ICSMNR

International Conference on Sustainable Management of Natural Resources

Proceedings of the First International Conference in Sustainable Management of Natural Resources

15th -17th October 2018, Bolivia Lodge, Polokwane, South Africa

EDITORS

Dr. Joshua Edokpayi
Department of Hydrology and Water Resources
University of Venda, South Africa

Prof. Wilson M Gitari
Department of Ecology and Resource Management,
University of Venda, South Africa

Dr. Eduard M Stam
Department of Ecology and Resource Management,
University of Venda, South Africa

Mr. Sphiwe E Mhlongo
Department of Mining and Environmental Geology,
University of Venda, South Africa

"Innovations and Technologies for Sustainable Management of Natural Resources"

School of Environmental Sciences
University of Venda,
University Rd, Thohoyandou,
South Africa, 0950

Cover and book design by Leach Printers & Signs,
Louis Trichardt Town, Limpopo Province of South Africa

ISBN: 978-0-620-82267-1

AUTHOR'S DISCLAIMER

The information presented in this publication is only for general education and informative purposes. Any views and opinions presented in the articles published in these proceedings are solely those of the authors and do not necessarily reflect those of the School of Environmental Sciences University of Venda (South Africa). The authors take full and exclusive responsibility for technical content, language and accuracy of information published herein. The information presented in this publication is not intended nor implied to be a substitute for professional advice. The editors are not responsible for any damage to property or persons that may occur because of use of the information published in this volume of the proceedings of ICSMNR2018 conference.

ORGANIZING COMMITTEE

Prof. Wilson Gitari (Chairperson)
Mr. Emmanuel Mhlongo (Co-Chairperson)

SUBCOMMITTEES

Publications and editorial

Dr. Joshua Edokpayi
Prof. Wilson Gitari
Dr. Eduard Stam
Mr. Emmanuel Mhlongo

Finance and liaison

Prof Wilson Gitari
Mr. Confidence Muzerengi
Mr. Emmanuel Mhlongo

Administration, social activities and communications

Dr. Milton Kataka
Prof. Wilson Gitari
Mr. John Mokgoebo
Ms. Ndivhudzanyi Rembuluwani
Mr. Emmanuel Mhlongo
Mr. Stanley Lesufi
Mr. Takalani Ramagalela
Ms. Noxolo Mbebe
Mr. Takalani Thabo
Mrs. Welheminah Mabogo
Mr. Mulalo Masisi

IT

Mr. Frans Matsaung
Mr. Farai Dondofema

Logistics

Mr. Ally Mahlaule
Mr. Ndivhuwo Nemapate
Mr. John Mokgoebo

THE REVIEW PROCESS

Participants for the ICSMNR 2018 conference first sent their abstracts which were reviewed by experts in the respective field of study. Authors with accepted abstracts were encouraged to submit their manuscript for inclusion in the conference proceedings. The submitted manuscript were again reviewed by a different reviewer with requisite expertise. After the review, authors were advised to attend to all the issues raised by the reviewers before a final acceptance of their manuscript.

A broad stream of reviewers from both national and international universities and research institute participated in the review of the manuscript as seen in the Table below.

Compiled by:
Joshua Edokpayi, PhD
Conference Technical Director

TECHNICAL REVIEWERS

Dr J.N. Edokpayi
University of Venda, South Africa

Dr T. Dube
University of the Western Cape, South Africa

Dr S. Alayande
Obafemi Awolowo University, Ile Ife, Nigeria

Dr G. Thondhlana
Rhodes University, South Africa

Prof O.S. Bello
Ladoke Akintola University of Technology, Nigeria.

Prof T. Davis
University of Nsuka, Nigeria

Prof L. Makondo
Durban University of Technology, South Africa

Prof. B Odhiambo
University of Venda, South Africa

Prof. P.B. Bikam
University of Venda, South Africa

Prof M.P. Tshisikhawe
University of Venda, South Africa

Prof W. Landman
University of Pretoria, South Africa

Dr A. Etale
University of the Witwatersrand, South Africa

Dr G. Madzivire
Council for Geoscience, South Africa

Dr O Babajide
CPUT, South Africa

Dr Sipho Mavundla
University of Zulu Land, South Africa

Dr M. Mujuru
University of Limpopo, South Africa

Dr A. Ramelo
The Council for Scientific and Industrial Research, SA

Dr E. Stam
University of Venda, South Africa.

Dr T. Kanyerere
University of Western Cape, South Africa

Prof C. Munyati
University of North West, South Africa

Prof E. Fosso-Kankeu
North West University, South Africa

Prof T. Nhiwatiwa
University of Zimbabwe, Zimbabwe

Prof. V. Somerset
The Council for Scientific and Industrial Research, SA

Prof. W.M. Gitari
University of Venda, South Africa

Dr. N. Davis
University of Pretoria, South Africa.

Prof W. Shivoga
Masinde Muliro University of Science & Technology, Kenya

Prof H. Tutu
University of the Witwatersrand, South Africa

Dr S. Nyale
Council for geoscience, South Africa

Dr M. Muchindu
Mintek, South Africa

Prof P. Ndungu
University of Johannesburg, South Africa

PREFACE

The world is becoming increasingly aware of the inter-connectivity and interdependence of the environment, human well-being and the economy. In South Africa this is captured in the National Development Plan (NDP): Vision 2030. Moreover, the NDP also recognizes the need for sustainable development which takes into account sustainable management of natural resources. The environment provides the basic services such as water, air and other natural resources which people depend on. In addition, the economy depends on these natural resources to provide economic growth, social development and human well-being. These function and services can only be rendered by a healthy and functional biophysical system. There has to be a balance between provision of these services and the maintenance of the capacity and integrity of the biophysical system to provide these services.

The first international conference for sustainable management of natural resources (ICSMNR2018) is the inaugural biannual conference to be organized by School of Environmental Sciences, University of Venda.

This series of biannual conference seeks to create a platform for national and international discussion on emerging trends, issues, innovative tools, technologies and experiences in exploration, sustainable exploitation and protection of natural resources. Moreover, this platform will create a space for promoting collaboration between academics, policy makers, environmental practitioners, environmental engineers, town planners, mining houses, researchers, students and socially responsible corporations. This conference proceedings is the product of the First International Conference for Sustainable Management of Natural Resources.

The conference attracted 85 abstracts in both oral and poster presentations. Out of these abstracts 38 were converted into full peer reviewed manuscripts. The manuscripts address various aspects of natural resources management and will be a good resource material for professionals, academics, government officials in the field of natural resources management and also resource material for environmental sciences and natural resources undergraduate and graduate students.

We hope that this inaugural conference serves as a beginning for the launch of bigger conferences, robust debates around natural resources management in future and creation of a fulfilling learning space.

Prof. Mugera M Gitari
Chairperson: Organizing committee

SPONSORS

University of Venda

WATER RESEARCH COMMISSION

environmental affairs
Department:
Environmental Affairs
REPUBLIC OF SOUTH AFRICA

TABLE OF CONTENTS

Contents **Page**

Diatomaceous earth: the future of ultra-pure silica - a review

O Izevbekhai[1,*], W Gitari[1] and N Tavengwa[2]

[1]Department of Ecology and Resource Management, University of Venda, South Africa
[2]Department of Chemistry, University of Venda, South Africa
*Email of corresponding author: mugera.gitari@univen.ac.za

Abstract
Diatomaceous earth (DE), which consists of fossils of prehistoric unicellular organisms (mainly diatoms) contains about 80 to 90% silica but this ubiquitous substance has not been used much as the source of this very useful oxide which ironically makes up most of its constituent. Silica, which is one of the main component of roads, bricks, windows, windscreens and all items made of glass and ceramics, is also used as filler for paints, plastics and in water filtration and agriculture. In its pure form, it is also used as precursor for silica gels, useful in wastewater remediation, ferrosilicon and elemental silicon which is used in modern day technology in optical data transmission fibers and precision casting, semiconductors, integrated circuits (microchips) and in solar – hydrogen energy systems. To date, quartz has been used as source of top-notch silica but there are predictions of the depletion of high quality quartz reserves in the near future as a result of the increasing demand of silica as precursor in many manufacturing industries, hence the need to look for a good alternative. This review presents the characteristics and uses of DE and compares it to that of silica, the various methods of extraction of silica from DE, comparing the purity of silica obtained using these methods and finally discusses the future of silica extraction from DE and its possible application in wastewater and groundwater remediation.

Keywords: *Diatomaceous earth, silica, extraction, remediation, wastewater*

1. Introduction

On the earth's crust, silicon is only second to oxygen in abundance making silica (SiO_2) one of the most abundant compounds. Silica is most commonly found in nature as quartz, and also in sand, in living organisms and plants usually in combination with other elements like aluminum, boron and some other trace elements, and oxides like Fe_2O_3, K_2O and others, depending on the source of the silica [1]. Although the oxide can be mined naturally, the various utilizations outweigh its availability [2]. As a result of this, there is the need for cheap and innovative ways to extract and purify silica present in other sources. Furthermore, its purity is a key parameter that determines the use it can be put to. Quartz is a relatively pure form of crystalline silica but it is difficult to use in areas like semiconductor manufacture that requires ultrapure silica because it is chemically stable [3]. Amorphous silica, the form in which it is present in DE [4] and a few other natural sources, on the other hand, can easily be purified since it readily dissolves in sodium hydroxide and other alkaline solutions. This review does not only discuss the characteristics and uses of DE but also compares it to that of silica, and also examines the various methods of extraction of silica from DE, comparing the purity of silica obtained using these methods. It further considers the future of silica extraction from DE and its possible application in wastewater and groundwater remediation.

Sources of silica

Commercially, silica is obtained from quartz but it can be obtained from biomass material such as rice husk, cassava periderm, sugarcane bagasse, maize stalk, corn cob, palm ash and pumice. It can also be obtained from soil, sand and diatomaceous earth. The yield that can be obtained from biomass is limited as there is also a large amount of organic matter and carbon contained in biomass materials. Sand and soil have several other uses and as such using them for large scale production of silica may not be achievable.

Diatomaceous Earth

When diatomite is crushed into a powder, it is normally referred to as diatomaceous earth, sometimes abbreviated as DE, also known as diatomite, tripolite or kieselgur. DE is a white powder occurring naturally as a soft sedimentary rock containing about 80 to 90% silica [5, 6] with size ranging from between 0.75m – 1500m [7]. Sometimes called infusorial earth or mountain meal [7], DE is formed naturally due to the accumulation of the silica cell walls of dead, microscopic, single celled, aquatic algae called diatoms (diatomea and radiolarian) [5]. Older deposits of diatomite have a different texture and crystalline phase as a result of the action of tectonic forces. DE contains mainly silica hydrate with varying degrees of water with metal oxides (mainly aluminum, iron and potassium oxides [8], carbonate salts, clay and organic matter as the major impurities [9]. The nature and amount of impurities are determined by atmospheric contact, chemical precipitation and environmental conditions [7].

Uses of DE

In its natural state, it has been used in making of bricks [5]; as stabilizer of trinitroglycerine in dynamite [5]; as filter aid for water, sugar, sweetener liquors, oils, fats, alcoholic beverages, chemicals, and pharmaceuticals etc. It can be used in this way because it is highly porous, has low density and high surface area [7, 8]. This accounts for half of its worldwide use [7]. It has also been used as filler in paints, plastics, Portland cement, as catalysts and as absorptive carrier in pesticides etc. [10]. It has been used as absorbent for industrial spills (oils and toxic liquids) [8], as abrasive in polishes, in insulation material [5], in grain preservation [11] as a natural insecticide [12], as an anticaking agent [5, 13]; in analysis, it is used in chromatographic columns [12].

Characteristics of DE

Diatomite is highly siliceous and relatively inert, has a low specific gravity and high surface area, and is very porous and has small particle size. These properties are what make it useful in the areas previously listed [14]. Three DE deposits were obtained from natural deposits at Kariandusi in Gilgil district, Nakuru County, Kenya [4], Eco – Earth, South Africa (SA) and Kolubara basin, Belgrade, Serbia [15]. The most abundant oxide in DE is silica and the second most abundant is aluminium oxide (CaO for SA DE) though the percentage composition of these oxides vary depending on the DE deposit (Table 1). The Kenyan deposit is richer in silica than the one from Serbia. The most abundant trace metal is Zirconium (Table 2) and completely amorphous having no crystalline mineral phases (Figure 1). The surface dimensions of DE are given in Table 3.

Definition and uses of silica

Silica, which is contained in high amounts in DE, can be mined from natural ores but the supply that can be gotten from these ores is limited and not sufficient when compared to the vast amount of uses the oxide and elemental silicon can be put to [2]. There is therefore the need to consider other sources of silica. DE can be used as natural source of silica because of its high silica content. Silica is the main component of roads, bricks, windows, windscreens and all items made of glass and ceramics. It is used as filler for paints, plastics, rubber and in water filtration and agriculture. It is also used as precursor for silica gels, ferrosilicon and elemental silicon which is used in modern day technology in optical data transmission fibres and precision casting and in solar – hydrogen energy systems. Basically, most of the uses of DE are as a result of its high silica content.

TABLE 1. Physicochemical parameters of DE

Oxide	Chemical composition of DE deposit (%)		
	Kenya	SA	Serbia
SiO_2	84.17	81.65	73.68
Al_2O_3	4.01	0.89	12.28
Fe_2O_3	2.96	-	3.29
Na_2O	0.61	-	0.12
K_2O	0.75	0.28	1.01
CaO	0.24	15.69	0.72
TiO_2	0.17	-	-
MgO	0.11	1.08	0.44
ZrO_2	0.06	-	-
MnO	0.04	-	-
P_2O_5	0.04	0.126	-
LOI[a]	(7.52)	-	8.26

Note: [a] Loss on ignition, [b] pH at point-of-zero-charge, [c] Water retention capacity (mL/g)

TABLE 2. Concentration of trace metals in DE [4]

Trace element	Concentration (mg/kg)	Trace element	Concentration (mg/kg)
Sc	3.85	Rb	44.7
Pr	13.0	Ho	2.05
V	25.2	Sr	26.7
Nd	49.8	Er	6.13
Cr	11.8	Y	51.5
Sm	9.65	Tm	0.91
Co	1.43	Zr	453
Eu	0.90	Yb	6.24
Ni	7.38	Nb	85.4
Gd	8.42	Lu	0.89
Cu	17.6	Mo	2.36
Tb	1.48	Hf	11.3
Zn	86.9	Cs	1.20
Dy	9.41	Ta	5.04
		Ba	31.0
		Pb	11.1
		La	58.5
		Th	13.7
		Ce	109
		U	2.95

TABLE 3. Surface dimensions of DE by BET

Parameter	Quantity		
	Area (m^2/g)	Volume (cm^3/g)	Pore (nm)
Single point surface area	31.1740		
BET surface area	31.8861		
Single point adsorption total volume		0.082691	
Adsorption average pore width (4 V/A by BET)			10.37335

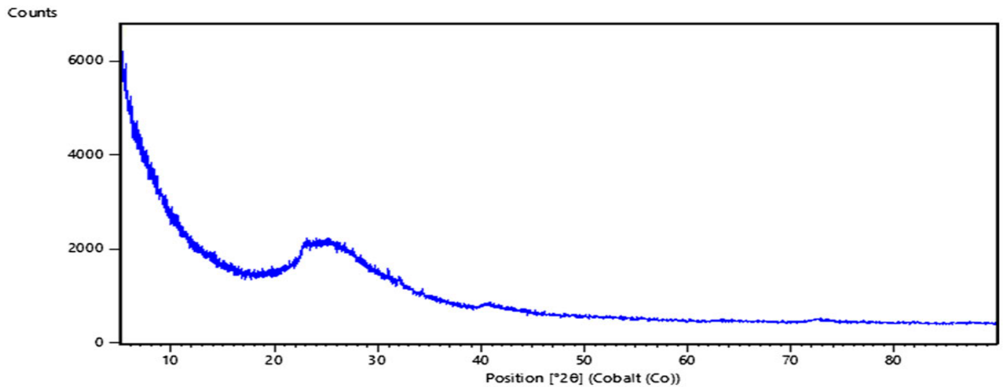


Figure 1. X-ray diffractogram of raw DE. [4]

Extraction of silica from commonly used sources

Silica has been extracted by several researchers from a variety of sources, mainly of agricultural origin, in very pure form (about 99.9%). The purity of the silica obtained is dependent on the purification method used with the purest obtained when hydrothermal method is used (Table 4). Even though some authors did not give information about the particle size of silica extracted, it is evident from literature that the extraction method influences the particle size with thermal treatment giving the highest particle size.

Extraction procedure from DE

Not many studies are available on the extraction of silica from DE but the purity obtained in the few studies cited is comparable to that from agricultural sources (Table 5). Majorly, silica is extracted from DE using alkali (mainly NaOH) because it dissolves readily to form alkali silicates, but one major drawback of this method is that precipitate all the silica from solution.

Justification

DE is a good source of silica because it occurs naturally and contains a very high amount of the oxide (70-90%) with a few soluble oxides and elements. Most DE deposits are completely amorphous [4] and so can easily be purified since it dissolves readily in caustic alkali. It is ubiquitous and does not have many competing uses.

Modification of silica

Even though silica gels are good adsorbents because of their relative inertness and large surface area, their application in water treatment is limited because they are hydrophobic and have poor mechanical properties [36]. Modification of silica makes them applicable in this and other areas by improving on its attributes and giving them required properties [37] (Tables 6 and 7). For example, the surface area, pore size and pore volume are all improved, making the silica better adsorbents.

TABLE 4. Extraction of silica from other sources

Source		Procedural highlights	Particle size (nm)	Percentage purity (%)	References
Biomass	Rice husk	Acid pre-treatment, combustion, leaching, pyrolysis, sol-gel. Maximum temperature-500°C, 700°C, 1000°C	6	96.5- 98.8	[16]
	Rice husk from two sources	Leaching and calcination. Maximum temperature: 650°C	181.2-294.7	33-35	[17]
	Corn hob	Pyrolysis, sol-gel, calcination. Maximum temperature: 700°C	305		[18]
	Rice, sylvan horse tail, scouring horse tail and larch needles	Hydrolysis, calcination, metallothermic reduction. Maximum temperature: 700°C	2000-100000	>99	[19]
	Rice husk	Acid pretreatment, combustion. Maximum temperature: 600°C	200-220	97	[20]
	Cassava periderm	Sol-gel. Maximum temperature: 600°C	62.69	61.53	[21]
	Sugarcane bagasse, cassava periderm and maize stalk	Calcination	-	38	[22]
	Rice husk	Hydrolysis, neutralization	-	36-99	[23]
	Corn cob	Sol-gel, Maximum temperature: 550°C	44-98	-	[24]
	Rice husk	Hydrothermal, Maximum temperature 150°C	-	99.9	[25]
	Rice husk	Acid leaching, alkaline extraction, thermal treatment, maximum temperature: 800°C	-	99.3-99.6	[26]
	Palm ash	Leaching. Maximum temperature: 700°C	-	>90	[27]
	Sorghum bargasse	Acidification			[28]
	Sugarcane leaves and bargasse	Acidification			[1]
Soil		-	-	-	[29]
Sand		Hydrothermal	72	>98	[30]
Sand			100	98.9	[31]
Sand		-	-	81.5	[32]
Pumice		Precipitation. Maximum temperature: 100°C	-	90.1	[33]
Quartz		Chemical leaching, thermal treatment. Maximum temperature: 50°C	-	-	[3]

TABLE 5. Extraction of silica from diatomaceous earth

Procedural highlights	Particle size (nm)	Percentage purity (%)	References
Dissolution, precipitation	-	-	[2]
Leaching	-	86-98	[34]
Alkaline extraction	-	77.3	[35]

TABLE 6. Physical modification

Modifying material	Purpose of modification	Pore volume (cm^3/g)	Surface area (m^2/g)	Pore diameter (nm)	References
Water	-	-	18	288.2	[37]
Methanol	-	-	190	7.8	
N – propanol	-	-	290	5.3	
N – hexanol	-	-	316	4.6	
bis(2,2'-methylenephenol) diaminoethane	Separation and spectrophotometric determination of Cu (II) from Ni(II) ions	-	-	-	[38]

TABLE 7. Chemical modification

Modifying material	Purpose of modification	Pore volume (cm^3/g)	Surface area (m^2/g)	Pore diameter (nm)	References
Trimethylchlorosilane	The reduce gel shrinkage	-	-	-	[39]
Aldehyde and	For effective release of	0.60	407	4.9	[40]
dexamethazone	dexamethasone to diseased sites	0.45	316	3.8	
Alkoxysilane	-	-	972.3	-	[41]
vinyltriethoxysilane	Increased strength	0.58	788	2.6	[42]
Ammonium	Adsorption of phosphates and nitrates	0.66	890	1.9	[43]
Tetraethoxysilane	Adsorption of dyes	1.47	582.52	12.5	[36]
Trimethylchlorosilane		1.48	515.38	12.5	
3-pentadecylcatechol	Rubber enforcement	-	-	-	[44]
Trimethylchlorosilane	-	0.889	945.8	3.8	[45]
Ammonium	Acidic support for iridium hydrogenation catalyst	0.66^b 0.72^a	247^b 405^a	10.8^b 7.1^a	[46]
3-mercaptopropyl-ethyoxyl-di(tridecyl-pentamethoxy)-silane	Silica/natural rubber composites	-	-	-	[47]

Note: ^{a}Acidic conditions, ^{b}Basic conditions

Future trends and challenges

In the future, there is likely to be a shift from quartz and biomass to DE in the production of ultra-pure silica because DE does not have much competing uses and the type of silica found in DE is completely amorphous making it easier to purify. Also, the yield obtained from the extraction and purification of silica is much higher than that from biomass. However, the yield obtained is dependent on the extraction procedure obtained. The most common extraction procedure is conventional solvent extraction using alkali, but this method reduces the yield because not all the extracted silica is recovered from solution. In the future, researchers will opt for a different extraction method, one that will allow for complete recovery.

DE is already being used as filter aid and has been applied in defluoridation of ground water mostly because of its great surface area and porosity. Extraction and modification of silica from it will make it better applicable in these areas and also in wastewater remediation where it has not really been applied much because as can be seen from Tables 3, 5 & 6 and from other literature, extracted silica and modified silica have better surface area and porosity than DE

Conclusion

DE is a good source of ultra-pure silica because it is found in nature to contain almost 80% of amorphous silica which can be purified easily. It does not have a lot of competing uses and so can be a good replacement or supporting 'partner' for the already overburdened quartz.

References

1. Harish, P.R.; Arumugam, A.; Ponnusami, V. Recovery of silica from various low-cost precursors for the synthesis of silica gel. *Der Pharmacia Lettre,* 2015, Volume 7, pp. 208-213.
2. Bessho, M.; Fukunaka, Y.; Kusuda, H.; Nishiyama, T. High-Grade Silica Refined from Diatomaceous Earth for Solar-Grade Silicon Production. *Energy & Fuels,* 2009, Volume 23, p. 4160–4165.
3. Zahan, M.S.; Tanmi T.; Rahman, M.S. Extraction of High purity SiO2 from Raw Quartz. *Imperial Journal of Interdisciplinary Research (IJIR),* 2017, Volume 3, pp. 1999-2005.
4. Izuagie, A.A.; Gitari W.M.; Gumbo, J.R. Defluoridation of groundwater using diatomaceous earth: optimization of adsorption conditions, kinetics and leached metals risk assessment, *Desalination and Water Treatment,* 2015, pp. 1-13.
5. Antonides, L.E.; Diatomite, *https://minerals.usgs.gov/minerals/pubs/commodity/diatomite/250497.pdf* , 1997, Retrieved 05 31, 2017
6. Izuagie, A.A.; Gitari W.M.; Gumbo, J.R. Effects of calcination temperature and solution pH on the defluoridation potential of Al/Fe oxide-modified diatomaceous earth: metal leaching and sorbent reuse, *Water Science & Technology: Water Supply, in press*, 2016, pp. 1-10.
7. Bakr, H. Diatomite: Its Characterization, Modifications and Applications, *Asian Journal of Materials Science,* 2010, Volume 2, pp. 121-136.
8. Hakamada, M.; Fukunaka, Y.; Oishi, T.; Nishiyama T.; Kusuda, H. Carbothermic reduction of amorphous silica refined from diatomaceous earth, *Metallurgical and materials transactions B,* 2010, Volume 41B, pp. 350-358.
9. Mendioroz, S.; Belzunce, M.J.; Pajares, J.A. Thermogravimetric study of diatomites, *Journal of Thermal Analysis,* 1989, Volume 35, pp. 2097-2104.
10. Mazidi, M.; Behbahani, R. M.; Fazeli, A. Screening of treated diatomaceous earth to apply as V2O5 catalyst support, *Materials research and innovations,* 2016, pp. 1-10.
11. Subramanyam, B.; Swanson, C.; Madamanchi; N.; Norwood, S. Effectiveness of insecto, a new diatomaceous earth formulation in suppressing several stored-grain insect species, Proceedings of the 6th international working conference on stored-product protection, Canberra, 1994.

12. Tsai, W.; Hsien, K.; Chang, Y.; Lo, C. Removal of herbicide paraquat from an aqueous solution by adsorption onto spent and treated diatomaceous earth, *Bioresource Technology,* 2005, Volume 96, pp. 657-663.
13. Tsai, W.T.; Hsien, K.J.; Yang, J.M. Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution, *Journal of Colloid and Interface Science,* 2004, Volume 275, pp. 428-433.
14. EFMA, Dynamic Diatomite: The Universal Uses of Diatomaceous Earth, 2016. Available online: http://www.efma.org/diatomite/. (Accessed on 15 05 2018).
15. Šaponjić, A.; Babić, B.; Devečerski, A.; Matović, B. Preparation of Nanosized Non-Oxide Powders Using Diatomaceous earth, *Science of Sintering,* 2009, Volume 41, pp. 151-159.
16. Rafiee E.; Shahebrahimi, S.; Feyzi, M.; Shaterzadeh, M. Optimization of synthesis and characterization of nanosilica produced from rice husk (a common waste material), *International Nano Letters,* 2012, Volume 2, pp. 1-8.
17. Carmona, V.; Oliveira, R.; Silva, W.; Mattoso, L.; Marconcini, J. Nanosilica from rice husk: Extraction and characterization, *Industrial Crops and Products,* 2013, Volume 43, pp. 291-296.
18. Ogunfowokan, A.; Ezenwafor T.; Imoisili, P. E. Synthesis of nanoporous silica membrane from corn hob ash (zea mays) by sol-gel method, *Nigerian materials congress (NIMACON 2011)*, Akure, 2011.
19. Zemnukhova, L. A.; Egorov, A. G.; Fedorishcheva, G. A.; Barinov, N. N.; T. A. Sokol'nitskaya; Botsul, A. I. Properties of Amorphous Silica Produced from Rice and Oat Processing Waste, *Inorganic Materials,* 2006, Volume 42, pp. 24-29.
20. Ghorbani, F.; Sanati A. M.; Maleki, M. Production of Silica Nanoparticles from Rice Husk as Agricultural Waste by Environmentally Friendly Technique, *Environmental Studies of Persian Gulf,* 2015, Volume 2, pp. 56-65.
21. Adepoju, A. D.; Adebisi, J. A.; Odusote, J. K.; Ahmed I. I.; Hassan, S. B. Preparation of silica from cassava periderm, *Journal of solid waste technology and management,* 2016, Volume 42, pp. 216-221.
22. Adebisi, J. A.; Agunsoye, J. O.; Bello, S. A.; Kolawole, F. O.; Ramakokovhu, M. M.; Daramola M. O.; Hassan, S. B. Extraction of Silica from Sugarcane Bagasse, Cassava Periderm and Maize Stalk: Proximate Analysis and Physico-Chemical Properties of Wastes,» *Waste Biomass Valor,* 2017, pp. 1-14.
23. Arefieva, O. D.; Zemnukhova, L. A.; Kovshun, A. A.; Kovekhova, A. V. Processing Methods of Alkaline Hydrolysate from Rice Husk, *Rice Science,* 2017, Volume 24, pp. 235-240.
24. Okoronkwo, E. A.; Imoisili, P. E.; Olubayode S. A.; Olusunle, S. O. O. Development of Silica Nanoparticle from Corn Cob Ash, *Advances in Nanoparticles,* 2016, Volume 5, pp. 135-139.
25. Todkar, B. S.; Deorukhkar O. A.; Deshmukh, S. M. Extraction of Silica from Rice Husk, *International Journal of Engineering Research and Development,* 2016, Volume 12, pp. 69-74.
26. Fernandes, I. J.; Calheiro, D.; Sánchez, F. A. L.; Camacho, A. L. D.; Rocha, T. L. A. d. C.; Moraes C. A. M.; Sousa, V. C. d. Characterization of Silica Produced from Rice Husk Ash: Comparison of Purification and Processing Methods, *Materials Research,* 2017, Volume 20, Suppl. 2, pp. 512-518.
27. Pa, F. C.; Chik A.; Bari, M. F. Palm Ash as an Alternative Source for Silica Production, 2nd International Conference on Green Design and Manufacture, Thailand, 2016.
28. Mupa, M.; Hungwe, C. B.; Witzleben, S.; Mahamadi C.; Muchanyereyi, N. Extraction of silica gel from Sorghum bicolour (L.) moench bagasse ash, *African Journal of Pure and Applied Chemistry,* 2015, Volume 9, pp. 12-17.
29. Saccone, L.; Conley, D. J.; Koning, E.; Sauer, D.; Sommer, M.; Kaczorek, D.; Blecker S. W.; Kelly, E. F. Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems, *European Journal of Soil Science,* 2007, Volume 58, pp. 1446-1459.
30. Munasir; Triwikantoro; Zainuri M.; Darminto, Synthesis of SiO2 nanopowders containing quartz and cristobalite phases from silica sands, *Materials Science-Poland,* 2015, Volume 33*, pp. 47-55*
31. Munasir; Sulton, A.; Triwikantoro; Zainuri M.; Darminto, «Synthesis of Silica Nanopowder Produced from Indonesian Natural Sand via Alkalifussion Route, The 2nd International Conference on Theoretical and Applied Physics (ICTAP-2012) 1555, Central Borneo, 2013.
32. Email, I. W.; Sani, N. A.; Abdulsalam, A. K.; Abdullahi, U. A. Extraction and quantification of silicon from silica sand obtained from Zauma river, Zamfara state, Nigeria, *European Scientific Journal,* 2013, Volume 9, pp. 160-168.

33. Dewati, R.; Suprihatin; Sumada, K.; Muljani, S.; Familya M.; Ariani, S. Precipitated Silica from Pumice and Carbon Dioxide Gas (Co2) in Bubble Column Reactor, *Journal of Physics,* 2018, Conf. Series 953, p. 012226.
34. Bessho, M.; Umehara, K.; Takaura, T.; Nishiyama T.; Shingu, H. The potential of the production of high-purity silica from biogenic diatomaceous earth, *Shigen-to-sozai,* 2001, Volume 117, pp. 736-742.
35. Kadri, L.; Khiat, A.; Tsubouchi K.; Hamzaoui, S. Chemical purification of silica from raw diatom, 3rd conference on energy and sustainable development, Adrar, 2017.
36. Zong, S.; Wei, W.; Jiang, Z.; Yan, Z.; Zhu J.; Xie, J. Characterization and comparison of uniform hydrophilic/hydrophobic transparent silica aerogel beads: skeleton strength and surface modification, *RSC Advances,* 2015, Volume 5, pp. 55579-55587.
37. Leboda, R.; Mendyk, E.; Sidortchuk V.; Tertykh, V. Methods of simultaneous physical and chemical modification of silica gels, *Materials Chemistry and Physics,* 1994, Volume 38, pp. 146 - 156.
38. Onwu F. K.; Uguru, P. I. Physical modification of silica gel with bis(2,2'-methylenephenol) diaminoethane for separation and spectrophotometric determination of Cu(II) from Ni(II) ions, *Der Chemica Sinica,* 2015, Volume 6, pp. 73 - 81.
39. Hilonga, A.; Kim, J.-K.; Sarawade P. B.; Kim, H. T. Low-density TEOS-based silica aerogels prepared at ambient pressure using isopropanol as the preparative solvent, *Journal of Alloys and Compounds,* 2009, Volume 487, p. 744–750.
40. Numpilai, T.; Witoon, T.; Chareonpanich M.; Limtrakul, J. Impact of physicochemical properties of porous silica materials conjugated with dexamethasone via pH-responsive hydrazone bond on drug loading and release behavior, *Applied Surface Science,* 2017, Volume 396, pp. 504-514.
41. Torres, C. C.; Urbano, B. F.; Campos, C. H.; Rivas, B. L.; Reyes, P. Composite hydrogel based on surface modified mesoporous silica and poly[(2-acryloyloxy) ethyl trimethylammonium chloride], *Materials Chemistry and Physics,* 2015, Volume 152, pp. 69-76.
42. He, J.; Shen, Y.; Evans D. G.; Duan, X. Tailoring the performance of polymer composites via altering the properties of the intrapore polymers of MCM-48 nanocomposites as fillers, *Composites: Part A: Applied science and manufacturing,* 2006, Volume 37, p. 379–384.
43. Hamoudi, S.; Saad R.; Belkacemi, K. Adsorptive Removal of Phosphate and Nitrate Anions from Aqueous Solutions Using Ammonium-Functionalized Mesoporous Silica, *Industrial and Engineering Chemistry Research,* 2007, Volume 46, pp. 8806-8812.
44. Yan, X.; Hamed G. R.; Jia, L. Modulating silica-rubber interface by a biorenewable urushiol derivative. Synthesis, surface modification, and mechanical and dynamic mechanical properties of vulcanizates therefrom, Journal of *applied polymer sciences,* 2017, Volume 135, pp. 1 - 10.
45. Feng, Q.; Chen, K.; Ma, D.; Lin, H.; Liu, Z.; Qin S.; Luo, Y. Synthesis of high specific surface area silica aerogel from rice husk ash via ambient pressure drying, *Colloids and Surfaces A,* 2018, Volume 539, pp. 399 - 406.
46. Janiszewska, E.; Kot M.; Zielinski, M. Modification of silica with NH4+ agents to prepare an acidic support for iridium hydrogenation catalyst, *Microporous and mesoporous materials,* 2018, Volume 255, pp. 94-102.
47. Zheng, J.; Han, D.; Ye, X.; Wu, X.; Wu, Y.; Wang Y.; Zhang, L. Chemical and physical interaction between silane coupling agent with long arms and silica and its effect on silica/natural rubber composites, *Polymer,* 2018, Volume 135, pp. 200 - 210.
48. Hassan, S.; Ojo, O.; Agusoye J.; Adebisi, J. Synthesis of amorphous silicon nanoparticles from agricultural wastes for solar applications-A review, Proceedings of materials science and technology society of Nigeria, Lagos, 2014.

African indigenous criteria used for domestic firewood selection by the Bapedi households of Senwabarwana villages, South Africa

K Semenya* and F Machete

College of Agriculture and Environmental Sciences, UNISA, Republic of South Africa
*Email of corresponding author: semenk@unisa.ac.za

Abstract
This paper presents the African indigenous criteria which Bapedi households in Senwabarwana village use for selecting domestic firewood. In total, 69 households in the village were purposively selected to participate in structured interviews. Purely qualitative data were collected and analysed using descriptive statistical methods. The study found that, in the main, 43 indigenous plant species are used as firewood; and of those, the ten-priority firewood species were identified using African indigenous criteria. The most frequently used and preferred species were *mohweleri*, *moretshe*, *motswiri*, *mokgwa*, *mushu*, *motshe*, *mokata*, *mphata*, *mokgalo* and *mogwana*, in order of preference. The authors found commonalities between the respective criteria which Western and African indigenous communities use to choose a specific log of wood, or other natural materials for making fire. The four primary factors influencing the Bapedi households in Senwabarwana village when choosing firewood are that certain woods (1) form long-lasting embers during combustion, (2) have higher heat value, (3) have low ash content and (4) are available within the area. To conclude, the authors suggest that the ethnobotanical knowledge of the Bapedi households in Senwabarwana village needs further research and documentation, prior to the development of a model for sustainable wood use in the future.

Keywords: firewood; firewood properties; indigenous knowledge systems; local ethnobotanical knowledge; selection criteria for firewood

1. Introduction

African communities have a rich history of undocumented knowledge systems that have survived colonialism and modernisation, conveyed mainly through oral accounts. Many of these knowledge systems are still prevalent and continue to be practised in non-urban areas of South Africa, as the ultimate means of securing a livelihood for rural communities. One such system outlines the criteria, which the Bapedi households of Senwabarwana village – amongst many others – use to decide on the suitability of wood or plant materials to use as firewood. Naturally, most tree species and plant materials can be used as firewood, yet their combustibility differs from one plant species to the next. This variance is associated with different species' unique properties [1]. The available literature [2, 3] outlines a number of factors which modern communities use to decide on the suitability of different types of firewood, with little (if any) such texts focusing on the different criteria which African indigenous communities utilise to do the same.

Another author [4] identify (1) a hot flame, (2) a flame that is long lasting, (3) long-lasting embers and (4) wood that is easy to split and ignite as the primary factors informing firewood selection in Uganda. In addition to these factors, the preferred firewood plant species should burn without producing too much smoke be able to lose moisture fast and produce embers such that (even when the burning wood is covered in ash) they retain fire overnight. Such firewood should have a flame that does not produce sparks. The wood should also be readily available, i.e., within reach of the user or community and easy to harvest (preferably without thorns). Other studies have identified prerequisites such as high heat or energy content, high wood density, low ash content and low moisture content [4-6]. The most commonly mentioned negative attributes relate to wood being difficult to ignite, quickly to burn out, or as producing too much smoke or ash. Western botanical knowledge generally saw firewood primarily being selected based on its heat (calorific) value, which is commonly measured using a bomb calorimeter [3]. According to [3], the heat value of firewood is dependent on its moisture content, density and ash content.

Heat value, which is synonymous with calorific value, is the amount of heat released when one kilogram of dry wood is burned, and all water created during the burning process is condensed [2]. Heat value is a variable used to determine the energy content of a fuel – in this instance; it depends on the chemical composition and moisture content of the wood in question. According to the available Western knowledge, the heat value of wood does not vary much from one tree species to another (18.7–21.9 MJ/kg). However, the heat value is slightly higher in coniferous species than for broadleaved or deciduous tree species [7], due to their higher lignin and resin contents. Furthermore, the available literature [8, 9,4] shows that the bark, crown and stump of trees typically have somewhat higher effective heating values than the wood of the stem.

Moisture content

Moisture content refers to the amount of water present in wood. The moisture content of wood has a significant effect on the net heat value reached during the wood-burning process [2], but it also markedly influences the net calorific heating value. The moisture content of wood varies from 20–65% and is mostly influenced by (1) climatic conditions, (2) the time of year, (3) tree species, (4) the part of the wood stem, and (5) the storage phase [7,2,1]. Hence, a dry wood has a high calorific value. The available literature suggests that heat emanating from a dry firewood combustion process should be drawn away from the combustion chamber to prevent overheating and consequent damage to the equipment used. In contrast, wet wood has a low calorific value per kilogramme of total wood weight, thus such firewood needs to be dried to 10–20% moisture content, to ensure that it burns well.

Wood density

According to the Food and Agriculture Organization [7], wood density refers to its dry weight per unit volume in kilogrammes per cubic metre (kg/m^3). Previous studies have associated denser or heavier woods with more heat per volume and longer burning time [1-2]. According to [3], denser species naturally have a higher heating value per cubic metre of solid stem wood.

Ash content

Ash content refers to the amount of solid waste that remains once the burning process has been completed [3, 7]. It can be expressed as the weight percentage of the dry base or of the received material. High ash content in a fuel generally reduces its heating value. The ash content of biomasses such as firewood ranges from 0.08–2.3 percent [1, 10]. According to [2], ash has a significant influence on the heat transferred to the surface of a fuel, as well as the diffusion of oxygen to the fuel surface during char combustion. Since ash is an impurity that will not burn, firewood with low ash content is better suited for thermal utilisation than types of wood with a high ash content.

What the authors of this paper wish to bring to the fore is the fact that contemporary Western knowledge of firewood differs from the local ethnobotanical knowledge of, for instance, the Bapedi households of Senwabarwana village, given that the former is well documented while the latter is not. This undocumented ethnobotanical knowledge base is under threat of extinction [11, 12]. According to [13,14], ethnobotanical knowledge originates from local communities, of which the inhabitants of Sewabarwana village are an example, with such knowledge being centrally important to the spiritual, physical and social interests of local communities [15]. Ethnobotanical knowledge might alleviate some of the shortcomings of contemporary Western knowledge, given that local knowledge has been in existence for centuries. This knowledge is transferred from one generation to the next within a community and is intertwined with its cultural values [14]. Apart from energy (fuel) provision, plants have multiple uses, serving a medicinal purpose and/or providing food and timber, to mention but a few. Lastly, although indigenous African communities such as the Bapedi households of Senwabarwana village commonly use firewood as the primary energy source for cooking food and heating water, no formally or officially documented criteria are used when selecting which plant species to harvest as firewood. Notably, this community does not use just any plant species as firewood – specific and selected tree species are preferred. In closing the identified gap in the literature, the aim of this paper is to present the African indigenous criteria for domestic firewood selection used by Bapedi households in Senwabarwana village, South Africa.

2. Materials and methods

The study was conducted in Senwabarwana, a village in the Blouberg Local Municipality in Limpopo Province, South Africa. According to [16], the village is home to 172 601 people and 43 747 households. A survey study was conducted, and data were collected using structured interviews. Convenience sampling was undertaken, using the visibility of stockpiled wood within a household, the visibility of people and the identification of a potential fire-making site (e.g., a kitchen or braai area) in or outside the home. Structured interviews were conducted in Sepedi, the local indigenous language of the Senwabarwana villagers. Lastly, all nominal, ordinal and interval data were analysed and presented through statistics.

3. Discussion of results

Thirteen main factors were identified as being used by the indigenous Bapedi households of Senwabarwana village to qualify twigs, logs or other flammable natural materials as the preferred types of firewood (see Figure 1). The results in Figure 1 present a ranking of the 13 major elements that the Bapedi households of Senwabarwana village use to select firewood, from the highest to the lowest priority factors. Notably, 98 per cent of households prefer a wood that burns longer, followed by wood that makes good coal (85%). The lowest ranking was for wood that does not rot (preferred by only 1% of households). Figure 2 present a matrix of the criteria and priority tree species selected as ideal firewood species in Senwabarwana villages.

Using the 13 factored criteria presented in Figure 2, the matrix shows three important issues, namely (1) the criteria per factor, (2) the number of respondents who rated each of the factors of the criteria and (3) the ten priority firewood species rated by respondents according to the 13-point criteria. It is worth noting that the trees, which made the list, tended to rank higher across most factors – particularly in respect of priority characteristics such as longer burning time. Although Figure 2 only presents the top ten trees, it is important to highlight that initially the community identified 43 tree species, which they commonly used for firewood – of those, the ten most favoured trees, were used to generate the matrix (Figure 3). The list of remaining trees and scientific names are attached (Appendix A).

 ISBN 978-0-620-82267-1

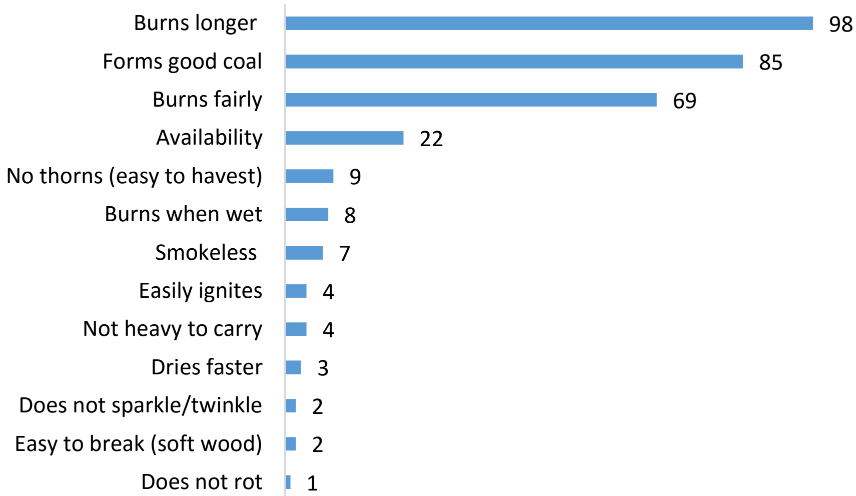
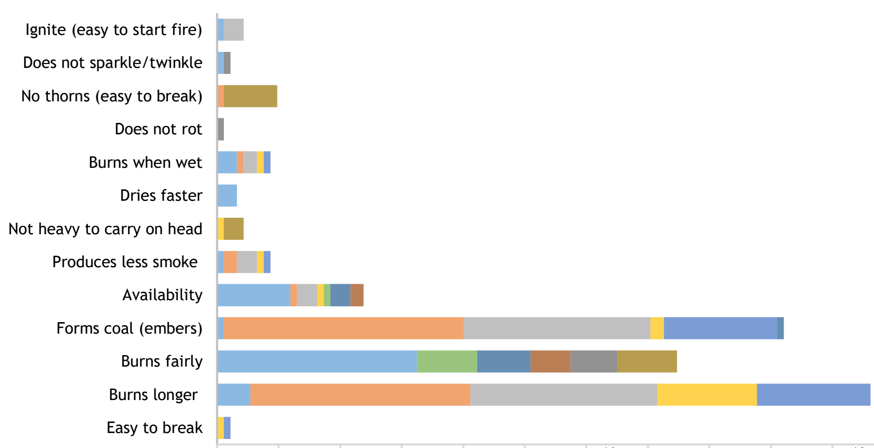


Figure 1. Firewood qualities used as factors for firewood selection



	Easy to break	Burns longer	Burns fairly	Forms coal (embers)	Availability	Produces less smoke	Not heavy to carry on head	Dries faster	Burns when wet	Does not rot	No thorns (easy to break)	Does not sparkle/twinkle	Ignite (easy to start fire)
Mushu		5	30	1	11	1		3	3			1	1
Mohweleri		33		36	1	2			1		1		
Moretshe		28		28	3	3			2				3
Motshe	1	15		2	1	1	1		1				
Motswiri	1	17		17		1			1				
Mokata			9		1								
Mokgwa			8	1	3								
Mokgalo			6		2								
Mphata			7							1		1	
Mogwana			9				3				8		

Figure 2. Firewood selection matrix with ten priority firewood tree species selected

The final outcome of the development and use of African indigenous criteria for firewood selection, based on the study conducted in Bapedi households of Senwabarwana villages, was a list of ten priority firewood species (Figure 3), which shows that *mohweleri*, *moretshe* and *motswiri* are preferred for their ability to form heat-retaining embers, whereas *mushu* is preferred for its ability to burn fairly (i.e., produce a strong flame) and for the fact that it is the most freely available wood species in the area. *mushu* meets most of the criteria identified, which might explain why it is the most commonly used species – in the absence of *mohweleri*, *moretshe* and *motswiri*, the community might thus revert to *mushu*. *Mogwana* is only preferred since the species does not have thorns, thus making it easy to harvest. The other tree species (e.g., *mokata*, *mokgwa* and *mokgalo*) do not meet many of the criteria identified by the participants and are used when the preferred species are not available. All these species are indigenous to the Senwabarwana area, and are used for medicine, food and timber [12, 17,18].

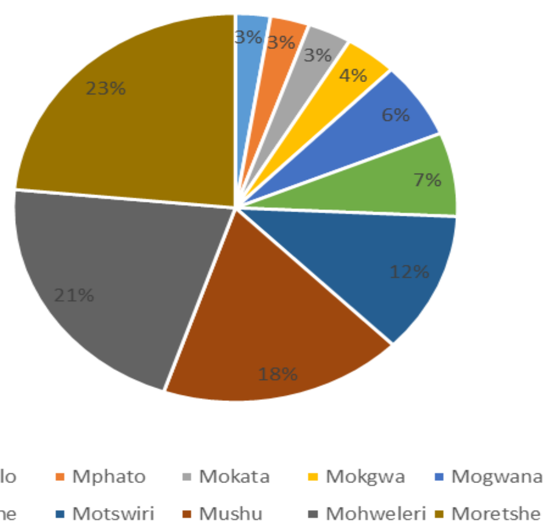


Figure 3. The most preferred firewood species selected through African indigenous criteria

4. Conclusion

The study found that, in the main, 43 indigenous plant species are used as firewood; and of those, the ten-priority firewood species were identified using African indigenous criteria. The most frequently used and preferred species were *mohweleri*, *moretshe*, *motswiri*, *mokgwa*, *mushu*, *motshe*, *mokata*, *mphata*, *mokgalo* and *mogwana*, in order of preference. The authors found commonalities between the respective criteria which Western and African indigenous communities use to choose a specific log of wood, or other natural materials for making fire. The four primary factors influencing the Bapedi households in Senwabarwana village when choosing firewood are that certain woods (1) form long-lasting embers during combustion, (2) have higher heat value, (3) have low ash content and (4) are available within the area. To conclude, the authors suggest that the ethnobotanical knowledge of the Bapedi households in Senwabarwana village needs further research and documentation, prior to the development of a model for sustainable wood use in the future.

References

1. Sigaud, P., & Luhanga, J. (2001). SADC Sub-Regional Workshop on Forest and Tree Genetic Resources. Forest Genetic Resources, 28, 41–44.
2. Glassman, I., & Yetter, R. A. (2007). Combustion, 4th ed., Academic Press, Burlington, MA.
3. Atkins, P., & De Paula, J. (2006). Physical Chemistry, 8th ed., Freeman, New York.
4. Tabuti, J.R.S., Dhilliona, S. S., & Lyea, K.A. (2003). Firewood Use in Bulamogi County, Uganda: Species Selection, Harvesting and Consumption Patterns. Biomass and Bioenergy, 25, 581–596.
5. Munalula, F., & Meincken, M. (2009). An Evaluation of South African Fuelwood with Regard to Calorific Value and Environmental Impact. Biomass and Bioenergy, 33, 415–420.
6. Tietema, T., Dithlogo, M., Tibone, C., & Mathalaza, N. (1991). Characteristics of Eight Firewood Species of Botswana. Biomass and Bioenergy, 1 (1), 41–46. Retrieved from http://dx.doi.10.1016/0961-9534(91)90050-M
7. Food and Agriculture Organisation. (2017a). Incentivizing Sustainable Wood Energy in sub-Saharan Africa: A Way Forward for Policy-makers, FAO, Rome, Italy.
8. Food and Agriculture Organisation of the United Nations (2017b). Sustainable Wood Fuel for Food Security – A Smart Choice: Green, Renewable and Affordable. Retrieved from http://www.fao.org/publications.
9. Jin, S.L., Schure, J., Ingram, V., & Yoo, B. (2017). Sustainable Wood Fuel for Food Security. A smart choice: green, renewable and affordable. Food and Agriculture Organization of the United Nations, Rome. Retrieved from http://www.fac.org/publications
10. Cardoso, M.B., Ladio, A.H., & Lozada, M. (2012). The use of firewood in a Mapuche community in a semi-arid region of Patagonia, Argentina. Biomass and Bioenergy 46, 155–164.
11. Giday, M., Asfaw, Z., Elmqvist, T., & Woldu, Z. (2003). An Ethnobotanical Study of Medicinal Plants used by the Zay People in Ethiopia. Journal of Ethnopharmacology, 85 (1), 43–52.
12. Mongalo, N.I., & Makhafola, T.J. (2018). Ethnobotanical Knowledge of the Lay People of Blouberg Area (Pedi Tribe), Limpopo Province, South Africa. Journal of Ethnobiology and Ethnomedicine, 14 (46). Retrieved from https://doi.org/10.1186/s13002-018-0245-4.
13. Martin, G.J. (1995). Ethnobotany: A Method Manual, Chapman & Hall, London, UK.
14. Berkes, F. (1999). Sacred Ecology: Traditional Ecological Knowledge and Resource Management, Taylor & Francis, New York.
15. Getahun, A. (1976). Some Common Medicinal and Poisonous Plants used in Ethiopian Folk Medicine, Addis Ababa University, Addis Ababa, Ethiopia.
16. Statistics South Africa. (2016). Community Survey 2016: Provinces at a Glance. Pretoria: Statistics South Africa. Retrieved from http://www.statssa.gov.za/wp-content/uploads/2016/.../Annual_Report_2016_Book_1_.pdf
17. Muthee, J.K., Gakuya, D.W., Mbria, J.M., Kareru, P.G., Mulei, C.M., Njonge, F.K. (2011). Ethnobotanical study of anthelmintic and other medicinal plants traditionally used in Loitoktok District of Kenya. Journal of Ethnopharmacology, 135, 15–21.
18. Semenya, S.S., Potgieter, M.J., Erasmus, L.J.C. (2013). Indigenous plant species used by Bapedi healers to treat sexually transmitted infections: Their distribution, harvesting, conservation and threats. South African Journal of Botany, 87, 66-75.

The relationship between rainfall variability and irrigated citrus production in the Greater Tzaneen Municipality, Limpopo Province, South Africa

T Tshitavhe* and E Kori

Department of Geography and Geo-Information Sciences, University of Venda, South Africa
*Email of corresponding author: tshitavhetangie@gmail.com

Abstract
Rainfall variability has the potential to adversely affect crop production in the semi-arid regions of South Africa. The effect is both on rain fed and irrigated crops, including citrus trees. Citrus production is done under both irrigation and natural rainfall in the Greater Tzaneen Municipality. Citrus is vulnerable to rainfall variability. Moisture stress is a limiting factor for citrus production. Irrigation is necessary during dry and low rainfall seasons. The aim of this paper is to analyse the relationship between rainfall variability and irrigated citrus production in the Greater Tzaneen Municipality. Rainfall statistics from 2006 to 2016 for three weather stations linked to three farms were obtained from South African Weather Service. The three farms provided irrigation patterns and production data. The Precipitation Concentration Index (PCI) at seasonal scale (citrus growth cycle) was used to analyse seasonal rainfall characteristics in the study area for the period 2006 to 2016 based on the citrus calendar. Results show a strong irregularity in the distribution of rainfall with values in the range of 21-50. Using rainfall variability as a predictor, the relationship between rainfall variability and citrus production was established using simple linear regression analysis. Results show a weak positive relationship between rainfall variability and citrus production (p>0,05 and r^2 <0,5) in all three farms during the period under review. The relationship was consistent showing ±5% margin of error at 95% confidence level. Such data suggests that rainfall variability leads to variation of citrus productivity. It is concluded that rainfall variability influences citrus production. However, its influence is insignificant indicating the power play of other factors. As a result, it is recommended that farmers should not only focus on rainfall variability as the main factor influencing citrus production. They must also consider other factors such as temperature increases, soil fertility, topography, diseases and pest infestation among others.

Keywords: Rainfall variability, Citrus production, Irrigation, Moisture stress, Precipitation Concentration Index

1. Introduction

According to the Intergovernmental Panel on Climate Change (IPCC) [1] the scientific community worldwide agrees that climate change is an inevitable phenomenon and a reality. Changes in rainfall patterns are occurring globally at rates that are projected to be remarkable in recent human history [2]. Rainfall is extremely erratic and unpredictably varying in both space and time during the cropping season. The Department of Agriculture Forestry and Fisheries (DAFF) [3] emphasised that rainfall variability has a negative impact on crop production particularly in the semi-arid regions that are already marginal for crop production and vulnerable to extreme climatic events. Variations in rainfall have devastating effects in areas where crop production is predominately rain-fed and hence any irregularity in weather conditions has adverse implications [4].

Climate and soil conditions in South Africa enable the country to cultivate and produce a variety of fruit crops including citrus [5]. Citrus is done under irrigation and natural rainfall in the Greater Tzaneen Municipality (GTM). Farming citrus in rain-fed agricultural areas with erratic and low rainfall is challenging [4]. Citrus production is largely affected by the amount of water received during the current and previous growing seasons. When citrus trees do not get enough water, growth and development rates are reduced [6, 7]. Adequate amounts of water are important during flowering and fruit set season to achieve good production [8].

Rainfall is not sufficient to meet the commercial citrus production water requirements [3]. Citrus trees are evergreen, require consistent moisture and should be irrigated all year-round, especially during active growth periods [9], except where severe droughts cause restrictions in water that is available for irrigation [3]. Moisture stress is a limiting factor in citrus production because rainfall is often poorly distributed and deficient in most cases [10]. It is necessary to supplement moisture by irrigation during dry and low rainfall seasons to ensure that moisture stress does not supress growth, development and production of citrus fruits [11]. Drip irrigation, micro-sprinkler and overhead sprinkler irrigation systems are commonly used in citrus production [12]. Citrus irrigation and nutrition are cultural practices that attempt to cope with rainfall variability [13]. Citrus trees require a balanced nutrition program and a good water management system formulated to provide specific needs for maintenance and for expected yield and fruit quality [13].

Global climate changes have led to changes in rainfall patterns, rainfall reduction and an increase in dry spells and droughts reducing soil moisture [14]. Increases in temperature coupled with more rainfall variability due to the changing climate reduce crop productivity. Where most crops are not irrigated, food production will drop. Rainfall is an important variable which have direct and indirect effects on agricultural crops. Rainfall is erratic and unpredictable [15]. Therefore, rainfall variation increases moisture stress in citrus trees, which then affects the productivity. It is important to understand the consequences of rainfall variability on citrus production as it has implications on food security. This paper looks at the relationship between rainfall variability and citrus production. Materials and methods used in this research are outlined following this introduction. The major findings of this research are discussed and presented in the next section before drawing concluding remarks.

2. Materials and Methods

Data used for this study were secondary monthly rainfall data, monthly irrigation practices and annual citrus production statistics from relevant government departments and farm records from 2006 to 2016. Due to the confidentiality of production data farm names are not mentioned. Three irrigated citrus farms, Farm 1, 2 and 3, respectively, linked to three weather stations were used for this study. Farm 1 is linked to New Agatha-BOS, Farm 2 is linked to Westafalia while Farm 3 is linked to Vergelegen weather station.

Monthly rainfall data for Westafalia, Vergelegen and New Agatha-BOS weather stations was obtained from South African Weather Service (SAWS) to examine rainfall variability. Monthly citrus irrigation hours for the growing phase were obtained from the three farms to establish the water requirements for citrus fruit trees for each season. Secondary annual citrus production data was obtained from the three farms to assess the influence of rainfall variability on citrus production. The citrus calendar in South Africa starts in spring (September) of the previous year and ends in winter (May) of the following year. Annual rainfall data was divided into three periods (citrus growth cycle) which are the flowering, growth and maturity seasons based on the citrus calendar. The three periods were divided to justify the importance of rainfall on the life cycle of citrus fruit crops.

The Precipitation Concentration Index (PCI) at seasonal scale (citrus growth cycle) was applied to examine seasonal rainfall characteristics in the study area for the period 2006 to 2016 based on the citrus production calendar. PCI is a tool used to determine annual or seasonal rainfall variability. PCI represents rainfall variability for each cropping season and shows the characteristics of the seasons [16]. It should be noted that rainfall variation as measured by PCI is about rainfall distribution through the specific season. The distribution is not concerned with the total amount of precipitation received, but when precipitation is received during the season. Whether a season was a drought or not is of no consequence to PCI. Therefore, PCI indicates whether rain was spread evenly through the season or not. The following equation was used to calculate the seasonal rainfall distribution:

$$PCI_{seasonal} = \frac{\sum_{i=1}^{4} pi^2}{(\sum_{i=1}^{4} pi\ )^2} . 100$$

Where: *PCI* = Precipitation Concentration Index; *Pi* = Monthly precipitation in month *i* and *Σ* = summation over 4 months.

According to Oliver [16] PCI values of less than 10 indicate uniform precipitation distribution (low precipitation concentration). Values between 11-15 indicate moderate precipitation concentration, values between 16-20 indicate concentrated (irregular distribution), values between 21-50 indicate highly concentrated (strong irregularity) and values greater than 50 indicate isolated (irregular). Simple linear regression analysis was adopted to establish the relationship between rainfall variability and irrigated citrus production. The r^2 statistic determined the direction and strength of the relationship. The *p*-value was used to determine the statistical significance of the relationship.

3. Results and Discussion

Seasonal Rainfall Characteristics

Results of seasonal rainfall characteristics of the Greater Tzaneen Municipality within the period 2006 to 2016 are presented in Table 1, 2 and 3. PCI calculated on seasonal scale of the citrus growth cycle varies across the study area from the lowest value of 25 in the 2012/2013 season during the flowering quarter to the highest value of 99 in the 2013/2014 season of the maturity quarter (Table 3). Results of the three tables show a strong irregularity in the distribution of rainfall with values in the range of 21-50. The reason for the irregular seasonal rainfall distributions is that some months of the seasons received rainfall above and below normal. This explains the motive for the general use of supplementary irrigation to make up the water requirements for citrus fruit trees during the flowering, growth and maturity periods. According to the study by Nsubuga *et al.* [17] locations with higher mean rainfall have relatively lower rainfall concentrations, while areas with lower mean rainfall have relatively higher rainfall concentrations.

Seasons which experienced isolated rainfall received most of the rain during the wet period (January-April) as shown in Table 2. The results agree with that of Ngongondo *et al.* [18] who analyzed rainfall distribution for the seasons from 1960 to 2007 for several locations across Malawi using the PCI. The results of the study indicated that most of the locations had high to very high concentrations of rainfall. Higher PCI values are an indication that rainfall is more concentrated or confined to a few rainy days during the months of the seasons. Results show that rainfall in the study area is usually highly concentrated. Similar studies in other parts of Africa such as Malawi [19] and Ghana [20] point out that varying degrees of rainfall concentration and seasonality characterize the distribution of rainfall in Africa.

TABLE 1. Seasonal Rainfall Distribution (Westafalia Weather Station)

Period	(September - December) Flowering			(January- April) Growth			(May- Aug) Maturity		
Season	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics
2006/2007	544	26	Highly concentrated	207,4	46	Highly concentrated	54,6	41	Highly concentrated
2007/2008	509,6	29	Highly concentrated	304	40	Highly concentrated	31,8	35	Highly concentrated
2008/2009	384	42	Highly concentrated	530,2	36	Highly concentrated	108,6	36	Highly concentrated
2009/2010	423,2	44	Highly concentrated	545,4	26	Highly concentrated	41,6	49	Highly concentrated
2010/2011	515,8	44	Highly concentrated	851,6	39	Highly concentrated	38,6	31	Highly concentrated
2011/2012	192,4	38	Highly concentrated	386,4	34	Highly concentrated	19,4	33	Highly concentrated
2012/2013	469,7	27	Highly concentrated	797,4	54	Isolated	22,8	33	Highly concentrated
2013/2014	388,2	43	Highly concentrated	594,6	29	Highly concentrated	36,6	30	Highly concentrated
2014/2015	215,2	42	Highly concentrated	275,4	26	Highly concentrated	10	75	Isolated
2015/2016	213,6	35	Highly concentrated	275,8	38	Highly concentrated	45	49	Highly concentrated

Rainfall variability and Citrus production

Results of the relationship between rainfall variability and citrus production in the study area for the period 2007 to 2016 is presented in Figure 1. The relationship was consistent showing ±5% margin of error at 95% confidence level. Results show a weak positive relationship between rainfall variability and citrus production (p>0,05 and r^2 <0,5) in all three farms during the period under review. This can be attributed to increasing temperatures and high rainfall variability in the area. Result indicated that the annual amount of rainfall in Greater Tzaneen Municipality is not stable and this reflects on the annual yield of citrus. It can be observed from Figure 1 that the annual output of citrus crops varies significantly with the annual rainfall distribution. According to the results rainfall variability does not significantly affect citrus productivity. This suggests that other production factors also influence citrus production. The experience of low rainfall between 2007-2016 particularly during the flowering and growing seasons could have affected the establishment of citrus fruit crops. Rainfall variability from season to season greatly affects soil water availability, and thus pose great risks to citrus production.

TABLE 2. Seasonal Rainfall Distribution (Vergelegen Weather Station)

Period	(September - December) Flowering			(January - April) Growth			(May - August) Maturity		
Season	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics
2006/2007	525.1	46	Highly concentrated	454	28	Highly concentrated	62.5	52	Isolated
2007/2008	1030	27	Highly concentrated	862.8	37	Highly concentrated	49.2	37	Highly concentrated
2008/2009	748.7	36	Highly concentrated	953.2	37	Highly concentrated	105.6	35	Highly concentrated
2009/2010	666.8	43	Highly concentrated	1134.1	31	Highly concentrated	54.2	34	Highly concentrated
2010/2011	771.2	47	Highly concentrated	1353.2	49	Highly concentrated	69.4	31	Highly concentrated
2011/2012	635.3	35	Highly concentrated	572.7	32	Highly concentrated	13.8	28	Highly concentrated
2012/2013	808.7	26	Highly concentrated	1345.1	49	Highly concentrated	85.8	30	Highly concentrated
2013/2014	690	38	Highly concentrated	611.4	31	Highly concentrated	23.9	69	Isolated
2014/2015	419	43	Highly concentrated	464.4	34	Highly concentrated	13.1	35	Highly concentrated
2015/2016	433.7	29	Highly concentrated	708.7	47	Highly concentrated	80.1	45	Highly concentrated

TABLE 3. Seasonal Rainfall Distribution (New Agatha-BOS Weather Station)

Period	(September - December) Flowering			(January - April) Growth			(May - August) Maturity		
Season	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics	Total Precipitation	PCI	Characteristics
2006/2007	768,3	48	Highly concentrated	398,3	30	Highly concentration	61,1	44	Highly concentrated
2007/2008	877,5	27	Highly concentrated	736,4	35	Highly concentrated	51,4	33	Highly concentrated
2008/2009	478,6	39	Highly concentrated	877,8	41	Highly concentrated	110	31	Highly concentrated
2009/2010	644,3	52	Isolated	898,1	30	Highly concentrated	47,5	36	Highly concentrated
2010/2011	666,2	48	Highly concentrated	1151,7	42	Highly concentrated	78,8	45	Highly concentrated
2011/2012	485,2	38	Highly concentrated	476,8	32	Highly concentrated	12,9	27	Highly concentrated
2012/2013	642,2	25	Highly concentrated	949,1	54	Isolated	76,9	46	Highly concentrated
2013/2014	621,7	41	Highly concentrated	803,1	30	Highly concentrated	20	99	Isolated
2014/2015	357,3	43	Highly concentrated	454,9	28	Highly concentrated	16,5	56	Isolated
2015/2016	319,7	29	Highly concentrated	658,2	53	Isolated	74,6	47	Highly concentrated

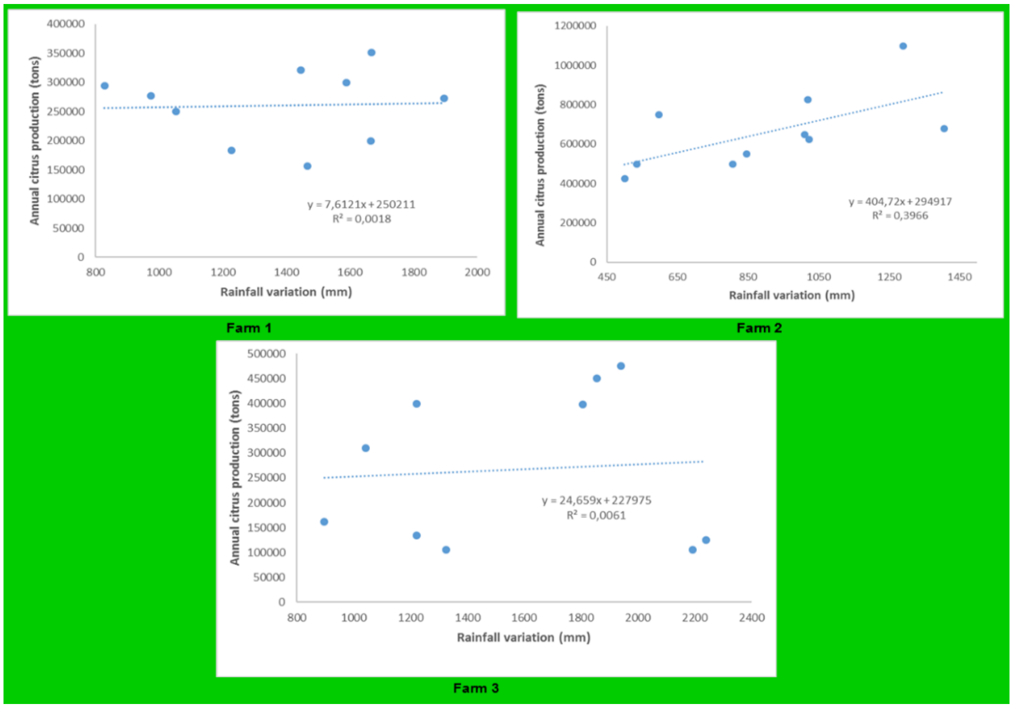


Figure 1. Rainfall Variability and Citrus Production Relationship

4. Conclusions and Recommendations

Citrus farmers in Greater Tzaneen Municipality rely on rainfall and irrigation to achieve good production. This study has shown that rainfall in the area does not have a definite distribution pattern. The above analysis revealed a weak positive relationship between rainfall variability and citrus production. It was observed that rainfall variability influences citrus production, as rainfall is the main source of water for citrus growth. However, its influence is insignificant indicating the power play of other environmental factors such as temperature increase, wind, topography, humidity, atmospheric pressure, soil fertility, pest infestation and diseases among others. Therefore, farmers should also invest in other production factors other than water availability because it is but one of the pieces of the citrus production puzzle. such investments may include soil enhancement to reduce soil moisture loss during the dry and dry-wet periods. This has the potential to reduce moisture stress that can suppress citrus growth, development and production.

It is recommended that further research be carried out on the effect of other weather elements such as temperature increases on citrus production. Research is also required on the selection of citrus varieties that will do well with limited rainfall and on the effects of rainfall variations on the citrus market. Since irrigation and rainfall are related, research is required to find a proxy variable that will constitute both irrigation and rainfall on the influence of rainfall variability on citrus production.

Acknowledgments: We appreciate the National Research Foundation (NRF) Research and Innovation for funding this research project. Irrigated citrus farm owners in Greater Tzaneen Municipality for the provision of production data. South African Weather Service (SAWS) for the provision of rainfall data.

References

1. IPCC (Intergovernmental Panel on Climate Change)., 2011. Extreme Weather and Climate Change. Working Group II Report (WGII).
2. Intergovernmental Panel on Climate Change. 2012: Managing the Risks of Extreme Events and Disasters to Advance Climate Change Adaptation. A Special Report of Working Groups I and II of the IPCC. Cambridge and New York: Cambridge University Press.
3. DAFF (Department of Agriculture, Forestry and Fisheries). 2016. Local market fruit sales data. Pretoria: Directorate of Agricultural Statistics.
4. Meza-Pale, P. and Yúnez-Naude, A., 2015. The Effect of Rainfall Variation on Agricultural Households: Evidence from Mexico. In 2015 Conference, August 9-14, 2015, Milan, Italy (No. 212457). International Association of Agricultural Economists.
5. Potelwa, X.Y., Lubinga, M.H. and Ntshangase, T., 2016. Factors Influencing the Growth of South Africa's Agricultural Exports to World Markets. European Scientific Journal, ESJ, 12(34).
6. Morgan, K.T., Zotarelli, L. and Dukes, M.D., 2010. Use of irrigation technologies for citrus trees in Florida. Horttechnology, 20(1), pp.74-81.
7. Obreza, T.A. and Schumann, A., 2010. Keeping water and nutrients in the Florida citrus tree root zone. HortTechnology, 20(1), pp.67-73.
8. Shirgure, P.S., 2013. Research review on irrigation scheduling and water requirement in citrus. Scientific Journal of Review, 2(4), pp.113-121.
9. Shirgure, P.S., 2012. Micro-irrigation systems, automation and fertigation in citrus. Scientific Journal of Review, 1(5), pp.156-69.
10. Dabrowski, J.M., Murray, K., Ashton, P.J. and Leaner, J.J., 2009. Agricultural impacts on water quality and implications for virtual water trading decisions. Ecological economics, 68(4), pp.1074-1082.
11. Asif, M., Ahmad, M., Mangrio, A.G., Akbar, G. and Wahab, A., 2015. Design, Evaluation and Irrigation Scheduling of Drip Irrigation System on Citrus Orchard. Pakistan Journal of Meteorology, 12(23).
12. DAFF (2013). Climate Change Adaptation and Mitigation Plan for the South African Agricultural and Forestry Sectors. Pretoria: RSA, Department of Agriculture, Forestry and Fisheries (in preparation).
13. Zekri, M., 2011. Factors affecting citrus production and quality. Trees.
14. Mupangwa, W., Walker, S., Masvaya, E., Magombeyi, M. and Munguambe, P., 2016. Rainfall risk and the potential of reduced tillage systems to conserve soil water in semi-arid cropping systems of southern Africa. AIMS Agriculture and Food, 1(01), pp.85-101.
15. Bewket, W., 2009. Rainfall variability and crop production in Ethiopia: Case study in the Amhara region. In Proceedings of the 16th International Conference of Ethiopian Studies (pp. 823-836). Trondheim, Norway: Norwegian University of Science and Technology.
16. Oliver, J.E., 1980. Monthly precipitation distribution: a comparative index. The Professional Geographer, 32(3), pp.300-309.
17. Nsubuga, F.N.W., Olwoch, J.M. and Botai, O.J., 2014. Analysis of mid-twentieth century rainfall trends and variability over southwestern Uganda. Theoretical and applied climatology, 115(1-2), pp.53-71.
18. Ngongondo, C., Xu, C.Y., Gottschalk, L. and Alemaw, B., 2011. Evaluation of spatial and temporal characteristics of rainfall in Malawi: a case of data scarce region. Theoretical and applied climatology, 106(1-2), pp.79-93.
19. Kumbuyo, C.P., Yasuda, H., Kitamura, Y. and Shimizu, K., 2014. Fluctuation of rainfall time series in Malawi: An analysis of selected areas. Geofizika, 31(1), pp.13-28.
20. Ndamani, F. and Watanabe, T., 2014. Rainfall variability and crop production in Northern Ghana: The case of Lawra District.

Techno-chemical assessment of clayey materials for potential industrial application in Thulamela Municipality of the Limpopo Province, South Africa

GO Akintola*, F. Amponsah-Dacosta and SE Mhlongo

Department of Mining and Environmental Geology, University of Venda, South Africa
*Email of corresponding author: georgeakintola540@gmail.com

Abstract

Thulamela Municipality has vast deposits of clayey materials which are locally used for manufacturing of burnt bricks. The socio-economic development and expansion have consequently increased the demand of this material for other purposes apart from brick making. This study aimed at determining the mineralogical, chemical and mechanical properties of the clayey materials found in Thulamela Municipality so as to establish its suitability for industrial utilization. These properties were determined using X-ray diffractometry (XRD), X-ray fluorescence spectroscopy (XRF), and Atterberg Limits as well as sieve analysis techniques. Other determined properties of the clayey materials were cation exchange capacity (CEC), pH and colour of the material, and their particle size distribution. The studied materials were found to be composed of silt to sand fractions while conspicuously dominated by kaolinite with few chlorite clay minerals. Relatively high concentration of silica, alumina and ferric oxide marked the material and the CEC values ranged from 17.6 to 42. 73 meq/100g. Technological test reveals high to medium compressibility inorganic silt and clay with grain sizes ranging from silt to sand fractions. Based on these characterization and empirical evaluation of properties, the studied clayey materials indicated their possible suitability for sanitary wares, table wares, refractory material, floor tiles and pottery making.

Keywords: clayey materials, industrial utilization, thermal behavior, clay characteristics, Thulamela Municipality

1. Introduction

South Africa is well-known for mining of high value minerals such as diamond, gold and platinum group elements. However, industrial minerals such deposits constitute suitable raw material for industrial products. In Thulamela Municipality, the use of clayey materials of the Sibasa Formation for making of burnt bricks has a long history because of the abundance of the clayey deposit. Due to the socio-economic development and expansion of the municipality, the demand for various clay products other than bricks is increasing. This has been primarily driven by increase in construction activities, paint and plastic productions as well as a ceramic water filter factory in the region and elsewhere in the country. This demand cannot be met with the traditional methods of manufacturing the products thus there is a need to gain better understanding of the characteristics of clay in the Thulamela Municipality and to establish the suitability of the variety of clay for different industrial applications. Some studies assessed the application of clayey materials in different industries such as mining, oil and gas, agriculture, construction and engineering, environmental and processing industries [1, 2]. Harnessing the several clayey materials in the study area for these various applications requires in-depth understanding of their properties.

Knowledge of clay properties for industrial application in many regions of South Africa is well documented but inexhaustive. The Vryheid Formation of the Karoo sequence was investigated and found to have properties suitable for refractoriness and brick making. The extensive shale underlying Grahamstown exhibited diverse properties in terms of mineralogy, vitrification, plasticity and particle size distribution in a manner similar to Jurassic-Early Cretaceous clay deposits in Tunisia used for ceramic purposes [3, 4, 5]. The portion of Fundudzi Formation found in Makhado Municipality which is an adjoining region to the present study area was investigated by Dacosta et al. [6] and found suitable for water filter production. Presently, the clayey deposit is being exploited for the commercial manufacturing of water purification filters in Makhado Municipality.

The Thulamela region is endowed with vast clayey deposits whose properties are poorly known. This study was conducted with the aim of assessing the clayey materials of the Sibasa Formation found in Thulamela Municipality for their possible industrial utilization. The assessment was based on the clayey material's thermal, morphological, mechanical, mineralogical, chemical and physical properties. The main outcome of the characterization is expected to provide a baseline information for prospective investors in various products such as ceramics, water filters, building bricks, tiles, insulators, plastics and paints. Moreover, this study is the first conducted to valorise the Sibasa clayey Formation underlying the larger parts of Thulamela Municipality of South Africa. This is significant for expansion of the social-economic development of the region which has a potential to empower the human capital of the region through employment opportunities that can potentially reduce poverty in the region.

Description of the Study Area

The study area is situated between latitude of 22° 15´ 00"S and 22° 30´ 00"S and the longitude of 30° 09´ 00"E and 31°00´56"E but largely underlain by the rocks of the Sibasa Formation of the Soutpansberg Group. Barker et al. [7], indicated that the Sibasa Formation which is about 3000m thick comprises pyroclastic lava with minor intercalation of sedimentary and tuffaceous rocks which are found underlain the Thulamela Municipality. In addition, Barker [8] noted that the pyroclastics rocks of Sibasa Formation can reach estimated thickness of 200m in the Mutshindudi Natal House agglomerate north of Thohoyandou and best developed in the Kruger National Park. The geological formations that underlain the different parts of Thulamela Municipality are shown in Figure 1.

2. Methods and Materials

The study was conducted on the clayey deposits of Sibasa Formation which widely underlies the Thulamela region. A total of fifteen clayey soil samples were collected from five different locations designated as Lwa, Nan, Mat, Mav, and Man. Based on texture and colour variation, three samples were randomly collected from each location and thoroughly mixed until homogeneity was achieved. The samples were then quartered into 3kg samples. The five representative samples corresponding to each location were taken to the laboratory for analyse. Prior to the laboratory analysis, the colours of raw clayey samples were determined using the Munsell colour chart. The chart consists of standard colours in different hues, value and chroma.

Mineralogical analysis of clayey materials

The mineralogical composition of fine powders of the bulk fractions of the samples were semi-quantitatively determined using X-ray Diffraction (XRD) analysis. The XRD is used mainly to reveal the crystallinity and concentrated clay mineral phases present in the samples. The powder of finely ground homogenous clay fractions (i.e. <2μm) were obtained by timed sedimentation. After glycolation and oven-drying the samples at 300 °C for 1 hour, each sample was tightly mounted on an oriented sample holder with very little pressure using black loading preparation technique for XRD analysis. The analysis was performed using a PANalytical X'Pert Pro powder diffractometer equipped with an X'Celerator detector coupled with receiving slits, variable divergence and Fe-filtered Cu-Kα radiation. While the receiving slit was set at 0.040°, the counting area was from 5° to 70° on a 2θ scale at 1.5s. The clay phases were identified using X'PertHighscore plus software. Rietveld refinement (Autoquan Program) employed a least square matching algorithm based on sample parameters and instrumental parameters to estimate relative phase amounts in percentage.

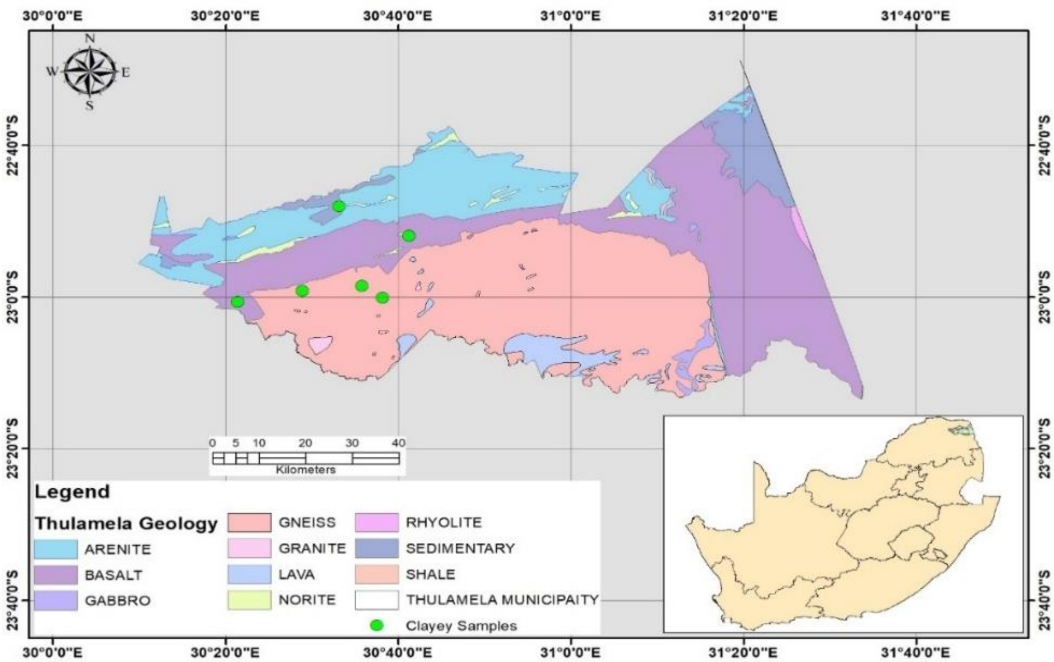


Figure 1. The map showing the distribution of different geology that underlies Thulamela Municipality.

Major and trace element analysis of clayey materials

The major and trace element geochemical analyses of the fine bulk clay were quantitatively estimated using the PANalytical AXios X-Ray fluorescence (XRF) spectrometer. The samples were pulverized to obtain <32μm fractions and then calcined at 1 000 °C for a minimum period of three hours to oxidize iron (ii) oxide (Fe^{2+}) and sulphur (S). Pressed powder pellets for XRF analyses were prepared using 6g of sample powder and 12g of boric acid as a binder. The mixture was fused into a steel cup and pressed at a pressure of 30 tons in a hydraulic set. The XRF instrument equipped with a 4 KW Rhodium (Rh) tube was used to analyse major oxides by inserting a glass disks containing 1g calcined sample, 8 g flux composed of 35% alkali borate ($LiBO_2$) and 64.71% lithium tetra borate ($Li_2B_4O_7$) as oxidant at 1050 °C in the XRF equipment.

Sieve analysis of the samples

The grain size analysis was conducted by first air-drying the soil samples until a constant mass was achieved and about 500g of each weighed soil sample was shaken through a stack of sieves with openings of decreasing size from top to bottom using a mechanical shaker. The mass of soil retained and passing each sieve was weighed and recorded after the soil was shaken on a mechanical shaker. The percent of fines on each sieve size was determined. The 50g soil sample which passed through No 200 sieve or <75µm fractions were treated with a hydrogen peroxide (H_2O_2) solution to oxidize organic material. The resultant slurry was mixed with 125 ml of 4% sodium hexametaphosphate ($NaPO_3$) solution which acted as the deflocculating agent. Agitation was achieved by turning the sedimentation cylinder upside down and back 60 turns for a period of one minute and later placed beside the control cylinder filled with distilled water. Measurement of sedimentation started at time-t, as the hydrometer and thermometer were inserted into the soil suspension.

Determination of plasticity and CEC

The degree of plasticity of studied samples was achieved through determination of Atterberg's liquid (LL) and plastic limit (PL) using Casagrande apparatus in accordance with the ASTM standard. The CEC of the clay sample was determined using exchangeable cation extraction and an atomic absorption spectrometer. About 25 g of the sample was initially oven-dried at 110 °C for six hours until constant weight was achieved. The sample pH was later adjusted to near-neutral when diluted with 1 litre of NH_4OH inside a 500 ml conical flask. The near-neutral solution was then thoroughly mixed with 125 ml of 1M NH_4O_{AC} for 12 hours using a mechanical shaker. With the aid of a suction machine, the solution was poured into a funnel lined with filter paper. The filtrate was re-filtered until the solution was clear by pouring 25 ml of 1M NH_4O_{AC} into the suction clay solution. The cleared filtrate was then poured into a beaker for determination of exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} using the atomic absorption spectrometer. The results of detected cations were displayed on the computer screen connected to the spectrometer and given as ml/g when were then later converted to meq/100g.

pH of the samples

To determine the pH of the soil, about 100 ml of de-ionized water was added to 100 g of pulverized clay samples placed in a 100 ml beaker. The clay solution was stirred continuously for an hour using a stirring rod until a homogeneous solution was achieved. This was to allow the pH of the soil slurry to stabilize. The pH meter was calibrated with buffer solutions of the pH values of 4.00 and 7.00 to standardize the acid-base condition. The thermometer was used to measure the temperature after which the pH meter electrodes were inserted into the soil slurry. After two minutes, the value displayed on the pH meter was read and recorded.

3. Results

The results of the mineralogical analysis of clay from the Thulamela Municipality are presented in Table 1. The results showed the presence of kaolinite and chlorite clay minerals and non-clay minerals which included quartz, feldspar, talc and Hornblende. In most samples, kaolinite content ranged from 22.80% to 59.26% with the samples from Lwa having the highest value. The kaolinite mineral was found as a main clay mineral in samples from Lwa (59.26%) and Mat (25.19%) whose values were comparatively higher than Man (22.80%) although absent in chlorite content. Chlorite was present in all samples except in

Lwa and Mat samples while the materials from Man and Nan had higher values of 9.07% and 8.83% respectively.

The geochemical result for the studied clay showed the presence of major element such as Si, Al, Na, K, Mg, Ca, Ti, Fe and Mn in their oxide forms. The result showed varying amount of silica (34.1-59.5%), alumina (14.30-22.4%), sodium oxide (0.1-1.3%), potassium oxide (0.3-3.0%), magnesia (0.1-1.3%) and calcium oxide (0.1-1.7%) in the studied samples (see Table 2). The fluxing oxides of the samples include K_2O, Na_2O, CaO, MgO, MnO and P_2O_5 which varies slightly in content with average abundance ranging from 0.06% to 1.78% (see Table 2). The Fe_2O_3 and TiO_2 contents in all studied samples average at 9.2% and 1.3% respectively.

TABLE 1. Mineralogical analyses of the raw clay from Thulamela Municipality.

Location		Mineral composition (%)						
		Kaolinite	**Chlorite**	**Quartz**	**Plagioclase**	**Microcline**	**Hornblende**	**Talc**
Lwa	L1	59.26	-	22.61	-	-	9.23	
Nan	L2	-	8.83	37.39	33.09	16.35	4.34	-
Mat	L3	25.19	-	59.87	-	-	1.95	5.79
Mav	L4	-	8.03	42.02	38.16	7.53	4.26	-
Man	L5	22.80	9.07	34.88	24.82	4.66	-	13.35

TABLE 2. Mineralogical analyses of the raw clay from Thulamela Municipality.

Location		Major oxides composition (%)							
		SiO_2	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**
Lwa	L1	34.1	22.4	25.5	0.2	0.1	0.1	0.1	0.5
Nan	L2	59.5	16.0	4.8	0.1	1.3	1.2	1.3	3.0
Mat	L3	48.3	20.10	14.6	0.1	0.4	0.3	0.1	0.3
Mav	L4	54.1	14.30	5.9	0.1	1.2	1.7	0.9	1.6
Man	L5	47.0	19.50	9.8	0.1	0.8	1.3	0.1	1.3

All samples showed homogeneous distribution of sand size fractions (2 to 0.05mm) with compositional values ranging from 86.98-98.66% (see Figure 2a). This abundance was on the decreasing order of Mav > Nan > Mat > Man > Lwa samples. Similarly, the fines fraction with size diameter ranging from 2µm to 0.05mm showed heterogeneous abundance with average value greater than 10% particularly in Lwa sample. Meanwhile, the gradational estimation depicted that all the soils collected from Lwa, Man, Mav and Mat showed a well sorted and graded pattern with exception of soils from Nan area. This could be due to the presence of relative higher sand size fractions and lowest fines sizes compared to other samples.

The plasticity properties of the clay deposits exhibited heterogeneous behaviors as revealed in plastic limit (PL), liquid limit (LL) and plastic index (PI) values presented in Figure 2b. In Figure 2b, the A-line separated the inorganic clay above the line from the inorganic silts below the line. Hence, the Lwa samples indicate inorganic silts of high compressibility and organic clays properties due to their location below the A-line in the plasticity chart. The samples from Nan, Mav and Man had LL values that are greater than 50 but lower PI value (<30) when compare with Lwa samples. Hence, it indicated that these soils are inorganic silts with high compressibility and organic clays properties since it plotted below the A-line of plasticity chart. The Mat samples were found to be having medium plasticity properties with LL values ranging from 30 to 50 and plotted below the A-line on the chart where intermediate PI value ranged from 15 to 21. According to the Unified Soil Classification System, soils from Lwa can be considered elastic silt (MH) due to their coefficient of uniformity (C_u) that is greater the 3 and that they have a liquid limit values that are greater than 50% which plotted above the "A" line (See Figure 2b). Furthermore, soils from Man which plotted below the "A" line can be inorganic silt (ML) while those from Nan, Mat and Mav are regarded as clayey sand.

The raw clays varied in hue/value/chroma with their corresponding tonality shades (see Table 3). Their hue/value/chroma ranged from 2.5YR/5/8 to 10YR/5/1 with corresponding tonality of red and gray. Clay that exhibited pale yellow to gray colour suggested reducing depositional environment due to leachable Fe resulting from hydromorphic conditions. The reddish to very pale brown clay indicated that they formed or deposited under oxidizing zones where Fe was enriched in the study area such as Lwa and Nan. Samples from Mat, Mav and Man whose Fe content is relatively high (>5%) exhibited a deep tonality.

The CEC values of the samples widely varied from 17.60 to 42.73 meq/100g and the pH exhibited similar near-neutral-pH values ranging from 6.13 to 7.50. Samples from Man and Mav had relatively high CEC values which were recorded to be above 30 meq/100g compared to other samples in which their CEC values were below 30 meq/100g.

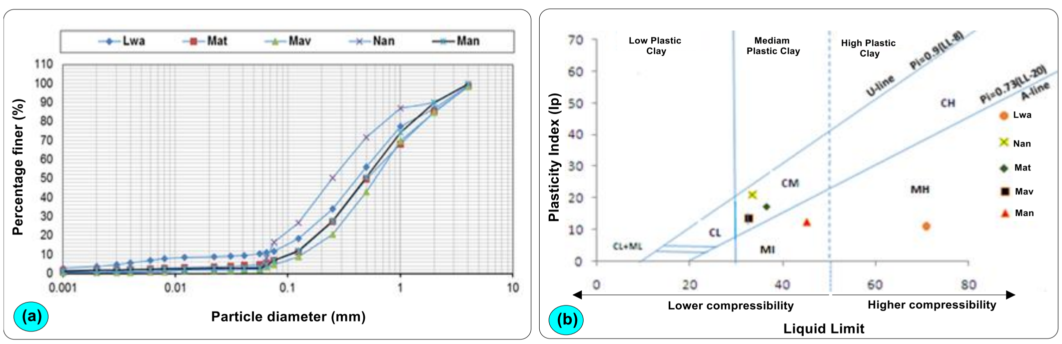


Figure 2. The gradational curves of the soil studied (a) and the plasticity of the soil (b).

TABLE 3. Summary of physical properties of studied clay samples

Location	Hue/value/chroma	Colour	Soil pH	CEC (Meq/100g)
Lwa	5YR/5/8	Yellowish red	6.13	20.69
Nan	7.5YR/5/4	brown	7.02	17.60
Mat	7.5YR/4/6	Strong brown	6.99	27.86
Mav	7.5YR/5/8	Strong brown	7.5	37.05
Man	2.5YR/5/8	Red	6.78	42.73

4. Discussions

The Sibasa clayey material underlying Thulamela region mainly composed of kaolinite and chlorite clay mineral in addition to non-clay minerals. The kaolinite minerals suggested that the clayey deposits in the Municipality were deposited in deltaic environment where fluvial influence could rapidly remove the Mg^{2+} and K^{+} ions from weathered solution of parent mineral [9, 10]. This environment suggests tropical humid condition with alternating and more pronounced wet seasons and less dry season which tend to increase water movement for rapid and adequate removal of the ions in the weathered solution. The presence of chlorite clay mineral suggested deep burial of the Sibasa Formation and possible low temperature regional metamorphism. The absence of smectite clay mineral in Thulamela region indicated that the region is not one of the low-lying surfaces which are indicative of marine environments under dry seasons with alternating less pronounced wet season and characterized with poor drainage or water movement [11, 12]. Implicitly, the weathering condition largely determines whether soils containing kaolinite and smectite can develop from same parent rock. High shrinkage properties were synonymous with materials enriched with kaolinite mineral [13, 14]. This shrinkage may be less when compared to smectite mineral which could shrink rapidly at temperature above 450°C due to expulsion of interlayer and surface water. Furthermore, samples which were rich in chlorite minerals exhibited relatively low shrinkage. However, the drying trends of the studied clayey material encourage their suitability for fast drying processes like refractory since they could withstand temperature >1000°C and showing characteristics to other clays used in Tunisia [15].

The chemical, mineralogical, particle size, plasticity and mechanical properties were used to assess the possible industrial application of the studied samples from Thulamela Municipality. Based on the chemical results of the samples enriched in kaolinite mineral were plotted into the Whitebody domain using the Riley's diagram after Fabbri and Fiori [16] as shown in Figure 3a. The samples from Nan and Mav that plotted outside the Whitebody domain may be due to dominances of chlorite mineral and absence of kaolinite and smectite clay minerals. In comparison with other studies [17-19], a raw material comprising kaolinite mineral ranging from 20 to 85% and medium to high plasticity and compressibility could be suitable for sanitary application. However, the content of iron and titanium oxide in Lwa, Mat and Man samples might require reduction since they impart various colors such as red, yellow and brown of Whitebody product such as sanitary wares. The work of Fabbri and Fiori [16] noted that the clays with chemical composition of 47% of SiO_2, 43 % of Al_2O_3 and 10% of total oxides can be an ideal composition for manufacturing of whiteware products

Furthermore, it was observed that the Al_2O_3 content has a direct relationship to refractoriness and mechanical strength properties of the soil. Samples from Lwa, Mat and Man which were enriched with kaolinite mineral had higher Al_2O_3 content and increasing thermal stability value. This may result from the chemical covalent bonding that formed between Si-Al in the crystal lattice which required higher temperature to break. The higher SiO_2 content in most of the clayey samples suggested their capability to resist chemical attack although may decrease its plasticity for ceramic use but increase the drying and calcination processing for refractoriness uses. However, raw clay with mineral composition range of quartz (26-36), feldspars and non-clay minerals (30-40) and clay minerals (20-24) were suggestive to be ideal for manufacturing of ceramic porous body. Several studies have alluded that as the Al_2O_3 content increases the refractoriness and mechanical strength. The Winkler diagram shown in Figure 3b used the particle size (<2 μm - >20 μm) parameter to assess the clayey materials for manufacturing of common bricks, vertically perforated bricks, roofing tiles and light weight bricks and hollow products. The variation in the particle diameters Nan and Mav can be suitable for manufacturing hollow products while Lwa and Man clays showed possible use for hollow products such as pottery making.

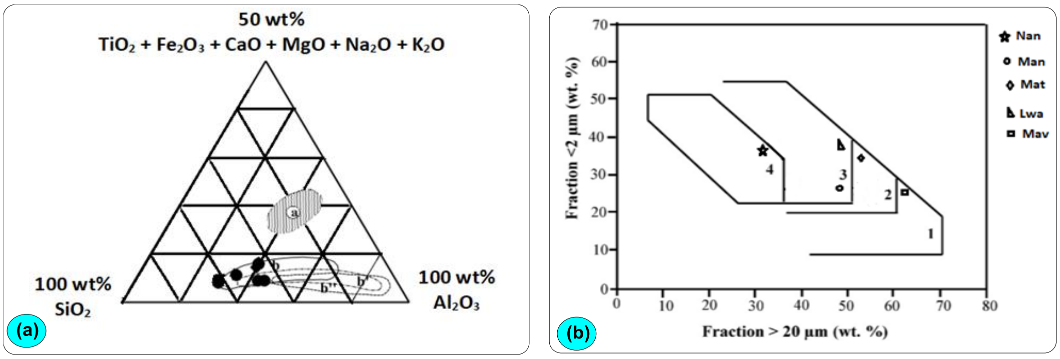


Figure 3. (a) Riley's plot showing possible clay utilization for a- red stoneware; b, b', b'' white stoneware B: (b) Winkler's chart showing potential use of clay for (1) common bricks, (2) vertically perforated bricks, (3) roofing tiles and masonry bricks (4) hollow products. (b) Workability chart showing possible industrial use of the studied clays (after Bain,1987)

5. Conclusion

The clayey materials of Sibasa Formation underlying the Thulamela Municipality are mainly composed of kaolinite and chlorite minerals but associated with quartz, plagioclase, microcline, goethite, anatase and talc. The iron and titanium oxides content are relatively high thus influenced the material's firing colour and probable suitability for whiteware products. Most of the clayey material exhibited relatively low shrinkage due to kaolinite and chlorite minerals contents. The clays showed inorganic silt and clayey sand with medium plasticity properties. The clayey material or soils also showed interesting properties for potential application in refractory, water purification and tableware's industries apart from bricks in which it is currently being used. However, beneficiation of the clayey materials is recommended to be conducted to determine their technological application.

Acknowledgements: The research grant provided by the University of Venda Research office is highly appreciated. The authors acknowledged the supports received from Mr, Muzerengi Confidence and Nemapate during sample preparation at the University of Venda Geology laboratory. We extend our special thanks to the XRF and XRD units of University of Pretoria and Mineralogy division of Mintek for their assistance during laboratory analyses.

References

1. Murray, H.H. Traditional and new applications for kaolin, smectite, palygorskite: A general overview. Applied Clay Sciences, 2000, 17, pp. 207–221.
2. Mahmoudi, S., Bennour, A., Srasra, E. and Zargouni, F. Characterization, firing behavior and ceramic application of clays from the Gabes region in South Tunisia. Applied Clay Science, 2017,135, 215-225.
3. Heckdroodt, R.O. Clay and Clay materials in South Africa. Journal of the South African Institute of Mining and Metallurgy,1991,91(10) pp. 343-363.
4. Mahmoudi, S., Bennour, A., Maguebli, A., Srasra, E., Zargouni, F. Characterization and traditional ceramic application of clays from the Douiret region in South Tunisia. Applied Clay Science, 2016, 127-128, pp. 78-87.
5. M'barek-Jemai M.B., Sdiri, A., Salah, I.B., Aissa, L.B Bouaziz, S., Duplay, J. Geological and technological characterization of the Late Jurassic-Early Cretaceous clay deposits (Jebel Ammar, northeasternTunisia for ceramic industry. Journal of African Earth Sciences, 2017, 129, pp. 282-290.

6. Dacosta, F.A., Muzerengi, C., Mhlongo, S.E., and Mukwevho G.F. Characterization of Clay for Water Filters at Mukondeni Village, Limpopo Province, South Africa. ARPN Journal of Engineering and Applied Sciences, 2013, 8 (1) pp. 927-932.
7. Barker, O.B., Brandl, G., Callgha, C.C., Erikson, P.G and Van der Neut, M. The Soutpansberg and Water Groups and the Blouberg Formation. In: Johnson, M.R., Anhaesser, C.R. and Thomas, R.J. (2006). The Geology of South Africa, Geological Society of South Africa, Johannesburg and the Council of Geosciences, Pretoria, pp. 304-318.
8. Brandl, G. (1999). Soutpansberg Group. In Johnson. M.R. (Ed), Catalogue of South African Lithostratigraphic Units, South African Commission of Stratigraphy pp. 6-41.
9. Santos, A.E., Rossetti, D. Depositional model of the Ipixuna Formation (Late Cretaceous-Early Tertiary), Rio Capim Area, Northern Brazil. Latin American Journal of Sedimentology, 2006 13, 101-117.
10. Refaey, Y, Boris. J, El-Shater, A.H, El-Hadda, A.A., Kalbitz, K., (2015). Clay minerals of Pliocene deposits and their potential use for the purification of polluted wastewater in the Sohag area, Egypt. Geoderma Regional 5 (2015) pp. 215–225.
11. Odoma, A.N., Obaje, N.G., Omada, J.I., Idakwo, S.O., Erbacher, J. Paleoclimate reconstruction during Mamu Formation (Cretaceous) based on clay mineral distributions. Journal of Applied Geology and Geophysics, 2013, 1 (5), pp. 40–46.
12. Ehrmann, W., Schmiedl, G., Hamann, Y., Kuhnt, T., Hemleben, C., Siebel, W. Clay Minerals in late glacial and Holocene sediments of the northern and southern Aegean Sea. Palaeogeogr. Palaeoclimatol. Palaeoecol, 2007, 249, 36–57.
13. Bennour, A., Mahmoudi, S., Srasra, E., Hatira, N., Boussen, S., Ouaja, M., Zargouni, F. Identification and traditional ceramic application of clays from the Chouamekh region in south-eastern Tunisia. Applied Clay Science, 2015, 118, pp. 212-220.
14. Zaied, F.H., Abidi, R., Slim-shimi, N., Somarin, A.k. potentiality of clay raw materials from Gram area (Northern Tunisia) in the ceramic industry. Applied Clay Science, 2015, 112, pp. 1-9.
15. Hajjaji, M., Hachani, B., Moussi, K., Jeridi, M., Medhioub, A., Lopez-Galindo, F., Rocha, J.A., Labrincha, A., Jamoussi, F. Mineralogy and plasticity in clay sediments from north-east Tunisia. Journal of African Earth Sciences, 2010, 57 (1-2), pp. 41-46.
16. Fabbri, B., Fiori, C. Clays and complementary raw materials for stoneware tiles. Mineralogica et Petrographica Acta, 1985, 29A, pp. 535– 545.
17. Burst, J.F. (1991). The application of clay minerals in ceramics. Applied Clay Science 5 (5-6), pp. 421-443.
18. Mikhalev, V.V and Vlasov, A. S. Properties of clays for manufacturing sanitary ware. Glass and Ceramics,2007, 64 (3 – 4), pp. 10 – 13.
19. Manoharan, C., Sutharsan, P., Dhanapandian, S., Venkatachalapathy, R. Characteristics of some clay materials from Tamilnadu, India, and their possible ceramic uses. Ceramica 2012, 58, pp. 412-418

Harnessing waste plant material, rice husk ash, for the production of high-quality silica

L Mulaudzi, WM Gitari* and O Izevbekhai

Department of Ecology and resource management, University of Venda, South Africa
*Email of corresponding author: mugera.gitari@univen.ac.za

Abstract
Silica is one of the most valuable inorganic multipurpose chemical compounds which exists in gel, crystalline and amorphous forms. It is the most abundant oxide on the earth crust. Natural silica can be obtained from rice husk, corn cob ash, cassava periderm, maize stalk, sugarcane bagasse and other agricultural wastes which consists of organic materials and hydrated silica. Disposal of these waste plant parts is a major problem for farmers, they discard them by open incineration or burying which results in environmental pollution. The best approach to manage this waste is to convert them into valuable materials like silica. Silica has also been used as a major precursor for a variety of inorganic and organometallic materials which have applications in synthetic chemistry as catalysts, and in thin films or coatings for electronic and optical materials. This review looks at simple chemical processes for extraction of silica from rice husk ash which is one of the most silica rich raw materials containing about 90-98% silica after complete combustion. Using rice husk as raw material for precipitated silica is superior, cost effective and consumes much lower energy compared to present technology of its production from quartz. Extracting silica from rice husk helps solve the disposal problem and at the same time generates a valuable product.

Keywords: silica, rice husk, extraction, plant material

1. Introduction
Silica (Figure 1), one of the most abundant chemical compounds on earth, is an ubiquitous and widely used chemical compound that exists in three physical forms; crystalline, amorphous and gel [48]. It is found in nature as quartz, in sand, in living organisms and in plants usually combined with a few elements and oxides like aluminum, boron Fe_2O_3, K_2O and others, depending on the source [2]. Even though silica can be mined from ores, the amount that can be obtained from these ores cannot meet the industrial demand [3]. As a result of this, there is the need for alternative sources. Silica has wide and diverse applications and uses [4, 5] but most of these processes require pure silica, manufacture of which requires high energy [48]. Natural silica can be obtained from rice husk, corn cob ash, cassava periderm, maize stalk, sugarcane bagasse and other agricultural wastes [5, 6] This review looks at the chemical processes for extraction of silica from rice husk.

2. Rice production
Rice is an important primary food for about half of the world's population, supplying 20% of the calories consumed worldwide. It is the second most grown crop which produces large quantity of waste. Rice is mostly produced in China, India, Indonesia, Thailand, Vietnam and some parts of Africa. Studies reported by the International Rice Research Institute (IRRI) in the year 2000 estimated that the world's rice production will be 800 million tons in 2025 [7]. According to Dang [8], in 2009 the total rice plantation was 7.3 million ha and production of rice was 38.7 million tons. The Food and Agriculture Organization (FAO) in 2017 reported that the world's rice production is 430 000 tons. Production of rice at this quantity, indicates that there is the likelihood of high quantity of waste.

3. Rice husk

Disposal of waste generated from rice production (rice husk) is poorly managed. It is disposed in an open land which occupies large spaces or burned, this causes environmental and human health problems [9]. Rice husks (Figure 2) are by-products from rice milling industries [10]. They are unavoidable food waste and are mostly available in rice producing countries [11]. Rice husk are produced in abundance at about 80 million tons per year worldwide [12] and since they are from a staple food, its production cannot be reduced, but its waste can be best managed by reuse and recycling [9]. This husk has light weight and high surface area and is one of the most silica rich raw materials containing about 90-98% silica [10]. The use of rice husk as the raw material to extract silica helps reduce waste disposal problems [11]. Extraction of silica from rice husk in an environmentally-friendly manner can reduce the disposal of large quantities of rice husk materials that pollute land, water, and air. By using these wastes, pollution can be reduced, and the wastes can be used as secondary resource to produce valuable materials [5].

Figure 1. Silica

Figure 2. Rice husks

4. Uses of Silica

Silica has been used in different industries, in catalysis, pigments, detergents, pharmaceutical products, electronics, chromatography column packing, ceramics, polymer materials, thin film substrates, thermal insulators, and humidity sensors [5, 13]. It can be used for agricultural purposes as it increases resistance to plant fungal diseases. Silica also can improve environmental stress tolerance and crop productivity [11]. Apart from that, Silica acts as an adsorbent for removing heavy metals from wastewater [14]. It can be used as; an adsorbent, a dehumidifying agent for air and other gases and as filtering agent for clearing juices and in beer purification [48]. Silica is also used to improve mechanical properties of poly vinyl chloride (PVC) flooring, it aids the floor to last longer and prevents damage to the environment since it can absorb moisture. It can also be used in reinforcement of elastomeric products like shoe soles, and in tires.

5. Extraction of Silica

Renewable nature and availability of agricultural wastes have stimulated researchers to explore the policy of waste to wealth creation. Activated carbon, cellulose, lignin, construction materials, biofuels, silica and silicon have been extracted from agricultural wastes [59, 60]. Silica has been prepared from agricultural wastes like, cassava periderm [59], sugarcane bagasse [16], coffee husk [17], wheat husk [18], corn cobs [5], which have organic materials and 60-90% hydrated silicon (Table 1) as their major components [5], using different techniques including vapor phase reaction, thermal decomposition technique and sol-gel. These methods are expensive, and they limit wide silica application.

TABLE 1. Silica content in different agricultural wastes

Agricultural waste	Silica percentage	References
Cassava peels	62.69	[59]
Sugar cane Bagasse	50.36	[16]
Diatomaceous earth	80-90	[19]
Corn cobs	60.20	[5]
Wheat husk	90	[18]
Coffee husk	41.68	[17]
Rice husk	99.66	[20]

Several methods have been established to extract silica from rice husk at low cost. Table 2 shows different methods used to extract silica. A study by Della [21] showed that burning rice husk to give rice husk ash (Figure 3), has a significant effect on the amount of silica extracted, this study shows that amount of silica extracted from rice husk ash was 95% after complete combustion at 700°C. YalcË [20] established that burning rice husk between 600°C and 800°C before thermal and chemical pretreatment produce high purity silica of above 99%. Kalapathy [22] proved that it is possible to obtain amorphous silica from rice husk ash by alkaline extraction at low temperature. A study by Mochidzuki [23], showed that using hot water to extract silica dissolves small silica quantity which only affects the particle morphology not the nature of amorphous silica. The authors used different chemical and thermal treatment approaches but reported that acid leaching pretreatment followed by oxygen-rich incineration and combustion of rice husk produced the highest silica content.

Figure 3. Rice husk ash

TABLE 2. Methods of silica extraction

Extraction method	Condition characteristics	Results	References
Alkaline media	Silica was extracted in alkaline media as silicate which was precipitated in the form of silica gel by the acid addition. the silica gel obtained was then heated at 80°C for twelve hours to obtained silica xerogels	- Silica percentage of 93%. - Large surface area - Yield percentage of 91%	[22]
carbonaceous materials	Silica is extracted using carbonaceous materials that were derived from rice husk by burning them at different temperature for different period.	- 94.95 silica percentage - High surface area - Small pore size	[21]
Washing rice husk with acidic or alkaline solution	silica is extracted from rice husk by washing rice husk with acidic or alkaline solution and then incinerate at 600°C in the atmospheric static air for converting husk into ash.	- High surface area - Small particle size - 99.66% of silica	[20]
Fluidized bed.	Rice husk was burned under controlled conditions in a fluidized bed. The ash was purified and used to extract silica	- Silica percentage of about 95% - High surface area	[24]
Glycerol treatment	Rice husk ash was treated with glycerol to produce glyceosilicate solution. The glyceosilicate was then titrated against aqueous glycerol solution of $Ba(O H)_2$	- Amorphous silica was obtained h the purity silica percentage of 82.86	[25]
Hydrothermal and steam explosion processes	Silica was extracted from rice husk in hydrothermal and steam explosion processes	- Low silica quantity and High purity	[23]
Extraction of silica in a reactor with NH_4F	Rice husk was leached with sulfuric and hydrochloric acid separately, the silica extraction was done in a reactor with NH. The solution was then washed and incinerated in a muffle furnace	- Small particle size varying from 0.43-0.94μm - Purity of silica leached with hydrochloric acid was 99.58% and the one leached with sulfuric acid is 99.08% - Large surface area with fine pore size	[26]

6. Why silica from Rice Husk

The use of rice husk ash to precipitate silica is superior and cost effective, unlike extracting silica from quartz using todays' technology. Use of rice husk ash which is waste has little cost and the process is more energy efficient than other processes which involves fusion of selected quality of sand [48]. Compared to other products that silica can be extracted from, and rice husk ash has small number of contaminants which makes it easy and less expensive to purify (Table 3) [72].

Silica in rice husk exists in the hydrated amorphous form which makes it easy to extract at low temperatures. Energy which could be recovered in the form of heat or electricity is also produced in the process [12]. Using rice husk to extract silica saves energy while on the other hand producing heat/electricity. An ongoing study shows that high purity silica can be extracted from rice husk at room temperature (Table 3).

TABLE 3. XRF characterization of rice husk, rice husk ash and extracted silica

Element Name	Rice husk	Rice husk ash	Extracted Silica
MgO	0.597	0.683	0
SiO_2	42.138	85.205	92.982
P_2O_5	0.153	0.322	0.079
S	0.133	0.018	0
Cl	0.111	0	0
K_2O	0.640	1.147	0
CaO	0.468	0.628	0
TiO_2	0.034	0.032	0
Cr	0.004	0	0.016
MnO	0.163	0.291	0
Fe_2O_3	0.227	0.151	0
Cu	0.022	0.002	0.003
Rb	0.008	0.006	0
Ti	0	0	0.005
V	0	0	0.001
Mn	0	0	0.005
Fe	0	0	0.038
Zn	0	0	0.003
Sr	0	0.003	0

7. Conclusions

Silica is a very important and useful compound which can be extracted from different agricultural wastes and high purity silica can be produced from rice husk using simple, energy saving and cost-effective methods. Different methods of extracting silica from rice husk have been established, leaching pretreatment followed by incineration of rice husk was reported to have the best silica content percentage (>99%). More research can be done to reduce the energy required for extraction of silica while improving its purity. More cost reduction in silica extraction from waste will make it more effective to use in future.

References

1. Todkar B.S, Deorukhkar O.A and Deshmukh S.M, Extraction of silica from rice husk, International Journal of Engineering Research and Development, 2016, vol. 12, no. 3, p. 6.
2. Harish P. R, Arumugam A and Ponnusami V, Recovery of silica from various low-cost precursors for the synthesis of silica gel, Der Pharmacia Lettre, 2015, vol. 7, no. 6, pp. 208-213.
3. Bessho M, Fukunaka H. Kusuda H and Nishiyama T, High-grade silica refined from diatomaceous earth for solar-grade silicon production, Energy & Fuels, 2009, vol. 23, p. 4160–4165.
4. Kalapathy U, Proctor A and Shultz J, A simple method for production of pure silica from rice hull ash, Bioresource Technology, 2000, vol. 72, no. 2000, p. 7.
5. Velmurugan P., Shim J., Lee K, J, Cho M. Lim S.-s., Seo S.-K., Cho K.-M. Bang K.-S and. Oh B.-T, Extraction, characterization, and catalytic potential of amorphous, Journal of Industrial and Engineering Chemistry, 2005, vol. 29, no. 2015, p. 6.

6. Adebisi J. A., Agunsoye J. O., Bello S. A., Haris M., Ramakokovhu M. M., Daramola M. O. and Hassan S. B, Extraction of silica from cassava periderm using modified sol-gel method, Nigerian Journal of Surgical Research, 2018, vol. 15, no. 2, p. 9.
7. Kubo M. and Purevdorj M., The future of rice production and consumption, Journal of food didtribution research, 2014, vol. 35, no. 1, p. 15.
8. Dang K. and Nguyen H. T., Management of agricultural waste and potential for cobenefits, ministry of agriculuture and rural development, Haiphong, China, 2010.
9. Moraes C. A.,Fernandes I. J, Calheiro D., Kieling A. G., Brehm F. A., Rigon M. R., Berwanger J. A., Schneider I. A. H. and Osorio E., Review of the rice production cycle: Byproducts and the main applications focusing on rice husk combustion and ash recycling, Waste Management & Research 2014, vol. 32, no. 11, p. 15.
10. Patil R. Dongre R. and Meshram J., Preparation of silica powder from rice husk, IOSR Journal of Applied Chemistry, 2014, vol. 2, no. 2014, p. 4.
11. Tyagi V., Pandit S., Sharma A. and Gupta R. K., Extraction and characterization of silica from rice husk for use in food industries, International Journal of Food Science and Nutrition, 2017, vol. 2, no. 4, p. 4.
12. Gandhi H., Tamaskar A. N., Parab H. and Purohit S., Extraction of silica from rice husk ash, Basic and Applied Engineering Research, 2015, vol. 2, no. 4, p. 4.
13. Okoronkwo E. A., Imoisili P. E. and Olusunle S. O., Extraction and characterization of amorphous silica from corn, Chemistry and Materials Research, 2013.vol. 3, no. 4, p. 6.
14. Kumar S., Sangwan P., Dhankhar R., Mor V. and Bidra S., Utilization of rice husk and Their ash: A Review, Research Journal of Chemical and Environmental Sciences, 2013, vol. 1, no. 5, p. 4.
15. Adepoju A. D., Adebisi J. A., Odusote J. K., Ahmed I. I. and Hassan S. B., Preparation of silica from cassava periderm, Journal of Solid Waste Technology and Management, 2016, vol. 42, no. 3, p. 6.
16. Affandi S. , Setyawan H., Winardi S., Purwanto A. and Balgis R., A facile method for production of high-purity silica xerogels from bagasse ash, Advanced Powder Technology, 2009. vol. 20, no. 2009, p. 5.
17. Espı´ndola-Gonzalez A., Martı´nez-Herna´ndez A. L., Angeles-Cha´vez C., Castan˜o V. M. and Velasco-Santos C., Novel crystalline SiO_2 Nanoparticles via annelids bioprocessing, Nanoscale Research Letters, 2010, vol. 5, p. 10.
18. Javed S. H., Anam S., Umair A. and Tajwar S., Precipitated silica from wheat husk, Pakistan Institute of Chemical Engineers,2011, vol. 39, p. 4.
19. Bakr H. E. G. M. M., Diatomite: Its characterization, modifications and applications, Asian Journal of Materials Science, 2010, vol. 2, no. 3, p. 16.
20. YalcË in N. and Sevinc V., Studies on silica obtained from rice husk, Ceramics International, 2001, vol. 27, no. 2001, p. 6.
21. Della V., Ku¨hn I. and Hotza D., Rice husk ash as an alternate source for active silica production, Materials Letters, 2002, vol. 57, no. 2002, p. 4.
22. Kalapathy U., Proctor A. and Shultz J., An improved method for production of silica from rice hull ash, Bioresource Technology, 2002, vol. 85, no. 2002, p. 6.
23. Mochidzuki k., Sakoda A., Suzuki M., Izumi J. and Tomonaga N., Structural Behavior of Rice Husk Silica in Pressurized Hot-Water Treatment Processes, Industrial and Engineering Chemistry Research, 2001, vol. 40, no. 24, p. 5705–5709.
24. Huang S., Jing S., Wang J., Jin Y. and Wang Z., Silica white obtained from rice husk in a fluidized bed, Powder Technology- Lausanne, 2001, vol. 117, no. 3, pp. 232-238.
25. PayaÂ J. MonzoÂ, J. Borrachero M. V., Mellado A. and OrdonAez L. M, Determination of amorphous silica in rice husk ash by a rapid, Cement and Concrete Research, 2001vol. 31, no. 2001, pp. 221-231.
26. Ma. X, Zhou. B, Gao. W, Qu. Y, Wand. L, Wang. Z and Zhu Y., A recyclable method for production of pure, Powder Technology, 2012, vol. 217, pp. 479-501.
27. Fernandes I. J., Calheiro D., Sánche F. L., Camacho A. L., Avila de Campos Rochac T. L. Mendes Moraes C. A and Caldas de Sousa V., Characterization of silica produced from rice husk ash: comparison of purification, Materials Research, 2017 vol. 20, no. 2, p. 7.

Chromium tanning, management challenges and environmental legislation in Sub Saharan African tanneries

RO Oruko [1]*, JO Odiyo [2] and JN Edokpayi[2]

[1]Department of Ecology and Resource management, University of Venda, South Africa.
[2]Department of Hydrology and Water Resources, University of Venda, South Africa.
*Email of corresponding author: richardoruko@gmail.com

Abstract
Tanning of hides and skins are common practices in Sub-Saharan Africa. Tannery-based chromium wastes are sometimes crudely dumped in soils, thereby posing a risk to the population. This review paper was undertaken to understand chromium waste management and challenges on the continent. This covered chromium tanning technology, growth of the tanning industry, contemporary use of chromium tanning agent, leather tanning stages that generate chromium wastes and their management, the environmental legislation challenges. It also presents the unresolved debate about replacing chromium as a tanning agent, health effects and the future of tanneries in sub Saharan Africa. The challenges associated with tannery-based chromium waste management in Africa is also presented. From the information and data gathered we conclude that the management of chromium-based tannery waste is inadequate as these wastes continue to degrade soils ecosystems at crude dumpsites. There is a knowledge gap in the remediation of soil contaminated with chromium-based tannery waste.

Keywords: Environmental legislation challenges, Remediation, Sub Saharan Africa tanneries, Tannery based chromium waste.

1. Introduction

Chromium is the 21st most abundant element in the earth's crust and exist in levels up to 100 ppm [1-2]. It is an essential micronutrient for living organisms. Cr (III) is an essential trace element known for its particular role in the maintenance of normal carbohydrate metabolism in mammals. [3]. Chromium III is widely used as major chemicals in leather tanning because of its stability that helps protect raw skin from degradation by the microbes, enzymes and environmental factors. However, it remains a subject of environmental controversy and dispute because of its toxicity and hazardous nature in the environment [2]. Environmental impacts of Cr (III) wastes from tanneries have been a subject of extensive scientific and technical debate. Assumptions that complete oxidation of all forms of Cr (III) to Cr (VI) will occur and that Cr (VI) will be completely reduced to Cr (III) if the wastes are mixed with soil at crude dumpsites as commonly practised in Africa currently are untenable and not based on scientific findings [2]. Thus, the need to review chromium wastes disposal in the sub Saharan African tanneries and propose practical techniques for policy makers and tannery managements to adopt in future.

2. Methods

Desktop review of one hundred and fifty-nine publications was undertaken; on topical areas like historical evolution of chromium tanning technology, contemporary use of chromium, growth of the tanning industry on the continent, the unresolved debate about replacing it as a tanning agent, its wastes, their management and the environmental legislation challenges in the sub Saharan African tanneries. It was supplemented with administration of questionnaires to more than seven key informants in the sector from selected countries in the continent to generate and correlate more data.

3. Result and Discussion

Historically leather tanning came about either by accident or by trial and error as man discovered methods of preserving and softening leather by treating raw animal skins with smoke, oils, minerals and bark extracts from plants [4]. Infogalactic states that, the first use of animal skins is attributed to *Australopithecus habilis* was roaming East Africa some two million years ago [5]. They used skins structures believed to have been warmed by fire which created a curing effect. This dried the skins slowly. The other earliest tanning methods were based on the use of vegetable and alum but in the nineteenth century, these tanning techniques were later supplemented with chrome tanning. This method is still in use today and accounts for about 80-90% of all tanning done globally [6]. Chrome tanning became the tanning method for modern footwear and fashion leathers. It produces soft, supple, beautiful and fine leathers [7]. The technique was discovered in 1858 by Knapp. The first commercial chrome tanned leather was produced in 1884 by Augustus Schultz of New York [8,9].

The main reaction between chrome and collagen fiber takes place when the positive charged chrome tanning agent bind with negative charged collagen carboxyl group by coordinate bond to fix the structure of collagen fiber and to give tanning effects, such as thermostability, chemical resistance and flexing endurance as shown in Figure 1.

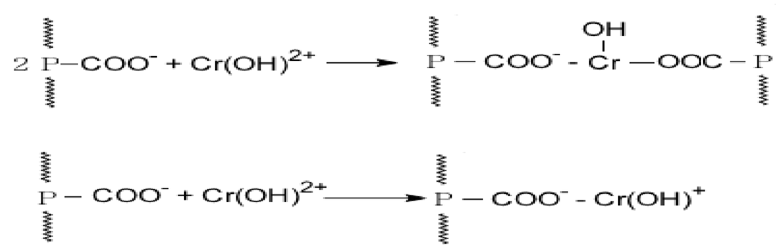


Figure 1. Cross link between hydrated chromium ion and carboxyl group of the collagen [10].

In most African countries, commercial chrome leather industries were established as export-based industry of semi-processed raw hides and skins with no consideration given to linking them to the development of a finished leather and leather products industry [11]. African leather industry development can therefore be categorized into three levels: developed – Egypt, Morocco, Tunisia and South Africa; Fairly developed – Eastern and Southern African countries including Ethiopia and Zimbabwe; Relatively under-developed – most of West African countries [12]. Figure 2 gives their regional distribution and total numbers in the continent.

Tanneries found in Africa range from modern and well-equipped commercial ones to the small and outdated ones known as artisanal tanneries, respectively [13,14]. Most tanneries in the continent face a lot of challenges that range from lack of space (to install waste management facilities), technical expertise, adequate capital (to build up individual wastewater treatment plants), poor quality of raw materials, market access, political changes and civil unrest. Other challenges include the importation of second-hand tannery products such as footwear and counterfeit footwear. Inadequate infrastructure and transportation, lack of foreign direct investment (FDI), inadequate infrastructure and processing equipment and facilities. These challenges often lead to the generation of toxic waste [11-14].

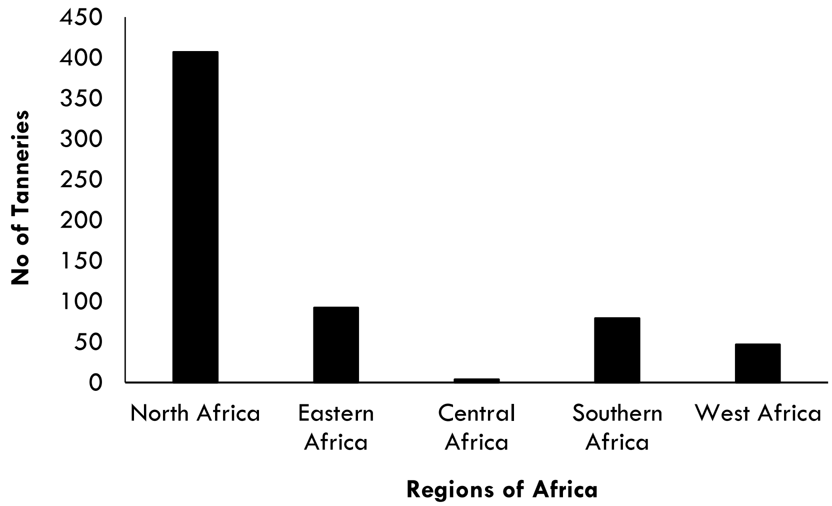


Figure 2: Regional distribution of tanneries in Africa [14].

To overcome these challenges, requires joint efforts of governments and tannery owners. There are also environmental concerns associated with the discharge of unused chromium effluent and the safe disposal of solid waste containing the metal ion. This has also brought the debate on how to replace chromium with other safe tanning agents like zirconium and titanium, but they have low shrinkage temperature in comparison to chromium. Some expert believe it is hardly feasible to reproduce all the features of chrome tanning with another material. They argue that the mechanism of chrome tanning has not been understood to the required level of resolution to help the development of alternatives [15, 16]. Therefore, there might be a need for a review to find areas for tanners and research institutes to collaborate and carry out more detailed studies. This could help with the development of the most appropriate tanning agent to replace chromium.

70% of the key informants and the reviewed literature confirmed that, the two most polluted waste streams in a tannery are the beam house wastes and the tan yard wastes. Beam house waste is highly alkaline and usually has high organic contents. The tan yard wastes are highly acidic and contain high concentrations of chromium [9]. The forms of wastes generated range from chrome sludge, splits, wet blue shavings, trimmings, crust trimmings, buffing dust, vegetable tanning extracts, mineral acids, alum, fatliquors, acid dyes, solvent coatings, pigments, and sodium chloride. In addition to dirt, manure, fleshings, grease, residual hair, proteins, oils, unfixed tan liquors and accidental spillover of chromium chemicals [9]. These wastes often end up in the environment without proper treatment.

The current waste treatment technologies employed in Africa include landfilling, open dumping, incineration, composting and occasional recycling (Figures 3-4). The tannering waste is either packed in sacks or crudely dumped in the open spaces as shown in Figure 4. Combustion of chromium containing wastes (Figure 3) can lead to the oxidation of trivalent chromium into hexavalent chromium, which is considered a carcinogenic compound [17]. This poss a direct health risks to tannery workers and other people living or working in close proximity to the tannery.

Figure 3: Tannery wastes crudely dump in sacks and burnt in the open space and kiln in a tannery in Kenya (Oruko, 2017).

Figure 4. Dried chromium cake dump inside a tannery compound in Kenya (Oruko, 2018).

During precipitation events rain water percolates into the dumped tannery waste leading to the formation of highly toxic leachates which often infiltrate through the soil and contaminate groundwater. There is also a possibility of the oxidation of Cr (III) to Cr (VI) during disinfection of Cr- contaminated water for human consumption. This poses a threat to public health. Large areas around such dumpsites are also rendered unsuitable for living and other activities [18].

Landfills remain the prefered disposal method globally for most solid wastes, but well managed landfills are not available in many African countries. Chromium wastes end up, polluting the ecosystems like soils and endangering human health. Therefore, a number of tanneries have been closed in a number of countries in Africa for failure to meet wastewater sewer acceptance limits, odour nuisance and polluting small water courses [13, 19]. Although some governments have closed polluting tanneries but there are weak policies in place on how to remediate such sites. Sustainable bioremediation techniques may be required for contaminated sites in future. This is necessary due to the fact that those sites continue to pose a health risk to tannery workers who grow food crops like kales, spinach and tomatoes on them as shown in Figure 5.

Figure 5. Spinach and Kales grown next to tannery dumpsites in South Africa and Kenya respectively (Oruko, 2018).

Despite the many difficulties faced in implementing tannery pollution control in Africa, important regulations and pollution prevention measures have been introduced, especially in Ethiopia, Kenya, Namibia, Tanzania, Tunisia, Zambia and Zimbabwe [12]. Some legislations have a check on the quality of treated effluents; while others on the quality of the recipient water bodies; some specify the permissible levels of impurities to be discharged per day into the recipient water body, whereas in some cases specifications are linked to the total amount of waste water discharged. Some countries have also made regulations related to production, import and sale of leather products with regard to hazardous substances. These legislations face challenges like low parameters values that seems impossible to reach. Their imposition by politicians who have no knowledge of environment problems, lack of capability to manage and implement the norms and lack of structures and experts to control and implement environmental laws need the attention and review of policy makers [13, 20]. In some cases, industries are encouraged to keep their plants operating as laws requiring treatment of wastes sometimes result in low production capacity that does not enable them to compete with other industries globally.

In developed countries, leather industries have invested time and resources in conforming to environmental protection laws. This has been achieved mainly by relocating most tanneries to tanning districts where centralised treatment plants are constructed, thus achieving economies of scale [14]. The reviewed literature and response from 45% key informants show that the tanning sector in Africa is finding it difficult to comply with environmental regulations, when there is strict enforcement of norms. They face challenges in cost effectiveness. Therefore, there may be a need in future for the governments to work with tanners and other stakeholders to address these shortcomings in the sector.

4. Conclusion

The tanning sector in Africa is still faced with numerous challenges which are summatable if all the relevant stakeholders from the government, private enterprise and tanneries owners work together. The management of chromium waste from tanning industries is inadequate on the continent. The waste will continue to degrade soil and water ecosystems at crude dumpsites. Thus, the need for policy makers and tanners to come up with sustainable management and remediation strategies for chromium contaminated sites.

References

1. Cervantes, C., Campos-Garcia, J., Devars, S., Gutierrez-Corona, F., Loza-Tavera, H., Torres-Guzman, J.C., and Moreno-Sanchez, R., (2001). Interactions of Cr with microorganisms and plants, *FEMS Microbiology Reviews*, 25, 335–347
2. Deborah, M., Proctor Brent, L.,Finley Mark, A.,Harris Dennis J.,Paustenbach David Rabbe (1997). Soil: perspective in chemistry, health and environmental regulation: special issue. Journal of soil contamination Vol.6/No 6.
3. Focardi. S, Pepi. M, and Focardi S E. (2013). Microbial Reduction of Hexavalent Chromium as a Mechanism of Detoxification and Possible Bioremediation Applications. http://dx.doi.org/10.5772/56365.
4. Leather resource LLC (2008). file:///C:/Users/oruko/Desktop/history%20of%20leather/History%20of%20Leather%20-%20Leather%20Resource.htm Downloaded at 12.41 pm
5. Infogalactic news: the planetary knowledge core (2016), Conservation and restoration of Leather. https://infogalactic.com/w/index.php? Title =conservation and restoration of leather objects& oldid=714576737. **82**. 6. Simply leather (Wales) ltd (2017).
6. http://www.simplyleather.co.uk/acatalog/History_of_Leather.html downloaded at 12.40 pm
7. 7. BLC Leather Technology Centre Ltd (2007). BLC Leather Technology Centre Ltd - Kings Park Road - Moulton Park - Northampton - NN3 6JD - UK - Registered No: 07009052 (England)///C:/Users/oruko/Desktop/history of leather/Where does leather come from How is leather made.htm. Downloaded at 12.43pm
8. The Columbia Electronic Encyclopedia, (2013). Columbia University Press. Licensed from Columbia University Press. www.cc.columbia.edu/cu/cup/.
9. Kolta,V.R., Tock,R.W., Ramsey,R.H.,Mollhagen, T.R., (1996). An assessment of the process, the leather properties and the potential for chromium reduction. Texas Tech university civil Engineeringfaculty.https://ttuir.tdl.org/ttuir/bitstream/handle/2346/12968/31295009805069.pdf?sequence=1
10. Xiaoxing.L, (2016). The technology of Leather manufacture. China leather and footwear industry research institute. https://leatherpanel.org/content/china-leather-footwear-industrial-research-institute.
11. Jabbar M.A., Kiruthu S., Gebremedh B., and Ehui S., (2002). 'Essential Actions to Meet Quality Requirements of Hides and Skins and Semi-Processed Leather from Africa: Case Studies in Four African Countries' (CFC), presented at the Expert Group Meeting on Trade Development of the Leather Industry in Africa, October 7-9, in 'Meet in Africa Tunis, October 6-13, 2002. http://www.unido.org/fileadmin/import/10197_Jabbar.2.pdf
12. Kiruthu S., 'Benchmarking the African leather sector' (UNIDO- ESALIA) presented at the Expert Group Meeting on Trade Development of the Leather Industry in Africa, October 79, in 'Meet in Africa 2002', Tunis, October 6-13, 2002.https://www.unido.org/fileadmin/user_media/Publications/Pub_free/A_blueprint_for_the_African_leather_industry.pdf
13. Favazzi. A, (2002). Study of the impact of the main policies and environment protections measures in Africa's leather industry. http://www.unido.org/fileadmin/import/10203_StudioFavazzi.4.pdf.
14. Cipriani S., 'Quality Control and Management of the African Leather Sector' (ASSOMAC) presented at the Expert Group Meeting on Trade Development of the Leather Industry in Africa, October 7-9, in 'Meet in Africa 2002' Tunis, October 6-13, 2002.

https://www.unido.org/fileadmin/user_media/Publications/Pub_free/A_blueprint_for_the_Africa leather_industry.pdf. Downloaded on 23/11/2017 at 8.30am
15. Covington, A.D., (2000). Journal society of leather technologist and chemist; 92. *http://www.sciencedirect.com/science/article/pii/S0141813012004266*.
16. Buljan, T. Ramasami, B. Shi, A.D. Covington, D.G. Bailey, W. Frendrup (2000). What is the future of (chrome) tanning? Leather manufacture in the new millennium Casablanca, Moroccohttps://leatherpanel.org/sites/default/files/publicationsattachments/futureofcrtanning.pdf-2017.11.22 *at 9.20pm*.
17. Oruko, R.O., Moturi, W.N., and Mironga, J.M. (2014). Assessment of tannery based solid wastes management in Asili Tannery Nairobi Kenya.International Journal for Quality Research8(2) 227–238ISSN 1800-6450Center for Quality, Faculty of Engineering, University of Kragujevac Serbia.
18. Kolomaznik, K; Adamek,M; Andel, I and Uhlirova. M. (2008); Leather Waste-Potential Threat to Human Health and a New Technology of Its Treatment. J. Hazardous Material.160, 514–520
19. Swartz, C.D., Moss, J.C., Rowswell, R.A., Mpofu, A.B., Welz, P.J., (2017). Water and waste water management in the tanning and leather finishing industry: NATSURV 10(2nd Edition). Water research commission project K5/2490 of South Africa.
20. Amit, K., Gupta, S., (2006). Phytoextraction capacity of the plants growing on tannery sludge dumping sites.*Ecotoxicology and bioremediation group, national botanical research institute, Ana pratap marg*. Bioresource Technology. Volume 98, Issue 9, Pp 1788-1794 *Lucknow*, India.
21. Madiha, S., Saleem, T., Rehman, S.M.D., Iqbal, M.A., Muhammed, F.J., Khan, S.B., (2010). Effects of leather industry on health and recommendation for improving the situation. Archives of environmental and occupational health journal volume 65-issue 3.

Physico-chemical assessment of treated and untreated effluents from two paint industries in Lagos, Nigeria

T Aniyikaiye[1]*, J Odiyo[2], T Oluseyi[3], J Edokpayi[2]

[1]Department of Environmental Resource Management, University of Venda, South Africa
[2]Department of Hydrology and Water Resources, University of Venda, South Africa
[3]Department of Chemistry, Faculty of Sciences, University of Lagos, Nigeria
*Email of corresponding author: lizaniyi@gmail.com

Abstract
Effluents from paint industries are a major source of pollution to the environment. This study evaluates the physicochemical parameters of both raw and treated wastewater, the treatment plants efficiencies as well as the compliance level of two understudied paint manufacturing companies in Lagos with National Environmental Standards and Regulations Enforcement Agency (NESREA), World Health Organization (WHO) as well as Department of Water Affairs (DWA) guidelines for discharge of effluent into a water resource. The physicochemical properties such as TS, TSS, TDS, BOD, COD, oil and grease, nitrate and phosphate were determined. The obtained values for the treated effluents are as follow: pH: 4 and 7; EC (mS/m): 311.8 and 149.2; TSS (mg/L): 460 and 740; TDS (mg/L): 2330 and 1180; DO (mg/L): 1.6 and 0; O and G (mg/L): 50 and 100; BOD (mg/L): 502.9 and 595.8; COD (mg/L): 629 and 1231; Nitrate (mg/L): 12.89 and 211.2 and Phosphate (mg/L): 0.02 and 0 for companies A and B, respectively. The results indicated that the Effluent Treatment Plants (ETPs) of the understudied paint companies were ineffective in reducing the TSS, BOD, O and G and COD of the effluents to acceptable discharge limits of the regulatory bodies.

Keywords: Effluents, ETPs, paint, physicochemical parameters.

1. Introduction

Industries perform key role in the socio-economic growth of any country. However, global industrialization, has place much pressure on natural resources. Consequently, various devastating ecological and human disaster, have resulted in environmental deterioration as well as pollution problems of various dimensions [1]. It is widely known that in many low-income nations, industrial environmental standards are non-existent, and where they are available, the mitigation instruments are inefficient. This is mainly due to lack of reliable and extensive monitoring systems for industrial emissions as well as enforcement of compliance with the industrial standards [2].

The compromise in the quality of the environment as a result of effluent discharge from the industrial sectors is becoming an environmental issue for many countries especially the developing nations like Nigeria [3]. In the past century there has been a rapid expansion in industries. This has led to an increase in the complexity of toxic effluents [4] Release of this industrial wastewater into the environment creates a remarkable impact on the receiving water bodies. This is especially true for chemical and allied process industries like the paint industry [5]

Emulsion paints are complex mixtures composed of both organic and inorganic pigments, latexes, extenders, cellulosic and non-cellulosic thickeners, emulsifying agents, etc. [6]. Paint effluent often contains all components of precursor paints with insignificant dilution [7]. They could be clean-up water composed of residual acids, plating metals and toxic chemicals [2]. The numerous chemicals used for the production of paint are responsible for the high concentrations of organic compounds, suspended solids, pigments and hazardous pollutants like heavy metals in the generated wastewater [6]. Some components of these wastes contain hazardous chemical elements which when discharged into the environment may penetrate and leach into the sub-surface environment and subsequently settle in the soil and bed sediment of water bodies [8]. Heavy metals are known to be persistent and can become bioavailable for uptake by other aquatic organisms under favorable conditions. Health challenges like genetic mutation, deformation, cancer, kidney problems etc., have been linked to pollution by heavy metals [2].

Non-restricted disposal of several tonnes of effluents into the lagoon, rivers and streams had become a threat to the aquatic environment. Olaniyi et al. [9] revealed that discharges of untreated or partially treated waste composed of algal nutrients, non-decomposable organics, heavy metals and other toxicants will compromise the quality of the receiving water bodies. Treatment of wastewater prior to discharge into the environment is therefore essential to prevent pollution [9].

Lagos is surrounded by various transboundary water bodies. Due to erratic supply of potable water, people often use water from some neighbouring rivers for domestic purposes. The water bodies in Lagos are also used for other activities such as fish farming, irrigation, transportation, cooling, etc. To safeguard the lives of humans, aquatic animals as well as plants depending on these water bodies, it is therefore of paramount importance that the quality and compliance level with the relevant regulatory standards; NESREA [10], WHO [11] and DWA [12] of the effluents being released into these water bodies be ascertained. Hence, this study assesses the effluent quality of two paint industries in Lagos, Nigeria.

2. Materials and Methods

Description of study area

Based on land mass, Lagos is the smallest state of Nigeria, located in the southwestern part of the country. Lagos has coordinates of Latitude 6°27′14″N and Longitude 3°23′40″ E (Figure 1). It is situated at an elevation 11m above sea level. The state has a total area of about 3,577 square kilometres with water bodies inclusive. It is bounded at the north and east by Ogun State, and shares common boundaries with the Coast of the Atlantic Ocean and the Republic of Benin at the south and west, respectively.

Figure 1. Map showing the study area (adopted from Maphill [14])

The major vegetation of Lagos State is the tropical swamp forest which is made up of fresh water and mangrove swamp forests. Lagos experiences two major seasons annually, which include wet season (April to October) and dry season (November to March). The atmospheric temperature ranges between 30°C and 38°C. The main water bodies in Lagos are the Lagos and Lekki Lagoons, Atlantic Ocean, Yewa and Ogun Rivers [9]. According to Lagos State Government, Lagos to had a population of about 17 million in 2009. The sporadic population growth had been attributed to industrialization coupled with other factors such as urbanization, telecommunication revolutions and mass transportation [13].

Sample Collection

Both raw and treated effluent samples were collected from two paint companies in Lagos, Nigeria. Clean 1 L plastic bottles were used for the collection of the samples. The bottles used were carefully rinsed with the wastewater sample prior collection and labelled appropriately. Onsite measurement of pH using a pH meter was performed and immediately transported in ice chest to the laboratory.

Determination of Total Dissolved Solids, Total suspended solids and Total Solids

A clean petri dish was dried at 100°C in an oven, cooled in a desiccator and then weighed to constant weight. The collected wastewater sample was filtered into a clean conical flask using a pre-weighed filter paper. 10mL of the filtrate was poured into the petri-dish and placed in the oven at 180°C. The residue was then cooled in the desiccator and weighed to a constant weight. The increase in mass of the dry filter paper was then determined after drying the filter paper at 105°C overnight.

$$\text{Total Dissolved solids } (\text{mgL}^{-1}) = \frac{(\text{A}-\text{B})\text{ X }1000}{\text{Volume of Sample (mL)}} \qquad (1)$$

Where: A is the weight of dried residue + evaporating dish in mg, B is the weight of the evaporating dish in mg

$$\text{Total suspended solids } (\text{mgL}^{-1}) = \frac{(\text{A}-\text{B})\text{ X }1000}{\text{Volume of Sample (mL)}} \qquad (2)$$

Where: A is the weight of the filter + residue in mg, B is the weight of the filter alone in mg

A known volume of water sample was poured in a pre-weighed petri dish and heated in an oven at 180°C. The residue was then cooled in the desiccator and weighed to a constant weight.

$$\text{Total Solids } (\text{mgL}^{-1}) = \text{Total Suspended Solids} + \text{Total Dissolved Solids} \qquad (3)$$

Oil and Grease determination

Oil and grease in the wastewater samples were analysed using the liquid-liquid extraction technique with hexane serving as the extracting liquid. A known volume of wastewater sample was poured into a separating funnel and 25 mL hexane added. Two layers of immiscible liquids were obtained with hexane forming the upper layer. The aqueous layer was collected through the tap of the separating funnel while the organic phase (hexane) was poured into a conical flask. The sample was sequentially extracted with three aliquots of hexane in the separating funnel. The solvent extracts were collected together and evaporated to dryness at ambient temperature (20-25°C) in a fume cupboard. The difference in weight is equivalent to oil and grease in the sample.

$$\text{Oil and Grease } (\text{mgL}^{-1}) = \frac{\text{A}-\text{B(mg)} \times 1000}{\text{Volume of sample (ml)}} \quad (4)$$

Where: A is the total gain in weight for experimental sample (mg), and B is the gain in weight for blank (mg)

Dissolved Oxygen (DO) Measurement

Winkler's method was used for the determination of DO. The Winkler method involves completely filling a sample bottle with water. The dissolved oxygen in the wastewater sample was then "fixed" by reacting it with series of reagents resulting in the formation of an acid compound. The obtained acidic compound was then titrated with an appropriate neutralising reagent. The change in colour signifying the end point is equivalent to the quantity of DO in the water sample [15].

Biochemical Oxygen Demand

Dilution water was made by addition of 10 mL of each of the reagents; phosphate buffer, magnesium sulphate, calcium chloride, ferric chloride, sodium sulphite and ammonium chloride into 10 L of water. A known quantity of wastewater sample was diluted with dilution water to 1 L mark of a standard flask. Two 300 mL amber bottle was completely filled with the diluted water. One of the bottles was incubated at 20⁰C for 5 days. $MnSO_4$ solution, alkali-iodide-azide reagent and concentrated sulphuric acid were added into the other amber bottle. DO_0 was determined by titrating 50 mL aliquot of the solution against sodium thiosulphate solution using starch solution as indicator, until a colourless end-point was attained. At the end of the 5 days, the sample in the incubator was brought out, DO_5 was determined by following the same procedure used for the determination of DO_0. A blank was prepared in a transparent bottle for DO_0. Another blank was prepared in an amber bottle and incubated with the sample for DO_5.

$$\text{BOD}_5 \ (\text{mg L}^{-1}) = \frac{(\text{DO}_0 - \text{DO}_5) \times \text{Volume of BOD bottle}}{\text{Volume of sample}} \quad (5)$$

Where, BOD_5 is the biochemical oxygen demand of the water sample on the 5th day of incubation, DO_0 is the dissolved oxygen level of the water sample prior to incubation in mg/ L, and DO_5 is the dissolved oxygen level of the water sample on the 5th day of incubation in mg/ L

Chemical Oxygen Demand

COD of the wastewater sample was determined by the addition of mercuric sulphate and sulphuric acid into a known volume of waste water sample in a reflux flask. On cooling, the obtained solution was reacted with known concentration of Potassium dichromate and known volume of sulphuric acid. The solution was refluxed for 2 hours and cooled. The obtained solution was diluted to twice its volume, cooled to room temperature and excess $K_2Cr_2O_7$ in it determined by titrating with ferrous ammonium sulphate (FAS) using ferroin indicator. Similarly, a blank with all reagents added to 25 mL of distilled water was titrated.

$$\text{COD (mg L}^{-1}) = \frac{(\text{A}-\text{B})\times\text{C}\times 8000}{\text{Volume of the sample (ml)}} \quad (6)$$

Where A = volume of titrant used for the sample (mL), B = volume of titrant used for the blank sample (mL), C = the normality of the ferrous ammonium sulfate.

Nitrate Determination

Calibration standards for nitrate in the range 0.1–1.0 mg/L were prepared by serial dilutions from a stock solution. A series of reaction tubes was set up in test tube stand and placed in a cold-water bath. A known volume of wastewater sample was poured into the reaction tubes, NaCl solution and diluted sulphuric acid were added sequentially. Brucine-sulphanilic acid reagent was added and the mixture heated for some minutes in a boiling water bath. The samples were then allowed to cool and the absorbance of each sample at 410 nm in the UV spectrometer was measured, with reference to the reagent blank. NO^{-}_{3}-N concentration in the wastewater samples was determined from the calibration curve of the standard nitrate solutions.

Phosphate determination

For the detection of phosphate, conditional reagents were prepared by mixing appropriate quantities of sulphuric acid, potassium antimonyl tartrate solution, ammonium molybdate solution and diluted ascorbic acid solution. Dilute sulphuric acid and some conditional reagent were added to a known quantity of wastewater sample using phenolphthalein as indicator. The absorbance of each sample at 880 nm was measured, using reagent blank as the reference solution. A calibration curve was plotted taking various concentrations of the standard phosphate solution with specified amount of conditional reagents.

Compliance Study and Calculation of Percentage Reduction Efficiencies

National Environmental Standards Regulatory and Enforcement Agency [10], World Health Organisation [11] and Department of Water Affairs [12] guidelines were used as benchmarks to evaluate the acceptability of the effluent from the ETP due to the prevailing environmental conditions in Nigeria and the scope of parameters stated in the guidelines. The reduction efficiencies of the various parameters were calculated by Equation below [16]:

$$\text{Reduction efficiency} = \frac{\text{Concentration in the influent} - \text{Concentration in the effluent}}{\text{Concentration in the influent}} \times 100 \quad (7)$$

3. Results and Discussion

pH

The pH of wastewater during treatment is essential for the removal of organic compounds and heavy metals. Alkaline pH favours the precipitation of most metals as insoluble solids [16]. The pH of the raw water of both paint industries did not need any pH adjustment as they fell within the recommended guidelines for wastewater discharge (Figures 1a & 1b). However, the pH of treated effluent from company A (pH 4) did not fall within NESREA [10] and WHO (Jordanian Standard) [11] for release of effluent into the surface water (6.5 to 8.5), as well as specification of 5.5 – 9.5 (DWA [12]). The acidic nature of the effluent obtained could be as a result of the excessive use of $Ca(OH)_2$ or the use of inadequate amount of lime for the wastewater treatment. The pH of effluent is very important as it can negatively impact the receiving watershed. Alteration in the pH of natural water bodies may disrupt aquatic organisms biochemical reactions by harming or killing the organisms. Acidic pH is known to favour the bioavailability of most metals in river systems with its attendant consequences [17]. There was however no change in the pH of company B after treatment.

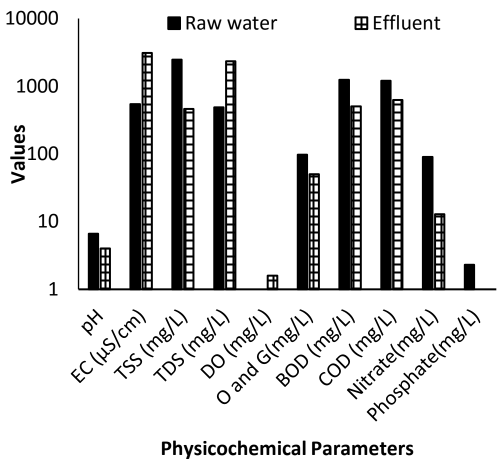


Figure 1a: Company A

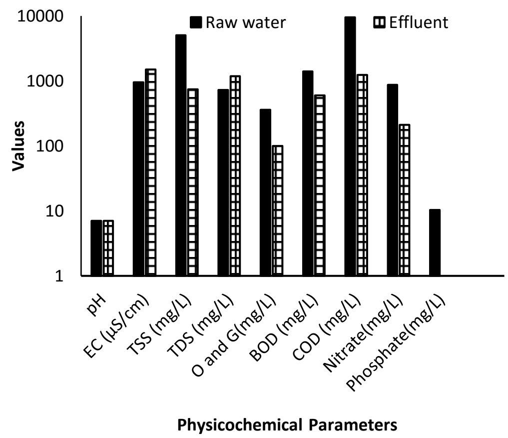


Figure 1b: Company B

Electrical Conductivity (EC)

EC is the measure of a solution's ability to conduct electric current which is greatly dependent on the availability of ionic species [18]. High values of EC show that inorganic ions are in abundance in the wastewater. Such ions have major influence on the conductivity of water. EC is directly proportional to the total dissolve solids (TDS) concentration. In essence, high EC in wastewater is an indication of high total dissolved solids concentration. This also implies that the ability of an electric current to pass through the wastewater is proportional to the concentration of ionic solutes dissolved in the water [19]. Although NESREA [10] and WHO [11] do not have specifications for effluent discharge, however Electrical conductivity measurements of raw wastewater obtained from company A (54.2 mS/m) and B (95 mS/m) fell within DWA, [12] limit of 70 - 150 mS/cm, applicable to discharge of effluent into water resource. Treatment of wastewater from both companies resulted in an increase in Electrical conductivity from 54.2 to 311.8 mS/m and 95 to 149.2 mS/m, respectively. This sporadic rise in EC could be as a result of dissolved ions of the reagents used for the wastewater treatment. The effluent discharge from Company B's ETP met the DWA [12] specification. The inability of the EC of the effluent from company A to fall within the required regulatory limit, showed that reagents were excessively used for the treatment of the effluent, hence the effluent is not suitable for irrigational purpose.

Total suspended Solids (TSS)

TSS is a measure of particulate maters suspended in water. It is used to describe the extent of pollution in wastewater. In addition, TSS serves as a good indicator for the turbidity of the water [20]. The TSS values for the raw wastewater from paint companies A and B were 2470 mg/L and 5070 mg/L, respectively. However, on treating, percentage reduction efficiencies of 81.4% (reduction to 460 mg/L) and 85.4% (reduction to 740 mg/L) were obtained for the ETPs of companies A and B, respectively. This showed that the ETPs of both companies were efficient in reducing the level of TSS but this removal was not sufficient as the TSS in the effluents from both companies did not comply with NESREA [10], WHO [11] and DWA [12] wastewater discharge limit of 0.75 mg/L, 60 mg/L and 25 mg/L respectively. The high level in TSS could be as a result of the presence of inorganic particulate matters such as extenders, pigments and additives present in paint. The result obtained is comparable with that obtained on the analysis of TSS in effluent samples from different paint companies in Ethiopia [21].

Total Dissolved Solids (TDS)

Total Dissolved Solid (TDS) is a measure of inorganic salts, organic matter and other dissolved materials in water. Industrial effluent is a major cause of TDS concentrations in natural waters [22]. Treatment of raw wastewater from both company A and B had resulted in a tremendous increase in the TDS level from 490 mg/L to 2330 mg/L and 730 mg/L to 1180mg/L, respectively. This increase could be as a result of the presence of dissolved ions of the chemical reagents used for the effluent treatment in both paint companies. This corroborates with the findings recorded for EC. Although, NESREA [10], and DWA [12] have no standard for effluent discharge into surface water, however, for effluent to be reused for irrigation purpose, it should not exceed 2000 mg/L [11]. In addition, water is said to be unpalatable and may begin to loss its commercial and domestic worth when the TDS level exceeds 1000 mg/L. High concentration of TDS in water is responsible for excessive scaling in water pipes, boilers, heaters, and household appliances [23]. The treated effluent from company A slightly exceeds the WHO [11] limit for effluent discharge, however the influent obtained from company B fell within the accepted limit. High concentration of TDS can result in dehydration of aquatic animals [22].

Dissolved Oxygen (DO)

Dissolved oxygen is essential for the survival of many types of marine life, and thus it serves as an important indicator of ecosystem condition. Dissolved oxygen concentrations are directly dependent on oxygen generation through photosynthesis and consumption by living organisms especially bacteria. In addition, dissolved oxygen is influenced by water temperature, water movement and salinity among others. Excessive nutrient loading can lead to depletion of dissolved oxygen by stimulating algae bloom consequently suffocation and death of aquatic organisms [24]. Prior to treatment, the DO level of raw wastewater from both Companies A and B were 0. However, the treatment of the influent in company A brought about an improvement in DO to 1.6 mg/L, an indication of DO improvement efficiency in Company A's ETP. Low DO concentration in effluent is an indication of high microbial activities in the water due to presence of biodegradable organic compounds like styrene acrylate binder, cellulosic thickener, etc in the effluent. DO level of company B even after treatment remains 0 this showed that the ETP is not efficient for the improvement of DO. With respect to NESREA [10] of 4 mg/L, both company A and B are non-compliant, however based on WHO [11] standard of 1 mg/L, only company A with DO concentration of 1.6 mg/L fell within the specification for effluent discharge into the surface water. Hence only the company A's ETP is effective in the improvement of DO to the acceptable WHO standard.

Oil and grease (O and G)

Oil and Grease is a highly viscous semisolid lubricant which floats on water due to its low density. The presence of high level of O and G in the water bodies can reduce productivity in the water [25]. The treatment of paint influents of Companies A and B had brought about O and G reduction from 97 mg/L to 50 mg/L and 360 mg/L to 100 mg/L which are equivalent to 49.5% and 72.2% reduction efficiencies in their respective ETPs. Although WHO [11] do not have standard for O and G, based on NESREA [10] and DWA [12] wastewater discharge limits of 0.1 mg/L and 2.5 mg/L respectively, all of the analysed wastewater samples greatly exceeded the required regulatory limits and therefore unsafe for disposal. High oil and grease concentration in effluent discharged into water bodies contributes to the emigration and death of aquatic animals. In addition, oil and grease on the surface of the water prevents the penetration of sunlight necessary for the photosynthetic activities of aquatic flora consequently reducing oxygen concentration in the water bodies [25].

Biochemical Oxygen Demand (BOD)

BOD is the amount of oxygen utilised by microbial organisms to decompose organic compounds in water and wastes. BOD test is used to determine the extent of pollution of a wastewater and the efficacy of effluent treatment methods. DO is greatly influenced by the BOD level in water. The higher the BOD, the greater the extent of oxygen depletion in the water bodies. This results in the reduction of oxygen available for higher forms of aquatic life. The aquatic animals become disturbed and exhausted, they suffocate and die [22]. The treatment of the influents brought about 59.6% and 57.7% reduction of the BOD in companies A and B, respectively. The effluents from both companies (502.9 mg/L and 595.8 mg/L) did not comply with NESREA [10] and WHO [11] BOD standards of 6 and 60 mg/L respectively. The percentage reduction efficiencies obtained from both companies A and B are indications that the ETPs used by both companies are averagely efficient but not sufficient to bring about reduction of BOD to the desired level. The high BOD level in the effluent could be attributed to the availability of organic compounds such as pure acrylic and styrene acrylic binders, cellulose thickener and organic pigments which could be broken down by micro-organisms. Microbial activities in the effluent results in the depletion of DO in the wastewater. The high BOD levels in the effluent samples from the two companies corroborates with the low DO concentrations obtained in the analysis of their respective effluent samples. The obtained values correlate with BOD of 535.8 mg/l and 600 mg/L obtained in the assessment of physicochemical parameter of paint effluents in India and Ethiopia carried out by Ram et al. [26] and Tesfalem and Abdrie [21] respectively. These results show that removal of BOD by ETPs in the paint industry is a global challenge. The discharge of wastewater with high levels of BOD into waterbodies can cause serious dissolved oxygen depletion and death of aquatic animals in the receiving water bodies.

Chemical Oxygen Demand (COD)

Chemical Oxygen Demand is the measure of oxygen equivalent of the organic content of the sample that is susceptible to oxidation by a strong chemical oxidant. It is an evaluation used to measure the level of water contamination by organic matter [20]. The COD value is usually higher than the BOD because some organic materials in the water that are resistant to microbial oxidation and hence not involved in BOD could be easily chemically oxidized. COD measurements can be made in a few hours while BOD measurements usually take five days (BOD_5) [26]. The COD of the untreated effluents from companies A and B are 1198 mg/L and 9481 mg/L, respectively. Results obtained after treatment gave 47.5% and 87% reduction efficiencies in COD levels of ETPs used in Companies A and B, respectively to 629 and 1231 mg/L. However, despite these ETP efficiencies, the resulting COD values greatly exceeded the NESREA [10], DWA [12] and WHO [11] limits for effluent discharge of 30, 75 and 150 mg/L respectively. The presence of oxidizable inorganic compounds like extenders, pigments and additives are accountable for the high concentration of chemical oxygen demand. This shows that ineffectiveness of ETP to reduce COD in wastewater to acceptable regulatory limit is a major challenge which cuts across the paint industry in Lagos, Nigeria. In addition, several studies in other parts of the world had revealed ineffectiveness of paint industry's ETP in the removal of COD (Tesfalem and Abdrie [21], Ram et al. [26], Onuegbu et al. [28]). This shows that the non-compliance of paint industry to regulatory standards with regards to COD is a global issue.

Nitrates, Phosphate

Nitrates are the end product of the aerobic decomposition of organic nitrogenous matter [27]. Phosphorus is an essential nutrient for the organisms that make up the aquatic food web. Excessive presence of phosphate in conjunction with nitrates and potassium, causes algal blooms which result in the death of aquatic organisms [22]. Effluents from companies A and B had nitrates concentrations of 90.56 mg/L and 871.9 mg/L, respectively. ETP nitrate reduction efficiencies of 85.8% and 75.8% for companies A and B, respectively to 12.89 and 211.2 mg/L were obtained. Only effluent from company A met the effluent discharge specifications of all the regulatory bodies; NESREA [10], WHO [11] and DWA [12] limit of 40, 45 and 15 mg/L respectively. Despite the high removal efficiency of 75.8% recorded for company B, the ETP was ineffective in the reduction of the nitrate to acceptable NESREA [10]/ WHO [11]/ DWA [12] limits. Availability of nitrogenous compounds such as nitrocellulose resin and thickener in the effluent could be responsible for the high level of nitrate in effluent from company B. The discharge of such effluents can lead to nutrient loading of the receiving watershed resulting in eutrophication. Conversely, the phosphate level of paint influents from both companies A; 2.3 mg/L and B; 10.3 mg/L, complied with the discharge guidelines of WHO [11], DWA [12] and NESREA [10] of 15, 10 and 3.5 mg/L, respectively. Treatment of these influents resulted in the reduction of the phosphate to negligible levels. This showed that the phosphate level in both raw and treated effluents from the two understudied companies fell within the acceptable regulatory effluent discharge limits for phosphate and the effluents are therefore suitable for reuse.

4. Conclusion

The results obtained from the two paint industries understudied, greatly showed a non-compliance to various regulatory standards as most of the physicochemical investigated exceeded the levels recommended for discharge. For some parameters, there was enrichment of the contaminants which further showed a failure in the treatment system. Routine monitoring of paint industries is recommended to prevent the risk of contamination to the receiving watershed which many communities depends as source for domestic water.

Reference

1. Nkwocha, A.C.; Ekeke, I.C.; Kamen, F.L.; Oghome. Quality Assessment of Effluent Discharges from Vegetable Oil Plant. Ethiopian J. of Environ. Stud. Manage. 2013, Vol. 6 Supplement, pp. 717- 723. Available online: URL http://dx.doi.org/10.4314/ejesm.v6i6.2S 2013

2. Chidozie, K.; Nwakanma, C. Assessment of Saclux Paint Industrial Effluents on Nkoho River in Abia State, Nigeria. J. Ecosyst. Ecography 2017, 7(2), DOI: 10.4172/2157-7625.1000240
3. Ohioma, I.; Luke, N.O; Amraibure, O. Studies on the pollution potential of wastewater from textile processing factories in Kaduna, Nigeria. J. Toxicol. Environ. Health Sci. 2009, Vol.1 (2) pp. 034-037, Available online at http://www.academicjournals.org/JTEHS
4. Sewvandi, G.A.; Adikary, S.U. Removal of heavy metals from wastewater using chitosan. Soc. Social Manage. Sys. Int. J. 2011, Vol.07, pp. 1-8. Available online: URLhttp://hdl.handle.net/10173/836
5. Ranade, V. V.; Bhandari, V. M., Industrial Wastewater Treatment, Recycling, and Reuse: An Overview. Industrial Wastewater Treatment, Recycling, and Reuse Oxford: Butterworth-Heinemann. Elsevier Inc., pp. 1-80. DOI: 10.1016/B978-0-08-099968-5.
6. Krithika, D.; Ligy P. Treatment of Wastewater from Water Based Paint Industries Using Submerged Attached Growth Reactor Int. Biodeter. Biodegr. J. 2016, Vol.107, pp. 31-41, Available online: URL https://doi.org/10.1016/j.ibiod.2015.10.017
7. Żak, S.; Rauckyte-Żak, T; Laurinavičius, A; Siudziński, P. Research on Physico-chemical Pretreatment of Wastewater from the Production of Wood Coating Materials. Ecol. Chem. Eng. J. 2014 21(1), pp.101-112. DOI: 10.2478/eces-2014-0009
8. Olaoye, R. A.; Oladeji, O. S. Preliminary Assessment of Effects of Paint Industry Effluents on Local Groundwater Regime in Ibadan, Nigeria. Int. J. Eng. Res. 2015, Vol.4 (10), pp. 518-522.
9. Olaniyi, I.; Raphel, O.; Nwadiogbu, J.; Onyebuchi. Effect of Industrial Effluent on the Surrounding. Environment Archives of Applied Science Research Scholars Research Library, USA, 2012, Vol. 4 (1), pp. 406-407.
10. Federal Ministry of Environment, Federal Republic of Nigeria Official Gazette, 2011, Vol. 98(49), pp. B693-B728 The Federal Government Printer, Lagos, Nigeria, FGP 71/72011/400 (OL 46)
11. World Health Organisation, Regional Office for the Eastern Mediterranean Regional Centre for Environmental Health Activities CEHA 2006, A compendium of standards for wastewater reuse in the Eastern Mediterranean Region, pp. 1-19.
12. Department of Water Affairs – General and Special Authorisation, 1999, Discharge limits and conditions set out in the National Water Act, Government Gazette No. 20526, Wastewater limit values applicable to discharge of wastewater into a water resource.
13. Oyegoke, S.O.; Adeyemi A.O.; Sojobi A.O. The Challenges of Water Supply for A Megacity: A Case Study of Lagos Metropolis. Intern. J. of Sci. Eng. Res. 2012, Volume 3 (2), pp. 1-10. Maphill, 2011, available online: URL https://www.google.co.za/search?biw=1280&bih=610&tbm=isch&sa=1&ei=vSPLW7 _ RJMG0gAaX LbACQ&q=map+of+nigeria+showing+lagos&oq=map+of&gs_l=img. (accessed on 23/10/2018)
14. United State Environmental Protection Agency. Water monitoring and Assessment. Available online: URL https://archive.epa.gov/water/archive/web/html/vms52.html (accessed on 19/07/2018).
15. Edokpayi, J.N; Odiyo, J.O; Msagati T.A.M; Popoola, E.O. Removal Efficiency of Faecal Indicator Organisms, Nutrients and Heavy Metals from a Peri-Urban Wastewater Treatment Plant in Thohoyandou, Limpopo Province, South Africa. Intern. J. of Environ. Res. Public Health 2015, Vol.12, pp. 7300-7320, DOI: 10.3390/ijerph120707300.
16. Missouri Department of Natural Resources. Available online: URL dnr.mo.gov. (accessed on 20/07/18).
17. Julian, K.T; Marianne S.; Shaun, R. Contaminated Groundwater Sampling and Quality Control of Water Analyses. Environmental Geochemistry. 2nd Edition, British Geological survey, Nottingham, United Kingdom, 2018; pp. 25- 45.
18. Uwidia, I.E.; Ukulu, H.S. Studies on Electrical Conductivity and Total Dissolved Solids Concentration in Raw Domestic Wastewater Obtained from an Estate in Warri, Nigeria. Greener J. of Phys. Sci. 2013. Vol. 3(3), pp. 110-114.
19. Sulaiman, A.A.; Attalla, E.; Sherif, M. A. S. Water Pollution: Source & Treatment. Am. J. Environ. Eng. 2016, Vol. 6(3), pp. 88-98, DOI: 10.5923/j.ajee.20160603.02.
20. Tesfalem, B.W.; Abdrie, S.H. Toxicity Study of Heavy Metals Pollutants and Physico-chemical Characterization of Effluents Collected from Different Paint Industries in Addis Ababa, Ethiopia. J. Forensic Sci. & Criminal Invest 2017, Vol.5 (5), pp. 1-6. DIO:10.19080/JFSCI.2017.05.55568
21. Rachna, B.; Disha, J. Water Quality Assessment of Lake Water: A Review. Sustain. Water Resour. Manag. 2016, Vol. 2, pp. 161–173, DOI 10.1007/s40899-015-0014-7
22. World Health Organization. WHO Guidelines for Drinking-water Quality, Fourth Edition, , WHO Library Cataloguing-in-Publication Data, Malta Publisher: Gutenberg, 2011, available online: http://www.who.int, pp. 1-541, ISBN. 978 92 4 154815

23. State of Narragansett Bay and its Watershed 2017 Technical Report. Bay Ecosystem Condition Indicators Chapter 15: Dissolved Oxygen. Pp 277- 278. Available online: URL http://nbep.org/01/wp-content/uploads/2017/09/Bay-Ecosystem-Condition-Indicators.pdf (accessed on 16/08/2018)
24. Olaniyi, R.A. Impacts of Effluent Discharge on Water Ecosystem. Advanced Environmental Biology University of Lagos, Nigeria, 2009, pp. 1.8.(viewed on 16/08/2018),
25. Ram, S.L; Pravin, U.S; Deepali, S.P. Study on Physico-chemical Parameters of Waste Water Effluents from Taloja Industrial Area of Mumbai, India. Int. J. Ecosys. 2011, Vol. 1(1), pp. 1-9, DOI: 10.5923/j.ije.20110101.01.
26. Walakira, P.; Okot-Okumu, J. Impact of Industrial Effluents on Water Quality Receiving Streams in Nakawa-Ntinda, Uganda. J. Appl. Sci. Environ. Manage. 2011, Vol. 15 (2), pp. 289 – 296.
27. Onuegbu, T.U; Umoh, E. T; Onwuekwe, I.T. Physico – Chemical Analysis of Effluents from Jacbon Chemical Industries Limited, Makers of Bonalux Emulsion and Gloss Paints. Int. J. Sci. Technol. 2013, Vol. 2, No. 2,pp 169.

Preparation, characterization and assessment of mechanochemically activated clay soils for groundwater defluoridation and antibacterial potency

OA Obijole[1]*, MW. Gitari[1] and A Samie[2]

[1]Department of Ecology and Resource Management, University of Venda, South Africa
[2]Department of microbiology, University of Venda, South Africa
*Email of corresponding author: objid21@gmail.com.

Abstract

In this study, aluminosilicate rich clay soils were prepared through mechanochemical activation. The chemical and mineralogical properties were investigated using XRF and XRD. The functional groups, morphology and the surface area were evaluated using FTIR, SEM and BET. Batch experiments were used to assess defluoridation efficiency of the activated clay while the antibacterial capacity was evaluated using the well assay method. The maximum adsorption capacity of the mechanochemically activated clay soil was found to be 1.87 mg/g with 32% fluoride removal at 2 g/100 mL adsorbent dosage, initial fluoride concentration of 3.2 mg/L, pH 6.0, 60 minutes contact time and 250 rpm at 298 ^{0}K. Fluoride adsorption was found to reduce in the presence of chloride and slightly increase in the presence of sulphate and nitrate. However, phosphate and carbonate ions competed with fluoride uptake in the adsorption process as the percentage fluoride removed reduced from 36.65% to 30.61% and 36.65% to 17.5%, respectively. The equilibrium pH ranged between 6.8 and 7.9. Adsorption data fitted well to Freundlich isotherms, hence, confirming multilayer adsorption. The antibacterial studies reveal no zones of inhibition for all the activated clay samples thereby suggesting that they were not active against the bacterial strains of *Escherichia Coli* (*E. Coli*) used in this study. The results showed that mechanochemically activated clay can be used for defluoridation of groundwater, however its effectiveness in pathogen removal is limited. It is however, recommended that further studies be conducted to improve the sorption capacity of the activated clay as well as its antibacterial potency.

Keywords: Adsorptive capacity, Bacteria, Clay soils, Escherichia Coli, Fluoride, Mechanochemical activation

1. Introduction

Clay minerals are naturally occurring fine grained phyllosilicate materials which impart plasticity to clay and hardened when dried or fired [1]. The knowledge about the structure of clay minerals has significantly increased and the use of clay has widened greatly due to advances in instrumental analytical methods such as X-ray diffraction, electron microscopy and spectroscopy. Attention is now focusing on clay properties as natural nano-sized particles which are applied in adsorption, catalysis, and in nanoscience research [1, 2]. Clays contain the following main elements aluminum, silicon and oxygen, others are iron, magnesium, alkali metals, alkaline earths, and other cations present either in the interlayer space or in the lattice framework by isomorphous substitution [3]. Adsorption studies on clays and bauxite shows that bauxite has the best adsorption capacities followed by bentonite and palygorskite while kaolinite had the lowest adsorption capacities [2]. Studies on other adsorbents for defluoridation are laterite [4], mechanochemically activated kaolinites [5], China clay [6], bentonite and montmorillonite [7]. Various independent studies carried out by subjecting clay to high temperatures produced clay wares with optimal fluoride binding capacity. The results of these studies showed that clay could be a promising choice as efficient adsorbent for defluoridation of water [8]. Studies have been done on the use of red mud, coal fly ash and clay for defluoridation [9, 10, 11, 12]. Some of the metal oxides coated adsorbents from aluminosilicate materials including clay are good for defluoridation, but not totally active against microbial strains [13, 14]. The main objective of this work is to determine the physico-chemical and mineralogical characteristics of the clay soil from Mukondeni Village, South Africa, with a view to ascertain its suitability as adsorbents for defluoridation and pathogen removal from groundwater. This was done by investigating (i) the geological fluoride present in the activated clay, point of zero charge and CEC. (ii) the chemical and mineralogical properties using XRF and XRD. (iii) the functional groups, morphology and the surface area using FTIR, SEM-EDS and BET (iv) Evaluation of the activated clays' adsorptive capacities by batch mode. (v) antibacterial potency assessment using the assay method.

2. Materials and Methods

Sample collection and preparation

Clay soil samples used were sourced from Mukondeni village in Vhembe district, Limpopo, South Africa. The clay materials were cleaned, dried, ground and made to pass 250 µm sieve. The finely ground dry clay powder was then mechanochemically activated at different times and kept in zip lock bags until use.

Preparation of mechanochemical activation of clay sample

To prepare activated clay, the optimum milling time was investigated as follows: 10g of dried clay was weighed and transferred into the milling pot and clay was milled for 5, 10, 20, 30, 40 and 60 minutes at 700 rpm using Retsch RS200 milling machine. The obtained clay powder of <250 µm particle size was then stored in clean corked plastic bottle. The optimum milling time was obtained by evaluation of the mechanochemically activated clay at different times for defluoridation at a specific pH. Furthermore, the geological fluoride level was determined in activated clay with a view to determining its suitability for defluoridation in groundwater.

Physicochemical characterization

Surface area, specific surface area pore sizes and volumes was evaluated by using Brauner-Emmett-Teller (BET) method. Mineralogical composition of the activated clay was analyzed using a PANalytical X'Pert Pro powder diffractometer. Elemental composition was evaluated by using PAN analytical Axios X-ray fluorescence spectrometer. The activated clays were investigated for its morphology (size and shape at the surface) using SEM. The FT-IR analysis of the activated clay was carried out using Bruker: ALPHA FT-IR Spectrophotometer. The point of zero charge (pH_{pzc}) was determined by titration at 0.1 M, 0.01 M and 0.001 M KCl concentrations using Eggleson *et al* methods [15]. The concentration of exchangeable cations was determined using flame atomic absorption spectra (600 PerkinElmer). The Cation Exchange Capacity (CEC) was evaluated by using ammonium acetate buffers at pH 5.4 and 7.4 respectively, using Chapman method [16].

Defluoridation Experiments-Optimisation procedures

Batch adsorption experiment were used to assess the activated clays capacity for defluoridation of fluoride rich simulated water: The following parameters were optimized:

Contact time; adsorbent dosage; pH and fluoride concentrations. The effect of co-existing ions was also evaluated. Modelling of the adsorption isotherm was done from the data generated using Langmuir and Freundlich equations.

Antibacterial Studies

Antibacterial activities of the six mechanochemically activated clays were evaluated with *Escherichia*. *Coli* (*E. Coli*) strains by using well diffusion assay method. Mueller-Hinton agar plates were inoculated with *E. coli* (ATCC 35218). Wells with a diameter of 6 mm were cut using a cork borer and filled with 30 µl of the six activated clay soils. (A-F). Plates were incubated for 24 hours at 37°C. After incubation, the growth inhibition zone diameters were measured in millimeter (mm).

3. Results and Discussions

Geological fluoride levels in the mechanochemically activated clays

The geological level in the activated clay was done using batch experiments at different contact times and the percent fluoride removal calculated. The geological fluoride levels in the activated clays at different contact times of 5 to 60 minutes ranges between 0.0401 and 0.0638 mg/L. This was found to be much lower than the World Health Organization [17] and South African National Standards [18], whose recommended maximum fluoride limit is 1.5 mg/L. Hence the geological fluoride in the clay is within the safe threshold, therefore promising for defluoridation.

Physicochemical and Mineralogical Characterization

Surface Area by Brunauer-Emmett-Teller (BET)

The results of analysis of the mechanochemically activated clay samples (A-F) at different times shows that they are mesoporous in nature. That is, pore sizes ranged between 5-15 nm. Surface area ranged between 13-18 m^2/g. Specific surface area ranged between 12-17 m^2/g while pore volumes gave an average value of 10 cm^3/g. Clay sample D had the largest surface area (17.19m^2/g), specific surface area (16.66m^2/g), pore volume of 10.07 cm^3 and pore size14.93nm indicating the roughness of pore walls and increase of additional active sites while sample F have the smallest surface area (13.23 m^2/g), specific surface area (12.58 m^2/g), a low pore volume (10.05 cm^3/g) and pore size of 14.68 nm, respectively. Hence clay sample D which was activated for 30 minutes is considered optimum for the modification process.

Cation Exchange Capacity (CEC)

The CEC values of clay soil at pH 7.4 and 5.4 (milli equivalent/100 g) was calculated to be 74.5 and 82.1, respectively. From results obtained, it can be seen that the CEC is not dependent on pH because there was no significant difference in the concentration of cations at different pH. The results correlate with that reported by Mudzielwana *et al*. [19] and Gitari *et al*. [20] who concluded that CEC is independent of pH. From the values obtained above, it can also be concluded that the CEC of the clay soil is generally moderate.

Point of zero charge of activated clay

pH_{pzc} of the clay soil evaluated was found to be 6.1 (Adsorbent dosage: 1.0 g/50 ml, contact time: 24-hour, agitation speed: 250 rpm and 298 K). This value is close to smectite rich (pH_{pzc} 6.0) clay reported by [19] and lower than bentonite clay soil (pH_{pzc} 8.2) reported by [10]. pH_{pzc} refers to the pH at which the clay has zero net charges on the surface. Above the pH_{pzc} the clay is negatively charged and below the pH_{pzc} the clay is positively charged. Therefore, the implication of this is that adsorption of fluoride anions will most likely be high at a pH below 6.1 due to the clay surface being entirely occupied by positive charges. Furthermore, the close pH_{pzc}values of (pH_{pzc} 6.1) in this study and that of [19] which is (pH_{pzc} 6.0) could be attributable to both clays being smectite rich.

Morphology of the mechanochemically activated clay

Scanning electron microscopy (SEM) (Figure1 a–d) shows the surface structure of the most activated clay. This consist of the fine particles of irregular shape and size on external surface with a micro-rough texture, some of which can promote the adherence of fluoride. The morphology of the clay in Figure 1a and b shows an irregular porous structure at lower magnifications. At higher magnifications, the clay soils images show a smooth irregular surface, and an expanded honeycomb, flared, "cornflake" and platy like texture (Figure 1c and d). The characteristics of images shows typical smectite clay surfaces which aids fluoride sorption unto the clay surfaces.

The Energy Dispersion Spectroscopy (EDS) of the activated clay is presented in Figure 2a. The elemental concentrations are shown with Si, Fe, Al and O having high concentrations in the sampled powdered clay material. The EDS results is corroborated the XRD and XRF results. The EDS analysis was carried out at the University of Cape Town, South Africa.

X-Ray Diffraction (XRD)

XRD analysis shows that the activated clay soil sample is mainly composed of Plagioclase, Quartz, Chlorite, Kaolinite, Actinolite, Muscovite, Microcline, Calcite and Albite. The quantitative results in Figure 2b further confirm the presence of plagioclase (smectite rich clay soil) (31.09%) and quartz (24.55%) as the major minerals and the presence of Chlorite (13.71%) and kaolinite (11.62%) as minor minerals (Figure 2b).

X-Ray Fluorescence (XRF)

The XRF analysis of the activated clay shows that silica (SiO_2) is the main component at 52.48%, followed by Al_2O_3 at 14.62%. High concentrations of SiO_2 and Al_2O_3 reveal that they are rich in aluminosilicate material. Minor elemental compositions are P_2O_5, TiO_2, Na_2O, MnO, K_2O, CaO, MgO and Fe_2O_3.

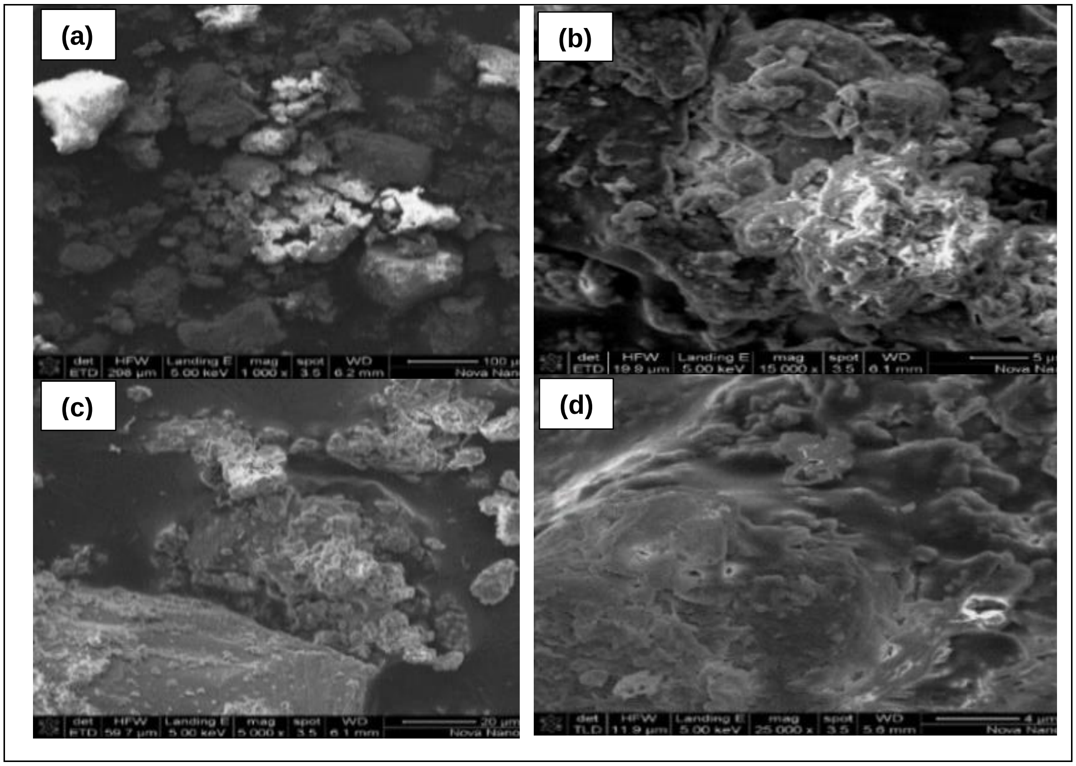


Figure 1a, b, c and d. Scanning electron microscopy (SEM) micrograph of the most mechanochemically activated clay at different magnifications.

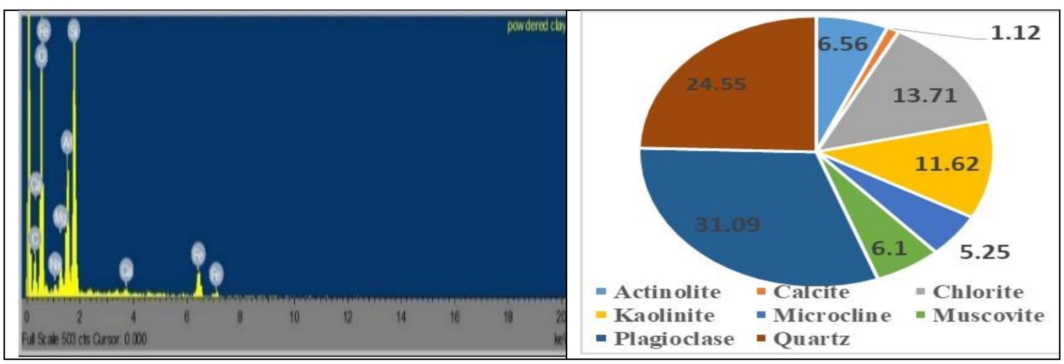


Figure 2. (a) Energy dispersal spectroscopy (EDS) and (b) XRD Quantitative results of the activated clay

Fourier Transform Infra-Red (FTIR) Analysis

The activated clay samples were scanned in the range between 4000 and 500 cm^{-1} and the spectra obtained is shown in Figure 3. The spectra show three main absorption regions of 3000-3800 cm^{-1}, 1300-1800 cm^{-1} and 500-1200 cm^{-1}. The hydroxyls stretching absorption bands are well established at around 3700 cm^{-1}. The absorption bands observed at 3400-3500 cm^{-1} and 1600-2700 cm^{-1} could be due to the OH vibrational mode of the hydroxyl molecule, which is observed in natural hydrous silicates. The bands between 3400 and 3700 cm^{-1} are attributed to the OH stretching mode. The H-O-H bending of water is observed at 1620-1640 cm^{-1}. In the 1000 cm^{-1}-500 cm^{-1} region, main functional groups were Si-O-Si and Al-O-H. The IR peak at 970 cm^{-1} may be attributed to Al-OH-Al. The IR spectra also showed Si-O stretching between 780 cm^{-1}-690 cm^{-1} and around 465 cm^{-1} which is indicative of quartz presence in the clay.

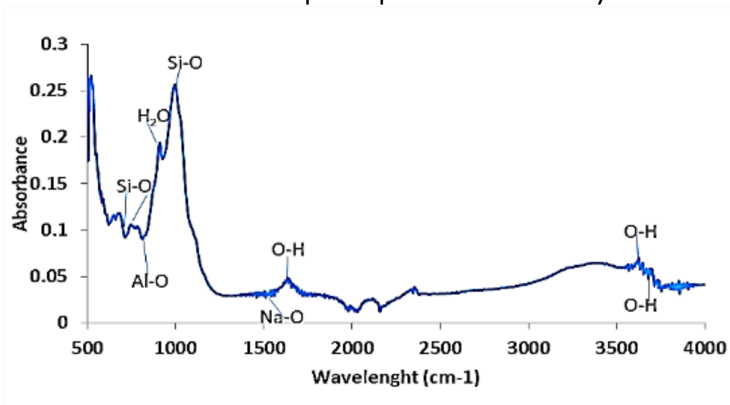


Figure 3. FT-IR Spectra of the activated clay

Defluoridation of simulated fluoride water with mechanochemically activated clay

The percent fluoride removal of clays activated at different times of between 5 and 60 minutes gave between 21.81% and 28.49%. Sample D exhibited highest removal of 28% indicating optimum activation time of 30 minutes. The plot of adsorption capacity versus activated time is presented in Figure 4.

The adsorption capacities increase from 0.94 mg/g to 1.195 mg/g at 30 minutes activation time and reduces thereafter to 0.915 mg/g at 60minutes activation, hence indicating that the activation had effect on the adsorption capacity of the clay soils. This was probably due to increase in the surface area which peaked at 30 minutes activation.

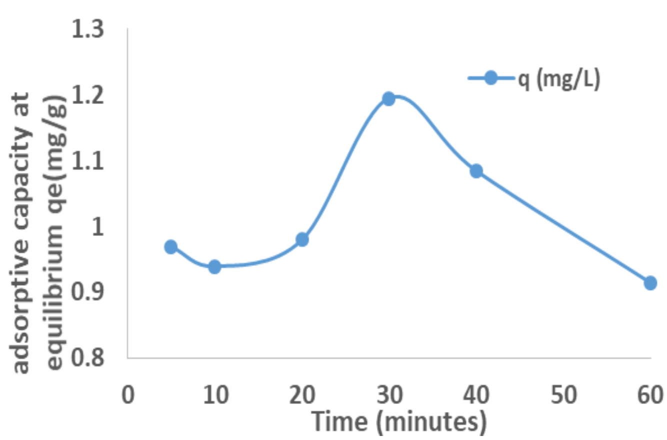


Figure 4. Plot of adsorptive capacity (mg/g) versus time (minutes)

Optimization of fluoride adsorption conditions

Effect of contact time

An increase in the percent fluoride removal with an increase in contact time was observed (Figure 5a). The reaction kinetics were very rapid within 20 minutes of contact and thereafter stabilized at ≈60 minutes (24.5% fluoride removal). After 60 minutes, the fluoride removal rate stabilizes, indicating that the reaction has reached equilibrium. Therefore, 60 minutes was taken as the optimum contact time and was used for subsequent experiments.

Effect of adsorbent dosage

Percent fluoride removal was observed to increase with an increase in the clay dosage (Figure 5 b). As dosage increases, more sites and surfaces become available for fluoride uptake. From 0.1 to 2.1g dosage, the fluoride uptake was observed to increase gradually (percent fluoride removal ≥38). At low adsorbent dosage, there is rapid fluoride adsorption rate since the active sites are more readily available while at high adsorbent dosage, the adsorbate species increasingly find it difficult to access the adsorption sites, hence gradual stabilization in adsorption process. Therefore, it can be concluded that the optimum dosage of the activated clay for defluoridation is 2.0 g/100 mL, hence it was adopted for subsequent experiments.

Effect of pH

The percent fluoride removal increases as pH increases from 1 to around 5 and thereafter decreases steadily until pH 10-12 is reached. This shows that at lower pH from 1-5, the positive sites on the adsorbent are being filled up by the fluoride, hence increased percent fluoride removal. Above pH 6, percent fluoride removal decreases. There was an increase in percent fluoride removal (from 22% to 48%) as the pH increases up to about 5. (Figure 5c). Hence it could be concluded that fluoride removal is dependent on the pH of the media. The chemistry of fluoride removal at different pH could be explained by relating it to the point of zero charge (pH_{pzc}) of the activated clay adsorbent. pH_{pzc} refers to the pH at which the adsorbent has zero net charges on the surface. Above the pH_{pzc} the clay adsorbent is negatively charged and below the pH_{pzc} the clay adsorbent is positively charged. Therefore, adsorption of more fluoride anions was observed to be at a lower pH up to about 5 which is around the point of zero charge of our clay adsorbent which was earlier determined to be 6.1. Higher adsorption at lower pH range lead to the assumption that chemisorption predominates while lower adsorption at higher pH range than the point of zero charge of 6.1 is suggestive of physisorption which predominates at these range.

Effect of fluoride ion Concentration

There is a sharp decrease in percent fluoride removal (from 32% to 18%) as the initial fluoride concentration increases from 1-5mg/L and thereafter stabilizes with further increase in the initial fluoride concentration from 5-90mg/L (Figure 5d). The decrease in fluoride adsorption was due to more fluoride ions in solution at higher fluoride concentrations, competing for fewer binding sites on the clay surfaces. Hence an initial fluoride concentration of 3.2mg/L was taken as the optimum concentration for subsequent experiments. It can thus be concluded that optimized adsorption conditions are at 60 minutes contact time, 2.0g dosage, 3.2 mg/L initial fluoride concentration, pH 6.0, agitation speed 250rpm and 298 ^{0}K.

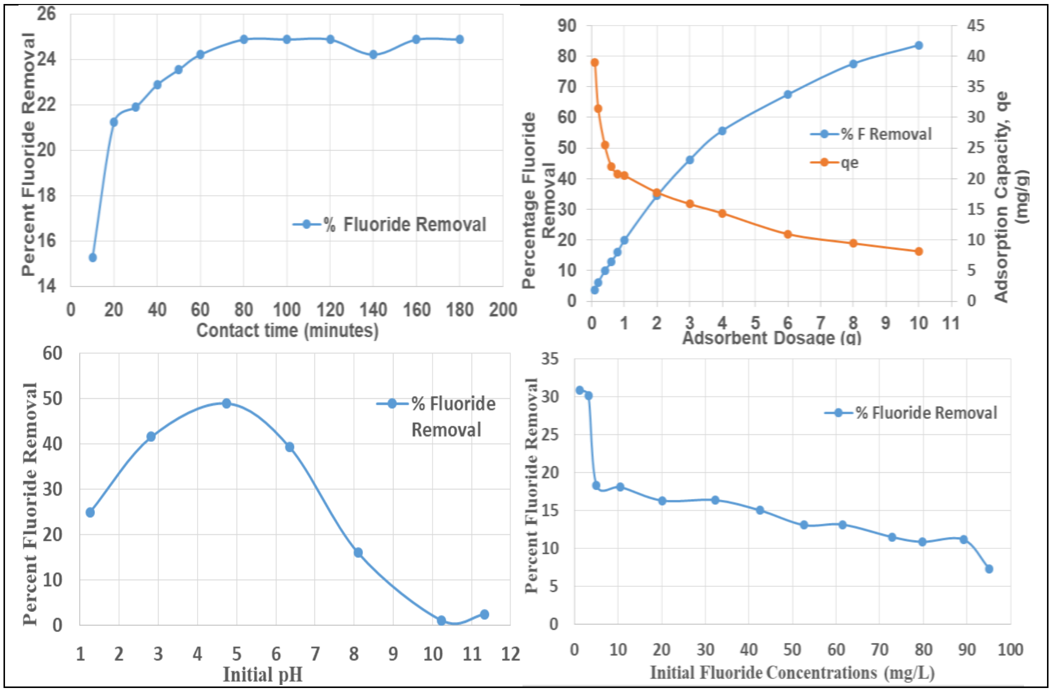


Figure 5. Optimization of fluoride removal by the activated clay (a) effect of contact time, (b) effect of adsorbent dosage, (c) effect of initial pH and (d) effect of initial concentration.

Effect of co-existing anions on the defluoridation process

Groundwater generally may contain other types of anions, in addition to F ions, which may be interfere with the defluoridation processes. Figure 9 shows the results of the effect of some co-existing anions on the adsorption of fluoride ions by activated clay. The adsorption of Fluoride ions onto the activated clay is slightly influenced by the Chloride ions, as there is little decrease in percentage fluoride removal from the blank while Sulphate and Nitrate ions gave some slight increase in percentage fluoride removal. However, Phosphate and Carbonate ions tends to be competing with the fluoride in the defluoridation process as the percentage fluoride removed was reduced from 36.65 to 30.61 and 36.65 to 17.5 respectively. Generally, negatively charged ions are naturally attracted to positively charged ions. The extent of attraction is dependent on the magnitude of charge and size of ion. Usually higher (multivalent) charged anions are more strongly attracted to cations for bonding than the univalent anions. This probably explains why Phosphate and Carbonate ions competed more with Fluoride for adsorption than other anions. The equilibrium pH ranged between 6.88 and 7.98.

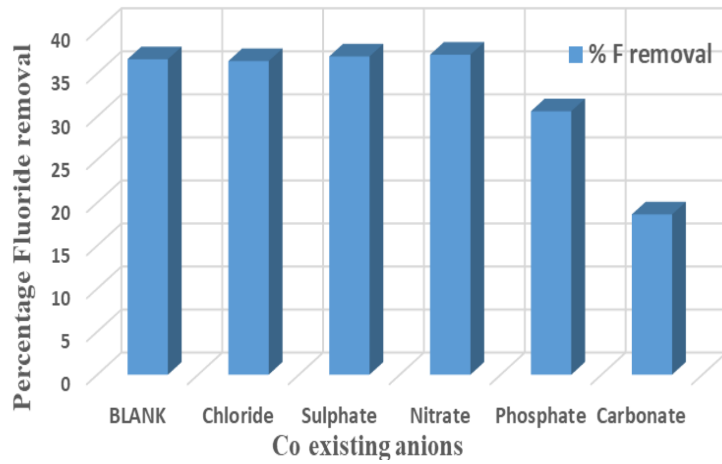


Figure 9. The percent fluoride removal in the presence of co-existing anions. (Contact time= 30 minutes; pH= 6.3; Initial fluoride concentration= 10 mg/L; Initial co-existing anions concentration= 10 mg/L; Adsorbent dosage= 2 g; Volume of solution= 100 mL; agitation speed= 250 rpm; Temperature= 298 ^{0}K).

Adsorption isotherms

Langmuir [20] and Freundlich [21] adsorption models are equilibrium test used to provide a general idea of the adsorbent effectiveness in defluoridation. The adsorption capacity of the activated clay for fluoride and the nature of the adsorbent surface were determined by analyzing the sorption data to fit into Langmuir and Freundlich isotherms.

Langmuir adsorption isotherm models the monolayer coverage of the adsorption surfaces and assumes that adsorption takes place on a structurally homogenous surface of the adsorbent. The linear form of the Langmuir model is given as Langmuir, (1916), [20]

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \quad (3)$$

Where Ce is the concentration of fluoride at equilibrium, qe is the adsorption capacity, q_{max} is the monolayer capacity of the adsorbent and b is the Langmuir adsorption constant. The values of Langmuir parameters, q_{max} and b was calculated from the slope and intercept of the linear plots of $\frac{1}{qe}$ versus $\frac{1}{Ce}$, with regression coefficient (R^2) in Figure 11a. The plot of Ce/qe values against Ce for the sorption data at 298 ^{0}K gave straight lines with high correlation coefficients of $R^2 = 0.85$ (Figure 11a); an indication of a favorable adsorption, possibly a monolayer adsorption of fluoride on the smooth surface of the adsorbent. Freundlich equation is derived to model the multilayer adsorption on heterogenous surfaces. The linearized form of Freundlich model is given as Freundlich [21]:

$$\text{Log } q_e = \log k_F + \frac{1}{n \log C_e} \quad (4)$$

Where $C_e$is the equilibrium concentration, q_e is equilibrium adsorption capacity and $\frac{1}{n}$ are Freundlich constants related to minimum adsorption capacity and adsorption intensity respectively. The values of k_F and $\frac{1}{n}$ are obtained from the slope and intercept of the linear Freundlich plot of log qe versus logCe . [21]. The plot of log qe against log Ce for the sorption data at 298K gave straight lines with high correlation coefficients (R^2) as shown in Figure 11b.This is also an indication of favorable adsorption. The correlation coefficient is however higher than those of Langmuir isotherm with (R^2 =0.98). Therefore, Freundlich isotherm gave a better fit to the sorption data, thereby confirming heterogeneous (multilayer) adsorption process.

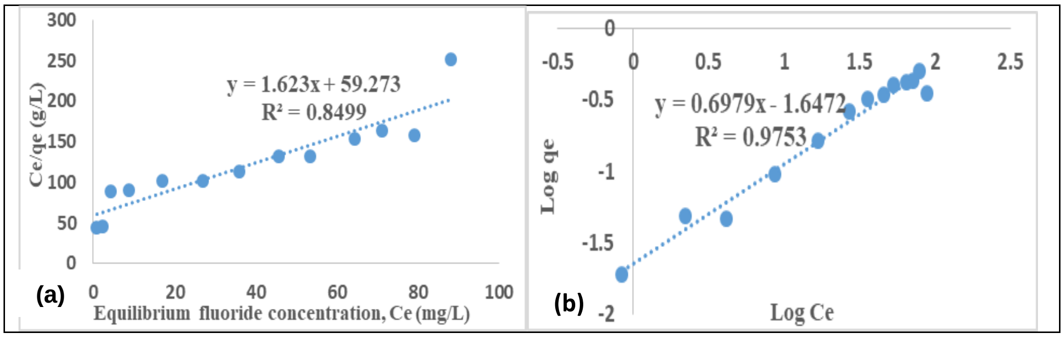


Figure 11. (a) Langmuir, and (b) Freundlich adsorption isotherms. (10 mg/L fluoride concentrations, 2.0 g/100 mL adsorbent dosage and 60 minutes contact time at 250 rpm. Fluoride concentration was varied from 1 to 100 mg/L).

Antimicrobial experiment Using Well diffusion assay method

Antibacterial activities of the clay samples were determined by using assay method. Figure 12 shows pictorial view of the zone of inhibition of the six clay samples investigated. All the six samples have zero zone of inhibition, thereby indicating that they do not have any potent activities against the *E. Coli* strains.

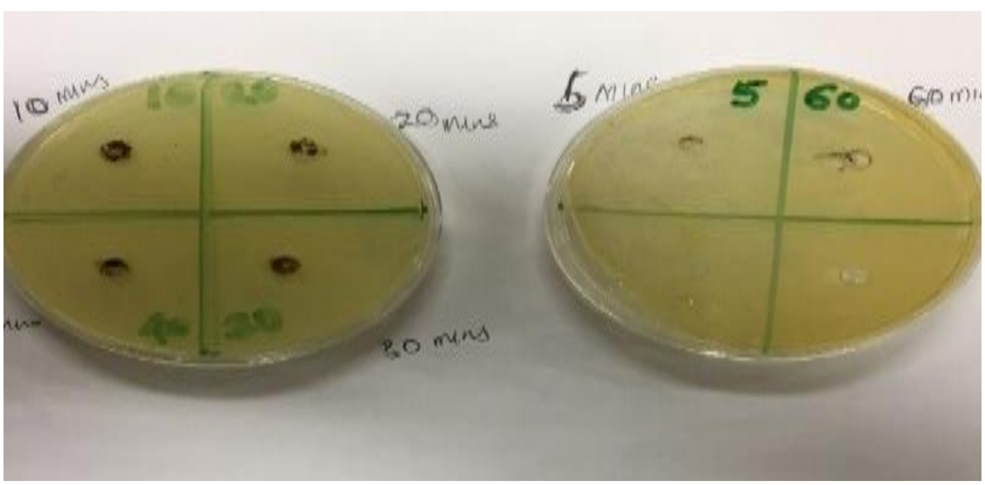


Figure 10. Pictorial view of zone of Inhibition of *Escherichia Coli* (*E. Coli)* strains against activated clay samples (A-F).

4. Conclusion

The search for low-cost, simple and an acceptable material for efficient simultaneous defluoridation and pathogen removal from water, for rural household usage lead to the choice of clay among others, since clay soil minerals are widespread and are in great abundance around the world. Evaluation of the mechanochemically activated clays' adsorptive capacities was found to be 1.87 mg/g with optimum defluoridation of 32% at 60 minutes contact time, 2.0g dosage/100 mL, 3.2 mg/L initial fluoride concentrations, pH 6.0, 250 rpm at 298K. Studies on the effect of co-existing anions showed that fluoride adsorption was reduced in the presence of chloride and increase slightly in the presence of sulphate and nitrate. However, phosphate and carbonate ions competed with defluoridation during the adsorption process as the percentage fluoride removed reduced from 36.65% to 30.61% and 36.65% to 17.5%, respectively. Adsorption data of the clay fitted well to Freundlich isotherms, therefore, confirming multilayer or heterogenous adsorption. All the activated clay does not show any activity against the *Escherichia Coli* (*E. Coli*) strains. Thus, suggestive of low or absence of antibacterial properties on the clay's surfaces. The adsorption efficiency and antibacterial potency of the activated clay for groundwater defluoridation and pathogen removal could therefore be probed further with a view to improving its sorption capacity and enhancement of the antibacterial potency.

Acknowledgments: The authors hereby acknowledge the financial support from Research & Innovation Directorate, University of Venda (Project no. SES/17/ERM/10) and Ecology and Resource Management department, University of Venda, South Africa.

References

1. Guggenheim, S. and Martin, R. T. Definition of clay and clay mineral: Joint report of the AIPEA and CMS nomenclature committees. Clays and Clay Minerals. 1995, 43, 2, 255–256.
2. Coetzee, P. P., Coetzee, L. L., Puka, R., and Mubenga, S. Fluoride adsorption modelling and characterization of clays for defluoridation of natural clays. Water SA. 2003, 29, 3, 331-338.
3. Konta, J. Clay and Man: Clay raw materials in the service of man. Applied Clay Sci. 1995, 10, 275-335.
4. Sarkar, M., Banerjee, A., Pramanick, P. P. and Sarkar, A. R. Use of laterite for fluoride removal from contaminated drinking water, J. Colloid Interface Sci. 2006, 302, 432–441
5. Meenakshi, S., Sairam Sundaram, C. and Sukumar, R. Enhanced fluoride sorption by mechanochemically activated kaolinites, J. Hazard mater. 2008, 153, 164–172.
6. Chaturvedi, K., Yadava, K. P., Pathak, K. C., Singh, V. N. Defluoridation of water by adsorption on fly ash. Air Soil Pollut. 1990, 49, 51-61.
7. Tor A, N Danaoglu, G, Arslan, Y. Cengeloglu. Removal of fluoride from water by using granular red mud: Batch and column studies. J. Hazard Mater. 2009, 164, 271-278.
8. Hauge, S., Osterberg, R., Bjorvatn, K. and Selvig, K. A. Defluoridation of drinking water with pottery: Effect of firing temperature. Scandinavian J. of Dental Res. 1994, 102, 329-333.
9. Bjorvatn, K., Bardsen, A., Tekle-Haimanot, R. Defluoridation of drinking water by use of clay/soil. In Defluoridation; Laboratory Experiences, Proceedings of the 2nd International Workshop on Fluorosis Prevention and Defluoridation of Water, Nazareth, Ethiopia, Nov 19–25. Dahi, E, Nielsen, J. M, (Eds). The Int. Soc. for Fluoride Res. New Zealand, 1997, 100–105.
10. Gitari, W. M., Ngulube, T., Masindi, V. and Gumbo, J. R. Defluoridation of groundwater using Fe^{3+}-modified bentonite clay: optimization of adsorption conditions. Desal. Water Treat. 2013, 53, 6, 1578–1591.
11. Gitari, M.W., Petrick, L.F., Musyoka, N.M. Hydrothermal conversion of S.A. CFA into pure phase zeolite Na-P1. In *Metals and Non-metals 'Zeolites-Useful minerals'* Claudia Belviso (Ed). 2016, 25-42.
12. Masindi, V., Gitari, M.W. and Ngulube, T. Defluoridation of groundwater using Cryptocsrystalline magnesite. J. of Water Reuse and Desalination. 2015, 05.3, 283-292.
13. Hauge, S., Osterberg, R., Bjorvatn, K. and Selvig, K. A. Defluoridation of drinking water with pottery: Effect of firing temperature. Scandinavian J. of Dental Res. 1994, 102, 329-333.

14. Dhillion, A. and Kumar, D. Development of nanoporous adsorbents for the removal of health-hazardous fluoride ion from aqueous systems. J. Mater. Chem. A. 2015, 3, 4215-4228.
15. Eggleson, C. M., and Jordan G. A new approach to pH of point of zero charge measurement: Crystal-face specificity by scanning force microscopy (SFM). Geochimica et Cos. Acta. 1998, 62, 11, 1919-1923.
16. Chapman H, D. Cation-exchange capacity. In C, A. Black (ed). Methods of soil analysis-chemical and microbiological properties. Agronomy 1965, 9, 891-901.
17. WHO. Water Sanitation/Health. http://www.who.int/water_sanitation_health/diseases. 25/08/18 2015
18. SANS 241. South African National Standard (SANS) 241 Drinking Water Specification. South African Bureau of Standards (SABS) SANS 241. Pretoria, South Africa, 2006.
19. Mudzielwana, R., Gitari M. W and Msagati, T. A. M. Characterisation of smectite-rich clay soil: Implication for groundwater defluoridation. S Afr J Sci. 2016,112, 11/12, 1-8.
20. Langmuir, J. The properties of solids and liquids. J. Am. Chem. Soc. 1916, 38, 2221-2295
21. Freundlich, H. M. F. (1906). Uber die adsorption in losungen. Z. Phys. Chem. 57A 385-470.

Biosynthesis of Ag-MgO-nanohydroxyapatite on nanofibrous cellulose for fluoride and bacterial removal in groundwater

WB Ayinde[1]*, WM Gitari[1], M Munkombwe[2] and A Samie[3]

[1]Department of Ecology and Resource Management, University of Venda, South Africa.
[2]Mintek, South Africa, Advanced Materials Division (Nanotechnology Innovation Centre).
[3]Department of Microbiology, University of Venda, South Africa.
*Email of corresponding author: twasiu33@gmail.com

Abstract

The present work focused on sustainable and innovative approach via bio-reduction route using Citrus paradisi peel extracts in the assembly of modified nanofibrous cellulose blended with Ag-MgO-nanohydroxyapatite (CNF-AgMgOnHaP) as a multifunctional adsorbent towards simultaneous defluoridation and pathogen removal in groundwater. Surface morphology and mineralogical properties of the nanocomposite were examined by UV–vis spectroscopy, SEM-EDS and FTIR respectively. Effects of contact time, adsorbent dose, pH, initial concentration along with antibacterial potency was investigated on removal of fluoride and typical pathogenic water strain using CNF-AgMgOnHaP adsorbent. The CNF-AgMgOnHaP composite has a BET surface area of 160.17 m^2/g. The sorption of fluoride by the adsorbent was found to be strongly dependent on the different sorption conditions. The experimental data indicated that the linear adsorption isotherms are well described by the Langmuir isotherm equation with maximum adsorption capacity of 8.9 mg g^{-1} at 303 K. The kinetic study indicated that the pseudo second-order model was the most suitable model that best describes the fluoride sorption behavior on the adsorbent surface. The synthesized nanocomposite adsorbent also exhibits antibacterial activity against both gram negative and positive water bacteria strains. Results obtained suggests that CNF-AgMgOnHaP nanocomposite has an improved potential for simultaneous defluoridation and antibacterial application in groundwater.

Keywords: Bio-reduction, nanocomposite, C*itrus paradisi*, simultaneous microbial-fluoride removal

1. Introduction

Water is a constant factor in human life. Drinking water sources are increasingly deteriorating because of natural processes and anthropogenic activities. The most appropriate and widely used source of drinking water for many rural communities in Sub-Saharan Africa and other developing countries is groundwater [1]. However, groundwater can become unsuitable for drinking due to the high concentration of naturally occurring and human-induced chemical species as well as microbial pollution [2-4]. Fluoride is important for normal mineralization in formation of bones and dental enamel; however, at higher concentration becomes detrimental to health [5-6]. Fluoride epidemics in drinking water have become a global problem with over 200 million people suffering from high health effects (dental or crippling skeletal fluorosis) and morbidity in a number of regions [7-9]. In addition to fluoride epidemics, the majority of acute water-related diseases are often associated with microbiological contamination. The inefficiency of conventional water treatment methods to filter and disinfect these pathogens and remove toxic chemical species from water has led scientists and engineers to look into new sustainable and innovative technologies, which utilize simple, eco-friendly and inexpensive technology for the supply of potable water. The techniques towards such removals are based on the principle of sorption as well as chemical-cell death by disrupting the cell walls of the microbes, especially at the point of use [10-11]. Various techniques have been reported for the removal of fluoride in drinking water, such as precipitation, reverse osmosis, electrodialysis, ion exchange, nanofiltration and adsorption [12]. Of these methods, adsorption is the most appropriate method due to its effectiveness, energy saving, economical in nature, and simplicity in small water resource layout [13-14]. Hence, this study focuses on the green synthesis, characterization and application of reusable Ag-MgO loaded on nanohydroxyapatite on a cellulose matrix via a natural bio-reductive, capping and a stabilizing agent (aqueous C. *paradisi* peel extracts) for simultaneous defluoridation and pathogen removal from groundwater.

2. Materials and Methods

Synthesis of CNF-AgMgOnHaP composite

CNF-AgMgOnHaP composite was synthesized by incorporating nanohydroxyapatite bound to Ag-MgO nanoparticle into a cellulose nanofiber matrix via bio-reduction and in-situ precipitation method at room temperature. 10 g of colloidal cellulose suspension from sawdust (CNF) was added to a mixture of solutions containing 40 mL of aqueous C*itrus paradisi* peel extract, 60 mL 1 mM $AgNO_3$ and 20 mL 0.1M $Mg(NO_3)_2.6H_2O$. The solution was mixed under continuous stirring for 12 h at 40 °C. The bio-reduction process seed growth kinetic of the nanocomposite through color variation was monitored using UV–Vis spectroscopy. 5 g of nanohydroxyapatite (nHap) was thereafter dispersed into the reaction mixture (CNF-AgMgO) and the mixture was agitated in a magnetic stirrer for 8 h to achieve homogenous mixing. The mixture was filtered, and oven dried at 60 °C for 24h and then ground to obtain (CNF-AgMgOnHaP) composite powder.

Adsorption experiment: Kinetics and Isotherms

The sorption studies to defluoridates groundwater by the CNF-AgMgOnHaP adsorbent was evaluated using batch experiment. The effects of contact time, pH, adsorbent dose, initial adsorbate concentration, etc. on the equilibrium adsorption capacity were optimized. 1000 mg/L standard stock solution of fluoride was prepared by dissolving 2.210 g NaF into 1000 mL of ultrapure water (18.2 MΩ/cm) at ambient condition. The desired fluoride solution was prepared by appropriate dilution of the standard stock solution. Batch adsorption experiments were carried out by mixing 0.225 g of CNF-AgMgOnHaP with 50mL of 10 mg/L F- solution. The mixture was shaken thoroughly using a thermostatic water bath shaker (STUART SSL2) at 250 rpm. The solution was then filtered, and the residual fluoride ion concentration was determined. All the experiments were conducted in triplicate, and the mean of the results computed. Equations 1 and 2 were used to determine the percentage fluoride removal and adsorption capacity, q (mg/g) of the adsorbent.

$$\%\text{ Adsorption } = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1); \qquad q = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

Where: C_o is the initial F- concentration (mg/L); C_e is the F- concentration at equilibrium (mg/L); V, volume of solution (L) and m is the dried mass of the adsorbent (g). The equilibrium data were then fitted using the linear Langmuir [15], Freundlich [16] and Dubinin-Radushkevick (D-R) [17]. The linear form of Langmuir isotherm equation;

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_a} + \frac{C_e}{Q_m} \quad (3); \qquad R_L = \frac{1}{1 + K_a . C_i} \quad (4)$$

The logarithmic form of Freundlich isotherm equation;

$$logq_e = logK_F + \frac{1}{n} logC_e \qquad (5)$$

Dubinin–Radushkevich isotherm equation is expressed as;

$$q_e = q_s \exp(-B\varepsilon^2) \qquad (6) ; \qquad \varepsilon = \mathrm{RT} \ln\left[1 + \frac{1}{C_e}\right] \qquad (7)$$

$$E = \frac{1}{\sqrt{2\beta_D}} \qquad (8)$$

Where: Q_m (mg/g) is the maximum adsorption capacity for a complete monolayer of an adsorbent, C_e (mg/L) is the adsorbate equilibrium concentration, q_e (mg/g) is the amount of F- ion adsorbed at equilibrium, K_a (L/mg) is the Langmuir adsorption equilibrium constant, K_F [(mg/g)/(mg/L)n] and 1/n are empirical Freundlich constant describing sorption capacity and sorption intensity parameters respectively. Also, β_D (mol^2/kJ^2) is the activity coefficient constant related to mean sorption energy; ε is the Polanyi potential; and E (kJ/mol) is the mean adsorption energy. In order to evaluate the mechanism and time dependence kinetic parameters of F- sorption by CNF-AgMgOnHaP surface, Pseudo first order kinetic model [18] (Eq. (9)), Pseudo second order kinetic [19] (Eq. (10)) and intra-particle diffusion model [20] (Eq. (11)) were used to test the experimental data.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \qquad (9)$$

$$\frac{t}{q_t} = \frac{1}{q_e} \times t + \frac{1}{k_2 . q_e^2} \qquad (10) ; \qquad q_t = k_{id} * \sqrt{t} \qquad (11)$$

Where: q_e and q_t are the amounts of adsorbate uptake per mass of CNF-AgMgOnHaP adsorbent ($mg.g^{-1}$) at equilibrium and at time t (min), respectively; with K_1, K_2 and K_i (min^{-1}) representing the rate constant of the pseudo-first-order, pseudo-second-order and intraparticle diffusion rate constants respectively.

2. Results and Discussion

Characterization

The morphological profile of the CNF-AgMgOnHaP with the inherent elemental distribution (Figures 1a-c) revealed a rough and heterogeneous surface with specific surface area 160.17 m^2/g with a micropore and mesopore area of 5.46 m^2/g and 196.12 m^2/g respectively.

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

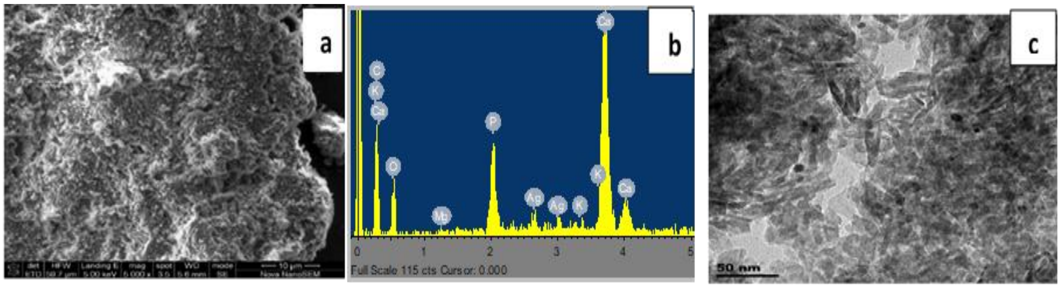


Figure 1. (a) SEM, (b) EDX, (c)TEM of CNF-AgMgOnHaP.

Effect of contact time

Figure 2 showed the effect of contact time on fluoride sorption by the composite. As shown, the fluoride sorption process evidently increased sharply as the time increases within the first 10 min contact time with about 93 % of F- removal. Subsequently, the adsorption rate became slower (10-20 min) with no appreciable difference in the percent fluoride removal until complete saturation was achieved. The rate of fluoride removal within the rapid equilibration time was due to the presence of free and abundant binding sites across the adsorbent surface. The optimum fluoride removal performance was assigned to contact time 10 min equilibration time; these were used in subsequent sorption experiments.

Effect of pH

Figure 2 displays the effect of initial solution pH (3-12) on fluoride sorption by CNF-AgMgOnHaP adsorbent using 0.25 g/50 mL of sorbent at 10 mg/L fluoride solution. It was observed that the removal efficiency of fluoride by the synthesized adsorbent was pH-dependent as it tends to increase with a maximum F- removal of 94% at pH of 5 increasing pH value. As shown on the plot, further increase in pH of the solution medium shows a gradual decrease in fluoride sorption percentage from pH 7 (87 %) to pH 12 (54 %). This variation showed the influence of solution pH on the sorption mechanism occurring at the adsorbent-sorbate interface. At higher pH, the concentration of the -OH is higher, which competes with the sorption sites of the composite thereby leading to lower % fluoride removal. Furthermore, the changes in the solution pH change the surface charge and protonation/deprotonation of the binding functional groups across the CNF-AgMgOnHaP adsorbent, as well as the solubility of fluoride ion species during the process [21-22].

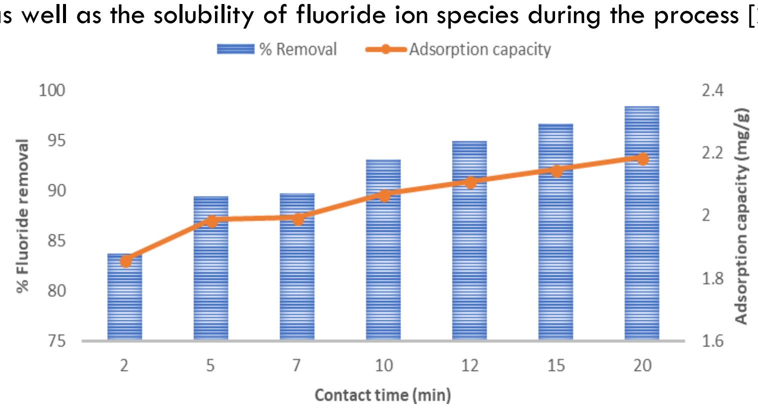


Figure 2. Effect of contact time

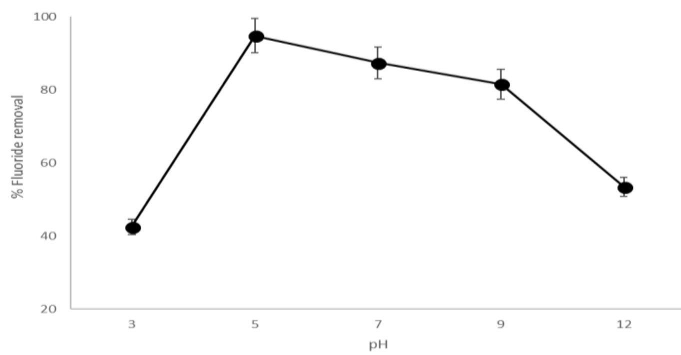


Figure 3. Effect of pH on fluoride adsorption by CNF-AgMgOnHaP

Effect of sorbent dosage

The adsorption efficiency of F- ion as a function of CNF-AgMgOnHaP dosage was investigated and the result is depicted in Figure 4. From the figure, the removal efficiency of F- is dependent on the adsorbent dosage varying from 0.1 g to 0.35 g (~69.0 to ~99 %). This may be attributed to the fact that increasing the dose of CNF-AgMgOnHaP creates more vacant available surface binding charge sites favoring the fluoride ions sorption-adsorbent interaction. In addition, increasing the sorbent dosage resulted in a decrease in the adsorption capacity (Figure 4).

Effect of co-existing anions

Figure 5 illustrates the variation of F- removal efficiency by the adsorbent with other coexisting anions (such as Cl^-, NO_3^-, CO_3^{2-}, and SO_4^{2-}) in water. The result showed that the presence of anions like Cl^-, NO_3^-, and SO_4^{2-} had a slight effect on fluoride sorption by CNF-AgMgOnHaP, with NO_3^- interfering in the least when compared with the anion-free water. However, CO_3^{2-}competed with the F- sorption for surface binding sites leading to reduction in the amount of fluoride removal from ~93 % to ~80%.

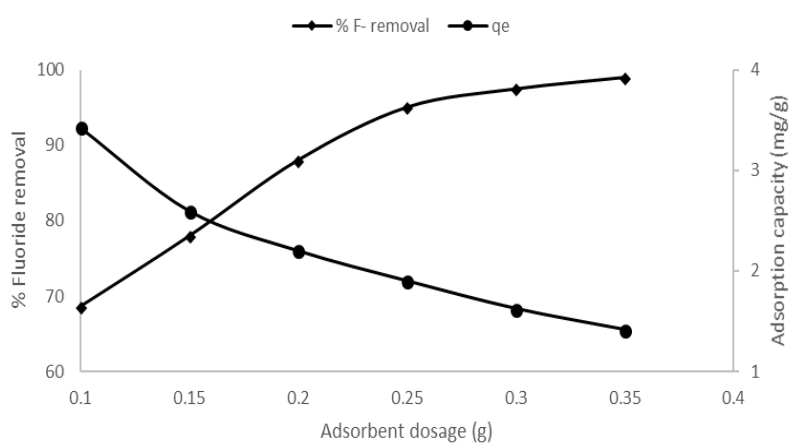


Figure 4. Effect of adsorbent dosage on fluoride adsorption.

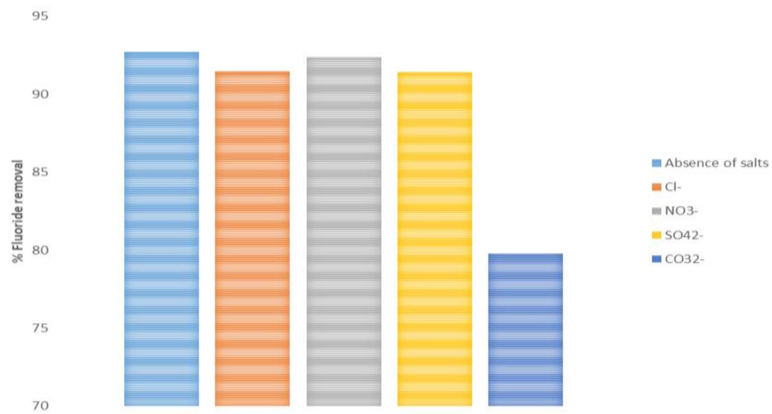


Figure 5. Effect of co-existing anions

The Batch adsorption isotherms

Table 1 shows the adsorption isotherms plots together with the corresponding calculated parameters of the sorbed F- on CNF-AgMgOnHaP composite at 303 K. Based on the higher correlation coefficients (R^2) values comparison (Table 3), it was found that the fluoride sorption onto the CNF AgMgOnHaP was best described by Langmuir isotherm model at the operating temperatures studied. (Langmuir > Freundlich > D-R), indicating that the adsorption of fluoride onto the CNF-AgMgOnHaP corresponds to monolayer adsorption [15]. The R_L values obtained ranged between 0 and 1 confirming favourable adsorption. Furthermore, the physical adsorption mechanisms of F- onto the adsorbent was supported by both the values of n, which falls between 1 and 10 as well as the E (kJ/mol) values from D-R [23] as shown in Table 1.

TABLE 1. Fitting isotherm parameters for fluoride sorption by the CNF-AgMgOnHaP adsorbent at 303 K.

Models	Parameters	Values
Langmuir	Q_{max} (mg.g^{-1})	8.92
	K_a (L.mg^{-1})	0.406
	R_L	0.198
	R^2	0.984
Freundlich	K_f	2.685
	n	3.359
	R^2	0.957
D-R	β_{DR} (mol^2/kJ^2)	4.00E-08
	q_{max}(mg/g)	5.046
	E (kJ/mol)	3.535
	R^2	0.749

Batch adsorption kinetic studies

Table 2 summarizes the kinetic parameters for fluoride adsorption by CNF-AgMgOnHaP composite. The calculated parameter values showed that pseudo-second-order model (Figure 6) best described the kinetic process of fluoride adsorption onto CNF-AgMgOnHaP. Therefore, the initial fluoride adsorption rate was extremely rapid and defluoridation occurred through chemisorption in contrast to physisorption characterized by weak van der Waal's force [5].

TABLE 2. Fitting kinetic parameters for fluoride sorption unto CNF-AgMgOnHaP adsorbent

Kinetic models	Parameters	Values
Pseudo first order	$q_e/(mg.g^{-1})$	0.843
	k_1 (min^{-1})	0.233
	R^2	0.89
Pseudo second order	$q_e/(mg.g^{-1})$	2.241
	k_2 (g/min mg)	0.67
	R^2	0.99
Intraparticle diffusion	K_{id} ($mg/g\ min^{1/2}$)	1.723
	R^2	0.97

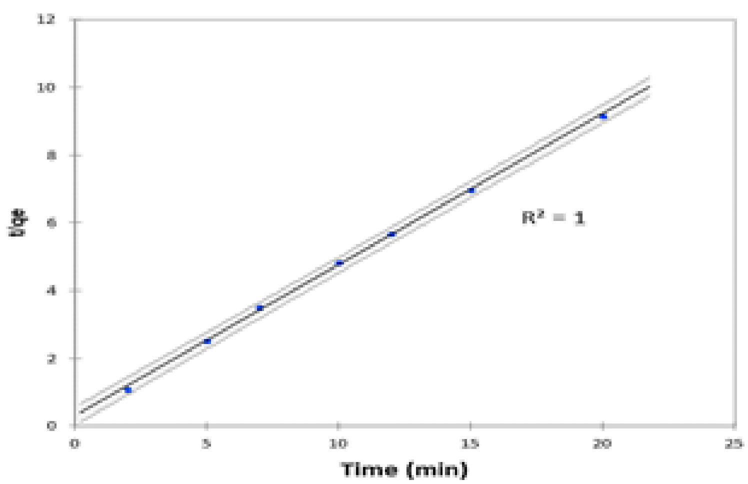


Figure 6. Pseudo-second-order kinetics plot.

Antibacterial activity

Table 3 shows the observed antibacterial property of CNF-AgMgOnHaP adsorbent through the values exhibited by the zone of inhibition against gram-negative and gram-positive bacterial strains. The diameter of the zone of inhibition was found to increase with an increase in the concentration of the adsorbent. The antibacterial property of the CNF-AgMgOnHaP adsorbent may be due to the diffusion of Ag-MgO nanoparticles within the adsorbent through the release of metal ions disrupting the cell wall structure of the bacteria genome in producing intracellular reactive oxygen species (ROS) resulting in the microbial cell death [24-25]. The observed zone of inhibition demonstrated that the CNF-AgMgOnHaP adsorbent possess antibacterial activity against both bacterial strains tested.

TABLE 3. Antibacterial property of CNF-AgMgOnHaP

Adsorbent concentration (mg/ml)	***E. coli*** Inhibition zone (mm)	***S. aureus*** Inhibition zone (mm)
1	4	3
5	7	6
7	10	8
10	13	11

4. Conclusion

CNF-AgMgOnHaP composite was successfully biosynthesized through the impregnation and dispersion of Ag-MgO and nHap nanoparticles by a simple hydrothermal method. The structural morphology provided evidence showing the aggregation of nanoparticles on the biopolymeric cellulose fiber matrix after modification. The sorption of fluoride by the adsorbent was found to be strongly dependent on the different sorption conditions with the optimum adsorption conditions determined at 10 min (25 ± 3 °C), 0.25g adsorbent dose, pH 5, with maximum defluoridation capacity of 8.92 mg/g at 303K. The synthesized composite also provides some antibacterial activity against both gram negative and gram-positive water bacteria strains. Consequently, the synthesized CNF AgMgOnHaP composite can be used as a suitable and viable adsorbent in the simultaneous removal of fluoride and pathogen for drinking water purification.

Acknowledgments: Authors would like to acknowledge financial support from USAID-PEER Cycle 6-Award No: AID-OAA-A-11-00012; National Research Foundation Grant No: 114726; University of Venda, South Africa (RPC grant Number: SES/17/ERM/03) and Mintek, South Africa.

References

1. Gitari, W. M., Ngulube, T., Masindi, V., & Gumbo, J. R. (2015). Defluoridation of groundwater using Fe3+-modified bentonite clay: optimization of adsorption conditions. Desalination and Water Treatment, 53 (6), 1578-1590.
2. Fuller, T., (2006). Rural water supplies and water-quality issues. Healthy Housing Reference Manual, pp.1-12.
3. USGC., (2016). Contaminants Found in Groundwater Available online: http://water.usgs.gov/edu/groundwater-contaminants.html (accessed on July 2017)
4. Snson J.S., Baker, L.A., Fox, P., (1999). Geochemical transformations during artificial groundwater recharge: soil–water interactions of inorganic constituents, Water research, 33 196–206.
5. Loganathan, P., Vigneswaran, S., Kandasamy, J., & Naidu, R. (2013). Defluoridation of drinking water using adsorption processes. Journal of Hazardous Materials, 248, 1–19.
6. Anthony A. Izuagie, Wilson M. Gitari & Jabulani R., Gumbo (2015): Defluoridation of groundwater using diatomaceous earth: optimization of adsorption conditions, kinetics and leached metals risk assessment, Desalination and Water Treatment, DOI: 10.1080/19443994.2015.1083894
7. Mumtaz, N., Pandey, G. and Labhasetwar, P.K., (2015). Global Fluoride Occurrence, Available Technologies for Fluoride Removal and Electrolytic Defluoridation: A Review, Critical Reviews in Environmental Science and Technology, DOI: 10.1080/10643389.2015.1046768
8. Chai, L., Wang, Y., Zhao, N., Yang, W. and You, X., (2013). Sulfate-doped Fe3O4/Al2O3 nanoparticles as a novel adsorbent for fluoride removal from drinking water. Water Research, 47(12), pp.4040-4049.
9. WHO, (2011) Guidelines for drinking water quality, forth ed., World Health Organization, chronicle, 38(4), 104-8.

10. Dankovich, T.A., Levine, J.S., Potgieter, N., Dillingham, R. and Smith, J.A., (2016). Inactivation of bacteria from contaminated streams in Limpopo, South Africa by silver-or copper-nanoparticle paper filters. Environmental Science: Water Research and Technology, 2(1), pp.85-96.
11. Pradeep, T., Anshup, in: Savage, N., Diallo, M., Duncan, J., Street, A. and R. Sustich (Eds.)., (2009). Nanotechnology Applications for Clean Water, William Andrew Publication, USA.
12. Dhillon, A. and Kumar, D. (2015). Development of a nanoporous adsorbent for the removal of health-hazardous fluoride ions from aqueous systems, Journal of Materials Chemistry A, 3 (8) 4215–4228.
13. Onyango, M.S. and Matsuda, H., (2006). Fluoride removal from water using adsorption technique. Advances in Fluorine Science, 2, pp.1-48.
14. Bhatnagar, A., Kumar, E. and Sillanpää, M., (2011). Fluoride removal from water by adsorption—a review. Chemical Engineering Journal, 171(3), pp.811-840.
15. Langmuir I., (1916). The constitution and fundamental properties of solids and liquids, Journal of the American chemical society, 38 2221–2295.
16. Freundlich, H.M.F. (1906) Uber die Adsorption in Losungen. Zeitschrift für Physikalische Chemie, 57, 385-470.
17. Dubinin, M., Radushkevich, L., (1947). Equation of the characteristic curve of activated charcoal. Chem. Zentr. 1 (1), 875-890.
18. Lagergren S., (1898). Zur Theorie der sogenannten adsorption geloster stoffe, K. Sven. Vetenskapsakad. Handl. 24 1–39.
19. Ho Y.S., (2006). Second-order-kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Research. 40 119–125.
20. Weber, W. J., Morris, J. C., (1964). Equilibria and capacities for adsorption on carbon, Journal of the Sanitary Engineering Division. 90 79–91
21. Tran, H.N., You, S.J., Hosseini-Bandegharaei, A. and Chao, H.P., (2017). Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. Water Research, 120, pp.88-116.
22. Samadi, N., Hasanzadeh, R. and Rasad, M., (2015). Adsorption isotherms, kinetic, and desorption studies on removal of toxic metal ions from aqueous solutions by polymeric adsorbent. Journal of Applied Polymer Science, 132(11).
23. Swain, S. K., Padhi, T., Patnaik, T., Patel, R. K., Jha, U., & Dey, R. K. (2010). Kinetics and thermodynamics of fluoride removal using cerium-impregnated chitosan. Desalination and Water Treatment, 13(1-3), 369-381.
24. Durán, N., Durán, M., de Jesus, M.B., Seabra, A.B., Fávaro, W.J. and Nakazato, G., (2016). Silver nanoparticles: a new view on mechanistic aspects on antimicrobial activity. Nanomedicine: Nanotechnology, Biology and Medicine, 12(3), pp.789-799.
25. Kuppusamy, P., Yusoff, M.M., Maniam, G.P. and Govindan, N., (2016). Biosynthesis of metallic nanoparticles using plant derivatives and their new avenues in pharmacological applications–An updated report. Saudi Pharmaceutical Journal, 24(4), pp.473-484.

Response of Orthoptera and Hymenoptera to mining activities in Tarkwa Gold Mine concession, Ghana

S Adu-Acheampong[1]*, R Kyerematen[2], D Acquah-Lamptey[2], RS Anderson[3]

[1]Department of Agronomy, University for Development Studies, Nyamkpala-Tamale, Ghana
[2]Department of Animal Biology and Conservation Science, University of Ghana, Ghana
[3]African Regional Postgraduate Programme in Insect Science, University of Ghana, Ghana
*Email of corresponding author: nanaakyampon@gmail.com

Abstract

One of the most important bioindicators of change in anthropogenically impacted environment especially in tropical Africa is change in insect diversity. In line with that we studied the population dynamics of Orthoptera and Hymenoptera insect orders as surrogates for measuring ecosystems health within the Tarkwa Mine concession of Gold Fields Ghana Limited (TGM). The study was conducted as part of environmental impact assessment in accordance with the Environmental Management Plan of TGM between 2014 and 2017. We sampled families of Orthoptera and Hymenoptera insect orders within the mine and characterised them based on diversity indices. Transect counts, sweep netting, Malaise trapping and flight interception trapping methods were employed to sample insect assemblages. Results showed that the mine concession had a relatively lower diversity and dominated by generalists and degraded forest indicator species of the two insect orders. The high presence of generalists and degraded forest species can be used as surrogate measure of rapid deteriorating ecosystems health within TGM. Recommendations are made to management to increase conserved forest blocks through land sparing and other active land reclamation efforts to serve as refugia for impacted animals because in this study there were few forest blocks within the concession that housed majority of healthy forest indicator species for this study.

Keywords: bioindicator, concession, environment, Hymenoptera, mining, Orthoptera

1. Introduction

Mining of precious metals come at a cost to the environment [1, 2], notably among them are biodiversity loss, pollution of water bodies and soil structure and nutrient degradation [1, 3]. Mining in Ghana has over the years been plagued with these environmental degradation issues [2, 4]. To regulate mining activities and mitigate its impacts on the environment the government of Ghana passed the Environmental Assessment Regulations act in 1999 which is supervised by the Environmental Protection Agency (EPA) of Ghana. This act also highlights the potential impact of mining operations on the environment and steps put in place to regulate and mitigate these impacts including defined environmental and occupational health and safety action plans, monitoring programmes and rehabilitation and decommissioning plans.

Biodiversity assessment is one of the methods employed by TGM as part of Environmental Impact Assessment within the concession as per EPA requirements for undertaking mining operations in Ghana. To be cost effective and quick in the biodiversity assessment surrogate species was used as a measure of the state of biodiversity and a measure of environmental health within TGM. To be efficient in using surrogate species, the selected group must be easy to sample and most importantly very sensitive to small changes in the environment [5, 6]. Due to their ease of sampling and sensitivity to the environment these two insect orders were used as surrogate species for assessment of biodiversity in general within the concession [6, 7, 8, 9]. This is in line with such other studies using very sensitive insect groups such as grasshoppers, [7, 8], butterflies [10, 11], dragonflies [12, 13] and ants [9, 14] as surrogates to measure the impact of environmental stressors.

Orthoptera and Hymenoptera are among the most important insect groups known for being environmentally sensitive and hence any change in their diversity or abundance can directly be linked to the health status of the environment in which they are located [5, 6]. Orthoptera and Hymenoptera were used as surrogates for this study because they are very conspicuous and easy to sample and also their biology has been well studied and hence can be easily related to conditions within the environment [5, 6].

We carried out this research to assess the diversity of Orthoptera and Hymenoptera within the Tarkwa gold mine concession to determine the level of impact of mining and related activities on biodiversity. Our hypothesis for this research was that, mining and other related activities has no impact on biodiversity of Orthoptera and Hymenoptera insect orders within the concession. If ecosystems within the concession are in good health or condition, we expect a very high diversity of species related to the vegetation zone within which the mine is located (endemic insect species of wet and moist evergreen forest). If more generalist and degraded indicator species are recorded in the study, we can assume that ecosystems health within the TGM is deteriorating due to mining activities and such activities are having negative impacts on biodiversity. Findings from this survey will be essential as it will serve as the first approach of using these groups as part of indicator tools for subsequent monitoring and assessments of the ecological quality within the mining concession.

2. Materials and Methods

Study area

Vegetation at TGM comprises of regenerated, re-vegetated and secondary forests with interspersed mining activities. Elevation in this area ranged from 74 m to 213 m above mean sea level (amsl). The landscape is dominated by opencast mining with artificial lakes created from large excavated pits. The entire mining concession of TGM was divided into North, Central and Southern divisions for sampling purposes for this work. The concession can be located on the south-western part of Ghana near the southern end of the Tarkwa Basin, approximately 300 km west of Accra at latitude 5°15’N and longitude 2° 00’N [15]. The TGM concession falls within two protected forest areas. The Ankasa Resource Reserve and Nini-Suhien National Park and Kakum National Park and Attandanso Production Reserve all within Moist or wet Evergreen Forest zones.

Orthoptera and Hymenoptera sampling

Orthoptera were sampled using aerial nets, visual observations and approximately 100-metre transect walk-and-counts. We also sampled Hymenoptera using pit fall traps [16] visual observations, aerial nets and malaise traps. Seventeen study locations with each divided into 5 sampling sites (17x5=85) were sampled. Five of each of the traps (one per sampling site) were set up at each study area for both Orthoptera and Hymenoptera separately. The smallest inter-site distance within an area of study was 50 m with the largest inter-site distance being 250 m. Random walks were employed by three persons for three hours per day during sampling for these two insect orders. Each of the sites was sampled on four occasions. Orthoptera and Hymenoptera identification were done to the family. And when needed to the species level using reference collection at the Museum of department of Animal Biology and Conservation Science, University of Ghana.

Data analysis

We used insect diversity indices to assess the quality of sites [17] and treated them as indicators for biodiversity assessment as has been done in previous studies elsewhere [18]. We used one-way ANOVA to find out the differences in Hymenoptera and Orthoptera species recorded for the study. We estimated differences between diversity of species known to be indicators of healthy ecosystems (e.g. specialists of endemic vegetation within the forest area) and indicators of degraded environment (e.g. generalist and invasive species) within the concession using Kruskal-Wallis test conducted in Statistica 13.2 [19]. This analysis was done because Shapiro Wilk's test of normality showed non-normal distribution ($W = 0.35$, $P < 0.01$).

3. Results

A total of 374 and 5440 individuals belonging to Orthoptera and Hymenoptera respectively were recorded. The most abundant Orthoptera recorded was Gryllidae, followed by Acrididae and Tettigonidae (figure 1a). The Formicidae family was the most abundant Hymenopteran family recorded followed by Apidae and Ichneumonidae (figure 1b). The most dominant of the Gryllidae and Acrididae were generalist's species (e.g. *Anaeolopus dorsalis*) that thrives in highly impacted environments. The study also recorded high numbers of invasive, Formicidae such as Argentine ants (*Linepithema humile*), Apidae and Ichneumonidae family members. These invasive species are also known to dominate highly impacted environments.

There were significant differences between the diversity of good ecosystems health indicator species such as endemic plant species specialists and indicator species for degraded ecosystems health e.g. generalist and invasive species that can also persist in highly impacted habitats for both Orthoptera and Hymenoptera orders in this study ($\chi2 = 12.30$ $p < 0.01$; $\chi2 = 8.45$ $p < 0.05$, respectively, Figure 2).

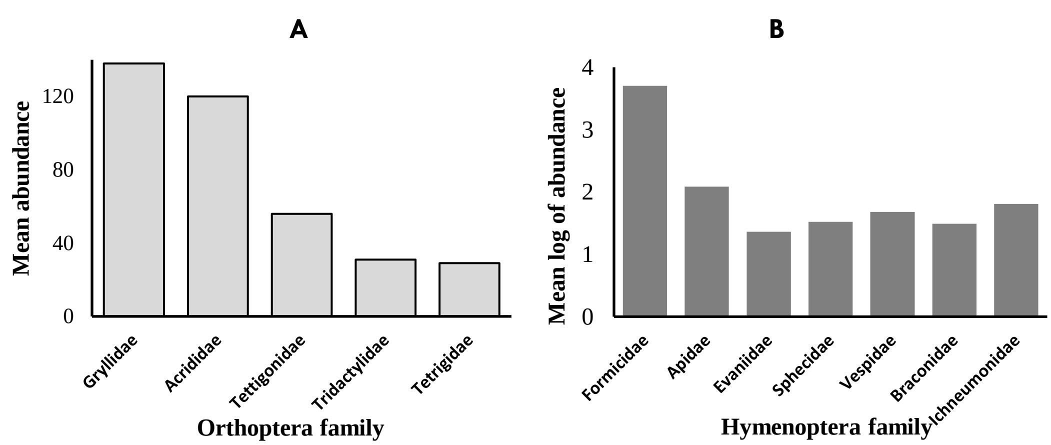


Figure 1. Mean relative abundance of Orthoptera and Hymenoptera families in Tarkwa Gold Mine. **B** was log transformed to minimise differences in visual effect between the least and the most abundant families within the Hymenoptera order recorded for the study.

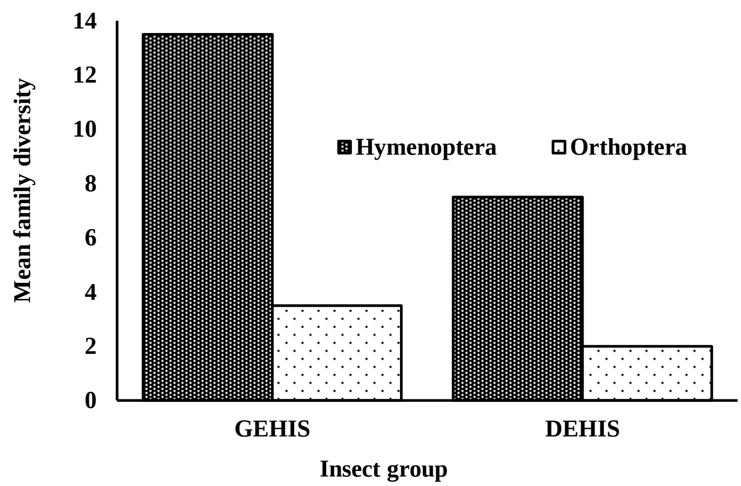


Figure 2. Mean family diversity of Hymenoptera and Orthoptera insect families at TGM. GEHIS = Good Ecosystems Health Indicator Species e.g. specialists of endemic forests, DEHIS = Degraded Ecosystems Health Indicator Species e.g. generalists and invasive species.

4. Discussion

The results of this study show a high influence of mining on diversity of both Orthoptera and Hymenoptera at TGM. There was a high diversity of indicator species which is an indication of high level of degradation and possibly ongoing destruction of vegetation and habitat within the concession. The high presence of invasive Hymenopterans mostly belonging to the family Formicidae which is known to dominate highly impacted environments is an indication of a changing environment [13, 21, 22, 23, 24].

Also, there were high abundance of generalists Orthoptera groups especially the Acrididae and Gryllidae which include species that are more adapted to highly impacted environments. Despite a relatively high diversity of generalists and invasive species indicating degradation in the study area, there were other species known to be specialist's indicators of forests in good health. Those species belonged mostly to Tettigonidae, Tetrigidae, Tridactylidae, Evanidae, Braconidae, Ichneumonidae and Sphecidae. The relatively large presence of species within these groups is an indication that there is a fair amount of natural vegetation in good health within TGM.

One of the most important bioindicators of change recorded within the concession is the dominant invasive Hymenoptera, the Argentine ant (*Linepithema humile*) which belongs to the family Formicidae. This species has been reported to dominate highly impacted environments such as mining environments. The aggression and dominance of Argentine ants displaces many native ants in an ecosystem. Such displacements can result in reduction or local extinction of vital species that may be important plant pollinators. When such displacements occur, the cascading effect could result in the death or extinction of some plants that make up key habitats and food for other organisms and hence affecting the ecosystem in general. Evidence of mine activities impacting negatively on the vegetation and habitats can be deduced from the ecology of the Argentine ant which is known to have population explosion under high anthropogenically impacted environment [25, 26].

Also, the high abundance of *Anaeolopus dorsalis*, an Acridid known to dominate highly impacted environment is further evidence of the extent of degradation within the concession.

Anaeolopus dorsalis is known to dominate agricultural lands and bare grounds hence their high presence is an indication of highly impacted environment [6]. However, the presence of pockets of habitats which contain less impacted secondary and re-vegetated forests with more records of wet or moist evergreen forested species show that there are places which could serve as refugia for impacted animals within the concession.

5. Conclusions and recommendations

Even though there were low diversities of Orthoptera and Hymenoptera indicator families in the study area. The biology and ecology of the majority of the Hymenoptera and Orthoptera families and species recorded in the study show that mine related activities are negatively impacting on biodiversity and hence the ecosystems health within the concession. This general observation agrees with a previous study which reported that butterfly diversity has been impacted negatively by mine activities within the concession [17]. Vegetation cover and diversity affect Hymenoptera and Orthoptera diversity within a community. Hence, destruction and subsequent change in vegetation structure and diversity will have a direct impact on their diversity, abundance and sometimes distribution [6, 27] which eventually affects ecosystems health. Pockets of secondary forests within the mine concession are possibly serving as refugia for displaced species within the concession.

We recommend management of TGM to increase conserved forest blocks through land sparing, active land reclamation efforts and other eco-friendly practices to serve as refugia for impacted and displaced animals during mining operations.

Acknowledgement: We thank the Tarkwa Gold Mine concession of Gold Fields Ghana Limited for granting us permission to collect insects as part of their Environmental Impact Assessment.

References

1. Ogola JS, Mitullah WV, Omulo MA. Impact of gold mining on the environment and human health: a case study in the Migori gold belt, Kenya. Environ. Geochem. Hlth. 2002, 24, 141-57.
2. Amankwah RK, Anim-Sackey C. Strategies for sustainable development of the small-scale gold and diamond mining industry of Ghana. Resour. Policy 2003, 29, 131-8.
3. Bian Z, Dong J, Lei S, Leng H, Mu S, Wang H. The impact of disposal and treatment of coal mining wastes on environment and farmland. Environ. Geol. 2009, 58, 625-34.
4. Hilson G, Hilson CJ, Pardie S. Improving awareness of mercury pollution in small-scale gold mining communities: challenges and ways forward in rural Ghana. Environ. Res. 2007, 103, 275-287.
5. McGeoch MA. The selection, testing and application of terrestrial insects as bioindicators. Bio. Rev. 1998, 73, 181-201.
6. Samways MJ, McGeoch MA, New TR. Insect conservation: a handbook of approaches and methods. Oxford University Press. 2010.
7. Adu-Acheampong S, Bazelet CS, Samways MJ. Extent to which an agricultural mosaic supports endemic species-rich grasshopper assemblages in the Cape Floristic Region biodiversity hotspot. Agr. Ecosyst. Environ. 2016, 227, 52-60.
8. Adu-Acheampong S, Samways MJ, Landmann T, Kyerematen R, Minkah R, Mukundamago M, Moshobane CM. Endemic grasshopper species distribution in an agro-natural landscape of the Cape Floristic Region, South Africa. Ecol. Eng. 2017, 105, 133-40.
9. Coelho IR, Ribeiro SP. Environment heterogeneity and seasonal effects in ground-dwelling ant (Hymenoptera: Formicidae) assemblages in the Parque Estadual do Rio Doce, MG, Brazil. Neotrop. Entomol. 2006, 35, 19-29.
10. Bonfantti D, Di Mare RA, Giovenardi R. Butterflies (Lepidoptera: Papilionoidea and Hesperioidea) from two forest fragments in northern Rio Grande do Sul, Brazil. Check List. 2009, 5, 819-29

11. Kyerematen, R., Kaiwa, F., Acquah-Lamptey, D., Adu-Acheampong, S., Andersen, R.S. Butterfly Assemblages of Two Wetlands: Response of Biodiversity to Different Environmental Stressors in Sierra Leone. Open J. Ecol. 2018, 8, 379-395.
12. Lee Foote A, Rice Hornung CL. Odonates as biological indicators of grazing effects on Canadian prairie wetlands. Ecol. Entomol. 2005, 30, 273-83.
13. Acquah-Lamptey D, Kyerematen R, Owusu EO. Using Odonates as markers of the environmental health of water and its land related ecotone. Int. J. Biodivers. Conserv. 2013, 5, 761-9.
14. Majer JD, Orabi G, Bisevac L. Ants (Hymenoptera: Formicidae) pass the bioindicator scorecard. Myrmecol. News. 2007, 10, 69-76.
15. Kyerematen, R., Adu-Acheampong, S., Acquah-Lamptey, D., Andersen, R.S., Owusu, EH., Mantey, J. Butterfly diversity as indicator for environmental health within Tarkwa Gold Mine, Ghana. Environ. Nat. Resources Res. 2018, 8, 69-83.
16. Lasmar CJ, Queiroz AC, Rabello AM, Feitosa RM, Canedo-Júnior EO, Schmidt FA, Cuissi RG, Ribas CR. Testing the effect of pitfall-trap installation on ant sampling. Insect Soc. 2017, 64, 445-51.
17. Magurran AE. Measuring biological diversity. Blackwell Publishing USA. 2013.
18. Marshall JC, Steward AL, Harch BD. Taxonomic resolution and quantification of freshwater macroinvertebrate samples from an Australian dryland river: the benefits and costs of using species abundance data. Hydrobiologia. 2006, 572, 171-94.
19. StatSoft Incorporated. Electronic statistics textbook. 2013. Tulsa, UK: StatSoft. Accessed on 2/5/2015: http://www.statsoft.com/textbook.
20. Hill T, Lewicki P. Statistics: methods and applications. 2006. Tulsa, UK.
21. Mack, R.N., Simberloff, D., Mark Lonsdale, W., Evans, H., Clout, M. and Bazzaz, F.A. Biotic invasions: causes, epidemiology, global consequences, and control. Ecol Appl, 2000, 10, 689-710.
22. Andersen AN, Fisher A, Hoffmann BD, Read JL, Richards R. Use of terrestrial invertebrates for biodiversity monitoring in Australian rangelands, with particular reference to ants. Austral Ecol. 2004, 29, 87-92.
23. Uehara-Prado M. Effects of land use on ant species composition and diaspore removal in exotic grasslands in the Brazilian Pantanal (Hymenoptera: Formicidae). Sociobiology. 2005, 45
24. Heterick BE, Lythe M, Smithyman C. Urbanisation factors impacting on ant (Hymenoptera: Formicidae) biodiversity in the Perth metropolitan area, Western Australia: Two case studies. Urban Ecosyst. 2013, 16, 145-73.
25. Suarez AV, Bolger DT, Case TJ. Effects of fragmentation and invasion on native ant communities in coastal southern California. Ecology. 1998, 79, 2041-56.
26. Munyai TC, Foord SH. Ants on a mountain: spatial, environmental and habitat associations along an altitudinal transect in a centre of endemism. J. Insect Conserv. 2012, 16, 677-95.
27. Hendrickx F, Maelfait JP, Van Wingerden W, Schweiger O, Speelmans M, Aviron S, Augenstein I, Billeter R, Bailey D, Bukacek R, Burel F. How landscape structure, land-use intensity and habitat diversity affect components of total arthropod diversity in agricultural landscapes. J. Appl. Ecol. 2007, 44, 340-51.

Impact of pollution and restoration of water resources on real property estates and agriculture

SM Liphadzi[1]* and SN Mpandeli[1,2]

[1]Water Research Commission of South Africa, South Africa
[2]Department of Hydrology and Water Resources, University of Venda, South Africa
*Email of corresponding Author: StanleyL@wrc.org.za

Abstract
The study was based on case studies that focused on the impacts of polluted freshwater on built properties situated near or on waterside. Water quality was used in determining the desirability and value of the property situated in or near water resources. The impact of water quality on agricultural productivity was also investigated. The results showed that poor water quality is one of the key factors that has a negative impact on property value. With regard to agricultural productivity, again the results showed that high value crops such as citrus produce less when irrigated with poor quality (saline) water. The farmer suffers a severe financial loss if supplied or using saline irrigation water. The costs associated with remediation of polluted water or soils are far higher than protecting the water resource itself.

Keywords: agriculture, citrus, impact, pollution, properties, waterfront, water quality salinity

1. Introduction

As population increase and industrialization intensify, more wastes are generated and the key natural resources such as water, air and soil get degraded when those pollutants reach the environment. More understanding of the impact of pollution on people and their livelihoods is needed especially during this time of climate change and increased population explosion. According to [1], contamination of water has become a global crisis and communities are facing worst consequences of poor water quality. Polluters often do not bear the full cost of pollution or the negative externalities they cause in the environment, society, and economy. However, people exposed to pollution of natural resources such as soil, freshwater, and air suffer many life and economic threatening risks [2,3]. A society may suffer severe loss of human capital as people get sick and then incapacitated or die due to water contaminants [2,4]. A huge agricultural produce and livestock losses due to poor water quality in rural communities of India were reported [2].

Water as natural capital and being central to human livelihoods, its degradation negatively affects all the water ecosystem services that people depend on [3; 5]. Some of the services provided by healthy water ecosystems include aesthetic beauty, cultural support, provision of food and medicine, biodiversity and thus tourism [3]. These services become much costly to a society when water resources are polluted because a society may have to pay for drinking water treatment and for other human interventions aimed at improving water quality [5]. However, water protection (prevention of degradation) is far cheaper and more sustainable than treatment or remediation [1].

According to [6], the insufficient data and limited studies focusing on the impact of environmental (or water) pollution was striking. This is even startling when focusing on South Africa and many other developing countries. This paper is based on previous studies conducted in South Africa and data generated in studies done in other countries. Case studies that focused on the socio-economic impacts of polluted freshwater on built properties situated near or on waterside of these water bodies were considered for this paper. In addition, the paper also included the impact of polluted irrigation water on the sustainability of crop farming, especially those that produce high value crops which earn the country substantial foreign currency through export. Salinity of irrigation water was used as the main water quality factor determining crop yields. The cost and benefits of restoring both water resources and affected agricultural land were analyzed in relation to the productivity of land and the budget required to restore land and water resources to suit agricultural use in terms of quality. This aspect is important since most studies focused either on negative impacts of pollution or on positive impact of reducing pollution of the environment [5]. This paper is bringing together both aspects (costs and benefits) together using lessons from chosen case studies. The main aim of this study is to evaluate or analyses the impact water quality and rehabilitation of water resources on property value and agricultural productivity.

2. Water Quality and Property Values

There is generally a high demand of properties in or closer to water bodies because aquatic ecosystem provides services that can be capitalised in to property values [7]. High demand for waterside properties has resulted in premium pricing of those entities (5, 8). Investments are made in properties in or near waterfront with the expectation of higher financial returns [9]. However, any factor that can negatively impact these investments causes a significant dent on personal finances and economic growth of the country or city [10]. The waterside properties are impacted by the physicochemical attributes of water, and some of these attributes affect the aesthetic beauty of the area, the smell, and usability of water [1, 9].

More water bodies and dams are becoming mesotrophic in South Africa [11], and this does not only decrease access to and usability of water but also the economic growth of the country [12]. Pollution of water resources happened when toxic or wastes are dumped or allowed to get in to water bodies or rivers, which degrade water quality, destroys the aesthetic beauty, or cause unpleasant smell [9,1,13]. Several studies have linked or associated water quality with property value [5, 8, 9]. In fact, most of the studies found that poor water quality negatively impacts the sale and the value of waterside properties [12,14, 15, 16].

Figure 1 (here below) shows how property values or prices (based on hedonic model) are negatively impacted by poor water quality (or pollution). Hedonic is a term that refers to a person acting in his or her own interest to select a property with most desirable set of characteristics [15, 17]. While structure, size and location are important in property valuation, water quality (eutrophication) was found to be a key determinant for properties closer to water bodies [7, 17], and this kind of impact of water quality or properties is more relevant in developed countries as compared to poor countries. Poor countries have other many socio-economic challenges that are likely to determine property prices or choices.

Most of the studies conducted in this subject have shown a high association (R^2 range of 0.65-0.75) and reduction of property prices by 11%- 30% [6, 18,19, 20, 21]. The analysis showed that property's price growth in estate near mesotrophic dams in South Africa either stayed stagnant or had a sluggish growth over a period of five years. Most of these dams have prevalent algal blooms that give off odours especially in summer. The results based on houses with an average of three [3] bedrooms showed a sluggish price growth of houses within 500m from polluted water bodies as compared to those that were more than 1000m from the polluted water resource.

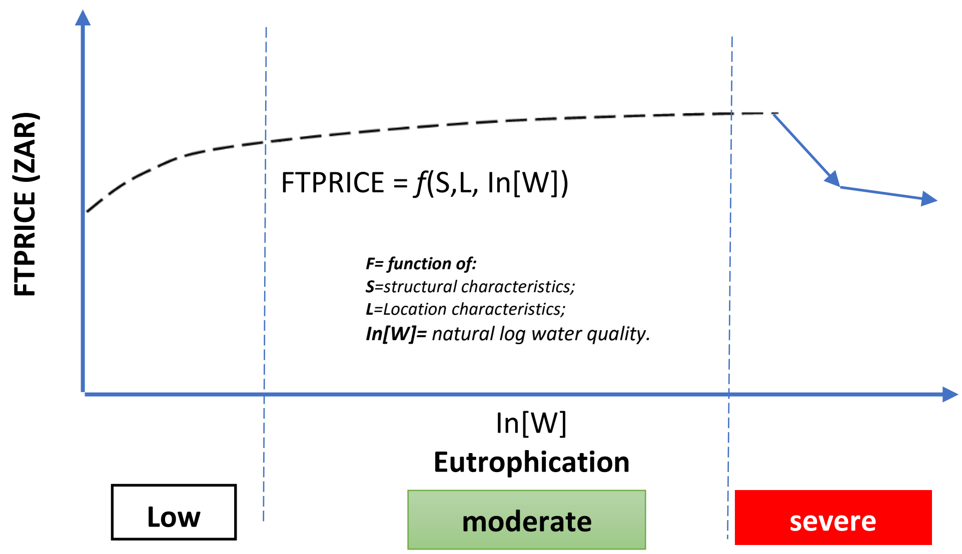


Figure 1. Association between water quality and property values determined using the hedonic model [adapted from 15, 17].

3. Agriculture Productivity and Water Quality

Various water users require specific water quality ranges to produce or support their operations. Agriculture is one of those businesses that can break or make due to the state of water quality [6]. Unfortunately, the availability of good quality irrigation water has decreased and will continue to deteriorate in future because the development of new water supplies won't be able to keep pace with escalating demand by industries and municipalities [4]. Therefore, farming is faced with a shortage of water and in some cases a poor irrigation water quality to use to meet the food requirement of the growing population [4,11]. Moreover, poor water quality (pollution) negatively impacts the health and quality of soil and thus reduce the production of crops and livestock [3].

Several crops have specific water quality requirements that if not met negatively impact their productivity or growth. Irrigating crops with saline (poor quality) results in the built up of salts in soil [4, 11] and the salts reduce water uptake by plant roots. Soil salinization affects crop yields and product quality, and the type of crops to be grown or produced on that farm land [4]. When productivity of the farm or land is reduced due to pollution, its value also takes a deep dive [19].

Table 2 shows the decline of citrus fruit yields as a result of decreasing quality (increasing salinity) of irrigation water. Citrus trees thrive and optimise their fruit production at salinity levels below 900 mg/L and can produce fruits worth ZAR74 250 per ha per year. Sanity levels above this threshold of 900 mg/L reduce citrus crops yield and cause plants to be non-productive when salinity increased to 1700 mg/L. A farmer surfers' greater financial loss when farm's productive potential declines due to salinity built-up in soil.

The farmer can choose either to change the crop to farm with or invest in restoring the land or soil. Both options are expensive because the possible crops to switch to are mostly grass or grain crops such as barley and wheat which tolerate high salinity [22]. Unfortunately, these grain crops produce lesser yields and are not high-value crops like citrus. In case the farmer or landowner decides to rehabilitate the soils (or land) contaminated by salts, getting enough clean freshwater supply is difficult and expensive. In fact, it would be wasteful and unethical to use such a scarce resource for flushing down salts to rehabilitate polluted soils, while there are still many people with no access to water and sanitation in South Africa. South Africa is one of the 30th driest countries in the world and restoration of saline soil requires huge volumes of clean water to flush down the salts, which can result in groundwater pollution. Moreover, it is counterproductive to flush down salts to groundwater because there are communities and farmers which depends on groundwater as their only water supply or resource. The other option for the farmer may be to sell the land with polluted or degraded soil. However, selling polluted land or farm that is no longer at its prime productive potential (for high value crops), will attract a low selling price, which is a big loss for the farm (property) owner.

TABLE 2. Impact of salinity on citrus fruit production in South Africa [Adapted from 11].

Salinity (TDS) mg/L	**Yield** (kg/ha)	**%Yield decline** (from 45 000kg/ha)	**Financial value** (ZAR/ha)- @R1.65/kg	**Financial loss** (ZAR/ha)
<900	45 000	0	74 250	0
900	45 000	0	74 250	0
1300	23 900	47	39 435	34 815
1400	17 100	62	28 215	46 035
1500	10 800	76	17 820	54 430
1600	4 050	91	6 683	67 567
1700	0	100	0	74 250
1800	0	100	0	74 50

4. Discussions and Conclusions

The case studies showed the importance of water quality as one of the key factors used in determining or influencing the property value. The value of properties near water bodies can be impacted by the quality of water. A hedonic model may not be the perfect model for investigating all the factors that impact property price or value, but it provides the basic understanding of the importance of clean environment on property market. Property owners, as individuals, are mostly worried about water quality adjacent to their property in case they want to use water, swim in or fish from it [6]. Poor water quality is a concern when the water has very high concentration of nutrients, toxic contaminants or faecal coliform bacteria. High nutrients levels result in water that is not clear (muck), which may give off unpleasant smell and water with faecal coliform pose hazard to human health and wellbeing [6].

Unfortunately, as land uses continue to change, population increase, and climate changing, poor water quality has become a global crisis [5]. As a result, better understanding the buyers' response to water conditions (especial water quality) is showing to become critical and a game changer in the property market. The loss of property value near polluted environment sites has a potential to cause civil actions and disobedience by property owners which may negatively affect the tax revenue stream of government. The state, just like property owners, can also lose money (tax) when potential buyers stop buying properties near polluted water or demand low prices for those properties. However, one should not be paranoid to think that fixing water quality alone would immediately make ordinary houses attract prime sale prices. It is generally known that location, size, conditions and age of the property (house) also influence the sale price or demand. In most circumstances, the impact of water quality on property value was high around big lakes or dams as compared to rivers or streams [7].

Data from different areas have shown that higher and quicker financial gains with regard to waterfront property values can be realised when water resources are protected as compared to implementing remediation or restoration interventions [5,18,21]. Therefore, restoration is much costly than protecting or preventing water pollution [5].

In most cases, industrial and municipality wastes are carried with return flows or dumped in water bodies to cause pollution. Properties near public parks, noisy neighbourhood, factories or slums (informal settlements) sell very cheap because wealth people frown to any suggestion of buying properties in or near those areas. However, the impact of water quality on property values should be different between developed and developing countries due to the manner in which bylaws are implemented and enforced. Deteriorating water quality, in rivers or any other water bodies is mostly reported to the public in the developed countries to create awareness of water and environmental conditions in their areas. These reports create perceptions which both buyers and evaluators of the properties consider in the sale of the property [6,19].

There are indeed several factors other than water quality that determine the water front property values in the developing world. Therefore, more studies are needed to determine the most impacting factors driving property markets in the developing and poor countries. In South Africa, it is common to see properties closer to public parks, streams, dams or green spaces being guarded by heavily armed security personnel or with electrified high walls due to fear of crime. These properties are no longer in high demand or priced high as they used to be 20 years ago, and this trend has taken a knock-on value of those properties.

The negative impact of increased salinity (pollution) in irrigation water on sensitive crops like citrus shows that crop farming in South Africa and global is threatened by increasing freshwater pollution. As indicated by [19], buyers pay reduced property prices for land or farms near polluted water resources or with polluted water supply. Studies conducted in India indicated huge loses in agriculture and increased vulnerability of rural poor communities when water quality deteriorated [2]. The study by [2] also reported huge costs to a society in the form of chronic diseases in people and their livestock. The loss of livestock due water pollution resulted in the reduction of income, which threatened farmers livelihoods, while the burden of diseases reduced working hours and labour. Water pollution has become a real threat that weigh heavily on plans to increase access to water for domestic and economic use as well as for increasing food security, which support UN's sustainable development goals.

Acknowledgments: We are grateful for the support from the Water Research Commission of South Africa

References

1. Haseena, M., Malik, M.F., Javed, A., Arshad, S., Asif, N., Zulfiqar, S., and Hanif, J. Water pollution and human health. Environ Risk Assess Remediat. 2017, 1,16-19.
2. Reddy, V.R. and Behera, B. Impact of water pollution on rural communities: An economic analysis. Ecological Econ. 2006, 50, 520-537.
3. Khan M.A. and Ghouri, A.M. Environmental pollution: Its effects on life and its remedies. Journal of Arts , Science and Commerce 2011, 2, 276-285.
4. Suresh, K.R. and Nagesh, M.A. Experimental studies of effect of water and soil quality on crop yield. Aquatic Procedia 2015, 4, 1235-1242.

5. Nicholls, S. and Crompton, J. A comprehensive review of the evidence of the impact of surface water quality on property values. Sustainability, 2018, 10,1-30.
6. Leggett, C.G. and Bockstael, N.E. Evidence of the effects of water quality on residential land prices. Journal of Environmental Economics and Management 2000, 39, 121-144.
7. Sklarz, M. and Miller, N. 2018. The impact of waterfront location on residential home values. Collateral Analytic Res. 2018, 1, 1-6.
8. Nikolaos, K., Dimitra, V. and Agapi, X. Real estate values and environment: A case study on the effect of the environment on residential real estate values. International Journal of Academic Res. 2011, 3, 861-868.
9. Walsh, P., Griffiths, C., Guignet, D., and Klemick, H. Modelling the property price impact of water quality in Chesapeake Bay counties. Ecological Econ.2017, 135,103-113.
10. Yao, H., You, Z. and Liu, B. Economic estimation of the losses caused by surface water pollution accidents in China from the perspective of water bodies' functions. International J. of Environmental Research and Public Health 2016, 13,154. 10.3390/ijerph13020154.
11. De Lange, W.J, Mahumanil, B.K., Steynl, M. and Oelofsell, S.H.H. Monetary valuation of salinity impacts and microbial pollution in the Olifants Water Management Area, South Africa. Water SA. 2012, 38, 241-248.
12. Colwel, P.F. and Dehring, C.A. The pricing of lake lots. The Journal of Real Estate Finance and Econ. 2005, 30, 267-283.
13. Anderson, H., Jonsson, L. and Ogren, M. Property Prices and Exposure to Multiple Noise Sources: Hedonic Regression with Road and Railway Noise. Environ Resource Econ. 2010, 45,73–89.
14. EPP, D. and Al-Ani, K.S. The effect of water quality on rural non-farm residential property values. American J. of Agricultural Econ. 1979, 61,529-534.
15. Michael, H.J., Boyle, K.L. and Bouchard, R. Does the measurement of environmental quality affect implicit price estimate from hedonic models? Land Econ. 2000, 76, 283-298.
16. Krysel, C., Boyer, E.M., Parson, C. and Welle, P. Lakeshore property values and water quality: Evidence from property sales in the Mississippi headwaters region. Walker, M.N. Mississippi Headwater Board, USA, 2003.
17. Graham M., Blignaut, J., de Villiers, L., Mostert, D., Sibande, X., Gebremedhin, S., Harding, H., Rossouw, N., Freese, N.S., Ferrer, S., and Browne, M. Development of a generic model to assess the costs associated with eutrophication. WRC Report No. 1568/1/12, Pretoria, SA, 2012.
18. Ara, S., Irwin, E., and Haab, T. The influence of water quality on the housing price around Lake Erie. Paper prepared for presentation at the American Agricultural Economics Association Annual Meeting, Long Beach, California, July 23-26. 2006.
19. Chamblee, J.F., Dehring, C.A., Depken, C.A., and Nicholson, J.R. Water contamination, land prices, and the stature of repose. J. Real Estate Finan Econ. 2015, DOI 10.1007/s11146-015-9514-3.
20. Gulgnet, D., Walsh, P.J., and Northcutt, R. Impacts of groundwater contamination on property values: agricultural run-off and private wells. Agricultural and Resource Economics Rev. 2016, 45, 293-318.
21. Jewit, G. Costs, benefits and financial flows from water at a catchment scale: Linking green and grey infrastructure. Presentation during World Water Week Conference, Stockholm, Sweden, 2018.
22. Liphadzi M.S., Kirkham, M.B, and Mankin, K.R. Remediation of Ammonium-Contaminated Abandoned Animal Waste Lagoon Soil: Physical Properties and Growth of Barley. Soil and Sediment Contamination: An International J.l 2000,11, 789-807

Harmful algal blooms occurrence and perception in the Upper Ngerengere Catchment, Morogoro, Tanzania

ON Kimambo[1]*, JR Gumbo[2] and H Chikoore[3]

[1]Department of Ecology and Resource Management, University of Venda, South Africa
[2]Department of Hydrology and Water Resources, University of Venda, South Africa
[3]Department of Geography and Geo-Information Sciences, University of Venda, South Africa
*Email of corresponding author: offoro@gmail.com

Abstract
Cyanobacteria are photosynthetic bacteria that occurs both in marine and freshwater environment. They produce toxins which are harmful to other aquatic organisms and human health. Their dense proliferation of harmful algae is commonly referred to as Harmful Algal Blooms (HABs). Aquaculture as an alternative source of income among small-scale farmers has received inadequate attention. Similarly, water pollution and interaction between social-economic activities and domestic water supply reservoirs remain an outstanding challenge in the Ngerengere catchment situated in Morogoro, Tanzania. The study aimed to survey the occurrence and perception of HABs in aquaculture systems in the upper Ngerengere catchment. A cross sectional survey focus group discussion, key informant interviews and anecdotal evidence-based approaches were used. A sample population was drawn from ponds owners, registered water users, government officials especially in water sector in the catchment. For data analysis, a chi-squared test statistics and constant comparison methods were used. From the survey, respondents (93.5%) were able to recognize the image of blooms displayed to them via the SurveyCTO application. On the other hand, respondents were uncertain regarding the health impacts associated with HABs. There was a consensus that water quality has been deteriorating and that blooms occur during the dry season (67.7%). There was also an agreement among the respondents that water pollution is a serious problem (71%), with most of the respondents attributing the source of pollution to other sources other than industrial discharge. The current study findings suggest a need to raise awareness on HABs in the catchment. The findings also provide a basis for the future scientific discussion.

Keywords: Cyanobacteria; Harmful Algal Blooms; HABs; Water pollutions; Aquaculture systems: Ngerengere Catchment; Morogoro

1. Introduction

Cyanobacteria are photosynthetic and microscopic bacteria that are naturally occurring in marine and freshwater ecosystems. Cyanobacteria produce secondary metabolites (toxins), for example, Microcystins, Cylindrospermopsin, Anatoxins, and Saxitoxins which are harmful [1] to the environment including human. Harmful algal bloom (HABs) is the term which is used for cyanobacteria that produce toxins. A recent global discussion on HABs focus on cyanobacteria (HABs) in freshwaters with changing environment [2-3]. A study by Brooks et al. [4] suggests the magnitude, frequency and duration of HABs are poorly understood while monitoring and surveillance of HABs are limited. In Tanzania fish production stands at 1% for aquaculture, 14% for marine and 85% for Inland waters [5] and nearly 25 to 50% of the consumed animal protein is from fish [6]. The statistics, for Tanzania mainland indicates an increase in aquaculture fish farmers from 3347 to 17511 between 2000 and 2013 with a corresponding increase in fish ponds from 4000 to 19930 which heighted the production from 200 tons to 2989.5 tons [7]. Small-scale fish farmers or traditional fisheries have been and will continue to be the most vulnerable to HABs [8] if business as usual continues. The challenges are attributed to startup capital, operating resources, and poor farming practices [8]. East Africa is an economic water scarcity area [6], and there has been a resistance in financing aquaculture projects [9]. In addition, environmental factors, such as land degradation [10]; pollution (point and non-point sources), climate and hydrological variability [11], habitat loss are also adding pressure on small-scale fisheries. Cyanobacteria (HABs) are not well captured or addressed as a problem in the Ngerengere catchment. Few studies have directly worked in the Ngerengere catchment, a recent survey [12] suggest water pollution to be a major problem. The survey recommended awareness rising and ecotoxicological studies. The profile of Morogoro region [13] shows the most common causes of morbidity including diarrhoea [14] and skin diseases which are also the symptoms of some cyanotoxins exposure [13]. Another evidence [15] suggest occurrence of C*ylindrospermopsis* species, which is among the toxin-producing species, although no toxic levels were reported. This study aimed to survey the occurrence and perception of Cyanobacteria (harmful algae) in the Ngerengere Catchment, in Morogoro region of the United Republic of Tanzania.

2. Materials and Methods

The Ngerengere catchment is the sub-catchment of the main Wami Ruvu basin and located in Morogoro region, Tanzania within longitudes and latitudes of 37°32´E 6°51´S, 38°09´E 6°69´S, 37°38´E 7°09´S and 38°38´E 7°05´S, respectively. It covers approximately an area of 2780 km^2 and is characterized by a tropical climate [16]. Mindu Dam is the main source of water and freshwater fishery supplies in urban and peri-urban of Morogoro [17]. The current study is more of exploratory which consisted of mixed methods (observation, questionnaires, and interviews). A questionnaire coded both in English & Kiswahili languages was designed using the Survey CTO (available at https://www.surveycto.com/index.html) and installed in a Samsung Tab4 as android application to gather the required information. Thirty-one (31) respondents was drawn from small-scale fish farmers, officials of the MORUWASA, WRBO, and the registered water users. We also conducted two focus group discussion (FGD), one meeting with Moruwasa officials, and contacted five key informants. Data were downloaded from computer server provided by the SurveyCTO in Excel format, transferred, and cleaned for the analysis. Images of blooms, mat and foam from field observations are presented. Jeffreys's Amazing Statistics Program (JASP) computer software (version 0.9.0 of 2018) was used to produce descriptive plots and Chi-Square tests statistics for inferential statements. Additionally, a constant comparison method was used for analyzing the qualitative information. The ethical clearance certificate (SES/17/ERM/09/2006) was issued by the Research Ethics Committee (REC) in the Directorate of Research & Innovation of the University of Venda, South Africa.

3. Results and Discussion

Respondents general particulars and experiences

The description of the significance and interpretation of the results in all the table was adopted from [18]. The prevailing point of view in the field is that gender inequalities in Tanzania is common in fishery sector [19]. In the current study, significantly ($p < 0.05$) (Table 1), most respondents were males and married. Most ponds activities including harvesting

 ISBN 978-0-620-82267-1

and monitoring of fish farming were dominated by men. The same was observed in Kilombero by [20], a district neighbouring the study area and in the same fish farming livelihood activity. These findings signify the level of participation of women in fish farming and regarding the risk associated with the presence of HABs, men are more exposed.

Significantly ($P<0.05$) most respondents stayed in the study area at about 5 to 10 years of the assessed groups. On the other hand, many respondents had high levels ($P< 0.05$) of education which might have positively affected our survey. Significantly, a higher number of respondents were "very well" informed about water problems in the study area. This corroborates with the survey of [21].

Significantly ($P<0.05$) most respondents stayed in the study area at about 5 to 10 years of the assessed groups. On the other hand, many respondents had high levels ($P< 0.05$) of education which might have positively affected our survey. Significantly, a higher number of respondents were "very well" informed about water problems in the study area. This corroborates with the survey of [21].

3.2. Water quality and algal bloom formation

The National Water Sector Development Strategy of 2006-2015 stresses the links between water quality and fisheries but also the impact of pollution on fisheries [22]. Asked about whether water problems in the region is serious or not serious, respondents collectively agreed that water problems in the catchment are "serious" and this dovetails nicely with the previous surveys e.g. [21; 27] in the study area. From the particular surveys, conflicts between downstream and upstream communities were evident. These were also confirmed during experts' interview that water quality is an issue of concern (Moshi, M, personal communication, 7/8/2018). Some other interesting results is that, respondents were uncertain about changes in water quality over the years ($p< 0.05$) (Table 1). These findings hint that there is a need for pollution monitoring and interventions in the catchment. Some previous studies [24], [25] have indicated that the standards and guidelines for fishing and environment are yet to be established in Tanzania.

Respondents were presented with multiple options question on "what are the reasons for poor water quality" following responses on “if water has been deteriorating” (Figure 1A). The result showed that, overuse of water for agriculture scored high followed by nutrients loads and industrial effluents. Although it is widely accepted [26] that agricultural activities can lead to nutrient leaching to the receiving waters. The method used suffers from the limitation that nutrients loads cannot be affirmed. To overcome that a common-sense method was an override. The same was also confirmed during expert interviews which revealed that controlling agricultural activities upstream of the Mindu dam was lacking in the plans (Angumbwike, N personal communication, 29/08/2018).

TABLE 1. Multinomial test for all the studied parameters

Parameter	Level	Counts	Proportion (out of 31)	Chi Squire (χ^2)	Degree of Freedom	P Value	Vovk-Sellke Maximum P Ration (VS-MPR[a])
Gender	Female	8	0.258	7.258	1	0.007	10.522
	Male	23	0.742				
Marital Status	Married	24	0.774	9.32	1	0.002	26.684
	Single	7	0.226				
How many years have you stayed in the region?	11 to 20	8	0.258				
	31 to 40	4	0.129	21.258	3	<.001	425.916
	5 to 10	18	0.581				
	>50	1	0.032				
How well are you informed about the problems facing water sources in the region?	Don't know	2	0.065				
	Very Well	18	0.581	12.452	2	0.002	29.877
	Well	11	0.355				
How serious is water-related problem?	Not a serious problem	9	0.290	5.452	1	0.020	4.782
	Serious Problem	22	0.710				
How are the changes in water quality for the time you have been in the region?	Don't know	1	0.032	17.903			
	Has deteriorated	12	0.387		3	<.001	103.970
	Has improved	3	0.097				
	Stayed the same	15	0.484				
Have you ever seen blooms (image of bloom displayed for recognition) before?	No	2	0.065	23.516			
	Yes	29	0.935		1	<.001	21834.894
How regular do you see blooms?	Once in a month	1	0.032				
	Once in a season	21	0.677	45.935	4	<.001	7.318e+6
	Once in a week	1	0.032				
	Once in every three month	5	0.161				
	Throughout a year	3	0.097				

ISBN 978-0-620-82267-1

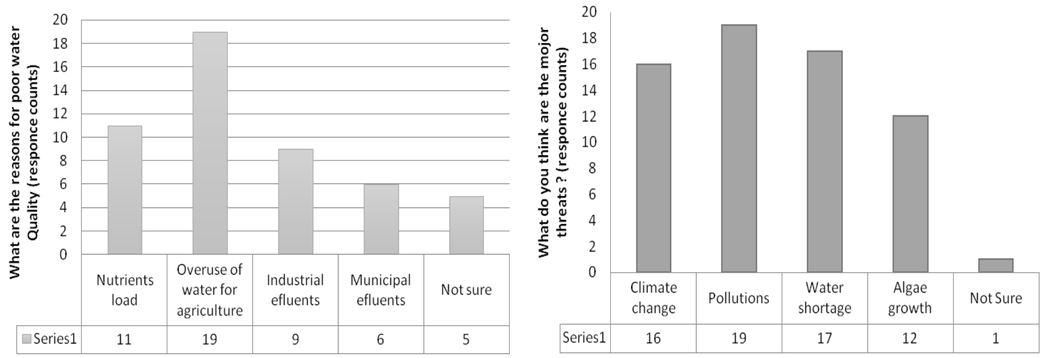
Continued

Do you have any idea on HABs in river/ponds/dam/reservoir?	No	13	0.419				
	Yes	18	0.581	0.806	1	0.369	1
Any idea about health effects associated with algal blooms?	No	14	0.452				
	Yes	17	0.548	0.290	1	0.590	1
Sometimes I see a noticeable discharge from industries	Agree	13	0.419				
	Disagree	2	0.065	8.097	3	0.044	2.675
	Strongly Agree	9	0.290				
	Strongly Disagree	7	0.226				
Sometimes we document history of discharge	Agree	12	0.387				
	Disagree	8	0.258				
	Strongly Agree	5	0.161	3.710	3	0.295	1.022
	Strongly Disagree	6	0.194				
Sometimes I see crystal clear water	Agree	17	0.548				
	Disagree	3	0.097				
	Strongly Agree	10	0.323	20.484	3	<.001	306.378
	Strongly Disagree	1	0.032				

Continued

Sometimes I see crystal clear, yellowish and brownish apparent	Agree	24	0.774				
	Disagree	1	0.032	28.226	3	<.001	8941.006
	Strongly Agree	5	0.161				
	Strongly Disagree	1	0.032				
Sometimes I see the severity of algal blooms with one or more of the following, massive floating scum, strong foul odour and or dead fish	Agree	16	0.516				
	Disagree	7	0.226				
	Strongly Agree	7	0.226	14.806	3	0.002	29.726
	Strongly Disagree	1	0.032				

Note: [a] Vovk-Sellke Maximum *p* -Ratio: Based the *p*-value, the maximum possible odds in favour of H_1 over H_0 equals 1/(-e *p* log(*p*)) for $p \leq .37$ [18]. Here, respectively p-values of 0.007 and 0.002 are only 10.522 and 26.984 times more likely in favour of Alternative hypothesis than the Null hypothesis (more clarification can be obtained at http://www.shinyapps.org/apps/vs-mpr).



A **B**

Figure 1. Ranks (response counts) for the reasons of poor water quality (A) and ranks for the major threats as perceived by the respondents (B) in the study area

When respondents asked about the major threats, pollution ranked high responses followed by water shortage and climate change which altogether accounts for more than 50% of the respondents (Figure 1B) and in fact are real [27]. Though some cited Algal growth as a problem, the rating was lower than other options. This could be attributed to low and /or lack of awareness on HABs. The test statistics reveal that respondents were highly aware of algal blooms from provided images of algal bloom ($P < 0.05$). Respondents also agreed that blooms normally occur once in a season. This corroborates findings by [28] on tropical cyanobacteria blooms and the verbatim comments from the respondents in clarifying the season as a factor in algae blooming" *green algae blooms in Mindu Dam proliferate during the dry season*". The observation appended (Figure 2 as supplementary materials agrees with key informant interview findings that algal blooms occur mostly during the dry season (July, August, September, October and November) (Angumbwike, N, personal communication, 29/08/2018). Similar arguments came from the surveys likewise, focus group discussions (FGD) and the interviews which were held during the 2018 Nane Nane (88) exhibitions in Morogoro, Tanzania. This indicates that the best timing for studying cyanotoxins occurrence and mobility may be during the dry season but toxins can form any time of the year [29].

A (6.9035585S, 37.5925432E) **B** (6.755683S, 377543226E)

C (6.755683S, 377543226E)

D (6.9035585S, 37.5925432E)

Figure 2. Visible foam like algae as observed at Konga, Kidangawa (A), Greenish colorations as observed at Kingolwira fish ponds (B) and next to it is red algae (C) and finally mat like algae as observed at Konga Kidangawa (D); specific location i.e. latitude and longitudes in the brackets. All photos were taken by the Author during the survey.

It is widely accepted that some species of harmful algal blooms can cause skin irritations [30]. During a focus group discussion with the fish farmers, it was revealed that farmers have experienced the same, but the current study could not scientifically prove the argument. “I must make sure that I have some soap with me and change clothes after fishing because I normally feel skin irritation just after fishing” (Raphael, I., personal communication, 10/08/2018). From the interviews, there was a claim that current guidelines and standards for the management of algal blooms are yet in place (Maly, R., personal communication, 7/8/2018). From the same interview, the conservation training and awareness raising were considered as an immediate solution for managing harmful algal blooms. Along the similar line, the issue of HABs is not well addressed in policies which were also identified by Miraji et al., [24]. Most of the respondents commended the current study in the catchment, for example, “the project will help us solving problems of water quality in the catchment” (Angumbwike, N., personal communication, 29/08/2018). The ideas from the interviews are in line with most respondents’ verbatim comments that there is a need for increased awareness and intervention. Overall, these findings challenge policymakers to specifically include the issue of HABs in the fishery, environmental policy for close follows up. When asked about any idea on HABs in the ponds/dam or river (Table 1) and any idea about health effects associated with algal blooms there was no significant difference between the groups ($p= 0.369$ and $p = 0.590$, respectively) even number of odds in favor of alternative hypothesis that the null hypothesis was 1 for all (Table 1). The uncertainty for example “*I was told some species of algae can be toxic, but I am not sure*” could be captured during interviews with the experts. Respondents collectively agreed that sometimes there is a noticeable discharge from the industries ($p = 0.044$), and sometimes respondents see a crystal-clear water as per. Collectively, respondents agreed that they sometimes see algal blooms limited with clarity odour apparently. On the other hand, there was no significant difference between the groups. When asked about documenting the history of discharge ($p= 0.295$) (Table 1). Moreover, the majority of respondents agreed to have seen the severity of algal blooms and also dead fish ($p < 0.05$) (Table 1). When asked about the conventional methods used in controlling HABS, most respondents said no treatment method is applied. However, some mentioned filtering and chemical treatment. During the focus group discussion and interviews, farmers revealed the use of hand palm (mimicking Secchi depth technique) for monitoring the turbidity in their ponds. Water is added into the pond if they cannot see the palm of their hand, baseline being the Elbow. Some ponds management techniques, for example, the use of lime [31] have been tested for sterilization, nutrient enrichment and or for regulating pH changes. This was also revealed during the focus group discussion with fish farmers. "I apply chalked lime (Chokaa in Kiswahili) surrounding the pond before I introduce Fingerlets or just after harvesting" (Mlegu, D., personal communication, 10/08/2018).

4. Conclusions

In conclusion, respondents were very well (58%) informed about the problems of water quality and the reasons for the cause including overuse of water for agriculture, and nutrients load for example over-fertilization of ponds. The anecdotal observations indicate the occurrences of blooms and some had a red hue. Respondents (93.5%) were able to identify (when an image of bloom displayed to them) algal blooms and that algal bloom proliferates more during dry seasons (67.7%). The study further found the community was uncertain regarding the health effects associated with HABs. In addition, respondent collectively agreed that they sometimes see the severity of algal blooms and dead fish. The findings challenge policymakers, technical specialists (e.g. medical practitioners), and researchers all together to address problems associated with algal blooms specifically HABs. The findings can be used as a basis for the development of HABs management framework (i.e. education and extension programs, monitoring, identification, and control).

Acknowledgements: This study was funded by the University of Venda, Limpopo South Africa (Project Number SES/17/ERM/14). The Tanzania Government through the Ministry of Water and Irrigation, Sokoine University of Agriculture (SUA), MORUWASA, WRBO, Morogoro Regional, Districts, Wards Administrations and Fish farmers all are thanked for making this study possible. Specifically, we also acknowledge the SurveyCTO group (https://www.surveycto.com/index.html) for their technological supports.

References

1. E. Testai, F. M. Buratti, E. Funari, M. Manganelli, and S. Vichi, "Review and analysis of occurrence, exposure and toxicity of cyanobacteria toxins in food," Rome, 2016.
2. B. Greer, R. Maul, K. Campbell, and C. T. Elliott, "Detection of freshwater cyanotoxins and measurement of masked microcystins in tilapia from Southeast Asian aquaculture farms.," Anal. Bioanal. Chem., vol. 409, no. 16, pp. 4057–4069, Jun. 2017.
3. D. Anderson, "HABs in a changing world: a perspective on harmful algal blooms, their impacts, and research and management in a dynamic era of climactic and environmental change.," Harmful algae 2012 Proc. 15th Int. Conf. Harmful Algae Oct. 29 - Novemb. 2, 2012, CECO, Chang. Gyeongnam, Korea. Int. Conf. Harmful Algae (15th 2012 Chang. Gyeongnam, Kore..., vol. 2012, pp. 3–17, 2014.
4. B. W. Brooks et al., "Are harmful algal blooms becoming the greatest inland water quality threat to public health and aquatic ecosystems?" Environ. Toxicol. Chem., vol. 35, no. 1, pp. 6–13, Jan. 2016.
5. The United Republic of Tanzania, "The Tanzania Fisheries Sector Challenges and Opportunities," Dar es Salaam, 2016
6. WorldFish, "The threat to fisheries and aquaculture from climate change," Penang, Malaysia, 2007.
7. The United Republic of Tanzania, "Basic data for livestock and fisheries sectors," Dar es Salaam, 2013.
8. R. Pomeroy, "A research framework for traditional fisheries: Revisited," Mar. Policy, vol. 70, pp. 153–163, 2016.
9. A. R. Kaliba, K. O. Osewe, E. M. Senkondo, B. V Mnembuka, and K. K. Quagrainie, "Economic Analysis of Nile Tilapia (Oreochromis niloticus) Production in Tanzania," J. World Aquac. Soc., vol. 37, no. 4, pp. 464–473, Dec. 2006.

10. M. Natkhin, O. Dietrich, M. P. Schäfer, and G. Lischeid, "The effects of climate and changing land use on the discharge regime of a small catchment in Tanzania," Reg. Environ. Chang., vol. 15, no. 7, pp. 1269–1280, 2015.
11. P. Z. Yanda and P. K. T. Munishi, "Hydrologic and landuse /cover change analysis for the Ruvu River (Uluguru) and (Sigi River (east Usambara) Watersheds," Dar es Salaam, 2007.
12. GLOWS-FIU, "Tanzania Integrated Water, Sanitation and Hygiene (iWASH) program Environmental Flow Recommendations for the Ruvu River Basin," 2014.
13. I. Sanseverino, D. Conduto, L. Pozzoli, S. Dobricic, and T. Lettieri, "Algal bloom and its economic impact," 2016.
14. IHME, "Tanzania | Institute for Health Metrics and Evaluation Measuring what matters." [Online]. Available: http://www.healthdata.org/tanzania. [Accessed: 08-Nov-2018].
15. D. Mushi, "Bacterial community structure and composition of tropical river and drinking water – insights from deep sequencing and correlation to environmental drivers," Technical University Braunschweig (TUB), 2015.
16. M. C. Gomani et al., "Establishment of a hydrological monitoring network in a tropical African catchment: An integrated participatory approach," Phys. Chem. Earth, vol. 35, no. 13–14, pp. 648–656, 2010.
17. R. H. Mdegela, M. Braathen, A. E. Pereka, R. D. Mosha, M. Sandvik, and J. U. Skaare, "Heavy Metals and Organochlorine Residues in Water, Sediments, and Fish in Aquatic Ecosystems in Urban and Peri-Urban Areas in Tanzania," Water. Air. Soil Pollut., pp. 1–11, 2009.
18. T. Sellke, M. J. Bayarri, and J. O. Berger, "Calibration of p Values for Testing Precise Null Hypotheses," Am. Stat., vol. 55, no. 1, 2001.
19. S. Fröcklin, M. de la Torre-Castro, L. Lindström, and N. S. Jiddawi, "Fish traders as key actors in fisheries: gender and adaptive management.," Ambio, vol. 42, no. 8, pp. 951–62, Dec. 2013.
20. R. Y. M. Kangalawe and E. T. Liwenga, "Livelihoods in the wetlands of Kilombero Valley in Tanzania: Opportunities and challenges to integrated water resource management," Phys. Chem. Earth, vol. 30, no. 11–16 SPEC. ISS., pp. 968–975, 2005.
21. J. Ngana, F. Mahay, and K. Cross, "Ruvu Basin: A Situation Analysis," 2010.
22. The United Republic of Tanzania, "National Water Sector Development Strategy," 2006.
23. FAO, "AQUASTAT - FAO's Information System on Water and Agriculture," 2016, 2016. [Online]. Available: http://www.fao.org/nr/water/aquastat/countries_regions/TZA/index.stm. [Accessed: 09-Oct-2018].
24. H. Miraji, O. C. Othman, N. Ngassapa, and W. Mureithi, "Research Trends in Emerging Contaminants on the Aquatic Environments of Tanzania," Sci. Hindawi Publ. Corp., vol. 2016, pp. 1–6, 2016.
25. P. Hawkins, "National Water Quality Management and Pollution Control Strategy," 2010.
26. H. W. Paerl and T. G. Otten, "Duelling 'CyanoHABs': unravelling the environmental drivers controlling dominance and succession among diazotrophic and non-Nitrogen -fixing harmful cyanobacteria," Environ. Microbiol., vol. 18, no. 2, pp. 316–324, Feb. 2016.
27. World Bank-Tanzania, Water Resources in Tanzania. 2006.
28. M. A. D. Mowe, S. M. Mitrovic, R. P. Lim, A. Furey, and D. C. J. Yeo, "Tropical cyanobacterial blooms: a review of prevalence, problem taxa, toxins and influencing environmental factors," J. Limnol., vol. 73, no. AoP, Dec. 2014.
29. D. Van der Merwe, "Freshwater cyanotoxins," Biomarkers Toxicol., pp. 539–548, Jan. 2014.
30. R. P. Rastogi, D. Madamwar, and A. Incharoensakdi, "Bloom Dynamics of Cyanobacteria and Their Toxins: Environmental Health Impacts and Mitigation Strategies," Front. Microbiol., vol. 6, p. 1254, Nov. 2015.
31. A. M. Lazur, C. E. Cichra, and C. Watson, "The Use of Lime in Fish Ponds," Florida, 2013.

Seasonal variation of microbiological and physico-chemical properties of groundwater in selected rural community of Vhembe District, South Africa

AM Enitan*, N Mutileni, JO Odiyo and JN Edokpayi

Department of Hydrology and Water Resources, University of Venda, South Africa.
*Email of corresponding author : enitanabimbola@gmail.com

Abstract
Potential effects of anthropogenic activities, on groundwater were evaluated around Muledane by the use of hydrochemical, and bacteriological analyses. Seasonal water samples were collected from eight different boreholes for bacteriological analysis (*Escherichia coli* and *Enterococcus faecalis*) and physico-chemical parameters (pH, turbidity, electrical conductivity and anions) during summer, autumn and winter. This was aimed at determining whether the borehole water of the region is safe for domestic and drinking purposes across the seasons. The values of most of the measured hydrochemical and bacteriological parameters were found not to meet the standard guidelines set by WHO and DWAF for drinking water, especially during summer and autumn. The pH values for all boreholes were higher during wet season (summer) as compared to winter (dry), while the mean NO_3 concentration for most of the boreholes failed to comply with the recommended guidelines throughout the season. High microbial load of *E. coli* (2.0×10^1 – 4.6×10^3) and *E. faecalis* (2.0×10^0 - 6.0×10^2 CFU/100 mL) were recorded in the wet season than in the dry season (*E. coli:* 0.0 – 7.0×10^2 and *E. faecalis:* 0.0 – 1.0×10^1 CFU/100 mL). The water sources classification analysis showed that most of the boreholes were prone to contamination during summer and autumn which correlates with the measured data obtained for microbial contamination. The results are of importance because water from these boreholes are used for drinking purposes and could pose major public health risks to the consumers, if not properly treated. Therefore, the study recommends regular testing and treatment of groundwater around Muledane area, in order to protect the households from water borne diseases.

Keywords: Bacteriological analysis, Groundwater quality, Muledane, Quality classification, Waterborne diseases.

1. Introduction

In most developing countries, the risk of groundwater contamination with bacteria, viruses, nitrates and chemicals from pit latrines is increasing due to improper design, location and construction of septic systems and/or lack of boreholes maintenance [1]. Unfortunately, unsafe water is an effective carrier of pathogens that are capable of transmitting waterborne diseases to a huge number of the population with devastating effects [2]. South Africa is water stressed due to high demand for potable water, unpredictable rainfall and high evaporation rate. Available groundwater resources (around 7500 million m^3/a) are extensively utilised in rural and urban areas of South Africa to reduce the pressure on surface water resources [3]. Reports in South Africa have shown that water-borne diseases remain one of the most important causes of illnesses and death in children due to lack of access to safe water infrastructure by almost 2.11 million people [4].

Water supply and sanitation in Muledane area of Vhembe district, Limpopo Province, South Africa is inadequate with significant percentage of people relying on groundwater as a source of water supply for domestic use. There is limited information on the bacteriological and chemical quality of these boreholes [5] with no available epidemiological and sufficient clinical evidences to conclude that pathogenic bacteria in the water supplies from the study area could pose health related risk. Thus, this study was undertaken to determine the quality, acceptability and fitness of borehole water supplies in Muledane for human consumption based on national and international drinking water guidelines. The objectives of the present study were to examine the hydrochemical and bacteriological quality of borehole water in rural communities in Muledane in Vhembe district. Classification based on lifetime usage of water supply proposed by Kempster, et al. [6] was adopted to know the impact of chemical contaminants on the quality of water obtained around this area.

2. Materials and Methods

Sample collection and analyses

Water samples were collected from eight selected boreholes in Muledane catchment area of Thohoyandou, Limpopo province, South Africa during summer, autumn and winter. A total of 48 groundwater samples were collected into sterile Schott bottles, immediately stored on ice and then transported to the University of Venda laboratory at -4°C so as to prevent multiplication of the microorganisms as well as to slow down the chemical reactions in the water. Samples were divided into analytical and microbiological samples for further analysis. Microbial analysis was carried out within 3-6 hours of sample collection. Direct count of Escherichia coli and Enterococcus faecalis based on membrane filtration technique was carried out using m-Enterococcus agar (E. faecalis) and mFC agar (E. coli) to isolates at 45.5°C for 48 hrs and 37°C for 24 hrs, respectively. Number of colonies were enumerated and expressed as number of bacteria colonies per 100 ml of water.

Temperature, pH, electrical conductivity (EC) and turbidity were measured on-site using H1 8014 HANNA instrument, turbidity and Cyberscan 500 conductivity (AQ2010 LABOTEC) meters, respectively. Appropriate portion of the collected groundwater samples from different boreholes were tested for nitrate concentrations using an ion chromatography (Methrohm 850 Professional IC) according to manufacturer's instruction to check the groundwater's suitability for domestic use.

Classification system of water sources

Classification system proposed by Kempster et al. [6] was adopted in this study based on chemical composition of the boreholes (Table 1).

Statistical analysis

Pearson's correlation coefficient (r) at $P<0.05$ confidence level was used to evaluate the relationship between physico-chemical parameters and the mean concentration of bacterial counts in the water samples. XLSTART statistical package was used for the analysis.

TABLE 1. Classification and human health effect of water quality as described by Kempster et *al*. [6].

Class	Chemical description	Impacts on human health
Class 0	Ideal water suitable for lifetime use with excellent and good quality.	No adverse effects on the users.
Class 1	Good water: The water is safe for lifetime use but falls short of the ideal water quality.	Suitable for use, rare instances of adverse health effects, usually mild health effects, almost sub-clinical and difficult to demonstrate.
Class II	Conditionally acceptable.	Negative effects may occur in some sensitive groups with adverse health effects if use for a prolonged period of time, or with lifetime use.
Class III	Poor water quality and not suitable for use as drinking water without adequate treatment to shift the water into a lower and safer Class".	Chronic effects may occur with serious health effects particularly in infants or elderly people with short-term use, and even more so with longer term use.

3. Results

Bacteriological composition of borehole water

Surveillance of water quality to ensure microbiological and chemical safety is a vital public health function, especially in developing countries. Water samples from the selected groundwater in Muledane Catchment, tested positive for both *E. faecalis* and *E. coli* bacterial. The results showed that there is high vulnerability of boreholes to microbial contaminants with high *E. coli* bacterial counts throughout the season. The mean *E. coli* counts recorded during summer was high in BH5 (4600 CFU/100 mL) followed by BH1 (3000 CFU/100 mL). During the winter season, no *E. coli* were isolated from boreholes BH4 and BH5 while, high concentrations were recorded in BH1 (150 CFU/100 mL), BH2 (700 CFU/100 mL) and BH7 (70 CFU/100 mL) samples. The *E. faecalis* counts during summer and autumn had mean counts above the standards limits set by WHO and DWAF for drinking water with the exception of BH3 (summer and autumn) and BH8 (autumn and winter) which had 0 colony per 100 mL. However, the concentration of *E. faecalis* throughout the winter period was very low with no detection in BH2, BH5 and BH8 boreholes.

Physico-chemical parameters of the selected water sources

The physico-chemical parameters of the measured boreholes in summer, autumn and winter were generally within the target water quality ranges (TWQR) for domestic and recreational uses as set by DWAF and WHO [8, 9]. On the contrary, nitrate and turbidity concentrations from selected sites were quite high which indicates potential quality challenges (Table 2). High nitrate concentrations were observed during summer from BH1 (121.64 mg/L) and BH8 (125.18 mg/L) boreholes (Table 2). The average concentration in water samples collected from BH6 during autumn (72.71 mg/L) as compared to other sample site was above the recommended limits set by WHO [9] and DWAF [8] for domestic and recreational purposes (< 22 and < 50 mg/L, respectively). High nitrate concentrations in BH1 throughout the season and BH8 in summer and autumn above the recommended limits by WHO and DWAF indicates a red flag on water quality as compared to other boreholes water samples as shown by the classification analysis (Table 2).

Classification of water quality

Extreme nitrate classification, class III was observed in the borehole water collected at BH1, while BH4 water falls under the ideal and suitable water quality for lifetime use (Class 0) throughout the season. Borehole BH5 fell under Class I during summer and class 0 during autumn and winter (Table 2). The water quality in BH7 need further treatment during summer (Class III). Likewise, boreholes BH2 and BH6 during winter fall into category III, this means that the water cannot be used for short term or emergency purposes without adequate treatment. If used it could lead to negative health effects especially in infants or elderly people.

4. Discussion

Detection of pathogenic bacteria in borehole water that is intended for human consumption is a cause for public health concern, especially if they are harbour virulent genes. All the boreholes had *E. coli* and *E. faecalis* cells beyond the guideline values of 0 CFU/100 mL during the wet season as compared to winter period. Osvalda *et al.* [10] mentioned the presence of faecal bacteria such as *Salmonella,* total coliform, *E. coli* and *Enterococcus* sp. in groundwater. Thus, the detection of *E. faecalis* and *E. coli* could be due to high dilution of faecal matter by rainwater and surface runoff into the aquifer or selective removal of nitrates transport in the soil [11]. Variation of nitrates (Table 2) in the boreholes across the seasons has weak correlation with bacterial indicators. This may be explained by the differences in contaminants entry point and physico-chemical parameters [12]. High nitrate concentration in the groundwater may be due to non-point sources such as septic tanks precipitation, geology and/or improper use of fertilisers and animal manures [7,12]. Accumulation of this nutrient in borehole water and long-time exposure or consumption of nitrate rich water could lead to serious health risks. Ingestion of high nitrate concentration water by humans could lead to blue baby syndrome (methemoglobinemia) in infants and could cause carcinogenic diseases in adults [2,3,13]. It is noteworthy that most of the water sources fell into class III because of its relatively high nitrate concentration (Table 2) which means that the water can be used for only short term and if used for a prolonged period without adequate treatment, it could pose adverse negative health effects in humans especially in infants or elderly people.

5. Conclusions

In general, all the selected borehole water taken from Muledane catchment of Limpopo, South Africa have ideal water quality in terms of pH and EC values and were within the acceptable limits set by WHO [9] and DWAF [8]. Most boreholes required further treatment before they can be used continuously or for a long period of time. In addition, the classification analysis showed that most of the boreholes are prone to contamination during summer due to rainfall. The boreholes are vulnerable to microbial contamination through groundwater seepage from the pit latrines which could pose major public health risks to the consumers. Therefore, effective, regular operation and maintenance of the drinking water sources through the adoption and promotion of appropriate water safety plans set by the policy maker or government sector are highly required.

TABLE 2. Concentration of physico-chemical parameters of selected boreholes in Muledane catchment and their water quality classification.

Sampling site	Month of sampling	Turbidity (NTU)	pH	EC (mS/cm)	NO_3^-	Chemical Classification constituent
BH1	Summer	0.65	7.17	61.90	**121.64**	**3**
	Autumn	0.99	6.51	63.70	53.13	3
	Winter	1.16	6.96	64.00	51.55	3
BH2	Summer	1.12	6.75	40.90	14.23	1
	Autumn	0.54	6.22	42.90	5.81	0
	Winter	0.94	6.79	43.70	**57.38**	**3**
BH3	Summer	4.10	6.82	32.90	30.49	2
	Autumn	14.9	6.22	18.68	11.97	1
	Winter	1.28	6.39	20.18	11.84	1
BH4	Summer	1.22	7.19	4.48	0.70	0
	Autumn	3.50	6.17	31.90	0.60	0
	Winter	1.11	7.20	16.28	0.65	0
BH5	Summer	1.00	6.95	11.30	16.08	1
	Autumn	5.76	6.13	16.29	2.2	0
	Winter	1.04	6.71	19.47	9.16	0
BH6	Summer	1.38	6.76	12.70	16.37	1
	Autumn	1.62	6.22	8.99	0.85	0
	Winter	1.16	6.28	9.78	**72.71**	**3**
BH7	Summer	2.26	6.62	28.20	47.86	3
	Autumn	0.94	6.04	15.11	5.03	0
	Winter	1.66	6.57	9.81	2.25	0
BH8	Summer	0.33	6.98	61.30	**125.18**	**3**
	Autumn	0.79	6.49	40.90	**63.73**	**3**
	Winter	1.01	6.59	51.10	2.27	0
Standard limit for WHO for drinking water quality [9].		<1.0	6.0–9.0	≤ 70	50	-
Standard limit for DWAF for drinking water quality [8].		<5	-	-	< 22	-
South African National Standards (SANS) [14]		≤1	6.0–9.0	-	< 11	-

References

1. Mbugua, H. The Effect of Septic Tanks Sewage Disposal System Distances on Borehole Water Quality In Ongata Rongai, Kajiado County, Kenya. University of Nairobi, 2016.
2. Lukubye, B.; Andama, M. Bacterial Analysis of Selected Drinking Water Sources in Mbarara Municipality, Uganda. Journal of Water Resource and Protection 2017, 9, 999.
3. Palamuleni, L.; Akoth, M. Physico-Chemical and Microbial Analysis of Selected Borehole Water in Mahikeng, South Africa. International Journal of Environmental Research and Public Health 2015, 12, 8619-8630, doi:10.3390/ijerph120808619.
4. WWF-SA. Water: Facts and Futures; 2016.

5. Edokpayi, J.N.; Enitan, A.M.; Mutileni, N.; Odiyo, J.O. Evaluation of water quality and human risk assessment due to heavy metals in groundwater around Muledane area of Vhembe District, Limpopo Province, South Africa. Chemistry Central Journal 2018, 12, 2.
6. Kempster, P.L.; Van Vliet, H.R.; Kuhn, A. The need for guidelines to bridge the gap between ideal drinking-water quality and that quality which is practically achievable and acceptable. Water S. A. 1997, 23, 163-167.
7. Grimason, A.; Morse, T.; Beattie, T.; Masangwi, S.J.; Jabu, G.C.; Taulo, S.; Lungu, K. Classification and quality of groundwater supplies in the Lower Shire Valley, Malawi–Part 1: Physico-chemical quality of borehole water supplies in Chikhwawa, Malawi. Water SA 2013, 39, 563-572.
8. DWAF, D.o.W.A.a.F. South African Water Quality Guidelines. Domestic Water Use. Department of Water Affairs and Forestry. Pretoria, South Africa 1996, 1, 2nd Edition.
9. WHO. Guidelines for Drinking-Water Quality, Addendum to Volume 1: Recommendations. 3rd ed. Geneva: World Health Organization. 2006.
10. De Giglio, O.; Caggiano, G.; Bagordo, F.; Barbuti, G.; Brigida, S.; Lugoli, F.; Grassi, T.; La Rosa, G.; Lucentini, L.; Uricchio, V., et al. Enteric Viruses and Fecal Bacteria Indicators to Assess Groundwater Quality and Suitability for Irrigation. International Journal of Environmental Research and Public Health 2017, 14, 558.
11. Haruna, R.; Ejobi, F.; Kabagambe, E.K. The quality of water from protected springs in Katwe and Kisenyi parishes, Kampala city, Uganda. African Health Sciences 2005, 5, 14-20.
12. Adeniyi, A.; Yusuf, K.; Okedeyi, O.; Sowemimo, M. Classification and health risk assessment for borehole water contaminated by metals in selected households in Southwest Nigeria. Journal of Water Resource and Protection 2016, 8, 459.
13. Trivedi, P.; Bajpai, A.; Thareja, S. Comparative study of seasonal variation in physico-chemical characteristics in drinking water quality of Kanpur, India with reference to 200 MLD filtration plant and ground water. Methods 2008, 2009.
14. South African National Standards, S. Drinking water. Part 1: Microbiological, physical, chemical, aesthetic and chemical determinants. SABS Standards Division. Pretoria, South Africa. 2011, 14.

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

Appraisal of solid waste disposal along Muungamunwe River at Hamutsha Village, Limpopo Province, South Africa

D Mugari* and NV Mudau

Department of Geography and Geo-Information Sciences, University of Venda, South Africa
*Email of corresponding author : dzivhumugari@gmail.com

Abstract

The challenge of solid waste disposal in rivers has become a serious environmental threat, mostly in the developing countries around the world. Solid waste dump's problem is growing rapidly day by day due to the lack of proper dumping sites and absence of waste management strategies. To highlight the main cause of improper solid waste management in developing countries, the study aimed at analyzing the state of solid waste pollution at Muungamunwe River and how waste management strategies can be implemented to prevent or to minimize it. The objectives of the study were to identify types of solid wastes disposed in the river, to analyze factors that contribute to solid waste disposal in the river, to determine the possible risks of solid waste in the river, to establish alternative waste management strategies to prevent/ minimize solid waste disposal in the river. The study employed descriptive research design. Thus, the study was conducted using both quantitative and qualitative research approaches. The study followed quantitative, descriptive survey design through questionnaires and an instrumental descriptive design in the form of structured interviews. In structured interview, the set of predetermined questions were prepared by the interviewer in advance. Close and open-ended questions were used to interview respondents. Field observations was carried out using a checklist, to identify the types of solid waste disposed at Muungamunwe River. Convenience sampling method was used to get respondents for interviews based on their availability and accessibility. The study was analyzed in two different ways, qualitative data was analyzed using inductive whereas quantitative data was analyzed using IBM-SPSS 23 statistical software. Analyzed data were presented through tables and graphs.

Keywords: Solid waste, river, illegal disposal

1. Introduction

Disposal of solid waste in rivers has become a complex issue in developing and developed countries around the world. However, the nature (quantity and quality) of solid waste vary from place to place and are largely dependent upon the way waste production is managed by both the government and the public [8]. Solid waste are substances and masses resulting from the various human activities that must be dumped. As far as solid waste is concern it has been observed that it primarily rises from anthropogenic activities [3]. The problem of solid waste pollution in rivers grows rapidly day-by-day due to lack of proper dumping sites and absence of active waste management strategies in developed and developing countries around the world. These results in direct threat to the public human health and the environment [6].

In most of rural areas, disposal of solid waste in water bodies puts the lives of people and other living and non-living organisms at risk. Solid waste pollution makes it problematic for people to access water from most water bodies as the waste disposed, mostly in rivers largely blocks the water pathways and makes the river fail to transport water sufficiently from one catchment to another. The World Health Organization report [12] estimated that about quarter of the diseases facing people today occur due to prolonged exposure to environmental pollution. More than 2 million people die every year due to water-borne diseases such as diarrhoea and cholera, and most of them are children less than 5 years of age.

Muungamunwe River is a perennial river that provides water to the community and other individual subsistence farmers around the area. Due to lack of municipal waste collection and absence of municipal services in the area, the citizens dump waste on the watersheds and in the river. As such, the waste disposed affect river waterways. The waste blocks it from providing water to the other parts of the community and to other individual subsistence farmers.

2. Materials and methods

Sampling method

Population within 300m radius from the river under study were selected because they observe almost everything that occurs in the river and were able to provide valid answers to the research study. Convenience sampling method was used in order to gather information from available and accessible participants in the study area. A total of 70 households out of 459 households within 300m (Meters) were sampled. Four subsistence farmers who extract water from the river were also selected purposively that is only those that are affected by the obstruction caused by illegal waste disposed into rivers. Makhado Municipality governmental stakeholders was also selected purposively because they have information about solid waste national strategies and they provided relevant information about alternative solid waste management strategies.

Data collection methods

Primary data was collected using interviews and field observations. Secondary data was collected through reviewing literature from documents and journals that have information related to the research topic. Secondary data about the risks (impacts) associated with the disposal of solid waste was conducted through documents from different scholars that have related information about solid waste pollution in rivers. Other than that, documents that contained information about solid waste management practice, solid waste governmental reports, solid waste national strategies and solid waste management policies were also reviewed.

The researcher used a checklist to check the types of solid waste disposed in the river and on its watershed next to the river. Furthermore, the researcher conducted face-to-face interview with the participants to gather information about factors that contribute to the solid waste disposal at the river. Interviews were conducted conveniently from household to household depending on the availability of the respondents. The researcher used open and close-ended questionnaire to undertake interviews from respondents. The researcher also probed to the questions, especially to illiterate people (elders and young participants) so that they can understand the content of the research problem and what was needed from them.

Data analysis

Qualitative data was analyzed using inductive content analysis. The researcher grouped information acquired on the field and data obtained were used to develop coding and category schemes. Coding schemes were tested, so that a conclusion can be drawn from the coded data. Afterwards, the themes were created incorporating the most important categories. Quantitative data obtained was analyzed using factor analysis through descriptive statistic IBM-SPSS 23 statistical software. Data obtained was presented through bar graphs, pie charts and tables.

3. Results and discussion

Solid waste disposal at the river

Muungamunwe River faces high concentration of different types of solid waste disposal. The findings indicated that the types of solid waste found were both non- biodegradable and biodegradable in nature. Figure 1 entails solid waste in the river and the ranking of solid waste that were found. Non-biodegradable waste includes plastics, napkins, tin cans, bottles, metals, aluminums, car parts, toys, electric wastes (E-waste), paint tins, batteries, spray cans and pesticides containers. The biodegradable solid waste found includes dead animals, food waste, dead animals, damaged furnisher, cardboards and tree branches that have been thrown in the river. The study also found that most of the above-mentioned waste rises from anthropogenic activities within the community as stated by [10].

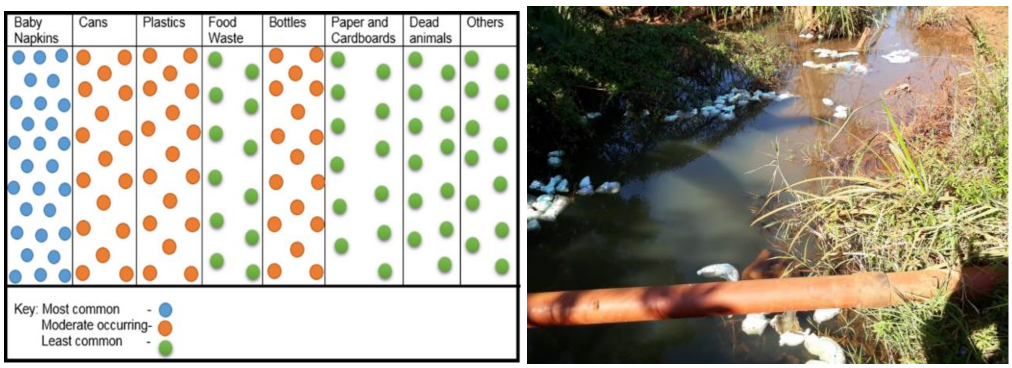


Figure 1. Ranking of solid waste dumped at Muungamunwe river

The findings point out that most people within Ha-Mutsha village lack awareness about the dangers of illegal dumping of solid waste at rivers. Of all respondents (70), 23% indicated that the rate of ignorance on participants is high. About 16% of respondents indicated that their main problem of disposing solid waste in water is the absence of disposal facilities and waste collection by responsible authorities.

Almost 14% of the respondents indicated that the distance from the river and their homes also contributed to the disposal of waste. Furthermore, about 11% of the respondents showed that there is a need to address people about the importance of conserving water and how can one avoid illegal dumping as a way of respecting water bodies. The study also revealed that about 11% of respondents are dumping at the water bodies because there is no provision of municipal services, such as rubbish bins within the village and 13% believed that lack of municipal collection is the main cause or factor that influences people to dump waste materials in rivers. The challenge is caused by lack of capacity by the local municipality as indicated by [8].

Subsistence farmers' states that illegal disposal of solid waste at Muungamunwe River gave rise to the loss of agricultural activities that usually took place at the community level. Most of subsistence farms are situated next to the river and their farming activities depends on the river to grow crops and to feed their livestock. However, a large amount of waste disposed at Muungamunwe River blocks its water pathways and affect the crop production of smallholder farmers.

Identified solid waste disposal into the river pose environmental risk that carries the potential of creating adverse effects on the physical and live environment through waste, pollution, emission or other effects [11]. However, human perception varies among individuals, which poses some conflicts in the perception of environmental risk, or the consequence of human behaviour. Most participants (14%) mentioned waste disposed at Muungamunwe River as a major problem to them. The solid waste disposed at the river blocks its pathways and affects the potential subsistence farmers within the community. The results also indicate that 30% of the respondents are affected negatively by contaminated water due to illegal dumping of waste in the river. Twenty nine percent of the respondents residing next to the river indicated that they are experiencing the problem of unpleasant odours from the river, mostly during the day and sunset mostly in winter.

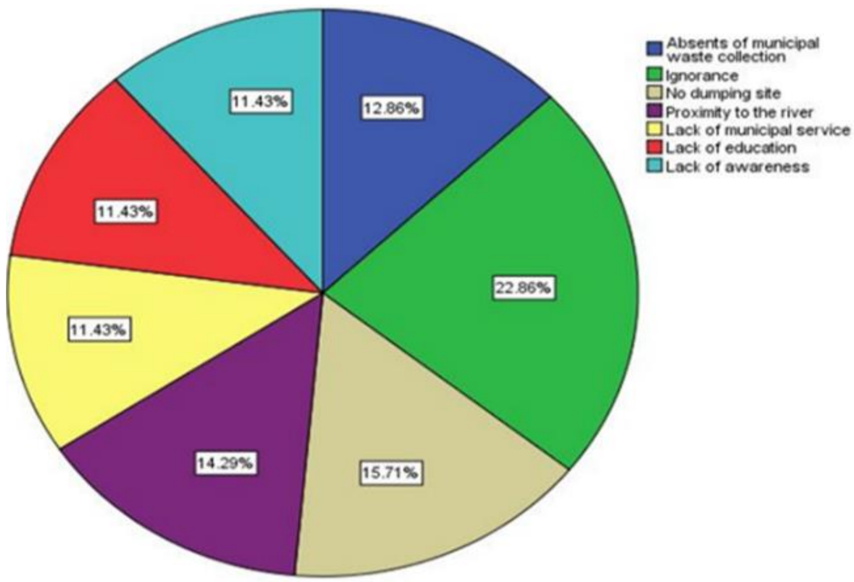


Figure 2. Factors that contributed to the disposal of solid waste in rivers.

Impacts of illegal dumping to rivers

There is potential risk of riverbank vegetation degradation, reduction in biodiversity as the dumped material can interfere with revegetation at the riverbank. Runoff from dumped materials at the riverbank can contaminate soil and water affecting aquatic ecosystem. There might be an increase in flooding and erosion risk as dumped items change natural water courses. There is loss of recyclable resources as the material once collected may not be recycled. Social impact includes decreased visual appearance of rivers leading to reduced use by the public, increased health risk as dump sites may attract vermin and rodents. Often there might be dumping from copy-cat offenders who will dispose in rivers. Decreased community pride and increased anti-social behaviour. There is a need of proactive stakeholder engagement and partnerships between community and environment section stakeholders.

A rapid increase in volume and types of waste generated such as disposable napkins contribute to the escalating problem for waste management in national and local governments in developing countries [4, 7 & 2]. Local municipalities should adopt the principles of waste management that include understanding the local conditions, obtaining official and political buy-in, and ensuring that the basic cleansing waste management systems are in place [1;12].

Responses from the households showed that there was an urgent need to educate people about caring for the rivers. Programmes such as "adopt a river" should be encouraged as initiatives in rural areas where there is no waste collection by the municipality [5]. Municipalities need to communicate effectively through well-known media outlets and convey the message of creating awareness of the need to actively participate in the protection and management of water resources. From the results, it can be concluded that the general public can only be partly to blame for their action on illegal disposal of waste in rivers because they might not have been aware of what was expected of them. Therefore, in municipalities, there is a need to identify potential communication strategies for use in effectively reaching out to the general public.

Disposable napkins as seen in Figure 1, were problematic because of the smell. Therefore, residents tend to dump them illegally in rivers because they could not burn them. The napkins seem to be affordable and save time and cost in washing baby linen. This is one of the reasons why there was a high volume of napkins introduced to the general waste stream of household waste. In addition [2] stressed the importance of analysing waste role players needs in waste management system. The municipality and traditional leaders should create awareness amongst households about unacceptability of illegal dumping and littering, and penalties for illegal dumping and littering. Zavodska [13] also emphasise the importance of increasing environmental education and awareness, using the cases of Ireland and the Czech Republic.

Alternatives for minimizing solid waste pollution in rivers.

About 19% of respondents viewed education and environmental awareness as the best implementation strategy to solve solid waste disposal at Ha-Mutsha village. Due to the high concentration of solid waste within the river, most of the pollutants found at the study were napkins, bottles, tins and plastic bags of which they are non-biodegradable. The study found that women contributed more to solid waste pollution at the river because baby napkins were the most common waste. Therefore, community stakeholders must pay more attention to women, by educating them about the impacts of solid waste disposal in water and to be made aware on how those impacts can affect their health. Education and environmental awareness will be achieved by engaging community members into awareness campaign and community meetings.

In addition, from the findings obtained, 13% of respondents stated that requesting for municipal collection can be an effective solution as most waste needs to be disposed in proper dumping sites. About 12% of the respondents suggested that siting of proper waste dumping sites can reduce illegal waste disposal at the river. Another 10% of the respondents showed that the planting of warning sign at the prohibited dumping areas such as river environments can help to solve the waste problem while 12% indicated that the development of Non-Profit Organizations (NPOs) which can adopt the river can be a good solution towards waste management. Implementations of NPOs can help people to clean waste at the river and can be implemented by unity engagement in the community.

Almost 10% of the participants believed that pay as you dump/ throw strategy can help to solve the problem, whereas 9% of respondents showed that composting (digging holes to dump waste) can help solve the problem. Respondents showed that people need to dig their own dumping sites at their homes where they can bury their waste there. About 14.43% of the respondents indicated that the reuse, reduce and recycle strategy can be more useful when solving this problem. 3R strategy is the most desirable option on waste management hierarchy and they helped to solve waste problem in many places. The Reduce strategy helped people to minimize waste produced at local scale.

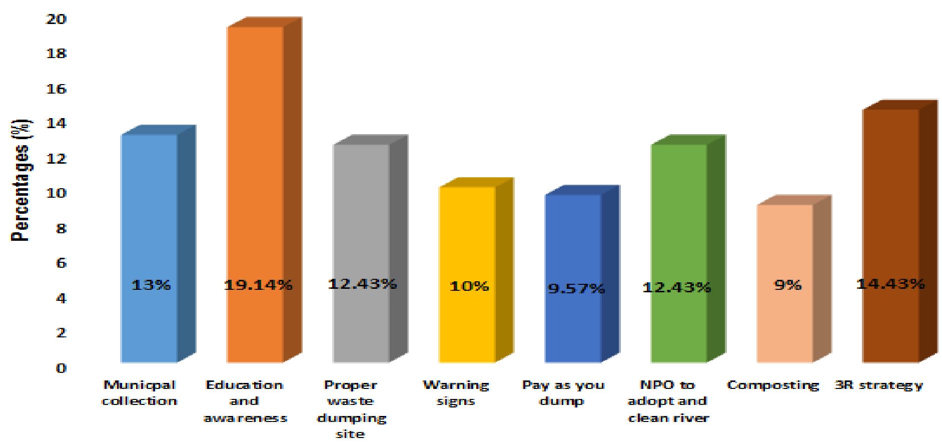


Figure 3. Alternative strategies to minimize illegal dumping in rivers

Alternative illegal dumping strategies provides action on how to prevent and manage illegal dumping in rivers of rural. This can be achieved by providing physical barriers as a deterrence to illegal dumping in key hotspots such as water bodies. Improve community awareness and services approach to reduce illegal dumping, increase investigations, widen enforcement exposure and intelligence gathering activities across the target area. Furthermore, develop and maintain effective local community reporting and accountability.

Community engagement is a key to environmental management in rural areas. Engage with residents, formal and informal businesses and where illegal dumping is an ongoing issue. Maintain and improve partnerships with key land owners to seek cooperation in minimizing and removing illegal dumping. Develop and distribute illegal dumping awareness material for a range of dumping types such as renovators, properties adjoining open space, builders, multi-unit dwelling tenants. Promote illegal dumping messages at community events and publicize illegal dumping enforcement activities. It is significant to develop and install 'report it' signage in identified hotspots. Promote incident reporting protocol that is easy for the community to use. Encourage community waste management plan, in all new development sites approvals, to ensure appropriate disposal practices of solid waste

4. Conclusion

The study concluded that solid waste pollution has severe risks on public human health and the environment. This study therefore portrays significant point sources of solid waste river pollution, which require priority control. To improve environmental management in rivers it is recommended that operational control measures of the waste hierarchy and disposal facilities should be implemented and maintained in all areas including rural areas. There is lack of monitoring of waste disposal facilities and illegal dumping hot spots in accordance with policy plans and management procedures by relevant authorities such as local municipalities. Community engagement is a key element in mitigating environmental issues in rural municipalities with lack of capacity to carry its mandate.

Acknowledgments: Special appreciation to Dr. N.V Mudau for supervision and NRF for research funds.

References

1. Arukwe, A., Eggen, T., and Moder, M., 2012. Solid waste deposits as a significant source of Contaminants of emerging concern to the aquatic and terrestrial environments – A developing country case study from Owerri, Nigeria. Science of the Total Environment, 438, 94-102.
2. Contreras, F. K., Hanaki, T., Aramaki and Connors, S., 2008. Application of analytical hierarchy process to analyze stakeholder's preferences for municipal solid waste management plans, Boston, USA. Resources, Conservation and Recycling, 52, 979-991.
3. Daniel, J and N, Parinez. (2012). "Assessment of plastic waste generation and its potential recycling of household waste in Can city, Vietnam" Environmental monitoring and assessment, vol.175, no.1-4, 2011, pp 23-35.
4. Ezeah, C., and Roberts, C.L., 2012. Analysis of barriers and success factors affecting the adoption of sustainable management of municipal solid waste in Nigeria. Environmental Management, 103, 9-14.
5. DEA (Department of Environmental Affairs), 2010. National Domestic Waste Collection Standards. DEA, Pretoria.
6. Goorah, S, Esmyot, M, Boojwon, R. (2009). The health impact of non-hazardous solid waste disposal in a community: the case of the Mare Chicose landfill in Mauritius. Journal of environmental health, 72(1) 48-54
7. Igoni, A. H., Ayotamuno, M.J., Ogaji, S.O.T., and Probert, S. D., 2007. Municipal solid waste in Port Harcourt, Nigeria. Applied Energy, 84, 664-670.
8. Mudau, N.V., (2015). A process mapping appraisal of municipal waste management system compliance in Limpopo province South Africa (Doctoral dissertation).
9. Naidoo, K. (2009). An analysis of municipal solid waste management in South Africa using the Msunduzi Municipality as a case study. University of Natal, Pietermaritzburg South Africa.
10. Shekdar, A.V. (2009). Sustainable solid waste management: an integrated approach for Asian countries. Waste management. New Dheli: India, 29(4), pp.1438-1448.
11. Steg, L. (2013). Environmental psychology: An introduction. Hoboken, NJ: Wiley-Blackwell.
12. WHO (World Health Organization) (2010). World health statistics 2010. World Health Organization.
13. Yau, Y. (2010). Domestic Waste Recycling, collective action and economic incentive: The case in Hong Kong. Waste Management. 30, 2440-2447.
14. Zavodska, A., Benesova, L., Smith. B. (2014). A comparison of biodegradable municipal waste management strategies in Ireland and the Czech Republic and lessons learned. Resources, Conservation and Recycling, 92, 136-14

Effect of selective conditions on various composite sorbents for enhanced removal of copper (II) ions in aqueous solution

RO Adeeyo[1,2], JO Odiyo[1], AO Adeeyo[2] and JN Edokpayi[1]

[1]Hydrology and Water Resource Department, University of Venda, South Africa
[2]Ecology and Resource Management Department, University of Venda, South Africa

Abstract
Heavy metals are one of the major contaminants reported in wastewater and wastewater effluents. The persistence of these metals, non-biodegradable and transformation from a less toxic form to more toxic form in environmental media under favorable conditions is of concern. Copper is one of the predominant heavy metals in wastewater effluent. In this work, various performance of different polymer adsorbent is presented for establishment of various optimum conditions. Nano-polymer composite were also reviewed with their optimum conditions to establish the resultant remediation effect as well as amount of copper removed, and time taken. This procedure allows the establishment of a valid conclusion of reduced time and high Cu II ion removal in association with nano-polymer adsorbents. Nano-polymer composites are therefore seen as good candidates for remediation of Cu ions at pH 5-6 and temperature between 24 and 27°C as mostly the optimum performance reported. The procedure reported can be applied for other metal remediation and development of potent novel adsorbents and process conditions.

Keywords: Polymer adsorbent, Nano-polymer adsorbent, copper, remediation, optimum condition.

1. Introduction

Sustainable access to water supply with good quality and quantity is significant to both human and aquatic life. Copper II ions is one of the widely spread heavy metal contaminant in the environment that poses great ecological problems due to its significance in urbanization and industrialization. Moreover, it is reported that high demand of copper due to its economic importance will cause a significant increase copper concentration in the environment by 2050 [1]. Therefore, regulation to reduce the concentration of copper has been established to protect man and its environment. According to World Health Organization, the permissible limit value for Cu (II) in drinking water guidelines is 2.0 mg/L while United State of Environmental Protection Agency (USEPA) reported that the content of copper ions in industrial effluent should not exceed 1.3 mg/L [2, 3]. This paper presents a review of polymer modified adsorbent as well as emerging hybrid Nano-composites adsorbents developed via different techniques by several researcher with emphasis on optimum conditions (contact time, pH, temperature, initial concentration, etc.) for adsorption process as factor to enhance adsorption in the removal of Cu II ions. Their strength and future challenges discovered are discussed.

2. Occurrence of Copper in Environmental Media causing Pollution

The combination of both unique chemical and physical characteristics of copper pave ways for its production and usage in the environment. The physical properties of copper, such as malleability, ductility, high thermal conductivity and high electrical conductivity enable its application in electrical power, electronics, petrochemicals, transportation, machinery and metallurgy. Thus, global production of copper is certain and amounts to 12 million tons per year with exploitable reserves around 300 million ton [3]. Figure 1 present the global percentage usage of copper.

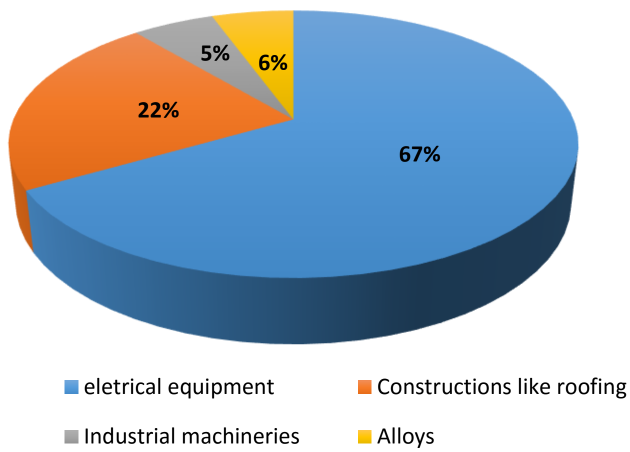


Figure 1. Global Percentage application of Copper

The human economic activities such as the production of copper, usage of copper and its compound result into different distribution of copper in various environmental media. Copper is a naturally occurring element that is present in the earth's crust, oceans, lakes and rivers [4]. Table 1 summarized the concentration of copper in various environmental media.

TABLE 1. Concentration of copper in different environmental media [5]

Environmental media		Concentration	unit
Soil	Total content in soil	2 -100	ug/g
	Soluble content in soil	< 1	ug/g
Atmosphere	Aerosol	1×10^{-7} - 3.82×10^{-4}	ug/l
Hydrosphere	Fresh water	8×10^{-5}	ug/l
	Sea water	0.01 2.8	ug/L
Biota	Plant	1- 110	ug/g
	Animal	2.4	ug/g

Natural sources of copper pollution

Natural sources of copper include wind-blown dust, volcanoes, decaying vegetation, forest fires, sea spray, urban run offs and aerosol particles and soil erosion [6]. Hazardous impacts release from volcanic eruptions into the environment, climate and health of exposed individuals has been reported.

Anthropogenic sources of copper pollution

The major anthropogenic sources of copper are Industrial, domestic and agricultural activities. High concentration of copper from industrial activities such as metal working, mining operation, refining process, batteries and electronic manufacturing, textile, nuclear power and painting are often deposited into their wastewater stream, although atmospheric deposition is also possible. For instance, Copper concentration in wastewater from metal finishing industry can be extremely high to concentration of about 10,000 mg/L [7]. The annual industrial discharges of copper into fresh water environments is estimated to be 1.4 x 10^{10} g/year, as well as the amounts of copper in industrial wastes and sewage sludge that have been dumped into the ocean as 1.7 x 10^{10} g/year globally [8].

Moreover, agricultural activities such as application of fertilizers on farmland, fungicidal spraying, and use of animal wastes lead to water pollution through copper deposits [9]. Another anthropogenic source of copper is leachate from municipal landfills and domestic wastewater. Copper concentration in leachates varies depending on the age of the landfill and the kind of waste that is deposited including the socioeconomic status of the people the landfill is serving. Copper concentrations in leachate from municipal landfills have been established to range from 0.005 to 1110 ppm [10].

3. Toxicity of Copper II Ion

Copper is micronutrient necessary for plant, animals and human at low concentration. Its unavailability could lead to serious limitation to the functioning of living cell, but if its level exceeds the regulated concentration in water, negative impact on aquatic and human health may be inevitable [8].

Excessive intake of copper can prompt oxidative stress and serious neurodegenerative diseases, such as Menkes disease, amyotrophic lateral sclerosis, Wilson disease, and Alzheimer's therefore causing long-term potential threat to living organisms and aquatic ecosystems [6]. Similarly, Copper ions affect the environment by inducing the damage of aquatic ecosystem, osmo-regulatory mechanism of the fresh water animals. Though, it is an essential element to plants, exceptionally high concentrations of copper may be toxic to plants by affecting mainly the growth of the roots [8].

As a result of this, several regulatory bodies (e.g. EPA) came up with standards for regulating copper discharge into the environment. Table 2: summarizes the maximum permissible concentration standard for copper

TABLE 2. Permissible Concentration standard for copper [11]

Element	Copper
PC in soil (mg/kg)	100
PC in water (mg/L)	0.1
PC in wastewater discharge into public sewage (mg/L)	1.0
PC in wastewater discharge into surface water (mg/L	0.1

4. Conventional Methods of Removing Cu II ions

Several techniques such as chemical precipitation, membrane filtration, electro deposition, ion exchange, adsorption, and membrane separation have been used to remove copper (II) ions from wastewater. Conversely, these technologies are either expensive or ineffective at low concentrations [1]. Table 3 summarizes the advantages and disadvantages of the physicochemical methods of removing copper ions from waste water. Adsorption technique is usually preferred over others because of its effectiveness, design, simplicity and low cost [1].

TABLE 3. Advantages and drawback of conventional methods for the removal of copper ions from waste water [12].

Methods	Advantages	Disadvantages
Ion exchange	Treatment even at low concentration	Expensive, Interference of composite ion and regeneration
Coagulation-flocculation and sedimentation (CFS)	Simplicity and low cost	Large volume of sludge with low density
Membrane Technology	High Efficiency and small foot print	High Energy, Concentrated Disposal and difficulty in maintenance
Electrolysis	Ease of operation, No requirement of chemical use	Expensive
Reverse Osmosis		Expensive
Chemical Precipitation	High percentage removal and simplicity of operation.	Bulky Hydroxide and Colloidal particles, Expensive
Membrane Filtration	High efficiency, low energy requirement, a small space due to high parking density low driving force	Expensive
Electrodialysis	Treatment of highly concentrated waste water	Membrane replacement and corrosion process.

5. Polymer based adsorbent

Polymer adsorbent has adjustable surface chemistry, vast surface area, pore size distribution, perfect mechanical strength and very easy to regenerate [13]. This make Polymer adsorbent a potential material for the sequestration of Cu (II) from water streams. Polymer adsorbent can be classified into two as bio polymer and synthetic polymer.

Biopolymer such as chitin, cellulose alginate, polysaccharides are from renewable resources, biodegradable, non-toxic and have excellent capability to associate with variety of molecules by physical and chemical interactions [14]. They are equally excellent adsorbent due to the presence of hydroxyl, amine, amide and carboxyl functional groups.

Synthetic polymer has been reported to perform excellently in the removal of copper ion in waste water when functionalized with amino or carboxylic group for specific interaction. The synthetic polymers enhanced the adsorption capacity with direct association to the chelating groups in the polymer structure [13]. Table 4 presents the optimized conditions of the use of polymer for Cu (II) sequestration.

7. Nano polymer composite based adsorbent

The emerging nano-composite materials have shown a high adsorption capacity, granulometric properties, chemical and thermal stabilities, reproducibility, with better selectivity for the copper ions removal compared to pure organic and inorganic materials [16].

Nano-composites adsorbent enhanced with polymer display some unique properties like easy preparation, cost-effectiveness, environmental stability, effective binding sites along the walls of the polymers with large surface area and pore volume thus, make it efficient toward the removal of copper ion from wastewater [20]. Table 5 summarized some polymer based nano composite with the factors affecting the removal.

TABLE 4. Summarized maximum adsorption conditions and their functional group for various natural and synthetically modified polymer

Adsorbent	Functional group	Adsorption (mg/g)	Time (min)	pH	Temp (K)	Initial Conc. (mg/l)	Reference
Amine functionalized silica magnetite	$-NH_2$	10.41	1440	5.5-6.5	298	150	[15]
Chitin biopolymer	$-NH_2$	13-15	480	5	298	100	[8]
Grafted cassava starch with 5-chloromethyl-8-hydroxyquinoline (CMQ).	-OH	25.75	90	6	-	50	[16]
Polyamine immobilized triethyleneamine	-C=O	1.47	-	5	-	-	[17]
Chitosan coated with Polyvinyl Chloride	$-NH_2$, -OH	87.9	210	5		100	[18]
(E)-2- [(1H-Imidazo lyl) methylene]-Hydrazinecarbo thioamide ligand (EIMH)	$--NH_2$, -OH	0.05	20	2-8	-		[19]

TABLE 5. Summarized maximum adsorption conditions and their functional group for various Nano-polymer adsorbent

Adsorbent	functional Group	Adsorption Capacity (mg/g)	Contact time (mins)	pH	Temp. (K)	Initial Conc. (mg/L)	Reference
CMC Magnetic Nanoparticles by co-precipitation Method	$-COO^-$, $-NH_2$	232	-	5.2	Room Temp.	-	[21]
CDs NPs by Chemical Precipitation Method	-	166.7	15	6	298k	100	[22]
rGO-PDTC/Fe3O4 by bromination, nucleophilic Substitution Polyethyelemide Method	N-CS_2, -C=S	3.84	45	6	-	-	[23]
SYONs by combustion Synthesis.	N-O, -C-H	772	720	6.5	-	400	[24]
Functional Eletcro spinning Polymer with IDA	-OH, C=O	80	293	3	-	50	[25]
MWCNT by RAFT method	$-CH_3$, -CH, -OH	89	7	-	-	-	[26]
Si02 – CMCS Ultrailtration/Si02-cyclam	-	68/61	-	-	-	-	[27]

8. Factors affecting the removal of copper ions

Reviewed literatures showed that adsorption capacity of polymer adsorbents depends on the experimental conditions like pH, initial concentration, contact time, temperature and nature of the material. Comparing Tables 4 and 5, the trend in the optimum conditions are the same. The trend in pH shows that Cu II ions optimum adsorption occurs mostly in circum-neutral medium. pH variation can determine the surface properties of an adsorbent and the ionization degree of an adsorptive molecule. For example; adsorption of copper unto synthesized poly[N-(4-[4-(aminophenyl) methylphenylmethacrylamide])] [28]. The trend in contact time revealed that adsorption is proportional to the amount of contact time. Therefore, it is evident that appreciable amount of contact time is required to attain equilibrium in polymer adsorbents [29]. The contact time in polymer adsorbent however is an extended one for adsorption process which may in turn require higher cost and investment. The contact time needed is greatly reduced in emerging nano-polymer composites due to large active sites are availability for the sorbate, thus the process proceeds very fast. However, as the active sites are filled up, the adsorption proceeds slowly until the equilibrium is reached [30]

The initial concentration in the removal of copper provides an important driving force to overcome all mass transfer resistances of the copper ion between the aqueous and solid phases [31]. Hence, a higher initial concentration of metal ion will enhance the adsorption amount of cu ions. From the tables, it indicates a low temperature favours removal of copper ion (i. e. increase in temperature decreases the adsorption capacity). This may be due to a tendency of copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution.

9. Conclusions

Increase in the adsorption capacity of nano-polymer composites for the removal of copper ion can be attributed to outstanding properties of nano-sized materials for development of novel functional materials which offer high specific surface area, volume ratio and increase surface active sites.

Thus, the use of nano-based adsorbent will influence high adsorption capacity in the purification of wastewater. This review established the circum-neutral pH and ambient temperature requirement for effective removal of Cu ions from solution. This conditions as well as nano-composite based adsorbents can therefore be recommended and used for development of effective bioprocesses in removal of this metal from aqueous solutions.

10. Future Researches

In spite of the significance of the adsorption condition contributing to the efficient removal of copper ions, some gaps still need to be filled to overcome some challenges in this line of research.

The use of polymer and Nano-polymer based composite adsorbent for large scale treatment should be investigated taking into consideration the effect of the adsorption conditions, in order to encourage patenting and commercialization.

Environmentally friendly methods (organic methods) should be researched into during the synthesis. Although some polymer is natural based, but their techniques of synthesis involved large use of chemicals. Moreover, environmentally friendly disposal of laden adsorbent should be of great concern.

References

1. Ekmekyapar F, Aslan A, Bayhan A, Çakıcı A, Biosorption of copper (II) by nonliving lichen biomass of Cladonia rangiformis Hoffm, Journal of Hazardous Material, 2006, vol. 137 p 293–98. doi: 10.1016/j.jhazmat.2006.02.003
2. Aydın H, Bulut Y and Yerlikaya C, Removal of Copper (II) from Aqueous Solution by Adsorption onto Low-Cost Adsorbents, Journal of Environmental Management, 2008, vol. 87, no. 1, p. 137-145.
3. Pugazhendhi A, Ranganathan K, Kaliannan T, Biosorptive removal of copper (II) by Bacillus cereus isolated from contaminated soil of electroplating industry in India, Water Air Soil Pollution, 2018 vol. 229 no. 76.

4. Georgopoulos, P.G., Tan, H.C., Wang, S.W., Vyas, V.M., Georgopoulos, I.G., Yang, Y.C., and Lioy, P.J. 2002. A Framework and Data Sources for the Assessment of Exposures to Copper: Technical Report Prepared for the International Copper Association (Draft) (available at http://www.CERM.org/copper).
5. Pais, I., and Benton Jones, J., Jr. The Handbook of Trace Elements. Boca Raton, (1997) FL: St. Lucie Press.
6. Georgopoulos A. R. G, Yonone-Lioy M. J, Opiekun R. E, Lioy P. J, Environmental copper: its dynamics and human exposure issues, Journal of Toxicology Environmental Health Critical Review, 2001, vol. 4, p. 341–394.
7. Aguado J, Arsuaga J. M, Arencibia A, Lindo M. and Gascon V, Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica, Journal of Hazardous Material, 2009, vol.163, p. 213–221.
8. Saravanan D, and Sudha P.N, Batch Adsorption Studies for the removal of copper from wastewater using Natural Biopolymer, International Journal of Chemical Technology research, 2014, Vol. 6, no. 7, p. 3496-3508.
9. Majumdar, S.S., Das, S.K., Saha, T., Panda, G.C., Bandyopadhyoy, T., Guha, A.K., Adsorption behaviour of copper ions on Mucor rouxii biomass through microscopic and FTIR analysis. Colloids Surfaces Biointerfaces, 2008, vol. 63, no. 138, p.145.
10. Tanner M. S, Leone A, and Mercer J. B. F, Copper Transport and its Disorders, Plenum Press, New York, NY, Eds, 1999, p. 127–13.
11. Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from Contaminated water: a review. J. Hazard. Mater. B97, 219–243.
12. Arbabi M, Golshani N, Removal of copper ions Cu (II) from industrial wastewater, International Journal of Epidemiology Research, 2016, vol. 3, no.3, p. 283–293.
13. Mahmoodi N. M, Najafi F, and Neshat A, Poly (amidoamine-co-acrylic acid) copolymer: synthesis, characterization and dye removal ability, Industrial Crops Production, 2013, vol. 42, p. 119–125.
14. Qu X, Alvarez P. J. J, and Li Q, Applications of nanotechnology in water and wastewater treatment. Water Research, 2013, vol. 47, no. 12, p. 3931–3946.
15. Lin Y, Chen H, Lin K, Chen B, and Chiou C, Application of Magnetic particles modified with amino group to remove copper ions from aqueous solution, Journal of Environmental Science, 2011, vol. 23, no. 1, p. 44-50
16. Sharma G, Pathania D, and Naushad M, Preparation, characterization, and ion exchange Behavior of nanocomposite polyaniline zirconium (IV) selenotungstophosphate for the separation of toxic metal ions, Ionics, 2015, vol. 21, p. 1045-1055.
17. Liu C, Liang X, Liu J, and Yuan W, Desorption of copper ions from the polyamine Functionalized adsorbents: Behaviour and Mechanism. Adsorption Science and Technology, 2016, vol. 34, no. 7- 8, p. 455-468.
18. Popuri S. R, Vijaya Y, Boddu V. M, Abburi K, Adsorptive removal of copper and Nickel ions from water using chitosan coated PVC beads. Bio resource Technology, 2009, vol. 100, no. 1, p. 194-199.
19. Houari B, Louhibi S, Tizaoui K, Boukli-hacene L, Benguella B, Roisnel T, and Dorcet V, New synthetic material removing heavy metals from aqueous solution and waste water. Arabian Journal of Chemistry, 2016.
20. Ansari R. and Delavar A. F, Application of poly 3-methylthiophene for removal of silver ion from aqueous solutions, Journal of Applied Polymer Science, 2009, vol. 113, p. 2293–2300.
21. Charpentier T. V. J, Neville A, Lanigan J.L., Richard B, Smith M. J, Richardson T, Preparation of Magnetic carboxylmethyl chitosan Nanoparticle for adsorption of heavy metals ions 2016
22. Golkhah S, Mousawi Z. H., ShirKhanloo H, Khaligh A, Removal of Pb (II) and Cu (II) ions from aqueous solutions by cadmium sulphide Nanoparticles, International Journal of Nano science and Nano technology, 2016, vol. 13, no. 2, p. 105-117.
23. Fu W, Huang Z, Magnetic dithiocarbamate functionalized reduced grapheme oxide for the removal of cu (II), cd (II) Pb (II) and Hg (II) ions from aqueous solution: synthesis, adsorption and regeneration chemosphere, 2018, vol. 209 p. 449-456.
24. Pradhan S. K, Panwar J, Gupta S, enhanced heavy metal removal using silver –yttrium oxide nanoparticles as novel adsorbent system, Journal of Environmental Chemical Engineering, 2017, vol. 5, no. 6, p 5801-5814.
25. Kamaruzaman S. Aris N. I. F, Yahaya N., Hong S. L., Rasak M. R, Removal of Cu (II) and Cd(II) ions from environmental water samples by using cellose Acetate Membrane. Journal of Environmental Analytical Chemistry 2017, Vol. 4, No. 4
26. Hosseinzadeh H, Pashaei S, Hosseinzadeh S, Khodaparast Z, Preparation of novel multi walled carbon-nano tubes nanocompositeAdsorbent via RAFT technique for the adsorption of toxic copper ion. Science of the Total Environment, 2018, Vol. 640– 641, p. 303-314.

27. Mokhter M. A, Magnenet C, Lakard S, Eurard M, Aden M, Clement S, Mehdia A, Larkard B, Use of Modified colloids and membranes to remove metals ions from contaminated solution, Colloids and interfaces, 2018, vol. 2, no. 19, p.
28. KumarKushwaha A., Neha Gupta N., Chattopadhyaya M. C.,Dynamics of adsorption of Ni(II), Co(II) and Cu(II) from aqueous solution onto newly synthesized poly[N-(4-[4-(aminophenyl)methylphenylmethacrylamide])] Arabian Journal of Chemistry (2017) Volume 10, 2, Pages 1645-S1653
29. Thakur L. S, and Parmar M, Adsorption of heavy metal (Cu2+, Ni2+ and Zn2+) from synthetic waste water by tea waste adsorbent International, Journal of Chemical and Physical Sciences, 2013, vol. 2, no. 6, p6-19.
30. Zhao, D., Gao, X., Wu, C., Xie, R., Feng, S., Chen, C., 2016. Facile preparation of Amino functionalized graphene oxide decorated with Fe3O4 nanoparticles for the adsorption of Cr(VI). Appl. Surf. Sci. 384, 1-9.
31. Ahmad, A. Rafatullah, M., Sulaiman, O., Ibrahim, M. H., Hashim R., Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. Journal of Hazardous. Material, 170 (2009), pp. 357-365.

An investigation of poaching of endangered traditional medicinal plant, Brackenridgea zanguebarica in Brackenridgea Nature Reserve

T.M Ndou[1]* and M.J Mokgoebo[2]

Department of Geography and Geo-Information Sciences, University of Venda, South Africa.
*Email of corresponding author: tshianeomellda@gmail.com

Abstract

Plant poaching is referred to the illegal harvest of plants species and this has led to the loss plant population. The *Brackenridgea Zanguebarica* plant is being poached for its medicinal use. Street vendors and herbalist poach and sell the plant to support their families. The main aim of the study is to assess the current conservational strategies and the impact of poaching on the *B. zanguebarica* plant species. Snow ball sampling was used to locate 15 street vendors and 10 traditional healers, whereas Random walk sampling was used to make 10 quadrants inside the reserve. To analyze the data SPSS IBM Statistical software and descriptive analysis was used. About 111 trees were poached. Statistical data from the reserve shows that poaching is directly proportional to years. It was found that 73% street vendors trade in *B. zanguebarica* and 27% of the traditional healer do not trade it. Furthermore, 55% trade the bark of *B. zanguebarica*, 18% in roots and 27% in both the bark and roots. From the interviews conducted 90% of traditional prefer traditional/indigenous conservational strategies to protect and conserve traditional medicinal plants species. It can be concluded that poaching is accelerating, and server measures need to be taken to protect and conserve the endangered medicinal plants species.

Key words: *Brackenridgea zanguebarica*, Poaching, Conservation, Nature Reserve, Street vendors.

1. Introduction

Brackenridgea zanguebarica Oliv is a traditional medicinal plant which is commonly known as the Yellow peeling plane and locally known as Mutavhatsindi. It is a small tree that grows up to 5 m high and 3 m wide. *B. zanguebarica* has a wide range of biological activities against eukaryotic cells, bacteria and viruses Moller et al. [1]. The species has a restricted distribution in South Africa and has been classified as Critically Endangered (CR) by the IUCN Red List categories in South Africa Raimondo et al. [2]. Furthermore, the population distribution of *B. zanguebarica* is found and only restricted in Mafukani village inside a reserve called Brackenridgea nature reserve. *B. zanguebarica* is the most sought after traditional medicinal plant in the Vhembe District Municipality. It is a single stemmed tree with a rough bark that has yellow pigment. The bark of the tree becomes yellow if scratched or peeled. The leaves are elliptic to obviate, approximately 40-50 mm long, glossy dark green and hairless. According to Netshiungani and Van Wyk [3], to the Vhavenda people *B. zanguebarica* is also a plant of great medicinal importance. Due to its demand in the market place, B. zanguebarica is being poached for its medicinal value. There has been high rate of poaching activities inside the reserve and this has led to the reduction of its population [4,5]. It can be added that *B. zangueabarica* will face extinction if severe measures are not taken to protect and preserve the species.

It is believed that Mutavhatsindi can be used to protect people against witchcraft, protect the whole homestead from evil people, perform magical activities, treat wounds, worms, amenorrhea, swollen ankles and aching hands and discourage opponents in sporting events such as soccer [6].

2. Materials and Methods

Sampling methods

Sampling is a method that deals with the selection of a subset of individuals from within a statistical population to estimate characteristics of the whole population [7]. For the field survey a random walk sampling procedure was used. Random walk sampling involves a researcher walking in a field of site to gather data. The researcher randomly selected an area inside the reserve were the population of the *B. zanguebarica* is dense and where most poaching activities are occurring. Snow ball sampling method was used to selected street vendors and traditional healers that have more knowledge about the *B. zanguebarica* plant.

Field survey

The Brackenridgea nature reserve is a 110-ha reserve. Site measurements were used to create a 20 × 20m (400m^2) quadrant using a tape measure. Random walk sampling was used to sample quadrat with higher plants densities. Random walk sampling was used to locate quadrants inside the reserve where poaching activities where taking place. Ten quadrats were made and *B. zanguebarica* trees in each quadrant were counted and analyzed based on the total number of species which were poached and non-poached.

Interviews

Interviewed participants were selected using Snowball sampling (Chain referral) based on their knowledge about B. *zanguebarica* plant species and work experience. Snow ball sampling is a non-probability sampling method which is used when characteristics to be possessed by samples are rare and difficult to find, it involves primary data sources nominating another primary data source to be used in the research. Interview was conducted with eight workers inside the nature reserve because the reserve only consists of eight workers. Four of the respondents were interviewed using a cell phone due to their un-availability in the reserve during the scheduled day that the researcher was collecting data. The interview with the workers was very essential because they have more information on the poaching activities occurring within the reserve.

Questionnaires

Open-ended questionnaires were distributed to the traditional healers, herbalist and street vendors using Snowball sampling technique. A total number of eight traditional healers and fifteen street vendors were sampled. The Snowball technique was used because this study is rare and hard to locate the participants. Questionnaires which contained eight questions were distributed to the traditional healers and questionnaires containing ten questions were distributed to street vendors. For this study, the questions were translated from English to Tshivenda by the researcher. The researcher also completing the questionnaires for the participants.

Primary data

In this research primary data was collected using questionnaires, interviews and field survey and observation. Open ended questionnaire was used to collect data from street vendors and traditional healers.

Secondary data

Secondary data was obtained from journals, books and internet. The researcher used information from the internet to find out more about poaching of traditional medicinal plants. Red list data was used to find out more about the *B. zanguebarica* plant species as an endangered plant [8].

Data analysis

Quantitative data from the questionnaire was analyzed using SPSS Microsoft excel where it was used to draw tables and graphs. Furthermore, SPSS Microsoft excel was used to analyze the data from the field to get the percentage of trees which were being poached, regenerating, dead and the ones which were not poached. Data from the interview with the workers from the reserve was analyzed using interpretive analysis

3. Results and discussion

Field survey data

TABLE 1. Total number of poached and non-poached trees

Quadrant no.	Total no. of species	No. of Poached plants	Non-poached plants	Item used for poaching
1	9	9	0	Blade
2	8	8	0	Blade and saw
3	20	14	6	Blade and axe
4	8	4	4	Blade and knife
5	16	15	1	Blade and knife
6	18	13	5	Blade saw and
7	24	18	6	Blade saw and
8	15	9	6	Blade saw and
9	11	10	1	Blade and knife
10	17	11	6	Blade saw and
Total	**146**	**111**	**35**	

Thus, data shows the number of poached *Brackenridgea zanguebarica* trees inside the reserve. From the 10 quadrants that were made a total number of 146 trees of *B. zanguebarica* plant species were found and identified. Out of the 146 trees 111 trees were poached and 35 were non-poached. This makes 76% of poached trees and 23% non-poached trees. Different items or tools were used to poach the trees and each tool leaves a trace behind which can be used to identify the method which was used, For instance, after poaching the *Brackenridgea zanguebarica* plant species a rough surface shows that an axe was used, a smooth surface shows that a Saw was used meanwhile a yellow pigment skin shows that a blade or a knife was used. According to Tshisikhawe et al. [5] poaching the traditional medicinal plants has negative impacts on the species because the population might decrease, and it can lead to extinction. Furthermore, poaching activities also disrupt the environment as well as the ecosystem.

TABLE 2. Data from the reserve

Years	No. of poached trees	Percentage per annum (%)
2012	96	8
2013	204	17
2014	264	22
2015	298	24.8
2016	456	38
2017	766	63.8

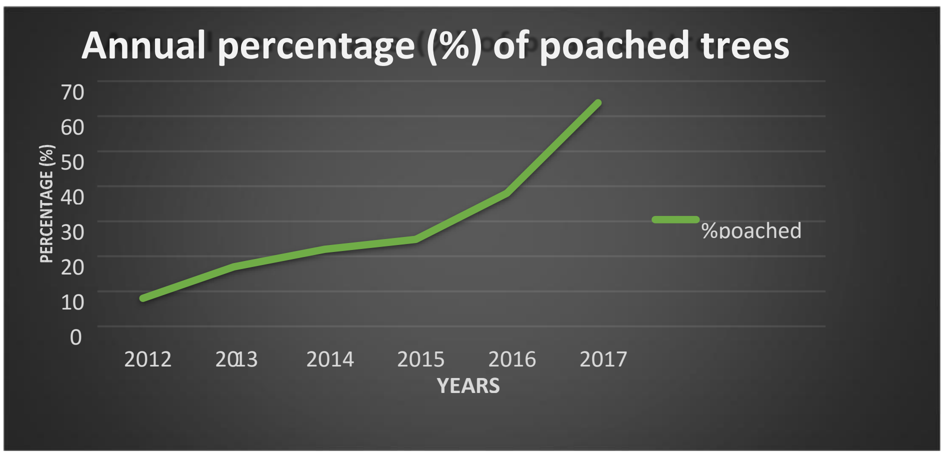


Figure 1. Percentage of poached trees

It can be said that poaching is inversely proportional to the increase in number of years. This trend shows that overtime the *B. zanguebarica* plant species will extinct if serious conservational measures are not put in place. Traditional healers believe that if a plant is initially utilized for its medicinal bark such can hardly be substituted with leaves since according to them, they may not have the same strength [5].

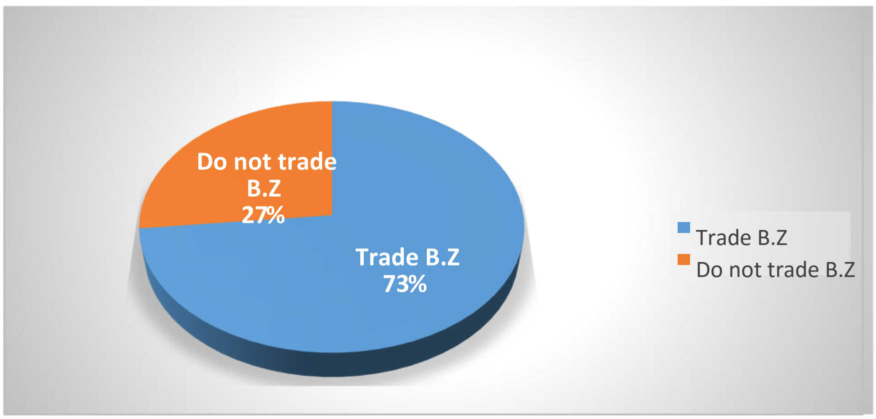
Evidence of poaching

Figure 2. Evidence of poaching

Yellow pigment shows that the tree was poached using a blade where the poacher extracts the buds of the tree. A rough surface shows that an axe was used to poach the tree. After poaching some trees regenerate, while others do no regenerate. The regenerating capacity of the tree depends on the mode and item of poaching that was used. It was found that trees which were poached using an axe do not regenerate. The regenerating capacity of the *B. zanguebarica* is difficult and in most cases the tree does not regenerate rather a new tree protrude next to the old poached tree.

Questionnaire data

Street vendor data



Traded parts

Medicinal plants are traded in a variety of forms, ranging from raw material (leaves, roots, and buds/bark) to unprocessed fragmented material (chips and slices) [5]. Moreover, the *Brackenridgea zanguebarica* can be sold for R300 per kilogram (kg) and sometimes the prices vary depending on the street vendor Tshisikhawe [6]. The investigated street vendors indicated that they only trade the roots and buds of the *B. zanguebarica* plant species thus, 18% trade the roots, 55% buds/bark of the tree, 27% trade both the roots and the buds. This confirms why high number of trees are poached using axes and blades.

TABLE 3. Traditional healer Demography

Gender	Total No.	No formal education	Only primary education	Only secondary education	Higher education
Male	**8**	3 (37%)	3 (37%)	2 (26%)	0 (0%)
Female	**2**	1 (50%)	1 (50%)	0	0 (0%)

Out of all the traditional healers Ten who were interviewed, all of them prefer traditional conservation strategies and myths as ways of conserving the traditional plants. No traditional healer harvest or extracts the traditional medicinal plants however they have people who harvest the plants for them and they are called *Tshigomamutanda*. These are unemployed boys who dropout from school or a family member who has acquired the knowledge from their parents or relatives who are traditional healers. It is a taboo for traditional healers to extract the traditional medicinal plants by themselves. The boys (*Tshigomamutanda*) get instruction from the traditional healers on how to extract or harvest the medicinal plants [5].

Conclusion: This study has shown that there is high rate of poaching activities occurring within the nature reserve and it has also revealed that serve measures needs to be taken to protect the *Brackenridgea. zanguebarica* species.

Acknowledgement: Sincere gratitude to my Supervisor Mr. Mokgoebo for all the assistance and NRF for funding this project.

References

1. Moller, M, Suschke, U, Nolkemper, S., Schneele, J., Distl, M., Sporer, F., Reichling J. and Wink, M. 2006. Antibacterial, antiviral, antiproliferative and apoptosis-inducing properties of Brackenridgea zanguebarica (Ochnaceae). Journal of Pharmacy and Pharmacology 58: 1131-1138.
2. Raimondo, D., Staden, L.V., Foden, W., Victor, J.E., Helme, N.A., Turner, R.C., Kamundi, D.A. and Manyama, P.A., 2009. Red list of South African plants 2009. South African National Biodiversity Institute.
3. Netshiungani, E.N. & van Wyk, A.E. 1980. Mutavhatsindi: Mysterious plant from Venda. Veld & Flora 66:87-90
4. SANBI. 2006. A South African response to the Global Strategy for Plant Conservation. SANBI Biodiversity Series 1. South African National Biodiversity Institute, Pretoria.
5. Tshisikhawe, M.P., van Rooyen, M.W. and Gaugris, J.Y. (2013). Is the Present Brackenridgea Nature Reserve Large Enough to Ensure the Survival of Brackenridgea zanguebarica Oliv? Koedoe, 55(1): 1-5.
6. Tshikhawe, M.P. 2002. Trade of indigenous medicinal plants in the Northern Province, Venda region: their ethnobotanical importance and sustainable use. M.Sc. Thesis. University of Venda for Science and Technology. Thohoyandou, RSA.
7. Chambers, R L, and Skinner, C J (editors) (2003), *Analysis of Survey Data*, Wiley, ISBN 0-471-89987-9.
8. Van Wyk, A.E & Van Wyk, P.1997. *Field guide to trees of southern Africa*. Struik, Cape Town.

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

The use of macroinvertebrates population to assess the river health status of Madanzhe River, Limpopo Province, South Africa

P Dlamini[1]*, Mokgoebo MJ[2]

[1]Department of Geography and Geo-Information Sciences, University of Venda, South Africa
*Email of corresponding author: pre0797916525@gmail.com

Abstract
The aim of this study is to use the macroinvertebrates population in order to assess the health status of Madanzhe River. The research objectives are, to identify the type of macroinvertebrates found in Madanzhe River, to measure the physio-chemical properties of Madanzhe River, and to examine the relationship between macroinvertebrates abundance found and physiochemical properties of water measured in madanzhe River. A field survey was implemented to find or to identify the types of macroinvertebrates found in the river and to determine the factors that influence the abundance of macroinvertebrates. The method used for collecting data was the D-nets which was used for sampling of macroinvertebrates and the measurement of water physiochemical properties using their different kinds of parameters. And lastly the use of ANOVA, to examine the means of sampling sites if differed markedly and to show the differences between the means of the macroinvertebrates from different sampling areas. Based on the results found the study showed that madanzhe river is polluted regarding to the macroinvertebrates found and the relationship between the macroinvertebrates and the water physiochemical properties

Keywords: macroinvertebrates, physiochemical properties

1. Introduction

Water is the basic resource upon which society relies for the quality of its life, including its health and recreation [1]. It is also the primary source upon which social and economic developments are based and sustained. Aquatic ecosystems must therefore be effectively protected and managed to ensure that they retain their inherit vitality and remain fit for domestic, industrial, agricultural and recreational uses for present and future generations [2]. Water pollution caused by sewage and agriculture, and occasionally pollution events from industries have become a significant stress on aquatic macroinvertebrates. Macroinvertebrates play an important role in the aquatic biological system to balance the natural flow of energy and nutrients. Therefore, the condition of benthic macroinvertebrates community reflects the stability and diversity of the large aquatic food web [3].

Macroinvertebrates are valuable indicators of biological monitoring of an aquatic system, because of their visibility to the naked eye, ease of identification, rapid lifecycle and are relatively easy to sample [4; 3]. Each macroinvertebrates species has specific sensitivity of tolerance towards pollutants. Macroinvertebrates are appropriate bio-indicators of ecosystem health, and their richness and diversity can be used to predict or estimate a system's ecological integrity [5].

Pollution affects the biodiversity of the aquatic community and the species composition changes from natural species to tolerant species. Macroinvertebrates are often the most abundant and diverse group of animals found in freshwater, and they include insects, mussels, snails and all crustaceans [6]. Macroinvertebrates are a primary food base for many fishes, birds, amphibians, reptiles and mammals such as bats and raccoons [7]. Macroinvertebrates are part of all aquatic food webs, representing every major feeding type, including predators, scrapers, collectors, shredders and filterers [6]

Changes in water quantity, water quality and the physical structure of the channel have almost without fail led to changes in the composition of the biotic community inhabiting the river, usually with a reduction in the biological diversity of the aquatic ecosystem [8]. Benthic macroinvertebrate communities typically consist of a variety of species that exhibit a wide range of feeding modes, stress tolerances and abilities to withstand disturbances [10; 9] in such a way that species composition and abundance are related to major environmental factors. Moreover, human induced changes on benthic communities include shifts in abundance of stress tolerant, opportunistic and sensitive species [4], and thus these species can be used as bio indicators. Macroinvertebrates are used for bioassessment because they are relatively easily sampled and are a very biodiverse group of species inhabiting waters that is contaminated to a different extent from clean to highly polluted [11].

2. Materials and methods

Field observation

Field observation was done prior to the collection of primary data. This was done by going to the field in Madanzhe River to examine the characteristics of the area and to check were samples can be taken. And to check the substrates of the river of in which macroinvertebrates are more likely to be found. Ten sampling sites were selected which differed from river characteristics such as riffles, pools and runs.

Physiochemical Monitoring

The geology, soils, and vegetation of a region influence water chemistry. Water chemistry data on the nutrients and major ions in a watershed thus provide a baseline for characterizing current conditions and assessing future changes. The physiochemical monitoring was done at Madanzhe river in ten sampling sites which differed according to river characteristics which are runs, pools, riffles, aquatic and marginal vegetation.

Determination of temperature and Dissolved oxygen

Temperature was measured at noon in order to standardize water temperature measurements immediately after sampling using a 2A JENWAY 970 Dissolved Oxygen meter which measures both temperature and dissolved oxygen at the same time. While oxygen was measured in the morning between 5 and 6a.m.in the summer season, this was done in order to obtain the correct oxygen concentration as it decreases as temperature increase.

This was done by inserting the meter on the different sampling sites and readings were made to evaluate the levels of temperature on the sampling points. The meter was placed inside the water for 2 minutes after the reading stabilized the data was then recorded in a data sheet. The Stream temperature was measured in degrees Celsius (°C). Dissolved oxygen was measured as percentage (%) of air saturation. The meter was calibrated according to manufacturer's guidelines prior use by Department of Water Affairs and Tourism [12].

Determination of Conductivity

Conductivity was measured in the field at midday together with temperature and pH, and it was measured in µm.cm. it was measured in different sampling points which had runs, pools and riffles. According to, Kney and Brandes, [13] if conductivity differs from one point to another within the stream or river of a uniform geology, then the possibility is that anthropogenic ionic pollutants will have altered it.

Determination of pH

pH was measured at midday around 13H00 to 15H00 PM using pH meter to avoid dissimilarity of results this was done by inserting in a standard pH meter on collected water in the different points and the readings were noted down and used to assess the levels of pH on the different sampling points. A scale of 1 to 14 was used to precise pH values for all collected samples where 7 represented neutral and any value less than seven was considered acidic and values above 7 were considered alkaline.

Determination of Nitrates

The water samples were collected in 2 litres for nitrates determination and analysis samples were immediately transported to the laboratory for further analysis using the Metrohom 850 Chromatography that was equipped with two columns namely Metrosep A Supp 5-100/4.0 with flow rate of 0.7 mL/min and Metrosep C4-250/4.0 with low rates were and 0.9 mL/min for anion and cation, respectively. For the analysis of anions carbonate eluent was used and for the cations, dipiclonic acid eluent was used. Prior to analysis, the column was equilibrated for 60 minutes.

Macroinvertebrates sampling procedure

The macroinvertebrates sampling was carried out from early October to late November in 2017 because it is the good season for collecting samples since it is summer and macroinvertebrates flourish and breed during the rainy season, as their short lifespan prescribes reproduction 'maxima' during the period, thereby facilitating the greatest chances for survival [14]. Some of the organisms (e.g. insects) exhibit part of their life cycle, such as cocoon instars, eggs or juveniles, only during the rainy period. The D-nets method was used for collecting the different types of macroinvertebrates. A small sieve net was used. This was done by scooping the sieve net into appropriate sampling habitats in the water. In each sampling point the scooping was done five times. After couple of minutes of scooping in each sampling point the sieve net was rinse into the water to remove the mud that had attached on it since some of the sites were macroinvertebrates collected contained a lot of mud. The jabs were typically combined for the site and were sorted on site

The sampling points were divided according to the stream length, the length of the river is 300m and the points were divided in an interval of 30m. A total of 81 samples were collected during daytime and some in the morning before sunrise because different macroinvertebrates respond differently in river temperature some prefer lower temperature, and some prefer higher temperature.

At each sampling points scooping was done for a sampling duration of five minutes. Within this time frame, stones and boulders in currents and at the bottom of the river channel were kicked to loosen macroinvertebrates from them. And some were collected in the runs, riffles and aquatic vegetation. The samples of macroinvertebrates collected were then spread in a tray to be separated from mud, small vegetation and small rocks.

Macroinvertebrates were later transferred in a consol glass jar of honey 350ml with ethyl alcohol so that the macroinvertebrates can be able to freeze in order to provide its good shape in order to be able to identify them. After freezing the macroinvertebrates were sorted and identified according to their family level in the laboratory using the Aquatic Invertebrates of South African Rivers field guide developed by Gerber and Gabriel [15]

3. Results and discussion

Macroinvertebrates gathered

Six different types of macroinvertebrates were gathered in different points and which differ according to their tolerance of pollution and with different numbers. The macroinvertebrates were collected in different types of biotopes which are riffles, runs, aquatic vegetation, pools and algae zone. Table 1 and Figure 1 shows the types of macroinvertebrates that were collected from the Madanzhe River.

Figure 3.1 shows that there were no macroinvertebrates found which are intolerant of pollution in Madanzhe River during sampling period however, the macroinvertebrates found were the ones which are moderately tolerant of pollution such as Elmidae, Aeshnidae, chironomidae, physidae, oligochaeta, and coenagrionidae.

The observed data showed that coenagrionidae and oligochaeta are more commonly along the river and eashnidae which moderately tolerant to pollution with the average of 23%, 25% and 19% respectively. The macroinvertebrates found with the highest abundance was oligochaeta and coenagrionidae which are both highly tolerant of pollution the abundance of this macroinvertebrates shows that madanzhe river is highly polluted since none of the macroinvertebrates which are intolerant of pollution were found therefore this tells us that madanzhe river needs to be assessed frequently to ensure that it is in good state and however the availability of elmidae and aeshnidae may act as an early warning that the river needs to be assessed since they are moderately tolerant of pollution.

TABLE 1. Macroinvertebrates gathered and their sensitivity to pollution

Organism	Order	Family	Pollution tolerance level	Abundance data	Percentage %
Riffle beetle adult	Coleptera	Elmidae	9	16	19.75
Dragonfly nymphy	Odonata	Aeshnidae	8	14	17.28
Midge larvae	Diptera	Chironomidae	2	10	12.35
Left handed snail	Mollusca	Physidae	3	2	2.47
Aquatic worms	Annelid	Oligochaeta	1	19	23.46
Blood worms midge	Odonata	Coenagrionade	4	20	24.69

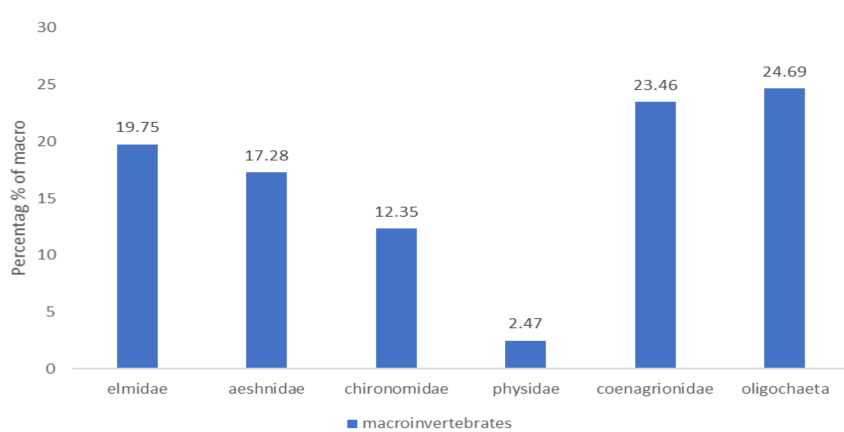


Figure 1. Percentage of macroinvertebrate abundance (Field data, 2017)

Macroinvertebrates diversity along Madanzhe River

Table 2 shows the macroinvertebrates according to their taxonomic groups. The results of this study found different types of macroinvertebrates in Madanzhe River in different sampling points. The macroinvertebrates include Elmidae, Aeshnidae, Chironomidae, Physidae, Oligochaete and Coenagrionidae. Most of the macroinvertebrates found are pollution tolerant this means that the macroinvertebrates they more likely to survive in poor water quality, therefore it shows that Madanzhe River is polluted due to farming activities, sewage leakage and different anthropogenic activities along the river.

Table 2 presents the macroinvertebrates richness for all the sites sampled from October to November. From the samples collected from madanzhe river, sample 1 showed that aeshnidae was found 22 percent of a total sample, chironomidae was found to be 30 percent; however, physidae, oligochaete, coenagrionidae and, elmidae were found to be 50%, 16%, 30%, and 0% respectively. Sample 1 and sample 4 where characterized by areas with high vegetation and riffles, this influenced the number of macroinvertebrates found in madanzhe river. Krull [16], showed that high vegetation support larger amount of macroinvertebrates population. This study agrees with Krull [16], which shows that high vegetation area in Madanzhe River supported high number of macroinvertebrates.

Also, since majority of macroinvertebrates are more likely to be found in riffles because the flow of water over the riffles provides plentiful oxygen and food particles. Therefore, this resulted in sample 1 and sample 4 having a lot of macroinvertebrates. The overall average of macroinvertebrates population showed that coenagrionidae was found the most with an average of approximately 25 percent. From the result oligochaete, elmidae, aeshnidae, chironomidae and physidae were found to be approximately 23%, 20%, 17%, 12%, and 2% respectively.

TABLE 2. Macroinvertebrate composition per sampling site.

Sites	**Macroinvertebrates according to groups**						
Order	**Coleptera**	**Odonata**	**Diptera**	**Gastropoda**	**Annelid**	**Odonata**	
Family	**Elmidae (%)**	**Aeshnidae (%)**	**Chironomidae (%)**	**Physidae (%)**	**Oligochaeta (%)**	**Coenagrionidae (%)**	**Total**
S1	0 (0)	3 (22)	3 (30)	1 (50)	3 (16)	6 (30)	16(20)
S2	0 (0)	0 (0)	1 (10)	0 (0)	6 (31)	3 (15)	10(12)
S3	2 (12.5)	2 (14)	0 (0)	0 (0)	3 (16)	0 (0)	7(9)
S4	3 (19)	5 (36)	1 (10)	1 (50)	0 (0)	4 (20)	14(17)
S5	1 (6)	1 (7)	0 (0)	0 (0)	3 (16)	2 (10)	7(9)
S6	4 (25)	0 (0)	1 (10)	0 (0)	3 (16)	1 (5)	9(11)
S7	0 (0)	2 (14)	0 (0)	0 (0)	0 (0)	3 (15)	5(6)
S8	1 (6)	1 (7)	0 (0)	0 (0)	0 (0)	1 (5)	3(4)
S9	2 (12.5)	0 (0)	3 (30)	0 (0)	0 (0)	0 (0)	5(6)
S10	3 (19)	0 (0)	1 (10)	0 (0)	1 (5)	0 (0)	5(6)
Average	**1.6 (19.75)**	**1.4 (17.28)**	**1 (12.35)**	**0.2 (2.47)**	**1.9 (23.46)**	**2 (24.69)**	
Total	**16 (100)**	**14 (100)**	10 **(100)**	**2 (100)**	**19 (100)**	20 (**100**)	**(81) 100)**

4. Conclusion

Based on the results of the study it was then concluded that the macroinvertebrates found in Madanzhe River showed the level of pollution impact on the river health status. The results indicated that richness along Madanzhe River was affected by the discharge of sewage and little excess of fertilizers from the agricultural activities situated next to the river. A group of taxa sampled during the period of the study indicated that most of the taxa found were highly tolerant of pollution, since 51 can be regarded highly tolerant to inorganic pollution, and 30 moderately tolerant to inorganic pollution were sampled. None were found which belonged to sensitive family which is highly intolerant of pollution during sampling period. The taxa of moderately tolerant organisms could act as indicators in the event of pollutant entering the system and they can therefore be seen as early warning.

Acknowledgements: I appreciate the national research funding (NRF) for funding this research and also my supervisor M.J. Mokgoebo for his guidance through the fulfilment of this research.

References

1. Westman, W.E., 1978. Measuring the inertia and resilience of ecosystems. Bioscience 28:705-710.
2. Roux, D.J., 1999. Design of a national programme for monitoring and assessing the health of aquatic ecosystems, with specific reference to the South African river health programme. *Biomonitoring of polluted water: reviews on actual topics. Trans Tech, Uetikon-Zurich, Switzerland*, pp.13-32.
3. Lai, J. 2013. Impact of anthropogenic pollution on selected biota in Loskop Dam. University of Pretoria.
4. Pinedo, S., Jordana, E. and Ballesteros, E., 2015. A critical analysis on the response of macroinvertebrate communities along disturbance gradients: description of MEDOCC (MEDiterranean OCCidental) index. *Marine Ecology*, *36*(2), 141-154.
5. Dlamini, V., 2009. Impact of agricultural activities on the diversity of aquatic macroinvertebrates as an indicator of ecosystem health along Lower Komati River, Swaziland. Unpublished Master of Science Thesis. Department of Civil Engineering, Faculty of Engineering. University of Zimbabwe
6. Baldwin, B.S., Carpenter, M., Rury, K. and Woodward, E., 2012. Low dissolved ions may limit secondary invasion of inland waters by exotic round gobies and dreissenid mussels in North America. *Biological Invasions*, *14*(6), 1157-1175.
7. Chapman, D., 1996. Water quality assessments. A guide to the use of biota, sediment sand water in environmental monitoring. 2nd edition. Chapman and Hall. University Press. Great Britian.
8. Boon P.J., 1992. Essential elements in the case for river conservation. River Conservation and Management (Eds P.J. Boon, P. Calow and G.E. Petts), pp. 11-33.
9. Ashton P.J. 2002. Avoiding conflicts over Africa's water resources. Ambio 31: 236-242.
10. Resh, V.H. and Rosenberg, D.M., 2010. Recent trends in life-history research on benthic macroinvertebrates. *Journal of the North American Benthological Society*, *29*(1), pp.207-219.
11. Cheimonopoulou, M.T., Bobori, D.C., Theocharopoulos, I. and Lazaridou, M., 2011. Assessing ecological water quality with macroinvertebrates and fish: a case study from a small Mediterranean river. *Environmental management*, *47*(2), pp.279-290.
12. DWAF (Department of Water Affairs and Forestry., 1996. South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems, DWAF, Pretoria.
13. Kney, A.D. and Brandes, D., 2007. A graphical screening method for assessing stream water quality using specific conductivity and alkalinity data. *Journal of environmental management*, *82*(4), 519-528.
14. Regina, N.M.M., 2002. Biological monitoring and pollution assessment of the Mukuvisi River, Harare, Zimbabwe.
15. Gerber A. & Gabriel M.J.M., 2002. Aquatic Invertebrates of South African Rivers. Field Guide. Institute for Water Quality Studies, Pretoria
16. Krull, J.N., 1970. Aquatic plant-macroinvertebrate associations and waterfowl. *The Journal of Wildlife Management*, 707-718.

Towards indigenous ecological water bio-disinfection: ethanolic extract from *T. glaucescens, Z. zanthoxyloides and G. latifolium* as effective biocide against water microbial pollutants

AO Adeeyo[1]*, JO Odiyo[2], E.M Enitan[2], KA Odelade[3] and JN Edokpayi[2]

[1]Department of Ecology and Resource Management, University of Venda, South Africa.
[2]Hydrology and Water Resources, University of Venda, South Africa
[3] Department of Biological Sciences, Northwest University, South Africa.
*Email of corresponding author: firstrebby@gmail.com

Abstract
Water and sanitation facilities in sub-Saharan Africa and Africa in general are appalling and for the most part absent. Progress continues with respect to the development of plant materials as potent adsorbents, disinfectants, coagulants, flocculants, wetland species and lots more as substitutes for the dangerous chemical disinfectants. This research presents the potential of phyto-active components of three native African plants as effective biocides against water microbial contaminants. Dry powder of *Terminalia glaucescens, Zanthoxylum zanthoxyloides and Gongronema latifolium* were extracted and prepared into different concentrations with ethanol, ranging from 25 mg/ml to 500 mg/ml. These fractions were then examined for antimicrobial activities against inherent bacterial and fungal water contaminants using disc diffusion assay. Fractions were afterward screened for phytochemical active compounds using standard methods. Crude extracts of the different plant examined selectively comprise saponins, tannins, reducing sugars, anthraquinones, flavonoids, terpenoids, phlobatanins and alkaloids. All plant extracts showed broad spectrum antibiosis against selected gram positive and gram-negative bacteria including *E. coli*, *P. aeruginosa*, *Klebsiella* sp, *S. pneumoniae* and *B. cereus*, as well as tested fungi, including *A. niger, A. flavus, Trichoderma sp and Candida sp.* While all extracts exhibited maximum antibiosis at 500 mg/ml, the ethanolic extract of *Z. zanthoxyloides* was the most effective in inhibiting the growth of test organisms. *Z. zanthoxyloides* recorded zone of inhibition of 25.50 mm against *E. coli* and *S. pneumoniae* each, while *G. latifolium* and *T. glaucescens* recorded 22.00, 20.00 mm as well as 24.00, 20.50 mm against *E. coli* and *S. pneumoniae* respectively. Activities of all extract at 500mg/ml recorded against *E.coli* and *S. pneumoniae* were significantly higher than activities of commercial streptomycin (10.50 mm) and gentamycin (13.50 mm) used against *E.coli* and *S. pneumoniae* respectively. *Z. zanthoxyloides* recorded highest antifungal activity of 23.50 mm against *Trichoderma* sp. which is significantly higher than the activity of commercial nystatin recorded as 14.00 mm. Antimicrobial activities of crude extract of plant tested were in the order of *Z. zanthoxyloides*>*G. latifolium*>*T. glaucescens*. The result indicated that plant materials investigated can be developed as effective biocides against water microbial contaminants.

Keywords: Bio-disinfection, *G. latifolium, T. glaucescens,* Water, *Z. zanthoxyloides.*

1. Introduction
About 70 % of African population live in rural areas and lack access to quality water supply [1]. This population, therefore depends on surface and ground water like small streams, ponds, rivers and dug wells [2;3] and are regularly treated with chemical disinfectants (3;4]. Chemical disinfection is associated with the generation of harmful chemical precursors with potentials to cause hemolytic anaemia, cancer, nervous disruption, dementia and emergence of waterborne pathogens resistant to chemical disinfections [3;5]. This water is also regularly contaminated through poor waste disposal facilities, open field defecation as well as untreated cum poorly treated wastewater from factories. Hence,

waterborne diseases constitute 80 – 90 % of the disease burden in Africa [1] and currently beckons for attention. Rural communities do not have access to public water supplies. The disinfection of water in rural areas is thus a unique problem. Therefore, there is an urgent need for development and widespread promotion of simple disinfection and green techniques for rural water treatment.

Plant materials have been implicated in oral and written traditional knowledge as alternative methods for contaminated water treatment [6] for human consumption [3]. Plants are known to possess various secondary metabolites with profound antimicrobial properties and have been used in extensive disinfection of water, air and skin. Various formulations of herbs such as hand washes, sanitizers, gels, creams, ointments, dentifrices and herbal fumigants have also been reported. A few reported commonly used herbs with disinfecting properties are *Azdirachta indica, Eucalyptus robusta, Aloe barbadensis*, *Aloe vera, Withania somniferum, Andrographis paniculata, Aegle marmelos, Berberis vulgaris, Cinnamomum verum, Piper nigrum, Rhamnus purshiana, Capsicum annuum, Syzygium aromaticum, Eucalyptus globulus, Gaultheria procumbens, Cassia angustifolia, Cassia fistula, Mentha piperita,* etc. These plants with proven disinfecting activity are also referred to as plant antiseptics [7]. Number of herb-based products are being formulated and introduced into the market to overcome problems associated with chemical disinfections. Hence, ethnopharmacologists, botanists, microbiologists, and natural-products chemists are searching for phytochemicals and "leads" which could be developed into antimicrobials. It is also observed that the microorganisms are increasingly becoming resistant to antibiotics.

Adeeyo et al. [5] previously explained the principle of herbal antibiosis and water purification; the mechanisms of antimicrobial actions of phytochemicals may be via cell membranes perturbations [8] involving diverse molecular modes, such as binding with and increasing the permeability of cell wall and membrane component [9], inducement of membrane destabilization, leakage of cytoplasmic contents, loss of membrane potential, change of membrane permeability, lipid distribution, the entry of the peptide and blocking of anionic cell components or the triggering of autolytic enzymes and the final death of the microbial cell [10]. Phyto-purification of water involve flocculation, coagulation and disinfection [11]. Polysaccharides as well as protein associated phyto-chemicals have been implicated in water purification. Phytochemicals are capable of forming flocs which slowly settles after binding with suspended impurities in water. The net charge of phytochemicals and impurities; negative, positive or neutral combine with active sides of impurities; and produces a bridging effect which binds impurities and phytochemicals together and then settles under the action of gravity. Disinfection properties of plant extracts in water have also been associated with ability to alter the pH of water, making it unsuitable for some living contaminants [1;12].

2. Materials and Methods

Terminalia glaucescens, *Zanthoxylum zanthoxyloides* and *Gongronema latifolium* samples were collected from Oja Igbo market at Ogbomoso North local government, Oyo State. The samples were washed, air dried and grounded to powder, then sieved to get a fine powdered form.

Preparation of samples

50 g of dried and grounded samples of *Terminalia* glaucescens, *Zanthoxylum zanthoxyloides* and *Gongronema latifolium* was extracted by maceration using 150 ml of ethanol as extraction solvent for 48 hours. The solvents fractions were separated using

vacuum filtration aided by a sterile Whatmann No 1 filter paper and filtering crucible. The filtered extract was then dried with the help of a freeze drier and stored in sterile polypropylene airtight container at 4°C or dispensed in appropriate sterile dissolving solution when required.

Antimicrobial Activity

Preparation of antimicrobial disc and sensitivity test

Different concentrations of crude extracts of *T. glaucescens, G. latifolium* and *Z. Zanthoxyloides* ranging between 25 and 500 mg/ml were prepared by dissolving appropriate amount of crystalised extract into ethanol. Solutions were then embedded in 6.0 mm diameter sterile disc prior to antimicrobial sensitivity testing by disc diffusion method as described by Lattef and Adeeyo [13]. Briefly, the test organism was swabbed evenly on the surface of the agar plate using surface spread method. Impregnated paper discs with different concentrations of crude extracts were then arranged serially and radially and pressed slightly but firmly to the surface of inoculated agar. The plates were afterward incubated at 37 °C for 24 hours. The fungi plates were incubated at room temperature (27 ± 2 °C) for 48 hours. The degree of sensitivity was determined by measuring the diameter in millimeter of the visible zone of inhibition of microbial growth produced by the diffusion of the extract. Test concentrations of crude extract were 500 mg/ml, 250 mg/ml, 100 mg/ml, 50 mg/ml and 25 mg/ml. Standard reference commercial antibiotics disc for gram negative (streptomycin), gram positive (gentamycin) and the fungi (nystatin) were used for a comparative study.

Phytochemical analyses

The phytochemical screening of the extracts was investigated according to standard methods and as modified by Harborne [14] and Adeeyo et al. [5]. Screening for tannins, saponnin, reducing sugars, alkaloids, terpenoids, flavonoids, steroids, anthraquinones and phlobatannins were carried out on extracted crude products.

Statistical Analysis

The Statistical Package for Social Scientists (SPSS, version 19.0) was used for the analysis of the data obtained. ANOVA test was used to compare mean of the differences determine the level of significance of the crude extracts at different concentration. Also, the general antimicrobial effects of the extracts were compared with the standard antibiotics and antifungal disc statistically.

3. Result

Antibacterial activities

The antibacterial activities of plants investigated are presented in Table 1. *T. glaucescens* exhibited antibacterial activities against all strains of bacteria in the study. The minimum concentration of the extract that exhibited significant antibiosis over commercial streptomycin was observed at 100 mg/ml and 500 mg/ml against *E. coli*. and *P. aeruginosa* respectively. No significant difference was observed in the activities of *T. glaucescens* over streptomycin against *Klebsiella* sp. *T. glaucescens* also exhibited significant antibiosis over the activities of gentamycin at 250 and 500 mg/ml against *B. cereus* and *S. pneumoniae*. *G. latifolium* like *T. glaucescens* exhibited antibacterial activities against all strains of bacteria studied, though no significant difference was recorded against *Klebsiella* sp. The minimum concentrations that exhibited significant antibiosis over commercial streptomycin on *E. coli* and *P. aeruginosa* was 50 mg/ml while 100 mg/ml was needed to exhibit significant antibiosis on *Klebsiella* sp. For *S. pneumoniae* and *B. cereus*, 100 mg/ml of *G. latifolium* was the concentration that exhibited significant activity over the activity of gentamycin. *Z. zanthoxyloides* exhibited significant antibiosis at a concentration of 25 mg/ml against *E. coli* and at 50 mg/ml against *Klebsella* sp, *S. pneumoniae* and *B. cereus*. 100 mg/ml was needed to exhibit significant antibiosis on *P. aeruginosa* over the activities of streptomycin and gentamycin. All significant antibiosis was greater than the activities of streptomycin and gentamycin reported.

TABLE 1. Antibacterial activities of *T. glaucescens, G. latifolium and Z. zanthoxyloides*

		T. glaucescens	*G. latifolium*	*Z. zanthoxyloides*
P. aeruginosa	STR	11.50± 0.707	11.50± 0.707	11.50± 0.707
	C	8.50±0.707	9.50±0.707	8.50±0.707
	C1	9.50± 0.707	13.00± 1.414	11.00± 1.414
	C2	11.50± 0.707	16.50± 0.707*	13.50± 0.707
	C3	11.50± 0.707	18.00± 1.414*	16.00± 1.414*
	C4	13.50± 0.707	19.00± 1.414*	18.50± 0.707*
	C5	14.50± 0.707*	20.00± 1.414*	22.00± 1.414*
Klebsiella sp	STR	10.50± 0.707	10.50± 0.707	10.50± 0.707
	C	9.00 ±1.414	8.50±0.707	7.50±0.707
	C1	8.50±2.121	11.00± 1.414	11.50± 2.121
	C2	9.50± 0.707	14.50± 0.707	15.50± 0.707*
	C3	11.50± 0.707	16.00± 1.414*	16.00± 1.414*
	C4	12.00± 1.414	18.00±0.000*	18.00± 1.414*
	C5	13.50± 0.707	19.00± 1.414*	19.50± 2.121*
E. coli	STR	10.00± 0.000	10.00± 0.000	10.00± 0.000
	C	8.50±0.707	10.50±0.707	7.00±0.0000
	C1	10.50± 0.707	13.50± 0.707	13.50± 0.707*
	C2	14.00± 1.414	15.00 ±0.000*	16.50± 0.707*
	C3	15.00± 1.414*	16.00± 1.414*	21.00± 1.414*
	C4	18.00± 1.414*	19.50± 0.707*	24.50± 0.707*
	C5	20.00± 1.414*	22.00± 1.414*	25.50±2.121*
S. pneumonia	GEN	13.50± 0.707	13.50± 0.707	13.50± 0.707
	C	8.50±0.707	10.50±0.707	8.50±0.707
	C1	12.00± 1.414	14.00± 1.414	15.00± 1.414
	C2	14.00± 1.414	17.00± 1.414	19.00± 1.414*
	C3	17.00± 1.414	19.50± 0.707*	22.50± 0.707*
	C4	19.00± 0.000	21.00± 1.414*	24.00± 1.414*
	C5	20.50± 0.707*	24.00± 1.414*	25.502.121*
B. cereus	GEN	13.00± 0.000	13.00± 0.000	13.00± 0.000
	C	8.50±0.707	8.50±0.707	7.50±0.707
	C1	12.00± 1.414	12.50± 0.707	12.00± 1.414
	C2	15.00± 1.414	15.50± 0.707	14.50± 0.707*
	C3	16.00± 1.414	17.50± 0.707*	16.00± 1.414*
	C4	18.50± 0.707*	18.50± 0.707*	17.50± 2.121*
	C5	19.00± 1.414*	19.50± 0.707*	20.50± 2.121*

Values are expressed as mean ± SD for n=2 for each concentration. Values with (*) are significantly higher than the control (antibiotics) at $p < 0.05$. C- ethanol only, C1-25ml, C2-50ml, C3-100ml, C4-250ml, C5-500ml extract. STR- Streptomycin, GEN- Gentamycin.

Antifungal activities

Table 2 presents the antifungal activities of various plant investigated. *T. glaucescens* exhibited antifungal activity against all fungal isolates tested. However, comparative activity to nystatin was only observed at 100 mg/ml and above. No significant differences were observed in the antifungal activities of *T. glaucescens* when compared to the activity of nystatin across all isolates and concentrations tested. In a similar manner, *G. latifolium* exhibited antifungal activity on all tested fungal isolate with comparative activity to nystatin observed mostly from 100 mg/ml and above. Significant difference in activity of *G.*

latifolium on *Trichoderma* sp. was observed only at 500 mg/ml. Z. *zanthoxyloides* exhibited antifungal activity on all fungal strains and recorded notable significant difference from activities of nystatin on *A. flavus* (500 mg/ml), *A. niger* (500 mg/ml) and *Trichoderma* sp (250 mg/ml).

Phytochemical screening

The results obtained from the qualitative phytochemical screening of the plant extracts are presented in Table 3. The result indicates a selective presence of phytochemicals including tannins, alkaloids, flavonoids, terpenoids, reducing sugars, saponins, steroids and anthraquinones. The phytochemical contents of the plants material is in the order of *T. glaucescens>G.latifolium>Z. zanthoxyloides.*

TABLE 2. Antifungal activities of *T. glaucescens, G. latifolium and Z. zanthoxyloides*

		T. glaucescens	*G. latifolium*	*Z. zanthoxyloides*
A. flavus	NIS	15.00± 0.000	15.00± 0.000	15.00± 0.000
	C	8.50±0.707	7.50±0.707	11.00±1.414
	C_1	12.00± 2.828	11.50± 0.707	14.00± 1.414
	C_2	13.50± 2.121	13.50± 0.707	16.00± 1.414
	C_3	17.00± 1.414	16.00± 1.414	17.00± 2.828
	C_4	17.50± 0.707	18.50± 0.707	20.00± 1.414
	C_5	19.00± 1.414	16.00± 1.414	23.00± 1.414*
A. niger	NIS	16.50± 0.707	16.50± 0.707	16.50± 0.707
	C	7.50±0.707	8.50±0.707	9.50±0.707
	C_1	11.00± 1.414*	13.00± 1.414	13.00± 1.414
	C_2	14.00± 1.414	14.00± 1.414	15.50± 0.707
	C_3	17.50± 0.707	16.50± 0.707	18.00± 1.414
	C_4	18.50± 0.707	17.00± 1.414	19.00± 1.414
	C_5	19.00± 0.000	20.00± 1.414	21.50± 0.707*
Trichoderma sp	NIS	14.00± 0.000	14.00± 0.000	14.00± 0.000
	C	8.50±0.707	9.50±0.707	10.50±0.707
	C_1	9.00± 1.414	13.00± 1.414	13.50± 0.707
	C_2	10.00± 1.414	16.00± 1.414	16.00± 1.414
	C_3	11.00± 1.414	18.00± 1.414	18.00± 1.414
	C_4	14.00± 1.414	18.50± 0.707	22.00± 1.414*
	C_5	19.00± 1.414	22.00± 1.414*	23.50± 2.121*
Candida sp	NIS	14.00± 0.000	14.00± 0.000	14.00± 0.000
	C	8.00±1.414	9.00±1.414	9.00±0.000
	C_1	11.00± 1.414	11.50± 0.707	12.00± 1.414
	C_2	13.00± 1.414	13.50± 0.707	14.00± 1.414
	C_3	12.00± 1.414	15.00± 1.414	15.00± 1.414
	C_4	13.50± 0.707	16.00± 1.414	17.00± 1.414
	C_5	15.00± 1.414	17.00± 1.414	19.00± 1.414

Values are expressed as mean ± SD for n=2 for each concentration. Values with (*) are significantly higher than the control (Nystatin) at $p < 0.05$. C-ethanol only, C1-25ml, C2-50ml, C3-100ml, C4-250ml, C5-500ml of extract. NIS- Nystatin.

TABLE 3. Phytochemical compositions of *T. glaucescens, G. latifolium and Z. zanthoxyloides*

Analysis	*T. glaucescens*	*G. latifolium*	*Z. zanthoxyloides*
Saponins	+	-	-
Tannins	+	+	+
Reducing Sugars	-	+	-
Alkaloids	+	+	+
Flavonoids	+	+	+
Terpenoids	+	+	+
Phlobatannins	-	-	-
Steroids	+	-	-
Anthraquinones	+	-	-

Phytochemical Analysis Results + = Present, - = Absent

4. Discussion

Comparative antimicrobial activities of plant and commercial antibiotics

In this study, ethanolic extract of all tested plant compared favourably against commercial gentamycin, streptomycin and nystatin which were used as standards and possess significant statistical differences. The plants investigated possesses potent antibacterial activities than that observed in commercial antibiotics while the antifungal activities were comparable to that of nystatin; a common antifungal agent. These reports points to the efficacy of herbs as potent antimicrobials as reported in these findings. When the disinfection of water was carried out using the leaves and fruits of *Hardwickia binata, Cyperus rotundus*, *Andropogon muricatus* and *Luffa cyllindrica,* a kinetic model was formulated to predict the disinfection of water. Results showed that all herbs showed effective removal of *E.coli* [15]. During the evaluation of disinfectant activity of *Ocimum sanctum, Azadirachta indica, Triticum aestivum, Phyllanthus emblica* and *Strychnos potatorum* in water purification, it was observed that all herbs maximum removal of *E.coli* was found at 30 minutes contact time [2]. This work is also similar to the report of Fagbemi et al. [16] on the activity of ethanolic extracts of selected plant materials. Fagbemi et al. [16] reported that ethanolic extracts of unripe banana, lemongrass, and turmeric were effective against *E. coli* ATCC25922, *P. aeruginosa*, *Salmonella paratyphi*, *S. flexneri*, *K. pneumoniae*, *S. aureus* ATCC 25921, and *B. subtilis* with MIC range of 4 to 512 mg/mL and MBC range 32 to 512 mg/mL depending on bacterial isolates and extracting solvent. *S. aureus* ATCC 25921 was killed in less than 2 h with unripe banana extract, *E. coli*, in less than 3 h with turmeric and *S. paratyphi* in just over 3 h with lemongrass. The overall results revealed that antimicrobial activities of the plant extracts are dose dependent with comparative activity greater than that of commercial antibiotics at the concentration of extracts tested [17]. The doses of antimicrobial samples used in this work were found to be effective in the treatment of the microbial isolates investigated with effectiveness against all bacterial and fungal isolates. Phytochemical products that produce minimum inhibitory concentrations (MIC) in the range 100–1000 mg mL^{-1} in *in vitro* susceptibility tests have been classified as antimicrobials [17].

The result of this work has established the ability of *T. glaucescens*, *G. latifolium* and *Z. zanthoxyloides* to effectively inhibit inherent water microbial contaminants and is in agreement with previous study on antimicrobial activities of herbal extracts. In this study, the plants investigated exhibited antibiosis that were significantly higher than common commercial antibiotics and points to the fact that plant materials investigated can be developed into potent eco-friendly biocides for possible application in water treatment as supported by previous studies.

Phytochemical activities and antimicrobial mechanisms

All plant extracts revealed the presence of tannins, alkaloids, flavonoids and terpenoids. However, *G. latifolium* contains reducing sugars while *T. glaucecens* contains saponins, steroids and anthraquinones. With respect to antibiosis and observed phytochemical result of this work; tannins, alkaloids, flavonoids and terpenoids seems to be the main active component responsible for antibiotic actions of the plant; these were the detectable component found in *Z. zanthoxyloides* which possessed maximum antibiosis. Reducing sugars, saponins, steroids and anthraquinones are likely to have a less- or no-contribution to antibiosis; individually or in synergistic form; these compounds were found in addition to tannins, alkaloids, flavonoids and terpenoids in *T. glaucescense* and *G. latifolium* but with reduced antibiosis when compared to *Z. zantholoides* (Table 1 and Table 3). The presence of antifungal and antimicrobial substances in higher plants is well established as they have provided a source of inspiration for novel drug compounds [18]. The phytochemical effectiveness of ethanolic extract in this work is therefore in agreement with several past reports including that of Nwachukwu and Uzoeto [19], Peni et al. [20], and Adeniyi et al. [21].

5. Conclusion

This study which is aimed at bioprospecting for eco-friendly biodisinfectant with focus on treatment of water microbial contaminants has revealed that *T. glaucescens, G. latifolium* and *Z. zanthoxyloides* are good source of antimicrobial agents with equal or better performance than selected commercial antibiotics. In addition, the plants are consumed in large quantities by animals and are applied as local mouth wash in rural African communities. It has been established that the extracts under study were effective against inherent fungal and bacterial water contaminant with broad spectrum of antibiosis against gram positive and gram-negative bacteria. References were made to indicate that active compounds of these plants may possess potent antiviral activities. It can therefore be concluded that the plants under investigation are potential candidates for treatment of fungal, bacterial and viral contaminants which are emerging issues in the field of water quality control. Thus, *T. glaucescens, G. latifolium* and *Z. zanthoxyloides* are recommended as potent sources of therapeutic antimicrobials and for further development as eco-friendly bio-disinfectants for rural African use.

Acknowledgement: The authors appreciates the University of Venda work study program and the Research and Publication Committee of the university for the grant given to Mr. Adeeyo (Grant number SES/17/ERM/13) for this research.

References

1. Yongabi K.A (2010). Biocoagulants for water and waste water purification: a review. International Review of Chemical Engineering 2:444-458
2. Somani S.B., Ingole N.W., Patil S.S (2011). Performance evaluation of natural herbs for antibacterial activity in water purification. Int J of Eng Sci & Tech 3: 7170-74.
3. Bhattacharjee T., Gidde M.R, Bipinraj N.K (2013). Disinfection of drinking water in rural area using natural herbs. International Journal of Engineering Research and development 5: 7-10.

4. Parthiban L., Porchelvan P., Rasamy T., Gowri S (2017). Clarification and disinfection of water using natural herbs (neem and tulasi) Azadirachta indica and Ocimum sanctum. Journal of Chemical and Pharmaceutical Sciences 10: 507-510
5. Adeeyo, A.O.; Odiyo, J.; Odelade, K. Chemical profiling and antimicrobial properties of phyto-active extracts from Terminalia glaucescens stem against water microbial contaminants. Open Biotechnol J 2018, 12,3-17.
6. Sundaramurthi P., Dhandapani S., Ponnusamy S., Subbaiyan M (2012). Effect of Tulsi as a water Treatment. Hitek J Bio & Bioengg.pg.1-7.
7. Khanam S., Afsar Z (2013). Herbal disinfectant: a review. World Journal of Pharmaceutical Research 3: 258-273
8. Esimone C.O., Iroha I.R., Ibezim E.C., Okeh C.O., Okpana E.M (2006). In vitro evaluation of the interaction between tea extracts and penicillin G against *Staphylococcus aureus*. Afr J Biotechnol 5: 1082-1086.
9. Chuang P.H., Lee C.W., Chou J.Y., Murugan M., Shieh B.J., Chen H.M (2007). Anti-fungal activity of crude extracts and essential oil of *Moringa oleifera* Lam. Bioresour Technol 98: 232-6.
10. Zasloff M (2002). Antimicrobial peptides of multicellular organisms. Nature 415: 389-95.
11. Burkill H.M (1985). The useful plants of West Africa. 92nd ed. Kew: Families A-D, Royal Botanical Gardens pp. 101-20.
12. Hindi N.K., Chabuck, Z.A (2013). Antimicrobial activity of different aqueous lemon extracts. J Appl Pharm Sci 3: 074-8.
13. Lateef A., Adeeyo A.O (2015). Green synthesis and antibacterial activities of silver nanoparticles using extracellular laccase of *Lentinus edodes*. Not Sci Biol 7: 405-11.
14. Harborne J.B (1998). Phytochemical Methods, A Guide to Modern Techniques of Plant analysis. 2nd ed. London: Chapman and Hall pp. 54-84.
15. Somani S.B., Ingole N.W (2012). Formulation of kinetic model to predict disinfection of water by using natural herbs. Int J Env Sci 2: 1344-54
16. Fagbemi J.F, Ugoji E, Adenipekun T, Adelowotan O (2009). Evaluation of the antimicrobial properties of unripe banana (*Musa sapientum* L.), lemon grass (*Cymbopogon citratus* S.) and turmeric (*Curcuma longa* L.) on pathogens. Afr. J. Biotechnol. 8 (7), 1176–1182.
17. Abreu, A.C.; McBain, A.J.; Simoes, M. Plants as sources of new antimicrobials and resistance-modifying agents. Nat Prod Rep 2012, 29, 1007-1021. DOI: 10.1039/c2np20035j.
18. Viji M., Sathiya M., Murugesan S (2010). Phytochemical analysis and antibacterial activity of medicinal plant *Cardiospermum helicacabum* linn. Pharmacologyonline 2: 445-56.
19. Nwachukwu E., Uzoeto H.O (2010). Antimicrobial activities of leaf of *Vitexdoniana* and *Cajanus cajan* on some bacteria. *Researcher* 2:37–47.
20. Peni I.J., Elinge C.M., Yusuf H (2010). Phytochemical screening and antibacterial activity of *Parinari curatellifolia* stem extract. *Journal of Medicinal Plants Research* 4:2099–2102.
21. Adeniyi T.A., Adeonipekun P.A., Omotayo, E. A (2014). Investigating the phytochemicals and antimicrobial propertiesof threesedge (Cyperaceae) species. *Notulae Scientia Biologicae* 6:276–281.

Characterization of acid mine drainage potential of coal and coal bearing rocks: A case study at Bloekembos coal project, Mpumalanga in South Africa

S Tshusa[1,*] and SJ Moja[1,2]

[1]Department of Environmental Sciences, University of South Africa, South Africa
[2]Sustainable Resources and Environment Competency, Council for Geosciences, South Africa
*Email of corresponding author: shudufhadzotshusa@gmail.com

Abstract
Coal mining generates noteworthy environmental impacts with varying severity depending on the geologic and climatic conditions, as well as the mining methods employed. This study aims to determine the geochemical characteristics and to predict acid mine drainage potential of the overburden and coal at Bloekembos coal project in the Witbank coalfields. A total of 11 samples comprised of 5.0 overburden samples and 6.0 coal samples were collected from the borehole core samples over a period of two months in 2017. These samples were characterized using various laboratory-based experiments, namely: sulphur speciation, mineralogical characterization (XRD), chemical characterization (XRF) and acid base accounting (ABA). Sulphur speciation results showed that coal has high sulphur content than the overburden and this means that coal may have high potential to generate acidic drainage. XRD results showed that pyrite occurs in a range of 0.1- 0.35 % in coal and 0.27-0.3% in overburden. Carbonates minerals such as dolomite (0.0-0.01 %), calcite (0.0-0.06 %) and siderite (0.0-3.81 %) occurs in rare to minor phases in both coal and overburden samples. ABA results shows that coal have high acid forming potential than the overburden. The low NNP in (0-30.5) kg $CaCO_3$ per ton confirmed that due to the high presence of acid forming minerals as compared to acid consuming minerals, coal have high potential to generate acid mine drainage than the overburden. The ABA results has a direct correlation with the sulphur speciation and XRD results. The lower NAG value in coal shows that the coal requires high quantity of base to increase the pH to neutral. This study has revealed that both the coal and overburden from the study area have the potential to generate acid mine drainage however with coal having higher potential than the overburden coupled with liberation of metals such as Fe, Mn, Se and Si.

Keywords: Characterization, overburden, coal, acid drainage generating potential

1. Introduction

Coal mining is known to create environmental impacts ranging from increased chemical contamination of water by acid mine drainage (AMD) caused by oxidation of sulphide minerals contained in the upturned disintegrated earth of coal bearing rocks seeping into water resources to subsidence in underground mining. Furthermore, it creates blemishes caused by heaps of overburden spoils contaminated with uneconomic low-grade coal seams or coal scalped in strip mining [1] Environmental liabilities that results after coal mining include acid contaminated water bodies and barren land that stay contaminated for several years until proper rehabilitation or remediation has taken place. Coal seams in South Africa are hosted in layers of sedimentary rocks of the Karoo Basin. The coal and the coal bearing rocks known to contain reactive sulphide minerals such as pyrite, but the pyrite mineral is more copious in coal layers. Coal mining takes place either by underground mining or opencast/strip mining methods [2] Another stage of coal mining that introduces toxic elements to the environment is coal processing. Coal is processed to enhance the quality and to remove impurities such as sulphide minerals and non-coal material. The washing of coal produces tons of solid waste called discards and slurries that are disposed in waste management facilities called discard dumps. The discard dumps often leach acidic water and toxic heavy metals such as Cu, Fe, Mn, Al, As and Cr [3].

There are limited published studies on geochemical and mineralogical characterization of coal bearing strata in the South African coalfields [4]. Acid mine drainage is one of biggest threat to South African water resources and long-term supply of fresh water. Highly toxic water enriched with metals, metalloids and sulphate decants into river systems and destroys aquatic life. Moreover, it poses serious threats to the people dependent on these resources [5]. Drainage chemistry is mostly influenced by the mineralogical properties of the material coupled with the geochemical characteristics. The change in the drainage chemistry is caused by a combination of physical and chemical weathering that occurs during the handling, use and storage of the material [5]. Learnings from the impacts of coal mining across the world and particularly in countries such as Pennsylvania, West Virginia, South Africa and India show that historical liabilities of mining can be severe if not well managed [6, 7, 8]. This study determines the geochemical characteristics and predicts acid mine drainage potential of the overburden and coal at Bloekembos coal project in the Witbank coalfields.

2. Materials and Methods

Materials

The geochemical core samples were collected at Bloekembos coal project during drilling campaign in the month of June 2017 using a diamond core drilling machine. Sampling took place in the month of July 2017 and a total of 11 samples were collected from 5 diamond core drilled boreholes (BH01, BH02, BH04, BH05 and BH06), BH03 was excluded because it was in close proximity with BH04. 06 coal samples and 05 overburden samples, boreholes sampled were selected taking into consideration the lithological units and areal coverage within the planned mining pit. Two samples per borehole (i.e. 1 coal and 1 overburden sample per borehole) beside borehole BH05 where there was a parting occurrence of the coal seam (i.e. 2 coal samples were collected). The overburden is comprised of the highly weathered and competent material sandstone/mudstone and the coal is seam 2#. The core was broken into pieces using a geological hammer, packed in a plastic sample bag, labeled, weighed (approximately 3.5kg each) and tied with cable ties. The samples were stored in a box and transported to the laboratory.

Preparation and characterization

Samples were sent to a SANAS (per ISO 17025) accredited Laboratory. The solid coal and overburden samples were oven dried and then crushed using jaw crushers, pulverized into homogeneous finer particles, put through a stainless-steel sieve for screening. To get a representative sample, the samples are coned and quartered or split using a riffle splitter boxes. All samples were milled to the required size fraction for relevant analysis. The bulk sample preparation is based on SANS 3082: 2011 [9]. For sulphur speciation the method reported by Sobek *et al*. (1978) was employed with slight modification

Mineralogical composition of the Samples was determined using X-ray diffraction. The samples were prepared using back loading method and were analyzed using a PANalytical Empyrean diffractometer with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. Phases were identified using the PANalytical Highscore plus analytical software. The weight percentages of the mineral were determined using the Rietveld method [10]. Major oxides, minor and trace elements by X-ray fluorescence (XRF) spectroscopy using

ThermoFisher instrument, ICP-OES using Perklin Elmer Optima 5300DV instrument and ICP-MS using Perkin Elmer Nexion 300D instrument. The major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO and MgO etc.) were determined by X-ray fluorescence (XRF) spectroscopy using the fusion or pressed powder pellets method and minor elements (Sr, Ba, Cr, Cu, Ni and Zn etc.) were analyzed using inductively coupled plasma optical emission spectrometry [11].

The analysis of other trace element and rare earth elements in coal and overburden samples were dissolved in a multi-acid total digestion using the microwave digestion technique. The total trace elements were determined using inductively coupled plasma mass spectrometry instrument. The instrument was calibrated with a series of NIST (National Institute of Standards and Technology) traceable calibration solutions. static tests performed for the characterization are based on Sobek *et al* (1978) and in line with the methods as outlined by Usher *et al* (2003). Australian Standard leaching procedure [12] was used for the leaching of the coal and overburden. The leachate solution was collected for analysis. The ICP-MS Perkin NexION 300 Instrument was used to analyze metals in the leachate solution, the Ion Chromatography and Spectrophotometer was used to analyze the anions in the leachate solution and other parameters were analysed by and Ion selective probe.

Quality assurance and quality control (QA/QC)

All samples received at the lab were checked against the submitted sample list, any discrepancies were discussed with the researcher before the samples are logged onto the Laboratory Information Management System (LIMS). Once the samples were logged, LIMS assigns a work number to the project and each sample is assigned a unique bar-coded sample number. Worksheets are generated for the samples and worksheets includes the QC standards, duplicates and blanks. Methods at the lab are accredited by SANAS as per ISO 17025. Only staff declared competent for the test procedures and analysis method can perform the test procedure. Suitable certified and standard reference materials were used to calibrate the instruments and as quality control standards during sample runs. Reference material were added in between the sample runs to check the quality throughout: Batch size < 100: QC (RM) after every 10th sample and Batch size >100 samples: QC (RM). Results were reported for the LIMS system and all reports were authorized by a competent person.

3. Results and discussion

The XRD results (Figure 1) illustrate that, on average, composition of acid forming mineral such as pyrite (0.1-0.35%) is more than the fast acid consuming/neutralizing minerals such as dolomite (0.0-0.01%), calcite (0.0-0.06%) and siderite (0.0-3.81%). Neutralization potential is anticipated to be delivered by calcite and dolomite and further, by alumino-silicate minerals such as kaolinite, microcline and muscovite even though their rate of weathering is slow to very slow.

The XRF results (Table 1) show abundance of SiO_2 in a range of 4.89 - 84.87% and Al_2O_3 in a range of 3.17 - 26.49 followed by Fe_2O_3 in a range of 0.3 - 3.38% and TiO_2 in a range of 0.15 - 1.18% in both coal and overburden. Overburden has the highest concentration of SiO_2, Al_2O_3, TiO_2 and Fe_2O_3 compared to coal. CaO and MgO are very low in a range of 0.04 and 0.45% in both coal and overburden. This interpretation directly correlates with the mineralogical composition of coal and overburden samples which are dominated by quartz, kaolinite and magnetite is some coal and overburden samples. Minor elements such as Sr, Ba, Ni, Pb, V, Zr and Zn occurs in very low concentration ranging from 0.00% - 0.21% were as C and S occurs in considerable concentration ranging from 4.10% - 69.9% and 0.04 - 0.98% respectively (Figure 2).

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

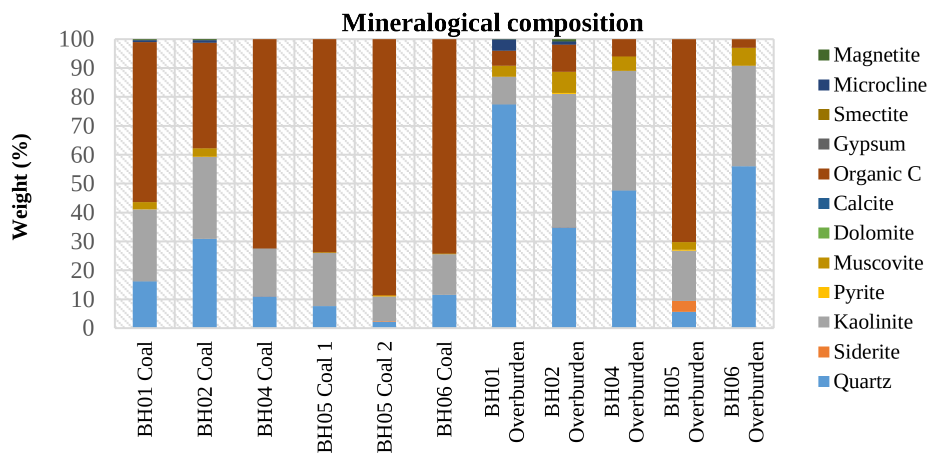


Figure 1. Mineralogical composition of the samples.

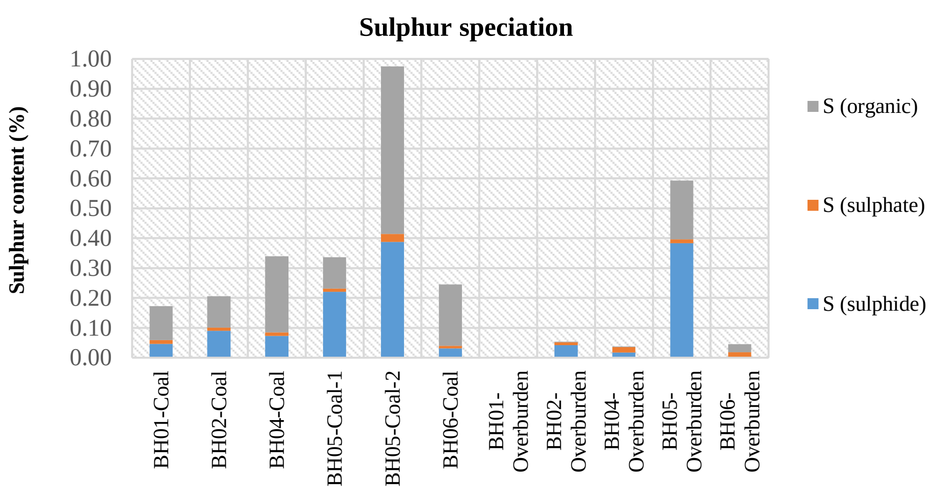


Figure 2. Sulphur Speciation of the samples

TABLE 1. XRF oxides of major elements results of coal and overburden (weight %)

Parameter	BH01 Coal	BH02 Coal	BH04 Coal	BH05 Coal-1	BH05 Coal-2	BH06 Coal	BH01 Overburden	BH02 Overburden	BH04 Overburden	BH05 Overburden	BH06 Overburden
SiO_2	28.47	43.38	17.60	15.25	4.89	14.26	84.87	56.52	47.89	13.55	71.93
Al_2O_3	12.14	15.42	8.05	8.45	3.17	5.50	6.04	26.49	16.99	9.17	12.37
Fe(total)	0.32	0.28	0.21	0.38	0.72	0.10	0.71	0.96	2.36	2.64	0.31
Fe_2O_3	0.46	0.40	0.30	0.54	1.03	0.14	1.02	1.38	3.38	3.78	0.45
TiO_2	0.85	1.17	0.47	0.36	0.15	0.44	1.75	1.18	1.16	0.39	1.60
CaO	0.05	0.05	0.09	0.06	0.11	0.07	0.05	0.70	0.45	0.29	0.04
MgO	0.10	0.10	0.05	0.04	0.06	0.04	0.04	0.24	0.23	0.16	0.07
Na_2O	0.03	0.03	0.02	0.04	0.01	0.02	0.04	0.06	0.06	0.03	0.04
K_2O	0.28	0.24	0.08	0.15	0.08	0.08	1.30	0.91	0.51	0.10	0.62
P_2O_5	0.02	0.03	0.01	0.01	0.01	0.01	0.03	1.27	0.08	0.04	0.03
Ni	0.08	0.02	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.01	0.02
V	0.02	0.01	0.00	0.00	0.01	0.00	0.01	0.02	0.01	0.00	0.01
C	29.83	30.74	56.18	56.69	69.99	61.30	0.50	12.88	11.87	49.73	4.10
S	0.17	0.21	0.34	0.34	0.98	0.25	0.00	0.05	0.04	0.59	0.04

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

TABLE 2. Acid base accounting results of coal and overburden

Sample ID	Paste pH	Total %S	AP Kg CaCO3/t	NP Kg CaCO3/t	NNP Kg CaCO3/t	NPR (NP/AP)	Rock Type %S	Rock Type NP/AP
BH01-Coal	6.60	0.167	5.22	1.08	-4.14	0.21	I	I
BH02-Coal	6.21	0.183	5.72	0.91	-4.81	0.16	I	I
BH04-Coal	5.24	0.339	10.59	2.16	-8.4	0.20	I	I
BH05-Coal-1	4.24	0.336	10.50	2.05	-8.5	0.20	I	I
BH05-Coal-2	3.70	0.975	30.47	0.00	-30.5	0.00	I	I
BH06-Coal	5.36	0.245	7.66	2.11	-5.5	0.28	I	I
BH01-Overburden	6.55	0.002	0.06	0.06	0.00	0.96	II	I
BH02-Overburden	5.92	0.053	1.67	1.27	-0.40	0.76	II	I
BH04-Overburden	5.31	0.037	1.16	0.00	-1.2	0.00	II	I
BH05-Overburden	4.59	0.593	18.53	0.00	-18.5	0.00	I	I
BH06-Overburden	5.60	0.045	1.40	0.00	-1.4	0.00	II	I

The ABA results (Table 2) show that paste pH of overburden and coal samples ranges from 3.7-6.6 which is slightly acidic to neutral (Figure 3). Total sulphur in coal ranges from 0.245-0.34 % and ranges from 0.002-0.593 % in the overburden as shown in Figure 4. According to Usher et al (2003) and Price (1997) at least 0.3 % of sulphide – S is needed for long term acid generation. Samples such as BH05-Coal-2 and BH05-Overburden have total sulphur percentage of 0.336 % and 0.593 % respectively and this two samples have the highest acid generating potential than all the other samples. Acid Potential (AP) in coal samples ranges from 5.2-30.5 CaCO3 per ton while in the overburden ranges from 0.1-77 CaCO3 per ton and figure 6 shows that the more the sulphur in the sample the higher the AP. The NP is very low in all samples due to the absence of fast dissolving/weathering carbonaceous mineral such as calcite and dolomite. The NNP ranges from 0.00 kg-30.5 kg CaCO3 per ton and this is due to the high presence of acid forming minerals such as pyrite Sulphur as compared to acid consuming minerals such as dolomite and calcite. Therefore, the results from the samples indicate that the coal and overburden have potential to generate acid mine drainage (Figure 5).

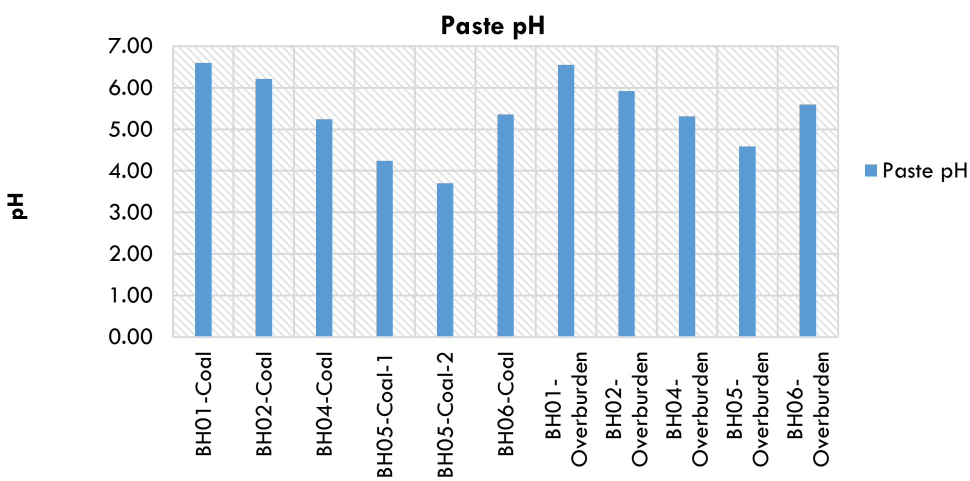


Figure 3. Paste pH of the samples

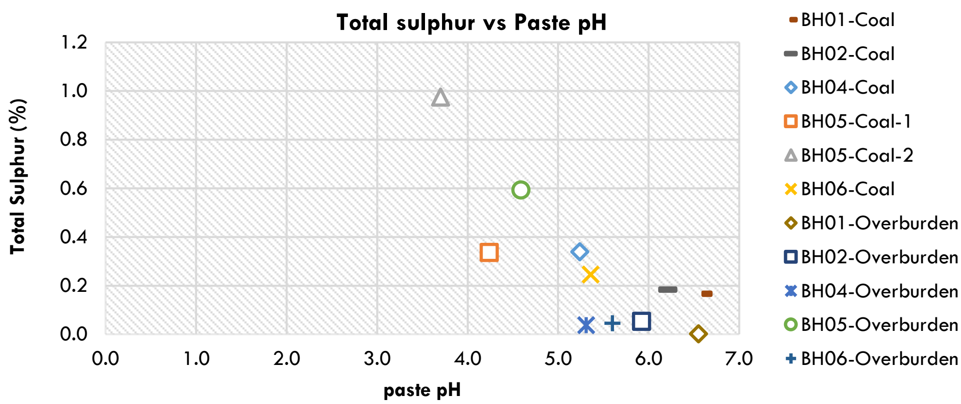


Figure 4. Total sulphur vs Paste pH of the samples

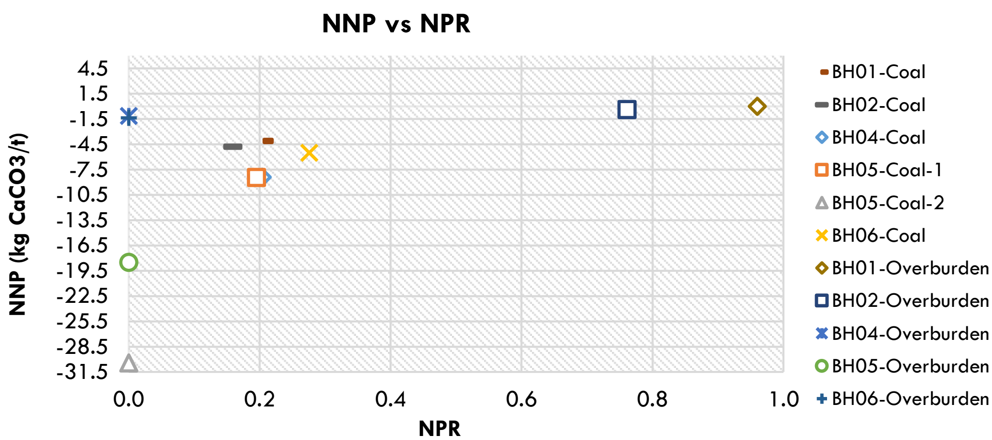


Figure 5. NNP vs NPR of the samples

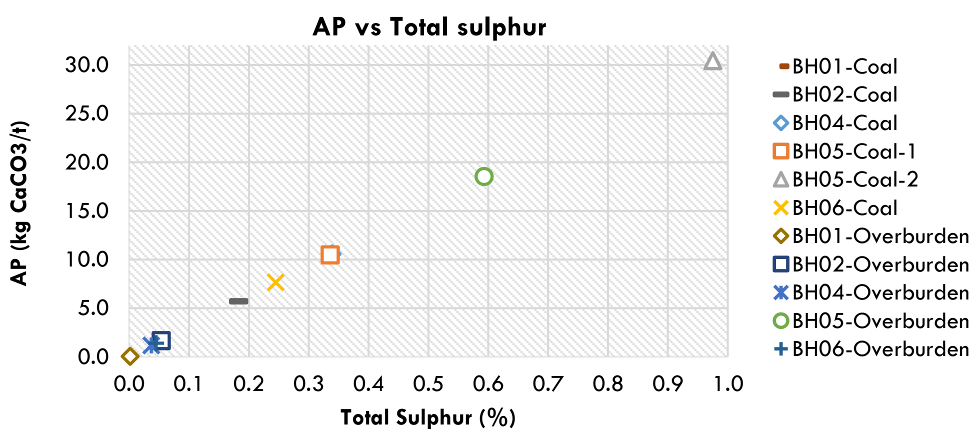


Figure 6. AP vs Total sulphur of the samples

The NAG test (Table 3) illustrates the quantity of base required to increase the pH to a neutral pH. All coal samples have a NAG pH of < 2. 4 and the overburden samples have a NAG pH ≤ 3.00. Only BH01 overburden have NAG pH of < 4.0 (Table 4.6). According to the NAG test screening method used by Miller et al (1997), all coal samples and 04 overburden samples (BH02, BH04, BH05 and BH06) have high capacity of forming acid, only BH01 overburden has lower capacity of forming acid. This can be attributed to adequate concentration of pyrite/sulphide and total sulphur as depicted in the sulphur speciation results and the acid base accounting results.

TABLE 3. Net acid generation (NAG) test results of coal and overburden

Sample ID	Description/ Rock Type	NAG pH: (H2O2)	NAG (kg H2SO4/t) at pH 7	NNP (Kg CaCO3/t)	Rock Type
BH01-Coal	Coal	1.90	49.36	-4.1	Rock Type Ia. High Capacity Acid Forming
BH02-Coal	Coal	1.70	73.18	-4.8	Rock Type Ia. High Capacity Acid Forming
BH04-Coal	Coal	1.66	54.35	-8.4	Rock Type Ia. High Capacity Acid Forming
BH05-Coal-1	Coal	1.75	41.13	-8.5	Rock Type Ia. High Capacity Acid Forming
BH05-Coal-2	Coal	1.60	55.75	-30.5	Rock Type Ia. High Capacity Acid Forming
BH06-Coal	Coal	1.89	35.55	-5.5	Rock Type Ia. High Capacity Acid Forming
BH01-Overburden	Mud/Sandstone	3.92	7.89	0.0	Rock Type Ib. Lower Capacity Acid Forming
BH02-Overburden	Mud/Sandstone	3.00	20.82	-0.4	Rock Type Ia. High Capacity Acid Forming
BH04-Overburden	Mud/Sandstone	2.18	37.77	-1.2	Rock Type Ia. High Capacity Acid Forming
BH05-Overburden	Mud/Sandstone	1.99	55.58	-18.5	Rock Type Ia. High Capacity Acid Forming
BH06-Overburden	Mud/Sandstone	3.53	10.72	-1.4	Rock Type Ia. High Capacity Acid Forming

The Short-term leach test was conducted to determine the mobility of salts and metals in the coal and overburden samples. The pH of the overburden and coal samples ranges from acidic to neutral. Coal samples from BH05 and BH06 indicates pH of less than 5, this indicates acid producing reaction. Overburden samples shows slightly acidic to neutral pH. The relationship between pH and TDS of the Leachate is shown in figure it further shows that TDS increase with increase in acidity (Figure 7). Coal-2 in BH05 shows that at pH of 3.34 and TDS become 366 mg/L respectively. Furthermore, coal in BH01 shows that at pH 6.98 and TDS become and 30 mg/L. On average, coal samples will generate more salinity than the overburden samples. The main anions contributing to salinity is likely to be the SO_4^{2-} and NO^{3-} due to their concentrations in the different coal and overburden samples (Figure 8). SO_4^{2-} concentration in coal samples ranges from 5 - 248 mg/L whereas in overburden it ranges from 10 - 48 mg/L and NO^{3-} concentration in coal samples ranges from 0.1-2.14 mg/L whereas in overburden, it ranges from 0.28-1.71 mg/L. The Coal in BH05 have the highest concentration of SO_4^{2-} among coal samples as shown in Figure 8.

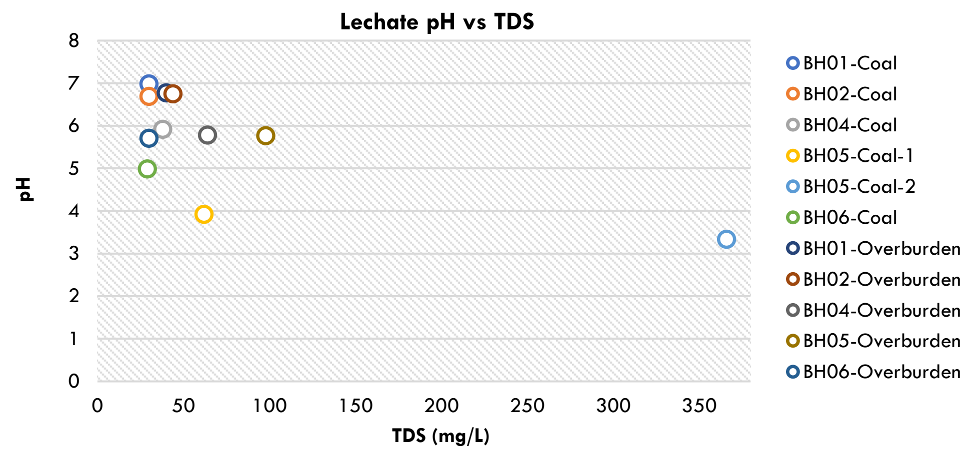


Figure 7. Leachate pH and TDS of the samples

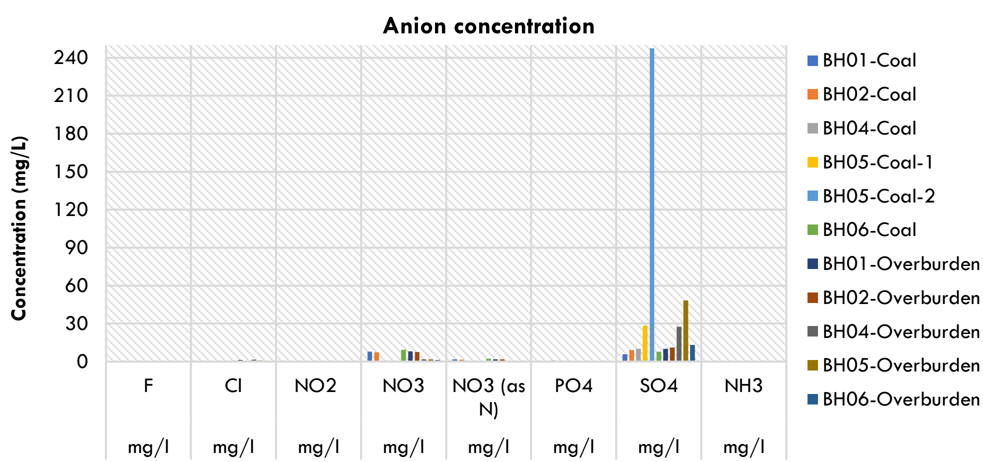


Figure 8. Anion concentration of the samples

4. Conclusions

This study shows that the coal and overburden samples are mainly composed of siliceous minerals such as quartz and kaolinite; followed by phyllosilicate minerals such as muscovite and microcline. Sulphide minerals such as pyrite and carbonates including dolomite, calcite and siderite occur in rare to minor phases in both coal samples and overburden samples. The overburden and coal samples are mostly composed of minerals that are inert and slow weathering or weak acid consuming mineral with enough acid forming mineral. Paste pH of overburden and coal samples ranges from slightly acidic to neutral. The coal and overburden show very high acid potential (AP) and coal shows higher AP than overburden. Because of the salinity associated with the acidity of the coal and overburden cations such as Na, K and Mg will be liberated and mobilized from the coal and overburden.

Acknowledgements: We appreciate the management of Bloekembos coal project for allowing this study and also the University of South Africa Masters bursary for funding this research, as well as the professional inputs from the Council for Geoscience.

References

1. Bell, F. G., Bullock, S. E.T., Hälbich, T. F. J., and Lindsay, P., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. International Journal of Coal Geology, 45, 195-216
2. McCarthy, T.S., 2011. Impacts of acid mine drainage in South Africa. South African Journal of Science, 107(5/6), Art. #712. DOI:10.4102/sajs. v107i5/6.712.
3. Zhao, B., Jacobs, P., and Schwegler, F., 2009. Geochemical assessment of the potential impact of Durban navigation colliery dumps on the environment, South Africa. International Mine Water Conference.
4. Pinetown, K. L., Ward, C. R., and van der Westhuizen, W. A., 2007. Quantitative evaluation of mineral in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage.
5. Kusuma, G. J., Shimada, H., Sasaoka, T., Matsui, K., Nugraha, C., Gautama, R. S. and Sulistianto, B., 2012. Physical and Geochemical characteristics of Coal mine overburden dump related to acid mine drainage generation. Memoirs of the faculty of engineering, Kyushu University
6. McCarthy, T.S. and Humphries, M. S., 2013. Contamination of the water supply to the town of Carolina, Mpumalanga, January 2012. South African journal of science, 109(9/10), Art. #2012-0112, 10. http://dx.doi.org/10.1590/sajs.2013/20120112
7. Skousen, J., Simmons, J., McDonald, L. M. and Ziemkiewicz, P., 2002. Acid-Base Accounting to predict post-mining drainage quality on Surface mines. Published in the Journal of environmental quality, 31,2034-2044.
8. Department of Water Affairs and Forestry, 2008. Best Practice Guideline G4: Impact Prediction (Pretoria, Department of Water Affairs and Forestry).
9. International Standard ISO 3082, 2009. Iron Ores-Sampling and sample preparation. ISO 3082: 2009. Fourth edition https://www.iso.org/obp/ui/#iso:std:iso:3082:en.
10. Mguni, N. G., 2015. Determination of hazardous trace elements in select Hwange, Zimbabwe coal samples with a comparison to select South African coal samples. MSc Thesis (unpublished), University of Witwatersrand, Johannesburg, South Africa.
11. Van Grieken, R.E. and Markowicz, A. A., 1993. Handbook of X-Ray spectrometry: Methods and Techniques. Marcel Dekker, Inc., New York.
12. Standards Australia, 1997: Australian standard leach procedure (ASLP).

Geochemical and isotopic compositions of the geothermal springs within Soutpansberg, Limpopo Province, South Africa

OS Durowoju[1]*, JO Odiyo[1] and GE Ekosse[2]

[1]Department of Hydrology and Water Resources, University of Venda, South Africa
[2]Directorate of Research and Innovation, University of Venda, South Africa
*Email of corresponding author: durotunde@gmail.com

Abstract

Limpopo Province has the highest number of geothermal springs, which were classified according to the residing mountains: Soutpansberg, Waterberg and Drakensberg. Mphephu, Sagole, Siloam and Tshipise geothermal springs fell within the Soutpansberg. This study was aimed at using the geochemical and isotopic compositions to understand the origin, age and geochemical processes controlling the water chemistry which could inform effective potential utilisation of the resources. Geochemical and isotopic ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{3}H$) analyses were undertaken, which was supported by conventional hydrogeological information. The dominant hydrochemical facies for geothermal springs within Soutpansberg were Na-Cl and Na-HCO_3. The reservoir temperature of these springs ranged between 95 – 185°C (Na-K geothermometer) indicating that most of the waters were mature water (not native). The isotopic composition of the springs ranged from −0.48‰ to −5.41‰ for $\delta^{18}O$, from −33.3‰ to −24‰ for $\delta^{2}H$, and from 0 to 1.6 TU for tritium. The $\delta^{2}H$ and $\delta^{18}O$ signatures revealed a significant infiltration before evaporation. This implied that the geothermal water originated from local rainfall with evidence of paleoclimate effect. Hence, geothermal springs water is a mixture of the rainwater and sea water. $\delta^{3}H$ values showed that the recent rainfall contributed more to the geothermal spring recharge particularly in summer compared to winter. The geothermal spring waters were not fit for drinking due to high fluoride content but could be used for direct heating in refrigeration, green-housing, spa, therapeutic uses, aquaculture, sericulture, concrete curing and coal washing.

Keyword: Geochemical process, hydrochemical facies, isotopic composition, Soutpansberg, Limpopo Province.

1. Introduction

Geothermal springs are natural geological phenomena which occur on all continents. They originate either from geologic platonic activity (volcanic origin) or from rainwater that percolates into the ground through permeable rocks or via conduits such as joints, faults and fracture zones in less permeable rocks (meteoric origin) [1]. South Africa is inclusively endowed with geothermal springs having about 78 known geothermal springs out of which Limpopo Province has about 30%. [2-3]. The geothermal springs in the Province were classified according to the residing mountain: Waterberg Group, Soutpansberg Group and Drakensberg Group [4]. The optimal utilisation of geothermal springs is largely dependent on their physical, geochemical, isotopic composition and the geological formation found at the depth of origin. Documentary and oral history reveal that geothermal springs were used for bathing, therapeutic, medicinal, religious, hygienic and social purposes across the world, for instance, India, Crete, Egypt, Turkey, Japan, Brazil and Canada [5-6].

Hydrogen and oxygen isotopes has proven to be ideal tracers of water system since they are incorporated in the water molecules and therefore their behaviour and variations reflect the origin, the hydrological and geochemical processes that affect natural water bodies [7]. These isotopes ($\delta^{18}O$, $\delta^{2}H$ and $\delta^{3}H$) with geochemical data are viable tools for understanding groundwater dynamics within the Soutpansberg because they provide critical information about sources of groundwater recharge, timing of recharge, water-rock interaction along flow paths, and mixing of distinct groundwater bodies [8]. This is despite the fact that groundwater is greatly affected by the geochemical processes occurring within the groundwater and interaction with the aquifer material leading to seasonal and spatial variations in the groundwater chemistry [9]. Hence, the geochemical characteristics of groundwater depend on the different geochemical processes and chemistry of water at the recharge area [10].

Some studies have been carried out on Limpopo geothermal springs ranging from hydrogeology, water quality and impacts on the surrounding soils and vegetation [11-18]. None of these studies elucidated the isotopic compositions in relation to the geochemical parameters of the geothermal springs. There is need to understand the groundwater system and chemical processes governing the resources such as sources, water types, and groundwater recharge, among others. The knowledge of the groundwater system and chemical processes will help to improve on the sustainability and development of the water resources within the locality. Already, some of the geothermal springs in Limpopo Province experience reduction in their yield and even dry up. For example, the hottest geothermal spring in the country found at Siloam village has dried up. Therefore, to avert these occurrences in the future such studies have to be undertaken to improve knowledge of the hydrogeological systems of the geothermal springs for effective sustainability of the resources.

2. Study Area

Mphephu and Siloam, Sagole, and Tshipise springs are located in Makhado, Mutale and Musina municipalities, respectively, in Vhembe District, Limpopo Province of South Africa (Figure 1). The study areas fall under quaternary catchments of the Nzhelele River catchment (within the Soutpansberg Group) which is in the northern region of Limpopo Province, South Africa [19]. The study areas are categorised under the hot semi-arid region with mean annual rainfall of Nzhelele ranges from 350-400 mm per annum [19]. More than 80% of the rainfall occurs in the summer and only about 20% occur in the winter [20]. The study areas are underlain by block-faulted Karoo Supergroup and Soutpansberg Supergroup rocks in the northern part of the Limpopo Province [15, 18]. These rocks have very low primary porosity, permeability and storage capacity, with limited groundwater flow [15, 18]. Groundwater occurrence is mainly related to secondary hydrogeological features; that is, faults and joints, which present preferential pathways and thus enhance the potential for groundwater flow in the region. The geology determines the extent to which the reaction with the host rock proceeds, depending on the chemical composition of the rock and the rate at which water passes through the rock.

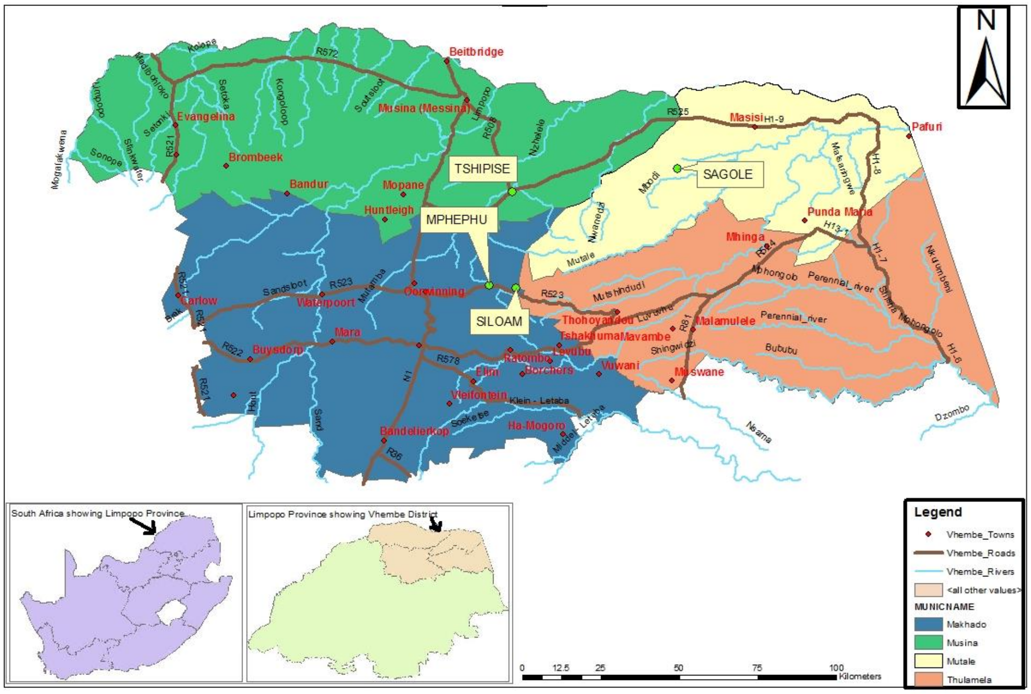


Figure 1. Map of study areas

3. Materials and Methods

Water samples were collected at the geothermal springs during winter (May – July 2016) and summer (October, 2016 – February, 2017) seasons. The samples were collected thrice per season to include seasonality variations (Yahaya et al., 2009). The geothermal water/borehole samples were collected at the source using acid-washed high-density polythene (HDPE) containers, chilled to between 3°C to 5°C (USEPA, 2004) and dispatched in a cooler box to Agricultural Research Council (ARC-ISCW) laboratory, Pretoria. The Samples were analysed for hydrochemical parameters in the laboratory using the standard recommended methods (APHA, 1998). The samples for anions (F^-, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, HCO_3^-) and major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) analyses were filtered and analysed using the Ion chromatography method (Dionex Model DX 500).

Stable isotopes analysis of the samples were performed using Thermo Delta V mass spectrometer connected to a Gasbench at Environmental Isotope Laboratory (EIL) iThemba LABS Johannesburg, South Africa. The water samples were equilibrated along with platinum (Pt) catalyst in preparation for deuterium measurements [21]. The equilibration time of the water samples with hydrogen gas was 40 minutes; whereas carbon dioxide gas was equilibrated with water samples in about twenty hours (20 hrs). Laboratory standards, calibrated against international reference materials, were analysed with each batch of the samples. The isotope ratios of $^2H/^1H$ and $^{18}O/^{16}O$ in the water samples were expressed as per mil (‰) deviation relative to the Standard Mean Ocean Water (SMOW) as follows:

$$\delta\ (‰) = \frac{R_{sampLe} - R_{smow}}{R_{smow}} \times 1000 \quad (1)$$

Where R represents the ratio of heavy to light isotopes (D/H or $^{18}O/^{16}O$) in the sample and standard respectively. The oxygen and hydrogen isotopic ratios were henceforth expressed individually as $\delta^{18}O$ and δD, respectively, or collectively as δ values. The enriched water samples from electrolytic processes were measured for tritium (^3H) using liquid scintillation counter. The samples were analysed in triplicate to obtain the mean values of the concentrations

The following empirical formulae were used to calculate the reservoir temperature of the geothermal system;

$$T\ (°C) = \frac{933}{0.993 + log\ (\frac{Na}{K})} - 273.15 \quad (2)$$

$$T\ (°C) = \frac{1217}{1.438 + log\ (\frac{Na}{K})} - 273.15 \quad (3)$$

$$T\ (°C) = \frac{1390}{1.75 + log\ (\frac{Na}{K})} - 273.15 \quad (4)$$

4. Results and Discussion

Hydrochemical parameters of the geothermal springs and hot boreholes were used to understand the geochemical processes governing their formation; prediction of sub-surface temperature using chemical geo-thermometers and assess suitability of the waters for domestic and irrigation purposes. Table 1 shows the results of the hydrochemical composition of the geothermal spring water and geothermal boreholes. Generally, the measured pH values range from 7.98 to 9.39 which implies that the waters are alkaline in nature. Most of the groundwater pH falls within recommended South African National Guidelines for Domestic Water Quality [20] values of 7-9 except for Siloam geothermal spring water (SAW) and Siloam hot borehole (SH2) having pHs of 9.39 and 9.19, respectively. The TDS values were generally less than 450 mg/l ranging from 120.84 to 423 mg/l for all the samples with a slight difference across seasons. Hence, the TDS values fall within the South African Guidelines for Domestic Water Quality [20] value of 450 mg/L. Although, previous studies showed that the TDS values for Tshipise geothermal spring was found in higher than 450 mg/L (Olivier et al. [15]; Durowoju et al. [18], this study recorded a lower value than then. This could be as a result of the decreased in water temperature (decreasing from 58°C to 55.4°C in this present study) of the spring in this present study.

The hydrochemical compositions of groundwater were not uniform but varied over a wide range. This implies that the groundwater compositions were heterogeneous in nature. This could be attributed to the underlying geology of the study areas [15]. The major water types are Na-Cl and $Na\text{-}HCO_3$ which are typical of marine and deep/deeper groundwaters which are influenced by the ion-exchange process (Figure 2). There is no variation in the water type with season for the studied geothermal spring/groundwater. The Na^+ and HCO_3^- ions were also present, making the water type fall under class C (temporary hard carbonate water) as reported by Olivier et al. [15]. Hence, the presence of Na+ in groundwater in the area was due to water-rock interaction as a result of oxidisation and evapotranspiration processes. These findings support the previous studies by Olivier et al. [15] and Durowoju et al. [18].

TABLE 1 Geochemical and isotopic compositions of the geothermal springs and boreholes within Soutpansberg

	SGW	SGS	TSW	TSS	MPW	MPS	SAW	SH1	SH2
Temp (°C)	42.4	44.8	54.6	55.4	41.3	42.7	67.7	45.2	48.4
Na-K(°C) Arnorsson	99.45	109.23	95.33	100.5	131.1	133.21	104.13	81.74	108.28
Na-K(°C) Fournier	139.53	148.69	135.65	140.51	168.91	170.85	143.92	122.75	147.81
Na-K(°C) Giggenbach	153.1	161.63	149.47	154.02	180.36	182.14	157.19	137.36	160.82
pH	8.82	7.98	8.46	8.47	8.05	8.15	9.39	8.86	9.19
SAR	33.88	19.20	25.75	25.45	2.07	2.18	7.39	17.25	19.04
EC (µS/cm)	330	347.33	746.67	745	335	365	340	630	330
TDS (mg/L)	133.13	196.70	377.48	390.61	124.38	120.84	215.18	305	130.12
Na (mg/L)	64.20	57.13	157.67	154.50	42.50	42.35	78.77	118	62.7
K (mg/L)	1.98	2.04	4.55	4.84	2.06	2.11	2.61	2.73	2.21
Ca (mg/L)	0.29	4.27	2.84	2.79	12.20	11.90	5.69	3.53	0.81
Mg (mg/L)	0.00	3.47	0.00	0.00	10.50	10.35	1.04	0±0.00	0
F (mg/L)	0.77	2.60	5.01	5.98	2.69	4.16	6.51	4.55	4.95
NO_3 (mg/L)	0.99	1.71	2.13	5.85	3.02	6.25	0.60	0.17	1.31
Cl (mg/L)	41.34	81.15	151.86	156.67	33.90	98.82	24.11	153.3	38.9
SO_4 (mg/L)	16.95	27.89	45.81	51.78	9.21	21.14	8.99	16.45	10.55
PO_4 (mg/L)	0.92	13.09	1.38	2.14	1.28	22.6	0.42	1.15	1.52
CO_3 (mg/L)	1.50	0.00	0.58	0.60	0.00	0.00	16.13	1.8	2.4
HCO_3 (mg/L)	9.76	7.93	12.38	11.90	15.25	7.32	98.75	8.54	9.76
$\delta^{18}O$ (‰)	-5.82	-5.08	-5.73	-4.98	-4.92	-4.82	-5.41	-5.34	-5.25
$\delta^{2}H$ (‰)	-30.7	-30.4	-33.5	-33.2	26.1	-24.6	-27.2	-27.14	-27.46
^{3}H (TU)	0.4	0.8	0.6	1.4	0.6	0.9	0.8	-	-

SGW-Sagole (Winter), SGW-Sagole (Summer), TSW-Tshipise (Winter), TSS-Tshipise (Summer), MPW-Mphephu (Winter), MPS-Mphephu (Summer), Siloam (geothermal spring), SH1- Siloam (Hot borehole), SH2-Siloam (Hot borehole).

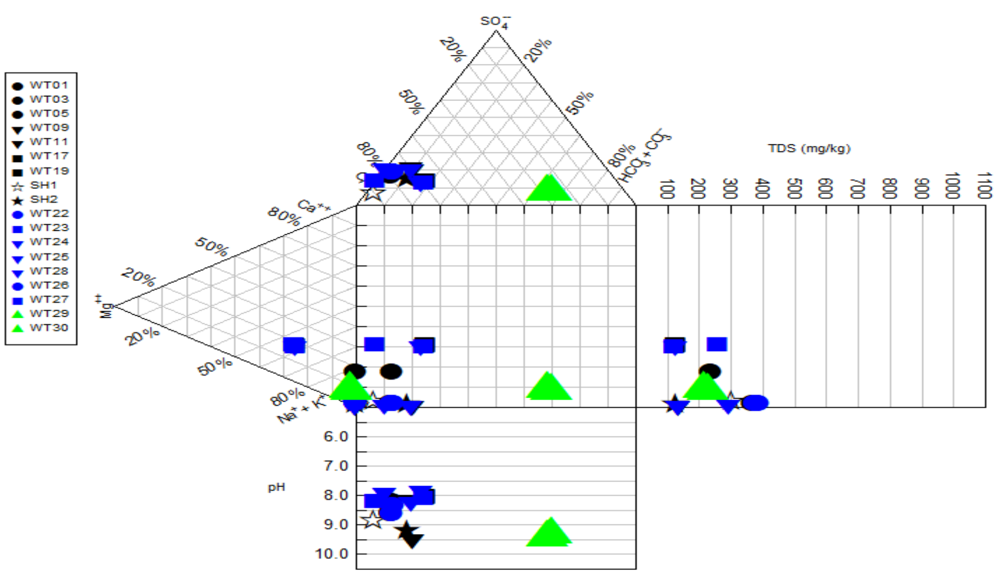


Figure 2. Durov diagram of geothermal springs and boreholes within Soutpansberg region.

The reservoir temperature of all the geothermal springs and boreholes within Soutpansberg regions were concentrated in the range between 80°C to 185°C from three Na-K geothermometer empirical formulae. This finding is relatively satisfied with the normal geothermal regime of earth's continental crust [25]. The variations of the reservoir temperature received by various Na-K thermometers empirical equations ranged within the stipulated temperatures above. Outcomes from Arnorsson's empirical formula gives the least temperatures compared to that of Fournier and Giggenbach. The results obtained from Fournier and Giggenbach's empirical formulae were close (±15°C) and hence, this study proposes the use of these formulae to complement one another. Information about water types and geothermometer of the springs and boreholes combined inferred that ratio of Na-K is dominated by percolation resulting to Na-Cl waters after partial or mixed equilibrium in large reservoirs.

$\delta^{18}O$ and $\delta^{2}H$ values were indicative of meteoric origin (Figure 3), which implies that rainfall is the fundamental source of these groundwaters. That is, the groundwater was derived from the infiltration of local precipitation with significant contribution of another type of water in the deeper part of the aquifer (sea water). That is, there is mixing of meteoric water with sea water. The measured tritium concentrations of the geothermal spring/boreholes are shown in Table 1. The tritium value ranged from 0.4 to 1.9 TU, which implied that the water fell on "submodern" (recharged before 1952) and "mixture of the submodern and modern" (recharged before 1952 and after 1952). This variation of the tritium concentrations in the aquifer indicates two types of water;

i. Old (submodern) deep water circulating with less or no influence by the modern recharge (deep aquifer) and;
ii. Water near the surface made of modern recharge (shallow aquifer).

This study showed the existence of two water types; groundwater recharged by present day meteoric water (rainwater) with a higher tritium concentration in the summer (wet) and older groundwater in deeper parts of the aquifer system with lower tritium concentrations. In summer, evidence of modern rainfall was prominent in this study in all the geothermal springs, resulting to a mixture of submodern and modern waters.

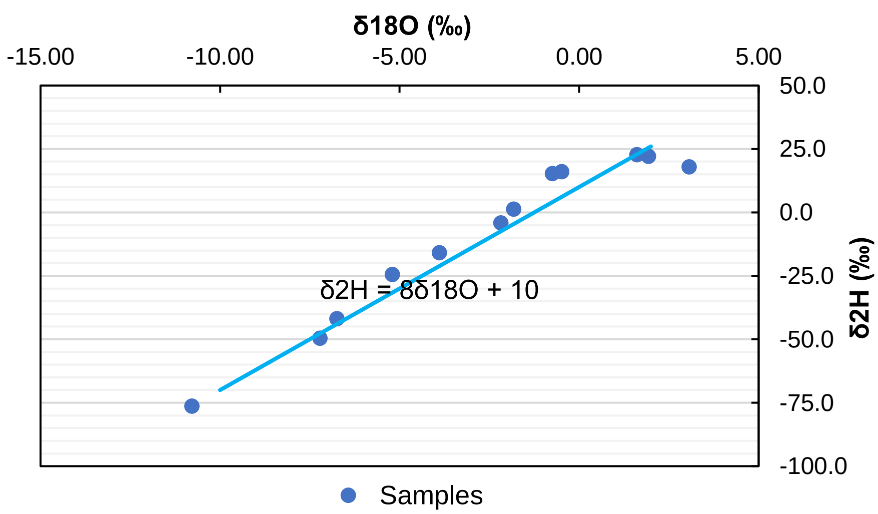


Figure 3. Plot of $\delta^{18}O$ against $\delta^{2}H$

4. Conclusion

Generally, the geothermal spring waters/boreholes are not fit for drinking due to high fluoride content. But these waters could be used for direct heating in refrigeration, green-housing, spa, therapeutic uses, aquaculture, sericulture, concrete curing and coal washing. The δD and $\delta^{18}O$ values of the geothermal spring water/boreholes confirm that the waters are of meteoric origin, which implies that rainfall is the fundamental component of these groundwaters. The geothermal springs have higher tritium values in summer compared to winter season. This implies that the geothermal springs were recharged before 1952 (submodern) for winter and recharged before and after 1952 (Mixture of modern and submodern) for the summer season. This is an indication that the present rainfall contributes more to the geothermal spring recharge, particularly in summer compared to winter.

Reference

1. La Moreaux, P.E and Tanner, J.T. (2001). Springs and Bottled Waters of the World, Ancient History, Source, Occurrence, Quality and Use, Springer: Berlin.
2. Kent, L.E. (1969). The Thermal Waters in the Republic of South Africa, International Geological Congress, Report of the Twenty-Third session, Czechoslovakia, Proceedings of Symposium II, Mineral and Thermal Waters of the world-Overseas countries, 19, 143-164.
3. Olivier, J., Venter, J.S. and Van Niekerk., H.J. (2010). Physical and Chemical Characteristics of Thermal Springs in Limpopo Province, South Africa, proceedings of World Geothermal Congress 2010, Bali, Indonesia, pp. 13.
4. Durowoju, O.S., Odiyo, J.O. and Ekosse, G.E. (2015). Hydrogeochemical setting of geothermal springs in Limpopo Province, South Africa - A Review. Res. J. Chem. Environ., 19, 77–88.
5. Van Vuuren K. (1990). Die Warmwaterbronne van Suidwes-Kaapland: HulleVerbreiding, Eienskappe en Benutting. B.A. Honours dissertation, University of Stellenbosch, South Africa
6. Lund, J.W. (2000). Balneological use of thermal water in the USA, GHC Bulletin, September, pp. 31-34.
7. Gonfiantini, R. (1998). On the Isotopic Composition of Precipitation. Hydrologie et Geochimie Isotopique In: Causse, C., Gasse, F. (Eds) 1998. Proc. Int. Symposium in memory of J.-Ch.Fontes, Paris, June 1995,ORSTOM, Paris.pp.3-2
8. Fawzia, M.A and Mohamed, S. (2004). Hydrochemical Processes and Environmental Isotopic Study of Groundwater in Kuwait, Water International, 29:2, 158-166, DOI: 10.1080/02508060408691765
9. Rajmohan N and Elango L. (2004). Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. Environmental Geology 46: 47-61DOI 10.1007/s00254-004-1012-5
10. Ako, A.A., Shimada, J., Ichiyanagi, K., Koike, K., Hosono, T., Eyong, G.E.T., Iskandar, I. (2010). Isotope hydrology and hydrochemistry of water resources in the banana plain (mungo-division) of the Cameroon Volcanic line, Journal of Env. Hydrology, 18(4), 1-20
11. Kent, L.E. (1948). The warm springs of Loubad, near Nylstroom, Transvaal. Trans. Royal Soc. South Afr. 31:151-168
12. Kent LE and Russell HD. (1950). The warm spring of Buffelshoek, near Thabazimbi, Transvaal. Trans. Royal Soc. S. Afr. 32:161-175
13. Mazor, E. and Verhagen, B.Th. (1983). Dissolved ions, stable and radioactive isotopes and noble gases in thermal waters of South Africa. J. of Hydrol. 63, 315-329.
14. Olivier, J., Van Niekerk, H.J. and Van Der Walt, I.J. (2008). Physical and chemical characteristics of thermal springs in the Waterberg area of Limpopo Province, South Africa. Water SA, 34 (2), 163-174.
15. Olivier, J., Venter, J.S. and Jonker, C.Z. (2011). Thermal and Chemical Characteristics of Thermal Springs in the Northern Part of the Limpopo Province, South Africa. Water SA, 34, 163–174.
16. Durowoju, O.S, Odiyo, J.O., and Ekosse, G.E. (2016a). Variations of heavy metals from geothermal spring to surrounding soil and *Mangifera indica*-Siloam Village, Limpopo Province, *Sustainability*, 8, 60; doi:10.3390/su8010060
17. Durowoju, O.S, Odiyo, J.O., and Ekosse, G.E. (2016b). Horizontal variation in trace elements and soil characteristics at Siloam and Tshipise geothermal springs, Limpopo Province, South Africa, *Water SA*, 42(4), 694-702.
18. Durowoju, O.S, Odiyo, J.O. and Ekosse, G.E. (2018). Geochemistry of Siloam and Tshipise Geothermal Springs, Limpopo Province, South Africa, *American J. of Environmental Sciences*, DOI: 10.3844/ajessp.2018.

19. Makungo, R., Odiyo, J.O., Ndiritu, J.G. and Mwaka, B. (2010). Rainfall–runoff modelling approach for ungauged catchments: A case study of Nzhelele River sub-quaternary catchment.
20. Department of Water Affairs and Forestry (DWAF) (2001). Luvuvhu/Letaba Water Management Area: Water resource situation assessment report NO P0200/00/030/. WSM (pty) Ltd.
21. Dolnikowski GG. (1995). A New Sample Preparation Method for Isotope Ratio Mass Spectrometry of 2H-Enriched Samples Generated by the Doubly Labeled Water Method. Obesity, DOI: 10.1002/j.1550-8528.1995.tb00010.x
22. Arnorsson, S., Gunnlaugsson, E. and Svavarsson, H. (1983). The chemistry of geothermal waters in Iceland III. Chemical geothermometry in geothermal investigations. Geochim. Cosmochim. Acta, 47, 567-577
23. Fournier, R.O. (1979): A revised equation for the Na/K geothermometer. Geothermal Resources Council Transactions. Volume 3, 221-224.
24. Giggenbach, W.F. (1988). Geothermal solute equilibria. Geochimica. Cosmochim. Acta, 52, 2749 - 2765.
25. Doan, V., Tran Anh, V. and Nguyen, T.T. (2014). Geochemical Characteristics of Geothermal Hot Water Sources on the Territory of Vietnam, Proceedings, Thirty Eighth Workshop on Geothermal Reservoir Engineering Stanford University, Stanford, California, February 24-26, SGP-TR-202

Hydrogeochemical characteristics and groundwater quality of the Shingwedzi and Mphongolo River Basins in Kruger National Park, Limpopo Province, South Africa

JO Odiyo*, F Ramusiya and N Bukalo

School of Environmental Sciences, University of Venda, South Africa
*Email of corresponding author: John.Odiyo@univen.ac.za

Abstract
A study has been carried out to characterise the groundwater chemistry in order to determine the type of water and confirm the suitability of groundwater quality for human and livestock or game utilisation. Groundwater in the Kruger National Park (KNP) generally occurs in the fractured gneiss, basalt, gabbro, schist, diabase and sandstone, dolerite-conglomerate, and also limestone rhyolite. Characterisation of the aquifers along the Shingwedzi and Mphongolo River Basins requires an understanding of the spatial and temporal variations of the hydrogeochemical parameters of the area. Analyses for major ions (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and HCO_3^{-}) were carried out using inductively coupled plasma - optical emission spectrometry. Physico-chemical parameters such as EC, pH and alkalinity were also determined using portable EC, pH and alkalinity meters. The results were compared to the South African National standards for drinking water 241 and South African water quality guidelines for livestock (or game) waterlog for domestic and game purposes, respectively. Groundwater in the study area is characterised as Na^{2+}-K^{+}-HCO_3^{-} and Na^{2+}-K^{+}-Cl^{-}-SO_4^{2-} water types, dominated by sodium from alluvial clay materials in alluvial aquifers, basalt aquifers and also from the weathering of granite. Surface water in the study area is characterised as Ca^{2+}-Mg^{2+}-HCO_3^{-} water type. Water quality is suitable for domestic and game use even though some of the elements (chloride and sodium) have concentrations above the guidelines, though not harmful to human and game health. Shingwedzi River and the granite quarry waters are also suitable for both domestic and livestock (or game) watering. The low concentration of TDS makes the water to be classified as fresh water. Generally, groundwater quality along the Shingwedzi and Mphongolo River basins has been classified as good quality water.

Keywords: Groundwater quality, human and game health, hydrogeochemical parameters, Kruger National Park, water type

1. Introduction
Hydrogeochemical characterisation reveals the quality of water that is suitable for its different purposes [1]; as reactions between groundwater and aquifer constituent minerals have a significant role on water quality [2]. Several factors control the chemical composition of groundwater. These include the composition of precipitation, the general geology and the degree of chemical weathering of the various rock types, aquifer's characteristics, climate and topography [3]. These factors all combine to create diverse water types and a complex groundwater quality that change temporally and spatially [3,4].

Water resources in South Africa are significantly affected by climate change, which causes scarcity of rainfall and makes the country a dry and drought prone country. South Africa in general, and Limpopo in particular, therefore rely on groundwater. This water is mainly used for irrigation, rural domestic supply, municipal supply, mining and livestock needs [5]. However, over 80% of the aquifer systems in South Africa have relatively low storage capacities and hydraulic conductivities, due to the nature of its geology [6]. Bearing in mind that groundwater quality is fundamental to groundwater resource management, determining hydrogeochemical characteristics and groundwater quality of the Shingwedzi and Mphongolo River Basins in Kruger National Park is crucial.

Kruger National Park is an enormous nature reserve stretching 350 Km along the Mozambican border and is 60 km wide on average [7]. Groundwater in KNP generally occurs in fractured gneiss of the Goudplaats Formation, basalts, gabbro, schist, diabase and sandstone, sandstone, dolerite-conglomerate, limestone and rhyolite. Groundwater, in some cases, also occurs in gneiss-schist contacts and in alluvial materials to a limited extent [8, 9]. The Quaternary Formations composed of alluvium sand, gravel and volcanic rocks are also present along the Shingwedzi, Mphongolo, Bububu, and also the Phugwane river basins. Alluvial aquifers along the lower reaches of Shingwedzi and Mphongolo rivers are of limited extent and of local importance [10] in supporting both the ecosystem and human consumptions.

Characterisation of the aquifers along the Shingwedzi and Mphongolo River Basins requires an understanding of the hydrogeochemical parameters of the area. This generally includes spatial and seasonal variations of groundwater quality and availability. Therefore, the objective of this study was to characterise the groundwater chemistry in order to: (i) determine the water type, and (ii) confirm the suitability of groundwater quality for human utilisation.

2. Study area

The study area is situated within the northern part of the Kruger National Park (KNP); about 60 km south of the Punda Maria gate and about 100 km northeast of the Phalaborwa gate. It is located within latitudes 23°00', 23°30'E and longitudes 31°00', 31°30'S. The area falls within the low-veld groundwater region in South Africa [11], within the Shingwedzi catchment area of the KNP. It is a semi-arid region, dominated by cool dry season (winter) from June to August, warm dry season (spring) from September to November, warm wet season (summer) from December to February and autumn from March to May [12]. Rainfall normally occurs in summer, with the mean annual precipitation between 400-600 mm [13], and little rainfall between March and April (autumn).

The study area is drained by two major rivers, the Shingwedzi River and Mphongolo River. The Mphongolo River drains from the north western side to the south eastern side before it joins the Shingwedzi River, which flows past the Shingwedzi Rest Camp. The Shingwedzi River drains the area from the west, flowing to the eastern part of the Shingwedzi Rest Camp. The Bububu and Phugwane Rivers are the two tributaries within the area. The Bububu River discharges water into the Shingwedzi River, while the Phugwane River discharges water into the Mphongolo River. During the dry season (May to October), some of these river courses tend to contract into strings of pools while during the rainy season, these rivers flow as a result of rainfall.

3. Geology of the study area

The geology of the study area is dominated by the Karoo Supergroup (Letaba Formation), the Basic Complex of the Goudplaats gneiss and the Gravelotte Group within the Goudplaats gneiss and also undifferentiated materials. The Goudplaats gneiss lies between the Mphongolo River and the Murchison greenstone belt [14]. The Timbavati gabbro comprises of maffic to ultramafic rocks that intrude the various older granites and gneiss. The Letaba Formation which occurs in the eastern part of the KNP consists of extrusive mafic volcanic rocks which rest comfortably on the Clarens Formation [14]. The basalts are considered to represent flood basalts that extruded along fissures associated with the fragmentation of the Gondwanaland. Venter [15] indicated that the Letaba basalts (olivine rich) area easily weathered and have formed large dark clays, which generally contain an excessive amount of calcium carbonate. In some places, cementation of soil particles have been sufficient as to form continuous layers of hardpan calcrete. The Clarens Formation within the area consists of a fine grained, pink argillaceous sandstone, containing irregular patches of cream coloured sandstone [14]. Recent Quaternary alluvial materials, including alluvium sand, river terrace gravel, and high terrace gravel, are found along the Mphongolo, Shingwedzi, Bububu, and Phugwane river basins [8,11].

4. Materials and Method

Groundwater samples were collected using a hand bailer. Before sampling, each borehole was subjected to purging using a 1-litre hand bailer. Borehole purging was done in order to remove stagnant water in the borehole casing prior to sampling so as to obtain representative sample of *in-situ* groundwater. Purging was performed by inserting a bailer in the boreholes and removing water several times (for a minimum of 10 times) until the stabilisation of Electrical Conductivity (EC) and temperature (T) was achieved; a sample was then taken. pH, EC and temperature were measured *in situ* in the field during sampling of each borehole using portable EC, pH and alkalinity meters. These parameters are the main source of salinity in groundwater and they determine the general character of the water [16]. The bailed water was transferred into a sample bottle and placed in a cooler bag with ice pack.

Water samples were submitted to the Council for Scientific and Industrial Research (CSIR) laboratory for analysis of major ions (Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}) employing inductively coupled plasma - optical emission spectrometry (ICP-OES). Some of the boreholes are located closer to the Shingwedzi Rest camp (Fig. 1). Hence, results obtained were compared to the [17] for domestic purposes and livestock (or game) watering. Since there are no game watering standards available, the DWAF livestock watering guidelines were used for game watering. Groundwater Chart 1.23.3.0 was used to draw Piper's trilinear diagram to determine the different hydrochemical facies in the area. This was used to characterise the type of water within the Shingwedzi and Mphongolo River Basins.

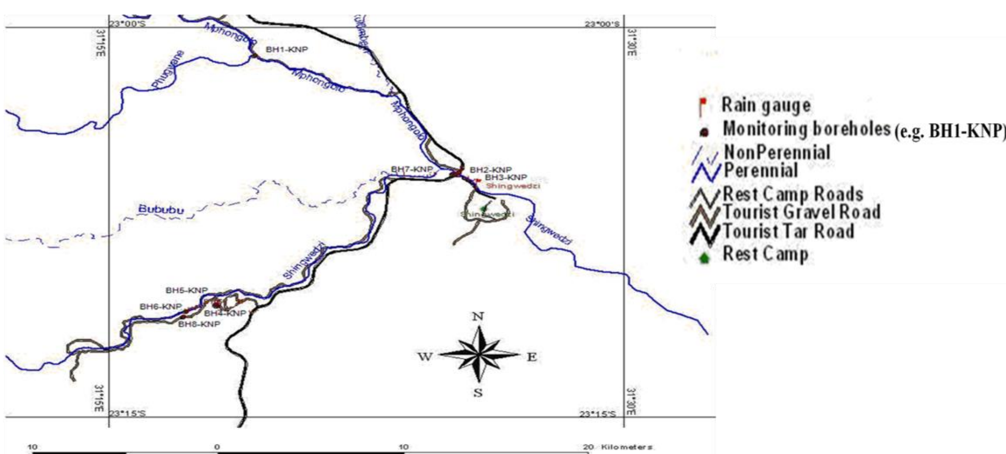


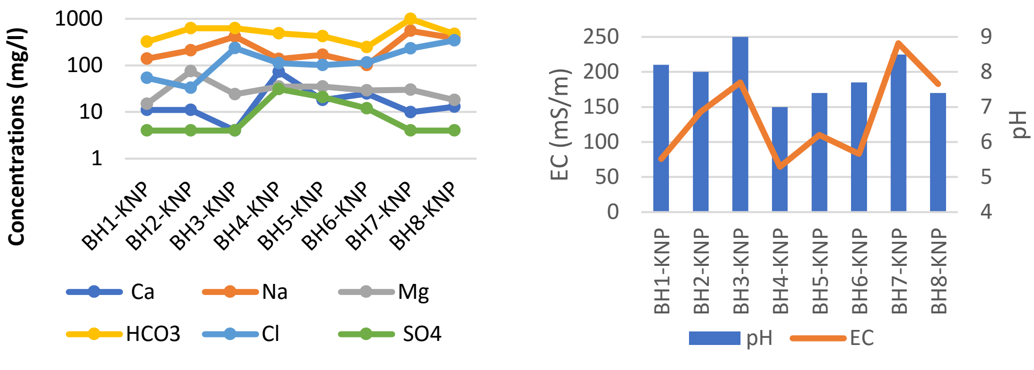
Figure 1. Location of boreholes and rainfall station along the Shingwedzi and Mphongolo River Basins.

5. Results

The first sampling exercise occurred in February 2005, which is the end of the summer season, the second occurred in April 2005, and the third (final) occurred in March 2006. The chemical and physico-chemical characteristics of water at each sampling point for the three sampling exercises are presented in Table 1 and plotted in Figures 2-4. HCO_3^- is largely the most dominant anion, varying from 248-991 mg/*l*, 140-702 mg/*l* and 48-1022 mg/*l* for February 2005, April 2005 and March 2006, respectively. While Na^+ is the most dominant cation for the three periods with concentrations ranging from 101-548 mg/*l*, 57-311 mg/*l* and 11-511 mg/*l*. The pH ranged from 7-9 in February 2005, 7.7-8.9 in April 2005 and 6.9-8.5 in March 2006 while EC ranged from 64.6-241 mS/m, 33.5-147 mS/m and 20.3-245 mS/m for the same periods respectively.

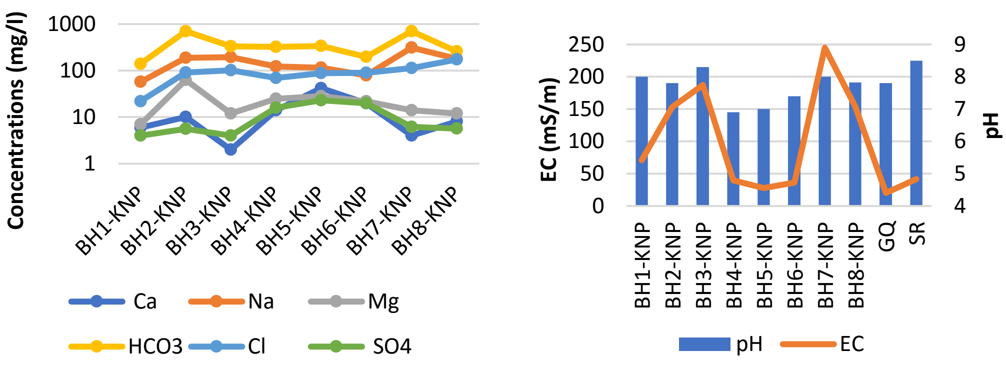
TABLE 1. Physico-chemical and chemical parameters of studied groundwater and surface water samples

Sample Id	Sample exercise	Parameters								
		Alkalinity	EC (mS/m)	pH	$CaCO_3^{2-}$ (mg/l)	Ca^{2+} (mg/l)	Cl^- (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	SO_4^{2-} (mg/l)
BH1-KNP	*Feb-05*	329	76	8.2	324	11	54	15	140	<5
	Apr-05	141	33.5	8	140	6	22	7	57	<5
	Mar-06	304	71.1	8	301	9	56	16	125	<5
BH2-KNP	*Feb-05*	634	143	8	628	11	33	75	211	<5
	Apr-05	710	128	8.3	696	10	91	63	189	5.6
	Mar-06	630	153	7.8	626	12	748	72	216	7
BH3-KNP	*Feb-05*	678	185	9	622	4	235	24	417	<5
	Apr-05	358	96.1	8.9	335	2	102	12	195	<5
	Mar-06	638	187	8.3	627	7	269	39	316	<5
BH4-KNP	*Feb-05*	484	64.6	7	484	73	111	35	138	31
	Apr-05	326	79.7	8	323	14	69	25	123	16
	Mar-06	141	39.6	6.9	141	21	34	9	32	14
BH5-KNP	*Feb-05*	423	110	7.4	422	18	102	35	169	21
	Apr-05	340	93.3	7.8	338	42	88	28	116	23
	Mar-06	48	27.9	7	48	2	26	6	29	23
	Feb-05	249	82.9	7.7	248	25	116	29	101	12
BH6-KNP	*Apr-05*	197	65.1	7.7	196	20	89	22	79	20
	Mar-06	130	36.2	7.4	130	10	38	11	42	<5
BH7-KNP	*Feb-05*	1023	241	8.5	991	9.9	233	30	548	<5
	Apr-05	720	147	8.4	702	4	114	14	311	6.2
	Mar-06	1033	245	8	1022	9	250	28	511	<5
	Feb-05	475	183	7.4	474	13	344	18	385	<5
BH8-KNP	*Apr-05*	261	98.7	8.2	257	8	173	12	179	5.7
	Mar-06	468	154	7.8261	465	22	245	34	261	21
Granite Quarry (GQ)	*Mar-06*	86	20.3	7.8	85	18	8	5	11	6.4
Shingwe dzi River (SR)	*Mar-06*	164	41.9	8.5	159	22	38	14	40	<5



(a) (b)

Figure 2. Chemical and physico-chemical characteristics of water at each sampling point in February 2005



(a) (b)

Figure 4. Chemical and physico-chemical characteristics of water at each sampling point in March 2006

Sodium and bicarbonate are the most dominant ions in groundwater of the Shingwedzi and Mphongolo River basins. Surface water and groundwater from the Shingwedzi and Mphongolo river basins are mainly rich in calcium, sodium, magnesium, bicarbonate and chloride. Sodium, calcium and magnesium are likely to have resulted from the weathering of granitic and basaltic rocks in the study area, which eventually resulted in the formation of the clays.

Figure 5 shows the correlation between EC and the major cations and between Na^+ and Mg^{2+}. The highest correlation coefficient is between Na^+ and EC (0.97). Mg^{2+} and EC have a correlation coefficient of 0.47; while there is almost no relationship between EC and Ca^{2+} ($r^2 = 0.04$). There is also a weak positive correlation between Mg^{2+} and Na^+. From the correlation coefficients between EC and the major cations, it shows that Na^+ and Mg^{2+}greatly contribute to the salinity of groundwater in the area. The weak, though positive correlation between Mg^{2+} and Na^+ shows that there is no evidence of cation exchange between sodium and magnesium.

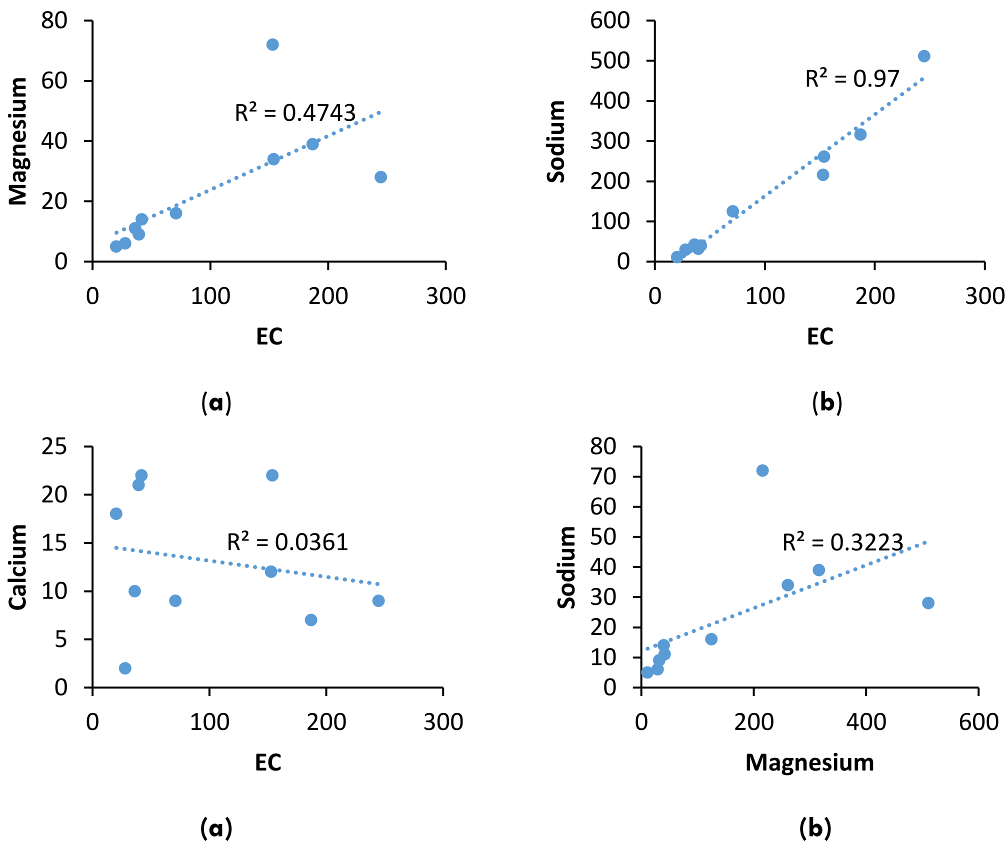


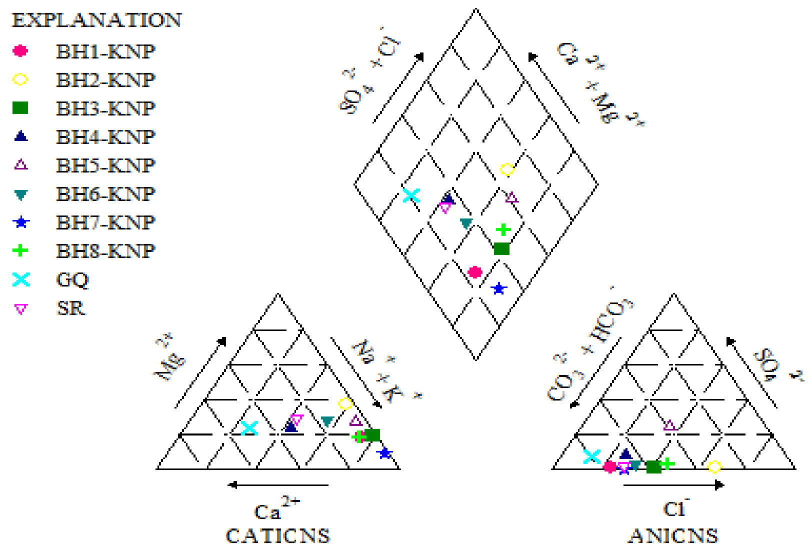
Figure 5. Correlations between a) Mg^{2+} and EC, b) Na^{+} and EC, c) Ca^{2+} and EC, and d) Na^{+} and Mg^{2+}

The major ionic composition of the water samples (in %-meq/l) is visualised using a Piper plot (Figure 6). The hydro-chemical data show that groundwater in the study area falls within two hydrochemical water types, namely, the Na-Mg-HCO_3-Cl and Na- HCO_3-Cl water types (Table 2). The major ionic composition of the water samples (in %-meq/l) is visualised using a Piper plot (Figure 6). The hydro-chemical data show that groundwater in the study area mainly falls within two hydrochemical water types, namely, the Na^{2+}-K^{+}-HCO_3^{-} and Na^{2+}-K^{+}-Cl^{-}-SO_4^{2-} water types (Table 2). Alluvial aquifer boreholes (BH3-KNP, BH6-KNP and BH7-KNP) are dominated by Na^{2+}-K^{+}-HCO_3^{2-} water type. These boreholes are situated at approximately 100 m away from each other. Surface waters are made up of a Ca^{2+}-Mg^{2+}-HCO_3^{-} water type.

The average groundwater quality laboratory analysis values for each parameter analysed from each borehole in the Shingwedzi and Mphogolo river basins were compared to the South African National Standards [17] and to the South African Water Quality Guidelines (SAWQG) for stock watering use in order to assess the suitability of groundwater quality use in KNP.

The water quality results for the samples collected at BH1-KNP, BH4-KNP, BH5-KNP, BH6-KNP, as well as the surface water samples collected at the Granite Quarry next to

BH4-KNP and BH5-KNP and at Shingwedzi river (near BH2-KNP, BH3-KNP and BH7-KNP) fall within Class I of [17] standards. Employing the same standard, water from BH2-KNP, BH3-KNP and BH8-KNP fall within Class I and Class II. The elevated EC (BH3-KNP and BH7-KNP), chloride (BH3-KNP and BH8-KNP) and sodium (BH2-KNP, BH3-KNP and BH8-KNP) are within Class II of the SANS 241standards [17]. The water quality results of BH7-KNP fall within Classes I, II and outside the SANS 241 [17]. The result falling outside the SANS 241[17] recommended class is due to high concentration of sodium (456.7 mg/l).



Key: SR- Shingwedzi River Water, GQ – Granite Quarry Water

Figure 6. Mphongolo and Shingwedzi hydrochemistry Piper diagram

TABLE 2. Groundwater types summary at the Shingwedzi and Mphongolo River Basins

Borehole Number	Groundwater Type (March 2006)	Geology (Aquifer)
BH1-KNP	Na^{2+}-K^{+}-HCO_3^{-}	Basalt
BH2-KNP	Na^{2+}-K^{+}-Cl^{-}–SO_4^{2-}	Basalt
BH3-KNP	Na^{2+}-K^{+}-HCO_3^{-}	Alluvium
BH4-KNP	Ca^{2+}-Mg^{2+}-HCO_3^{-}	Granite-Gneiss
BH5-KNP	Na^{2+}-K^{+}-Cl^{-}–SO_4^{2-}	Granite
BH6-KNP	Na^{2+}-K^{+}-HCO_3^{-}	Alluvium
BH7-KNP	Na^{2+}-K^{+}-HCO_3^{-}	Alluvium
BH8-KNP	Na^{2+}-K^{+}-HCO_3^{-}	Granite
Granite Quarry	Ca^{2+}-Mg^{2+}-HCO_3^{-}	n/a (Surface Water)
Shingwedzi River	Ca^{2+}-Mg^{2+}-HCO_3^{-}	n/a (Surface Water)

The surface water at the Granite Quarry was compared to that of the nearby boreholes water at BH4-KNP and BH5-KNP, while the surface water at the Shingwedzi River was compared to that of nearby boreholes BH2-KNP, BH3-KNP and BH7-KNP. The results

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

show that the water quality of the Granite Quarry and that of boreholes BH4-KNP and BH5-KNP belong to Class I, though the values of the measured parameters are much higher in the boreholes (Table 3). However, for Shingwedzi River, the water quality is in Class I while that of the boreholes falls in Classes I and II and outside SANS 241 [17], indicating that the borehole water has some elevated geochemical parameters. These are interesting results indicating that surface water from Shingwedzi River flowing through Kruger National Park has safe levels of the measured chemical parameters, while groundwater has elevated concentrations in some of the parameters signifying geochemical pollution.

The electrical conductivity is elevated at BH3-KNP (156.03 mS/m) and BH7-KNP (211.00 mS/m) (Table 3), which are above the recommended livestock water use [18]. The estimated TDS of the quality of water in the area is within the range of 0-1000 mg/l, and hence the water in the study area is characterised as fresh water. The higher EC values at BH3-KNP and BH7-KNP, located within 100 m from each other, may be associated with the distance away from the stream, probably indicating a longer residence time as compared to the relatively low EC values at BH6-KNP and BH1-KNP that are located approximately 30 m away from the river.

TABLE 3. Average groundwater quality analysis results compared to the South African National Standards [17] and [18] livestock watering

Parameters	EC (mS/m)	TDS (mg/L)	pH	Ca^{2+} (mg/L)	Cl^{-}(mg/L)	Mg^{2+}(mg/L)	Na^{+}(mg/L)	SO_4^{2-} (mg/L)
SANS 241 (2005)	**Class I (recommended operational limit)**							
	< 150	< 1 000	5.0 – 9.5	< 150	< 200	< 70	< 200	< 400
	Class II (max. allowable for limited duration)							
	150 – 370	1000 – 2400	4.0 – 10.0	150 – 300	200 – 600	70 – 100	200 – 400	400 – 600
	Class II water consumption period							
	7 years	7 years	None	7 years	1 Year	7 years	7 years	7 years
DWAF (1996) - Livestock Watering (SAWQG)	0 – 150	0 – 1000	NS	0 – 100	NS	0 - 500	0 – 2000	0 – 1000
BH1-KNP	60.4	39.26	8.2	8.67	44	12.67	107.33	<5
BH2-KNP	141.33	91.86	8.05	11	90.67	70	205.33	5.3
BH3-KNP	156.03	101.42	8.6	4.33	202	25	324.33	<5
BH4-KNP	59.65	38.77	6.9	36	71.33	23	97.67	20.33
BH5-KNP	77.07	50.09	7.6	20.67	72	23	104.67	22.33
BH6-KNP	61.4	39.91	7.6	18.33	81	20.67	74	12.33
BH7-KNP	211	137.2	8.45	7.63	199	24	456.7	5.4
BH8-KNP	145.23	94.39	7.8	14.33	254	21.33	275	10.57
Granite Quarry	20.3	13.19	7.8	18	8	5	11	6.4
Shingwedzi River Water	41.9	27.23	8.5	22	38	14	40	<5

6. Discussion

Leyland *et al.* [19] conducted a study in the KNP and indicated that the increased Na concentration can be assigned to the Karoo lava. Most of the boreholes were drilled in or through alluvial materials, which are dominated by clay. High sodium in both groundwater and surface water at KNP could also be due to salt-affected soils of the KNP, which form distinct patches in the landscape [20]; and from groundwater-surface water interactions.

The bicarbonate dominance suggests recently recharged water, resulting in intense silicate weathering and favouring mineral dissolution [21]. A general reaction for the weathering of silicate rocks with carbonic acid is: (Cations) silicates + H_2CO_3 = H_4SiO_4 + HCO_3^- + cations + solid products (mostly clays) [22].

The source of calcium ion could be attributed to the presence of calcrete in alluvial materials along the Mphongolo and Shingwedzi River basins. The main source of chloride in groundwater in the study area could be a result of erosion and weathering of granites, having sodalite, apatite, mica and hornblende in the rock matrix [23]. The major source of magnesium in groundwater could be ion exchange of minerals in rocks and soils by water [23]; while low potassium concentrations might be due to the resistance to weathering of potassium-bearing minerals and its fixation in the formation of clay minerals [22]. Though some boreholes in the study area are characterised by Na^{2+}-K^+-Cl^--SO_4^{2-} water type, the source of Cl in the area is not known. du Toit [9] indicated that high chloride concentration shows that it is old water, which is probably caught up with the sediments during deposition.

7. Conclusion

Groundwater in the study area is characterised as Na^{2+}-K^+-HCO_3^- and Na^{2+}-K^+-Cl^--SO_4^{2-} water types, dominated by sodium which is assigned to alluvial clay materials in alluvial aquifers and basalt aquifers and also from weathered granite materials (mica). Surface water in the study area is characterised as Ca^{2+}-Mg^{2+}-HCO_3^- water type. Water quality in the area is suitable for domestic use even though some of the elements (chloride and sodium) have concentrations above the guidelines, though not harmful to human and game health, except groundwater in borehole BH7-KNP that might be slightly harmful to human and game health, if sodium is not managed. Shingwedzi River and the granite quarry waters are also suitable for both domestic and livestock (game) watering. The low concentration of TDS makes the water to be classified as fresh water. Generally, groundwater quality along the Shingwedzi and Mphongolo river basins is of good quality.

Acknowledgments: The authors are grateful to CSIR through Christine Colvin for funding this research through a Water Research Commission Research Project.

References

1. Prasad, D.S.R.; Sadashivaiah, C.; Rangnna, G. Hydrochemical characteristics and evaluation of groundwater quality of Tumkur Amanikere Lake watershed, Karnataka, India. *E-journal of Chemistry* 2009, *6* (S1), S211-S218.
2. Nagaraju, A.; Sreedhar, Y.; Kumar, K.S.; Thejaswi, A.; Sharifi, Z. Assessment of Groundwater Quality and Evolution of Hydrochemical Facies around Tummalapalle Area, Cuddapah District, Andhra Pradesh, South India. *Journal of Environmental Analytical Chemistry* 2014, *1*, 1-6.
3. Hussein, M.T. Hydrochemical evaluation of groundwater in the Blue Nile Basin, eastern Sudan, using conventional and multivariate techniques. *Hydrogeology Journal* 2004, *12*, 144-158.
4. Ganyaglo, S.Y.; Banoeng-Yakubo, B.; Osae, S.; Dampare, S.B.; Fianko, J.R.; Bhuiyan, M.A., Hydrochemical and isotopic characterisation of groundwaters in the Eastern Region of Ghana. *J. Water Resource and Protection* 2010, *2*, 199-208.
5. Busari, O. Groundwater in the Limpopo Basin: occurrence, use and impact. *Environment Development and Sustainability* 2008, *10(6)*, 943-957, DOI: 10.1007/s10668-007-9094-3.
6. Woodford, A.; Rosewarne, P.; Girman, J. *How much ground- water does South Africa have?* Report for the Groundwater Phase 2 Project, Department of Water Affairs and Forestry, Pretoria, South Africa, 2005.
7. Dennis, N.; Brett, M. *Images of a great African Park*;New Holland Publishers: UK, 2001; pp 144.
8. du Toit, W.H. *Abridge geohydrology of the Kruger National Park*. Report No: GH 3888, DWAF, Pretoria, 1996.

9. du Toit, W.H. *Geohydrology of the Kruger National Park based on the evaluation of existing borehole information*. Report No: GH 3806, Vol. 1, 1998; pp 124.
10. Vegter, J.R. *Hydrogeology of groundwater region 19, Lowveld*. Prepared for WRC, Report No. TT 208/03, 2003.
11. Vegter, J.R. *Groundwater development in South Africa and an introduction to the hydrogeology of groundwater regions*, prepared for WRC, Report No. TT 134/00, 2001.
12. Zambatis, N. Determinants of grass production and composition in the Kruger National Park, MSc (Agric.) dissertation, 2003, University of Natal, Pietermaritzburg, unpublished.
13. Schulze, R.E.; Maharaj M.; Lynch, S.D.; Howe, B.J.; Melvil-Thompson, B. South African atlas of agrohydrology and –climatology, Report TT82/96, Water Research Commission, Pretoria, 1997.
14. Schutte, I.C. The general geology of the Kruger National Park, *Koedoe* 1986, *29*, 13-37.
15. Venter, F.J. Soil Patterns associated with the major geologic units of the Kruger National Park, *Koedoe 1986*, 29,125-138.
16. Weaver, J.M.C.; Cave, L.; Talma, A.S. *Groundwater sampling: A comprehensive guide for sampling methods*. WRC, Report No TT 303/07, 2007.
17. SANS 241 (South African National Standards). *Drinking water*, 6th ed.; Pretoria, South Africa, 2005.
18. DWAF. *South African Water Quality Guidelines – Field Guide*, 8th ed.; Department of Water Affairs and Forestry, Pretoria, South Africa, 1996; Volume 8.
19. Leyland, R.C.; Witthuser, K.T. *Regional description of the groundwater chemistry of the Kruger National Park*, Water Research Commission – Report No. KV 211/08, 2008.
20. Dye, P. J.; Walker, B. H. Vegetation-environment relations on sodic soils of Zimbabwe Rhodesia. *Journal of Ecology* 1980, *68*, 589-606.
21. Subba Rao, N.; Vidyasagar, G.; Surya Rao, P.; Bhanumurthy, P. Chemistry and quality of groundwater in a coastal region of Andhra Pradesh, India. *Applied Water Science* 2014, DOI 10.1007/s13201-014-0244-0.
22. Rajmohan N.; Elango, L. Hydrogeochemistry and its relation to groundwater level fluctuation in the Palar and Cheyyar river basins, southern India. *Hydrological Processes* 2006, *20*, 2415-2427.
23. Sujatha, D.; Reddy, B.R. Quality characterization of groundwater in the south-eastern part of the Ranga Reddy district, Andhra Pradesh, India. *Environmental Geology* 2003, *44*, 579–586.

A procedural approach for prioritization of rehabilitation of gold tailings dumps of abandoned mine sites in the Giyani Greenstone Belt, South Africa

SE Mhlongo[1]*, F Amponsah-Dacosta[1] and A Kadyamatimba[2]

[1]Department of Mining and Environmental Geology, University of Venda, South Africa
[2]Department of Business Information System, University of Venda, South Africa
*Email of corresponding author: emmanuel.mhlongo@univen.ac.za

Abstract

South Africa has many abandoned mines and it is estimated that it will take hundreds of years to rehabilitate them. Preliminary assessment of these mines to establish and quantify their problems is an important step towards their rehabilitation. This paper presents a methodological approach for prioritization of rehabilitation of abandoned mine waste dumps. Such method was developed to take into consideration the contamination potential of the dumps, their dispersion to the surrounding areas as well as landscape and visual impacts of the waste on ranking the dumps for rehabilitation. The application of the method on tailings dumps of abandoned gold mines found in different parts of the Giyani Greenstone Belt demonstrated the simplicity and robustness of the use of the method in different areas of abandoned mine tailings dumps. The fact that the method uses both qualitative and quantitative approaches in ranking the waste dumps for rehabilitation make it to easily accommodate site-specific issues in the rehabilitation prioritization process. This was identified as the major strength of this method. It is recommended that the method be used as a tool for priority setting in the rehabilitation of abandoned mine waste dumps.

Keywords: Tailings dumps, abandoned mines, rehabilitation prioritization, ranking tools.

1. Introduction

Mining and processing of solid minerals produces large volumes of waste material which include spoil dumps, tailings, and waste rocks [1]. Tailings dumps are known for having serious impacts on the environment and the health of people and animals [2]. This is because of their high toxic metal content which are sometimes at levels greater than those in the ore mined [3]. According to Olobatoke and Mathuthu [4], the composition of mine waste depends largely on the type of ore mined, the gangue associated with the ore, and the extraction method used. The most common toxic metals in tailings are Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Manganese (Mn), and Asenic (As) [5]. The impacts these metals have on people and animals are generally aggravated by their long-term persistence on the environment [6]. Their accumulation in soils, water and air are direct ways the metals enter the human food chain [7]. The transportation of tailings material through different forms of erosion can result to pollution of the environment that is far from the mining site.

The rehabilitation of abandoned mine sites (including mine tailings dumps) has taken different forms in different areas or regions. The focus of rehabilitation of these mines in South Africa has mainly been on addressing the safety and health risks they present as well as their environmental problems. Although this has been the case, the method used to set such priority of rehabilitation of abandoned mines in the country has not been broadly communicated or published. Some of the known tools for compilation of abandoned mines inventory and prioritization of rehabilitation were documented by Mhlongo et al. [8]. However, there are several challenges in adopting these tools outside the context which they

ISBN 978-0-620-82267-1

were developed and used. These challenges include lack of model calibration and transparency, some important parameters and reclamation methods are not taken into account, and that they are mostly data demanding and time consuming [9]. In this work, a case study of abandoned mines in the Giyani Greenstone Belt (Limpopo Province) was used to develop a less data demanding, less computational, methodological and robust tool for prioritization of abandoned mine waste dumps for rehabilitation in the country. This priority setting method is expected to considerably reduce the work, cost and timeframe for characterization and prioritization of rehabilitation of abandoned waste dumps.

Description of the study area

This work used three tailings dumps found in three abandoned mines in the Giyani Greenstone Belt, namely; Fumani Mine, Louis Moore Mine and Klein Letaba Mine shown in Figure 1. These mines operated in the belt from the 1870s to late 1980s. According Ward and Wilson [10], gold mining operations in Louis Moore, Fumani and Klein Letaba ceased in 1978, 1991 and 1995 respectively. The exploitation and processing of gold in these mines left behind large volumes of tailings material which are currently unprotected.

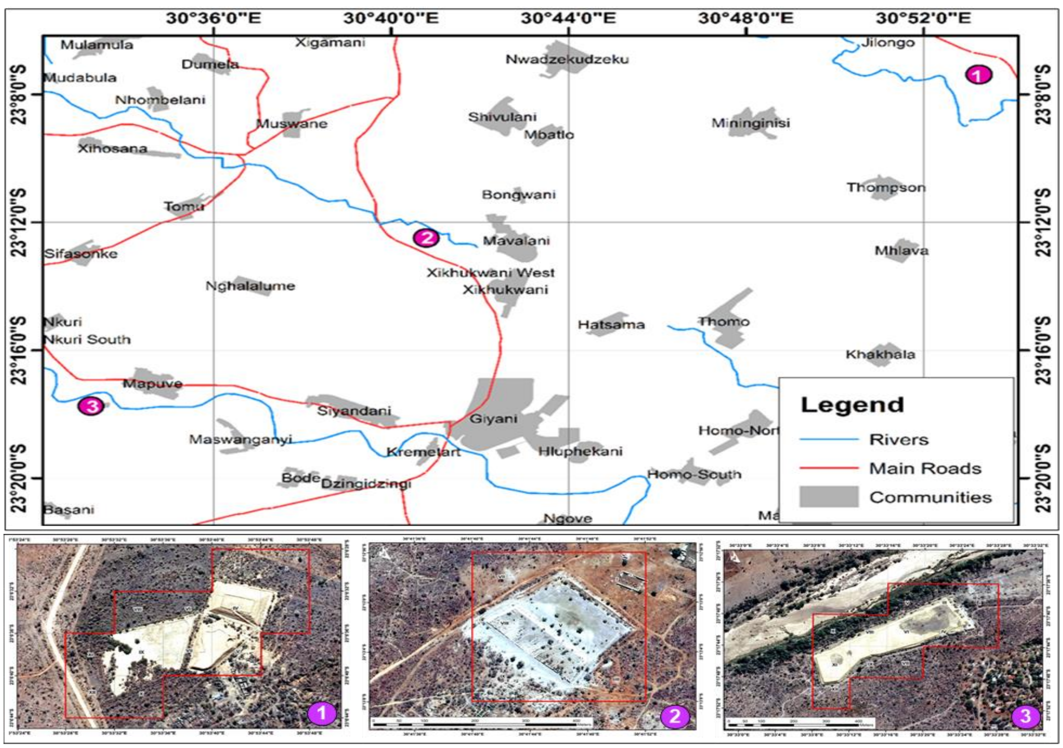


Figure 1. The geographical location of the tailings dumps in the study area. (1) is the Fumani Mine, (2) the Louis Moore Mine, and (3) the Klein Letaba Mine tailings dumps.

2. Methodology

The tool developed for prioritization of rehabilitation of abandoned mine tailings dumps involves use of the index of contamination (IC), tailings material or dump susceptibility to erosions and impact of the dumps on the landscape and appearance of the site. Using the generated numerical scores relating to the seriousness of these factors, the rehabilitation prioritization scores ($\mathrm{RP_{Score}}$) of the dumps were determined using Equation (1). In this equation IC is the index of contamination, ID is the value indicating the potential of the tailings to escape or be dispersed to the surrounding environment, and ILVI is the index of landscape and visual impact of the tailing dumps.

$$\mathrm{RP_{Score}} = (\mathrm{IC} \times \mathrm{ID}) + \mathrm{ILVI} \tag{1}$$

The index of contamination

The index of contamination which is the technique for evaluating multiple metal contamination of soils was determined using the method known as mean hazard index [11,12]. The method involved dividing the concentration (mg/kg) of toxic metals in tailings by their respective maximum allowable limits of metals in soils [13, 14]. The sum of the quotient values obtained was then divided by nine which is the number of toxic metals ratios considered in the study (see Equation 2). An Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) instrument was used to determine the concentration of these metals in tailings material.

$$\mathrm{IC} = \frac{\frac{\mathrm{Cd}}{7.5} + \frac{\mathrm{Pb}}{20} + \frac{\mathrm{As}}{5.8} + \frac{\mathrm{Cr}}{6.5} + \frac{\mathrm{Zn}}{240} + \frac{\mathrm{Cu}}{16} + \frac{\mathrm{Co}}{300} + \frac{\mathrm{Hg}}{0.93} + \frac{\mathrm{Ni}}{91}}{9} \tag{2}$$

Material dispersion to the surrounding environment

The value (ID) that describe the potential of tailings material being dispersed to the surrounding areas was calculated using Equation 3. Where; $\mathcal{A}$ is the area occupied by the dump (i.e. in hectares), i_e is the textural properties of the material, $\mathrm{i}_{\not{f}}$ is the nature of waste dump cover, i_d is the efficiency of the design characteristics of the dump in controlling potential pollution of the surrounding environment, i_a is the average distance of the dump from the surface water body. The criteria used to assign scores to these factors is shown in Table 1.

$$ID = \mathcal{A} \times (i_e + i_{\not{f}} + \mathrm{i}_d + i_a) \tag{3}$$

The exposure of the dumps and their landscape and visual impact analysis

The determination of the ILVI commenced with selecting viewpoints from which the tailings dumps can be observed by the members of the public. These points were selected in critical areas at 0.5-1.5km and 1.5-2.5km distance zones from the dumps. In each viewpoint (VP), the area of the dump visible ($\mathcal{A}_{\mathrm{vis}}$) was estimated and used to calculate the value known as the index of the dump exposure (IdE) using Equation 4. From this equation $\mathcal{AV}_{\mathrm{Total}}$ is the total area occupied by the dump.

$$\mathrm{IdE} = \frac{\mathcal{A}_{\mathrm{vis}}}{\mathcal{AV}_{\mathrm{Total}}} \tag{4}$$

The value representing the total exposure of the dump ($\mathrm{IdE_{Total}}$) was computed using Equation 5. Where; (IdE_{av}) is the average index of exposure of the dumps in the viewing distance area and (n_i) is the number of viewpoints considered in each distance area. The $\mathrm{IdE_{total}}$ was used to multiply the weights of the factor of chromatic contrast (i_c), morphology and shape of the dump (i_r), and the relationship of the nature of the dump with the surroundings (i_n) as shown in Equation 6 modified from [2] to incorporate the exposure of the dumps in quantifying their impact on the aesthetic appearance of the landscape. The criteria used to assign weights to the factors i_c, i_r and i_n are depicted in Table 2.

$$\mathrm{IdE_{Total}} = \sum_{i=1}^{n} \frac{\mathrm{IdE}_{av}}{n_i} \quad (5)$$

$$\mathrm{ILVI} = \mathrm{IdE_{Total}} \times (\mathrm{i}_c + \mathrm{i}_r + \mathrm{i}_n) \quad (6)$$

TABLE 1. The criteria for scoring of the factors for determination of the index of dispersion of tailings material to the surrounding environs.

Description	Weight
The factor relating to the general configuration and design of the tailing dumps	i_d
The classification of mine waste dumps	
▪ Heaped fill: waste pile in the form of mound (normally in flat, undulating slopes and slightly inclined)	1.00
▪ Side hill fill: waste pile located on the side of a hill.	0.80
▪ Ridge crest fill: waste pile located on top of a ridge, straddling the crest of the ridge.	0.60
▪ Valley fill: waste dump that completely fills the valley (extend upstream to the valley head	0.40
▪ Cross valley fill: waste dumps that crosses the valley but does not fill up the entire upstream portion of the valley (include outlet for controlling floor flows without temporal storage)	0.20
The textural properties of the waste material	i_e
▪ Gravel soil (>0.25mm): 50% or more of course fraction is retained in No.4 sieve	0.1
▪ Sandy soil: 50% or more of course fraction passes the No.4 sieve	0.5
▪ Clayey soil: 50% of fine fraction passes 2.0µm	0.8
▪ Silt soil: 50% of fine fraction is retained between 0.6mm and 0.002mm sieves	1.0
The properties of the waste dump cover material	i_f
▪ Both slopes and top surface of the dumps are without any cover	1.00
▪ The top surface is covered by indigenize plant/grass species	0.75
▪ Slopes are covered by indigenize plant/grass species	0.50
▪ The dump is complete covered by indigenize plant/grass species	1.25
Factor relating to the distance of the dumps from surface water bodies	i_a
▪ < 100m	1.0
▪ 100-300m	0.75
▪ 300-600m	0.5
▪ 600-1000m	0.25
Factor relating to the dump's area coverage (ha)	$\mathcal{A}$
▪ Dumps occupying a planner area greater than 625ha	1.00
▪ Dumps occupying about 25-625ha planner area	0.80
▪ Dumps occupying about 5 - 25ha planner area	0.60
▪ Dumps occupying 1 - 5ha planner area	0.40
▪ Dumps occupying less than 1ha planner area	0.20

TABLE 2. The criteria for scoring of the factors for landscape and visual impact analysis on the tailings dump [2].

Description	Weight
Impact factor by chromatic contrast	
Appearance	i_c
▪ Visual similarity (no significant difference from over 1km)	0-1
▪ Significant chromatic contrast (yellow-brown, gray-black)	3-6
▪ Clear differences of colour: natural colours	6-8
▪ Clear differences of colour: artificial colours	8-10
Impact factor on the morphology or shape of the physical environment	
Deposit shape	i_r
▪ Shape of the deposit filling into the natural morphology	0-1
▪ Divergence only in shape, but not in volume	2-4
▪ Divergence in volume and shape	4-10
Impact factor related to the nature of the deposit and its relationship to the surroundings	
Nature of the deposit	i_n
▪ Mining waste like the natural surface materials	0-1
▪ Mining waste different from the natural surface materials	1-4
Waste dumps located in arid zones	
▪ With natural colours	1-2
▪ With unnatural (anomalous) colours	3-5
Waste dumps located in humid zones	
▪ With natural colours	0-1
▪ With artificial colours	2-3

3. Results

The method for prioritization of rehabilitation of abandoned mine waste disposal facilities was applied on tailings dumps of Klein Letaba, Louis Moore and Fumani gold mines in the GGB. These dumps are generally unprotected with highly eroded slopes and are at close proximity to major surface water bodies such as Nsami and Klein Letaba Rivers. They were found to be highly contaminated with Cd, As, Cr, and Cu while Ni and Pb was found to be above the maximum permissible limit in Louis Moore and Fumani mines (see Figure 2a). The concentration of Co, Hg and Zn was detected at levels below the permissible limit in all studied tailings material. The computed index of contamination (IC) of the tailings revealed that all the dumps are highly contaminated by multiple toxic metals. This is because the determined IC values of all tailing dumps were greater than 1 which suggest extreme contamination by anthropogenic and geologic activities [11, 12, 15]. As depicted in Table 3, the calculated IC values for the dumps were in the decreasing order of Fumani Gold Mine Tailings (FGMT) > Louis Moore Mine Tailings (LMMT) > Klein Letaba Mine Tailings (KLMT). The high IC value (19.2) of Fumani tailings indicated that this dump has very high potential for polluting the environment.

The textural characteristics of the tailing material showed that the dumps were dominated by sand fraction of particles. According to the Unified Soil Classification System (USCS), the tailings material from Fumani Mine can be classified as well-graded sand while that from Louis Moore and Klein Letaba can be classified as poorly-graded sand (see Table 3). In view of this, the tailings material from Fumani Mine can be considered less susceptible to erosion than that of Louis Moore and Klein Letaba mines. The reason for this is the fact that well-graded sand is generally less erodible than poorly-graded sand [16]. According to the method used in this work, the tailings dumps in the study area showed to be having almost equal potential of being spread to the surrounding areas or environment (see ID values of the dumps in Table 3). Although the number of points from where the tailings dumps could be viewed varied, this did not influence the determined ILVI values in any specific way. The ILVI values were found to be in the decreasing order of KLMT> FGMT> LMMT (see Table 4). This indicated that the Klein Letaba tailings dump affected the aesthetic beauty of the natural landscape more than Fumani mine tailings and Louis Moore mine tailings.

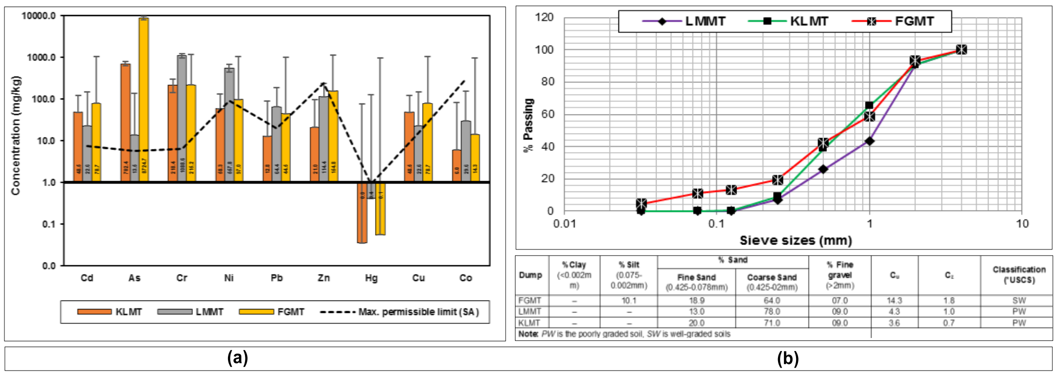


Figure 2. (a) is the comparison of the average concentration of toxic metals in tailings with the maximum permissible limit and (b) in the textural properties of tailings material.

TABLE 4. The results of the assessment of the tailings dumps in the study area.

Dump	VP	IdE	IdE_{av}/n_i		IdE_{total}	$(i_c + i_r + i_n)$	ID	ILVI	IC
			Zone – A	**Zone – B**					
Klein Letaba	KL-VP-01	0.4	0.4	0.7	1.1	23.0	1.4	24.8	2.0
	KL-VP-02	0.7							
	KL-VP-03	0.6							
	KL-VP-04	0.5							
Louis Moore	LM-VP-01	0.3	0.7	0.5	1.2	13.0	1.1	15.6	2.3
	LM-VP-02	0.6							
	LM-VP-03	0.8							
	LM-VP-04	0.7							
Fumani	FM-VP-01	0.1	0.1	0.7	0.7	23.0	1.2	16.4	19.2
	FM-VP-02	0.7							

4. Discussion

South Africa has several abandoned mine waste disposal facilities which present different types and degree of environmental problems as well as social and economic concerns. Efforts of addressing the problems of some of the mine waste dumps in different parts of the country have been made [17]. The environmental problems and potential health risks of mine waste dumps have been widely used as factors for prioritization of rehabilitation of abandoned tailings dumps in the country. For example, asbestos mines and mines with uranium bearing mine waste or acid water generating tailings have been the primary focus of the country's abandoned mines rehabilitation programme [17, 18]. In view of this, a tool for prioritization of rehabilitation of abandoned tailings dumps presented in this work was developed to take into consideration the pollution potential of the dumps as well as their landscape and visual impact (LVI) issues. The use of LVI to set rehabilitation priority for abandoned mining sites was first explored by Rodrıguez et al. [2], and Mavrommats and Menegaki [19]. The use of this approach in the method developed for this work is due to the fact that exposure of old dumps to the public turn to create negative reaction to observers who are not prepared to accept the alteration of the landscape instigated by the presence of the dumps in the area. According to Dentoni et al. [20], the negative reaction due to old mining activities on the landscape may present serious concerns in areas where tourism industry has a potential to grow.

The application of this method in abandoned gold tailings dumps in the GGB demonstrated that the rehabilitation of the dumps should begin with the most toxic tailings dumps of the Fumani Gold Mine. The Klein Letaba tailings dump which is about 120m from the Klein Letaba River is to be considered second on the rehabilitation programme (see Figure 3). The Louis Moore Mine tailings is to be rehabilitated last. The areas of the tailing dumps which were visible in different viewpoints and not blending well in the surrounding environment should be addressed in a way that enhance the aesthetic appearance of the tailings dumps area. The rehabilitation requirement scores and the ranking of the studied tailings dumps for rehabilitation are shown in Figure 3.

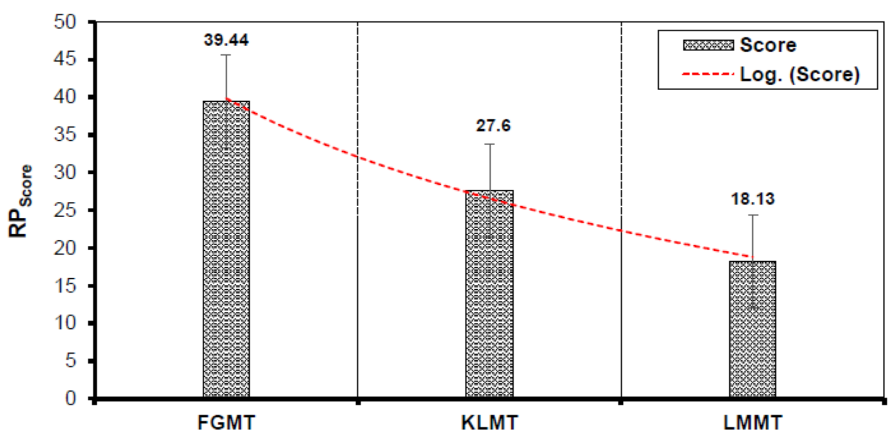


Figure 3. The priority of rehabilitation of abandoned gold tailings dumps in the Giyani Greenstone Belt.

5. Conclusion

The concentration of Cd, As, and Cu was considerable high in all gold tailings while Hg, Zn, and Co was below the permissible limit in all tailing dumps. The calculated values of the index of contamination revealed that the tailings dump in the study area are contaminated with multiple metals and the pollution contamination is at the increasing order of FGMT>LMMT>KLMT. However, the impact of the tailings dumps on the visual appearance of the landscape is in the increasing order of KLMT> FGMT> LMMT.

In situations where the rehabilitation of mine tailings is required, the priority setting tool used in this work can assist in generating the list showing dumps to be given attention first in the rehabilitation programme or project. However, in the case of ongoing rehabilitation project, it can assist in identifying the areas of the dump to be given maximum attention. Based on these, the tool can be used to set a priority of rehabilitation at any stage of the rehabilitation project. Moreover, this method was developed to integrate qualitative and quantitative aspects of abandoned mine tailings to rank them over each other to set priority of their rehabilitation. The integrative approach of the tool allowed it to easily accommodate site-specified issues of abandoned mine waste dumps facilities. This was also identified as a strength and robust characteristics of this method.

Acknowledgment: The methodology used in this research is currently being used in an ongoing PhD study, Department of Mining and Environmental Geology, University of Venda. The authors thank the University of Venda for financial support.

References

1. Kim, M.; Jung, Y. Vertical Distribution and Mobility of Arsenic and Heavy Metals in and around Mine Tailings of an Abandoned Mine. Journal of Environmental Science and Health: Part A - Toxic/Hazardous Substances and Environmental Engineering, 2004, A39 (1), pp. 203–222.
2. Rodrıguez, R.; Dıaz, M.B., Vigil, H.; Rodrıguez, A. Development of a user-friendly method to assess the present condition of old abandoned mining waste dumps in Asturias (Spain). International Journal of Mining, Reclamation and Environment, 2011, 25 (1), pp. 6–31.
3. Choi W, Jeong S and Chae Y. Study on Recycling and Utilization of Abandoned Mine Waste, Geosystem Engineering, 2005, 8 (3), pp. 57-62. DOI:10.1080/12269328.2005.10541237
4. Olobatoke R.Y.; Mathuthu M. Heavy metal concentration in soil in the tailing dam vicinity of an old gold mine in Johannesburg, South Africa. Can. J. Soil. Sci., 2016, 96, pp. 299–304.
5. Li X.; Huang l. Towards a view paradigm for tailings phytostabilization-nature of the substrates amendment option, and anthropogenic pedogenesis. Crit. Rev. Environ. Sci. Technol. 2015, 45 (8), pp.813-839.
6. Mani D.; Kumar, C. Biotechnological Advances in Bioremediation of Heavy Metals Contaminated Ecosystems: An Overview with Special Reference to Phytoremediation. International Journal of Science and Technology, 2014, 11(3), pp. 843-872.
7. Kamunda, C.; Mathuthu, M.; Madhuku M. An Assessment of Radiological Hazards from Gold Mine Tailings in the Province of Gauteng in South Africa. Int. J. Environ. Res. Public Health, 2016, 13, 138; doi:10.3390/ijerph13010138
8. Mhlongo, S.E.; Amponsah-Dacosta, F.; Kadyamatimba, A. Development and use of hazard ranking system for abandoned mine entries: A case study of the mine shafts in Giyani and Musina areas of South Africa. Cogent Engineering, 2018, 5: 1491776. https://doi.org/10.1080/23311916.2018.1491776
9. Kubit, O.E.; Pluhar, C.J.; De Graff, J.V. A model for prioritizing sites and reclamation methods at abandoned mines. Environment Earth Sciences, 2015, 73 (12), 7915–7931. doi:10.1007/s12665014-3949-3
10. Ward, J.H.W.; Wilson, M.G.C. Gold Outside the Witwatersrand Basin. In: Wilson, M.G.C. and Anhaeusser, C.R., (editors) The Mineral Resources of South Africa. Council for Geosciences, 1998, pp. 350-386.
11. Reis, A. P.; Ferreira da Silva, E.; Cardoso Fonseca, E.; Patinha, C.; Barrosinho, C.; Matos, J. Environmental Assessment of the Caveira Abandoned Mine (Southern Portugal): Part 1: Characterization of Metal Contaminated Soil. Soil and Sediment Contamination: An International Journal, 2012, 21 (2), pp. 227-254.
12. Chon, H.T.; Cho, C.H.; Kim, K.W.; Moon, H.S. The occurrence and dispersion of potentially toxic elements in areas covered with black shales and slates in Korea. Applied Geochemistry, 1996, 11, pp. 69-76.
13. Department of Environmental Affairs: DEA. The framework for the management of contaminated land, South Africa, 2010. Available online: http://sawic.environment.gov.za/documents/562.pdf (accessed on 5 February 2016).
14. Kamunda, C.; Mathuthu, M.; Madhuku, M. Health risk assessment of heavy metals in soils from Witwatersrand Gold Mining Basin, South Africa. International Journal of Environmental Research and Public Health, 2016, 13, 663.
15. Nimick, D.A.; Moore, J.M. Prediction of water-soluble metal concentrations in fluvially deposited tailing sediments, Upper Clark Fork Valley, Montana, USA. Appl. Geochem, 1991, 6, pp. 635–646.
16. Gray, D.H.; Sotir, R.B. Biotechnical and Soil Bioengineering Slope Stabilization: A Practical Guide for Erosion Control. John Wiley and Sons, Inc, New York, 1996.

17. Department of Mineral Resources: DMR. The national strategy for the management of derelict and ownerless mines in South Africa, 2010. Available online: http://cer.org.za/news/dmrs-national-strategy-forthemanagement-of-derelict-and-ownerless-mines2009
18. Mhlongo S.E.; Amponsah-Dacosta F.A. Review of Problems and Solutions of Abandoned Mines in South Africa. International Journal of Mining, Reclamation and Environment, 2016, 30 (4), pp. 279-294.
19. Mavrommats, E; Menegaki, M. Setting Rehabilitation Priorities for Abandoned Mines of Similar Characteristics According to their Visual Impact: A case of Milos Island, Greece. Journal of Sustainable Mining, 2017, 16, pp. 104–113. doi:10.1016/j.jsm.2017.10.003
20. Dentoni, V.; Massacci, G.; Radwanek-Bak, B.D. Visual impact of quarrying in the Polish Carpathians. Geological Quarterly, 2006, 50 (3), pp. 383-390.

Communication for development in water quality related risk reduction planning: a conceptual framework

TE Volenzo *, JO Odiyo and L Munyai

School of Environmental Sciences, University of Venda, Republic of South Africa
*Email of corresponding author: volenztom@gmail.com or Tom.Elijah@univen.ac.za

Abstract
Water is a key driver for socio-economic development, livelihoods and ecosystem integrity. This is reflected in the emergence of unified paradigms such as Integrated Water Resource Management (IWRM) and the weight accorded to it in the Sustainable Development Goals agenda. This paper interrogated the effectiveness of existing participatory planning and assessment models adapted from IWRM model on water quality and public health at community level. The analysis was built around public health ecology perspective and drew useful lessons from critique of basin wide integrated Modeling approaches and existing community participatory models envisaged under Water Users Associations (WUA) in South Africa. The study concludes that the inherent "passive participation" adapted from IWRM model fail to adequately address water quality and public health dimensions in its pillars. Since water quality has direct bearing on disaster risks in public health, building a coherent mitigatory vision requires the adoption of active participatory assessment and planning models that incorporate livelihoods, agency, social learning dynamics and resilience through recognition of communication for development approaches in community empowerment.

Keywords: Community empowerment; Communication for Development. Ecological Public Health; IWRM; Participatory planning and assessment; Public Health Risks; Water quality related risks

1. Introduction

Poor management of water resources causes health, environment and economic losses on a scale that impedes development and frustrates poverty reduction efforts [1] The observation has informed policy action at local and global scales over the last 3 decades [2]. For example, the Sustainable Development Goals (SDGs) agenda on water seeks to ensure availability and sustainable management of water, sanitation and maintenance of water-related ecosystems. Sustainable management and development of water resources is fundamental to poverty alleviation and inclusive growth [3]. Furthermore, water resources management underpins and interacts with all the pillars of the green economy, including environmental protection, food and energy. The universality of water in terms of social and environmental externalities is largely responsible for emergence of collaborative frameworks, protocols, treaties and convections [4]. Such mechanisms and models have been cascaded to the local levels in many countries, such as, South Africa.

The Integrated Water Resource Management (IWRM) paradigm informs institutional frameworks on water resources management in many countries of the world [1]. IWRM is defined as a process that promotes the coordinated development and management of water, land, and related resources to maximise the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems [2]. The paradigm aims at ensuring efficient, equitable and sustainable development and management of the world's limited water resources and for coping with conflicting demand [1,5,6]. The paradigm is especially invaluable in addressing intricate policy matrices, water related risks and conflict among policy makers, decision makers and researchers [6,7], hence its dominance as a paradigm for transformation of water management globally. Participatory assessment and planning, as well as, consideration for livelihood lenses and disaster risk reduction paradigms could be critical in the implementation of IWRM across the broad policy sectors, subsector purposes and adaptation to ecological public health perspectives.

Risk and resilience are related and interrelated analytical lenses in public health [8]. Risk and resilience are critical in water resources management due to existence of many drivers of risks and uncertainties. This is particularly critical in rural based water supply systems. The role of community agency in resilience building has been explored by different authors. Community resilience refers to the existence, development, and engagement of community resources by community members to thrive in an environment characterised by change, uncertainty, unpredictability, and surprise or social sustainability [9]. Community resilience is critical in facing the multiple challenges, risks and uncertainties in water resource management. Community resilience can be enhanced through community-based disaster risk reduction approaches adaptation initiatives [8].

As an integrative approach, IWRM, can be improved by focusing on transformative processes and structures of a social system. Public health ecology has been proposed as an appropriate approach for addressing the multiple transitions that currently affect human health and sustainability [10]. The view resonates with analysis in this study on water related public health risks. Exploring the institutional framework in water resource management, its limitations and its ramifications on public health could improve and provide innovative analytical lenses from which ecological public health perspectives are framed and enhanced. As one of the water scarce countries [11] of South Africa provides an important case study for analysing ecological public health perspectives. In addition, South Africa is one of the countries with high morbidity and mortality from water borne diseases [12], especially among formally disadvantaged areas and rural communities. The undesirable conditions are exacerbated by climate change risks [13].

Ecological Public health thinking places particular emphasis on the interplay of ecosystems health and human health, as well as, consideration for economic factors [10] and suggests a paradigm shift through investment in sustainability for a steady state economy from which equitable conditions for health are expected to accrue [14]. In practice ecological public health supports capacity building, coherence and vision into integrative frameworks that address sustainability and disaster risk reduction, e.g. the development of low carbon economy and massive retrofitting of housing [10]. This requires medium and long-term changes with clear shared understanding among public health actors [10]. However, its weakness lies in its failure to recognise the role of individual effort in resilience building [15]. This study attempts to close this gap by focusing on how individual and collective participation in water resources management can be harnessed for positive public health outcomes.

Historically rooted institutional biases are key elements of community health outcomes and the inherent social costs of illness [8]. Some authors [15, 16], have argued that 'ecological public health' should be the prominent approach to improving health in the 21st Century. However, this observation is based on findings that largely focus on economic dimensions such as the Gross Domestic Product (GNP) and how this affects human health and welfare. The economic, social and environmental factors in South Africa mirrors this analysis especially in relation to water resources and provide a good case study for researchers, community of practice and policy makers. This review provides useful insights into the effect of institutional frameworks on public health from ecological public health perspectives.

Drawing upon findings on participatory planning from a water Users Association (WUA) in a South African municipality and basin wide modelling approaches from other regions, existing weaknesses and limitations were identified to suggest a model that can enhance effective participation. In doing so, the study drew from sustainable livelihood frameworks [17], socioecological systems [18] and communication for development paradigms [19,20] to address the limitations of IWRM in relation to ecological health perspectives. The study in particular examined the role of communication for development approaches and the concept of participation as a unifying concept that underpins ecological public health and IWRM. The main contribution through the article is in resolving existing policy–practice gaps on integrative models and participatory planning [21]. Focusing on the institutional framework from a participatory angle broadens and enhances the robustness of ecological public health perspective as an integrative model that encapsulates individual knowledge and interests. The central contribution of this article is thus a robust analytical framework for the integration of knowledge, attitudes and behaviour into ecological public health perspective in planning mitigation of water related public health risks.

2. Ecological Public Health and Participatory Assessment and Planning

One-way communication, a form of passive participation, is one of pervasive superficial tactics power holders use to claim occurrence of community participation in rubberstamping decisions during planning processes. In such situations the community has less opportunity to influence the programme [22]. The shortcomings are reflected in [23,24] who identified lack of moderation, suspicion and window dressing as some of the shortcomings during conventional participatory processes. Given that different actors with different agendas often subjectively interpret participation, there is need to account for interests and knowledges of all stakeholders and livelihood perspectives from political ecology lenses [25]. A "transformative" participation that empowers and transforms involved communities is proposed by [26], while [27], and conceptualizes participation from a two-way flow of communication perspective in terms of information dissemination to passive participants or "communication" and gathering information from participants or "consultation. In this study exploration for the integration of transformation angle by [26], and [27], concepts from communication for development lenses were carried out.

Communication for development is built around the principle of empowerment in the identification of problems, development of solutions and implementation strategies, monitoring and evaluation [19]. Empowerment refers to the capacity of people to make effective choices, envision alternatives, participate in decision making, negotiate with influence, control and hold accountable institutions that affect their lives and livelihoods [28]. The three basic components of communication for development are advocacy, social mobilisation and behavioural change (or behavioural development) communication. Effective communication relies on the synergistic use of the three strategic components [19]. Advocacy informs and motivates community leadership to create a supportive environment to achieve programme objectives and the related development goals. In essence, the advocacy component is aimed at changing policies, allocating resources, public dialogue and conversation on critical issues.

Social mobilization engages and supports participation of institutions, community networks, social/civic and religious groups to raise demand for or sustain progress towards a development objective by strengthening participation in activities at the grass-roots level. The backbone of developing the social mobilisation component of a communication strategy comes from a combination of data, participant and behavioural analyses [19,20], as well as, Community input. Methodologies and approaches to stakeholder, participant and behaviour analysis and the end product in terms of a communication objective and strategy are provided by [19]. Since human health is a product of human- environmental interactions [10], communication for development is a critical tool for transforming participatory processes and increasing community resilience. In the next section, review of the legal and institutional framework on water in South Africa in the context of ecological public health and community participation were done.

3. IWRM in the Context of South Africa's Community Participation in Development and Management of Water Resources

Several legislations and institutions are involved with water management in South Africa. The legislations and institutions include the National Water Policy [29], the National Water Act (Act 36 of 1998) and the Water Services [30]. The Water Services Act delegates water quality monitoring and management to Water Services Authorities (WSAs), Department of Water Affairs (DWA), Department of Health (DoH), Local Government and Civil society [31]. The primary responsibility for ensuring the provision of safe drinking water and monitoring quality rests with WSAs. The traditional leaders (chiefs and headmen) are the heads of their communities and give guidance on many issues including development as given under Traditional Leadership and Governance Framework Act, 2003 [32]. Communities hold meetings at the traditional leaders' courts where various issues including development are discussed. The traditional leaders' courts could as such provide a forum for deliberation on local issues before they cascade to higher levels [33].

The National Water Act, aims at ensuring that the nation's water resources are protected, used, developed, conserved, managed, and controlled in ways that take into consideration such factors as, inter alia, meeting the basic human needs of present and future generations, promoting equitable access to water, redressing past discrimination, facilitating social and economic development, and protecting aquatic and associated ecosystems. The need for equity and fair procedures is found throughout the Principles 12- 25 of the water policy [29]. The National Water Act of 1998 divides South Africa into Water Management Areas and prescribes processes by which strategies and management institutions ought to evolve in Water Management Areas. It advocates the use of stakeholder participation principle in development of Institutional and management systems, Catchment Management Agencies, Catchment Management Strategies, and Water Users' Associations.

The water policy in South Africa mirrors the policy sectors under the IWRM paradigm. The policy is anchored on post-apartheid constitutional order, international customs and practice and land mark international instruments such as the Mar del Plata (1997), the 1992 Dublin world conference on water and Environment, Agenda 21, the 1996 Stockholm Global Water Partnership (IWRM), ratification and domestication of international treaties and protocols such as the Ramsar on wetlands and shared water systems under SADC protocols [29]. The policy mirrors global trends on sustainability, water availability per person focus, concerns on rising pressure on water resources and need to address potential conflicts.

Unbundling Participatory Dilemmas from Ecological Public Health Perspective: The Case of a South Africa's Water Management Area

To capture the Human-Environment interactions and potential impacts on public health, water was sampled from points 3 sampling points on River Luvuvhu, namely, upstream (point

A), mid-stream (point B) and downstream (point C) before and after rainfall. The physicochemical parameters were analysed in the laboratory and compared with DWAF guidelines on water for domestic use [34]. The location of sampling Point C captures cumulative human-environment interactions in terms of sources of pollution (agricultural activities, urban runoff and municipal waste water treatment plant). Point B is located near Levubu, a major agricultural area. Point A is majorly a conservation area within Louis Trichardt (near a hill and has a forest plantation) with isolated agricultural activities. The results of physicochemical analysis are presented in Table 1 and 2.

Table 1 provide chemical parameters. The electro conductivity (EC) at point B was 111.65µS/cm before rainfall and within DWA guidelines for domestic use but increased to 162.43 µS/cm after rainfall which is above DWAF guidelines for domestic use. High EC at this point may be due to high ion content leached from agricultural fields. At Point C, mean EC was 139.87 µS/cm and 189.00 µS/cm before and after rainfall, respectively, and turbidity was 4.02 NTU and 9.93 NTU before and after rainfall, respectively. According to DWA guidelines for domestic use, turbidity levels above 5 NTUs is visible and objectionable aesthetically undesirable to majority of water users. The high adsorption capacity of the particulate particles carries increased risk of microbial disease transmission, as well as, increase chemical toxicity.

TABLE 1. Physicochemical parameter differences between sampling points on River Luvuvhu.

Physiochemical Parameters	**Point A**		**Point B**		**Point C**	
	Before Rainfall	**After Rainfall**	**Before Rainfall**	**After Rainfall**	**Before Rainfall**	**After Rainfall**
Ph	7.20	7.41	7.33	7.12	7.46	7.24
EC (µS/cm)	83.90	98.17	111.65	162.43	139.87	189.00
TDS (mg/L)	50.30	59.00	67.02	96.57	83.93	101.93
COD (mg/L)	17.50	11.83	15.50	21.33	32.00	41.17
Turbidity (NTU)	9.87	11.17	4.53	6.62	4.02	9.93

Source, Authors Analysis of field data, 2018.

The fluoride concentration at A are 0.003 mg/L and 0.05 mg/L before and after rainfall respectively and within the required range of (0–1.00mg/L) guidelines for domestic water use by [35]. Nitrate is the end product of the oxidation of ammonia or nitrite. The health risks of nitrate are reviewed by [35]. Presence of nitrates in drinking water is a health concern because it is easily reduced into nitrite by gastrointestinal bacterial [35].

TABLE 2. Concentration of chemical parameters before and after rainfall.

Chemical Parameters	**Point A**		**Point B**		**Point C**	
	Before Rainfall	**After Rainfall**	**Before Rainfall**	**After Rainfall**	**Before Rainfall**	**After Rainfall**
Fluoride (mg/L)	0.003	0.05	0.21	0.18	0.14	0.70
Chloride (mg/L)	9.08	7.61	41.33	16.29	21.07	33.49
Nitrate (mg/L)	0.17	0.10	25.89	11.65	15.10	37.02
Phosphate (mg/L)	0.44	0.17	1.17	1.31	1.25	2.01
Sulphate (mg/L)	1.29	0.05	0.30	0.06	3.20	0.38

Potential Solution to Participation Dilemmas in Water Quality Management

The assessment of possible disaster events (disaster risks) is a very important issue when mitigating disasters. The design of a comprehensive model revolves around six main components: strategic planning, hazard assessment, risk management, disaster management actions (four fundamental phases of disaster management), monitoring and evaluation and environmental effects [36]. This resonates with the ecological public health perspective. The results of, and assessments derived from the comprehensive model can be utilised as an input for a dynamic evaluation in a monitoring and evaluation system. The evaluation of all measures, and feedback to the strategic planning module is recommended in addressing environmental issues, an important aspect in ecological health perspective. Pollution and contamination levels as disaster risks in water can be assessed through Grey water footprints [37]. In an evaluation of quality of water and spatial distribution of diarrhoea cases, from River Khandanama and ground water source used by Tshikuwi community in South Africa by [38], presence of *Vibrio*, *Salmonella*, and *Shigella* species and the detection of total coliforms, faecal coliform, and enterococci counts exceeded the acceptable limits and increased the vulnerability of the communities to episodes of diarrhoea. This is reflected in the outbreak of diarrhoea cases in the area [38].

In assessment of community participation on water quality monitoring and management, in Luvuvhu catchment, Limpopo province of South Africa, [33] concludes that, though the legal and policy framework in South Africa, may be supportive of community participation, the integration of attitudes, indigenous knowledge, practices and leadership structures in the sustainable management of water resources though critical, remains low to non-existent. The latter study proposes that the apparent policy- practice divide requires a community-based water quality management model anchored on a trialage of technology, empowerment and communication. The model recommends increased linkages between local government level structures and community level structures in improving the articulation of the opinions of the majority of the people and allowing information flow from the grass root level to the national level.

Planning of water projects (especially identification and construction phases) is by default based on top- down planning models with the community being incorporated only at late stages e.g. through the establishment of water users' associations as discussed in previous sections. This planning approach negates policy interventions such as those envisaged under various acts of parliament in South Africa. The suggested model by [33], which is a bottom-up approach has some potential in addressing the oversight. However, the reliance on structural lenses is prone to limitations cited by [39,40]. The gender aspect is particularly important in light of findings by [34]. We contextualize the weaknesses to suggest a model that can be used to realize effective community participation in water quality monitoring. The model identifies community knowledge, attitudes and behavior as critical elements that influence water quality outcomes. Our observation is particularly relevant in the context of observation by [38], that reducing health-risks from contaminated water supplies not only require the monitoring of groundwater and other water sources but also use of sustained health-education programmes in the communities. Thus, mitigating health risks associated with human-environmental interactions should focus on cognitive failures and livelihood lenses.

South Africa has one of the most vibrant legal and policy frameworks on water quality management. However, from the above literature, it is evident that though physicochemical risks are largely under control, microbiological risks are wide spread in rural community's drinking water supply systems and a threat to public health. Available literature and our findings suggest such risks are livelihood related hence the need for a comprehensive risk-based community participatory planning framework on mitigation. The observation resonates with [41], in their recommendation for a comprehensive assessment of water quality and water use practices in rural areas of Limpopo. Given that all-natural sources of water have presence of E. coli [42], recommended needs and risk assessments approaches in mitigation of water related health risks. Figure 1 presents the suggested community risk-based planning framework with communication for development lenses as the main pillar

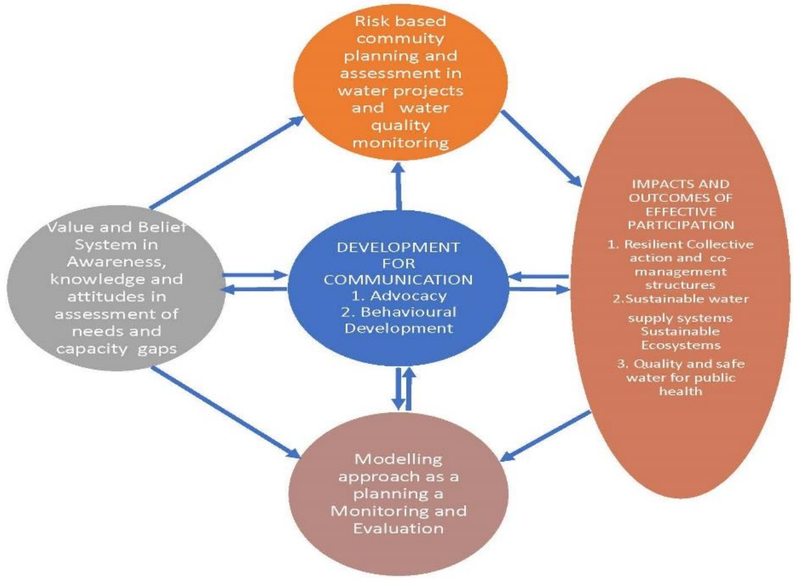


Figure 1. Community based risk reduction model for interfacing planning and public health in water projects (Authors synthesis, 2018).

4. Conclusions

In recognition of the role water plays in public health and human welfare, the relevance of IWRM as a paradigm for transformation of water management globally through ecological public health lenses has been interrogated. The article has been contextualised to a water resource management area, Limpopo province of South Africa. The focus on participation from institutional perspectives intended to enrich the utility and coherence of ecological public health model in integrating human agency from political ecology lenses. It is concluded that, participatory planning, institutional and cultural change are some of the requisite dimensions in assessment of public health risks and building resilient social systems. This necessitates the assessment of knowledge, attitudes and existing practices and the extent to which they are integrated into water resources management and their integration with public health. Though the policy and legal frameworks recognize the role of participation, implementation of the same does not support integration of public health disaster risks. Communication for development has been realized to be central to unbundling cognitive failure and biases among planners, community, development practioners, and policy and decision makers. Since effective participation is dependent on utilization of a two-way communication feedback mechanism to transform culturally embedded knowledge, attitude and behavioural norms (at individual, community, collective and institutional levels), the use of advocacy, behavioural change and social mobilization is critical. In particular a community-based planning approach for planning of water projects should encompass risk reduction principles in addressing health perspectives.

Author Contributions: V.T.E was the originator of research idea and conceptual framework and wrote the manuscript, J.O revised the manuscript and advised on corrections, L. M sampled water and Laboratory analysis

References

1. GWP. "Integrated Water Resources Management (IWRM) and Water Efficiency Plans by 2005 " Why, What and How? by," Elanders Infologistics Väst AB, 10, 2005.
2. UNEP, "UN-Water Status Report on The Application of Integrated Approaches to Water Resources Management," Nairobi, Kenya, 2012.
3. UN, "Transforming the world: the 2030 Agenda for Sustainable Development," A/RES/70/1, 2015.
4. Namara, R.E., & Giordano, M.. Economic rationale for cooperation in international waters in Africa: A Review. A Review. Washington DC, USA; 2017, https://doi.org/10.1596/26071
5. Grigg, N, S. "Integrated water resources management: Balancing views and improving practice," Water Int; 2008, 33(3), pp 279–292
6. Snellen, W.B. & Schrevel, A. IWRM: for sustainable use of water 50 years of international experience with the concept of integrated water management. FAO/Netherlands Conference on Water for Food and Ecosystems. Wageningen; 2004, https://doi.org/10.1016/j.pce.2008.02.002
7. GWP. Global Program Review Working for a World Free of Poverty the World Bank (Vol. 4). Washington DC, USA: Independent Evaluation Group, The World Bank Group; 2010.
8. Davis, R., Cook, D., & Cohen, L. A community resilience approach to reducing ethnic and racial disparities in health. American Journal of Public Health; 2005, 95(12) 2168–2173. https://doi.org/10.2105/AJPH.2004.050146
9. Magis, K. Community resilience: An indicator of social sustainability. Society and Natural Resources; 2010, 23(5) 401–416. https://doi.org/10.1080/08941920903305674
10. Hanlon, P. Unhealthy Glasgow: a case for ecological public health ? Public Health; 2015, 129(10), 1353–1360. https://doi.org/10.1016/j.puhe.2015.08.006
11. DWAF. National Water Strategy (2nd Edition 2013). Pretoria, South Africa: DWAF. Pretoria, 2013
12. DWAF (Department of Water Affairs and Forestry). Guideline for the Management of Waterborne Epidemics, with the emphasis on Cholera Management(Guideline Document U1.5 No. Management. Pretoria ; 2002, Retrieved from http://www.dwa.gov.za/Dir_WQM/docs/CHOLERA.pdf
13. DEA. National Climate Change Adaptation Strategy. National Adaptation Strategy. Pretoria, South Africa; 2017
14. Jackson, T. Prosperity Without Growth: Economics for a Finite Planet. London: Earthscan; 2009, https://doi.org/http://dx.doi.org/10.1016/j.biocon.2014.02.018
15. Lang, T., & Rayner, G. Ecological Public Health. The 21st century's big idea. Biomedical Journal ; 2012, 5466(August), 1–5. https://doi.org/10.1136/bmj.e5466
16. IRIS. Global Health Survey: Experienceand Perception in 28 Countries. IRIS: Amsterdamm, Ireland, 2011. Retrieved from www.irisnetwork.org
17. Scoones, I. Sustainable Rural Livelihoods a Framework for Analysis; IDS Working Paper 72 (Volume 72); The Institute of Development Studies: Brighton, UK, 1998, doi:10.1057/palgrave.development.1110037.
18. Holing, C.S. Understanding the Complexity of Economic, Ecological, and Social Systems. Ecosystems; 2001, 4(5), 390–405. https://doi.org/10.1007/s10021–
19. UNICEF, "Writing a communications strategy for development for Development Programmes: Aguideline for Programme Managers and Communication Officers," Dhaka, Bangladesh; 2008
20. FAO, "Collaborative change: a communication framework for climate change adaptation and food security," FAO, Rome, Italy; 2010.
21. Medema, W., Mcintosh, B.S. B.B. S., & Jeffrey, P.J. P. From Premise to Practice: a Critical Assessment of Integrated Water Resources Management and Adaptive Management Approaches in the Water Sector. Ecology and Society; 2008, 13(2), 29. https://doi.org/29

22. Hobley, M. Participatory forestry: the process of change in India and Nepal. Rural Development Forestry Study Guide 3, Rural Development Forestry Network Overseas Development Institute; 1996
23. Chambers, R. Paradigm Shifts and the Practice of Participatory Research and Development (No. 2; 1994, Retrieved from http://opendocs.ids.ac.uk/opendocs/handle/123456789/1761#.VeYN8PlViko
24. Birkhoff, J. Community conflict over water reuse. Perspectives from conflict analysis and resolution. Appendix C. In: Hartley, T. W (Ed.). Water reuse. Understanding public perception and participation. Water Environment Research Foundation, Alexandria, Virginia, USA; 2003.
25. Bixler, R.; Dell'Angello, J.; Mfune, O.; Roba, H. The political ecology of participatory conservation: Institutions and discourse. J. Political Ecol. 2015, 22, 165-182. [CrossRef]
26. Lawrence, A. No personal motive? Volunteers, biodiversity, and the false dichotomies of participation. Ethics Place Environ. 2006, 9, 279–298, doi:10.1080/13668790600893319.
27. Rowe, G. & Frewer, L.J. Public participation methods: A framework for evaluation. Science Technology and Human Values; 2000, 25(1) 3–29, https://doi.org/10.1177/016224390002500101
28. World Bank. Empowerment in Practice: Analysis and Implementation (No. 37272). Washington DC; 2007, http://siteresources.worldbank.org/WBI/Resources/EmpowermentLearningModulebody.pdf
29. DWAF. White paper on a national water policy for south africa. South Africa: DWAF; 1996b, http://www.polity.org.za/polity/govdocs/white_papers/water.html%5Cnhttp://www.dwaf.gov.za/Documents/Policies/nwpwp.pdf
30. Republic of South Africa. National Water Act 36 of 1998, Pub. L. No. vol 398. No.1091, Government Gazette 1 (1998). Republic of South Africa; 199
31. Hodgson, K & Manus, L. A drinking water quality framework for South Africa. Water SA 2006, 32, https://doi.org/10.4314/wsa.v32i5.47853
32. Republic of South Africa. Traditional Leadership and Governance Framework Act (2003). South Africa: Republic of South Africa; 2003
33. Nare, L., Odiyo, J.O., Francis, J., & Potgieter, N. Framework for effective community participation in water quality management in Luvuvhu Catchment of South Africa. Physics and Chemistry of the Earth; 2011, 36(14–15), 1063–1070, https://doi.org/10.1016/j.pce.2011.08.006
34. DWAF. South African Water Quality Guidelines. South African Water Quality Guidelines vol.1: Domestic Water Use 2nd Edn. (Vol. 1). Pretoria, South Africa; 1996a
35. WHO. Nitrate and nitrite in drinking water. Drinking-water Quality (Nitrate and nitrite in drinkingwater Background document for development of WHO Guidelines for Drinking-water Quality Rev/1: No. WHO/SDE/WSH/07.01/16/Rev/1), Geneva, Swirtzeland; 2011
36. Asghar, S., Alahakoon., D. Churilov, L. A. dynamic integrated model for disaster management decision support systems. J. Simul. 2005, 6(10 and 11).
37. Miglietta, P. P., Toma, P., Fanizzi, F. P., DeDonno, A., Migoni, D. & Serio, F. A Grey Water Footprint Assessment of Groundwater Chemical Pollution: Case Study in Salento (Southern Italy). Sustainaibility; 2017, 9(5). https://doi.org/10.3390/su9050799
38. Bessong, P., Odiyo, J.O., Musekene, J. & Tessema, A. Spatial distribution of diarrhoea and microbial quality of domestic water during an outbreak of diarrhoea in the Tshikuwi community in Venda, South Africa. Journal of Health, Population and Nutrition; 2009, 27(5) 652–659, https://doi.org/10.3329/jhpn.v27i5.3642
39. Ostrom, E. Background on the Institutional Analysis and Development Framework. Policy Studies Journal 2011, 39, 7–27
40. McGinnis, M. Costs and challenges of polycentric governance. Political Thoeory and Policy Analysis : Analyzing Problems of Polycentric Governance in the Growing EU. Bloomington; 2005, Retrieved from http://www.indiana.edu/~workshop/papers/mcginnis_berlin.pdf
41. Edokpayi, J., Odiyo, J.O., Popoola, E. ., & Msagati, T.A. Evaluation of microbiological and physicochemical parameters of alternative source of drinking water: A case study of Nzhelele river, South Africa. Open Microbiology Journal, 2018, https://doi.org/10.2174/1874285801812010001
42. Edokpayi, J., Rogawski, E., Kahler, D., Hill, C., Reynolds, C., Nyathi, E., Odiyo, J.O., Dillingham, R. Challenges to Sustainable Safe Drinking Water: A Case Study of Water Quality and Use across Seasons in Rural Communities in Limpopo Province, South Africa. Water; 2018, 10(2)18, https://doi.org/10.3390/w10020159

Geotechnical analysis of aggregate rock for use in road and construction: A case study of Mukula Stone Crusher

N Rembuluwani* and TU Khumeleni

Department of Mining and Environmental Geology, University of Venda, South Africa.
*Email of corresponding author: Ndivhudzannyi.rembuluwani@univen.ac.za

Abstract

The road is one of land transportation infrastructure which is very important in supporting the economy for both regional and national development. The quality of material for road construction influences road performance. Aggregate material plays a major role in road and construction and it forms about 95% weight of the total concrete mixture. This study was conducted to determine the suitability of the rock aggregate produced in Mukula Stone Crushers for use in road and construction as per South African National Standard (SANS). Flakiness test was carried out in conjunction with strength test. Specimens of fragmented rock material were collected and subjected to an in-house crusher. Crushed material was graded to determine fraction passing 14mm and retained on 10mm sieve, this fraction was used to determine the Aggregate Crushing Value (ACV). Retained 14mm material was prepared to determine flakiness index. Results indicated that the materials from Mukula Stone Crushers have strong properties and are of good quality. The values obtained from the tests were 13.7% ACV and 14% flakiness index, which does not exceed maximum percentages required by SANS of 29% and 35%, respectively. These results show that the material has high strength and is well rounded. Sufficient roundness and hardness of aggregate is required in road and building construction to avoid crushing of buildings and to make road surface balanced and difficult to damage. The study indicated that the aggregate produced in Mukula Stone Crusher can be used for road and building construction.

Keywords: Aggregate, Flakiness Index, ACV, Construction

1. Introduction

The main operational function of road is to provide accessibility and connectivity between centers, for transportation of people and goods during its service life. Roads in South Africa are typically designed to provide a service of 20 years during this time deterioration of the material should be minimal. It is therefore essential that the aggregate material used in road layers should be durable and their deterioration be minimal. Aggregate rocks consist of hard materials which are generally derived from the crushing of solid rock or boulders [1]. Compared with many other countries, South Africa has a plentiful supply of hard rock, which can be obtained by quarrying naturally occurring deposits of hard rock. The importance of using the recommended type and quality of aggregate cannot be overemphasized [2]. Not only that aggregates should be strong and durable, they should also possess proper shape and size to make the pavement act monolithically.

The choice of the method or a combination of the test methods for durability evaluation depends on the required parameters to meet material specifications for pavement design and the type of rock [3]. There are several commonly used test methods to determine the suitability of rock aggregates for use in pavements and they provide a better understanding of the quality of aggregates. The test methods to evaluate the durability or quality of aggregates involving some form of particle to particle interaction under load are mostly the mechanical tests which include Aggregate Crushing Value (ACV). To determine the suitability of the aggregate for use in pavement construction, ACV test was conducted to determine the strength of the material. The shape and volume parameters can be used to define the flakiness index of the aggregates. In South Africa, aggregate shape properties are quantified by flakiness index [4]. This paper focuses on analyzing the materials found in Mukula to determine their suitability in road construction.

2. Materials and Methods

ACV Test

From the field sampling, three specimens of fragmentated rock material were collected and subjected to the in-house crusher. According to South African National Standard [5], the standard test is carried out on the fraction passing 14mm sieve and retained on the 10mm sieve. Therefore, crushed material was prepared by sieving out enough quantity to yield a test fraction aggregate passing a 14mm sieve and retained on a 10mm sieve, of 2.98kg per specimen sample, enough to fill the cylindrical measure for ACV test. The crushing cylinder was placed on its base plate, retained specimens were filled on a container in three layers and each layer was tamped with 25 light strokes of the tamping rod using the hemispherical end. Surface of the aggregate was leveled, and plunger was inserted. Care was taken to ensure that it did not jam in the cylinder until it rested horizontally on the surface of the aggregate.

The aggregated crushing assembly was placed centrally on the bearing platen of the compression testing machine, and a load at a uniform rate of 40KN/min at plus or minus 5KN/min was applied. The applied load was released upon reaching 400KN. All material from the crushing cylinder was removed, and the aggregate was loosened with care. All loosened dry material was sieved on a 2mm sieve into a pan as described in SANS 3001-AG10 [6]. Both materials retained on the 2mm sieve and the material passing the 2 mm sieve retained in the pan was weighed and their masses were recorded to the nearest 1g. ACV was determined using the following formulas:

$$P_{Ci} = 100\left(\frac{M_{CiP}}{M_{1i}}\right) = A_C$$

Where P_{Ci} is the percentage of fines generated and M_{CiP} is the mass of the fraction that passes through the 2 mm sieve, expressed in grams and A_C is ACV.

Flakiness Index

The flakiness index of coarse aggregate is a measurement of the flatness of an aggregate, which influences many uses in the construction industry. For example, it affects the bulk density of the aggregate used for concrete and the performance of road surfacing aggregates. As described in SANS 3001-AG1 [7], it is recommended that a flakiness index test is carried out in conjunction with the strength test (ACV). The flakiness index parameter gives an indication of the flatness of a selection of aggregate particles [8].

Retained 14 mm material after crushing was prepared to determine the FI. The sample was divided by riffling to a test size that complies with the slot dimensions, size and mass of fractions table. As described in SANS 3001-AG1 [9], grading analysis was carried out, separating the test sample into the relevant fractions. Each fraction was weighed to be gauged to the nearest 1g and the masses were recorded. All particles were gauged in each fraction size.

3. Results and Discussion

Grading Results

Grading is the particle-size distribution of an aggregate as determined by a sieve analysis [10]. This study is focused on course aggregates, the standard sieves for course aggregates have openings ranging from 2mm to 100mm [11]. The grading sizes for these aggregates apply to the amounts of aggregate (by mass) in percentages that pass through an assortment of sieves. For a coarse aggregate to be used in concrete making, it should fall within the standards [12]. Sieve analysis was conducted to determine the grading of the crushed aggregate samples. The results were determined and are shown in Table 1 and expressed in the graph in Figure 1.

The sieve analysis, known as the gradation test, is a basic and essential test for all aggregate utilization [12]. This test determines the distribution of aggregate particles, by size, within the collected sample. This test in conjunction with ACV and Flakiness index is a very good quality control and acceptance tool [13]. The sample was collected from the G1 material which is a sound rock from a quarry. The grading of the tested material fell around or close to the standard and the gradation curve is S-Shaped (Figure 1) which shows that the material of different sizes is well distributed. Therefore, the material has a good quality for construction.

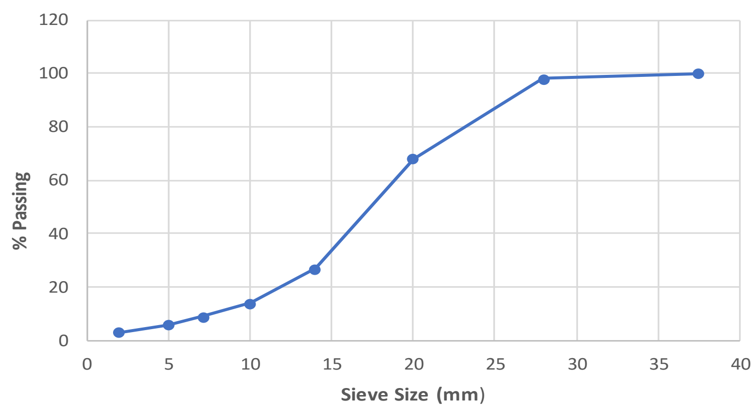


Figure 1. Grading curve, parentage passing by mass.

TABLE 1. Sample grading results

Sieve size	Accumulative Mass Retained(g)	% Retained	% Passing
37.5		0	100
28	39.7	2	98
20	730.9	30	68
14	1663.1	41	27
10	1957.6	13	14
7.1	2072.4	5	9
5	2128.2	3	6
2	2202.1	3	3

ACV Test Results

These test results are used for the quality control of the concrete, by means of particle strength, of aggregates. For this study, aggregate crushing value was tested and the 10% fines aggregate crushing (FACT) test was conducted. This test method is classified as group A, rating 5 and activity AG, in accordance with the requirements of the South African Construction education and training authority (CETA) and its value is not supposed to exceed 29 [10]. During the test, mass of the material before test was weighed and measured to be 2649g. After the test, the mass of fines was measured to 362 grams. The ACV was then calculated as follows:

$$ACV(\%) = \frac{\mathrm{b}}{a} \times 100 = \frac{362\mathrm{g}}{2649\mathrm{g}} \times 100 = 13.7\% \text{ (the stone has high strength)}$$

Therefore, from the test results the ACV was calculated to be less than the standard value of 29 and from the results it shows that the stone is very strong.

Flakiness index Test Results

This is the test of coarse aggregate used to measure the flatness of an aggregate, which influences many uses in the construction industry such as bulk density of the aggregate used for concrete and the performance of road surfacing aggregates [14]. This test method is classified as group A, rating 3 and activity AG, in accordance with the requirements of the South African Construction education and training authority (CETA) and its value is not supposed to exceed 35 [10]. The results of the test are shown in Table 2.

TABLE 2. Flakiness test results

Sieve Size(mm)	Mass of Fraction (M_S) (g)	Mass pass Flakiness slot (M_F) (g)
18.7	39.7	0
14	691.2	78.8
10	932.2	128.8
7	294.5	43.7
5	114.8	31.3
3.5	55.8	20.1
Total	**2128.2**	**302.7**

Fineness modulus

The fineness modulus of coarse aggregate according to ASTM C 125 is calculated by adding the cumulative percentages by mass retained on each of a specified series of sieves and dividing the sum by 100, shown in Table 3.

TABLE 3. Determination of finesses modulus

Sieve size (mm)	% Retained(a)	% Passing	Cumulateive retained (b)
37.5	0	100	0
28	2	98	2
20	30	68	32
14	41	27	73
10	13	14	86
7.1	5	9	91
5	3	6	94
2	3	3	97
Pan	3	0	-

$$\text{Fineness Modules} \quad = \frac{\sum b}{\sum a} = \frac{475}{100} = 4.75$$

FM is an index of the fineness of an aggregate, when the FM is high it shows that the aggregate is coarser. Different aggregate grading may have the same FM. FM of fine aggregate is useful in estimating proportions of fine and coarse aggregates in concrete mixtures. from the above results it shows that the mixture is well balanced with enough fines and enough coarse aggregate [15].

4. Conclusion

The study has shown that the aggregate produced in Mukula Stone Crusher can be used for road and building construction. Aggregate shape and surface texture are some of the characteristics that play a huge role in the selection of material for construction and these should comply with the requirements. The materials which were tested have flakiness of 14%, which complies with the minimum requirements for construction. Sufficient hardness is required so that the aggregate does not crush during construction. To ensure adequate hardness and toughness the ACV should not exceed the maximum value of 29%. From the test conducted the ACV of 13.7% was determine which shows that the material has high crushing strength making the material most suitable for construction of high-volume roads.

Acknowledgments: The authors will like to thank Mukula Stone Crushers for allowing this study and Pakama Crushers for the laboratory analysis and guidance throughout this study.

References

1. McNally, G. (2002). Soil and rock construction materials. CRC Press.
2. SANS. (2014a). Aggregates from natural sources Aggregates for concrete. Pretoria: SABS Standards Division.
3. Paige-Green, P. (2007). Durability testing of basic crystalline rocks and specification for use as road base aggregate. Bulletin of Engineering Geology and the Environment.
4. TMH 1. Standard Methods for Road Construction Materials. 1986. DoT, Pretoria, South Africa.
5. SANS. (2012). Civil Engineering Test Methods PartAG10: ACV (Aggregate Crushing Value) and 10% FACT (fines aggregate crushing test) values of coarse aggregate. Pretoria: SABS Standards Division.
6. Mgangira, M.B., Xungu, S.A. and Giani, J.C. (2018). An investigation of aggregate degradation in a high stress field. 37th Annual Southern African Transport Conference: Proceedings. Pretoria, South Africa.
7. SANS. (2014c). Civil Engineering Test Methods PartAG1: Particle size analysis of aggregates by sieving. Pretoria: SABS Standards Division.
8. Anochie-Boateng, J., Komba, J.J. and O'Connell, J.S. (2011). Laser-based approach for determining flakiness index of aggregates used in pavements.
9. Stark, T., Wilk, S. and Swan, R. (2018). Sampling, Reconstituting, and Gradation Testing of Railroad Ballast. In Railroad Ballast Testing and Properties. ASTM International.
10. South African National Roads Agency. (2013). South African pavement engineering manual: chapter 4: standards. South African National Roads Agency, Pretoria, South Africa.
11. Sneha, M. and Senthamarai, R.M. (2018). Design and Performance of Sustainable concrete. International Journal of Applied Engineering Research.
12. Little, D.N., Allen, D.H. and Bhasin, A. (2018). Aggregates. In Modelling and Design of Flexible Pavements and Materials. Springer, Cham.
13. SANS. (2014b). Civil Engineering test methods PartAG4: Determination of the flakiness index of course aggregate. Pretoria: SABS Standards Division.
14. Paul H.W., Karen K.D. (2003). Highway Engineering. USA: John Wiley & Son.
15. COLTO. 1998. Standard Specifications for Road and Bridge Works for State Road Authorities. Published by the South African Institute of Civil Engineering (SAICE), Pretoria.

Disappearance of wetland ecosystems and the role of participatory land use planning in Mathavelani Precinct in Limpopo Province of South Africa

E Ingwani* and MM Seaba

Department of Urban and Regional Planning, University of Venda, South Africa
*Email of corresponding author: ingwani@gmail.com

Abstract
The disappearance of wetland ecosystems in rural settlements is increasingly becoming a global concern. The aim of this paper is to contextualize the complexities flowing from the disappearance of wetland ecosystems and the role of Participatory Land Use Planning as a tool for sustainable management of wetland ecosystems using a case study of Matavelani Precinct in Limpopo Province of South Africa. This explorative case study adopted a mixed methods approach. Qualitative and qualitative data was collected from 75 households; the Village Head; and the municipal spatial planning experts from Thulamela Local Municipality, and urban and regional planning academics from the University of Venda. Spatial data was reproduced through ArcGIS and AutoCAD. The tragedy of the commons theory by Hardin (1968) is the mode of analysis. Wetland ecosystems of Matavhelani precinct are fast disappearing due to changes in land use. An inclusive Participatory Land Use Planning tool remains important to preserving wetland 'ecosystems in Matavhelani precinct.

Keywords*:* participatory land use planning; disappearance, wetland ecosystems

1. Introduction

The disappearance of wetland ecosystems is a global concern. Wetland ecosystems sustain diverse biotic and abiotic species [2]. Wetland ecosystems are spaces that are naturally saturated with water on a more or less permanent basis. In most cases, human interaction interferes with the ability of wetland ecosystems to provide functional relevance to a biodiversity of plants and animals. The increasing demand for services from wetland ecosystems leads to overuse and exploitation of wetland ecosystems. Participatory Land Use Planning emerges as a significant tool to the management and conservation of these wetland ecosystems.

Participatory Land Use Planning is a process, activity, and a methodology that emphasises community empowerment through discussions with experts to engender sustainable management of natural resources [3]. Communities and experts on land use from planning institutions such as local municipalities collaboratively make decisions at village level through PLUP in order to harmonize activities and land uses to avoid distortions and conflict.

This paper interrogates the disappearance of wetland ecosystems in South Africa, and the role of PLUP using a case study of Matavhelani Precinct. The paper focuses on these trajectories from 2013 to present (2018) - the period marked with the inauguration of the Spatial Planning and Land Use Management Act 16 of 2013 in South Africa. Matavhelani Precinct is endowed with a diversity of wetlands that provide many ecosystems services to local households. These ecologically sensitive spaces are however fast disappearing.

2. Materials and methods

This explorative case study adopted a mixed methods approach [4]. Qualitative and qualitative data was collected from 75 households through household questionnaires; an interview with the Village Head; and the Delphi Technique with municipal spatial planning experts from Thulamela Local Municipality, and urban and regional planning academics from the University of Venda. Extensive literature review, and observations triangulated evidence. Spatial data was reproduced through ArcGIS and AutoCAD. This paper employs the theory of space production [5], and the tragedy of the commons [6] as theoretical lenses to understand why wetland ecosystems in Matavhelani Precinct are disappearing. These two theories explain the reasons behind the disappearance of wetland ecosystems, and why adoption of the PLUP tool remains critical. Both modes of analysis also explain how individual interaction with space such as wetland ecosystems can engender an array of outcomes.

3. Results

Characterizing wetland ecosystems in Matavhelani Precinct

Five distinct categories of natural wetlands were identified in Matavhelani Precinct. These include swamps, fens, springs, marshes and a bog. In Matavhelani Precinct, ferns recharge underground acquirers, and release water when fully recharged. Springs draw underground water to sustain all life forms above the ground. The bog of Matavhelani Precinct on the other hand is a sacred religious space where community rituals take place. The bog is characterized by a thicket of tree and grass species soaked in muddy water. The swamps of Matavhelani Precinct are low lying areas with high amounts of vegetation and water that takes time to drain. Whereas, marshes are just waterlogged areas that drain water from time to time. Figure 1 shows the location of the wetland ecosystems in Matavhelani Precinct.

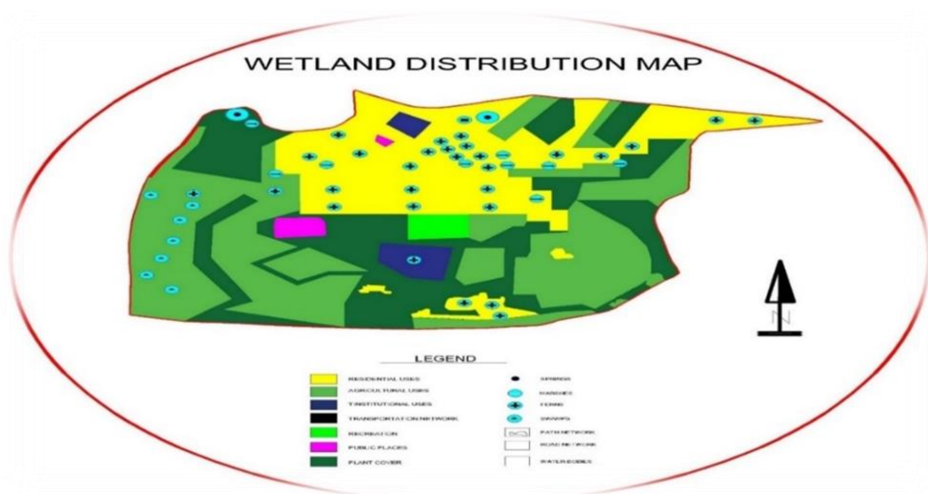


Figure 1. The distribution of wetland ecosystems in Matathavhelani Precinct

The location of wetland ecosystems in Matavhelani Precinct shows that wet lands coexist, and often occupy the same geographic location. Because of the mutual relationships 'between' the wetlands, the ecosystems support each other to boost services to people. Two distinct categories of wetland ecosystems, and use rights were identified in Matavhelani Precinct. These are the communal and private wetlands ecosystems use rights.

Communal wetland ecosystems are public goods accessed by all community members without restriction. According to heads of households, all wetland ecosystems classified as communal carry common property use rights. Any individual in Matavhelani Precinct can access and use communal wetland ecosystems without excluding others. In most cases, communal wetland ecosystems are located on grazing land and forests. On the other hand, private wetland ecosystems are private goods. The property use rights for private wetland ecosysytems are determined by the individual owners. Often, the privatized wetland ecosystems are fenced to exclude others. Private wetland ecosystems are located on private farms and individual heads of households' residential stands. Privately owned wetland ecosystems in Matavhelani Precinct comprise marshes, swamps and ferns. About 80% of the wetland ecosystems in Matavhelani Precinct are privately owned. Yet, wetland ecosystems in rural areas carry common property rights that allow access and use by all community residents without restriction. According to heads of households, privatization of wetland ecosystems engenders the sustainability of the water bodies as private owners pay less attention to the conservation of such wetlands.

3.2 Wetland ecosystems services in Matavhelani Precinct

Community residents of Matavhelani Precinct extract a variety of ecosystems services from the wetland ecosystems in their locality. These services include water for domestic and agricultural use; food from wild vegetables and tree species, as well as spiritual relevance from the bog. The research findings also show that both private and communal swamps, springs and marshes are the most frequently visited because they offer ecosystems services that are necessary for livelihoods of the everyday.

Captalizing and maximizing use of common property resources by people causes exploitation of these resources [7]. However, people tend to capitalize the use of common property resources differently depending on the access dynamics at their disposal. In Matavhelani Precinct, privatized wetland ecosystems tend to suffer degradation due to over exploitation by individual households compared to those that are communally owned. Individual households use water from the privatized wetland ecosysytems to grow crops and vegetables throughout the whole year without giving the wetland ecosystems time to replenish. Whereas, the cultural norms and values that regulate use of communal wetland ecosystems are significant in conserving the communally owned wetland ecosystems such as the bog. Lack of individual initiatives to regulate use of privatized wetlands leads to disappearance of the ecosystems

The disappearance of wetland ecosystems in Matavhelani Precinct from 2013 to 2018

The state of wetland ecosystems in Matavhelani Precinct from 2013 to 2018 reveals significant change. Approximations show an increase in land for cultivation while wetland spaces decreased from 2013 to 2018 (See Figure 2).

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

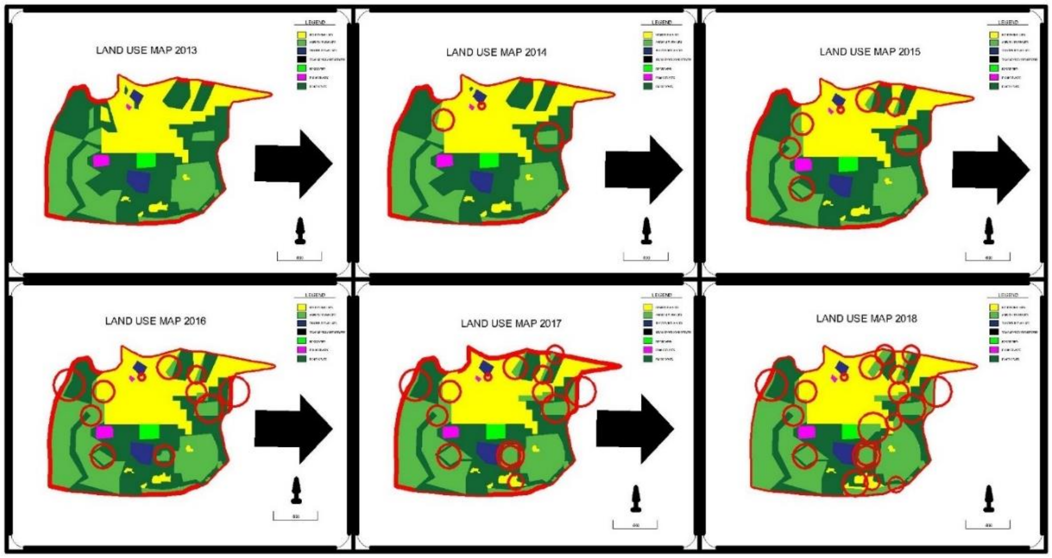


Figure 2. The disappearance of wetland ecosystems from 2013 to 2018

The change in land uses from wetland ecosystems, to arable and residential land between 2013 and 2018 in Matavelani Precinct is attributed to rapid population growth, and an increased need for shelter, food, water, and firewood. Furthermore, population increase induced the need for new developments such as social institutions. For example, the new clinic under construction requires a viable road network to promote accessibility and connectivity.

Contrary, conversion of wetlands into land for cultivation increased the number of subsistence farmers in the precinct. Water from wetland ecosysytems sustains growing of crops, and this promotes household livelihoods. The precinct lies on top of a ground water stream and thus generates water in the different wetland ecosysytems. This also explains why boreholes in the precinct never run dry as wetland ecosystems play a natural role of refiling the boreholes.

In Mathavelani Precinct, many private farmlands are located in proximity to wetland ecosystems. The heads of households indicated that growing of crops next to water bodies such as wetland ecosysytems simplifies labour in agricultural production. As a result, most heads of household prefer to own farmlands that are located in proximity to wetland ecosystems than those located far from the farmland. The traditional leader as a local level land administrator is responsible for extending individual land rights to heads of households. In some cases, land use rights are extended into ecologically sensitive areas such as wetland ecosystems. According to heads of households of Matavhelani, the traditional leader is therefore responsible for transacting land adjacent and within wetland ecosystems. This is because of the strong social ties between the traditional leader and community residents. Under these circumstances, permission to farm on common property resources such as wetland ecosysytems is always granted. Clearly, the nexus between tragedy of the commons and production of spaces is largely determined by how people interact. Thus, production of space through individual interaction can generate wider implications to the communities. For example, disappearance of the common property resources such as wetland ecosystems.

4. Discussion: The role of Participatory Land Use Planning

Wetland ecosystems of Matavhelani Precinct are fast disappearing. As community residents individualize and exploit wetland ecosystems, they interfere with the ecological functions of these aquatic features. The research findings show that swamps, springs and marshes are the most frequently visited because they offer services that are necessary for household livelihoods of the everyday. This shows not only the significance of wetland services towards domestic and livelihood activities, but also the vulnerability of the wetland ecosystems particularly springs due to overuse. People have a capitalist behaviour towards common property resources, and this causes them to over exploit these resources to meet their personal needs [8]. Clearly, individual interaction with spaces such as wetland ecosystems is determined by individuals' present gains, and not what will become of the ecologically sensitive areas in future.

Participatory Land Use Planning (PLUP) thus emerges as a spatial planning and land use planning technique that can mitigate further conversion of wetland ecosystems in Matavhelani Precinct. Participatory Land Use Planning makes use of other planning techniques such as transect walks, livelihoods analysis, and community mapping. Participatory Land Use Planning is a people-oriented bottom-up approach that recognizes adapting to the uniqueness of land uses to local circumstances [9].

A PLUP exercise was conducted in Matavhelani to isolate competing interests among community residents themselves, as well as between community residents and wetland ecosystems. Community residents of Matavhelani 'mapped' the land use activities they regarded as adaptable. The views of the community residents were captured through PLUP with regards to conservation and management of wetland ecosystems. Participatory Land Use Planning emerged as a spatial planning tool that does not only ensure sustainable land use, but also assists the management of wetland 'left overs' in the precinct. Participatory Land Use Planning techniques generate distributive decision-making processes capable of balancing community interests on accessing the remaining patches of wetland ecosystems. Through PLUP the existing land uses and and the wetland ecosystems in the precinct were interfaced through community engagement. Spatial planning experts also concurred that PLUP is an important tool in generating sustainable solutions to deal with disappearing wetland ecosystems. Adoption of partcipatory approaches in land use planning for the management and conservation of ecologically sensitive areas such as wetlands is important to reconcile apparent competing interests and needs for ecosystems services.

5. Conclusions

Land use change in Matavhelani Precinct is a result of population growth. Wetland ecosystems are slowly changing to other land uses mainly residential and cultivation. Change in wet land uses engendered disappearance of wetland ecosystems. As wetland ecosystems disappear, the ecosystems services also diminish thereby impacting on household livelihoods dependent upon these services. Clear strategies on interfacing the different land uses in the precinct and ecologically sensitive areas such as wetland ecosystems is critical to manage and conserve and the existing 'left overs' of wetland ecosystems. Adoption of community partcipatory approaches such as PLUP as an inclusive spatial planning tool that encourages learning from parrallel efforts of community residents and physical planning experts is important. Communities elsewhere experiencing similar circumstances on disappearance of wetlands can adopt PLUP to conserve such ecologically sensitive ecosysytems.

Acknowledgement: This paper is based on Mashudu Mulweli Seaba's unpublished BURP Honors thesis at the University of Venda. Mashudu Mulweli Seaba conducted fieldwork in Matavhelani Precinct between June 2017 and April 2018 [10].

References

1. Hardin, G. The tragedy of the commons. *Science* 1968, *162(3859)*:1243-1248.
2. Ramsar Convention on Wetlands. *Call to action to ensure and protect the water requirements of wetlands for the present and the future*. Gland: Switzerland, 2015.
3. International Institute for Environment and Development. Participatory Land Use Planning as a tool for community empowerment in Northern Tanzania. IIED, United Kingdom, 2010.
4. Creswell, J. W. *Research Design: Qualitative, Quantitative and Mixed Methods Approaches*, 4th ed., SAGE: London, 2014; pp. 215, ISBN 978-14522-2610-1.
5. Lefebvre, H. *Everyday life in the mordern world, 1st ed.,* Penguin Press: USA, 1971; pp. vii-x.
6. Hardin, G. The tragedy of the commons. *Science* 1968, *162(3859)*:1243-1248.
7. Hardin, G. The tragedy of the commons. *Science* 1968, *162(3859)*:1243-1248.
8. Hardin, G. The tragedy of the commons. *Science* 1968, *162(3859)*:1243-1248.
9. Engel, A. *Land use planning. Concept, tools, and application,* GIZ: Germany, 2011; pp. 74-78.
10. Seaba, M.M. The Impact of land use change on wetland ecosystems: A case of Matavhelani Precinct of Limpopo Province in South Africa, University of Venda, 2018.

Removal of As(III) and As(V) from groundwater using Fe-Mn bimetal oxide modified kaolin clay mineral: Adsorption modelling and mechanistic aspect

R Mudzielwana[1]*, WM Gitari[1] and P Ndungu[2]

[1]Department of Ecology and Resource Management, University of Venda, Thohoyandou, South Africa,
[2]Department of Applied Chemistry, University of Johannesburg, South Africa
* Email of corresponding author: mudzrabe@gmail.com

Abstract
A promising As(III) and As(V) adsorbent was successfully developed by impregnating Fe-Mn oxides onto the interlayer surface of kaolin clay mineral. The physicochemical composition of the synthesized adsorbent were characterized using X-ray fluorescence (XRF), Brunauer-Emmett-Teller (BET) and Fourier Transform Infrared (FTIR). The synthesized adsorbent has BET surface area of 29.8 m^2/g and a pore diameter of 8.5 nm making it a mesoporous material. Batch experiments were used to evaluate the applicability of the adsorbent in As(III) and As(V) removal from the solution. A maximum As(III) and As(V) percentage removal of 82.75 and 81.64%, respectively were achieved at initial pH of 6 from initial concentration of 5 mg/L using adsorbent dosage of 0.4 g/100 mL and agitation time of 60 min at 250 rpm shaking speed. The adsorption kinetics data was successfully described by the pseudo second order of reaction kinetics while the adsorption isotherm data was described by Langmuir isotherm model. The results showed that Fe-Mn modified kaolin clay mineral developed in this study is a promising adsorbent for arsenic removal from groundwater.

Keywords: Kaolin clay mineral; adsorption; arsenic; kinetics; isotherms.

1. Introduction

Contamination of groundwater by arsenic is now viewed as an environmental and public health issue globally with countries like India, Bangladesh, China, Mexico and Chile being the worst affected [1, 2]. It is estimated that more than 200 million people worldwide are at risk of arsenic poisoning from arsenic contaminated groundwater [3]. Symptoms of arsenic poisoning includes various types of cancer, skin thickening and neurological disorder diseases after a long period of exposure [4]. The World Health Organization (WHO) reduced the standard for arsenic in drinking water from 50 µg/L to 10 µg/L in 1993 with the aim of reducing arsenic poisoning risk to human beings [5]. Today, majority of communities living in developing countries still depend on groundwater with arsenic concentration beyond 10 µg/L due to lack of alternative sources of arsenic free water.

In natural water, arsenic primarily occur in inorganic form as arsenite [As(III)] and arsenate [As(V)], depending on the redox conditions [6]. Arsenite is more mobile, highly toxic and difficult to remove as compared to arsenate for most arsenic extraction processes. This is because it is neutrally charged at most pH ranges [7]. Available arsenic removal techniques such as coagulation, ion-exchange, adsorption and precipitation have been proven to be more effective to the removal of As(V) than As(III) which is highly toxic [8]. In convectional water treatment, pre-oxidation of As(III) to As(V) is necessary and recommended in order to achieve higher As(III) removal [9]. This process is more complex and highly expensive. As such it is of high priority to develop alternative technique that is sustainable and feasible and capable of effectively removing both As(V) and As(V) simultaneously.

Clay and clay minerals are largely found in nature at little or no cost. Furthermore, clays have shown higher adsorption efficiency towards the removal of inorganic contaminants from water. The higher sorption capacity of clay minerals originates from their physicochemical properties such as larger specific surface area, higher cation exchange capacity, and chemical and mechanical stability [10]. Moreover, clays can be modified to enhance their adsorption capacity. Mishra and Mahato [11] pillared montmorilonite clay mineral with respective iron and manganese oxides and evaluated their efficiency for As(III) and As(V) removal. The Mn oxide pillared clay showed higher efficiency for As(III) than As(V) while the Fe oxide pillared clay showed higher efficiency for As(V) than As(III). These findings have triggered the idea of developing Fe-Mn binary modified clay mineral. Therefore, is aimed at synthesizing Fe-Mn bimetal oxide modified clay mineral and evaluate its use in As(III) and As(V) removal from groundwater. The physicochemical parameters of the synthesized adsorbent were evaluated using available techniques such as BET, XRF and FTIR. The parameters such as contact time, adsorbate concentration and solution pH were also evaluated and optimized.

2. Material and Methods

Locally available kaolin clay (RK) containing quartz and kaolinite as main minerals was collected from Dzamba Village, Limpopo Province, South Africa. All chemical reagents were purchased from Rochelle Chemicals & Lab Equipment CC, South Africa Ltd and were of analytical grade and they were used without further purification. Stock solutions containing 1000 mg/L As(III) and As(V) were prepared by dissolving 0.1733 g $AsNaO_2$ and 0.476 g $HAsNa_2O_4$, respectively in a 100 mL flask using Milli-Q water (18.2 MΩ/cm). The solutions were preserved by adding few drops of 3 M HNO_3. Working solutions were prepared by appropriate dilutions.

2.1 Synthesis of Fe-Mn oxide modified kaolin mineral

The Fe-Mn bimetallic oxide modified kaolin mineral (FMK) was synthesized as follows: solutions containing 0.25 M Fe and Mn, respectively were mixed together at a volume ratio of 7.5 mL: 2.5 mL (3: 1) in a 250 mL plastic bottle to make up a final volume of 10 mL. To this, 1 g of clay was added, and the mixture was agitated for 10 min to ensure proper soaking. This was followed by addition of 20 mL of 2 M NaOH to the mixture to precipitate Fe and Mn into their respective oxides. The mixture was agitated on a Table shaker for further 60 min at 250 rpm and then aged for 48 hours for further precipitation. Thereafter, the mixture was centrifuged at 3000 rpm and the residues were washed with Milli-Q water to remove excess supernatants till the pH was close to neutral and then oven dried for 12 hours at 110 ^{O}C. Modified clay was then milled to pass through 250 µm sieve and then stored in a zip lock plastic bag.

2.2 Physicochemical Characterization

The elemental composition of the modified clay was examined using S1 titan handheld XRF (Bruker, Germany). Functional groups were determined using ATR Diamond FTIR (Bruker, Germany). The pore size distribution, pore volume, and pore diameter were determined by Barrett Joyner Halenda (BJH) sorption model using a specific surface area analyzer (Autosorb-iQ & Quadrasorb SI, USA). Nitrogen adsorption-desorption isotherms were used to determine specific surface area of the adsorbent according to Brunauer Emmett Teller (BET) model.

2.3 Batch Experiments

The efficiency of Fe-Mn oxide modified kaolin mineral (FMK) in As(III) and As(V) removal was evaluated using batch experiments. Parameters such as contact time, adsorbent dosage, adsorbate concentration and initial solution pH were evaluated. To evaluate the effect of contact time, 100 mL solution containing 5 mg/L As(III)/As(V) was pipetted onto 250 mL plastic bottle and 0.1 g of the modified clay was added. Mixtures were agitated for various contact times ranging from 10 to 120 min on a Stuart Reciprocator Table Shaker. For the effect of adsorbate concentration, the intial As(III)/As(V) concentration was varied from 1 to 30 mg/L and to evaluate the effect of pH the initial solution pH was adjusted from 2 to 12 using 0.1 M NaOH and 0.1 M HCl. After agitation, samples were filtered using 0.45 µm pore filter membrane using a vacuum pump. The solution pH was measured using JENWAY 3510 pH meter. The residual As(III)/As(V) concentration was measured using ScTRACE Gold electrode attached to 884 professional VA Polarography (Metrohm, SA). A composite solution containing 1 mol/L sulfamic acid, 0.5 mol/L citric acid and 0.45 mol/L KCl was used an electrolyte. For total As concentration, $KMnO_4$ was added as an oxidizing agent. All experiments were carried out in triplicate and the mean values were reported. Equation 1 and 2 were used to compute the percentage of removal and the adsorption capacity respectively.

$$\%\,removal = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_i - C_e}{m}\right) \times v \quad (2)$$

Where C_i and C_e represent the initial and equilibrium As(III) concentration (mg/L) respectively and m represent mass of the dry adsorbent (g). V is the volume (*L*) and q_e is the adsorption capacity (mg/g).

3. Results and Discussion

Adsorbent characterization

Table 1 presents the chemical and surface properties of raw kaolin (RK) and Fe-Mn modified kaolin clay (FMK). The results showed that SiO_2 and Al_2O_3 are the major chemical oxides of RK averaging 56.06 and 22.05%, respectively. Fe_2O_3 was observed as one of the minor oxides averaging 3.88%. After modification the percentage composition of Fe_2O_3 and MnO increased to 16.66 and 4.02%, respectively. The results suggest that the clay surface was successfully coated by Fe and Mn oxides. Surface area of the clay increased from 19.2 to 29.8 m^2/g after modification. This could be attributed to propping up of the parent clay mineral interlayer structure during modification. Furthermore, the pore diameter decreased from 9.54 nm to 8.5 nm after modification. The decrease in pore diameter could be an indication that the Fe and Mn oxides were diffused into the pores of RK during modification. Based on the average pore diameter range, the clay is classified as a mesoporous material.

TABLE 1. Chemical composition and surface properties of RK and FMK.

	SiO_2 (w/w %)	Al_2O_3 (w/w %)	Fe_2O_3 (w/w %)	MnO (w/w %)	MgO (w/w %)	CaO (w/w %)	K_2O (w/w %)	Surface area (m^2/g)	Pore diameter (nm)
RK	56.06	22.05	3.88	0.01	0.57	0.95	0.16	19.2	9.54
FMK	39.39	10.08	16.66	4.02	LOD	0.55	0.13	29.8	0.08

Figure 1 present the FTIR spectrum of RK, FMK and arsenic loaded FMK. The band observed at 3625.11 cm^{-1} in RK spectra can be ascribed to vibration of physiosorbed water molecules. The bands at 2077 and 1644.2 can also be ascribed to the hydroxyl groups located between the octahedral and tetrahedral sheets of the clay. The band at 1005 and 911.88 cm^{-1} could be attributed to the vibration and stretching of Si-O-Si and Al-OH-Al groups, respectively. The bands at 779.25 cm^{-1} could be attributed to the vibration of Si-O groups. After modification, a decrease in the intensity of all the bands was observed. This could be attributed to loss of SiO_2 and Al_2O_3 content during modification. A new band was observed at 1409.6 cm^{-1} which could be attributed to Fe-OH and Mn-OH vibration. After arsenic adsorption a further decrease in bands at 3625.11 cm^{-1} 2077 and 1644.2 cm^{-1} was observed. Which could be due to exchange of OH- groups for arsenic species. A slight increase was observed in the bands at 1005 and at 911.88 cm^{-1} this could be ascribed to formation of arsenic containing mineral complexes. As such ion exchange and complexation are suggested as the main mechanisms for arsenic adsorption.

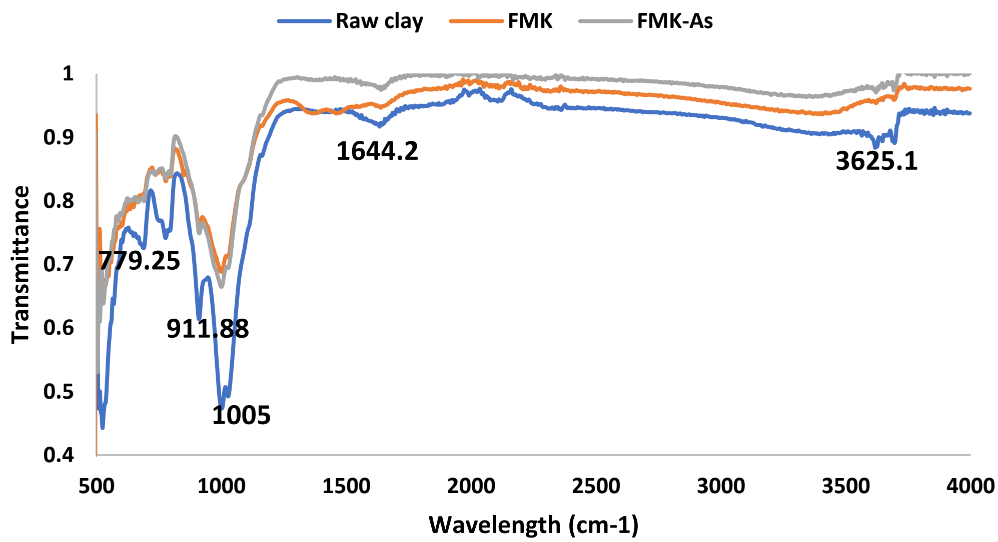


Figure 1. FTIR spectra for RK, FMK and FMK-As.

3.1 Effect of contact time and adsorption kinetics

The effect of contact time on As(III) and As(V) removal is presented in Figure 2. It is observed that the percentage As(III) and As(V) increased with increasing contact time. After 60 min, no significant change in the percentage of removal for both arsenic species was observed. Therefore, 60 min was chosen as the optimum contact time for subsequent experiments.

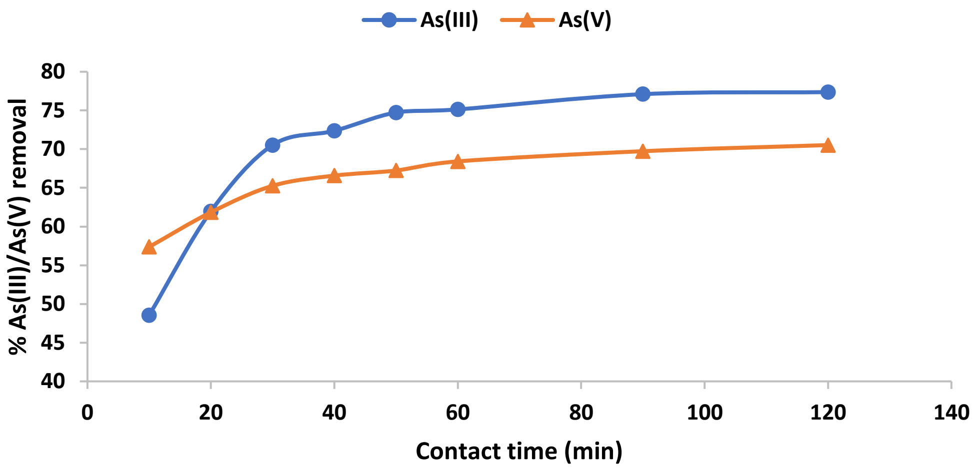


Figure 2. Effect of contact time in percentage As(III) and As(V) removal by FMK (initial As(III)/As(V) concentration of 5 mg/L, adsorbent dosage of 0.1 g/100 mL, pH 6.2)

To further elucidate the As(III) and As(V) possible adsorption mechanism the linear equations for pseudo first and second order reaction models were used [12,13]. The linear equations 3 and 4 represent the pseudo first and second order reaction kinetics models, respectively.

$$\log(q_e - q_t) = -\frac{K_1 t}{2.303} + \log q_e \tag{3}$$

$$\frac{t}{q_t} = \left(\frac{1}{q_e}\right) t + \frac{1}{K_2 q_e^2} \tag{4}$$

Where q_e and q_t (mg/g) are the adsorption capacities of As(III) and As(V) of the adsorbents at the equilibrium and at time t (min), K_1 (min^{-1}) and K_2 (mg/g. min^{-1}) are the rate constants of the pseudo first order equation and pseudo second order equation, respectively. The value of K_1 is determined from the slope of log q_e-q_t vs time while the value of K_2 is determined from the slope of t/q_t against time. The constant values for pseudo first order and second order models are presented in Table 2. Based on the R^2, adsorption data for both arsenic species was described better by the pseudo second order (R^2=0.99). This suggest that adsorption of both As(III) and As(V) was more of chemisorption.

TABLE 2. Parameters for pseudo first and second order reaction kinetics model.

	Pseudo first order				Pseudo second order		
	$q_{e\ exp}$ (mg/g)	K_1 (min^{-1})	$q_{e\ cal}$ (mg/g)	R^2	K_2 (mg/g. min^{-1})	$q_{e\ cal}$ (mg/g)	R^2
As(V)	5.36	0.011	1.42	0.89	0.05	5.49	0.99
As(III)	5.63	0.034	2.34	0.94	0.02	6.0	0.99

3.2 Effect of adsorbate concentration and adsorption isotherms

The adsorption isotherms were studied by varying the As(III) and As(V) initial adsorbate concentration. The results are presented in Figure 3 in terms of As(III) and As(V) against adsorbate concentration. It is observed that the percentage of removal decreases with increasing arsenic species concentration. This could be attributed to increasing ratio between the active adsorption sites and the adsorbate molecules as the concentration increases.

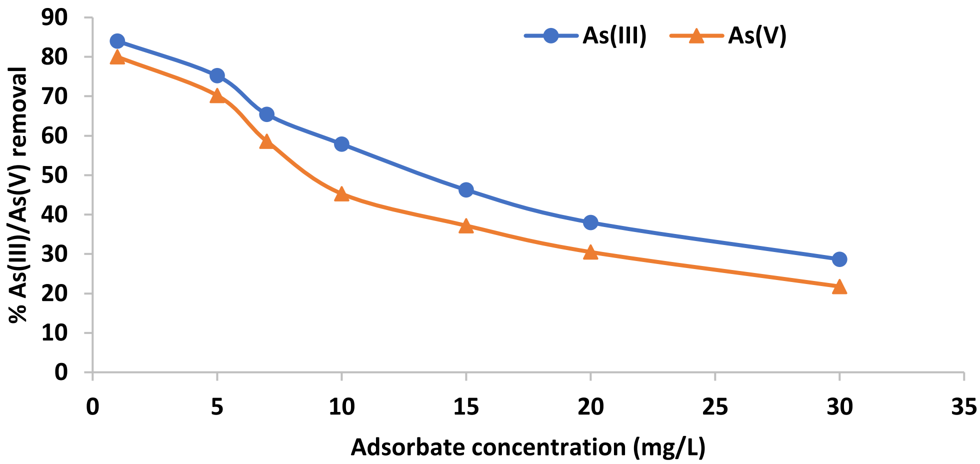


Figure 3. Effect of adsorbate concentration on As(III)/As(V) removal by FMK (0.4 g/100mL adsorbent dosage, 60 min contact time at 250 rpm and initial pH of 6.5).

To further illustrate the relationship between the adsorbate concentration and the adsorbent the linear equations for Langmuir (Equation 6) and Freundlich (Equation 7) isotherm model were used [12].

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{max}}\right) C_e + \frac{1}{Q_{max} K_L} \qquad (6)$$

$$\log q_e = n \log C_e + \log K_F \qquad (7)$$

Where C_e (mg/L) is the As(III)/As(V) concentration at equilibrium, q_e (mg/g) is the adsorption capacity at equilibrium, Q_{max} (mg/g) is the maximum saturated monolayer adsorption capacity, K_L (L/mg) is the constant related to the affinity between adsorbent and adsorbate, K_F (mg/g) is the Freundlich constant related to adsorption capacity and n is the Freundlich intensity parameter which indicate the magnitude of the adsorption driving force or the surface heterogeneity. The value of Q_{max} and K_L are determined from the slope and intercept of C_e/q_e vs. C_e while the value of K_f and n are determined from the slope and intercept of log q_e vs. log C_e. The constant values for Langmuir and Freundlich adsorption are presented in Table 3. Based on the regression coefficient values obtained, the experimental data showed better fit to Langmuir adsorption isotherm model (R^2=0.99). The better fitting to Langmuir isotherm model suggests monolayer uniform adsorption on the surface of the adsorbent.

TABLE 3. Parameters for Langmuir and Freundlich isotherm models.

	Langmuir isotherm				Freundlich		
	q_e (mg/g)	q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	1/n	R^2
As(V)	1.63	2.12	2.76	0.99	1.81	0.42	0.90
As(III)	2.15	3.04	3.2	0.99	1.97	0.47	0.93

3.3 Effect of initial pH

The effect of pH onto As(III) and As(V) removal is presented in Figure 4. The percentage As(III) removal remained almost constant at pH levels between 2 and 8 and decreased at pH >10. While the percentage As(V) removal decreased with increasing pH. At acidic pH values, the adsorbents surface is positively charged and this will enhance As(V) removal through electrostatic attraction. At alkaline pH values, the adsorbent surface is largely negatively charged, this enhances electrostatic repulsion between As(V) and As(III) species and adsorbent charges hence the decrease in percentage of removal.
Equation 8-12 hypothesize the adsorption of As(V) and As(V) onto FMK.

$$\equiv MOH + H_3AsO_4 \leftrightarrow \equiv MH_2AsO_4 + H_2O \quad (8)$$
$$\equiv MOH + H_2AsO_4^- \leftrightarrow \equiv MHAsO_4^- + H_2O \quad (9)$$
$$\equiv MOH + HAs_4^{2-} \leftrightarrow \equiv MAs_4^{2-} + H_2O \quad (10)$$
$$\equiv MOH + H_3As_3 \leftrightarrow \equiv MH_2As_3 + H_2O \quad (11)$$
$$\equiv MOH + H_2As_3^- \leftrightarrow \equiv MHAs_3^- + H_2O \quad (12)$$

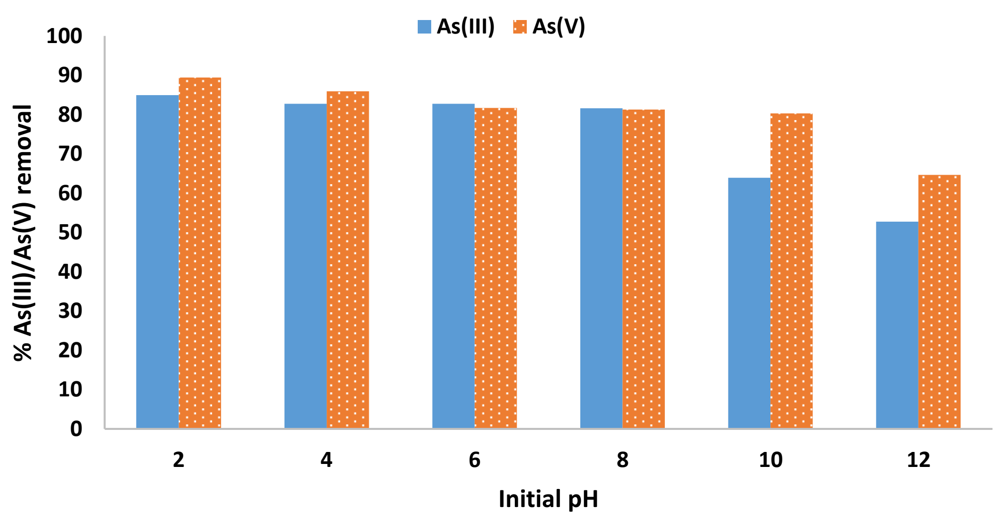


Figure 4: The effect of initial pH on As(III)/As(V) removal onto FMK (initial As(III)/As(V) concentration 5 mg/L, 0.4 g/100 mL adsorbent dosage, 60 min contact time at 250 rpm shaking speed).

4. Conclusions

Fe-Mn binary oxide modified kaolin clay mineral was successfully prepared and used as As(III) and As(III) adsorbent. A maximum As(III) and As(V) percentage removal of 82.75 and 81.64%, respectively were achieved at initial pH of 6 from initial concentration of 5 mg/L using adsorbent dosage of 0.4 g/100 mL and agitation time of 60 min at 250 rpm.

Fixed bed column experiment showed that a volume of 80 mL of groundwater with spiked arsenic concentration of 4.45 mg/L was treated at breakthrough point. The adsorption kinetics data was successfully described by the pseudo second order of reaction kinetics while the adsorption isotherm data was described by Langmuir isotherm model. The results showed that FMK developed in this study is a promising adsorbent for arsenic removal from groundwater.

Acknowledgment: Authors would like to acknowledge financial support from NRF, Saif and University of Venda RPC grant Number: SES/17/ERM/03, TESP-ESKOM grant and Prof Gitari Environmental Remediation and Water Pollution Chemistry Research groups DHET research incentive funds.

Reference

1. Bhowmick, S., Pramanik, S., Singh, P., Mondal, P., Chatterjee, D., Nriagu, J. Arsenic in groundwater ofWest Bengal, India: A review of human health risks and assessment of possible intervention options. Science of the Total Environment, 2018, 612, 148–169.
2. Rahman, M.A. Rahman, A. Khan, M.Z.K. Renzaho, A.M.N. Human health risks and socio-economic perspectives of arsenic exposure in Bangladesh: A scoping review. Ecotoxicology and Environmental Safety, 2018, 150, 335–343.
3. Naujokas, M.F. Anderson, B. Ahsan, H. Aposhian H.V. Graziano, J.H. Thompson, C. Suk, W.A. The Broad Scope of Health Effects from Chronic Arsenic Exposure: Update on a Worldwide Public Health Problem. Environmental Health Perspectives, 2013, 121(3), 295-302.
4. Mandal, B.K., Suzuki, K.T. Arsenic round the world: a review. Talanta, 2002, 58, 201–235.
5. World Health Organization (WHO). 2011 Guidelines for drinking-water quality, Fourth edition, Volume 1.
6. Smedley, P.L, & Kinniburgh, D. G. A review of the source, behavior and distribution of arsenic in natural waters. Applied Geochemistry, 2002, 17, 517-568.
7. Qi, J. Zhang, G. Li, H., 2015. Efficient removal of arsenic from water using a granular adsorbent: Fe–Mn binary oxide impregnated chitosan bead. Bioresource Technology, 2015, 193, 243–249.
8. Li, X. He, K. Pan, B. Zhang, S. Lu, L. Zhang, W. Efficient As(III) removal by macroporous anion exchanger-supported Fe–Mn binary oxide: Behavior and mechanism. Chemical Engineering Journal, 2012, 193(194), 131–138.
9. Cui, H.J. Cai, J.K. Zhao, H. Yuan, B. Ai, C.L. Fu, M.L. Fabrication of magnetic porous Fe–Mn binary oxide nanowires with superior capability for removal of As(III) from water. Journal of Hazardous Materials, 2014, 279, 26–31.
10. Bhattachryya, G.K., Gupta, S.S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Advances in Colloid and Interface Science, 2008, 140, 114–131.
11. Mishra, T. Mahato, D.K. A comparative study on enhanced arsenic(V) and arsenic(III) removal by iron oxide and manganese oxide pillared clays from ground water. Journal of Environmental Chemical Engineering, 2016, 4, 1224–1230.
12. Tran, H.N. You, S.J. Bandegharaei, A.H. Chao, H.P. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. Water Research, 2017, 120, 88-116.
13. Ho, Y.S., 2004. Citation review of Lagergren kinetic rate equation on adsorption reactions. Scientometrics, 2004, 59(1), 171-177.

The impacts of climate change on water, energy and agriculture sectors: Adaptation strategies in southern Africa

S Mpandeli[1,4]*, D Naidoo[1], T Mabhaudhi[2], C Nhemachena[3], L Nhamo[3] and S Liphadzi[1]

[1]Water Research Commission of South Africa, Pretoria, South Africa
[2]Earth and Environmental Sciences, University of KwaZulu-Natal, South Africa
[3]International Water Management Institute, Southern Africa (IWMI-SA), South Africa
[4]School of Environmental Sciences, University of Venda, South Africa
* Email of corresponding author: sylvesterm@wrc.org.za

Abstract
Climate change is adversely affecting the water, energy and agriculture sectors in southern Africa. Current climate change adaptation strategies are developed and implemented along sectoral lines, and they are threatening to derail the sustainability of adaptation interventions. This review assesses climate change adaptation opportunities in southern Africa through the water-energy-food (WEF) nexus and recommends strategies to sustainably cement resilience and adaptation initiatives. Challenges hindering the three sectors to successfully build adaptive capacity are highlighted. A well-coordinated and integrated nexus approach results in strong resilient systems, creates opportunities to harmonise activities and manages trade-offs and synergies. Southern Africa has witnessed an increased frequency and intensity of extreme weather events resulting in reduced rainfall totals, low crop yields and energy shortfalls. As climate change is projected to result in 20% reduction in annual rainfall by 2080 in southern Africa, the socio-economic insecurities are expected to worsen if no action is not taken. The WEF nexus presents opportunities for greater resource coordination, resource mobilisation, and policy convergence across sectors and thus promoting a cross-sectoral resource management. Besides promoting regional integration, a cross-sectoral approach to resources management at regional level promotes an integrated regional development and improves the livelihoods of people as resources are transboundary in nature. Despite regional WEF nexus initiatives, the momentum has been slow due to lack of science evidence and political will. Overall, the WEF nexus approach has potential to increase the resilience of marginalised communities of southern Africa and contribute towards attaining the Sustainable Development Goals (SDGs 1, 2, 6 and 7).

Keywords: SADC; WEF nexus; climate change; resilience; adaptation; socio-economic development.

1. Introduction

Extreme climate events, such as recurring droughts and flooding, have emerged as the biggest threats to the rapid growth of many emerging economies in southern Africa. Across the region, it is expected that climate change will continue warming and changing rainfall patterns [1]. These impacts will be felt variably across the region, with some areas becoming warmer and wetter, while others will become warmer and drier [2]. Climate models concur that the latter scenario will be more dominant across southern Africa, with the impacts of climate change being mostly associated with declining rainfall totals [2,3]. According to Niang et al. [1] rainfall changes remain uncertain as climate change models struggle to simulate observed climate variability and teleconnection patterns. In terms of development, climate change is described as a wicked problem, because it is complex and straddles various sectors and levels [4]. Responses to climate change therefore necessitate transdisciplinary or cross-sectoral approaches [5]. Current approaches to climate change adaptation are similar to how development is framed in the region and they have been sector-based. This has often led to mal-adaptation as trade-offs are not accounted for.

Within the region, the dominant narratives comprising ambitious development plans are common and often based around sectors that are highly exposed to climate variability, especially agriculture, hydropower and infrastructure [6]. The sectoral approach has been cited as another obstacle to sustainable development and efficient resource utilisation [5,7]. As such, there is a need to approach development from a cross-sectoral perspective as the challenges faced are cross-cutting. In this regard, emerging cross-sectoral approaches such as the water-energy-food (WEF) nexus approach could be useful. The WEF nexus is broadly defined as an approach that considers the interactions, synergies and trade-offs between water, energy and food when undertaking the management of these resources [7]. WEF resources are inextricably linked with usage within one sector influencing the use and availability in the adjacent sectors. The WEF nexus has been researched by many actors, each approaching their analyses with their niche or sector in mind, be they political, social, or scientific perspectives [8]. Unlike Integrated Water Resource Management (IWRM), which is water-centric in nature, the goal of the WEF nexus is to approach resource management more holistically by utilising a multi-centric philosophy with each resource sector within the WEF nexus having an equal weighting [5].

While it is widely recognised and accepted that climate change poses, perhaps, the single greatest threat to regional growth and development, most climate change adaptation strategies and plans are formulated and implemented from a sectoral approach. This tends to negate the complexity of climate change and the need for a systems approach in developing adaptation plans. The absence of a cross-sectoral approach to resource management may lead to cases of mal-adaptation.

2. Climate change impacts on WEF resources

In southern Africa climate change impacts would mostly be felt through water resources [3]. Reductions in water resources could severely affect food production and energy generation. The estimated reductions of about 20% in rainfall by 2080 could exacerbate water, energy and food insecurity if no action is taken. The region is already marked by a great spatio-temporal variability in climate and water resources, particularly in southern drier countries and the region has become arid, receiving less than 350 mm of rainfall. Reduced annual rainfall totals are impacting on energy generation and food production, compromising regional security and exacerbating regional vulnerabilities, as they threaten to reverse economic gains made in the past [9]. For example, the 2015/16 El Niño Southern Oscillation (ENSO) induced drought affected the whole region, resulting in more than 40 million people (14% of the SADC population) to be food insecure [9]. To counter these challenges, the region needs to adopt water management practices that reduce the use of water. Such practices include cultivation of indigenous underutilised crops that suit the current harsh environmental conditions [10]. Cultivating underutilised crops will reduce water allocated to agriculture which currently stands at 70% of available water resources [11]. Also turning to other sources of energy would result in saving a lot of water. Southern Africa can take advantage of its abundant cleaner sources of energy such as solar and wind [12]. Changes in climate are expected to severely affect performance of the agriculture sector with detrimental effects on progress in achieving food security and nutrition [13,14]. The Fourth and Fifth Assessment reports (AR4 and AR5) reported with medium confidence that agricultural systems in Africa (including southern Africa) were vulnerable to climate change impacts. Agricultural productivity in SADC would be significantly affected by projected

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds) ISBN 978-0-620-82267-1

changes in climate. For example, agricultural productivity in the region will decrease from 15% to 50% by 2080 due to climate change [15]. The adaptation of the agriculture sector to climate change through the WEF nexus enhances resilience through the production of enough food and fibre for the increasing population through innovative farming practices that suit the changing environment [16]. Adaptation in agriculture requires proactive policy interventions and integration into wider sustainable development agenda at local, national and regional levels to effectively build resilient communities and systems. For example, investing in improving efficiency in agricultural production systems will be an important intervention to address projected impacts of climate change on agriculture in the region. More efforts are required to build resilience on African agriculture systems to climate change and variability in addition to current adaptation initiatives [13]. Overall, it is critical that readily available sustainable adaptations in agriculture are implemented to help improve efficiency in resource use and simultaneously build resilient production systems. Ensuring that the resources for farmers to access such adaptation measures are important if they are to use them and build their resilience in the face of projected changes in climate.

The SADC region is endowed with vast energy resources, although availability varies from country to country. The untapped potential of hydropower generation in Angola, The DRC, Mozambique and Zambia (countries with reliable water resources) has capacity to supply the whole region with electricity [17]. The region currently shares power grids whose electricity is generated from shared watercourses. Nevertheless, biomass remains the most used source of energy as only 24% of the total population and 5% of rural people have access to electricity [18]. Over dependency on biomass energy contributes deforestation and desertification in the region [7]. The failure by the region to tap into the abundant cleaner energy resources has been lack of investment and financing. As the demand for energy continues to increase due to population and industrial growth and urbanisation, energy insecurity has been severe in the region causing power blackouts in most regional countries. As current hydro-electricity is failing to meet demand, turning to alternative cleaner sources of energy could be a solution. For example, the average outage of electricity in 2008-2009 was 6.70 hours with corresponding losses of 5.4% of annual sales [19]. Consequently, the success of the region's industrialisation and job creation goals is hampered by reliance on hydro-power which is in short supply due to recurring droughts. According to the SADC Regional Infrastructure Development Master Plan (RIDMP) of 2012, assuming an average economic growth rate of 8% per annum, energy demand is expected to increase to more than 77 000 MW by 2020 and to over 115 000 MW by 2030, exerting more pressure on water resources [20].

3. Climate change adaptation through the WEF nexus

Climate change adaptation through an integrated and cross-sectoral management of resources remains important for regional economic development in the advent of climate change and improve the livelihoods of people [21]. Responses to climate change range from autonomous coping strategies to reactive interventions towards climate variability and extreme events, and proactive interventions to long term changes in climate. Reactive/ autonomous adaptations include changes in production and management practices (such as changes in crop mixes, and crop varieties) in response to changes in local climatic and growing conditions. Proactive interventions on the other hand involve, planned policy and investment decisions to enhance adaptive capacity of target agricultural systems such as investments in efficient irrigation systems and new crop varieties [21]. While reactive/autonomous responses are useful in the short term, it is proactive interventions that will contribute to long term adaptation and sustainability. In that regard, it is important for the region to implement these interventions in a sustainable manner that will contribute to resilience building and improved productivity.

4. Current SADC WEF nexus initiatives

The SADC region produced the WEF Nexus Action Plan, which is incorporated in the RSAP IV, in realisation of the importance of the nexus in regional socio-economic security and cooperation and integration as well as due to the need to respond to the recurrence of drought in the region [22]. The aim of the WEF Nexus Action Plan (Figure 1) is to create an enabling environment for accelerated industrial growth and pilot the nexus to facilitate better understanding of the nexus benefits. The action plan recognises the role of the nexus in adapting to the challenges posed by population growth and climate variability and change, as well as in optimising resource use in order to achieve regional goals and targets. The plan calls for a regional nexus assessment study to provide policy recommendations as well as strategic actions that are informed by research and scientific evidence.

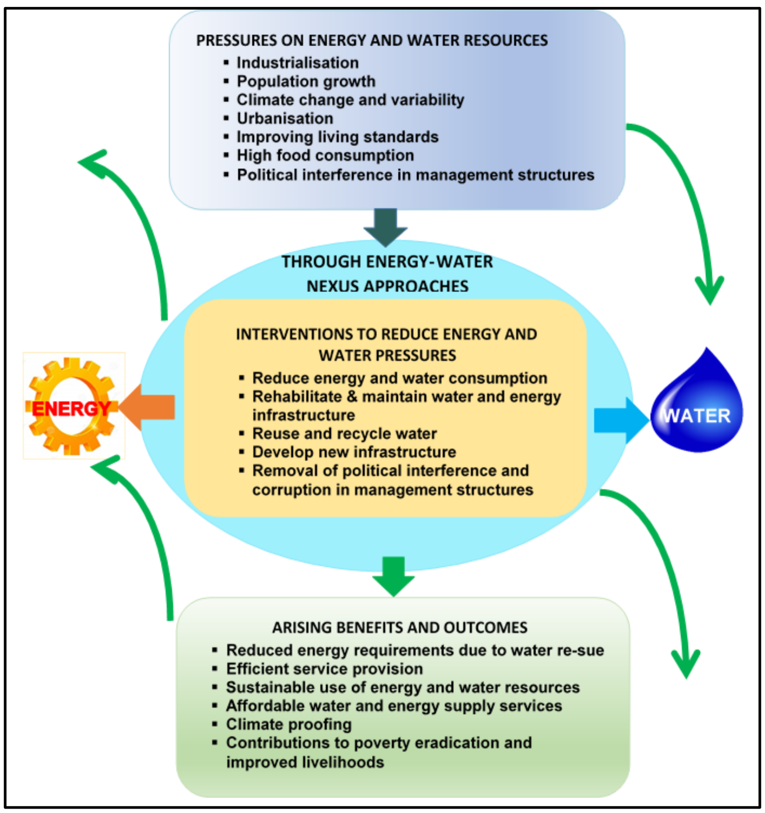


Figure 1. Energy-Water Action Plan conceptual framework.
Source: Adapted from The World Bank, 2016.

Key activities include mobilising resources for a regional nexus study in collaboration with other sectors and identifying and implementing regional nexus demonstration projects and studies. Despite the presence of the WEF Nexus Action Plan, there is little or no evidence of cross-sectoral linkages in institutions, policies and current projects. Some activities in recognition of the importance of the nexus include the SADC multi-stakeholders water dialogue and that focus on exploring nexus opportunities in providing coherent and well-planned development and use of resources. The multi-stakeholder dialogues also focus on regional value chains and job creation through the WEF nexus. While these efforts are commendable, there is a need to start developing action plans with clear timelines on how the WEF nexus initiatives and projects.

5. Conclusions

The WEF nexus draws on holistic, systems perspective that recognise the value of all sectors in equal terms. Climate change is a cross-cutting challenge that needs to be tackled by more than one climate sensitive sector. The integration of climate change adaptation strategies into the WEF nexus offers opportunities to create proper resource coordination, harmonisation of activities across all sectors, improves resilience and reduction of vulnerabilities to attain regional development targets. Resource scarcity is one of the primary constraints for individual sectors to meet the ambitions of the SDGs, and in general the development aspirations of SADC. The WEF nexus presents an opportunity for policymakers, researchers and development agencies to integrate the sectors to optimise the use of the resource base, maximise synergies and minimise trade-offs, and has grown to be an essential tool to achieve the SDGs on poverty alleviation, zero hunger, provision of water and sanitation, and access to affordable and reliable energy (Goals 1, 2, 6, and 7, respectively). There are also significant implications for health and sanitation as higher temperatures and lower rainfall are projected in the region, which may result in mal-nutrition, disease outbreaks and prevalence. The WEF nexus offers opportunities to integrate and manage these challenges in a more sustainable manner and promote regional peace and cooperation, harmonisation of legislations, policies and strategies in a region of transboundary resources like southern Africa. Sectoral policies that are not linked to each other are the cause of unsustainability and unbalanced resource development. However, successful implementation of the nexus at regional level requires political commitment, supported by technological innovations that allow producing more with less resources.

References

1. Niang, I.; Ruppel, O.C.; Abdrabo, M.A.; Essel, A.; Lennard, C.; Padgham, J.; Urquhart, P. In: Climate change 2014: Impacts, adaptation, and vulnerability. Part B: Regional Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge: United Kingdom and New York, NY, USA, 2014; p 199-1265.
2. Nhamo, L.; Mabhaudhi, T. Preparedness or repeated short-term relief aid? Building drought resilience through early warning in southern Africa. Water SA 2018.
3. Schulze, R. A 2011 perspective on climate change and the south african water sector; 1843/2/11; Water Research Commission (WRC): Pretoria, South Africa, 2012.
4. Sun, J.; Yang, K. The wicked problem of climate change: A new approach based on social mess and fragmentation. Sustainability 2016, 8, 1312.
5. Nhamo, L.; Ndlela, B.; Nhemachena, C.; Mabhaudhi, T.; Mpandeli, S.; Matchaya, G. The water-energy-food nexus: Climate risks and opportunities in southern Africa. Water 2018, 10, 18.
6. Butterfield, R.; Coll Besa, M.; Burmeister, H.; Blair, K.; Kavonic, J.; Bharwani, S.; Cullis, J.; Spires, M.; Mwalukanga, B. Inspiring climate action in African cities: Practical options for resilient pathways; FRACTAL Working Paper 4. Stockholm Environment Institute Oxford Centre, Oxford, UK: 2017.
7. Mabhaudhi, T.; Mpandeli, S.; Madhlopa, A.; Modi, A.T.; Backeberg, G.; Nhamo, L. Southern Africa's water–energy nexus: Towards regional integration and development. Water 2016, 8, 235.
8. Leck, H.; Conway, D.; Bradshaw, M.; Rees, J. Tracing the water–energy–food nexus: Description, theory and practice. Geography Compass 2015, 9, 445-460.

9. SADC. SADC regional humanitarian appeal, June 2016; Southern Africa Development Community (SADC): Gaborone, Botswana., June 2016, 2016.
10. Chivenge, P.; Mabhaudhi, T.; Modi, A.T.; Mafongoya, P. The potential role of neglected and underutilised crop species as future crops under water scarce conditions in sub-saharan africa. International journal of environmental research and public health 2015, 12, 5685-5711.
11. Nyagwambo, N.; Chonguiça, E.; Cox, D.; Monggae, F. Local governments and IWRM in the SADC region; Institute of Water and Sanitation Development (IWSD) Harare, Zimbabwe, 2008; p 58.
12. Banks, D.; Schäffler, J. The potential contribution of renewable energy in South Africa. Sustainable Energy & Climate Change Project (SECCP): 2005.
13. Müller, C.; Cramer, W.; Hare, W.L.; Lotze-Campen, H. Climate change risks for African agriculture. Proceedings of the National Academy of Sciences 2011, 108, 4313-4315.
14. Challinor, A.; Wheeler, T.; Garforth, C.; Craufurd, P.; Kassam, A. Assessing the vulnerability of food crop systems in africa to climate change. Climatic change 2007, 83, 381-399.
15. Ahlenius, H.; UNEP/GRID-Arendal. Projected agriculture in 2080 due to climate change; UNEP/GRID-Arendal: Oslo, Norway, 2009.
16. Chemnitz, C.; Hoeffler, H. Adapting african agriculture to climate change. International Journal of Rural Development 2011, 45, 32-35.
17. Stiles, G.; Murove, C. SADC renewable energy and energy efficiency status report; Renewable Energy Policy Network for the 21st Century (REN21): Paris, France, 2015.
18. Schreiner, B.; Baleta, H. Broadening the lens: A regional perspective on water, food and energy integration in sadc. Aquatic Procedia 2015, 5, 90-103.
19. Mandelli, S.; Barbieri, J.; Mattarolo, L.; Colombo, E. Sustainable energy in africa: A comprehensive data and policies review. Renewable and Sustainable Energy Reviews 2014, 37, 656-686.
20. SADC. SADC regional infrastructure development master plan: Executive summary; Southern Africa Development Community (SADC): Gaborone, Botswana, August 2012, 2012; p 40.
21. Hassan, R.; Nhemachena, C. Determinants of african farmers’ strategies for adapting to climate change: Multinomial choice analysis. African Journal of Agricultural and Resource Economics 2008, 2, 83-104.
22. SADC. Regional Strategic Action Plan on Integrated Water Resources Development and Management Phase IV; Southern African Development Community (SADC): Gaborone, Botswana, 2016; p 64.

Future Exploitation of the North Leader Conglomerate at No: 5 Shaft of Blyvooruitzicht Gold Mine, South Africa

NA Mahlaule* and F. Amponsah-Dacosta

Department of Mining and Environmental Geology, University of Venda, South Africa
*Email of corresponding author: ally.mahlaule@gmail.com

Abstract

Blyvooruitzicht Gold Mine (BGM) has been established within the West Wits Line of the Witwatersrand Basin. Three renowned auriferous horizons such as North Leader (NL), Carbon Leader (CL) and Middelvlei (MR) were identified at BGM. Massive gold exploitations have been conducted from CL and MR using both longwall and scattered mining methods respectively. As for NL conglomerate, no mining activities have taken place as yet and this was impeded by the findings from previous studies that had shown that gold grades were generally less than 0.5 g/t. Recent studies conducted on NL conglomerate based on drillholes and development samplings have shown great potentials that warrant future exploitation. BGM employed scattered mining method for stope areas with erratic gold values such as those of the Middelvlei reef. The introduction of scattered mining method has resulted in unacceptably high stress levels and Energy Release Rates (ERR) at BGM. BGM called for a more amenable mining method due to highly inconsistent gold grades as well as the presence of multiple geological anomalies. The purpose of the study was to establish a mining method suitable for exploitation of the NL conglomerate, considering the erratic nature of the reef. The methods used were diamond drilling, core logging, core sampling, development sampling (bulk sampling), fire assay and inverse distance of power as interpolation method in Datamine Studio 3.21. Results from the study conducted showed erratic trend with high gold values being in association with carbon seams and fine pyrite. Sequential grid mining method was suggested for exploitation of this ore body due to erratic nature of the grades as well as the safety of this method. The proposed mining method is envisaged to provide regional support on stabilizing pillars and to serve as bracket pillars to support major geological structures, hence keeping ERR and Average Pillar Support(APS) within allowable levels.

Keywords: Future exploitation, North Leader conglomerate, Sequential grid method, Witwatersrand Basin

1. Introduction

According to Engelbrecht [1] and McCarthy [2], Blyvooruitzitcht Gold Mine is situated on the North-Western boundary of the Witwatersrand Basin in South Africa. It is located near the Carletonville town and is 80 km south-west of Johannesburg at latitude of 26° 23' S and longitude 27° 15' E in Gauteng province of South Africa [3]. Figure 1 provides a locality map of the study area with other mines occurring within the West Wits Line area.

Searle [3] indicated that BGM had only employed Longwall mining method for exploitation of Carbon Leader and Middelvlei reefs, however, secondary mining method such as scattered mining was lately introduced due to erratic nature of the grades in the Middelvlei reef. Searle [3] highlighted that the alternative of a longwall mining system with strike stabilizing pillars would be equally good based on Energy Release Rate (ERR), however, would be deemed inappropriate due to variation in ore grade. Sequential grid mining combines the scattered mining concept with a system of partial extraction [4]. Mahlaule [5] modeled and evaluated economic aspects of the North Leader conglomerate, the results showed erratic trend. The erratic nature of the results obtained from the study conducted by Mahlaule [5] strongly influence the type of mining method to be employed. According to Laurie [6], the mining method anticipated is of critical importance in the evaluation of a mineral deposit. Handley [7] revealed that sequential grid mining has been employed as the principal mining method at the AngloGold West Wits since the commencement of stoping operations from the sub-vertical shaft system in 1988. Since good face length and flexibility in a variable orebody would be of prime importance, a breast mining system with panels advancing along strike is preferable [3]. According to Applegate [7], partial extraction of mineralized orebody reduces the entire stress levels while also avoiding holing of panels into mined out areas.

Applegate [7] highlighted that the Energy Release Rate (ERR) peak could be kept at acceptable levels by implementing a proper sequence of mining. In other words, the ERR for breast panels mining on strike can be controlled by limiting stope span, subsequently mining on only one side of a raise at a time. This shows that sequential grid mining has huge potential in improving mine safety through promotion of correct mining configuration. Jooste [8] conducted a comparative analysis of seismic hazards associated with both Longwall and Sequential Grid mining methods and the results revealed less hazards associated with Sequential Grid mining method as opposed to longwall mining method. According to Jooste [9], in recent years deep-level mines situated in the West Rand region of the Witwatersrand goldfields adopted layouts that incorporate the systematic use of dip stabilizing pillar. Engelbretcht [1] emphasized the significance of sequence of mining and that the overall direction of mining should be from the shaft pillar outwards, moving from raise line to another towards the boundaries.

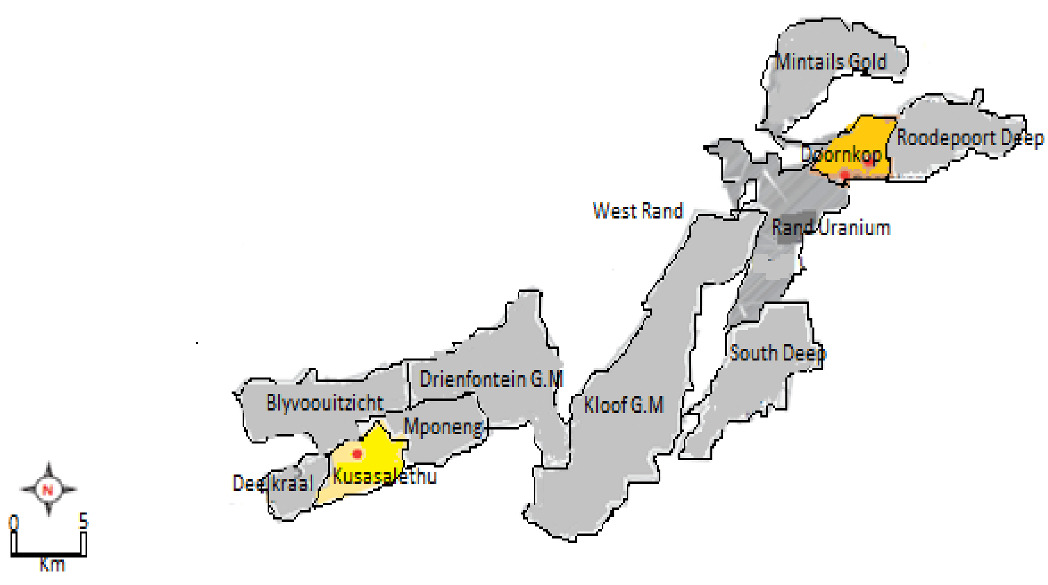


Figure 1. Locality map of the study area [10].

2. Methodology

Diamond drilling, core logging, development sampling (bulk sampling) and core sampling; fire assay and inverse distance of power were employed during the study.

Data collection

A total of 111 samples of well mineralized NL conglomerate were sampled. The samples were collected from various locations at Blyvooruitzitcht Gold Mine (BGM using various methods. Diamond drilling was employed in order to acquire lithological data of the North Leader (NL) conglomerate. Core logging was done to define stratigraphic position of the NL. Sampling methods such as core and development sampling were employed to determine vertical and lateral continuity and distribution of gold mineralization within the NL in the study. Core sampling was employed to attain raw data from drillholes. Development sampling method was enhanced by means of sampling reef intersection points in the cross cuts. Sampling of reef intersection points has enabled the definition of physical position of NL. Bulk sampling was employed during data collection phase and the sample size was $15x10$ cm, with a minimum weight of 400 g. Figure 2 provides detailed of various sampling points carried at the study.

Data analysis

The raw data acquired from both drillholes and development sampling was sent to BGM analytical laboratory for gold processing. Fire assay method was employed for metallurgical treatment of ore to liberate gold. In other words, the analysis of gold mineralization was enhanced through fire assay technique. About 111 samples of NL conglomerate were treated at BGM analytical laboratory. Fire assay incorporated various phases such as preparation, sample combustion, cupellation and parting. The above-mentioned sample preparation phases were carefully followed in order to liberate gold grains from gangue. The samples were thoroughly dried overnight, then crushed in a jaw crusher and placed at as a sieve split. About 85% samples were then reduced to < 150 µm in the Vertical Spindle Pulverize. In order to avoid contamination, a 150 g of crushed quartz was passed through the pulverizer between each sample. Later, compressed air was used to clean each crusher after each sample was processed. The finely ground samples were fused with a suitable flux under reducing conditions. Fusing of the samples was done to promote the separation of the precious metals from the gangue. Each batch of samples was identified by adding a small quantity of copper <0.5 g into crucibles. The crucibles containing the charge and the flux was loaded into the furnace and pre-heated to 1000 ^{0}C. The flux was combined with the charge to form a fluid slag. The lead button containing the precious metals was detached from the slag by striking the interface with a sharp blow by a hammer. Subsequently, the lead was removed by oxidizing fusion (cupellation) and the precious metals, thus isolated to make the samples available for measurement. During cupellation, lead was oxidized to molten litharge. Oxidation of lead resulted in an orange-yellow tinged cupel. Absorption of carbon resulted in dirty patches in the cupels. Small quantities of other base metals were absorbed because of high surface tension that could oxidize. The final product of cupellation was a prill (tiny, circular mass) of precious metals that contained gold trace. The flattened prill was heated until the water evaporated, producing a black, amorphous spec. Two drops of nitric acid were added to the cups, to ensure a total parting of gold. Final annealing for about five minutes unveiled golden-yellow characteristics of gold which was then measured in an assay balance. Thus, the assay values were determined and expressed in grams per ton (g/t). Inverse distance of power was used for data interpolation and mineral resource evaluation was accomplished through the application of Datamine studio 3.21 software.

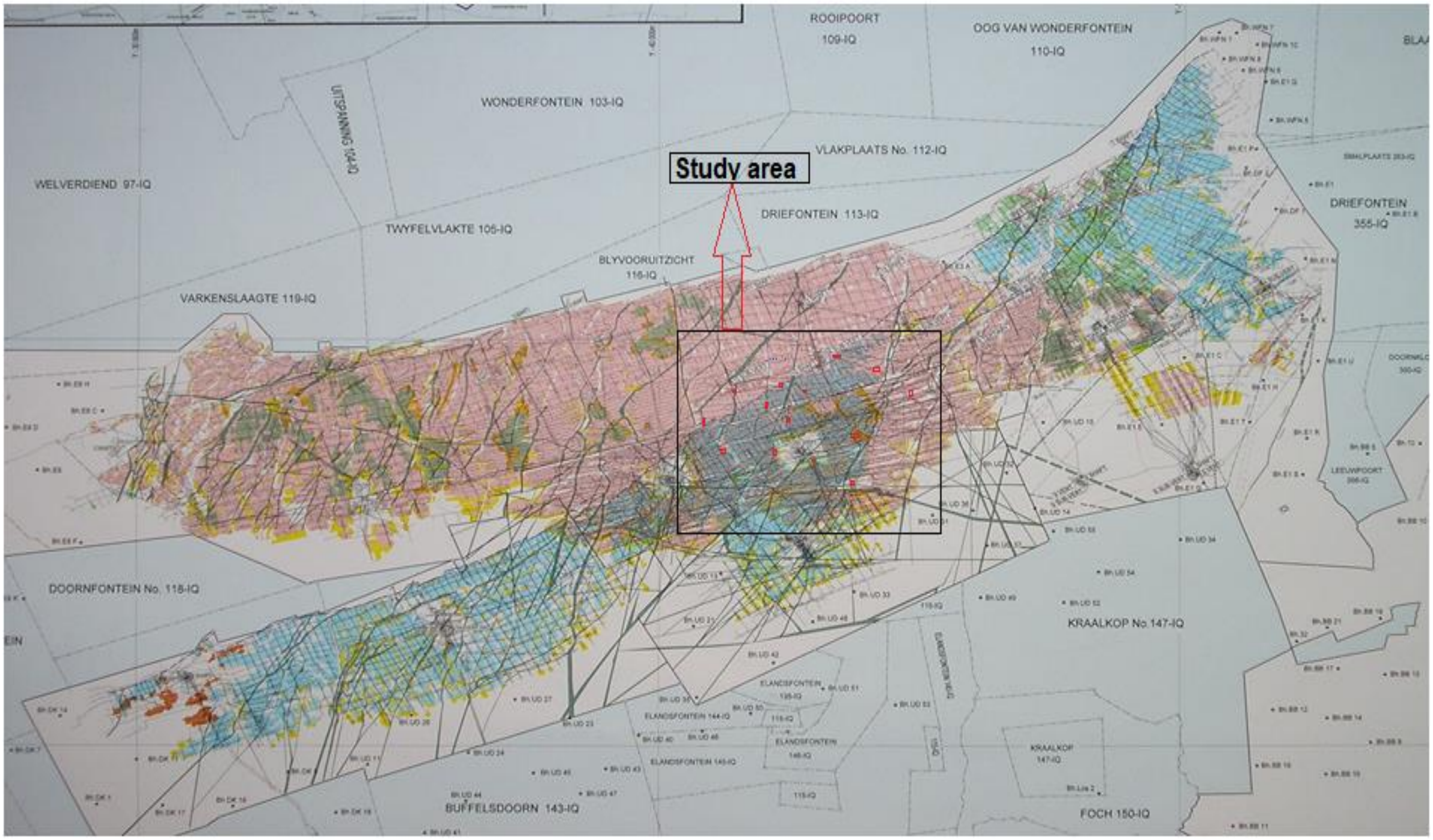


Figure 2. BGM work plan showing various sampling points

3. Results and Discussion

Results obtained from the study carried at Blyvoouitzicht Gold Mine are presented in this section. The results include those from fire assay and inverse distance of power.

Fire assay

Assay results obtained from drillholes show that gold grades range from 0.2 to 18.11 g/t while those of development sampling are in the region of 1.20 and 15.30 g/t. It is believed that carbon content might have influenced the distribution of gold mineralization within the North Leader (NL). For instance, high gold value of 18.11 g/t and 15.30 g/t in both drillholes development sampling results could be due to high carbon content material. On the other hand, the low values 0.2 and 1.20 g/t in drillholes and development might have been initiated by the introduction of water which later removed flyspeck carbon materials from the cementing matrix during drilling exercises. Table 1 and Table 2 provide detailed results of drillholes and development sampling.

TABLE 1. Drillhole data

BHID	X-Reef coords	Y-Reef coords	Z-Reef coords	Bearing	Dip	Au(g/t)
38/21-80	24813	33783	2957	45	90	0.92
38/21-80	24813	33783	2951	45	90	0.20
38/21-80	24813	33783	2942	45	90	0.33
38/21-80	33783	33783	2924	45	90	0.88
38-23 -1c	29814	33782	2482	90	5	0.35
38-23 -1c	29827	33782	2981	90	5	0.26
38-23 -1c	29835	33619	2980	90	5	0.52
38-23-1c	29862	33619	2978	90	5	0.63
38-23-1c	29886	33782	2975	90	5	18.11
38-23-1c	29901	33782	2974	90	5	0.82
38-23-4p	24529	33619	2925	90	60	0.03
38-23-4p	24838	33619	2909	90	60	0.81
38-23-4p	24847	33619	2894	90	60	0.94
38-23-4p	24848	33619	2892	90	60	0.45
38-23-4p	24849	33619	2890	90	60	0.18
38-23-4p	24852	33619	2886	90	60	0.25
38-23-5p	24819	33797	2925	180	75	0.19
38-23-5p	24819	33794	2911	180	75	0.87
38-23-5p	24819	33790	2898	180	75	0.99
38-23-5p	24819	33789	2894	180	75	1.46
38-23-5p	24819	33788	2891	180	75	0.58
38-23-5p	24819	33786	2882	180	75	0.6
38-23-6p	24827	33770	2882	180	75	0.8
38-23-6p	24827	33766	2915	180	75	0.27
38-23-6p	24827	33763	2802	180	75	0.91
38-23-6p	24827	33762	2897	180	75	12.17

Table 2. Development data

Locality	X-Reef coords	Y-Reef coords	Z-Reef coords	From	To	CW (cm)	Au(g/t)
SECT-A	24813	33783	2957	0	5	15	5.50
SECT-A	24813	33783	2951	5	10	20	2.40
SECT-A	24813	33783	2942	10	15	30	8.00
SECT- B	24813	33783	2924	0	5	12	6.90
SECT- B	29814	33783	2982	5	10	17	8.70
SECT- B	29827	33782	2981	10	15	19	8.60
SECT- C	29855	33619	2980	0	5	28	10.10
SECT- C	29862	33619	2978	5	10	8	1.30
SECT- C	29886	33619	2978	10	15	11	2.00
SECT- D	29901	33782	2974	0	5		2.80
SECT- D	24829	33619	2925	5	10	25	7.80
SECT- D	24838	33619	2909	10	15	16	9.70
SECT- E	24847	33619	2894	0	5	21	15.50
SECT- E	24848	33619	2892	5	10	29	10.30
SECT- E	24849	33619	2890	10	15	50	1.20
SECT- F	24852	33619	2886	0	5	22	1.26
SECT- F	24819	33797	2925	5	10	27	9.12
SECT- F	24910	33794	2911	10	15	28	5.6
SECT-G	24819	33790	2898	0	5	11	15.3
SECT-G	24810	33789	2894	5	10	15	2.4
SECT-G	24810	33788	2891	10	15	18	6.1
SECT- H	24819	33876	2882	0	5	10	2.9
SECT- H	24827	33770	2928	5	10	9	5.2
SECT- H	24827	33766	2915	10	15	15	2.2
SECT- I	24827	33763	2902	0	5	19	2.1
SECT- I	24827	33762	2902	5	10	22	1.7

Mineral resource estimation

Gold grades from drillholes and development sampling are presented in Figure 3. It can be noted from the graph that gold grades from both drillholes and development sampling show asymmetrical trend. Gold grades of development sampling are higher as compared to those of drillholes. Development sampling was done in situ, hence the samples had high carbon content as opposed to drillholes samples whose carbon content is assumed to have been washed away during drilling. The weighted data obtained from drilling and development sampling reveal variability in gold mineralization as shown in the quintile graph. The peaks and the troughs in the quantile graph denote positive correlation from the two datasets. The difference in the existing relationship could be due to difference in carbon contents. The relationship between drillholes and development results is depicted in Figure 3.

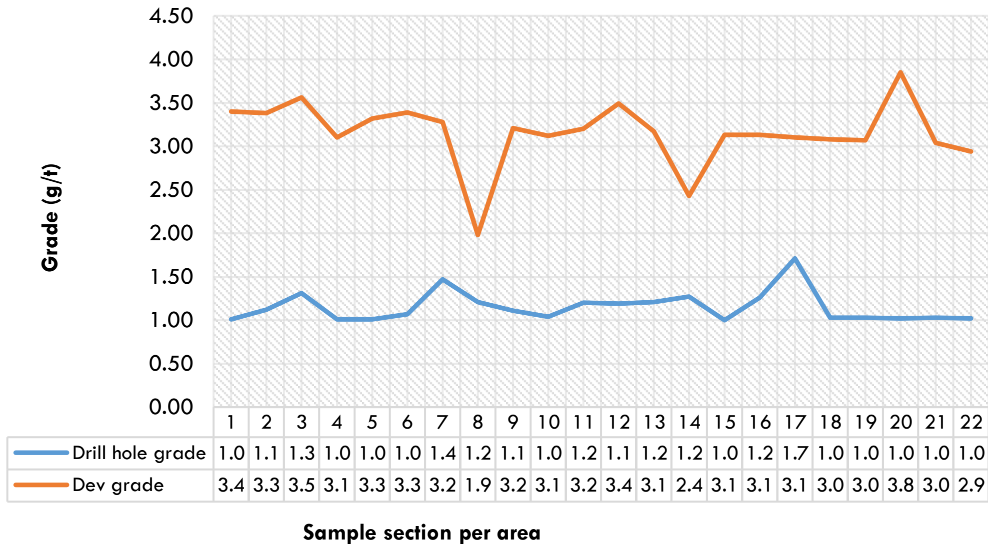


Figure 3. Relationship between drillholes and development evaluation results

Choice of mining method

Choice of mining method was determined based on various factors such as nature of grade distribution; mining depth and seismicity build up as well as the nature of geological materials.

Nature of grade distribution

Gold grades in the study are generally checkered or erratic in nature. The results obtained from both drillholes and development samplings have proven the erratic nature of the grades. The nature of grade distribution is one of the fundamental factors to be taken into account when making a choice mining method.

Mining depth and seismicity build up

When considering the current mining depth of between 2700 and 3000 m, erraticism of the grades, gold distribution and cut off grade, it is therefore recommended that the reef under consideration be exploited using sequential grid mining method. In other words, sequential grid mining method will be ideal for exploitation of this type of orebody. Reason being that the mining will be in sequence, then the stress can be easily distributed or shared among the in situ geological materials. Figure 4 provides a layout of proposed sequential grid mining method.

The nature of geological material

The rock strata above the North Leader form the footwall of the Carbon Leader and it comprises heterogeneous succession of siliceous and argillaceous, yellowish green, cross-bedded quartzites. The strata of the North Leader conglomerate consist of mature medium-grained, greyish white, frequently cross-bedded quartzites. In other words, North Leader conglomerate is the first conglomerate unit to be intersected within the Main conglomerate Formation. This implies that it forms the bottom statigraphic marker within the Main

Conglomerate Formation. Development in the south eastern portion of the mine and prospect drilling to the south revealed that North Leader is well developed. The North Leader is underlain by the upper square pebble of the Maraisburg Quartzite Formation, the member of the West Rand Group. From Figure 4, S1, S2, S3 and S4 denote stope 1 to 4, in which the panels in these stopes can be planned to mine in zigzag and stop at the pillars as indicated by arrows. The pillars should be in situ geological materials of ±10 m width to allow maximum stress absorption.

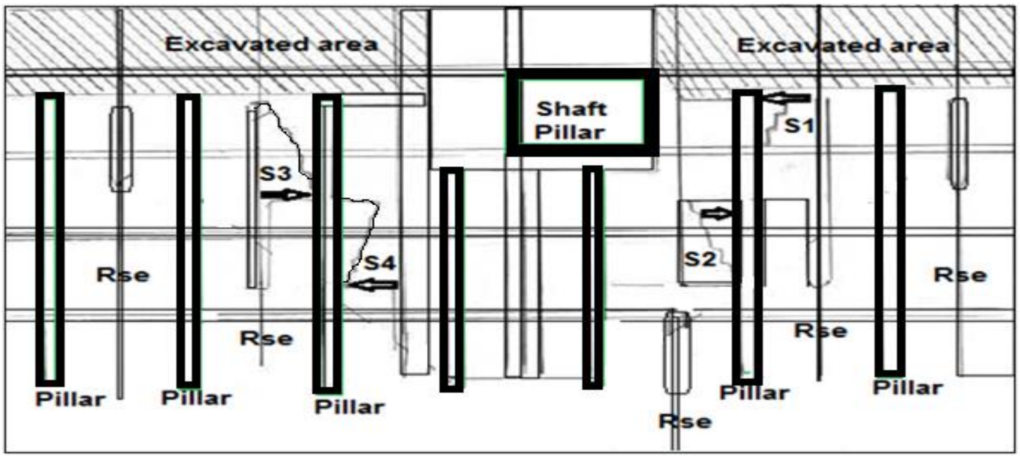


Figure 4. Layout of proposed sequential grid mining method

4. Conclusion

Results from the study conducted showed asymmetric trend with high gold values being in association with high carbon seams and fine pyrite. Sequential grid mining method was proposed for the exploitation of the North Leader (NL) conglomerate due to erraticism of the grades, gold distribution, current mining depth as well as the safety of this method. The study concluded that the proposed mining method will provide extensive support on clamping pillars. It was also noted that Sequential grid mining method in conjunction with clamping pillars will provide regional support on major geological structures, hence keeping Energy Release Rate (ERR) and Average Pillar Support (APS) within tolerable levels. Based on the findings, the study has recommended that pillars for supporting major geological anomalies should be kept within 10 m width to allow maximum stress fascination.

Acknowledgement: We would like to thank University of Venda Research and Publication Committee for funding this work.

References

1. Engelbrecht, C.J., Baumbach, G.W.S., Matthysen, J. L. and Fletcher, P. (1986). The West Wits Line. In: Anhaeusser, C.R. and Maske, S. (Eds.), Mineral Deposits of Southern Africa, Vol. 1. Geological Society of South Africa.pp. 599 – 625.
2. 8. McCarthy, T.S. (2006). The Witwatersrand Supergroup. In: Anhausser C.R., Johnson, M.R. and 9.
3. Searle, J.P. (1992). A Sedimentological study of Middelvlei reef on Doornfontein Gold Mine. Masters Dissertation (Unpublished), Camborne School of Mines, UK, 4-5pp.
4. Handley, M.F., de Lange, J.A.J., Essrich, F. and Banning, J.A. (2000). A review of the sequential grid mining method employed at Elandsrand Gold Mine.pp.158-167.

5. Mahlaule, N. A. and Amponsah-Dacosta, F. (2017). Evaluation of New Ore Body for Future Exploitation at No: 5 shaft of Blyvooruitzicht Gold Mine, South Africa. In: Emery,E.,Moreno., Arryo,C.,Bisso,C., Brickey,A.,Echeverreria,M., Freire,R.,Gomez,D., Gopfert,H. and Ibbara.F.(Eds). Proceedings of Geomin & Mine Planning Conference, Santiago, Chile.pp.1-10.
6. Laurie, J. (2008). South African Geology for Mining, Metallurgical, Hydrological and Civil Engineering, 10th revised edition, Lupon Publishing, Johannesburg. pp. 153-155.
7. Applegate, J.D. (1991). Rock Mechanics Aspects of Sequential Grid Mining. Masters Project Report, University of the Witwatersrand, Johannesburg, South Africa.pp.16-64.
8. Jooste, Y. and Malan, D.F. (2015). Rock engineering aspects of a modified mining sequence in a dip pillar layout at a deep gold mine.pp.2-16.
9. Jooste,Y. (2013). Modified sequential grid layout to increase production rates in deep level hard rock mines. Masters Dissertation--University of Pretoria, South Africa.pp.60-122.
10. Smith, A. J.B, Beukes, N. J. and Gutzmer, J. (2013). The Composition and Depositional Environments of Mesoarchean Iron Formations of the West Rand Group of the Witwatersrand Supergroup, South Africa. Society of Economic Geologists, published on January 2013, 108(1). pp. 1-15.

Suitability of copper tailings as additives in the preparation of concrete materials: strength and water absorption properties

R Thobakgale[1, 2], WM Gitari[1, 2*], SA Akinyemi[2, 3]and C Muzerengi[3,4]

[1]School of Environmental Sciences, University of Venda, South Africa
[2]Department of Ecology and Resources Management, University of Venda, South Africa
[3]Department of Geology and Applied Geophysics, Ekiti State University, Nigeria
[4]Department of Mining and Environmental Geology, University of Venda, South Africa
[*] Email of corresponding author: mugera.gitari@univen.ac.za

Abstract
Mine waste disposal is a worldwide problem. Mine tailings, for instance, if poorly managed, can become a source of severe environmental contamination. This realization has prompted a great body of work aimed at improving current mine waste disposal technology, as well as beneficiation practices, such as using mine waste admixtures in the production of concrete materials. The present study looks at how copper tailings finely ground solid mine waste residue from processing of copper ore can be usefully applied. Copper tailings consist of fine particles with a wide range of uneconomic and inorganic toxic metals primarily bounded to a variety of gangue minerals present within the tailings. The safe disposal of fine particulate copper tailings is essential due to the hazard it poses to human health, largely through inhalation, and the ease of erosion to nearby aquatic systems to contaminate domestic and irrigation water. This study reports on the feasibility of blending copper tailings as an additive in cement concrete and the effect on strength and water absorption properties, to sustain the building and construction industry. The copper tailings in this study contain high amount of silica (58.12%) and substantial amounts of Fe (11.7%) and Al (14.17%) oxides, which makes them excellent pozzolanic materials for use in cement concrete. Concrete materials incorporating copper tailings at 5 and 10 % and cured for 3 and 28 days improved compressive strength and water absorption properties of the resulting concrete materials when compared with the control mix containing 100% Ordinary Portland cement. It is submitted that copper tailings can successfully be utilized in the preparation of concrete material to sustain the building and construction industry, and this will further reduce the environmental risk posed by the tailings disposal worldwide.

Keywords: Mine waste; copper tailings; unconfined compressive strength; environmental pollution

1. Introduction
South Africa has a long history of mining activities dating back a century ago, and as a consequence large volume of tailings are generated and disposed of in landfills or tailings impoundments [1]. The disposed tailings occupy large hectares of hitherto valuable land, and, because in many instances, tailings were unsafely disposed of, or poorly managed, they have become potential sources of environmental contamination [2]. In South Africa, some of the tailings from past mining activities include: the Musina copper tailings, gold tailings in the Giyani Greenstone Belt and Witwatersrand, and cassiterite tailings in Mokopane, within the eastern limb of the Bushveld complex [3]. Generally, tailings contain a wide range of toxic chemical species primarily bounded to a variety of gangue minerals present within the tailings, process chemicals including reagents such as cyanide and sulphuric acid, and leachates from treated ore [4]. The chemical composition, geochemical and mineralogical characteristics of the tailings vary depending on the type of the ore mined, type of equipment used during beneficiation or mineral processing, type of process chemicals added during ore separation, particle size of the mined ore and moisture content [2].

Some of the chemical constituents and gangue minerals within the tailings are very unstable and reactive, especially when the tailings are exposed to atmospheric oxygen and infiltrating rainwater, resulting in the partial release of weathering products to nearby aquatic systems, hence contaminating water used for drinking by animals and that used for irrigation (Hiller et al. [5]). Furthermore, fine particulate matter released from air-dried tailings may also prove to be hazardous to human health [2]. However, as part of a tailings disposal management system, a few researchers and some private companies have considered rehabilitation and recovery of tailings, although this approach proved has proven to be costly, and with a low recovery rate for certain tailings [3,6,7]. Nevertheless, other researchers have recently identified the reuse of tailings in the construction industry as the best eco-friendly management approach for tailings disposal [8,9]. Understanding the effect of tailings as admixtures on concrete will elucidate their durability in the construction industry. In the reuse management system approach for tailings disposal, a large volume of tailings is put into good use, thus alleviating problems associated with tailings disposal and their environmental impact and reclamation of the previously usurped land.

The present study represents an implementation of the reuse management approach on tailings disposal, through an evaluation of the feasibility of utilizing copper tailings as admixtures on Portland cement concrete in the construction industry. The effect of copper tailings as admixtures on the mechanical properties of Portland cement concrete containing copper tailings will be elucidated.

2. Materials and Methods

Materials (conforming to IS: 40311988-Methods of physical tests for hydraulic cement)

The binders used in preparing Portland cement concrete mixtures were Ordinary Portland cement and copper tailings obtained at various depths at an abandoned copper tailing in Musina, Limpopo Province, South Africa. The tailing samples were air-dried and homogenised before usage. Natural river sand sourced from Dzindi river was used as fine and course aggregates.

Physical and chemical properties of copper tailings and Natural river sand

Particle size distribution was performed on both the copper tailings and Natural River sand using sieve analysis in accordance with ASTM D 422 [10]. The initial moisture content was determined on tailings samples in accordance with the ASTM D 2216 [11], and subsequently the specific gravity tests was determined according with ASTM D 854 [12]. Finally, an oxide analysis of the copper tailings was performed by X-ray fluorescence spectrometry (XRF) (Thermo Fisher ARL9400 XP+ Sequential XRF with WinXRF software) to determine the pozzolanic properties or chemical composition of the copper tailings.

Mixture proportions

A dry mixture of 4500 g of standard sand sieved at grade 1 (2mm-1mm and grade 2, coarse and medium) and grade 3 (1 mm-500 µm, fine particle size), and 2000g of cement was weighed and transferred into a mechanical mixer, mixed thoroughly in a dry state for 4 minutes before the addition of water. The prepared mixture was added 0% (C0), 5% (C5), and 10% (C10) dry copper tailings by mass of cement concrete. A standard w/b ratio of 0.3 in accordance with ASTM C109 [13] guidelines was used in the preparation of mixtures, taking into consideration the settling time of cement concrete (3-5 minutes). The mixture proportions are summarised in Table 1. Design mixtures were filled within the assembled mould with an area of 10000 mm². The moulds were then covered with plastic bag for 24 hours to maintain humidity at about 27±3°C. After 24 hours of maintaining humidity, the cubes were then de-moulded and placed in water bath for curing or aging for 3 and 28 days, respectively, prior to the determination of unconfined compressive strength and water absorption tests, respectively.

TABLE 1. Mixture proportions.

Mixture ID	Copper tailings (% by mass)	W/B ratio	Quantities (g)					
			Water	Cement	Tailings	Coarse	Medium	Fine
C0	0	0.3	600	2000	0	2250	563	1690
C5	5	0.3	600	1900	100	2250	563	1690
C10	10	0.3	600	1800	200	2250	563	1690

Unconfined compressive strength test

Unconfined compressive strength was measured on the casted specimens at 3 and 28 days in accordance with ASTM C 109 guidelines [13]. The values obtained for crushing load or compressive strength on each cube were compared with those obtained for the control specimen (C0) for the respective curing days (3 and 28 days).

Water absorption test

Similarly, the rate of water absorption was determined on representative specimens in accordance with ASTM C 1403 [14]. Cured surface of specimens were placed inside water bath and the rate of water absorption was determined at 8 and 24h.

3. Results and Discussion

Physical and chemical properties of copper tailings and Natural river sand.

Some physical and chemical properties of copper tailings and natural river sand are shown in Table 2, while Figure 1 shows the particle size distribution of copper tailings and natural river sand

TABLE 2. Physical and chemical characteristics of copper tailings and natural river sand.

Component	Copper tailings	Natural river sand
Chemical composition (wt.%)		
SiO_2	58.12	-
Al_2O_3	14.17	-
Fe_2O_3	11.7	-
CaO	7.5	-
Loss On Ignition	<10	-
Physical properties		
Specific gravity	2.14	2.2
Fineness modulus	2.77	4.06
Initial moisture content	1.39	-
USCS	SM-SC silty, clayey sand	SP

USCS (Unified Soil Classification Scheme); SM (Sand-Silt); SC (Sand-Clay); SP (Poorly Grade Sand).

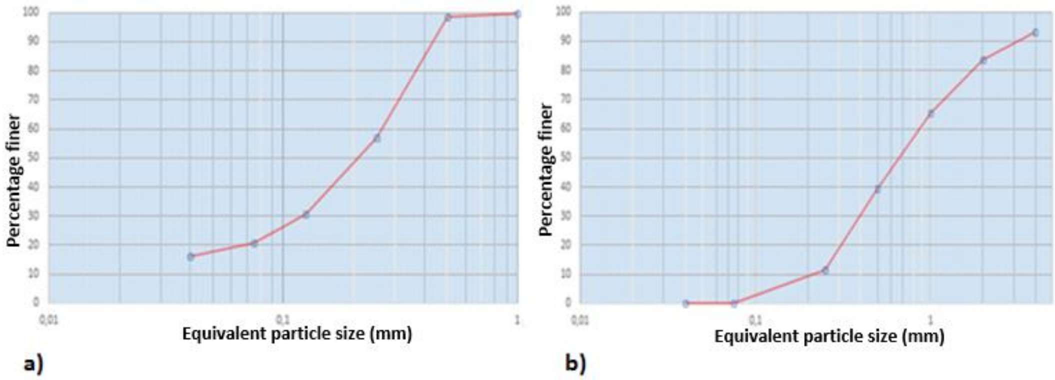


Figure 1. Particle size distribution of a) copper tailings, and b) natural river sand.

From Figure 1, about 25 % of the copper tailings are less than 0.1mm in particle size with the fineness modulus of 2.77, while about 6 % particles in river sand particles are less than 0.1 mm with a fineness modulus of 4.06. The reduced fineness of the copper tailings was attributed to the low initial moisture content of the tailings (Table 2). According to the unified soil classification scheme (USCS) copper tailings were classified as silty clayey sand i.e., sand with great deal of fines, while the natural river sand was classified as poorly graded sand i.e., low percentage of fines. The specific gravity of copper tailings and natural river sand is 2.14 and 2.2 respectively. The relatively low specific gravity of the copper tailings was attributed to the substantial content of Fe_2O_3 present in the copper tailings. Similar observations were made by Thomas et al [15] on copper tailings from India. Furthermore, copper tailings contain high amount of silica and substantial amounts of iron and aluminium, and that makes them pozzolanic material best suitable for use in Portland concrete (Janković et al [16]).

Unconfined compressive strength

Figure 2 shows the unconfined compressive strength of mixtures at 3 and 28 days, respectively. Mixtures incorporating copper tailings yielded higher compressive strength compared to those of the control specimens at 3 and 28 days of curing. Thomas et al. [15] observed similar trend whereby copper slag addition enhanced concrete compressive strength compared to the control mixtures.

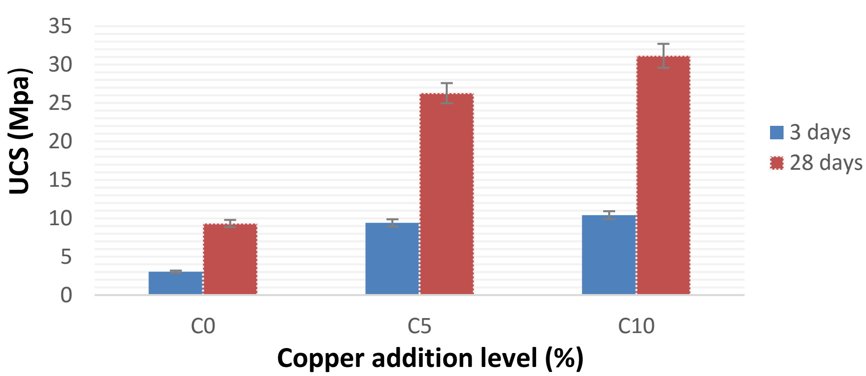


Figure 2. Unconfined compressive strength (UCS) of specimens.

It is speculated that the low W/B ratio, high density of copper tailings and natural river sand as attested by the specific gravity contributed to compressive strength enhancement observed.

Water absorption potential

One important mechanical property that influence the durability of concrete is its absorption potential to the ingress of water and other potentially deleterious substances [15]. Figure 3 shows the water absorption potential for mixtures immersed deep in water bath for 8 and 24h. The water absorption increased as copper tailings content on mixtures increased. Similar observations were made by [8] on copper tailings in Cyprus. It is suggested that the high percentage of fine particles in copper tailings contributed to decrease in porosity of the particles, thus high-water absorption of mixtures containing copper tailings compare to the control concrete mixture.

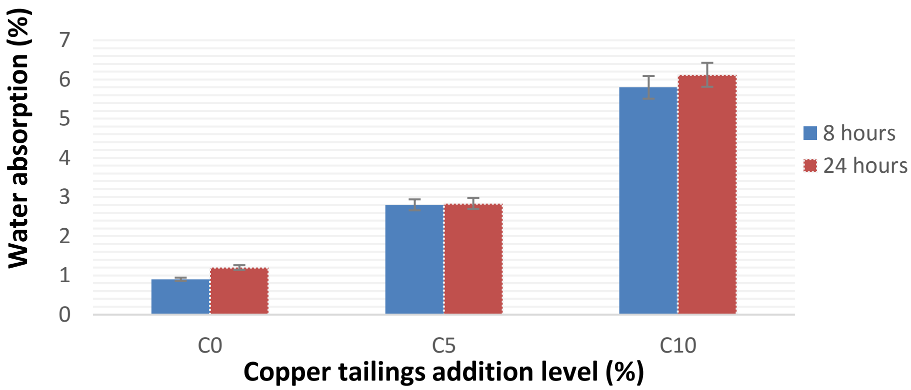


Figure 3. Water absorption of specimens.

4. Conclusions

The high silica (SiO_2) content and substantial amounts of Fe_2O_3 and Al_2O_3, and the percentage of fines in the copper tailings makes them good pozzolana material that are moderately reactive in concrete mixtures. The addition of copper tailings at 3 and 28 days improved the compressive strength of mortar mixtures compared to the control mixture. Equally, the potential water absorption of mixtures incorporating copper tailings increased gradually with time. The potential application of copper tailings as admixtures in the preparation of concrete mortars will improve the durability of concrete, limit the use of Ordinary Portland cement, and most importantly, alleviate potential environmental risks induced by copper tailings disposal. Although, this work focused on copper tailings, it is hoped that this information will be relevant to other researchers investigating the blending of tailings of similar composition with cement in the construction industry or other markets.

Acknowledgements: The authors express their gratitude to the Department of Ecology and Resource Management of the University of Venda, the Department of Civil Engineering of the University of Johannesburg, and National Research Foundation (UID: 114573) for their interest and access to logistic and financial support.

References

1. Department of Mineral Resources (DMR). The National Strategy for the Management of Derelict and Ownerless Mines in South Africa. 2009. Available at: https://cer.org.za/news/dmrs-national-strategy-for-the-management-of-derelict-and-ownerless-mines-2009 (accessed 21.08.2018).
2. Lottermoser, B.; G. Mine Wastes: Characterization, Treatment and Environmental Impacts (3rd edition). 2010. 204-240.
3. Matshusa, K.; Makgae, M. Overview of Abandoned Mines in the Limpopo Province, South Africa: Rehabilitation Challenges. J. Environ. Science, and Eng., B 3. 2014 156-161.
4. Joeng, J. Solid-Phase Speciation of Copper in Mine Wastes. Bull. Korean. Chem. Soc. 2003, 24, 209-218.
5. Hiller, E.; Petrák, M.; Tóth, R.; Voleková, B.; L.; Jurkovic, L.; Kučerová, G.; Radková, A.; Šottník, P.; Vozár, J. Geochemical and mineralogical characterization of neutral, low-sulfide/high-carbonate tailings impoundments, Markušovce, eastern Slovakia. Environ. Sci. Pollut. Res. 2013, 20, 7627-7642.
6. Mhlongo, E.; Dacosta, F.;A. A review of problems and solutions of abandoned mines in South Africa. Int. J. Min. Recl. Environ. 2015, 30, 4, 1188.
7. Engineering and Mining Journal. Resurgence in Johannesburg's Gold Tailings Reclamation. 2008. Available at: http://www.womp-int.com/story/2008vol4/story018.htm (accessed 22.08.2018).
8. Onuaguluchi, O.; Eren, O. Recycling of copper tailings as an additive in cement mortars. Construction and Building Materials. 2012, 37, 723-727.
9. Mahmood, A.; A.; Mulligan, C.; N. Investigation of the use of mine tailings for unpaved road base. Proceedings of the Annual International Conference on Soils, sediments, water and energy. 2007,12, 1166.
10. ASTM D 4228. Test Methods for particle size distribution and moisture content. 1998.
11. ASTM D 2216. Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass. 2014.
12. ASTM D 854. Test Methods for Specific Gravity of Soil Solids by Water Pycnometer. 2014.
13. ASTM C 109. Standard test methods for compressive strength of hydraulic cement mortars. ASTM International, West Conshohocken, PA. 2008.
14. ASTM C 1403. Standard test method rate of water absorption of masonry mortars. ASTM International, West Conshocken, PA. 2006.
15. Thomas B. S.; Damare A.; Gupta R.C. Strength and durability characteristics of copper tailing concrete, Constr. and Building Material. 2013, 48, 894–900.
16. Janković, K.; Bojović, D.; Stojanović, M.; Lončar, L. The use of mine tailings as a partial aggregate replacement in SCC concrete. 41th International conference contemporary achievements in civil engineering, Subotica, Serbia. 2015.

Treatment of acid mine drainage using magnesite: a comparison with conventional mechanical agitation of reaction mixtures

RJ Novela*, WM Gitari, WB Ayinde

School of Environmental Sciences, University of Venda, South Africa,
* Email of corresponding author: e-mail: rirhandzumahansi@gmail.com

Abstract
This work reports on sonochemical treatment of the AMD/Magnesite reaction mixtures and a comparison of the product water quality with the conventional agitation. Magnesite, a locally mined alkaline reagent in Limpopo, South Africa was utilized in our experiments. Operational parameters evaluated included pH, contact time and percentage chemical species removal. Various S/L ratios of magnesite and AMD were shaken in a Table shaker or subjected to sonochemical waves using a sonochemical processor for selected time intervals. pH, EC, TDS and chemical species attenuation were recorded over time. XRF and SEM were utilized in characterization of the raw and reacted magnesite and these indicated increased concentration of Fe, S, Al and Mn in the reacted magnesite indicating formation of Fe, S, Al and Mn bearing mineral phases and deposition on unreacted magnesite grains. Contact of magnesite with AMD at S/L of 1g/100 mL for 60 mins of conventional agitation led to decrease in EC and increase in pH to 9.4. Al, Mn, Fe and Zn were removed to levels > 99% while SO_4^{2-} were removed to levels ≥ 50 %. Sonication of the same magnesite/AMD mixtures for 60 mins led to an increase in pH to 8.6 and sulphate removal ≥ 99%. Sonication was observed to be fast in attainment of final alkaline pH than conventional shaking and also superior interms of sulphate removal. Sonochemical treatment was observed to introduce superior mechanistic aspects that enhanced sulphate removal and can be enhanced through selective seeding with various salts to enhance superior chemical species removal and recovery of beneficial products.

Keywords: Acid Mine Drainage, Metal Species, Sulphate, Magnesite, Cavitation, pH, precipitation

1. Introduction
South Africa is a nation that is blessed with the occurrence of large quantities of many minerals of economic importance [1], such as Gold, Diamond, Copper and many more. During mining activities sulphide minerals in rocks are exposed to oxygen and water and produce environmentally harmful mine water that is not only acidic but contains high concentrations of sulphates and metals [1-4], this water is called acid mine drainage (AMD). Thus, acid mine drainage is an inevitable waste water of the mining industry characterized by its strongly acidic nature and significant levels of metals ions, especially iron and sulphate [5], resulting primarily from the dissolution of the metallic sulphide, and its subsequent oxidation to sulphuric acid [6; 7]. Acid mine drainage need to be treated urgently to prevent or reduce the risk of ground and surface water contamination. Many treatment technologies that are currently used have limitations for example, cost factor, treatment inefficiencies, implementation inconveniencies and materials availability [8]. There is thus a need to come-up with cheap and effective technologies for treatment of acid mine drainage. This study was designed to develop a novel technology of using magnesite under the influence of ultrasound for remediation of AMD. Advantages of sonication include generation of reactive oxidative radicals which are able to oxidize almost all toxic contaminants present in the environments without generating secondary pollutants, potential chemical-free and simultaneous oxidation, shear degradation, and enhanced mass-transfer processes [9].

2. Materials and methods

Magnesite collection and preparation

Magnesite was collected from Folovhondwe magnesite mine Limpopo province, South Africa. The magnesite was crushed using a hammer. A milling machine was then used to mill the magnesite into fine powder. During milling, the milling pot was thoroughly cleaned before the magnesite could be milled. Magnesite was milled for at least 5 minutes at a rotation speed of 700 rpm. The samples were kept in a zip-lock plastic bag until utilization for AMD treatment.

Characterisation of magnesite

The milled magnesite and the AMD-reacted magnesite was characterized using x-ray fluorescence. Magnesite was prepared as pressed powder pellets with binding agent Boric Acid with approximately 15-20 g of the milled powder being pressed in a Die Set of 40 mm diameter. Approximately 3 g of boric acid was used as a binding agent during the preparation of the pellets. Magnesite was pressed using about 30 tons of pressure on the hand operated pressing machine. The pellets were then placed in plastic cups for XRF analysis. Magnesite analysis were performed on an S2 Ranger (Bruker) for a least 10 minutes per sample. The morphology of the raw magnesite and AMD-reacted magnesite was examined using a scanning electron microscopy.

Preparation of acid mine drainage

The AMD was simulated by dissolving the following quantities of salts in 1000 mL of Milli-Qultra-pure water (18MΩ), 0.895g $Fe_2(SO_4)_3$. H_2O, 2.685g $FeSO_4$, 0.494g $Al_2(SO_4)_3{\cdot}18H_2O$, 0.08015 g $MnCl_2.4H_2O$, 1.1393g $MgSO_4$, 2.421g $CaCl_2.2H_2O$, 0.08793g $ZnSO_4.7H_2O$ and 0.03 ml H_2SO_4. This was expected to give 250 mg/L Fe^{3+}, 540 mg/L Fe^{2+}, 40 mg/L Al^{3+} and 35 mg/L Mn^{2+}, 230 mg/L Mg^{2+}, 660 mg/L Ca^{2+}, 20 mg/L Zn^{2+} and 524 mg/L SO_4^{2}.

Characterization of Aqueous solutions

Temperature, electrical conductivity and pH were measured using an Orion multi-parameter analyser. Thereafter each sample was divided into two halves, the first half was acidified with 3 drops of concentrated HNO_3 to prevent aging and immediate precipitation of Al, Fe, Mn and SO_4^{2-} ions and stored in a refrigerator at 4^0C until analysed for cations using ICP-MS and the second half was analysed for anions using metrohm professional 850 IC.

Batch experiments: optimization of inorganic contaminant removal conditions

To study the effect of agitation time 9 samples containing 100 mL of the synthesized solution were pipetted into 9 bottles of 250 mL and 1g of magnesite was added to each sample. The mixtures were agitated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 250 rpm using the Stuart reciprocating shaker. To study the effect of sonication time 9 samples containing 100 mL of the complex solution were pipetted into 9 bottles of 250 mL and 1g of magnesite was added to each sample. The mixtures were sonicated for 1, 5, 10, 15, 30, 60, 90, 120 and 180 minutes at 60% amplitude and a cycle time of 50%, using the ultrasonic processor UP400S. The mixtures were then filtered through sterilized membrane 0.45µm filters.

3. Results and discussion

Physicochemical characterization of magnesite, magnesite residues, AMD and product water

Elemental composition by X-ray fluorescence

Analysis showed that magnesite comprises of MgO as a major oxide and minor component of SiO_2 and CaO. These findings are in line with studies done by [10]. The high concentration of MgO could be attributed to the fact that magnesite is a magnesium carbonate mineral. After AMD treatment a decrease in MgO was observed. This is as a result of $MgCO_3$ dissolution into the solution. There was an increase in Mn and Fe oxides in an AMD reacted magnesite. An increase in Fe, Ca and Mn indicates the precipitation of Fe bearing minerals, formation of Ca rich precipitates and Mn carbonates.

TABLE 1. Chemical composition of magnesite and AMD reacted magnesite

Metal Oxides (%)	Raw magnesite	AMD-Reacted magnesite
MgO	87.28	52.33
SiO_2	8.66	8.36
CaO	1.84	3.44
Fe_2O_3	0.38	10.08
TiO_2	0.04	0.048
K_2O	0.02	0.04
P_2O_5	0.036	0.056
MnO	0.011	0.29

Morphology of the raw and reacted magnesite by Scanning Electron Microscope

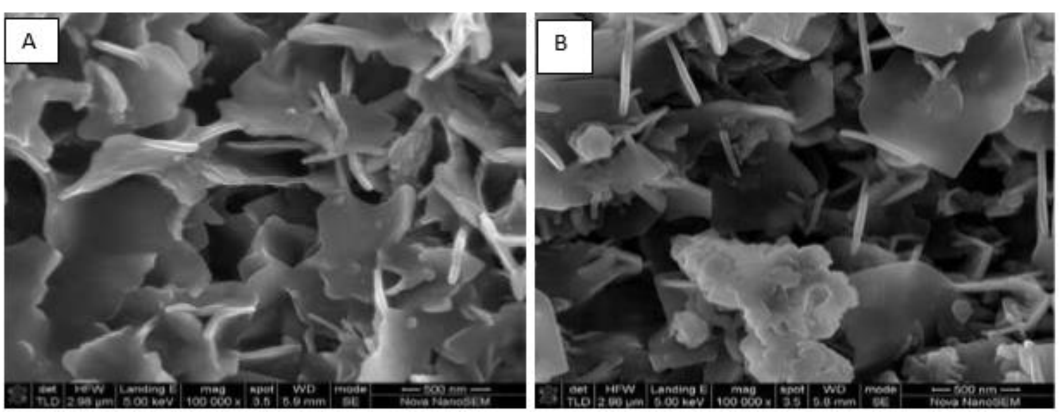


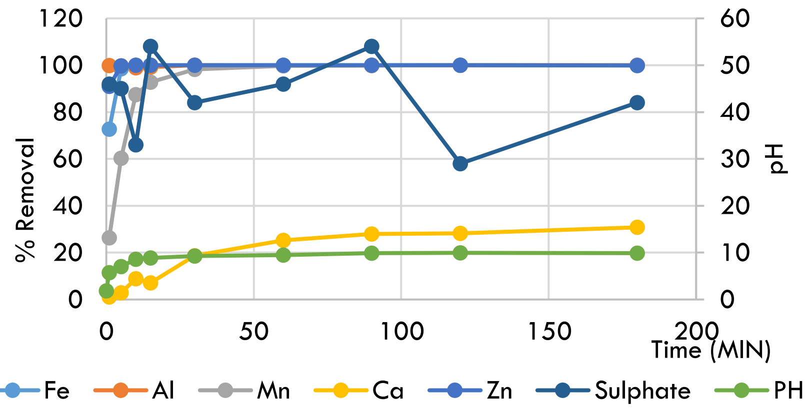
Figure 1. SEM Images of raw magnesite (A) and AMD-reacted magnesite (B)

Figure 1 shows the micrographs of raw magnesite (A) and AMD reacted magnesite (B) at 100 000x magnifications. The micrographs show that raw magnesite has a leafy like morphology and a bundled rod-shaped structure in its matrices. The analysis also show that magnesite is a porous material. This is observed at both magnification levels. After AMD treatment, the morphology of AMD reacted magnesite show a disappearance of the leafy like structures and an introduction of sheet structures and spherical structures. The difference in raw magnesite micrographs (image A) with AMD-reacted magnesite (image C) indicates the formation new minerals, which was supported by XRF results (Table 1). For example, decrease of some oxides (MgO, CaO), and an increase of some oxides (MnO and Fe_2O_3) and a complete introduction of new elements can be seen from the XRF results.

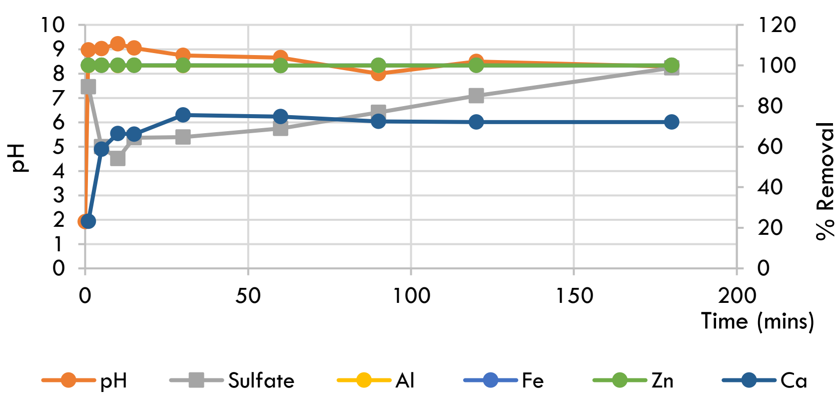
Optimization Results

Effect of mechanical shaking time and sonication time

Figure 3.3 shows the results for neutralization and metal removal efficiency as a function of mechanical shaking time and sonication time.



(a)



(b)

Figure 3a. Variation of Al, Fe, Mn pH and sulphate with increasing shaking time (250 mg/L Fe^{3+}, 540 mg/L Fe^{2+}, 40 mg/L Al^{3+} and 35 mg/L Mn^{2+}, 230 mg/L Mg^{2+}, 660 mg/L Ca^{2+}, 20 mg/L Zn^{2+} and 524 mg/L SO_4^{2-}, 250 rpm, 1g/100ml). Figure 3b. Variation of pH and sulfate with increasing sonication time (250 mg/L Fe^{3+}, 540 mg/L Fe^{2+}, 40 mg/L Al^{3+} and 35 mg/L Mn^{2+}, 230 mg/L Mg^{2+}, 660 mg/L Ca^{2+}, 20 mg/L Zn^{2+} and 524 mg/L SO_4^{2}, Cycle 0.5, Amplitude 60%, 1g/100ml).

An increase in pH was observed after 1 minute of agitation from 1.7 to 5.7, the pH continued to increase drastically up to 9.4 after 60 minutes and stabilizes at 9.9 after 180 minutes. The removal of Ca was very low, with only 1% removal after 1 minute and only 30% was removed after 180 minutes. The removal of Mn after 1 minute was observed to be 26.3% and increased drastically to 99.99% after 60 minutes. The removal of Fe at 1 minute was observed to be 72% and stabilizes at 99.9%. Zn removal was observed to be 90% after 1 minute and 99.9% removal was attained after 5 minutes. The removal of Al after 1 minute was observed to be 99.9%. Sulfate removal was observed to be 46% after 1-minute, maximum removal was 54% after 15 minutes and 90 minutes. This could be attributed to an increase in the pH of the solution. 60 minutes was chosen as an optimum time. The lower % removal of sulphate compared to that for metals, could be attributed to the formation of MgSO4 and, partly, CaSO4, which remains in solution until saturation and only precipitates at elevated dosages [10].

The pH increased drastically up to 8.9 in 1 minute, and reaches the equilibrium after 10 minutes, and thereafter, there was no increase in pH. Sulfate removal was observed to be 59% after 5 minutes and it continued to increase as the sonication time was increased. Sonication was found to be quicker in raising the solutions pH as compared to shaking since pH of 8.9 was attained after 15 minutes when shaking while in sonication attained it in 1 minute. A pH of 9.2 was attained after 30 minutes of shaking, whilst the same pH was attained after 5 minutes when using sonication. Sulfate removal while using an ultrasonic processor was 98.7%, and as a result the treated water will not require further polishing. Metals removal was greater 99.90% for most species. Sonication was shown to be better in removing calcium, with a maximum of 77.55% whereas shaking achieved a maximum of 30.58%. The lower removal of calcium can be attributed to the diverse existence calcium; $CaCO_3$, Ca^{2+} , $CaOH^+$, $CaSO_4$, $CaHCO_3^-$, $CaHSO_4^+$.

High removal of metal species by sonication can be as a result of the high energy microenvironment resulting from generation of free radical and/or high temperature or pressure in the cavitation bubble during cavitation [11]. The generated primary and secondary radicals and the formation of new relatively stable chemical species that can diffuse further into the solution to create chemical effects increase chemical activity in the solution [12]. Hydroxyl radical has a very high oxidizing power [13] and thus can oxidize the metal species in the solution. Chemical reactions occur at three different regions during sonication, Interiors of collapsing bubbles where extreme conditions of temperature and pressure exist transiently [13]; Interfacial regions between the cavitation bubbles and bulk solution where a high temperature and a high gradient is present, Bulk solution where the radicals, being produced in the interior of bubble and in the interfacial region, that survive migration from the interface can undergo radical reactions with solute present in the bulk solution [13].

4. Conclusion

This study has shown that magnesite can be used to remediate AMD. Contact of AMD with magnesite, 1g: 100 ml for 60 minutes of agitation at 250rpm, led to decrease in EC and an increase in pH to 9.4 and removal of Al, Mn, Fe, Zn (> 99%) and sulfate (<50%), while sonication at 400W, 24 kHz, 0.5 cycle and 60% amplitude for 60 minutes has led to an increase in pH from 1.8 to 8.6 and sulfate removal (>60%). Sonication was found to be quicker in increasing the pH of the solution compared to agitation with a shaker since a pH of 8.9 was attained after 15 minutes when agitating with a shaker whereas the same pH was attained within 1 minute when using sonication. The pH of the solution increased to 9.2

within 30 minutes while using a shaker, while the same pH was attained after 5 minutes when using an ultrasonic processor. Of importance was the removal of sulfate which was found to be improved by sonication as compared to shaking, with 98.7% removal achieved when using sonication as compared to 54% removal when using agitation with a shaker. Sonication was also found to be much more effective in removing metal in acid mine drainage as compared to agitation using a shaker. As a result, further treatment of the water is required to remove sulphate, after treatment of AMD with magnesite using a shaker. Further experiments need to be carried out using higher amplitude and suitable pulse time and lower adsorbent dosage in order to reduce sludge generation.

Acknowledgements: This study was funded by Prof Gitari DHET research incentives fund. This support is gratefully acknowledged.

References

1. Akcil, A. Koldas, S. (2006) 'Acid Mine Drainage (AMD): causes, treatment and case studies', Journal of Cleaner Production, 14
2. Bowell, R.J., 2004. A Review of Sulfate Removal Options for Mine Waters. In: Mine water 2004 Proceedings International Mine Water Association Symposium 2, Newcastle upon Tyne, pp. 75–91.
3. Brown, M., Barley, B., Wood, H., 2002. Mine Water Treatment Technology. IWA Publishing, London, Application and Policy.
4. Tolonen, E.T. Sarpola, A. Tao, H. Rämö, J. Lassi, U. (2014) 'Acid mine drainage treatment using by-products from quicklime manufacturing as neutralization chemicals', Chemosphere
5. Pérez-López, Castillo, J. Quispe, D. Nieto, J.M. (2010) 'Neutralization of acid mine drainage using the final product from CO2 emissions capture with alkaline paper mill waste', Journal of Hazardous Materials, 177
6. Evangelou, V.P., 1995. Pyrite Oxidation and Its Control. CRC Press, Boca Raton, Florida.
7. Watten, B.J. Sibrell, P.L. Schwartz, M.F. (2005) 'Acid neutralization within limestone sand reactors receiving coal mine drainage', Environmental Pollution, 137
8. Masindi, V. (2016) 'A novel technology for neutralizing acidity and attenuating toxic chemical species from acid mine drainage using cryptocrystalline magnesite tailings' Journal of Water Process Engineering 10, 67–77
9. Wu, T.Y. Guo, N. Teh, C.Y. Hay, J.X.W. (2013) 'Advances in Ultrasound Technology for Environmental Remediation', Springer, Briefs in Green Chemistry for Sustainability, DOI: 10.1007/978-94-007-5533-8_2.
10. Masindi, V. Gitari, W.M. Tutu, H. and De Beer, M. (2015) 'Passive remediation of acid mine drainage using cryptocrystalline magnesite: A batch experimental and geochemical modelling approach' Water SA, 41
11. González-García, J. Sáez, V. Tudela, I. Díez-Garcia, M.J. Esclapez, M.D. and Louisnard, O. (2010) 'Sonochemical Treatment of Water Polluted by Chlorinated Organo compounds', A Review. Water, 2Masindi, V. Gitari, W.M. Tutu, H. and De Beer, M. (2015) 'Passive remediation of acid mine drainage using cryptocrystalline magnesite: A batch experimental and geochemical modelling approach' Water SA, 41
12. Wan Ishak, W.M.F. Rowson, N.A. (2009) 'The Effect of Ultrasound Pre-Treatment on Froth Flotation Performance', International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering, 3
13. Yang, C. (2008) 'The feasibility studies on sonochemical processes for treating used oil: Toxin reduction for eliminating recycle interference'. A Dissertation Presented to the faculty of the graduate school University of Southern California in partial fulfilment of the requirements for the degree Doctor of Philosophy (Environmental Engineering)

Hemical and physicochemical characterization of Grootvlei Power Station coal fly ash and assessment of the bioavailability and translocation of chemical species

AS Mashau* and MW Gitari

Department of Ecology and Resources Management, University of Venda, South Africa
*Email of corresponding author: shirldor.mashau03@gmail.com

Abstract
The present study aims to examine the physicochemical and mineralogical properties of Grootvlei Power Station coal fly ash and chemical species bioavailability. The elemental composition and mineralogical properties were determined using X-ray fluorescence (XRF), and X-ray diffraction (XRD), respectively and scanning electron microscopy (SEM) was used to examine the morphology. SEM showed that surface morphology of FA has a lower degree of sphericity with irregular agglomerations of many particles. The XRF revealed that FA contains 43.65 %, 22.68 % and 10.89 % of SiO_2, Al_2O_3 and Fe_2O_3, respectively which indicate that FA is an alumino-silicate material and can be categorized as class F (SiO_2-rich) South African FA. Pot culture experiments were carried out to assess the bioavailability of FA chemical species in plants. *Brassica juncea* and *Spinacia oleracea L* plants were planted using FA and soil as a growth medium. In terms of the overall accumulation of chemical species, Fe, Mn, B, Ba and Zn were the highest for most plant parts of both plant species. However, *B. juncea* experienced highest overall accumulation of chemical species than *S. oleracea L*. Bioconcentration factor and Translocation factor showed that *B. juncea* was the most effective for phytoremediation of FA dumps since it was able to translocate most chemical species to shoots.

Keywords: fly ash, leachates, chemical species, pot culture experiments, growth media.

1. Introduction

Coal fly ash (CFA) dumps are the major sources of metal contamination of the environment as a whole. Agricultural lands have been continuously contaminated by direct discharge of industrial effluents, runoff wastewater from ash dumps, overflow of ash dykes during rainy seasons or through atmospheric fall out of fly ash [1]. If soil and water get contaminated with industrial effluents containing high levels of metals, the metals find their way into food crops and vegetables and consequently enter the food web. Most of these metals at high concentrations are toxic and persistent, while some are toxic even at very low concentrations and accumulates over time. They are regarded as environmental pollutants and pose a threat to the environment and human health [2]. Thus, improper FA dumping will continue to cause land degradation, water, air and soil pollution if preventive measures are not implemented.

Phytoremediation is a cost-efficient and ecologically benign way to go about this pollution of air, soils and water sources caused by CFA through which the chemical species also end up in food chain, affecting human life. This is because conventional remediation methods such as acid leaching, land-filling, and excavation process are very expensive and not eco-friendly [3]. Something similar was mentioned that it is aimed at providing an innovative, economical, environment-friendly approach for removing toxic metals from hazardous waste sites [1]. As phytoremediation involves techniques such as rhizofiltration, phytostabilization, phytovolatilization and phytoextraion, the current study focuses on phytoextration. The aim of this study was to determine the potential of *Spinacia oleracea L* and *Brassica juncea* in the phytoremediation of chemical species from coal fly ash. This was done by evaluating the morphology, chemistry, and mineralogy of coal fly ash and the physicochemical properties of leachates from coal fly ash on contact with water at different conditions. Together with the assessment of the growth of *Spinacia oleracea L* and *Brassica juncea* in pot culture experiments using FA and evaluating temporal evolution of chemical species in leachates from the pots. The concentrations of chemical species accumulated by roots, stems, and leaves of selected plants were also evaluated. Most importantly, the phytoremediation potential of the selected plants was evaluated using the bioconcentration factor (BCF) and translocation factor (TF). Plant species which were used includes *Spinacia oleracea L* with the common name "spinach", coming from the Amaranthaceae family and is native to South West Asia; and *Brassica juncea* with a common name "indian mustard", coming from the Brassicaceae family and native to Asia. They both tolerate partial shade and they are fast growing

2. Methodology

Materials and sampling of plants

The dry coal FA used was collected from Grootvlei Power Station which is one of ESKOM's power stations. Good and viable seeds of *Spinacia oleracea L* and *Brassica juncea* were purchased and sown in seed trays then transplanted to the pots for pot culture experiments. Plant samples were collected from pot culture experiments within three successive harvest time.

Characterization of coal fly ash

Chemical and mineralogical composition of CFA and soil were determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. Scanning Electron Microscopy (SEM) was used to examine the morphology of FA.

Preparation of plants samples for analysis and biomass estimation

Samples of the whole plant was collected, then cut to separate parts: leaves, stems and roots in order to determine chemical species' concentrations in each part of the plant and for the estimation of biomass. The biomass of the plants was estimated by weighing the mass (g) for the plant sample after air drying. To estimate the chemical species bioaccumulation, dried samples were ground into a fine powder and 0.5 g was weighed for digestion through aqua regia (HCl: HNO_3 = 3:1 (v/v)) to near dryness or until a white-colored solution was formed. The acid digestion was carried out on a hotplate. After complete digestion of samples, 100 mL of MilliQ water (18.2 MΩ/cm) was added and left to cool down. Samples were then filtered through 0.45 µm pore membrane. Samples were then analyzed using ICP-MS. Blanks and internal standards were set for quality assurance.

Experimental design

Pot culture experiments were conducted for four successive months (April to July 2015). Prior to experiments, pots were washed thoroughly with Milli-Q water and filled up with different compositions of soil and coal FA. Experiments were conducted in four sets. The first set (set 1) was filled up with FA, the second set (set 2) with soil only, the third set (set 3) with a mixture of FA and soil at ratio 1:1 (50% FA: 50% soil), and the last set (set 4) was for control with only FA. *Spinacia oleracea L* and *Brassica juncea* plants were grown in three sets of pots (sets 1 to 3). No plant was grown in set 4. Seeds were sawn in seed trays and irrigated daily until germination, then transplanted to pots. The pots were kept in a nursery to replicate the natural environment. The pots were monitored (measuring plant heights for growth performance) and leachates were collected daily, including record of the heights of plants. Plants were irrigated daily, and the collected leachate was analyzed using ICP-MS. The first harvest was of seedlings, second harvest was done after 46 days of growth and the last harvest was done after 115 days of growth.

Bioconcentration and Translocation factors

Bioconcentration factor (BCF) was calculated for each plant part (root, stem, leaf). BCF was calculated for each plant part (root, stem, leaf) using the following equations for the FA and soil:

$$\text{BCFa} = \text{Metal in leaves} / \text{Metal in FA or soil.} \quad (1)$$

$$\text{BCFb} = \text{Metal in stem} / \text{Metal in FA or soil.} \quad (2)$$

$$\text{BCFc} = \text{Metal in roots} / \text{Metal in FA or soil.} \quad (3)$$

Where BCFa is the bioconcentration factor of the stem, BCFb is the bioconcentration factor of the roots, and BCFc is the bioconcentration factor of the leaves.

Then translocation factor (TF) which is an asset to assess a plant's potential for phytoremediation purpose was also calculated. TF is based on the ratio of metal concentration in plant stem as compared to that of the plant root and leaves [4].

Thus: $$\text{TF} = \text{BCFa} / \text{BCFb} \quad \text{i.e. leaf/stem.} \quad (4)$$

$$\text{TF} = \text{BCFb} / \text{BCFc} \quad \text{i.e. stem/root} \quad (5)$$

3 Results and Discussion

Physicochemical characterization of Grootvlei power station coal FA

Figure 1 depicts the morphology of FA as determined by SEM at different magnification levels. It is observed that the morphology of FA has lower degree of sphericity with irregular agglomerations of many particles while there were dominant spherical particles and smaller sharp needle like particles.

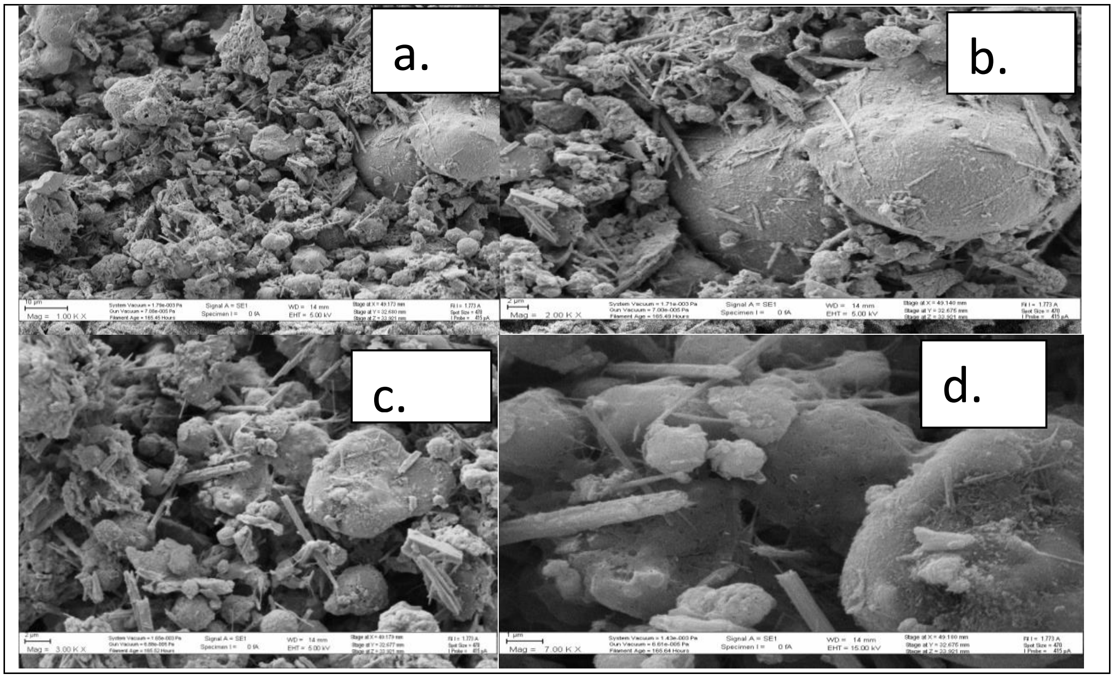


Figure 1. SEM micrographs of Grootvlei Power Station FA at (a) x10 000 (b) x20 000 (c) x30 000 and (d) x70 000 magnifications.

Figure 2 presents the XRD spectrum of the FA. The spectra showed the presence of mullite, quartz, calcite, hematite, magnetite and albite as mineral phases in the FA. The quantitative results from XRD showed that mullite is the dominant mineral (48.14 %) followed by quartz (28.51 %). Other mineral phases were at trace levels.

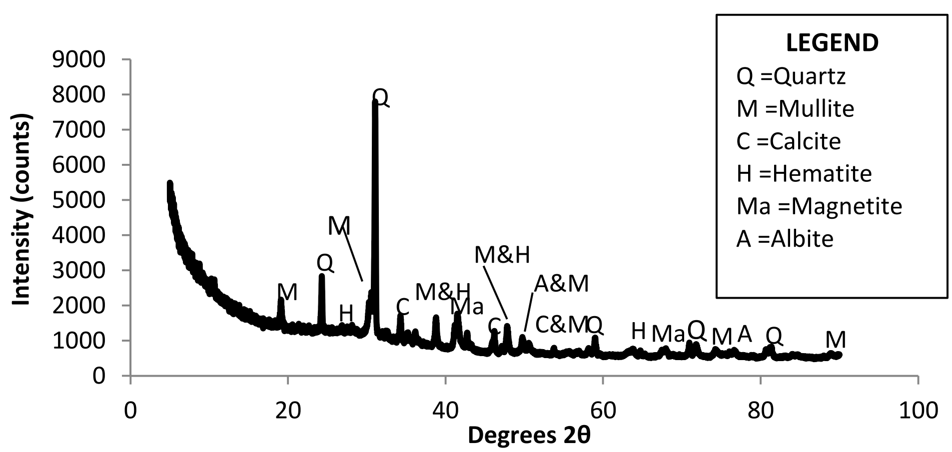


Figure 2: XRD spectrum of the FA.

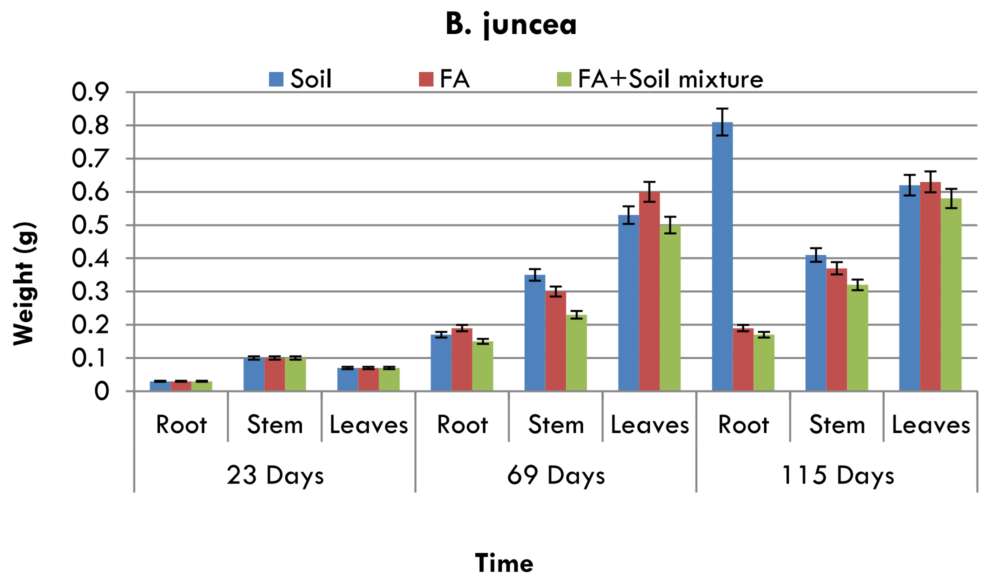
Table 1 depicts the chemical composition of FA and soil as determined by XRF. The analysis revealed that FA consists of Fe_2O_3 (10.89%), SiO_2 (43.65 %) and Al_2O_3 (22.68 %). The total percentage of these three oxides amount >70% indicating that this South African fly ash can be categorized as class F (SiO_2-rich), which is either derived from anthracitic or bituminous coals [6]. High concentration of Fe_2O_3, SiO_2 and Al_2O_3 confirms that this fly ash is an alumino-silicate material [7]. The soil had SiO_2 (82.9 %) as the main component, while Fe_2O_3 and Al_2O_3 were available in small amounts. Elements such as Ni, Cu, Zn, Zr, W, Sr, Ni, As, Rb and Mo were observed at trace levels in both FA and soil (Table 1).

TABLE 1. Comparison of the chemical composition of FA and soil samples.

Fly ash sample				Soil sample			
Major elements (as oxides)	(w/w) %	Trace elements	mg kg^{-1}	Major elements (as oxides)	(w/w) %	Trace elements	mg kg^{-1}
SiO_2	43.65	As	22	SiO_2	82.90	As	24
TiO_2	1.23	Cu	57	TiO_2	0.54	Cu	17
Al_2O_3	22.68	Ga	35	Al_2O_3	7.33	Ga	9
Fe_2O_3	10.89	Mo	9	Fe_2O_3	3.31	Mo	8
MnO	0.06	Nb	31	MnO	0.03	Nb	9
MgO	1.88	Ni	63	MgO	0.25	Ni	20
CaO	7.04	Pb	29	CaO	0.36	Pb	6
Na_2O	0.19	Rb	39	Na_2O	0.71	Rb	51
K_2O	0.81	Sr	2001	K_2O	1.09	Sr	46
P_2O_5	0.54	Th	41	P_2O_5	0.05	Th	13
Cr_2O_3	0.18	U	28	Cr_2O_3	0.01	U	5
NiO	0.01	W	48	NiO	0.00	W	235
V_2O_5	0.02	Y	65	V_2O_5	0.01	Y	10
ZrO_2	0.07	Zn	40	ZrO_2	0.07	Zn	21
CuO	<0.01	Zr	507	CuO	0.00	Zr	405
SO_3	0.36			LOI	3.02		
LOI	9.50			**TOTAL**	**99.69**		
TOTAL	**99.11**						

Assessment of biomass of plant species in pot culture experiments

The biomasses of *B. juncea* and *S. Oleracea L* over time in different growth media are presented in Figure 3. Results showed that in both growth media, roots, stems and leaves biomasses were increasing gradually with increasing days. This was observed in both plants species. Based on the roots and stem masses, *S oleracea L* showed a better tolerance in FA as compared to *B. juncea* in FA growth media. Jamil *et al.* [8] stated that plants with extensive root system are capable of trapping more heavy metals due to better exploration in soil or growth media, hence such increase in the biomass and growth performance of roots is an advantage for the current study in phytoremediation.



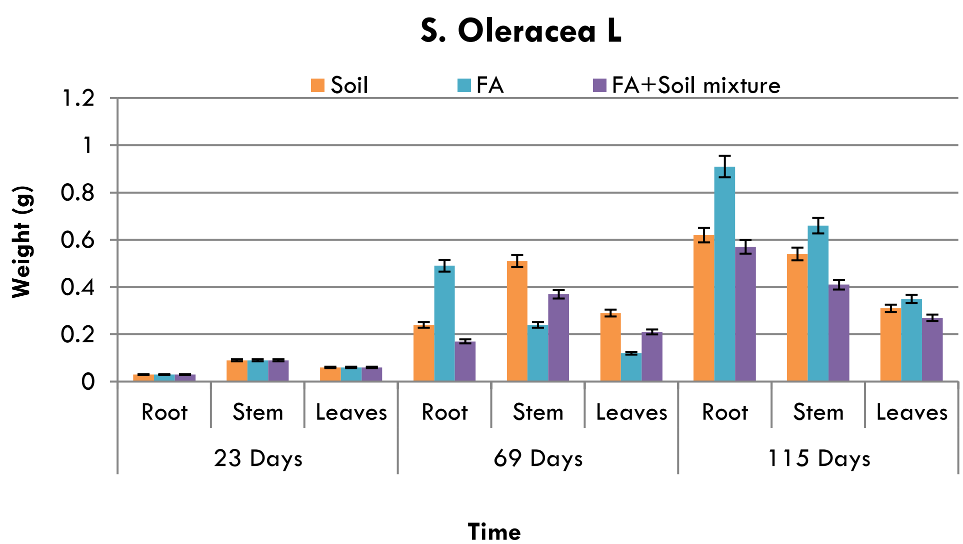


Figure 3. Above and below ground biomass for *B. juncea* and *S. Oleracea L* in all growth media.

Potential of the plant species for phtytoremediation.

The phytoremediation potential of a plant is accessed by computing the bioconcentration factor (BCF) and translocation factor (TF) of chemical species throughout the plant. The BCF value of more than 1 indicates that the plant is a potential accumulator of chemical species, while the TF value greater than 1 indicates that the plant is a potential translocator of chemical species

Table 2 shows the BCF of chemical species accumulating in *B. juncea* and *S. Oleracea L* in day 115 for all growth media. Higher BCF values were observed for Fe, Mn, Zn, Cu and Ni in plant parts of both plants. Conversely, lower values were observed for Mo, B, Ba and Cr having BCF values less than 1 for most growth media over time. From the results it was concluded that *B juncea* is more suitable for the accumulation of many chemical species than *S. Oleracea L* in FA and soil as a growth media (Table 2). For the FA+soil growth media, *S. Oleracea L* accumulated many different chemical species than *B juncea* from 69 days to 115 days.

TABLE 2. BCF for chemical species accumulating in both plant species in day 115 for all growth media.

B. juncea									
Growth media	**Soil**			**FA**			**FA+Soil**		
	Leaf	**Root**	**Stem**	**Leaf**	**Root**	**Stem**	**Leaf**	**Root**	**Stem**
B	2.67	1.01	2.40	0.12	0.08	0.06	0.07	0.02	0.03
Cr	5.66	4.37	2.06	1.00	1.08	0.55	2.13	0.58	0.65
Mn	24.00	15.79	7.72	309.84	200.39	262.18	315.57	118.69	106.95
Ni	1.20	1.32	0.59	24.57	24.32	11.75	10.66	3.47	3.28
Cu	6.53	5.96	2.46	27.58	19.96	25.26	9.31	4.44	3.78
Zn	16.43	28.56	11.90	185.73	181.15	196.67	85.29	44.32	35.85
Mo	7.29	1.12	3.24	0.28	0.15	0.15	0.03	0.02	0.03
Ba	2.72	2.36	1.86	1.22	1.10	1.38	1.32	0.50	0.52
Fe	68.31	50.51	17.89	979.08	692.36	1098.15	4046.11	1128.22	1047.44
S. Oleracea L									
Growth media	**Soil**			**FA**			**FA+Soil**		
	Leaf	**Root**	**Stem**	**Leaf**	**Root**	**Stem**	**Leaf**	**Root**	**Stem**
B	0.11	0.11	0.11	0.01	0.01	0.01	0.01	0.01	0.01
Cr	1.13	1.13	1.13	0.38	0.38	0.38	1.24	1.24	1.24
Mn	6.92	6.89	6.90	97.36	97.28	97.32	8.01	8.00	8.00
Ni	0.51	0.51	0.51	11.24	11.23	11.23	6.10	6.10	6.10
Cu	1.94	1.93	1.93	17.62	17.61	17.61	9.36	9.36	9.36
Zn	5.67	5.65	5.66	42.96	42.93	42.95	91.92	91.91	91.92
Mo	0.24	0.24	0.24	0.01	0.01	0.01	0.01	0.01	0.01
Ba	0.34	0.34	0.34	0.48	0.48	0.48	0.35	0.35	0.35
Fe	0.22	0.22	0.22	957.95	957.33	957.31	257.23	257.19	257.20

Table 3 shows the translocation factor of various chemical species over time (115 days) in studied plants grown in different growth media. Ten sampled plant species were revealed to have the potential to be used in phytoextraction of Zn (TF and BCF>1) [9]. In the current study, TF further proved this because the *B. juncea* species was proved to be an effective phytoremediation plant species since it is effective in the translocation of many chemical species (including Zn) for different growth media to shoots with TF values >1; while *S. oleracea L* failed to translocate most chemical species from roots to shoots. Translocation was high enough from stems to leaves of *B. juncea* plant species in soil growth media, followed by FA and then lastly FA + soil growth media. Hence, the *B. juncea* plant species has a potential of being used as a coal FA dump phytoremediator since it accumulated and translocated many chemical species to shoots than *S. oleracea L*.

TABLE 3. Translocation factor (TF) of various chemical species for 115 days in *B. juncea* and *S. oleracea L* grown in different growth media. TF=BCFb /BCFc. i.e. stem/root and TF=BCFa /BCFb i.e. leaf/stem.

	B. juncea						***S. oleracea L.***					
	leaf/stem.			stem/root			leaf/stem.			stem/root		
	Soil	**FA**	**FA+ Soil**	**Soil**	**FA**	**FA+ Soil**	**Soil**	**FA**	**FA+ Soil**	**Soil**	**FA**	**FA+ Soil**
B	3.57	5.15	1.79	2.37	0.74	1.33	1.06	0.68	2.75	1.21	1.85	0.77
Cr	4.84	3.32	1.03	0.47	0.51	1.13	2.55	0.25	0.45	0.77	1.35	0.66
Mn	3.86	4.44	1.08	0.49	1.32	0.91	0.63	18.75	3.70	0.45	0.05	0.59
Ni	4.04	2.90	1.01	0.45	0.48	0.94	0.98	1.58	0.57	0.46	0.16	0.40
Cu	4.35	3.34	1.20	0.41	1.27	0.85	1.17	1.75	0.62	0.61	0.24	0.42
Zn	4.22	3.26	1.24	0.42	1.09	0.81	0.80	0.44	1.42	0.55	1.25	0.65
Mo	8.95	5.46	3.36	2.88	0.97	1.72	1.72	1.30	3.59	0.76	1.12	0.66
Ba	2.64	3.10	1.22	0.79	1.26	1.05	0.60	1.50	1.16	0.65	0.38	0.56
Fe	5.38	3.68	0.91	0.35	1.59	0.93	2.39	2.80	0.59	0.60	0.17	0.61

4. Conclusions and Recommendations.

The findings of the current study show that coal FA from Grootvlei power station is a class f FA which is also an aluminosilicate material. The FA morphology showed that FA has lower degree of sphericity with irregular agglomerations of many particles while there were dominant spherical particles and smaller sharp needle-like particles. There is similarity in terms of the elemental composition of FA and soil since SiO_2 is available in both mediums as a major oxide which gives expectation of similar growth of the plants in both mediums. In leachates from pot culture experiments, chemical species like B, Ba, Mo and Cr were occurring at higher concentrations for most weeks in the pot culture experiments. In terms of the biomass estimation of both plants, *S. oleracea L* had higher biomass for FA growth media over time, representing better growth in that specific growth media; while *B. juncea* did best in soil as a growth media. Even though that was the case, when it comes to BCF and TF, *B juncea* was found to be the most effective in terms of accumulating and translocating chemicals species to shoots than *S. Oleracea L*. Hence it is further recommended that *B. juncea* is an effective plant species and can be used for phytoremediation of coal FA dumps. There is still a need for the assessment or investigation of other plant species which can be more resistant and effective in phytoremediation than *B. juncea* since it was not tolerant enough to grow on FA, for instance some plants had to be replanted again after death in pot culture experiments. Future studies should also assess the concentration of chemical species that remain after the last harvest of plants to assess if all chemical species were removed from the coal FA.

Acknowledgements: Authors would like to acknowledge Sasol Inzalo Foundation, National Research Foundation (NRF), the University of Venda Research Publication Committee (RPC) for their financial support and Environmental Remediation and Nanosciences group DHET incentive funds.

References

1. Kisku, G.C, Kumar, V., Sahua, P., Kumar, P. and Kumar, N. Characterization of coal fly ash and use of plants growing in ash pond for phytoremediation of metals from contaminated agricultural land. International Journal of Phytoremediation 2018, 20 (4), India, pp. 330–337.

2. Maiti, D. and Prasad, B. Revegetation of fly ash – A review with emphasis on grass-legume plantation and bioaccumulation of metals. Academy of Scientific and Innovative Research (AcSIR), Environment Management Divison, CSIR-Central Institute of Mining and Fuel Research, Applied Ecology and Environmental Research 2016, 14(2), Budapest: Hungary, pp. 185-212.
3. Tiwari, S., Singh, N.S. and Garg, S.K. Induced phytoremediation of metals from fly ash mediated by plant growth promoting rhizobacteria. Journal of Environmental Biology 2013, 34, Triveni Enterprises, Lucknow India, pp. 717–727.
4. Pandey, V.C., Singh, K., Singh, R.P. and Singh, B. Naturally growing Saccharum munja on the fly ash lagoons: a potential ecological engineer for the revegetation and stabilization. Ecological Engineering 2012, 40, pp. 95–99.
5. Mattigod, S., Rai, D., Eary, L. and Ainsworth, C. Geochemical Factors Controlling the Mobilization of Inorganic Constituents from Fossil Fuel Combustion Residues. In. Review of the Major Elements, Journal of Environmental Ouality 1990, 19 (188).
6. Gitari; W.M., Petrik; L.F., Key. DL. and Okujeni, C. Partitioning of major and trace inorganic contaminants in fly ash acid mine drainage derived solid residues. International Journal of Environmental Science and Technology 2010, 7 (3), South Africa, pp. 519–534.
8. Jamil, S., Abhilasha, P.C., Singha, N. and Sharma, P.N. Jatropha curcas: A potential crop for phytoremediation of coal fly ash. Journal of Hazardous Materials 2009, 172, ELSEVIER: India, pp. 269–275.
9. Subhashini, V., Swamy A.V.V.S, and Hema Krishna R. Pot experiment: To study the uptake of zinc by different plant species in artificially contaminated soil. World Journal of Environmental Engineering 2013, 1 (2), Science and Education Publishing, Ontario; Canada, pp. 27–33.

A method for assessing vegetation development on restoration sites

EM Stam* and ND Thovhakale

Department of Ecology and Resource Management, University of Venda, South Africa
*Email to corresponding author: ed.stam@univen.ac.za

Abstract
During ecological rehabilitation destroyed or damaged ecosystems are assisted to recover to a predetermined state. During this process the ecosystems will undergo ecological succession. The direction of this succession depends *inter alia* on how the area is managed. In order to evaluate the results of management strategies, the managed areas need to be monitored regularly by performing vegetation surveys. Interpreting the data emanating from these surveys is, however, not straightforward. Here we propose a method by which one can assess whether a rehabilitated vegetation is developing towards the predetermined goal. The method requires that a benchmark site is identified as the goal to be achieved. The benchmark site needs to be surveyed only once, but the rehabilitated area repeatedly (interval: one or two years). It is essential that the repeat samples are taken at the same points. The data resulting from this procedure are analysed in a correspondence analysis after which the site points of the repeat samples are connected by arrows. These arrows are vectors which indicate in which direction the species composition is developing in each site. If the vectors are pointing in the direction of the cluster of points belonging to the benchmark site, this indicates that the rehabilitated vegetation is developing towards the target; if they point in random directions there may be no directional succession and if they point away from the benchmark cluster a different benchmark site may have to be identified. The method will be illustrated with a data set from a mine in Mpumalanga, South Africa.

Keywords: mining rehabilitation, vegetation, correspondence analysis, benchmarking

1. Introduction

Various human activities may lead to land being denuded of vegetation, following which attempts are made to rehabilitate or restore the vegetation to a predetermined desired state. Examples are open-cast mining [1], removal of dense alien vegetation [2, 3], dam removal [4] and/or rewilding of former agricultural land [5]. Often the sites where such restoration efforts are made are closely monitored to enable managers to intervene when there are indications of land degradation. Such monitoring entails *inter alia* performing vegetation surveys to assess how the vegetation is developing. Different criteria are used to make this assessment, depending on the management goals. It could be ground cover, amount of alien *vs.* indigenous plants, amount of ruderals or pioneer species *vs.* climax species, amount of palatable *vs.* less palatable species or resemblance to benchmark vegetation. In cases where resemblance to benchmark vegetation is the criterion the starting point may be quite far removed from the target. It would be useful, in such cases, to be able to monitor the succession taking place after rehabilitation, whether it is proceeding towards the benchmark site and at which rate. Monitoring in this case will entail performing vegetation surveys at regular intervals. Since the aim of the monitoring is to appraise development, i.e. change over time, it would be advisable to repeatedly survey the same sample sites. Over time this procedure yields a dataset consisting of a series of tables with abundance data for plant species within each site where each table represents a point in time. In order to assess whether the system is developing in the direction of the benchmark vegetation, we need to be able to visualize the trajectory of the succession. Here, we propose a method for this based on correspondence analysis. In correspondence analysis (CA), sites are arranged in scatter diagrams, such that sites which are similar in species composition are close together and sites that are very different in species composition are far apart [6]. In the proposed method we use this property of CA to determine whether over time the rehabilitation sites are becoming more or less similar to sites in a preselected benchmark area which represents the target for the rehabilitation effort. The proposed method significantly facilitates the interpretation of consecutive survey data and subsequently the management of the rehabilitation sites.

2. Methods

A new use for correspondence analysis

A typical correspondence analysis (CA) diagram is highlighted in Figure 1. In this case, only the points representing sites have been plotted, with the species having been left out. The interpretation of the figure is that sites are similar in species composition if their points are close to each other, while they are very different in species composition if their points are far apart. In the fictitious example of Figure 1 site 6 and 8 are similar while site 1 and 11 are very different in species composition.

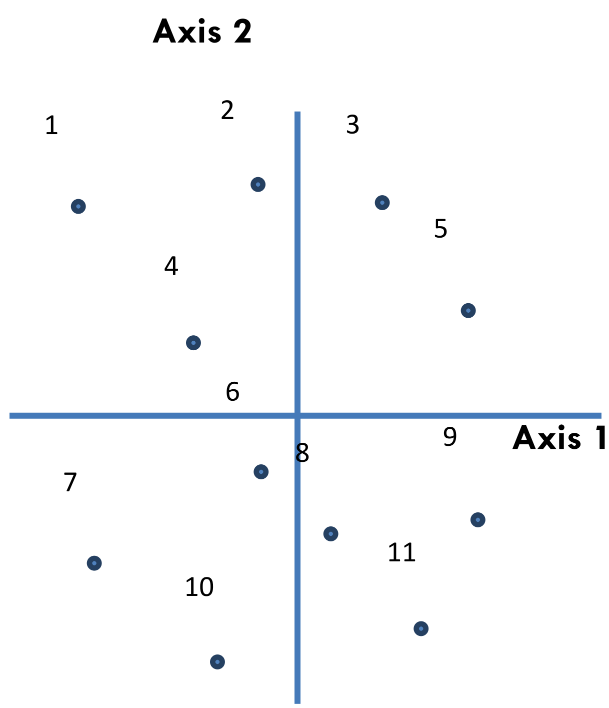


Figure 1. Fictitious example of a correspondence analysis diagram showing only sites.

This property of CA can be used to make comparisons between different areas e.g. a rehabilitation area and benchmark area (Figure 2). When the points for the benchmark area are interspersed between the points of the rehabilitation area, i.e. they are inseparable, this indicates that the two areas are highly similar in species composition (Figure 2A). On the other hand, a more common scenario is where the benchmark area points are clustered together and relatively far from the points of the rehabilitation area (Figure 2B). Thus, the species composition in the two areas are quite different, and the rehabilitated area has not yet reached the point where its managers can be satisfied that they have achieved their target.

To estimate whether a target is likely to be met in future it is necessary to know whether the rehabilitated area is developing in the direction of the benchmark area or, in other words, whether it is becoming more similar to it. This can be monitored with repeated surveys of the same sites. After all the sites have been surveyed twice, the two resulting datasets can be merged and plotted in one correspondence analysis graph (Figure 3). The two points belonging to the same sites, but in different years are subsequently connected by a vector which indicates both the direction and the degree of the change in species composition at the sites. There are three possible results which correspond to different scenarios (Figure 4). First, the vectors may be pointing in the direction of the target. In that case the rehabilitation sites are developing towards the target and no intervention is required. Second, the vectors may be pointing in all directions. This may mean that the interval between the surveys was too short to be able to see the signal in the noise.

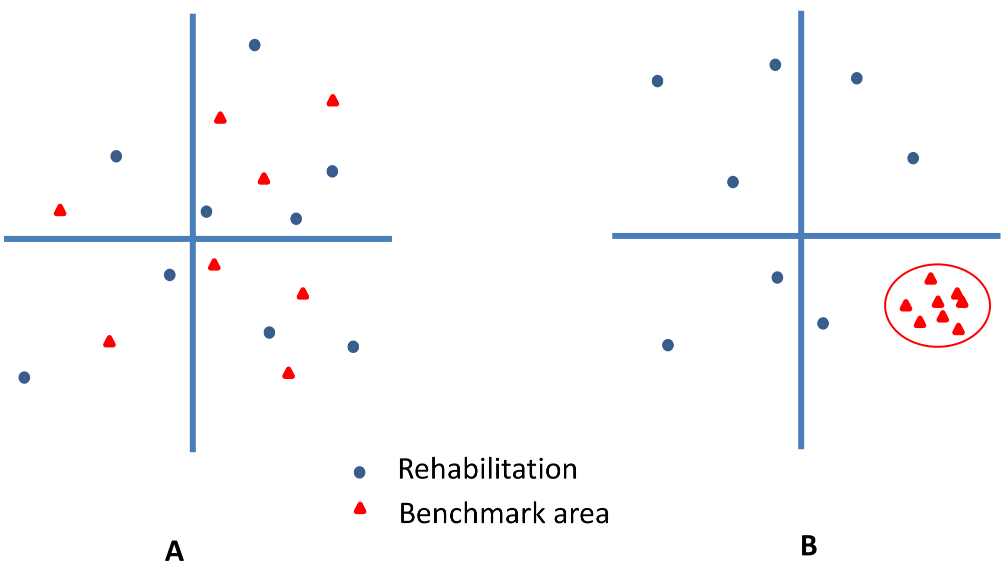


Figure 2 Fictitious correspondence analysis graphs with sites of a rehabilitation and a benchmark area combined. A: high similarity between the two areas B: low similarity.

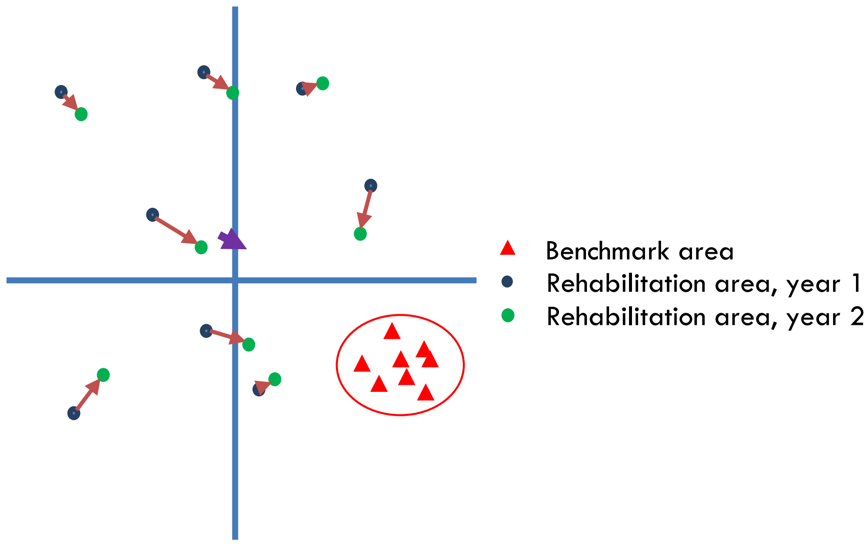


Figure 3 Results of repeated surveys in one CA plot. Blue dots indicate results from the first year and green dots from the second year. The dots which are connected by a vector correspond to the same sites. The vector indicates the direction in which the sites have changed over the year, as well as the amount of change. The thicker vector indicates the average change of the whole rehabilitation area.

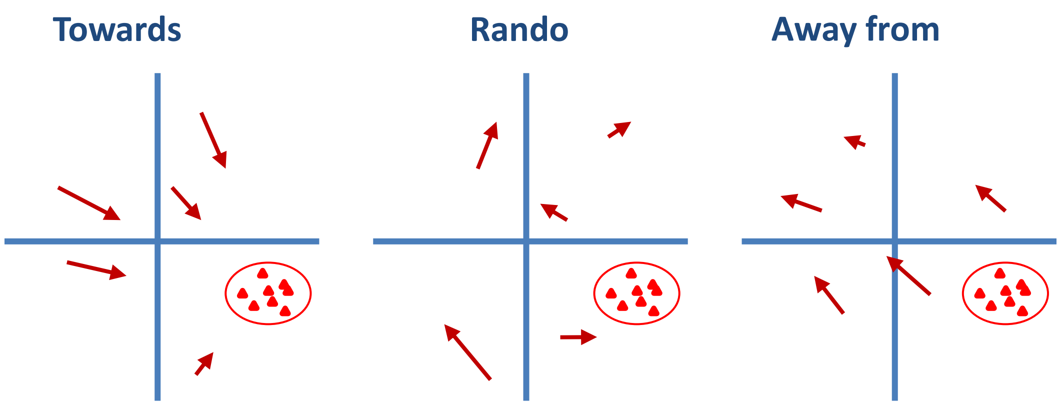


Figure 4 Three possible scenarios for the results of correspondence analysis of repeated vegetation surveys in a rehabilitated area. As in figure 3 the vectors connect the results of a first survey with those of a second survey (points not shown). The encircled points represent the benchmark site.

In that case another survey would be required. It may also mean that the rehabilitation area is stagnant, i.e. that there is no succession taking place. Or different parts of the area are developing in different directions. In the latter two cases the rehabilitation will not reach its target without a management intervention. Third, the vectors may point away from the target. This means that succession is taking place, but it is away from the benchmark. The most likely cause is that abiotic conditions are different between the rehabilitation and the benchmark area. In this case no management intervention can force the rehabilitation area to become like the benchmark area as it will always tend to develop away from it to a different climax. This result indicates that a wrong benchmark area was chosen and a new one may need to be identified.

Testing the method using field data

The method was tested on a dataset from a project at a rehabilitation area of an opencast coal mine in Mpumalanga. The project aimed at assessing the effect of cattle grazing on the rehabilitation process and for this purpose ten 5 x 5 m exclosures had been erected. Linked to each exclosure are six one square meter sites where vegetation surveys were performed; three inside and three outside. Thus, the total number of sites in the rehabilitation area is 60. In addition, there are two benchmark areas, each of which has ten sites. The rehabilitation sites have been surveyed twice, in April 2017 and March 2018. During the surveys, cover percentages were estimated for each species using sketches on graph paper. The data for both years and all three areas were combined in one matrix which was the input for a CA performed with Statistica™. In the resulting plot, the 2017 and 2018 points for each site in the rehabilitation area were manually connected by vectors.

3. Results and discussion

Figure 5 shows the result of the CA of the mine rehabilitation data. The two ellipses encircle the points for the two benchmark sites, BM1 and BM2. Because of the large number of points in the figure (140) the density of the vectors is too high to be able to see a pattern. The figure enlargement, however, clearly shows that the vectors are pointing in all directions and hence the result therefore corresponds to the random scenario (Figure 4). This means that either the interval of one year between the vegetation surveys was not long enough or that the vegetation on the rehabilitated area is not displaying a clearly directional succession. To exclude the first possibility a third vegetation survey would have to be carried out on the rehabilitated area. If this does not change the result, it means that a management intervention may be required to reach the target.

A number of publications in the ecological restoration literature stress the importance of setting clear targets for restoration projects [7-10] and/or benchmark sites [8, 10-12]. However, methods for monitoring of vegetation development against a benchmark and evaluation of whether this development is in an anticipated direction are uncommon. In one publication principal component analysis (PCA) is used to visualize the trajectory along which a recovering vegetation develops [11], but the vegetation development is not evaluated relative to a benchmark area as is proposed in the current study.

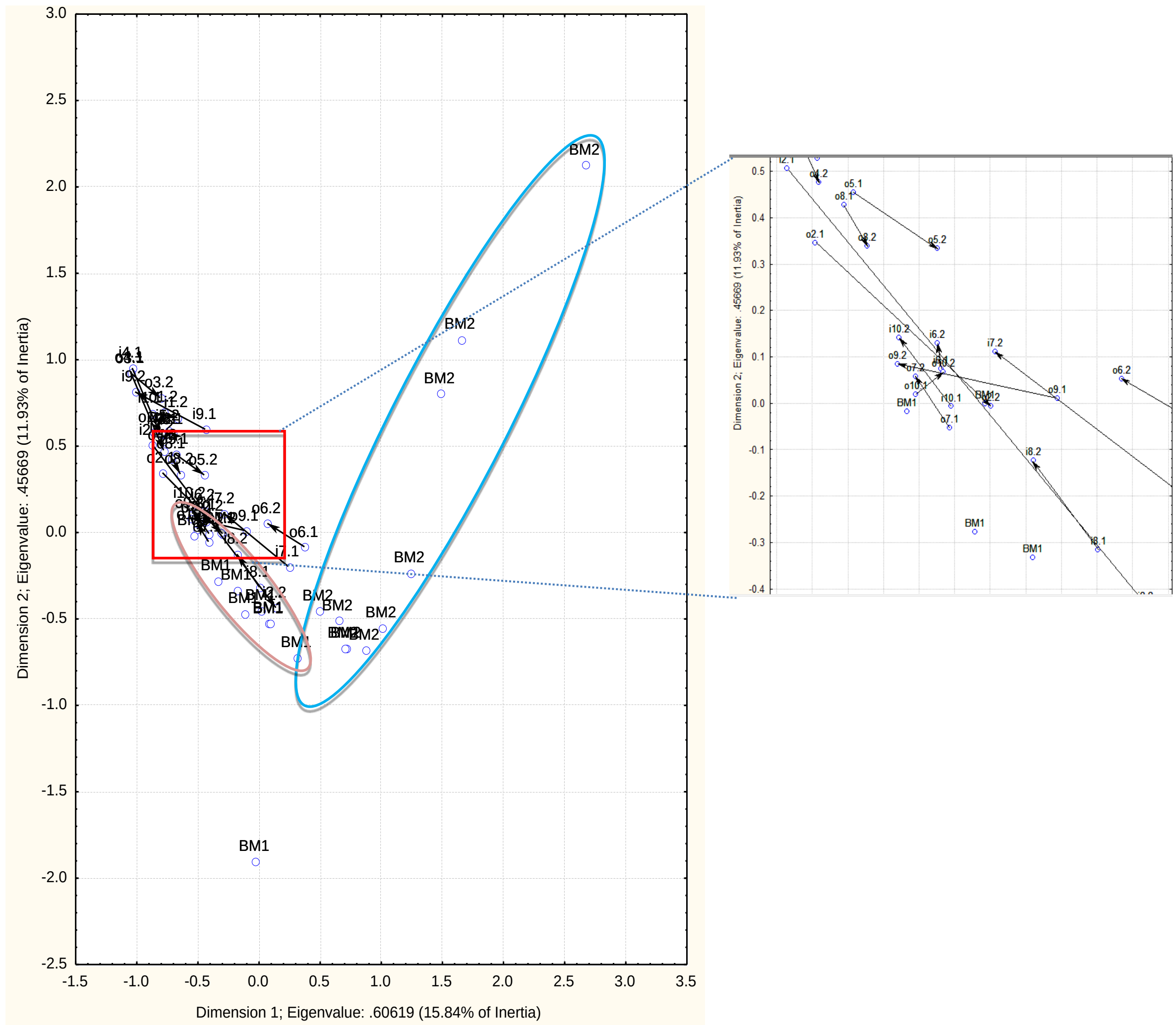


Figure 5. CA on vegetation surveys in a post mining rehabilitation area and two benchmark areas. Points of repeat surveys in the rehabilitation areas are connected by vectors. The points of the benchmark areas have been encircled by ellipses. The red square indicates an area in the graph which has been enlarged.

4. Conclusion

The proposed method using CA to visualize the direction of vegetation development in restoration/rehabilitation sites may have the potential to be a valuable evaluation tool in restoration ecology. What still needs to be established is whether it can distinguish between the three scenarios highlighted in Figure 4. Thus, for this purpose it needs to be tested on other datasets of repeated vegetation surveys.

Acknowledgements: The data used in this article were generated in a project funded by the Coaltech Research Association.

References

1. Baasch, A., A. Kirmer, and S. Tischew, Nine years of vegetation development in a postmining site: effects of spontaneous and assisted site recovery. Journal of Applied Ecology, 2012. 49(1): p. 251-260.
2. Fill, J.M., S. Kritzinger-Klopper, and B.W. van Wilgen, Short-term vegetation recovery after alien plant clearing along the Rondegat River, South Africa. Restoration Ecology, 2018. 26(3): p. 434-438.
3. Richardson, D.M., P.M. Holmes, K.J. Esler, S.M. Galatowitsch, J.C. Stromberg, S.P. Kirkman, P. Pysek, and R.J. Hobbs, Riparian vegetation: degradation, alien plant invasions, and restoration prospects. Diversity and Distributions, 2007. 13: p. 126-139.
4. Orr, C.H. and E.H. Stanley, Vegetation development and restoration potential of drained reservoirs following dam removal in Wisconsin. River Research and Applications, 2006. 22(3): p. 281-295.
5. Sandom, C., C.J. Donlan, J.C. Svenning, and D. Hansen, Rewilding, in Key Topics in Conservation Biology 2, D.W. Macdonald and K.J. Willis, Editors. 2013, John Wiley & Sons, Ltd. p. 430-451.
6. Jongman, R.H.G., C.J.F. Ter Braak, and O.F.R. Van Tongeren, Data analysis in community and landscape ecoloy. 1987, Wageningen: Pudoc.
7. Miller, J.R. and R.J. Hobbs, Habitat Restoration—Do We Know What We're Doing? Restoration Ecology, 2007. 15(3): p. 382-390.
8. Pastorok, R.A., A. MacDonald, J.R. Sampson, P. Wilber, D.J. Yozzo, and T.J. P., An ecological decision framework for environmental restoration projects. Ecological Engineering, 1997. 9: p. 89-107.
9. Prach, K., S. Bartha, C. Joyce, P. Pyšek, R. van Diggelen, and G. Wiegleb, The role of spontaneous vegetation succession in ecosystem restoration: A perspective. Applied Vegetation Science, 2001. 4: p. 111-114.
10. Wortley, L., J.-M. Hero, and M. Howes, Evaluating Ecological Restoration Success: A Review of the Literature. Restoration Ecology, 2013. 21(5): p. 537-543.
11. Anand, M. and R.E. Desrochers, Quantification of Restoration Success Using Complex Systems Concepts and Models. Restoration Ecology, 2004. 12(1): p. 117-123.
12. Andrade, B.O., C. Koch, I.I. Boldrini, E. Vélez-Martin, H. Hasenack, J.-M. Hermann, J. Kollmann, V.D. Pillar, and G.E. Overbeck, Grassland degradation and restoration: a conceptual framework of stages and thresholds illustrated by southern Brazilian grasslands. Natureza & Conservação, 2015. 13(2): p. 95-104.

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

Reduction of Vehicular Pollutants Using Phytoremediation Method: A Review

IT Enitan[1]*, JN Edokpayi[2], J.O Odiyo[3] and AM Enitan[2]

[1]Department of Ecology and Resource Management, University of Venda, South Africa
[2]Department of Hydrology and Water Resources, University of Venda, South Africa
*Email to corresponding author: ronkmodel2003@gmail.com

Abstract
Air pollution has become an alarming issue worldwide and especially in the developing countries due to the adverse effects the pollutants have on human health and the ecosystems. Vehicular emissions one major source of air pollution containing NO_2, Pb, SO_2, C_6H_6, CO_2, CO and particulate matters (PMs) has reached its critical level and could pose major threat to humans and ecosystem. Thus, there is urgent need for an environmentally friendly remediation technique for a sustainable population-pollution nexus. One of the solutions to reduce pollutants is phytoremediation. Plants growing in contaminated environment, especially at roadsides could be used as eco-sustainable filter through absorption of deposited PM and heavy metals at high concentrations. The spatial distribution of roadside plants, tolerance limit, potential health risks has been determined by different researchers in both developed and developing countries. Several eco-friendly plants such as *Eucalyptus globus, Ficus religiosa, Mangifera indica, Codiaeum interuptum* and *Cassia fistula* among others were employed for phytoremediation and act as biological filters for particles in air. However, the causes and effects of air pollution on plants, animals and humans are yet to be fully unraveled. Thus, this paper review plants (ornamental and trees) that could absorb and reduce air pollution in the environment based on their properties like air pollution tolerant index (APTI).

Keywords: Vehicular emissions, sustainable population-pollution nexus, Phytoremediation, Air pollution tolerant index (APTI)

1. Introduction

Atmosphere is a complex and dynamic gaseous system that is essential to support life on earth but has been polluted due to human activities [1]. Air pollution is currently of much environmental concern due to increasing emission from anthropogenic activities across the world. Air pollution is harmful to humans, animals and are susceptible to bioaccumulation in food chain. Monitoring and management of air pollution has been carried out for a long time. One of the major air pollutants is atmospheric particulate matters (PMs) that may cause adverse health effect on humans, affect plants life, ecosystem and become global environmental problems [2,3]. Other major air pollutants from different sources include gaseous pollutants such as ground-level ozone (O_3), sulphur dioxide (SO_2), nitrogen dioxides (NO_2), nitrogen trioxide (NO_3), heavy metals and volatile organic compounds (VOCs). The concentrations of these pollutants in the atmosphere vary widely depending on the sources of pollution [4]. However, the causes and effects of air pollution on plants, animals and humans are yet to be fully unraveled.

2. Vehicular emissions as source of air pollution

Motor vehicle emissions are a major source of air pollution in the world. Pollution caused by traffic activities is increasingly and becoming a great threat to human health, worldwide. This has led to high concentration of pollutants that have reached their critical level in many cities. The concentrations of air pollutants vary widely depending on their area, distribution, meteorological conditions and the topographical features in the vicinity [5]. Motor vehicles are a very significant source of different pollutants that could affect plant growth adversely [6,7].

Vehicular exhaust from combustion of fuels, engine oils, tyre wear and tear, brake wear, vehicular exhaust catalysts (VEC) and road abrasion contains a wide range of pollutants and metals. Some of these metals are directly deposited on the exhaust pipe, while the remainders are released into the surrounding environment [8]. Pollutants from motor vehicles can react in the atmosphere to form different and even more reactive (and dangerous) pollutants such as photochemical smog [9]. Also, heavy metals originated from different sources are transferred to the biosphere constituents of airborne particles [10].

Study has shown that Pb contamination of roadside soils and *Amaranthus* leaves was a function of traffic density, as mediated by atmospheric deposition and distance from roads in Uganda [11]. In India, Singh *et al*. [12] reported that pollutants from vehicles account to 60-70% of the pollutant found in the urban area in which the two major pollutants were Pb and SO_2. Heavy metals concentration like Pb and Mn in roadsides wheat and soil samples has been reported to originate from the traffic in Turkey [13]. In another study, Hassan and Basahi [14], assessed concentrations of heavy metals in ambient air of Jeddah city, Saudi Arabia through elemental analyses of foliar dust and leaf tissues of lettuce plants.

In South Africa, vehicle emissions in Cape Town have been identified as one of the sources of brown haze [15]. In a recent study by Mabusela and Mamakoko [16], increase of road traffic in the City of Johannesburg was reported to contributes significantly to high levels particulate matter and greenhouse gas emissions in the city. For a sustainable environment, study have suggested that decrease in air pollutants may result in the mitigation of global burden and outbreak of endemic diseases [17]. Sadly, management of air pollution is still facing challenges due to lack of availability of suitable tools and techniques for monitoring and removal of air pollutants from the atmosphere.

3. Phytoremediation an Eco-friendly method in reducing air pollution

In the quest of an alternative eco-friendly technology, impacts of air pollutants on biochemical, physiological and morphological parameters of plant are now being explored as a vital part of air pollution science. Plants have been labelled as the -lungs of cities acting as natural biofilters in reducing air pollution [18]. Phytoremediation is now being considered as an alternative eco-friendly technology for treating NO_2, Pb, SO_2, C_6H_6, CO_2, CO, particulate matters (PMs) and VOC contaminated air. Study on the elemental composition and distribution of dust adsorbed on leaves and their tissues have reported that plants are suitable bio-monitors and bio-indicators of air pollution [19]. The impact of air pollution and the effects of PM on plants have been reported by some researchers [2,20]. The roadside deposition studies across the world have demonstrated that significant quantities of vehicle pollutants are deposited on plants in China [21] and India [20] which has drawn attention to the gaseous pollutant, PM, and heavy metal accumulation in plants at high concentrations. Several previous reports have proposed treating air pollutants by various plant parts [22—25]. However, sensitivity, response and tolerance of plants to air pollutants varies and this differential behaviour are being employed in the world to develop appropriate environmental indicators and phytoremediation strategies.

The ability of plant to maximally absorb pollutants from the air without negative impact on the plant is determined using air pollution tolerant index (APTI) which expresses the capacity of a plant to battle against air contamination. Air Pollution Tolerance Index was calculated by using the equation 1 [26].

$$APTI = {[A + (T + P) + R]}/{10} \quad (1)$$

Where, A= Ascorbic acid (mg/g dry wt.), T= Total Chlorophyll (mg/g dry wt.), P= pH of leaf extract and R= Relative water content of leaf tissue (%).

The plant species with low index values are more sensitive to air pollution and act as biological indicators of air pollution and tool for monitoring environmental pollution (Table 1) [27]. Tolerant plant species represent the greatest possibility for reducing the injury caused by air pollutants.

TABLE 1. Air Pollution Tolerance Index (APTI).

Range of APTI	Tolerance level
30-100	Tolerance
17-29	Intermediate
1-16	Sensitive
<1	Very sensitive

Identified Plant species for Phytoremediation

Impatiens balsamina an ornamental plant that locally known as Garden Balsam are of Southeast Asian origin, it is found growing in different part of the world, throughout tropical Africa, and including India, southwest Asia, southern China, Japan, as well as parts of Europe, Russia, Malaysia and North America. Nawahwi et al., [22] showed that *Impatiens balsamina* could be used to remediate and reduce organic contaminants because of its ability in Malaysia. Also, research conducted by Sriprapat et al., [28] showed that *Sansevieria trifasciata* was efficient for toluene removal and *Chlorophytum comosum* was effective for ethylbenzene removal out of the twelve-sample studied for air pollution by volatile organic compound. Likewise, according to the study carried out by Dzierżanowski and Gawroński [29], Silver birch and whitebeam were the most effective for PM among the best phytoremediator. Some other plants with varied species have been identified for phytoremediation of air pollutant based on their morphological characteristics (leaf area index, leaf hair, thick epicuticular wax layer) and air pollution tolerance level (higher APTI) as summarised in Table 2.

Out of 19 species reviewed for pollution assimilation, 3 species showed APTI values ranging from 80.45 to 95.20 which falls within the tolerance ranges of 30 to 100 (Figure 1 and Table 3). Other plant species are having APTI ranging from 16.02 to 10.78 (Table 1), which are sensitive and intermediate species.

However, some of the reported disadvantages of bioaccumulation of automobiles pollutants on plants include reduction in the concentration of photosynthetic pigment when absorbed by the leaves and various patches on the leaves [38]. This induces structural and functional changes of the leaf [2]. The impacts of PM on the biochemical, physiological and morphological characteristics of urban roadside plants (species) have been recorded by several researchers [33,39].

TABLE 2: Plant species for Phytoremediation based on APTI value and some biological characters

Plant species	Air pollutants	Air pollution tolerance index (APTI	Morphological Characteristics	Literature
Sansevieria trifasciata	VOC (highest toluene)		Epicuticular wax	[28]
Chlorophytum comosum	VOC (highest ethylbenzene)			
Mangifera indica	SPM	12.27		
Acacia nilotica	Suspended particulate matter	10.78		[30]
Moringa pterydosperma	(SPM), SO_2 and NO_X	12.17		
Cassia renigera		12.07		
Ailanthus excelsa	SPM, SO_2 NO_X and F	11.03		
Swietenia macrophylla				
Polyathia fragrans	CO		Canopy structure	[31]
Pongamia pinnata		11.58		
Albizia saman		11.62		[32]
Tamarindus indica		11.59		
Swietenia mahogany		12.22		
Azadirachta indica		13.16		
Cassia fistula	SPM, SO_2 and NO_X	13.79		*[33]*
Ficus bengalensis		15.38		
Psidium gujava		15.76		
Saraca indica		15.91		
Azadirachta indica		16.02		
Bougainvillea spectabilis	SPM, SO_2 and NO_X			[34]
Ageratum conyzoides				
Bungur (*Lagerstroemia speciose*)				
Gmelina (*Gmelina arborea*)	NO_2			[35]
Tanjung (*Mimusops elengi*)			Tree Canopy structure	
Dialium indum	PM_{10}		Epicuticular wax layer, foliage,	[36]
Pterocarpus indicus	CO		and leaf surface	
Codiaeum interuptum (decorative plant)	CO			
Cassia fistula (decorative plant)	PM_{10}			
Eucalyptus globus		95.20		
Ficus religiosa	SPM	85.45		[37]
Magnifera indica		80.52		

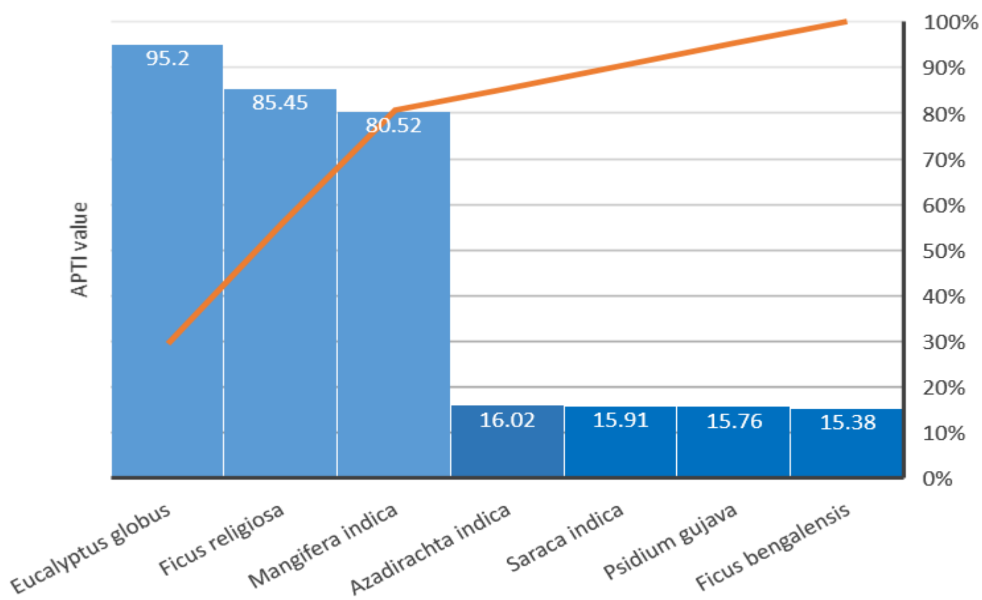


Figure 1. APTI level in different plant species

TABLE 3. Various categories of tree species based on APTI

Tree species	APTI (mean value)	Tolerance
Eucalyptus globus	95.2	Tolerance
Ficus religiosa	85.45	Tolerance
Mangifera indica	80.52	Tolerance
Ficus bengalensis	15.38	Sensitive
Psidium gujava	15.76	Sensitive
Saraca indica	15.91	Sensitive
Azadirachta indica	16.02	Intermediate
Acacia nilotica	10.78	Sensitive

4. Conclusions

This review shows that eco-environment conservation and pollution abatement through phytoremediation may be used in mitigation of air pollution risks by means of the plant APTI, leaf structure, tree canopy, roughness, and Epicuticular wax. Based on the plant APTI level reviewed, it can be concluded that *Eucalyptus globus*, *Ficus religiosa* and *Mangifera indica* in the following order, have high tolerance level. Used as tree or ornament planting programs, such plants have the potential to improve air quality and at the same time utilized for passive monitoring of air pollution. Proper knowledge of tree quality is required to achieve maximum benefit. Therefore, such practices should be adapted in environs as it can positively affect ecosystems in many ways and help to attain sustainable population-pollution nexus.

References

1. Steffen, W., Sanderson, R.A., Tyson, P.D., Jager, J., Matson, P.A., Moore III, B., Oldfield, F., Richardson, K., Schellnhuber, H-J., Turner, B.L., 2006. Global change and the earth system: a planet under pressure. Springer Science & Business Media.
2. Rai, P.K. and Panda, L.L., 2014. Dust capturing potential and air pollution tolerance index (APTI) of some road side tree vegetation in Aizawl, Mizoram, India: an Indo-Burma hot spot region. Air Quality, Atmosphere & Health, 7(1), pp.93-101.
3. Seinfeld, J.H. and Pandis, S.N., 2016. Atmospheric chemistry and physics: from air pollution to climate change. John Wiley & Sons.
4. Phalen, R.F. and Phalen, R.N., 2012. Introduction to air pollution science. Jones & Bartlett Publishers.
5. Chattopadhyay, S. 2014. Spatial and temporal variations of ambient air quality in Burdwan town, West Bengal, India.
6. Krzyżanowski, M., Kuna-Dibbert, B. and Schneider, J. eds., 2005. Health effects of transport-related air pollution. WHO Regional Office Europe.
7. Sharma, N., Agarwal, A.K., Eastwood, P., Gupta, T., Singh, A.P.,2018. Introduction to Air Pollution and Its Control. Air Pollution and Control. Springer, 3-7.
8. Winther, M. and Slento, E., 2010. Heavy metal emissions for Danish road transport. National Environmental Research Institute, Aarhus University.
9. Desai, A.A., 2018. A review on Assessment of Air Pollution due to Vehicular Emission in Traffic Area.
10. Odiyo, J.O., Bapela, H.M., Mugwedi, R. and Chimuka, L., 2005. Metals in environmental media: A study of trace and platinum group metals in Thohoyandou, South Africa. Water SA, 31(4), pp.581-588.
11. Nabulo, G., Oryem-Origa, H. and Diamond, M., 2006. Assessment of lead, cadmium, and zinc contamination of roadside soils, surface films, and vegetables in Kampala City, Uganda. Environmental Research, 101(1), pp.42-52.
12. Singh, N., Yunus, M., Srivastava, K., Singh, S.N., Pandey, V., Misra, J.A. and Ahmad, K.J., 1995. Monitoring of auto exhaust pollution by roadside plants. Environmental Monitoring and Assessment, 34(1), pp.13-25.
13. Ekmekyapar, F., Sabudak, T. and Seren, G., 2012. Assessment of heavy metal contamination in soil and wheat (Triticum aestivum L.) plant around the Corlu–Cerkezkoy highway in Thrace region. Global Nest J, 14(4), pp.496-504.
14. Hassan, I.A. and Basahi, J.M., 2013. Assessing roadside conditions and vehicular emissions using roadside lettuce plants: HARD, POST-OFFICE BOX, 10-718 OLSZTYN 5, POLAND, 22(2).
15. Chiloane, K.E., 2006. Volatile organic compounds (VOC's) analysis from Cape Town haze II study (Doctoral dissertation).
16. Mabusela, X. and Mamakoko, T. 2017. An overview of Joburg's vehicular emissions measurements and control methods.
17. Franklin, B.A., Brook, R. and Pope III, C.A., 2015. Air pollution and cardiovascular disease. Current problems in cardiology, 40(5), pp.207-238.
18. McPherson, E. G. 2005. Trees with Benefits. American Nurseryman April 1: 34-40.
19. Ram, S.S., Majumder, S., Chaudhuri, P., Chanda, S., Santra, S.C., Chakraborty, A. and Sudarshan, M., 2015. A review on air pollution monitoring and management using plants with special reference to foliar dust adsorption and physiological stress responses. Critical Reviews in Environmental Science and Technology, 45(23), pp.2489-2522.
20. Rai, P.K., 2016. Biodiversity of roadside plants and their response to air pollution in an Indo-Burma hotspot region: implications for urban ecosystem restoration. Journal of Asia-Pacific Biodiversity, 9(1), pp.47-55.
21. Zhang, H., Zhang, Y., Wang, Z., Ding, M., Jiang, Y., Xie, Z., 2016. Traffic-related metal(loid) status and uptake by dominant plants growing naturally in roadside soils in the Tibetan plateau, China. Science of the Total Environment 573, p. 915–923.
22. Nawahwi, M.Z., Aziz, K.M., Mohamed, S.M., Shariff, S.M., Taib, M.N.A.M. and Abdullah, M.A., 2014. Phytoremediation Potential of Impatiens balsamina Towards Naphthalene Contaminated Soil in Different Parts of Plant.
23. Kapoor, M., 2017. Managing Ambient Air Quality Using Ornamental Plants-An Alternative Approach. Universal Journal of Plant Science, 5(1), pp.1-9.
24. Reshma, V.S., Kumar, P. and Chaitra, G.S., 2017. Significant Role of Ornamental Plants as Air Purifiers– A Review. Int. J. Curr. Microbiol. App. Sci, 6(8), pp.2591-2606.
25. ElAziz, N.G.A., Mahgoub, M.H., Azza, M.M., Farahat, M.M. and Abouziena, H.F., Potentiality of Ornamental Plants and Woody Trees as Phytoremidators of Pollutants in the Air: A Review.

26. Singh, S.K. and Rao, D.N., 1983, November. Evaluation of plants for their tolerance to air pollution. In Proceedings of symposium on air pollution control (Vol. 1, pp. 218-224).
27. Ogunrotimi, D. G., Adereti, F. K., Eludoyin, A. O. & Awotoye, O. O. 2017. Urban air pollution control: selection of trees for ecological monitoring using anticipated performance indices in a medium-size urban area in Southwest Nigeria. Interdisciplinary Environmental Review, 18, 40-54.
28. Sriprapat, W., Suksabye, P., Areephak, S., Klantup, P., Waraha, A., Sawattan, A. and Thiravetyan, P., 2014. Uptake of toluene and ethylbenzene by plants: removal of volatile indoor air contaminants. Ecotoxicology and environmental safety, 102, pp.147-151.
29. Dzierżanowski, K. and Gawroński, S.W., 2011. Use of trees for reducing particulate matter pollution in air. Challenges of Modern Technology, 2.
30. SHANNIGRAHI*, A.S., Fukushima, T. and Sharma, R.C., 2004. Anticipated air pollution tolerance of some plant species considered for green belt development in and around an industrial/urban area in India: an overview. International journal of environmental studies, 61(2), pp.125-137.
31. Sulistyantara, B., Nasrullah, N., Fatimah, I.S. and Pratiwi, P.I., 2016, January. Study of the Effectivity of Several Tree Canopy Types on Roadside Green Belt in Influencing the Distribution Vertically and Horizontally of CO gas Emitted from Transportation Activities to Vicinity of The Road. In IOP Conference Series: Earth and Environmental Science (Vol. 31, No. 1, p. 012031). IOP Publishing.
32. Kumar, M. and Nandini, N., 2013. Identification and evaluation of air pollution tolerance index of selected avenue tree species of urban Bangalore, India. International Journal of Emerging Technologies in Computational and Applied Sciences, 4(5), pp.388-390.
33. Joshi, N., Bora, M. and Haridwar, U., 2011. Impact of air quality on physiological attributes of certain plants. Report and Opinion, 3(2), pp.42-47.
34. Deepalakshmi, A.P., Ramakrishnaiah, H., Ramachandra, Y.L. and Radhika, R.N., 2013. Roadside plants as bio-indicators of urban air pollution. IOSR Journal of Environmental Science, Toxicology and Food Technology, 3(3), pp.10-14.
35. Desyana, R.D., Sulistyantara, B., Nasrullah, N. and Fatimah, I.S., 2017. March. Study of the effectiveness of several tree canopy types on roadside green belt in influencing the distribution of NO2 gas emitted from transportation. In IOP Conference Series: Earth and Environmental Science (Vol. 58, No. 1, p. 012045). IOP Publishing.
36. Putri, A.E., Humairo, M.V. and Agustina, U., 2017. Reduction effort of Pm10 And Co with phytoremediation method using trees and decorative plants in surabaya, Indonesia.
37. Lohe, R.N., Tyagi, B., Singh, V., Tyagi, P., Khanna, D.R. and Bhutiani, R., 2015. A comparative study for air pollution tolerance index of some terrestrial plant species. Global Journal of Environmental Science and Management, 1(4), pp.315-324.
38. Joshi, P.C. and Swami, A., 2007. Physiological responses of some tree species under roadside automobile pollution stress around city of Haridwar, India. The Environmentalist, 27(3), pp.365-374.
39. Rai, P.K., Panda, L.L., Chutia, B.M. and Singh, M.M., 2013. Comparative assessment of air pollution tolerance index (APTI) in the industrial (Rourkela) and non-industrial area (Aizawl) of India: An ecomanagement approach. African Journal of Environmental Science and Technology, 7(10), pp.944-948

Reviewing the National Household Travel Surveys public transport trends in South Africa (2000-2016): Implications for the green transport agenda

J Chakwizira*

Department of Urban and Regional Planning, University of Venda, South Africa
* Email to corresponding author : jameschakwizira@gmail.com

Abstract

This paper reviews and analyses the findings and results of the 2003 and 2013 National Household Travel Surveys (NHTS). Public transportation trends in South Africa show preponderance towards the use of private cars and small and inefficient minibus taxis at the expense of mass public transport systems such as buses and trains. Such a set-up presents commuting challenges and opportunities that cascade into the physical, social, economic and political realms. This paper, making use of a public transport commuting systems theory and a green transport innovation framework of analysis, identifies key transport issues and presents implications for a green commuting transport agenda. The findings indicate a green commuting transport implementation framework emphasizing the need for up-skilling institutions and enterprises to support innovation and development in the transport sector.

Keywords: Household survey, public transport, commuting, green transport

1. Introduction

The history of public transport and commuting in South Africa is complex and linked to the socio-economic development context of South Africa [1]. Firstly, the geography of settlements and landscapes explain the fragmentation of transport and commuting patterns in South Africa. Secondly, the apartheid handwork exacerbated spatial fragmentation making efforts aimed towards re-shaping and transforming the transportation and commuting architecture in the country a challenging task [2,3]. Transport, commuting patterns and systems have over centuries undergone circular transformations that present a narrative turn in which missed opportunities, forgotten dimensions and emergent issues play out differently for different areas as transport authorities and practitioners embarked in actions and interventions aimed at advancing sustainable transport and commuting solutions for any given country.

Previous research by the Financial and Fiscal Commission (FFC) acknowledged advancements in the South African transport policy and legislative frameworks yet bemoaned inadequate implementation follow-through [4]. The report further questioned whether the full value chain of research and development was being realized in a context of financial, physical and governance constraints. The National Development Plan (NDP, 2030), acknowledges the historical roots of the transportation constraints with particular emphasis being placed on the need to turn-around the delivery and provision of rural and urban passenger transport systems [5]. Contemporary South African cities are characterised by long commuting distances and costs with implications for transport solutions and technologies [6,7]. With respect to the transport sector's significant contribution to anthropogenic greenhouse gas (GHG) emissions, the NDP read together with climate change and development planning frameworks enjoins targets for GHG emission reduction with strong requirements for setting up a framework for green transport infrastructure, services and related incentives as important dimensions towards transiting to a low carbon economy in South Africa. Emergent green transport technologies, solutions and alternatives to overcoming commuting barriers and bottlenecks that characterize and highlight transportation gridlocks instead of transportation networks of flows, exchange and development in South Africa are discussed.

Concepts for the green transport agenda and policy frameworks in South Africa

The concepts for the green transport agenda and policy framework have links to both organic and structured interventionist approaches aimed at promoting sustainable transport. Throughout history humankind has always developed systems and mechanism to respond to climate change with green transport being no exception. Romans developed the aqueduct water system in which water was transported from areas of excess to areas of deficit through a navigable constructed water channel to convey water; drought lead to the need for irrigation for societies in the Ancient Near East (for example in parts of what is now modern Syria and Turkey about 12 000 years ago); *et cetera* [8]. However, these systems are usually not patented and as part of indigenous inter-generational transfer of transport adaptation and mitigation coping mechanism not easily transferable. These range from using drought resistant animal transport power as represented by donkeys and camels to eating traditional herbs and nutrition that reduces sweating and loss of water from the body for long periods [9]. However, the scientific transport solutions are linked to the development of circular economy transport frameworks and policies aimed at promoting sustainable transport. Three main paradigms have evolved so far. These are Lee Schipper's World Bank's Framework Approach: the Activity, mode Share, Intensity and Fuel mix (ASIF) framework [10], and the simplified United Nations Environment Programme (UNEP's) Approach: Activity, Shift and Improve (ASI) [11]. These two frameworks focused on the leading role that improving transport energy efficiency plays in reducing carbon emissions. A new variation and improvement of the ASI framework has been developed by the World Bank - the Enable, Avoid, Shift and Improve (EASI) Framework Approach [10]. This new framework approach introduces an adaptive sustainable transport institutional and governance component. EASI is premised on the need to enable, avoid, shift and improve green transport interventions aimed at reducing carbon emissions for both the primary transport sector and allied sectors.

2. Materials and Methods

This study utilises Statistics South Africa's databases of the 2001 [12] and 2011 [13] census as well as the 2009 [14, 15] and 2016 [14] Statistics South Africa Community surveys. The study also draws heavily on the Department of Transport's 2003 [16] and 2013 [17] National Household Travel Survey (NHTS) databases. The analysis and cross-referencing to these national data sets has the effect of providing for a trend analysis and longitudinal survey approach to understanding transport commuting and travel patterns including the spatial geography of South Africa. Table 1 presents the list of data sets employed in conducting the study.

TABLE 1. List of Datasets consulted in conducting the research study

Survey Name	Dataset Custodians	Study Year	Sampling	Av. Monthly Income	Av. no. of cars per household	Mean Household Size
Gauteng Transportation Study	GDoRT	2000	22 944	3 247	0.5	3.56
National Household Travel Survey	DoT	2003	45 556	-	0.40	--
National Household Travel Survey	DoT	2013	51 341	-	-	-
Gauteng Household Travel Survey	GDoRT	2014	29 779	5 767	0.5	2.94
General Household Survey	StatsSA	2016	54 432	-	-	-

Key: DoT - Department of Roads and Transport; StatsSA - Statistics South Africa, GDoRT - Gauteng Department of Roads and Transport [12-18]

3. Results

Urban population densities

South Africa's urban form and structure leads to patterns of demand which are extremely expensive to service. Low average population densities imply that public transport systems operate over relatively longer distances and with relatively fewer passengers than higher population densities [6,7]. Figure 8 compares population densities in the built-up areas of a sample of cities across the world. From Figure 1, we can deduce that South Africa's cities spatial structure is fragmented and characterized by low densities.

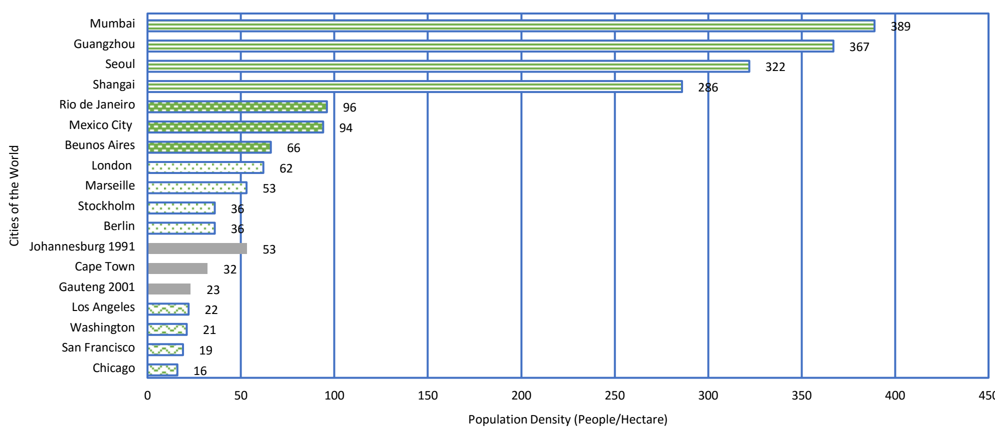


Figure 1. Selected population densities in built-up areas of selected metropolitan areas Source: [3,4]

Household and transport expenditure patterns in South Africa

Figure 2 presents household expenditure patterns on transport items in South Africa disaggregated by province for the year 2016. From Figure 2 we can deduce that transport

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A *JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds)* *ISBN 978-0-620-82267-1*

expenditure in South Africa has remained above the World Bank norm of 10% of household expenditure [19]. This is inconsistent with both the national and provincial policies of reducing household public transport cost to less than 10% of disposable household income [20].

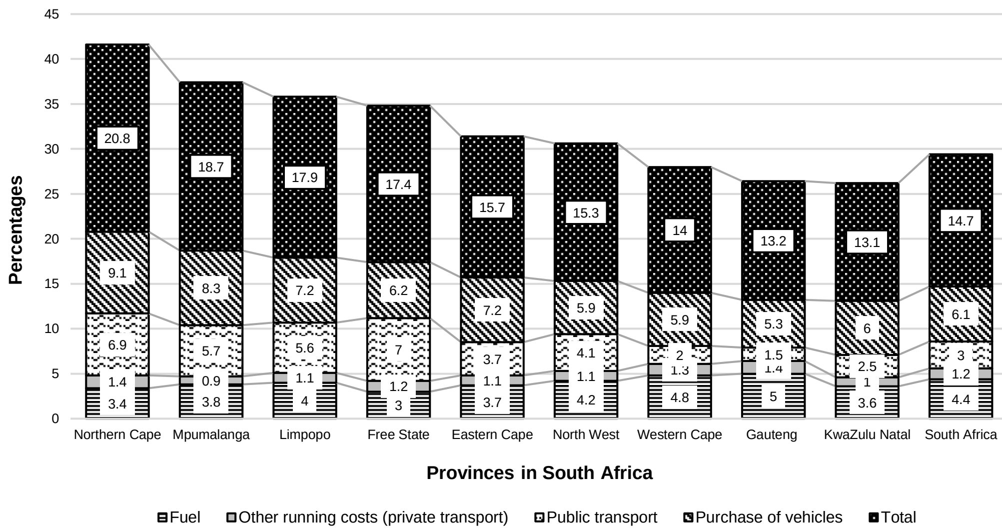


Figure 2. Household expenditure patterns on transport items in South Africa disaggregated by province, 2016 [14,15]

With respect to Figure 2, in countries like South Africa that are reliant on rapidly increasing quantities of crude oil to fuel its transport system, there are additional risks to energy security and a negative impact on the national balance of payments. In terms of foreign currency requirements for importing oil. With respect to fluctutations. In oil prices, the local market has to respond to changes in fuel prices, prices of goods and protests as industry, residents and employees seek for solutions to the impact of oil in the economic sectors. This attests to the fragmented and spatially distorted and inefficient apartheid geography in South Africa [5]. In order to address these shortcomings, there is need to implement sustainable, compact and transit orientated urban developments that are based on bus rapid transit systems [18]. given this context the developments of the bus rapid transport (BRT) Rea Vaya, BRT Areyeng and the BRT Harambee are initiatives in the right direction [14]. However, the introduction of mass public transit systems has been seen to lead to a switch of between 2-5% of private motorists, pedestrians and mini-bus taxi users to public transport [10]. With respect to such findings, it is therefore important to realise that BRT systems are not enough in spatially changing and transforming commuting and settlement induced transport choices in any area.

Transport and externalities

Transport enables trade, commerce, employment and social interactions, but concomitant to these advantages also presents health and emission related challenges [1,2]. Reliance on fossil fuel and transport infrastructure is associated with urban congestion, local air pollution as well as accidents (6,7,18]. Figure 3 presents air quality ratings of municipalities in South Africa.

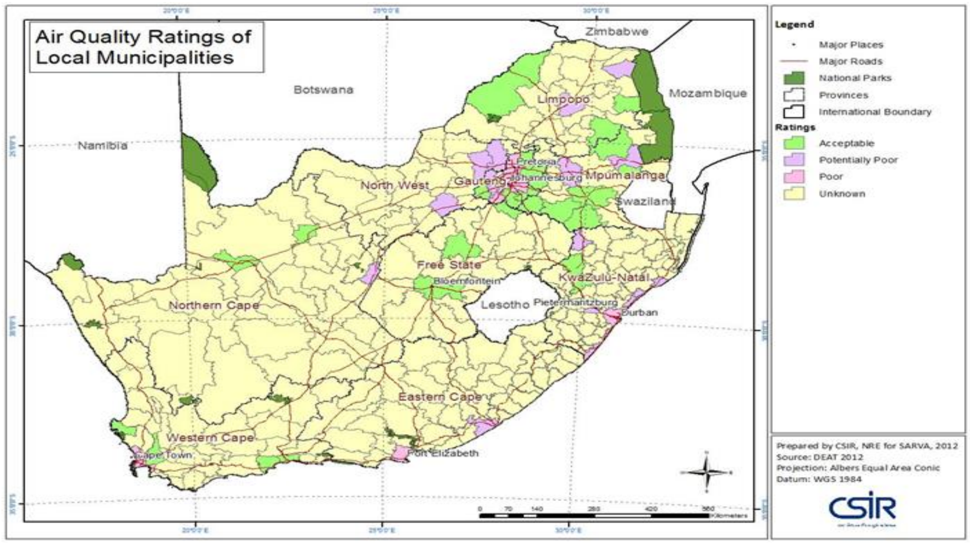


Figure 3: Air Quality Ratings of Municipalities in South Africa [20]

From Figure 3, we can deduce that the majority of the potentially poor and poor air quality areas are found in major cities as well as mining dominates settlements of South Africa. In such areas, deaths due to environmental causes are mostly attributable to air pollution exposure with respect to populated and congested cities as compared to rural and agricultural landscapes. Air-related health outcomes include lung cancer, stroke, chronic respiratory diseases e.g. asthma & chronic obstructive pulmonary disease (COPD).

Selected Sustainable Transport Implementation Measures for Local Municipalities in SA

A number of implementation measures, appropriate to local municipalities that must be aligned to the EASI framework for the promotion of sustainable transport in South Africa are presented in Table 2.

TABLE 2. Selected Sustainable Transport Measures for Local Municipalities in South Africa

Type of Measure	Examples of Measure
Taxes	Congestion charges, vehicle registration fees, road tolls (e-tolls).
Incentives	Reduction of parking costs and relaxation of access restrictions for low emission vehicles.
Regulations	Regulatory restrictions to encourage modal shifts (road to rail).
Planning	Development of non-motorised transport (NMT)/bus/public-transport lanes/zones.
Standards	Emissions standards for public transport fleets and municipal vehicle fleets.
Information Programmes	'Green/Eco Driving' Campaigns.
Green Procurement	Low emission vehicle procurement for Integrated public transport network (IPTN) systems.
Direct Infrastructure Investment	Investment in alternative fuel infrastructure e.g. solar charging points for electronic vehicles (EVs).
Institutional Measures	Creation of a Transport Authority and green transport system engineering and curricula.

4. Discussion

The results show that the modes of transport for daily commuting from home to work are private car (48.4%), minibus taxi (29.3%), walking (11.1%), bus (2.9%), train (2.4%), lift club (1.7%), and other (4.2%) [21]. Average travel times across all modes of transport have increased [24]. The average travel time increased by 44% from 32 to 46 minutes [6,7,17]. This could be the result of a combination of factors which include increased congestion and location of residential areas further away from places of work [1,2,6,7,21-25]. To incentivize a modal shift to public transport, tax rebates for car-pooling, shared mobility as well as car registration and retirement policies cam play significant roles in ensuring that there is transition from private automobile dominant travel systems to public transport dominated transport systems thereby contributing to reducing green house gases (GHG) contribution by the transport sector [20].

Urban fragmentation and sprawl in South Africa encourages long travelling and commuting with implications for carbon outputs. This set-up results in passenger travel demand being increasingly absorbed by low capacity transport modes. This is revealed in terms of the increased proportions of private cars and minibus taxis that serve the travel demand needs relative to proportionately reduced demand serviced for the use of buses and trains by commuters [5]. The use of private car travel has increased markedly between 2001 - 2016. Trend analysis highlight how buses tend to be used more for purposes of education-related trips rather than work and shopping/leisure trips. The main reason for not using higher capacity public transport modes is that the modes are not accessible [17-19]. These results are consistent with similar survey results undertaken as they show that the modes of transport for daily commuting from home to work are private car (48.4%), minibus taxi (29.3%), walking all the way (11.1%), bus (2.9%), train (2.4%), lift club (1.7%), and other (4.2%) [17-19, 24].

A review of household and transport expenditure in South Africa reveals interesting results. It is not unexpected for inhabitants of the Northern Cape to spend a higher portion of their income on transport as it is geographically the largest province in the country and the towns/stores and other places of interest are further apart [17,19]. Gauteng, KwaZulu-Natal and Western Cape are the provinces where there are more job opportunities for South Africans, given the high economic activity in these provinces [14,15,17,19]. Therefore, transport is more easily accessible as government transport infrastructure programmes are targeted to these provinces to facilitate those economic activities [6,7]. For example, the Bus Rapid Transit (BRT) system and Gautrain were implemented in Gauteng. Limpopo, Eastern Cape and Mpumalanga are among the poorest provinces in South Africa and they have proportions that are higher than the national percentage.

5. Conclusions

This paper has presented the link between transport, commuting, travel patterns and urbanisation prototypes encouraging sprawled and fragmented development that has lead to inefficient low carbon transition models of development in South Africa. At the same time, the paper also explored how compact and transit orientated urbanisation prototypes increased chances for efficient low carbon transition models of development in South Africa. Compact and green friendly cities entail new spatial thinking in which townships economies are developed for high density jobs concentration. In this way, employees need not travel long distances to access work opportunities as jobs and socio-economic opportunities would have been brought to the local neighbourhoods. With respect to embedding carbon friendly and smart urban transportation and commuting systems of advanced green transport circular economies, South Africa has immense opportunities to on-ramp initiatives for creating better carbon city footprints provided the right mix of land use policies, carbon tax incentives as well as spatial transformation approaches are employed. However, a failure to capture the full urban transportation and commuting value chain will result in missed opportunities for creating carbon neutral cities and settlements that have the innate ability to overcome the fragmented and sprawled automobile dominant paradigms of city growth and development in South Africa.

Acknowledgments: The author acknowledges the University of Venda, Directorate of Research and Innovation for funding support that enabled the publication of this manuscript.

References

1. DoT. 1996. White Paper on National Transport Policy. Pretoria: DoT. South Africa
2. DoT. 1998. Moving South Africa action agenda: urban passenger module. Pretoria: DoT. South Africa
3. Gauteng Department of Roads and Transport. 2002. The 2002 Gauteng household travel survey data. Johannesburg: Gauteng Department of Roads and Transport. Johannesburg, South Africa
4. Financial and Fiscal Commission. 2010. Technical Report: Submission for the 2011/2012 Division of Revenue Act. Technical Report RP: 72/2010. Midrand: FFC. South Africa
5. National planning commission NPC (National Planning Commission). 2011. National Development Plan: Vision for 2030. Pretoria: NPC. South Africa
6. Chakwizira, J. 2016. Access and Constraints to Commuting in Gauteng Province, South Africa. 2016: University of Venda. Thohoyandou, South Africa
7. Chakwizira, J. Bikam, P. Aina Adeboyejo, A.T. 2018. Different strokes for different folks: Access and Transport constraints for public transport commuters in Gauteng province, South Africa, Volume 8 (1), p. 58 – 81, ISSN 2217-544X (print), ISSN 2217-5652 (online), DOI: 10.7708/ijtte.2018.8(1).05
8. S. Riehl, K. E. Pustovoytov, H. Weippert, S. Klett, F. Hole. Drought stress variability in ancient Near Eastern agricultural systems evidenced by 13C in barley grain. Proceedings of the National Academy of Sciences, 2014; DOI: 10.1073/pnas.1409516111
9. Alley, R., and A. Agustsdottir. 2005. "The 8k Event: Cause and Consequences of a Major Holo-cene Abrupt Climate Change." Quaternary Science Reviews 24.10–11:1123–1149.; Roberts, N., W.J. Eastwood, C. Kuzucuoğlu, G. Fiorentino, and V. Caracuta. 2011. "Climatic, Vegetation and Cultural Change in the Eastern Mediterranean during the Mid-Holocene Environmental Transition." The Holocene 21.1:147–162.
10. The World Bank. 2015. Policies for sustainable accessibility and mobility in urban areas of Africa, Africa Transport Policy Programme (SSATP), TRANSITEC Consulting Engineers Ltd (M. Stucki), in collaboration with ODA, CODATU and Urbaplan, Washington DC, USA.
11. UNEP. 2011. Towards a Green Economy – Transport – Investing in Energy and Resource Efficiency. United Nations Environment Programme.
12. Stats SA. 2001. October Household Survey (OHS), 2000. Pretoria: Stats SA.
13. Stats SA. 2011. General household survey, 2010. Pretoria: Stats SA.
14. Stats SA. 2016. An analysis of household expenditure and income data using the LCS 2014/2015, Pretoria, South Africa
15. Stats SA. 2010. General household survey, 2009. Pretoria: Stats SA., South Africa
16. DoT. 2003. The National Household Travel Survey datasets. Pretoria: DoT., South Africa
17. DoT. 2013. The National Household Travel Survey datasets. Pretoria: DoT., South Africa
18. Gauteng Department of Roads and Transport (2014) Gauteng Household Travel Survey, Johannesburg, South Africa
19. Stats SA. 2014. NHTS Provincial Report Gauteng profile. Pretoria: Statistics South Africa.
20. Dawood, G. and Mokonyama, M. 2016. Towards a More Optimal Passenger Transport System for South Africa: Design of Public Transport Operating Subsidies, Chapter 7, Submission for the 2015/16 Division of Revenue, Treasury, Pretoria, South Africa
21. Serebrisky, T, Gomez-Lobo, A, Estupin, N and Munoz-Raskin, R. 2009. Affordability and subsidies in public urban transport: what do we mean, what can be done? Transport Reviews: A Transnational Transdisciplinary Journal. Vol. 29(6): 715–739.

22. Nunez, L, Forrester, C and De Wet, T. 2008. Sub-study on Credit and Savings. Johannesburg: University of Johannesburg, Centre for Social Development in Africa.
23. Nagdee, Q. 2004. The debt trap: The indebtedness of the poor in South Africa. Cape Town: University of the Western Cape, South Africa.
24. Stats SA. 2012. Income and expenditure of households 2010/2011. Statistical release P0100. Pretoria: Stats SA.
25. Chakwizira, J. Question of road traffic congestion and de-congestion in the Greater Johannesburg area: some perspectives. 2007. Conference Planners.

Evaluation of groundwater defluoridation potential of Mg/Ce/Mn-diatomaceous earth in a fixed bed using gravity flow mode

TL Budeli, WM. Gitari * and R Mudzielwana

Department of Ecology and Resource management, University of Venda, South Africa
*Email to corresponding author: mugera.gitari@univen.ac.za

Abstract
In this study, Mg/Ce/Mn-modified diatomaceous earth (DE) was synthesized for groundwater defluoridation. The chemical characterization of the raw and modified diatomaceous earth was carried out using XRF and FTIR techniques. Column experiments were conducted to evaluate the fluoride removal efficiency of the synthesized adsorbent on a gravity flow mode. The experiments were conducted to evaluate the effects of bed height and the effect of initial concentration. The column adsorption capacity decreased from 1.69 mg/g to 1.51 mg/g as the bed height increase from 1.3 cm to 3 cm respectively. Conversely, increasing initial concentration reduced the adsorption capacity from 3.31 mg/g at 5 mg/L to 1.69 mg/g at 10 mg/L. A maximum volume of 1318 mL was treated after 73 hours at initial concentration of 10 mg/L and bed height of 3 cm. The results obtained from the study proved and showed that synthesized Mg/Ce/Mn-modified DE has the potential for use in groundwater defluoridation. However, further studies are recommended to enhance the flow of water during treatment.

Keywords: Diatomaceous earth, fixed bed, groundwater and defluoridation

1. Introduction

Groundwater is the most affordable, accessible and reliable source of water in developing countries [1]. The contamination of groundwater by elements such as fluoride is of great concern because of health impacts on human beings [2]. The concentration of fluoride in drinking water above 1.5 mg/L as recommended by the World Health Organization (WHO) is associated with health impacts such as dental and skeletal fluorosis [3]. It was reported four areas that are affected by high prevalence of fluoride in groundwater in South Africa which are Limpopo, Northern Cape, North-West and Kwa-Zulu-Natal Provinces [4]. Moreover, Odiyo and Makungo [5] conducted a survey in Siloam Village, Limpopo province and found that out of the 87% households that use groundwater, 85% have members with mottled teeth and 50% of school learners between the ages of 11 and 14 also have mottled teeth. Researchers have developed several techniques for remedying fluoride contaminated drinking water including adsorption methods, membrane techniques, ion exchange and precipitation methods [6]. Amongst the available techniques, adsorption technique is the most affordable and effective of all defluoridation techniques due to factors such as cost efficiency, socio-cultural acceptance, environmental benignity and simplicity. Al-Ghouti *et al.,* [7] reported that recent studies have focused on different types of low-cost adsorbent materials such as kaolinite, bentonite, amorphous alumina, montmorillonite and diatomaceous earth and other natural materials. Diatomaceous earth (DE) is widely used especially in industries owing to its unique physical and chemical properties such as high porosity, inertness, natural abundance and cost effectiveness [8,9].

Work has been done on the use of modified DE to remove fluoride from groundwater. Izuagie *et al.,* [10] reported that binary metal Al/Fe oxide-modified DE is more effective sorbent than either Al or Fe oxide-modified DE for groundwater defluoridation. It was found that Al/Fe oxide-modified DE's maximum fluoride removal capacity was 93.1% [10], whereas the maximum fluoride removal capacity of raw DE was found to be 26.52% [11]. Furthermore, a trimetal oxide-modified DE of magnesium (Mg), Cerium (Ce) and Manganese (Mn) was also evaluated for fluoride removal using batch experiment and the sorption capacity of approximately 97.1% was recorded [12]. The main objective of the study was to synthesize and characterize the Mg/Ce/Mn modified-DE and evaluate its applicability on groundwater defluoridation using fixed bed column on a gravity flow mode. Therefore, the study was designed to evaluate the applicability Mg/Ce/Mn-modified DE in a rural household setup.

2. Materials and methods

Materials

Diatomaceous earth (DE) was used in the study obtained from Eco-Earth Traders, South Africa. All chemicals and reagents were purchased from Rochelle chemicals at Johannesburg, South Africa and they are of analytical grade. These include magnesium tetraoxosulfate (VI) ($MgSO_4$), cerium (III) chloride heptahydrate ($CeCl_3.7H_2O$), manganese (II) chloride tetrahydrate ($MnCl_2.4H_2O$), sodium hydroxide (NaOH), sodium fluoride (NaF) and total ionic strength adjustment buffer (TISAB III). Field water used in this experiment was collected from Siloam community borehole in Siloam Village, Makhado Local Municipality, Vhembe District, South Africa. Fluoride stock solution was prepared by dissolving a known amount of 2.21 g NaF into 1000 mL volumetric flask.

Methods

Synthesis of Mg/Ce/Mn oxide-modified diatomaceous earth (DE)

Mg/Ce/Mn oxide was synthesized according to the method developed previously by Gitari *et al.,* [12]. Briefly, modification of DE with Mg/Ce/Mn oxides was carried out as follows: 50 ml of 0.25 M $MgSO_4$, 50 ml of 0.25 M $CeCl.7H_2O$ and 100 ml of 0.25 $MnCl_2.4H_2O$ solutions were prepared by dissolving 1.5 g, 4.7 g and 4.9 of salts, respectively in Milli-Q water. The three solutions were added together in 250 mL plastic bottle in a ratio of Mg/Ce/Mn: 5/5/10 mL. Thereafter, 3 g of prepared DE was weighed into the solution and shaken for 20 min at 100 rpm, for proper soaking. The pH of the solution was adjusted to 8.2 by adding 2 M NaOH and vigorously mixed. The bottle was corked, and suspension was then shaken in a reciprocating shaker at 150 rpm for 30 min. The content was exposed to air for 10 h for possible oxidation Mn^{2+} to Mn^{4+}. The mixture was washed with Milli-Q water and centrifuged to remove the supernatants. The solid was then dried in the oven at 110 °C for 8 h, and then cooled in a desiccator. Finally, the bottle was corked and stored to avoid moisture.

Characterization of raw and modified DE

Fourier Transform Infrared (FTIR) (Bruker Alpha Platinum-ATR) was used to determine the functional groups of the raw DE, modified DE and fluoride-loaded modified DE. X-ray fluorescence (XRF) (Bruker SI Titan/Tracer Handheld XRF) was used to determine the chemical composition of the raw DE and modified DE.

Column experiments

The base of a 500 mL water bottle with a diameter of 5.8 cm and a height 21 cm was cut. Its lid was perforated, and a perforated filter paper was placed on the lid as a base. The column was packed with 100 g of river sand, a filter paper was placed on top of the river sand then Mg/Ce/Mn-modified DE was packed in the column to a desired bed height. Filter paper was placed on top of the adsorbent material. Finally, 100 g of river sand was packed in the column. The column was held up by a retort stand. The continuous defluoridation experiment was performed under gravity flow mode as shown by figure 1 below. To evaluate the effect of adsorbate concentration, synthetic solutions containing 5 and 10 mg/L were prepared through appropriate dilutions from the stock solutions. Solutions were poured continuously to pass through column bed packed with 20 g of DE to make up a bed height 1.3 cm. To evaluate the effect of bed height, two columns were packed with 20 and 40 g of DE to make up a bed height of 1.3 and 3 cm, respectively were set in parallel. A feed water containing initial F^- concentration of 10 mg/L was poured continuously to pass through the bed. Effluent were collected at intervals of 2 hours throughout the experiment until the effluent concentration was almost equivalent to the initial concentration. Field water collected from Siloam community borehole containing 4.5 mg/L natural fluoride concentration was treated using a column packed with an adsorbent dosage of 40 g and a bed height of 3 cm.

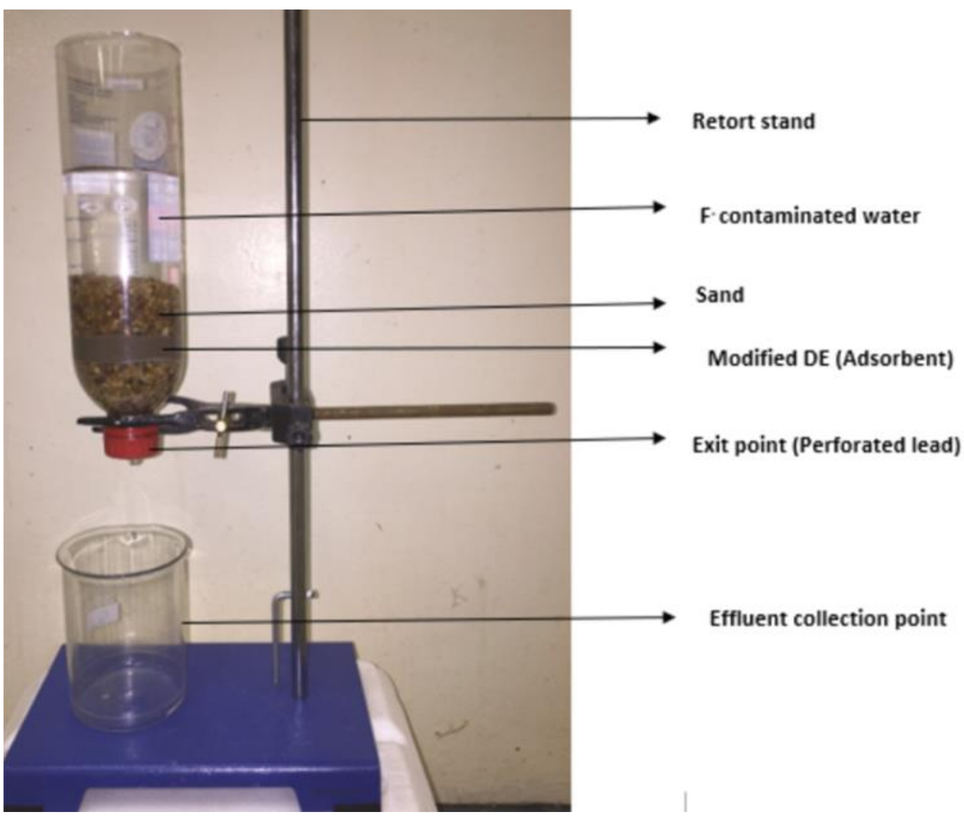


Figure 1. Experimental setup

Sample analysis

The fluoride concentration in the treated water sample was measured using ion selective electrode 9609 BNWP Orion (USA) attached to Thermo Scientific Orion VersaStar A215 ISE/pH meter. To calibrate the fluoride ISE electrode different standards 0.1, 1, 10 and 100 mg/L F^- from the stock solution. The standard solutions were mixed with TISAB III ratio of 10:1 and for 10 minutes. Same ratio was maintained for samples. TISAB III was added to decomplex fluoride ions (F^-) from Al^{3+}, Fe^{3+} and Si^{4+} complexes and to maintain pH at between 5.2 and 5.5, optimum for the F^--selective electrode. TDS, EC and pH of the treated water samples were measured using ion selective electrode 430-231 Jenway attached to Jenway Code 430 pH/Cond. meter.

Calculating the adsorption capacity at breakthrough point and exhaustion point

The adsorption capacity at breakthrough point and at exhaustion point were calculated using Equation 1 and 2 [13], respectively.

$$q_B = \int_{V_0}^{V_B} \frac{(C_0 - C_e)}{m} d_v \quad (1)$$

Where: q_B is the adsorption capacity at breakthrough point (mg/g); V_B is the through put volume (mL) at breakthrough point; C_0 is the initial F^- concentration (mg/L); C_e is the F^- concentration at equilibrium (mg/L); m is the mass of the adsorbent (g) and d_v is the volume of solution (L)

$$q_E = \int_{V_0}^{V_E} \frac{(C_0 - C_e)}{m} d_v \quad (2)$$

Where: q_E is the adsorption capacity at exhaustion point (mg/g); V_B is the effluent discharged volume at exhaustion point (mL); C_0 is the initial F^- concentration (mg/L); C_e is the F^- concentration at equilibrium (mg/L); m is the mass of the adsorbent (g) and d_v is the volume of solution (L)

3. Results and discussion

Characterization of raw and modified DE

Elemental composition by X-ray fluorescence

Table 1 shows the comparison of major oxides/element in the raw and Mg/Ce/Mn modified DE. The percent compositions of MnO, MgO and Ce in the modified species were observed to increase in the modified sample. The increase was most probably due to the use of the metal oxides in the modification of DE. A notable decrease was observed in the percent composition of SiO_2 from 82.42% of which could be attributed to the replacement of the oxides by the introduced metals during DE modification process.

TABLE 1. Comparison of the major elements (%) in the raw and Mg/Ce/Mn oxide-modified diatomaceous earth.

	SiO_2	Al_2O_3	MgO	Fe_2O_3	K_2O	CaO	MnO	Ce
Raw DE	82.42	0.84	1.05	0.66	0.39	6.63	0.01	<LOD
Mg/Ce/Mn	71.86	0.61	1.1	0.48	0.26	0.59	1.68	5.56

Fourier Transform Infra-Red (FTIR) spectroscopy

Figure 2 represents the absorption spectra of raw DE, modified DE and Fluoride reacted DE. There was an increase in intensity of absorbance of all the IR spectrum peaks at 800 cm^{-1} and 1052 cm^{-1}, these bands can be attributed to the stretching of alumino-silicate of the DE. The absorption band between 3200 and 3500 cm^{-1} is due to stretching vibrations of structural OH- groups of DE and water. The raw DE showed a small absorbance band at 1440 cm^{-1}, which is not observed in the modified DE and Fluoride reacted DE which could be attributed to the vibration of the Mg-O bond frequency. Fluoride reacted DE showed an increased intensity of absorbance of all the IR spectrum peaks indicating the formation of fluoride complexes.

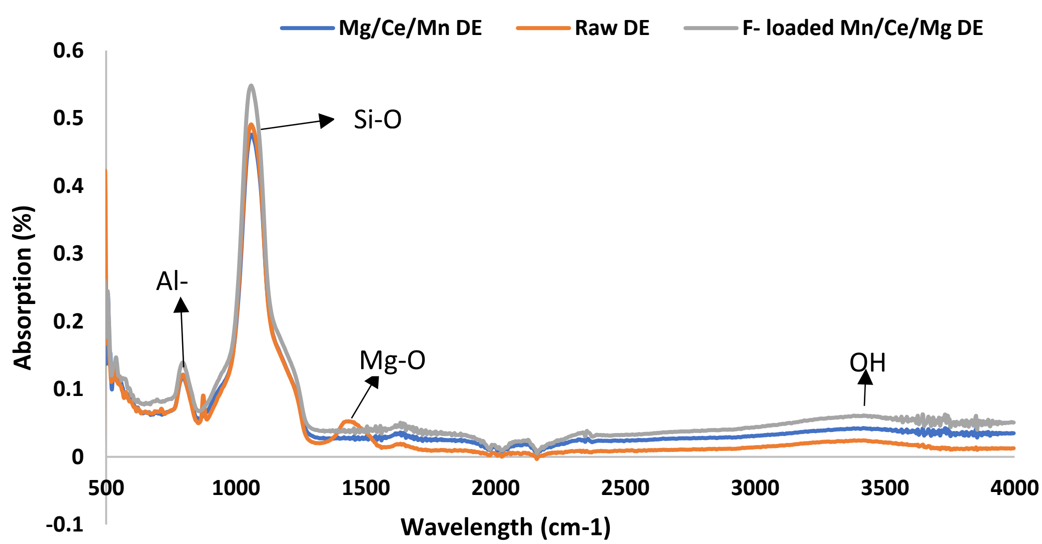


Figure 2. FTIR spectra of raw DE, Mg/Ce/Mn oxide-modified DE and F-loaded Mg/Ce/Mn oxide-modified DE

Column experiment

Effect of bed height

Figure 3 shows the fluoride breakthrough curve as a function of bed height. It is observed that as the bed height increases the volume of the sample treated increases. This could be attributed to an increase of adsorption active site as the bed height increases. At a low bed height, there are fewer active sites for F^- to adsorb, hence the adsorbent is saturated faster, resulting in low volume of treated sample at breakthrough point.

Conversely, at higher bed height there are more active sites for adsorption hence more volume of treated sample at breakthrough point. The column with a bed height of 1.3 cm reached the breakthrough point at a volume of 792.4 mL in 35 hours. The adsorption capacity at breakthrough point was 1.69 mg/g. The bed was saturated after treating 2394.5 mL of fluoride contaminated water after 79 hours. When the bed height was increased to 3 cm the column reached the breakthrough point at the volume of 1318 mL after 73 hours of treatment. The adsorption capacity at breakthrough point was 1.51 mg/g. The bed was saturated after treating 3218 mL of fluoride contaminated water after 136 hours.

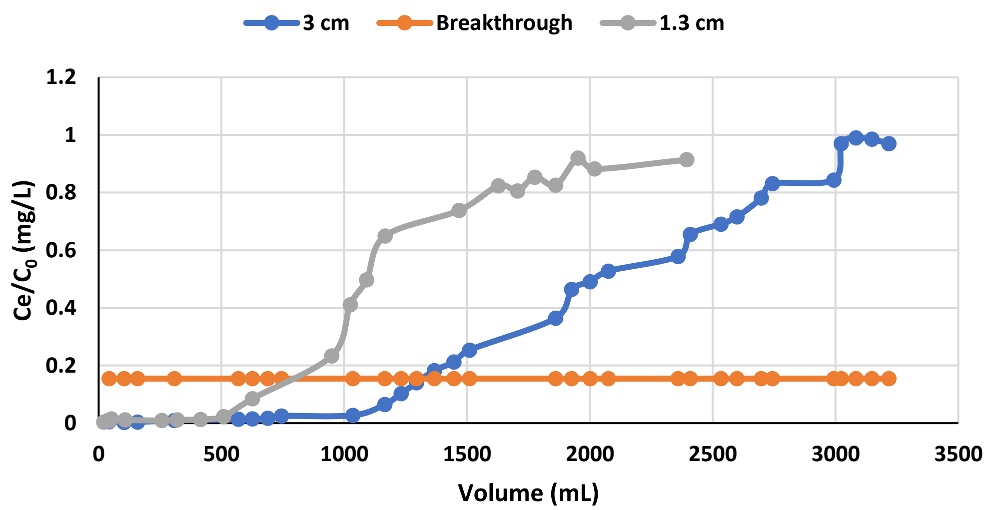


Figure 3. Breakthrough curves for adsorption of F^- onto Mg/Ce/Mn-modified DE with the same adsorbate concentration (10 mg/L) but different bed heights (1.3 and 3 cm).

Effect of adsorbate concentration

Figure 4 shows the fluoride breakthrough curve as a function of adsorbate concentration. It is observed that as the initial F^- concentration increases the volume of treated sample decreases at breakthrough point. At increased initial F^- concentrations, the higher driving force for mass transfer leads to a faster saturation of the adsorbent's sorption sites, hence a decrease in sample treated at exhaustion point [13]. Therefore, as the adsorbate concentration increases, the driving force for mass transfer and F^- loading rate increase which decreases the adsorption zone length. The column with adsorbate of concentration 5 mg/L had an adsorption capacity at breakthrough point of 3.31 mg/g. Adsorption capacity of the column with adsorbate concentration of 10 mg/L at breakthrough 1.69 mg/g. It is observed that the breakthrough point of 5 mg/L adsorbate was higher than the breakthrough points of the 10 mg/L adsorbate. This is because at lower adsorbate concentration there is low driving force for mass transfer which leads to slower saturation of the adsorbent's sorption sites, hence an increase in sample treated at breakthrough point [13].

Proceedings of ICSMNR2018
15-17 October 2018, Polokwane, S.A JN Edokpayi, WM Gitari, EM Stam, SE Mhlongo (eds) ISBN 978-0-620-82267-1

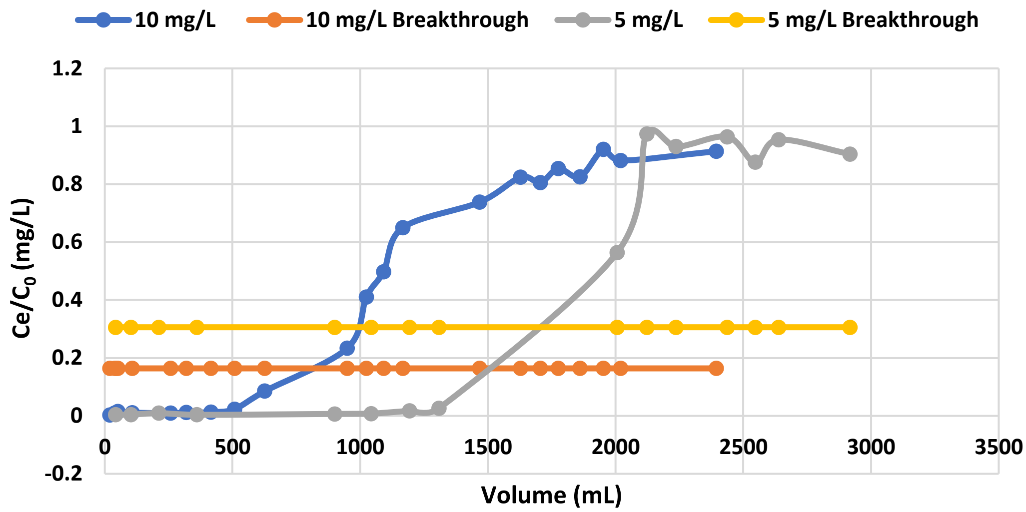


Figure 4. Breakthrough curves for adsorption of F^- onto Mg/Ce/Mn-modified DE with the same bed height (1.3 cm) but different adsorbate concentrations (5 and 10 mg/L).

Field water defluoridation

Table 2 shows the physicochemical properties of field water before treatment and at breakthrough point. Figure 5 shows the breakthrough curve for adsorption of F^- in groundwater onto Mg/Ce/Mn-modified DE with an adsorbate concentration of 4.29 mg/L and a bed height of 3 cm. The column treated 1198 mL of water at breakthrough point within 41 hours. The adsorption capacity at breakthrough point was 2.19 mg/g. To provide drinking water for a family of 5 daily living around Siloam village, 667.78 g of DE will be needed to treat 20 litres of fluoride contaminated water and this process will take 684.5 hours (28 and half days) which indicates that the adsorbent is not time efficient for its application in household setup. The pH and TDS of the Siloam borehole were within the WHO guidelines [14]. The EC was way beyond the guidelines set by WHO [14]. Although the EC has decreased at breakthrough, it was still above the WHO guidelines. This could be due to the presence of co-existing ions; chloride, phosphate and sulphate in groundwater. At breakthrough point, chloride and sulphate recorded higher than the initial values, and also recommended levels. The reason for this could be the leaching of the ions from the adsorbent during the experiment since the material was modified by Cl^- and SO_4^{2-} containing salts. Phosphate was totally removed at breakthrough point which showed that the material was effective because it removed other pollutants. The presence of nitrates was found at breakthrough point and its source could be the sand which supported the adsorbent since it was washed by nitric acid during its preparation prior the experiment.

TABLE 2. Physicochemical properties of field water before treatment and breakthrough point.

Parameters	Siloam borehole water (Initial parameters)	Parameters at breakthrough treatment	WHO guidelines [14]
pH	7.54	6.9	6-9
EC (μS)	333	177.8	0-150
TDS (mg/L)	200	106.9	0-500
F^-(mg/L)	4.29	1.5	1.5
Cl^-(mg/L)	36.76	450.74	0-100
NO_3^-(mg/L)	<LOD	5.58	0-50
PO_4^{3-} (mg/L)	3.84	<LOD	0-1
SO_4^{2-} (mg/L)	15.16	262.33	0-250

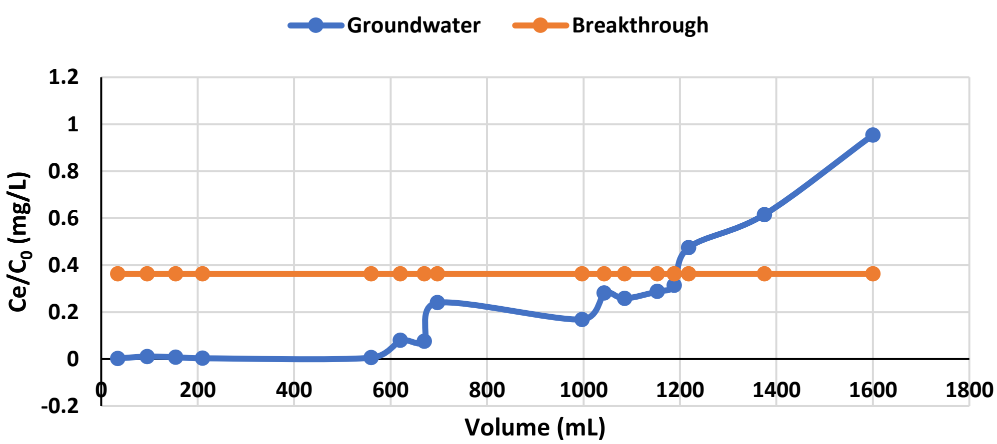


Figure 5. Breakthrough curve for adsorption of F^- in groundwater onto Mg/Ce/Mn-modified DE with an adsorbate concentration of 4.29 mg/L and a bed height of 3 cm. see my previous comments on your figures

Performance indicators

Table 3 shows the performance of the adsorbent. It is observed that column treating 5 mg/L F^- adsorbate concentration is the most effective since it has the lowest adsorption exhaustion rate and the highest bed volume processed before the breakthrough point was reached.

TABLE 3. The performance of the adsorbent

	Bed height (cm)		Adsorbate concentration (mg/L)	
	1.3	3	5	10
Bed volume	39.62	32.95	88.1	39.62
Adsorption exhaustion rate (g/L)	10.2	12.1	9.4	10.2

4. Conclusion

The aim of this study was to evaluate the groundwater defluoridation potential of Mg/Ce/Mn-diatomaceous earth in a fixed bed on gravity flow mode. The parameters varied were bed height and adsorbate concentration. The column sorption process was found to perform better at lower adsorbate concentration and higher bed height. At breakthrough point, high bed volumes and low adsorption exhaustion rate values were attained at lower adsorbate concentration and higher bed height implying a good bed performance. The column with lower adsorbate concentration of 5 mg/L treated 1.8 L within 27 hours and a column with higher bed height of 3 cm treated 1.3 L at breakthrough point within 73 hours. The bed height was further used to treat groundwater. In this case, the bed treated 1.2 L of water at breakthrough point within 41 hours. The results obtained from the study proved and showed that synthesized Mg/Ce/Mn-modified DE has the potential for use in groundwater defluoridation. However, further studies are recommended to enhance flow rate of the column during treatment in order to improve time efficiency.

Acknowledgments: The study was funded by SasolInzalo Foundation. Its support is highly appreciated.

Reference

1. Mudzielwana, R., Gitari, M. W. & Msagati, T. A., 2016. Characterisation of smectite-rich clay soil: Implication for groundwater defluoridation. South African Journal of Science, 112, pp. 1-8
2. Abiye, T., Bybee, G. and Leshomo, J., 2018. Fluoride concentrations in the arid Namaqualand and the Waterberg groundwater, South Africa: Understanding the controls of mobilization through hydrogeochemical and environmental isotopic approaches. Groundwater for Sustainable Development, 6, pp.112-120.
3. WHO, 2011. Guidelines for Drinking Water Quality. Volume 1. 4th ed. Geneva: WHO press.
4. Ncube, E. J. & Schutte, C., 2005. The occurrence of fluoride in South African groundwater: A water quality and health problem. Water SA, 31(1), pp. 35-40.
5. Odiyo, J. O. & Makungo, R., 2012. Fluoride concentrations in groundwater and impact on human health in Siloam Village, Limpopo Province, South Africa. Water SA, 38(5), pp. 731-736.
6. Meenakshi & Maheshwari, R., 2006. Fluoride in drinking water and its removal. Journal of Hazardous Materials, 137, pp. 456-463.
7. Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J. and Ahmad, M.N., 2003. The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. Journal of Environmental Management, 69(3), pp.229-238.
8. Antonides, L., 1998. Diatomite. US Geological Survey Mineral Commodity Summaries, pp. 56-57.
9. Aue, W. & Hastings, C., 1961. The distribution of support-bounded silicones on chromosorbs. Journal of Chromatography, 52(2), pp. 295-310.
10. Izuagie, A. A., Gitari, W. M. & Gumbo, J. R., 2016. Synthesis and performance evaluation of Al/Fe oxide coated diatomaceous earth in groundwater defluoridation: Towards fluorosis mitigation. Journal of Environmental Science and Health, Part A, 51(10), pp.810-824.
11. Izuagie, A. A., Gitari, W. M. & Gumbo, J. R., 2016. Defluoridation of groundwater using diatomaceous earth: optimization of adsorbtion conditions, kinetics and leached metal risk assessment. Desalination and Water Treatment, 57(36), pp.16745-16757 p. 1-13.
12. Gitari, W., Izuagie, A. & Gumbo, R., 2017. Synthesis, characterization and batch assessment of groundwater fluoride removal capacity of trimetal Mg/Ce/Mn oxide-modified diatomaceous earth. Arabian Journal of Chemistry, In press. http://dx.doi.org/10.1016/j.arabjc.2017.01.002
13. Setshedi, K.Z., Bhaumik, M., Onyango, M.S. and Maity, A., 2014. Breakthrough studies for Cr (VI) sorption from aqueous solution using exfoliated polypyrrole-organically modified montmorillonite clay nanocomposite. Journal of Industrial and Engineering Chemistry, 20(4), pp.2208-2216
14. World Health Organization, 2017. Guidelines for drinking-water quality: first addendum to the fourth edition.

Assessment of Spatial Distribution of Heavy Metals within the Klein Letaba Tailings Dam, Limpopo Province, South Africa

N Nemapate*[1], JS Ogola[1] and GE Ekosse[2]

[1]Department of Mining and Environmental Geology, University of Venda, South Africa.
[2]Research and Innovation, University of Venda, South Africa.
* Email to corresponding author: nemapaten@gmail

Abstract
Mining in the Giyani Greenstone Belt produced large quantities of rock waste dumps and tailings. Mine waste is regarded as a principal source of heavy metal dispersion and contamination. The extent of heavy metals spatial distribution has not been adequately established in the Klein Letaba tailings dam. The overall assessment of the distribution pattern of heavy metals at the Klein Letaba tailings dam showed erratic distribution that may be attributed to the nature of tailings at the initial stages of tailings disposal. The tailings dam has not matured enough to produce acid mine drainage, hence there was no distinct oxidation boundary between the reducing zone. The distribution of the metals literally varied from one drill hole to the other, although a general trend was noted with some metals decreasing in the value, whereas others increase in values with depth. Along a number of drill holes, Ag, Cd, Cu and Mn decrease in values with depth, whereas As, Co, Cr and Ni increase with depth. Erratic distribution of metals was noticeable amongst Co, Cr, Mn and Ni. The study involved sampling of tailings material, logging of the thickness of different layers of the dam and determination of heavy metals concentration in the material using an atomic absorption spectrometry instrument. Sampling of the tailings dam was done to the depth of 8 m and samples were collected at every 1 m interval using a hand-held auger drill. The samples were taken to the laboratory for heavy metal analysis. The presence of Pb, As, Cu, Co, Cd, Mn and Ni within the tailings was confirmed with relatively high values of As, Cr, Ni and Mn established, being 3943 ppm, 759 ppm, 731 ppm and 383 ppm respectively. The distribution of metals with depth within the dam was found to be erratic and this can be attributed to the erratic distribution of these metals within the ore.

Keywords: Heavy metals, Spatial distribution, Tailings dams

1. Introduction

Exploration of mineral resources is an extremely important venture for economic development of any country. Nevertheless, the legacy of past and current mining activities results in the production of mine wastes, which when not managed properly, can have devastating efforts on the environment and human health. Environmental management of mine sites has therefore become mandatory, especially with enactments of environmental laws and regulations. Environmental degradation due to mining activities have led to issues such as pollution and waste management, zero emissions, eco-taxes, life-cycle analysis, polluter pays. Today, mine closure does not only mitigate or deal with environmental issues such as acid mine drainage, but also looks at the social, economic and development issues. Many mining companies now see their relationships with the public as being important and as regulatory compliance Macdonald *et al.* [5], thus public acceptance of future mining activities is strongly determined by its vision of ecological programme at today's site. Mine closure should be planned in a way that both the company and community benefit. This is what De Sa [5] describes as sustainable community development with a focus on mine closure. In South Africa, there are over 5, 900 abandoned mines [9]. In Limpopo Province alone, there are about 729 abandoned mines Matshusa *et al.* [7] that contain heavy metals such as Pb, Zn, Cu, As, Co, Cd, Ni and Mn. It is imperative to undertake a study of the tailings dams so as to ascertain the level and the distribution of the heavy metals in the tailing dams. The mean annual precipitation of the area varies between 700 mm and 150 mm in the mountainous zone. The annual rainfall over the remainder of the sub-catchment ranges from 450 mm to 800mm. More than 85% of the annual rainfall occurs during Summer [3]. The mean annual temperature ranges from 12° C to 17°C in Winter and from 22°C to 30°C in Summer [3]. Klein Letaba tailings dam is located about 22 km in the northwestern part of Giyani town. The tailings dam is geographically situated at latitude 23°17'44.95''S and longitude 30°33'12.19''E (see Figure 1).

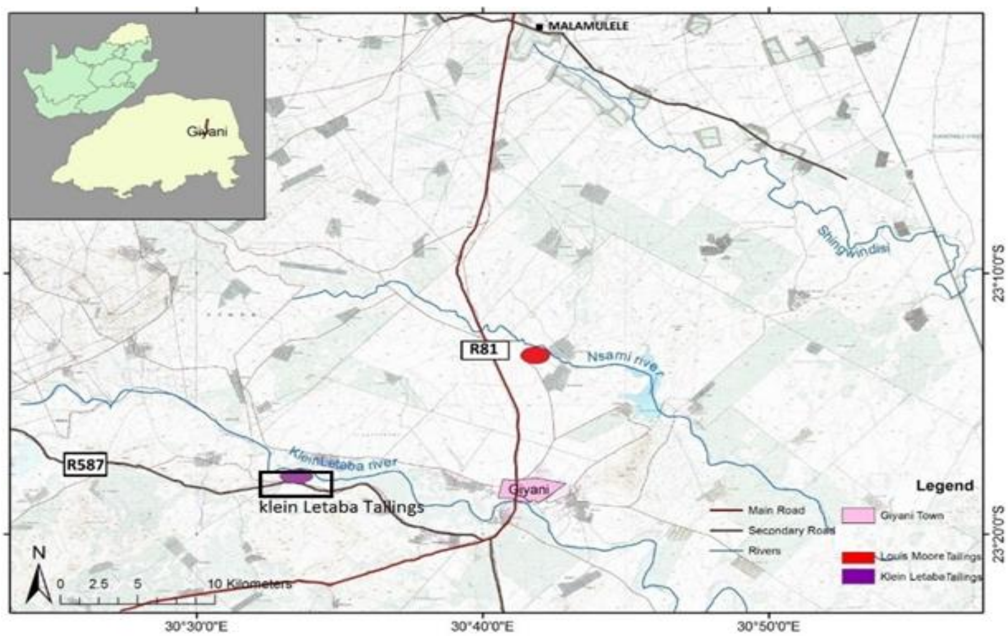


Figure 1. Location Map of Klein Letaba tailings dam

2. Materials and Methods

The study involved both fieldwork and laboratory work as well as data analysis and interpretation. Fieldwork included augering, sampling and profile logging of tailings with depth, whereas laboratory work comprised sample preparation and analysis.

Augering and Logging

A hand auger was used to drill through the tailings. Three profiles of equal spacing of 50 m apart were projected over the Klein Letaba tailings dam and the sampling interval along the profiles was 150 m. The profiles were numbered P1, P2, P3 and boreholes were numbered P1A1, P1A2, P1A3, P1A4, P2A1, P2A2, P2A3, P2A4, P3A1, P3A2, P3A3, P3A4 starting from the northern edge to the southern. Twelve boreholes were drilled through the tailings from the surface to a depth of 8 m. Changes in physical properties of the tailings such as colour, moisture content and hardness with depth were carefully recorded in a logbook. This information was used to correlate logs along the profiles.

Tailings Sampling

Tailings sampling was conducted simultaneously as augering and profile logging were taking place Nengovhela *et al.,* [8]. Each borehole was sampled at an interval of 1 m up to 8 meters from which 95 samples were collected, each weighing about 5 kg. The samples were put in a clean and properly marked polyethylene sample bags.

Sample Preparation

The collected samples were prepared at the Mining and Environmental departmental laboratory, University of Venda. Preparation included splitting, drying, milling and digestion of samples.

Sample Splitting

The samples were split in order to get a representative sample to be used for geochemical analysis. Using a riffle splitter, the sample was first homogenized, this was achieved by repeatedly pouring the sample through a riffle splitter and combining the halves between passes until a small portion of sample was left. The sample was then placed in a sample bag which was marked.

Sample Drying

The obtained portion of the sample was placed in a Bench Vacutec laboratory oven to dry for 6 hours so as to remove any moisture within it. The dried sample was then allowed to cool at room temperature before being milled.

Sample Milling

The oven dried samples were transferred into a milling pot and placed in a Retsch Model RS 200 milling machine wherein it was milled for 5 minutes at 700 rpm to reduce the particle size. Quartz was used to clean the milling pot after every sample was milled. The milled samples were then transferred into sample bags which were marked, ready for weighing and digestion.

Weighing and Digestion of samples

Samples were weighed using an analytical balance (Redwag Model AS220/C/2). The weighed 5 g of each sample was placed in a decomposition beaker for acid digestion upon adding 2-5 ml of deionized water to moisten the sample. Two grams of certified reference material from MINTEK were also weighed. Aqua-regia composed of 15 ml nitric acid and 45 ml hydrochloric acid was added to the sample in a decomposition beaker. The beaker was then placed on the hot plate for at least 90-120 minutes for decomposition. The samples were then removed from the hot plate and allowed to cool to room temperature. The samples were then transferred to a 100 ml volumetric flask and accurately made up to the mark with deionized water before shaking vigorously and allowed to settle for 2 hours ready for geochemical analysis.

Sample analysis

The samples were analysed at the Department of Mining and Environmental laboratory, University of Venda, using atomic absorption spectrometry (AAS Perkin Elmer AAnalyst 400). The analysis was conducted for Pb, Zn, Cu, As, Cd, Co, Ag, Ni, Cr and Mn. A total of 95 samples were analysed for heavy metals.

3. Results and Discussion

Correlation of drill hole logs along Profile 2 and distribution of Borehole P1A4 over the Klein Letaba Tailings dam are explained in the figures below.

Correlation of Tailings Profiles

The correlation of the drill holes was done in order to show the oxidation, transition and un-oxidized zones along profiles of the tailings dam. This was used to determine the extent of tailings oxidation and the potential for acid mine water generation within this dam.

Correlation along Profile P2

Correlation was done to understand the continuity of layers with depth throughout Profile 2 over the Klein Letaba tailing dam (Figure 2). It was observed that along each borehole the colour of the tailings changed from orange and grey to brown up to a depth of 3.2 m for P2A1, 2.9 m for P2A2, 2.1 m for P2A3 and 1 m for P2A4. Variations indicate that the tailings were not being oxidized uniformly within the dam. The oxidation zone, however, was up to a depth of 3.2 m to the east and 1.0 m to the west. The transitional zone was not identified. As was observed in the previous case, there was uneven oxidation of the tailings with depth, a phenomenon that is attributable to uneven topography of the tailings dam and the retention of water on the tailings dam surface.

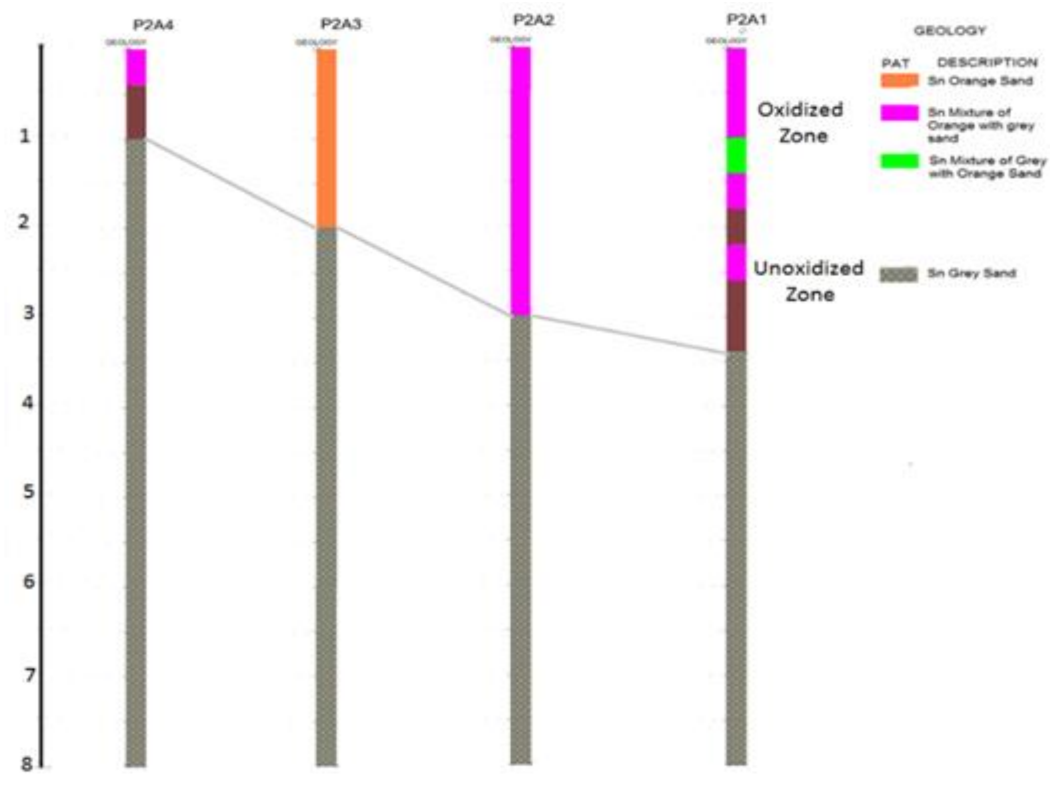


Figure 2. Correlation of drill hole logs along Profile 2 over the Klein Letaba Tailings dam showing the oxidized and unoxidized zones.

Statistical Analysis of Metals at Klein Letaba Tailings Dam

The statistical analysis of heavy metals within the Klein Letaba tailings dam was undertaken so as to determine the mean values, standard deviation and threshold of the metals within the tailings dam (Table. 1). A total of 95 samples were analysed. Range is the difference between the highest and lowest values within a set of numbers. Mean is the average of all samples and is sometimes called the arithmetic mean. Standard deviation is a measure that is used to quantify the amount of variation or dispersion of a set of data values. The threshold values of metals are defined as the mean multiplied by two times the standard deviation or: Bland et al., [1].

$$Threshold = x \times 2\sigma \tag{1}$$

Where: x is mean and σ Standard deviation

Metals with the highest range were As, Ni and Cr. These metals had the highest mean values of (mg/kg) 1462, 431 and 447 respectively as well as the highest standard deviation of 890, 172 and 129 respectively. For As the erratic distribution pattern may be attributed to the distribution of arsenopyrite within the ore body.

TABLE 1. Statistical Parameters for Metals within the tailings dam

Sample ID mg/kg	Pb	Zn	Cu	As	Cd	Cr	Co	Ag	Ni	Mn
Number of samples	95	95	95	95	95	95	95	95	95	95
Minimum	3.18	3.48	41	335	0.20	133	10	0.39	63	114
Maximum	127	113	138	3943	1.58	759	80	2.78	731	383
Range	124	109	97	3609	1.38	625	70	2.38	668	270
Mean	20	50	74	1462	0.57	447	46	0.65	431	205
Median	16	36	73	1261	0.40	457	48	0.60	422	186
Standard deviation %	17	26	20	890	0.23	129	15	0.31	172	55
Threshold	54	101	114	3242	1.03	706	75	1.27	774	315

Distribution of Heavy Metals within the Klein Letaba Tailings Dam

Borehole P1A4

Ag and Cu showed a general decrease with depth whereas Co, Cr and Ni indicated the opposite (Figure 3) Cd also registered a general decrease with depth except between 1 – 2 m. As showed a general increase with depth except at an interval of 5 – 6 m where there was an abrupt decrease in values. Mn showed a relatively uniform distribution from the first 1 m then erratic distribution between 1 to 4 m after which it had uniform distribution with depth. Pb on the other hand had uniform distribution from the top to 5 m with abrupt increase of values between 1 to 2 m and after the 5 m mark, it had a general increase with depth. Zn on the other hand had abrupt decrease in value from a depth of 1 m to 4 m then uniform distribution from 4 to 7 m then increase in value with depth.

The overall assessment of the distribution pattern of heavy metals at the Klein Letaba tailings dam showed erratic distribution that may be attributed to the nature of tailings at the initial stages of tailings disposal. The tailings dam has not matured enough to produce acid mine drainage, hence there was no distinct oxidation boundary between the reducing zone. The distribution of the metals literally varied from one drill hole to the other, although a general trend was noted with some metals decreasing in the value, whereas others increase in values with depth. For example, along a number of drill holes, Ag, Cd, Cu and

Mn decrease in values with depth, whereas As, Co, Cr and Ni increase with depth. Erratic distribution of metals was noticeable amongst Co, Cr, Mn and Ni.

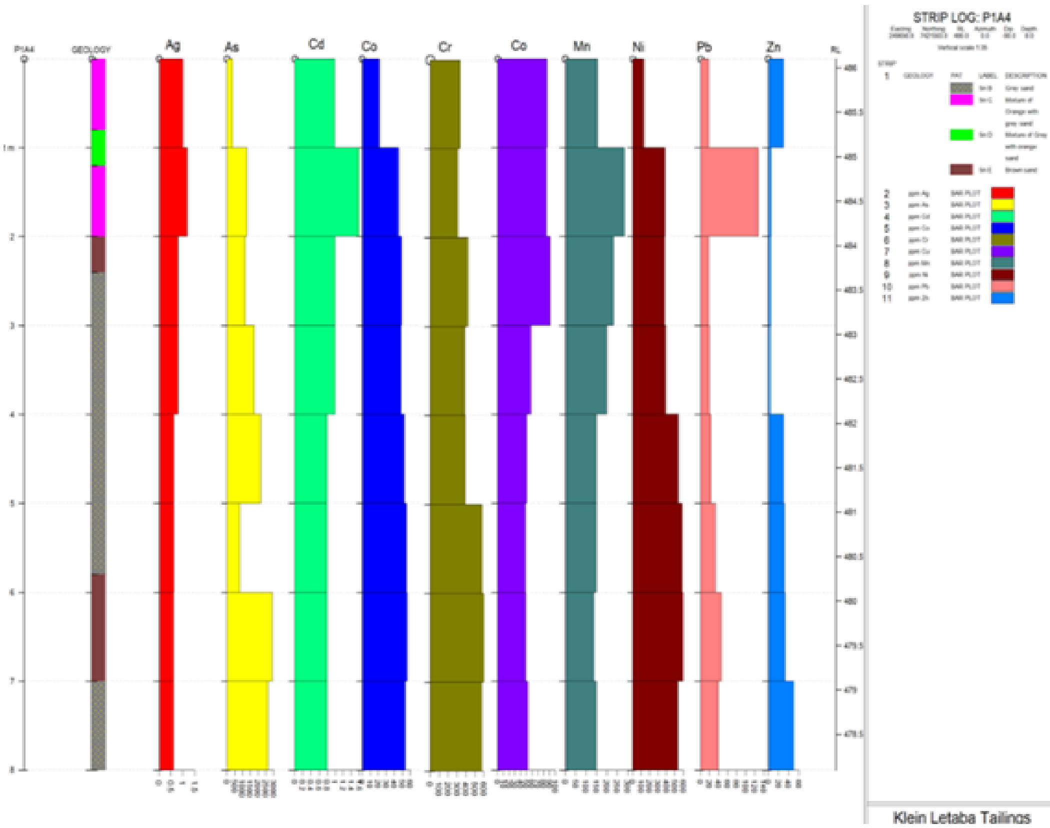


Figure 3. Distribution of metals in Borehole P1A4.

Comparison of Concentration Levels of Metals and Soil Quality Guidelines

The mean concentrations of the metals in the tailings were compared with the soil quality guidelines (Table 2). This was done in order to determine the potential threat that these tailings dams pose to the environment. The mean concentration of As, Cu, Ni, Cr and Mn were found to be higher than the recommended soil pollution monitoring standards. This means that Klein Letaba tailings are a threat to the nearby land, farms and rivers to which the tailings are eroded through either wind or water erosion.

TABLE 2. A comparison of the mean metal values and soil pollution monitoring standards [4].

Trace elements in (mg/kg)	As	Cd	Cr	Cu	Ag	Ni	Pb	Zn	Mn	Co
Soil Quality	5.8	7.5	6.5	16	10	91	20	240	740	300
Mean Klein Letaba concentration values	1462	0.57	447	74	0.65	431	20	50	205	46

4. Conclusion

Heavy metals distribution pattern within the Klein Letaba tailings dam was rather erratic as some increased or decreased with depth. Based on the soil quality standard, it was established that the Klein Letaba tailings had higher mean values of As (1462 mg/kg), Cr (447 mg/kg) and Ni (431 mg/kg). This means that the tailings have the potential to pollute the environment and impact negatively on human health through the food-chain and air pollution.

Acknowledgement: We are sincerely grateful to the University of Venda that financially supported this project.

References

1. Bland, J.M. and Altman, D.G. (1996). Statistics notes: measurement error. BMJ. 312 (7047): 1654. PMC 2351401. PMID 8664723. doi:10.1136/bmj.312.7047.1654. Pp. 20-23.
2. De Sa, P. (2005). Mineral Policy: A world Bank Perspective. In E. Bastida, T. Waide and W. Ferriandezo (eds.): International Comparative Mineral and Policy: Trends and Prospects, The Hague, Kluwer Publ. Pp 403-504.
3. DWAF (2003). Luvuvhu/Letaba water management area: Overview of water resources availibity and utilization. National water resource planning, Polokwane, South Africa, Report No. PWMA 02000/00.0203. Pp. 4.
4. Government Gazette (2012). National Environmental Health Norms and Standards for Premises and Acceptable Monitoring Standards for Environmental Health Practitioners.
5. Macdonald, C., Megure, G. and Westorn., H. (2006). Integrated Closure Planning Review. Report prepared for IEMM, Uk. Pp. 14.
6. Map of South Africa, by South Africa channel, http://www. South Africa.com/maps.
7. Matshusa, K., Ogola, J.S. and Maas, K. (2012). Dispersion of metals at Louis Moore gold tailings dam. Limpopo province, South Africa. International mine water association. Pp. 334.
8. Nengovhela, A.C., Yibas, B. and Ogola, J.S. (2006). Characterisation of Gold Tailings Dams of the Witwatersrand Basin with Reference to their Acid Mine Drainage Potential, Johannesburg, South Africa. ISSN 0378-4738=Water SA Vol.32 No.4 October. Pp. 60.
9. SAI (2016). Report of the Auditor General to Parliament on a Perfomance Audit of the rehabilitation of Abandoned Mines at the Department of Mineral and Energy. Pp. 1-3.

A spatial analysis of public places of amusement, and right to the city for the youths in Thohoyandou Town, South Africa

E Ingwani[1]* and K Mudau[2]

[1] Department of Urban and Regional Planning, University of Venda, South Africa
[2]Tswane Metropolitan Municplaity, South Africa
Email to corresponding author : ingwani@gmail.com

Abstract
Public places of amusement are designed to offer entertainment. Many small rural towns of South Africa such as Thohoyandou lack evenly distributed public places of amusement for the youths. This interferes with the right to the city of the youths. This study analyses the spatial distribution of public places of amusement for youths in Thohoyandou Town. The study employed qualitative and quantitative data collection and analysis techniques. Private and public places of amusement are sparsely located in the urban core; suburban; urban periphery; and town villages. Youths of Thohoyandou Town travel by bus or taxi to access public places of amusement. The Right to the City is not only determined by the spatial distribution of public places of amusement, but also other factors such as affordability.

Keywords: green spaces, public places, spatial analysis, youths

1. Introduction

Public places of amusement are special attraction centres usually located in the core of settlement structures. Facilities for public places of amusement are specifically designed to offer entertainment, fun, and enjoyment. The aim of this paper is to present an analysis of the spatial distribution of public places of amusement and right to the city for youths in Thohoyandou Town - a small rural town of Limpopo Province of South Africa. The objectives of this paper are: (1) to characterize public places of amusement for the youths in Thohoyandou Town, and (2) to map the spatial distribution of places of amusement for youths in Thohoyandou Town.

Many small rural towns of South Africa such as Thohoyandou lack evenly distributed public places of amusement for the youths thereby interfering with these youths' right to the city. As such, youths often travel from small rural towns to big cities to access public places of amusement where these resources are perceived by the youths as fairly and spatially distributed. Little research has been done to interrogate the spatial distribution of public spaces in small rural towns of previously disadvantaged spaces of South Africa such as Thohoyandou Town. Unequal spatial distribution of public places of amusement is a problem affecting many small towns in South Africa [1].

Thohoyandou Town is located in Thulamela Local Municipality of Vhembe District of Limpopo Province in northern South Africa. Thohoyandou Town is a significant administrative hub for Thulamela Local Municipality, and Vhembe District. Thohoyandou Town lacks public places of amusement such as cinemas, theatres, museums, dance halls, music studios and amusement parks. Lack of public spaces of amusement in Thohoyandou makes the town lack liveliness, and 'boring' for many local youths. However, Thohoyandou Town emerges as a nodal point that serves the needs of the rural population in this region.

2. Materials and methods

This explorative case study adopted both qualitative and quantitative approaches to data collection and analysis – the mixed methods [2,3]. Two hundred questionnaires were administered at ten different public places of amusement identified during a reconnaissance. The Delphi technique (serious brainstorming with experts) was applied to interview three municipal spatial planners at Thulamela Local Municipality. The spatial configuration of public places of amusement were reproduced through AutoCAD ArcGIS, and Word Paint software. The Right to the City theory by Henri Lefebvre [4] is the primary mode of analysis.

3. Results

The research findings were analysed following themes from the research objectives. The public places of amusement formed the unit of analysis.

Characterization of public places of amusement in Thohoyandou Town

Twenty public places of amusement were identified in Thohoyandou Town. These were simply categorised as public and private. Sixty percent of the public places of amusement were public; whereas 40% were private. Clearly, most of the public places of amusement in Thohoyandou Town are public compared to private spaces. Public places of amusement are defined as those provided by the government - Thulamela Local Municipality.

The spatial configuration of public places of amusement in Thohoyandou Town

All the public places of amusement categorised as private places (40%) are nucleated in the urban core of Thohoyandou Town. This can be because public places of amusement provided by private providers are business and profit oriented, and hence are nucleated in places that promote economies of agglomeration to maximize profit and returns. In some cases, places of amusement categorised as public places are also nucleated in the urban core. This is because public places are not profit driven but needs driven; hence are located in suburban radii where they would serve the needs of communities better. Agglomeration of economic activities enables the urban core to become a service centre [5]. Figure 1 shows the spatial location of public places of amusement in Thohoyandou Town.

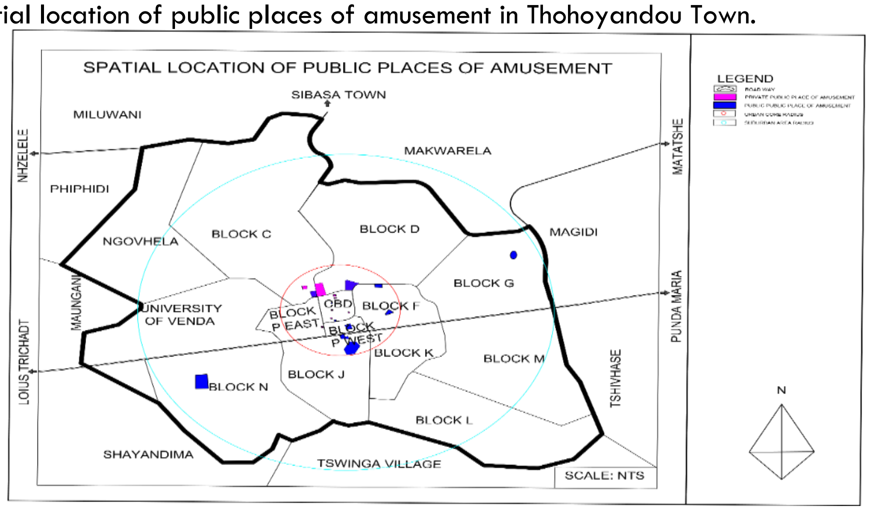


Figure 1. The spatial location of public places of amusement in Thohoyandou Town

4. Discussion

The spatial spread of spaces of public places of amusement in Thohoyandou town are driven by both private and public (municipal) practices. Figure 2 shows the radii of the neighbourhoods where the youths came from to access public places of amusement in Thohoyandou Town.

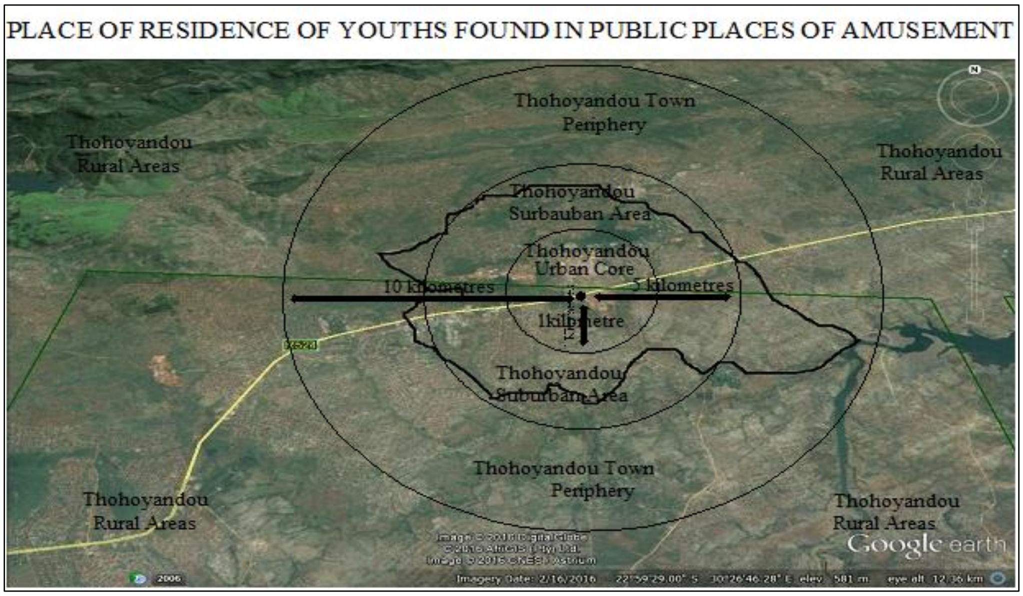


Figure 2. Residential areas of the youths in Thohoyandou Town and public places of amusement

The spatial configuration of public places of amusement in Thohoyandou Town engendered both negative and positive impacts on the youths' right to the city. Positive aspects are linked to mere provisioning of services to all inhabitants of the city and its peripheries regardless of differential social constructs. On the other hand, the negative impacts flow from provisioning practices relating to distortions from clustering the services in the urban core at the expense of the settlements in the outskirts of the town. From the Growth Pole theory, Thohoyandou Town has four rings namely; urban core ring, suburban ring, urban periphery ring and town village ring. The provisioning of public places of amusement is concentrated on the nodal ring or radius which is the central place that serves all the residents from all the different rings such as suburban, the urban periphery and the town villages. Private places of public places are largely located in the urban core. Most of the public places of amusement categorised as public places are also distributed in the urban core of Thohoyandou Town.

Since, most of public places of amusement are nucleated in the urban core of Thohoyandou Town, this promotes economies of agglomeration as the various public places amusement are agglomerated in the urban core which was established as a nodal point to serve the various city needs of residents. However, this distribution of public places of amusement favours the youths who reside in neighbourhoods found in the urban core since they can walk to the public places of amusement, whereas those who stay in the town village ring of Thohoyandou Town such as Ha-Matsa pay taxi or bus fares to access these public places of amusement in the urban core of Thohoyandou Town. This makes it difficult for these youths to access public places of amusement at night. Furthermore, the findings show that the indoor facilities are located in the CBD since they require small portions of land. The CBD has limited land hence cannot be distributed outdoor facilities such as Thohoyandou Stadium that require a huge portion of land. In terms of the Growth Pole theory, this means that the agglomeration of some facilities such as stadiums in the urban centres may be denied by lack of sufficient land.

However, public places of amusement located in the urban core of Thohoyandou Town are easily reachable by all youths from different places since they are in close proximity with bus and taxi termini. This is because there are two bus and two taxi termini in the urban core of Thohoyandou Town. Youths using different modes of transport such as taxis and buses can reach the public places of amusement found in the urban core of Thohoyandou Town. The public places of amusement located in the suburban radius are easily reachable only by the youths who reside in the neighbourhoods where they are found. Youths from other places need to pay extra taxi or bus fares to reach these places. This means that these public places of amusement are distributed to serve the needs of youths whose neighbourhoods are located close to the urban core. This is similar to what youths in Dhaka in Senegal are experiencing where Sikkatuli Park is a public open park which located in the Gulshan-Baridhara residential neighbourhood biased to serve the needs of the residents of this neighbourhood [6]. This implies that public parks located in residential neighbourhoods are geared towards serving the communities where they are found, although they often serve the needs of other people from other places.

Public places of amusement categorised as private places are distributed on land zoned for business practises because they are business oriented. The public places of amusement categorised as public places are distributed on residential land use, institutional land use, industrial land use and open space land use. This is due to that public places of amusement are allowed to be located on these land uses according to Thulamela Local Municipality LUMS of 2006. The findings also show that there is available vacant land and open space for future development in Thohoyandou Town. According to Thulamela Town Planner, such land amounts to 8.5 km^2. The development of public places of amusement in the vacant land occurs only if there is a requirement from the residents of Thohoyandou Town for a public place of amusement. This entails that the Right to the City is granted to the youths since they are allowed to shape what is in place in the Thohoyandou Town.

Thulamela Local Municipality is responsible for the provisioning of public places of amusement; the budget allocation of public places of amusement; the maintenance of public places of amusement, and also the formulation of policies that guide the provisioning of public places of amusement in Thohoyandou Town. With regards to provision, the Thulamela Local Municipality only provides public places of amusement which are categorised as public places such as Thohoyandou Stadium and Riverside Park. Thulamela Local Municipality provides the public places of amusement needed by the community since it is regulated by Batho-Pele principles, and Thulamela Sports and Recreation Policy of 2008. Thulamela Local Municipality is currently facilitating the development of a cricket stadium and Block-G Park; of which these were identified as needs of the youths Thohoyandou Town. According to the theory of Social Production, this means that the provision of public places of amusement in Thohoyandou Towns by Thulamela Local Municipality is based on the lived spaces which assume giving power to residents to shape what exists in space [7].

Most youths in Thohoyandou Town indicated that they preferred visiting night clubs as spaces where they can get amusement of which these are private public places. These private places are perceived by the youths as the best facilities since they offer the youths opportunities to enjoy partying, dancing and listening to loud music. Observations revealed a huge influx of youths in night clubs. The only private public places of amusement which the youths do not prefer are casinos because the youths were not interested in gambling. Most of the public places of amusement categorised as public places such as sports field and the tennis court were less preferred by the youths in Thohoyandou due to lack of distinct program facilitation in these places. However, there are some public places of amusement categorised as public places which the youths preferred. These places experienced a huge influx of youths particularly during events or programmes. For example, huge numbers of youths were observed in Thohoyandou Indoors Centre during a Venda Rap Music contest event. This means that programmes and events help promote complete and full usage of these places which the Right to the City demands. This means that these public places of amusement are of significance to the youths only when they are programmes in place. Therefore, public places of amusement without programmes may be regarded as not of existence since during days when they are no events a handful of youths are observed in these places.

In this study, the state of infrastructure of all public places of amusement categorised as private places such as Khoroni Casino Hotel and Jerusalem Night Club was perceived as good by youths. This is because private service providers, provide public places of amusement that have good state of infrastructure that attracts many people so that they may be able to maximise profit returns. As for those categorised as public places, a few of these public places of amusement in Thohoyandou Town were perceived as bad, for example, the Thohoyandou Stadium and Thohoyandou Tennis court. However, huge influx of youths was observed in these places during events such as soccer matches in Thohoyandou Stadium. This means that for the youths it is not about the state of maintenance which matters the most, but what matters is being in these places of amusement. This means that the right to the city is determined not by the conditions of the infrastructure, but by the needs of individuals being met [8]. For example, in Zimbabwe hockey stadiums such as Magamba and Khumalo have bad infrastructure but were being utilised for hockey national games in the country [9]. Clearly, when choices are limited, people often get satisfied with what is currently provided.

5. Conclusion

In conclusion, a total of twenty public places of amusement were identified in Thohoyandou Town. Most of these were categorised as public compared to private places. Most public places of amusement in Thohoyandou Town are in the urban core. Youths who reside in the suburban, urban periphery and town village radii travel by bus or taxi to access public places of amusement. However, the distribution of public places of amusement in Thohoyandou Town has less influence on limiting the Right to the City since youths from different radii frequent these places. It can therefore be concluded that the Right to the City of youths to places of public amusement is not determined by spatial configuration, but by other factors such as individual needs, and access fees.

Acknowledgement: This paper is based on Kingsley Mudau's unpublished BURP Honors thesis at the University of Venda. Kingsley Mudau conducted fieldwork in Thohoyandou Town between August 2015 and May 2016 [10].

References

1. Turok, I. Urbanisation and development in South Africa: Economic imperatives, spatial distortions and strategic responses. International Institute for Environment and Development: London, 2012; pp. 19-20, ISBN:978-1-84369-890-6.
2. Creswell, J. W. Research Design: Qualitative, Quantitative and Mixed Methods Approaches, 4th ed., SAGE: London, 2014; pp. 215, ISBN 978-14522-2610-1.
3. Neuman, W. L. 2013. Social research methods: Qualitative and quantitative approaches, 7rd ed.; Boston: Allyn and Bacon: London, 2013; ISBN:9780205615964.
4. Lefebvre, H. Everyday life in the modern world, 1st ed., Penguin Press: USA, 1971; pp. vii-x.
5. Nhede, N.T. The Zimbabwe growth point phenomenon: Impact and implications on public service delivery. AP 2013, 21(4), 117-129, URI: http://hdl.handle.net/2263/41546
6. Tabassum, S.; Sharmin, F. Accessibility analysis of parks at urban neighbourhood: the case of Dhaka. AJASE 2013, 2(2), 48-61, ISSN2305-915X.
7. Purcell, M. Excavating Lefebvre: The right to the city and its urban politics of the inhabitant. GJ, 2002, 58(2-3), 99-108, DOI:https://doi.org/10.1023/B:GEJO.0000010829.62237.8f
8. Huchzermeyer M. Cities with slums- From Informal settlement eradication to a Right to the City in Africa. UCT Press: University of Cape, South Africa, 2011; EAN 978191989539.
9. Madzivanzira, A. Stadiums call for attention. The Patriotic: Zimbabwe, March 16 2016.
10. Mudau, K. A spatila analysis of public places of amusement for the youths in Thohoyandou Town, South Africa, Honors Thesis, University of Venda, South Africa, 2016.

Seasonal variations in the physicochemical and microbial components of municipal wastewater discharge in Shikwambana River and its environmental impacts

ML. Nsovo*; BW Ayinde and W.M Gitari

Department of Ecology and Resource Management, University of Venda, South Africa.
*Email to corresponding author : nsovolouisa@gmail.com

Abstract

Indiscriminate release of sewage and poor wastewater management changes physicochemical and microbial characteristics of water and causes a hazard to environmental quality, including human health and aquatic ecosystem. The present work was undertaken to assess the seasonal variation effects of releasing incompletely treated sewage in the Shikwambana River, Limpopo province, South Africa from March to December 2017. The experiment was conducted based on water samples obtained from four different points namely: upstream (A); middle-stream (B); downstream (C) and the point where the river is suspected to be clean (D). The physicochemical parameters such as temperature, turbidity, pH, electrical conductivity (EC), nitrate, sulfate, phosphate, Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and heavy metal contents as well as bacteriological contents of the water were analyzed in order to assess the quality of the river. The experimental results showed different pH values ranging from 6.60-13.48. Higher turbidity contents of 50.17 NTU were at point C in summer as compared to other points. EC values range between (3.5-1395.5 µS/cm). Turbidity and EC values exceeded the WHO limits. Nitrate, phosphate and sulfate concentrations were below the WHO limits. Generally, the data shows significant distributions of physicochemical components in point C, especially in summer throughout the sampling period. Heavy metals such as iron (Fe), arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg) and anion fluoride were within the recommended DWAF limits. Microbial load contents of the river showed the presence of *E. coli* with higher coliform counts in most cases than *Aeromonas sp.*, *Shigella sp.*, and *Staphylococcus sp.*, which exceeded the WHO standard (<10cfu/ml). To avoid health risk and further deterioration of the environment, there should be rehabilitation and upgrading of the sewage system in Shikwambana.

Keywords: Water quality; sewage; physicochemical and microbial components, Shikwambana River.

1. Introduction

Environmental pollution is a wide-reaching problem, and it is likely to influence the health of human and aquatic populations [1]. 40% of the world's population lack basic sanitation facilities and billions of people are still using unsafe drinking water sources [2]. Protecting the quality of a nation's water is critical to sustain human health as well as the entire ecosystem. Water pollution is characterized by waste from society, treatment plants, industrial and commercial activities, agricultural or surface runoff, geological materials, and other pollutants [3-4]. Many of these Surface waters, often serve as waste disposal systems for untreated domestic sewage, mining and manufacturing industries as well as Agricultural effluents, especially in developing and sub-Saharan African countries [5-7]. This influences the breeding of pathogenic micro-organisms and accumulation of toxic chemical pollutants, which affects the quality of the environment and human population. According to World Health Organization reports, [8] around 3–6 million people die each year due to water related diseases and disasters from unsafe water treatment and poor sanitation. Urbanization and industrialization have resulted in many environmental issues in developing countries, including South Africa. The South African Water Services Act, 1997 (Act 108 of 1997) was prescribed for municipalities to manage the water and sanitation infrastructure under their control according to national standards and norms. However, this is contrary due to the dilapidating state of water and sanitation infrastructure in the rural communities leading to outbreaks of diseases; thereby, impeding local economic development [9]. The Shikwambana river in Mopani district, Limpopo province, South Africa is a major source of water that is used for domestic and other activities. The river is gradually losing its fresh water status, due to release of untreated or partially treated sewage water. Hence, becoming unsuitable for domestic activities. Furthermore, this waste water is often characterized by many inorganic chemical species, nutrients like nitrogen, phosphorus, as well as organics and pharmaceutical constituents posing a great risk of eutrophication-related and health risk problems to human and aquatic organisms [10; 4]. In Shikwambana, the two major sewage treatment plants near the river have been abandoned. Waste water coming from the nearby township is channeled into the oxidation ponds and from there into the river without being properly treated by the treatment plants. The only method used in treating this wastewater is chlorination, which apparently is not an effective and sufficient treatment method for removing toxic chemical constituents and eliminating all pathogenic microorganisms in the rivers. The potential impacts and risk of untreated domestic water discharge into the river system to both human health and aquatic communities in and around Shikwambana town has not been reported. Therefore, this present study is aimed to ascertain and identify the different level of toxic pollutants discharged into the river that receive untreated wastewater and to assess the potential adverse effects corresponding to various discharges for optimum water quality monitoring and management.

2. Materials and methods

Study area and sample collection

Water samples were collected once a month between January to December 2017 covering the major seasons of the year in South Africa. The river is found between Shikwambana village and Lenyenye with geographical coordinates of 23° 57'43.0956''S 30° 16'19.4952''E. The water samples were obtained from four different points: the upstream (A), middle stream (B), downstream (C), and the last point where the water is suspected to have naturally cleaned itself (D). Precautionary measures were taken to remove any air bubble present. All samples collected were via standardized sample bottles in duplicates, carried in a cooler bag which was filled with ice cubes from sample area to the laboratory and stored in the refrigerator at 4 °C till further analysis.

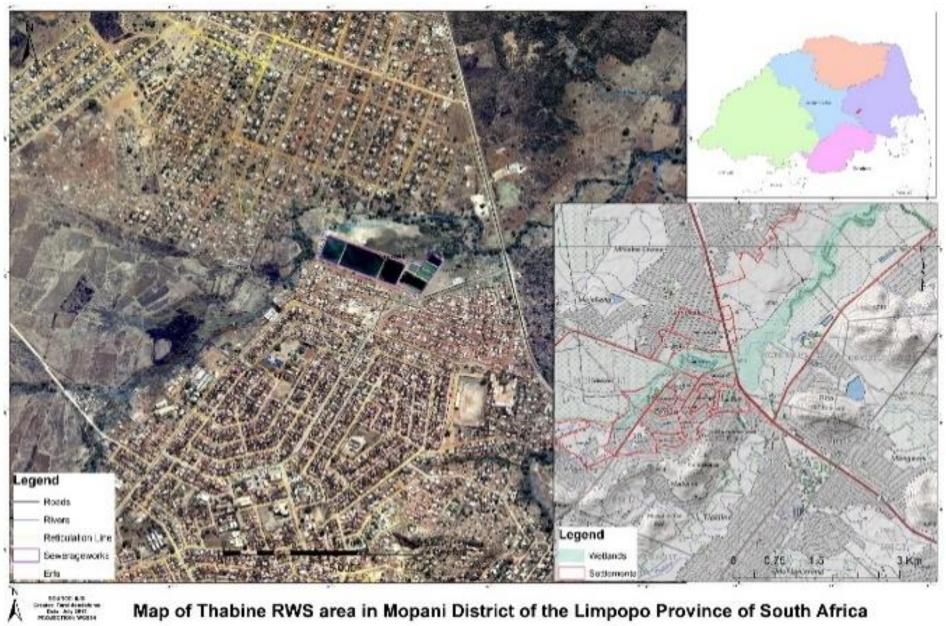


Figure 1: Location of study area (Shikwambana Village, Mopani district, Limpopo, South Africa)

Physico-chemical and microbial sampling analysis methods

The physical parameters such as pH, Electrical conductivity (EC), Turbidity and temperature were measured using the Thermo Scientific Orion Versa star ISE/pH/ EC meter, Orbelo Hellige TB 200 Turbidimeter. The nutrient (nitrates and phosphates) and chemical parameters (TOC, COD, sulphate and fluoride) were measured using Spectroquant Spectrophotometers (Pharo 100 with a Thermo-reactor, TR 620) through the photometric method. The procedures for each of the parameters were carefully followed according to the standard methods stated in their respective reaction cell kits (Merck). Each chemical parameter cell kit reagents used in the respective determination and quantifications contained different standard compositions as prepared by the manufacturer (Merck). Furthermore, heavy metals were measured using ICP-MS (Thermo ICap 6200 ICP-AES). The microbial loads determination and quantifications in the sample waters were subjected to microbial screening using the total coliform counts method; therefore, incubated at 37°C and grown in their respective agars media (Eosin Methylene Blue Agar, MacConkey Agar, Aeromomas agar, and Mannitol salt agar for E-coli, Salmonella, Staphylococcus, Shigella and Aeromonas hydrophilia respectively). These media were prepared according to the standard instructions provided therein by the manufacturer.

3. Results and discussion

Physical parameters

Figures 2 (a-d) shows the physical parameters' measurements of water samples from different sampling points across all the seasons of the year. From the results (Fig 2(a)), there was a general increase in temperature for all the seasons, which ranged from 20.05 °C to

26.8 ℃. The highest temperature was recorded in winter at 26. 80 ℃ at downstream where sewage effluents meet the river water, followed by the upstream with 26.6 ℃. Lowest temperatures were observed in autumn, between 20.05 ℃ and 20.95 ℃ in all study sites. Although, temperature of the water is dependent on the source depth and time of the season. The temperature values obtained in all the sampling points and throughout the season were within the recommended limit of 20°C - 30°C in water. Fig. 2 (b) depicts the water pH across the period of study, there were fluctuations in the pH which ranges from 6.6 to 13.48. Point C had the highest value in summer than all the seasons. The lowest value was observed in spring at point C than all the other seasonal periods of the year. Generally, pH is influenced by chemicals coming from waste water, agricultural runoff or industrial effluents, CO_2 through respiration, photosynthesis as well as geological processes [11]. The pH in autumn, winter and spring were all within the acceptable WHO limits but in summer at point C, the pH exceeds the limits to 13.48 which is highly alkaline.

As shown in Fugure 2 (c), electrical conductivity for all the seasons were fluctuating and ranges from 3.5 to 1395.5 (µS/cm). The conductivity variations may generally be due to the geology of the river bed, storm water runoff and the continuous sewage effluent flowing into the stream. The highest EC value was obtained at point C with 1395.5 (µS/cm) in all the seasons, and this exceeded the WHO permissible value (400 µS/cm). This is likely to be associated with high salt contents. Furthermore, Fig. 2 (d) illustrates the turbidity across all the water samples, which may be due to the presence of suspended matter such as clay, silt, organic and inorganic matter, plankton, and other microscopic organisms [12-14]. Higher turbidity values were observed mostly in the wet season (summer) than the rest of the seasons with the highest value of 50.17 (NTU). This is expected due to high rainfall during this period, which accelerate runoff and increase streamflow. Most of the values exceeded the allowable WHO limit (3 NTU).

Chemical parameters

Figure 3 (a-f) depict the results obtained from the measurements of the chemical parameters of water samples across all the seasons. From the obtained data in Fig 3 (a), nitrate levels gradually increase in winter and spring with the highest peaks observed in both seasons 15.025mg/L and 25.25 mg/L respectively especially in point C. Nitrate is among the most common nutrient contaminants of water sources worldwide, and these could be as a result of leaching of nitrates from farming activities around the area as well as the incomplete treated waste water from the sewage. The nitrate concentrations across all sampling points were within the WHO limits of 50 mg/L. Phosphates, as shown in fig. 2 (b), indicate that there was a general increase in all the seasons ranging from 0.3 - 4.55 mg/L. The main sources of phosphates in this river are drainage from farming activities (fertilizers, runoff from manure, etc.) and sewage effluent. In addition, Fig 2 (c), depicts sulphate values ranging from (3-24.25 mg/L) in all the seasons with a sharp increase at point C in spring. This might be due to end of dry seasons and accumulation of nutrients due to shortages or no rainfall. The sulphate concentrations observed were within the recommended DWAF [15] limits of 0 to 200 mg/L for human consumption.

The values recorded for fluoride ranges between 0.0128-0.0525 mg/L fig.2 (d) for all seasons with the highest value in summer and the lowest in winter. Fluoride is a naturally-occurring chemical species essential for normal bone growth, but beyond certain concentrations can be detrimental. All fluoride values are within the acceptable World Health Organization (WHO) limits (1.5 mg/L). Fig.2 (e), shows Total organic carbon (TOC) with highest values in summer, followed by winter and spring, especially in point C. But point D had the highest value of 51.5 mg/L in spring, which could cause a reduction in available oxygen in water thereby affecting aquatic organisms. Moreover, the amount of Chemical Oxygen Demand (COD) as illustrated in fig. 2 (f) ranges between 10.75 to 71.5 mg/L in all the seasons, with highest peaks at point C. This might be caused by anthropogenic materials leading to higher nutrient levels in water, which ultimately decreases the dissolved oxygen level in water needed by aquatic organisms to survive.

Heavy metals

The released of heavy metal without proper treatment possess a significant threat to public health because of its persistence, bio-magnifications and accumulation in the food chain [16-17]. Metals with the highest concentration across all the points are Sodium (Na) (101.10 mg/L), Calcium (Ca) (56.95 mg/l), magnesium (Mg) (28.53 mg/L) and phosphorus (P) (7.40 mg/L). Heavy metals are influenced by natural sources, anthropogenic activities, the burning of fossil fuels, mining and smelting of metalliferous ores, municipal and industrial wastes, pesticides, and fertilizers [18-20]. Although all these metal cations are present, some like iron (Fe), arsenic (As), lead (Pb) fall within the recommended DWAF [15] limits for human use because of their presence in trace concentrations.

Micro-organisms

Surface waters are usually contaminated with fecal coliform bacteria. High levels of fecal coliform in the water can pose a serious health threat and affect the economy as well as the environmental quality of a community [21]. In all the microbial results, *E-coli* was calculated with the highest colony growths (cfu /ml) as compared to other microbial species. The viable bacterial cell values range from 7×10^3 - 9.99×10^5, 2×10^3 - 9.99×10^5, 3×10^3-9.99×10^5, and 1×10^3-3.8×10^4 cfu/ml for *E-coli, Shigella, Staphylococcus* and *Aeromonas species* respectively in all the sampling points. It was generally observed that even after chlorine treatment, the bacterial colonies were greater than the recommended WHO guideline of <10 cfu/ml.

4. Conclusion

The present study shows that there were great seasonal variations in the parameters under study. The data obtained shows that most of the parameters remained within the acceptable WHO guidelines. Generally, the data also shows that the water from point (D) where the river is suspected to have naturally cleaned itself has a lot of organic materials than the upstream and middle stream of the river, especially TOC and COD. Microbial load in the river are higher than the recommended guidelines as well, therefore, pose health problems and affect the water quality. There is a need for proper discharge and management of wastewater in the environment. To have a clean environment, the challenges faced in water bodies must be properly addressed, in order to restore aquatic environments for a sustainable economic growth.

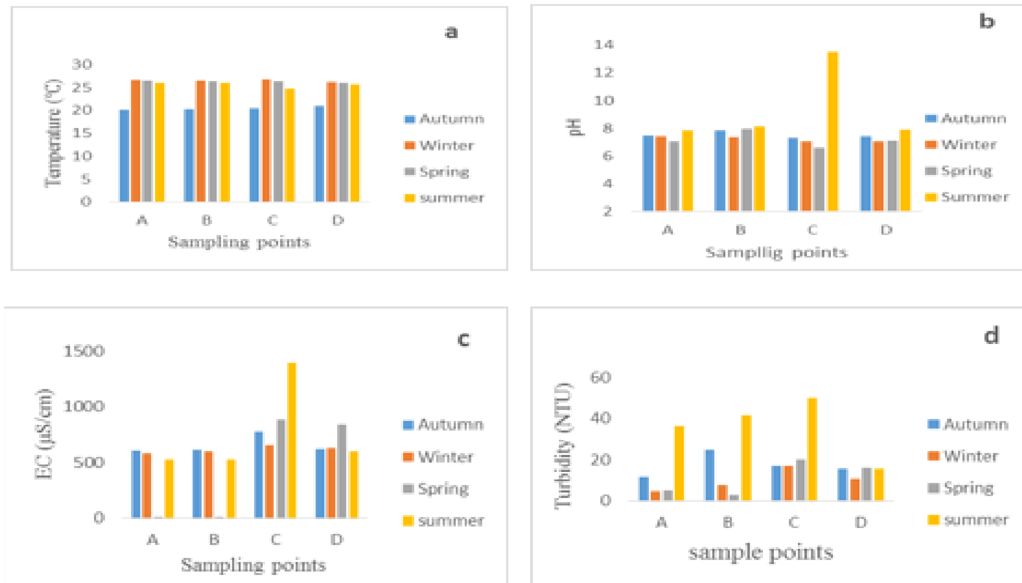


Figure 2. Mean seasonal variations of (a) temperature; (b) pH; (c) EC; (d) Turbidity from summer to spring at Shikwambana River for the year 2017.

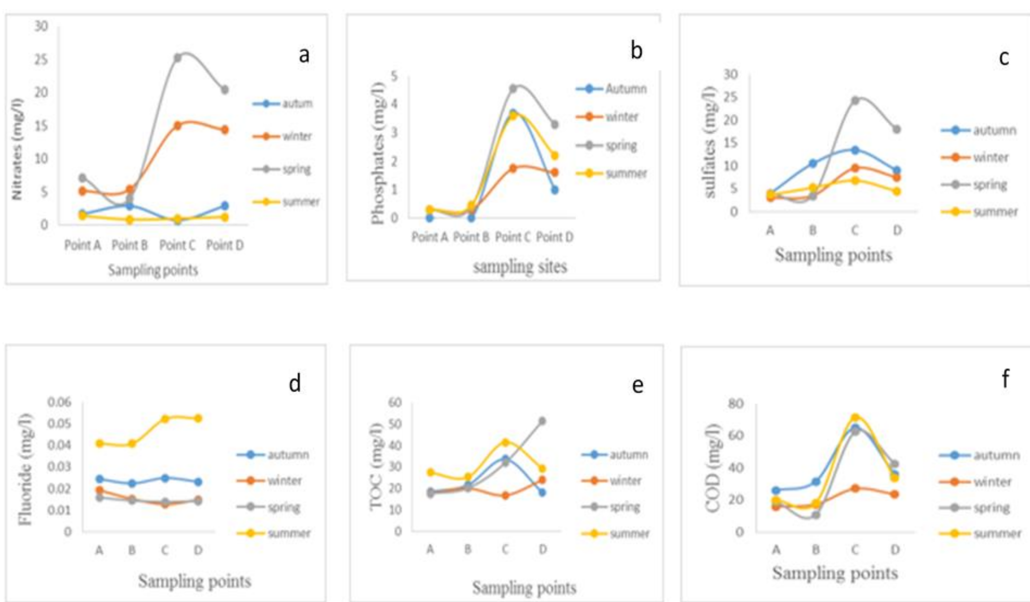


Figure 3. Mean seasonal variations of (e) Nitrate; (f) Phosphate; (g) Sulphate; (h) Fluoride; (i) TOC; (j) COD from summer to spring at Shikwambana River for the year 2017.

Acknowledgment: Authors would like to acknowledge the Department of Water and Sanitation, South Africa for their financial support in this project.

References

1. Khan, M and Ghouri A. M. (2011). Environmental pollution: its effects on life and its remedies. Journal of Arts, Science & Commerce, 2 (2): 276-285.
2. Egun, N. K., (2010). Effect of Channelling Wastewater into Water Bodies: A Case Study of the Orogodo River in Agbor, Delta State. J Hum Ecol, 31 (1): 47-52.
3. Henze, M., 1992. Characterization of wastewater for modelling of activated sludge processes. Water Science and Technology. 25(6): pp 1-15.
4. Akpor O. B. and Muchie, M. (2011). Environmental and public health implications of wastewater quality. Afr J. Biotechnology 10(13): 2379-2387.
5. Dyer, S.D., Peng, C., McAvoy, D.C., Fendinger, N.J., Masscheleyn, P., Castillo, L.V. and Lim, J.M.U. (2003). The influence of untreated wastewater to aquatic communities in the Balatuin River, The Philippines. Chemosphere, 52 (1): 43-53.
6. Kuang, Q ; Bi. Y ; Xia. Y and Hu. Z. (2004). Phytoplankton community and algal growth potential in Taipinhu reservoir, Anhui Province, China, Lakes & Reservoirs: Research & Management. 9(2): 119–124.
7. Wang, H., Wang, T., Zhang, B., Li, F., Toure, B., Omosa, I.B., Chiramba, T., Abdel-Monem, M. and Pradhan, M. (2014). Water and wastewater treatment in Africa–current practices and challenges. *CLEAN–Soil, Air, Water*, *42*(8), pp.1029-1035.
8. World Health Organization and UNICEF. (2017). Progress on drinking water, sanitation and hygiene: 2017 update and SDG baselines. World Health Organization
9. Christo Owen VanderReede, (2015). SA municipalities are discharging raw sewage into our river systems and wetland areas Accessed fromhttp://www.sacarpsociety.co.za/ArticlesDisplay.asp?ID=205
10. Welch E.B and Lindell T. (1980). Ecological effects of waste water. Cambridge University Press, London, United Kingdom.
11. Fondriest Environmental, (2013). "pH." Fundamentals of Environmental measurements. Accessed from http://www.fondriest.com/environmental-measurements/parameters/water-quality/pH/
12. American Public Health Association. (1975). Standard methods for the examination of water and wastewater, 14th ed. American Public Health Association, New York.
13. Kavanaugh, M. C., and Trusiell, A. R. (1979). Measurement of turbidity. In American Water Works Association Water Quality Technology Conference Proceedings, Advances in laboratory techniques for quality. 41-53
14. Constantin, S., Doxaran, D. and Constantinescu, Ș. (2016). Estimation of water turbidity and analysis of its spatio-temporal variability in the Danube River plume (Black Sea) using MODIS satellite data. *Continental Shelf Research*, *112*, pp.14-30.
15. DWAF (1996). South African Water Quality Guidelines. Vol. 1: Domestic water use: 71.
16. Rajendra, P., J. Muthukrishnan and P. Gunasekaran. (2003). Microbes in heavy metal remediation. Indian J. Exp. Biol. 41(9): 935-944.
17. Moore, J.W. and Ramamoorthy, S. (2012). *Heavy metals in natural waters: applied monitoring and impact assessment*. Springer Science & Business Media
18. Han F. X, Banin A, Kingery W. L, Triplett G. B, Zhou L. X, Zheng S. J, Ding W. X. (2003). New approach to studies of heavy metal redistribution in soil. Advances in Environmental Research. 8: 113-120.
19. Al-Bahry S, Mahmoud I, Al-Rawahi S, Paulson J. (2011). Egg contamination as an indicator of environmental health. In: Impact of Egg Contamination on Environmental Health. Nova Science Publisher, Inc. New York, USA. ISBN: 978-1-62100-125-6.
20. Al-Musharafi, S.K., Mahmoud, I.Y. and Al-Bahry, S.N. (2012). Heavy metal contamination from treated sewage effluents. In Proceedings of 11th International Conference on Modelling, Monitoring and Management of Water Pollution (pp. 381-389).
21. Brown and Caldwell. (2001). A guidebook For Local Governments for Developing Regional Watershed Protection Plans. https://epd.georgia.gov/sites/epd.georgia.gov/files/related_files/site_page/devwtrplan.pdf.(2/16/16)