Multi-elemental analysis of heavy metals present in dust emitted from cement plants located in Pretoria and Thabazimbi, South Africa

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Declaration

I, **Matodzi Vhahangwele,** declare that this dissertation: '**Multi-elemental analysis of heavy metals present in cement dust emitted from cement plants located in Pretoria and Thabazimbi, South Africa,'** is my original work and has not been submitted for any degree at any other university or institution. This thesis does not contain other persons' writing unless specifically acknowledged and referenced accordingly.

Signed (Student): …………………………………………………... Date: …………………

List of publications

This thesis is based on the following papers:

I. Effectiveness of the wetlands to phytoremediation of selected heavy metals discharged from a cement brick making factory
Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda Tavengwa

(Manuscript in preparation)

II. Determination of heavy metals in soil and sediments using Modified BCR sequential extraction procedure around a cement brick making factory in Thohoyandou, South Africa
Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda Tavengwa

(Manuscript in preparation)

III. Spatial distribution of heavy metals in dust contaminated urban streets around a Cement Plant in Pretoria, South Africa
Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda Tavengwa

(Manuscript in preparation)

IV. Determination of platinum group metals in dust enhanced by dust suppressants along a gravel road next to a Cement Plant in Thabazimbi, South Africa
Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda Tavengwa

(Manuscript in preparation)

Supplementary
V. Heavy metal accumulation in fruits and vegetables planted on contaminated soils in Thohoyandou
Barbra Moyo, Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda

Water SA (submitted)

Contribution of the authors

Paper I

Principal author, involved in sampling, performed samples preparation and analysis, evaluation of the results and writing of the article. Co-authors revised the draft manuscript and made suggestions for improvement.

Paper II

Principal author, involved in sampling, performed samples preparation and analysis, evaluation of the results and writing of the article. Co-authors revised the draft manuscript and made suggestions for improvement.

Paper III

Principal author, involved in planning, performed samples preparations and analysis, evaluation of the results and writing of the article. Co-authors revised the draft manuscript and made suggestions for improvement.

Paper IV

Principal author, involved in planning, performed samples preparation and evaluation of the results and writing of the article. Co-authors revised the draft manuscript and made suggestions for improvement.

Paper V

Co–author, involved in planning, performed preparation and analysis and evaluation of the results and writing of the article. Co-authors revised the draft manuscript and made suggestions for improvement.

Abstract

Increasing health and environmental concern about the effects of most toxic heavy metals emitted from cement plants in developing countries, which are going through rapid development, has led to this study. Cement industry in South Africa has been the primary industry over the years contributing immensely to infrastructure development and economic growth. Cement has been used to build many large cities, industries, homes, bridges and shopping malls around the country and still continue to be used by constructors. At this point, there has been no other substitute for cement and it will continue to be produced for decades to come. Unfortunately, this industry is now known to be amongst the major environmental polluters. Less has been done to address the adverse effects that comes with the production of cement, especially in the developing countries where there is huge demand for cement. This study focusses on dust emanating from production processes especially cement manufacturing from rotary kiln stage during production of cement and cement bricks. The production of cement and cement bricks generate dust, which is distributed over large areas of the environment.

In South Africa, there are a number of factories in operation without proper planning of pollution prevention and compliance to environmental legislature. Since the production of cement is associated with the release of dust containing heavy metals, the dust is atmospherically deposited on the land, water surfaces and residential areas. The soil, street pavements, wetlands and water surfaces have become the sinks of heavy metals. Heavy metals that are being deposited include arsenic, cadmium, chromium, manganese, cobalt, copper, barium, antimony, selenium, vanadium, nickel and lead. Such metals pose health threat to the animals, plants and human beings living around the cement factories. These metals can easily be leached out from the soil and washed to the water bodies causing water pollution. Old processing techniques have been found to be inefficient to prevent emission of dust to the atmosphere. Hence, the emission of the toxic heavy metals to the environment was uncontrollable.

Since cement is used to produce cement bricks, the whole process is subjected to heavy metals being discharged with dust from the factory to the surrounding environment. Four papers (**I**, **II**, **III and V**) were written to assess the level of heavy metals.

In **paper I,** water and plants samples (*Bidens Pilosa*, *Phragimites Australis* and *Xanthium Strumarium)* were collected in the Mvudi River nearby a cement factory. Sampling was done before, within and after the wetland. Samples were digested with nitric acid for analysis. The concentration of zinc, chromium and lead were determined in the samples using a graphite furnace atomic absorption spectromentry. Results showed that the concentrations of zinc, chromium and lead were above the permissible limits in different parts of the plants analysed and water. The pH of water samples were below the threshold recommended by Department of water affairs and forestry (DWAF) and World health organisation (WHO).

In **paper II,** seven soils at different distance, seven soils below soil surface at seven different layers and a bulk were sampled nearest to the cement brick making factory. Bulk sample was separated into five particle sizes (2 - 3 mm, 1 - 2 mm, 0.5 - 1 mm, 0.5 mm). Five sediments samples were also collected before, within and after the wetland along Mvudi river. Modified three step BCR sequential extraction was applied to the 23 samples in order to obtain the metal distribution in the samples. Heavy metal concentrations of nickel and chromium were determined using graphite atomic absorption spectrometry. Results showed that the levels of nickel and chromium exceeded the permissible limits recommended by WHO. Elevated concentrations Ni and Cr in soil and sediments also showed that the cement brick making factory is the main source of pollution in the area.

To assess the contribution of cement dust to heavy metal pollution from the cement plants to the surrounding environment, two studies were carried out in the vicinity of two cement plants one in Thabazimbi and the other in Pretoria. Two papers (**III and IV**) were written from the studies and were summarised as follows:

In **paper III,** dust samples were collected along the road leading to and passing by the cement plant in Thabazimbi, South Africa. The samples were collected using a brush and pan into sampling bags. After sampling dust samples were sieved into three particle size fractions (PM_{125}, PM_{75}, and PM_{32}). A bulk and five samples were collected beneath the soil at different depth for depth analysis nearest to the cement plant. Water samples were collected along the Crocodile River before and after the cement plant site. The samples were digested using aqua ragia and extracted using Modified BCR sequential extraction. The samples were analysed using inductive coupled plasma optical emission spectrometry (ICP-OES) for concentration of platinum group metals and x-ray fluorescence for elementary analysis (XRF). Analysis of samples included characterisation of the dust samples using x-ray diffraction (XRD). The concentrations were also compared to that of the control study (blank) area to find out if the metals were discharged from the cement factories of interest.

In **paper IV**, street dust samples were collected randomly on the paved surfaces, on the streets and accessible residential and roadsides on locations close to the cement plant in Pretoria. Some samples were collected along the road leading to the gate of the factory and also on the road near the cement plant. The samples were collected into sampling bags using a brush and pan. After sampling dust samples were sieved into three particle size fractions (PM_{125}, PM_{75} and PM_{32}). A bulk and five samples were collected beneath the soil at different depth for depth analysis nearest to the cement plant. Water samples were collected along the Apies River before and after the cement plant. All samples were kept in a cooler box with ice bags to keep them in good condition. The samples were digested using aqua ragia and extracted using Modified BCR sequential extraction. Results were used to establish spatial distribution of the heavy metals around the urban streets. The samples were analysed using ICP-OES for concentration of heavy metals and XRF. Analysis of samples included characterisation of the dust samples using XRD. The concentrations were also compared to that of the control study (blank) area to find out if the metals were discharged from the cement factories of interest.

In **paper V,** seven different vegetables (spinach/*Spinacia oleracea*, Chinese cabbage/*Brassica rapa*, onion/*Allium cepa*, beetroot/*Beta vulgaris*, sweet potatoes/*Ipomoea batatas*, tomatoes/ *Lycopersicon esculentum* and cabbage/*Brassica pekinensis*), fruits (bananas/*Musa acuminate*) and their soils taken after uprooting them were sampled in farming area close to Thohoyandou town and the cement factory. The concentrations of cadmium, nickel and manganese were measured using the graphite atomic absorption spectrometry (GFAAS). Cadmium, nickel and manganese levels were found above permissible limits proposed by Food agricultural organisation (FAO) and WHO in edible parts of vegetables, fruits and soils and hence, may pose a health risk to consumers. Similarly the results from XRF also showed high concentration of the heavy metals in soil analysed.

The aim of this project is to determine the levels of toxic heavy metals carried with dust emanating from cement factories. This assessment is meant to identify and highlight the levels of heavy metals in areas that are close to cement factories. The study will develop a database of heavy metals in affected areas and the pollution impact to the affected environments.

Dedications

This work is dedicated to my grandmother Mrs Mukhadakhomu Sarah and to my late grandmother Manari Makwarera for being there for me and encouraging me throughout my studies.

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Conference presentation

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Vhahangwele Matodzi, Malebogo Andries Legodi and Nikita Tawanda Tavengwa, Effectiveness of wetlands to phytoremediation of selected heavy metals discharge a cement brick making factory, SACI 2018 Conference, 2 - 7 December 2018, CSIR, Pretoria, South Africa, Poster presentation

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List of abbreviations and acronyms

AAS	Atomic absorption spectrometry
BACT	Best available control technology
BCR	Community Bureau of Reference
BEI	Backscattered electron images
CEM	Cement
CEMBUREAU	European cement association
CPCB	Central pollution control board
CRM	Certified reference material
CSIR	Council for Scientific and Industrial Research
DEA	Department of Environmental Affairs
DWAF	Department of Water affairs and Forestry
EC	European commission
EC	Electrical conductivity
ESP	Electrostatic precipitator
FAO	Food and Agriculture Organisation
GFAAS	Graphite furnace atomic absorption spectrometry
GIS	Geographic information systems
ICP-OES	Inductive couple plasma optical emission spectrometry
IUPAC	International Union of Pure and Applied Chemistry
MAL	Maximum allowable limits
NAAQS	National ambient air quality standards
NPC	Natal Portland cement
PC	Portland cement

PGMS	Platinum group metals
pH	Hydrogen ion
PM	Particulate matter
PPC	Pretoria Portland cement
SACI	South African Chemical Institute
SANAS	South African National Accreditation System
SEM-EDX	Scanning electron microscope-energy dispersive X-ray detector
SPM	Suspended particulate matter
SQGs	Sediment quality guidelines
TDS	Total dissolved solids
TOC	Total organic compounds
UK	United Kingdom
US EPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
WBCSD	World Business Council for Sustainable Development
WHO	World Health Organisation
XRD	X-ray diffraction
XRF	X-ray fluorescence

Chapter 1

1 Introduction

This chapter gives the background to the study, research problem, rational of the study and motivation as to why the research was carried out. It concludes by giving the outline on how the work is presented in this thesis.

1.1 Background of the study

Cement is in many ways an essential material that is used worldwide, mainly as a component of concrete (Theron and Niekerk, 2017). In 2009, the estimated yearly production of cement exceeded 3 billion tonnes and this figure continued to grow during 2010 and 2011 (van Oss, 2012). This corresponds to about 0.5 tonne of cement produced per person on the planet each year. In South Africa, despite the lacklustre macro-economic backdrop over the recent past, cement sales have been fairly resilient (Emeran, 2013). The census data shows South Africa has been increasing in population since 1980 at approximately 2% per annum (Kok and Collinson, 2006). Similarly, the country's cementitious sales have steadily risen from 14.9 million tonnes in 2012 and was expected to reach 18.1 per million tonnes in 2018 owing to the addition of new cement manufacturing plants in South Africa, Zambia and Zimbabwe (Emeran, 2013). Economists allude to the fact that as population increases, there is likely to be a corresponding rise in demand for the basic necessities of life with housing as top priority. However, if unchecked, such growth may lead to the unsustainable consumption of scarce natural resources. To meet structural and infrastructural demands, one of the most important building and construction materials in use is concrete which has cement as a basic component (Ohanyere and Alexander, 2012). The most common cement, Portland cement (PC), is derived from the calcining of clay, sand and limestone (a natural resource), with limestone being its predominant constituent (Ohanyere and Alexander, 2012). Currently, there are 20 grinding functional plants across South Africa with a production capacity of 21.7 million tonnes.

Cement is the most important basic material used in building and civil engineering. It constitutes the foremost construction ingredient around the world and playing a key role as a construction material throughout the history of civilisation and urbanization (Supino et al., 2016). The development of cement industry has immensely contributed to economic development of South Africa as a country since the start of civilisation. Cement is widely used as an adhesives or binders by the construction industry for the formation of concrete. Concrete is formed by mixing of aggregate, water and cement. Concrete is also used for cement brick making one of the most important component of building. The concrete has been used for construction of many settlements, schools, towns, cities, shopping centres, roads and etc. Recently, it was in very high demand during the construction of stadiums for the 2010 Soccer World Cup which was hosted in South Africa.

Most cement plants are normally located on limestone deposits and shale or clay reserves to mine this locally (Abdel Moneim et al., 2013). Limestone is the predominant raw material, therefore, most plants are situated near a limestone quarry or receive this material from a source via inexpensive transportation (Zimwara et al., 2012). It also is among the most important non-metallic raw material used for industrial and agricultural purposes (Alnawfleh et al., 2015). Other raw materials that are combined with limestone to have a desired chemical composition include clay and chalk. Clay is mainly composed of the fine grained platy mineral kaolinite; a white hydrous aluminium silicate, $Al_2Si_2O_5(OH)_4$, containing 23.5% alumina, 46.5% silica. Chalk is a fine grained white limestone or micrite. On average, it consists of 97.5 – 98.5% calcium carbonate, containing clay and quartz as its most common impurities (Alnawfleh et al., 2015).

The cement industry has been found to be the second largest cause of CO_2 emission in the world. This include the emission of hazardous pollutants such as greenhouse gases, particulate matter, polyaromatic cyclic compounds and dust which pollute the environment. Particulates and particulate bound metals and ions emitted from various industrial sources are dispersed into the atmosphere due to atmospheric dynamics (Barouti et al., 2006).

The potential sources of fugitive dust (with heavy metals) emissions in cement plants include raw material handling, grinding, blending and delivery, clinker storage, grinding, cement storage, bulk loading and packaging of final product, making cement industry a major emitter of particulate matter (Kalafatoğlu et al., 2001). Nadal et al. (2009) indicated that most of the particulate matter are derived from the physic-chemical reactions involving the raw material calcination and fuel combustion in the kiln system. The clinker burning process is the most important step in cement manufacturing where temperature increases, a series of reactions occurs, ranging from evaporation of free water to decomposition of raw materials and combination of lime and clay oxides (Supino et al., 2016). During this process, heavy metal emissions are common, since metals may be present in both raw materials and conventional fuels (Jones et al., 1994). Heavy metal emissions in a cement plant occur mostly through the stacks attached to the raw mill, rotatory kiln, coal mill, grate cooler and cement mill (Gupta, 2012). The emissions of heavy metals during the production of the clinker leads to a wide spread of environmental contamination and human exposure to heavy metals. Despite this, some human settlements, schools, and towns are located within the vicinity of the cement plants and are found to be exposed to the hazards posed by the emissions from the cement plants processes. This also pose a great danger to the animals and plants in the environments exposed to the emissions from the cement plants.   .

Raw materials in cement production contain majority of heavy metals that emanate from cement dust during production. Achternbosch et al. (2003) reported that typical cement raw materials contain 25 mg kg^{-1} of Cr, 21 mg kg^{-1} of Cu, 20 mg kg^{-1} of Pb and 53 mg kg^{-1} of Zn and about 50% of the total Cd, Cu and Zn load in cement are introduced through raw materials. In spite of the fact that metals are frequently blocked within the clinker, some of them are volatilized and condense on the dust particles (Schuhmacher et al., 2002; Isikli et al., 2003; Isikli et al., 2006). Heavy metal emissions from cement manufacturing are common, since metals may be present in both raw materials and conventional fuels (Jones and Herat, 1994). A relevant study identified raw material feed as the principal source of metal input and also indicated contribution from fuel, e.g. coal (Gupta, 2012).

Particulate and associated metal emissions from cement plants may have serious environmental and health implications. When considering the lack of information on the extent of emissions of particulates and metals from cement plants, it is important to investigate the extent at which the environment is being polluted (Gupta, 2012). The impact of a cement plant and/or of other anthropogenic activities occurring in industrial and urban areas are a reason for heavy metals and polycyclic aromatic hydrocarbons depositions. Heavy metals and organic compounds, such as polycyclic aromatic hydrocarbons, as well as dust and other pollutants, have been identified in the emissions from cement plants (Koren and Bisesi, 2003). The use of solid wastes, as supplementary fuel or as raw material substitute, and several processes associated with cement manufacturing result in high emissions of heavy metals (Baldantoni, et al., 2014).

The emissions can be transported through air mass movements, deposited at local and long–range, determining impacts and imbalances in the receiving environment. Heavy metals and polycyclic aromatic hydrocarbons are toxic pollutants altering ecosystems. They are hazardous for human beings as particles to which these pollutants are associated can be inhaled and ingested (Domingo, 1994; Chang, 1996; IARC, 2013; Baldantoni, et al., 2014).

Some studies highlighted the negative impact of cement dust on soil community and the effect of the altered soil composition on vegetation growth (Ade–Ademilua and Umebese, 2007). The contamination of soil by heavy metals can be problematic on several levels because they do not degrade biologically (Emmanuel et al., 2009) and this always result in several soil dysfunctions leading to concerns about the environmental quality. Metal contaminated soil poses risks to humans and animals through ingestion of plants that have bioaccumulated toxic metals from contaminated soil (Turner, 2009).

Several methods or techniques have been introduced to reduce the burden of environmental pollution caused by cement production, especially in developed countries. According to the European Cement Association, CEMBUREAU, the co-processing of alternative fuels provides a solution in terms of reducing fossil fuel dependency as well as a contribution towards the lowering of atmospheric emissions. The shift from coal to secondary raw materials (e.g., biomass, waste and waste-related materials such as tyres, sludge and slag) could allow a substitution rate of about 80% from a technical point of view (Hasanbeigi et al., 2012).

In this work studies were carried out to measure the level of heavy metals that were emitted from two cement factories in Thabazimbi and Pretoria and a cement brick making factory in Thohoyandou town around their surrounding environments. Though five studies were conducted to analyse different samples such soil, sediments, water, cement dust, fruits and vegetables, this was done to show the impact of heavy metals associated with cement and raw materials used for its production to the environment. The distance, and depth at which the heavy metals are exposed to the surrounding enviroments will help to determine severity of heavy metal pollution. This study paves a way towards the development of database of heavy metals in the affected environments. This was one of the few studies conducted in such environments in South Africa.

1.2 Research problem

Cement is an essential component for infrastructure development for developing countries. However, heavy metals in cement dust may pose a great threat to health of the plants, animals and residents in and around the factory. Finer particles made up of high surface areas with heavy metals bounded to them are a great risk to human health since they appear to evade the body's natural defence mechanism, with a consequence of redistribution into other sites of the body, causing systematic health effects (Yalala, 2015). Cement dust that contain high concentration of heavy metals such as chromium, copper, aluminium, cobalt and lead causes diseases such as central nervous system disorders, anaemia, ulcer, respiratory organs, visual, asthma, skin, and lung cancer (Mahurpawar, 2015). The nuisance dust close to cement process is associated with haze and poor visibility (Engelbrech et al., 2013). The cement dust suspended in the atmosphere may settle on the house roofs, furniture, and roadways and became source of heavy metals. Some cement factories still profess that their activities are environmentally friendly though studies show otherwise. There has been many complaints with regard to the dust emitted from the cement plants, that it causes breathing problems. There has not been proper regulation of heavy metals emanating from cement industries operating in South Africa (Yalala, 2015). Most of the studies done in South Africa focus on cement plants in cities and towns. There is little work done in remote areas where some cement plants are close to rural settlements, like in Limpopo.

1.3 Rationale of study

The area of toxic air pollutants has been the subject of interest and concern for many years. Exposure to metal containing particulate matter can cause adverse health effects such as respiratory organs, asthma and lung cancer. In South Africa, some cement plants are located next to the communities which are highly populated like in Pretoria (PPC Hercules) can affect residents in Pretoria West. Mamba cement factory in Limpopo can affect Thabazimbi residents and Sephaku cement factory in North West can affect Rustenburg residents. These communities are subjected to the emissions of cement dust that contain heavy metals almost every day. Many studies have been done on both dust and metals in developing countries such as India, Nigeria, and Zambia and the results showed that people staying next to the cement plants are more likely to get sick from the dust emitted from cement factories (Akeem, 2008; Nkhama et al., 2015; Schumacher, 2004). It is also important to analyse the heavy metals in the soil and water in these communities that are next to cement plants in South Africa. The results will give some information about South African cement industry, when it comes to the emission of cement dust (containing heavy metals), and the adverse effects to the communities living around the cement plants. This will also help the regulators moving forward on what needs to be done to reduce the emission of cement dust so that the industry may become environmentally friendly and save lives of people living close to these plants.

1.4 Outline of the dissertation

The outline of the dissertation (comprising of five chapters) is presented as follows:

Chapter 1: A general introduction and background to cement industry and its emission of dust to the surrounding environment. This chapter also spells out the research problem which brings out the motivation for carrying out the research.

Chapter II: A concise review of the cement industry, cement production and environmental impact of cement dust, South African regulations of dust pollution. The chapter also reviews methods of sampling, sample analysis and techniques for analysis.

Chapter III: The research objectives are provided in this section.

Chapter IV: This chapter lists manuscripts (**paper I-V**) presented for my MSc examination. The work carried out, results and discussion are presented in each paper.

Chapter V: General conclusions and future work based on experimental findings are discussed in this section.

References: List of the references for introduction and literature review.

Appendix: List of raw data and extra materials

Chapter 2

2 Literature review

This chapter reviews main sources of dust. The chapter gives a detailed information about the cement industry looking at the cement production, pollutants that are emitted during its production and the impact of metals to the surrounding environment. It also present some methods that have been used to analyse dust.

2.1 Sources of dust

Industrial processes have been implicated, among many anthropogenic process, as possible sources of hazardous metals in the environment (Wufem et al., 2013). Examples of anthropogenic sources of dust include power generation activities, industrial processes, waste disposal, transportation (private and public vehicles), biomass burning, domestic fuel burning, landfill sites, and agriculture (DEA, 1999). Cement industry is among those industries implicated, which produce important binding agent for construction industry, and is produced world-wide in large amounts (Achternbosch et al., 2003). Cement industry is one of the 17 most polluting industries listed by Central Pollution Control Board (CPCB) (Schuhmacher et al., 2004). However, cement industry is also associated with the emission of particulate matter which cause environmental degradation, serious pollution and health hazards which have placed the industry under intense scrutiny from environmentalists and governments (Sarujan, 2014). Cement production activities which are known to cause emission include crushing, blasting, screening, transportation, stockpiling, stacking and burning of raw materials. The cement forms part of the industries that are well known to be problematic with regards to the introduction of heavy metals into the environment through dust emanating from their operations (Olowoyo et al., 2015).

Quality of the environment is vital for sustainable development, especially in the face of rapid developmental programs from developing countries. The emissions of particulate matter to air by cement industries during the burning of raw materials have constituted a major problem in most third World countries mostly due to economic constraints (Wufem et al., 2014). Some companies are making efforts to decrease any negative impacts their activities may have on the environment while some have continued to pollute the environment but professing to be environmentally conscious (Tajudeen et al., 2011).

2.2 South African cement industry

South African cement industry was started in 1892, where the first Portland cement was produced. Since then, the industry has been growing in terms of production capacity. Almost 18 million tonnes per annum of cement are produced in South Africa (Achternbosch et al., 2003). The industry has grown because of rapid economic development across South Africa in recent decades. This growth has necessitated massive construction and building works and resulting in an increased demand for cement production (Olowoyo et al., 2015). The government plays a huge role in relation to the amount of the cement to be produced because of its developmental programmes.

The industry has four main companies which produce almost 95% of the cement in South Africa. The major companies are Pretoria Portland Cement (PPC), Lafarge, Afrisam and Natal Portland Cement (NPC). There are other latest new companies from the cement industry which are Sephaku and Mamba companies. The PPC Company, has eight cement production factories and three milling depots in the Southern African region. PPC has the capability to produce 8 million tonnes of cement annually. Lafarge was created in 1998 and it is capable of manufacturing 3 million tonnes of cement annually (Lafarge, 2010). Afrisam has six manufacturing facilities, nine cement depots, 16 quarry and aggregate operations all of which combine to enable the company have almost 4.6 million tonnes cement production capacity on annual basis. NPC has the capacity to manufacture 1.5 million tonnes of cement on an annual basis. Mamba cement has the capacity of 1.1 million tonnes per annum and Sephaku has a capacity to produce of 2.65 million tonnes of cement per annum.

2.2.1 Cement dust

Cement industry processes, especially crushing and burning of raw materials, are associated with the emissions of particulate matter whose depositions may be accompanied by potential impacts caused to human and animal health, vegetation and soil (Wufem et al., 2014). The main processes that regularly cause pollution are those concerned with mineral extraction and burning of raw materials. Particulate matter refers to gases, dust, fumes and others. Dust consist of solid matter in such a fine state of subdivision that the particles are small enough to be raised and carried by wind. Cement dust released from the kiln (80 - 90%) may be of the size 30 µm in diameter (Akeem, 2008). As a result of its fine particle size, dust travels over long distances and the total suspended particulate matter in the atmosphere is thus increased (Wufem et al., 2014). Dust suppression in these operations is more difficult and dust levels can be very high. Mineral extraction to get raw materials for cement production is raising in many developing countries in order to meet high cement demand.

According to the glossary of atmospheric chemistry terms (IUPAC, 1990), dust is small dry, solid particles projected into the air by natural forces, such as wind, volcanic eruption, and by mechanic or man-made processes such as crushing, grinding, milling, drilling, demolition, shovelling, conveying, screening, bagging, and sweeping (Khambekar and Pittenger, 2013). Dust particles are usually in the size range from about 10 to 100 µm in diameter, and they settle slowly under the influence of gravity (WHO, 1999). Airborne dust is classified according to its effects that include: environmental, occupational health and physiological effects (see Figure 1) and size distribution (Petavratzi et al., 2005).

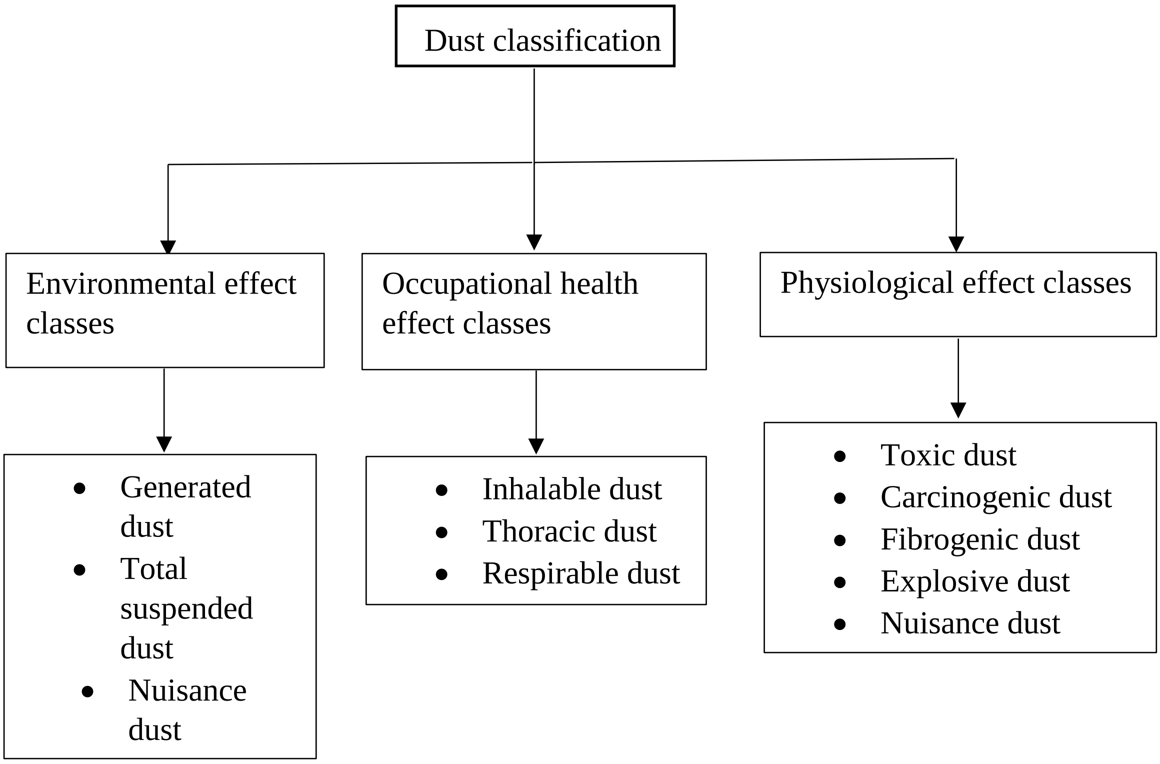

Figure 1. Dust Classification (adapted: Petavratzi et al., 2005)

2.3 Ambient air monitoring system in South Africa

The National Ambient Air Quality Standards (NAAQS) uses PM_{10} and $PM_{2.5}$ concentrations as criteria to evaluate the amount of particulate matter entrained in ambient air owing to the health risk associated with particulate matter equal or smaller than 10 microns in diameter. The standard specifies that PM_{10} levels may not exceed 120 $\mu g\ m^{-3}$ over an average of 24 h and 50 $\mu g\ m^{-3}$ for an averaging period of one year as shown in Table 1 (DEA, 2009).

Table 1: National Ambient Air quality Standards for Particulate Matter (State of Air Report, 2005; DEA, 2009).

Pollutant	PM_{10}		$PM_{2.5}$	
Authority	Maximum 24-hour concentration (µg m^{-3})	Average annual concentration (µg m^{-3})	Maximum 24-hour concentration (µg m^{-3})	Average annual concentration (µg m^{-3})
DEA	120	50	65	25
SANS limits (SANS 1929:2005)	75	40	-	-
EC	50	30	-	-
Australia	50	-	25	8
UK	50	40	-	-
World Bank (General Environmental Guidelines)	70	50	-	-
US EPA	150	50	35	15
WHO	50	20	-	-

ABBREVIATIONS: EC, European Commission; SANS, South African National Standard; SA standards (AQA); UK, United Kingdom; US EPA, United States Environmental Protection Agency; WHO, World Health Organization; and Department of Environmental Affairs (DEA).

Note: – not given

The problem of air pollution is being recognized as a growing source of socio-ecological concern for many African countries. Significantly higher levels of air pollution are currently being experienced in major cities in Africa. African countries are now recognizing air pollution as having significant adverse impacts on national economic developments. These calls for urgent programmes to solve existing air pollution problems in Africa (Hicks et al., 2004).

The National Framework for Air Quality Management in South Africa makes provision for the establishment of air quality objectives for the protection of human health and the environment as a whole (The South African National Standards (SANS) 1929, 2011). Such air quality objectives include limit values, alert thresholds and target values. The proposed guideline criteria for dust deposition are outlined in SANS 1929:2005, Edition 1.1. The target, action and alert threshold are used in the evaluation of dust fallout. The proposed guideline for "Target" level is set at 300 mg/m^2/day annually with no permitted frequency of exceedance. The guidelines state that the "Action Residential" level of 600 mg/m^2/day, averaged over 30 days period may be exceeded three times within a year. However, the exceedance should not be in two sequential months. The "Action industrial" level is set at 1 200 mg/m^2/day averaged over 30 day's period within a year. The permitted frequency of exceedance is similar to "Action residential" level. Areas recording monthly average dust fallout rates that exceed 2400 mg/m^2/day under the "Alert threshold" have no permitted frequency of exceedance. However, the first incidence of dust fallout rate exceedance requires remediation and compulsory report to the relevant authorities (SANS 1929, 2011).

The City of Tshwane is one of the three large metropolitan areas in the Gauteng Province. It consists of five zones around Pretoria which are Pretoria Central East, Pretoria North, Pretoria Central West, Pretoria South and Pretoria East. The city has put in place several monitoring stations in different areas to monitor ambient levels of priority pollutants, mainly particulate matter, sulphur dioxide, ozone, volatile organic compounds, carbon monoxide, and nitrogen oxides in different areas of the city. While activities to monitor ambient air quality and introduced interventions for pollution reduction are underway, human health surveillance is presently not an integrated part of air quality management in the city or in South Africa. NAAQS were derived from international epidemiological studies of personal exposure (Engelbrech et al., 2013).

Presently, the only routinely indicator of impact of air pollution on the public is air related complaints lodged by residents of the city to municipal health services. Dust is frequently reported and most likely came from unsealed roads, open and non-vegetated plots and industrial and construction activities (Wright et al., 2011).

Waterberg District Municipality (Limpopo Province) is a mining area found in north of South Africa with large reserve of platinum group metals (PGMs) and coal. Due to the expected development within the Waterberg area and the existing mining and metallurgical activities in the western arm of the bushveld igneous complex, there were concerns of air pollution. The Waterberg priority area was declared in anticipation of the development of air quality problems associated with the mining activities in the Waterberg area (Feig et al., 2016). Three ambient air quality monitoring stations were established in the Waterberg Priority Area in October 2012. The stations are located at Thabazimbi, Lephalale and Mokopane. Each of the stations was fully equipped to monitor the following parameters at a temporal resolution of minute:

Sulphur Dioxide (SO_2)
Particulate matter of aerodynamic diameter > PM_{10}
Particulate matter of aerodynamic diameter > $PM_{2.5}$
Oxides of nitrogen ($NOx = NO + NO_2$) Ozone (O_3)
Carbon monoxide (CO)
VOCs (benzene, toluene, ethyl benzene, xylene) (Feig et al., 2016)

The initial analysis indicated that the area already may be facing air quality problems, prior to the initiation of the major planned developments in the area. Therefore, it is crucial to assess the pollutants concentration in the area and monitoring how the pollutant levels change with the implementation of the planned developments (Feig et al., 2016).

2.4 Cement production

The most common cement, Portland cement, is derived from the burning of clay, sand and limestone as its predominant constituents. The raw materials extracted from the earth through mining and quarrying include limestone, silica, alumina, and iron. These raw materials are mixed to obtain correct chemical composition with proper particle size and strength. (Supino et al., 2016). They are heated at high temperatures around 1500°C to produce an intermediate grey clinker which is the mixture of the heated raw materials in the rotary kiln. The clinker is then grounded into powder and gypsum is added to regulate setting time and then grinded to form cement. However, the production of cement is associated with the particulate matter emissions from the burning, crushing, grinding of raw materials and their storage, usage and storage of solid fuel, moving of materials and packaging activities (Schuhmacher et al., 2009). It has been found that the raw materials, fossil fuels, and waste fuel during their burning in the kiln contribute to the emission of heavy metals such as lead, cadmium and mercury (Sharma et al., 2013). Table 2 below shows six different types of cement that are produced by the four major cement companies without addition of calcium sulphate monohydrate ($CaSO_4 \cdot H_2O$).

Table 2: Cement types and their major and minor constituents (without gypsum).

Type	Denomination	Major	Minor constituents
CEM I	Portland cement	99.1% clinker	0.2% coal fly ash, 0.5% oil shale, 0.2% pozzolana
CEM II	Slag cement	65% clinker	0.5% coal fly ash
		30% slag	4.5% limestone
CEM II	Limestone cement	65% clinker	19% coal fly ash
CEM II	Shale cement	65% clinker	
		35% shale	
CEM II	Pozzolanic cement	65% clinker	1% coal fly ash
CEM III	Blast furnace	34% clinker	5% limestone
		19% clinker	
		76% blast furnace	

CEM abbreviation for cement

Production of cement may be subdivided into the areas of supply of raw materials, making of the clinker in the rotary kiln then the clinker is milled with other minerals to produce the powder we know as cement (Kosmatka et al., 2002). Cement production starts with the extraction of the limestone, marble and clay, and their subsequent pre-crushing in the quarry that is usually located within the vicinity of the cement works. With the ratio of raw materials being specified exactly, raw materials used in Portland cement manufacturing must contain appropriate proportion of calcium oxides, silica, alumina and iron oxides (Hewlett and Peter 1997). Apart from natural raw materials, waste containing lime, aluminate, silicate, and iron are increasingly gaining importance as raw materials substitutes (Yang et al., 2015). The mixture of raw materials is milled to raw mill and, at the same time, dried with the residual heat of the kiln off gasses. In the downstream electrostatic precipitator, the raw mill is separated and subsequently transported to raw mill silos via pre-heater, the dust like raw meal is fed then into the rotary kiln. By means of the burning process at 1250 to 1500°C, clinker granules are formed. Lime, silica, alumina and iron oxide react with one another in the kiln to form the main constituents for cement (Achternbosch et al., 2003). The composition of the clinker basically consists of the following four compounds:

Tricalcium silicate ($3CaO \cdot SiO_2$)

Dicalcium silicate ($2CaO \cdot SiO_2$)

Tricalcium aluminate ($3CaO \cdot Al_2O_3$)

Tetracalcium aluminate ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$)

The energy required is supplied by combustion of coal, oil, gas or secondary fuels in a burner at the end of the rotary kiln (primary combustion) and partly at the beginning of the rotary kiln (secondary combustion). The hot flue gasses generated by combustion flow through the rotary kiln and pre-heater in opposite direction to solids. The clinker leaving the rotary kiln gas is cooled down. This clinker is then ground together with gypsum and other additives, to influence the properties of the cement and setting time (Worrell et al., 2001). The entire production process is shown in Figure 2. Table 3 shows some of the regular and non-regular materials that are used for cement production.

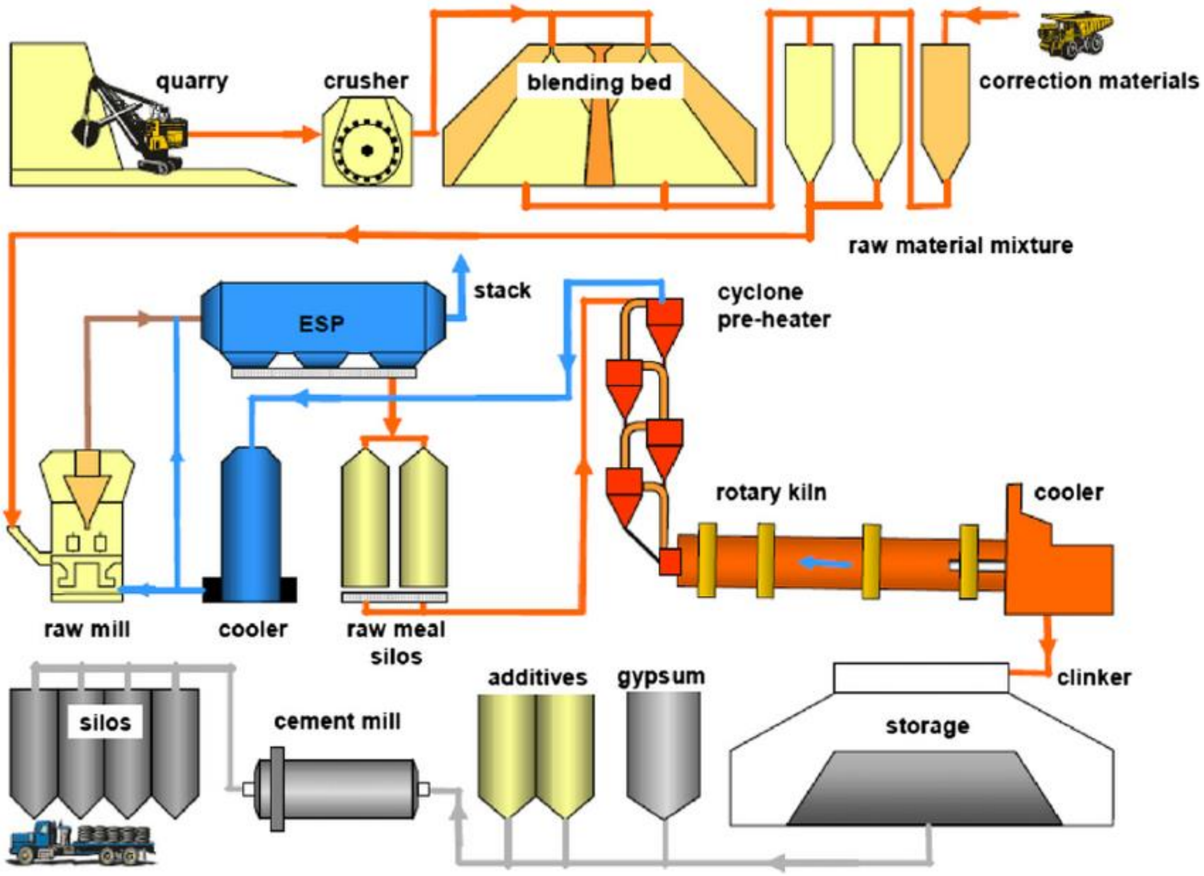

Figure.2. Schematic representation of cement production (Ohanyere and Alexander, 2012).

Table 3: Input materials during cement production (Achternbosch et al., 2003).

Class	Input materials
Primary raw materials	Limestone, marlstone, clay stone, sand, trass
Regular fuels	Hard coal, brown coal, oil coke, oil shale
Secondary fuels	Used tyres, waste oil, scrap wood, fractions from municipal, industrial, and commercial wastes, including paper wastes, plastic wastes, automobile, textiles, paper/plastic mixtures
Secondary raw materials	Iron ore, materials from iron and steel works, pyrites cinder, mill scale, contaminated ore, foundry sand, ashes from burning process, coal fly ash
Interground additives	Natural gypsum, anhydrite, gypsum from flue gas desulphurisation, fly ash, oil shale, foundry sand, trass
Intermediate and final products	Raw meal, clinker, Portland cement, blast furnace cement

2.4.1 Impact of alternative materials and fuels

The cement manufacturing industry is one of the leading industry contributing enormously to environmental pollution and it is under pressure to reduce emission of pollutants. The industry has resulted in the use of alternative fuels and raw materials. Due to sustainability of the cement dust production cost, most manufacturers have resorted to using alternative raw feeds and secondary fuels derived from industrial by-products (Bhatty, 1995; Yan et al., 2010). Alternative source of fuels are solvents, used tyres, waste oil, paints residue, biomass such as woodchips, and sewage sludge (Bhatty, 1995). Sources of alternative raw materials are iron and steel industry, coal fly ash, iron ore and ashes from other industries (Abdel Moneim et al., 2013). The use of alternative fuels for cement clinker production is of high importance for the cement manufacturers as well as for the environment. Alternative fuel utilization at commercial level in cement industry is as old as about 30 years now. Reports show that in some kilns, up to 100% substitution rates have been achieved (Cemex News, 2011), while others are facing some limitations regarding environmental, social and product quality issues. However, switching to alternatives fuels presents several challenges as they have different characteristics compared to the conventional fuels. Poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher SO_2, NOx, and CO emissions, and dusty kilns are some of the major challenges which need to be addressed (Trezza and Scian, 2000). The alternative fuel and raw materials might have contributed to elevated heavy metals release from cement factories. One potential constraint on the implementation of alternative fuels is the final clinker composition since the combustion by-products are incorporated into clinker (Chinyama, 2011). With the use of alternative fuels and raw materials on the rise, environmental pollution associated cement production might be reduced. The usage of alternatives fuels in cement manufacturing not only helps to reduce the emission but also has significant ecological benefits of conserving non-renewable resources (Trezza and Scian, 2000). The substitution rate of fossil fuel and raw material varies from country to country. Most of the European countries are way ahead in the usage percentage of alternative fuels than the rest of the world. Alternative fuel substitution rate of different countries is shown in Table 4 (WBCSD Report, 2005).

Table 4. Percentage substitution rate of alternative fuels of different countries.

Country	(%)Substitution	Country	(%)Substitution
Netherlands	83	Czech Republic	24
Switzerland	48	EU (prior to expansion in 2004)	12
Austria	46	Japan	10
Norway	35	United States	8
France	34.	Australia	6
Belgium	30	United Kingdom	6
Germany	42	Denmark	4
Sweden	29	Hungary	3
Luxembourg	25	Finland	3

2.4.2 Emission of pollutants

Cement manufacturing is associated with the emission of pollutants either transferred into the product cement or emitted with the exhaust gas into the environment. The emissions include CO, NOx, and SO_2, organic compounds, heavy metals and dust (Zimwara et al., 2012). Dust emissions at cement plants originate mainly from quarrying and crushing, raw material storage, grinding and blending (in the dry process only), clinker production, finish grinding, and packaging and loading (Karstensen, 2007). The largest emission of cement dust has been related to the pyroprocessing system that includes the kiln and clinker cooler exhaust stacks (Bhatty, 1995). Often, dust from the kiln is collected and recycled into the kiln thereby producing clinker from the dust. However, if the alkali content of the raw materials is too high, some or all of the dust is discarded or leached before returning it to the kiln. In many instances, the maximum allowable cement alkali content of 0.6 percent (calculated as sodium oxide) restricts the amount of dust that can be recycled. Bypass systems sometimes have a separate exhaust stack. Additional sources of dust are raw material storage piles, conveyors, storage silos, and unloading facilities (U.S. EPA, 2009).

As flame temperature increases, and long residence times prevailing in cement kilns, this result in significant amount of NOx generated with the quantity of nitrogen in the fuel during the calcining process (Akgun, F., 2003). In the cement manufacturing process, NOx is generated in the burning zone of the kiln and the burning zone of a precalcining vessel. Sulphur dioxide may be generated both from the sulphur compounds in the raw materials and from sulphur in the fuel. The sulphur content of both raw materials and fuels varies from plant to plant and with geographic location. However, the alkaline nature of the cement provides for direct absorption of SO_2 into the product, thereby mitigating the quantity of SO_2 emissions in the exhaust stream (U.S. EPA, 2009). Carbon dioxide is released during the production of clinker, a component of cement, in which calcium carbonate ($CaCO_3$) is heated in a rotary kiln to induce a series of complex chemical reactions (Conneely et al., 2001). Specifically, CO_2 is released as a by-product during calcination, which occurs in the upper, cooler end of the kiln, or a precalciner, at temperatures of 600 – 900°C, and results in the conversion of carbonates to oxides. The simplified stoichiometric relationship is as follows:

$CaCO_2 + heat \rightarrow CaO + CO_2$

If the combustion reactions do not reach completion, CO and volatile organic pollutants, which are typically measured as total organic compounds (TOC), VOC, or condensable organic particulate, can be emitted. Incomplete combustion also can lead to emissions of specific hazardous organic air pollutants, although these pollutants are generally emitted at substantially lower levels than CO or TOC. Atmospheric emission from the plants include heavy metals such as As, Cd, Cr, Ni and Pb from cement production (Pacyna et al., 2007). Al, Be, Cu, Mn and Zn have also been distinguished in the emissions from cement plants (Schuhmacher et al., 2002). Heavy metal emitted from Portland cement kilns can be grouped into three general classes: volatile metals, including Hg and Tl; semivolatile metals, including Sb, Cd, Pb, Se, Zn, K, and Na; and refractory or nonvolatile metals, including Ba, Cr, As, Ni, V, Mn, Cu, and Ag. Although the partitioning of these metal groups is affected by kiln operating conditions, the refractory metals tend to concentrate in the clinker, while the volatile and semivolatile metals tend to be discharged via the primary exhaust stack and the by-pass stack, respectively (US.EPA, 1994). Figure 3 provides a process flow diagram of the general cement manufacturing process and the associated inputs and emissions during various steps of the production process.

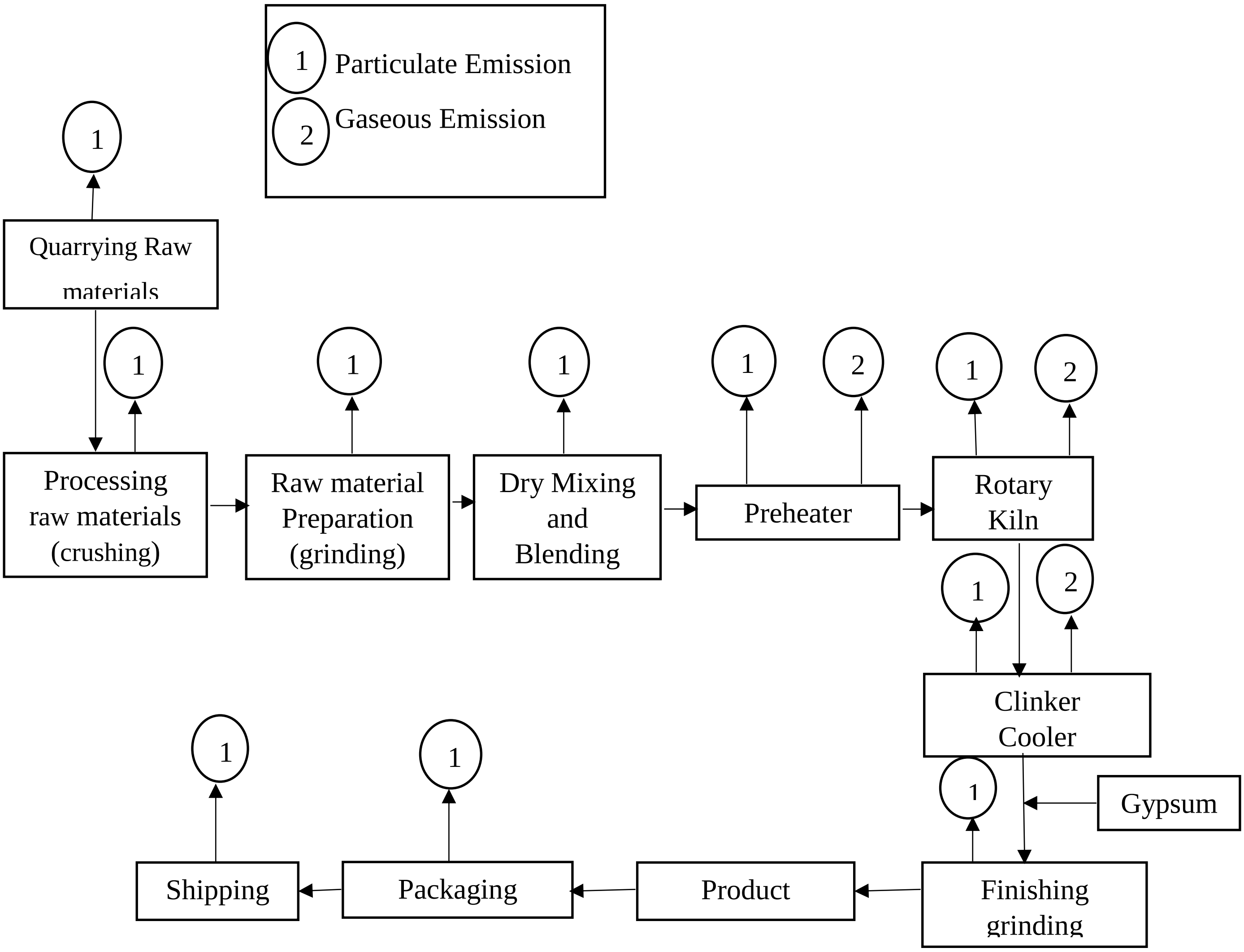

Figure. 3. Process flow diagram for the cement manufacturing process, showing gaseous and particulate emissions (Huntzinger and Eatmon, 2009).

2.4.3 Health and environmental effects of cement dust emission

Emissions of heavy metals from cement plants are one of the major sources of environmental pollution. Cement factories have been reported to be a major source of heavy metals emission to the environment with several reports showing higher concentrations of heavy metals around them (Ogunbileje et al., 2013). Contamination of the environment by metals is of major concern because of their toxicity and threat to human life and the environment (Sakai et al., 2000; O'Brien et al., 2003; Rana, 2008; Ceccatelli et al., 2010). Heavy metals toxicity appears to be dependent on dose, route of exposure, duration, and frequency of exposure (Ogunbileje et al., 2013). Heavy metals like Pb and Hg in contaminated soil can be transported by water, wind and other human activities with their resultant health impacts and effects on the environment (Ogunbileje et al., 2013).

Some trace metals (e.g, Cu and Zn) at low concentrations are harmless, but others (e.g, Pb and Cd) at extremely low concentrations are toxic and initiators or promoters in many diseases including cancer (Willers et al., 2005).

Several studies have revealed the negative impact of cement dust to the workers and residents living around the cement factories. Health risk to communities around cement plants has also been studied (Schuhmacher et al., 2004). Dietz et al. (2004) reported a significant correlation between cement dust exposure and laryngeal cancer among workers exposed to cement dust in an epidemiological study, while Abimbola et al. (2007) reported increased incidence of diseases linked to heavy metal toxicity in residents living around cement dust factory. Dietz et al., (2004) and Smailyte et al. (2004) reported increased risk of lung and bladder and laryngeal cancers in cement factory workers in Lithuania and Germany, respectively. Moreover, pollutants emitted from cement plants, especially metals, get distributed in soils also and may affect vegetation and enter food chain via crops and water (Schuhmacher et al., 2009). Evidently, human health can be indirectly affected through the intake of drinking water, contaminated foodstuffs and skin absorption of chemicals from contaminated soils apart from direct exposure to ambient dust generated by stack emissions from cement plants (Gupta, 2012). To residents living along unpaved roads, the traffic-generated dust penetrates their homes causing a nuisance and health problems such as hay fever and allergies. Crops and vegetation near unpaved roads can be covered with the airborne dust stunting their growth due to the shading effect and clogging of the plant’s pores (Jonathan et al., 2004). Fine particles resulting from traffic actions can also be washed off during precipitation events and carried into nearby creeks, streams, and lakes increasing their respective particulate loading. For motorists using the unpaved roads the traffic-generated dust can reduce visibility and cause driving hazards (Jonathan et al., 2004).

Heavy metals pollution accumulates in the street dust, soil, and surface and influences both the population health and ecosystem (Tüzen, 2003 and Ferreira-Baptista and De Miguel, 2005). Street dust has a particular concern due to its potential health risk to children through hand-to mouth activities, important source of house dust and urban atmospheric particulate matter and being inhaled by those traversing the streets and those residing in the vicinity of the streets (Ljung et al., 2005). Street dust carries a high loading of contaminants such as metals and organic pollutants (Kim et al., 1998; Li et al., 2001 and Yunker et al., 2002). In urban areas, elevated levels of metals in soils in playgrounds may pose risks to human health.

The risk is especially high for children because of their low tolerance to toxin as well as the inadvertent ingestion of significant quantities of dust (or soils) through dermal and hand-to-mouth pathways (Davies et al. 1990; Watt et al. 1993; Al-Rajahi et al., 1996; Li et al., 2001; Banerjee, 2003; Ljung et al., 2006). In addition, elderly people who are frequent visitors to parks might be sensitive to high loadings of metals in urban soils (Acosta et al., 2009).

2.4.4 Measures used to control emissions from cement production

The cement industry contributes significantly to the imbalances of the environment; in particular air quality. The key environmental emissions are NOx, SO_2 and particulate matters (Albeanu et al., 2004). Particulate matter include dust, soot, liquid droplets (except pure water droplets), and consist of fine particles that can remain suspended in the air. This particulates matter with presence of metallic elements are emitted from crushing, grinding and burning of raw materials in cement manufacturing (Ibrahim et al., 2012). Generally, NOx emissions are generated during fuel combustion by oxidation of chemically-bound nitrogen in the fuel and by thermal fixation of nitrogen in the combustion air. The emissions of SO_2 are generated from sulphur compounds in the raw materials and, to a lesser extent, from sulphur in the fuel (Ibrahim et al., 2012).

The measures used to control emissions from fugitive dust sources are comparable to those used throughout the mineral products industries. Vehicular traffic controls include paving and road wetting. Controls that are applied to other open dust sources include water sprays with and without surfactants, chemical dust suppressants, wind screens, and process modifications to reduce drop heights or enclose storage operations. Typically, emissions from these processes are captured by a ventilation system and collected in fabric filters. Some facilities use an air pollution control system comprising one or more mechanical collectors with a fabric filter in series. Because the dust from these units is returned to the process, they are considered to be process units as well as air pollution control devices (U.S EPA, 1994).

The cement kiln itself has been designated as best available control technology (BACT) for the control of SO_2. The highly alkaline conditions of the kiln system enable it to capture up to 95% of the possible SO_2 emissions. However, if sulphide (pyrites) is present in the kiln feed, this absorption rate can decline to as low as 50% (Zimwara et al., 2012). Therefore, sulphur emissions can be decreased through careful selection of raw materials. The cement kiln system itself has been determined to provide substantial SO_2 control. Fabric filters on cement kilns are also reported to absorb SO_2. Generally, substantial control is not achieved.

An absorbing reagent (e.g., CaO) must be present in the filter cake for SO_2 capture to occur. NOx is generated in the burning zone of the kiln and the burning zone of a precalcining vessel (U.S EPA, 1994). The use of natural gas combustion with a high flame temperature and low fuel nitrogen generates a larger quantity of NOx than does oil or coal, which have higher fuel nitrogen but burn with lower flame temperatures. Co-incineration of liquid wastes, including waste solvents from ink and paint manufacturing processes and liquid industrial wastes, in coal-fired cement kilns has been shown to result in substantial (up to 40%) reductions in NO_x emissions (Jones and Herat, 1994).

2.5 Heavy metals

Heavy metal pollution is one of the major problems facing the environment surrounding cement plants. Industrialization and urbanization have also increased the anthropogenic contribution of heavy metals in biosphere (Nagajyoti et al., 2010). The term ‘‘heavy metals’’ refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech Water Treatment and Air Purification, 2004). Heavy metals do not naturally bio-degrade, thus they remain one of the most persistent environmental pollutants associated with anthropogenic activities (Callender, 2003; Osman and Kloas, 2010; Sekabira et al., 2010; Bednarova et al., 2013). Generally, heavy metals have higher densities (Alloyways and Ayres, 1993). However, chemical properties of the heavy metals are the most influencing factors compared to their density (Nagajyoti et al., 2010). The industrialization of the world dramatically increased the overall environmental load of heavy metal (McBride, 1994). The human body requires trace amounts of some heavy metals such Zn, Cu, Fe, Co and others, but these can be dangerous at high levels. Other heavy metals such as Hg, Pb, As and Cd have no known benefits and their accumulation over time can cause serious illness and even premature death (Singo, 2013). Heavy metals also occur naturally, but rarely at toxic levels. Heavy metals are emitted with cement dust and tend to accumulate in the streets, soil, water and sediments. Non-essential heavy metals, such as Hg, are not required for growth and are considered to be most harmful to humans and freshwater biota (Corbett, 1995; Wasik and Namiesnik, 2001; Ouyanget al., 2002; Jarup, 2003; Fasinu and Orisakwe, 2013). Beyond their optimum threshold, low concentrations of nonessential metals are as harmful as high concentrations of the essential metals (Newman and Clement, 2008; Hariprasad and Dayananda, 2013). Cd, Cr, Cu, Ni, Pb and Zn are commonly classified as trace heavy metals (Shozi, 2015).

Trace metals

The term 'trace metals' is used when referring to heavy metals of low natural concentration (less than 0.01%) in the environment and may be toxic at relatively high concentrations (Alloway, 1995; Duffus, 2002; Callender, 2003; Jarup, 2003; Yao and Gao, 2007; Appenroth, 2010). Trace metal toxicity can be defined as the concentration level required to exhibit acute (may lead to death) or a sub-lethal biological response in organisms (Smith, 1985). Zinc is an essential nutrient for the human body and thus is important for human health (Ohnesorge and Wilhelm, 1991).

In humans, health effects of zinc poisoning include gastrointestinal distress, diarrhoea, slow reflexes, anaemia and metabolic disorder (Ohnesorge and Wilhelm, 1991). Pb is hazardous to most forms of life at any concentration and is relatively bioavailable to freshwater organisms (Jarup, 2003). The symptoms of acute Pb poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system (Jackson et al., 2009). Cd is a rare mineral in the earth's crust and is highly toxic to humans, animals and freshwater organisms even at concentrations as low as 1µg L^{-1} (Callender, 2003; Jarup, 2003). Cd has also been reported to have significant effect on the respiratory tract which has been the major focus of most studies on cement factory workers (Hart, 2000). Among other effects, an *in vitro* study indicated that Cd caused dose-dependent decrease in the percentage of macrophages in bronchial lavage and whole blood (Coin and Stevens, 1986). The effect of Cd toxicity in humans includes kidney damage and bone pains. Cd also has mutagenic (changes in genetic make-up), carcinogenic (cancer-causing) and teratogenic (causing developmental malformations) effects (Johri et al. 2010; Nawrot et al., 2010). Ni is a non-essential and toxic heavy metal which occurs as Ni (II) in the environment. Ni has been considered to be an essential trace element for human and animal health (Nazir et al., 2015). Cr on the other hand, is a relatively common element found in many minerals in the earth's crust (Callender, 2003; Guertinet al., 2004). The eastern part of South Africa harbours the largest reservoirs of chromium in the world (as chromite) (Callender, 2003). Cr can exist as Cr (III) and as Cr (VI) but Cr (VI) is 100 to 1000 times more toxic than Cr (III) as it causes severe skin damage in humans (Sharma et al., 2012).

2.5.1 Impact of heavy metals in surface water

Heavy metals emanating from the cement plant may contaminant surface water. Surface water may be contaminated with heavy metals through a runoff from the plant after water has being used in the cement production or by atmospheric deposition of cement dust. Heavy metal contamination in aquatic ecosystems due to discharge of industrial effluents may pose a serious threat to human health (Rai, 2008). In the water column, trace metals may exist as free or complexed ions or they may be adsorbed onto solids. Metals also occur in small amounts naturally and may enter into aquatic systems through leaching of rocks, airborne dust, forest fires and vegetation. As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, thus causing heavy metal pollution in water bodies (Nazir et al., 2015).

The presence of heavy metals in water may have a profound effect on the microalgae which constitute the main food source for bivalve mollusks in all their growth stages, zooplankton (rotifers, copepods, and brine shrimps) and for larval stages of some crustacean and fish species (Nazir et al., 2015). Moreover, bioconcentration and magnification could lead to high toxicity of these metals in organisms, even when the exposure level is low (Nazir et al., 2015). Some trace metals are incorporated within insoluble organic or inorganic matter in bottom sediments where they are partitioned within the geochemical fractions (Filipek and Owen, 1979; John and Leventhal, 1995). One of the main processes that governs distribution and partitioning of heavy metals between phases is sedimentation (Förstner and Salomons, 1980; Forstner et al., 1986). Sedimentation is not a simple or straightforward process and it allows heavy metals to be removed from surface water as they become trapped in the bottom sediments (Ayoub et al., 2001; Peijnenburg and Jager, 2003; Yao and Gao, 2007). Heavy metals form compounds with low solubility and the degree of solubility is controlled by pH. That is, acidic conditions will result in increased solubility of the metal complexes thus releasing metals in the environments (Förstner and Wittmann, 1979; Fergusson, 1990; John and Leventhal, 1995; Peijnenburg and Jager, 2003; Violante et al., 2010).

2.5.2 Impact of heavy metals in soil

Soil is a crucial component of rural and urban environments, and in both places land management is the key to soil quality. Therefore, it is important to monitor heavy metals causing soil contamination, in order to manage and protect the soil. In most cases, soils may become contaminated by the accumulation of heavy metals through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition

(Khan et al., 2008; Zhang et al., 2010). Excess heavy metal accumulation in soils is toxic to human beings, plants and animals. Exposure to heavy metals in soil over a long period of time is normally chronic, due to food chain transfer. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Maslin et al., 2000).

Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (McLaughlin et al., 2000; McLaughlin et al., 2000; Ling et al., 2008). Therefore, the determination of free metal ion concentrations in soil becomes important. The free metal ion concentration not only depends on the total metal content in soils, but also on the metal species that exist in the soil. In addition, some environmental conditions (e.g., pH, concentration of complexing ligands in solution, and the soil colloid) are important. (Ene et al., 2009).

2.5.3 Impact of heavy metals in sediments

Heavy metal contamination in sediment could affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes et al., 2007; Abdel-Baki et al., 2010). Elevated concentration of heavy metals in sediments, in comparison to sediment quality guidelines (SQGs), are an indication of anthropogenic input into the environment. Sediment quality, as a method to measure freshwater quality, has been widely studied on a local and global scale (Burton, 1991; Aprile and Bouvy, 2008). Over the last few decades the study of the sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments (Harikumar and Nasir, 2010; Rosales-Hoz et al., 2003) Sediments and suspended particulate matter (SPM) play an important role in the adsorption of dissolved heavy metals. They can also be a potential reservoir of metals, by releasing them to the water column under changing physical and chemical conditions (Karbassi et al., 2007). Sediment cores can be used to study the pollution history of aquatic ecosystem (Karbassi et al., 2005; Viguri et al., 2007). Within an individual sediment core, differences in pollutant concentrations at different depths reflect how heavy metal input and accumulation changes over time (Shine et al., 1995; White et al., 2005).

The sediments are potential source of long-term heavy metal pollution in the catchment. Within freshwater systems, bottom sediments are regarded as heavy metal sinks due to the densities and chemical properties of metals. Gao et al. (2016) reported that sediments accumulated more metals than soils and aquatic plants. This confirmed that sediments are more useful for heavy metal assessment. Long-term partitioning within the sediments make them more useful for measuring heavy metal pollution than water analysis (Burton, 2002; Ayas et al., 2007; Chen et al., 2007; Osman and Kloas, 2010; Qiao et al., 2013; Shanbehzadeh et al., 2014).

2.5.4 Impact of heavy metals in wetlands

Wetlands areas are critical for water surfaces because they trap a large amount heavy metals from natural and anthropogenic sources. In general, the term “wetlands’ refers to transition zones between terrestrial and aquatic systems with soil saturated with water for at least part of the year or covered by shallow water along with characteristic wetland plant species (Kalff, 2002). They regulate the water regime, act as natural filters, and display amazing nutrient dynamics (Prabhat, 2008). This helps on improving the quality of water which is supplied to the communities for use in the households. They also play a role in preventing flooding. There are two types of wetlands which are natural and constructed wetlands. Natural wetlands are not manmade whereas constructed wetlands area are constructed mainly to remove pollutants in wastewater from industrial areas.

Plants in wetland areas use phytoremediation to remove toxic heavy metals in polluted water. Phytoremediation is an environmental friendly technology that make use of plants to degrade, remove, transform, or immobilize toxic heavy metals in soils, sediments, and polluted water in wetland areas (Jaak et al., 2015). The approach is generally one of ‘‘phytostabilization’’, where the plants are used to immobilize metals and store them below ground in roots and/or soil, in contrast to ‘‘phytoextraction’’ in which hyperaccumulators may be used to remove metals from the soil and concentrate them in aboveground tissues (Weis and Weis, 2004).

Vegetation comprising wetland plants is the most important component of a wetland system. The common plants in wetlands are common reed *(Phragmitesspp*.), cattail *(Typhaspp*.), rush *(Juncusspp.)*, and bulrush *(Scirpusspp*.). However, the most common plant species worldwide is *Phagmites Australis* (Cav.) Trin. ex Steud (Kadlec et al., 2000; Scholz, M., 2006). The different actions of plants and their associated rhizosphere bacteria on contaminants include phytoextraction, rhizofiltration, phytostabilization, phytodegradation, rhizodegradation, and phytovolatilisation (Salt et al., 1995; Williams, 2002). Wetland plants also take up heavy metals from the environment but tend mainly to accumulate them in below ground tissues (Peverly, Surface, and Wang, 1995; Stoltz and Greger, 2002; Weis and Weis, 2004). These latter plants must be, in turn, harvested and disposed of to prevent recycling of accumulated metals when the plants decompose (Prabhat, 2008).

2.5.5 Phytoremediation of heavy metals

Due to increasing anthropogenic activities it became critical to develop methods that will remediate the environment and return it to its prior condition. Phytoremediation is a cost effective and environmentally friendly technology which has been successfully developed to remediate soils contaminated with various pollutants. According to (Cunningham and Berti, 1993), phytoremediation is defined as the use of green plants to remove, contain, or render harmful environmental contaminants. Phytoremediation is currently one of the best low cost available technique especially for developing countries.

In this process specially selected or genetically engineered plants are used which are capable of direct uptake of pollutants from the environment (Macek et al., 2000). It has been reported that phytoremediation is increasingly used as a technological complement for treatment of polluted water in different types of treatment wetlands (Horne 1999; Zhang et al. 2010). Phytoremediation can be applied to both inorganic and organic pollutants present in solid and liquid substrate (Salt et al. 1998). Generally, phytoremediation of contaminants by a plant involves the following steps: uptake, translocation, transformation, compartmentalization, and sometimes mineralization (Schnoor et al. 1995).

Inorganic contaminants (heavy metals and radionuclides) can be either taken up from the soil and immobilized by the roots (phytoimmobilization), or transported to the plant shoot (phytoextraction) (Reichenauer and Germida, 2008). Nearly 450 hyperaccummulator plants ranging from annual herbs to perennial shrubs and trees (e.g. tobacco, sunflower, mustard, maize, pennycress, brake fern, Russian thistle, rattlebush, python tree, willow, poplar, etc.) have been described to accumulate and detoxify extraordinary high levels of metal ions, such as Ni, Co, Pb, Zn, Mn, Cd, etc. in their above ground tissues (Meagher, et al., 2000; Padmavathiamma and Li, 2007; Shah and Nongkynrih, 2007). After the contaminants have been remediated plants are harvested and removed from the site for disposal or recovery of the contaminants (Susarla et al., 2002).

2.5.6 Impact of heavy metals in plants

Accumulation of heavy metals in crop plants is of great concern due to the probability of food contamination through the soil root interface. Though, heavy metal like, Cd, Pb and Ni are not essential for plant growth, they are readily taken up and accumulated by plants in toxic forms (Nazir et al., 2015). Presence of toxic heavy metals in agricultural soil may adversely affect crop production or crop quality. This may also affect human beings through food chain. However, there are plants that can tolerate toxic heavy metals in soil and aquatic systems. In general, plants have a tendency to release excessive metal ions through transpiration, reducing the toxic concentration in the plant tissues of leaves which is common to *Phragmites australis* (Berk and Colwell 1981; Burke et al., 2000). Some of the heavy metal such as Cd, Hg and As are strongly poisonous to metal-sensitive enzymes, resulting in growth inhibition and death of organisms. An alternative classification of metals based on their coordination chemistry, categorizes heavy metals as class B metals that come under non-essential trace elements, which are highly toxic elements such as Hg, Ag, Pb, Ni (Nieboer and Richardson, 1980). Plants growing in metal-polluted sites exhibit altered metabolism, growth reduction, lower biomass production and metal accumulation. Various physiological and biochemical processes in plants are affected by metals (Nagajyoti et al., 2010). Heavy metal toxicity in plants varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many heavy metals are considered to be essential for plant growth. The essential heavy metals (Cu, Zn, Fe, Mn and Mo) play biochemical and physiological functions in plants and animals. Two major functions of essential heavy metals are the following: (a) Participation in redox reaction, and (b) Direct participation, being an integral part of several enzymes (Nagajyoti et al., 2010).

2.6 Methodology

2.6.1 Particle size analysis

Dust emitted from industrial activities contain very small particles that are normally less than 90 µm in size. It is therefore imperative to separate the dust into different sizes in order to conduct a proper presentative study of particles involved. Small particles with a large surface area to mass ratio allow more adsorption of heavy metals than larger particles (Förstner and Salomons, 1980; Lin et al., 2003; Jain, 2004). Wang et al. (2006) also reported that fine particles have high specific area that retains high amounts of metals. Studies had shown that concentration of metals in soils increases with decreasing particle size (Al-Rajahi et al., 1996; Ljung et al., 2006).

Particle size of particulate matter plays a major role in the distribution of dust, and determines the depth of penetration and deposition in the respiratory system, where trace metal absorption efficiency ranges from 60 - 80% resulting in impairing the physiological function of the lung based on bioavailability of toxic metals (Yalala, 2015). Based on their potential to cause adverse health effects, particles are defined into 3 categories, namely: (1) ultrafine particles, < 0.1 µm, (2) fine particles, < 1 µm, and coarse particles, > 1µm (Yalala, 2015). They are also categorised as: (1) respirable fraction, < ($PM_{2.5}$), (2) inhalable fraction, < (PM_{10}) (Charlesworth et al., 2011), while according to European Committee for Standardization and British Standard Institute (1993) classification, particulate matter is classified as inhalable (< 100 µm); thoracic (10 - 25 µm) and respirable particulates (0 – 10 µm).

To determine the particle size distribution of a solid sample the sample must be dried and sieved using sieves of smaller sizes other methods include laser diffraction. The laser diffraction technique has gained increasing popularity as the method of choice for particle size analysis as it is simple and rapid, yet accurate (Eshel et al., 2004; Rawle, 2005).

2.6.2 Vertical distribution

Vertical distribution of pollutants is a significant method used to assess the depth at which pollutants are being transferred from the topsoil to the lower layers of the soil. This method is carried out close to the source of pollution as emission of heavy metals pose a risk to biota and human health occupying the surrounding environment. Soil samples are collected from the upper layer, middle layer, and deep layer. In most instance the level of pollutants decrease with the increase of profile depth to lower most soil (Abdu et al., 2010). The presence of organic compounds, and macro-elements such as Fe and Mn in the soil also play a critical role in distribution of heavy metals in different layers. Mobility and bioavailability of heavy metals in soil profile depends on their bonds between organic compounds, Fe and Mg (Al-Mur et al., 2017). It is also important to investigate the factors that control the behaviour of heavy metals in soil such as the pH and electrical conductivity. The pH is generally the main factor governing the concentrations of soluble metals, and metal solubility tends to increase at lower pH and decrease at higher pH values (Brallier et al., 1996; Wang and Qin, 2005).

According to some studies, the lower layers of the soil can also contain elevated levels of heavy metals. For example, a soil profile study in Elin Pelin, Bulgaria Atanassov et al. (2015) reported that concentrations decrease along the soil depth with some elements, such as Zn, Cu, and especially Mn and Pb showing elevated contents in the middle part of the soil profile. Abdu et al. (2010) also reported higher concentrations of some heavy metals at lower profile depth. Apparently many investigation are conducted for the surface soil only. The previous studies were only focused on the total heavy metal contents in soil surface layer (Chen et al., 2005; Wang and Qin, 2005; Zhang et al., 2005). Therefore, studies that involves the vertical distribution of heavy metals are significant for monitoring and carrying out suitable remediation measures in order to minimise soil pollution around industrial areas.

2.6.3 Spatial distribution

Spatial distribution is sampling strategy that is used to assess human and ecological risk especially in urban areas with industrial emission to measure the amount of pollutants around the source of emission. It is also critical to understanding the spatial distribution of pollutants for environmental management (Raulinaitis et al., 2012). To describe these spatial structures, mapping based on geographical information systems (GIS) and geostatistical methods are useful approaches (Maas et al., 2010). The presence of pollutants and the potential sources are captured from the map created. The gathered information about the pollutants can be used by the environmental monitors to identify areas of concern, where risks are high and locations where remediation efforts should be focused. The success of assessment of pollutants using spatial distribution mostly in case of dust samples may depend upon the source of emission and the particle size. Particle size and anthropogenic influences were dominating factors controlling the spatial variations of heavy metals (Aprile and Bouvy, 2008). Few studies have been carried out in African towns although human demography and subsequent urban development would need spatially explicit development plans (Maas et al., 2010).

For example, In Annaba, the fourth largest city of Algeria, no spatial mapping of contaminated soils exists yet, although industrial activity is quite high in the city (Broutin, 2009), and the population continues to increase. In such cities, the identification of the different sources of contamination maybe particularly difficult, because those sources are numerous and located at different scales (Rodriguez Martin et al., 2006) and a geostatistical approach based on a large-scalefield study maybe useful to identify the different sources of soil contamination. As in the study of settled dust around the city Qingdao, China Xu et al. (2019) there were significant spatial distribution differences of heavy metals in settled dust, contents of Cu, Pb, Zn, Ni and Hg were higher in the old city areas due to human activities (Xu et al., 2019).

A study of agricultural soils around Zagreb, Croatia (Romic and Romic, 2003), the spatial distribution of metal trace elements concentrations was explained by various anthropogenic activities including urban traffic (Pb and Zn), local industrial contamination (Cd and Cr) and agriculture (Cu) (Maas et al., 2010). These methods are used commonly for urban development or risk assessment in European or North American cities. To prevent further environmental pollution in developing countries such methods are critical to sustainable development in the growing cities of Africa.

2.6.4 Partitioning of heavy metals in soil and sediments

Partitioning, or fractionation, refers to the distribution of heavy metals among the different binding phases of a complex substrate (Baeyens et al., 2003; Lin et al., 2003). Partitioning enables the complete extraction of metals bounded with different compounds. This method determines the bioavailability and mobility of the metals in the soil and sediments. Speciation of the metals involved is achieved by examination of the bonds the metals makes with the compounds in the soil or sediments. This is known as sequential extraction and the idea behind the method is that the selected extractant could stepwise liberate the metals associated with a specific substrate fraction. These include carbonates, iron-manganese (Fe-Mn oxyhydroxides), sulphides/organic material (these three fractions are known as the mobile forms) and the crystalline lattice (known as the non-mobile form) (Tessier et al., 1979; Tessier and Campbell, 1987; Eggleton and Thomas, 2004; Dominik et al., 2007). The mobile forms may be potentially available for uptake by plants and freshwater biota if released in their respective substrate fractions. The metals bound in crystalline structures and silicates, are not bioavailable, unless they undergo geochemical weathering (Forstner et al., 1986; Ayas et al., 2007).

2.6.5 Total metal analysis

Sample preparation is the most important step, when determining total metal concentrations with an analytical instrument for analysis in aqueous solution. Sample preparation consumes the largest share of time for any analysis, this technique has economic significance (Matusiewicz, 2003; Okoro and Fatoki, 2012). The reliability of the technique depends upon the reagents selected for extraction. In addition to the task of transforming the solid sample into an aqueous solution, the acid extraction technique suffers from limitations due to the fact that the fraction of the total metal extracted by any partial technique will depend on the reagent used (Sabra et al., 2011).

Aqua regia was used for extraction of heavy metals sediments and soil samples in this research. Aqua regia 1:3 (HNO_3: HCl) procedure is strong enough to extract metals associated with sediment and soil fractions.

Two methods that are normally used for digestion are microwave-assisted digestion and Open beaker acid digestion. Microwave-assisted digestion is a type of closed wet acid digestion procedure used in determining elements in a solid sample by transferring the analytes, into solution form (Matusiewicz, 2003; Sakan et al., 2011). In open beaker, acid digestion take place in an open beaker on a hot plate. Closed microwave digestion is faster, safe and reliable and can achieve higher temperatures than open beaker digestion. This makes closed microwave digestion to be the most preferred method.

2.6.6 Sequential analysis

Sequential extraction method is the most appropriate procedure for extraction of heavy metals in solid samples such as soil and sediments. Application of sequential extraction procedure provide more useful information about the bioavailability and mobility and transfer of heavy metals. The success of partitioning or fractionating heavy metals into specific fractions depends on the selected reagents. The metals in the fractions can be selectively extracted using the appropriate reagent and the metal concentrations are related to the extractant used instead of the simulated environmental conditions (Baeyens et al., 2003; Jain, 2004). Three-step extraction protocol was developed based on an acetic acid extraction in step 1, a hydroxyl ammonium chloride extraction in step 2 and a hydrogen peroxide attack followed by an ammonium acetate extraction in step 3 (Rauret et al., 2001). This three-step procedure was first tested in 1992 in an inter-laboratory trial in which the extraction was conducted on sediment samples from the Netherlands (Ure et al., 1993). Subsequent studies resulted in the improvement and validation of this protocol, as well as the preparation of certified reference material (CRM 601) for the three-step BCR protocol (Quevauviller et al., 1997). The three-step BCR protocol was then modified, in the late 1990s, from the findings of the validation of CRM 601, which had some discrepancies at the 95% confidence interval (Rauret et al., 2001). This modified procedure, along with the addition of the aqua regia stage, was used to certify the newly developed CRM 701 for lake sediments.

The aqua regia extracts were considered to be an important tool for internal control, and this is now the preferred protocol and CRM according to the European Community

Standards Measurement and Testing Programme (Rauret et al., 2001). Researchers have used some variation of the BCR protocol in their speciation studies (Yuan et al., 2004; Kartal et al., 2006). More recently, a fourth step was added to the BCR protocol, in which the residual (crystal lattice) is extracted by means of aqua regia (HNO_3/HCl; 1:3). The aqua regia acts a strong oxidising agent which is able to destroy the remaining minerals and resistant oxidisable material. The total concentration is obtained by summing the relative concentrations of the metal in the three steps and to that of the residual fraction.

2.6.7 Inductively coupled plasma-optical emission spectrometry

ICP – OES is an analytical technique that uses inductively coupled plasma as an excitation source. The “plasma” is a luminous volume of partially ionised gas (Skoog et al., 2004; Velez, 2009). ICP-OES is a type of emission spectroscopy that is based on the fact that atoms from different elements emit electromagnetic radiation at characteristic wavelengths. This allows for simultaneous, quick, accurate detection of a broad range of elements metals. It not only measures major macro-elements, but can also detect trace elements, therefore, a large number of samples may be analysed using ICP-OES. The most commonly used plasma gas is argon as it can simultaneously excite and ionise most elements (Huang et al., 2006).

Liquid samples are introduced by means of a peristaltic pump and then go through a nebuliser which forms a fine aerosol. The aerosol is transported to the centre of the plasma which decomposes the sample into atoms, at temperatures in excess of 7000°C. Some of the atoms are ionised and excited and electrons from the ground state are excited to vacant higher energy levels (Skoog et al., 2004). As they revert to their ground state the atoms they emit light at a wavelength characteristic to that element and this emission is measured with an optical spectrometer. The intensity of the emission has a direct relationship with the concentration of that element in the sample being analysed (Skoog et al., 2004; Huang et al., 2006; Ojeda and Rojas, 2007).

ICP-OES is a widely-used and robust trace element technique that provides accurate, precise results with low detection limits. Due to its multi-element capabilities, it is ideal for a large number of samples for routine analysis. ICP-OES requires minimal dilution, even in samples high in salt content (Skoog et al., 2004; Velez, 2009). However, the technique has its limitations. It consumes a larger volume of the introduced sample than other ICP techniques and cannot determine isotopic ratios. The absence of self-absorption in the argon plasma results in linear calibration lines over a large concentration range (Ojeda and Rojas, 2007).

Although the high temperature of the plasma reduces interferences, it cannot eliminate all spectral and non-spectral interferences (Dams et al., 1995). When electrons revert to their ground state an emission spectral line is generated. If the electrons move to more than one vacant energy level a series of spectral lines may be produced. A sample containing a number of different elements may then produce complex emission spectra (Dams et al., 1995; Skoog et al., 2004; Huang et al., 2006; Ojeda and Rojas, 2007).

2.7 Health risk assessment

Health risk assessment is used to establish the probability of adverse health effects in humans exposed to hazards chemicals in contaminated environments using both local and international levels (WHO). According to WHO guidelines, health risk assessment focusses on health hazard characterisation and health impact assessment. The health characterisation process involves the identification and assessment of the hazard in environment and its effects in the environment, its effects on the human health based on the evidence from epidemiology studies. The health impact assessment involves identification of expected population, the potential exposure pathways and estimation of contaminants intake for each pathway for range of scenarios and land use (Yalala, 2015). Table 5 below shows some of the maximum allowable limits (MALs) for elements in water, air and land as derived by Environmental Protection Agency (EPA), South African National Accreditation System (SANAS), and the Department of Environmental Affairs (DEA).

Table 5: Maximum allowable limits of different elements in different matrix

Elements	Matrix	MAL	Reference
Arsenic	Air	2	EPA/SANAS
	Soil	5.8	DEA/EPA
	Water	0.01	EPA/DEA
Cadmium	Air	0.02	EPA
	Soil	0.005	DEA/EPA
	Water	0.003	WHO/SANS/DEA
Cobalt	Air	0.05	EPA/SANAS
	Soil	50	DEA/EPA
	Water	0.5	SANAS/DEA
Chromium	Air	0.5	EPA/SANAS
	Soil	46000	DEA/SANAS
	Water	0.1	SANAS/DEA
Chromium (IV)	Air	0.001	EPA/SANAS
	Soil	6.5	SANAS/DEA
	Water	0.05	EPA/SANAS
Copper	Air	1	EPA/SANAS
	Soil	16	EPA/DEA
	Water	2.0	WHO/EPA/SANAS
Mercury	Air	0.1	EPA/SANAS
	Soil	0.93	EPA/DEA
	Water	0.006	EPA/SANAS
Manganese	Air	1000	EPA/SANAS
	soil	1000	EPA/DEA
	water	0.5	EPA/SANAS
Nickel	air	15	EPA/SANAS
	soil	91	EPA/SANAS
	water	0.07	WHO/EPA/SANAS
Lead	air	50	EPA/SANAS
	soil	20	EPA/SANAS
	water	0.01	WHO/EPA/SANAS
Antimony	air	500	EPA/SANAS
	soil	10	EPA/DEA
	water	0.02	WHO/EPA/SANAS
Selenium	air	200	EPA/SANAS
	soil	10	EPA/SANAS
	water	0.01	WHO/EPA/SANAS
Vanadium	air	50	EPA/SANAS
	soil	150	EPA/DEA
	water	0.2	EPA/SANAS

Units of concentration in air (μg kg^{-1}), soil (mg kg^{-1}) and water (mg L^{-1})

Chapter 3

3 Research objectives

This chapter gives the purpose and the main objectives of the study. The specific objectives, problem statement and general approach of the study are also presented.

3.1 General objectives

The general objectives of this study was to establish the concentrations of heavy metals such as manganese, nickel, arsenic, lead, platinum, ruthenium, rhodium, cadmium, palladium, zinc and chromium that are emitted with cement dust in the vicinity of cement factories in Thabazimbi and Pretoria in Limpopo and Gauteng provinces, South Africa.

3.2 Specific objectives

- To investigate the effectiveness of *Bidens Pilosa*, *Phragmites Australis and Xanthium Strumarium* plants within a wetland area's ability to remove heavy metals through phytoremediation from the Mvudi River (**paper I).**
- To extract nickel and chromium in soil and sediments using modified BCR sequential extraction and to determine their concentrations using samples of collected at different distances, soil depth and separated into different particles size fractions (**paper II**).
- To assess the level of heavy metals on streets dust using their spatial distribution on urban streets close to a cement plant in Pretoria (**paper III**).
- To determine the concentrations of platinum group metals in dust collected at various distance on a dust suppressed roadway close to a cement plant in Thabazimbi (**paper IV**).
- To evaluate the level of cadmium, chromium and manganese in edible parts of vegetables and fruits and soil, irrigated using contaminated water next to cement brick making factory (**paper V**).

3.3 Research questions

Why are the levels heavy metals analysed before, within and after a wetland area are different?
What is importance of determining the concentration of heavy metals in different soil depth, spatial distribution, different distances and different particle size fractions?
What is the importance of evaluating the level of heavy metals on a dust suppressed road and streets close to a cement plant?
What is causing the concentration of heavy meals in edible parts of fruits and vegetables and soil to exceed the permissible limits?

3.4 Hypothesis

The hypothesis of this study is that the samples collected from the cement brick making factory, cement plants will show high levels of heavy metals, which could be contributing to severe health problems. The concentrations of heavy metals are expected to be very high close to the cement plants than in residential areas. Samples of the finer particle size fraction will show high concentration of heavy metals.

3.5 General Approach

- Selected samples (soil, water, plants, vegetables and fruits and dust samples) were collected on the basis of the site to be investigated and sampling method to be used.
- Water samples were acidified with nitric acid for preservation and parameters such as pH, temperature, total dissolved solids (TDS) and electric conductivity (EC) were measured in the field.
- Plant, soil and sediment samples were left to dry until they reach a constant weight at room temperature in the laboratory
- Solid samples were converted into solutions using total metal digestion and modified BCR sequential extraction
- Obtained solutions were analysed using GF-AAS and ICP-OES techniques for the total concentrations of heavy metals
- Bulk samples were characterised with XRF and XRD

The overall flow chart of the general approach used for the five papers is shown in Figure 3.

Selected samples were collected next to a cement bricking making factory (**paper I-II-V**) and physico-chemical parameters of water were measured for **paper I-V**. Dust samples were sampled along the streets, tar road and gravel roadway next to a cement plant for **paper II-IV**. All samples were dried at room temperature after collection (**paper I-V**). Vegetables and fruits were microwave digested (**paper V**) and plants were digested with nitric acid and analysed with GF-AAS (**paper I**). Water samples were analysed with GF-AAS and ICP-OES (**paper I-V)**. Modified BCR sequential extraction was applied for the soil, dust and sediments samples to extract metals. Aqua regia digestion was also applied dust samples and analysed with ICP-OES (**paper II-IV**). Bulk samples for soil and dust samples were characterised with XRF and XRD.

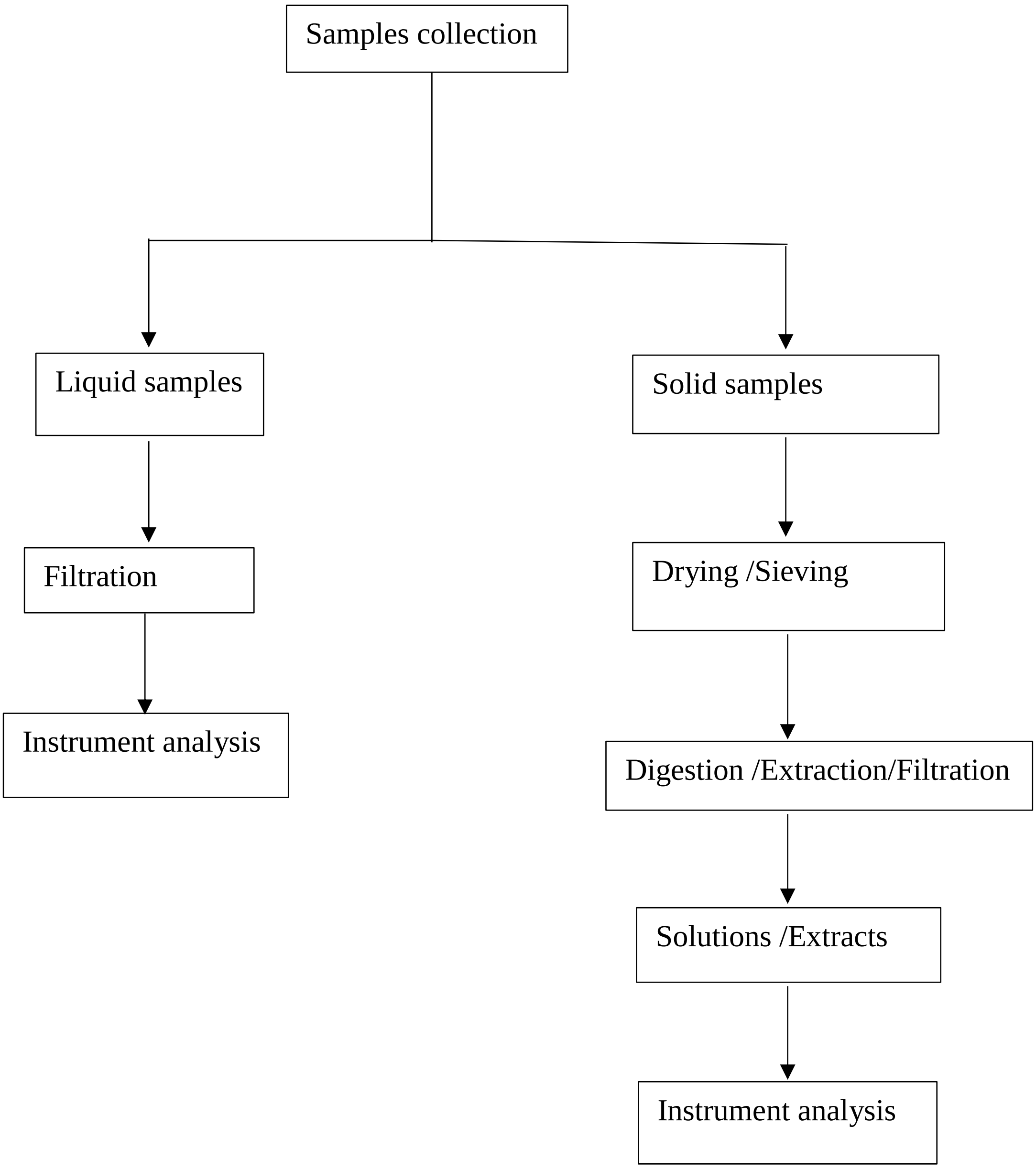

Figure 4. Schematic representation of the general approach.

Chapter 4

4 List of publications

This chapter lists all the five manuscripts submitted for examination. Each manuscript is formatted into the style as required by a particular journal. Note also that the reference styles are also different. **Papers I, II** and **V** have been submitted and are currently under review, whilst **paper III** and **IV** are a manuscript that will be submitted soon.

Paper I

This paper “Effectiveness of the wetlands to phytoremediation of selected heavy metals discharged from a cement brick making factory’’ evaluated the effectiveness of the plants within a wetland to phytoremediation of heavy metals and to show the role wetlands play on reducing water pollution**.**

Effectiveness of wetlands to phytoremediate selected heavy metals discharged from a cement brick making factory

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ABSTRACT

High concentrations of heavy metals in surface water remain a concern for developing countries as they threaten human life and the environment in general. This study was conducted to assess the levels of zinc, chromium and lead in the Mvudi River, located in Thohoyandou in the Limpopo province of South Africa. Due to recent development of using some plant species to remove contaminants such as heavy metals, plants were sampled for this study to assess the efficiency of phytoremediation. Phytoremediation is considered as one of the best technique for extracting heavy metals from a contaminated site. The surface water and plant samples were collected before, within and after a wetland area near a cement brick making factory. The samples were analysed to determine the concentrations of zinc, lead and chromium using an atomic absorption spectrometer. The results showed that zinc was the most concentrated metal in water and plants reaching a concentration of 4.52 mg kg^{-1} in the leaves of *Bidens pilosa* and 0.77 mg L^{-1} within the wetland. Chromium and lead were easily absorbed by the roots of the plants as showed by the significant decrease in concentration while moving into the wetland area. The highest concentrations of chromium in plants were 0.33 mg kg^{-1} in *Bidens pilosa* (leaves), 0.32 mg kg^{-1} in *Phragmites australis* (stem) and 0.41 mg kg^{-1} in *Xanthium strumarium* (stem). The standard deviation values were in the range of 0 to 0.41. Concentrations of zinc, chromium and lead in plants samples were found to be higher as compared to that of water samples and this shows that plants were absorbing large amounts of metals.

Keywords: Cement brick making, Heavy metals, Wetland, Wastewater, Phytoremediation

1. Introduction

South Africa is amongst the water scarce countries, therefore, it is very important to prevent pollution of water bodies around the country. The constitution of South Africa also state that safe water is the basic human right (Edokpayi et al. 2016). However, there are still people who do not have access to safe drinking water especially in rural areas (Heleba 2012). Surface water is still the primary source of water which can be used for the purpose of drinking, recreation, irrigation and industrial use (Edokpayi et al. 2016). The rivers continue to be polluted by the wastewater discharged from waste treatment factories, dumping of waste, industrial and agricultural activities (Gasana et al. 2002). Some of the pollutants are heavy metals which are very harmful to human beings and habitants in the rivers. Most of the pollutants may be attributed to the development of cities and towns.

Thohoyandou, in the Limpopo Province of South Africa, is one of the fastest growing towns in terms of infrastructure, hence there has been an increase in number of cement brick production plants to meet the demand of bricks. There is also an increase in number of people flowing into the town to access the modern shopping malls and high quality standard of living. Cement bricks may contain trace amounts of heavy metals such as arsenic, zinc, cadmium, antimony, lead and chromium (Achtembosch et al. 2003; VDZ 2000). This results from using raw ingredients which contain heavy metals such as cement, fly ash and aggregate (Amira et al. 2014; Achtembosch et al. 2003). Even though heavy metals are toxic at trace levels, their toxicity can be reduced in a wetland.

Wetlands are natural filters, helping to improve water quality of runoff water from the urban and agricultural lands by trapping pollutants. Wetland may contribute substantially to improving water quality by modifying or trapping a wide range of substances commonly considered to be pollutants (Bullock and Acreman 2003). Such pollutants include heavy metals emanating from industries, wastewater treatment plants and agricultural activities near rivers. Some wetland plants have the ability to remove small quantities of nutrients, trace metals and other compounds from the water and incorporate them into their tissue, which may later be recycled in the wetland through decomposition (Guslia et al. 2015). The selected plants *Bidens pilosa* and *Phragmites australis* are invasive plants except *Xanthium strumarium*, and can be found in a wetland. *Phragmites australis* is by far the most frequently used species for heavy metals analysis in the wetland, and probably the most studied macrophyte in natural wetlands. Phytoremediation evaluation studies of these plants as hyperaccumulators shows that they have high potential to bioaccumulate some heavy metals (Srivastava et al. 2013, Nariz et al. 2011).

Phytoremediation is a green emerging technology used to remove pollutants from environmental components (Laghlimi et al. 2015). Mechanisms used to remediate soils contaminated with heavy metal are: phytoextraction, phytostabilisation, phytovolatilization and rhizofiltration. The first two mechanisms are the most reliable (Laghlimi et al. 2015). The conventional soil remediation technologies have the advantage of immediately reducing the risk factors arising from metal contamination, but may only be considered temporary alternatives because the metals have not yet been removed from the soil environment (Chhotu 2009). However, conventional techniques are very expensive, reduce soil fertility and can damage the soil. Phytoremediation is an alternative process for removal of contaminants in the environment, and is sustainable, inexpensive and suitable for developing countries (Ghosh and Singh 2005; Cunningham and Ow 1996). Through phytoremediation, the environment is returned to its original state prior to contamination. After sufficient plant growth and metal accumulation, the above ground portions of the plant are harvested and removed, resulting in the permanent removal of metals from the site (Nandakumar et al.1995).

This study aims to assess the potential of selected wetland plants for their ability to remediate zinc, chromium and lead in the Mvudi River beside a cement brick making factory in Thohoyandou, South Africa. Studies in which the importance of wetlands as sources, sinks or transformers of dissolved solutes are uncommon, particularly in Southern Africa. Okonkwo and Mothiba (2005) found that there is inadequate knowledge and data on heavy metal concentrations in South Africa. This is one of the first attempts to assess heavy metals in the Mvudi River due to the influence of wastewater coming from a cement brickmaking factory in Thohoyandou. The outcome of this study will provide a baseline and data on heavy metals present in the Mvudi River as a result from cement brickmaking factory.

2. Materials and methods

2.1. Analytical reagents

Nitric acid (55%) used for digestion and acidification was purchased from Merck (Johannesburg, South Africa). All reagent stock solutions: 1000 mg L^{-1} stock solution of the metals salts of zinc sulphate, potassium dichromate and lead acetate 3-hydrate analytical reagent grade bought from Merck (Johannesburg, South Africa) were used to prepare standard solutions. Calibration curves were constructed for each metal ion to be tested and the correlation coefficients were determined.

2.2. Materials

A portable Multi-probe Boeco pH meter purchased from Rochelle (Johannesburg, South Africa) was used to take the pH, electrical conductivity (EC), temperature and dissolved oxygen (DO) of the water samples. Milli-Q for de-ionised water was purchased from Sigma Aldrich (Johannesburg, South Africa) was used for dilutions of all solutions. All glass and sampling water bottles used were first soaked in dilute HNO_3, thoroughly washed with liquid soap and then rinsed with de-ionised water and acetone. Thereafter, all glassware was dried in the oven at 100°C for 24 h, while the plastic were left to dry at room temperature and later used for water sample collection. Sieves from Rochelle (Johannesburg, South Africa) of different sizes were used to sort the dried plant powder samples into different size ranges. A refrigerator was used to store the samples at 4°C.

2.3. Instrument

A Perkin Elmer Pinaacle 900T Atomic Absorption spectrometer bought from Perkin Elmer (Johannesburg, South Africa) was used to analyse all the samples in the laboratory. Milli-Q water was used to blank the instrument before analysis. The auto-sampler cups were washed and rinsed using de-ionized water prior to use. Argon gas flow rate of (0.25 L min^{-1}) was used to protect and purge the graphite tubes during the furnace program procedures, and the data acquisitions were carried out using Syngistix for AA Spectra software. The absorbance of each metal was measured at appropriate wavelength using default instrument parameters for the GF-AAS. An amount of 20 µL of the working solutions was drawn into the graphite tube by the auto-sampler of the instrument and the absorbance readings were measured using a hollow cathode lamp at the appropriate wavelength for each metal: Zn at 216.86 nm (slit width 0.70 nm, lamp current 15 mA); Cr at 357.87 nm (slit width 0.70 nm, lamp current 25 mA) and Pb at 217.0 (slit width 0.70 nm, lamp current 13 mA). The heating programme for each metal was as follows: Zn (drying 110°C, ashing 700°C, atomisation 1800°C); Cr (drying 110°C, ashing 1500°C, atomisation 2300°C) and Pb (drying 110°C, ashing 850°C, atomisation 1600°C). All analyses were done in triplicate.

2.4. Sampling area

The Mvudi River in Thohoyandou (23.013 S, 30.2828 E) is a tributary of the Luvuvhu River, located in the north-eastern part of South Africa (Figure 1). The river is south of the University of Venda. It falls in the Lowveld of Limpopo Province, which forms part of the greater Limpopo River Basin with an elevation of 546 m above sea level (Edokpayi et al. 2015;

Mzezewa et al. 2010). It has a semi-arid climate, which is classified as humid subtropical with a subtropical dry forest biozone. Daily temperature in the catchment varies between 20 – 40°C (wet season) and 12 – 22°C (dry season) (Odiyo et al. 2012). The catchment average annual rainfall is about 800 mm, but it often varies between 340 mm and 2000 mm (DWAF 2003). The river is mainly used for domestic, recreational and agricultural purposes. Several land use activities in the river catchment that could constitute possible sources of pollution include agriculture, human settlements, schools, hospitals, solid waste disposal sites and effluents from wastewater treatment plants. Mvudi River is a major source of water to Nandoni dam (Edokpayi et al. 2016). The dam supplies water to the urban areas of Louis Trichardt, Thohoyandou and rural communities. However, on its course to Luvuvhu River it passes through a wetland around Maungani village. This is where wastewater from a cement brickmaking factory runs off into the river passing through the wetland. Fig. 1 shows a map of the cement the brick making factory, wetland and Mvudi River.

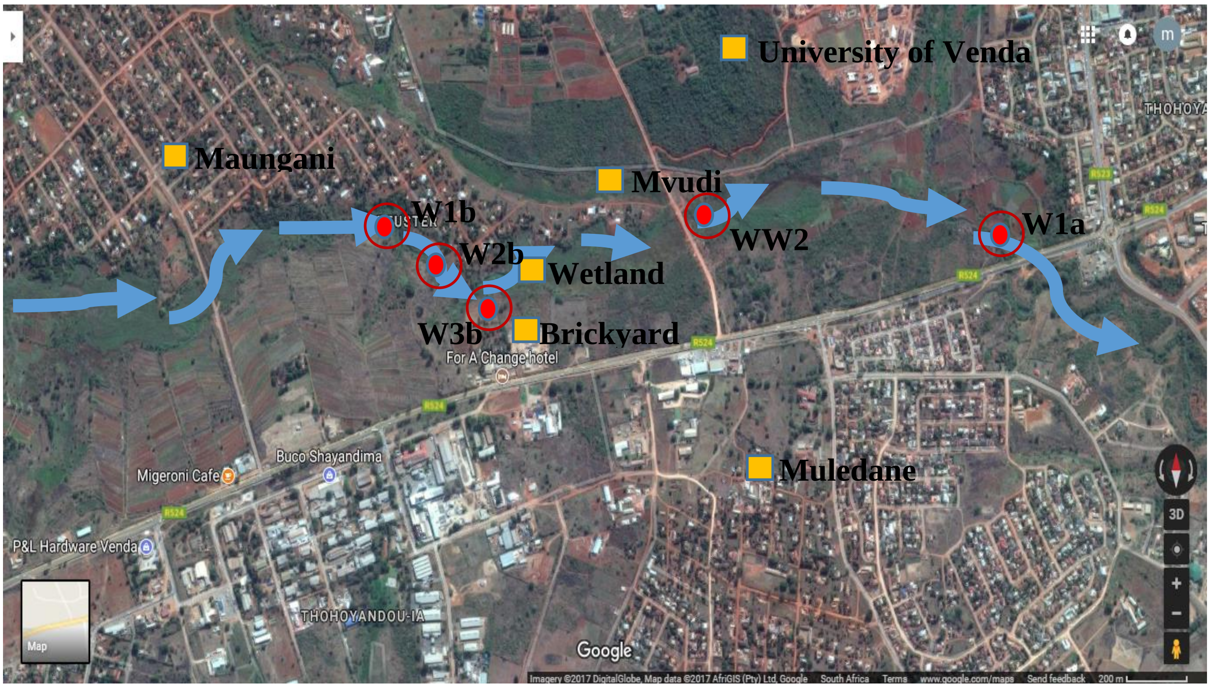

Fig. 1. Sampling site of water and plants samples encircled in the vicinity of a cement brickmaking company in Thohoyandou, South Africa.

2.5. Sample collection

The propylene containers were used for water sample collection. Before use, the propylene containers (500 mL) were first rinsed with the water samples and thereafter, immersed about

15 cm below the surface of the river. Water samples were collected at the river just before, within and after the wetland area, making a total of 5 samples and labelled according to the sampling site. The water samples were collected during summer season (wet and high flow). After collection, pH electrical conductivity, temperature and dissolve oxygen were determined in the field using portable measuring and data recording equipment. The samples for metal concentrations were acidified in the field with 5% HNO_3, to avoid microbial activity.

Three different plant species were selected and collected for the analysis of heavy metals of interest absorbed by the roots into their stem and leaves. Fig. 2 shows the pictures of the plants that were collected along the Mvudi River. The plants were later identified and characterised for their ability to absorb heavy metals at University of Venda (Botany department). The plants were collected, separated into leaves, stem and roots and dried at room temperature. The dried plants were then ground using a mortar and pestle and sieved through a size 2 mm sieve.

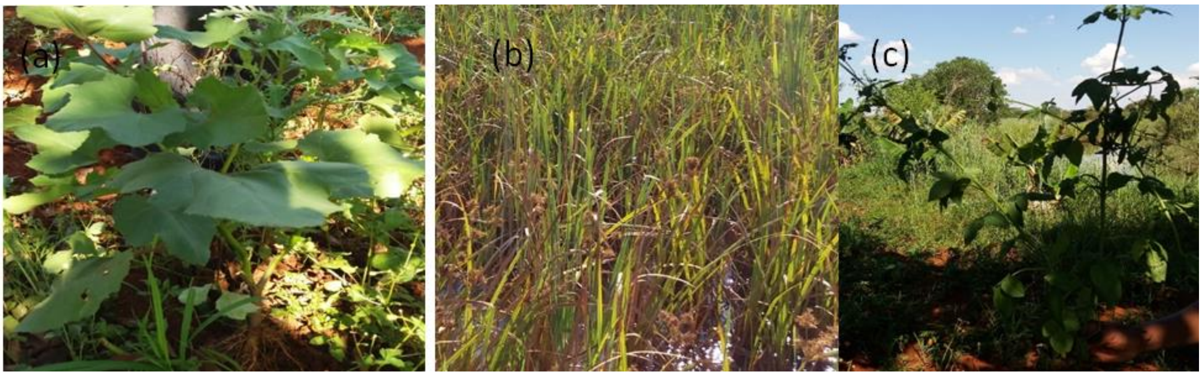

Fig. 2. Pictures of the sampled plants (a) *Xanthium strumarium*, (b*) Phragmites pustralis* and (c) *Bidens pilosa*.

2.6. Sample preparation

All water samples collected were preserved by being stored at 4°C. The samples were also centrifuged at 200 rpm for 10 min and filtered before analysis. The plant samples were washed with de-ionised water to remove any particulate deposited from the atmosphere and dried under room temperature, partitioned into three parts, namely root, stem, and leaves. These samples were weighed to find the initial weight and further dried until a constant weight for each part was obtained. The samples were cut into small pieces and grounded using porcelain mortar and pestle. A 0.2 g portion of each sample was transferred into a 250 mL beaker with 25 mL HNO_3 and heated to 80 – 100°C in fume hood. After heating for 20 min, the content of the flask was left to cool and later 10 mL of each sample solution was added to a centrifuge vial.

A 40 mL of de-ionised water was added to each solution in the centrifuge vial to bring the final volume to 50 mL. The centrifuge flasks were marked before determination of metals by GF-AAS.

3. Results and discussion

3.1. Physico-chemical parameters of the collected water samples

The pH values of the Mvudi River from the water samples collected were of the range 6.50 – 6.95 (Table 1). The highest pH value was after the wetland and the lowest pH value was just before the wetland. The pH values fell within the recommended limit 6 – 8.5 as set by the Department of Water Affairs and Forestry of South Africa (DWAF), and World Health Organisation (WHO) for domestic, recreational and agricultural water use. The pH plays an important role in the speciation and bioavailability of metals in the aquatic environment. A pH < 4 will increase the toxicity and bioavailability of most heavy metals (Edokpayi et al. 2015). At high pH > 9, heavy metals precipitate or adsorb to mineral surfaces and metal anions are mobilized (Evanko and Dzombak 1997; Takac et al. 2009).

The values of electrical conductivity (EC) usually gives an indication of the presence of dissolved ions in water and the presence of these ions can alter the taste of water and also contribute to the hardness of water. It also gives an indication of the total dissolved solids present in the water (Odiyo et al. 2012). Water with high EC values is not suitable for domestic purposes and irrigation as it can lead to the salinity of agricultural soils. The EC values (128.0-155.4 mS cm^{-1}) obtained in this study are within the water guidelines as set by DWAF (1996) and WHO (2011).

Temperature can exert great control over aquatic communities. Temperatures above 30°C are not suitable for benthic organisms such as clams, lobsters, crabs and other tiny organisms that live in the bottom sediments. High temperature may be lethal to these organisms. Open space and direct sunlight may have resulted in increased temperature of the water. The amount of sunlight absorbed by the water is controlled by shading of trees, water surface area, water volume, turbidity, streambed colour and orientation to the sun. The temperatures recorded were below 31°C (Table 1). Therefore this is good for organisms living in water.

Dissolve oxygen (DO) is a measure of the amount of oxygen dissolved in aqueous solution. The DO levels recorded were high for all water samples ranging from 76.4 to 94.8 mg L^{-1}. This indicated good water quality thus would sustain many sensitive aquatic lives (Gary 2013).

Table 1.

Water quality parameters from different samples of the Mvudi River.

Site	GPS coordinates	EC (mS cm⁻¹)	DO (mg L⁻¹)	pH	Temp (°C)
W1b	22.9847° S, 30.4350° E	128.0	76.4	6.74	24.3
W2b	22.9851° S, 30.4355° E	131.1	80.2	6.67	30.2
W3b	22.9856° S, 30.4360° E	129.8	78.1	6.50	27.8
WW2	22.9834° S, 30.4432° E	136.0	83.8	6.53	26.7
W1a	22.9835° S, 30.4536° E	155.4	94.8	6.95	27.4

Note: W1b = first water sampling point before the wetland, W2b second water sampling point before the wetland, W3b third water sampling point before the wetland, WW2 water sampling point within the wetland and W1a water sampling point after the wetland.

3.2. Concentration of heavy metals in water samples from the Mvudi River

Fig. 2 shows the concentrations of zinc, chromium and lead in water samples from the Mvudi River. These concentrations in water samples clearly indicate that there are anthropogenic sources nearby influencing the presence of heavy metals within the wetland area. The zinc concentrations in water samples ranged between 0.13 to 0.77 mg L⁻¹. The highest concentration of 0.77 mg L⁻¹ was observed within the wetland and there was no concentration which was above the permissible limit of zinc in all water samples of 5 mg L⁻¹ according to standards set by WHO (1991) and DWAF (1996). The presence of zinc may have been caused by some anthropogenic activities towards the wetland, possible sources include the brick making factory and sewage water from the nearby communities. It is also possible that the low cost houses rooted with corrugated sheets around Maungani and other rural communities may have contributed to the determined zinc level (Okonkwo and Mothiba, 2008). The concentration of chromium in water samples varied between ND to 0.06 mg L⁻¹. The level of chromium was very low just before the wetland (W3b) and after the wetland (Wa). The highest concentration of chromium was 0.06 mg L⁻¹ at the first sampling point (W1b). However, chromium with a low concentration of 0.01 mg L⁻¹ was determined within the wetland. A low concentration within the wetland (Ww) may be attributed to phytoremediation by some plants, such as *Xanthium strumarium*, *Phragmites australis* and *Bidens Pilosa*, within the wetland area. The maximum permissible limit of chromium in water is 0.1 mg L⁻¹, the values of Cr detected in all water samples were below the permissible limit. The level of lead ranged between 0.01 to 0.08 mg L⁻¹.

It is quite clear that the concentration of lead decreased moving downstream. Some plants may have accumulated lead entering the wetland area because it can easily be absorbed by the roots and by the sediments. According to the WHO standard, the permissible limit of lead in water is 0.05 mg L^{-1} and in all the collected water samples, it was above the permissible limit only before the wetland.

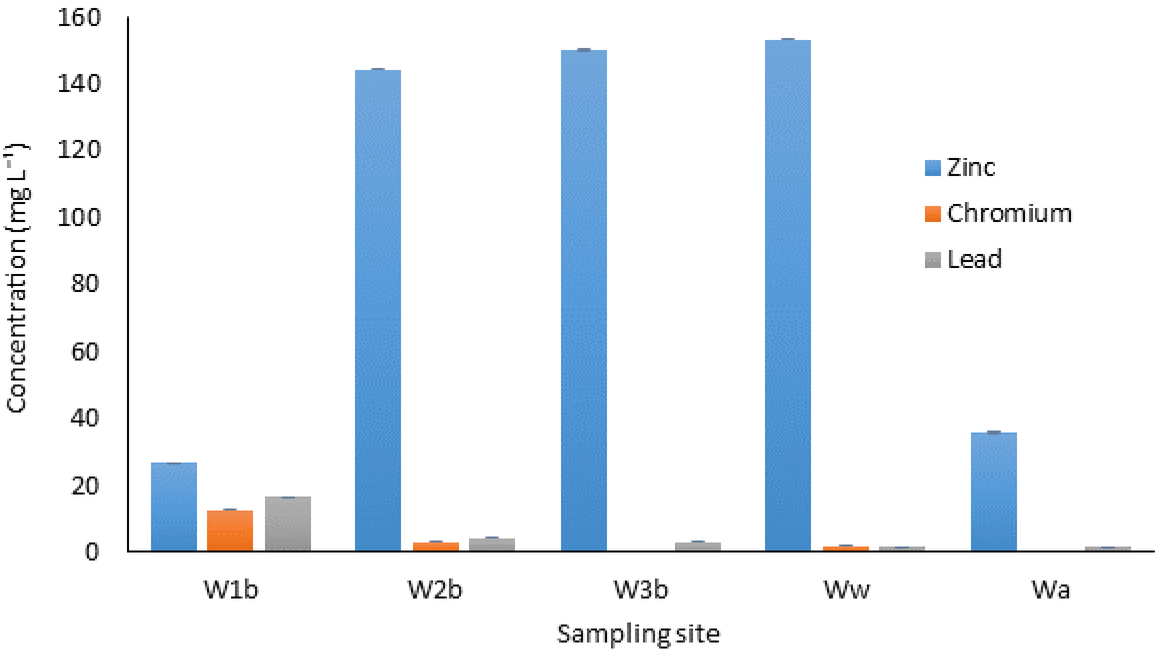

Fig. 3. Concentrations of Zn, Cr and Pb in water samples from the Mvudi River (SD, n = 3).

3.3. Percentage weight loss due to dehydration in selected plants

Plants contain some amount of water which can be released during dehydration to the surrounding. This process occurs when the sample is dried after collection. The amount of water lost due to dehydration can be calculated using Eq. 1.

$$\% \text{ weight loss due to dehydration} = \frac{Co-Ce}{Co} \times 100 \qquad (1)$$

where co (g) is the initial weight of the sample and ce (g) is the weight after dehydration. The reported percentage weight loss due to dehydration shows that stems from three plants had the highest water loss during the drying process as compared to their leaves and roots (Table 2). This might mean that the stems carry more water than leaves and roots because water moves slowly within the stem. The trend was observed for all three plants in this study. *Phragmites australis* was the only plant collected in all three plant sampling points.

Its percentage water loss for leaves and stem during the drying period were also the lowest than all other values calculated. Plant samples showed the following trend; the leaves had the lowest weight loss followed by the roots and the stem with the highest weight loss. This trend was evident for all three different plants with *Xanthium strumarium* having the highest water loss than other plants.

Table 2.

% Weight loss due to dehydration for the plant.

Plants	% weight loss to dehydration		
	Leaves	stem	Roots
W3b			
Bidens pilosa	13.0	43.1	16.5
Phragmites australis	4.4	71.0	
Xanthium strumarium	4.7	63.8	43.5
Ww			
Bidens pilosa	7.4	56.0	21.2
Phragmites australis	2.2	62.1	
Xanthium strumarium	26.5	67.5	46.2
Wa			
Phragmites australis	1.3	15.7	

3.4. Concentrations of heavy metals in plants samples

Zinc is one of the important trace elements that plays a vital role in the physiological and metabolic process of many organisms. Nevertheless, higher concentrations of zinc can be toxic to the organism (Nazir et al. 2015). The concentration of zinc in *Bidens pilosa* parts ranged between 0.04 to 4.52 mg kg^{-1} (Fig. 4). The highest concentration of 4.52 mg kg^{-1} was observed in the leaves within the wetland. There was an increase of zinc level in all parts of the plant moving along the Mvudi River, from the point of discharge to within the wetland area. All the zinc concentrations exhibited for plant were very high compared to recommended limit of 0.60 mg kg^{-1} according to WHO standards except for roots 0.04 mg kg^{-1} before the wetland. This showed that zinc can easily be absorbed by the roots to the shoots of the *Bidens pilosa* and eventually bio-accumulate in the leaves. It is clear that there are human activities contributing to the subsequent increase of zinc level going into the wetland area. The possible activities may include brick making, sewage water and agricultural activities.

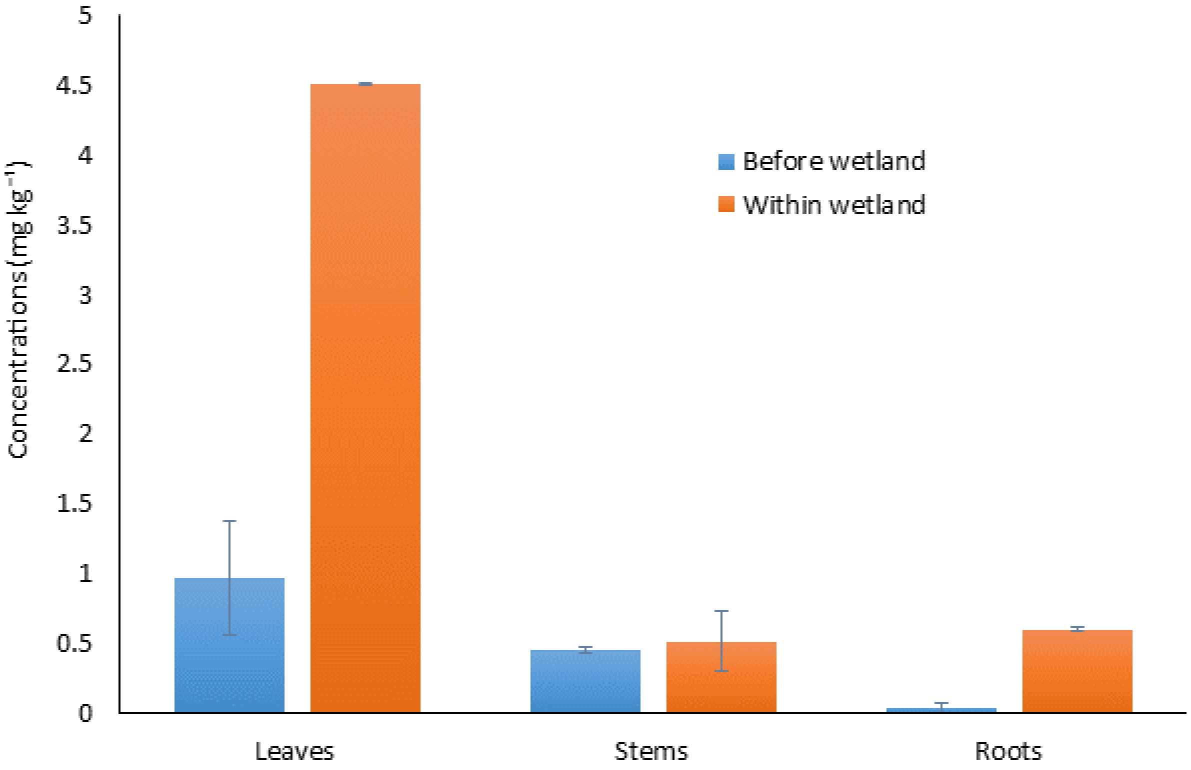

Fig. 4. Concentrations of zinc in *Bidens pilosa* parts before and within the wetland (SD, n = 3).

As illustrated by Fig. 5, zinc levels in *Phragmites australis* were between 0.003 to 1.93 mg kg^{-1} and were high above the permissible limit of set by WHO except for 0.003 mg kg^{-1} for the stems after the wetland. The value 1.93 mg kg^{-1} of the leaves was the highest found and it was recorded after the wetland. Previous studies reported high concentrations of heavy metals very substantially between stems and leaves with leaf concentration being often higher. Such a high concentration may be attributed to other sources after the wetland. After the wetland, the concentration of zinc in the stem decreased to 0.003 mg kg^{-1} due to unavailability of zinc. This is probably due to the effectiveness of the *Phragmites australis*in the wetland to phytoremediate zinc.

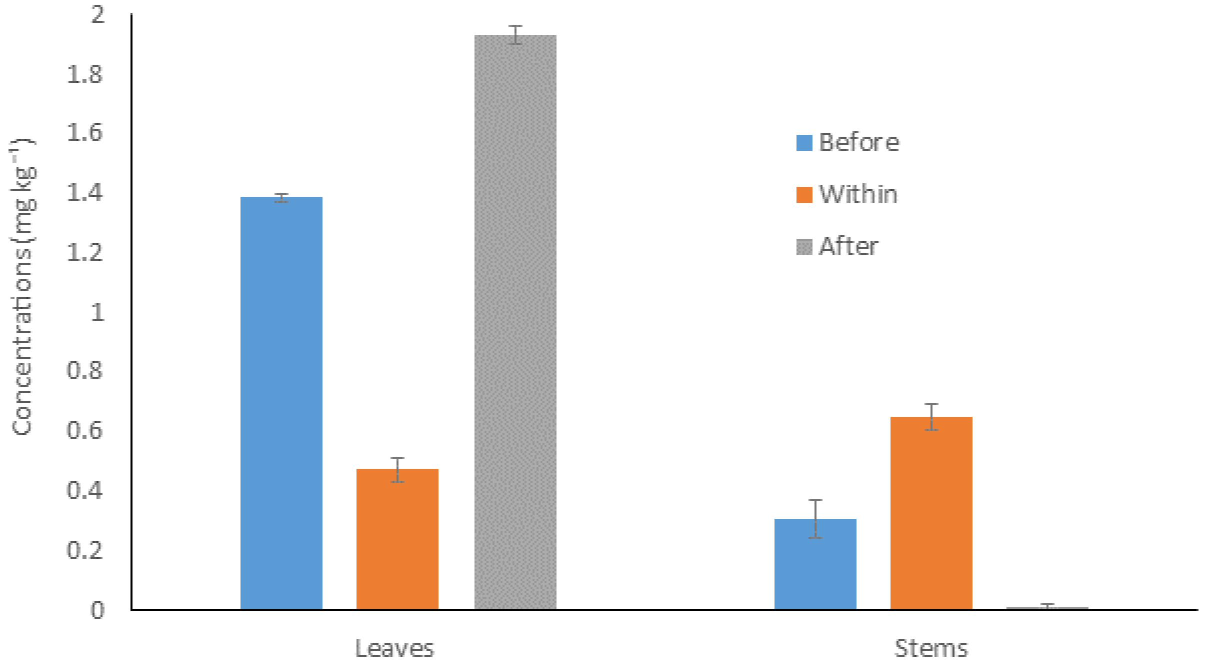

Fig. 5. Concentrations of zinc in *Phragmite australis* parts before, within and after the wetland (SD, n = 3).

The levels of zinc in *Xanthium strumarium* (leaves, stems, roots) are represented in Fig. 6. The concentration of zinc in *Xanthium strumarium* ranged between 0.73 to 4.73 mg kg^{-1} from before to within the wetland. The concentrations of zinc in different parts of this plant species were all above the WHO recommended limit. The trend from the graph depicted a decline of concentration from before the wetland to within the wetland and after the wetland. Variety of plants competing for zinc within the wetland may be the cause of this decline.

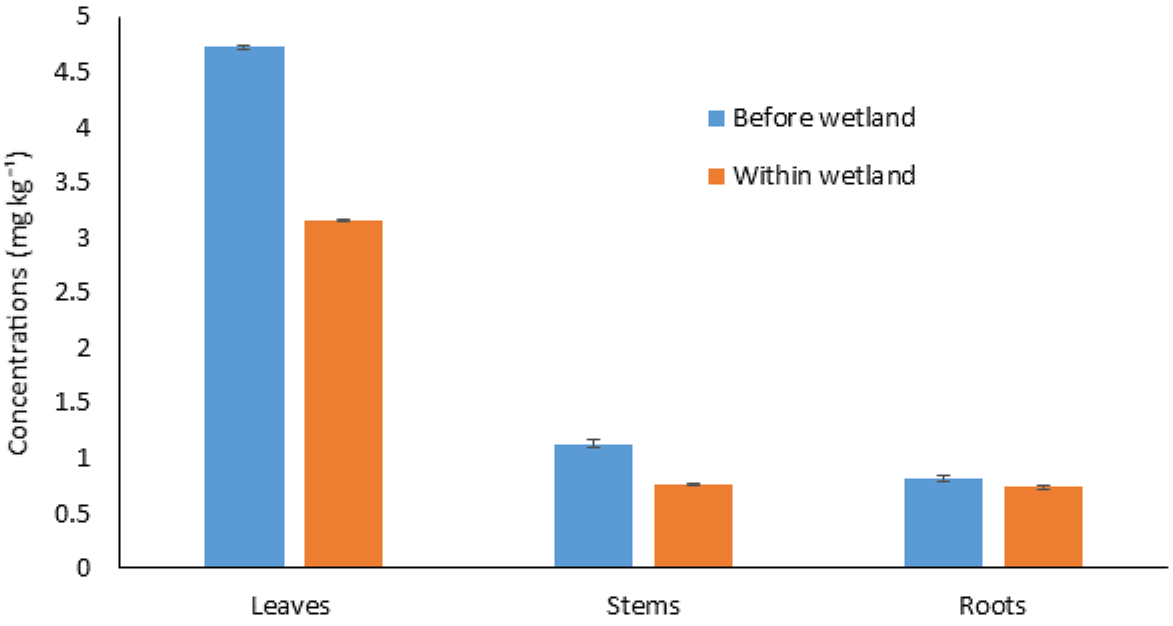

Fig. 6. Concentrations of zinc in *Xanthium strumarium* parts before and within the wetland (SD, n = 3).

The concentrations of chromium in *Bidens pilosa* parts are shown in Fig. 7. The permissible limit for chromium in plants is 1.30 mg kg^{-1} as recommended by WHO (1996). The concentration of chromium in *Bidens pilosa* varied from 0.03 to 0.33 mg kg^{-1} with the leaves within the wetland having the highest concentration. All chromium concentrations were below the permissible limit. The increase in *Bidens pilosa* level of chromium, depicted that the metal was absorbed by the roots to the leaves. This can be contributed to human activities discharging chromium to the river. A possible source of chromium is the cement brick making factory and sewage water from the rural and urban areas.

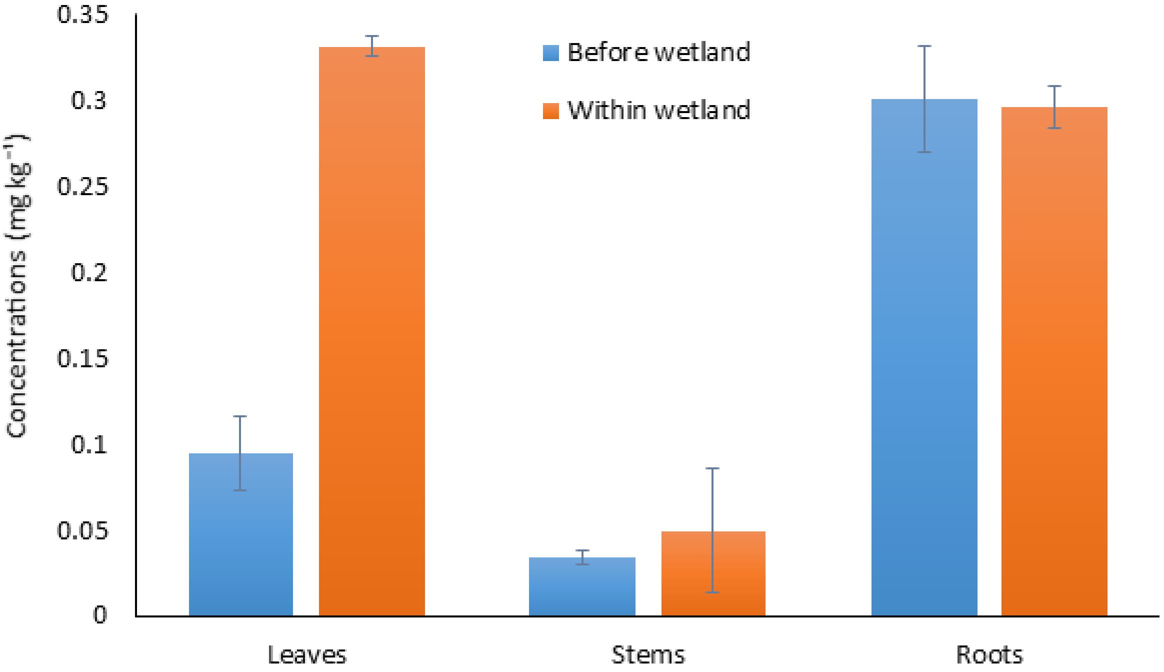

Fig. 7. Concentrations of chromium in *Biden pilosa* parts before and within the wetland (SD, n = 3).

As shown by Fig. 8, the concentration of the chromium in *Phragmites australis* ranged between 0.07 and 0.32 mg kg^{-1} with the stem having the highest concentration after the wetland. The concentrations recorded were below the permissible limit. High concentration of chromium in the stem after the wetland may be as a result of construction at the University of Venda and agricultural activities going on along the Mvudi River where a lot of cement containing heavy metals was being used.

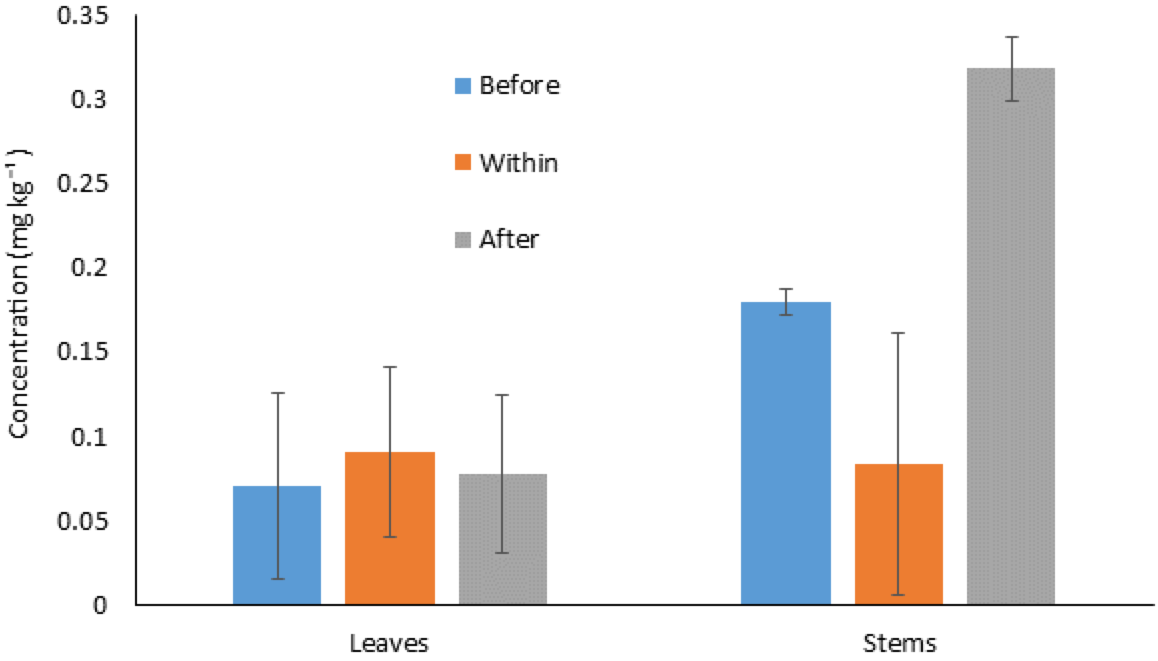

Fig. 8. Concentrations of Chromium in *Phragmites australis* parts before within and after the wetland (SD, n = 3).

Chromium levels in *Xanthium strumarium* are represented in Fig. 9. Chromium concentration in *Xanthium strumarium* varied between 0.07 and 0.41 mg kg^{-1} and the concentrations recorded were found to be below the permissible limit of 1.3 mg kg^{-1}. The levels of chromium in the plant may be attributed to the waste entering the water during leaching from the cement brick making factory.

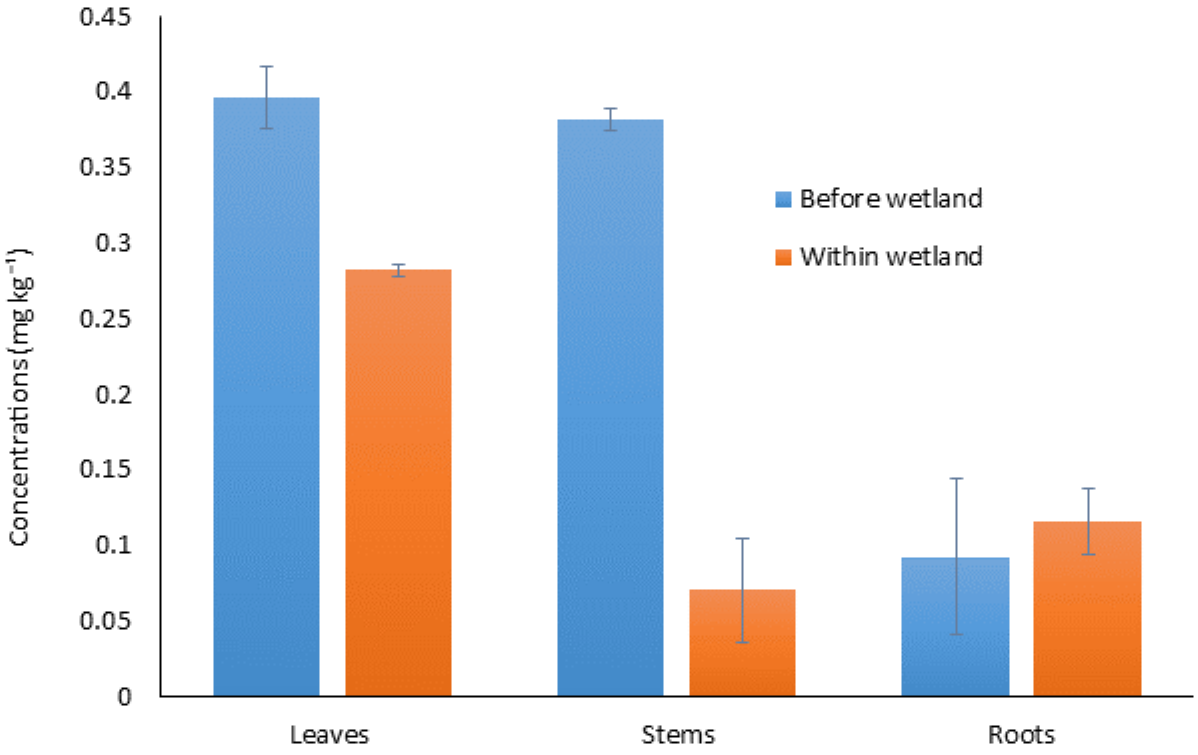

Fig. 9. Concentrations of chromium in *Xanthium strumarium* parts before and within the wetland (SD, n = 3).

In *Bidens pilosa* lead concentration varied between 0.01 to 0.04 mg kg^{-1} going to the wetland as shown in Fig. 10. The highest concentration of lead was recorded in the leaves within the wetland. According to WHO recommendations, the permissible limit of lead in plants is 2 mg kg^{-1}. In *Bidens pilosa*, the concentration of lead in the leaves and the stems was high whilst in the roots it was below the permissible limit. This shows that the lead can easily be absorbed by the roots but weakly transported to the shoots of a plant. A study by Okonkwo and Mothiba (2005) revealed that high concentrations of Pb in Mvudi River may have been influenced by the effluent from a nearby sewage treatment plant and a waste dumping site. Also the agricultural activities around the rivers may have contributed to the observed high levels of lead levels, since these metals can occur as impurities in fertilizers and in metal-based pesticides and compost and manure. The use of alkyl lead compounds such as anti-knocking agents in fuel might also be the main reason for elevated levels of Pb in the plant (Atayese et al. 2009; Suzuki et al. 2009). The cement brick making factory next to the wetland area may have contributed large amounts of lead observed in this study. Runoff from road sides and bricks industries around the river are possible sources of heavy metal contamination (Edokpayi etal.2016).

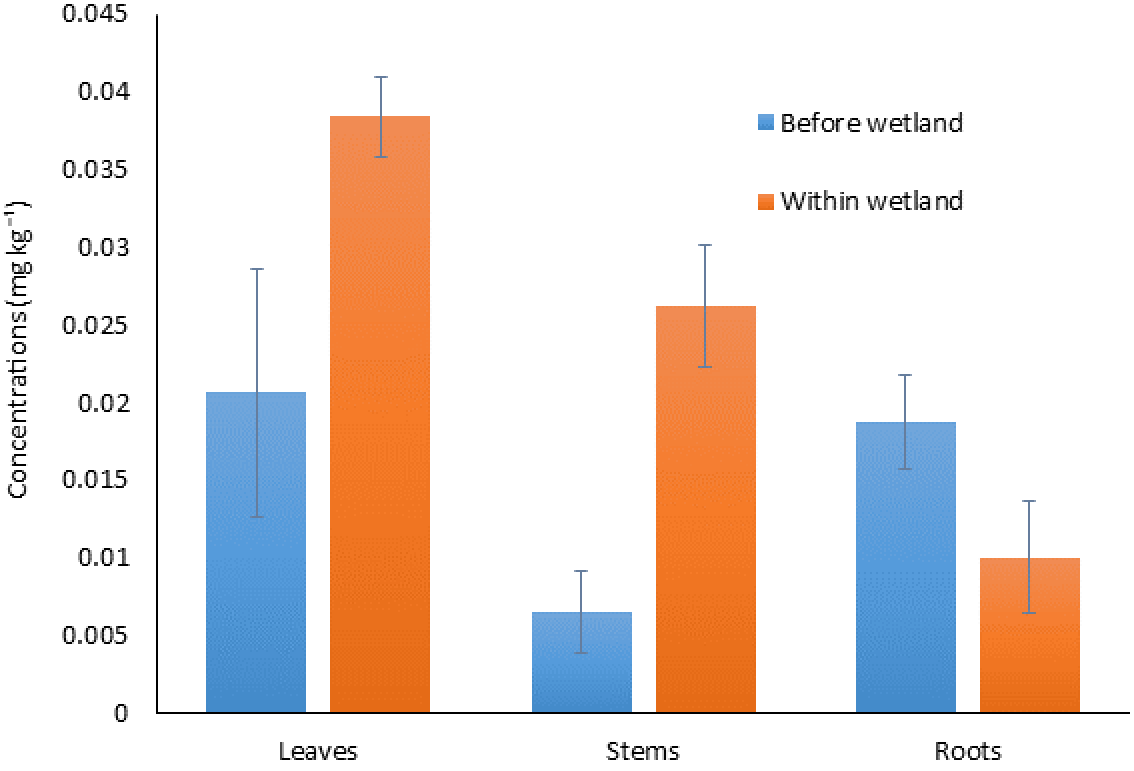

Fig. 10. Concentrations of lead in *Bidens pilosa* parts before and within the wetland (SD, n=3).

4. Conclusion

The main purpose of this research was to conduct an assessment of heavy metals focused on establishing the levels of zinc, chromium and lead, and evaluating the efficiency of some plants within a wetland in removing heavy metals around the Mvudi River. The concentrations of lead and chromium in water samples decreased going downstream while zinc concentrations increased. Most concentrations of zinc recorded were higher than the permissible limit for plants, while the recorded concentrations of chromium and lead were below the permissible limits, as set by WHO in plants and water samples. The highest concentrations of the selected heavy metals were found in plants. This implied that there was absorption of heavy metals by the roots of some plants within the wetland. Most of the high concentrations of zinc, chromium and lead in the selected plants were found within the wetlands. Therefore, large amounts of metals were absorbed by the selected plants within the wetland. The leaves contained majority of the heavy metals. This showed that plants within the wetland have the ability to effectively accumulate heavy metals. The runoff from road sides, panel beater, brick making industries, agricultural activities and road pavements to the Mvudi River are the possible sources of heavy metal contamination.

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Paper II

This paper “Determination of heavy metals in soil and sediments using modified BCR sequential extraction procedure around a cement brick making factory in Thohoyandou, South Africa’’ demonstrate the distribution of heavy metals emanating from a cement brick making factory to the surrounding environment.

Determination of heavy metals in soil and sediments using modified BCR sequential extraction procedure around a cement brick making factory in Thohoyandou, South Africa

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ABSTRACT

Assessment of heavy metals in the environment is significant for sustainable development in a developing country like South Africa. The purpose of this study was to determine the concentration of Cr and Ni in the soil and sediment samples, and to explain their possible sources. In this study, the distribution of Ni and Cr in various particle size fractions, sediments along the Mvudi River, distance from the pollution source, soil profile fractions and bulk soil was investigated. Modified community bureau of reference (M-BCR) sequential extraction method was applied to both soil and sediments samples to obtain the metal distribution. The content of Ni and Cr in the soil and sediments samples were measured by graphite furnace atomic absorption spectrometry (GFAAS) instrument. The concentrations of the Ni and Cr with distance moving away from the brick making factory ranged as follows; 100.06 – 165.78 mg kg^{-1} and 214.55 – 310.81 mg kg^{-1}, respectively. Elevated Cr level at site S6 (310.81 mg kg^{-1}) showed that the supplements applied in the agricultural land in the area influenced the level of Cr in soil. These results at various distances showed that most of the high contents of Ni and Cr were found very close to the brick making factory. Depth analysis of Cr and Ni concentrations in soil ranged from 228.17 – 365.36 mg kg^{-1}and 93.18 – 230.45 mg kg^{-1}, respectively. Results revealed that high metal contents were in the lower layers of the soil. Fractionation of Ni and Cr demonstrated the predominance of high contents in the residual fractions with ranges of 72 – 81% and 77 – 82% than in the non-residual fractions 4 – 23% and 0.54 – 20%, respectively. The high level of metals distributed in finer fractions can be attributed to the high surface area of the particles.

The level of Ni and Cr in sediments decreased from upstream to downstream and lowest levels were observed in the wetland area due to the plants uptake of the metals within the wetland. It was concluded that the presence of the brick making factory might be increasing the level of metals in soils and the sediments.

Keywords: Soil and Sediments Pollution · Heavy Metals · Cement Bricks · Modified BCR Sequential Extraction

1. Introduction

Rapid urbanisation and industrialisation in developing countries has caused serious contamination of the soil and sediments. Unlike in developed countries, the demand for economic, agricultural and industrial development outweighs the importance of environmental protection and it's conservation. This negligence by developing countries has been accompanied by considerable environmental pollution with necessary need for intervention. Currently, most data on heavy metals in African countries are as a result of regional investigations that have been limited to the area around the source of the heavy metals (Aguilar et al. 2002, Ikenaka et al. 2010). Heavy metal pollution has not yet been controlled effectively because anthropogenic activities are increasing, especially in developing countries. There is therefore concern around the world about the release of heavy metals and the behaviour of heavy metals in the environment (Yan et al. 2018). Exposure to toxic heavy metals such as Cr and Ni can cause wide variety of health problems.

Studies have shown that heavy metal contamination is mostly caused by industries, agriculture, wastewater discharge, domestic sewage discharge and atmospheric deposition (Yan et al. 2018). However, in many instances of environmental pollution, hot spots of heavy metal with high concentrations are found to be in industrial areas. Cement brick making industry is one of the small scale industry that is growing rapidly because cement bricks are now more favoured than the clay bricks. There is also an increase in demand for brick production because of the economic development and growing population in small towns such as Thohoyandou in Limpopo province, South Africa. Some of these cement brick making factories are found in sites that are close to water sources. The cement brick making industry is associated with pollution through the use of cement which contains heavy metals incorporated during its production (Achtembosch et al. 2003). This makes cement brick industry considered to be one of the environmental polluters. Cement contains metals such as Cd, Ba, As, Cu, Pb, Ni, Co, Cr and Mn (Achtembosch et al. 2003).

Excess of these metals in the environment can be a threat to the plants, animals and human beings. High quantities of Ni can cause diseases associate with lung, liver, and kidney damage. Ni can also result in cancer, respiratory failure, birth defects, allergies, dermatitis, eczema, diseases of nervous system and heart failure (Arora et al. 2017). Cr can lead to allergic cancer dermatitis in humans, bleeding of the gastrointestinal tract, cancer of the respiratory tract, and ulcers of the skin (Arora et al. 2017). The dust emanating during the production of the cement bricks can settle on the soil and sediments through atmospheric deposition. When it rains, wastewater from the factory is washed to the soil, sediments and water bodies. The environment becomes contaminated with heavy metals that have been accumulated by the soil, sediments and water bodies.

The assessment of the sediments is important in determining the level of pollution in water bodies and in identifying the possible source of pollution. Heavy metal contaminations in sediments could affect the water quality, the bio-assimilation and bioaccumulation of metals in aquatic organisms, resulting in potential long-term effects on human health and ecosystem (Snodgrass et al. 2008; Besser et al. 2009; Ip et al. 2007; Suthar et al. 2009; Lix et al. 2012). Soil is a major sink for heavy metals released into the environment by aforementioned anthropogenic activities (Wuana et al. 2011; Kirpichtchikova et al. 2006). The total amount of trace metals in the soil is controlled by significant factors including pH, Eh, composition and amount of organic matter in the soil, clay mineral content, salt concentrations, anion and cation complexing agents, and presence of Fe/Mn/Al oxides and hydroxides (Hursthouse, 2001; Horckmans et al. 2007; Wali et al. 2014).

South Africa is a developing country where advocacy over environmental protection is not well prioritised like economic development. There are no strict enforcements that have been put into place for industries that do not comply with recommended permissible limits of heavy metals. Environmental organisations are the ones that pressurise the industries to comply with the existing recommended limits. Soils and river sediments can be used in South Africa to measure the severity of environmental contamination.

In this study, the soil and sediments were used to assess the impact of heavy metal contamination in the environment discharged from a cement brick making factory. Several studies entail that, in polluted environment systems, sediments and soil have been increasingly recognized as the most important sink for contaminants and as a reservoirs and possible future sources of pollutants. The impact of heavy metals contamination emanating from cement brick making factories has not been extensively studied in South Africa, particularly in areas where the factories are near rivers.

It is therefore important to obtain basic information about the level of heavy metals contamination in the environment, especially in areas where industries are the possible source of pollution. Heavy metals contamination in soil may lead to the contamination of crops and river water which can cause reduction of crop production around the Mvudi River in Thohoyandou, South Africa. High levels of heavy metals in the Mvudi River which is a tributary to Nandoni dam may lead to health concerns with regard to the water which is being used by the communities around the area, as most of the water is supplied from Nandoni dam. This study seek to provide valuable information about the level of heavy metals in soil and sediments, the degree of contamination, as well as potential environmental and human health risks.

2. Materials and Methods

2.1. Analytical reagents

Chemicals for digestion and acidification H_2O_2, HCl, $NH_2OH{\cdot}HCl$, CH_3COONH_4, CH_3COOH and HNO_3 were purchased from Merck (Johannesburg, South Africa). $NiSO_4 (H_2O)_6$ and $K_2 Cr_2O_7$ salts of analytical reagent grade were bought from Merck (Johannesburg, South Africa).

2.2. Materials

Mesh sieves (3 mm, 2 mm, 1 mm and 500 µm) bought from Lasec (Johannesburg, South Africa) were used to sort the samples of soils and sediments into different sizes. A refrigerator bought from Labtech (Johannesburg, South Africa) was used to store the samples at 4.0°C. CNW water bath thermostatic vibrator purchased from Lasec (Johannesburg, South Africa) was used to mechanically shake the samples in 50 mL centrifuge vials. An MRC centrifuge purchased from Retsch (Johannesburg, South Africa) was used to separate the residue and the supernanted in the vials. A pH meter used to adjust the pH of the samples during the preparation of the samples for analysis was bought from Lasec (Johannesburg, South Africa). Distilled water was used to zero the instrument before analysis and for dilution of all solutions.

2.3. Instrument

The Perkin Elmer Pinaacle 900T atomic absorption spectrometer (AAS) bought from Perkin Elmer (Johannesburg, South Africa) was used to analyse all the samples in the laboratory. Perkin Elmer hollow cathode lamps were used to analyse the concentration of heavy metals. Calibration curves were constructed for each metal to be tested and the correlation coefficients were checked. Triplicate analysis method, which is an effective method for determining the precision of an analysis was used in this study.

2.4. Sampling area

The study area consists of the cement brick making factory, surrounding surface soil and the river sediments in the Mvudi River. It falls in the Lowveld of Limpopo Province of South Africa which forms part of the greater Limpopo River Basin with an elevation of 546 m above sea level. The study area also falls within Thohoyandou town in Vhembe district. Vhembe climate is typically subtropical with mild, moisture and wet, warm summers characterised by Lowveld (Arid and semi-arid (Poto and Mashela, 2008). Daily temperature in the catchment varies between 20 – 40°C (wet season) and 12 – 22°C (dry season).

The catchment average annual rainfall is about 800 mm, but it often varies between 340 mm and 2000 mm. The river is majorly used for domestic, recreational and agricultural purposes. Several land use activities in the river catchment that could constitute possible sources of pollution include agriculture, human settlements, schools, hospitals, solid waste disposal sites and effluents from Muledane wastewater treatment plant. Mvudi River is a major source of water to Nandoni dam. Which supplies water to the urban areas of Louis Trichardt, Thohoyandou and the surrounding rural communities. Due to intense cement brick making, there is atmospheric deposition of dust around the factory. When it rains, wastewater from a cement brick making factory run off to the surrounding environment. The soil is used for maize fields and small vegetables gardens. Fig. 1 shows the cement brick making factory and the entire study area.

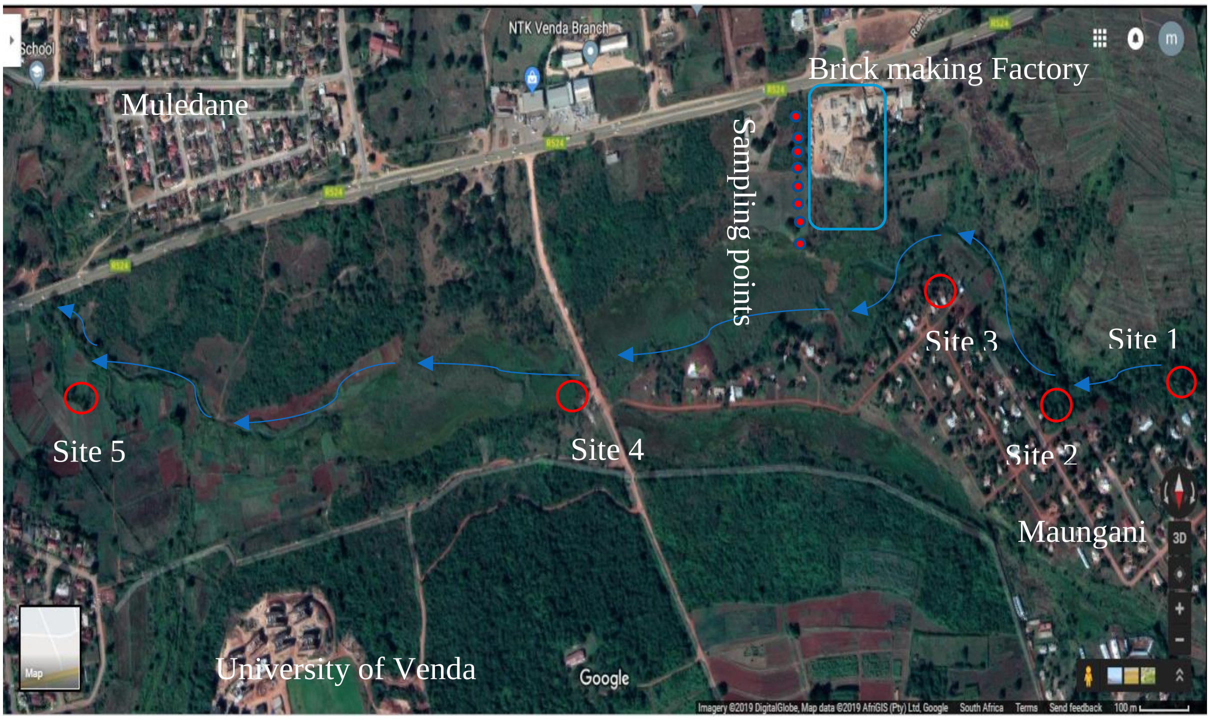

Fig. 1. Sampling sites (encircled in red) for sediments and (red dots) for soil samples in the vicinity of a cement brick making company in Thohoyandou, South Africa

2.5. Sample collection

Soil samples were collected and put in zip plastic bags, one large sample was collected just close to the factory and seven other soil samples were collected at different depths (0, 5, 10, 15, 20, 25 and 30 cm) and also collected at 5 cm below the soil surface on various distance moving towards the Mvudi River from cement brick making factory. Five sediments samples were also collected along the Mvudi River from before the wetland, within the wetland and after the wetland. GPS coordinates were also taken at each sampling point (Table 1). The samples were stored at 4°C before analysis.

Table 1

Sampling sites and GPS co-ordinates representing the geographical location of the sampling points.

Sampling sites	GPS coordinates
S1	22.9863° S, 30.4389° E
S2	22.9862° S, 30.4388° E
S3	22.9861° S, 30.4389° E
S4	22.9859° S, 30.4389° E
S5	22.9858° S, 30.4389° E
S6	22.9856° S, 30.4389° E
S7	22.9855° S, 30.4388° E
W1b	22.9847° S, 30.4350° E
W2b	22.9851° S, 30.4355° E
W3b	22.9856° S, 30.4360° E
Ww	22.9834° S, 30.4432° E
W1a	22.9835° S, 30.4536° E

Note: S1-S7 are sampling points at different distances from the cement brick making factory, W1b = first water sampling point before the wetland, W2b second water sampling point before the wetland, W3b third water sampling point before the wetland, WW2 water sampling point within the wetland and W1a water sampling point after the wetland.

2.6. Sample preparation

The soil and sediments samples were air dried at room temperature until constant weights were obtained. The bulk sample was sieved through sieves of the size (3 mm, 2 mm, 1 mm, 500 µm). The soil samples at different depth, at different distances and sediments samples were sieved through 1 mm sieve. From each sample, 1 g was weighed and added into a 50 mL centrifuge vials. The samples in the vials were prepared for analysis with a modified BCR sequential extraction procedure which involved three main steps described by Nemati et al. (2011) and Davutluoglu et al. (2011), and a fourth step as added by Rauret et al. (1999). The BCR sequential extraction stages can be summarised as follows; Step 1, the extraction of metals associated with carbonates and are weakly bound at cation exchange sites in the matrix; step 2, the extraction of metals associated with Fe and Mn oxides; step 3, the extraction of metals associated with organic matter and sulfides; step 4, the extraction of rmetals found in mineral lattice of the soil (Rumah et al. 2017). The exchangeable fraction is easily removed and used by organisms, whereas the reducible and oxidizable fractions can be solubilised depending on the physical and chemical parameters, such as the oxygen content, Eh, charges, salinity, and bacterial activity (Yap et al. 2006; Wali et al. 2014).

In the first step (exchangeable), the exchangeable and soluble fractions were extracted.

A portion of each sample mixed with 40 mL of 0.11 M acetic acid solution in a mechanical end-over-end shaker at 30 rpm at room temperature for 16 h. The extract was separated from the solid residue by centrifugation at 3000 rpm for 20 min and collected in centrifuge tubes. The residue was washed by shaking for 15 min with 20 mL of deionized water and centrifuged for 20 min at 3000 rpm.

In the second step (easily reducible oxides), the reducible fraction was extracted. A volume of 40 mL of 0.5 M hydroxyl ammonium chloride solution was added to the residue from the first step, and re-suspended the mixture by mechanical shaking for 16 h at room temperature. The acidity level of this reagent was adjusted to pH 1.5 with HNO_3. The extract was separated, and the residue was washed in the same manner as described in the first step.

In the third step (organic matter), the oxidizable fraction was extracted. A 20 mL solution of 8.8 M H_2O_2 was cautiously added to the residue from the second step and heated the mixture for 1 h at room temperature in 100 mL beakers on a single big hot plate for 1 h at 85 ± 2 °C in a fume hood. The volume was reduced to less than 3 mL. A second aliquot of 20 mL of H_2O_2 was added to the mixture, which was digested for 1 h at 85 ± 2 °C until the volume of the residue reached 2 to 3 mL. The residue was mixed with 50 mL of 1 M ammonium acetate solution, adjusted to pH 2 with HNO_3 and shaken for 16 h at room temperature. The extract was separated, and the residue was washed in the same manner as described in previous steps.

In the fourth step (residual), the residual fraction was extracted. The analysis of the residue was performed using aqua regia for metals insoluble in the previous steps. In this step, 20 mL aqua regia solution was prepared for each extract acquired from each extraction stage from previous step in a 250 mL beaker. After adding aqua regia solution to the beaker containing a residue, the solution was evaporated to near dryness on a hot plate covered with watch glass in a fume hood. A 20 mL solution of 2% HNO_3 was added to the extract in the beaker after digestion. The extract was filtered through a Whatman No. 42 filter paper into 100 mL volumetric flask and filled to the mark with deionised water. GF-AAS instrument was used to determine the concentration of extracted of Ni and Cr in the solutions from each of the three extraction steps of the BCR method, as well as that of the acid attack of the residue.

2.7. Distribution factor (DFx) calculation

In order to estimate the size fraction to which heavy metals are preferentially enriched, distribution factor (DFx) was calculated by use of Eq. 1 (Acosta et al. 2009)

$$DF_X = \frac{X_{fraction}}{X_{bulk}} \tag{1}$$

where X_{fraction} and X_{bulk} are contents (mg kg^{-1}) of heavy metal in a given fraction and bulk sample, respectively.

3. Results and Discussion

3.1. Concentration of Ni in soil and sediment samples

The concentrations of Ni obtained by the BCR sequential extraction are shown in Fig. 2(a). The availability as well as the mobility of the metals decreased in the order: exchangeable fractions > reducible fractions > oxidizable form > residual form. This is consistent with the findings made by Rumah et al. (2017) and Sunguret et al. (2014). The total concentrations recorded for the samples taken at various distances moving away from the source of pollution varied between 96.06 – 154.67 mg kg^{-1}. Ni concentration observed decreased gradually with increasing of distance from the source of pollution. This trend shows that the brick making factory was the main source of Ni polluting the soil. Low concentrations of Ni were recorded in the exchangeable and reducible fractions and predominantly recorded high in the oxidizable and residual fractions. This showed that the Ni was less mobile and bioavailable for plants uptake. Rumah et al. (2017) also reported similar findings for Ni.

Ni concentrations in depth analysis are shown Fig. 2(b). The results for depth analysis were determined for 0 – 30 cm and showed that the concentration of Ni increased with depth from the topsoil to lower most soil. The concentration of Ni at different layers varied from 93.18 – 230.45 mg kg^{-1}. The depth from 0 – 5 cm layer showed the highest concentration of 230.45 mg kg^{-1} followed by 121.94 mg kg^{-1} in depth (10 – 15 cm). This might be due to the percolation of Ni from the topsoil to the subsoil layer.

Fig. 2(c) shows the Ni concentrations recorded for sediments from the Mvudi River. The concentrations of Ni in the sediments varied between 104.08 – 204.15 mg kg^{-1}. The results showed that the concentrations decreased from the upstream to the wetland area and increased after the wetland. The highest concentration was at the first sampling point W1b before the wetland area because much of soluble Ni is partitioned into the sediments rather than water.

This shows that there was other source influencing the concentration of Ni in the sediment apart from the brick making factory. Such source may be agricultural activities and wastewater coming from nearby households around the area. The lowest amount of Ni was observed within the wetland area.

This might be as a results of wetland plants bio-accumulating Ni from the sediments in the river. The amount of Ni which could be exchanged by water showed that the Mvudi River could be at a risk of being polluted.

Ni concentrations obtained from different particle size are shown in Fig. 2(d). The concentration of Ni in different particle sizes showed a range of 197.55 – 221.00 mg kg^{-1}, where the 221.00 mg kg^{-1} was observed in the smallest particle size < 0.5 mm. The level of Ni increased with the decrease in the particle size. This results showed that most of Ni was held in finer fractions. Organic carbons in finer fractions are biologically stable, and hence heavy metals in this fraction are considered more persistent and harmful to the environment (Abdulfatahet al. 2009; Acosta et al. 2011; Semlali et al. 2001). These results agreed with earlier reports on preferential partitioning of metals to fine particle size fractions in soils (Al-Rajahi et al. 1996; Ljung et al. 2006; Acosta et al. 2009). With their findings that metals tend to accumulate in small particles due to high surface areas and negative charges associated with fine particles, especially on expanding types of clay minerals (e.g., smectite and vermiculite) and organic matter. The values of distribution factors DFx of the particle size fractions were as follows; 2 – 3 mm (0.69), 1 – 2 mm (0.68), 0.5 – 1 mm (0.69), and < 0.5 mm (0.76) which also showed that high concentrations of the metal were preferentially found in the smaller particles. This high amount of Ni indicated that fine particle size fractions of soils in this study may serve as major sink for metals. Analysis of the bulk also showed that the top soil is highly contaminated with Ni reaching a level of 289.0 mg kg^{-1}.

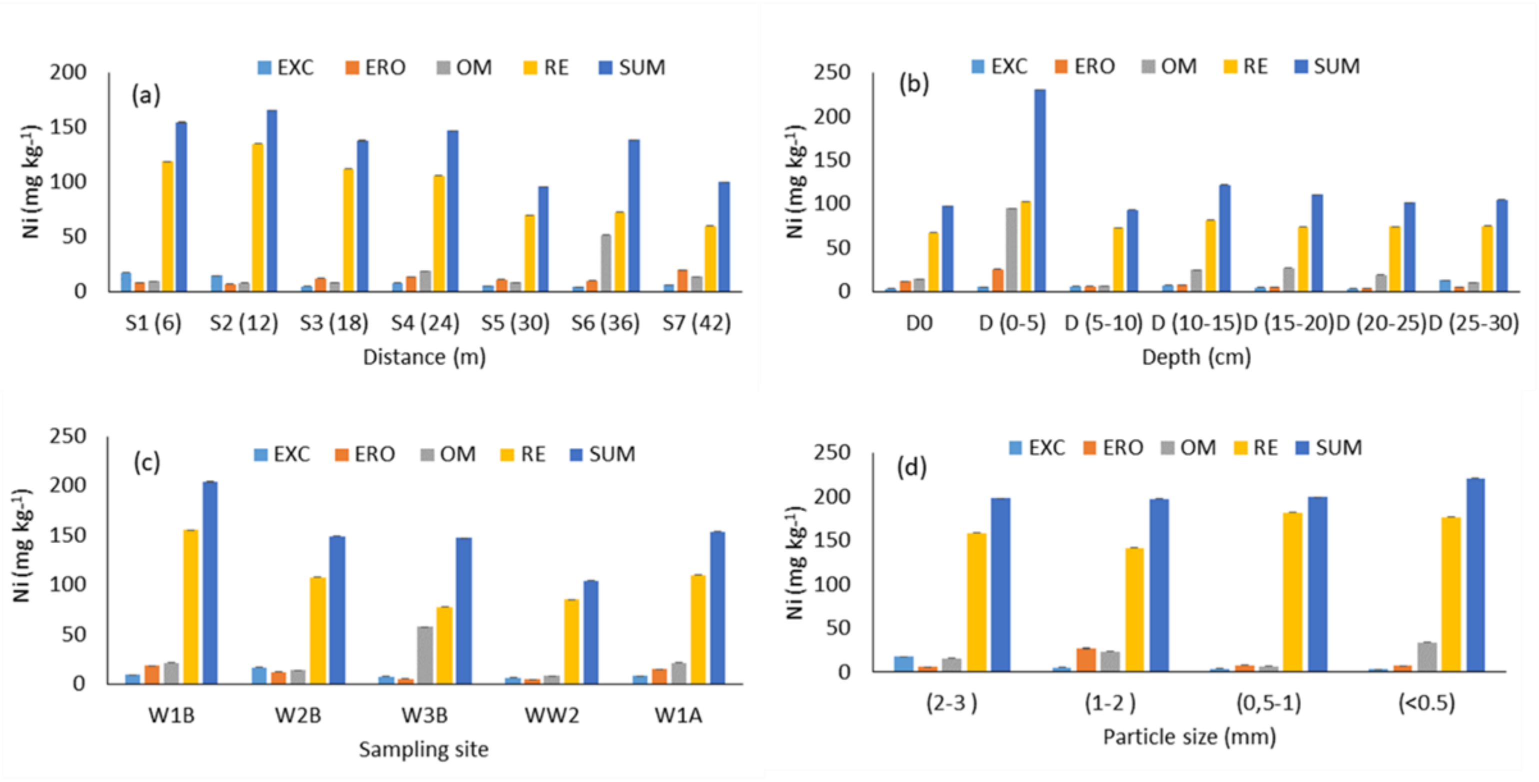

Fig. 2. Concentrations of Ni obtained in the four steps (exchangeable, reducible, oxidation, residual) of the BCR and the sum of extracted for (a) distance (b) depth (c) sediment and (d) particle size evaluations (n = 3).

3.2. Concentrations of Cr in soil and sediments samples

Concentrations of Cr extracted with BCR sequential extraction are in shown Fig. 3(a). Cr concentrations at different distance from a brick making factory varied between 214.55 – 310.81 mg kg^{-1}. Generally, the content of Cr decreased with the increase of distance from the pollution area. The highest concentration of 310.81 mg kg^{-1} at a farm 36 m away from the brick making factory might have been caused by the use of fertilizers when enhancing crop production. A significant amount of Cr recorded at a sampling point close to the factory showed that the brick making factory is the main source of Cr polluting the surrounding area. This was also shown by high amount in exchangeable fraction with the first two samples (S1 and S2) collected closest to the factory. High concentrations were recorded for residual fractions than non-residual fractions which implies that the Cr is less mobile and bioavailable for uptake by the plants. Other studies also made the same findings (Li, Q, 2012; Wali et al. 2014; Cuong and Obbard, 2006).

Fig. 3(b) shows Cr concentrations in depth analysis. The concentrations of Cr recorded for depth analysis in 0 – 30 cm varied from 228.17 – 365.36 mg kg^{-1}. The general trend observed from the results showed that the values increased with depth from top soil to the deeper soil. The general patterns observed in this area may be attributed to downward migration of the metal from a cement brick making factory while the bulk enrichment in the soil profile may be caused by the enrichment of organic matter content with depth in the soil.

Concentrations of Cr in the sediments are represented by Fig. 3(c). The concentration of Cr in sediments along the Mvudi River varied between 277.48 – 344.84 mg kg^{-1}. The highest concentration was recorded at the sampling point (W1a) before the wetland. Arora et al. (2017) reported that Cr can be transported by surface runoff waters in its soluble or precipitated form and ultimately deposited into sediments. This suggested that the high amount of Cr in the sediments were as a results of runoff from the factory to the surface water then into the sediments. The concentration recorded within the wetland area was the lowest due to accumulation of the metal by plants such as *Bidens pilosa*, *Phragmites australis* and *Xanthium strumarium* which were dominant plant species in the wetland. Cr in exchangeable fraction showed that there could be a possible pollution caused by the amount of metal which can easily dissolve in water. Although this amount was small, this could be an environmental risk point as the water is used for irrigation and by human beings in the surrounding communities. Metal fractionation showed that major portion of the metal was found in the residual fraction, indicating that this metal was strongly bound to the sediments (Davutluoglu et al. 2011).

Distribution of Cr in different particle sizes is shown by Fig. 3(d). The total concentration of Cr in particle size distribution observed for the bulk sample showed a range of 313.08 –356.04 mg kg^{-1}. The observed Cr concentrations in particle size fractions were almost the same. The distribution factors DFx of the particle size fractions were as follows; 2 – 3 mm, (1.06) 1 – 2 mm (1.09), 0.5 – 1 mm (0.96) and < 0.5 mm (1.04). These DFx values showed that the high level was in the large particles. The particle size fraction of 1 – 2 mm contained the highest amount of Cr as compared to other sizes. Cr concentration in the bulk sample also showed high level as those recorded in different particle sizes.

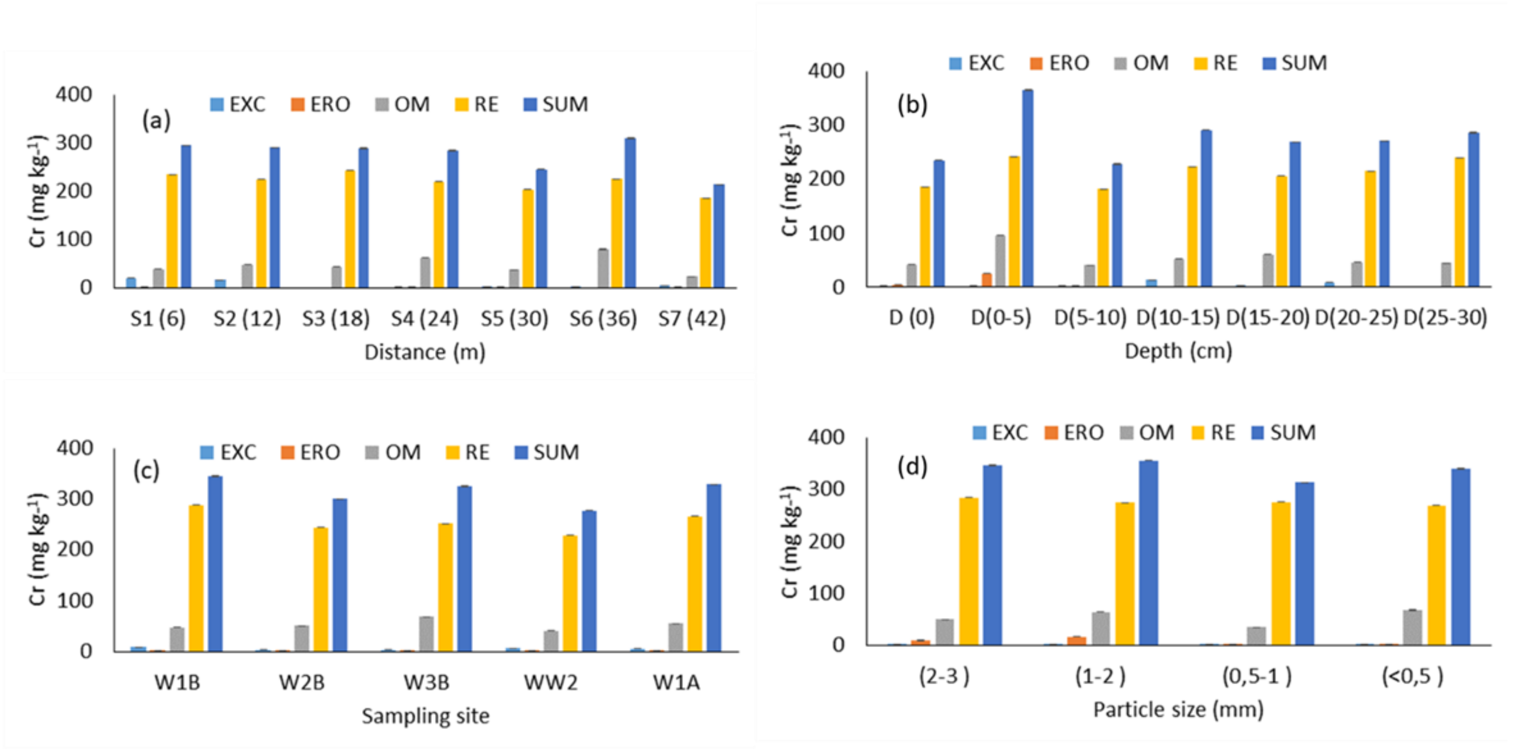

Fig. 3. Concentrations of Cr obtained in the four steps (exchangeable, reducible, oxidation, residual) of BCR and the sum of extracted for (a) distance (b) depth (c) sediment and (d) particle size evaluations (*n* = 3).

The distribution of Ni in extracts of BCR sequential extraction and digests of the residual phase using particle size of 0.5 mm and depth of 10 cm are represented in Fig. 4(a). The percentage of the metals extracted in each step was expressed as a fraction of the total metal content. Ni availability as well as the mobility of the metal decreased in the order: exchangeable fractions > reducible fractions > oxidizable fraction > residual fraction. Ramirez et al. (2005) also reported similar results. The highest amounts which could be bioavailable and mobile were observed for Ni contents at different distance with 7% in exchangeable and 9% in reducible fractions. The lowest Ni amount bioavailable and mobile were observed for particle size distribution with 6% exchangeable and 4% reducible. Ni concentrations in residual fractions were greater than 60% in all different samples. Similar results have also been reported by Martin et al. (1999), Davutluoglu et al. (2011) and Favas et al. (2011). A highest percentage of 81% was observed in the residual fraction of the particle size distribution samples. This might be due to the surface area of the smallest particles negatively charged attracting many metal ions.

Fractionation of Cr in soils by means of the BCR sequential extraction is shown in Fig. 4(b). Low Cr percentages for availability and mobility with respect to exchangeable and reducible fractions were observed. Generally, the availability as well as the mobility of Cr decreased in the order: exchangeable fractions > reducible fractions > oxidizable fraction > residual fraction. The lowest amounts were observed in the particle size and sediment samples were only 0.5% (EXC) and 0.6% (ERO). Highest amounts were in the residual fractions in all samples with the residual fraction of particle size sample as high as 82%. The moderately high percentages of the oxidizable (organic bound) fraction indicated the strong ability of the heavy metal to form complexes with organic matter thereby reducing its mobility and phytotoxicity (Kashem et al. 2007). High amounts of Cr with a mean of 72% were observed in the residual fractions. This suggested that most of Cr was strongly bound to minerals and other materials in the residual fraction (Wali et al. 2014). The results of the extraction indicated that Cr was mainly bound, and immobilized, in a mineral lattice of the sediments. Cr fractionation for the sediment showed a high content in residual fraction (RES and OM) than in non-residual fractions (EXC and ERO). This result was consistent with the distribution of Cr in the sediments of Taihu Lake in China (Yuan et al. 2004).

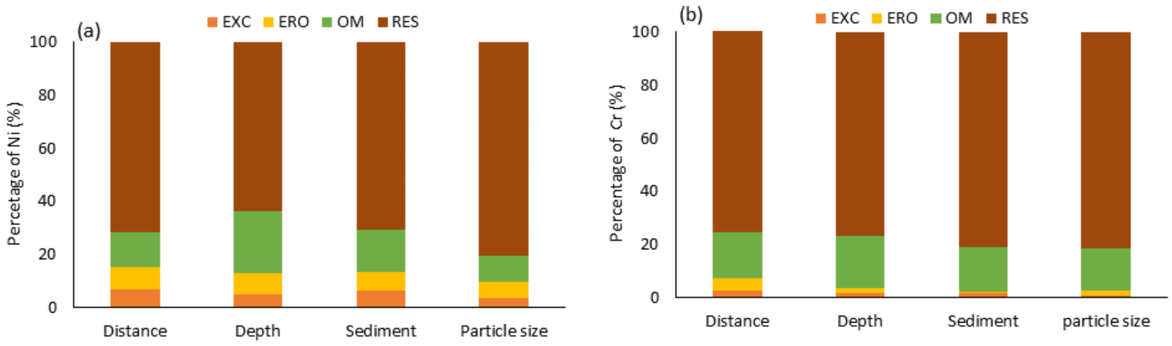

Fig. 4. Extractability order of the metals in each extraction stage of the BCR sequential extraction procedure and residual phase for (a) Ni and (b) Cr concentrations in soil and sediment samples.

Fig 5(a) shows soil profile of Ni with respect to depth for the four fractions including the sum of extracts. The general trend for the represented fractions is the initial increase from 0 to 5 cm, then a gradual decrease with depth. At the lower most soils (20 – 30 cm), the amount of Ni was almost the constant. This might be attributed to the high organic matter at this layer.

The results in Fig. 5(b) shows the soil profile of Cr in four fractions including the amount of sum of extracts from 0 to 30 cm below the topsoil. The general trend for the represented fractions showed that initially the level of Cr increased from 0 to 5 cm then gradually decreased with depth to the deep soil. The graphs in Fig. 4(b) showed that the concentration of Cr in the exchangeable and reduction fractions were lower than that of oxidizable and residual fractions.

In lower most soils in 20 – 25 cm, the level of Cr was almost the same for all fractions. However, the concentration slightly increased at the lower most soils for exchangeable, reduction and residual fractions. Cr bounded to high content of organic matter might have caused the rapid increase at the depth of 5 cm. The general reduction in contamination with depth could only be due to the anthropogenic origin of Cr (Wali et al. 2014).

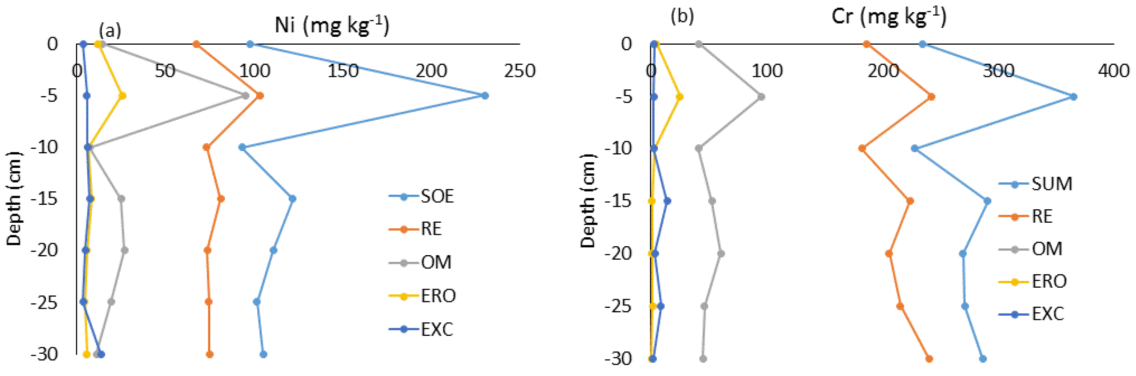

Fig. 5. Soil profile of (a) Ni and (b) Cr in soil samples from next to the cement factory

Conclusion

The present study has demonstrated that the level of Ni and Cr obtained from the depth analysis and at various distances released from brick making factory in the Thohoyandou area has caused severe to excessive pollution capable of serious ecological and public health hazard. High levels of Ni and Cr in the soil around the factory and in sediments of the Mvudi River implied that metal pollution levels in the study area are not of natural geology or the processes of weathering and deposition, but of anthropogenic activities. The study showed that Ni and Cr determined from distance and depth analysis appeared to indicate that the brick making factory is the main source of pollution. Since the soil samples collected close to the brick making factory and topsoil showed high concentrations. The observed low levels of Cr and Ni within the wetland for the sediment samples suggested that there were plants accumulating the two metals within the wetland area.

The fractionation of the studied samples showed that the availability and the mobility of the metals were of the order: exchangeable fractions > reducible fractions > oxidizable fraction > residual fraction.

The obtained order suggested that heavy metal concentrations found in the non-residual fractions were higher than those observed in the residual fraction indicating that high percentage of the metals was not bio-available and could not easily enter the food chain. Elevated concentrations of Ni and Cr were recorded for the different particle size fractions, this might be due to the surface area of the particles.

To reduce the impact of heavy metals pollution to the environment, the workers and the management of the cement brick making factory must receive proper training on waste management.

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Paper III

This paper “Spatial distribution of heavy metals accumulated in street dust emanating from a cement factory in Pretoria, South Africa’’ focusses on the pollution caused by a cement plant to its surrounding environment .

Spatial distribution of heavy metals accumulated in street dust emanating from a cement factory in Pretoria, South Africa

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Abstract

The present study was aimed at investigating the concentration of heavy metals in cement dust around a cement factory in Pretoria, South Africa in order to predict their contribution to pollution within the area. Cement dust samples were collected randomly in different streets in the vicinity of a cement factory, and were used to establish the spatial distribution of heavy metals around the studied streets. The samples were separated into three particles size fractions (<32, <75 and <125 µm) because the level of heavy metal contamination differ by the size of dust particles. The heavy metals concentration increased with the decrease of dust particle size in all samples. The total concentrations of As, Cr, Cd and Ni were determined in cement dust using inductively coupled plasma optical emission spectrometry (ICP-OES). High concentrations were observed for the samples collected close to the cement. The availability as well as the mobility of the heavy metals decreased in the order: exchangeable fractions (EXC) > reducible fractions (ERO) > oxidizable fraction (OM) > residual fraction (RE). The concentration of As in all analysed samples was the highest reaching a level of (16150 mg kg^{-1}) in dust sample GT2 followed by Cr, Ni and Cd. The results showed that there was a significant difference in the concentrations of heavy metals from different streets. The study revealed that the source of the heavy metals as pollutants cannot be attributed to the cement factory only, but also to vehicular emissions. It was concluded from the present study that monitoring plans and risk assessments are important to evaluate heavy metal concentration in dust in order to develop proper measures for reducing the risk of inhalation and ingestion of dust for human beings and the environment.

Keywords; Cement factory, Heavy metals, Street dust, Spatial distribution

Introduction

Heavy metals pollution caused by cement dust emission from the cement factories has become a major cause of environmental pollution. The cement industry forms part of the industries that are well known to be problematic as regards to the introduction of heavy metals from the dust emanating from their operations (Lafta et al., 2013; Mandal and Voutchkov, 2011; Addo et al., 2012). Several studies have reported cement factories to be a major source of heavy metals emission to the environment showing higher concentrations of heavy metals with their vicinity (Isikli et al., 2003; Al-Khashman and Shawabkeh, 2006; Abimbola et al., 2007; Gbadebo and Bankole, 2007; Mandal and Voutchkov, 2011). Large amount of heavy metals in cement dust emanate from the rotary kiln during pyro-processing in the plant.

In populated urban areas like Pretoria, elevated levels of heavy metals in dust may pose risks to human health. There is ample evidence that street dust is an important pathway in the exposure of people to toxic elements (Dietz et al., 2004; Abimbola et al., 2007; Acosta et al., 2009). The intake of dust particles with high concentration of toxic substances, especially potentially toxic metals, poses a potential threat to human health (Karmacharya and Shakya, 2012). The risk is especially high for children because of their low tolerance to toxic as well as the inadvertent ingestion of significant quantities of dust (or soils) through dermal and hand-to-mouth pathways (Davies et al., 1990; Watt et al., 1993; Al-Rajahi et al., 1996; Li et al., 2001; Banerjee, 2003; Ljung et al., 2006). Specifically, in relation to cement dust, Dietz et al. (2004) reported a significant correlation between cement dust exposure and laryngeal cancer among workers exposed to cement dust in an epidemiological study, while Abimbola et al. (2007) reported increased incidence of diseases linked to heavy metals toxicity in residents living around cement dust factory. In addition, elderly people who are frequent visitors to parks might be sensitive to high loadings of metals in urban soils (Acosta et al., 2009). Water bodies which supplies drinkable and irrigation water may also become contaminated by heavy metals through atmospheric deposition. This may pose adverse effects to plants and cause serious health concerns to human beings. In addition, small particles are soluble and are more likely to traverse the gastric mucosa and be more efficiently adsorbed in human tissues than coarse fractions (Acosta et al., 2009).

Dust may accumulate several heavy metals which include As, Pb, Cd and Cr on road surfaces depending on the source. Deposition of these heavy metals occur at various distances around the cement factories and are influenced by wind velocity, particle size, and stack fumes.

It was also reported that about 0.07 kg of dust is generated into the atmosphere when 1 kg of cement is manufactured (Olowoyo et al., 2015).

There is a lack of information on the concentrations of heavy metals in streets dust of Pretoria, which may provide vital information on the state of environmental pollution of urban areas around industrial areas. Besides, very little information is available about the distribution of metals in different particle size fractions of the dust from cement factory in urban areas (Karmacharya and Shakya, 2012). Although, several studies have noted the impact of the cement industry on the environment from developed countries, very few studies have been carried out in developing countries like South Africa (Olowoyo et al., 2015). The primary objective of the study was to determine the distribution of heavy metals in various streets, at different distance from the cement plant and particle size fractions to explain the influence of cement factory as a sources of heavy metals in street dust.

Materials and Methods

Analytical reagents

Analytical grade chemicals such as H_2O_2, $NH_2OH{\cdot}HCl$, CH_3COONH_4, CH_3COOH and HNO_3/HCl were used for extraction and digestion of soil and dust samples were supplied by Merck (Johannesburg, South Africa).

Materials

Sieves (125, 75 and 32 µm) purchased from Lasec (Johannesburg, South Africa) were used to sort the samples of soils and sediments into different sizes. A refrigerator bought from Labtech (Johannesburg, South Africa) was used to store the samples at 4.0°C. Ultrapure water obtained by a Milli Q system (Millipore, France) was used for dilutions. CNW water bath thermostatic vibrator purchased from Lasec (Johannesburg, South Africa) was used to mechanically shake the samples in 50 mL centrifuge vials. A portable multi-probe Boeco pH meter purchased from Rochelle (Johannesburg, South Africa) was used to measure the PH, electrical conductivity (EC), temperature and total dissolved solids (TDS). An MRC centrifuge purchased from Retsch (Johannesburg, South Africa) was used to separate the residue and the supernatants.

Instruments

ICP-OES 9000 Shimadzu equipped with a meinhard nebulizer, a glass cyclonic spray chamber and ICP WinLab software Data System was used to determine heavy metal contents.

Argon (purity higher than 99.995%) supplied by BOC gases, a member of Linde group (South Africa) was used to sustain plasma and as carrier gas. Axial view was used for metal determination, while 2-point background correction and 3 replicates were used to measure the analytical signal. The emission intensities were obtained for the most sensitive lines free of spectral interference. The calibration standards were prepared by diluting the stock multi-elemental solution (1000 mg L^{-1}) in 0.5% (v/v) nitric acid containing all analysed elements (As, Cd, Cr and Ni) supplied by Merck (Darmstadt, Germany) was used for calibration. The calibration curves for all the studied elements were in the range of 0.5 to 5 mg L^{-1}.

X-ray diffraction (XRD) was used to determine the mineral composition of bulk dust sample. Bulk dust sample was ground in an agate mortar and randomly mounted on petrographic slide prior to XRD analysis. The XRD powder pattern was recorded at 26°C using Bruker axs, (Karlsruhe, Germany). Measurements were performed using a multi-purpose x-ray diffractometer D8-Advance from Bruker operated in a continuous ϑ-ϑ scan in locked coupled mode with of Cu-Kα ($\lambda K\alpha_1$=1.5406Å) radiation and Lynx Eye (Position sensitive detector). A position sensitive detector, Lyn-Eye, was used to record the diffraction data at a typical speed of 0.5 sec/step which was equivalent to an effective time of 92 sec/step for a scintillation counter in the region of 6–90°. Data were background subtracted so that the phase analysis is carried out for diffraction pattern with zero background after the selection of a set of possible elements.

The Bruker handheld S1 Titan XRF (Cramerview, South Africa) spectrometer equipped with an Rh anode x-ray tube and a Maximum voltage of 50 kV was employed. The samples were air-dried in open air, to remove moisture content. Removal of moisture is significant because moisture content above 20% could interfere with the XRF analysis and also alter the soil matrix for which the XRF spectrometer has been calibrated with respect to solid (powdered) samples. The soil samples were thoroughly homogenized and sieved to fine particle sizes of 75 µm with Retsch aluminium test-sieves with vibratory electronic sieve shaker to reduce soil matrix.

Sampling area

The cement plant is situated next to a very busy Es’kia Mphaphle Drive (M1) road (GPS coordinates 25^{0}43’21 S, 28^{0}10’15 E) in Hercules west of Pretoria in Gauteng Province, South Africa. There is an Apies River flowing parallel to the Es’kia Mphaphle Drive and the cement plant. On the west part of plant there are several streets, two schools and factories.

Fig. 1. Sampling site for dust samples (5 point – stars) around the cement plant, water samples (7 point-stars) along the Apies River and factory effluent.

Sample collection

The dust samples were collected along Es'kia Mphaphle Drive, near a cement plant gate and at various streets around Hermastad urban area in Pretoria. A large bulk sample of dust and five soils layers at different depth in the soil were sampled next to the cement plant. Water samples were collected along the Apies River into 500 mL sample bottles and were collected during summer season (wet and high flow). The water samples were acidified with 5% (v/v) HNO_3 and the physico-chemical parameters were measured at the field.

Sample preparation

Samples were dried at room temperature until a constant weight was achieved and separated into particles size fractions (125, 75 and 32 μm) in the laboratory. All the samples were originally stored in closed paper bags until analysis. A mixture of aqua regia solution (20 mL) was used for digestion. The temperature was maintained at 110°C C for 2 h during digestion of 0.2 g of dust and soil samples on a hot plate in a fume hood. After cooling, 20 mL of 2% HNO_3 water was added to the sample and mixed. The mixture then filtered through filter paper and the solution was diluted to 100 mL with distilled water.

A bulk sample was treated by a three step modified BCR sequential extraction procedure as explained by Li et al. (2010), and the residue on the fourth step was subjected to aqua regia. The resulting solutions were then analysed for metal concentration using ICP-OES.

Results and Discussion

Characterisation of water and dust samples

Table 2 shows the results for pH, EC, TDS and temperature of collected water samples from the Apies River. The pH of water samples ranged from 7.1 to 8.9. The pH values were generally within WHO range of 6.5 – 8.5. The highest pH value of 8.9 was recorded from the effluent coming out from the plant. This suggested that the effluent was alkaline in nature. The effluent contained calcium carbonate, aluminium silicate, silica oxide and iron oxide used as raw materials during cement production in a rotary kiln. This resulting effluent from the production has potential of imparting high alkalinity to the effluent receiving Apies River. This observation is similar to the findings by Ipeaiyeda and Obaje (2017). The lowest pH value of 7.1 was recorded from the first sampling point before the plant site. Which shows that water in Apies River had not being affected by the alkalinity of the effluent.

The EC ranged from 189 to 361 µS cm^{-1}. The highest value was recorded before the plant site and lowest value was recorded at a small pool just out the plant. WHO normal range for electrical conductivity of water is 400 – 600 µS cm^{-1} and the recorded range was within WHO acceptable range. EC which is a measure of water's ability to conduct an electric current. It is related to the amount of dissolved minerals in water, but it does not give an indication of which element are present. High values of EC is a good indicator of the presence of contaminants such as sodium, potassium, chloride or sulphate (Nazir et al., 2015).

TDS values were in the range of 113 – 218 mg L^{-1} and were below the recommended limit of DWAF (2001) for domestic water use (450 mg L^{-1}) and higher than the guideline value of 0.4 mg L^{-1} for use in irrigation.

The temperature ranged from 22.1 to 27.6°C. Highest temperature of 27.6°C recorded was before the cement plant and the lowest temperature of 22.1°C was recorded at first sampling point. The recorded temperature fell within 30°C which is good for organisms living in water. Temperature above 30°C, is not suitable for organisms in water such as clams, lobsters, crabs and other tiny organisms that live in bottom sediments. High temperature may cause effects to the organisms living in water.

Table 1: Physico-chemical properties of water samples from the Apies River

Site	GPS	pH	EC (µS cm^{-1})	TDS (mg L^{-1})	Temperature (°C)
Ps1	25°72’88 S, 28°16’97 E	7.1	349	211	22.1
Ps2	25°72’78 S, 28°17’04 E	8.0	361	218	24.5
Ps3	25°72’66 S, 28°17’18 E	8.5	360	216	27.6
Ps4	25°71’57 S, 28°17’12 E	8.5	357	216	27.5
Ps5	25°71’50 S, 28°17’20 E	8.3	364	218	27.0
Psp	25°72’14 S 28°17’16 E	8.6	189	113	27.2
Psr	25°72’14 S, 28°17’01 E	8.9	334	200	27.5

Note: Ps1 to Ps5 are the sampling points of water along Apies river and Psp is sampling point of water at the pool and Psr is the sampling point of water at the runoff.

The pH values of the dust samples were determined in the de-ionized water with a ratio of 1:5 (v/w) dust to water as shown in Table 2. The pH of the dust samples measured varied from 7.1 to 7.9 and this range showed that the dust was slightly alkaline. The alkalinity of the dust might be due to the presence of high calcium carbonate content present in dust as shown by the XRF and XRD results in Table3. The highest pH of 7.9 was recorded for the dust sample collected along a heavy traffic road of Es’kia Mphahlele Drive and from Charl Cilliers Street which is far away from the cement plant. These high pH values along the Es’kia Mphahlele Drive and Charl Cilliers Street might be as result of dust deposition and vehicular emission along the road.

The measured EC values of dust samples varied from 98.7 to 2190 µs cm^{-1} as shown in Table 2. The elevated EC values of the dust samples showed that there were many charged ions in dust samples. The charged ions might be magnesium, sulphate, carbonate, chloride and calcium from limestone and clay. The highest EC value of 2190 µs cm^{-1} was recorded for a sample collected next to the gate of the cement plant, where most of the dust from the factory and from the heavy vehicles settles on the ground.

Table 2: Physico-chemical parameters of dust samples from around the cement plant

Sample site	MOO	Bulk	GT1	EPS1	CHA PS1
pH	7.5	7.1	7.2	7.9	7.9
EC (µs cm^{-1})	247.0	405.0	2190.0	98.7	361.0

Note: MOO is dust sample from Moost Street, Bulk the bulk of dust sample, GT the dust sample from the gate, EPS1 dust sample along Es’kia Mphahlele Road and CHA dust sample from Charl Cilliers Street.

Fig. 2 shows the XRD pattern of the minerals identified in the dust sample using XRD pattern. The mineralogy of the dust sample was recorded for the sample in order to know about the mineralogical composition and the crystalline nature of the minerals. The minerals contained in the samples were identified by making use of International Centre for Diffraction Data, Powder Diffraction File (ICDD PDF). The XRD patterns, identified the following minerals quartz, calcite, dolomite, muscovite and kaolinite. These minerals forms part of the raw materials that are used for cement manufacturing. The XRD pattern also revealed that quartz is the dominant mineral. The minerals in XRD pattern were crystalline in nature.

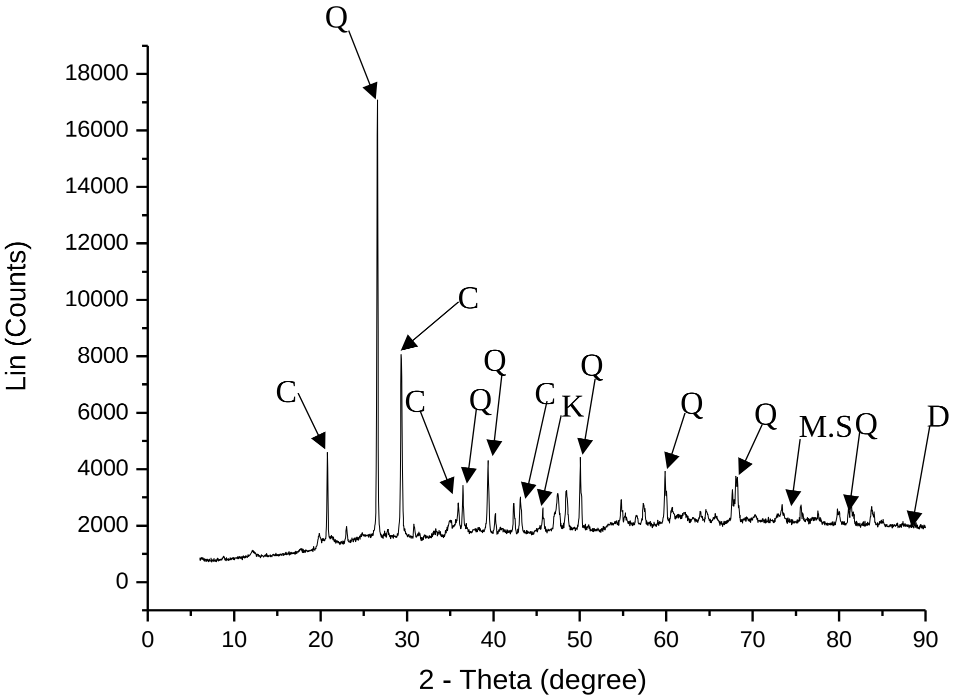


Fig. 2. The XRD diffractogram of the bulk sample showing (C – Calcite, D – Dolomite, K – Kaolinite, Q – Quartz, M,S – Muscovite) minerals.

The concentration of heavy metals and metal oxides identified and quantified by XRF spectrometry are recorded in Table 3. Ni and Cr were the only metals identified with concentrations of 0.003 and 0.030 mg kg^{-1}, respectively. The amount of Cd and As were below detection limit. However, the results showed high amount of metal oxides such as silica, alumina and lime which are the main component for cement production.

Table 3: Elemental analysis of the dust sample collected close the cement plant using XRF spectrometry (n = 3).

Heavy metals	(Concentration mg kg^{-1})	SD
Ni	0.003	0.002
Cr	0.030	0.003
As	Bdl	Bdl
Cd	Bdl	Bdl
Metal oxides		
Al_2O_3	7.02	0.23
SiO_2	27.85	0.29
CaO	12.05	0.05

SD standard deviation; bdl below detection limit

Concentrations of heavy metals in water samples and dust samples

The levels of heavy metals in the Apies River are presented in Fig. 3. The concentrations of each heavy metal along the river varied as follows As (5250 – 10050 mg L^{-1}), Cd (68 – 194 mg L^{-1}), Cr (408 – 1060 mg L^{-1}) and Ni (314 – 785 mg L^{-1}). The heavy metals concentrations decreased in the following order: As > Cr > Ni > Cd. High concentration of As were observed in all sampling sites with a highest at PS3 (10050 mg L^{-1}). Elevated concentrations of As in water might cause health problems to the urban communities, who are supplied with water from the Apies River. High concentrations recorded at sampling point PS3 might be caused by the atmospheric deposition of cement dust containing heavy metals. The heavy metals concentrations increased in water samples collected towards the cement plant from (PS1 to PS2) and decreased after the plant (PS4 to PS5). This might be showing that the main source of the detected heavy metals was the cement plant. PPCP and ROW represent the water samples collected in the influent, and the effluent, and it was evident that these streams also contain high level of the heavy metals.

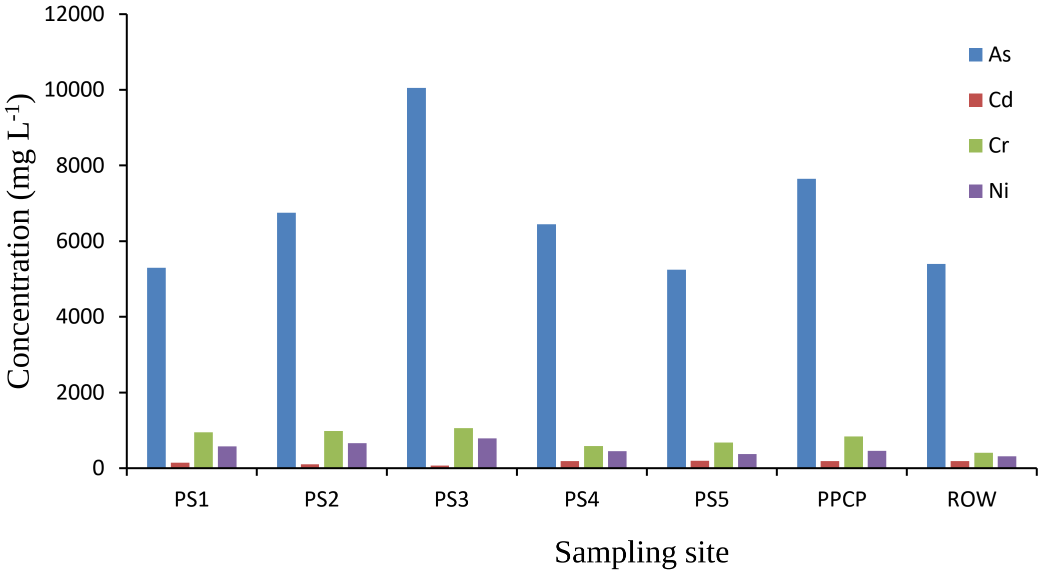


Fig. 3. Represent the concentrations of heavy metals in water samples from the Apies River and from the factory effluent.

The concentration of heavy metals in five different particle sizes is shown in Fig. 4. The level of heavy metals increased with the increase of particle size. Generally, the trend of the heavy metals was increasing in the following order: 32 µm < 75 µm < 250 µm < 500 µm < 1000 µm. In each particle size fraction As concentration dominated as compared to other metals. The highest concentrations of the heavy metals were observed in the particle size fraction of 1000 µm. The heavy metal concentrations varied as follows: As (3425 – 6300 mg kg^{-1}), Cd (201 – 230 mg kg^{-1}), Cr (313 – 725 mg kg^{-1}) and Ni (126 – 384 mg kg^{-1}). The highest concentration of 6300 mg kg^{-1} was recorded for As in 1000 µm. Such high concentration of As might be due to emissions from the cement production. The raw materials which are limestone and clay for cement manufacturing also contain As in small amount. High amount of heavy metals in large particle size indicate that the metals might be from parent rock (Facchinelli et al., 2001).

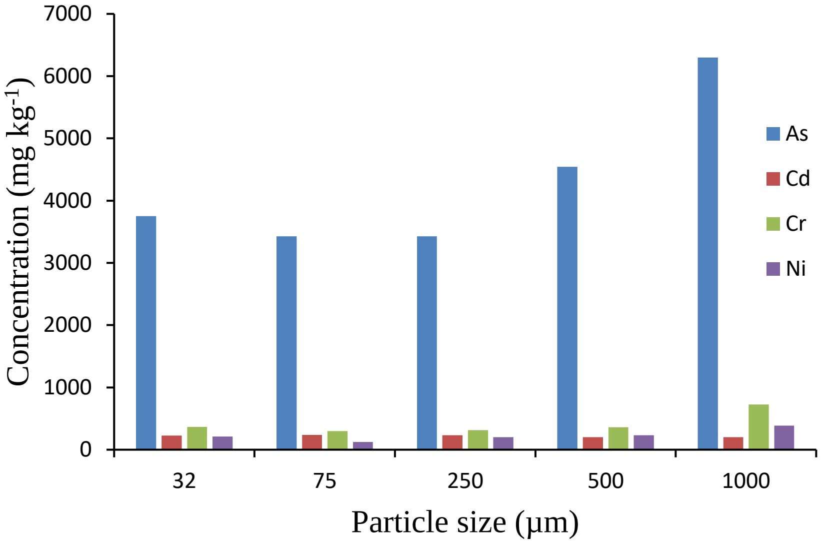


Fig. 4. Distribution of heavy metals in different particle sizes

Fig. 5 shows the distribution of heavy metals different fractions treated using BCR sequential extraction. Generally, the availability as well as the mobility of the heavy metals decreased in the order: exchangeable fractions (EXC) > reducible fractions (ERO) > oxidizable fraction (OM) > residual fraction (RE). This showed that the soil is contaminated with the selected heavy metals. High concentrations of the heavy metals in the exchangeable and reducible fractions suggest that the metals are bioavailable and mobile for uptake by the plants. The levels of the heavy metals in the non-residual fractions showed that the soil is polluted by heavy metals. Pollution of the soil pose health hazard to the urban communities around the cement plant.

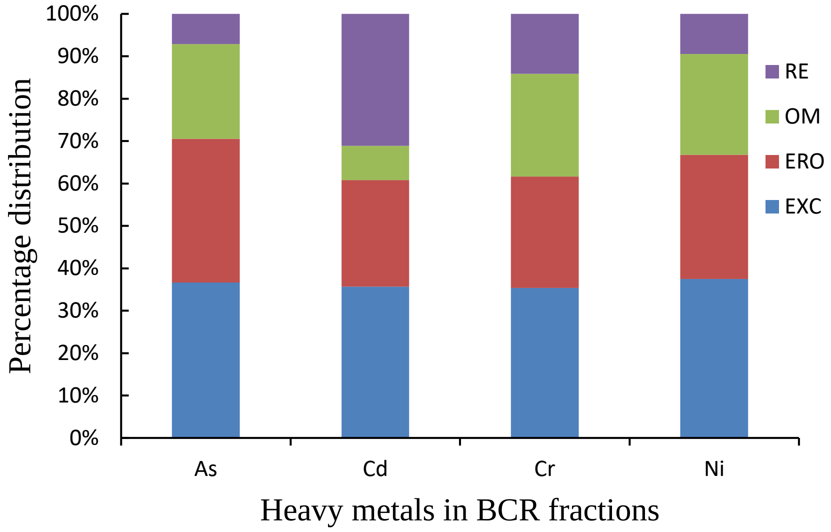


Fig. 5. Partitioning of heavy metals in BCR fractions for 32 µm particles of the bulk sample

Fig. 6 shows the distribution of heavy metals in soil profile. The general trend was the decrease of heavy metal concentration with the increase in depth. The concentration decreased from highest value of 5150 mg kg^{-1} from the topsoil (0 cm) to the middle soil (> 10 cm) but as the depth got deeper (20 cm) it decreased to a lowest concentration of 321 mg kg^{-1}. Cd in the lower depth increased to 359 mg kg^{-1} than its concentration in the upper soil of 182 mg kg^{-1}. This increase might have been caused by clay soil in the lower depth.

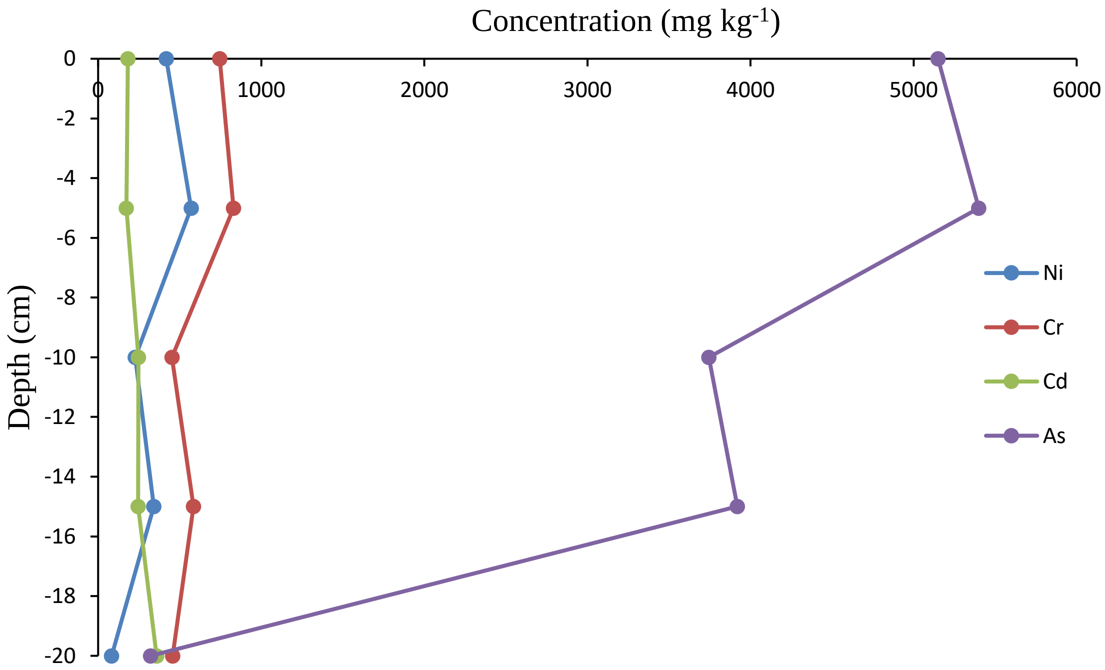
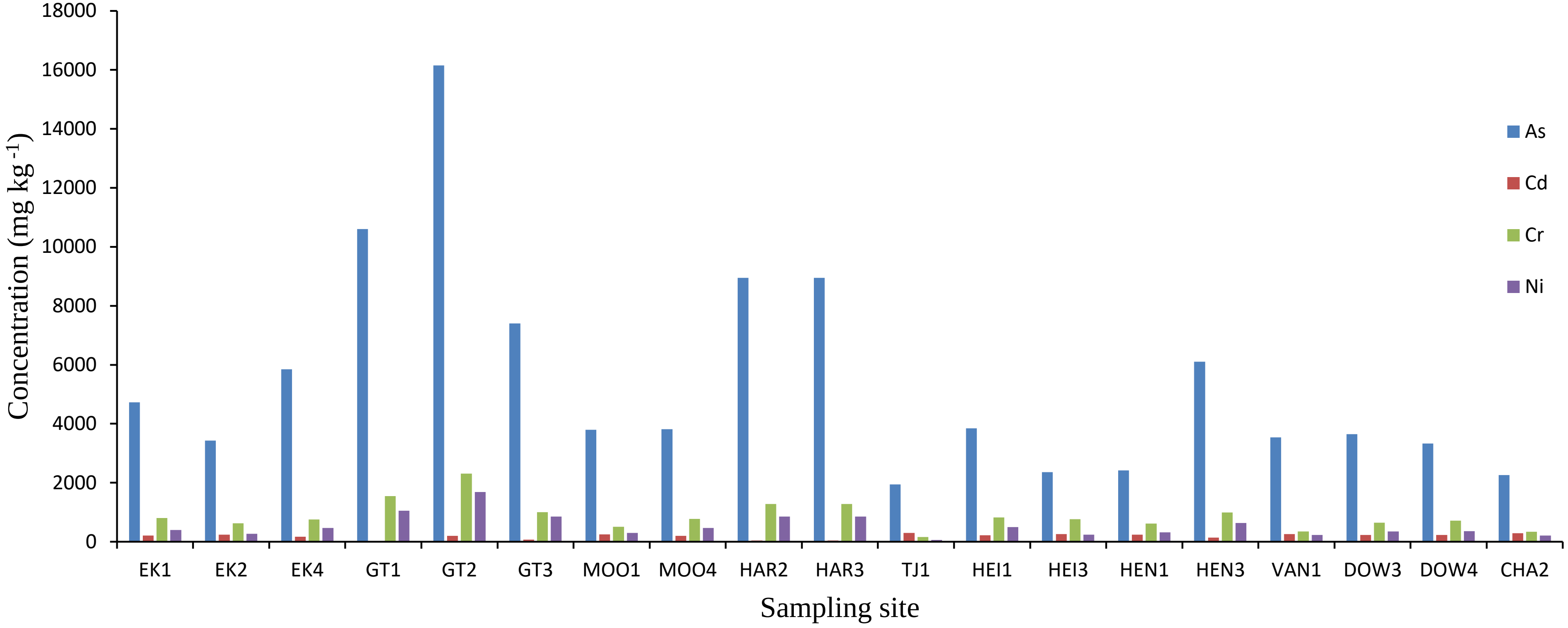


Fig. 6. Vertical distribution of heavy metals in soil sample collected next to a cement plant.

Spatial distribution of heavy metals on the street dust is shown in Fig. 7. The street dust were dominated by the concentration of As followed by Cr, Ni and Cd. This elevated concentration of As raises serious health concerns to the people living in such urban locations. High concentrations were observed in locations close to the cement plant, especially, along the road to the cement plant gate at sampling site GT2 with As (16150 mg kg^{-1}), Cd (195 mg kg^{-1}), Cr (2310 mg kg^{-1}) and Ni (1685 mg kg^{-1}). High concentrations were also observed along Es'kia Mphahlele Drive and the Moost Street. These elevated concentration might be due to the emissions from cement plant and vehicular. Low concentrations of heavy metals were recorded for the sampling site (CHA1) which is 2 km away from the industries. These results suggested that the streets behind the cement plant are contaminated with heavy metals from the emissions of the cement plant, vehicles and other industries in the area.



Note: EK1-EK4 are the sampling point along Es'kia Mphahlele Drive Road, GT1-GT3 are sampling points on the road to the gate of cement plant, MOO1and MOO4 are the sampling points on the Moost Street, HAR2 and HAR 3 are the sampling points along the Haarlem Street, TJ1 is sampling point on the Talijaard Street, HEl1 and HEl1 are sampling points along the Hellen Street, HEN1 - HEN3 are sampling points along the Hendrik street, VAN1 is the sampling point on the Van Riebeeck Road, DOW3 – DOW4 are the sampling points on the Van Der HOff Road and CHA2 is the sampling point on the Charl Cilliers Street.

Fig. 7. Spatial distribution of heavy metals on the streets of Pretoria close to a cement plant

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Conclusion

The water and dust sample were dominated by high concentrations of As which can results in serious health problems. The distribution of heavy metals in different locations indicated that the cement plant responsible for metal pollution as the highest metal concentrations were found close to the cement plant. The soil next to the cement plant was polluted with heavy metals emanating from the vehicle emission and from cement manufacturing. The results showed that the streets were contaminated with As and possible source of elevated concentrations were emissions from the cement plant and other industrial activities. Quartz dominated the minerals in the bulk sample followed by calcite from limestone and other minerals identified include dolomite, muscovite and kaolinite. There is need to take proper measures in order to reduce the risk of inhalation and ingestion of dust by human beings and pollution of the environment. This study demonstrated that the metal concentrations of the street dust can be used as a powerful geochemical tracers of monitoring the impact of anthropogenic activity.

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Paper IV

This paper “Determination of platinum group metals in dust samples enhanced by water suppressant along a gravel road next to a cement Plant in Thabazimbi, South Africa’’ determine the concentrations of PGMs in collected along a dust road suppressed by water and being contaminated by traffic emission and emissions from the cement production.

Determination of platinum group of metals in dust samples enhanced by water suppressant along a gravel road next to a cement plant in Thabazimbi, South Africa

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Abstract

Global economic growth has led to an increase of cement production to meet the demand of infrastructure development over the past decades. This has resulted in cement factories being the major sources of dust pollution. Dust emanating from the cements plants deposits on buildings, roadways, on road pavements and plants. The purpose of this study is to determine the concentration of platinum group metals (PGMs) emitted with cement dust on a dust suppressed roadway next to a cement factory in Waterberg, South Africa. This region is well known for large reserves and mining of PGMs such as Pt, Rh and Pd. Dust was sampled along the gravel roadway and separated into three different particle size fraction (PM_{32}, PM_{75} and PM_{125}). Water samples were also sampled along the Crocodile River. Highest levels were recorded for a sampling point CR5 with Pd (1465 mg kg^{-1}), Pt (8500 mg kg^{-1}), Rh (mg kg^{-1}) and Ru (3910 mg kg^{-1}). The concentrations of PGMs were determined using inductively coupled optical emission spectrometry (ICP-OES). The concentrations of heavy metals decreased in the following order; Pt > Rh > Ru > Ni. Concentration of the PGMs along the dust road varied as follows Pt, (150 - 16550 mg kg^{-1}), Rh (58.5 - 5100 mg kg^{-1}), Ru (381-7100 mg kg^{-1}) and Pd (71.5 – 2895 mg kg^{-1}). Elevated concentrations of Pt were observed in all samples and the highest concentrations partitioned to the small particle size fraction of 32 µm. The vehicular emissions were also found to be the major contributor to suspended particulate matter and atmospheric deposition of dust dominantly result from emission from the cement plant. The result revealed that the pH of the Crocodile River was slightly alkaline which was influenced by the effluent from the cement plant. The most common minerals identified were quartz and calcites.

Keywords; Dust suppressants, cement dust, platinum group of metals, cement factory, environment

Introduction

Thabazimbi local municipality is located within a belt of mining reserves of platinum, iron, chrome, limestone, etc. and within the Bushveld region of South Africa. Bushveld igneous complex is well known area for its rich in platinum group metals (PGMs) and some of the principal mines from which the PGMs are obtained. South Africa is the leading country with 85% of the world production of PGMs and has 82% of the world's economic resources (Rao and Reddi, 2000). There are also cement companies mining raw materials for cement production. Raw materials such as limestone and clay in the area are expected to contain some amount or platinum group metals. Due to availability of raw materials for cement production, there is cement plant located near Thabazimbi. The cement industry, due to the nature of its activities, is one of the industries which releases most of pollutants to the environment (Saffari et al., 2016).

The cement industry is faced with the problems of heavy metals emission with dust during the manufacturing of cement. Therefore, there is high possibility that PGMs might also be emitted with cement dust during pyro-processing from the plant to the surrounding environment. Dust emission usually occurs during the processes of quarrying and crushing, raw material storage, grinding and blending (in the dry process only), clinker production, clinker storage piles, finish grinding, and packaging and loading (Kalafatoglu et al., 2001). The largest emission source of dust within cement plants is the pyro-processing system that includes the kiln and clinker cooler exhaust stacks.

The PGM are currently receiving worldwide attention as they offer the dual attraction of rare, high-value precious metals as well as having major industrial uses (Rao and Reddi, 2000). Due to the expected development within the Waterberg area and the existing mining and metallurgical activities in the western arm of the bushveld igneous complex (Feig et al., 2016), there is concern regarding the future and current air quality in these regions. This led to the establishment of the Waterberg Priority Area ambient air quality monitoring network in 2012 to monitor the ambient air quality in the Waterberg Area.

Some people have expressed concern over inadequate dust control measures from cement plants because fallout from quarry dumps containing cement dust can be significant for adjacent landowners in the absence of buffers between the dumps and residential, agricultural, and recreational land use areas (EPA, 1994).

Depending on the type of production, the particle diameter of dust in different intervals and at different times can be harmful to health and environment. This is the most important factor to have a significant influence on the performance and health of people (Lei et al., 2011; Edalati et al., 2014). Chest pain, congestion, throat inflammation, cardiovascular disease, respiratory are some of diseases that can be caused by air pollution (Iman Akbari et al., 2016). Concerns may also arise from the farmers who have to handle cement dust during the application to agricultural fields (EPA, 1998). The effects of dust on the agriculture area are determined by the concentration of dust particles in the ambient air, size distribution, deposition rate and its chemistry (Petavratzi et al., 2005).

The measures used to control emissions from these fugitive dust sources are comparable to those used throughout the mineral products industries. Vehicular traffic controls include paving and road wetting. Controls that are applied to other open dust sources include water sprays with and without surfactants, chemical dust suppressants, wind screens, and process modifications to reduce drop heights or enclose storage operations (US.EPA, 1994). Road washing is one of the methods that might reduce the occurrence of dust re-entrainment by reducing the amount of dust on the road and/or by reducing their ability to suspend as the increased moisture might capture the particles on the road surface. In general, washing activities are applied in combination with sweeping (Amato et al., 2010). To reduce dust emissions from the haul road's surface, many cement plants employ some means and frequency of road wetting to suppress dust (EPA, 1998).

The primary aim of this study was to determine the contribution of road dust to platinum group metals next to a cement plant in Thabazimbi Municipality in South Africa. There are few studies that have been conducted to evaluate concentration of PGMs on the dust suppressed roadway. Therefore, this study focusses on the determination of PGMs emitted from a cement plant to establish severity of their contamination on the surrounding environment.

Materials and Methods

Analytical reagents

Analytical grade chemicals for sequential extraction H_2O_2, $NH_2OH{\cdot}HCl$, CH_3COONH_4, CH_3COOH and HNO_3/HCl for aqua regia were used from Merck (Johannesburg, South Africa).

Materials

Mesh sieves (125, 75 and 32 µm) bought from Lasec (Johannesburg, South Africa) were used to sort the dust into different sizes. Mechanic shaker bought from Retsch (Johannesburg, South Africa) was used to shake the sieves. A refrigerator bought from Labtech (Johannesburg, South Africa) was used to store the samples at 4.0°C. CNW water bath thermostatic vibrator purchased from Lasec (Johannesburg, South Africa) was used to mechanically shake the samples in 50 mL centrifuge vials. A MRC centrifuge purchased from Retsch (Johannesburg, South Africa) was used to separate the residue and the extracts in the vials. Ultrapure water obtained by a Milli Q system (Millipore, France) was used for dilutions. A portable Multi-probe Boeco pH meter purchased from Rochelle (Johannesburg, South Africa) was used to measure the pH and electrical conductivity (EC), temperature and total dissolved solids (TDS).

Instrument

Measurements were carried out with a sequential, axially viewed ICP-OES 9000 Shimadzu equipped with a Mein hard nebulizer, a glass cyclonic spray chamber and ICP WinLab software Data System. Argon (purity higher than 99.995%) supplied by BOC gases a member of Linde group (South Africa) was used to sustain plasma and as carrier gas. Axial view was used for metals determination, while 2-point background correction. The emission intensities were obtained for the most sensitive lines free of spectral interference. The calibration standards were prepared by diluting the stock multi-elemental standard solution (1000 mg L^{-1}) in 0.5% (v/v) nitric acid containing all analysed PGMs elements supplied by Merck (Darmstadt, Germany) was used for calibration.

The x-ray diffraction powder pattern was recorded at 26°C using Bruker AXS (Karlsruhe, Germany). Measurements are performed using a multi-purpose X-ray diffractometer D8-Advance from Bruker operated in a continuous ϑ-ϑ scan in locked coupled mode with of Cu-Kα ($\lambda K\alpha_1$ = 1.5406Å) radiation and Lynx Eye (Position sensitive detector).

The samples were air-dried in open air, to remove moisture content. Removal of moisture is significant because moisture content above 20% could interfere with the XRF analysis and also alter the soil matrix for which the XRF spectrometer has been calibrated with respect to solid (powdered) samples. The soil samples were thoroughly homogenized and sieved to fine particle sizes of 75 µm with Retsch aluminium test-sieves with vibratory electronic sieve shaker to reduce soil matrix.

In general, although results are element dependent, sieving samples to a particle size of < 250 µm is recommended (Urrutia - Goyes et al., 2017). The Bruker handheld S1 Titan XRF (Cramerview, South Africa) spectrometer equipped with an Rh anode X-ray tube and a Maximum voltage of 50 kV was employed.

Sampling area

The cement plant shown in Fig.1 is situated next to several agricultural fields cultivated with pastures farms (GPS coordinates 24°98’66 S, 27°54’65 E) and a busy gravel roadway parrallel to the Crocodile River flowing towards the west in Koedoeskop which falls under the jurisdiction of the Thabazimbi Local Municipality and the Waterberg District, South Africa. The gravel roadway joins the R511 road on both its ends. Thabazimbi area is characterised by three prominent east-west trending mountain ranges and the majority of the mining operations take place in these mountains where the deposits occur. The cement plant has a production capacity of 1.2 million tonnes per year (Govinda et al., 2016). There is Northam Platinum Mine on the far west of the cement plant. The gravel road is used by heavy traffic coming and going from the cement plant and there is also heavy traffic of trucks transporting raw minerals from the mines in the nearby area. Water from the Crocodile River is used for irrigation by the farmers, where the main agricultural activity is centred on pastures.

Water is also channelled from the Crocodile River to the cement plant and used for cooling the rotary kiln during the production of the clinker. During this process, water get contaminated with pollutants released from the formation of the clinker. Contaminated water is treated with lime to precipitate the pollutants and then released back to the river via pipes. This water is also sprayed over the gravel roadway to suppress dust. The residential area of Koedoeskop is far away from the cement plant.

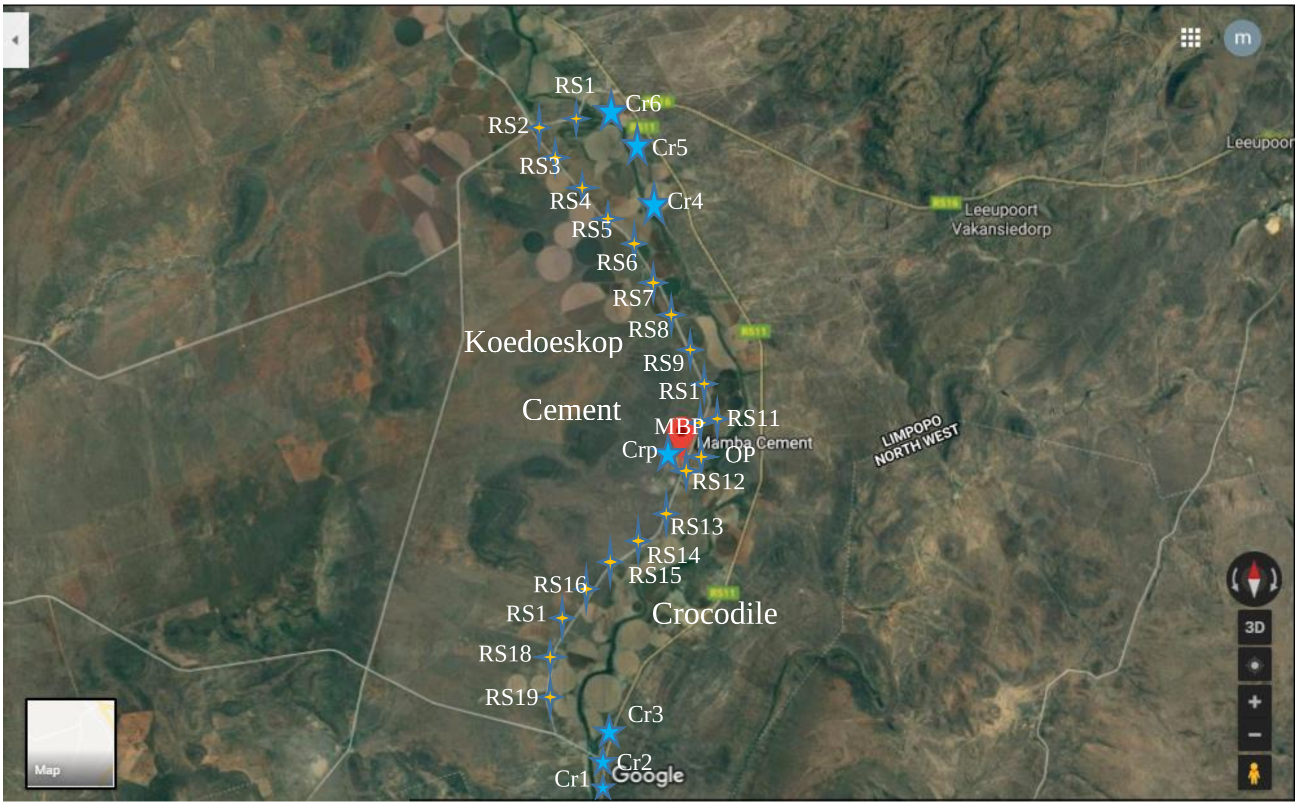


Fig. 1. Sampling sites for dust along the road (4 – stars), water samples (5 – stars) along the Crocodile River and factory effluent.

Sample collection

The dust samples were collected along the gravel roadway at a distance of 1 km apart from one end of the roadway to the other end of the gravel road passing by the cement plant. A large bulk sample of dust was sampled next to the cement plant for particle size analysis. Samples were dried at room temperature until a constant weight was achieved and separated into different particles size fractions (125, 75 and 32 µm) in the laboratory. All the samples were originally stored in closed plastic bags until analysis. Water samples were collected along the Crocodile River in 500 mL sampling bottles. The bottles were rinsed with the surface water before collecting a sample at each sampling point. The water samples were acidified with HNO_3 and the physico-chemical parameters were also measured at the field. In the laboratory, the water samples were passed through a 0.45 µm membrane filter prior to ICP-OES analysis.

Sample preparation

Aqua regia was used for digestion of the dust samples. The temperature was maintained at 110˚C for 2 h during digestion of 0.2 g of dust samples with 20 mL of 3:1 (v/v) HCl/HNO_3 mixtures on a hot plate and placed in a fume hood.

After cooling, 20 mL of 2% HNO_3 water was added to the sample and mixed. The residue was filtered through filter paper and then the sample was diluted to 100 mL with de-ionised water. A bulk sample was prepared through modified BCR sequential extraction as explained by Wali et al. (2014). ICP-OES instrument was used to determine the concentrations of PGMs in the solutions.

Results and Discussion

Characterisation of water and dust samples

Table 1 shows the results for pH, electrical conductivity, total dissolved solids and temperature of collected water samples from the Crocodile River. The pH ranged from 7.7 to 8.7 which shows that the pH was just above the neutral pH of 7. The highest pH value was 8.7, which was recorded along the river close to the cement plant and the lowest value was 7.7 due to neutralization of the plant wastewater by liming the effluent from the cement plant. This pH from the effluent shows that the water is almost clean which implies that the water was treated before being released to the Crocodile River. The pH values fell within the recommended limit of 6 to 8.5 set by World Health Organisation and adopted by the Department of Water Affairs and Forestry of South Africa (DWAF, 1996) for domestic, recreation and agricultural water use.

The Electric conductivity (EC) is the capacity of material to carry current. It is used as a measure of the mineral or ionic concentration of water (Singo, 2013). EC of the Crocodile River water samples is shown in Table 1. The EC value ranged from 510 to 1073 µS cm^{-1}. The highest conductivity of 1073 µS cm^{-1} was observed for water collected in the effluent next to the cement plant. This indicated that the water from the plant carried high mineral content. The EC values obtained in this study exceeded the water guidelines set by DWAF (1996) and WHO (2011).

The total dissolved solids of water samples from the Crocodile River ranged from 301 to 630 mg L^{-1}. TDS is the measure of dissolved mineral ions in water such as magnesium, calcium, sulphate, chloride, bicarbonate, sodium, nitrate and carbonate. It is a direct estimate of electrical conductivity of water because EC is the measure of charged ions in the solution (DWAF, 1996). The highest value of 630 mg L^{-1} was above the recommended limit of DWAF, (2001) for domestic water use 450 mg L^{-1} and higher than the guideline value of 0.4 mg L^{-1} for use in irrigation.

Table 1: Physico-chemical properties of water samples from the Crocodile River

Site	GPS coordinates	pH	EC (mS cm^{-1})	TDS (mg L^{-1})	Temperature (°C)
Cr1	25^{0}05’89 S, 27^{0}51’99 E	7.9	529	316	29.2
Cr2	25^{0}06’62 S, 27^{0}51’57 E	8.1	510	301	30.9
Cr3	25^{0}07’21 S, 27^{0}52’05 E	7.9	491	324	30.0
Cr4	24^{0}89’14 S, 27^{0}51’99 E	8.7	464	285	32.2
Cr5	24^{0}89’43 S, 27^{0}52’45 E	8.5	486	291	27.0
Cr6	24^{0}89’94 S, 27^{0}52’95 E	8.5	485	292	27.7
Crp	24^{0}98’22 S, 27^{0}54’82 E	7.7	1073	630	33.7

Note: Cr1 to Cr6 are the sampling points of water along the Crocodile River and Crp is the sampling point of water at the effluent outside the cement plant.

Dust pH and EC were measured in a 1:5 (w/v) ratio of dust to de-ionized water mixture. The pH and EC values were determined by using a pH meter as shown in Table 2. The pH and EC of the dust were determined to assess their possible influences on agricultural soil. The pH of the dust samples measured varied from 6.7 to 8.2, and this range showed that the dust is slightly alkaline. The alkalinity of the dust might be caused by the presence of high calcium carbonate content present in dust. The highest pH value of 8.2 was observed at the bottom surface sediment collected along the Crocodile River, this suggested that there was high percolation of lime on sediments.

The EC values of the dust and sediments samples are shown in Table 2. The recorded values of EC varied from 362 to1497 µS cm^{-1}. The highest EC value was observed for sample collected next to the cement plant were most of the dust emanating from the plant settle. This shows that the dust is predominantly loaded with ions. Such ions might have been carried by dust from the cement plant. The ions might be magnesium, sulphate, carbonate, chloride and calcium from limestone and clay. These elements may affect productivity of the agriculture soil of farms situated along the gravel road. The dust sample (RS16) collected along the road was slightly acidic due to the dust emanating from the heavy vehicles transporting minerals from the mines.

Table 2: Physico-chemical characteristic of dust samples and a sediment

Sample	CR1	CR3	RS8	RS16	Bulk
pH	7.3	8.2	7.8	6.7	8.0
EC (μs cm^{-1})	791	366	362	986	1497

Noted: CR1and CR3 are the sediment samples collected along the Crocodile River, RS16 and RS8 are the dust sample collected along the road, Bulk is the dust sample collected in bulk next to the cement plant.

The mineralogy of dust sample identified using XRD patterns

The XRD pattern of the dust sample collected close to the cement plant are shown in Fig. 2. The mineralogy of the dust sample was recorded for the sample in order to know about the mineralogical composition and the crystalline nature of the minerals. The minerals contained in the samples were identified by making use of International Centre for Diffraction Data, Powder Diffraction File (ICDD PDF). The XRD pattern identified the following minerals quartz, calcite, dolomite, microcline, muscovite and gypsum. These minerals observed in the XRD patterns of dust represent the composition of raw materials used in cement manufacturing with gypsum used as an additive for the clinker. XRD pattern showed that quartz dominated and minerals in XRD pattern were crystalline in nature.

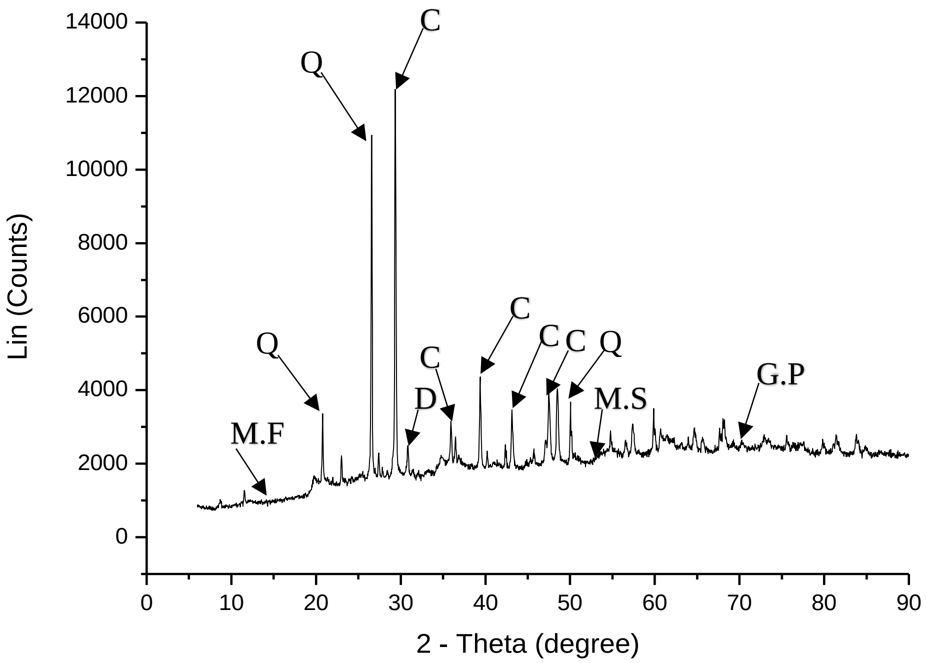


Fig. 2. A representative XRD diffractogram (Q –Quartz, M.F – Microline Feldspar, M.S – Muscivite, G.P – Gypsum, C – Calcite, D – Dolomite) of the minerals present in the bulk sample.

XRF analysis of elements in the bulk dust sample

The XRF results of the bulk sample collected close to cement plant are shown in Table 3. As for this study, Ni was the only heavy metal observed from the XRF analysis with a concentration of 0.002 mg kg^{-1} and the Pt, Pd and Rh were below detection limit. The metal oxides such as silicate, lime and aluminate were the major representative of dust sample as shown in Table 3. These metal oxides might be arising from the raw materials.

Table 3: Shows the concentration of heavy metals and metals oxides with their standard deviation obtained using the XRF analysis of the bulk sample collected close to the cement plant.

Heavy metals	Concentration (mg kg^{-1})	SD
Pt	bdl	bdl
Pd	bdl	bdl
Rh	bdl	bdl
Ni	0.002	0.002
Metal oxides		
Al_2O_3	9.545	0.26
SiO_2	38.43	0.36
CaO	15.72	0.05

SD: standard deviation bdl: below detection

Levels of PGMs in the road dust and the Crocodile River water samples

The concentrations of Pd, Pt, Rh and Ru in the Crocodile River are shown in Fig. 3. The general trend of the concentration of platinum group metals at each site was decreasing in the following order Pt > Ru > Rh > Pd. Fig. 3. Showed that the concentration of the PGMs generally increased moving along the sampling points in the Crocodile River. Elevated levels of the PGMs after the cement plant at sampling points Cr4, Cr5 and Cr6 might be due to contamination of water by the effluent from the cement plant, leaching of the metals to the water bodies and atmospheric deposition. Highest levels were observed at a sampling point CR5 with Pd (1465 mg kg^{-1}), Pt (8500 mg kg^{-1}), Rh (mg kg^{-1}) and Ru (3910 mg kg^{-1}). This sampling point CR5 might be an entry point to the Crocodile of the effluent or where the dust settlement most from the cement plant. High concentrations of Pt at all the sampling points might also be caused by large deposits of Pt in the area (Cawthorn, 2010). WHO (1991) reported that in highly industrialised areas, elevated amounts of platinum can be found in river sediments. It is assumed that organic matter, e.g., humic and fulvic acids, binds platinum, aided perhaps by appropriate pH and redox potential conditions in the aquatic environment.

The level of PGMs in the effluent sample showed that most of the metals in the Crocodile River emanate from the cement production plant.

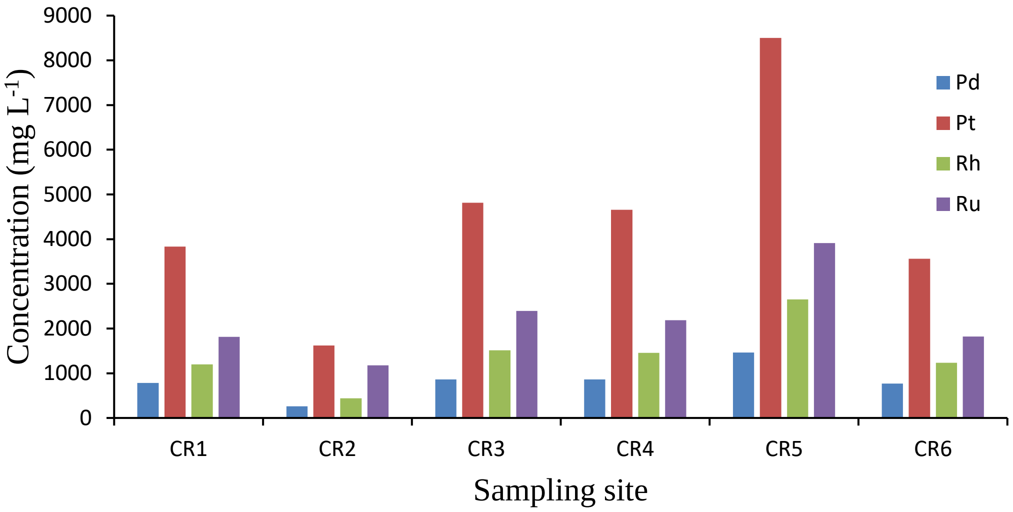


Fig. 3. Concentrations of PGMs in water samples of the Crocodile River and the factory effluent.

Fig. 4 shows the concentration of PGMs in different BCR fractions. The PGMs dominated the ERO fraction, followed by EXC, OM and RE fractions. Generally, the availability as well as the mobility of the PGMs decreased in the following order: reducible fraction (ERO) > exchangeable fraction (EXC) > oxidizable fraction (OM) > residual fraction (RE). The observed order suggest that metals were bioavailable and mobile, which can results to uptake by the plants. Platinum is mobile only in extremely acid conditions or in soil water with high chloride content (WHO, 1991). The highest concentration was observed for Pt with a concentration of 32 in the reducible fraction. The availability and the mobility of metals pose a concern to the surrounding communities as they might ingest these metals through food chain.

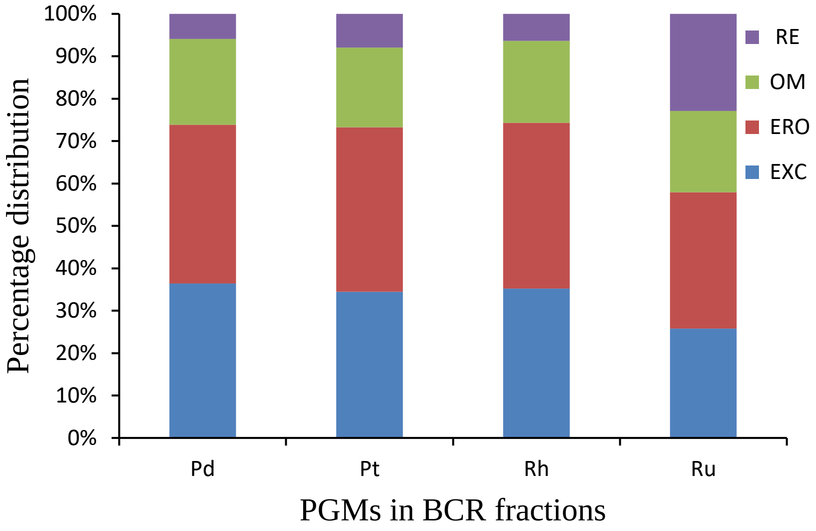


Fig. 4. Distribution of PGMs in BCR fractions with particle size of 32 µm

The concentration of PGMs in different particles size fractions are presented in Fig. 5. The level of Pt dominated all particle size fractions. Most of the PGMs were associated with the smaller particle size of $PM_{32.}$ The concentration of PGMs decreased with the increase of particle sizes. The preferential of the metals to the small particles was also observed by Wang and Chen, (2006). The level of the PGMs was high in small particle size fractions and the order was $PM_{32} > PM_{75} > PM_{125}$. This showed that PGMs in smaller particle sizes pose high risk to the people because such particles can be inhaled. The particles with small sizes are considered a major environmental and health hazard (Homolya, 1999). The general trend of each metal in the particle size fractions was decreasing in the following order; Pt > Ru > Rh > Pd. Similar metal abundance order was obtained in all three different particles size fractions. The trend depicted in the Fig. 5 shows that people living in the area around the cement plant are in danger of inhaling fine particles which can cause health problems associated with PGMs toxicity. The results suggested that size distribution of particles containing PGMs is important with respect to risk assessment of human inhalation.

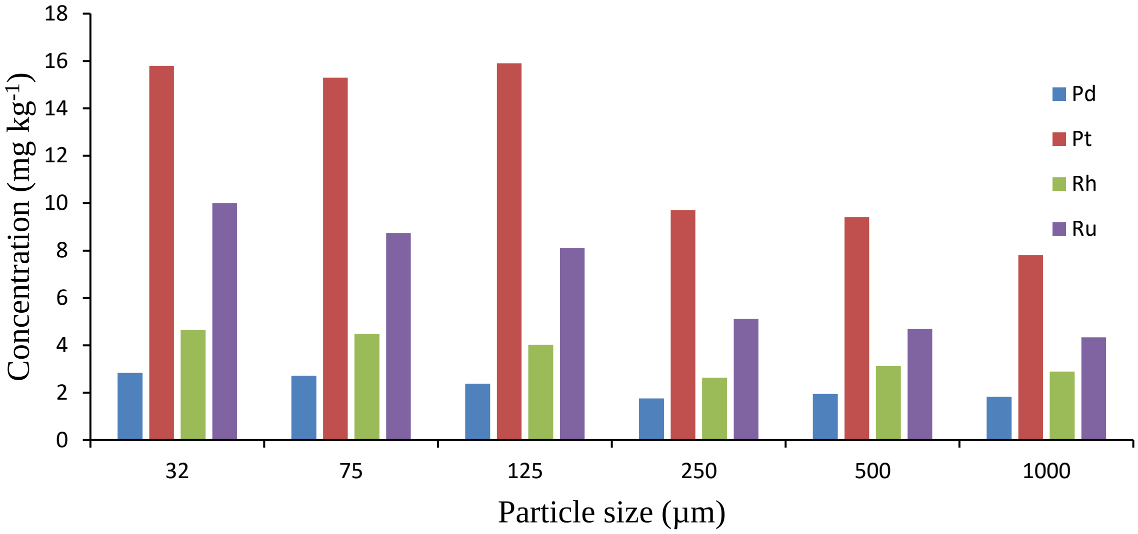


Fig. 5. PGMs concentrations in six different particle sizes fractions

The level of PGMs in different depth of the bulk soil sample collected next to the cement plant are shown in Fig. 6. The general trend was the decreasing of PGMs concentration with increasing depth from the topsoil to the deeper depth. A similar pattern was observed in Bongwha, Korea by Kim and Jung (2004). This uniform trend was observed for all PGMs from upper surface to deeper depth. The PGMs concentration decreased with depth in the following order; Pt > Ru > Rh > Pd. The concentrations of the PGMs showed that the actually topsoil is at 15 cm because of the sudden increase at this layer and a gradual decrease with depth.

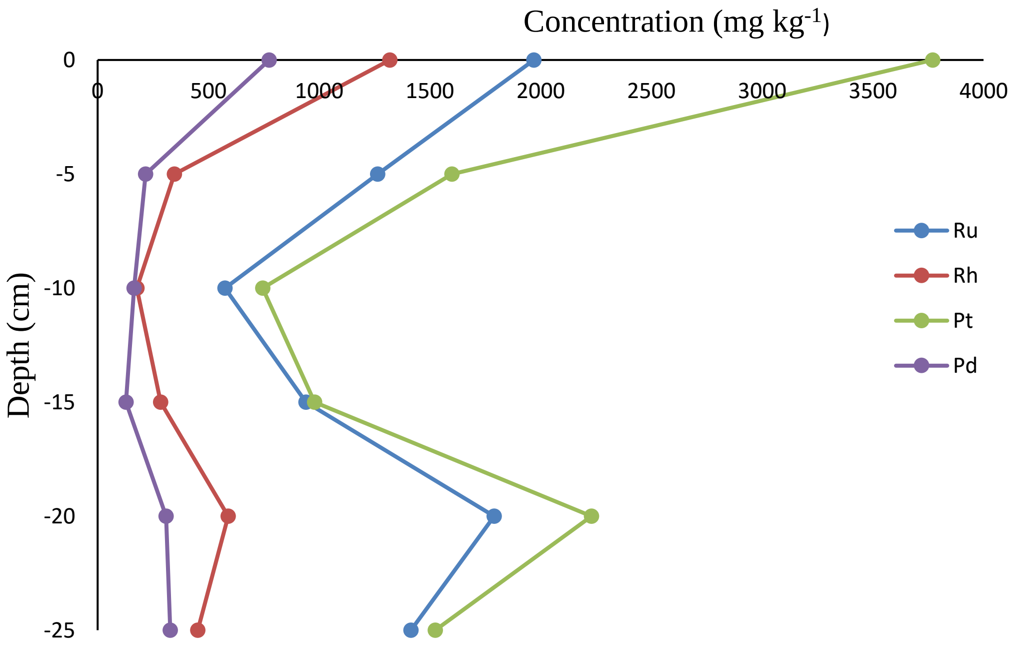
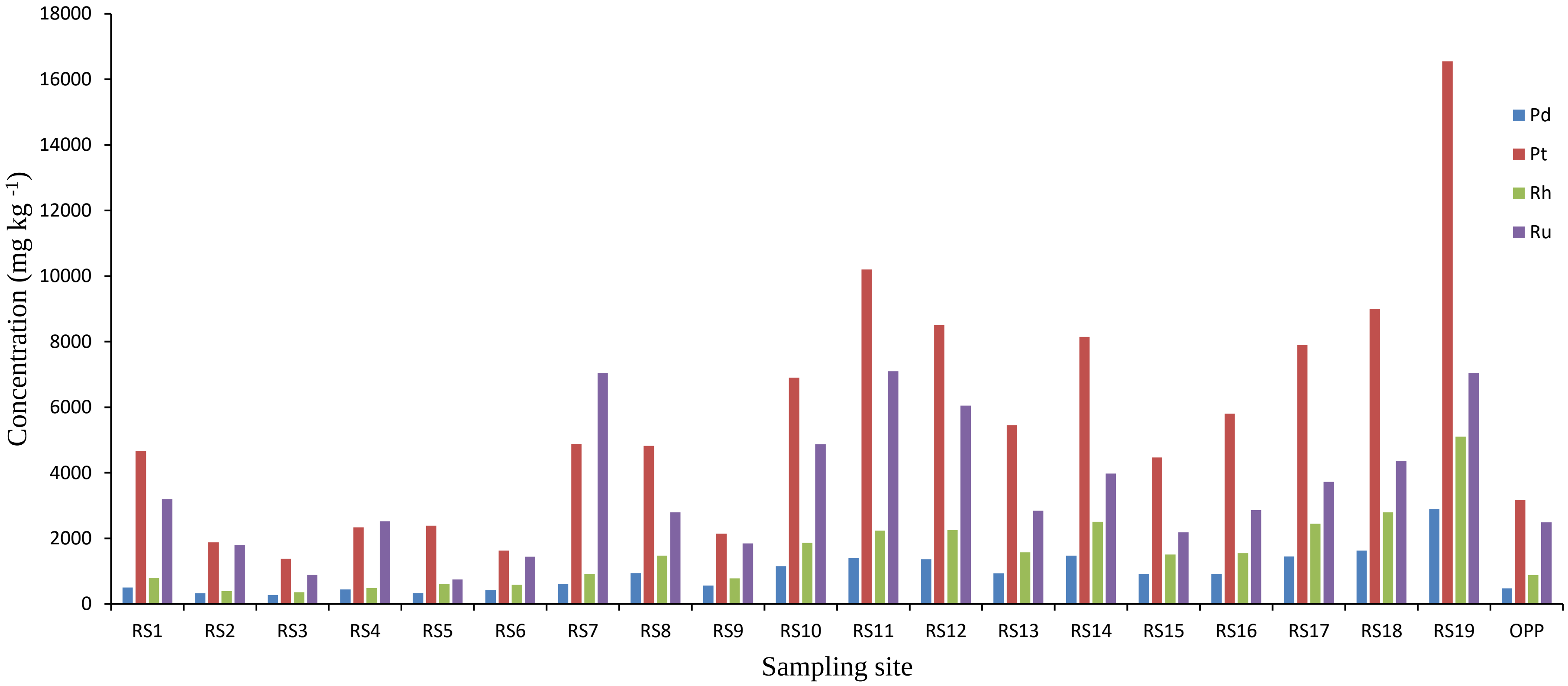


Fig. 6. PGMs concentrations in soil profile

The concentration of PGMs in particle size fraction of (PM_{32}) for dust samples collected along a gravel road are shown in Fig. 7. The highest concentrations in all the dust samples were that of Pt followed by Ru, Rh and Pd. The PGMs concentration along the dust road varied as follows Pt, (150 - 16550 mg kg^{-1}), Rh (58.5 - 5100 mg kg^{-1}), Ru (381-7100 mg kg^{-1}) and Pd (71.5 – 2895 mg kg^{-1}). Low concentration was observed at the first sampling point (RS1) which is 11 km away from the cement plant. This showed that the concentrations of the PGMs decreased with the increase of distance from the cement plant. High concentration was observed at the last sampling point (RS19) on a busy road where heavy vehicles pass by carrying cement bags and minerals. Traffic and industrial emissions are considered to be major contributors of metals pollution in road dust (Yuen et al., 2012). This high levels of PGMs on the dust road suggested that the dust road is polluted by emissions from the heavy vehicles and minerals falling on the road. It was observed that the concentrations of the PGMs were high for the dust samples collected in the eastern part than as compared to western part of cement plant. The wind direction might have influenced the direction of atmospheric deposition of dust on the eastern part from the cement plant. High amount of PGMs in the farm (OPP) might affect the crops. The results showed that dust contains high amount of PGMs than the soil because dust is much more exposed to the vehicular and rotatry kiln emissions.



Note: RS1 - RS19 are the sampling points along a dust road next to the cement plant and OPP is the sample point on a farm next to the cement plant.

Fig. 7. Distribution of heavy metals along a dust road next to the cement plant

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Conclusion

In this study, the results showed that the cement plant activities increased the accumulation of PGMs in soil and water around Koedoeskop. The level of PGMs in the samples was dominated by Pt, followed by Ru, Rh and Pd. The BCR method revealed that PGMs were available and mobile for the plant uptake, which pose health rick. The results indicated a preferential partitioning of metals to small particle size fractions in all samples. The dust contained minerals such as quartz, calcite, muscovite, dolomite, microline feldspar and gypsum. Dust road was highly contaminated with the PGMs especially in next to the cement plant and along the busy road. This study showed that monitoring and risk assessment are necessary to evaluate the PGMs concentration in dust in order to develop the proper measures for reducing health effects associated with inhalation and ingestion of dust. High level of PGMs showed that the water suppressant was not effectively suppressing the PGMs on the dust road. An efficient method that can suppress dust with the PGMs is required to avoid resuspension of the PGMs with dust, which pose health hazard to the people in the surrounding communities next to the cement plant.

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Chapter 5

5 General conclusions and future work

In this chapter, general conclusions based on experimental findings from the papers are discussed. The work carried out in this research and a discussion of the achieved objectives is also presented. The recommended future work is also presented at the end of this section.

5.1 Conclusions

Plants within a wetland of the Mvudi River were used to investigate their effectiveness to phytoremediation of heavy metals within a wetland **(paper I)**. The concentration of heavy metals showed that there was accumulation of heavy metals by the plants within the wetland, as shown by decrease of the heavy metals concentration in water samples within the wetland. The water samples showed that the heavy metals concentration decreased within the wetland when compared to the heavy metals concentration before the wetland. The study showed the importance of wetland on improving water quality in the river.

The soil samples collected next to the source of pollution were used to establish the distribution of heavy metals in soil depth and particle size fractions (**paper II, III and IV**). Soil samples were also collected at interval distances moving away from the source **(paper II)**. The results showed that the concentration of heavy metals generally decreased with distance from the source, increased with the decrease of particle size and decreased with the increase of soil depth. The results revealed that sediments samples accumulate high concentration heavy metals **(paper II**).

The application of BCR to soil and dust samples showed that the heavy metals were not mobile and bioavailable for plant uptake (**paper II, III and IV**). The availability as well as the mobility of the metals decreased in the order: exchangeable fractions > reducible fractions > oxidizable form > residual form. Spatial distribution of heavy metals bind to dust in urban streets showed that high amount of metals were concentrated to locations nearest to the plant (**paper IV**). The investigation of platinum group metals along a dust suppressant gravel road in Thabazimbi revealed that the metals were released with cement dust and existed naturally.

Analysis of fruit and vegetables showed that irrigation water and the soil were contaminated with heavy metals (**paper V**). The concentration of heavy metals were found to be higher than the recommended limits by WHO and FAO raising concerns to the health of people who consume the fruits and vegetables sampled from the farms affected. The overall study showed that indeed the surrounding areas of cement factories are in danger of heavy metal pollution of the soil, water and air.

5.2 Future work

A depth analysis of the areas surrounding the cement factories is imperative to develop a proper detailed information on how the factories affect the environment.

A sampling method that can sample dust from the air as it being released, collection of dust on plants leaves and nearby buildings can be used to improve the quality of the dust samples (**paper III and IV**). This can be used to obtain exact contents of dust as it is being released before settling on soil. Seasonal analysis can be conducted to compare the amount of heavy metals released seasonally. A study which involve a questioner to the people living next to cement factories may be used to find information about the effects of heavy metal.

The content of Fe, Mg and organic compounds in soil can also be analysed to found out how they influence the amount of heavy metals in depth analysis (**paper II, III and IV).** Water containing lime from cement plants which is used as dust suppressant can be analysed to find a role it can plays in preventing metal resuspension with dust on the gravel roads (**paper IV**).

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Supplementary paper

This paper “Heavy metal accumulation in fruits, vegetables and soils in Thohoyandou” investigated the level of Cd, Ni and Mn in edible parts of fruits and vegetables cultivated close to a cement brick making factory.

Heavy metal accumulation in fruits, vegetables and soils in Thohoyandou, South Africa

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ABSTRACT

The accumulation of heavy metals such as Cd, Mn and Ni was investigated in seven different vegetables (spinach/*Spinacia oleracea*, Chinese cabbage/*Brassica rapa*, onion/*Allium cepa*, beetroot/*Beta vulgaris*, sweet potatoes/*Ipomoea batatas*, tomatoes/ *Lycopersicon esculentum* and cabbage/*Brassica pekinensis*), fruits (bananas/*Musa acuminate*) and soil samples in Thohoyandou, Limpopo Province in South Africa. Heavy metals were quantified using graphite furnace atomic absorption spectrometry (GFAAS). Concentrations of heavy metals in fruits and vegetables were in the range of 0.23 – 2.94 mg kg^{-1} for Cd, 11.72 – 50.16 mg kg^{-1} for Mn and 5.73 – 44.11 mg kg^{-1} for Ni on a dry weight basis. Analysis of soils from where fruits and vegetables were sampled showed that Cd in the soil was in the range of 0.08 – 1.07 mg kg^{-1}, Mn levels were 204.99 – 249.13 mg kg^{-1} and Ni levels were 48.47 – 88.23 mg kg^{-1}. Cd was below the instrument detection limit for soils on which onions and bananas were grown. Vegetables showed different accumulation abilities, with leafy vegetables being the highest accumulators of heavy metals. The obtained results showed that concentrations of Cd in fruits, vegetables and soils exceeded the recommended maximum acceptable levels proposed by FAO/WHO and hence, may pose a health risk to consumers. Ni concentrations in bananas, onion, beetroot, spinach and Chinese cabbage exceeded recommended standards by FAO/WHO. The presence of heavy metals in soil, fruits and vegetables might be due to atmospheric deposition of cement dust on vegetables and vehicular traffic emissions.

Keywords: Heavy metals, fruits and vegetables, soil, bioaccumulation factor, toxicity, contamination

INTRODUCTION

Contamination of food by heavy metals is often due to environmental and industrial contamination such as industrial emissions, irrigation water and the harvesting processes (Huang et al., 2014). Cement production is among the anthropogenic activities that contribute to environmental pollution through the emission of cement dust (Bermudez et al., 2010). Cement dust contains pollutants such as heavy metals, particulates and dioxins, which may pose a health risk to humans (Tajudeen et al., 2011). Soils and plants serve as sinks for atmospheric deposition of heavy metals from industrial emissions (Bermudez et al., 2010; Hao et al., 2009; Hernández-Martínez and Navarro-Blasco, 2012). Wind and seepage waters can carry cement dust and result in its accumulation in soils and on plants (Taghipour et al., 2013; Li et al., 2015; Xu et al., 2014). Heavy metals that may be contained in cement dust include As, Cd, Pb, Hg, Tl, Al, Be, Cr, Cu, Mn, Ni, and Zn (Schuhmacher et al., 2002; Engelbrecht et al., 2013; Oganbileje et al., 2013).

Phytotoxicity and elevated heavy metal uptake by food crops are a result of excessive accumulation of these heavy metals in agricultural soils and hence contributing to food insecurity (Kabata-Pendias and Mukherjee, 2007; Nagajyoti et al., 2010). Furthermore, the potential of heavy metals to bioaccumulate in the food chain has led to health concerns. Excessive bioaccumulation of toxic heavy metals in vegetables may result in dietary nutrients being unavailable to humans or induce health problems to both humans and ecosystems (Ogunkunle et al., 2013; Wuana and Okieimen, 2011; Hu et al., 2013; Yang et al., 2009). Moreover, cement dust deposition on plants can cause stomatal clogging, and hence affecting the growth of plants (Abdel- Rahman and Ibrahim, 2012; Prajapati and Tripathi, 2008).

Heavy metals are harmful due to their long biological half-lives, non-biodegradable and persistent nature (Arora et al., 2008; Shalini et al., 2017). Continuous consumption of unsafe concentrations of heavy metals through foodstuffs may lead to chronic accumulation of heavy metals in the kidney and liver of humans, resulting in the disruption of numerous biochemical processes and hence leading to cardiovascular, nervous, kidney and bone diseases (Zhou et al., 2016; Sharma et al., 2009). Chronic Cd exposure can cause acute toxicity to the liver and lungs, induce nephrotoxicity and osteotoxicity and impair the function of the immune system

(Klaassen et al., 2009; Patrick, 2003). Acute health effects of Ni due to exposure to high concentrations of pollutants are shown by clinical symptoms such as nausea, vomiting, abdominal discomfort, diarrhoea, visual disturbance, headache, giddiness and cough (Duda-Chodak and Blaszczyk, 2008).

Vegetables are a rich source of vitamins, minerals and fibre, whereas fruits are a rich source of carbohydrates, proteins, vitamins, minerals and fibre, which are required for human health (Cherfi et al., 2014). Zn, Cu, Mn, Ni and Co are essential heavy metals that might be contained in fruits and vegetables. However, they can be toxic when their concentrations exceed the tolerable limit in living organisms. Non-essential heavy metals such as Hg, Pb, As, Cr and Cd are non-essential heavy metals and they are toxic to cells of the body even at low concentrations (Izah et al., 2016).

In this study the presence of Mn, Cd and Ni was investigated in soil, fruits and vegetables from a small scale farm in the vicinity of a cement brick laying company in Thohoyandou, South Africa. The close proximity of this farm to the cement brick laying company might result in the contamination of soil, vegetables and fruits with heavy metals from cement dust. Moreover, this small scale farm is close to one of the busiest roads in Thohoyandou. There have been few studies that have focused on heavy metal contamination on fruits and vegetables in South Africa (Bvenura and Afolayan, 2012). Furthermore, none of the previous studies examined heavy metals in soil, vegetables and fruits simultaneously in Thohoyandou, hence this was done as a first attempt. Monitoring levels of heavy metals can provide useful information for promoting food safety in South African food industries and setting national standard limits since there are none at the moment.

EXPERIMENTAL

Chemicals

Nitric acid, hydrochloric acid, manganese sulphate, cadmium sulphate and nickel sulphate analytical reagents were purchased from Merck (Johannesburg, South Africa). Polyethylene bags and all the glassware were purchased from Lasec (Johannesburg, South Africa).

Instruments and materials

Heavy metals concentrations were analysed using a graphite furnace-AAS technique (Perkin Elmer Model Pinnacle 900T, Perkin Elmer, Singapore/Germany), fully automated and PC-controlled using Syngistix AA. A Mars 5 microwave assisted digestion system (CEM Corporation, USA) was used for the digestion of fruits and vegetables. A Restch grinder and mesh sieves of 2 mm, 1 mm, 500 µm, 250 µm and 75 µm sizes were purchased from Retsch GmbH (Haan, Germany). A portable Multi-probe Boeco pH meter purchased from Rochelle (Johannesburg, South Africa) was used to measure the pH and electrical conductivity (EC) of soil samples.

Study area

Thohoyandou is a town in the Limpopo Province of South Africa. It is the administrative centre of Vhembe District Municipality and Thulamela Local Municipality. Daily temperatures in the town vary between 20°C and 40°C in wet seasons and 12°C and 22°C in dry seasons, respectively. The average annual rainfall in the town is approximately 800 mm, but it often ranges between 340 mm and 2000 mm. The prevailing wind direction is east to southeast in both the summer and the winter months. The average wind speed is 11 km hr^{-1} in summer and 15 km hr^{-1} in winter (Mzezewa et al., 2010). . The town is at its urbanization and development stage, with a modern shopping mall being the most recent big development. People are also building houses from time to time since the town is expanding. There are two brick laying companies which supply building materials that are situated on the western part of town. The brick laying company of which is the possible source of heavy metals of interest is about 1 km away from the sampling site in this study. Figure 1 shows the sampling area and the sampling points indicated by the red circles.

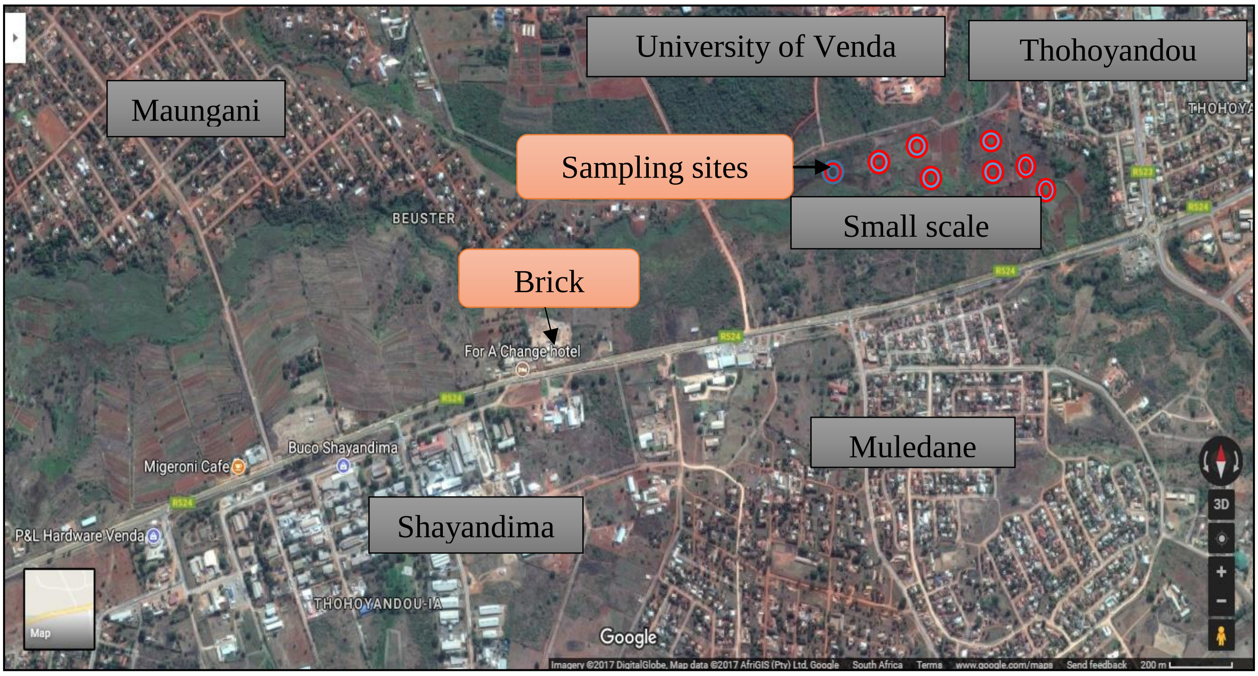

Figure 1

Sampling area showing a brick laying company and the nearby small scale farms including the red circled sampling points

Sample collection

A sampling method described by Zhou et al. (2016) and Sharma et al. (2009) was used. Bananas and seven vegetable samples of different vegetable species were collected from a small scale farm close to a bricklaying company in Thohoyandou using the random sampling method. Tomatoes are of the solanaceous vegetable species, onion is an allimus vegetable, sweet potatoes and beetroot are root vegetables whereas Chinese cabbage, spinach and cabbage are leafy vegetables. All samples were stored in polyethylene bags for transport at a constant temperature of 4°C. Soil samples were collected from the upper soil (0 – 20 cm) in the same location where vegetables were sampled using a stainless steel spade and stored in polyethylene bags for transport.

Sample preparation

Fruit and vegetable samples were cleaned with deionised water to remove dust and soil. The edible parts of the vegetables were separated from the plants, chopped into small pieces and air dried until the weight of the sample remained constant. All samples were ground to fine powder using a Restch grinder and passed through a series of sieves and the 75 µm fraction was used for analysis. Approximately, 0.2 g of each sample was weighed into a Teflon vessel and digested in 12 mL of HNO_3 using a Mars-5 microwave assisted digestion system according to the program shown on Table 1. The resulting solutions were filtered using Whatmann No. 42 filters into 50 mL volumetric flasks and filled up to the mark with deionised water and then analysed for concentrations of Mn, Cd and Ni using graphite furnace atomic absorption spectrometry. Standard solutions of the three elements under the study were prepared. The measurements were made using hollow cathode lamps of Mn, Cd and Ni at wavelengths of 193.7, 228.8 and 279.49 nm, respectively.

TABLE 1

Digestion program for the vegetables and fruits with a microwave assisted acid digestion system

Stage	Power (%)	Ramp time (min)	Pressure (psi)	Temperature (°C)	Hold time (min)
1	100	4	800	180	8
2	100	5	800	180	5

Soil samples were air dried at room temperature to constant mass and were passed through a 75 µm sieve plastic sieve to remove large debris, gravel-size materials, plant roots and other waste materials and stored in closed plastic bags until analysis. The pH and electrical conductivity (EC) of the soil slurry were measured with a pH multi-meter at 1:5 (w/v) ratio soil to water suspension. For the analysis of the total concentrations of soil metals, approximately, 0.2 g of each sample was weighed into a 250 mL beaker and digested using aqua regia (5 mL HNO_3 and 15 mL HCI). The mixture was heated for 3 hours on a hot plate to near complete evaporation, then 20 mL of 2% HNO_3 was added into the beaker. The solution was filtered through a Whatman No. 42 filter paper into a 100 mL volumetric flask and filled to the mark using a deionised water. The prepared samples were analysed using the GF-AAS.

RESULTS AND DISCUSSION

Chemical properties of soil

Table 2 shows some chemical properties of the composite soil sample. The pH of the composite soil sample was 6.73 indicating that the soil was near neutral pH. Soil acidification has an effect of reducing nutrient supply and increasing the dissolution of heavy metals such as Mn and Cd and hence increasing their absorption by plants (Dorraji et al., 2010). The pH of the soil is a critical factor in controlling the bioavailability of trace elements, especially for Cd (Adriano, 2001; Kabata-Pendias and Pendias, 2001). The soil electrical conductivity was 95.3 mS m^{-1}. The soil in this study was clayey, hence it has the ability to store and bind cations. XRF results showed that the composite sample contained 87.1 mg kg^{-1} of Ni which was above the standard value as stipulated by FAO/WHO. These results correspond to the concentrations of Ni in soils obtained by AAS as shown on Table 4. Cd was not detected.

TABLE 2
Chemical properties of soil

Sample name	pH	EC (mS m^{-1})	Mn (mg kg^{-1})	Ni (mg kg^{-1})	Cd (mg kg^{-1})
Composite	6.73	95.3	-	87.1	0
Standard value in soil*	-	-	-	50	0.3

-Not available, *FAO/WHO, 2011

Heavy metal concentrations in edible parts of fruits and vegetables

The concentrations of Cd, Mn and Ni found in fruits and vegetables are shown in Table 3. The range of concentrations of heavy metals in fruits and vegetables was in the order Mn > Ni > Cd. The same trend was obtained by Laniyan et al. (2014) in vegetables. The obtained concentration ranges were 0.23 – 2.94mg kg^{-1}, 11.72 – 50.16 mg kg^{-1} and 5.73 – 44.11 mg kg^{-1} for Cd, Mn and Ni, respectively. The concentrations of Cd in fruits and vegetables exceeded the recommended maximum acceptable levels proposed by FAO/WHO (2002 and 2011). Ni concentrations in bananas, onion, beetroot, spinach and Chinese cabbage exceeded recommended standards by FAO/WHO (2002 and 2011). The lowest concentrations of Cd, Mn and Ni were obtained in bananas and cabbage green outer leaves, whereas the highest concentrations were found in the spinach. Vegetable species differ generally in their ability to take up and accumulate heavy metals, even among cultivars and varieties within the same species (Saumel et al., 2012). Cd accumulation in vegetable species decreased in the order of leafy vegetables > root vegetables > allimus vegetables > solanaceous vegetables. Onion leaves showed a higher accumulation of Cd compared to the onion bulb. The concentrations of Mn were in descending order, leafy vegetables (spinach, Chinese cabbage, cabbage inner layer leaves) > allimus vegetables (onion leaves) > root vegetables (beetroot and sweet potatoes) > solanaceous (tomatoes) > fruit (bananas). This trend was similar to that found by Zhou et al. (2016). However, the concentration of which Mn in cabbage outer green leaves was lower compared to the rest of the leafy vegetables. The highest concentration of Ni was observed in spinach (leafy vegetable). However, there is no clear trend for the rest of the vegetables according to their species. High concentrations of heavy metals in leafy vegetables might be due to the interception of heavy metals emitted in the atmosphere by leaves, remaining on the leaf surface or entering the leaf tissues, although a selective metal uptake by roots can also affect metal contents in leaf tissues (Maisto et al., 2013). The exposed surface area of the leaves may influence the deposition of aerial dust (Prajapati, 2002).

Results of this study are in agreement with the results obtained by Ali and Al-Qahtaini (2012), who reported that Mn and Cd concentrations ranged from 4.16 – 94.16 mg kg^{-1} and 0.92 – 4.13 mg kg^{-1}, respectively in different vegetables. The concentrations of Cd and Mn in cabbage, onion, spinach and tomatoes correspond to the results reported by Bvenura and Afolayan (2012), except that the Cd concentration in spinach samples in this study were higher. In a more recent study by Shaheen et al. (2016) a concentration of 0.05 mg kg^{-1} of Cd in tomatoes was reported which was above the recommended standard limit by FAO/WHO. The high concentration levels of heavy metals might be due to atmospheric deposition of contaminated dust on the leaves. Cement dust from the bricklaying company might be responsible for the presence of heavy metals in vegetables and fruits. Cement dust maybe carried by wind and deposited on the vegetables and the soil. Automobiles might also be a source of heavy metal contamination. The sampling site is less than a kilometre away from one of the busiest roads that connect Thohoyandou and the town of Louis Trichardt. There is no recommended standard for manganese concentrations in fruits and vegetables.

TABLE 3

Concentrations of heavy metals in edible parts of fruits and vegetables (mg kg^{-1} dry weight) from a small scale farm in Thohoyandou

Sample name	Cd	Mn	Ni
Maximum permissible limit† (mg kg^{-1})	0.05 (fruits) † 0.05 (vegetables) *	NA (fruits) NA (vegetables)	0.80 (fruits) † 10.00 (vegetables)*
Cabbage green outer leaves	0.29	13.68	5.73
Cabbage inner layer leaves	0.54	22.58	6.55
Onion leaves	0.74	30.65	12.51
Onion bulb	0.91	22.65	10.84
Spinach	2.94	50.16	44.12
Chinese cabbage	0.77	31.78	11.38
Beetroot	1.08	29.95	19.07
Sweet potatoes	0.57	23.92	9.34
Tomatoes	0.60	15.75	7.97
Bananas	0.23	11.72	8.54

ND-not detected; NA-not available; † FAO/WHO, 2002; *FAO/WHO, 2011

Heavy metal concentrations in soil

The concentrations of Cd, Mn and Ni in soil samples collected where fruits and vegetable were grown are shown in Table 3. The concentrations of Cd, Mn and Ni ranged from 0.03 – 1.07 mg kg^{-1}, 204.99 – 249.13 mg kg^{-1} and 48.47 – 88.23 mg kg^{-1}, respectively. The concentrations of heavy metal were in the order Mn > Ni > Cd which is the same order in the samples of fruits and vegetables. Cd was below instrumental detection limits for soils where onions and bananas were grown. The Cd concentrations of soils where tomatoes and spinach were grown were above FAO/WHO standards. The concentration of Ni was below the FAO/WHO standard only for the soil where cabbage was grown. The concentrations of Cd obtained in this study were similar to the results obtained by Liu et al. (2015) where their Cd concentrations ranged between 0.0541 and 0.8487 mg kg^{-1} in vegetable soils. The concentrations of Cd and Mn were comparable to the results obtained by Bvenura and Afolayan (2012), although the concentration of Cd in the soil where spinach was grown was higher. However, Mn concentrations obtained by Bvenura and Afolayan (2012) are slightly higher and were ranging between 377.61 mg kg^{-1}and 499.68 mg kg^{-1}.

Phosphate fertilizers are an important source of heavy metals entering agricultural soils, especially Cd (Nicholson et al. 2003). Traffic pollution is also an important source of Cd and it is mainly from the aging and wear of automobile tires, gasoline and car body wear and brake lining wear (Weckwerth 2001).

TABLE 4

Concentrations of heavy metals in soil collected under the mentioned fruit/vegetable (mg kg^{-1} dry weight)

Sample name	Cd	Mn	Ni
Maximum permissible limit† (mg kg^{-1})	0.30 *	N/A	50.00 *
Cabbage	0.20	211.81	48.47
Onion	ND	223.26	74.71
Spinach	1.07	229.13	88.23
Chinese cabbage	0.03	204.99	68.83
Beetroot	0.08	210.14	83.50
Sweet potatoes	0.12	230.27	80.20
Tomatoes	0.32	245.13	74.32
Bananas	ND	249.13	66.52

ND-not detected, *FAO/WHO, 2011

Bioaccumulation factor in fruits and vegetables

The bioaccumulation factor (BF) can be used to estimate the ability of plants to accumulate heavy metals in their edible tissues. The bioaccumulation factor was calculated using the following equation.

$$\text{Bioaccumulation factor} = C_{plant}/C_{soil}$$

where C_{plant} is the heavy metal concentration in edible tissues of a plant and C_{soil} is the heavy metal concentration in soil.

The bioaccumulation factors for Cd, Mn and Ni were 1.45 – 25.67, 0.05 – 0.22 and 0.11 – 0.50, respectively and these results are shown on Table 5. Cd has the highest BF, hence the uptake of Cd by vegetables is higher than for Mn and Ni. The trend of the bioaccumulation factor for Mn and Ni is similar to the trend of the concentrations of these heavy metals in fruits and vegetables, with spinach having the highest BF for both heavy metals, showing that leafy vegetables have a greater ability to bioaccumulate heavy metals. Chinese cabbage (leafy vegetable) had the highest bioaccumulation factor for Cd and this corresponds to the findings by Zhou et al. (2016). The strong ability to accumulate Cd by all the vegetables might be due to acidity of the soil and water used for irrigation. Acidity increases the solubility of heavy metals and hence making them readily available for absorption by plants.

TABLE 5

Bioaccumulation factors of fruits and vegetables from a small scale farm in Thohoyandou

Sample name	Cd	Mn	Ni
Cabbage green outer leaves	1.45	0.06	0.12
Cabbage inner layer leaves	2.70	0.11	0.14
Onion leaves	-	0.14	0.17
Onion bulb	-	0.10	0.15
Spinach	2.75	0.22	0.50
Chinese cabbage	25.67	0.15	0.16
Beetroot	13.33	0.14	0.23
Sweet potatoes	7.58	0.10	0.12
Tomatoes	1.88	0.06	0.11
Bananas	-	0.05	0.13

-Not available

CONCLUSION

The range of concentrations of heavy metals in fruits and vegetables was in the order Mn > Ni > Cd. The obtained results showed that concentrations of Cd in fruits, vegetables and soils exceeded the recommended maximum acceptable levels proposed by FAO/WHO and hence this may pose a risk to public health. The concentrations of Ni in bananas, onion, beetroot, spinach and Chinese cabbage exceeded recommended standards by FAO/WHO. Vegetables showed different heavy metal accumulation abilities, with leafy vegetables being the highest accumulators of heavy metals. Heavy metal uptake and accumulation was high for leafy vegetables and low for tomatoes (solanaceous vegetables) and bananas.

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Appendix

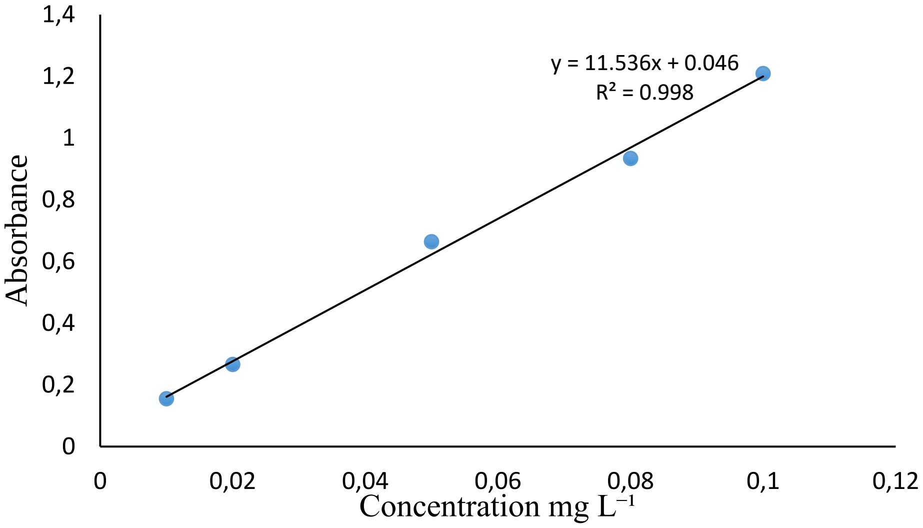

Fig. 1A. Calibration graph of chromium

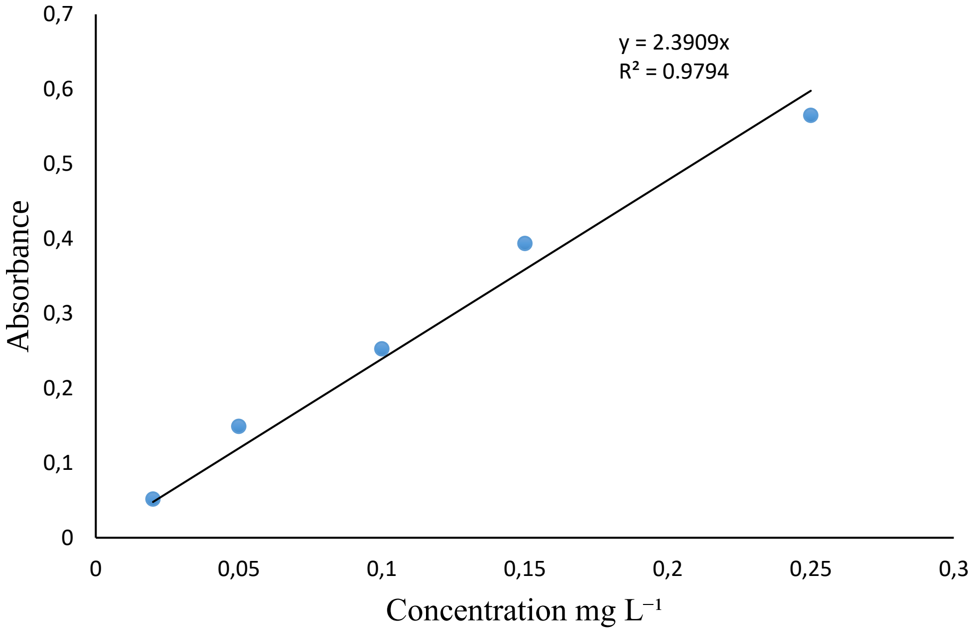

Fig. A2. Calibration graph of Lead

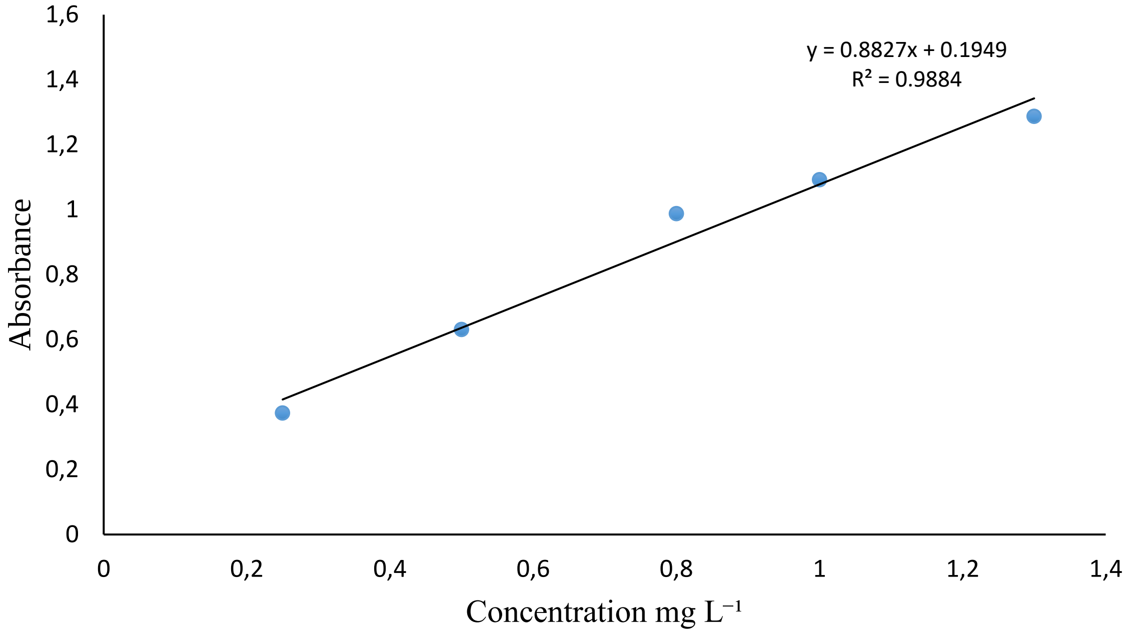

Fig.3A. Calibration graph of Zinc

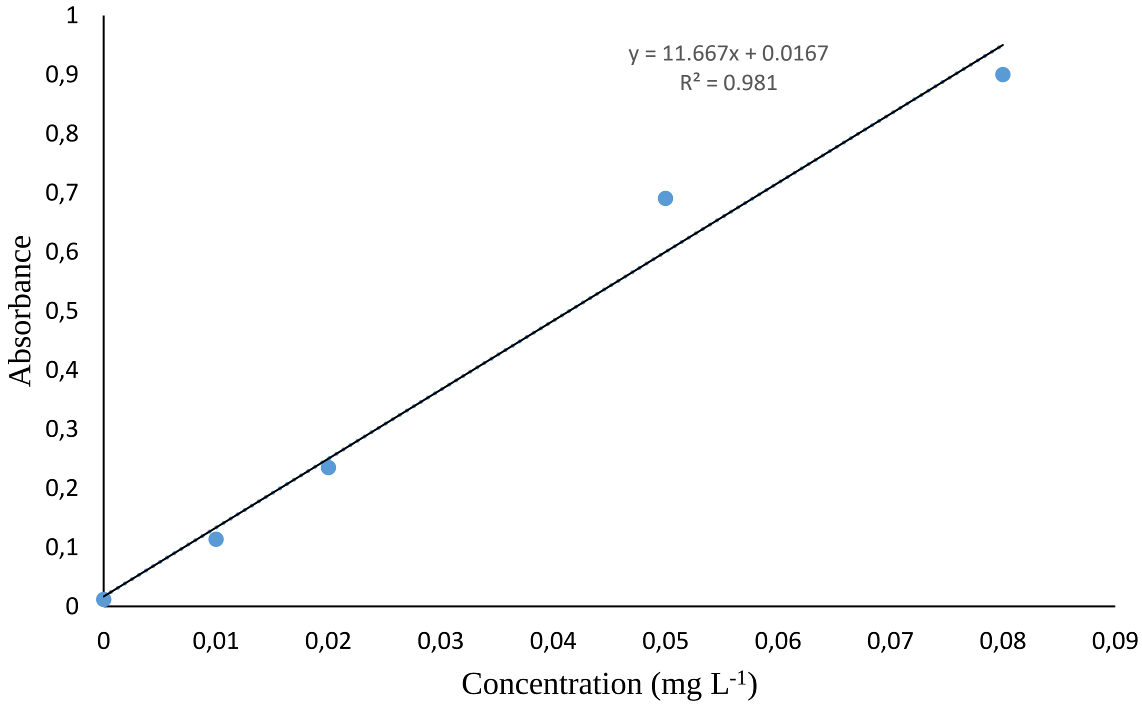

Fig. A4. Calibration graph of Cadmium

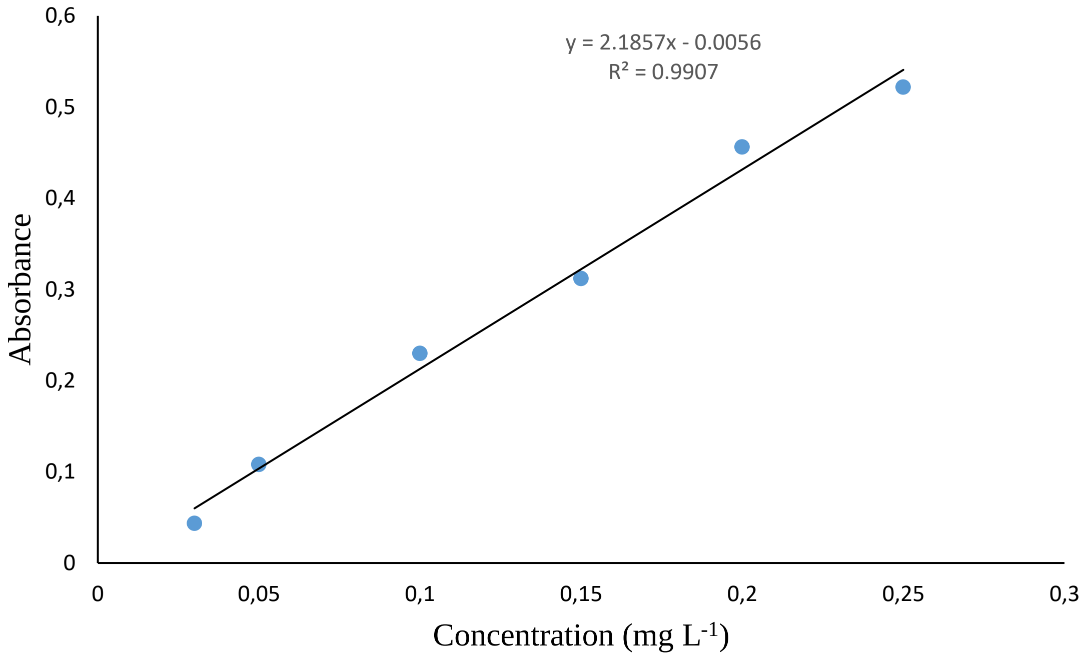

Fig. A5. Calibration graph of Nickel

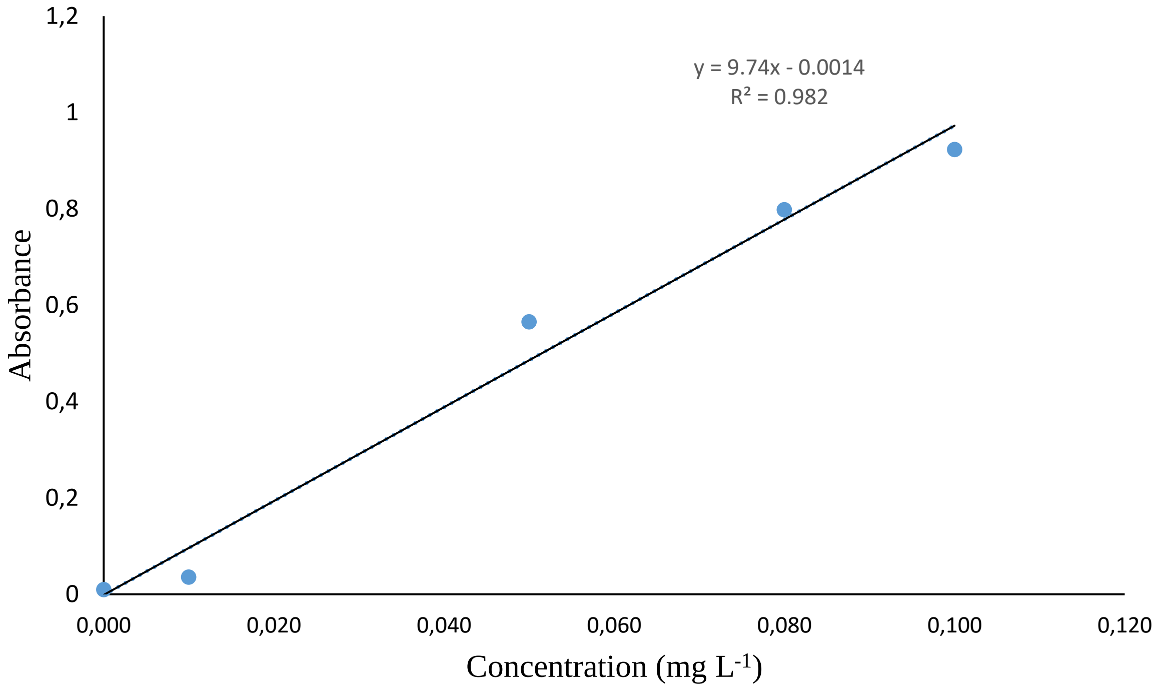

Fig. A6. Calibration graph of Manganese

Table 1A. The XRF analysis of BS0 sample

Element	Percentage (%)	-/+ [*3]
Mgo	0.674	0.684
Al_2O_3	11.273	0.281
SiO_2	36.936	0.348
P_2O_5	0.079	0.024
S	0.081	0.012
Cl	0.007	0.008
K2O	1.000	0.015
CaO	5.254	0.028
Ti	0.679	0.008
V	0.006	0.003
Cr	0.010	0.002
Mn	0.296	0.012
Fe	4.038	0.040
Co	0.000	0.005
Ni	0.003	0.002
Cu	0.005	0.001
Zn	0.003	0.001
Se	0.000	0.001
Rb	0.004	0.001
Sr	0.002	0.001
Y	0.001	0.001
Zr	0.018	0.001
Nb	0.000	0.001
Mo	0.001	0.001
Rh	0.000	0.002
Ag	0.000	0.002
Cd	0.000	0.003
Sn	0.002	0.020
Sb	0.000	0.004
Ba	0.046	0.018
La	0.000	0.030
Hf	0.000	0.003
Ta	0.001	0.002
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.000	0.001
Tl	0.000	0.001
Pb	0.000	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	0.000	0.006
Ce	0.000	0.003
Pd	0.000	0.001

Table 2A. XRF analysis of BS1 sample

Element	Percentage (%)	-/+ [*3]
Mgo	0.324	0.647
Al_2O_3	14.568	0.314
SiO2	43.435	0.379
P_2O_5	0.053	0.019
Cl	0.019	0.010
K_2O	1.230	0.016
CaO	0.938	0.014
Ti	0.860	0.009
V	0.007	0.003
Cr	0.015	0.002
Mn	0.062	0.007
Fe	4.288	0.039
Co	0.000	0.004
Ni	0.005	0.002
Cu	0.005	0.001
Zn	0.003	0.001
Se	0.000	0.001
Rb	0.004	0.001
Sr	0.024	0.001
Y	0.001	0.001
Zr	0.014	0.001
Nb	0.000	0.001
Mo	0.001	0.001
Rh	0.000	0.001
Pd	0.000	0.003
Ag	0.000	0.002
Cd	0.000	0.002
Sn	0.000	0.019
Sb	0.000	0.004
Ba	0.048	0.018
La	0.000	0.029
Hf	0.000	0.003
Ta	0.001	0.002
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.000	0.001
Tl	0.000	0.001
Pb	0.001	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	0.000	0.006

Table 3A. The XRF analysis of BS2 sample

Element	Percentage (%)	-/+ [*3]
Mgo	0.500	0.613
Al_2O_3	10.826	0.268
SiO_2	46.003	0.386
P_2O_5	0.057	0.018
Cl	0.195	0.010
K_2O	1.345	0.016
CaO	0.943	0.014
Ti	0.658	0.008
V	0.004	0.002
Cr	0.034	0.002
Mn	0.033	0.006
Fe	2.709	0.030
Co	0.000	0.003
Ni	0.005	0.002
Cu	0.004	0.001
Zn	0.002	0.001
Se	0.000	0.000
Rb	0.003	0.001
Sr	0.021	0.001
Y	0.000	0.001
Zr	0.011	0.001
Nb	0.000	0.001
Mo	0.000	0.001
Rh	0.000	0.001
Pd	0.000	0.003
Ag	0.000	0.002
Cd	0.000	0.003
Sn	0.002	0.019
Sb	0.000	0.004
Ba	0.038	0.017
La	0.000	0.028
Hf	0.000	0.003
Ta	0.001	0.001
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.000	0.001
Tl	0.000	0.001
Pb	0.000	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	1.000	0.005
Ce	0.000	0.006

Table 4A. The XRF analysis of BS3 sample

Element	Percentage (%)	-/+ [*3]
Mgo	0.241	0.622
Al_2O_3	13.339	0.296
SiO_2	41.686	0.365
P_2O_5	0.065	0.019
Cl	0.471	0.012
K_2O	1.191	0.016
CaO	0.767	0.013
Ti	0.709	0.008
V	0.004	0.003
Cr	0.061	0.003
Mn	0.032	0.006
Fe	3.767	0.036
Co	0.000	0.004
Ni	0.016	0.003
Cu	0.004	0.001
Zn	0.002	0.001
Se	0.000	0.000
Rb	0.003	0.001
Sr	0.020	0.001
Y	0.000	0.001
Zr	0.011	0.001
Nb	0.000	0.006
Mo	0.001	0.001
Rh	0.000	0.002
Pd	0.000	0.002
Ag	0.000	0.002
Cd	0.000	0.003
Sn	0.005	0.020
Sb	0.000	0.004
Ba	0.037	0.017
La	0.000	0.027
Ce	0.000	0.007
Hf	0.000	0.003
Ta	0.000	0.002
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.000	0.001
Tl	0.000	0.001
Pb	0.000	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	0.000	0.005

Table 5A. The XRF analysis of CBF sample

Element	Percentage (%)	-/+ [*3]
Mgo	0.484	0.647
Al_2O_3	12.962	0.296
SiO2	40.192	0.361
P_2O_5	0.051	0.020
Cl	0.000	0.011
K_2O	1.048	0.015
CaO	1.701	0.018
Ti	0.701	0.008
V	0.007	0.003
Cr	0.024	0.003
Mn	0.062	0.007
Fe	3.860	0.037
Co	0.000	0.004
Ni	0.006	0.003
Cu	0.005	0.001
Zn	0.003	0.001
Se	0.000	0.001
Rb	0.004	0.001
Sr	0.027	0.001
Y	0.001	0.001
Zr	0.015	0.001
Nb	0.000	0.001
Mo	0.000	0.001
Rh	0.000	0.002
Pd	0.000	0.002
Ag	0.000	0.002
Cd	0.000	0.002
Sn	0.002	0.020
Sb	0.000	0.004
Ba	0.046	0.018
La	0.000	0.029
Hf	0.000	0.003
Ta	0.001	0.002
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.001	0.001
Tl	0.000	0.001
Pb	0.000	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	0.000	0.006
Ce	0.000	0.003

Table 6A. The XRF analysis of MBP sample

Element	Percentage (%)	-/+ [*3]
Mgo	1.291	0.766
Al_2O_3	7.019	0.231
SiO_2	27.854	0.287
P_2O_5	0.226	0.033
Cl	0.090	0.008
K_2O	2.888	0.022
CaO	12.045	0.045
Ti	0.332	0.007
V	0.005	0.003
Cr	0.030	0.003
Mn	0.777	0.020
Fe	3.051	0.035
Co	0.000	0.004
Ni	0.003	0.002
Cu	0.004	0.001
Zn	0.002	0.001
As	0.000	0.000
Se	0.000	0.000
Rb	0.004	0.001
Sr	0.009	0.001
Y	0.002	0.001
Zr	0.022	0.001
Nb	0.001	0.001
Mo	0.001	0.001
Rh	0.000	0.001
Pd	0.000	0.003
Ag	0.000	0.002
Cd	0.000	0.002
Sn	0.019	0.023
Sb	0.000	0.004
Ba	0.039	0.016
La	0.000	0.026
Hf	0.000	0.001
Ta	0.001	0.001
W	0.000	0.001
Pt	0.000	0.002
Au	0.000	0.001
Hg	0.000	0.000
Tl	0.000	0.001
Pb	0.000	0.002
Bi	0.000	0.002
Th	0.000	0.003
U	0.000	0.005
Ce	0.000	0.003

Table 7B. The XRF analysis of PBP sample

Element	Percentage (%)	-/+ [*3]
Mgo	1.238	0.745
Al_2O_3	9.545	0.263
SiO_2	38.429	0.357
P_2O_5	0.182	0.033
Cl	0.000	0.010
K_2O	0.652	0.013
CaO	15.721	0.051
Ti	0.401	0.008
V	0.006	0.003
Cr	0.046	0.008
Mn	0.169	0.012
Fe	3.466	0.041
Co	0.000	0.004
Ni	0.002	0.002
Cu	0.007	0.001
Zn	0.009	0.001
As	0.001	0.001
Se	0.000	0.001
Rb	0.003	0.001
Sr	0.013	0.001
Y	0.001	0.001
Zr	0.015	0.001
Nb	0.000	0.001
Mo	0.001	0.001
Rh	0.000	0.002
Ag	0.000	0.002
Cd	0.000	0.002
Sn	0.000	0.017
Sb	0.000	0.005
Ba	0.024	0.018
La	0.030	0.036
Hf	0.000	0.003
Ta	0.000	0.001
W	0.000	0.001
Pt	0.000	0.001
Au	0.000	0.001
Hg	0.000	0.001
Tl	0.000	0.001
Pb	0.004	0.002
Bi	0.002	0.002
Th	0.000	0.003
U	0.000	0.006

Table 1C. Hollow cathode lamps parameters

Element	Current (mA)	Wavelength (nm)	Slit width (nm)
Zn	15	216.86	0.7
Cr	25	357.87	0.7
Pb	13	217.00	0.7
Ni	15	232.00	0.7
Cd	13	228.80	0.7
Mn	15	279.48	0.2

Table 2C. GFAAS operating conditions

Element	Drying (°C)	Ashing (°C)	Atomisation (°C)
Zn	110	700	1800
Cr	110	1500	2300
Pb	110	850	1600
Ni	110	1100	2300
Cd	110	500	1500
Mn	110	1300	1900

Table 3D. ICP-OES operating conditions

Instrument	ICPE-9000 Shimadzu
Ignition Mode	Normal(water)
RF generator power	1.20 kW
Plasma gas	10 L/min
Carrier gas	0.7 L/min
Gas Flow Auxiliary	0.60 L/min
Plasma torch	Mini torch
View Direction	Axial
View Position	low
Ar Gas	500 kPa
Ar Purge	Low
Peristaltic Pump	Low
Rotation Speed	20 r.p.m
High rotation speed	60 r.p.m