NORTH-WEST UNIVERSITY
YUNIBESITI YA BOKONE-BOPHIRIMA
NOORDWES-UNIVERSITEIT
MAFIKENG CAMPUS

Determination of metal concentrations in vegetation, soil, dust and water in the vicinity of a cement factory in North West Province, South Africa

M.H. Huyser

(20728921)

Dissertation submitted in fulfillment of the requirements for the degree *Master of Science in Environmental Sciences* at the Mafikeng Campus of the North-West University

Supervisor: Dr L.G. Palamuleni

Co-supervisor: Prof F. Winde

2012

DECLARATION

I declare that the work in this dissertation was carried out in accordance with the Regulations of the North-West University. The work is original except where indicated by special reference in the text and no part of dissertation has been submitted for any other degree. Any views expressed in the dissertation are those of the author and in no way represent those of the North-West University. The dissertation has not been presented to any other University.

Signed:......................................

Date: 25 April 2012

ABSTRACT

On a per capita basis, cement is the second most widely consumed product in the world and its demand is increasing globally due to population growth and urbanisation. Manufacturing plants produce cement kiln dust (CKD) as one of the by-products while coal provides the dominant energy source in the manufacturing process. Various metals are found in CKD and some of these are micronutrients with potentially toxic effects. If these are present in large quantities, they pose a direct threat to vegetation, animals and humans.

The aim of this study was to quantify a selected number of trace metal concentrations in vegetation, soil, dust and water samples near a cement manufacturing plant in the North West Province. Thirty-one samples at various distances from approximately 500m to 2700m from where the cement factory is situated, were collected. In addition, similar samples (except for water) were taken from a control site situated 72 kilometres in a north-western direction from the factory. The water control sample was collected from the Ditsobotla municipal water supply.

Soil, plant and dust samples as well as the sediment from the water sample were acid digested to obtain total metal concentrations. The acid digested samples were analyzed for selected metal concentrations using the ICP-MS. The relationship between soil metal concentrations and particle size distribution as well as the relationship between dust concentrations and Ca concentrations was established to determine the link with the presence on a CMP in the area. The control samples, reference standards and results from similar research performed were used to compare with metal concentrations found in this study.

The study revealed that Ni and Cu concentrations are higher in the silt fraction of the soil whilst V, Co, Zn and Pb in the silt fraction are only marginally higher than the complete soil sample. Only Cr and Mn concentrations were higher in soil samples than the control and reference values, while metal concentrations for Cr, Cu, Pb and Mn were higher in the dust samples than the control and the Emission Limit Value (ELV). Moreover, metal concentrations in the vegetation samples are not a concern as the concentrations are lower than reference values. Cadmium and As levels are of no concern in this study area especially since dust samples had undetectably low levels.

The condition of the environment in relation to pollution from the cement factory was established. Although some metals revealed lower concentrations, the study demonstrated the potential of metal contamination particularly Ni, Mn and Cr to the environment vis-a vis on the surrounding vegetation, animals and possibly on humans. It was therefore recommended that ELV limits for South Africa should be established and monitored for cement factories in South Africa coupled with sustainable land management policies.

Acknowledgements

I would like to express my genuine gratitude and appreciation to my thesis supervisor, Dr Lobina Palamuleni of North-West University, Mafikeng Campus. Her willingness to take me in despite her busy schedule and not only coming in to scrutinize finished products but also working through each chapter with me taught me a lot about thinking scientifically. Her positive encouragement is highly appreciated. I would also like to thank Prof Frank Winde, who guided me in shaping my research concept into a workable project.

Special thanks go to the staff of Biological Sciences and Geography & Environmental Sciences who were always giving words of encouragement. Especially Prof Malan who invested time in giving constructive advise as well as Prof Ruhiiga for his support.

I would like to express appreciation to Sammy Bett, M Sc student and post graduate assistant, Dept of Geography, NWU, who assisted me with the maps required for the project. Furthermore, my brother Ernie Venter, a geologist for valuable hints and help with the spatial mapping done.

Last but not least, I thank my family for their support and encouragement. A special thanks to my husband Jurie, who listened patiently to me right through the project. To my two girls, thank you for giving Mommy time to work at home.

Above all, I am grateful to the Lord God Almighty who is my source of strength and wisdom.

Table of Contents

List of Figures

List of Tables

List of Acronyms

CEC	Cation exchange capacity
CKD	Cement kiln dust
CMP	Cement manufacturing plant
EC	Electrical conductivity
EF	Exceedance factor
ELV	Emission limit value
EPA	Environmental Protection Agency
ESP	Electrostatic precipitator
GIS	Geographical information system
GPS	Global positioning system
ICP-MS	Inductively coupled plasma mass spectrometer
OEL	Occupational exposure limits
PM	Particulate matter
ppm	Parts per million
R^2	Coefficient of determination
rpm	Revolutions per minute
TSP	Total suspended particles

CHAPTER 1

1. GENERAL INTRODUCTION

1.1. Metal background information

Metal contamination is a concern to the environment as it has various negative effects on vegetation, animals and on humans (Bermudez, et al., 2010). This study focuses on quantifying metals in soil, plants, dust and water to evaluate the possible impact of metals on the environment. Chapter 1 gives background information about metal classification as well as information on the study area. Climatic data of the study area includes wind, rainfall, temperature, humidity, pressure, soil form, geology and vegetation.

The elements analyzed are referred to metals and not heavy metals due to inconsistency between different definitions. According to Duffus (2001) the term heavy metals is used although no consistency or reference is made to which classification of heavy metals is used. Duffus (2001) explained the different classifications that are used for heavy metals as follows:

- Density (or specific gravity) of elements: inconsistency occurs as Bjerrum (1936) defined heavy metals as elements with a gravity of more than 3.5, other definitions > 4, some > than 5 and others even with a density greater than 7 (Duffus, 2001).
- Atomic weight: various authors' classified heavy metals according to atomic weight vary as well. Some definitions refer to elements with a high atomic weight whilst giving examples like Cd, Hg and Pb. Other definitions specify metallic elements with an atomic weight greater than 40 (Lewis, 1993), whilst other definitions define heavy metals as metals with an atomic weight greater than Na that forms soaps on reaction with fatty acids (Bennet, 1986).
- Atomic number: heavy metals defined by atomic number vary from periodic table parameters, to any element with an atomic number greater than 20 as well as metals between 21 (Scandium) and 92 (Uranium) (Duffus, 2001).

- According to toxicity: heavy metals are defined in this instance according to the toxicity to animals and aerobic and anaerobic processes (Klaasen, 1996). These elements include As, Cd, Cr, Cu, Pb, Hg, Ni, Se and Zn although not everyone is dense and entirely metallic.

Some metals are important micronutrients for humans although at high levels metals may increase toxicological risk (Schuhmacher, et al., 2002) for instance Mn, Zn, Fe, Co, Ni, while other metals like Cd, Pb and Al are non-essential elements. Some metals are carcinogenic including As, Be, Cd, Cr, Co and Ni (Beyersmann, 2002). Most metals bioaccumulate whilst they are also carried through the soil-plant-human cycle. Anthropogenic activities contribute to elevated levels of metals in the environment. The metals emitted to the air may be directly or indirectly transmitted to humans through inhalation (Schuhmacher, et al., 2004) or accumulation in soil, water, vegetation and biota (Işikli, et al., 2003; Al-Masri, et al., 2006).

Background to metal emissions from cement plants

Cement is the second most consumed product in the world per capita basis after water (Zeman, 2009). Due to urbanization and population growth, the demand for cement is increasing whilst the environment may be affected / impacted by the manufacturing process. Cement manufacturing plants (CMPs) have a by-product called cement kiln dust (CKD). Coal burning is used in the cement manufacturing process as a source of energy. Cement clinker is formed during the burning process in the kilns and is grounded with additives to form cement (Tavares & Cerqueira, 2006). During the burning process in the kiln, CKD emissions occur, which expose the environment to various elements (Siddique, 2006). Cement kiln dust contains essential elements for example Cu, Fe and Zn as well as non-essential, toxic metals such as V, Cr, Mn, Co, Ni, As, Cd and Pb (Polat, et al., 2004; Al-Khashman & Shawabkeh, 2006; Abimbola, et al., 2007; Bermudez, et al., 2010).

Cement manufacturing plants emit dust during the various processes of cement production. Although dust released from CMPs is commonly referred to as CKD, dust is also released into the environment from almost every stage of manufacturing, including quarrying activities to packaging of the final product (Abdul-Wahab, 2006; Bermudez, 2010). Cement kiln dust is a fine-grained, solid, highly alkaline waste byproduct originating from the process of forming clinker in the kiln (Van Oss & Padovani, 2003). As CKD consists of unburned or partially burnt raw materials it is recycled back to the kiln as part of the kiln feed. Some of the CKD formed is released into the air by stacks even though air pollution control devices for example cyclones, electrostatic precipitators, or bag-houses are fitted to collect CKD. The emitted dust may accumulate on soil, vegetation, crops or on house roofs (Abimbola, et al., 2007). The dust emitted is classed according to size. Particulate matter less than 10 micron bigger than 2.5 micron is known as PM_{10} and dust particles smaller than 2.5 micron are known as $PM_{2.5}$. Metals may bind or accumulate on the dust particles (Constans, 1997) and reach the environment when dust is emitted to the air due to air pollution control devices not capturing the dust.

Element concentrations in CKD vary and are dependent on the composition of the coal used during the burning process and the coal combustion conditions (Polat, et al., 2004). Pollution of the environment with metals is toxic to different living systems and is carried through life-cycles (Işikli, et al., 2003; Işikli, et al., 2006). Cement kiln dust may contain metals and pollute the environment as the dust emissions spread through wind and rain (Işikli, et al., 2003; Al-Masri, et al., 2006), negatively affecting plants, animals and humans as explained in the literature review.

1.2. Problem statement

Cement manufacturing plants emit CKD which contains various metals including Cu, Zn, V, Cr, Mn, Co, Ni, As, Cd and Pb. Does the CMP in the study area consequently pollute the environment (soil, vegetation, dust and water) with metals? If so, what are the potential short effects on the environment?

1.3. Study area

In the northern region of the North West Province of South Africa, three CMPs are located in an area within an approximate radius of 45 km. For the purposes of this research project, samples were collected from one CMP located next to Lichtenburg (Figure 1), situated within the Ditsobotla Municipality. The factory also has a village located in a southern direction next to the plant where some of the employees live.

Lichtenburg was established in 1873 (North West Parks and Tourism Board, 2012) and has a population of approximately 65 863 inhabitants (GeoNames geographical database, 2012). The area is relatively flat although elevated 1459 m above sea level. The town is situated SW from the cement factory (Figure 1). To the west of the cement factory is an industrial area with various industries including transport companies, a cheese factory and engineering companies. Figure 1 shows the location of the study area.

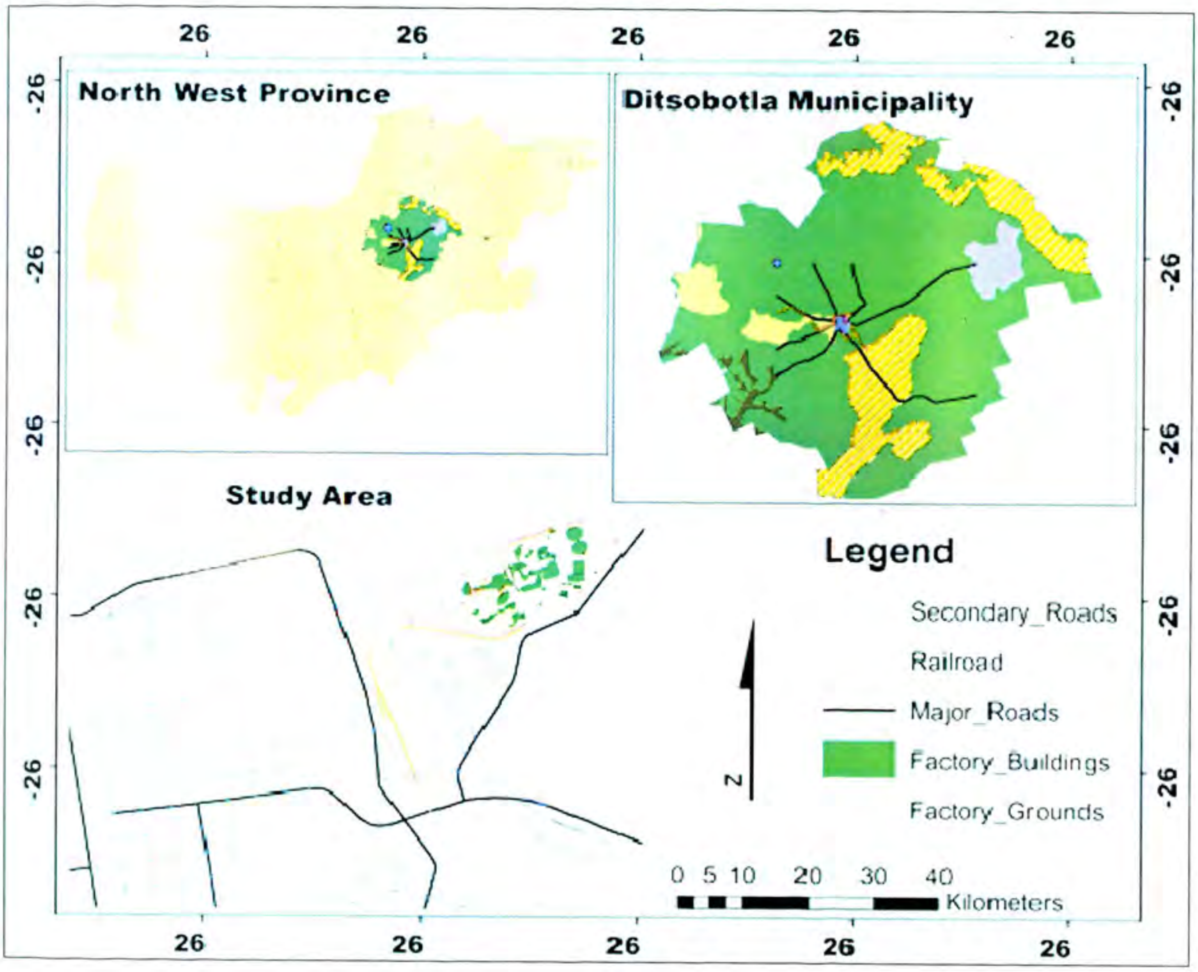


Figure 1: Location of the study area in the North West Province (Source: Created by Sammy Bett Geography Department, NWU)

The cement manufacturing plant is situated on the outskirts of Lichtenburg, approximately 1.8 km NE of the town centre (Figure 1). The CMP has been operational for approximately seven decades. This plant has three kilns and produces approximately 200 000 tons of cement clinker per month (Lafarge Cement, 2011). Cement kiln dust is monitored continuously in the kilns for total suspended particles (TSP) using a fixed monitoring system. At this specific factory, no tests have been performed for testing heavy metals in the CKD or in the environment {Personal communication, CMP Environmental Manager, Lichtenburg, 2009}.

The control site for comparing plant and soil concentrations is situated 72 kilometres in a north western direction from the factory. This site was chosen as no cement factories, other industrial activities or major roads are present in this area, thereby eliminating interference from motor vehicles and industrial pollution.

The North West Province plays a major role in the agricultural sector of South Africa. The major utilisation of land in the North West Province is farming. Farming consists mostly of maize production, cattle and game farming (North West Province Department of Agriculture, Conservation and Environment, 2002).

1.4. Environmental settings

The climate of Lichtenburg is hot and semi-arid with high temperatures during the summer months with cooler winter months (Sections *temperature* and *humidity*). The wind direction is predominantly from the North as shown in Figure 3.

Rainfall

Rainfall occurs during summer from September to April. The average rainfall for the last few 10 years and is an average 559 mm per annum (Figure 2) (South African Weather Service, 2011).

Figure 2: Average monthly rainfall for the period 2000 – 2010 (South African Weather Service, 2011).

Wind direction and wind speed

The prevailing wind direction at the CMP is predominantly from the north with wind speed reaching up to 8.7 m/s as shown in Figure 3 (South African Weather Service, 2011). Metal distribution is affected by the wind direction resulting in metal deposition downwind from the source (Işikli, et al., 2006). Wind speed influences the concentrations of pollutants in the air. Higher wind speeds result in higher dilution of pollutants in the air whereas light winds cause less mixing of pollutants with air, resulting in higher concentration of pollutants.

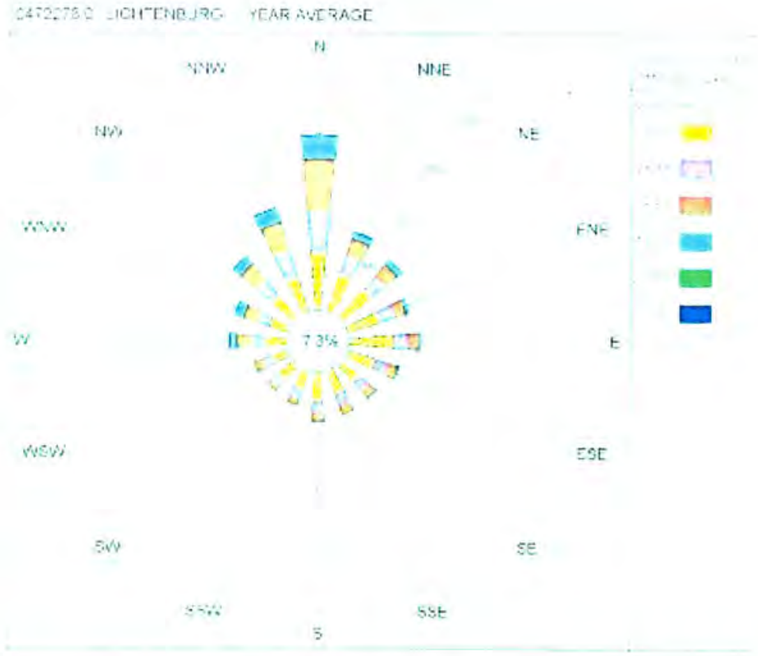


Figure 3: Average wind direction and speed for 2000 – 2010 (South African Weather Service, 2011).

Samples were collected in June and August 2009. Wind direction and speed for these periods are shown in Appendix A.

Air temperature, humidity and pressure

Figure 4 shows the average minimum and maximum temperatures recorded in the last ten years (South African Weather Service, 2011). The average temperature ranges from 1 °C in the winter to 29 °C in the summer.

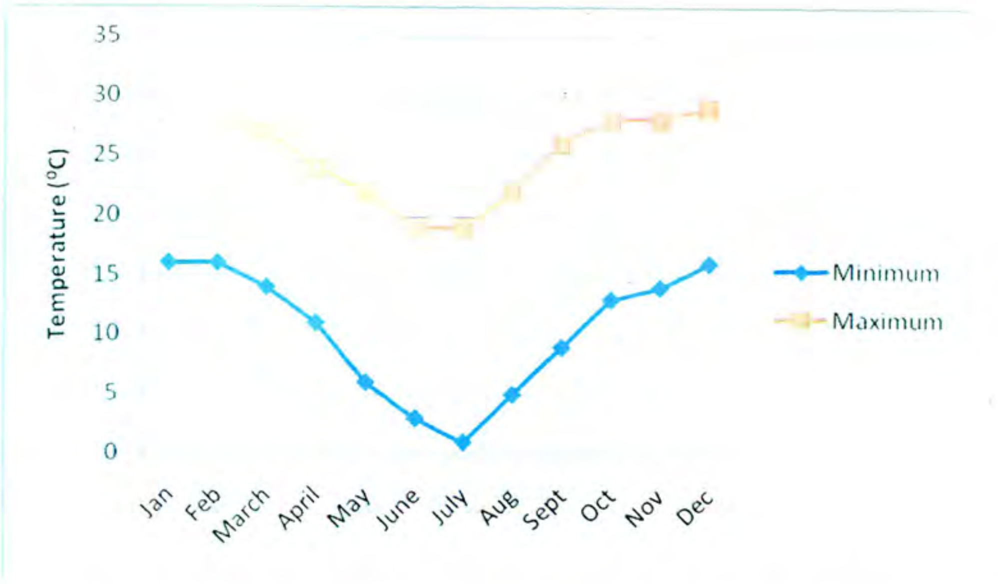


Figure 4: Average minimum and maximum temperatures 2000-2010 (South African Weather Service, 2011).

The average humidity in Lichtenburg for 2002 – 2010 is indicated in Figure 5 (South African Weather Service, 2011).

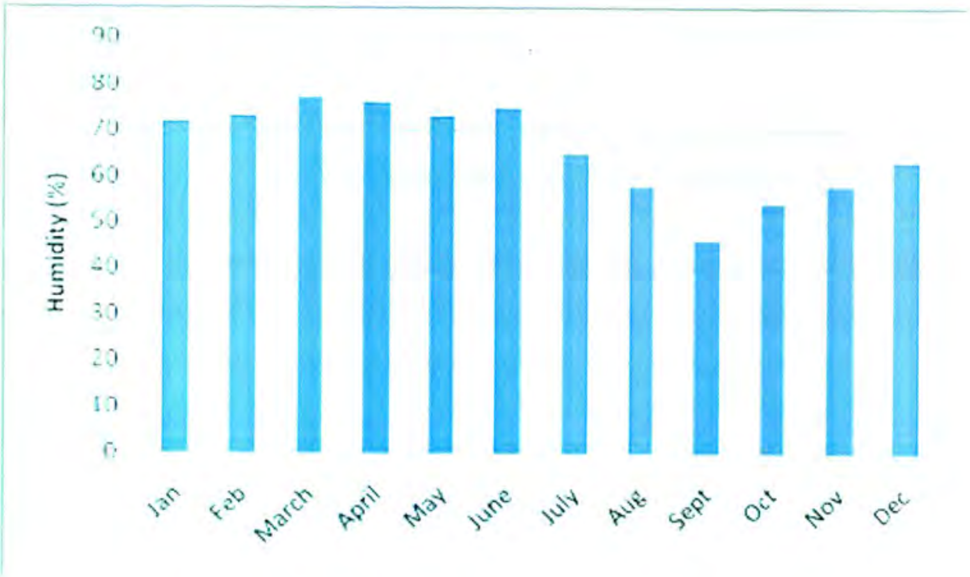


Figure 5: Average humidity (%) from 2002 – 2010 (South African Weather Service, 2011).

The average pressure measured at 08:00 am in hectopascal is shown in Figure 6 for the last ten years as supplied by the South African Weather Service (2011).

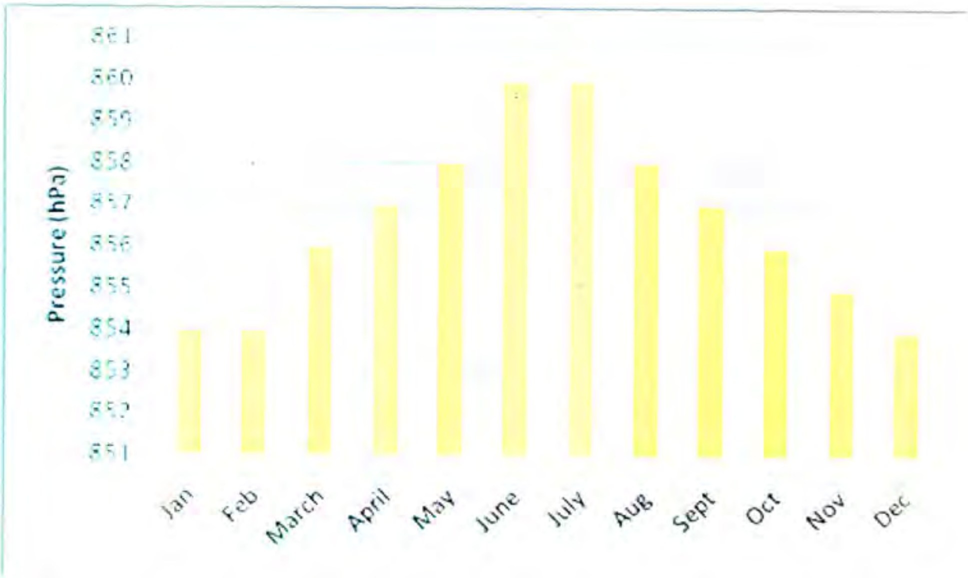


Figure 6: Average ground air pressure in Lichtenburg 2000 – 2010 (South African Weather Service, 2011).

Geology

Geology may also play a role in the distribution of the chemicals in the soil (Doerr, et al., 2005) and may thus influence the uptake of metals in plants. Figure 7 gives the geological data of the study area. The cement manufacturing plant is located on dolomite, tillite and sandstone which are all sedimentary rock (Van der Watt & van Rooyen, 1995).

Sedimentary rock is rock formed from materials deposited from suspension or precipitated from solution. The principal sedimentary rocks are sandstone, limestone and conglomerates (Van der Watt & van Rooyen, 1995). Sandstone is a sedimentary rock consisting mainly of grains of quartz. Sedimentary rock and sandstone are good aquifers (a layer of rock that contains abundant, freely moving ground water) (Strahler & Strahler, 2005). Hence, water will drain faster from the top soil to deeper soil during rainfall, as explained in section 3.2.

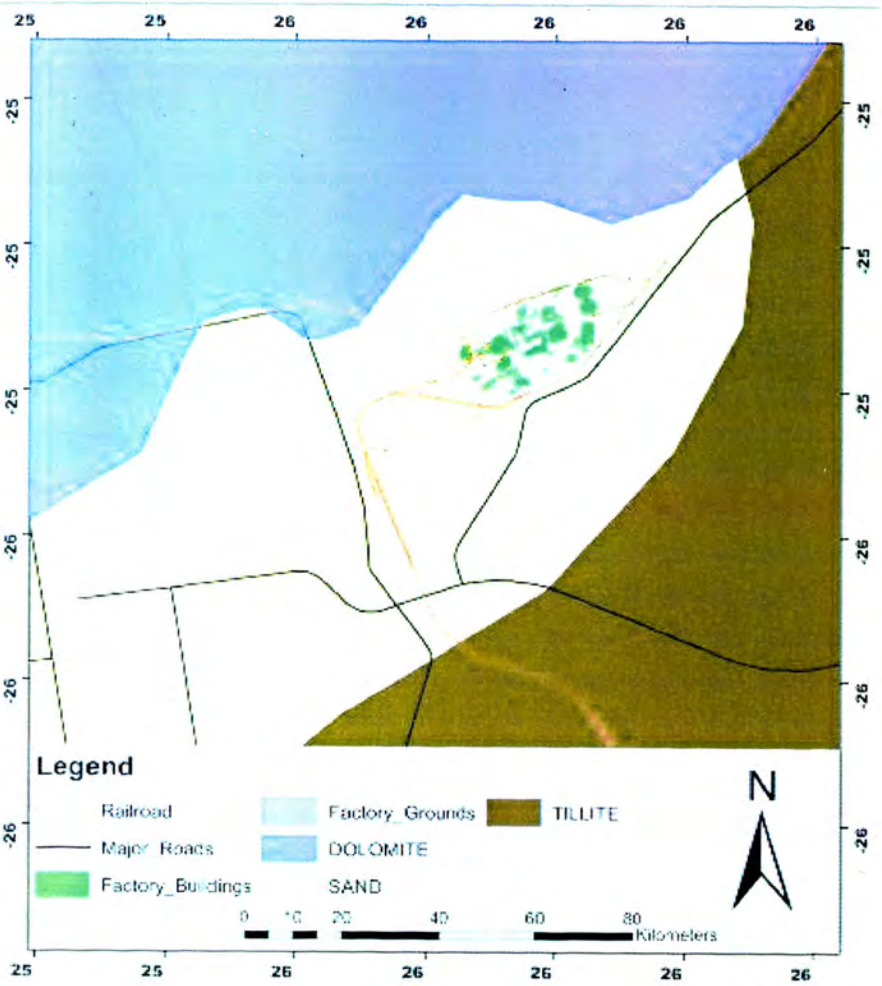


Figure 7: Geology of the study area (Source: Created by Sammy Bett Geography Department, NWU).

Soils

Figure 8 shows the various soil forms of the study area and indicates that the soil forms are Glenrosa, Mispah and Plinthic Catena.

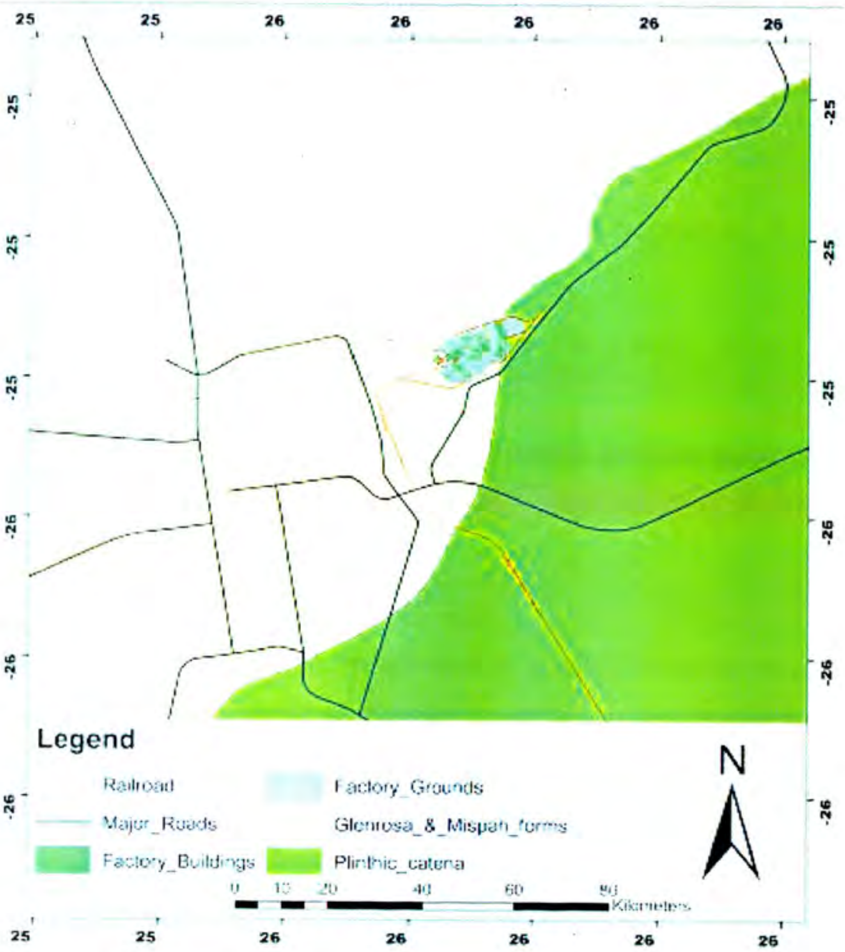


Figure 8: Soil forms within the study area (Source: Created by Sammy Bett Geography Department, NWU).

The dominant soil type in the study area is sandy loam soil as discussed in Chapter 4.

Vegetation of the study area

The vegetation in the study area is grasslands northwest, north and east of the factory. To the west of the factory is an industrial area. The residential area located next to the factory in a south to south western direction and the town Lichtenburg have landscaped gardens. Agricultural lands lie south east of the factory.

1.5. Aim and Objectives

The aim of the project is to determine the level of environmental pollution of soil, vegetation, dust and water by selected metals near the CMP next to Lichtenburg in the North West Province.

The selected metals include Cu, Zn, V, Cr, Mn, Co, Ni, As, Cd and Pb as some of these metals are toxic at high levels and are known to be present in CKD (Chen, et al., 2010).

The specific objectives are to:

- Determine concentrations of metals in soil, vegetation, dust and water in the vicinity of a cement factory;
- Compare levels of contamination to the control sample concentrations and reference standards;
- Map spatial concentration / contamination patterns using Geographic Information System (GIS) technology.

1.6. Significance of the Study

The cement factory is located south-east of a wildlife centre as well as next to residential areas lying south to south west of the factory. Land, north and east of the factory, is utilized mostly for animal husbandry. To the south-east from the factory land is used to grow crops. It will be of concern to the environment and the human population living in this area, if the cement factory pollutes the environment with metals.

1.7. The purpose of the Study

The purpose of this project is to determine metal concentration in the environment near a cement manufacturing plant. The findings will clarify if metals are released into the environment in the study area. Results may also assist in future to motivate downwind location of new factories with regard to residential areas. In addition, new environmental policies regarding location of factories that emit metals may be suggested to the appropriate authorities.

1.8. Structure of the Chapters

This dissertation is divided into five chapters. Chapter one comprises the general introduction with background information on metals. It also includes the aim and objectives of the study as well as the significance of the study. Literature is discussed in chapter two and consists of the findings of other similar studies and on similar aspects of heavy metal contamination in soil, vegetation, dust and water. It also gives more detail on the cement manufacturing process. Chapter three is the research methodology which describes the research design and the methods of data collection, sampling procedures and laboratory methods used. Chapter four presents results in relation to the research problem and the objective of the study. The results are presented in the form of tables, graphs and histograms. Statistical analyses are used to illustrate the relationships between the different variables and are discussed accordingly. Related research results are also used to interpret metal concentrations found. Maps indicate the spatial distribution of metal contamination in the study area. Chapter five provides conclusion and recommendations consisting of a summary of the whole research as well as suggestions on corrective measures for metal pollution and natural resources management. The dissertation ends with a section of Appendices which includes additional wind data, photos showing the collection of dust samples, a flow diagram of cement manufacturing, detection limits of the Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS) as well as coefficient of variance of analysis performed.

2. LITERATURE REVIEW

2.1 Introduction

Literature review is discussed in Chapter 2. The cement manufacturing process is also discussed to give background information about the source of potential pollutants. Photographs of the CMP in the study are included to show CKD emissions in the study area.

Cement manufacturing process

The cement manufacturing process is discussed to give background information about cement production. The effects of cement manufacturing on the environment are considered to be local as compared to other mining industries and other manufacturing processes (Van Oss & Padovani, 2003). Cement manufacturing involves various processes. These processes include mining for raw material, milling of the raw materials and a burning process to form clinker, the main product to manufacture cement. After clinker has been formed, it is milled and mixed with gypsum to form cement. A diagrammatic representation of the cement manufacturing process is shown in Appendix B. During the manufacturing process, particulate matter is emitted at every stage of processing.

Lime, the main raw material, is mined at a quarry where it is crushed to reduce the size and transported to the manufacturing plant. In this case study, the limestone is transported by railway from the quarry to the CMP. Other raw materials for the manufacturing of clinker include silica, alumina and iron oxide. Cement manufacturers combine these raw materials at different ratios. According to Huntzinger & Eatmon (2009), the ratios may vary as follows:

Table 1: Raw materials used in the cement manufacturing process

Raw materials	Sources	Mass percent
Lime	Limestone, shells, chalk	60-67
Silica	Sand, fly ash	17-25
Alumina	Clay, shale, fly ash	2-8
Iron oxide	Iron ore	0-6

At the specific manufacturing plant where samples were taken, raw materials are kept in dome-like structures (Figure 9). These structures were erected in 2006 and 2009 respectively and were developed to minimize dust generation as well as to improve the manufacturing process, as rain compacts the raw material affecting the manufacturing process negatively.

Figure 9: Dome structures at the CMP, Lichtenburg

The raw materials are crushed and milled in a raw mill to particle sizes less than 75 micron. The milled raw materials are known as kiln feed in the dry manufacturing process and slurry in the wet manufacturing process. The CMP in the project uses the dry method {Personal communication, CMP employee, Lichtenburg, 2010}. The kiln feed is pumped to blending tanks where it is homogenized. The homogenized material is stored in the silos until it is required. To produce one metric ton of clinker, approximately 1.5 to 1.6 tons of kiln feed is required (Van Oss & Padovani, 2003).

From the raw mill silo the materials are passed through a pre-heater. The reason for preheating the kiln feed is to improve production. Coal burning is used in the cement manufacturing process as a source of energy. Coal is finely milled in the coal mill and stored in a silo for later usage. Approximately 15-20 tons of coal is burned to produce 100 tons of clinker (Van Oss & Padovani, 2003). Alternative fuels are used as energy source in European and USA cement plants. South African CMPs are in the process of applying for permits to use alternative fuels as energy source.

The kiln feed of raw materials are fed to the kiln. As described by Van Oss & Padovani (2002), the kiln is the core function of the cement manufacturing process. A rotary kiln consists of a steel tube varying in length from 50 – 200 m. The internal diameter of the kiln is between 3.5 to 5.5 m and is lined with refractory bricks. The kiln is gently inclined and slowly rotates about its long axis. The core process of cement manufacturing occurs in the kiln and is known as pyroprocessing. The basic chemical reaction that occurs in the kiln is evaporating of all moisture and calcining the limestone to produce free calcium oxide (ESSROC, 2009). The calcium oxide reacts with the minor materials (sand, shale, clay and iron). The raw materials pass four thermal zones in the kiln. The temperature raise to approximately 900 °C during the first stage, then it increases to 1200 °C. During the third zone, the temperature typically rises to 1450 °C where clinker (Figure 10) is formed. The clinker diameter is 3 – 20 mm. The clinker is cooled to approximately 1250 °C in the last few meter of the kiln.

Figure 10: Cement clinker (Marsh Environmental Impact Assessment, 2009)

The clinker is stored in the clinker silos until it is required for cement manufacturing. The final step in manufacturing cement is the addition of additives to the clinker. The clinker and gypsum are ground to fine grey material and is stored to be packed and shipped at a later stage (Tavares

& Cerqueira, 2006). The final product, cement, is transported via railway or by truck to the distributor or end user.

During the burning process in the kiln, dust emissions occur, which expose the environment to various elements (Siddique, 2006). Gaseous emissions occur at the pre-heater, kiln and clinker cooling sections. Stacks are used for the release of emissions at the pre-heater and kiln systems. Air pollution control devices are installed at stacks to reduce particulate matter emissions. These devices are electrostatic precipitators (ESP), cyclones or bag houses. Electrostatic precipitators are older control devices used in the cement manufacturing industry while bag houses are modern technology used to control air emission. Some kiln dust is recycled back into the processing system while the rest is a waste by-product collected by the control devices or emitted into the air. The particulate matter collected by the air pollution control devices and particulate matter emitted by the stacks are referred to as CKD and is un-reacted raw material. The CKD is fine material (PM_{10} and $PM_{2.5}$) that is carried by hot gasses in a cement kiln.

According to Van Oss & Padovani (2003), CKD generation at cement plants are between 15 and 20 %. Two-thirds of cement kiln dust are transferred back to the kiln feed as it consists mostly of unburned or partially burned raw materials. The remaining CKD collected by the ESPs or bag houses is disposed of by landfill or sold. Recovery by the air control devices is generally high although ESPs are electric devices that may trip and cause CKD to be emitted. Cement kiln dust may also pass through bag houses if not changed when required or if they are faulty.

The cement factory investigated in this case study has 12 stacks varying in height from 60 - 90 meters above ground surface. Either ESPs or bag filters are installed and used at the various stacks. Stacks include the cooler, raw mills, coal mills, kilns and cement mills. Figure 11 shows CKD (in the form of a plume) released from the factory during technically unstable conditions (for instance, warming of the kiln or air control devices not functioning optimally). Under stable operating conditions, the emissions are not noticeable (Figure 9).

Photo taken West from factory (27 June 2010)　Photo taken South West from factory (13 November 2010)

Figure 11: Dust plume emitted from the CMP

2.2. Metals emitted by CMPs

Cement kiln dust spreads through wind and rain and accumulates in and on plants and soil (Işikli, et al., 2003; Al-Masri, et al., 2006). Chen, et al. (2010) stated that emissions of elements between cement factories may vary by 40 % due to inaccurate measurements of pollutants and annual flow, whilst indicating that cement kiln dust contain Cu, Mn, Ni, Zn, Co, Cd, As, Cr, Pb, V and Se. Metals are toxic to different living systems and are carried through life-cycles (Işikli, et al., 2006). Branquinho, et al. (2008) also explained that metal concentrations may vary from one area to another due to variations in local source, geomorphology and general weather conditions including rainfall and wind. Element concentrations may also vary between factories as a result of the composition of the coal used during the burning process and the coal combustion conditions (Polat, et al., 2004).

The CKD emitted consists of fine dust particles and is defined as either PM_{10} or $PM_{2.5}$. According to van Oss & Padovani (2003), approximately 42 % of dust emitted from a cement plant is PM_{10} and approximately 18 % is $PM_{2.5}$. Most base cations and metals released from the manufacturing process are bound to the PM_{10} (Grantz, et al., 2003) as compared to the $PM_{2.5}$ fraction. Due to more PM_{10} emitted, the impact of dust is close to the cement factories. Dust for this project was not divided into $PM_{2.5}$ and PM_{10} due to compacted dust or fall-out dust collected from surfaces. A dust collector with filters was not available or used to collect dust.

Abdul-Wahab (2006) and Branquinho, et al. (2008) stated that impact of CKD is local and that dust fall-out is in the region between 250 m – 1000 m downwind from a factory. Further than approximately 1000 m metal concentrations will decrease with increased distance from the factory (Işikli, et al., 2006).

Effects of metals on the environment

Metals are potentially toxic to living organisms and are transferred in the soil-plant-animal-human cycle (Işikli, et al., 2003; Işikli, et al., 2006). Total chlorophyll content is decreased in plants with the presence of certain metals for example chromium (Rodriquez, et al., 2007), cadmium and lead (Phetsombat, et al., 2006) causing the relative growth of the plant to decrease (Phetsombat, et al., 2006). If plants are grown in soil contaminated with metals, these plants take the metals up through their roots (Intawongse & Dean, 2006; Phetsombat, et al., 2006). The metals can also accumulate on the plant externally (Akinola & Ekiyoyo, 2006). In either case, they will be transferred to animals or humans if the plants are ingested (Islam, et al., 2007). Soil metal contamination also influences soil biota and the processes soil micro organisms regulate (Oliveira & Pampulha, 2006). Soil microbe diversity, abundance and activity may decrease because of metal contamination (Verma, et al., 2010). Metals may also contaminate ground water as a result of leaching from metal contaminated soil (Verma, et al., 2010).

Effects of metals on animal and human health

Wright & Welbourn (2002) described the effects of metals on humans and include As, Cd, Cr which are potential carcinogens, Hg and Mn may cause neurological effects and Ni may cause respiratory disease. Cu, Fe and Zn are micronutrients in the human diet (Wright & Welbourn, 2002) although at high levels Cu and Zn have been found to be toxic to soil organisms and humans (Spear, 1981). Dust contaminated with metals may have various toxic effects on humans resulting from inhalation and ingestion (Soriano, et al., 2011).

Other effects may be caused by Cr that is known for causing dermatitis in humans (Işikli, et al., 2003). High levels of Pd and Cd caused poisoning (Raven, et al., 2005; Fajimi, 2007) and are toxic to animals as well (Oluokun, et al., 2007). In a study performed by Sen & Sunlu (2007) it was found that cadmium negatively affected the development, survival and hatching of eggs.

Another study by Fajimi (2007) revealed that goats were poisoned after ingesting forage contaminated with lead released from a CMP.

2.3. Conclusion

According to Phetsombat, et al. (2006), Oluokun, et al. (2007) and Wright & Welbourn (2002) metal contamination may affect vegetation, animals and humans negatively. As shown in the photos (Figure 11), CKD is emitted from the CMP. The materials and methods are indicated and discussed in Chapter 3 that were used to determine the metal load in the environment emitted from the CMP as well as other tests performed that may influence the metal concentrations in the environment.

CHAPTER 3

3. RESEARCH METHODOLOGY

The research methodology on the concentrations of selected metals in vegetation, soil, dust and water samples near a cement manufacturing plant in the North West Province are presented. The data sources and the different analytical techniques employed are highlighted in this chapter. In order to distinguish different methods and their importance, the various methods for each objective set in Chapter 1 are discussed.

3.1. Introduction

A quantitative research approach was used for this research project. Spatial patterns were used to identify collection points and collection dates as it influences the distribution of CKD in the environment and ultimately the metals in the samples collected (Abdul-Wahab, 2006). Sampling in the study area was done to investigate metal concentrations in soil, vegetation, dust and water. The various types of samples were analyzed for total concentration V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb. Soil samples were also analyzed for pH, electric conductivity (EC), cation exchange capacity (CEC) as well as particle size distribution due to their influence on metal mobility and solubility (Al-Khasman, 2004). Additional analysis on the dust samples included quantifying of Ca, Mg, K and Al.

Research design

The research process is shown in Figure 12.

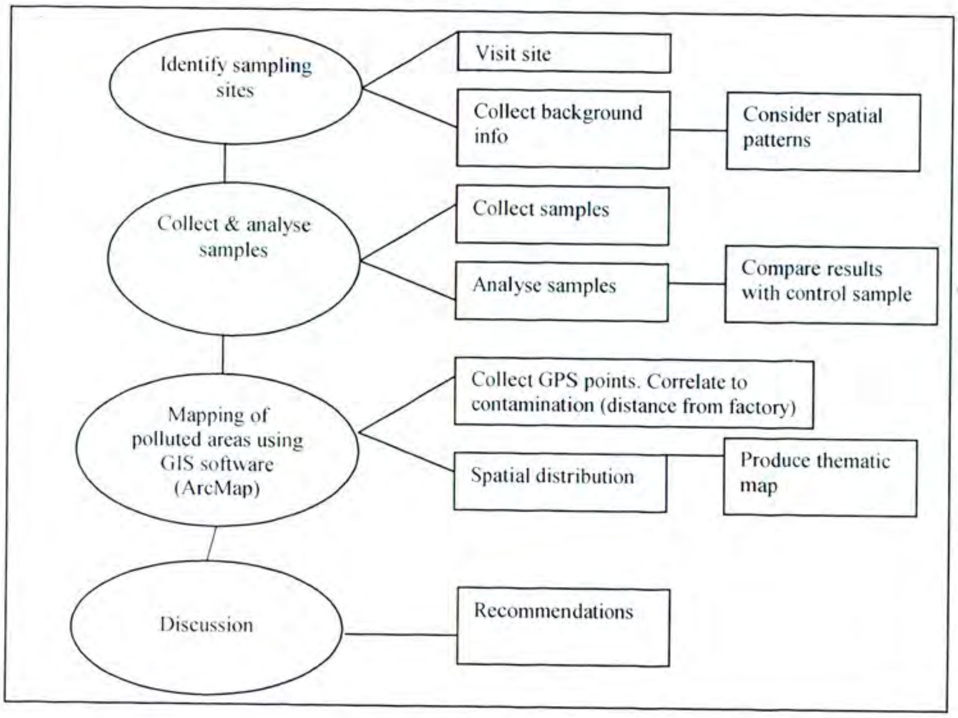


Figure 12: Flow chart showing the research design

3.2. Environmental settings on metal concentrations – sampling sites

Spatial patterns of various climatic factors were taken into account to determine possible contamination areas as well as the extent of contamination. The following spatial patterns were factors taken into account to determine sample collection points.

Wind

Wind direction plays an important role in the distribution of metals (Işikli, et al., 2003; Işikli, et al., 2006). The predominant wind direction is from the north with wind speed reaching up to 8.7 m/s as indicated in Chapter 1 (Figure3). The wind data were used to decide on collection points. Due to a northern prevailing wind, samples were collected mostly south from the factory, although some samples were collected SSW, SW and SE from the factory due to accessibility. One dust sample was also collected east from the factory.

Rainfall and soil type

Other factors that influence metal concentrations are rainfall and soil type. The soil type determines the storage capacity of the soil. Finer textures hold more water than coarser textures, meaning that sandy soil has a small storage capacity and clay soil has a large storage capacity (Strahler & Strahler, 2005). Therefore, once the rainfall increases, the metals present in the soil will drain through the sandy soil but in the clay soil, metals will not drain out. This in turn, may influence the uptake of metals in plants from the soil. Thus, in sandy soil, trees with deep roots will take up metals while uptake by grass will be less as the roots are shallow. Soil samples were collected during the dry season in June and August, although rainfall for those two months was 10 mm and 3 mm respectively (South African Weather Services, 2011).

Geology and soil forms

Sedimentary rock is the principal geology in the study area resulting in a low water holding capacity. Glenrosa and Mispah are the dominant soil forms; hence they contribute significantly to ground water. These soil forms are Xerosols (soils of dry areas) and contain small amounts of clay while mostly consisting of coarse sand and gravel (FitzPatrick, 1980). This characteristic gives the soil a small water storage capacity, indicating a higher infiltration capacity and loading potential.

3.3. Collection of Samples

Samples collected included soil, vegetation, dust and water (Figure 13). The samples were taken from the vicinity of a cement factory in the North West Province. In addition, similar samples (except for water) were taken from a control site situated 72 kilometres in a north-western direction from the factory. The control water sample was collected from the Ditsobotla municipality water supply.

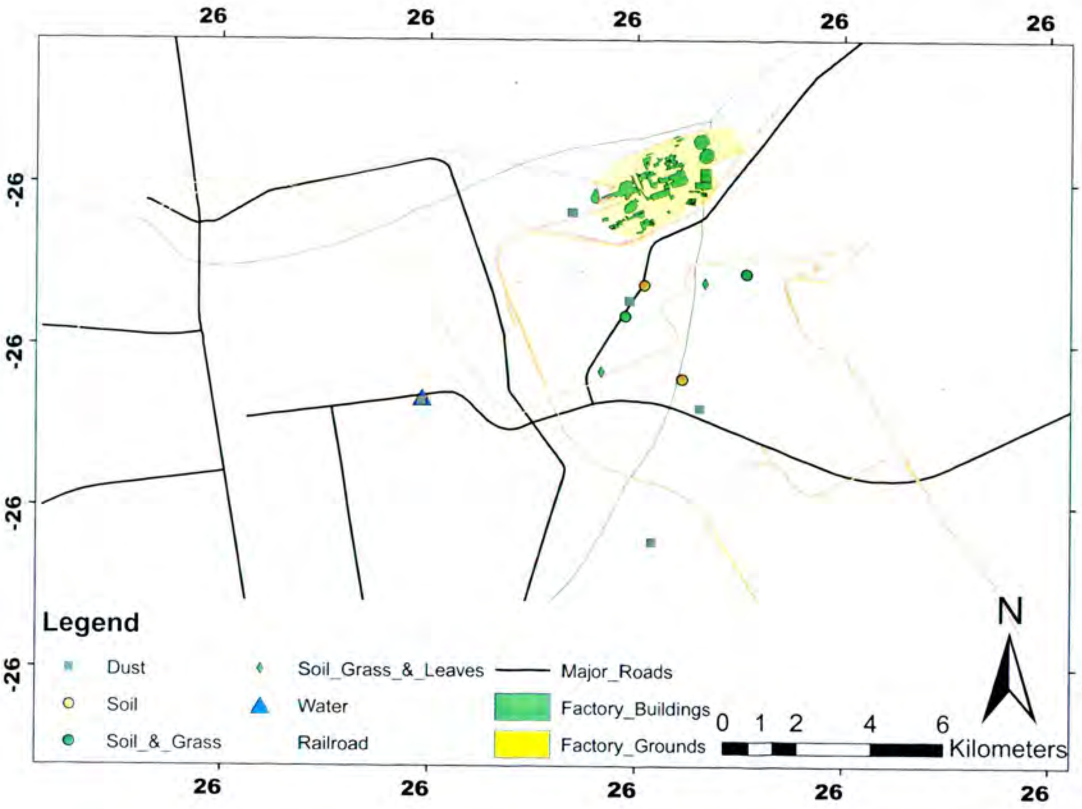


Figure 13: Collection sites of different samples (Source: Created by Sammy Bett Geography Department).

Soil Samples

Soil samples to determine the presence of metal concentration were collected in the following way:

Twelve soil samples were collected from land adjacent to the CMP. Eight samples were collected in June and four in August and one control sample in June. Accessibility to sample collection points played a major role in the selection of the points, as did the presence of vegetation at the points. Branquinho, et al. (2008) stated that the spatial dust impact seems to be local, and ranges from 250 m to 1000 m. Therefore, samples were taken at distances varying from 530 m to 1400 m. At a collection point, samples were taken at a depth of 0-10 cm and at 10-20 cm., Al-Khashman & Shawabkeh (2006) used similar depths which may indicate the difference in pollution at different depths.

The samples were collected with a spade and placed into a marked paper bag (Watts & Halliwell, 1996). Approximately 1 kg of each sample was collected for each point and each depth. A ruler was used to ensure that the first sample was collected from 0-10 cm and the deeper sample from 10-20 cm. Details of the soil sampling are shown in Table 2.

Table 2: Location of soil samples in the study area

							Control sample
Depth (cm)	0-10	0-10	0-10	0-10	0-10	0-10	0-10
	10-20	10-20	10-20	10-20	10-20	10-20	10-20
Distance from factory (m)	530	710	1100	1300	760	1400	72300
Direction from factory	S	SE	SW	SSW	SSW	S	NW
GPS co-ordinates	26°E11.21 26°S08.47	26°E11.44 26°S08.51	26°E10.82 26°S10.82	26°E10.84 26°S08.81	26°E10.96 26°S08.47	26°E11.15 26°S08.86	25°E36.53 25°S49.43
Date collected	2/6/2009	2/6/2009	2/6/2009	2/6/2009	16/8/2009	16/8/2009	2/6/2009

Vegetation Samples

Vegetation samples to determine the presence of metal concentration were collected in the following way:

Two vegetation types were analysed for metal contamination, namely grass and tree leaves. Grass and tree samples were collected to compare metal concentrations for shallow root plants and deep root plants. The grass species vary due to variance in the study area (Table 3) whilst tree leaves (Table 4) were collected from *Eucalyptus cladocalyx* as they were available in the study area and control site.

Two samples and a control sample were collected from *Eucalyptus cladocalyx* trees from the factory and control site respectively. Woody species have been found to accumulate metals in their leaves (Unterbrunner, et al., 2007); therefore, leaves were collected randomly from the tree canopy of *Eucalyptus cladocalyx* up to a reachable height of approximately 2 m. Samples were collected S and SSW from the factory according to availability. Five grass samples were taken at the same collection points as the first collected soil samples, due to accessibility and availability of the grass samples. Grass samples were collected by using a garden fork to loosen the roots from the soil. The whole plant (leaves and roots) was placed in a labeled brown paper bag.

Table 3: Grass samples - collected 2 July 2009

Sample collected	*Enneapogon cenchroides*	*Setaria incrassata*	*Eragrostis rigidior*	*Bothriochloa insculpta*	*Bothriochloa insculpta*	Control
Distance from factory	530 m	530 m	710m	1100m	1300m	72300m
Direction from factory	S	S	SE	SW	SSW	NW
GPS co-ordinates	26°E11.21 26°S08.47	26°E11.21 26°S08.47	26°E11.45 26°S08.51	26°E10.82 26°S10.82	26°E10.84 26°S08.81	25°E36.53 25°S49.43

Table 4: Leaves of trees collected for analysis on 2 July 2009

Sample collected	*Eucalyptus cladocalyx*	*Eucolyptus cladocalyx*	*Eucolyptus cladocalyx*
Distance from factory	530 m	1300m	72300m
Direction from factory	S	SSW	NW
GPS co-ordinates	26°E11.207' 26°S08.467'	26°E10.835' 26°S08.810'	25°E36.532' 25°S49.433'

Dust Samples

Preliminary analysis of soil samples indicated a correlation between soil particle sizes specifically the silt percentage and metal concentration. Hence, dust particles were collected for further analysis. Dust samples were collected from an adjacent business roof, from an old bus stop, from residential areas and a control sample from a storeroom where dust colligated (Table 5, Appendix C). Compacted dust was loosened with a spatula and placed in a marked brown paper bag. A small broom was used to sweep together loose dust which was then placed in a paper bag.

Table 5: Dust samples collected for analysis on 16 August 2009

Collected from	Bus stop	Industrial site - roof	Kraal – roof	Residential house - boat	Residential house - car	Control
Distance from factory	920 m	1000 m	1600 m	2600 m	2700 m	72300 m
Direction from factory	SSW	W	S	SW	S	NW
GPS co-ordinates	26°E10.898' 26°S08.525'	26°E10.644' 26°S08.414'	26°E11.219' 26°S08.964'	26°E10.002' 26°S08.971'	26°E11.003' 26°S09.564'	25°E36.543' 25°S49.432'

Water Samples

A water sample was collected from a portable swimming pool when it was evident three weeks after erecting it that prominent sediment was present in the water (Figure 14). Water was collected in a sterile 1 liter plastic bottle. Water was taken from the bottom of the pool (including the sediment) to analyze for the probable presence of metals. Tap water was collected to compare the results with the water collected from the swimming pool. Metal analyses were performed on the water sample (excluding sediment), on acid digested (Section 4.2) sediment and on the control water sample to compare metal concentrations.

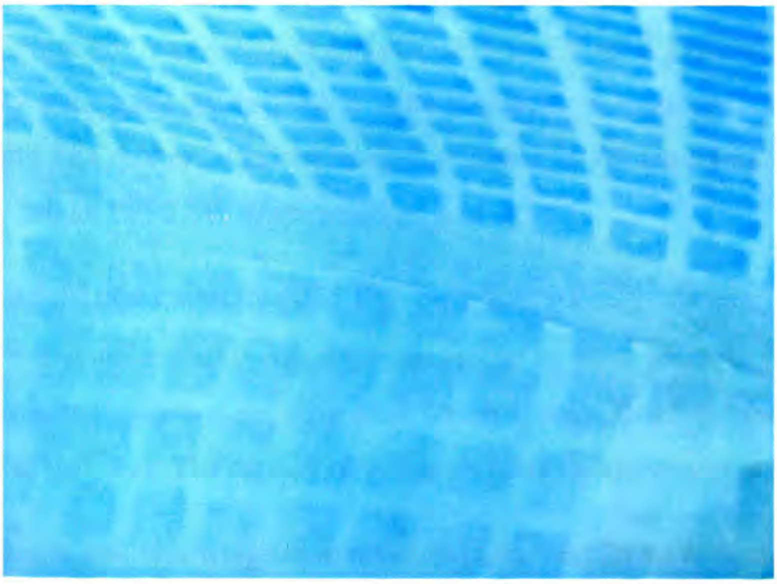


Figure 14: Dust and debris at the bottom of a pool

3.4. Data analysis techniques

Soil analysis

Soil samples were dried for 48 hours before analysis was performed. The soil was dried in an oven at temperatures not exceeding 40 °C. The soil was sieved through a 2mm sieve after drying and then homogenized. Stones in the soil were not crushed.

Soil samples were analyzed for pH, EC, CEC and soil texture analysis. The soil samples were digested with acids to perform metal analysis on an ICP-MS. A detailed description of each method follows.

pH analysis

Soil analyses were performed according to the Environmental Protection Agency (EPA) Method 9045D – Soil and waste pH (EPA Method 9045D). Twenty gram of soil was weighed in a 100 ml beaker and 50 ml de-ionized water was added to the soil. The suspension was then mixed with a glass rod for 5 seconds. The suspension was left to stand for 4 hours. The mixture was stirred once again after 4 hours and left to stand for 10 minutes. The pH was measured in the top liquid. A Copenhagen PHM 80 pH meter was used to take the pH reading.

Electrical conductivity (EC)

Fifty gram of soil was weighed and placed in an EC tube. De-ionized water was added to form a saturated mud paste by mixing it with a spatula or glass rod. The mixture was left to stand overnight. The mixture was centrifuged at 2000 rpm for ten minutes. The EC was measured with a WTW model LF92 EC-meter measuring in mS/cm.

Cation exchange capacity (CEC)

Cation exchange capacity was done according to EPA Method 9080 principle. Colloidal parts like clay usually have a negative load which is neutralized by the adsorption of cations on the surface of the parts. The capacity that the clay has to adsorb cations is referred to as the CEC.

Five gram of soil was weighed in a Schott bottle and 50 ml sodium acetate was added to the soil. The suspension was mixed for 15 minutes at 180 rpm. Filter flocculent was placed in the lye tube and compacted with a glass rod. The suspension was quantitatively transferred to the lye tube by washing the bottle out with sodium acetate to include all soil. The extra sodium was flushed out by adding 50 ml (1:1) Ethanol: distilled water to the lye tube. The lye tube was flushed an extra five times with ethanol. Then 30 ml of ammonium acetate was added to transfer the sodium from the binding sites, and this was repeated three times. The liquid was funneled into a 100 ml volumetric flask. The flask was filled up to volume with ammonium acetate and was well mixed. A tenfold dilution was made and analyzed for sodium concentration using an atomic absorption spectrophotometer (AAS). The AAS used was a Varian SpectrAA model 250 Plus. The unit to express CEC is cmol(+)/kg.

Particle size distribution

A 100 g of soil was weighed and sieved to separate soil (particles < 2 mm) from the bigger particles for example stones or organic matter like plants. The > 2 mm fraction was weighed and noted.

Soil < 2 mm was analyzed according to the particle size analysis of soils by means of the hydrometer method (Laker & Du Preez, 1982). Fifty grams of soil < 2 mm was weighed and saturated with distilled water. Ten milliliter of hydrogen peroxide was added to the soil paste and heated for 4 hours on a sand heater. Then 125 ml of Calgon, a sodium hexametaphosphate solution was added and mixed well. The mixture was quantitatively transferred to a 53 μm sieve. Soil was washed through the sieve with tap water into a one liter volumetric flask. The soil that did not pass through the sieve was washed into a beaker and placed in an oven to dry. After drying, the soil was weighed which represents the sand fraction of the soil.

The soil-water suspension in the volumetric flask was mixed. After 40 seconds a soil hydrometer was placed in the solution and the reading was noted. This reading represents the silt fraction of the soil. After seven hours the hydrometer was placed into the volumetric flask without mixing the mixture again. The reading was taken and represents the clay fraction of the soil. The size of sand particles analyzed is between < 2 mm and 53 μm. Silt size is between 53 μm and 2 μm whilst clay size is < 2 μm according to the Udden-Wentworth grain-size scale (Appendix D).

Soil type

The soil texture designation based on percentage of sand, silt and clay model was used to determine the soil types (Figure 15) (Owen & Chiras, 1995).

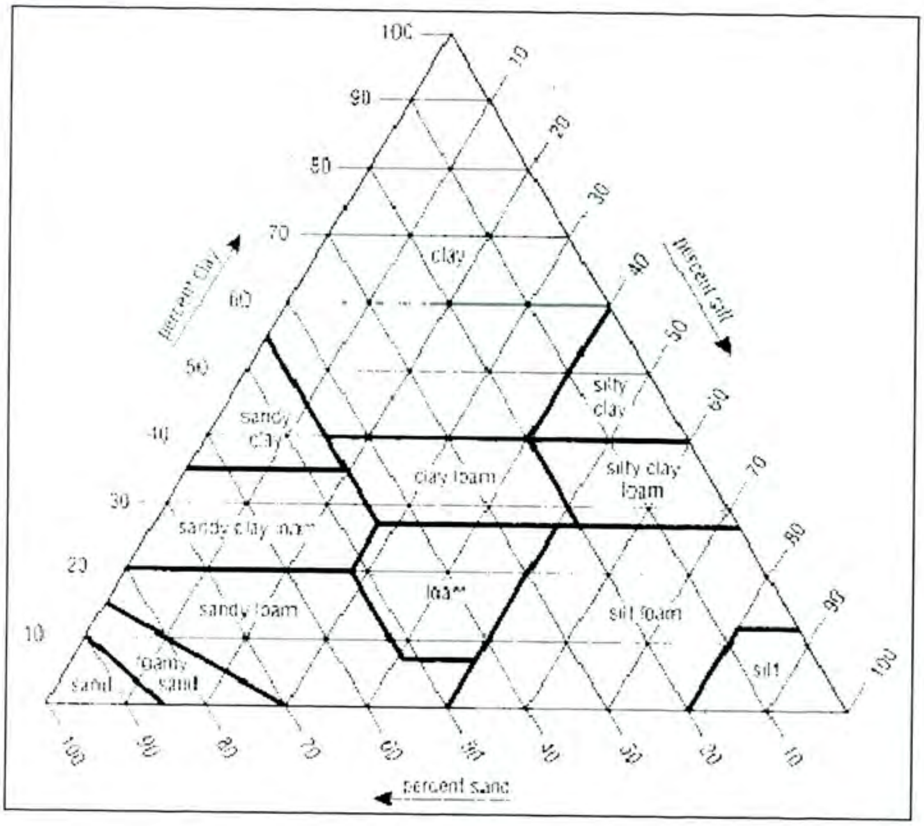


Figure 15: Soil texture designation based on percentage of sand, silt and clay (Owen & Chiras, 1995)

Determination of metal concentrations in vegetation, soil, dust and sub-aquatic sediments

Soil, plant and dust samples as well as the sediment from the water sample were acid digested (EPA Method 3050B) to obtain total metal concentrations. Two grams of sample was placed in a 150 ml beaker and 15 ml concentrated nitric acid was added to the sample. The sample was refluxed at 95 °C on a sand heater for at least an hour (or until fumes disappear) with an hour glass on the beaker. After digestion, the hour glass was removed to allow evaporation of acid. Evaporation was done until 5 ml was left in the beaker. The beaker was removed from the heater and allowed to cool down completely. Then 3 ml of 30 % hydrogen peroxide (H_2O_2) was added to the sample. Additional H_2O_2 was added until the reaction decreased. Then,10 ml 3N hydrochloric acid (HCl) was added and the beaker was covered with a watch glass. The sample was heated on a sand heater for at least an hour. The sample was removed from the heater and left to cool, and then filtered through a 0.22 μm filter into a 50 ml volumetric flask. The filter paper was washed with de-ionized water to transfer the sample quantitatively to the volumetric flask. The flask was filled up to volume.

The acid digested samples were analyzed for selected metal concentrations by the ICP-MS - Agilent 7500 series. Fluka standards were used for each metal and reproducibility was also performed on selected samples. Appendix E shows an estimated detection limit for the Agilent 7500 series ICP-MS as per manufacturer's specifications.

In addition, dust samples were also analyzed for Mg, Al, K and Ca concentrations. Ca concentrations assisted to trace if the source of metals in the dust was the CMP, as calcium oxide is one of the major raw materials of cement (Branquinho, et al., 2007; Galindo, et al., 2011).

Soil samples analysis

The mean as well as minimum and maximum value for the soil metal concentrations was calculated. Frequency tables were drawn and further cross tabulations were done to describe the relationship between the concentration of contaminants and variables like distance from the cement factory and soil depth. For example, the average top soil metal concentration was divided by the average deeper soil concentration per distance from the factory, to assess if metal concentrations are higher in the top or deeper soil. Equation 1 was used to calculate the exceedance factor (EF).

$$EF = [M]^X / [M]^0$$

Equation 1: Exceedance factor

> Where [M] is metal concentration, X is the average dust concentration, 0 is the control / reference standard and the control value / reference standard = 1

The results of the soil metal concentrations were checked against reference standards defined by Turekian & Wedepohl (1961) and the control sample concentrations by dividing the soil metal concentrations by the control and reference respectively.

In addition, Soriano, et al. (2011) refers to classification of polluted soil according to parts per million (ppm) metal concentration in soil (Table 6). This classification table was used to classify metal concentrations in the study area between unpolluted, light, medium, high and extreme pollution of soil.

Table 6: Concentrations of metals (ppm) in contaminated soil (Soriano, et al., 2011)

Element	Unpolluted soil	Light pollution	Medium pollution	High pollution	Extreme pollution
As	0 - 30	30 - 50	50 - 100	100 - 500	> 500
Cd	0 - 1	1 - 3	3 - 10	10 - 50	> 50
Cr	0 - 100	100 - 200	200 - 500	500 - 2500	> 2500
***Cu**	0 - 100	100 - 200	200 - 500	500 - 2500	> 2500
Mn	0 - 500	500 - 1000	1000 - 2000	2000 - 10000	> 10000
***Ni**	0 - 20	20 - 50	50 - 200	200 - 1000	> 1000
Pb	0 - 500	500 - 1000	1000 - 2000	2000 - 10000	> 10000
V	0 - 100	100 - 200	200 - 500	500 - 2500	> 2500
***Zn**	0 - 250	250 - 500	500 - 1000	1000 - 5000	> 5000
* available concentration of metal					

Soil metal concentrations were further compared to metal concentrations from similar studies performed by Abimbola, et.al (2007), Al-Khasman & Shawabkeh (2006), Bermudez, et al. (2010), Ross (1994) and Schuhmacher, et al. (2002). Correlations between soil particle size distribution and soil metal concentrations were also performed.

Dust sample analysis

Dust metal concentrations were compared to the control and metal concentration in CKD analyzed by Massicotte, et al. (2004). Equation 1 was also used to compare the metal concentrations to the control. In South Africa, no reference standards for metal emissions from cement factories are specified, hence results were also evaluated against reference values stipulated in the cement industry of Spain. In Europe, emission limits are available for cement factories producing more than 50 tons of cement clinker per day. Various countries, including Austria, Denmark, France, Germany, Spain and United Kingdom to name a few, have different emission limit values (ELV). Due to the inconsistency between reference conditions and grouping of various metals into a "sum of" concentration values, it is challenging to compare the ELVs as well as to compare dust concentrations to the ELVs. The emission limit values are for emissions from stack whereas samples in this project are fall-out dust.

Due to Spain specifying individual metal ELV, these limits were used to compare with metal concentrations found in the fall-out dust. The concentrations are given in mg/m^3 at a temperature of 0^{0}C and pressure of 1.013 barr or 760mm Hg. To convert mg/m^3 to ppm with a different temperature and pressure Equation 2 is used: (Nevada Division of Environmental Protection, Chemical Accident Prevention Program, 2007). Using Equation 2, ELV concentrations in mg/m^3 were converted to ppm based on average temperature (17.65°C) and average pressure 642 mm Hg (856 hPa) in the study area.

$$\text{TLV in ppm} = \frac{[R * T * (\text{TLV in mg/m}^3)]}{(P * MW)}$$

Equation 2: Converting mg/m^3 to ppm at different pressure and temperature

Where TLV is the threshold limit value, R = 62.4 when temperature (T) is in Kelvins, K (=273.16 + T°C), P is pressure (expressed in units of mm Hg) and MW is molecular weight

Table 7: ELV of Spain, CMP's

Metal	*ELV in mg/m^3	ELV in ppm
As	3	1.1
Cd	2	0.5
Cr	15	8.2
Cu	5	2.2
Ni	55	26.5
Pb	80	10.9
Zn	25	10.8

(European commission, Directorate General Environment, 2004)

ELV's used for comparison in Table 7 do not specify V concentrations, although Finland specify an ELV for V as 100 mg/m^3 which is 48 ppm (Equation 3).

$$\text{ELV}\left(\text{in ppm}\right) = \frac{\left(24.45 * \text{ELV in mg/m}^3\right)}{\text{molecular weight of substance}}$$

Equation 3: Converting mg/m^3 to ppm

Where measurements are taken at 25 °C and at 760mm Hg pressure

Correlations between metal concentrations and Ca concentrations were also performed to assess if the CMP is the source of metals present in the dust as calcium oxide is the major raw product of cement (Prodjosantoso & Kennedy, 2003).

Spatial distribution of metals

GPS co-ordinates on collection of each sample were taken with a Garmin eTrex Venture, indicating the collection point in degrees and minutes. Modelling software, SURPAC, version 6.2 was used to map the spatial distribution in terms of total metal concentration distribution. Inverse distance squared (ID^2) (Barber, 2011) was used by applying a weighted factor based on the X, Y coordinates and elevation. A regularized grid model was used at 100m intervals whilst the surge radius was specified at 2.5km. Equation 4 was used to indicate spatial distribution of various metal concentrations at different distances from the cement factory in a graphical form.

$$F(x, y) = \sum_{i-1}^{n} w_i f_i$$

Equation 4: Inverse distance equation

Where n is the number of scatter points in the set, f$_i$ is the values of scatter points and w$_i$ is weights assigned to each scatter points

3.5. Conclusion

Determination of sample collection points was guided by not only spatial patterns but also accessibility to collection points on the land adjacent to the CMP. Various sample types collected give a broader view of metals in the study area emitted from the CMP. The results are compared with the control sample results (Figure 18, 26, 31), international reference standards (Figure 18, 27) and similar research results from various other study areas. Reproducibility was performed by analyzing selected samples in duplicate. Chapter 4 presents the results and discussion obtained from the collected samples.

CHAPTER 4

4. RESULTS AND DISCUSSION

4.1. Introduction

This chapter presents results and discussion of the soil, vegetation, dust and water metal concentrations. The vegetation results include a brief discussion on metal concentrations found in the samples. The soil results include particle size distribution, pH, EC and CEC which influence metal distribution and availability in the soil. The dust results not only include the metal concentrations but also four additional elements analyzed. The metal concentrations in the dust are compared to the Ca concentrations found to assist in tracing the origin of the metals. A water sample and the sediment in the water were also analyzed for metal concentrations. All metal concentrations are reported in ppm.

Vegetation results

Vegetation samples included grass and tree leaves collected for analysis. The whole grass plant was collected, whilst only tree leaves were collected for the woody species. Table 8 shows results obtained from grass samples.

Table 8: Metal analysis of grass samples at different distances from the CMP

Distance from factory	530 m	530 m	710 m	1100 m	1300 m	Control
Direction from factory	S	S	SE	SW	SSW	NW
Grass type	*Enneapogon cenchroides*	*Setaria incrassata*	*Eragrostis rigidior*	*Bothriochloa insculpta*	*Bothriochloa insculpta*	
Metals analysed (concentrations in ppm)						
V	0.625	1.725	0.1	0.1125	0.95	1.95
Cr	0.875	3.25	3.25	7.25	4.75	3.75
Mn	95	135	105	92.45	65	235
Co	0.275	0.35	0.275	0.525	0.475	<0.0001
Ni	9	11.25	10.5	10.5	11.25	8
Cu	2.2	3.75	2.25	3	3	3.5
Zn	12.75	40	27.5	30	21.25	70
As	1.15	0.1775	0.7	0.8	0.525	1.15
Cd	0.0325	0.015	0.0425	0.0375	0.30	0.045
Pb	1.8	2.175	1.5	1.9	2.15	1.725

Table 9 shows results obtained from tree leave samples.

Table 9: Metal analysis of tree leave samples at different distances from the CMP

Distance from factory	530 m	1300m	Control
Direction from factory	S	SSW	NW
Tree type	*Eucolyptus cladocalyx*	*Eucolyptus cladocalyx*	*Eucolyptus cladocalyx*
Metals analysed (concentrations in ppm)			
V	0.19	2.2	0.65
Cr	3	0.1075	1.975
Mn	177.5	102.5	30
Co	0.5	0.3	0.6
Ni	8.75	9.25	10
Cu	1.1	1.175	7.75
Zn	37.5	37.5	35
As	0.8	0.525	0.875
Cd	0.0325	0.0275	0.0425
Pb	1.75	1	2.125

Pb concentrations are lower in this study area. However, Oluokun, et al. (2007) found elevated Pb levels in the blood of goats after eating forage contaminated with Pb (mean of 420ppm) emitted from a cement factory.

Table 10: Comparison between mean metal concentrations (ppm) in vegetation

Metals analyzed	Schuhmacher, et al. (2002) mean metal concentrations (ppm)	Mean metal concentrations (ppm) in vegetation (current project)
V	0.42	0.84
Cr	0.38	3.21
Mn	35.7	110.36
Co	0.05	0.39
Ni	1.44	10.07
Cu	5.52	2.35
Zn	19.9	29.5
As	Not detected	0.67
Cd	0.02	0.03
Pb	0.77	1.75

This case study does not have high Pb levels in the vegetation. Schuhmacher, et al. (2002) analyzed herbage samples for the same metal concentrations as this project. Table 10 compares the mean concentrations found by Schuhmacher, et al., (2002) and concentrations found in this study area.

Even though mean metal concentrations of all the metals except Cu is higher in this study area than the samples analyzed by Schuhmacher, et al. (2002), the vegetation metal concentrations are low compared to the control. Metal concentrations found in vegetation samples are also lower than the concentrations specified by Ross (1994) as toxic levels in plants (Appendix G). The difference in metal concentrations between this study area and Spain may be explained by Chen, et al. (2010) whose observations concluded that conditions and emissions differ from one cement plant to another.

The reason for low metal concentrations in the vegetation samples may be due to the alkaline pH levels of the soil which reduce mobility and bioavailability of the metals resulting in less uptake of metals by the trees as well as the grass. The sandy loam soil type also influences metal concentrations in the vegetation as metals drain through soil during rainfall. The metal concentrations in the vegetation samples are insignificant.

Soil results

The soil results including metal concentrations (ppm), soil properties and particle size distribution are shown in Tables 11 and 12.

Table 11: Analysis of soil samples at different distances from the CMP

Distance from factory		530 m	530 m	710 m	710 m	1100 m	1100 m	1300 m	1300 m	Control	Reference standard [a]
Depth		0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm		
Analysed metals (concentrations in ppm)											
V		130	125	130	137.5	107.5	95	130	200	52.5	-
Cr		300	300	240	250	230	210	195	275	150	90
Mn		1225	1550	2750	3000	975	900	2300	1950	575	850
Co		13.5	16.25	25	27.5	9.75	8.5	19.25	18.25	11.25	19
Ni		42.5	40	72.5	82.5	27.5	25	57.5	50	50	68
Cu		20.75	20.75	25	27.5	13	11	20	24.5	24.75	45
Zn		7.5	5	45	42.5	2.5	10	4.25	4.5	6.25	95
As		8	5.75	9.75	10	6.75	5.5	7	12.25	5.25	13
Cd		0.0325	0.025	0.0725	0.0375	0.03	0.0225	0.0725	0.04	0.025	0.3
Pb		14.5	13.25	23.75	20	15.5	12.75	21	16.75	8.25	20
Soil properties analysed											
pH (H_2O)		8.24	8.24	7.95	8.02	8.07	8.01	8.22	8.02	8.26	-
EC (mS/m)		49	48	64	65	57	42	38	36	90	-
CEC		13.17	11.83	42.88	47.36	12.9	11.93	19.36	14.89	15.64	-
Particle size distribution											
>2mm		4.4	4.2	0.6	0.9	4.0	1.6	1.3	22.9	30.5	-
% < as 2mm	Sand	75.8	75.7	27.1	19.5	75.8	78.7	56.3	73.3	74.4	-
	Silt	14.4	14.5	54.0	67.9	17.0	11.7	32.8	17.8	5.7	-
	Clay	9.8	9.8	18.9	12.6	7.2	9.6	10.8	8.9	19.9	-

[a] Turekian & Wedepohl (1961)

Table 12: Analysis of second soil samples at different distances from the CMP

Distance from factory		760 m	760 m	1400 m	1400 m	72300 m (Control)	Reference standard [a]
Depth		0-10 cm	Silt fraction	0-10 cm	10-20 cm	0-10 cm	
Metals analysed (concentrations in ppm)							
Mg		1983.75	2742.5	4265	3090	-	-
Al		2600	5217.5	7140	4732.5	-	-
K		344.5	659.25	1563.25	1230.5	-	-
Ca		56075	92325	41950	34800	-	-
V		122	149	196	151	52.5	-
Cr		264	180	227	160	150	90
Mn		974	575	688	546	575	850
Co		8	12	16	12	11.25	19
Ni		24	94	92	65	50	68
Cu		3	12	9	12	24.75	45
Zn		18	20	25	53	6.25	95
As		<0.000	<0.000	<0.000	<0.000	5.25	13
Cd		<0.000	<0.000	<0.000	<0.000	0.025	0.3
Pb		14	15	19	14	8.25	20
Soil properties analysed							
pH (H_2O)		7.86	-	8.49	8.18	8.26	-
EC (mS/m)		26	-	77	66	90	-
Particle size distribution							
>2mm		14.7	-	5.1	1.9	30.5	-
% < as 2mm	Sand	84.6	-	33.7	74.4	74.4	-
	Silt	8.2	-	36.7	5.7	5.7	-
	Clay	7.2	-	29.6	19.9	19.9	-

Particle size distribution

Sand, silt and clay percentages were determined on the fraction < 2 mm of the soil samples. The soil types are indicated in Table 13.

Table 13: Percentage sand, silt, clay and soil type of soil samples collected

Distance from factory	Sand %	Silt %	Clay %	Soil type
530 m	75.8	14.4	9.8	Sandy loam soil
710 m	27.1	54.0	18.9	Silt loam soil
760 m	84.6	8.2	7.2	Loamy sand soil
1100 m	75.8	17.0	7.2	Sandy loam soil
1300 m	56.3	32.8	10.8	Sandy loam soil
1400 m	34.1	41.3	24.6	Loam soil
72300 m (control)	74.4	5.7	19.9	Sandy loam soil

Soil samples are sandy loam, silt loam, loamy sand or loam soil. Not one of the samples is classified in the clay range. Sand soil does not have a high storage capacity. For this reason, it is expected that if metals are deposited on the top soil metals will drain through to lower soil in the rainy season due to the soil type. It will also influence the EC and CEC due to drainage of cations resulting in a lower EC.

Soil Properties

The pH, EC, CEC and metal concentration results are also shown in Table 11 and 12. The pH, EC and CEC affect the mobility and solubility of metals (Al-Khasman, 2004).

pH value

Soil pH was determined to interpret mobility of metals in soil as pH refers to the hydrogen ion concentration [H^+]. The pH values are higher than 8 for samples except for one sample which has a pH of 7.95 (Table 11). These pH levels found, define the soil as being slightly alkaline to medium alkaline (Foth, 1984). Due to the alkaline conditions of the soil, metals are not very mobile as metals are mobile under acidic conditions. With a lower pH, [H+] is high, resulting in metals which are also cations to be more mobile due to less binding sites available. In alkaline conditions, [H+] is less, resulting in less competitive binding sites for metals resulting in less mobile metals, except for vanadium that is mobile under neutral to alkaline conditions (Wright & Welbourne, 2002). It is evident from Figure 16 where total metal concentrations between samples collected 0-10cm and 10-20cm are compared, 63% of the total metal concentrations are higher in the top soil than the deeper soil. This indicates that mobility of metals are reduced in the study area. Due to the alkaline conditions of the soil which is influenced by the CEC of the soil (Al-Khashman, 2004) the low metal concentrations in the vegetation may also be explained.

EC and CEC

The clay content of the sample collected 710 m from the factory as well as the control sample is double the average of clay content of the other samples (Table 11). This may relate to the higher EC in these two samples, respectively 1.3 and 1.9 times higher than the average EC of the other samples. The CEC is also higher, 2.8 times more than the average of the other samples, in the sample collected 710 m from the factory (Refer to figure. This is due to the silt (> 2.5 times) and clay (> 2 times) content that is more than the average of the other samples collected (Table 11).

Metal concentration

Metal concentrations in the top soil and deeper soil were compared to determine if metals are deposited on the top soil or if metal concentrations found are background levels occurring naturally in the study area. The top soil metal concentrations were divided by the deeper soil metal concentrations. The columns in Figure 16 that exceed 1.00 (EF) on the y-axis represent metal concentrations higher in the top soil than the deeper soil whilst columns in the figure less than 1.00 represent metal concentrations that are higher in the deeper soil than in the top soil.

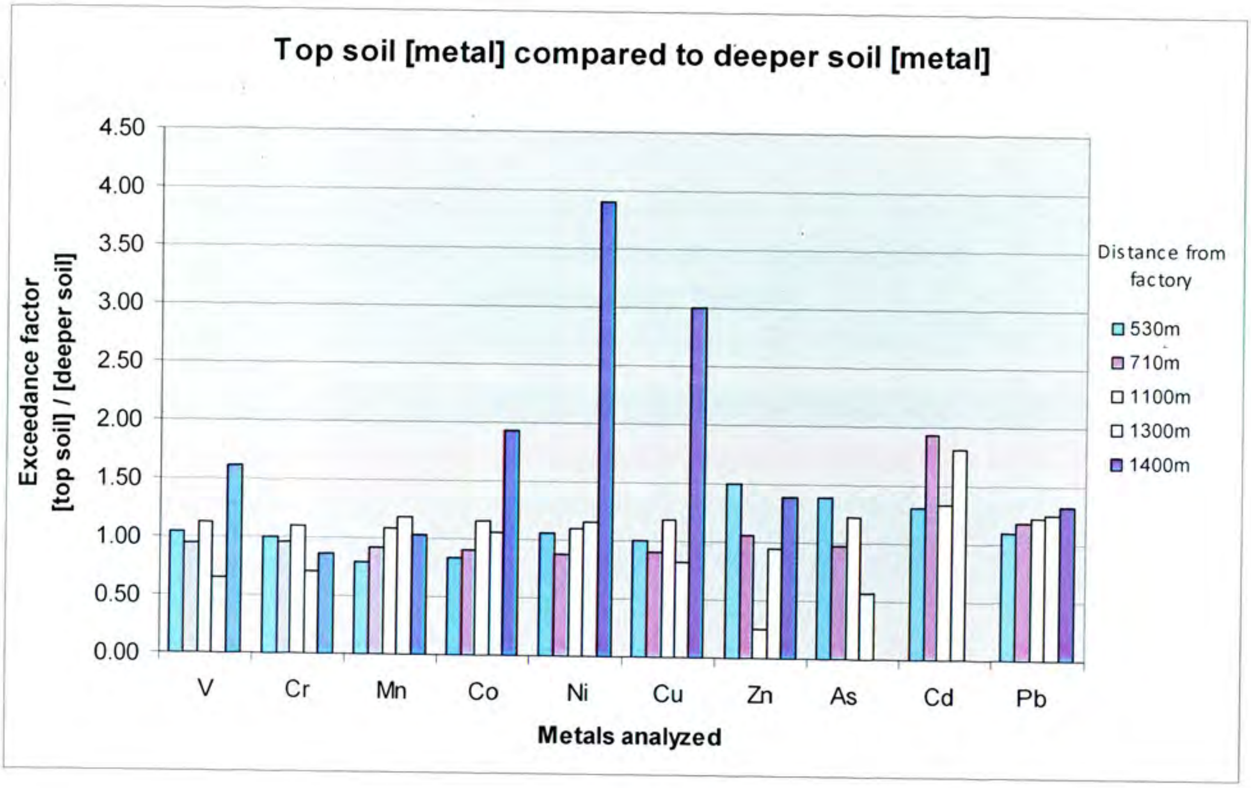


Figure 16: Top soil metal concentrations compared to deeper soil metal concentrations

If the exceedance factor is >1, the metal concentration is higher in the top soil, whereas exceedance factors <1 indicate metal concentration higher in the deeper soil. The concentrations of Cd and Pb are the only two metals that have consistently higher concentrations in the top soil (Figure 16). The other metals have varying concentrations in the top and deeper soil although the differences are not considerable. Due to the soil type (sandy loam soil), soil forms and geology in the study area, the soil water holding capacity is low. Three days before the first samples were collected it rained in the study area. The rainfall was 10 mm for the collection month (South African Weather Services, 2011). Due to the unimportant differences between the top and deeper soil, it may be presumed that metals drained through to deeper soil or groundwater after the rain.

Total metal concentrations of the various samples collected were plotted against the different distances of samples collected to observe if a relationship exists between distance and metal concentrations. Abdul-Wahab (2006) states that cement dust impact vary from 500m – 1000m. Metal concentrations will decrease with an increase in distance from the factory after approximately 1000m (Isikli, et al., 2006). Figure 17 shows the total metal concentration at various distances. No pattern is evident with regard to metal concentration and distance from factory, although the two highest concentrations of metals are at 710m and 1300m which have high silt percentages of 54% and 32.8 % respectively (Table 13).

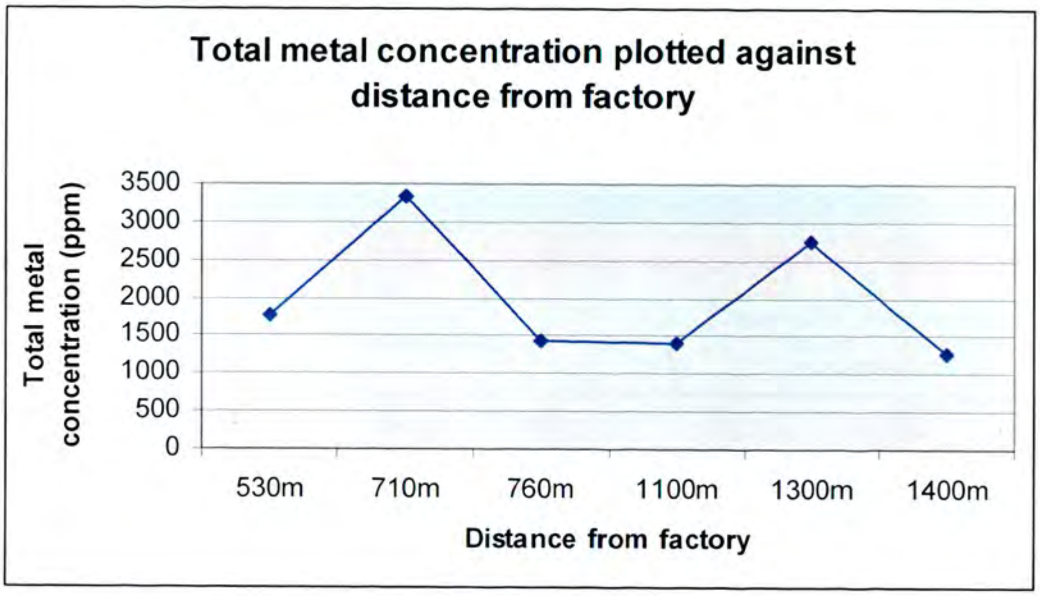


Figure 17: Total metal concentration vs. distance from factory

The average soil metal concentrations were compared with the control sample and the standard reference concentrations (Figure 18) using Equation 1.

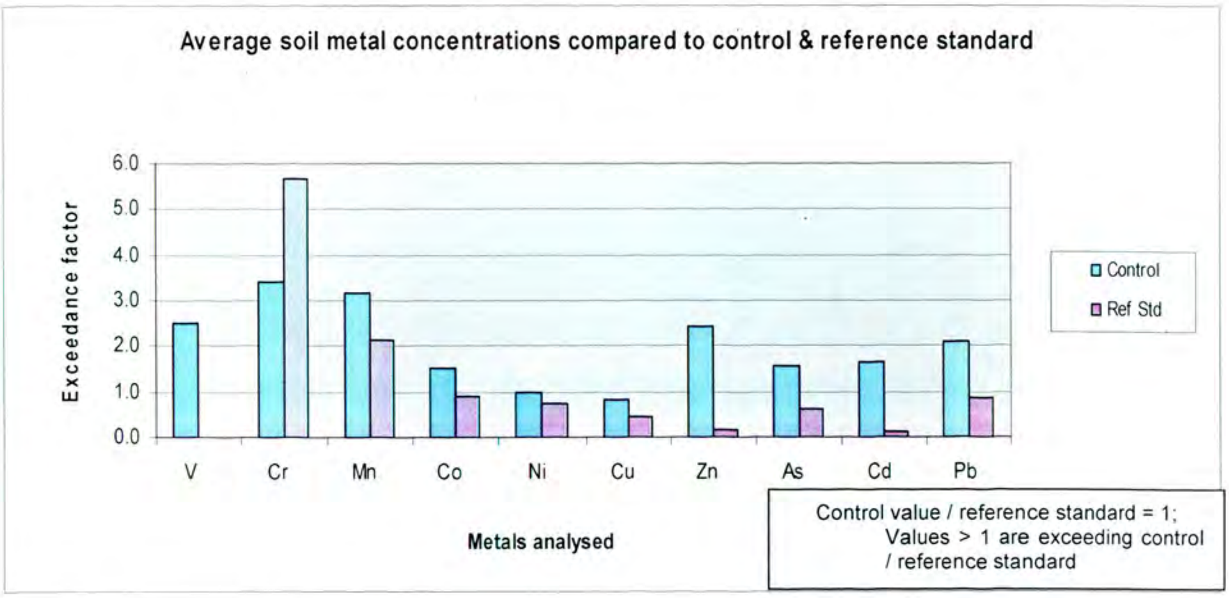


Figure 18: Average soil metal concentrations compared to control and reference standard

The reference standard used did not include values for V. Chromium and Mn concentrations were 3.4 and 3.2 times more than the control and 5.7 and 2.2 times exceeding the reference standard concentrations (Figure 18). No other metal concentrations had a concentration that exceeded the reference values (Figure 18). Compared to the control V, Zn and Pb exceeded the control by 2.5, 2.4 and 2.1 times whilst Co, As and Cd concentrations were marginally higher than the control, exceeding the control by 1.5, 1.5 and 1.7 respectively (Figure 18). It should be noted that soil samples were not collected in the rainy season. It is expected that fluctuations in soil metal concentrations may have been observed whilst dust sample concentrations should not be influenced by seasonal sampling.

Table 14 shows the mean concentration of metals in the soil analyzed as well as the minimum and maximum values to simplify the classification of soil pollution as stated by Soriano, et al. (2011). Arsenic and Cd concentrations in the second soil samples were below detection limits (Table 14).

Table 14: Metal concentration (mean, minimum and maximum) in soil samples (ppm)

Metal	Mean	Minimum value	Maximum value
As	5	<0.001	10
Cd	0.04	<0.001	0.07
Co	15	8	25
Cr	243	195	300
Cu	15	3	25
Mn	1435	674	2750
Ni	53	24	73
Pb	18	14	24
V	136	108	130
Zn	17	3	45

Comparing the mean soil metal concentration in Table 14, metals may be classified as non-pollutants or pollutants of soil (Table 15). Co is not classified due to a reference concentration not referred to in the referenced Table 6.

Table 15: Classifying soil pollution per metal concentration in the study area

Unpolluted soil	Light pollution	Medium pollution
As, Cd, Cu, Pb, Zn	V	Cr, Mn, Ni

Table 15 confirms the finding in Figure 18, where Cr and Mn were more than double the concentration of the reference standard and the control. Contradicting is the Ni classification in Table 15 indicating medium pollution, although concentrations compared to Turekian & Wedepohl (1961) and the control sample were low. According to Ross (1994), soil trace metals originate from fly ash residues from coal combustion, providing 34.2%, 62.86% and 51.3% of the annual inputs of Cd, Mn and Ni respectively. This statement correlates with the classification of medium polluted soil with regard to Mn and Ni, although low Cd concentrations are not polluting the soil.

Further data analysis to compare results with similar investigations is shown in Table 16 where the mean metal concentrations found in the study area are compared to other research results investigating metal distribution from cement factories.

Table 16: Metal concentrations compared to other studies

Metal analyzed	**Current project**	**Abimbola, et.al (2007)**	**Al-Khasman & Shawabkeh (2006)**	**Bermudez, et al. (2010)**	**Schuhmacher, et al. (2002)**
	Mean top soil concentrations in ppm				
As	5	-	-	8	6
Cd	0.04	0.72	5	-	0.3
Co	15	-	-	12	4
Cr	243	-	22	50	10
Cu	15	26	3	4	28
Mn	1435	-	-	281	214
Ni	53	15	-	3	11
Pb	18	37	55	8	16
V	136	-	-	-	9
Zn	17	56	45	93	38

Comparing the results with other metal concentrations found in different areas, it is apparent that correlations do exist between certain metals including As and Co. Nickel, Mn, Cr and V concentrations are higher in this study area (Table 16) than all the other studies performed, although V was analyzed by only Schuhmacher, et al. (2002). Due to V concentrations exceeding the control (Figure 18) it is challenging to interpret the result as no reference standard or other reference studies can be used to compare concentrations. Wright & Welbourne (2002) state that V shows low toxicity in humans even though V toxicity has been demonstrated in laboratory experiments using plants and animals. The concentrations used for the laboratory experiments were higher than concentrations found in the environment.

The higher Ni, Mn and Cr concentrations reiterate the classification of medium polluted soil by these three metals as seen in Table 15. Even though the metal concentrations of Ni, Mn and Cr are moderately elevated in the soil (Table 15), bioavailability of metals found in the soil seems to be of minor significance due to the low concentrations of metals found in the vegetation samples. Due to the reduced bioavailability of metals to plants, the metal concentrations in the soil are not of concern to human health via ingestion, although metals may drain to groundwater due to low water storage capacity soil forms in the study area. Although the metal concentrations in the soil are not of concern currently, over time metal may accumulate, and for that reason it needs to be monitored.

Soil particle size vs soil metal concentrations

To assist in determining the source of the metals in the soil, correlation between the soil particle size and average top soil metal concentrations of the first samples collected in the study area was performed. The metal concentrations were plotted against the particle size percentage (Figure 19, Figure 20, Figure 21). A correlation indicates that a relationship exists between metal concentration and particle size percentage and may either be a positive or negative correlation. If no correlation existed, the graph would show no relationship between metal concentrations and particle size i.e. points scattered on graph.

A negative correlation between the total metal concentrations and sand percentage is expressed (Figure 19). As shown in Figure 19, metal concentrations are lower when the sand percentage is high and vice versa. This negative correlation indicates that metal concentrations were not high in the sand fraction of the soil which may relate to lower background levels (naturally occurring) of metals in soil.

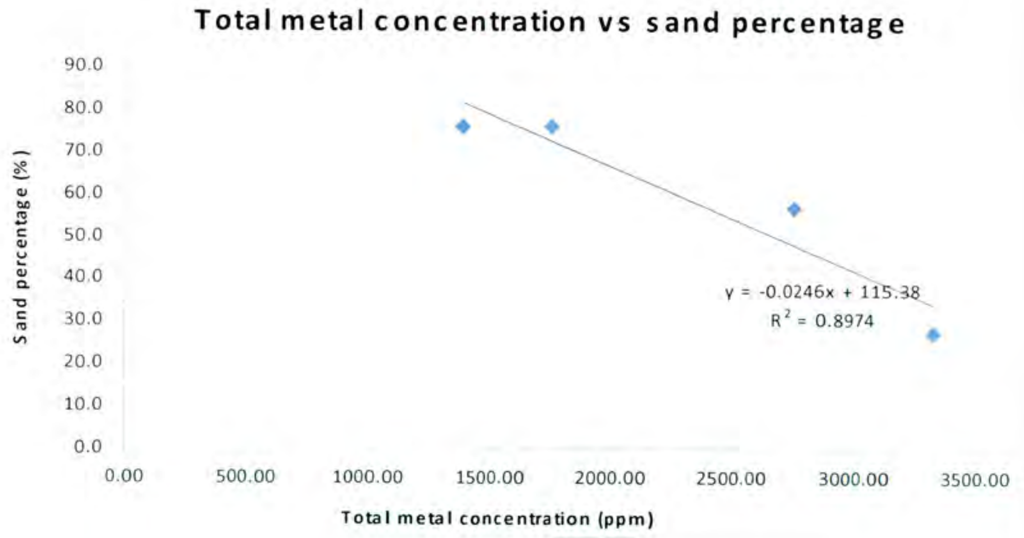


Figure 19: Correlation between total metal concentration and sand percentage

Total metal concentration showed a relationship with the clay percentage of the soil (Figure 20). A positive correlation exists and may be due to metals trapped within the clay particles as the clay percentage ranges from 7.2 to 18.9 (Table 11).

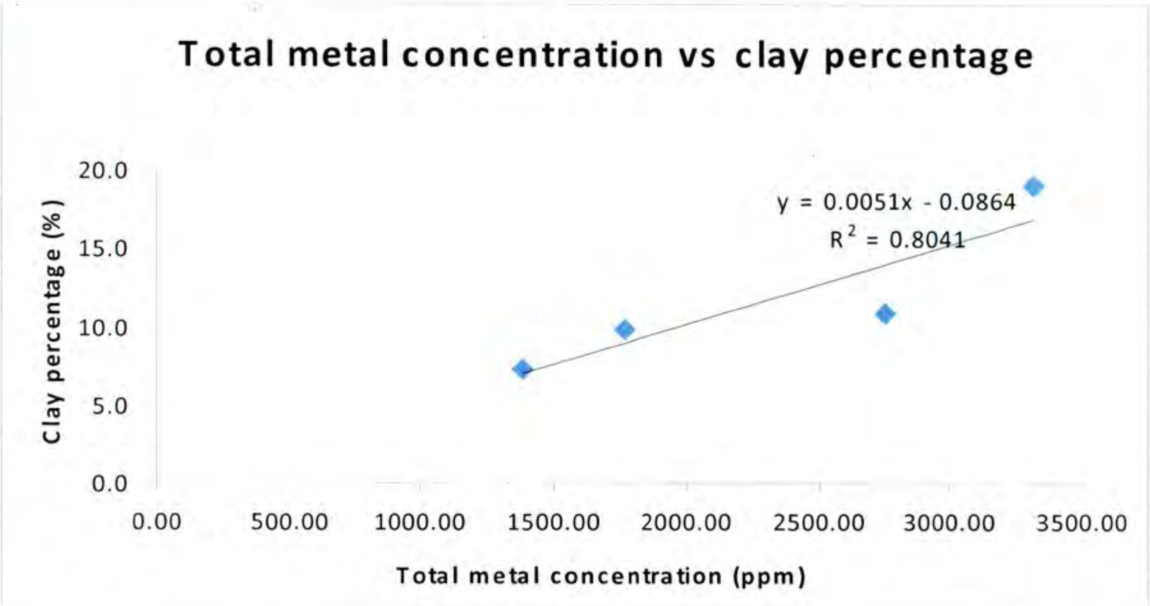


Figure 20: Correlation between total metal concentrations and clay percentage

A positive relationship also exists between total metal concentrations and silt percentage (Figure 21). Silt is the fraction of soil transported by the wind (Bermudez, et al., 2010) and it was found that metals are mostly bound to PM_{10} (Grantz, et al., 2003) when distributed to the environment from cement stacks. The correlation is also higher than clay correlation as the coefficient of determination (R^2) is 0.899 for silt (Figure 21) and 0.804 for clay (Figure 20).

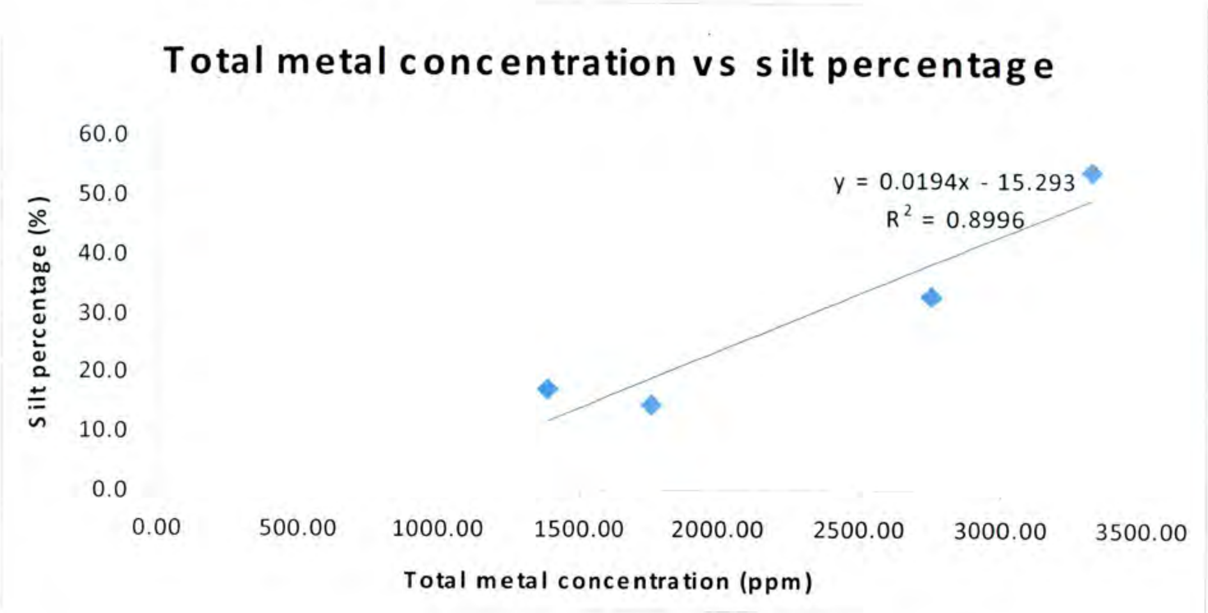


Figure 21: Correlation between metal concentrations and silt percentage

Bermudez, et al., 2010 analyzed soil particle size < 63 µm, as the dust fraction transported by wind for metal concentrations in the top soil. According to Lide, (1994) various dust sources have different sizes as indicated in the Table 17, although dust is referred to particles 1-100 µm in size (Boltovsky, 2003).

Table 17: Size of dust particles from different sources (Lide, 1994)

Particle Name	Size (µm)
Dust	1-10,000
Coal Dust	1-100
Cement Dust	3-100
Insecticide Dusts	0.4-10
Atmospheric Dust	0.001-20

Additional correlations were also performed between single top soil metal concentrations and the different soil fractions namely sand, silt and clay. The reason for correlating each metal to sand, silt and clay is to analyze if all metals analyzed have a relationship with silt percentage. A positive correlation with silt will indicate if the specific metal is transported by wind to the study area whilst a negative correlation may indicate that the metal concentration found is the natural background level in the soil.

Figure 22 shows Cd and As concentrations correlated to the three soil fractions. Due to undetectacble levels of Cd and As in the second soil samples collected, Figure 22 shows results of first collected soil samples.

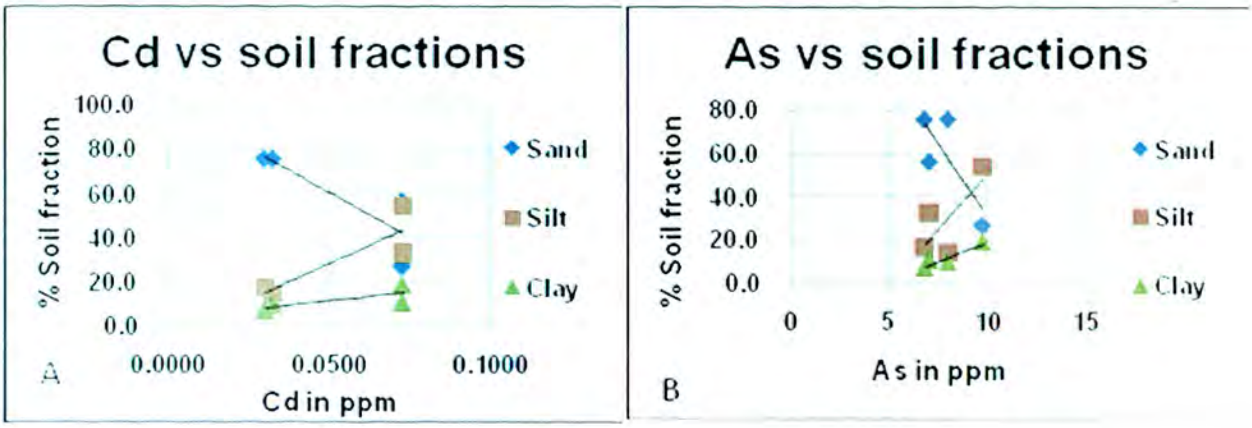


Figure 22: Correlation between Cd and As and soil texture

Even though the concentrations were too low in the second sample batch, a positive correlation was found between the silt percentage of the soil and the Cd (Figure 22 A) and As (Figure 22 B) concentrations respectively, whilst a negative correlation exists with the sand fraction of the soil.

Figure 23 shows the relationship between the various soil fractions and V, Cu, Mn and Zn respectively.

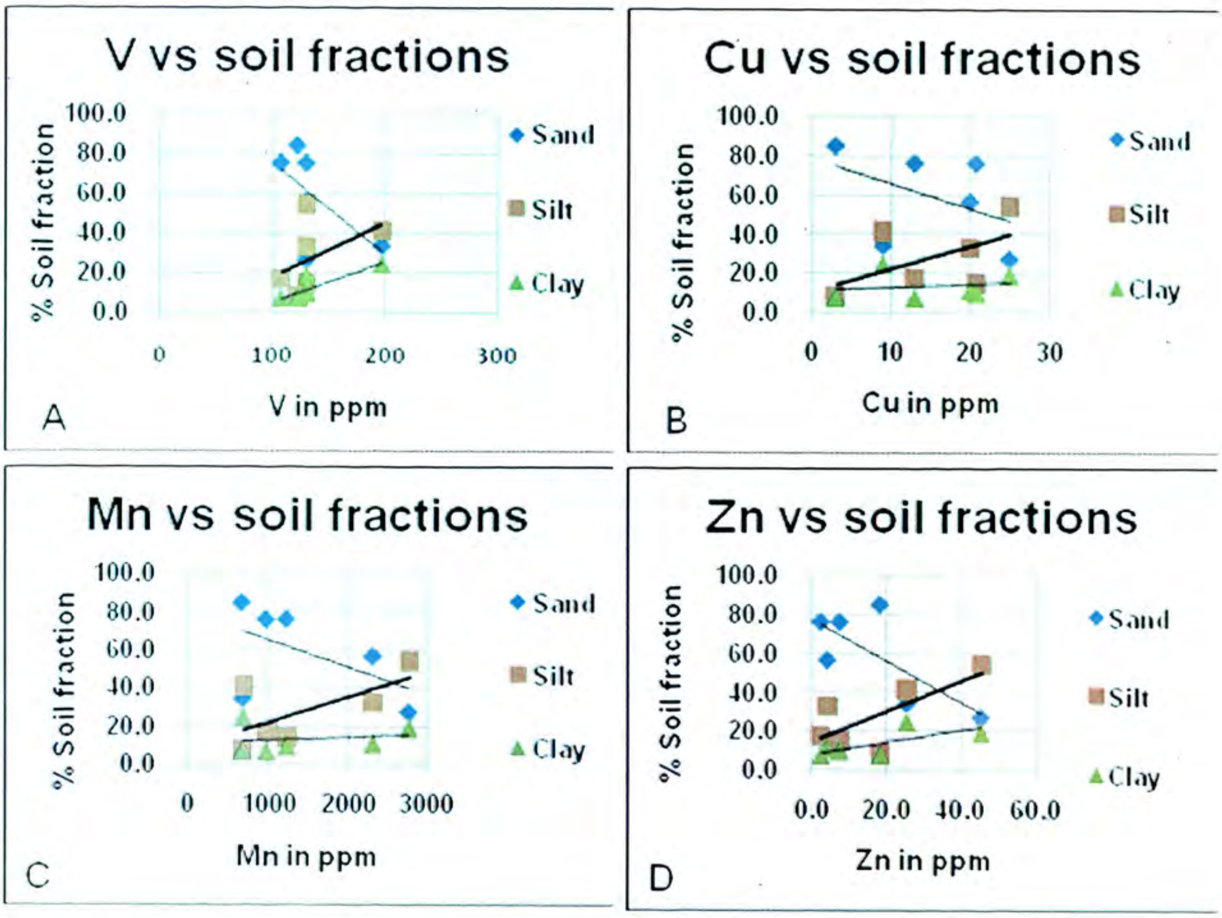


Figure 23: Relationship between metal concentration and soil fractions (silt vs. metal $R^2 < 0.7$).

Vanadium, Cu, Mn and Zn all show a positive correlation with silt percentage with a R^2 of 0.2224 (Figure 23 A), 0.2769 (Figure 23 B), 0.4344 (Figure 23 C) and 0.5237 (Figure 23 D) respectively. This result indicates that dust from the cement factory may be a potential source of the metals even though the correlation is low with a R^2 of less than 0.7.

Figure 24 shows positive correlations between metals and soil fractions with a relationship linking the metal concentrations and silt fraction with R^2 of more than 0.75.

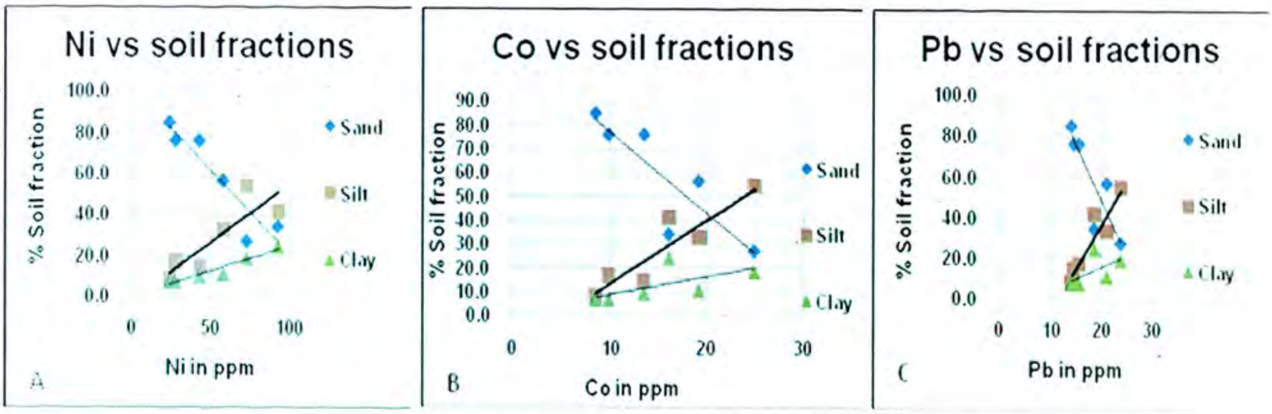


Figure 24: Relationship between metal concentration and soil fractions (silt vs. metal $R^2 > 0.75$).

The correlations for Ni (0.7542) (Figure 24 A), Co (0.8417) (Figure 24 B) and Pb (0.8756) (Figure 24 C) are all above $R^2 > 0.75$ with negative correlations between the sand fraction and an insignificant correlation with the clay fraction of the soil. Due to a positive correlation between the silt fraction and metal concentrations of the samples, it may be assumed that these metals are distributed to the soil through dust.

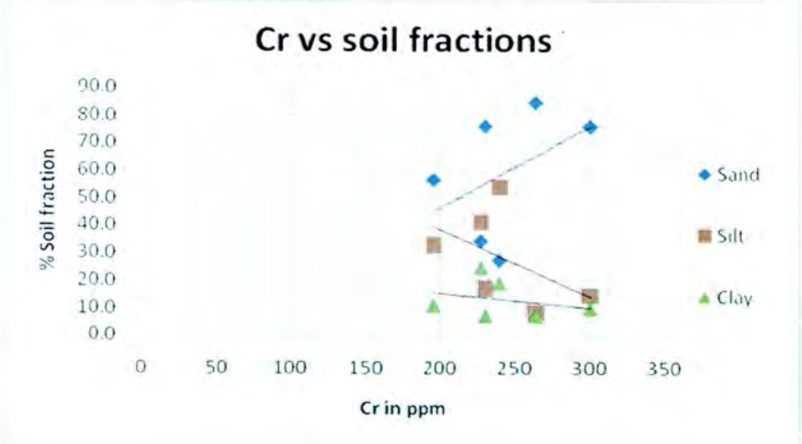


Figure 25: Correlation between Cr concentrations and soil fraction

Chromium was the only metal that showed a negative correlation with total metal concentration and silt percentage and a positive correlation with the sand percentage (Figure 25). This correlation relates to the Cr concentrations in the samples collected in soil 10-20 cm which show marginally higher levels than the samples collected 0-10 cm except for the sample collected 1400 m from the factory (Figure 16). Therefore, it may be concluded that Cr concentrations in the soil are not elevated due to anthropogenic activities (through dust), but rather natural levels occurring in the study area.

To confirm the assumptions that metals are distributed by dust, dust samples were collected as well as second soil samples. The soil sample collected 710 m from the factory was divided into two. One half of the sample (sand, silt and clay) was analyzed for metal concentrations. The other half of the sample was divided into the different soil fractions. Only the silt fraction of this sample was analyzed for metal concentrations. This enabled the researcher to evaluate if the metal concentrations in the silt fraction of the soil were higher than the metal concentrations in the sand, silt and clay fraction of the soil. This will assist to clarify if metals are occurring naturally in the soil or if the metals are distributed by dust. Table 18 shows the percentage of silt fraction metal concentrations exceeding the soil metal concentration.

Table 18: Metal concentration present in silt fraction > soil metal concentrations

Metals Analyzed	Silt metal concentration exceeding soil metal concentration (%)
V	22%
Cr	-32%
Mn	-41%
Co	50%
Ni	292%
Cu	300%
Zn	11%
Pb	7%

Comparing the metals in the silt fraction of the soil, metals are higher in the following order: Cu > Ni > Co > V > Pb > Zn as compared to the complete soil sample. Nickel and Cu concentrations were considerably higher in the silt fraction of the soil whilst V, Co, Zn and Pb in the silt fraction were marginally higher than the complete soil sample (Table 18). Cadmium and As are not indicated due to undetectable concentrations. Chromium and Mn concentrations were lower in the silt fraction of the soil sample (Table 18).

Although the dust fall-out was not causing concern with regard to metals deposited onto soil, further investigations were done to quantify metal levels in the dust.

Dust results

Dust sample results are shown in Table 19.

Table 19: Analysis of fall-out dust samples at different distances from the CMP

Sample	Dust	Dust	Dust	Dust	Dust	Dust (control)
Distance from factory	920 m	1000 m	1600 m	2600 m	2700 m	72300 m
Direction from factory	SSW	W	S	SW	S	NW
Analyzed elements (concentrations in ppm)						
Mg	5982.50	5295	2057.50	5800	4732.5	1938
Al	6567.50	6227.5	5985	7820	7072.5	2620
K	534.75	410.75	750	1599.25	720.75	1228.75
Ca	165650	96225	28352	87775	80350	8532.5
V	43.88	36.48	32.28	35.75	31.2	2.11
Cr	32.7	37.3	61.23	51.3	50.4	16.13
Mn	689.75	985.25	524.25	1295.25	769.25	198.28
Co	29.78	4.65	2.66	6.08	5.15	0.66
Ni	14.09	21.58	12.54	43.73	24.11	6.47
Cu	3.11	49.8	1.92	74	9.5	13.43
Zn	2747.5	878.5	129.13	3037.5	286	299
As	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Cd	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Pb	5.53	17.08	3.08	30.3	97.45	7.88
Other analysis						
pH (H_2O)	8.32	8.51	7.83	7.24	Too little	6.90
EC (mS/m)	407	202	198	655	Too little	763

Figure 26 shows the average fall-out dust concentrations compared to the control sample. Cadmium and As are not shown in Figure 26 due to concentrations below the detection limit.

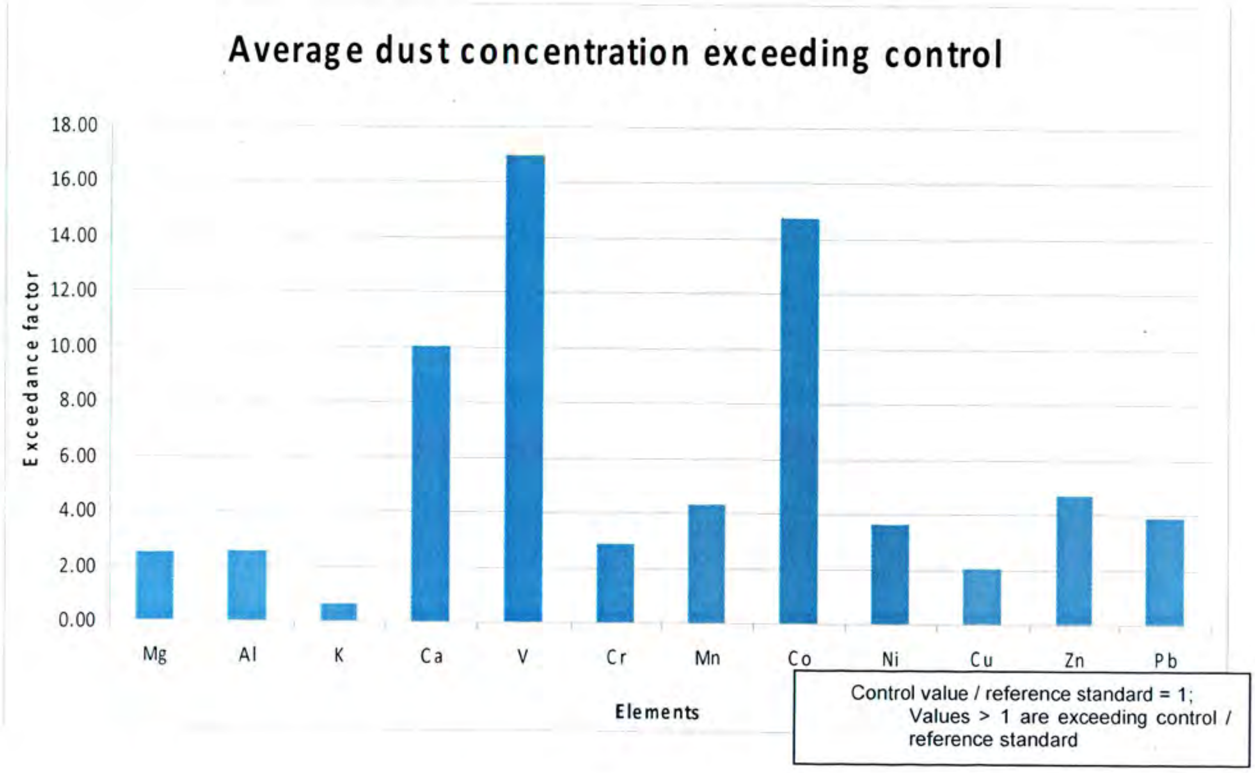


Figure 26: Average fall-out dust concentration compared to the control sample

Results in Figure 26 reveal that V and Co levels were 17.1 and 14.75 times higher than the control sample. The other metals Zn, Mn, Pb, Ni, Cr and Cu exceeded the control sample concentration by 4.73, 4.3, 3.9, 3.62, 2.89 and 2.06 respectively. Ca, which is the indicator element to assess if the elements are originating from the cement factory, is 10.04 times more than the control sample concentration.

Hindy, et al. (1990) found that V is released from a cement factory to the surrounding environment. The V concentrations in the soil compared to other studies were much higher and the dust concentration compared to the control sample is much higher. In the current study, the mean V concentration is 36 ppm, lower than the ELV for Finland (European commission, Directorate General Environment, 2004; Chapter 3, Equation 4) which is 48 ppm. Vanadium inhalation may cause DNA mutagenesis which may lead to lung cancer (Ehrlich, et al., 2008) if it is in the form of vanadium pentoxide.

Co was also significantly higher than the control sample. Even though cobalt is beneficial to humans as it plays a role in Vitamin B12 absorption (Armstrong, 1989), at high levels cobalt may affect human health. Cobalt inhalation may cause asthma-like diseases including dyspnea, respiratory sensitivity and decreased respiratory function (Lenntech, 2011). Cobalt is also a recognized carcinogen, with inhalation being the main exposure route targeting the lungs (Beyersmann, 2002). Nonetheless, Spain or other European countries do not specify an ELV

Massicotte, et al. (2004) analysed CKD for various elements. The concentrations of the metals found in the CKD are compared to the concentrations found in this study area (Table 20).

Table 20: Mean, minimum and maximum fall-out dust values compared to kiln dust (ppm)

	Statistical dust metal data (ppm)			
Metal	**Mean**	**Minimum value**	**Maximum value**	**Kiln dust ***
Mg	4773.50	2057.5	5982.5	9200
Al	6734.50	5985	7820	19500
K	803.10	410.75	1599.25	65700
Ca	85665.00	28352	165650	285000
V	35.92	31.2	43.88	-
Cr	46.59	32.7	61.23	<100
Mn	852.75	524.25	1295.25	300
Co	9.67	2.66	29.78	20
Ni	23.41	12.54	43.73	10
Cu	27.67	1.92	49.8	<10
Zn	1415.73	129.13	3037.5	300
Pb	30.69	3.08	97.45	200
*Massicotte et al. (2004)				

Metal concentrations in the fall-out dust that are higher than the concentrations found by Massicotte et al. (2004) in kiln dust are Mn, Cu, Ni and Zn, exceeding kiln dust by 2.84, 2.77, 2.34 and 4.72 respectively. These findings correlate with soil metal concentrations as specified in Table 15 for Mn and Ni whilst Cu and Zn concentrations in soil are classified as not polluting soil. Massicotte et al. (2004) did not test for V concentrations in kiln dust.

Manganese levels were higher than Mn kiln dust levels found by Massicotte et al. (2004) and are 4.3 times higher than the control sample. Unfortunately, ELVs are not specified for Mn. Manganese levels found in the soil are also higher than the control sample levels (Figure 26) and reference standard (Table 20). Due to the elevated levels of Mn in the dust, inhalation probability is high for humans living in the vicinity of the CMP. Manganese toxicity may occur from ingestion of high Mn levels, although more severe cases of neurotoxicity occur due to Mn inhalation as it creates a more effective entry pathway once inhaled (Normandin, et al., 2002). Inhalation of Mn is associated with psychosis and Parkinsonism if chronically exposed to Mn containing particles (HaMai, et al., 2006). Psychosis is a mental disorder marked by delusions while Parkinsonism is a common neurological disease associated with tremors of the fingers and hands and slow speech caused by deterioration of the brain cells that produce dopamine. Dopamine is a neurotransmitter regulating movement and emotions in conjunction with the brain. Normandin, et al., 2002 found deterioration of the brain cells due to decreased transcription levels of five out of ten genes associated with oxidative stress and inflammation following exposure to Mn. Occupational Exposure limits (OEL) are available though it may be disputed if OEL and fall-out dust concentrations are comparable.

Furthermore, dust concentrations are compared to the ELV specified by Spain (Chapter 3, Dust sample analysis). The ELVs are used to compare the fall-out dust sample results, hence the results should be used with caution. ELVs are for CKD emitted from the CMP whereas dust samples collected for this project were fall-out dust containing CKD.

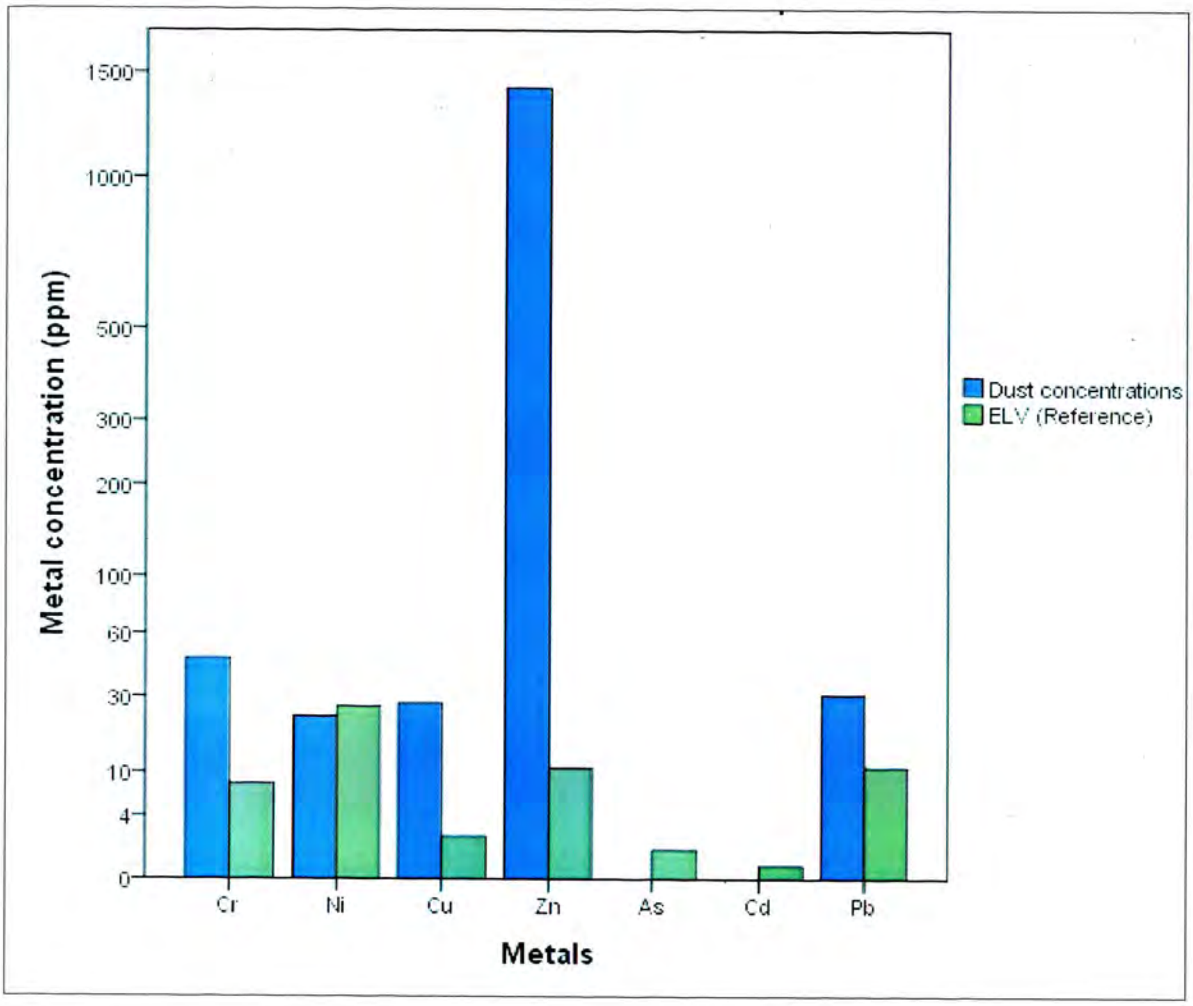


Figure 27: Average dust concentrations compared with ELV

The average Zn concentration of the dust in the study area was 1416 ppm whilst the ELV for Zn is 10.8 ppm. Even the minimum concentration of a dust sample found (129 ppm) is higher than the reference ELV. Zinc concentrations are also higher than the control sample (Figure 26), as well as kiln dust (Table 20). Although Zn is an essential element in a variety of cellular processes, at high concentrations it may cause toxicity. Inhalation of Zn may induce cardiovascular health complications (Wallenborn, et al., 2008) especially Zn found in high concentrations combustion source PM (Gilmour, et al., 2006). Contradictions exist with regard to Zn toxicity. As stated by Wright & Welbourn (2002), Zn toxicity is not generally of concern to humans and may accumulate in tissue although it does not biomagnify, whilst Fernandez, et al. (2003) state that Zn appears to cause lung injury when inhaled. This may be of concern due to elevated levels in the dust which may be inhaled by humans.

The average Cr concentration was 4.4 times higher than the ELV stated by Spain (European commission, Directorate General Environment, 2004). Although Cr concentration correlations to silt fraction (Figure 25) and Ca concentrations are negative (Figure 28), the impact of Cr in dust is discussed due to the increased levels present in the dust compared against the ELV (Figure 27) and the control sample (Figure 26). Chromium inhalation induces an inflammatory response in the lung which may contribute to early oncogenesis (Beaver, et al., 2009). Potgieter, et al. (2003) found hexavalent Cr in clinker formed during the cement manufacturing process. Further investigations are required to trace the origin of the Cr in the dust and to analyze for the various Cr species present in the dust.

The Cu concentration exceeded the ELV by 12.6 (Figure 27). Wright & Welbourne (2002) explain that Cu is an essential trace element for humans and that the liver and kidneys can detoxify high concentrations of Cu except in the case of a metabolic disorder like Wilson's disease. Copper concentrations thus do not pose a huge threat to human health.

Lead levels are 2.8 times more than the ELV although according to Ca concentration correlation with Pb concentrations (Figure 28) the levels are not related to CKD. This is reiterated by the low concentration compared to kiln dust concentrations tested by Massicotte, et al. (2004) (Table 20).

Only dust Ni concentrations in the study area are lower than the ELV relating to Figure 20, indicating that Ni concentrations in the soil are also lower than the control sample and reference standard, although Ni concentrations in the dust were 2.34 times higher than the control sample (Figure 26). Ni concentrations in the soil also show a high correlation with silt percentage (Figure 25) and are also classified as a metal in medium polluted soil (Table 15).

Association between the metal concentrations and Ca concentrations were performed to assess if the cement factory is the emitting source of the metals (Figure 28, 29, 30).

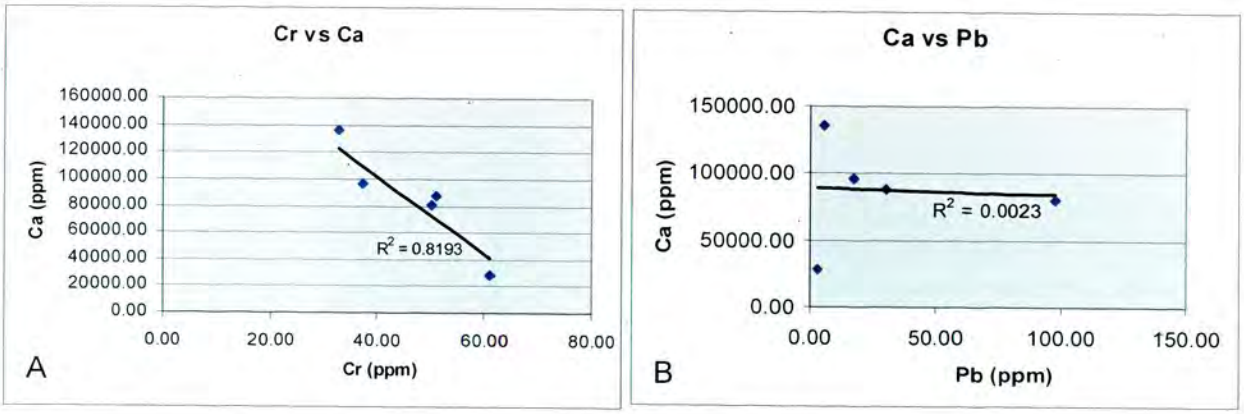


Figure 28: Negative correlations between Cr and Pb and Ca concentrations

Chromium (Figure 28 A) and Pb (Figure 28 B) have negative correlation with Ca concentrations found in the dust samples. This confirms what was found with soil Cr concentration compared with the silt fraction. The only plausible explanation for the negative Cr concentrations is that Cr is not emitted by the CMP, although high levels are present in the soil and dust samples collected compared to the control and reference values. The Pb correlation contradicts what was found when establishing a relationship between the soil Pb concentrations and the silt fraction (Figure 24 C). The relationship was high with the silt fraction, but has a negative correlation with the Ca concentrations in the dust. The only plausible explanation for the difference in Pb concentrations (2.8 times more than the ELV) (Figure 27) could be that Pb is not emitted by the CKD. The origin of the Pb in the soil may be due to other sources such as motor vehicles (Olowoyo, et al., 2010) since samples were collected in close proximity to roads.

The relationship between Ca concentrations and Mn (Figure 29 A) and Cu (Figure 29 B) is low with an R^2 of 0.0962 and 0.0102 respectively (Figure 29). This relates to correlations drawn between these metals and the silt fractions which did show a relationship although it was not significant.

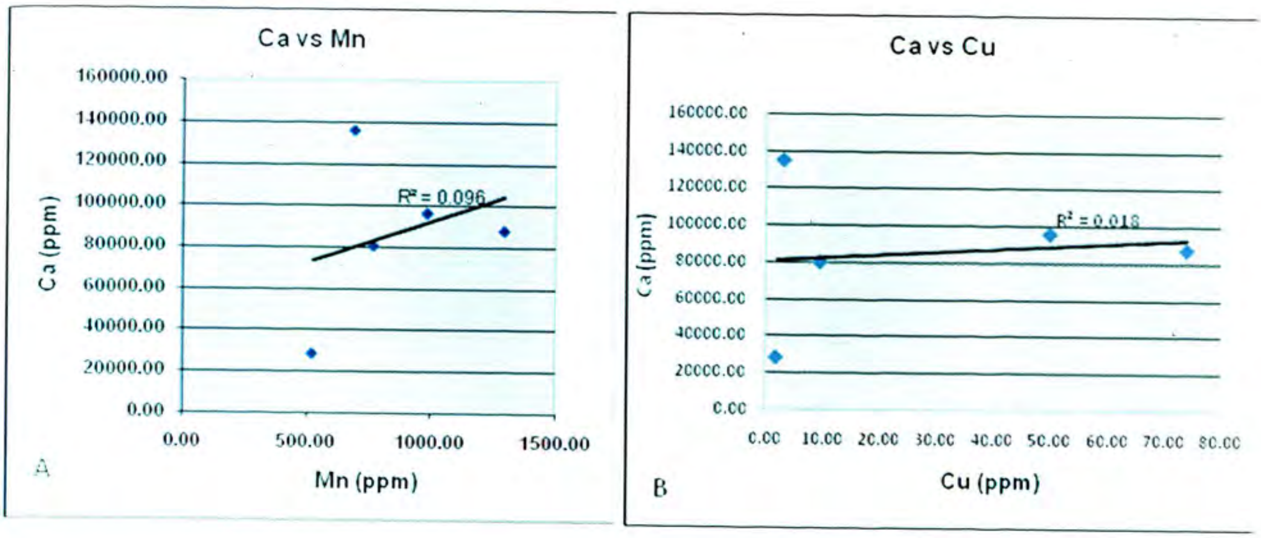


Figure 29: Correlations between Ca concentrations and Cu and Mn concentrations

A positive correlation between Ca concentrations and metal concentrations indicate that these metals are emitted by the CMP. The four metals that show a significant positive correlation with the Ca concentrations are Ni (Figure 30 A), Zn (Figure 30 B), Co (Figure 30 C) and V (Figure 30 D).

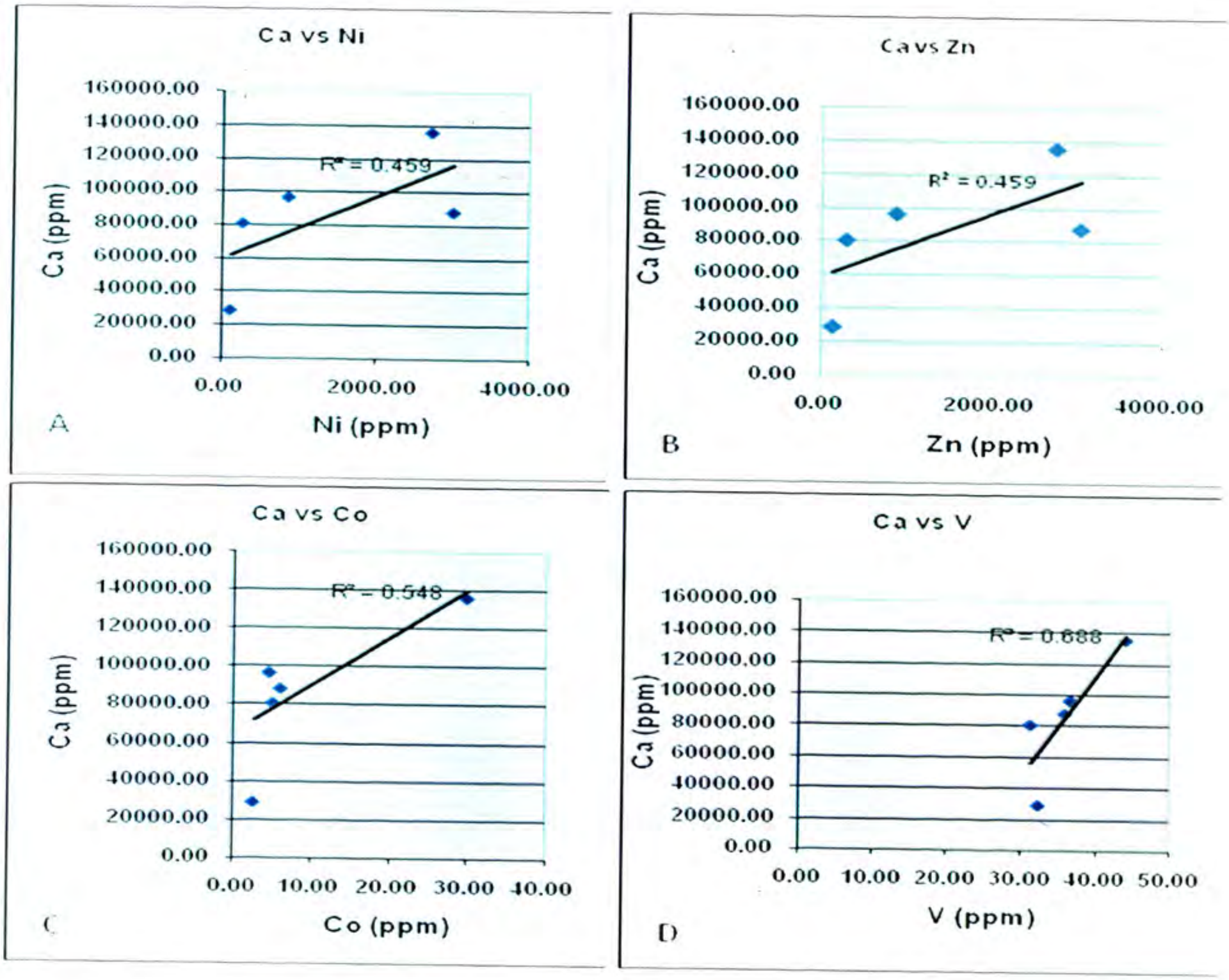


Figure 30: Correlations between Ca concentrations and Ni, Zn, Co and V.

The results agree with the findings in the soil analysis where Ni (Figure 24 A), Zn (Figure 23 D) and Co (Figure 24 B) revealed a high correlation with silt fraction, except for V compared with silt fraction which had a positive correlation of 0.688 (Figure 23 A). The concentration of metals in the dust emitted from the CMP may have possible health effects on the human population living in the town located next to the CMP. Schuhmacher, et al. (2004, 2009) found that emissions from a cement plant create low human health risk relating to toxicological and cancer risk although their calculated concentrations in the air (dust), soil and dust samples are lower than the analyzed concentrations of this study.

Even though Ni concentrations found in the dust are below the ELV (Figure 27), a high correlation exists between Ca concentration and Ni levels (Figure 30 A). The soil Ni levels are also higher than the control and other studies performed elsewhere (Table 16) and they are classified as levels present in polluted soil (Table 15). Humans are mainly exposed to Ni by inhalation. Inhaled Ni absorption is higher than ingested Ni (Wright & Welbourn, 2002). Although Ni may be an essential element for humans, occupational studies have found a correlation between Ni inhalation and respiratory tract diseases (Wright & Welbourn, 2002). Therefore, the presence of Ni in the air could be a potential threat to the health of both workers at the CMP and humans residing within the study area.

Water results

Table 21 summarizes results of metal concentrations in water and sediment samples. The water and sediment found in the water were tested for the same elements as the dust samples.

Table 21: Water sampling results

Sample analyzed	Water from pool	Sediment collected from pool (acid digested)	Tap water – used to fill the pool
Distance from factory	2600 m	2600 m	Control
Direction from factory	SW	SW	
Analyzed elements (concentrations in ppm)			
Mg	110	4268.25	100
Al	0.31	36585	0.1
K	7.5	853.65	5.6
Ca	120	49999.5	100
V	0.023	51.219	0.018
Cr	0.074	121.95	0.065
Mn	0.03	475.605	0.024
Co	0.0016	8.2926	0.0012
Ni	0.02	47.5605	0.0092
Cu	0.78	118291.5	0.16
Zn	2.3	256095	0.48
As	0.027	14.634	0.021
Cd	0.0012	11.9511	0.0012
Pb	0.0021	109.755	0.0026
Other analysis			
pH (H_2O)	7.94	-	7.31
EC (mS/m)	62	-	61

The control sample and the water sample collected from the pool (excluding the sediment) are compared to assess if metals were deposited into the water from dust fallout. Tap water was used as the control as it was used to fill the pool. Figure 31 shows results of metal concentrations in water samples.

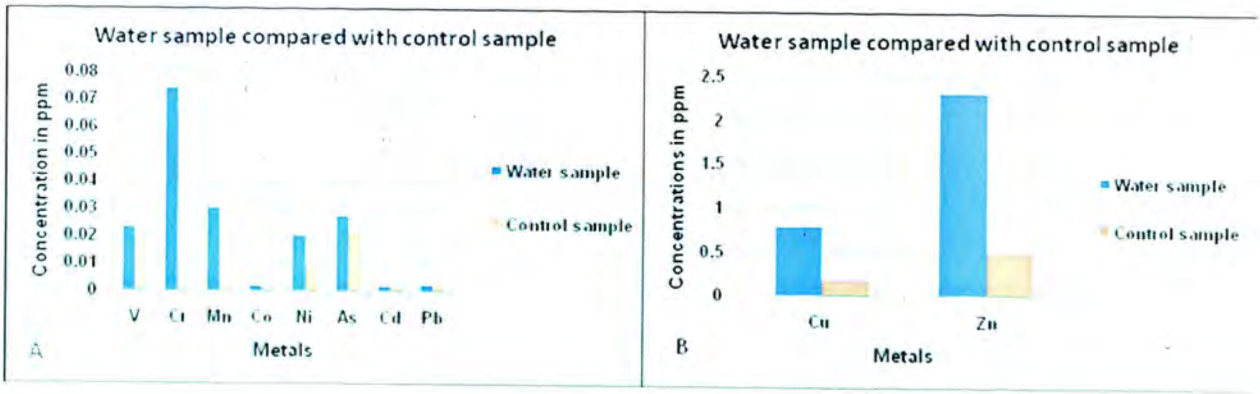


Figure 31: Metal concentrations from water sample compared with control sample

Results reveal that V, Cr, Mn, Ni, As, Cu and Zn are higher in the test sample than the control (Figure 31). Cobalt is slightly higher than the control whilst Cd has the same concentrations and Pb is lower in the test sample than the control. This corresponds with the correlations graph in Figure 28, specifically for Pb. The Ca concentration in the test water sample was also higher than the concentration in the control sample (Table 21).

Comparing the sediment total element concentrations with the straight water sample analyzed, it was evident that the metal concentrations as well as Ca concentrations (Figure 32) were higher in the sediment of the water than the water sample collected. It is known that metals accumulate in the sediments of water (Rybicka, et al., 2005).

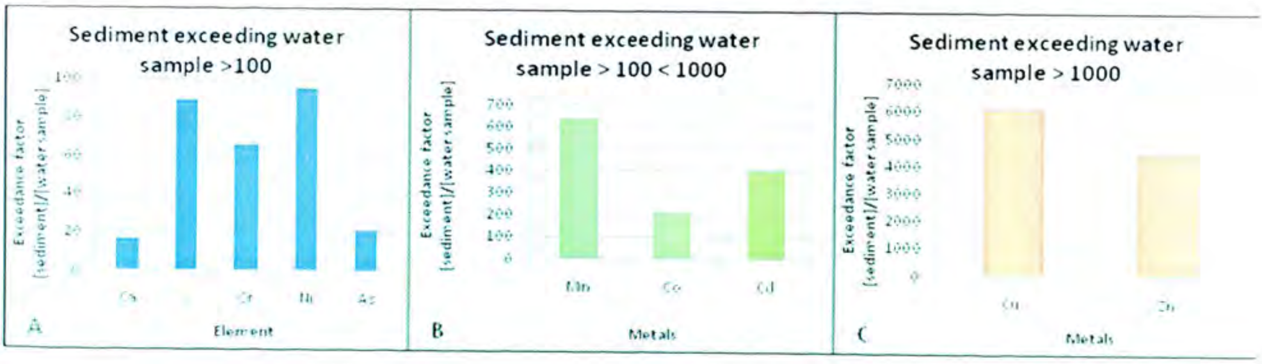


Figure 32: Sediment element concentrations exceeding water sample concentrations

The sediment results compared to the water sample shows that the metal concentrations are much higher in the sediments (Figure 32) whilst the metal concentrations in the water sample compared to the control is only marginally (Figure 31). It should be mentioned that results could not be conclusive because only one water sample was collected, which was divided into a sediment sample and the water sample.

Repeatability

Repeatability of the metal determination method was performed. Selected samples were analyzed in duplicate. Variance, standard deviation, and coefficient of variation are indicated in Appendix F. The average coefficient of variation for element analysis is 3.32% which falls within the acceptable level of 5% (Appendix F).

Spatial mapping

The metal concentrations were used to create spatial distribution maps to indicate spreading of metals within the study area. Figure 33 shows the soil metal concentrations within the study area.

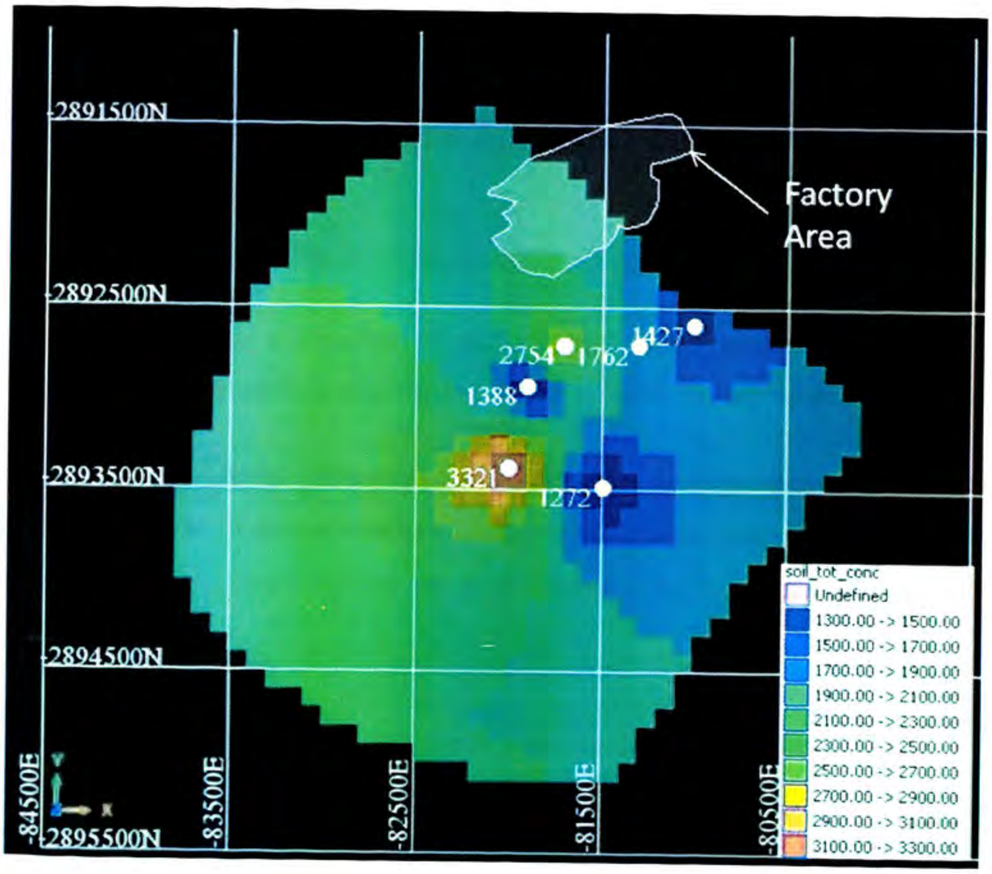


Figure 33: Spatial distribution of soil metal concentrations in the study area (Source: Created by Ernie Venter, Rock & Stock Investments, geoscience consultants)

The spatial distribution of the fall-out dust metal concentrations is shown in Figure 34.

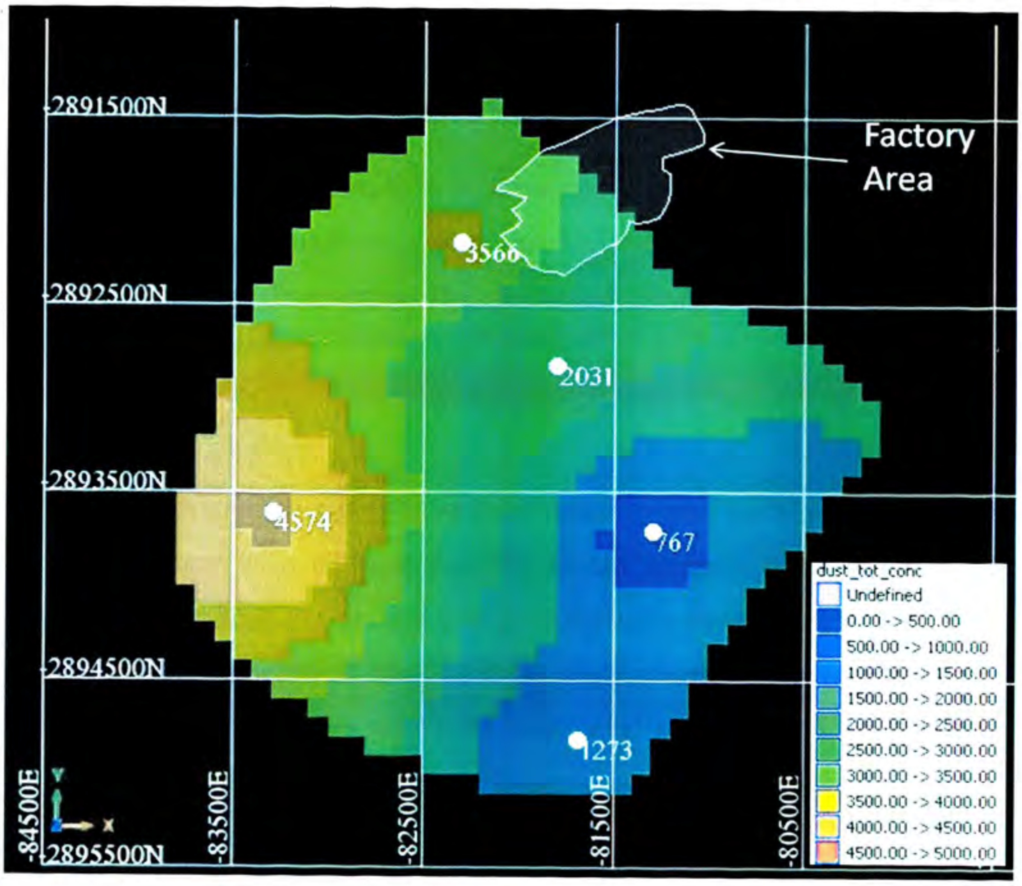


Figure 34: Spatial distribution of fall-out dust metal concentrations in the study area (Source: Created by Ernie Venter, Rock & Stock Investments, geoscience consultants)

Figure 33 and Figure 34 reveals that the highest distributions of metals are south-west from the factory. This is of major concern as the town Lichtenburg lies south-west from the factory and the fall-out dust concentrations are much higher than the total soil metal concentration.

4.2. Conclusion

The results and the effects the metal concentrations may have on the environment and human health were discussed in this chapter. The conclusion and recommendations for this project are discussed in the following chapter.

CHAPTER 5

5.1. CONCLUSION AND RECOMMENDATIONS

The results of the vegetation, soil, dust and water samples were given and discussed in the previous Chapter. Conclusions and recommendations based on Chapter 4 are given in this Chapter to end the dissertation with possible follow-up research and recommendations made to relevant stakeholders.

Conclusion

Cement manufacturing plants have been found to emit metals during various cement production processes. There is a concern that the metals released could have a negative effect on the environment and on the people living in the adjacent town. By quantifying the metals in the environmental samples, it may become clear whether environmental pollution is occurring. Therefore, various samples were collected including vegetation, soil, dust and water. The results of this study can be used to assist the appropriate local authorities to set emission limit values for cement manufacturing plants.

This study was based on the hypothesis that metals from cement manufacturing plants including Cu, Zn, V, Cr, Mn, Co, Ni, As, Cd and Pb could pollute the environment and be hazardous to human health. The study was aimed at answering the questions: Does the CMP in the study area pollute the environment (soil, vegetation, dust and water) with metals? If so, what are the potential short term and long term effects on the environment and public health? This study focused on quantifying metals in soil, plants, dust and water to evaluate the possible impact of metals on the environment and human health. These concentrations were compared to the control sample and the reference standards as shown and discussed in Chapter 4.

Results from the analysis of metals showed that some of the selected metals are released into the environment from the cement manufacturing plant. Of particular interest were the metal concentrations in the soil with the silt fraction that revealed Ni, Cu and Pb concentrations significantly higher in the silt fraction of the soil whilst V, Cu, Mn and Zn in the silt fraction were marginally higher than the complete soil sample. Only Cr and Mn concentrations were higher in soil samples than the control and reference values whilst metal concentrations for Cr, Cu, Pb and Zn were higher in the dust samples than the control and the ELV. However, correlation analysis indicates that Cr and Pb concentrations are unrelated to cement emissions. In addition, due to ELVs only being available for European countries and not in South Africa, comparing concentrations to a reference value was challenging.

Furthermore, water and sediment found in the water were tested for the same elements as the dust samples. The control sample and the water sample collected from the pool (excluding the sediment) were compared to assess if metals were deposited into the water from dust fall-out. Tap water was used as the control as it was used to fill the pool. The sediment in the water sample indicated that all metals analyzed were higher than the water sample analyzed. Comparing the sediment total element concentrations with the straight water sample analyzed, it is evident that these elements are present in the residue at the bottom of the pool.

Contradictory to other studies performed, metal concentrations did not show a distinct pattern compared to distance from the factory. This may be due to various factors including wind speed variations, wind direction fluctuations, rainfall and varying heights of stacks at the CMP. Bioavailability and mobility of the metals in the soil can be stated to be of minor significance due to the low metal concentrations in the vegetation samples. However, this research will serve as a base for future studies especially since CMPs are in the process of applying, to convert from using coal as energy source to alternative fuels.

The study was limited by insufficient number of samples due to the cost of analyzing each of the samples. The user should be aware of the following concerns: 1) limited number of samples collected per environmental factor, 2) dust emitted from the stack could not be sampled and fall-out dust was collected which may result in a buildup of metals in the accumulated dust samples. Due to fall-out dust collected, it is complicated to compare the concentrations to ELVs.

Recommendations

In view of the results obtained in this study, the following implementation strategies are worth noting.

- Pollution from the cement factory is of concern to the environment and the human population living in this area. The challenge for further study is the need for thorough assessment of metal concentrations in water and water sediments to determine if water sources are contaminated by CKD. Furthermore, due to increased Cr levels found, further research is required to determine the source of the Cr in the samples analyzed.

- The study recommends that further study should include analysis of dust emitted from the CMP, to ascertain in what oxidation state vanadium exists due to the high concentrations found in this study area compared to the control.

- European countries have ELVs applicable to the cement factories. However, in South Africa ELVs for metals are not specified. Due to some elevated metal concentrations found in the study area and other studies performed worldwide, it is recommended that ELV limits be established in South Africa and monitored for cement factories and other related industries.

- The location of new cement factories with respect to residential areas should be considered especially due to higher metal concentrations downwind from the factories. There is need for new CMPs to be located downwind from residential areas to decrease inhalation of PM containing metals.

- Except for metals in the CKD, PM inhalation is associated with acute respiratory distress in humans (Fernandez, et al., 2003), hence the need for ELVs for CMP to ensure that PM and the constituents of the PM comply with required ELVs. In addition, periodic (annually or every six months) monitoring should be executed. Such being the case, monitoring stations should be erected in close proximity to the CMP to quantify PM fall-out and the composition of the PM, specifically the metal concentrations. Once ELVs are available for metals, it will also be an advantage to compare the concentrations to required limits.

- Various cement factories in South Africa are currently applying for EIA (environmental impact assessment) in order to use alternative fuels other than coal as energy source. Once alternative fuels are used, a comparative study should be done to compare metal levels in the dust to concentrations found using coal as energy source. The metal concentrations found in this project can be used as reference values to assess if metal concentrations have increased or decreased in the environment.

References

Abdul-Wahab, S.A., 2006. Impact of fugitive dust emissions from cement plants on nearby communities. *Ecological Modelling*, 195, pp.338-348.

Abimbola, A.F., Kehinde-Phillips, O.O. & Olatunji, A.S., 2007. The Sagamu cement factory, SW Nigeria: Is the dust generated a potential health hazard? *Environ Geochem Health*, 29(2), pp.163-167.

Akinola, M.O. & Ekiyoyo, T.A., 2006. Accumulation of lead, cadmium and chromium in some plants cultivated along the bank of the river Ribila at Odo-nla area of Ikorodu, Lagos state, Nigeria. *Journal of Environmental Biology*, 27(3), pp.597-608.

Al-Khashman, O.A., 2004. Heavy metal distribution in dust, street dust and soils from the work place in Karak Industrial Estate, Jordan. *AE International – Asia*, 38, pp.6803-6812.

Al-Khashman, O.A. & Shawabkeh, R.A., 2006. Metals distribution in soils around the cement factory in southern Jordan. *Environmental Pollution*, 140, pp.387-394.

Al-Masri, M.S., Al-Kharfan, K. & Al-Shamali, K., 2006. Speciation of Pb, Cu and Zn determined by sequential extraction for identification of air pollution sources in Syria. *Atmospheric Environment*, 40, pp.753-761.

Armstrong, F.B., 1989. *Biochemistry.* Oxford: University Press.

Barber, J., 2011. *Geological Modelling.* Geology and Mine Planning for Stratified Deposits. Available at:http://www.gemcomsoftware.com/sites/default/files/whitepaper/Minex_GrowthMethod.pdf [Accessed 11 November 2011]

Beaver, L.M., Stemmy, E.J., Constant, S.L., Schartz, A., Little, L.G., Gigley, J.P., Chun, G., Sugden, K.D., Ceryak, S.M. & Patierno, S.R., 2009. Lung injury, inflammation and Akt signaling following inhalation of particulate hexavalent chromium. *Toxicology and Applied Pharmocology,* 235, pp.47-56.

Bennet, H., 1986. *Concise Chemical and Technical Dictionary.* 4th ed. London: Edward Arnold.

Bermudez, G.M.A., Moreno, M., Invernizzi, R., Plá, R. & Pignata, M.L., 2010. Heavy metal pollution in topsoils near a cement plant: The role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations. *Chemosphere*, 78, pp.375-381.

Beyersmann, D., 2002. Effects of carcinogenic gene expression. *Toxicology Letters*, 127, pp.63-68.

Bjerrum, N., 1936. *Bjerrum's Inorganic Chemistry.* 3rd ed. London: Heinemann.

Boltovsky, 2003. Diameter of a Speck of Dust. Available at: http://hypertextbook.com/facts/2003/MarinaBolotovsky.shtml [Accessed 10 December 2010]

Branquinho, C., Gaio-Oliveira, G., Augusto, S., Pinho, P., Máguas, C. & Correia, O., 2008. Biomonitoring spatial and temporal impact of atmospheric dust from a cement factory. *Environmental Pollution*, 151, pp.292-299.

Chen, C., Habert, G., Bouzidi, Y. & Jullien, A., 2010. Environmental impact of cement production: detail of the different processes and cement plant variability evaluation. *Journal of Cleaner Production*, 18, pp.478-485.

Constans, D.L., 1997. Why All Cement Kilns Should Test Their CKD. GCI Tech Notes, 3(6). Available at: http://www.gcisolutions.com/GCINOTES697.htm [Accessed 8 June 2009]

Doerr, N.A., Ptacek, C.J. & Blowes, D.W., 2005. Effects of a reactive barrier and aquifer geology on metal distribution and mobility in a mine drainage impacted aquifer. *Journal of Contaminant Hydrology*, 78(1-2), pp.1-25.

Duffus, J.H., 2001. Heavy Metals – A meaningless term. *Chemistry International*. 23(6), pp.1-6.

EPA Method 3050B – Acid digestion of sediments, sludges and soils. Available at: http://www.epa.gov/wastes/hazard/testmethods/sw846/pdfs/3050b.pdf [Accessed: 10 February 2012]

EPA Method 9045D – Soil and waste pH. Available at: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9045d.pdf [Accessed 24 March 2011]

EPA Method 9080 – Cation-exchange capacity of soils (ammonium acetate). Available at: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9080.pdf [Accessed 24 March 2011]

ESSROC. Available at: http://www.essroc.com/default.aspx?pageid=183 [Accessed 3 October 2009]

European commission, Directorate General Environment, 2004. Analysis of Member States' first implementation reports on the IPPC Directive (EU-15). Available at: http://ec.europa.eu/environment/air/pollutants/stationary/ippc/replies_and_opinions/final_report_ippc.pdf [Accessed: 23 June 2011]

Fajimi, A.K., 2007. Pb & Cd poisoning of goats raised in a cement kiln dust polluted area. *Journal of Food, Agriculture & Environmental*, 5(1), pp.382-384.

Fernandez, A., Wendt, J.O.L., Wolski, N., Hein, K.R.G., Wang, S. & Witten, M.L., 2003. Inhalation health effects of fine particles from the co-combustion of coal and derived fuel. *Chemosphere*, 51, pp. 1129-1137.

FitzPatrick, E.A., 1980. *Soils – Their formation, classification and distribution.* London: Longman.

Foth, H.D., 1984. Fundamentals of Soil Science. 7th ed. New York: John Wiley & Sons.

Galindo, N., Yebero, E., Nicolas, J.F., Crespo, J., Pastor, C., Carratala, A. & Santacatalina, M., 2011. Water-soluble ions measured in fine particulate matter next to cement works. *Atmospheric Environment*, 45, pp.2043-2049.

GeoNames geographical database, 2012. Available at: http://population.mongabay.com/population/south-africa/982899/lichtenburg [accessed: 10 February 2012]

Gilmour, P.S., Nyska, A., Schladweiler, M.C., McGee, J.K., Wallenborn, J.G., Richards, J.H. & Kodavanti U.P., 2006. Cardiovascular and blood coagulative effects of pulmonary zinc exposure. *Toxicology and Applied Pharmocology*, 211, pp.41.52.

Grantz, D.A., Garner, J.H.B. & Johnson, D.W., 2003. Ecological effects of particulate matter. *Environmental International*, 29, pp.213-239.

HaMai, D., Rinderknecht, A.L., Guo-Sharman, K., Kleinman, M.T. & Bondy, S.T., 2006. Decreased expression of inflammation-related genes following inhalation exposure to manganese, *NeuroToxicology*, 27, pp.395-401.

Hindy, K.T., Abdel Shafy, H.I. & Farag, S.A., 1990. The role of the cement industry in the contamination of air, water, soil and plant with vanadium in Cairo. *Environmental Pollution*, 66(3), pp.195-205.

Huntzinger, D.N. & Eatmon, T.D., 2009. A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies. *Journal of Cleaner Production*, 17, pp.668-675.

Intawongse, M. & Dean, J.R., 2006. Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. *Food Addit Contamination*, 23(1), pp.36-48.

Işikli, B., Demir, T.A., Űrer, S.M., Berber, A., Akar, T. & Kalyoncu, C., 2003. Effects of chromium exposure from a cement factory. *Environmental Research*, 91, pp.113-118.

Işikli, B., Demir, T.A., Akar, T., Berber, A., Űrer, S.M., Kalyoncu, C. & Canbek, M., 2006. Cadmium exposure from the cement dust emissions: A field study in a rural area. *Chemosphere*, 63, pp.1546-1552.

Islam, E., Yang, X.E., He, Z.L. & Mahmood, Q., 2007. Assessing potential dietary toxicity of heavy metals in selected vegetables and food crops. *Journal of Zhejiang University Science B*, 8(1), pp.1-13.

Klaasen, C.D., 1996. *Casarett and Doull's Toxicology: The Basic Science of Poisons.* 5th ed. New York: McGraw-Hill.

Lafarge Cement, 2011 http://www.lafarge.co.za/wps/portal/za/2-Cement [Accessed 9 November 2011]

Laker, M.C. & Du Preez, C.C., 1982. An investigation into the accuracy of hydrometers for soil particle size determination. *Agroplantae,* 14, pp.17-22.

Lenntech, Water Treatment solutions Available at: www.lenntech.com/perriodic/elements/co.htm) [Accessed 4 July 2011]

Lewis, R.J., 1993. *Hawley's Condensed Chemical Dictionary.* 12th ed. New York: Van Nostrand Reinhold.

Lide, D. R., 1994. *Handbook of Chemistry and Physics.* 75th ed. Florida: CRC Press.

Marsh Environmental Impact Assessment, 2009. PPC de Hoek secondary materials co-processing programme. Final EIA Report. Available at: http://www.marsh-africa.com/sector/environment/documents/Sec2-DeHoek.pdf [Accessed 21 June 2010]

Massicotte, R., Robidoux, P.Y., Sauvé, S., Flipo, D., Mathiot, A., Fournier, M. & Trottier, B., 2004. Immunotoxicological response of the earthworm *Lumbricus terrestris* following exposure to cement kiln dust. *Ecotoxicology and Environmental Safety*, 59, pp.10-16.

Nevada Division of Environmental Protection, Chemical Accident Prevention Program (NDEP-CAPP, 2007. Substance data sheet – conversions. Available at: http://ndep.nv.gov/bapc/capp/docs/chem/Conversion_Factors_071102.pdf [accessed: 27 January 2011]

Normandin, L., Carrier, G., Gardiner, P.F., Kennedy, G., Hazell, A.S., Mergler, D., Butterworth, R.F., Phillipe, S. & Zayed, J., 2002. Assessment of Bioaccumulation, Neuropathology and Neurobehaviour following subchronic (90 days) inhalation in Sprague-Dawley rats exposed to manganese phosphate. *Toxocology and Applied Pharmacology,* 183, pp.135-145.

North West Parks and Tourism Board, 2012. Available at: http://www.tourismnorthwest.co.za/central/lichtenburg.html [accessed: 10 February 2012]

North West Province Department of Agriculture, Conservation and Environment 2002. State of the Environment Report 2002. Directorate Environmental and Conservation Management, Mafikeng, South Africa.

Oliveira, A. & Pampulha, M.E., 2006. Effects of long-term heavy metal contamination on soil Microbial Characteristics. *Bioscience and Bioengineering*, 102(3), pp.157-161.

Olowoyo, J.O., van Heerden, E., Fischer, J.L. & Baker, C., 2010. Trace metals in soil and leaves of *Jacanranda mimosifolia* in Tshwane area, South Africa. *Atmospheric Environment*, 44, pp.1826-1830.

Oluokun, J.A., Fajimi, A.K., Adebayo, A.O. & Ayaji, F.T., 2007. Lead and cadmium poisoning of goats raised in cement kiln dust polluted area. *Journal of Food, Agriculture & Environment*, 5(1), pp.382-384.

Owen, O.S. & Chiras, D., 1995. *Natural resource conservation.* 7th ed. New-Jersey: Prentice-Hall.

Phetsombat, S., Kruatrachue, M., Pokethityook, P. & Upatham, S., 2006. Toxicity and bioaccumulation of cadmium and lead in Salvinia Cucullata. *Journal of Environmental Biology*, 27(4), pp.645-652.

Polat, R., Gürol, A., Budak, G., Karabulut, A. & Ertuğrul, M., 2004. Elemental composition of cement kiln dust, raw material and cement from a coal-fired cement factory using energy dispersive X-ray fluorescence spectrometry. *Journal of Quantitative Spectroscopy Radiative Transfer*, 83, pp.377-385.

Potgieter, S.S., Panichev, N., Potgieter, J.H. & Panicheva, S., 2003. Determination of hexavalent chromium in South African cements and cement-related materials with electrothermal atomic absorption spectrometry. *Cement and Concrete Research*, 33, pp.1589-1593.

Prodjosantoso, A.K. & Kennedy, B.J., 2003. Heavy metals in cement phases: on the solubility of Mg, Cd, Pb and Ba in $Ca_3Al_2O_6$. *Cement and Concrete Research*, 33, pp.1077-1084.

Raven, H.R., Johnson, G.B., Losos, J.B. & Singer, S.R., 2005. *Biology.* 7th ed. New York: McGraw-Hill.

Rodriquez, M.C., Barsanti, L., Passarelli, V., Evangelista, V., Conforti, V. & Gualtieri, P., 2007. Effects of chromium on photosynthetic and photoreceptive apparatus of the alga *Chlamydomonas reinhardtii. Environmental Research*, 105(2), pp.234-239.

Ross, S.M., 1994. *Toxic Metals in Soil-Plant Systems.* London: John Wiley & Sons.

Rybicka, E.H., Adamiec, E. & Aleksande-Kwaterczak, U., 2005. Distribution of trace metals in the Odra River system: Water-suspended matter-sedimens. *Limnologica,* 35, pp.185-198.

Schuhmacher, M., Bocio, A., Agramunt, M.C., Domingo, J.L. & de Kok, H.A.M., 2002. PCDD/F and metal concentrations in soil and herbage samples collected in the vicinity of a cement plant. *Chemosphere*, 48, pp.209-217.

Schuhmacher, M., Domingo, J.L. & Garreta, J., 2004. Pollutants emitted by a cement plant: health risks for the population living in the neighbourhood. *Environmental Research*, 95, pp.198-206.

Schuhmacher, M., Nadal, M. & Domingo, J.L., 2009. Environmental monitoring of PCDD/Fs and metals in the vicinity of a cement plant after using sewage sludge as a secondary fuel. *Chemosphere*, 74, pp.1502-1508.

Sen, H. & Sunlu, U., 2007. Effects of cadmium ($CdCl_2$) on development and hatching of eggs in European squid (*Loligo vulgaris* Lamarck, 1798) (Cephalopoda: Loliginidae). *Environmental Monitoring Assessment*, 133, pp.371-378.

Siddique, R., 2006. Utilization of cement kiln dust (CKD) in cement mortar and concrete. *Resources Conservation Recycling*, 48(4), pp.315-339.

Soriano, A., Pallares, S., Pardo, F., Vicente, A.B., Sanfeliu, T. & Bech, J., 2011. Deposition of heavy metals from particulate settleable matter in soils of an industrialised area. *Geochemical Exploration,* (Epub ahead of print).

South African Weather Service. Available at: http://www.weathersa.co.za/web/

Spear, P.A., 1981. Zinc in the aquatic environment; chemistry, distribution and toxicity. National Research Council of Canada, Association Committee on Scientific Criteria for Environmental Quality, Report NRCC No. 17589, Ottawa.

Strahler, A. & Strahler, A., 2005. *Physical Geography: Science and Systems of the Human Environment*. 3rd ed. New Jersey: John Wiley & Sons.

Tavares, L.M. & Cerqueira, M.C., 2006. Statistical analysis of impact-fracture characteristics and microstructure of industrial Portland cement clinkers. *Cement and Concrete Research*, 36(3), pp.409-415.

Turekian, K.K & Wedepohl, K.H., 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. *Geol. Soc. of Am. Bull.*, 72, pp.175-192.

Unterbrunner, R., Puschenreiter, M., Sommer, P., Wieshammer, G., Tlustoš, P., Zupan, M. & Wenzel, W.W., 2007. Heavy metal accumulation in trees growing on contaminated sites in Central Europe. *Environmental Pollution*, 148(1), pp.107-114.

Van der Watt, H.v.H. & van Rooyen, T.H., 1995. *A Glossary of Soil Science*. 2nd ed. Pretoria: Soil Science Society.

Van Oss, H.G. & Padovani, A.C., 2002. Cement Manufacture and the Environment Part I: Chemistry and Technology. *Journal of Industrial Ecology*, 6(1), pp.89-105.

Van Oss, H.G. & Padovani, A.C., 2003. Cement Manufacture and the Environment Part II: Environmental Challenges and Opportunities. *Journal of Industrial Ecology*, 7(1), pp.93-126.

Verma, R.K., Yadav, D.V., Singh, C.P., Suman, A. & Gaur, A., 2010. Effect of heavy matals on soil respiration during decomposition of sugarcane (*Saccharum officinarum L.*) trash in different soils. *Plant Soil Environ*, 56(2), pp.76-81.

Wallenborn, J.G., Evansky, P.E., Shannahan, J.H., Vallanat, B., Ledbetter, A.D., Schladweiler, M.C., Richards, J.H., Gottipolu, R.R., Nyska, A. & Kodavanti, U.P., 2008. Subchronic inhalation of zinc sulfate induces cardiac changes in healthy rats. *Toxicology and Applied Pharmacology*, 232, pp. 69-77.

Watts, S. & Halliwell, L., 1996. *Essential Environmental Science – Methods and Techniques.* London: Routledge.

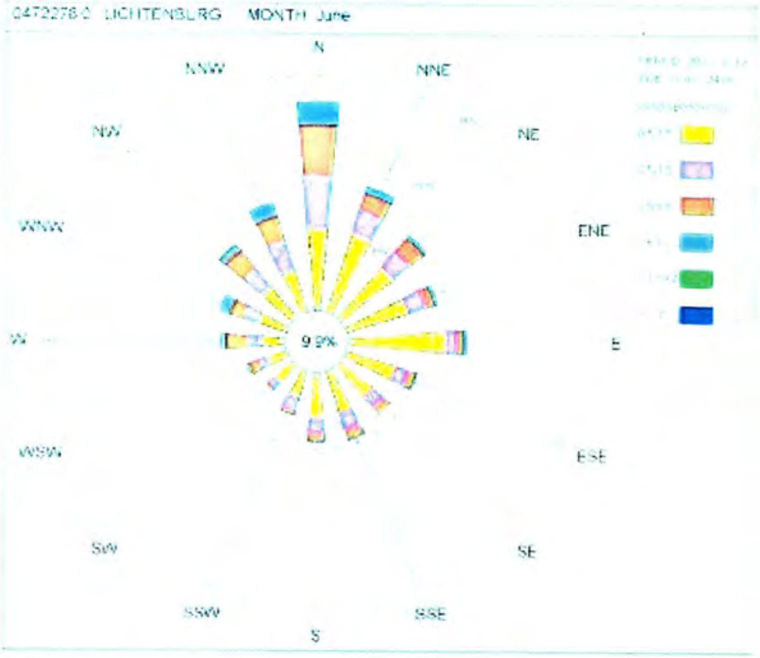
Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments, *J. Geology*, 30, pp.377-392.

Wright, D.A. & Welbourn, P., 2002. *Environmental Toxicology*. Cambridge: University Press.

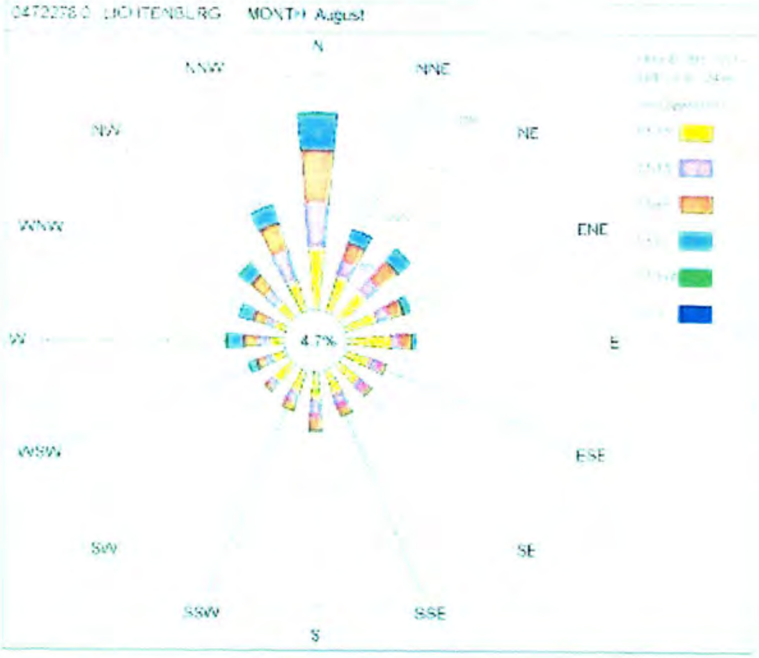
Zeman, F., 2009. Oxygen combustion in cement production. *Energy Procedia*, 1, pp.187-194.

Appendices

Appendix A: Additional wind data

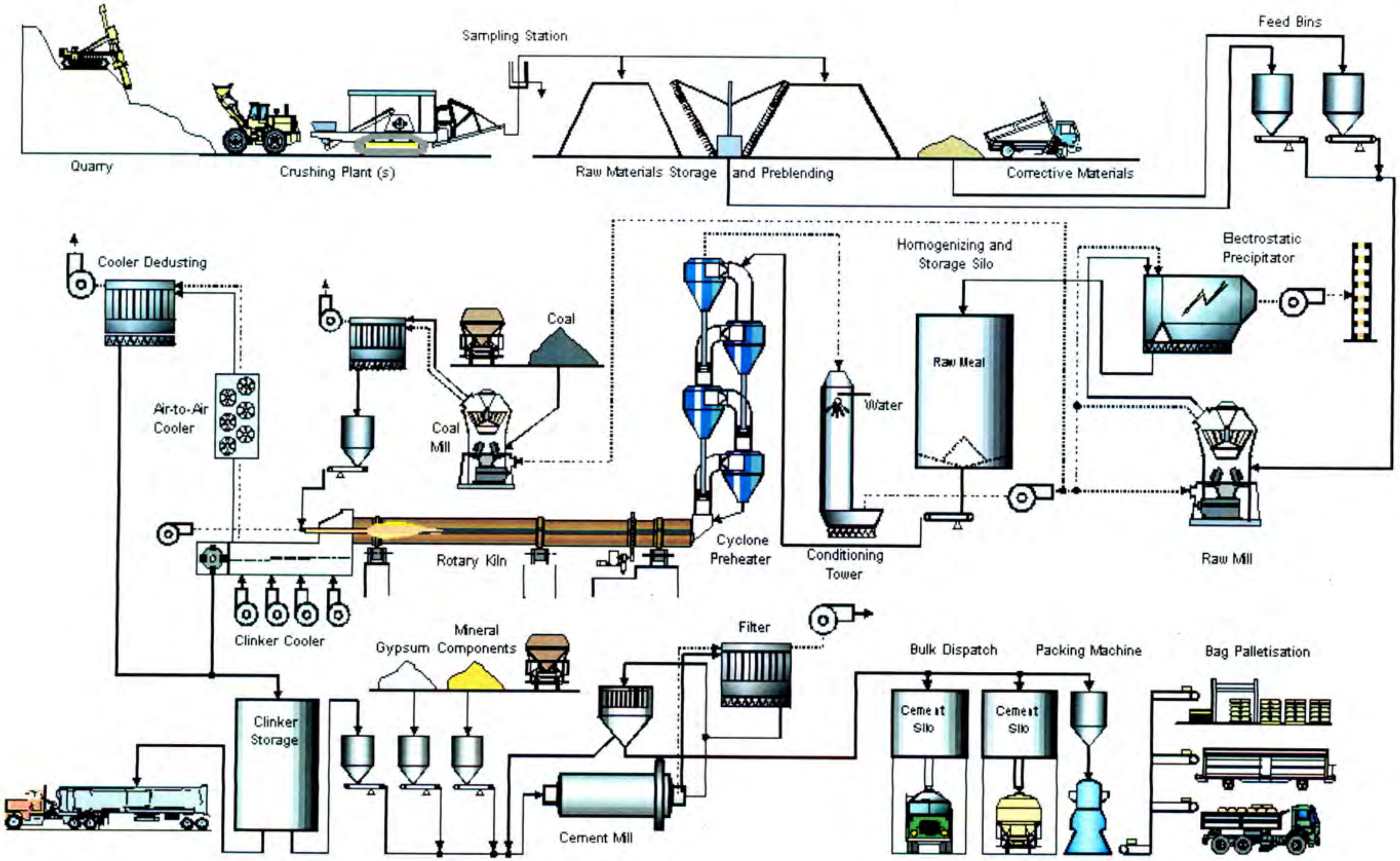


Average wind direction and speed for June 2000 – 2010.



Average wind direction and speed for August 2000 – 2010.

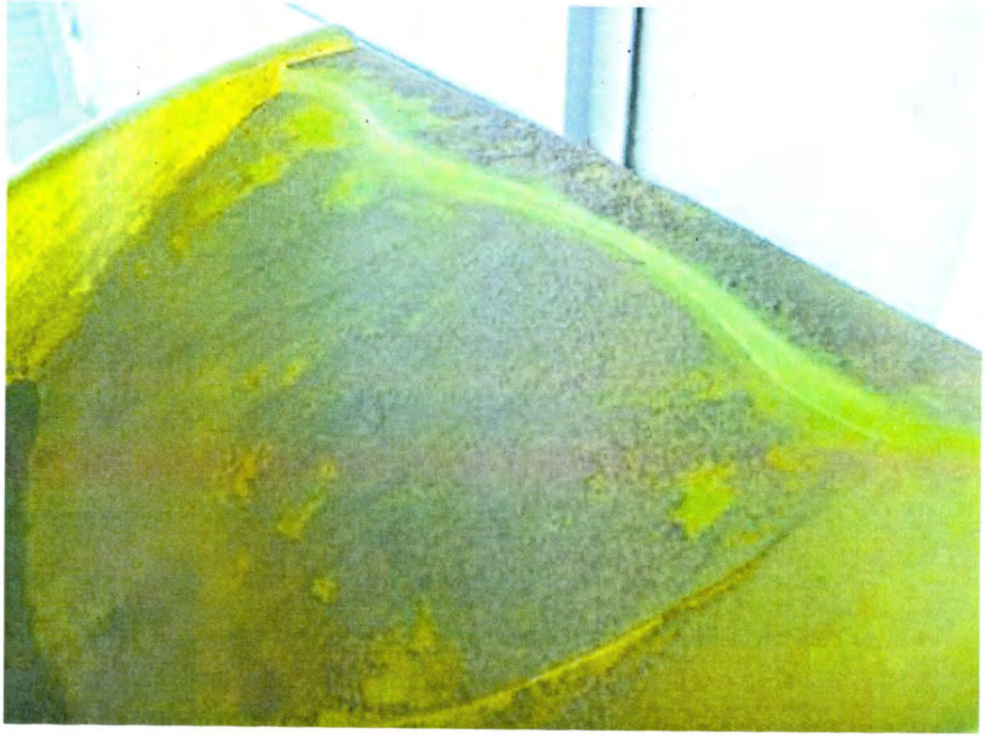
Appendix B: *Process Flow* diagram of the cement manufacturing process (Marsh Environmental Impact Assessment)



Appendix C: Photos – collecting dust samples

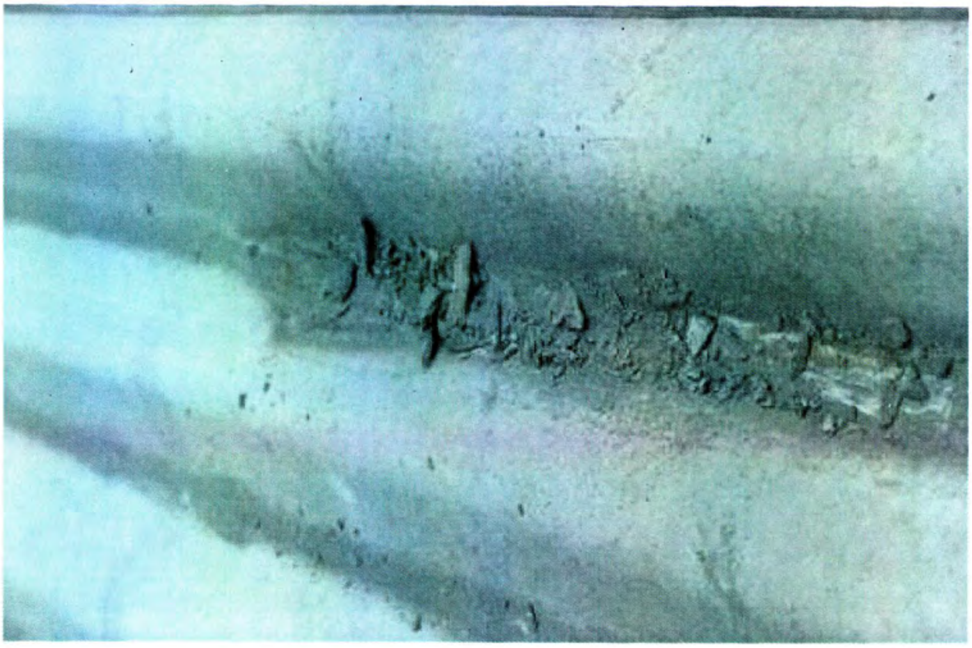
Bus stop from where dust samples were collected.

Inside panel of bus stop showing dust accumulation and compaction.



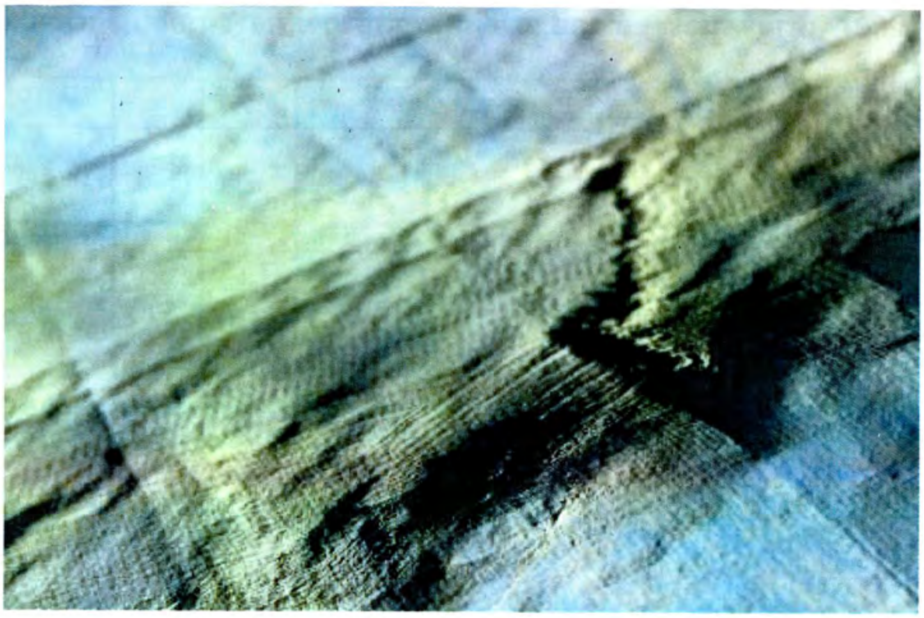
Dust collected in bus stop after scraping dust loose with spatula.

Compacted dust on roof at industrial collection site.



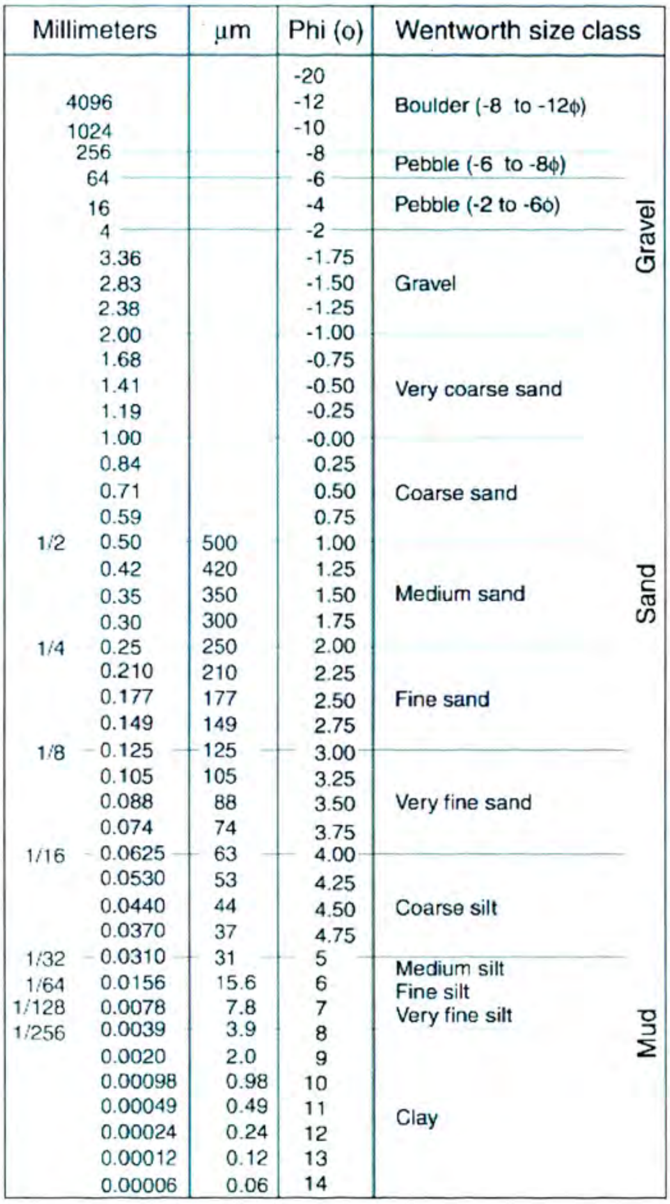
Loosened compacted dust on industrial roof.

Loose dust on the kraal roof.



Loose dust from collected from boat cover at residential house.

Appendix D: Udden-Wentworth grain-size scale (Wentworth, 1922)



Millimeters		µm	Phi (o)	Wentworth size class	
			-20		
	4096		-12	Boulder (-8 to -12ϕ)	
	1024		-10		
	256		-8	Pebble (-6 to -8ϕ)	
	64		-6		
	16		-4	Pebble (-2 to -6o)	
	4		-2		Gravel
	3.36		-1.75		
	2.83		-1.50	Gravel	
	2.38		-1.25		
	2.00		-1.00		
	1.68		-0.75		
	1.41		-0.50	Very coarse sand	
	1.19		-0.25		
	1.00		-0.00		
	0.84		0.25		
	0.71		0.50	Coarse sand	
	0.59		0.75		
1/2	0.50	500	1.00		
	0.42	420	1.25		
	0.35	350	1.50	Medium sand	Sand
	0.30	300	1.75		
1/4	0.25	250	2.00		
	0.210	210	2.25		
	0.177	177	2.50	Fine sand	
	0.149	149	2.75		
1/8	0.125	125	3.00		
	0.105	105	3.25		
	0.088	88	3.50	Very fine sand	
	0.074	74	3.75		
1/16	0.0625	63	4.00		
	0.0530	53	4.25		
	0.0440	44	4.50	Coarse silt	
	0.0370	37	4.75		
1/32	0.0310	31	5	Medium silt	
1/64	0.0156	15.6	6	Fine silt	
1/128	0.0078	7.8	7	Very fine silt	
1/256	0.0039	3.9	8		Mud
	0.0020	2.0	9		
	0.00098	0.98	10		
	0.00049	0.49	11	Clay	
	0.00024	0.24	12		
	0.00012	0.12	13		
	0.00006	0.06	14		

Appendix E: Estimated detection limits for the ICP-MS

	Detection Limit (ppb)
Aluminum	0.7
Antimony	0.1
Arsenic	0.1
Barium	0.1
Beryllium	0.1
Bismuth	0.1
Boron	3
Bromine	10
Cadmium	0.1
Calcium	50
Cerium	0.1
Cesium	0.1
Chromium	1
Cobalt	0.1
Copper	0.2
Dysprosium	0.1
Erbium	0.1
Europium	0.1
Gadolinium	0.1
Gallium	0.1
Germanium	0.1
Gold	0.1
Hafnium	0.1
Holmium	0.1
Iodine	0.1
Iridium	0.1
Iron	10
Lanthanum	0.1
Lead	0.1
Lithium	0.1
Lutetium	2
Magnesium	0.4
Manganese	0.1
Mercury	0.1
Molybdenum	0.1
Neodymium	0.1
Nickel	0.3
Niobium	0.1
Osmium	0.1
Palladium	0.1
Platinum	0.1
Praseodymium	0.1
Rhenium	0.1
Rhodium	0.1
Rubidium	0.1
Ruthenium	0.1
Samarium	0.1

Selenium	1
Silver	0.1
Sodium	5
Strontium	0.1
Tantalum	0.1
Tellurium	0.1
Thallium	0.1
Thorium	0.1
Thulium	0.1
Tin	0.4
Titanium	0.2
Tungsten	0.1
Uranium	0.1
Vanadium	0.2
Ytterbium	0.1
Yttrium	0.1
Zinc	0.2
Zirconium	0.1

Appendix F: Standard deviations and Coefficients of Variation for samples analyzed in duplicate

Standard deviations and Coefficient of variation for soil samples

	760 m (0-10 cm)				760m - silt				1400 m (0-10 cm)				1400 m (10-20 cm)			
Element	**Sample**	**Repeat**	**σ**	**CV**	**Sample**	**Repeat**	**σ**	**CV**	**Sample**	**Repeat**	**σ**	**CV**	**Sample**	**Repeat**	**σ**	**CV**
Ca	56075.0	54500.0	1113.69	2.01	92325.0	89550.0	1962.22	2.16	41950.0	38850.0	2192.03	5.43	34800.0	27025.0	5497.76	17.78
V	24.4	17.7	4.78	22.74	29.7	30.0	0.19	0.65	39.2	45.8	4.67	10.99	30.3	28.1	1.54	5.27
Cr	52.7	49.7	2.16	4.21	35.9	37.4	1.08	2.94	45.4	52.4	4.95	10.13	32.0	30.0	1.38	4.45
Mn	673.5	603.5	49.50	7.75	574.5	564.8	6.89	1.21	688.0	699.5	8.13	1.17	545.5	501.0	31.47	6.01
Co	1.7	1.6	0.09	5.33	2.4	2.3	0.03	1.29	3.2	3.2	0.03	1.00	1.4	1.3	0.05	3.36
Ni	4.7	4.9	0.12	2.57	18.7	18.9	0.11	0.59	18.4	18.9	0.35	1.87	9.0	8.8	0.08	0.93
Cu	0.6	0.5	0.02	3.29	2.5	2.5	0.03	1.41	5.2	5.0	0.16	3.16	1.4	1.3	0.05	4.04
Zn	91.0	89.3	1.24	1.37	98.3	98.0	0.18	0.18	126.6	131.3	3.29	2.55	264.3	274.5	7.25	2.69
Pb	2.7	2.7	0.02	0.72	3.1	3.1	0.00	0.12	3.7	3.7	0.03	0.72	2.8	2.8	0.03	1.02
			Mean CV	5.56			Mean CV	1.17			Mean CV	4.11			Mean CV	5.06

Standard deviations and Coefficient of variation for dust samples

	920 m from factory				1000 m from factory				72300 m from factory (control)			
Element	**Sample**	**Repeat**	**σ**	**CV**	**Sample**	**Repeat**	**σ**	**CV**	**Sample**	**Repeat**	**σ**	**CV**
Ca	135650.00	129175.00	4578.52	3.46	5295.00	4965.00	233.35	4.55	8532.50	7900.00	447.25	5.44
V	43.88	42.33	1.10	2.54	6227.50	5840.00	274.00	4.54	2.11	1.83	0.20	10.30
Cr	32.70	32.20	0.35	1.09	410.75	395.25	10.96	2.72	16.13	16.53	0.28	1.73
Mn	689.75	655.50	24.22	3.60	96225.00	94550.00	1184.40	1.24	198.28	198.08	0.14	0.07
Co	29.78	29.60	0.12	0.42	37.30	34.53	1.96	5.46	0.66	0.68	0.01	2.07
Ni	14.09	13.90	0.13	0.95	985.25	987.25	1.41	0.14	6.47	6.28	0.13	2.11
Cu	3.11	2.98	0.09	3.08	13742.50	13687.50	38.89	0.28	13.43	13.53	0.07	0.52
Zn	2747.50	2887.50	98.99	3.51	4.67	4.58	0.07	1.45	299.00	286.50	8.84	3.02
Pb	5.53	5.54	0.01	0.10	21.58	21.45	0.09	0.42	7.88	7.68	0.14	1.82
			Mean CV	2.08			Mean CV	2.24			Mean CV	3.04

Mean Coefficient of Variation of elements analyzed

Element	**Soil 760m**	**Soil Silt**	**Soil 1400m**	**Soil 1400m**	**Dust 920m**	**Dust 1000m**	**Dust Control**	**Mean CV**
Ca	2.01	2.16	5.43	17.78	3.46	1.24	5.44	5.36
V	22.74	0.65	10.99	5.27	2.54	7.18	10.30	8.52
Cr	4.21	2.94	10.13	4.45	1.09	5.46	1.73	4.29
Mn	7.75	1.21	1.17	6.01	3.60	0.14	0.07	2.85
Co	5.33	1.29	1.00	3.36	0.42	1.45	2.07	2.13
Ni	2.57	0.59	1.87	0.93	0.95	0.42	2.11	1.35
Cu	3.29	1.41	3.16	4.04	3.08	3.16	0.52	2.67
Zn	1.37	0.18	2.55	2.69	3.51	0.65	3.02	2.00
Pb	0.72	0.12	0.72	1.02	0.10	0.46	1.82	0.71
Mean Coefficient of variance of all elements analyzed								**3.32%**

σ = Standard deviation

CV = Coefficient of variation

As and Cd were omitted from the CV determination as the concentrations were below detection limit.

Appendix G: Typical concentrations of some trace metals in plants (Ross, 1994)

Element	Normal range in plant solution (µg g^{-1} fresh wt)[a]	Concentration in contaminated plants (µg g^{-1})[b]	Annual plant uptake (kg ha^{-1} $year^{-1}$)[c]
Chromium	0.03-15	5-30	Nd
Manganese	15-1000	300-500	1.0
Cobalt	0.05-0.5	15-50	0.0006
Nickel	0.02-5	10-100	Nd
Copper	4-15	20-100	0.006
Zinc	8-400	100-400	0.01
Cadmium	0.2-0.8	5-30	Nd
Selenium	0.2-6.8	60	0.001
Mercury	0.005-0.5	1-3	Nd
Lead	0.1-10	30-300	Nd

[a] Allaway, 1968; Bowen, 1979; [b] Kabata-Pendias & Pendias, 1984; [c] Bohn *et al.*, 1985.

Nd = Not determined