Automotive Trace Metal Concentrations on the South African National Road (N3) and its Impact on the Environment

By

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I, __Zaheer Batwa-Ismail____ declare that

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ABSTRACT

The environment is currently experiencing the negative effects of globalisation and unsustainable development with environmentally harmful activities increasing at an alarming rate in South Africa and other developing countries. This is due to these countries circumventing the implementation of environmental policies against foreign investors, such as vehicle manufacturers and chemical industries, to allow for a reduction in fiscal austerity by increasing the gross domestic product. The effects of these activities have a greater impact on the environment and population of developing nations than developed ones. Heavy metal contamination is one of the major concerns related to vehicle manufacturers and toxic chemical industries in terms of environmental management.

The aim of this research was to assess the impact of vehicle pollution along the South African National Road (N3) between Durban and Hilton as it is one of the major transportation routes from the harbour. The elemental concentrations in the leaves of *Bidens pilosa*, that are picked and cooked by communities that live along the roadside, were investigated. The concentrations of thirteen elements were selectively investigated to determine the impact of soil quality on elemental uptake by vegetation and to assess for potential metal toxicities. Soil was evaluated for metal pollution by calculation of geoaccumulation indices and enrichment factors. Common sources of contamination were identified by principal component analysis and spatial distribution of toxic elements; lead and cadmium was developed via geographic information system (GIS).

The study showed *Bidens pilosa* to contain high concentrations of toxic metals especially that of lead, which were linked to high soil concentrations. Soil quality indicators showed soils to be moderately to heavily contaminated in some areas and moderately contaminated in others. Enrichment results showed moderate to significantly enriched soils.

Statistical analyses indicated different sources for the toxic metals (cadmium and lead) and the Kriging interpolation study depicted and demonstrated the spatial diffusion of both cadmium and lead concentrations throughout the study area of the N3. The road transport sector is a key source for heavy metal contamination as it is the preferred method of transport by most industries in South Africa and other developing countries. This study therefore provides insight into the impacts of vehicle pollution in the surrounding environment.

ABBREVIATIONS

CBD – Central business district

CRM – Certified reference material

DOH – Department of Health, South Africa

DWAF – Department of Water Affairs and Forestry

EF – Enrichment factor

FAO – Food and Agricultural Organisation

GIS – Geographic information system

ICP-OES – Inductively coupled plasma – optical emission spectrometry

I_{geo} – Geoaccumulation index

ND – Not determinable

NEM: WA – National Environmental Management Waste Act

PM – Particulate matter

WHO – World Health Organisation

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CHAPTER 1 : INTRODUCTION

Whilst development in South Africa and other developing nations is increasing rapidly, the negative impact on the environment is increasing exponentially. Heavy metal contamination is one of the major concerns directly related to industrial development in terms of environmental management (Zaidi et al, 2005). Natural land has been transformed for urban land use at an increasing rate since industrialisation, with brought about chemical, physical and biological changes as well as changes in biodiversity (Nogaim et al, 2013). These impacts are due to an increase in all forms of waste and effluent from a plethora of land uses and alterations in the natural landscape, which alter properties of soil and concentrations of heavy metals (D'Mello, 2003). The soil along roads is a reservoir for pollutants and heavy metals which result from vehicular emissions and improper waste disposal (Nogaim et al, 2013). Pollution and soil contamination processes have become a serious environmental concern in both developed and developing countries. In particular, heavy metals and its impact on environmental health are of great concern as these metals are introduced into the food chain via plants that absorb them from the soil (Steenland and Boffetta, 2000).

The elemental content in plants is indicative of the surrounding environment. Trace metal analysis of edible vegetation and soil characteristics are excellent environmental indicators of the link between pollution and human impacts. Currently, the assessment of trace metals in soil has become increasingly important due to public awareness on the link between soil and food. Pollution of the environment by metals, whether essential or non-essential, poses major risks to living organisms as metals are not biodegradable and accumulate within soils over time which results in higher uptake by living organisms (Singh, 2005). Pollution by industries and other fossil fuel burning innovations, such as automobiles, are typically the cause of increased concentrations of trace metals in soils and the environment (Palige & Chmielewski, 1996). Rivers are also affected by the burning of fossil fuels. To assess for pollution by industries and potential toxicities to human health, the quality of soil needs to be determined and its influence on plant uptake evaluated.

The direct and indirect impact of pollution on the environment and humans are often unnoticed by local communities in third world countries due to the mind-set of individuals, cultivated by poverty and the basic need for survival (Steyn & Herselman, 2005). Rural communities in South Africa are alerted to pollution via the health of their livestock and wild animals. For example, chronic copper toxicities were found in ruminants in the vicinity of the Kruger National Park in Mpumalanga as the poisoning of cattle and impala occurred due to inefficient management of emissions from a copper mine (Herselman et al, 2005). A concerning detail is that mitigation measures were minimal and the impact on human health and other affected species of the food chain were not evaluated. Studies and assessment of the environment with regards to accumulation of trace metals should be prioritised, particularly metals such as arsenic (As), lead (Pb), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni), selenium (Se), mercury (Hg), and zinc (Zn), due to its adverse effects on human health, if at elevated levels (McLaughlin et al, 1999). By identifying sources of pollution and implementing change to manage pollution, soil and plant contamination can be reduced which would then reduce exposure to humans through the food chain. Sources of pollution can be identified and mitigation measures implemented if studies are conducted to assess this accumulating health risk. Total soil concentrations of heavy metals provide an estimate of the risk of exposure to plants and animals but it does not indicate the extent and effects thereof (Alloway, 2005).

Due to economic conditions and cultural preferences, people in both rural and urban areas have been moving towards indigenous vegetation which is picked from the wild, as these types of vegetation have a much lower commercial value and are abundantly available (Schippers, 2000). However, there has been an increase in food poisoning amongst both humans and animals due to contamination of these foods which results from many factors such as pesticides and other forms of pollution which contain heavy metals (D'Mello, 2003).

1.1 Problem Statement

Vehicular emissions are a crucial environmental concern in the twenty first century. South Africa is a developing country and a nation with a high poverty index; therefore, a large number of motor cars, trucks, taxis and buses are older model vehicles which emit higher levels of environmental contaminants compared to newer, more technologically advanced vehicles that are designed to abide by laws imposed on vehicle manufacturers. However, even these newer models emit cumulatively high levels of environmental contaminants including trace metals. Road infrastructure, which is generally in close proximity to agricultural land and along which wild edible vegetation grows, is a route of exposure to heavy metals in humans and animals alike. *Bidens pilosa* L. is a herb that forms part of a staple diet to many people living in rural areas across South Africa, due to traditional knowledge on creating dishes such as *imifino* and *isigwamba* and due to high poverty levels which force communities to eat these inexpensive and readily available forms of nutrition. Rural communities that live in close proximity to roads pick and eat this herb from the roadside due to accessibility. However, by consuming this herb along roadsides, there is danger of exposure to toxic chemicals emitted by vehicles.

1.2 Aims and Objectives

The aim of this study is to assess the impact of vehicle pollution in the surrounding environment of the South African National Road (N3) between Durban and Hilton as it is one of the major transportation routes from the harbour. The elemental concentrations in the leaves of *Bidens pilosa* which grows along the N3 and is picked and eaten by communities that live along the roadside is also investigated as a function of soil quality. This was achieved by collecting plant and soil samples from the roadside along the N3.

The objectives of the research are:

1. To determine the concentrations of selected elements As, Cd, Ca, Cr, Co, Cu, Fe, Mg, Mn, Ni, Pb, Se and Zn in soil and vegetation that grow along the South African National Road (N3), using inductively coupled plasma – optical emission spectrometry (ICP-OES).
2. To compare the elemental content in vegetation and to assess for potential toxicities by comparing to maximum permissible limits.
3. To evaluate the levels of contamination and enrichment in the soil for each metal by calculating the geoaccumulation index (I_{geo}) and enrichment factor (EF).
4. To investigate whether contamination, if present, is as a result of vehicular emissions or other sources.
5. To determine the spatial distributions of the two major toxic heavy metals, Pb and Cd, along roadside using geographic information system (GIS).

CHAPTER 2 : LITERATURE REVIEW

Particulate matter (both organic and inorganic forms) within urban atmospheres is mainly as a result of vehicular emissions. This includes metals, at trace amounts, due to different vehicular emissions with each source contributing a unique set of emissions. Exposure to particulate matter (PM) by humans occur simultaneously via PM_{10} (coarse dust particles between 2.5 and 10 µm in diameter) and $PM_{2.5}$ (fine particles 2.5 µm or smaller in diameter which can only be detected by a microscope) (Lohse, 2001). Heavy metal pollution is a problem on a global scale as heavy metals are imperishable and toxic at high concentrations. The trace metals, Cd, Cr, Pb, Zn, Fe and Cu are most prominent in contaminated soils (Wong, 2006).

Industrial activities together with vehicular emissions contribute substantially to heavy metal contamination in roadside soils. This affects vegetation, animals and humans that live in the vicinity of the road. The construction of road networks and infrastructure to meet industry demands has led to major changes in land use of many areas. These include de-forestation, loss of wetlands and natural habitats which, in-turn, affect the biodiversity of the area. Previous studies on trace metal concentrations of vehicular emissions have found concentrations of Pb, Cu, Zn, Cd and Ni to decrease with distance away from the roadside (Joshi et al, 2010; Pagotto et al, 2001). However, contaminated soils and dust particles were also found to be dispersed across a large area along the road due to the erosive properties of wind and rainfall.

Heavy metal concentrations in the environment are caused primarily due to air pollution which is via vehicular emissions, industrial effluents, and other waste producing activities (Figure 2.1). Vehicle congestion within road structures contributes significantly to particulate matter numbers. This occurs in both first and third world countries. Central business districts and peripheral industrial hubs of urban nodes have a higher concentration of emissions due to the high traffic flow and are therefore considered to act as a sink to chemicals and metals leaching into the environment. This is a serious health and environmental concern which would ultimately affect quality of life and increases mortality rates if allowed to accumulate without a proactive plan of rehabilitation and reduction (Fabietti et al, 2010).

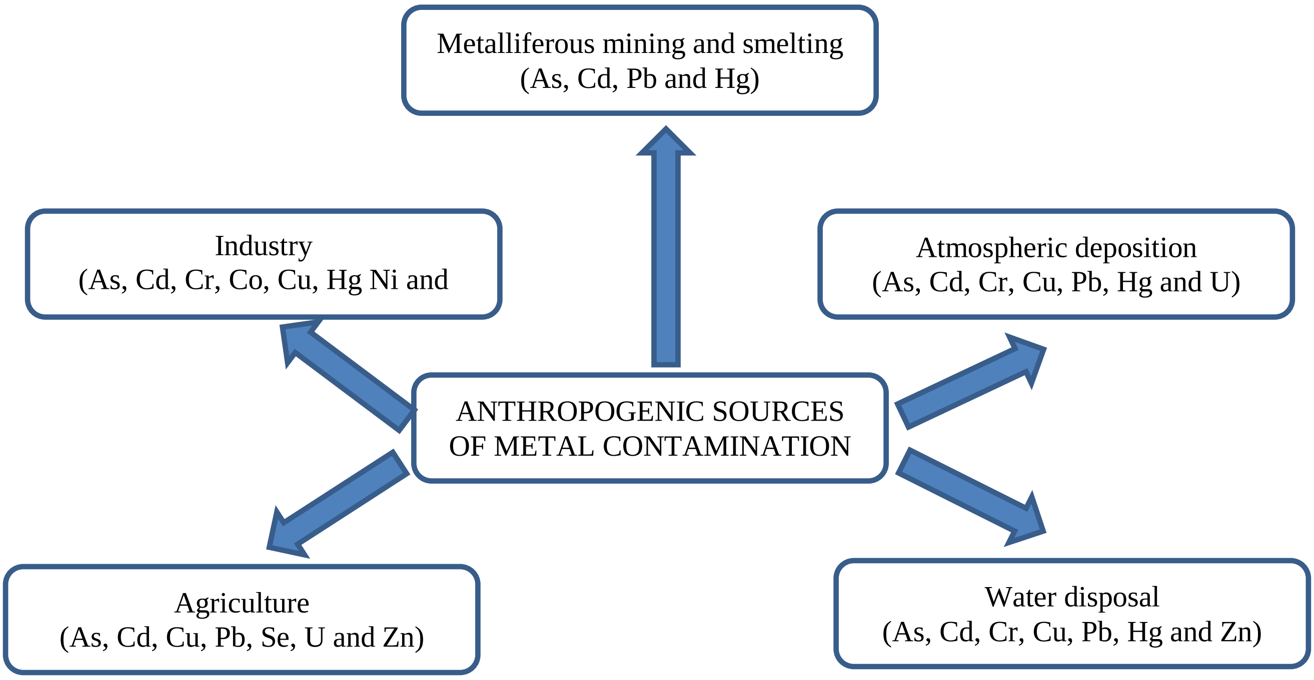

Figure 2.1: Anthropogenic activities leading to contamination of soils by heavy metals (Gupta et al, 2016).

2.1 Vehicular Emissions

Schauer et al (2006) conducted a study which assessed the composition of vehicular emissions such as exhaust emissions via a tunnel emissions test. These were compared to source profiles developed from road dust and road dust formed from brakes, tyres and other component wear (Table 2.1). They concluded that trace metal concentrations were dependent on many factors such as type of vehicles in an area (heavy, light, petrol, diesel and engine capacity), type of driving (high speed or stop and go) and environmental factors such as climate, topography and geology of the area.

Tunnel tests measure emissions of a large fleet under real-world driving conditions, but all measurements include brake wear which contributes significantly to metal emissions, notably for Fe (64%–84%), Cr (23%– 43%), Mn (53%–75%), Cu (72%–91%), Zn (17%–56%), Sr (22%–36%), Sb (99%–100%), and Ba (85%–92%). Gasoline tailpipe emissions contributed up to 20% to roadway emissions for Mg and Ca, up to 32% for Pb, and more than 20% for Zn and Mo. These emissions were also the sole source of Pt in some tests. Metals were also attributed to diesel tailpipe emissions, including Zn (up to 11%), Pb (up to 32%), Cd (up to 41%), and V (up to 34%) (Schauer et al, 2006).

Table 2.1: Average particulate matter ($PM_{2.5}$) tailpipe emission composition profiles (Schauer et al, 2006).

	Petrol Vehicles	**Diesel Vehicles**
As	41.3	565
Ca	3856	4004
Co	ND	ND
Cu	215	321
Cr	51.4	123
Cd	0.07	15.4
Fe	796	2797
Mg	1208	945
Mn	22.5	74.3
Se	ND	ND
Ni	ND	ND
Pb	83.5	137
Zn	4953	2966

The accumulation of heavy metals in the top horizons of soils is due to sedimentation, impaction and interception. The cumulative properties of soil and its retention capacity are of grave concern in terms of environmental impact and human exposure. Trace metals, being non-biodegradable and having long biological half-lives within biological beings, cause hepatic, renal, neurological and hematopoietic toxic effects which are detrimental to human health (Rimmer et al, 2006).

Ingestion of agricultural crops and affected animals via the food chain is another route of trace metals entering the human body (Logan et al, 1997). Leafy green vegetables have been shown to accumulate high concentrations of trace metals; the uptake of which is dependent on factors such as pH, soil organic matter and cation exchange capacity (Chaney et al, 1997).

Previous studies on trace metal concentrations within soil horizons have concluded that the traffic sector is a primary contributor to concentrations in soil in both rural and urban areas (Sorme, 2001). Previous studies have also shown vehicular emissions (tyre and brake wear, exhaust emissions and oil spillage) and traffic density to contribute significant amounts of heavy metals to the atmosphere and surrounding environment (Hjortenkrans et al, 2006; Okunola et al, 2008).

Nutrients are chemical elements or compounds that are vital to the physiology or metabolism of an organism. Essential elements are obtained from food and are not synthesised in the organism; non-essential elements are not required for proper functioning of the body. Elements essential to man include Ca, Cu, Co, Cr, Mg, Mn, Ni, Se, and Zn and most of these elements are essential at low concentrations (Harrison and Mora, 1996). The accumulation of trace metals, usually due to anthropogenic causes, in organs such as the liver and kidneys of humans are of concern due to adverse health effects which include abnormal functioning of many biochemical processes (WHO, 1992), the development of cancer (Trichopoulos, 1997) and the development of abnormalities amongst children (Gobbes and Chen, 1989). The metals of concern include As, Cd, Cr, Hg and Pb. Elements, both essential and non-essential, are found in soil; exposure of consumers to heavy metals is primarily via crops grown on contaminated soil.

2.2 Elements

2.2.1 Toxic elements

Lead (Pb) is a heavy, non-essential, toxic metal, which, in high doses, can affect the nervous system and other organs of the body. Lead can accumulate in the bodies of humans and animals even through long term, low-level exposure (Herselman, 2007). Lead, which was present in petrol, was phased out in South Africa in 2006. Industrial emissions, vehicle exhaust emissions and paint (including road-marking paint containing Pb) are the primary sources of Pb emissions into the environment and atmosphere (Bigdeli and Seilsepour, 2008). The breakdown of tyres from vehicles also introduces Pb into the environment (Giannouli et al, 2007). Gołuchowska and Strzyszcz (1999) found cement dust to contain high amounts of Pb.

Lead is toxic to humans since the body does not metabolise it and absorbs about 20% of ingested amounts directly into the bloodstream (Department of Environmental Affairs, 2010). Constant exposure to relatively low levels of Pb causes neurological impairment in children and constant or isolated exposure to relatively high levels of Pb causes serious damage to the brain and organs of the human body such as the liver and kidneys in adults and children, which ultimately leads to death (Singh, 2005). The acceptable limit for Pb in vegetables is 0.3 mg kg^{-1} (Nogaim et al, 2013). High levels of Pb are associated with high traffic areas since

Pb is released into the environment through the exhaust of internal combustion engines (Bigdeli and Seilsepour, 2008). In recent years, regulatory authorities have been on high alert due to contamination by Pb as a result of its highly toxic nature and adverse health effects for both humans and animals. Lead accumulation in humans and animals is via the respiratory tract by inhaling contaminated dust and via consumption of contaminated food (Bigdeli and Seilsepour, 2008).

Lead can be found in car batteries within a lead-acid or lead-oxide electro-chemical system and, on average, weighs 8 kg per 13 kg battery. It is also used to manufacture wheel balance weights which are placed, non-permanently, within the rims of the vehicle. These weights have a tendency to fall off after time due to rotation of the wheels and impact with roads and potholes; each vehicle, on average, contains 200 – 250 g of Pb per car (Root, 2000). Lead is also found within electrical components and circuit board solders (175 g per vehicle); spark plugs (1.8 g per vehicle) and lighting bulbs (12 g per vehicle). It is also used within many steel components of the vehicle to assist with improved machinability, which signifies a high usage of Pb in the vehicle manufacturing process and within the product itself. On average, these steel items contain 0.35% Pb by weight. Lead is found within copper alloys which are predominantly used within the internal combustion chamber of engines. A rough estimate of 8 to 12 kg of Pb containing copper alloys is found within a single vehicle. It is also found as a lining inside petrol tanks due to a hot dip process. Vibration dampers contain Pb of between 4.7 to 20 kg in newer vehicles to reduce road and motion noise and increase stability. Vulcanizing agents for high pressure fuel and water hoses contain Pb of up to 4.7% by weight. Stabilisers in protective paints contain Pb of between 10 and 50 g per vehicle. Lead forms, on average, 2% of the weight of materials used for brakes and brake linings (Lohse, 2001). The concentration range of Pb in South African soils is 0.93 – 11.9 mg kg^{-1}

(Herselman, 2007) and the worldwide mean (earth's crust) is calculated to be 17 mg kg^{-1} (Rudnick, 2014).

Arsenic (As) is a toxic and carcinogenic element which can lead to fatality if ingested in large quantities (Saldivar and Soto, 2014). Usual symptoms of an overdose of As are stomach related conditions. Arsenic is found in organic and inorganic states due to the weathering of parent rock, in soil, natural gas from shale and water. Arsenic is used in a few commercial products, for example, preservatives and fertilisers (Saldivar and Soto, 2014). The worldwide mean (earth's crust) of As is calculated to be 4.8 mg kg^{-1} (Rudnick, 2014) and the concentration range of As in South African soils is 0.4 – 7 mg kg^{-1} (Pillay et al, 2003).

Cadmium (Cd) is a naturally occurring, non-essential, toxic element. In recent studies, it has been shown to have adverse effects on environmental health such as in soil, plants, animals and human health. Cadmium accumulates in the bones and kidneys of humans and animals and can lead to adverse effects of the kidneys (Herselman, 2007). High levels of Cd found in soils indicate poor waste management from industries and public sectors relating to metal processing, fertilisers and raw sewage (Bremner and Beattie, 1995). Cadmium has been shown to be absorbed by the roots and leaves of plants. High levels of Cd in plants is due to uptake from contaminated soil as a result of fertilisers in agriculture, smelting of metals in industries and exposure to untreated sewerage in close proximity to waste water treatment works and unmaintained sewerage pipelines (Gulten, 2011).

Cadmium is found in automobiles and the manufacturing processes of vehicles. Cadmium is found in high levels in batteries designed for specific electric and hybrid vehicles which aid in a more efficient usage of battery power which extends the range of motion; each vehicle contains, on average, about 38 kg of Cd. It is used in electrical components in a glass matrix as it enhances the adhesion properties of thick films; approximately 10 µg are used per vehicle in this application (Lohse, 2001). The concentration range of Cd in South African soils is 0.89 - 1.17 mg kg^{-1} (Herselman, 2007) and the worldwide mean (earth's crust) is calculated to be 0.53 mg kg^{-1} (Rudnick, 2014).

2.2.2 Macro-elements

Calcium (Ca) is an element that is required for optimal functioning of the human body and its deficiency affects the skeletal structure of the body. Calcium is also vital for plants as it regulates the absorption of nutrients within different plant cells (Sela, 2012).

Magnesium (Mg) is a vital element which occurs in large quantities within our bones, tissues and organs. Magnesium is responsible for muscle, heart and nerve functions and is required by the immune system. Magnesium is found in chlorophyll therefore its uptake by humans is mainly via green leafy vegetables (Magnesium Resource Centre, 2012).

2.2.3 Micro-elements

Chromium (Cr) is an element which is essential for proper body functions of living organisms (Mertz, 1967). Chromium (III) is present in a plethora of fruit, vegetables, grains and meat. Industrial processes frequently produce Cr (VI), which may serve as an indicator of contamination within the environment due to Cr (VI) being more leachable than Cr (III). Elevated concentrations have been found in the run-off of Cr from stainless steel and concrete (Persson and Kucera, 2001). Chromium (VI) is extremely toxic to all organisms and is carcinogenic (Wetterhahn and Hamilton, 1987).

Copper (Cu) is a trace element which is essential to living organisms. Copper is required within the bodies of humans and animals for the formation of haemoglobin in blood and is also essential for bones (Herselman, 2007). Exposure to high levels of Cu to humans and animals occurs via dust inhalation primarily from industrial processing such as refineries and smelters (Department of Environmental Affairs, 2010). Copper enhancement in soils may be connected to the traffic sector as Cu is used in brake linings (Hjortenkrans et al, 2006). Possible health effects to humans and animals due to an ingestion of high concentrations of Cu are organ damage (liver and kidneys), gastrointestinal impacts and red blood cell disturbances (Department of Environmental Affairs, 2010).

Manganese (Mn) is an essential element for living organisms which is found naturally in soil, rocks, food and water. Although Mn is essential for plant growth, high concentrations can be toxic (McLaughlin, 1999). Plants are the main source of Mn and are the most important route of exposure to humans.

Nickel (Ni) is an essential element which performs a vital function in metabolism. Extensive distribution of Ni in the environment is due to anthropogenic activities such as the burning of fossil fuels in industrial and other processes. Nickel present in refinery dust is carcinogenic (Department of Environmental Affairs, 2010). Health effects to humans and animals due to ingestion or exposure to high concentrations of Ni directly affects the development of unborn offspring in pregnant females (Department of Environmental Affairs, 2010). Nickel released from concrete surfaces may also add to total Ni emissions (Persson and Kucera, 2001).

Zinc (Zn) is an essential element for the efficient functioning of an organism's physiology and metabolism. Above acceptable limits of Zn in plants can suppress crop yields and can render the soil unproductive (Shipp and Baker, 1975). Humans have a high tolerance for Zn. Zinc is an important material used in the galvanizing process and in processing other metals such as alloys, bronze and brass. Zinc exposure is primarily through ingestion. Elevated concentrations were observed in run-off for Zn from galvanised steel and surfaces painted with Zn-containing paints whilst most of the Zn enhancement may be connected to the traffic sector (Hjortenkrans et al, 2006). The present use of zinc oxide (ZnO) in rubber is a major source of Zn (Hjortenkrans et al, 2006). Zinc oxide is also used for concrete manufacture to improve the processing time and the resistance of concrete against water (Brown, 1976). Gołuchowska and Strzyszcz (1999) found cement dust to contain high amounts of Zn which can be released into the air and eventually settle onto the soil.

Iron (Fe) is one of the most abundant metals on earth; it is essential to most life forms and to normal human physiology. In humans, Fe is an essential component of protein involved in oxygen transport (Institute of Medicine, Food and Nutrition Board, 2001). Excess amounts of Fe can result in toxicity and even death (Department of Environmental Affairs, 2010).

Cobalt (Co) is also essential to the human body due to its vital role in a number of biochemical metalloenzyme reactions. In plants, it assists with nitrogen absorption and chlorophyll production (Petitto et al, 2004). Cobalt is required in minimal amounts for proper body functions in both humans and animals therefore, there is a possibility (although not common) for Co toxicity in humans and animals (Herselman, 2007).

Selenium (Se), found within the proteins of tissues in fauna and flora have a negative impact on human health if the acceptable levels are surpassed. Selenium is found in higher amounts within foods such as seafood and cereals due to the higher amounts of proteins within these foods. A high level of Se in plants is generally due to high levels in soil (Hathaway et al, 2014).

2.3 *Bidens pilosa* L.

Bidens pilosa L. (which is commonly known as the Blackjack plant in English, Ucucuza / Uqadolo in isiZulu, Gewone Knasekerel, Umhlabangubo, Mushiji and Muchize in other languages) comes from the plant family, Asteraceae (DAFF, 2011) (Figure 2.2). *Bidens* *pilosa*, which originated from South America grows in subtropical and tropical areas such as South Africa, China, Spain and Mexico (Weinberger and Msuya, 2004). *Bidens pilosa* usually grows in areas with higher average temperatures (Brazier, 2003) and is commonly recognised as an inedible weed which has a high tolerance to external factors, therefore, it grows wildly. It has been eaten for millennia as a vegetable or pot herb by cultural South African tribes such as the Zulu and Xhosa people (DAFF, 2011). The leaves are cooked as an herb which is called *imifino* in isiZulu; the addition of leaves to a mealie meal dish is called *isigwamba* in isiZulu. The plant is harvested across South Africa during seasons with plentiful rain and is found in the local markets at early hours of the morning to maintain freshness (DAFF, 2011). It has high nutritional value, serves as a medium for traditional medication for illnesses such as anaemia, toothache and blood flow problems, has antiseptic, anti-inflammatory and analgesic properties and is used as a tea and spice (Weinberger and Msuya, 2004). Due to the lack of literature on this plant and its increasing popularity as a food source, it is important to assess for its nutritional value by gathering information on its elemental content.

Figure 2.2: *Bidens pilosa* (http://www.tropilab.com/bidens-pil.html)

Minimal scientific literature is available on *Bidens pilosa* as a form of food due to a general misconception that this plant is an inedible weed. However, indigenous knowledge is available via elder members of communities in South Africa, which is gradually being lost with each new generation. *Bidens pilosa* has been identified as a possible hyper-accumulator, which is characterised as a plant species capable of absorbing and accumulating extremely high amounts of trace metals (Baker and Brooks, 1989). The hyper-accumulator plant can take up high concentrations of specific trace metals without indicating toxicity within the structure of the plant. Current trends in the science of combatting soil toxicity include the use of hyper-accumulators species for decontamination of soils. Few species of plants have the ability to accumulate trace metals without toxic effects. Sun et al (2009) conducted a study in which the responses by *Bidens pilosa* through the many stages of growth to Cd and As uptake and accumulation was investigated. The results confirmed *Bidens pilosa* to possess all the required characteristics for a Cd hyper-accumulator whilst excluding As. This relationship could be investigated for the phytoremediation of soils with As and Cd toxicities.

2.4 Geographic Information System (GIS)

The geographic information system (GIS) is a tool which is used for a plethora of applications. It is a technological cartographic tool in which data can be measured and modelled, manipulated and analysed in a spatial framework (Figure 2.3). Geographic information system can be used for geochemical mapping of trace metals in which the relationship between the trace metals, spatial and geographic features are visually represented by mapping analysed features and layers of the above-mentioned features (Awange, 2013).

An appropriate understanding of the interactions between human activities and natural processes is required, as negative consequences could delay the management and conservation of eco-systems and its dependants. The analysis of trace metals in the natural environment is fundamental to ecological research as it can be used to acquire a better understanding of human technological impacts on the environment and can assist in developing mitigation measures to control such impacts. The complex nature of trace metals in the natural environment creates difficulties in quantifying data which has a qualitative element in terms of social and agricultural best practice. However, advances in computer technology such as GIS, in the past decade, have allowed natural scientists and members of social and political backgrounds to converge requirements for assessments and policy implementation (Burrough and McDonnell, 2015).

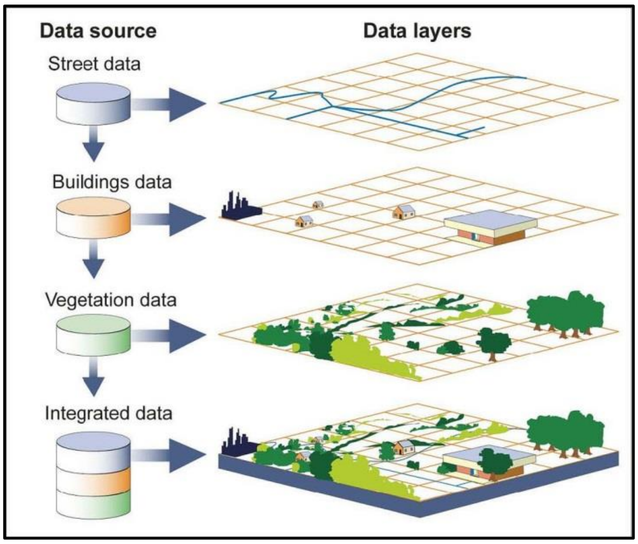

Figure 2.3: Geographic information system (GIS)
(https://www.nationalgeographic.org/encyclopedia/geographic-information-system-gis/)

2.5 Geographic Information System (GIS) Based Studies

Bakir et al (2015) conducted a study in the Hamedan Province of Iran, in which their objective was to use GIS coupled with soil analysis via inductively coupled plasma - atomic emission spectrometry (ICP-AES) to assess the effects of anthropogenic activities on trace metal concentrations. Total concentrations of trace metals (As, Cd, Co, Cr, Cu, Ni, Pb, V and Zn) in samples were analysed via ICP-AES and interpolated via Kriging. The analysis of interpolated maps such as in Figure 2.4 indicated As, Cd, Pb and Zn to be from geological and agricultural origins such as fertilisers whilst it indicated Cr, Co, Ni and V to be from geological origins.

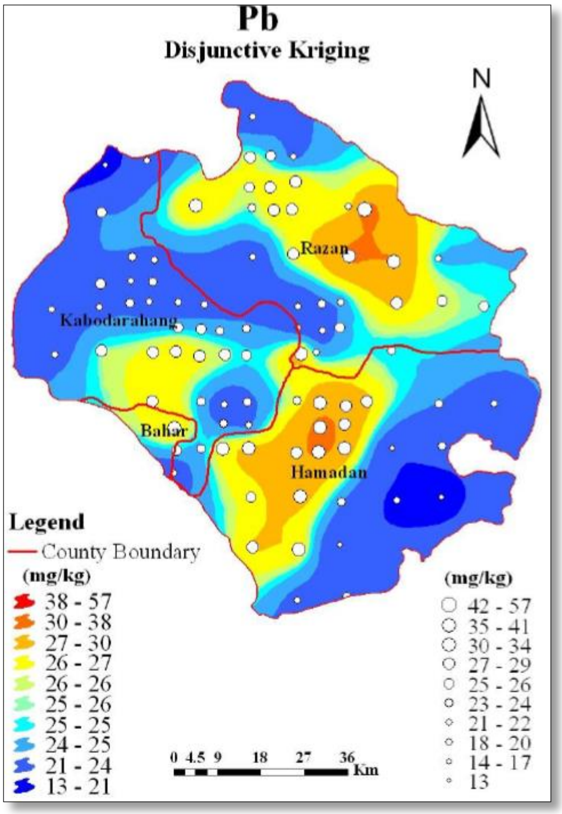

Figure 2.4: Interpolated map for lead (Pb)

2.6 Past Studies on Pollution Conducted in Africa

Mmolawai et al (2011) assessed for heavy metal pollution along roadside soils in Botswana. The geoaccumulation index (I_{geo}), enrichment factor (EF), contamination factor and pollution load index were calculated to assess for metal contamination. Five demarcated zones were classified for analysis, wherein three of the zones where impacted by trace metal pollution. Multivariate analysis indicated sources of pollution to be from mixed origins; Pb and Ni, were from vehicular emissions; Fe and Mn were from lithogenic processes. The findings of the study were targeted to policy makers in Botswana with regards to mitigation of pollution from vehicular emissions as there was minimal monitoring and policy implementation in this regard.

2.7 Past Studies on Pollution Conducted in South Africa

Herselman (2007) developed baseline concentrations for heavy and trace metals across South African soils in 2007 by analysing approximately 4500 soil profiles. Selected soil samples were analysed by inductively coupled plasma - mass spectrometry (ICP-MS) for total and exchangeable concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn.

Table 2.2: Baseline concentrations of trace metals in each class (mg kg^{-1})

	Cd	**Co**	**Cu**	**Ni**	**Pb**	**Zn**
Class 1	0.001-0.03	0.01-4.72	0.06-3.38	0.02-1.74	0.07-7.20	0.06-2.19
Class 1-2	0.001-0.04	0.01-13.4	0.06-6.16	0.02-4.18	0.07-12.6	0.06-3.33
Class 2-3	0.001-0.05	0.03-18.0	0.22-7.91	0.03-6.62	0.27-13.2	0.06-3.53
Class 3-4	0.002-0.05	0.07-29.1	0.30-12.3	0.04-11.9	0.3-14.7	0.06-3.98
Class 4-5	0.002-0.06	0.23-58.6	0.44-26.5	0.09-31.3	0.4-15.7	0.08-4.64
Verification: % correct	92	93	96	95	95	89

***class descriptions are displayed in figure 2.5**

The results were used to update the current framework on trace metal background concentrations in South Africa. Geographic information system maps of the distribution of trace metals were developed with 500 random samples serving as a comparison for accuracy.

The theoretical trace metal distribution map is depicted in Figure 2.5 (Herselman, 2007), with the corresponding baseline concentration of each metal within the class seen in Table 2.2. The resultant maximum threshold values for trace metals (in mg kg^{-1}) in South African soils are (total and exchangeable): Cd (2 and 3), Co (20 and 50), Cr (80 and 350), Cu (100 and 120), Ni (50 and 150), Pb (56 and 100), and Zn (185 and 200). Four-fifths of all soils were found to be Zn deficient, one-third Cu deficient and one-fifth Co deficient (Herselman, 2007).

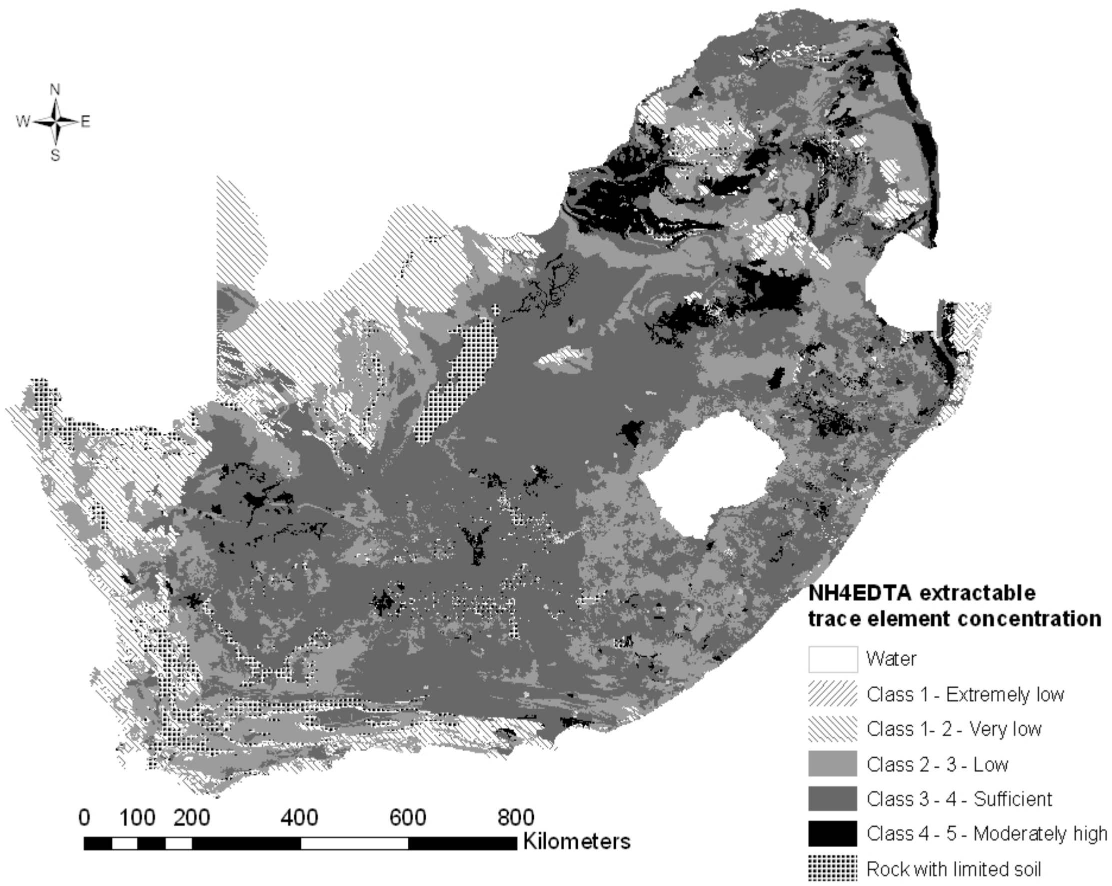

Figure 2.5: Theoretical trace metal distribution in South Africa

Olowoyo et al (2012) analysed the concentrations and sources of several trace metals in Pretoria, South Africa. The samples were collected from ten locations spread across Pretoria, in which, varying external factors affected trace metal concentrations. The samples were analysed by ICP-MS. Results revealed inconsistent concentrations of trace metals at all ten sites. The findings showed high concentrations of Pb, Cu and Zn to be linked to areas with high traffic densities such as highways and city centres. Vehicular emissions were determined to be one of the major contributing factors of high trace metal concentrations in soils.

Bvenura and Afokeyan (2012) studied the accumulation of the trace metals Cd, Cr, Mg, Pb and Zn in cultivated vegetables (cabbage, carrot, onion, spinach and tomato) in Alice, Eastern Cape, South Africa. Random samples were collected from subsistence farms in the locality. All samples were digested, and analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES). Results showed soils to have low levels of metals which made vegetation safe for human consumption.

Mahlangeni et al (2016) evaluated the distribution of trace metals in *Laportea peduncularis* as a function of soil characteristics. *Laportea peduncularis* was chosen because it is a medicinal plant which is consumed by many local South Africans. Trace metals (As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn) were assessed for total soil concentrations in the soil and leaves by ICP-OES. Geoaccumulation indices and enrichment factors were calculated and showed soil samples to be moderately contaminated with significant enrichment. The results indicated that concentrations of trace metals in *Laportea peduncularis* and the soil were affected by site specific conditions however, the accessibility and absorption of the metals exclusively relied upon the control of the plant.

2.8 Environmental Legislation in South Africa

2.8.1. National Environmental Management: Air Quality Act No.39 of 2004

The National Environmental Management: Air Quality Act No.39 of 2004 (NEM: AQA), which falls under the umbrella National Environmental Management Act (NEMA), has replaced the outdated Atmospheric Pollution Prevention Act (No. 45 of 1965) (APPA). However, NEM: AQA contains vague legislation against vehicle emissions as it focuses more on industries whilst local authorities, such as district and local municipalities, take responsibility for monitoring air pollution and meeting nationally to set ambient air quality limits. To reach these air quality limits, an Air Quality Management Plan (AQMP) is to be developed via an external consulting company in which strategies and an assessment on structures in place is to be analysed and documented. The AQMP then becomes a part of the integrated development plan of the Municipality. This encourages appropriate by-laws to be passed in accordance with the recommendations of the AQMP. However, sufficient legislation and by-laws in all municipalities against vehicular emissions requires immediate updating as the traffic sector and associated emissions from it are ever increasing due to increased population and current technological and industrial advancements (Department of Environmental Affairs, 2004).

2.8.2 National Environmental Management: Waste Act No.59 of 2008

The National Environmental Management: Waste Act No.59 of 2008 (NEM: WA), states that contaminated land refers to "the presence in or under any land, site, buildings or structures of a substance or micro-organism above the concentration that is normally present in or under that land, which substance or micro-organism directly or indirectly affects or may affect the quality of soil or the environment adversely" (Department of Environmental Affairs, 2012).

NEM: WA section 36 (5) provides that:

"An owner of land that is significantly contaminated, or a person who undertakes an activity that caused the land to be significantly contaminated, must notify the Minister and MEC of that contamination as soon as that person becomes aware, of that contamination" (Department of Environmental Affairs, 2012).

It is now obligatory by the owner of the contaminated land or by the individual responsible for the activities in which the contamination occurred, to notify the minister of such contamination. However, areas of contamination must also, by obligation, be noted and monitored for remediation by the minister. Such persons convicted of contaminating land are liable to a fine not exceeding five million or imprisonment not exceeding five years (Department of Environmental Affairs, 2012).

NEM: WA section 36 (6) provides that the minister can issue a written notice to any individual that has been identified as a potential polluter and section 36 (7) allows the minister to direct the individual identified in section 36 (6) to undertake a site assessment at their own cost.

NEM: WA provides screening values in which contaminated land should be rehabilitated to a specified concentration of trace metals (Table 2.3).

Table 2.3: National Environmental Management: Waste Act No.59 of 2008 (NEM: WA) screening values in which contaminated land should be rehabilitated to a specified concentration of trace metals (Department of Environmental Affairs, 2012)

Parameter	**SSV1**	**SSV2**	**SSV2**	**SSV2**	
Metals and metalloids	**All land uses protective of the water resources**	**Informal Residential**	**Standard Residential**	**Commercial/ Industrial**	**Protection of Ecosystem Health**
	mg kg $^{-1}$				
Arsenic	5.8	23	48	150	580
Cadmium	7.5	15	32	260	37
Chromium (III)	46000	46000	96000	790000	n/a
Chromium(VI)	6.5	6.5	13	40	260
Cobalt	300	300	630	5000	22000
Copper	16	1100	2300	19000	16
Lead	20	110	230	1900	100
Manganese	740	740	1500	12000	36000
Mercury	0.93	0.93	1	6.5	4.1
Nickel	91	620	1200	10000	1400
Vanadium	150	150	320	2600	-
Zinc	240	9200	19000	150000	240

2.8.3 Government initiatives

Scorgie (2005) states that government led initiatives to reduce vehicle emissions have been underway since post-apartheid policy implementation in South Africa. This includes:

- Removal of lead from fuel which had been implemented in 1996.
- Equipping vehicles with catalytic converters and other forms of technology to reduce emissions from the manufacturer.
- Recent changes in fuel compositions such as in reduction of sulphur in diesel.
- Adapting EURO technologies across manufacturers
- Taxation on CO_2 emissions
- Upgrading of public transport
- Upgrading of highways

South Africa is responding to its pollution challenges in various ways. These include legislative reform, revision of pollution limits, proactive planning by local authorities, and sector-specific controls.

CHAPTER 3 : EXPERIMENTAL

This chapter will discuss, in detail, the experimental techniques and methodologies adopted to meet the objectives of this study.

3.1 Experimental Techniques

3.1.1 Digestion

The total concentration of heavy metals in soil, water and crops can be determined by a number of sample preparation methods. Total metal concentration in soil is the metal concentration representing the total amount of metals determined in soil after digestion in a strong acid (Dean, 2005). For solid samples, the sample matrix has to be destroyed thereby liberating the metals present, before analysis. There are a variety of decomposition techniques, of which, acid-digestion is most common. Acid-digestion involves the use of oxidising acids e.g. nitric acid (HNO_3) and an external heat source to decompose the sample matrix. Usually, acid digestion is carried out in an open glass vessel like a beaker on a hot plate. An alternative approach to conventional heating involves the use of microwave heating (Figure 3.1). Microwave digestion is more efficient than conventional heating since the digestion mixture is heated directly and there is no loss of analyte if a closed vessel is used (Dean, 2005).

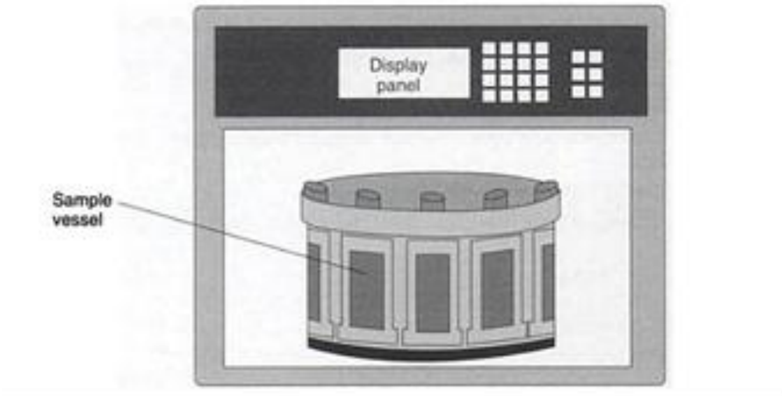

Figure 3.1: Pressurised microwave digestion system (Herbert and Hashemi, 2008)

3.1.2 Inductively coupled plasma - optical emission spectrometry (ICP-OES)

Techniques such as inductively coupled plasma-optical emission spectrometry (ICP-OES) are employed to measure the total metal content present in a medium (Dean, 2005). Inductively coupled plasma - optical emission spectrometry is one of the most versatile analytical techniques for quantitative multi-element analysis and it allows for the detection of low concentration levels (Dean, 2005). The ICP source produces a stream of high-energy ionized gas called plasma, by inductively coupling an inert gas such as argon with a high frequency field. When a sample is injected through the centre of the plasma, a temperature of 10 000 K allows for the desolvation, dissociation, atomization and excitation of the elements in the sample. This results in emission of light of unique frequencies for the given elements (Figure 3.2). The light is proportionate to the concentration of the elements in the sample and is measured by an emission spectrometer. The spectrometer is capable of separating the unique frequencies into discrete wavelengths and quantifies the results. Some advantages of ICP-OES due to its high temperatures are the wide linear dynamic range, increase in detection limits, lack of chemical interferences, minimum inter-element effects and high accuracy and precision.

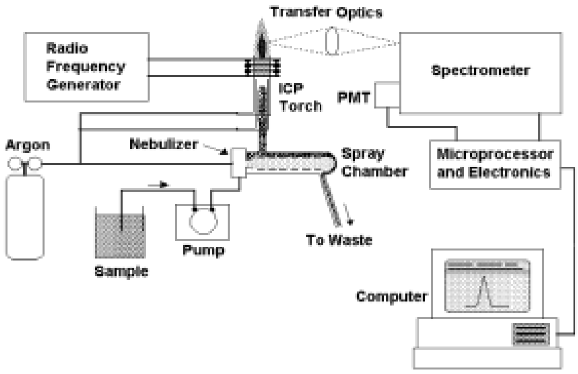

Figure 3.2: Instrumental set-up of ICP-OES (Charles and Fredeen, 1997)

3.2 Experimental Methods

3.2.1 Sampling

The study was conducted on the South African National Road (N3) from Hilton to Durban. The study area was selected due to high automobile activity and as a main logistic route for trucks from Durban harbour to Johannesburg. The South African National Road (N3) starts in the Central Business District (CBD) of Durban heading west via a dual carriageway through Westville and Pinetown, through to the Toll Plaza situated at Marianhill which leads to Cato Ridge, Camperdown and Pietermaritzburg, after which, is a steep incline up Townhill towards Hilton and Howick, en route to Johannesburg. To evaluate the impact of soil quality on elemental uptake by wild edible plants that grow across the study area, *Bidens pilosa* (a wild herb) was selected for analysis as the species is known to grow in the vicinity of the N3 (KwaZulu-Natal) and is picked and eaten by the surrounding rural communities. *Bidens pilosa* was selected and not agricultural or commercial crops, to reduce the impact on sample readings by other variables relating to the cumulative effects of fertilisers and pesticides on commercial and agricultural crops.

The soil samples were obtained from twenty pre-determined sampling locations along the N3 (Figure 3.3). The sampling locations were mapped out via GIS to be a proportionate and statistically reduced variation of 5 km apart while taking into consideration safe vehicle stopping areas. At each sampling location, three soil samples were collected. The first sample point was approximately one metre away from the roadside; the next sample point was ten metres away from the first point (11 m away from the roadside) and the last sample point was ten metres away from the second one (21 m away from the roadside). Sixty soil samples were collected in total to compare concentrations relative to distance from the road. Sampling was conducted in April 2015 on a warm day (24 ºC) with no rainfall or wind. Due to the horizon of the soil known as the plough layer which hosts plant roots that uptake nutrients from the soil, all soil samples were collected from a depth of 30 cm by the use of a hand auger (Nyangababo and Hamya, 1986).

Soil aliquots were manually homogenised using a plastic spoon after removal of extraneous material such as leaves and rocks. The composited soil volume (500 mg) was reduced to 100 mg by coning and quartering. Plant samples (*B. pilosa*) were collected from ten of the twenty soil sampling sites due to dispersed growing patterns of the plant. These samples were collected from roadside soils approximately one meter away from the road. All samples (plant and soil) were placed in polyethylene bags and stored in cooler bags for transportation. Schauer et al (2006) reported that trace metal concentrations in soil are dependent on many factors such as types of vehicles in the area, driving styles and environmental factors such as climate, topography and geology of the area. Table 3.1 lists the sample locations with environmental factors for the area.

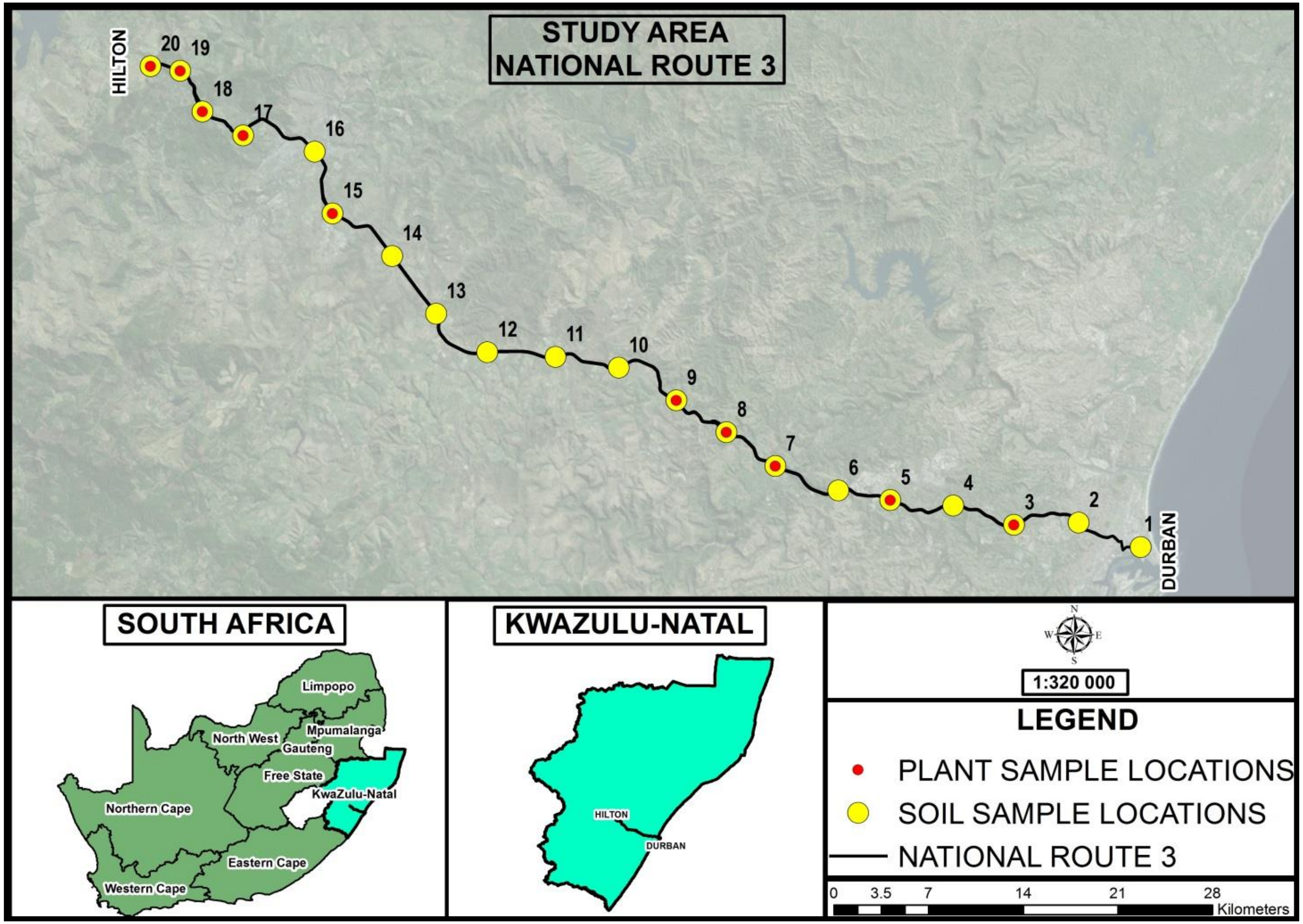

Figure 3.3: Study area in relation to country and province

Table 3.1: Soil and plant sample locations along the South African National Road (N3) and selected environmental factors

Site	Plant Sample	Town	Land use	Geological Formation	Mean annual temp (°C)	Rainfall Index (mm)	Latitude	Longitude	Altitude (m)
1		Durban Harbour	Urban area	Bluff/Berea (QB)	16 to 22	15 to 50	-29.861644	31.032464	7.73
2		Durban CBD	Urban area	Dwyka (C-Pd)	16 to 22	15 to 50	-29.845316	30.984819	81.18
3	1	Westville	Urban area	Natal (O-Sn)	16 to 22	15 to 50	-29.846915	30.935437	177.69
4		Pinetown	Urban area	Natal (O-Sn)	16 to 22	15 to 50	-29.834026	30.888884	267.44
5	2	Marianhill	Urban area	Natal (O-Sn)	16 to 22	15 to 50	-29.830242	30.840739	335.91
6		Marianhill Toll	Urban area	Natal (O-Sn)	16 to 22	15 to 50	-29.823759	30.801042	379.36
7		Hillcrest	Commercial sugarcane	Natal (O-Sn)	16 to 22	15 to 50	-29.807418	30.752936	568.65
8		Shongweni	Plantation	Maphumulo metamorphic suite (Nbi)	16 to 22	15 to 50	-29.784705	30.715724	726.41
9	3	Drummond	Grassland	Natal (O-Sn)	10 to 22	15 to 60	-29.763381	30.677502	515.08
10		Inchanga	Grassland	Dwyka (C-Pd)	10 to 22	15 to 60	-29.741661	30.63336	746.8
11		Cato-Ridge	Urban area	Dwyka (C-Pd)	10 to 22	15 to 60	-29.734245	30.585172	758.92
12	4	Camperdown	Grassland	Dwyka (C-Pd)	10 to 22	15 to 60	-29.730827	30.533137	755.53
13		Lynfield Park	Annual commercial crops dryland	Dwyka (C-Pd)	10 to 22	15 to 60	-29.70506	30.494042	795.19
14		Ashburton	Grassland/bush clumps mix	Dwyka (C-Pd)	10 to 22	15 to 60	-29.666533	30.460618	638.64
15	5	Scottsville	Urban area	Dolerite (Jd)	10 to 22	15 to 60	-29.637878	30.415325	693.47
16	6	Pietermaritzburg	Urban area	Pietermaritzburg(Pp)	10 to 22	15 to 60	-29.596508	30.401905	622.15
17	7	Town Bush	Urban area	Pietermaritzburg(Pp)	10 to 22	15 to 60	-29.585488	30.347501	815.82
18	8	Montrose	Plantation	Vryheid(Pv)	10 to 22	15 to 60	-29.569432	30.316402	1015.58
19	9	Hilton	grassland	Volkrust (Pvo)	10 to 22	15 to 60	-29.542249	30.299699	1137.21
20	10	Cedara	Bushland	Volkrust (Pvo)	10 to 22	15 to 60	-29.538983	30.27709	1061.65

3.2.2 Reagents and standards

Analytical reagent grade chemicals were used and were supplied by Merck (Kenilworth, NJ, USA). All glassware was soaked in HNO_3 (3M) then rinsed in double distilled water prior to use.

3.2.3 Sample preparation

Soil samples were air-dried, passed through a 2 mm mesh sieve to obtain the soil fraction and crushed using a mortar and pestle to reduce particle size to a powderised form, for microwave digestion. Plant samples were washed with double distilled water to remove extraneous matter, oven dried at 40 ºC then ground in a food processor (Russell Hobbs range) to obtain a powder. All samples (plant and soil) were placed in polyethylene bottles and stored in a refrigerator at 4 ºC until digestion, which was within a week of collection.

3.2.4 Digestion and elemental analysis of samples

Prior to analysis, the sample matrix has to be simplified by destroying the organic matrix; one of the ways to do this is by decomposition of the sample using strong oxidising agents such as nitric acid (HNO_3). Digested samples prevent carbon deposits on the cones of the instrument via ICP-OES and build-up of salt which maintains long-term stability of the instrument, reduces interferences (spectral and non-spectral), improves the overall throughput of the method and allows for the analysis of larger sample sizes (Moodley et al, 2012). In this study, microwave-assisted digestion was utilised. This method allows for rapid dissolution of the sample matrix, requires low volumes of oxidising reagents and minimises contamination due to the use of a closed vessel. For this study, digestions were performed using the CEM microwave accelerated reaction system (MARS 6, CEM Corporation, USA) according to the method as described by Moodley et al (2012). The maximum temperature was 260 ºC with maximum pressure of 75 bar. Three replicates each of plant material (*B. pilosa* leaves and certified reference material (CRM) (0.5 g)) and soil samples (0.25 g) were digested in HNO_3 (70%, 10 mL) in MARSXpress™ vessels (Teflon PFA, Dupont, Wilmington, DE, USA) after pre-digestion for 30 min. The microwave power was set at 100% at 1600 W and the temperature was ramped to 180 ºC for plant samples and 200 ºC for soil samples, where it was held for 15 min. After the digests were cooled (15 min) they were gravity filtered through Whatman No. 1 filter papers into volumetric flasks (50 mL) and the volume was made up to the graduation mark with double distilled water. All samples were stored in a refrigerator at 4 ºC in polyethylene bottles until elemental analysis which was done within a week of digestion.

All soil and plant samples were analysed for arsenic (As), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn) by ICP-OES. These metals are considered to be of most interest since they are the likely contaminants from vehicle emissions (Bushell and Williamson, 1995) and they include essential (Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Se and Zn) and toxic (As, Cd, Pb) elements. In order to eliminate matrix effects, external standards and reagent blanks were prepared for calibration by addition of double distilled water to 70% HNO_3 using the same volume as the samples. Working standards were prepared from stock standard solutions (1000 mg L^{-1}) and HNO_3 (70%) to match the matrix of digested samples. Calibration curves were obtained by preparing a blank and five standard solutions within the estimated ranges for each element. Wavelengths were chosen based on maximum analytical performance and minimum spectral interference. Spectral overlaps and inter-element interferences were eliminated by choosing the best of the three most sensitive lines. The Background Equivalent Concentration was checked daily by realigning the Hg lamp before analysis. Method validation was performed using the CRM, White Clover (BCR-402)

(Institute for Reference Materials and Measurement, European Commission, Joint Research Centre, Belgium) and Metals in Soil (D081-540) for soil samples (ERA, A Water Company, Milford, MA, USA). Certified reference materials were prepared and analysed similar to samples for method validation. All samples (plant material, soil and CRMs) were analysed in triplicate.

3.2.5 Statistical analysis

All statistical analyses were done using International Business Machines Statistical Package for the Social Sciences (IBM SPSS, Version 25, IBM Corporation, Cornell, New York). Principal component analysis (PCA) using the Varimax Rotation Method with Kaiser Normalization was used to reduce correlated observed variables to a smaller set of important independent variables. Cases used for statistics were based on cases with no missing values for any variable used.

3.3 Baseline/Background Concentrations

Defining background concentrations for trace and heavy metals in soils is essential for the recognition and management of pollution as well as deficiencies and toxicities for plants and animals (Herselman et al, 2005). The background concentration is intended to convey some idea of the natural range in concentration of elements in soil that can be expected prior to contamination through anthropogenic activities. With this natural range of concentrations, it is possible to assess the likelihood of contamination. Background concentrations (EPA 3050 method, acid extraction) were used from a study conducted by Herselman (2007) in which she updated the background concentration of soils in South Africa by analysing 4500 samples across South Africa as follows:

Table 3.2: Background concentrations of trace metals in soil (mg kg^{-1})

	South Africa (Herselman, 2007)	Upper continental crust (Rudnick, 2014)
Cd	0.1	0.09
Cr	71.9	92
Ni	38.7	47
Pb	21.7	17
Zn	45.2	67
Cu	29.5	28
Co	18	17.3
As	ND	4.8
Se	ND	0.09

Due to unavailability of baseline concentrations in South Africa for As and Se, trace element composition estimates of the upper continental crust were used in this study which were calculated by Rudnick (2014).

3.3.1 Geoaccumulation index (I_{geo})

The estimation of enrichment (contamination) of metal concentrations above background concentrations in soil can be accomplished by calculating the geoaccumulation index (I_{geo}) as proposed by Muller (1969). The degree of metal pollution in seven grades ranging from uncontaminated to extremely contaminated are assessed in this method. The degree of anthropogenic pollution is established in this study by calculating the I_{geo} according to the equation proposed by Muller (1969):

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5\ B_n} \right]$$

C_n is the concentration of element in sample and B_n is the background/baseline concentration of the same element. The factor 1.5 is incorporated into the equation to minimise any variations in the background value due to lithologic (rock composition) variations (Stoffers et al, 1986).

The background concentrations for this study were used from a study conducted by Herselman (2007) and Rudnick (2014) (Table 3.2). The following categories for soil were used for I_{geo} values: $I_{geo} \leq 0$ uncontaminated, $0 > I_{geo} < 1$ uncontaminated to moderately contaminated, $1 > I_{geo} < 2$ moderately contaminated, $2 > I_{geo} < 3$ moderately to heavily contaminated, $3 > I_{geo} < 4$ heavily contaminated, $4 > I_{geo} < 5$ heavily to extremely contaminated and $I_{geo} > 5$ extremely contaminated (Müller 1969).

3.3.2 Enrichment factor (EF)

An alternative method for determining levels of soil contamination is by use of the enrichment factor (EF). The EF compares the concentration of an element in the soil to concentrations of the element in the earth's crust. Due to Zn concentrations being known in South Africa, Zn is used as the reference element (Herselmann, 2005; Mendiola et al, 2008). Enrichment factors are calculated using the following equation:

$$\boldsymbol{EF = \left(\frac{\frac{C_x}{C_{ref}}}{\frac{B_x}{B_{ref}}}\right)}$$

C_x is the content of the examined element in the examined environment; C_{ref} is the content of the examined element in the reference environment, B_x is the content of the reference element in the examined environment and B_{ref} is the content of the reference element in the reference environment. The background concentrations for this study were used from a study conducted by Herselman (2007) and Rudnick (2014) (Table 3.2). EF values were interpreted as follows: EF < 1 background concentration, 1 > EF < 2 depletion to minimal enrichment, 2 > EF < 5 moderate enrichment, 5 > EF < 20 significant enrichment, 20 > EF < 40 very high enrichment, and EF > 40 extremely high enrichment (Sutherland, 2000).

3.4 Geographic Information System (GIS) Analysis

Soil samples were obtained from 20 predetermined points along the South African National Road (N3). Each soil sample consisted of three sampling points, ten meters apart, moving away from the roadside therefore, 60 soil sample points were obtained, in total. These points were interpolated, i.e. an estimation of a variable at an unmeasured location from observed values at surrounding locations. Each sample point was analysed in triplicate, and the mean was obtained and captured. This process was incorporated to reduce errors in the field and to adopt a constant and structured approach. Sample points were split into four subsets due to altitude and slope, which assisted in a higher accuracy in interpolation and assisted with visually representing the information in smaller subsets.

Subsets were broken up as follows: 1. Durban to Marianhill Toll (5 – 381 m above sea level), 2. Marianhill Toll to Cato Ridge (568 – 758 m above sea level), 3. Camperdown to Pietermaritzburg (758 – 625 m above sea level), 4. Pietermaritzburg to Hilton (820 – 1061 m above sea level). Each subset was interpolated via Kriging to a 200 m buffer of the N3 for Pb and Cd. The process depicted in Figure 3.4 was followed.

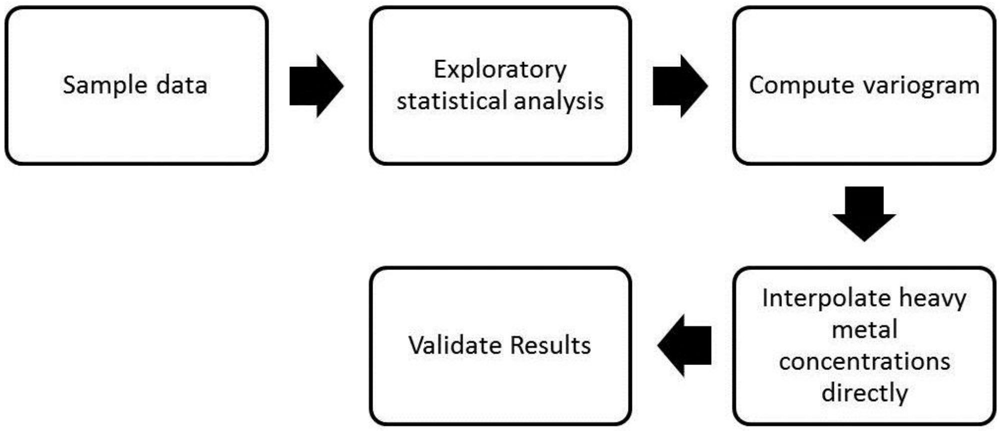

Figure 3.4: Geographic information system (GIS) interpolation process

3.4.1 Goodness of fit test

Data was assessed for normality via the Shapiro-Wilk test (Figure 3.5). Data was calculated by the following equation:

$$\mathbf{W} = \frac{\left(\sum_{i=1}^{n} a_i x_{(i)}\right)^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

Null hypothesis: The data are normally distributed. (α = 0.05)

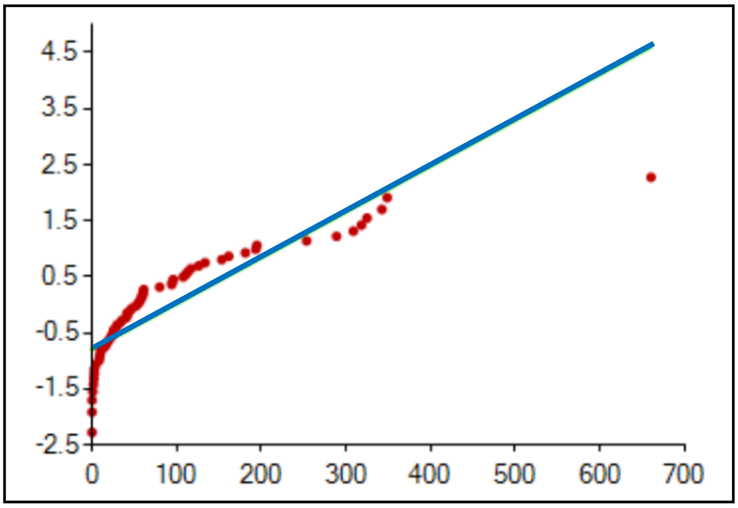

Figure 3.5: Shapiro-Wilks test: $P < 0.001$

P-value = 0.001 < 0.05, therefore the null hypothesis is rejected and we conclude with 95% confidence that the data is not normally distributed. Values were then transformed to normally distributed data via logarithmic transformation (Figure 3.6).

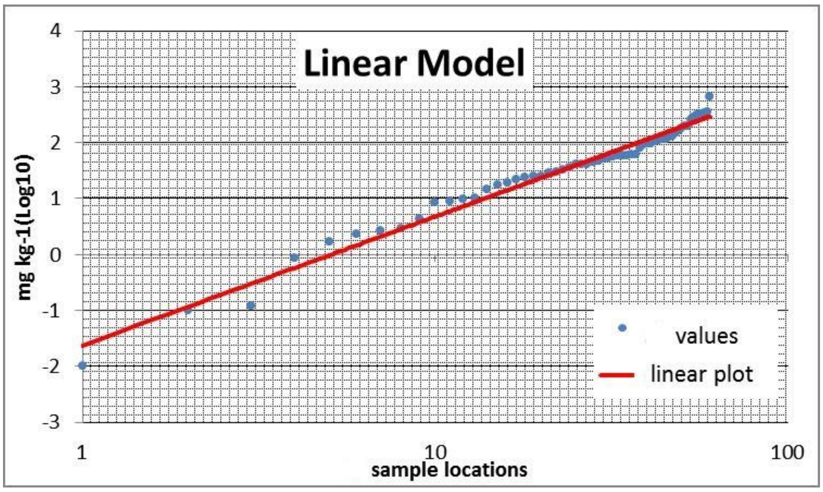

Figure 3.6: Logarithmic transformed data

A critical technique in interpolation via any Kriging technique is to create and fit an experimental variogram to the data. The model used is unimportant given that parameters such as the nugget effect and slope on the original are properly chosen and the modelled semi-variogram has the same estimation with the experimental data. Frequency distributions within the mining industry have predominantly skewed distributions with outliers. Fitting a semi-variogram based on the skewed data with many outliers proves difficult therefore transforming the data by logarithmic equation improves the semi-variogram model (Armstrong & Thurston, 1987).

Bohling (2005) defined the following terms in a semi-variogram as follows:

Sill: The semi-variance value at which the variogram levels off.

Range: The lag distance at which the semi-variogram reaches the sill value.

Nugget: Represents variability at distances smaller than the typical sample spacing, including measurement error.

The experimental semi-variogram was fitted to the model as depicted in Figure 3.7 to increase the accuracy in the Kriging process.

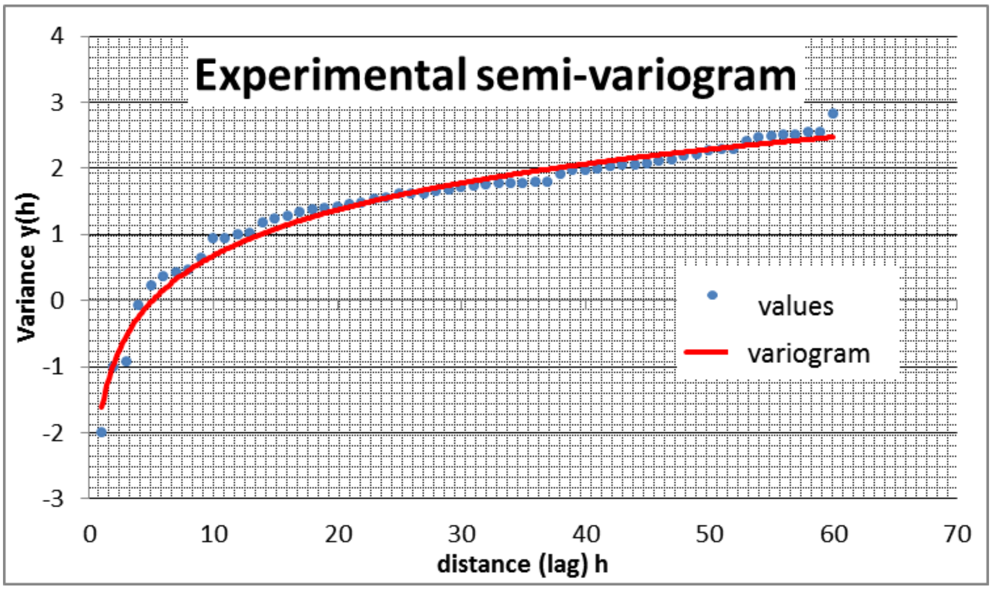

Figure 3.7: Exponential variogram was fitted for the model

The interpolation technique used was Kriging due to the type of data sets and the required output. Kriging is an interpolation technique in which the surrounding measured values are weighted to develop a predicted value for an unmeasured location. Weights are based on the distance between the measured points; Kriging is distinctive among the interpolation methods in that it provides an easy method in describing the variance, or the accuracy of predictions (Burrough and McDonnell, 2015). Kriging is based on Regionalised Variable Theory, which assumes that the spatial variation in the data is similar across the surface, therefore the same pattern of variation can be observed at all locations on the surface. Kriging is a method which weights of the value sum to unity. It uses an average of a subset of neighbouring points to produce a particular interpolation point (Bohling, 2005).

The Empirical Bayesian Kriging Method was used in this study, which is a geostatistical method of interpolation which automatically adjusts parameters via the sub setting and simulation processes in the Kriging model and accounts for errors introduced into the model via prediction of the semi-variogram to develop as accurate results as possible with the most user friendly application (Krivoruchko, 2012).

3.4.2 Accuracy assessment

Generally, the best model is the one that has the standardised mean nearest to zero, the smallest root-mean-squared prediction error and the standardised root-mean-squared prediction error nearest to one (Heuvelink, 2007).

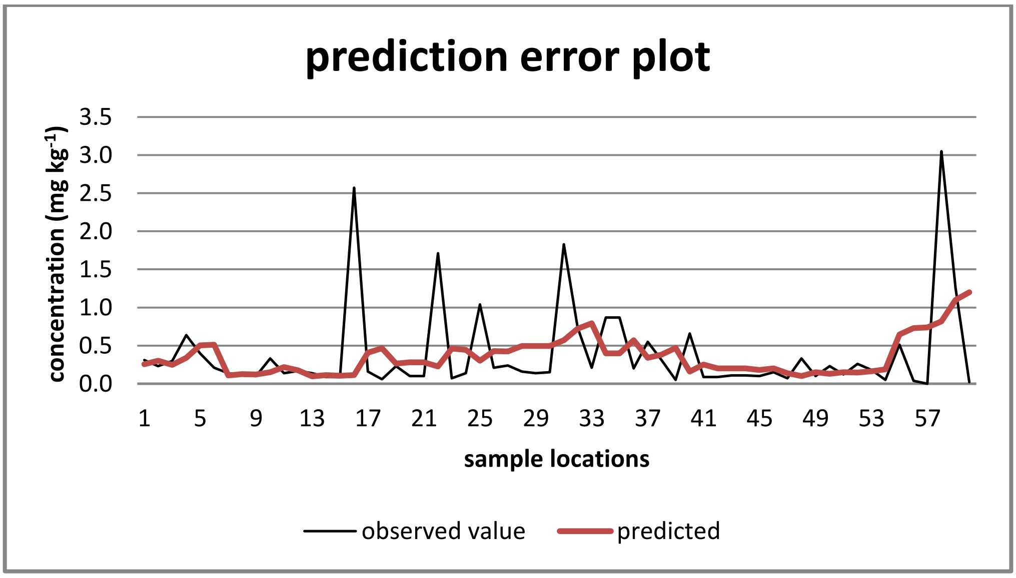

Figure 3.8: Prediction error plot

Mean = 0.0122, Root-mean-square error = 0.276, Mean standardized error = 0.043, Root-mean-square standardized error = 0.0984, Average standard error = 0.278, r = 0.585 which indicates that the accuracy of the interpolation is good.

There are two concerns to consider when comparing the results from different models which are optimality and validity (Figure 3.8). For example, the root-mean-squared prediction error may be smaller for a particular model. Therefore, one might conclude that it is the optimal model. However, when comparing to another model, the root-mean-squared prediction error may be closer to the average estimated prediction standard error. This is a more valid model as when you predict at a point without data, you have only the estimated standard errors to assess your uncertainty of that prediction. When the average estimated prediction standard errors are close to the root-mean-squared prediction errors from cross validation, you can be confident that the prediction standard errors are appropriate (Heuvelink, 2007).

CHAPTER 4 : AUTOMOTIVE TRACE METAL CONCENTRATIONS ON THE SOUTH AFRICAN NATIONAL ROAD (N3) AND ITS IMPACT ON THE ENVIRONMENT

4.1 Introduction

Heavy metal contamination in the environment is through both anthropogenic and natural sources. Vehicular emissions contribute substantial amounts of heavy metals in roadside soils, which biaccumulate and adversely affect biota. Heavy metals are also non-biodegradable and may remain in the environment for long periods of time, even if point sources of pollution are removed. Biotic effects of heavy metals vary depending on the type of metal and whether essential or non-essential.

In this chapter, the impact of vehicle pollution in the surrounding environment of the South African National Road (N3) between Durban and Hilton (a major transportation route from the harbour) will be discussed. The elemental concentrations of macro, micro and toxic metals in the leaves of *Bidens pilosa* and surrounding soils was determined to evaluate the impact of soil concentrations on elemental uptake by the plant. The analytes of interest included As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se and Zn. Soil contamination was determined by calculating I_{geo} and EF values for a metal. Statistical analyses were performed to determine sources of metals.

4.2 Results and Discussion

4.2.1 Quality assurance

The accuracy of the method used in this study was measured by comparing the certified values for the CRMs (White Clover (BCR-402) for plants and Metals in Soil (D081-540) for soil) with experimental values. Certified reference materials are reference materials accompanied by a certificate; the certified concentrations of elements are accompanied by an uncertainty at a stated level of confidence. Analysis of the CRM was to ensure that digestion was complete, instrument parameters were optimised and calibration errors were removed. The CRM was treated from start to finish in the same manner as dried and powdered plant and soil samples. The experimental values obtained on analysis of the CRM are presented in Table 4.1. The investigation showed that the experimental values compared well to certified values thereby validating the method.

Table 4.1: Comparison of measured and certified/indicative values (Mean (SD), n = 3), based on dry mass, in the certified reference materials for plant (BCR-402) and soil (D081-540)

	BCR-402 (µg g^{-1})		**D081-540 (µg g^{-1})**		
Element	Measured	Certified	Measured	Certified	Acceptable limit
As	0.20 (0.01)	0.09 (0.01)	98 (5.00)	101 (5.92)	61.0-116
Ca	-	-	6200 (20.00)	7530 (7.27)	6210-8850
Co	0.16 (0.02)	0.18 (0.01)	200 (10.50)	199 (4.10)	116-159
Cr	5.10 (0.15)	5.19	85.5 (4.8)	86.8 (6.1)	69.3-104
Fe	246 (10)	244	12780 (120)	12800 (180)	5380-20100
Ni	8.30 (1.0)	8.25	228 (10.34)	236 (4.17)	175-302
Zn	25.01 (0.10)	25.02	140 (2.11)	130 (11.50)	113-184

4.2.2 Analysis of the impact of soil concentrations on plant concentrations

The growth and development of flora is reliant on the accumulation of trace metals, within limits, which is a normal and essential process. Elemental uptake and distribution may also vary in different parts of the plants. Nickel, Cu, Zn, and Mn are trace metals that are readily taken up by plants but kill plants at levels below those associated with adverse health effects; therefore, phytotoxicity prevents transfer of these metals from soil through the food chain (McLaughlin et al, 1999). Golmohammed and Rezapour (2014) stated that the concentration and dynamics of soil trace metals in natural ecosystems, in particular, is dependent on the lithology of parent rock as well as topography and geopedological processes. The macro-nutrients that plants must obtain from their environment for growth and development include Ca and Mg; the micro-nutrients include Fe, Mn, Zn, Co and Ni.

Table 4.2: Acceptable limits for trace metals in vegetable (mg kg^{-1})

	DWAF[a] (2005)	**DOH[b] (2004)**	**CODEX[c] (2001)**	**FAO[d] (1985)**	**WHO[e] (1996)**	**This study**
Ca	175	-	-	-	-	16643.9
Co	0.7	-	-	-	-	0.95
Cu	2.3	30	40	0.2	10	54.3
Cr	0.11	-	2.3	-	-	11.2
Fe	-	-	-	5	150	743
Mg	-	-	-	-	-	5187.2
Mn	4.9	-	-	-	6.61	268.3
Ni	0.18	-	-	0.2	-	3.12
Zn	11	40	0.6	2	-	181.6

[a] - DWAF – Department of Water Affairs and Forestry, [b] - DOH – Department of Health, South Africa, [c] - CODEX – Codex Alimentarius International Food Standards, [d] - FAO – Food and Agricultural Organisation, [e] - WHO – World Health Organisation

Figure 4.1 shows the concentrations of Ca and Mg in the plant (*Bidens pilosa*) and soil samples from ten different sites across the N3. Plant Ca ranged from 11016 mg kg^{-1} (Pietermaritzburg) to 21074 mg kg^{-1} (Town Bush) whilst total soil Ca ranged from 593 mg kg^{-1} (Westville) to 4200 mg kg^{-1} (Pietermaritzburg) (Figure 4.1). Calcium concentrations in plant material are below the acceptable health limits (Table 4.2) (Department of Water Affairs and Forestry, 2005). Plant Mg ranged from 3189 mg kg^{-1} (Cedara) to 6414 mg kg^{-1} (Marianhill) whilst total soil Mg ranged from 191 mg kg^{-1} (Drummond) to 2773 mg kg^{-1} (Pietermaritzburg). Maximum permissible limits in South African soils for trace metals, Ca and Mg, have not been established. However, for both metals, the highest soil concentrations were obtained from the capital of KwaZulu-Natal (Pietermaritzburg). In this study, concentrations of both Ca and Mg were also found to be considerably higher in plant material than soil. This indicates that the plant tends to accumulate these metals to meet physiological needs.

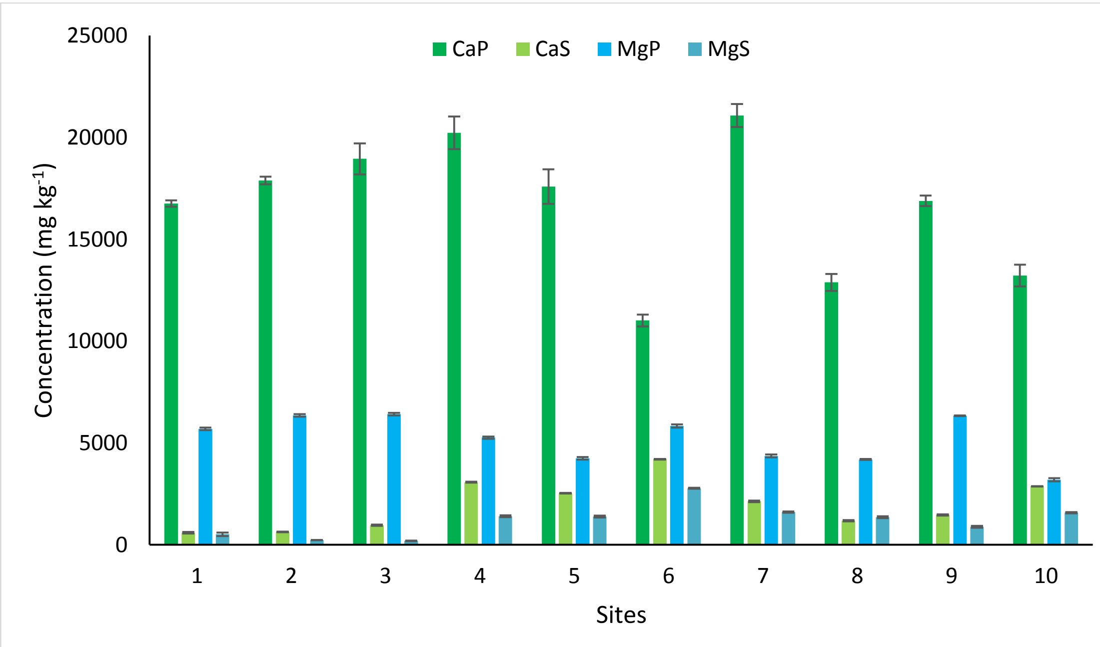

Figure 4.1: Concentration (in mg kg^{-1}, Mean (SD), n=3) of Ca and Mg in plants (P) and soil (S) from 10 sites along the South African National Road (N3)

Sites: 1. Westville, 2. Marianhill, 3. Drummond, 4. Camperdown, 5. Scottsville, 6. Pietermaritzburg, 7. Town Bush, 8. Montrose, 9. Hilton, 10. Cedara

Plant Fe ranged from 504 mg kg^{-1} (Westville) to 1104 mg kg^{-1} (Town Bush) whilst total soil Fe ranged from 101 mg kg^{-1} (Camperdown) to 47798 mg kg^{-1} (Hilton) (Figure 4.2). Excessive levels of Fe absorbed by plants are toxic and may inhibit their growth (Chaney, 1980). The plant had high concentrations of Fe across all samples, above the acceptable limit for Fe in vegetable (150 mg kg^{-1}) as set by the World Health Organisation (WHO) (World Health Organisation, 1996) (Table 4.2). However, Fe concentrations in the plant are consistent with previous studies on leafy vegetable in South Africa (Table 4.3). Maximum permissible limits for Fe in South African soils have not been established. However, in this study, total soil Fe was predominantly higher than concentrations in plant material. This indicates the plants ability to exclude the element. Sample areas with high concentrations of total soil Fe include areas which have shale as the predominant bedrock within Dwyka and Pietermaritzburg geological formations. De vos et al (2005) predicted a 4.7 mg kg^{-1} world mean concentration of Fe in shale bedrock which indicates Fe enriched soil content (Table 4.4).

Plant Mn ranged from 81 mg kg^{-1} (Westville) to 350 mg kg^{-1} (Scottsville) whilst total soil Mn ranged from 105 mg kg^{-1} (Westville) to 1680 mg kg^{-1} (Cedara) (Figure 4.2). The levels of Mn are high across all sites, which are above acceptable limits for Mn in vegetation (6.6 mg kg^{-1}) (Table 4.2) (World Health Organisation, 1996). When compared to other South African studies (Table 4.3), higher Mn values appear to be the trend, such as 260 mg kg^{-1} in *Laportea alatipes* (Mahlangeni et al, 2016). Maximum permissible limits for Mn in South African soils have not been established. However, Mn soil rehabilitation screening values as specified by the National Environmental Management: Waste Act (NEM: WA) in all land uses is 740 mg kg^{-1}. Three of the ten sites (Scottsville, Pietermaritzburg and Cedara) exceeded this limit.

This could possibly be due to high trucking activities in these areas and naturally high Mn levels in the soil as Mn is commonly found within the earth's lithosphere.

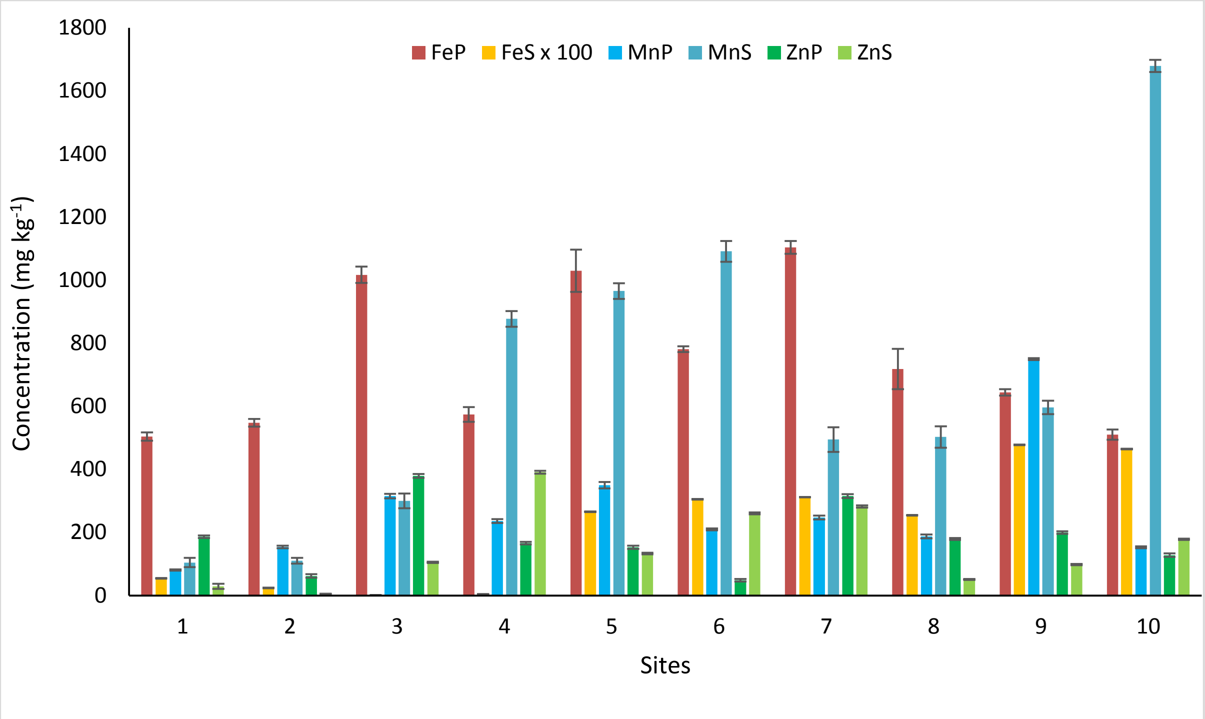

Figure 4.2: Concentration (in mg kg^{-1}, Mean (SD), n=3) of Fe, Mn and Zn in plants (P) and soil (S) from 10 sites along the South African National Road (N3)

Sites: 1. Westville, 2. Marianhill, 3. Drummond, 4. Camperdown, 5. Scottsville, 6. Pietermaritzburg, 7. Town Bush, 8. Montrose, 9. Hilton, 10. Cedara

Plant Zn ranged from 48 mg kg^{-1} (Pietermaritzburg) to 379 mg kg^{-1} (Drummond) whilst total soil Zn ranged from 5 mg kg^{-1} (Marianhill) to 391 mg kg^{-1} (Camperdown) (Figure 4.2). The maximum acceptable limit for Zn in foods, as set by the South African Department of Health, is 40 mg kg^{-1} (Department of Health, 2004). The average concentration of Zn in the plant was found to be 181 mg kg^{-1} which is much higher than the maximum acceptable limit. Plants are quite sensitive to Zn, with phytotoxicity of Zn being one of the primary concerns of excess Zn in soils (Brown et al, 2004). However, the results show the plant to accumulate Zn at most sites, as plant concentrations are higher than soil concentrations, with no phytotoxic effects. Zinc concentrations in the plant are also higher than those of other vegetation from previous studies done in South Africa (Table 4.3). The maximum permissible limit for Zn in South African soils is 185 mg kg^{-1} (Table 4.5). Zinc screening values for rehabilitation in all land uses as specified by NEM: WA is 240 mg kg^{-1}. Three of the ten sites (Camperdown, Pietermaritzburg and Town Bush) that are in close proximity to major urban areas are above these acceptable limits. High bedrock concentrations of Zn in shale, the predominant bedrock in the high concentration areas, are 50 to 90 mg kg^{-1}, which therefore indicates that Zn concentrations are much higher naturally in these areas (De Vos et al, 2005) (Table 4.4). Zinc enhancement may also be connected to the traffic sector since ZnO used in the rubber of motor vehicle tyres is a major source of Zn (Hjortenkrans et al, 2006).

Table 4.3: Average concentrations for trace metals in leafy green vegetable (mg kg^{-1})

Vegetation	Country	Co	Cr	Cu	Fe	Mn	Ni	Zn	References
Lettuce	Egypt	-	-	1.97	-	-	-	9.76	Radwan & Salam (2006)
	Greece	-	0.036	0.17	4.04	0.95	0.05	1.01	Stalikas et al (1997)
	Tanzania	-	-	5.8	-	-	-	15.9	Bahemuka & Mubofu (1999)
Spinach	Egypt	-	-	4.48	-	-	-	20.9	Radwan & Salam (2006)
	Greece	0.026	0.13	2.45	21.5	4.42	0.52	2.99	Stalikas et al (1997)
	South Africa	-	10.05	10.64	2840	140	5.11	70	Lion & Olowoya (2013)
	Tanzania	-	-	13.7	-	-	-	48.1	Bahemuka & Mubofu (1999)
Cabbage	South Africa	-	-	1.18	-	23.56	-	29.6	Bvenura & Afokeyan (2012)
	Tanzania	-	-	5.6	-	-	-	41.8	Bahemuka & Mubofu (1999)
	Zimbabwe	-	0.5	0.2	-	-	0.5	32.15	Mapanda et al (2007)
Laportea alatipes	South Africa	1.42	12.1	19.1	6114	260	6.36	60.7	Mahlangeni et al (2016)
Obetia tenax	South Africa	6.64	87.7	23.9	12045	206	15.8	34.3	Mahlangeni et al (2016)
Laportea peduncularis	South Africa	0.33	3.1	23	1310	152	4.79	26	Mahlangeni et al (2016)

Urtica dioica	South Africa	-	1.06	17.6	208	25.6	2.4	37.5	Mahlangeni et al (2016)
Bidens pilosa	South Africa	0.95	11.2	54.3	743	268.3	3.12	181.6	This Study

Table 4.4: Mean concentrations for trace metals in different bedrock (mg kg^{-1})[a]

	Cu	Fe	Zn	Cr	Pb	Ni	Co
Ultramafic	40	9.6	50	1600	1	-	0.09
Sandstone	-	0.5	-	35	10	20	-
Shale	50	4.7	50-90	90	23	90	0.8
Limestone	-	0.98	50	11	-	<5	-

[a] - (De vos et al, 2005)

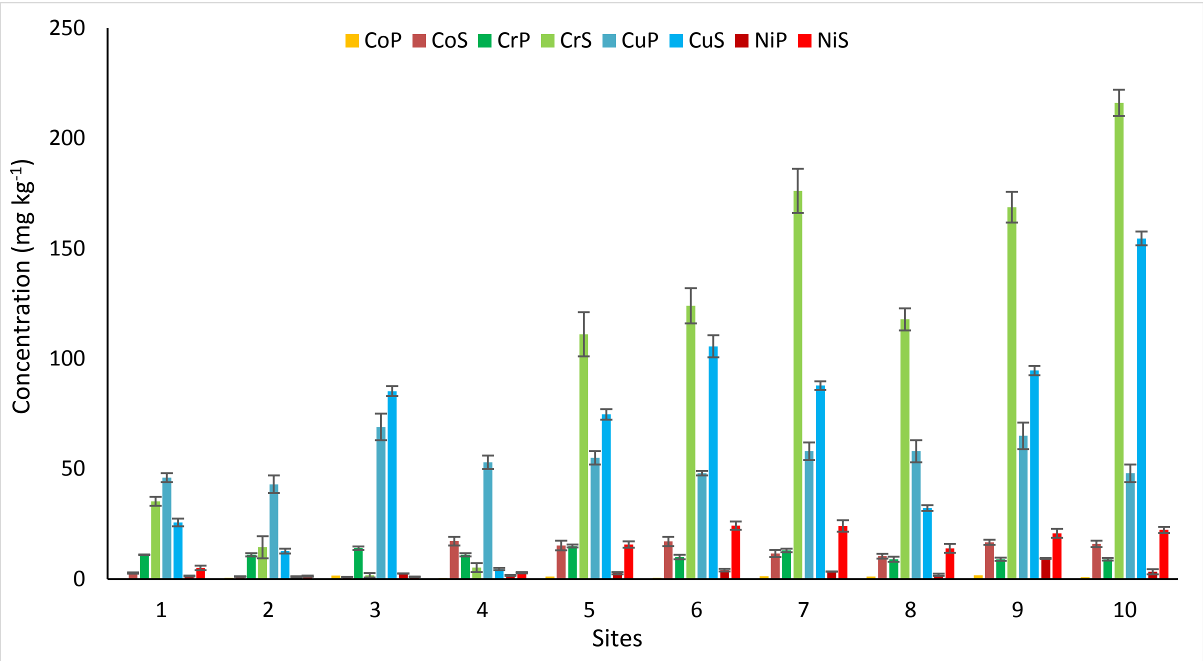

Figure 4.3: Concentration (in mg kg^{-1}, Mean (SD), n=3) of Co, Cr, Cu and Ni in plants (P) and soil (S) from 10 sites along the South African National Road (N3)

Sites: 1. Westville, 2. Marianhill, 3. Drummond, 4. Camperdown, 5. Scottsville, 6. Pietermaritzburg, 7. Town Bush, 8. Montrose, 9. Hilton, 10. Cedara

Plant Co ranged from 0.3 mg kg^{-1} (Westville) to 1.7 mg kg^{-1} (Hilton) whilst total soil Co ranged from 0.9 mg kg^{-1} (Drummond) to 17.2 mg kg^{-1} (Camperdown) (Figure 4.3). Cobalt concentrations in the plant are above the acceptable health limits of 0.7 mg kg^{-1} at Drummond, Town Bush, Montrose and Hilton (Table 4.2) (Department of Water Affairs and Forestry, 2005). However, Co concentrations in the plant are consistent with other vegetation from previous studies done in South Africa (Table 4.3). Maximum permissible limits in South African soils for Co have not been established. However, the Co soil screening value for rehabilitation in all land uses as specified by NEM: WA is 300 mg kg^{-1}. The world mean concentration of Co in shale, the predominant bedrock of the study area, is 0.8 mg kg^{-1} (Table 4.4).

Plant Cr ranged from 9 mg kg^{-1} (Montrose, Hilton and Cedara) to 15 mg kg^{-1} (Drummond) whilst total soil Cr ranged from 2 mg kg^{-1} (Drummond) to 216 mg kg^{-1} (Cedara) (Figure 4.3). Chromium concentrations across all samples of the plant exceed the threshold value of 2.3 mg kg^{-1} (Table 4.2) (Codex Alimentarius, 2001). However, Cr concentrations in the plant are consistent with other vegetation from previous studies done in South Africa (Table 4.3). The maximum permissible limit for Cr in South African soils is 80 mg kg^{-1} (Table 4.5). All soil samples are above the acceptable limit, with Hilton and Cedara having extremely high concentrations (168.7 mg kg^{-1} and 216.1 mg kg^{-1}, respectively). Accumulation of Cr within soil is primarily due to industrial wastes and untreated sewage exposure. Chromium is also used in corrosive preventative coatings in vehicle manufacture at approximately 10 g per vehicle. Herselman (2007) found the natural concentration of Cr in South African soils to be high, higher than the world mean concentrations of other landscapes such as bedrock shale (90 mg kg^{-1}) and sandstone (35 mg kg^{-1}) (Table 4.4).

Plant Cu ranged from 43 mg kg^{-1} (Marianhill) to 69 mg kg^{-1} (Scottsville) whilst total soil Cu ranged from 5 mg kg^{-1} (Camperdown) to 155 mg kg^{-1} (Cedara) (Figure 4.3). The maximum acceptable limit for Cu in foods set by the South African Department of Health is 30 mg kg^{-1} (Department of Health, 2004). The plant exhibited high levels of Cu with all samples exceeding permissible levels. Copper concentrations in the plant are considerably higher than other vegetable from previous studies done in South Africa (Table 4.3). The maximum permissible limit for Cu in South African soils is 100 mg kg^{-1} (Table 4.5). Except for Cedara, all sites had soil concentrations below this limit. The world mean concentration for Cu in bedrock shale, the predominant bedrock of the study area is 50 mg kg^{-1} (Table 4.4).

Plant Ni ranged from 1 mg kg^{-1} (Marianhill) to 9.3 mg kg^{-1} (Hilton) whilst total soil Ni ranged from 1 mg kg^{-1} (Drummond) to 24.2 mg kg^{-1} (Pietermaritzburg) (Figure 4.3). All plant samples had Ni concentrations above the permissible limit of 0.18 mg kg^{-1} for Ni in vegetable (Table 4.2) (Department of Water Affairs and Forestry, 2005). The maximum permissible limit for Ni in South African soils is 50 mg kg^{-1} (Table 4.5); all samples were below this limit. The world mean concentration for Ni in bedrock shale and sandstone is 90 and 20 mg kg^{-1}, respectively (Table 4.4).

Table 4.5: Guidelines for maximum permissible levels of micro-elements in soil (mg kg^{-1})

	EU[a]	**USA[b]**	**Germany[c]**	**Australia & New Zealand[a]**	**South Africa 1991[d]**	**South Africa 1997[e]**	**South Africa 2007[f]**	**This Study**
Cr	-	1500	400	50	80	80	80	84.96
Cu	50-140	750	135	60	100	66	100	130.02
Ni	30-75	210	75	60	15	50	50	12.15
Zn	150-300	1400	300	200	185	46.5	185	147.66

[a] - McLaughlin et al (1999), [b] – US EPA (1995), [c] - Adriano (2001), [d] - National Department of Health & Population Development (1991), [e] - Water Research Commission (1997), [f] - Herselman (2007)

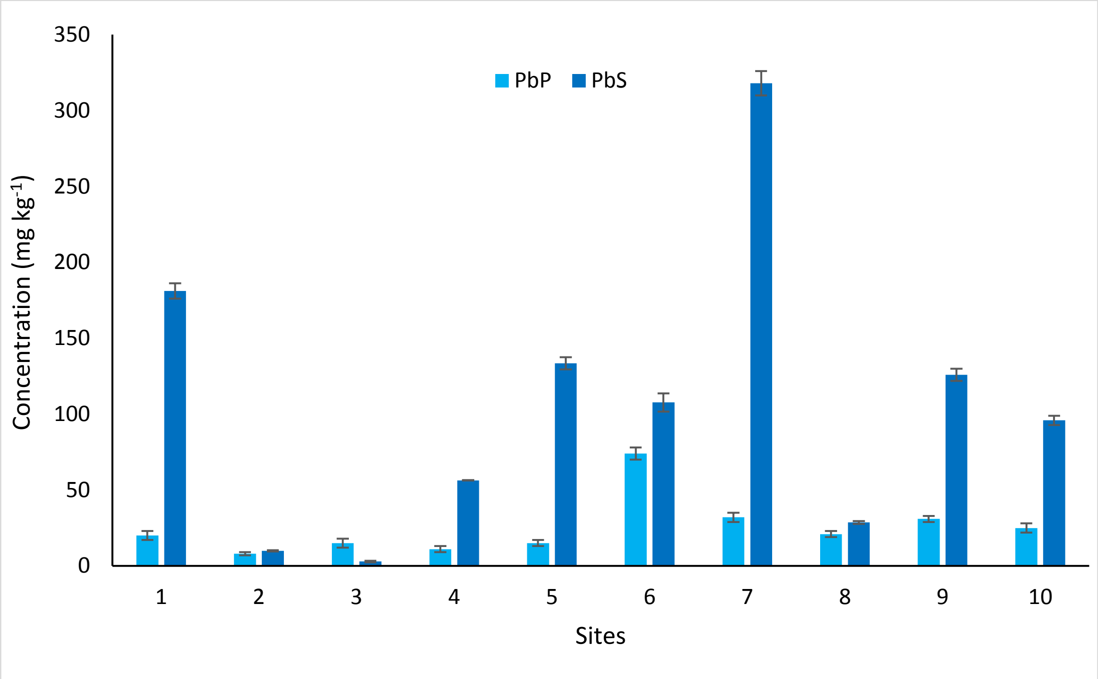

Figure 4.4: Concentration (in mg kg^{-1}, Mean (SD), n=3) of Pb in plants (P) and soil (S) from 10 sites along the South African National Road (N3)

Sites: 1. Westville, 2. Marianhill, 3. Drummond, 4. Camperdown, 5. Scottsville, 6. Pietermaritzburg, 7. Town Bush, 8. Montrose, 9. Hilton, 10. Cedara

Plant Pb ranged from 8 mg kg^{-1} (Marianhill) to 74 mg kg^{-1} (Pietermaritzburg) whilst total soil Pb ranged from 2.9 mg kg^{-1} (Drummond) to 318 mg kg^{-1} (Town Bush) (Figure 4.4). The maximum acceptable limit for Pb in vegetation is set at 0.3 mg kg^{-1} by the South African Department of Health (Table 4.2) (Department of Health, 2004); all plant samples exceeded this limit. An informal settlement, on-ramps and industrial activities, dense populations (Pietermaritzburg), forestry and increased motor vehicle strains and run-off due to topography (Town Bush) are likely contributors to high concentrations of Pb; these are activities of an urban setting as depicted in Figure 4.6.

Table 4.6: Acceptable limits for toxic metals (As, Cd and Pb) in vegetation (mg kg^{-1})

	DWAF[a] (2005)	DOH[b] (2004)	CODEX[c] (2001)	FAO[d] (1985)	WHO[e] (1996)	This Study
As	0.002	1	-	-	-	1.64
Cd	0.04	0.2	0.3	0.01	0.02	1.23
Pb	0.02	0.3	0.3	5	2	25.2

[a] - DWAF – Department of Water Affairs and Forestry, [b] - DOH – Department of Health, South Africa, [c] – CODEX Alimentarius – International Food Standards, [d] - FAO – Food and Agricultural Organisation, [e] - WHO – World Health Organisation

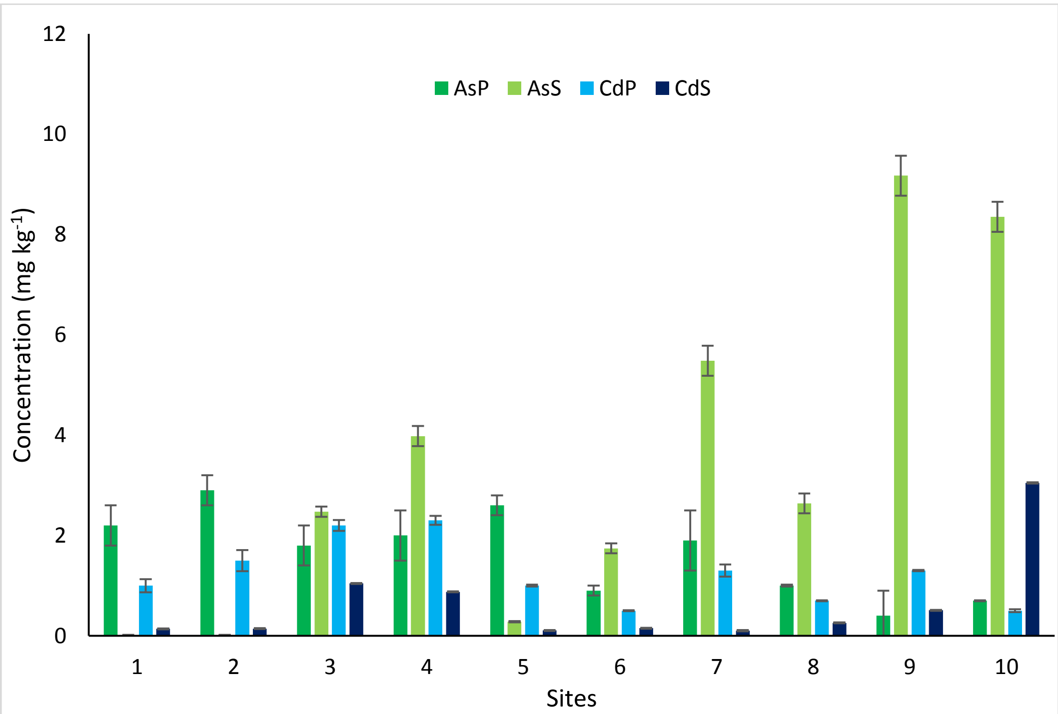

Figure 4.5: Concentration (in mg kg^{-1}, Mean (SD), n=3) of As and Cd in plants (P) and soil (S) from 10 sites along the South African National Road (N3)

Sites: 1. Westville, 2. Marianhill, 3. Drummond, 4. Camperdown, 5. Scottsville, 6. Pietermaritzburg, 7. Town Bush, 8. Montrose, 9. Hilton, 10. Cedara

Plant As ranged from 0.4 mg kg^{-1} (Hilton) to 2.9 mg kg^{-1} (Marianhill) whilst total soil As ranged from 0.01 mg kg^{-1} (Marianhill) to 9 mg kg^{-1} (Hilton) (Figure 4.5). Most samples have higher values than the acceptable exposure limit for As as set by the South African

Department of Health (Table 4.2) (Department of Health, 2004). Sites 1 and 5 have the highest values with all being two-fold the set limit, with an average concentration of 2.3 mg kg^{-1}. This indicates an increased As concentration in plants closer to the coast rather than inland. These areas are in close proximity to the two major industrial hubs, Pinetown and Mkondeni in an urban setting (Figure 4.6), which indicates a possible link between industrial effluents and increased As concentrations in surrounding plants.

Plant Cd ranged from 0.5 mg kg^{-1} (Pietermaritzburg and Cedara) to 2.3 mg kg^{-1} (Camperdown) whilst total soil Cd ranged from 0.1 mg kg^{-1} (Town Bush) to 3 mg kg^{-1} (Cedara) (Figure 4.6). Cadmium concentrations in the plant are also above the acceptable limit of 0.2 mg kg^{-1} as set by the South African Department of Health (Table 4.2) (Department of Health, 2004). Plants at Sites 3 (2.2 mg kg^{-1}) and 4 (2.3 mg kg^{-1}) have the highest concentrations in this study. This region is in close proximity to the tollgate and forestry (Figure 4.6). Possible fertiliser, herbicide and pesticide usage in the area, run-off due to topography and increased mechanical wear from vehicles due to the tollgate could be potential sources of Cd toxicity.

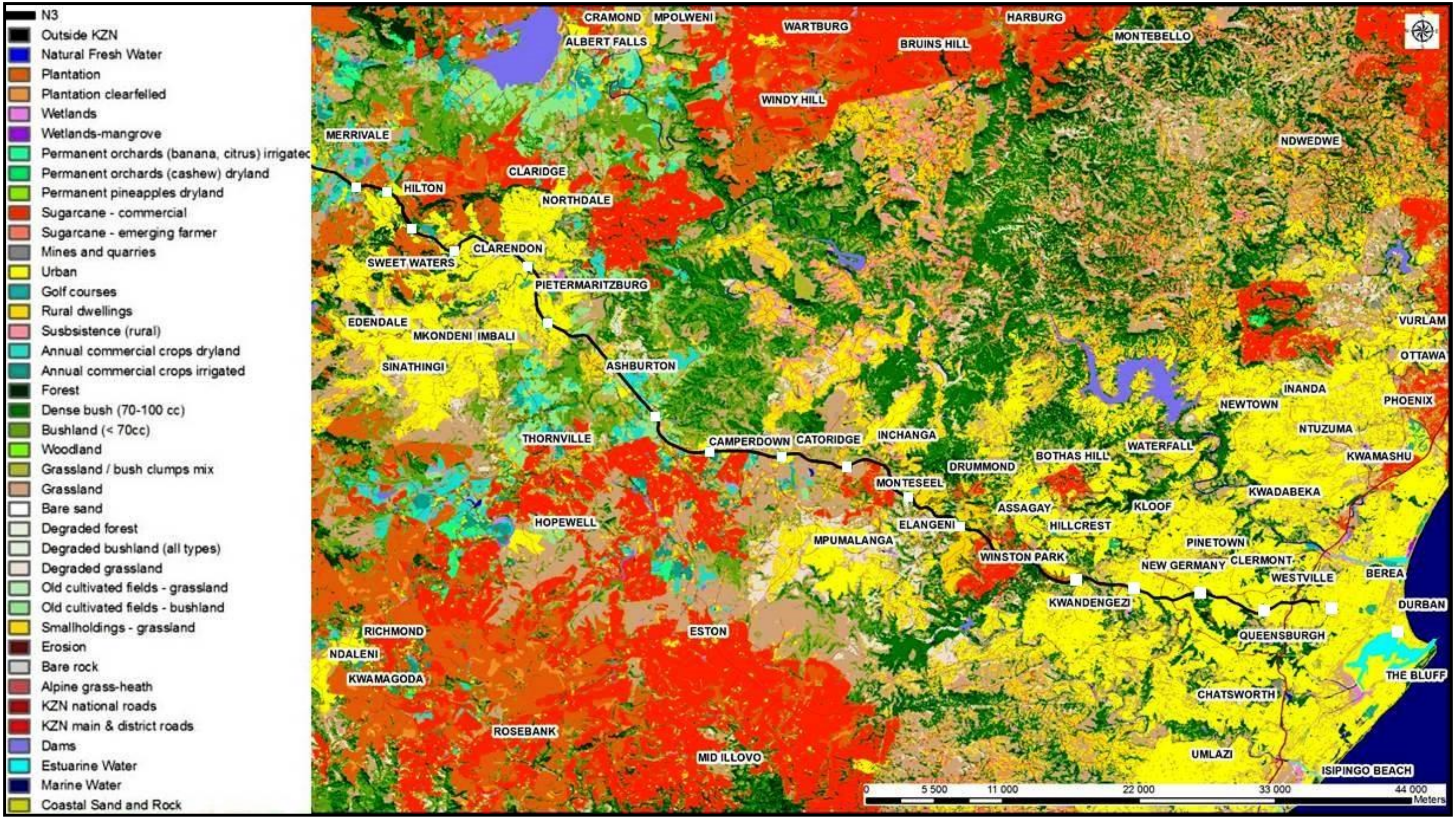

Figure 4.6: Land use map of the study area

4.2.3 Analysis of toxic metals (As, Cd and Pb) in soil samples collected across the South African National Road (N3)

The analysis of soil samples collected from 20 sites across the N3 and three distances away from the main road (one metre away from the roadside, ten metres away from the first point and ten metres away from the second point) will be discussed hereunder.

Previous studies on trace metal concentrations of vehicular emissions have shown Cu, Cd, Ni, Pb and Zn to decrease with distance away from the roadside (Joshi et al, 2010; Pagotto et al, 2001). Therefore, As, Cd and Pb, being the most toxic trace metals analysed in this study, will be analysed to determine the effects on concentration with regards to distance away from the road.

Table 4.7: Guidelines for maximum permissible levels of toxic metals (arsenic, cadmium and lead) in soil (mg kg^{-1})

	EU[a]	USA[b]	Germany[c]	Australia & New Zealand[a]	South Africa 1991[d]	South Africa 1997[e]	South Africa 2007[f]	This Study
As	-	21	-	20	2	2	2	2.32
Cd	1-3	20	3	3	2	2	2	0.77
Pb	50-300	150	300	300	56	66	56	118.93

[a] - McLaughlin et al (1999), [b] – United States, Environmental Protection Agency (1995), [c] - Adriano (2001), [d] - National Department of Health & Population Development (1991), [e] – Water Research Council, South Africa (1997), [f] - Herselman (2007)

The maximum acceptable limit for Pb in South African soils is 56 mg kg^{-1} (Table 4.7); only five of the 20 sites (Durban Harbour, Drummond, Inchanga, Cato-Ridge and Montrose) had Pb concentrations below this limit at D1 (1 m away from the roadside) (Figure 4.7). Herselman (2007) found a high natural total concentration of Pb in South African soils which would contribute to higher Pb concentrations in soil compared to other landscapes of the world. The mean world concentration for Pb in bedrock shale is 23 and sandstone is 10 (Table 4.4).

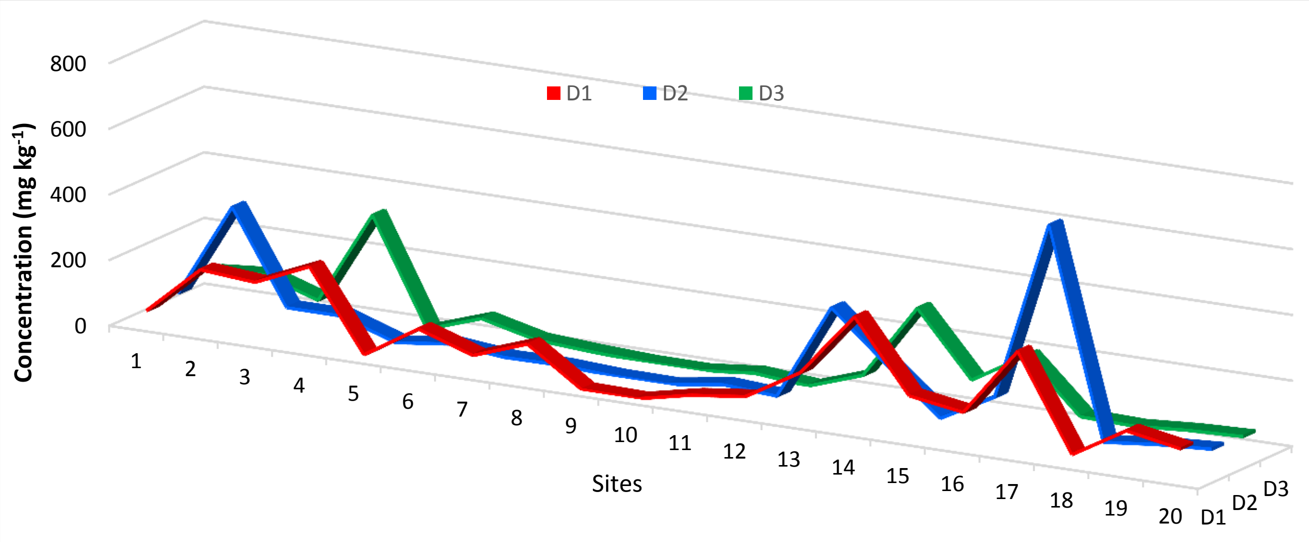

Figure 4.7: Concentration of lead (Pb) in soil samples collected along the South African National Road (N3) with distance away from the roadside (D1 - one metre away from the roadside, D2 - ten metres away from D1 and D3 - ten metres away from D2)

Sites - 1. Durban Harbour, 2. Durban CBD, 3. Westville, 4. Pinetown, 5. Marianhill, 6. Marianhill Toll, 7. Hillcrest, 8. Shongweni, 9. Drummond, 10. Inchanga, 11. Cato-Ridge, 12. Camperdown, 13. Lynfield Park, 14. Ashburton, 15. Scottsville, 16. Pietermaritzburg, 17. Town Bush, 18. Montrose, 19. Hilton, 20. Cedara

In terms of concentrations of trace metals in the soil with distance away from the roadside, the results show average Pb concentrations from samples closest to the road (D1) to be 118.93 mg kg^{-1}, 11 metres away from the road (D2) to be 99.40 mg kg^{-1} and 21 m away from the road (D3) to be 71.83 mg kg^{-1}. Typically soil Pb concentrations decrease with an increase in distance from the roadside.

High soil Pb concentrations close to the roadside (1 m away) are evident in the Ashburton and Mkondeni areas (Site 14) due to high industrial activities and truck depots. The emerging rural and small holding land uses in the area (Figure 4.6) could possibly be at risk as subsistence crops grown in contaminated soils could absorb high levels of Pb which may result in plant, human and animal toxicities.

Lead concentrations spike 11 m away from the roadside at Site 2 (Durban CBD), 13 (Lynfield Park) and 17 (Town Bush). Samples from Durban CBD were collected closer to the Spaghetti Junction, near Berea. This is a high traffic zone, with many on- and off-ramps and start-stop conditions for vehicles, which in turn, has the potential for higher emissions from different directions. High Pb concentrations at Lynfield Park are possibly due to leaching of fertilisers from agricultural activities in the vicinity and a rock quarrying mine and industrial activities very close to the N3 (Figure 4.6). High Pb concentrations at Town Bush or at the foot of Town Hill could be due to engine strain on vehicles and trucks to power up a steep hill, excessive breaking downhill and storm water run-off of herbicides, pesticides and fertilisers from plantations in the vicinity (Figure 4.6) which are carried further away from the roadside.

Lead concentrations spike 21 m away from the roadside at Site 4 (Pinetown) and 16 (Pietermaritzburg). Pinetown is a high industrial activity zone with high trucking activities. Pietermaritzburg is the capital and second largest city in KwaZulu-Natal. It is a regionally important industrial hub and the main economic hub of the UMgungundlovu District Municipality.

Areas with Pb toxicity are to be rehabilitated to a concentration of 20 mg kg^{-1} in all land uses and 100 mg kg^{-1} for the protection of ecosystem health in accordance with NEM: WA in South Africa. This indicates high Pb concentrations along the N3.

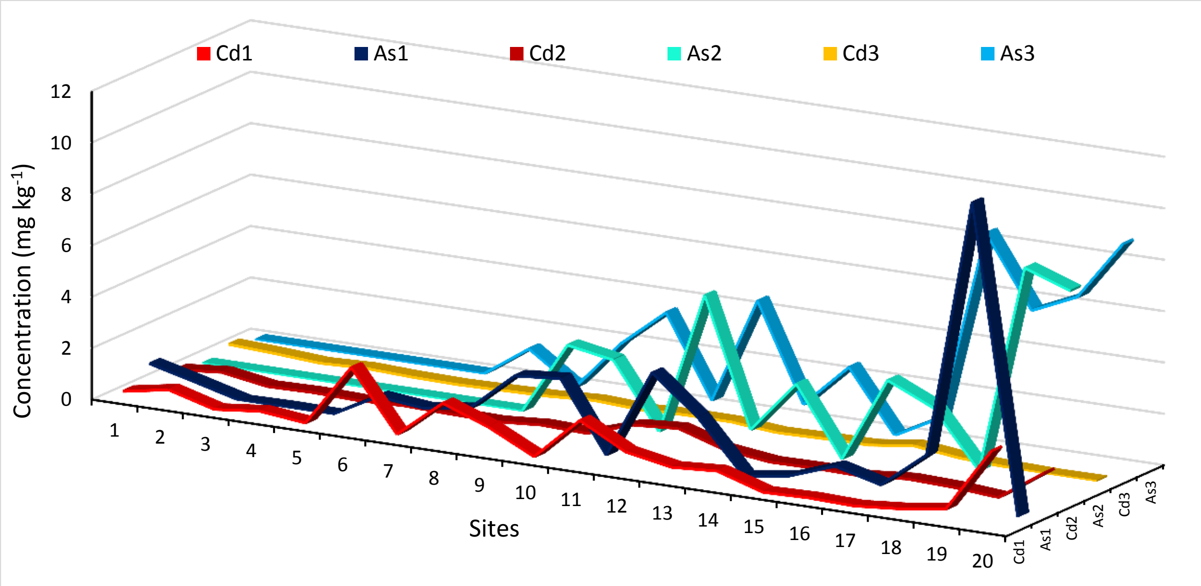

Figure 4.8: Concentration of arsenic (As) and cadmium (Cd) in soil samples collected along the South African National Road (N3) with distance away from roadside ((D1 - one metre away from the roadside, D2 - ten metres away from D1 and D3 - ten metres away from D2)

Sites - 1. Durban Harbour, 2. Durban CBD, 3. Westville, 4. Pinetown, 5. Marianhill, 6. Marianhill Toll, 7. Hillcrest, 8. Shongweni, 9. Drummond, 10. Inchanga, 11. Cato-Ridge, 12. Camperdown, 13. Lynfield Park, 14. Ashburton, 15. Scottsville, 16. Pietermaritzburg, 17. Town Bush, 18. Montrose, 19. Hilton, 20. Cedara

The maximum acceptable limit for As in South African soils is 2 mg kg^{-1} (Table 4.7); five of the 20 sites (Drummond, Inchanga, Camperdown, Lynfield Park and Hilton) had As concentrations above this limit at D1 (1 m away from the roadside) (Figure 4.8). In terms of concentrations of trace metals in the soil with distance away from the roadside, the results show average As concentrations from samples closest to the road (D1) to be 1.54 mg kg^{-1}, 11 metres away from the road (D2) to be 1.85 mg kg^{-1} and 21 m away from the road (D3) to be 2.25 mg kg^{-1}. It is clear from the results that soil As concentrations increase with an increase in distance from the roadside.

Arsenic concentrations spiked at Sites 12 (Camperdown), 14 (Ashburton), 19 (Hilton) and 20 (Cedara). The high concentrations of As at Hilton and Cedara could be due to forestry, plantations and agricultural practices (fertilisers, pesticides and herbicides) in close proximity to the sample points (Figure 4.6). Atafar et al (2010) found fertilisers used in agricultural practices to cause dramatic spikes in As, Cd and Pb concentrations in soils. Areas with As toxicity are to be rehabilitated to a concentration of 5.8 mg kg^{-1} in all land uses and 580 mg kg^{-1} for the protection of ecosystem health in accordance with NEM: WA, South Africa.

The maximum acceptable limit for Cd in South African soils is 2 mg kg^{-1} (Table 4.7). With the exception of Site 6 (Marianhill Toll, 2.8 mg kg^{-1}) and 20 (Cedara, 3.0 mg kg^{-1}), all soil samples were below this limit. High soil Cd at Marianhill Toll Plaza could be due to traffic density and the impacts thereof whilst high soil Cd at Cedara could be due to agricultural practices in the area (Atafar et al, 2010) and close proximity to a freeway interchange with moderate increase in traffic (not too high as the region is not densely populated) (Figure 4.6).

Areas with Cd toxicity are to be rehabilitated to a concentration of 7.5 mg kg^{-1} in all land uses and 37 mg kg^{-1} for the protection of ecosystem health in accordance with NEM: WA, South Africa.

4.3 Soil Contamination

Geoaccumulation indices (I_{geo}) and enrichment factors (EFs) were calculated for trace metals As, Cd, Co, Cr, Cu, Ni, Pb and Zn to evaluate for soil contamination (Table 4.8).

Geoaccumulation indices and EFs for Co indicate soil to be uncontaminated with background concentrations. Geoaccumulation indices and EFs for Cr indicate soil to be uncontaminated with minimal enrichment. Geoaccumulation indices for Cu indicate soil to be uncontaminated to moderately contaminated with Sites 2 (Durban CBD) and 6 (Marianhill Toll) being heavily contaminated. Enrichment factors indicate background concentrations and minimal enrichment with Sites 8, 9, 13, 14, 16, 17, 19 and 20 being moderately enriched and Sites 2 (Durban CBD) and 6 (Marianhill Toll) being significantly enriched. Geoaccumulation indices and EFs for Ni indicate soil to be uncontaminated with background concentrations. Geoaccumulation indices for Zn indicate soil to be uncontaminated to moderately contaminated with Sites 2 (Durban) and 17 (Town Bush) being moderately to heavily contaminated. Enrichment factors indicate background concentrations and minimal enrichment with Sites 4, 8, 13, 14, 15, 16, 17 and 20 being moderately enriched and Sites 2 (Durban CBD) and 12 (Camperdown) being significantly enriched.

For the toxic metals, I_{geo} values for Pb indicate soil to be uncontaminated to moderately contaminated with Sites 14 (Ashburton) and 17 (Town Bush) being moderately to heavily contaminated. Enrichment factors indicate background concentrations with minimal enrichment with Sites 3, 15, 16, 19 and 20 being moderately enriched and Sites 2 (Durban CBD), 14 (Ashburton) and 17 (Town Bush) being significantly enriched. Geoaccumulation indices for Cd indicate soil to be uncontaminated and moderately contaminated with Sites 6, 8, 11, 12 and 20 being moderately to heavily contaminated. Enrichment factors indicate background concentrations and minimal enrichment with Sites 2, 8, 9, 12 and 13 being moderately enriched and Site 6 (Marianhill Toll), 11 (Cato-Ridge) and 20 (Cedara) being significantly enriched. Geoaccumulation indices for As indicate uncontaminated soils; EF results indicate background concentrations and minimal enrichment.

Table 4.8: Geoaccumulation index (I_{geo}) and enrichment factors (EF) for each element from the twenty sites along the South African National Road (N3)

Sites	As		Cd		Co		Cr		Cu		Ni		Pb		Zn	
	EF	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}	**EF**	I_{geo}
1	0.1	-3.0	1.9	0.9	0.2	-2.3	1.1	0.1	1.6	0.6	0.2	-2.6	1.9	0.9	1.9	0.9
2	0.1	-3.9	2.8	1.5	0.4	-1.4	1.6	0.6	**11.5**	**3.5**	0.4	-1.2	**6.5**	**2.7**	**5.4**	**2.4**
3	0.0	ND	0.8	-0.4	0.1	-3.3	0.3	-1.6	0.6	-0.8	0.1	-3.5	2.9	1.5	0.4	-1.2
4	0.0	-7.7	1.4	0.5	0.7	-0.6	0.7	-0.6	**6.6**	**2.7**	0.3	-1.9	**6.6**	**2.7**	3.1	1.6
5	0.0	ND	0.7	-0.5	0.0	-4.6	0.1	-2.9	0.3	-1.8	0.0	-5.5	0.2	-2.6	0.1	-3.7
6	0.1	-2.9	**6.3**	**2.6**	0.5	-1.1	1.1	0.1	**14.5**	**3.8**	0.3	-2.0	2.0	1.0	0.2	-2.2
7	0.1	-2.8	1.0	-0.1	0.1	-3.6	0.4	-1.4	0.3	-1.7	0.1	-4.0	0.9	-0.2	0.4	-1.2
8	0.1	-2.8	4.3	**2.1**	0.2	-2.6	0.5	-1.1	2.2	1.1	0.1	-3.0	1.4	0.5	2.1	1.1
9	0.3	-1.5	3.4	1.7	0.0	-4.9	0.0	-6.0	2.0	0.9	0.0	-5.8	0.1	-4.2	1.6	0.6
10	0.4	-1.3	1.0	0.0	0.0	-8.3	0.0	-6.0	1.5	0.6	0.0	-7.4	0.0	-8.7	1.5	0.6
11	0.4	-1.2	**6.2**	**2.6**	0.4	-1.4	0.1	-4.3	1.1	0.1	0.0	-4.8	0.8	-0.3	1.6	0.6
12	0.6	-0.7	4.4	**2.1**	0.6	-0.7	0.0	-4.4	0.1	-3.3	0.1	-4.3	0.8	-0.4	**5.8**	**2.5**
13	0.2	-2.6	2.0	1.0	0.5	-1.1	0.7	-0.4	2.0	1.0	0.2	-2.2	**5.4**	**2.4**	2.5	1.3
14	0.4	-1.5	1.9	0.9	0.4	-1.3	0.7	-0.4	2.7	1.4	0.4	-1.5	**8.3**	**3.0**	2.4	1.3
15	0.0	-4.7	0.7	-0.5	0.6	-0.8	1.0	0.0	1.7	0.8	0.3	-1.9	2.6	1.4	2.0	1.0
16	0.2	-2.0	1.3	0.3	0.6	-0.7	1.2	0.2	2.4	1.3	0.4	-1.3	4.3	**2.1**	3.9	1.9
17	0.5	-0.9	1.0	0.0	0.4	-1.2	1.7	0.7	2.0	1.0	0.4	-1.3	**10.5**	**3.4**	4.2	2.1
18	0.4	-1.4	1.1	0.1	0.4	-1.4	1.1	0.1	0.7	-0.5	0.2	-2.1	0.8	-0.3	0.8	-0.4
19	1.3	0.3	1.2	0.3	0.6	-0.7	1.6	0.6	2.2	1.1	0.4	-1.5	2.2	1.1	1.5	0.5
20	1.2	0.2	**9.7**	**3.3**	0.6	-0.8	2.0	1.0	3.5	1.8	0.4	-1.4	2.0	1.0	2.7	1.4

*** High enrichment or contamination**

Sites - 1. Durban Harbour, 2. Durban CBD, 3. Westville, 4. Pinetown, 5. Marianhill, 6. Marianhill Toll, 7. Hillcrest, 8. Shongweni, 9. Drummond, 10. Inchanga, 11. Cato-Ridge, 12. Camperdown, 13. Lynfield Park, 14. Ashburton, 15. Scottsville, 16. Pietermaritzburg, 17. Town Bush, 18. Montrose, 19. Hilton, 20. Cedara

4.4 Statistical Analysis

Principal component analysis (PCA) is used to identify the source of metals in soil and is an effective tool to define anthropogenic or lithogenic sources of metals. Both the eigenvalues and percentage of variance calculated by PCA are shown in Table 4.9. Three principal components were extracted.

Table 4.9: Eigenvalues and percentage of variance calculated by principal component analysis

Total Variance Explained						
Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.56	46.335	46.335	3.286	27.382	27.382
2	2.23	18.584	64.918	3.225	26.872	54.254
3	1.576	13.131	78.05	2.855	23.796	78.05

Principal component 1, with high loadings of Mg, Co, Ni, Zn and Pb, explained 27.4% of the total variation (78.1%). Principal component 2, with high loading of Mn, Ca, Cu and Cd, explained 26.9% of the total variation and principal component 3, with high loadings of Fe, Cr and As, explained 23.8% of the total variation (Figure 4.9).

Lead in the environment results from industrial emissions, vehicle exhaust emissions and paint including road-marking paint containing Pb (Bigdeli and Seilsepour, 2008). The breakdown of tyres from vehicles introduces Pb into the environment and Pb is also used in other vehicle manufacturing processes (Giannouli et al, 2007). Elevated concentrations of Zn in the environment are due to run-off from galvanised steel and surfaces painted with zinc-containing paints while most of the Zn enhancement may be connected to the traffic sector (Gołuchowska and Strzyszcz, 1999). The use of ZnO in rubber of tyres is also a major source of Zn in the environment (Hjortenkrans et al, 2006). Extensive distribution of Ni has occurred due to anthropogenic activities such as the burning of fossil fuels in industrial and other processes such as vehicle emissions (Department of Environmental Affairs, 2010). Cobalt is used in car batteries and is critical to the proper functioning of electrical cars. Magnesium is preferred to Al for automotive use. When alloyed, Mg has the highest strength-to-weight ratio of all the structural materials (Total Materia, 2005). Therefore, vehicular emissions appear to be a possible common source for trace metals in the environment due to principal component 1.

High levels of Cd in the environment is usually attributed to fertilisers in agriculture, smelting of metals in industries and exposure to untreated sewerage in close proximity to waste water treatment works and unmaintained sewerage pipelines (Gulten, 2011). Cadmium is also found in many processes involved in the manufacturing of vehicles (Lohse, 2001). Copper emission sources are usually industrial processing such as refineries and smelters (Department of Environmental Affairs, 2010). Copper enhancement in soils may be connected to the traffic sector as Cu is used in brake linings (Hjortenkrans et al, 2006). The major anthropogenic sources of environmental Mn include municipal waste water discharges, sewage sludge, mining and mineral processing, emissions from alloys, steel and Fe production, combustion of fossil fuels and emissions from the combustion of fuel additives. Therefore, emissions given off by industries in the region and possibly by vehicles in the wear and tear processes appear to be possible common sources for trace metals in the environment due to principal component 2.

Arsenic is used in a few commercial and industrial products for example preservatives and fertilisers (Saldivar and Soto, 2014). Industrial processes frequently produce Cr which may serve as an indicator of contamination within the environment due to Cr leaching into the soil (Persson and Kucera, 2001). Iron is also commonly used in industrial and commercial activities. Therefore, industrial and commercial activities in the region and possibly contaminated groundwater appear to be possible common sources for trace metals in the environment due to principal component 3.

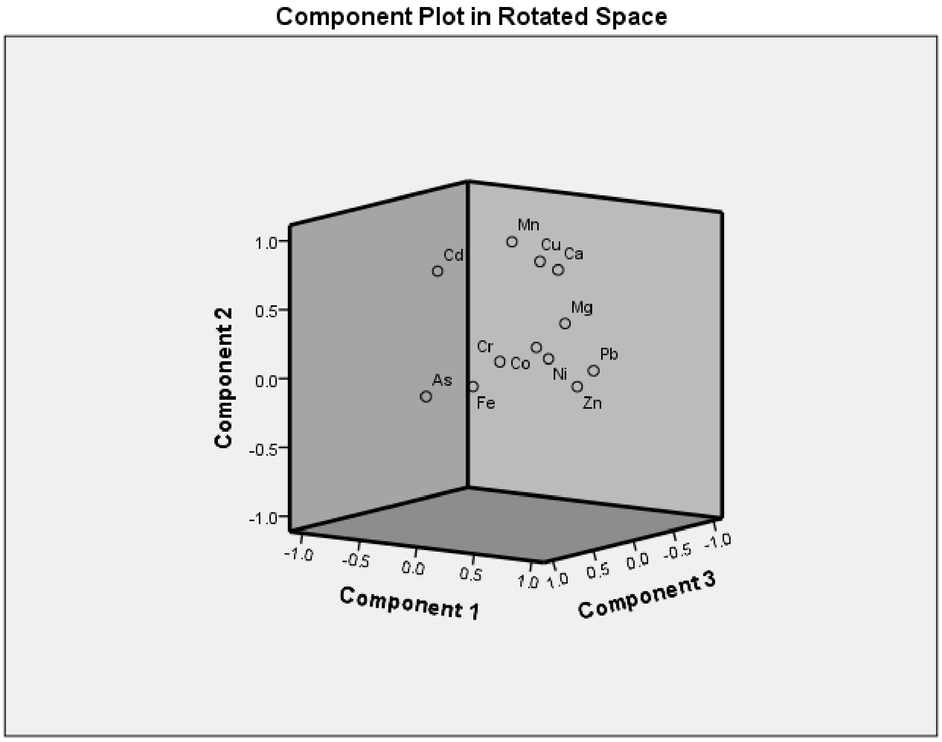

Figure 4.9: Component plot in rotated space

CHAPTER 5 : GEOGRAPHIC INFORMATION SYSTEM (GIS) ANALYSIS OF TOXIC TRACE ELEMENTS, LEAD AND CADMIUM, WITHIN THE STUDY AREA

5.1 Introduction

Mapping the spatial distribution of toxic trace metals in the soil is essential for accurately estimating areas which have been contaminated. These areas require attention and remediation from the responsible bodies of government, therefore a tool such as geographic information system (GIS) and the use of geostatistics and interpolation provides effective methods to quantify and depict the impact on soil in the specified area in a way that specialists across many fields of academia will easily understand. This will support effective and efficient decision-making processes (Burrough & McDonnell, 2015).

Lead and Cd are two of the most toxic trace metals that dominate vehicular emissions. These metals form part of the materials and manufacturing processes of vehicles and contribute to the total tail pipe emissions. Lead and Cd have been analysed via chemical analysis in this study; the GIS analysis was therefore conducted on the spatial data of these two toxic trace metals. The objective of determining the spatial distributions of the two major toxic heavy metals, Pb and Cd, in the roadside verges by using GIS as an analytical tool was determined in this chapter.

5.2 Results and Discussion

Interpolated distribution maps for Cd and Pb, with a 200 m buffer of the N3, with analysis of possible contributors to high emissions are depicted and discussed below.

Table 5.1: Lead and cadmium concentrations used for interpolation

Site	Town	Pb concentrations	Cd concentrations
1	Durban Harbour	59.61±18.11	0.28±0.04
2	Durban CBD	210.37±124.81	0.42±0.21
3	Westville	94.20±76.02	0.12±0.02
4	Pinetown	212.92±136.65	0.21±0.10
5	Marianhill	5.51±3.97	0.11±0.03
6	Marianhill Toll	65.70±44.68	0.93±1.42
7	Hillcrest	28.48±25.71	0.14±0.07
8	Shongweni	45.26±62.07	0.64±0.92
9	Drummond	1.82±1.03	0.50±0.47
10	Inchanga	0.08±0.06	0.15±0.01
11	Cato-Ridge	26.14±9.35	0.93±0.83
12	Camperdown	24.66±28.18	0.65±0.39
13	Lynfield Park	173.87±125.66	0.30±0.25
14	Ashburton	266.27±95.59	0.28±0.33
15	Scottsville	83.23±56.85	0.11±0.01
16	Pietermaritzburg	137.41±48.61	0.19±0.13
17	Town Bush	337.13±313.85	0.15±0.07
18	Montrose	27.23±3.08	0.16±0.11
19	Hilton	69.50±48.87	0.18±0.28
20	Cedara	65.00±26.82	1.44±1.52

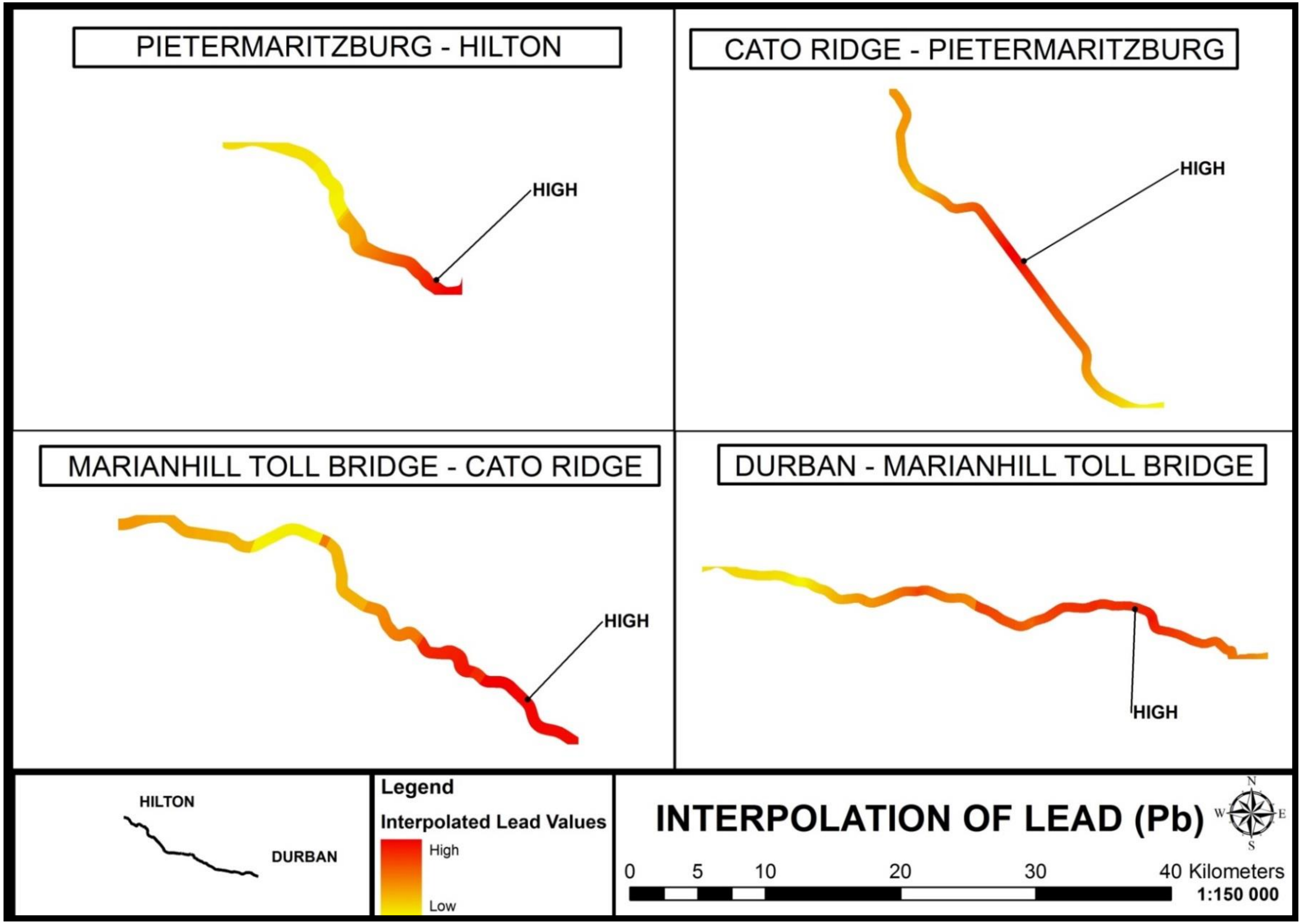

Figure 5.1: Interpolation of lead (Pb)

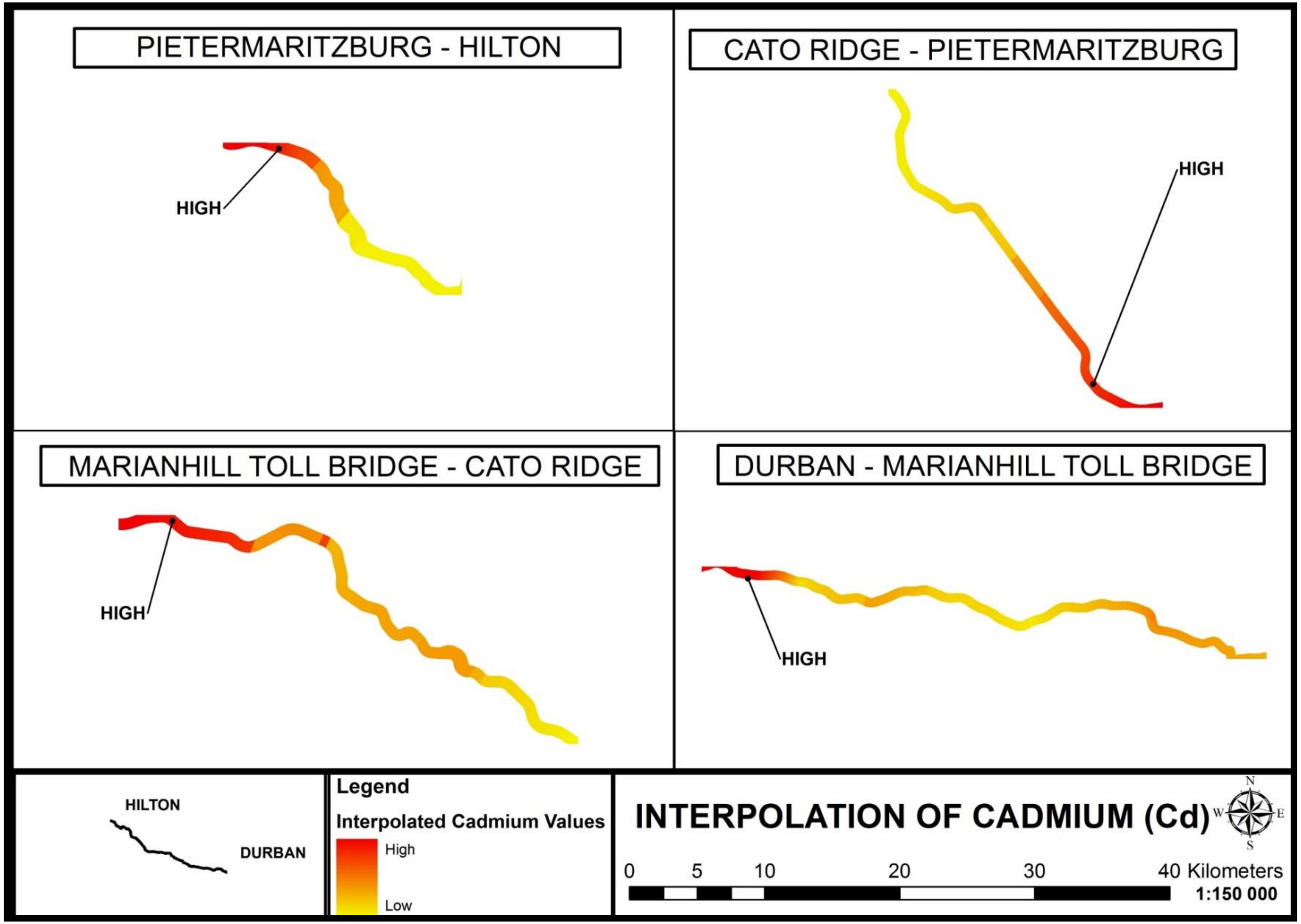

Figure 5.2: Interpolation of cadmium (Cd)

Mico et al (2006), Lu et al (2007) and Facchinelli et al (2001) found high Pb and Cd concentrations in soil to be predominantly due to anthropogenic sources such as the settling of vehicle emissions and the runoff from the use of fertilisers used in agricultural practices.

In this study, Pb concentrations spike closer to the Spaghetti Junction near Westville and Berea, due to high traffic density and an increase in start-stop conditions for vehicles, which in turn, has the potential for higher emissions (Figure 5.1). A major spike is evident in the vicinity of Pinetown due to industrial activities and higher trucking activities. High Pb concentrations are seen till Hillcrest due to atmospheric, water and other forms of pollution, transportation from the toll area and from industrial areas of Pinetown and its surrounding. Extremely high Pb levels are evident in the Ashburton and Mkondeni areas due to high industrial activities and truck depots; the prominence of rural and small holding land uses in the area could be at risk; crops from subsistence farming could absorb high levels of Pb and traverse the food chain.

High Pb concentrations are evident at Lynfield Park, which are possibly due to leaching of fertilisers from agricultural activities in the vicinity and a rock quarrying mine and industrial activities near the N3. High Pb levels at the foot of Town Hill which is at the bottom of a steep hill could be due to engine strain on vehicles and trucks, excessive breaking down and storm water run-off of herbicides, pesticides and fertilisers from plantations in the vicinity.

Golmohammed and Rezapour (2014) stated that the concentrations and dynamics of soil trace metals in natural ecosystems are dependent on the lithology of parent rock as well as topography and geopedological processes. When concentrations of Pb are overlaid onto a geological map, there is an apparent correlation between concentrations in the soil and the lithology of parent rock. However, further analysis of the composition of parent rock is required to accurately predict a correlation between the findings and the natural content of Pb within the soil which is related to the trace metal composition of the parent rock. Herselman (2007) stated that there is a high natural total concentration of Pb in South African soils, therefore Pb concentrations would appear higher than other landscapes of the world. The trend evident from the interpolated distribution maps of Pb indicates high concentrations in densely populated areas and the immediate surrounding areas. This indicates that high Pb concentrations are linked to anthropogenic causes even though there is a high natural Pb presence in the soils of South Africa.

Cadmium concentrations spike in Pinetown which is an industrial region and towards Marianhill Toll due to stop and go emissions from vehicles (Figure 5.2). Cadmium concentrations are generally high from the tollgate to Cato Ridge however, concentrations spike at Cato Ridge due to industrial activities in the area. High Cd concentrations continue till Camperdown from Cato Ridge due to industrial activities. Extremely high Cd levels are evident in Hilton and Cedara due to a truck weigh bridge in the vicinity of Hilton which increases vehicle stop-start emissions as well as agricultural practices and forestry in the vicinity. Forest ecosystems are usually characterised as being good receptors of heavy metals which remain trapped in the canopy via air transportation of soil and dust and is leached into the soil profile via rainfall and run-off.

Natural Cd concentrations in parent rock are usually below the threshold. It is evident in the interpolated distribution maps that high Cd concentrations are not correlating with high Pb concentrations, which therefore indicates different sources of these toxic elements and that the deposition characteristics of the two metals are different in relation to the natural environment. This was also seen by the statistical analysis (PCA). Concentrations of Pb and Cd in the study area are directly impacted by the topography and geopedological processes of the area. However, accurate correlations cannot be determined due to the scope of the study.

CHAPTER 6 : CONCLUSIONS AND RECOMMENDATIONS

The current research was aimed at assessing the impact of vehicle pollution in the surrounding environment of the South African National Road (N3) between Durban and Hilton by investigating the elemental concentrations in the leaves of *Bidens pilosa* and surrounding soils.

6.1 Conclusions

The findings for micro-elements (Co, Cr, Cu, Fe, Mn and Ni) in the plant are consistent with other studies conducted in South Africa. However, when compared to acceptable limits in vegetation Cu, Cr, Fe, Mn, Ni and Zn are above the acceptable limits with Zn being considerably higher. For the toxic metals (As, Cd and Pb), levels were higher than acceptable limits, with Cd being significantly high and Pb being extremely high.

The findings for soil indicate all concentrations of micro-elements were lower than the acceptable limits. For the toxic metals, As concentrations were marginally above the acceptable limit. Cadmium concentrations were below the acceptable limit at most sites. Lead concentrations were extremely high and above the acceptable limits across the study area. For soil contamination and enrichment analysis, the findings show uncontaminated soils for micro-elements with Cu and Zn showing moderate to heavy contamination in some areas. Also, results for micro-elements showed background concentrations, minimal enrichment and moderate enrichment across most sites with Cu and Zn having significant enrichment in some areas.

For the toxic element, As, the results indicate soils to be uncontaminated to moderately contaminated with background concentrations and minimal enrichment. For the toxic element, Cd, the results show soils to be moderately to heavily contaminated in some areas and uncontaminated and moderately contaminated in the rest. Enrichment results indicated background concentrations, minimal enrichment and moderate enrichment across the sample area with specific areas being significantly enriched. For the toxic element, Pb, the results show soils to be moderately to heavily contaminated in some areas and uncontaminated and moderately contaminated in the rest. Enrichment results show background concentrations, minimal enrichment and moderate enrichment with some areas being significantly enriched at a higher frequency than the other toxic elements.

The results show *Bidens pilosa* to accumulate the toxic metals Pb and Cd, but not As. This trend could be investigated for phytoremediation of soils with Pb and Cd toxicities. Statistical analyses indicated common sources for different metals. The sources could possibly be vehicle tail pipe emissions, wear and tear of vehicles, agricultural practices, commercial and industrial activities and contaminated groundwater.

Success in the reduction of accumulated toxic metals such as Pb and Cd in contaminated environments is possible. The advent of industrialisation, the transport sector, commercial agricultural practices and forestry have contributed the most to the pollution of the surrounding environments by toxic trace metals. The accumulation of these toxic trace metals could therefore be reduced, going into the future, by reducing the impacts by the sources via technological advancements in environmentally responsible forms of practises in the specific industry. Further to reducing future impacts, specific sectors should be required, via policy on social and environmental responsibility, to rehabilitate the impacts of the past by their specific industrial and commercial sector via proper implementation of the National

Environmental Waste Act (NEM: WA) which provides screening values in which contaminated land should be rehabilitated to a specified concentration of trace metals possibly via hyper-accumulator plant species as discussed and a plethora of other natural and technically engineered methods.

A health risk assessment for humans and animals, via food sources with metal contamination, may also be calculated with the data that has been obtained in this study.

The process of rehabilitation and reducing the concentration of toxic heavy metals in contaminated soils is very difficult and complex, such as in many areas, heavy metals may still be accumulated by plants and subsequently move into the food chain for many decades. However, via holistic thinking in terms of the technical, social and monetary requirements and a responsible industrial and commercial sector backed by proper policy and implementation by government and the private sector, reduction of past and future impacts to acceptable concentrations are achievable.

It is evident from the findings of interpolation that natural factors such as slope with regards to storm water run-off and other factors such as vehicle emissions due to engine strain, anthropogenic factors such as effluents from industrial areas, agricultural and forestry practices, and high traffic density, primarily contribute to high Pb and Cd concentrations along the N3. Areas of high Pb and Cd concentrations do not correlate as is evident in the interpolated maps (and seen by PCA) indicating different emission sources. The Kriging interpolation study depicted and demonstrated the spatial diffusion of both Cd and Pb concentrations throughout the study area of the N3 and a conclusion that Pb and Cd pollution dominate different regions of the study area can be determined due to the above-mentioned factors.

This study has demonstrated that vehicular emissions are the primary route of exposure to toxic heavy metals along transportation routes, such as the N3. However, high concentrations of toxic metals and other trace metals found in roadside soils are not solely due to vehicular emissions but also due to a combination of industrial, agricultural and social impacts.

6.2 Recommendations for Further Study

- Trace metal analysis of soils found along the South African National Road (N3) from Hilton to Johannesburg to complete the continuous route taken by logistics companies from the main harbour to the economic hub of South Africa.
- Potential usage of *Bidens pilosa* as a means for phytoremediation in South Africa.

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