Cape Peninsula
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Accumulation of lead and manganese in soil along the N1 highway in the City of Cape Town after the banning of leaded petrol in South Africa

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DECLARATION

I, Emmanuel Fon Mbakwa, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

ABSTRACT

Soil contamination by metals is a serious environmental problem that has significant implications for human health. Roadside soils have been shown to have considerable contamination due to depositions of metals by vehicles. Metal pollution poses significant environmental concerns because most metals are not biodegradable and often have long half-lives, thus predicating far reaching effects on biological systems, including the soil.

Unleaded petrol has been available in South Africa since 1996. The conversion from leaded to unleaded petrol has been a slow process. Leaded petrol has been totally phased out since January 2006. The manganese-containing fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) that was introduced to automobile fuel formulae as an octane boosting and “anti-knock” agent, to replace or reduce the lead content in petrol, was officially approved in some developed countries.

Despite the fact that metal contamination of soil has long been known, few studies have been carried out into its vertical distribution in the soil.

The objectives of this investigation were: firstly, to assess the accumulation of lead and manganese in soil along the N1 highway; secondly, to determine the vertical distribution of lead and manganese in soil along the N1 highway; and thirdly, to compare the concentrations of lead and manganese in soil along the N1 highway, before and after the banning of leaded petrol in South Africa.

Six soil samples were taken at each site approximately two meters from the road verges and at a depth of approximately 0-2cm of surface soil. The sampling period commenced on the 16th of February 2011 and ended on the 28th of December 2011. Once-off soil samples were also collected at sites 1, 5 and 6 at depths of 0-2cm, 30cm and 60cm, respectively. Samples were digested with 10 ml 55% nitric acid. Lead and manganese concentrations were determined by using Inductively Coupled Plasma Mass Spectrophotometer (ICP–MS).

The mean concentrations of lead found in the roadside soils of the N1 highway ranged between 7.32mg/kg and 2068.31mg/kg and these were of high concentrations when compared to studies done in other countries.

Results from the vertical distribution of lead investigation showed that lead concentrations ranged from 52.72mg/kg to 215.94mg/kg at surface level, from 15.80mg/kg to 164mg/kg at a depth of 30cm and from 14.06mg/kg to 216.07mg/kg at a depth of 60cm from the surface. It was also shown that there is a positive correlation between lead concentration and the amount of organic content (although not statistical), concluding that as the amount of organic content increases lead concentrations also increase.

The mean manganese concentrations found in the roadside soils of the N1 ranged between 12.17mg/kg and 221.47mg/kg. The levels of manganese in the soil were found to be relatively low when compared to other studies an indication of mild to low metal contamination of the sampled soils.

Results from the vertical distribution of manganese concentrations showed that concentrations in the soil ranged from 39.23 mg/kg to 63.32 mg/kg at surface level, from 14.4mg/kg to 310.86mg/kg for depths of up to 30cm, and from 4.42mg/kg to 343.96mg/kg for depths of up to 60cm.

No relationships of manganese levels in the soil were found at any of the sites when sites were compared prior to the banning of lead and after the banning of lead despite the increased traffic volumes and, thus, increased MMT usage over the years, indicating that manganese contribution from MMT is very low and does not significantly increase soil contamination along the N1 highway. However, further investigations are needed into the future to monitor manganese contamination that may possibly occur.

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DEDICATION

This thesis is dedicated to my beloved parents Mr and Mrs Mbakwa.

DEFINITION OF TERMS

MMT: Methylcyclopentadienyl manganese tricarbonyl

NICNAS: National Industrial Chemicals Notification and Assessment Scheme

TEL: Tetraethyl lead

$CaCO_3$: Calcium carbonate

Mn: Manganese

Pb: Lead

OM: Organic matter

ICP-MS: Inductively Coupled Plasma - Mass Spectrometry

USEPA: United States Environmental Protection Agency

WHO: World Health Organization

CBD: Central Business District

EEA: European Environment Agency

ATSDR: Agency for Toxic Substances and Disease Registry

DEAT: Department of Environmental Affairs and Tourism

DME: Department of minerals and Energy

CCT: City of Cape Town

CCME: Canadian Council of Ministers of the Environment

CSBEP: Criticality Safety Benchmark Evaluation Project

NSF: National Science Foundation

Toxic: Able to cause injury to living organisms as a result of physicochemical interaction (Duffus et al., 2007).

Hazard: Set of inherent properties of a substance, mixture of substances, or a process involving substances that, under production, usage, or disposal conditions, make it capable of causing adverse effects to organisms or the environment, depending on the degree of *exposure*; in other words, it is a source of danger (Duffus et al., 2007).

Ecotoxicology: Study of the toxic effects of chemical and physical agents on all living organisms, especially on populations and communities within defined ecosystems; it includes transfer pathways of these agents and their interactions with the environment (Duffus et al., 2007).

Emission: The release of a substance from a source, including discharges to the wider environment (Online Oxford English Dictionary, 2013).

Leach: With reference to a soluble chemical or mineral, drain away from *soil*, ash, or similar material by the action of percolating liquid, especially rainwater (Online Oxford English Dictionary, 2013).

Exposure: Concentration, amount, or intensity of a particular physical or chemical agent or environmental agent that reaches the target population, organism, organ, tissue, or cell, usually expressed in numerical terms of concentration, duration, and frequency (for chemical agents and microorganisms) or intensity (for physical agents) (Duffus et al., 2007).

Half-life: Time required for the concentration of a reactant in a given reaction to reach a value that is the arithmetic mean of its initial and final (equilibrium) values. For a reactant that is entirely consumed, it is the time taken for the reactant concentration to fall to one-half of its initial value (Duffus et al., 2007).

Pollution: The Introduction of pollutants into a solid, liquid, or gaseous environmental medium or any undesirable modification of the composition of a solid, liquid, or gaseous environmental medium (Duffus et al., 2007).

Bioaccumulation: Progressive increase in the amount of a substance in an organism or part of an organism that occurs, because the rate of intake from all contributing sources and by all possible routes exceeds the organism’s ability to eliminate the substance from its body (Rand, 1995).

Bioconcentration: Process leading to a higher concentration of a substance in an organism than in environmental media to which it is exposed (Rand, 1995).

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CHAPTER ONE: INTRODUCTION

1.1) Soil pollution

The soil is a dynamic and complex system in which any changes in the physico-chemical characteristics would alter its metallic composition and other important, deterministic parameters such as pH, soil type and organic carbon content. Soil contamination by metals is a serious environmental problem that has significant implications for human health (Moore et al., 2009).

Roadside soils have been shown to have considerable contamination due to depositions of metals by vehicles (Harrison et al., 1981). There have been a number of studies on metal contamination in soils along major roads because of the severe health and environmental effects caused by metals (Turer and Maynard, 2003). The deposition of metals from vehicles and the relocation of metals to roadside surface soil by air and runoff water have led to considerable soil contamination (Viard et al., 2004; Nabuloa et al., 2006; Ogbonna and Okezie, 2011).

Metal pollution poses significant environmental concerns because metals are not degradable and often have long decay half-lives, thus predicating far reaching effects on biological systems, including the soil (Adeniyi, 1996; Ram et al., 2000). According to Adeniyi (1996) these metals also get accumulated when plants and crops cultivated in soil close to major roads are consumed by humans and animals, especially livestock, either directly or indirectly. This bioaccumulation may reach lethal levels (Wang and Demshar, 1992). With advanced technologies and an increase in the use of vehicles in Cape Town, soil contamination may be of significant environmental concern, which is likely to become more serious and more widespread in the near future. In a study done by Meng Ke (1995), it was reported that lead concentrations in soils are greater under heavy traffic than light traffic.

1.2) Metals

Chemists define metals as being elements that have a characteristic lustrous appearance, are good conductors of electricity, and generally enter chemical reactions as cations (Walker et al., 2003). Metals comprise 75% of the known elements and can form alloys with each other and with non-metals (Sparks, 2005). They have useful properties such as strength, malleability and conductivity of heat and electricity. Some metals exhibit magnetic properties and others are excellent conductors of electricity. Their chemical reactivity is diverse and their toxic effect on biological systems is even more diverse (El-Hinnawi and Hashmi, 1982). Many metals are essential to life, although they occur only in trace amounts in the body tissues.

Background values are often used to determine if soil has become polluted with undesirable substances. Soil with concentrations exceeding the local normal background values are then deemed contaminated. If the soil becomes so contaminated that it has an environmental impact, it is deemed polluted. As discussed by Tiller (1992) there is a continuum of soil metal concentrations from the natural or pristine state through to highly polluted soils. The level at which soil is deemed polluted therefore depends on the concentrations of accumulated metals. Background values for metals in soil are often assessed in terms of background values documented in rural soils. Thus, normal background values are obtained from soils with mildly elevated accumulation due to normal agricultural fertilization practices. The higher background concentrations of metals found in Australian rural soils (Tiller, 1992) often exceed those quoted for Dutch soils (Moen et al., 1986). Due to human activities, modern industrial development and the diversity and heterogeneity of soil, background values of elements in soil can only be a statistical value within a basic range, not a definite value (CSBEP, 1990). Soil may be the most important sink of metals and other pollutants. Metal contaminations are introduced into the soil environment through a variety of human activities, such as waste disposal, mining and smelting (Wu et al., 2006).

Surface soil around roadsides is usually contaminated with metals from vehicular emissions and other associated sources. Many studies show that the extent of contamination is related to the traffic volume and proximity to the highway (Motto et al., 1970; Wheeler and Rolfe, 1979; Rodriguez-Flores and Rodriguez-Castellon, 1982; Nabuloa et al., 2006; Rossini-Oliva and Fernandez Espinosa, 2007).

Metal contaminations from industrial activities are also often indicated in surface soil near the industries. Elevated levels of copper, zinc, lead, cadmium, nickel and iron have been detected near smelting works (Burkitt et al., 1972; Beavington, 1975). Also, high levels of cadmium, lead and zinc have been detected around zinc refineries (Kobayashi et al., 1973), while a high prevalence of lead and zinc has been observed around lead smelters and industries making anti-knock compounds for vehicle engines (Lee, 1972; Bolter et al., 1974).

In past studies an increase in metal concentrations with increasing traffic density indicated a relationship between traffic and metal loads in the soil (Olajire and Ayodele, 1997). Roadsides receive considerable amounts of traffic-generated pollutants. High concentrations of these metals are of great concern due to their potential toxicity and biomagnification potential (Ragan and Mast, 1990).

Metals are non-biodegradable and therefore persist for long periods in aquatic as well as terrestrial environments. They may be transported also through soils to reach groundwater, or may be taken up by plants, including agricultural crops (Boularbah et al., 2006). Metals are considered as one of the main pollutants responsible for environmental contamination (Jozic et al., 2009) because of their high toxicity levels and constant availability in the environment.

Metals can migrate within the soil, some of them accumulate in it and often disturb soil processes and sometimes can even cause soil degradation (Poszyler-Adamska and Czerniak, 2007).

Metal pollution is one of the main ecological problems in the world (Gardea-Torresdey et al., 2005; Claus et al., 2007). Plants growing in contaminated environments can accumulate metals at high concentrations, causing a serious health risk to people or animals eating these plants (Kabata-Pendias and Pendias, 1984; Alloway et al., 2004). Metals may enter the human body through inhalation of dust, consumption of contaminated drinking water, direct ingestion of soil and consumption of food plants grown on contaminated soil (Cambra et al., 1999).

Metals and their compounds can bioaccumulate in the body's tissues, such as bones or nerves. They can cross the placenta and harm an unborn child in pregnant women. Children are most susceptible to health problems caused by metals because their bodies are smaller and still developing. The health hazards presented by metals depend on the level of exposure and the length of exposure. In some cases, the health effects are immediately apparent; in others, the effects are delayed (Thomson, 2005).

High levels of toxic metals deposited in body tissues and subsequently in the brain, may cause significant developmental and neurological damage, including depression, increased irritability, anxiety, insomnia, memory loss, aggression and many other disorders. Chronic effects of prolonged low-level exposure to arsenic poisoning cause skin pigmentation, keratosis, skin cancers and death if exposed to high levels. Mercury poisoning symptoms include blindness, deafness, brain damage, digestive problems, kidney damage, lack of coordination and mental retardation. One of the most famous cases of mercury poisoning resulting from chronic exposure was the disaster that occurred in Minamata, Japan, where methylmercury was discharged from a plastics manufacturing plant into the waters of Minamata Bay in the 1950s and 1960s. Fish in the harbour were contaminated and those who ate the contaminated fish were gradually poisoned (Harada, 1996). Lead poisoning may negatively affect the nervous system and kidneys and may consequently lead to developmental retardation (Von Schirnding and Fuggle, 1996).

1.3) Lead

Lead has a blue-gray colour. It is the softest and heaviest of the common metals. It is very malleable and ductile, but has no elastic strength. Recent work has suggested that seasonal increases in children's blood lead (BPb) levels relate to exposure through activity, summer days of outdoor play, as well as open windows and doors leading to increased contact with lead-contaminated soil (Mielke and Reagan, 1998; Yiin et al., 2000; Haley and Talbot, 2004). Children and adults living in urban areas where surface soils are contaminated with lead may become exposed through indoor and outdoor inhalation of lead in dust and ingestion of lead contaminated soil dust deposited within homes and outdoor surfaces (Laidlaw et al., 2005). Lead levels greater than 165 mg/kg in the soil have been associated with children's blood lead concentrations of more than 10 μg/dL (DEFRA and Environment Agency, 2002). Blood lead concentrations of more than 10 μg/dL is an indication of excessive exposure in infants and children (CDC, 2005). Wheeler and Rolfe (1979) found that lead levels in vegetation increased linearly in relation with traffic density and proximity to roadways. Rodriquez-Flores and Rodriquez-Castellon (1982) reported that lead levels in soil and vegetation decrease with increasing distance from the road.

Lead particles are emitted from motor vehicles in to the atmosphere as lead halides (eg. PbBrCl). Lead particles are emitted from mines and smelters primarily in the form of lead sulfate ($PbSO_4$), complex lead compounds ($PbO.PbSO_4$) and lead sulfide (PbS) (EPA, 1986). Evidence exists to show that atmospheric lead enters the soil as lead sulfate or is converted rapidly to lead sulfate at the soil surface. Lead sulfate is relatively soluble, and thus could leach through the soil if it were not transformed. In soils with pH levels greater than, or equal to 5, and with at least 5% organic matter, atmospheric lead is retained in the upper 2-5 cm of undisturbed soil (EPA, 1986). The higher content of Pb in the air and the accumulation of metals in the soil and plants have a negative influence on the quality and quantity of agricultural production (Vrubel et al., 1996).

The natural lead in the soil is strongly related to the composition of the parent rock. The mean lead concentration for surface soil on a worldwide scale could be estimated at ±25ppm. The upper limit for the lead concentration of a normal soil can be established at ±70ppm (CSBEP, 1990).

According to Swaileh et al. (2004) motor vehicles are sources of several pollutants in the environment; particularly lead (Sutherland and Tack, 2000). Harper et al. (2003) found that older cars are associated with higher emissions of pollutants and vehicles are on average older in South Africa than in developed countries. In studies done by Davis et al. (2001) and Van Bohemen et al. (2003) it was found that the main processes by which vehicles spread metals into the environment are combustion, the wear of vehicles (tyres, brakes, engine) and leaking of oil. Lead can be released by the combustion of leaded petrol.

The City of Cape Town (CCT) is a relatively densely populated metropolitan area, with about 48% of the population living in central Cape Town, as well as the southern and northern suburbs. Eighty five percent of all the job opportunities are localised in the above mentioned areas, resulting in a huge daily movement of people to and from work with high vehicular traffic on the major roads, especially during peak hours (CMC, 1997/8; CCT, 2002). Over the past decades, the number of vehicles in the CCT has increased by 85%, which is more than in most developing countries. Also, the rapid industrialisation and non-stop demand for land, housing and infrastructural development in the CCT expanded to such an extent in the past years (CMA, 1998) that there is a realistic chance that the local environment in the CCT has been put under increased toxic stress due to increased emission of metals.

Lead may mobilize from soil when lead-bearing soil particles run off to surface waters during heavy rains. Lead may also mobilize from soil to atmosphere by downwind transport of smaller lead-containing soil particles entrained in the prevailing wind (NSF, 1977). This latter process may be important in contributing to the atmospheric load of lead around some lead-smelting sites that contain elevated levels of lead in the soil.

The downward movement of lead from the soil by leaching is very slow under most natural conditions (NSF, 1977). The conditions that induce leaching are the presence of lead in the soil at concentrations that either approach or exceed the absorption capacity of the soil, the presence in the soil of materials that are capable of forming soluble materials with lead, and a decrease in the pH of the leaching solution (eg. acid rain) (NSF, 1977). Partially favourable conditions for leaching may be present in some soils near lead-smelting sites that contain elevated levels of lead in the soil.

1.3.1) Sources of lead

The soil is contaminated by lead from various sources (American Academy of Pediatrics, 1987). Lead particles are deposited in the soil from flaking lead paint, from old buildings, and from motor vehicles that use leaded petrol. The illegal disposal of waste in the environment may also cause soil pollution. Urban environments in general have received higher depositions of lead from vehicular emissions than have rural areas (Moen et al., 1986).

In many lead-mining environments, the predominant form of lead is galena or lead sulfide (Colorado Department of Health, 1990). Other mineral forms of lead are predominantly cerusite (lead carbonate), anglesite (lead sulfate) and massicot (lead oxide). Wide variations in soil lead levels have been reported, ranging from less than 100 ppm to over 11,000 ppm (National Research Council, 1980). Natural levels of lead in surface soils are usually below 50 ppm (Chaney et al., 1984; Reagan and Silbergeld, 1989). Soils adjacent to houses with exterior lead-based paints may have lead levels greater than 10,000 mcg/g (EPA, 1986). Lead has been shown many times to permanently reduce the cognitive capacity of children at extremely low levels of exposure (Needleman et al., 1990).

1.4) Manganese

Manganese is a gray–white metal, resembling iron. It is a hard metal and is very brittle, fusible with difficulty, but easily oxidized (Walker et al., 2003). Manganese is the second most abundant metal in nature (Wittmann, 1977). The chemical behaviour of manganese is very similar to that of iron, and manganese is frequently found in association with iron (CCME, 1992). Although manganese is widely distributed in the earth’s crust, it does not occur naturally in its native state but rather exists in many minerals, with oxides, carbonates and silicates, being among the most important (Moore and Ramamoorthy, 1984). Manganese originates from rock erosion (Birch and Taylor, 1999) but the concentrations of this metal are greatly increased in surface waters by anthropogenic activities (Moore and Ramamoorthy, 1984). Manganese is an important micronutrient (Cover and Wilhm, 1982). This element is essential and plays a vital role and has considerable biological significance for most living organisms (Förstner and Prosi, 1979). A substantial fraction of manganese is present in suspended forms in natural waters (Moore and Ramamoorthy, 1984; CCME, 1992), resulting in the removal of this metal from the water column by the process of sedimentation into river sediments.

The manganese-containing fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) that was introduced to motor vehicle fuel formulae as an octane boosting and “anti-knock” agent to replace or reduce the lead content in petrol, has officially been approved in some developed countries (Health Canada, 2003). MMT was introduced in South Africa in 2000 (DEAT and DME, 2003).

Manganese is considered an essential metal important to mitochondrial oxidative processes for all living mammals, but may also be toxic at elevated concentrations (Alessio and Lucchini, 1996). Manganese is less toxic than most other metals, such as lead but it may still pose a threat to organisms when it is present in high concentrations (Förstner and Prosi, 1979).

Manganese particulates have a low residence time in the air and their fate and transport depends on their size and density, wind speed and direction (ATSDR, 2000). Most of particulate manganese compounds emitted from cars are immediately deposited on the ground through gravitational settling, while others undergo chemical transformation in the atmosphere before sinking on soil and vegetation alongside major roads through wet deposition (Annegarn and Scorgie, 2002; Baird and Cann, 2005). About 50% of manganese emitted particles are retained after being deposited onto the soil surface, while the other half is reflected back into the air (Bhuie et al., 2005).

These compounds accumulate in urban roadside soils, vegetation and air alongside major roads (Annegarn and Scorgie, 2002; Ona et al., 2006). Manganese can be distributed in the environment by wind and water. Studies have shown a positive correlation between the levels of manganese and the distance from urban main roads (Ona et al., 2006).

Human activities are responsible for the higher than normal levels of manganese in the soil (ATSDR, 2000). Most contamination from manganese comes from anthropogenic activities related to mining and mineral processing, emissions from alloy plants as well as steel and iron production. Others include combustion of fuel in cars and industry, the discharges of municipal wastewater, sewage sludge and the use of pesticide (WHO, 2004).

Manganese is essential for normal physiological functioning in humans and animals (EPA, 2000). However, elevated levels of essential elements could be detrimental to human health (Rollin et al., 2005). The toxicity of a metal depends on its route of administration and the chemical compound with which it is bound (El-Hinnawi and Hashmi, 1982).

Long term exposure to high levels of manganese, mainly by inhalation in humans may negatively affect the central nervous system, visual reaction time, hand steadiness and coordination (EPA, 2000). Other exposures may be by absorption though the skin from accidental spills or the use of manganese based petrol as a solvent cleaner and from misuse such as petrol sniffing (Egyed and Wood, 1996). Highly exposed or susceptible sub-populations might be at increased risk from low-level manganese exposure. Those at risk include infants, pregnant women, the elderly, those with iron deficiency, people with Parkinson's disease, and workers exposed to petrol or exhaust fumes (Rollin et al., 2005).

MMT is highly toxic to humans in the raw concentrated form (NICNAS, 2003). The combustion of MMT in vehicles releases particles of manganese oxide (Mn_3O_4) that can be inhaled fairly easily (Annegarn and Scorgie, 2002). Excessive intake of manganese, either through inhalation or ingestion, may result in pathological damage, particularly to the central nervous system (Keen and Zindenberg-Cherr, 1990).

High levels of manganese can result in manganese-induced anaemia in fish (Martin and Coughtrey, 1975). Although studies reported that airborne manganese levels in Montreal (where MMT was used for more than 10 years) were similar to those areas where MMT was not used, the possibility of elevated human exposure to manganese both by inhalation and ingestion cannot be ruled out (Lynam et al., 1999). Recent animal studies performed on rats showed that inhalation of soluble forms of manganese resulted in higher brain manganese levels (Dorman et al., 2002; Brenneman et al., 2000).

The absorption of ingested manganese is regulated by homeostatic mechanisms that may be increased by iron deficiency thought to be prevalent in developing countries (Bothwell, 1995; Szarfac and de Souza, 1997). It was found that individuals with anaemia absorb almost twice the levels of manganese than healthy individuals with the same exposure. Infants have a greatly increased absorption and retention capacity for ingested manganese compared to that of adults (Mena et al., 1969). An association between manganese uptake during pregnancy and early psychomotor development of children was also recently reported (Takser et al., 2003).

1.4.1) Sources of manganese in soil

The major pool of manganese in soils originates from the crust of the earth. It is considered to be the twelfth most abundant element and the fifth most abundant metal. Manganese does not occur naturally in a pure state; oxides, carbonates and silicates are the most important manganese-containing minerals. The most common manganese mineral is pyrolusite (MnO_2), usually mined in sedimentary deposits by open-cast techniques (WHO, 1981).

Manganese contamination also results from direct atmospheric deposition, wash off from plants and other surfaces, leaching from plant tissues and shedding of excretion of material such as leaves, dead plants and animal material excrement. The anthropogenic source of manganese in the soil comes from the combustion of fuel additives through emission. One of the main sources of inorganic manganese as a pollutant in an urban environment is the combustion of MMT, particularly in areas of high traffic density (Sierra et al., 1998). In countries where the anti-knock fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) is used in motor vehicle engines; manganese is a component of motor vehicle exhaust fumes (Majestic et al., 2007). Some of the manganese deposit sites that are operational in the world include South Africa, South America, India and China (Schiele, 1991).

1.5) Vertical distribution of metals in soil

Despite the fact that metal contamination of soil has long been known, few studies have been carried out on the vertical distribution of metals in the soil. Godin (1986) evaluated the downward migration of metals. Samples were taken from boreholes, to a maximum depth of 1m, sampled by fixed depth intervals, without taking the pedological horizons into account. Lead and manganese profiles were carried out for soils chosen according to the parent material, soil use and distance from plants. This study showed that the metal concentrations decreased logarithmically with depth. However, the depth reached by the metals was not determined (Godin, 1986).

Godin (1986) concluded that there was a strong link between the metals and the organic matter of the soil and suspected that migration of contaminants was more pronounced in sandy soils.

While the studies of metal-contaminated sites around mining or metallurgical sites are numerous and relatively old (Freedman and Hutchinson, 1981; Dudka and Adriano, 1997), those which seek to evaluate the vertical migration of the contaminants of natural or cultivated soils are much rare (Kuo et al., 1983; Scokart et al., 1983; Merrington and Alloway, 1994). The profiles examined do not generally exceed 1m. Metals can be retained for a long period after entering an environmental medium such as the soil (Tokahoglu and Kartal, 2003).

The stability of elements in the soil is high in contrast to other components of the environment (ie. atmosphere, water), causing long-time or even permanent pollution (Kozák, 1991). The total contents and potential mobility of these elements depend on the chemical and physical properties of both the soil and the elements, and the soil metal content is gradually decreased by leaching, plant uptake, erosion and evaporation. Another significant factor affecting the behaviour of the elements in the soil is their rate of absorption into the soil (Kabata-Pendias and Pendias, 1984).

1.6) Lead and manganese as petrol additives

Lead and manganese are commonly used as metallic additives in petrol. They are added as petrol soluble chemicals that produce the desired effect at the part per million concentration range (Chevron, 2002).

The addition of these additives into petrol helps to prevent premature “knocking,” to protect engine valves against wear, and to increase the efficiency and power of the engine (Chevron, 2002). The use of high octane petrol allows vehicle manufacturers to increase engine compression ratios, which then helps to increase fuel efficiency and power (Blumberg and Walsh, 2004).

1.6.1) Tetral-ethyl lead (TEL)

Tetral-ethyl lead (TEL) is an organic metallic compound. TEL was found to be an effective anti-knocking agent in engines by Thomas Midgley in 1921 (NIHF, 2002). TEL is a viscous colourless liquid produced by reacting ethyl chloride with sodium lead alloy.

The addition of TEL in petrol, has been linked to various adverse environmental consequences, as well as health risks associated with their emission into the environment. TEL was also found to be damaging to the catalytic converters in motor vehicle engines (Kirk and Othmer, 2001). This resulted in its initial reduction and subsequent removal from petrol altogether (Chevron, 2002).

In a study conducted in Canada it was found that maximum lead content ranged between 200 and 400 mgL^{-1} in petrol (Loranger and Zayed, 1994). Similar studies were conducted in South Africa and found that the maximum lead content in petrol ranged between 400 and 836 mgL^{-1} (Von Schirnding and Fuggle, 1996).

The European Union phased out lead in petrol in 2000, Ghana in 2004, China and South Africa in 2006 (DEAT and DME, 2003). Despite the banning of leaded petrol by many countries, lead will continue to be a major ecological and human health concern in the world due to the fact that lead is persistent, has a long residence time and low desorption in soil (Von Schirnding and Fuggle, 1996; Rollin et al., 2005).

1.6.2) Methylcyclopentadienyl Manganese Tricarbonyl (MMT)

Methylcyclopentadienyl Manganese Tricarbonyl (MMT) is the most popular lead replacement compound in the world because of its lower production cost (Chevron, 2002). MMT is added to petrol in a smaller amount than TEL, with a maximum concentration of 18 mgL^{-1} used in Canadian and South African petrol (Chevron, 2002; DEAT and DME, 2003).

MMT was originally introduced into the market in 1958 as a supplement to the petrol additive tetral-ethyl lead or smoke suppressant in engines. After the banning of leaded petrol in the USA by the EPA in 1972; it was later used as an octane enhancer in unleaded petrol (Loranger and Zayed, 1997).

All leaded petrol was completely replaced by 1990 in Canada by MMT (Loranger and Zayad, 1994). The average MMT concentrations in Canadian petrol ranged from 6.3 to 10.8 mgL^{-1} of manganese, significantly below the 18 mgL^{-1} recommended limit value (Environment Canada, 2005). Higher levels of MMT in petrol are found in other countries. In Lithuania a survey was conducted and manganese levels in petrol were found to be up to 55 mgL^{-1} (Shindler, 2004).

The main source of airborne inorganic manganese pollution in urban areas comes from the combustion of MMT and is more significant in areas of high traffic density (Sierra et al., 1995). The same situation can be identified in Cape Town in areas with high traffic density; this being made feasible by the fact that the majority of vehicles in South Africa are older and set to use MMT-enriched petrol.

In countries such as Canada with extensive use of MMT for decades, MMT has been blamed for higher warranty cost (Ghitter and Kenny, 1997) and also numerous complaints have been received from customers of blocked and ineffective catalysts (Schindler, 2004).

1.7) Statement of the research problem

Unleaded petrol has been available in South Africa since 1996. The conversion from leaded to unleaded petrol has been a slow process. Leaded petrol has been totally phased out since January 2006 (Harper et al., 2003). However, there is still a real danger of lead contamination, at least in the area close to roads because of its long half-life decay (Pirkle et al., 1985). Lead is of particular concern because there is increasing evidence that relatively low concentrations of lead in the blood can affect children's mental development, an effect that persists into adulthood (Needleman et al., 1990). Therefore, it is important to investigate whether the banning of leaded petrol is having a positive effect on lead contamination in the environment.

The manganese-containing fuel additive methylcyclopentadienyl manganese tricarbonyl (MMT) that was introduced to motor vehicle fuel formulae as an octane boosting and “anti-knock” agent, to replace or reduce the lead content in petrol, has officially been approved in some developed countries (Health Canada, 2003). Manganese is considered an essential metal important to mitochondrial oxidative processes for all living mammals, but may also be toxic at elevated concentrations (Alessio and Lucchini, 1996).

1.8) Objectives of the research

- To assess the accumulation of lead and manganese in soil along the N1 highway.
- To determine the vertical distribution of lead and manganese in soil along the N1 highway.
- To compare the concentrations of lead and manganese in soil along the N1 highway, before and after the banning of leaded petrol in South Africa.

CHAPTER TWO: MATERIALS AND METHODS

2.1) Field Survey

2.1.1) Sampling sites

Site 1: This site is located at the turn-off into Sable Road which leads into the Century City Shopping Mall. This is the site closest to the Central Business District (CBD) of Cape Town, about 4 kilometers away. Site 1 is characterized by grassy vegetation.

Site 2: This site is located 2 kilometers away from site 1. Site 2 is found along the N1 near the Victoria Palms residential area. The vegetation around site 2 is characterized by palm trees and grass.

Site 3: This site is located along the N1 highway near the N1 City Shopping Centre. The vegetation at this site is characterized by the presence of Eucalyptus trees and grass.

Site 4: This site is located along the N1 highway near the Tygervalley residential area and surrounded by grassy vegetation.

Site 5: Located about 2.5 kilometers from site 4, site 5 is located alongside the N1 highway near the intersection of the N1 highway with the R300 highway. The Kuils River is close to this sampling site.

Site 6: Located at the turn-off into Brighton Road, site 6 is found along the N1 highway, 33 kilometers away from the CBD. This site is close to residential areas found along both sides of the N1 highway.

The N1 is one of the main routes to and from Cape Town and is chosen as the sampling area because of the high volumes of traffic it carries on a daily basis. The closest site is about 4 km from the Cape Town CBD and the furthest site about 33 km from the Cape Town CBD. The sampling sites were in or close to areas of high traffic density, residential areas and shopping malls. The soil type along the N1 highway was mostly sandy in nature (Tables 3 and 4). Rainfall data for the sampling period was collected from the Cape Town Weather Office. Vehicle counts for the sampling period were collected from Sanral.

2.2) Sampling procedure

At each of the sampling sites soil samples (±500g per sampling occasion) were taken at the inbound (traffic into the city) and outbound (traffic leaving the city) sides of the N1 highway.

This sampling was done every second month for a period of one year and for this purpose each sampling site was given a name and a number. The sampling period commenced on the 16th of February 2011 and ended on the 28th of December 2011. Six soil samples were taken at each site, approximately two meters from the road verges and at a depth of approximately 0-2cm. The soil from each sampling site was collected in labelled plastic vials and taken to the laboratory for analysis. Record was kept of the weather conditions and activities at and adjacent to sampling sites, prior to and at the time of sampling that could possibly influence the outcome of the results.

For the purpose of determining vertical distribution of metals, once-off soil samples were also collected at sites 1, 5 and 6 at depths of 0-2cm, 30cm and 60cm, respectively.

2.3) Acid digestion

The soil samples were placed in separate, labelled petri dishes and into a Memmert oven to dry for 48 hours at 60°C, in order to obtain the dry weight of the soil. The dried soil was then sifted through a 1 mm sieve and placed into clean, labelled petri dishes and weighed on a Precisa XB 220A balance to obtain a weight of between 0.2g and 0.3g.

The weighed soil was then placed into labelled, metal free test tubes for digestion. The test tubes with the soil samples, as well as a blank (test tube with only the 10ml nitric acid, to measure for possible contamination) were placed in a Grant UBD digester in a fume cabinet and digested with 10ml 55% nitric acid at a temperature of 40°C for one hour. The temperature was then increased to 120°C for a period of three hours. The method employed in this study was identical to that used by Odendaal and Reinecke (1999). After cooling, the samples were filtered through Whatman no 6 (90mm) filter paper and diluted to 100ml with distilled water using labelled volumetric flasks. The samples were finally filtered through Whatman 0.45 μm cellulose nitrate membrane filter paper using a syringe and Millipore filter holders. The prepared samples were stored in a fridge in plastic vials until it was ready to be taken to the ICP-MS laboratory at the University of Stellenbosch to determine the lead and manganese concentrations in the samples.

2.4) Metal analysis

The metal concentrations in the samples were determined with an Inductively Coupled Plasma - Mass Spectrophotometer (ICP–MS) and calculated using the following formula:

$$\frac{(\text{ICP reading} - \text{Blank}) \times [\text{dilution factor}]}{\text{Dry mass of soil sample (g)}}.$$

Metal concentrations were expressed as mg/kg.

2.5) Statistical analysis of data

The data in this study were analysed by using the Sigmastat 3.5 computer software package. The values are presented as the mean ±SD and the probability levels used for statistical significance were $P<0.05$.

The spatial and temporal comparison of lead and manganese concentrations over a one year period were analysed by means of the Kruskal-Wallis One Way ANOVA on Ranks. The reason for using this non-parametric test was due to the fact that the data was found to be not normally distributed.

The normality test is automatically done by the Sigmastat 3.5 package. If statistical differences were found, this test was followed up by the Student Newman Kuels post-hoc test.

There were no statistical tests done on the comparison of lead concentrations in the soil before and after the banning of lead in petrol. This was because the raw data of lead concentrations before the banning of lead in petrol was not available from a previous study (Kruger, 2008).

The comparison of manganese before and after the banning of lead in petrol was done by means of the Mann Whitney Rank Sum Test. The data in this case were also found to be non-parametric.

CHAPTER THREE: RESULTS AND DISCUSSION: LEAD

PART 1: RESULTS

3.1) Distribution of lead in soil along the road verges of the N1 highway over a period of one year

The mean lead concentrations for the outbound and inbound sides of the N1 highway for the sampling period February 2011 to December 2011 are presented in Table 1 and illustrated in Figures 1 to 6. Lead concentrations are expressed in mg/kg.

3.1.1) Comparisons of soil lead concentrations between sampling sites per sampling occasion

3.1.1.1) Outbound

On sampling occasion one, no significant differences ($P>0.05$) in pairwise multiple comparison of lead concentrations in the soil were recorded between sites 1 and 2, sites 3 and 4, sites 4 and 5, and between sites 1 and 6. There was a statistically significant difference ($P<0.05$) of lead concentration in the soil between sites 2 and 3.

On sampling occasion two, pairwise multiple comparisons in lead concentrations in the soil were significantly different ($P<0.05$) between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 5 and 6 and between sites 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparison of lead concentrations in the soil were recorded between sites 4 and 5.

On sampling occasion three, lead concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 4 and 5, sites 5 and 6 and between sites 1 and 6 were significantly different ($P<0.05$) in pairwise multiple comparisons. There were no significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil between sites 3 and 4.

On sampling occasion four, a statistically significant difference ($P<0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, sites 5 and 6 and between sites 1 and 6. No other statistically significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded.

On sampling occasion five , lead concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, and between sites 1 and 6 were significantly different ($P<0.05$) in pairwise multiple comparisons. There were no significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil between sites 5 and 6.

On sampling occasion six, pairwise multiple comparisons of lead concentrations in the soil were significantly different ($P<0.05$) between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 5 and 6, and between sites 1 and 6. No significant difference ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between sites 5 and 6.

3.1.1.2) Inbound

On sampling occasion one, there was a statistically significant difference ($P<0.05$) in pairwise multiple comparison of lead concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, sites 5 and 6, and between sites 1 and 6.

On sampling occasion two, pairwise multiple comparisons of lead concentrations in the soil were significantly different ($P<0.05$) between sites 2 and 3, sites 3 and 4, sites 4 and 5, sites 5 and 6, and between sites 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between sites 1 and 2.

On sampling occasion three , lead concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, and between sites 1 and 6 were significantly different ($P<0.05$) in pairwise multiple comparisons. There were no significant differences ($P>0.05$) in pairwise multiple comparisons in lead concentrations in the soil between sites 5 and 6.

On sampling occasion four, statistically significant differences ($P<0.05$) in pairwise multiple comparison of lead concentrations in the soil were recorded between sites 1 and 2, sites 3 and 4, sites 4 and 5, sites 5 and 6, and between sites 1 and 6. There were no significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil between sites 2 and 3.

On sampling occasion five, lead concentrations in soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, sites 5 and 6 and between sites 1 and 6 were significantly different ($P<0.05$) in pairwise multiple comparisons.

On sampling occasion six, pairwise multiple comparisons of lead concentrations in the soil were significantly different ($P<0.05$) between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between sites 4 and 5, and between sites 5 and 6.

3.1.2) Comparisons of soil lead concentrations over the sampling period per sampling site

3.1.2.1) Outbound

At site 1, there were statistically significant differences ($P<0.05$) in pairwise multiple comparisons of lead concentrations in the soil between occasions 3 and 4, occasions 4 and 5, 5 and 6, and between occasions 1 and 6. No statistically significant different ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 1 and 2, as well as occasions 2 and 3.

At site 2, pairwise multiple comparisons of lead concentrations in soil were significantly different ($P<0.05$) between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, and between occasions 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentration in the soil were recorded between occasions 5 and 6.

At site 3, there were statistically significant differences ($P<0.05$) in pairwise multiple comparisons of lead concentrations in the soil between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 4, significant differences ($P<0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 5, lead concentrations in soil between occasions 2 and 3, 3 and 4, 5 and 6 were statistically significantly different ($P<0.05$) in pairwise multiple comparisons. No significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 1 and 2, 4 and 5, and between 1 and 6.

At site 5, pairwise multiple comparisons of lead concentrations in the soil were significantly different (P<0.05) between occasions 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between 1 and 6. No significant differences (P>0.05) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 1 and 2.

3.1.2.2) Inbound

At site 1, there were statistically significant differences (P<0.05) in pairwise multiple comparisons of lead concentrations in the soil between occasions 1 and 2, 2 and 3, 3 and 4, and between occasions 4 and 5. No significant difference (P>0.05) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 5 and 6, and 1 and 6.

At site 2, pairwise multiple comparisons of lead concentrations in the soil were significantly different (P<0.05) between occasions 1 and 2, 2 and 3, 3 and 4, 5 and 6, and between occasions 1 and 6. No significant differences (P>0.05) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 4 and 5.

At site 3, there were statistically significant differences (P<0.05) in pairwise multiple comparisons of lead concentrations in the soil between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 4, significant differences (P<0.05) in pairwise multiple comparisons of lead concentration in the soil were recorded between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 5, lead concentrations in soil between occasions 2 and 3, 3 and 4, and between occasions 4 and 5 were significantly different (p<0.05) in pairwise multiple comparisons. No statistically significant differences (P>0.05) in pairwise multiple comparisons of lead concentrations in the soil were recorded between occasions 1 and 2, 5 and 6, as well as occasions 1 and 6.

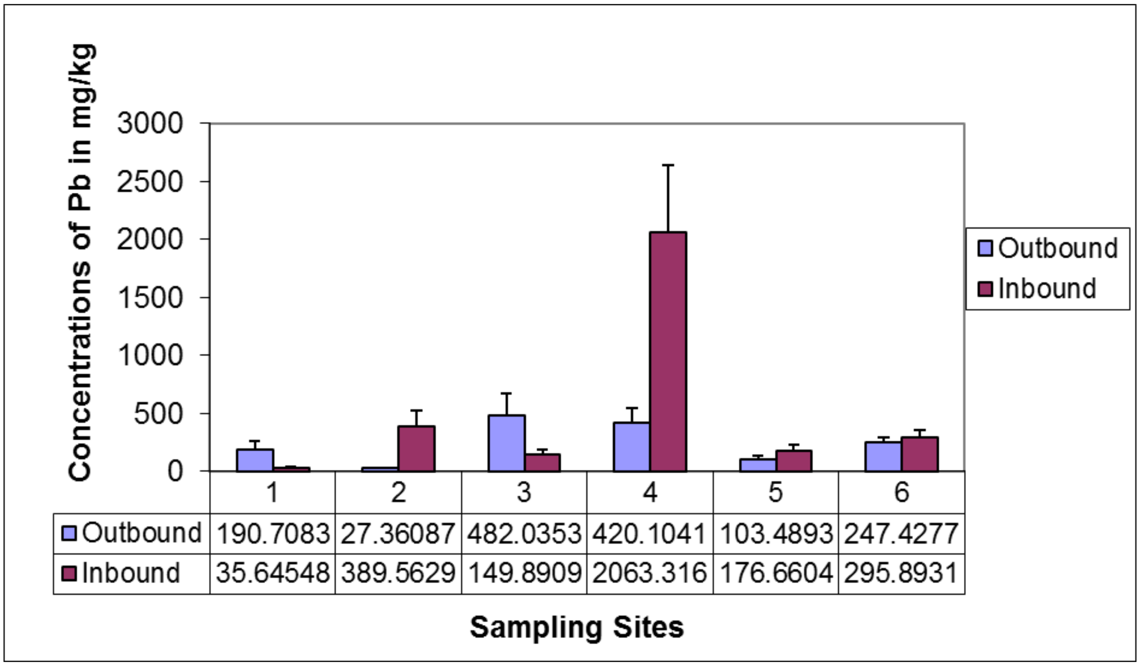
At site 6, pairwise multiple comparisons of lead concentrations in the soil were significantly different ($P<0.05$) between occasions 1 and 2, 3 and 4, 5 and 6, and between occasions 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of lead concentrations in soil were recorded at occasions 2 and 3, and at occasions 4 and 5.

Table 1: The mean lead concentrations (mg/kg) (± SD) for the outbound and inbound sides of the N1 highway for the sampling period February 2011 to December 2011. Numbers 1 to 6 in the left column represent the sampling sites.

SAMPLING SITE		SAMPLING OCCASIONS					
		Feb-2011	Apr-2011	Jun-2011	Aug-2011	Oct-2011	Dec-2011
1) Out	**Mean**	**$^{\mathrm{a}}$190.70^{1}**	**$^{\mathrm{a}}$125.26^{2}**	**$^{\mathrm{a}}$151.60^{2}**	**$^{\mathrm{a}}$39.95^{3}**	**$^{\mathrm{a}}$17.72^{4}**	**$^{\mathrm{a}}$61.46^{5}**
	SD	73.25	51.86	41.76	20.13	3.71	21.26
1) In	**Mean**	**$^{\mathit{a}}$35.64$^{\mathit{1}}$**	**$^{\mathit{a}}$194.03$^{\mathit{2}}$**	**$^{\mathit{a}}$30.58$^{\mathit{3}}$**	**$^{\mathit{a}}$8.34$^{\mathit{4}}$**	**$^{\mathit{a}}$49.07$^{\mathit{5}}$**	**$^{\mathit{a}}$52.71$^{\mathit{5}}$**
	SD	9.43	38.57	6.32	2.87	72.27	19.89
2) Out	**Mean**	**$^{\mathrm{b}}$27.36^{1}**	**$^{\mathrm{b}}$7.32^{2}**	**$^{\mathrm{b}}$28.58^{3}**	**$^{\mathrm{b}}$7.45^{4}**	**$^{\mathrm{b}}$167.46^{5}**	**$^{\mathrm{b}}$129.46^{5}**
	SD	6.97	4.97	9.18	5.40	71.89	40.07
2) In	**Mean**	**$^{\mathit{b}}$389.56$^{\mathit{1}}$**	**$^{\mathit{a}}$200.73$^{\mathit{2}}$**	**$^{\mathit{b}}$1371.11$^{\mathit{3}}$**	**$^{\mathit{b}}$468.32$^{\mathit{4}}$**	**$^{\mathit{b}}$499.55$^{\mathit{4}}$**	**$^{\mathit{b}}$558.33$^{\mathit{5}}$**
	SD	133.88	16.24	1401.5	66.20	63.50	35.28
3) Out	**Mean**	**$^{\mathrm{c}}$482.03^{1}**	**$^{\mathrm{c}}$151.04^{2}**	**$^{\mathrm{c}}$529.01^{3}**	**$^{\mathrm{c}}$1382.04^{4}**	**$^{\mathrm{c}}$853.79^{5}**	**$^{\mathrm{c}}$1018.81^{6}**
	SD	186.4	15.59	167.49	207.76	62.17	136.64
3) In	**Mean**	**$^{\mathit{c}}$149.89$^{\mathit{1}}$**	**$^{\mathit{b}}$377.26$^{\mathit{2}}$**	**$^{\mathit{c}}$517.56$^{\mathit{3}}$**	**$^{\mathit{c}}$398.95$^{\mathit{4}}$**	**$^{\mathit{c}}$61.74$^{\mathit{5}}$**	**$^{\mathit{c}}$398.37$^{\mathit{6}}$**
	SD	36.06	44.21	33.28	94.04	8.85	81.27
4) Out	**Mean**	**$^{\mathrm{c}}$420.10^{1}**	**$^{\mathrm{c}}$177.98^{2}**	**$^{\mathrm{d}}$633.70^{3}**	**$^{\mathrm{d}}$354.81^{4}**	**$^{\mathrm{d}}$214.94^{5}**	**$^{\mathrm{d}}$231.87^{5}**
	SD	124.95	20.53	75.58	61.24	65.41	38.99
4) In	**Mean**	**$^{\mathit{d}}$2063.31$^{\mathit{1}}$**	**$^{\mathit{c}}$149.70$^{\mathit{2}}$**	**$^{\mathit{d}}$122.82$^{\mathit{2}}$**	**$^{\mathit{d}}$1900.69$^{\mathit{3}}$**	**$^{\mathit{d}}$691.56$^{\mathit{4}}$**	**$^{\mathit{d}}$219.52$^{\mathit{5}}$**
	SD	581.03	6.91	12.64	716.38	199.02	41.82
5) Out	**Mean**	**$^{\mathrm{d}}$103.48^{1}**	**$^{\mathrm{d}}$99.55^{1}**	**$^{\mathrm{e}}$210.89^{2}**	**$^{\mathrm{e}}$31.75^{3}**	**$^{\mathrm{e}}$44.773^{3}**	**$^{\mathrm{e}}$128.86^{4}**
	SD	31.03	45.59	68.70	11.36	20.85	25.54
5) In	**Mean**	**$^{\mathit{e}}$176.66$^{\mathit{1}}$**	**$^{\mathit{d}}$227.70$^{\mathit{2}}$**	**$^{\mathit{e}}$491.95$^{\mathit{3}}$**	**$^{\mathit{e}}$123.91$^{\mathit{4}}$**	**$^{\mathit{e}}$251.02$^{\mathit{5}}$**	**$^{\mathit{d}}$215.94^{5}**
	SD	54.19	37.04	375.92	59.98	45.30	39.84
6) Out	**Mean**	**$^{\mathrm{e}}$247.42^{1}**	**$^{\mathrm{e}}$176.66^{2}**	**$^{\mathrm{f}}$69.20^{3}**	**$^{\mathrm{f}}$228.77^{4}**	**$^{\mathrm{f}}$40.81^{5}**	**$^{\mathrm{e}}$99.32^{6}**
	SD	42,51	37.56	15.60	65.26	11.59	15.60
6) In	**Mean**	**$^{\mathit{f}}$295.89$^{\mathit{1}}$**	**$^{\mathit{e}}$418.61$^{\mathit{2}}$**	**$^{\mathit{e}}$462.59$^{\mathit{2}}$**	**$^{\mathit{f}}$264.08$^{\mathit{3}}$**	**$^{\mathit{e}}$304.07$^{\mathit{4}}$**	**$^{\mathit{e}}$170.72$^{\mathit{5}}$**
	SD	62.29	58.23	92.33	114.21	30.11	41.04

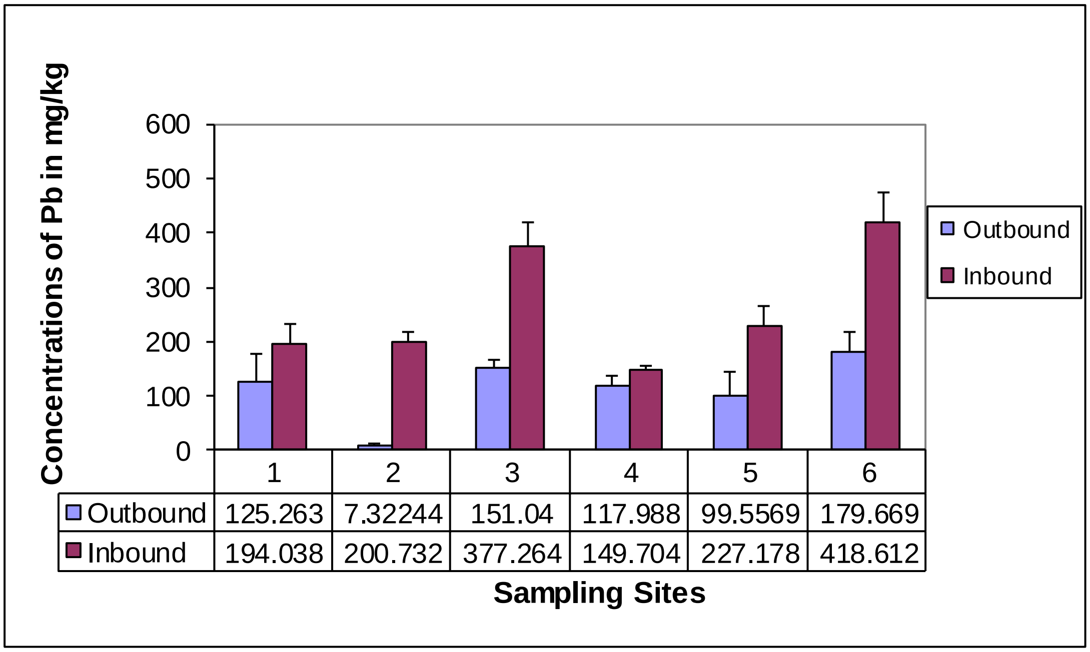
Statistically significant differences are indicated with different letters or numbers. Superscripts a to f (non-italicised) = mean value obtained from soil samples at outbound sides compared with each other for the different sites along the length of the highway; Superscripts a to f (italicised) = mean value obtained from soil samples at inbound sides compared with each other for the different sites along the length of the highway; Superscripts 1 to 6 (non-italicised) = mean value obtained from soil samples at the outbound side of one particular site compared with each other for different sampling occasions; Superscripts 1 to 6 (italicised) = mean value obtained from soil samples at the inbound side of one particular site compared with each other for different sampling occasions.

Graphs of the soil lead concentrations of the N1 highway over the sampling period February 2011 to December 2011



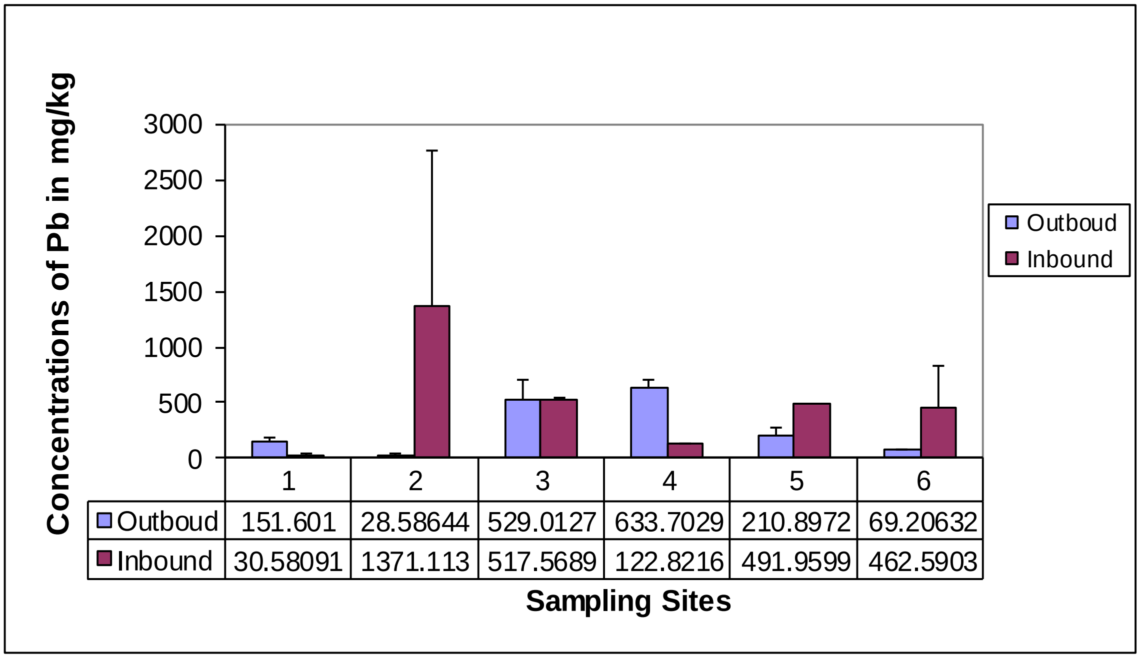
	1	2	3	4	5	6
Outbound	190.7083	27.36087	482.0353	420.1041	103.4893	247.4277
Inbound	35.64548	389.5629	149.8909	2063.316	176.6604	295.8931

Figure 1: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the February 2011 sampling occasion. N=6



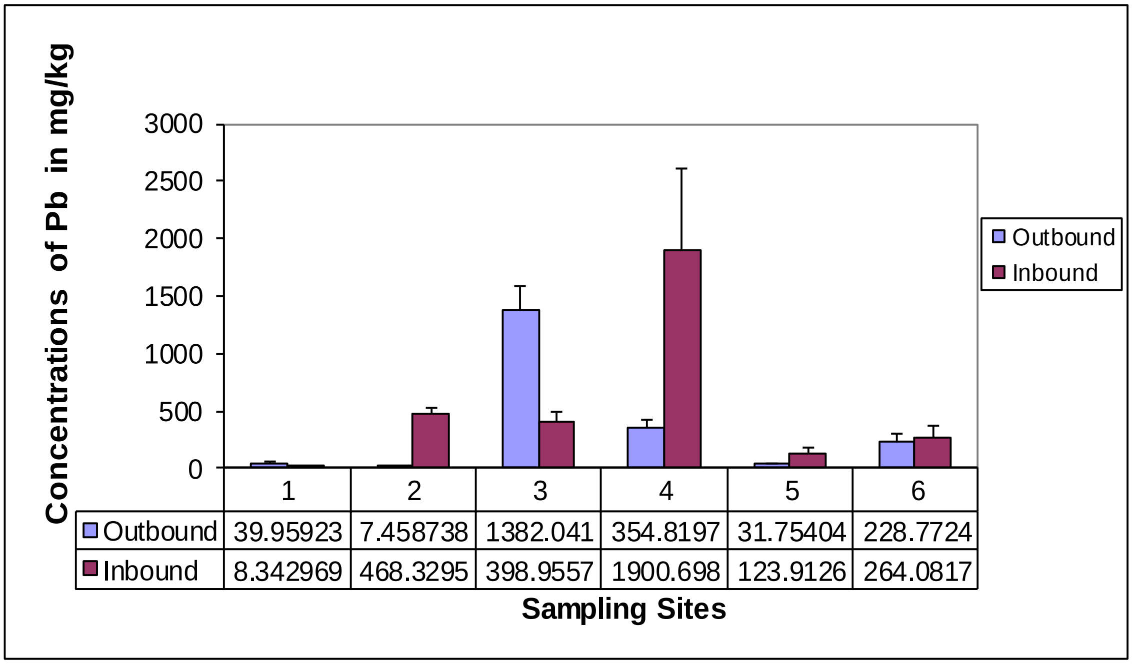
	1	2	3	4	5	6
Outbound	125.263	7.32244	151.04	117.988	99.5569	179.669
Inbound	194.038	200.732	377.264	149.704	227.178	418.612

Figure 2: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the April 2011 sampling occasion. N=6



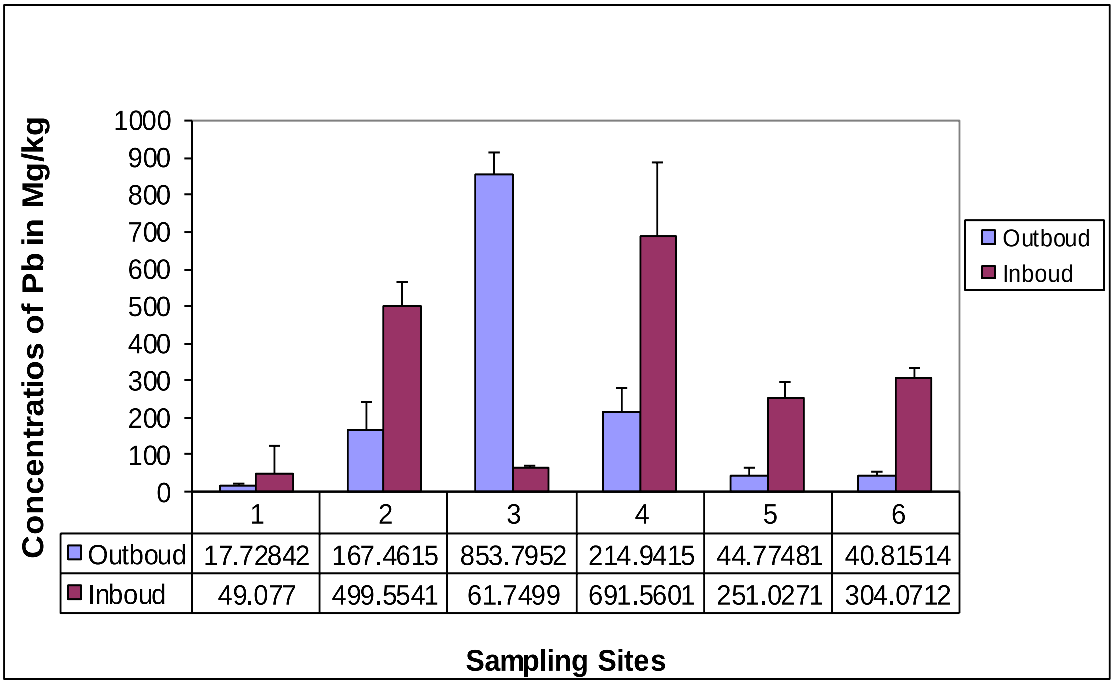
	1	2	3	4	5	6
Outboud	151.601	28.58644	529.0127	633.7029	210.8972	69.20632
Inbound	30.58091	1371.113	517.5689	122.8216	491.9599	462.5903

Figure 3: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the June 2011 sampling occasion. N=6



	1	2	3	4	5	6
Outbound	39.95923	7.458738	1382.041	354.8197	31.75404	228.7724
Inbound	8.342969	468.3295	398.9557	1900.698	123.9126	264.0817

Figure 4: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the August 2011 sampling occasion. N=6



	1	2	3	4	5	6
Outboud	17.72842	167.4615	853.7952	214.9415	44.77481	40.81514
Inboud	49.077	499.5541	61.7499	691.5601	251.0271	304.0712

Figure 5: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the October 2011 sampling occasion. N=6

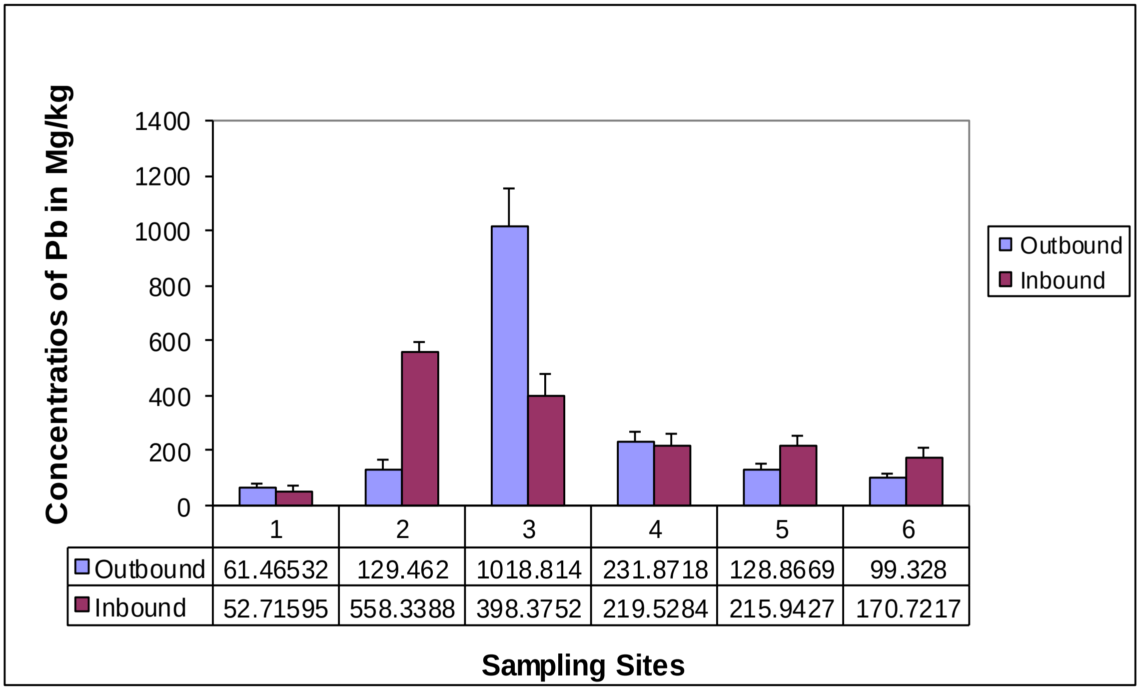


Figure 6: Mean lead concentrations (mg/kg) (± SD) for the N1 highway for the December 2011 sampling occasion. N=6

Table 2: Rainfall (mm) in the area of the N1 highway for the sampling period February 2011 to December 2011 (The Cape Town Weather Office)

Sampling occasions	**Average rainfall in mm**
Jan	38mm
Feb	**40mm**
March	40mm
April	**60mm**
May	70mm
June	**80mm**
July	79mm
Aug	**78mm**
Sept	41mm
Oct	**40mm**
Nov	37mm
Dec	**36mm**
Total Average	**53.25mm**

The values displayed in bold indicate the months of sampling and the respective average rainfall for the month (Table 2).

Table 3: Vehicle counts on the outbound side of the N1 highway documented during the sampling period of this study

	Sampling Sites					
	1 **(Sable Road)**	**2** **(Victoria Palms)**	**3** **(N1 City)**	**4** **(Tygervalley)**	**5** **(Kuils River)**	**6** **(Brighton Road)**
Sampling occasions						
Jan 2011	-	-	-	-	1003845	1084830
Feb 2011	**-**	**-**	**-**	**-**	**1067780**	**1107426**
Mar 2011	-	-	-	-	1126822	1060807
Apr 2011	**-**	**-**	**610746**	**662524**	**1032975**	**1090740**
May 2011	-	-	-	-	1020083	1118222
Jun 2011	**-**	**-**	**-**	**-**	**898645**	**1091609**
Jul 2011	-	-	-	-	1020268	1154429
Aug 2011	**-**	**-**	**-**	**-**	**1058241**	**1153925**
Sep 2011	-	-	-	-	1127175	1116825
Oct 2011	**461222**	**599960**	**545621**	**438605**	**1147356**	**1207781**
Nov 2011	344679	393423	309162	411227	1001402	1191982
Dec 2011	**-**	**-**	**-**	**-**	**1160254**	**1213319**
Total	**461222**	**599960**	**1156367**	**1101129**	**6365251**	**6864800**

The vehicle counts shown in Table 3 were taken by Sanral and were the only data available at the time. The values in bold indicate the sampling months and the respective vehicle counts.

Table 4: Vehicle counts on the inbound side of the N1 highway documented during the sampling period of this study

	Sampling Sites					
	1 **(Sable Road)**	**2** **(Victoria Palms)**	**3** **(N1 City)**	**4** **(Tygervalley)**	**5** **(Kuils River)**	**6** **(Brighton Road)**
Sampling Occasions						
Jan 2011	-	-	-	-	960052	1155154
Feb 2011	**-**	**-**	**-**	**-**	**982177**	**1177809**
Mar 2011	-	-	-	-	982383	1136579
Apr 2011	**-**	**-**	**596899**	**677639**	**984360**	**1156102**
May 2011	-	-	-	-	945352	1184382
Jun 2011	**-**	**-**	**-**	**-**	**826324**	**1152238**
Jul 2011	-	-	-	-	934449	1219626
Aug 2011	-	-	-	**-**	**1032607**	**1222732**
Sep 2011	-	-	-	-	1034659	1158475
Oct 2011	**402670**	**563828**	**491801**	**441027**	**1064317**	**1158475**
Nov2011	329522	381848	271187	415707	920154	1289428
Dec 2011	**-**	**-**	**-**	**-**	**1100040**	**1285721**
Total	**402670**	**563828**	**1088700**	**1118666**	**5989825**	**7153077**

The vehicle counts shown in Table 4 were taken by Sanral and were the only data available at the time. The values in bold indicate the sampling month and the respective vehicle counts.

3.2) Vertical distribution of lead in soil along the road verges of the N1 highway

3.2.1) Outbound

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in lead concentrations between the surface soil and the 30cm depth soil, and between the surface soil and 60cm depth soil at site 1. No significant difference ($P>0.05$) were found between the 30cm and 60cm depth samples at site 1 (Figure 7; Table 5).

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in lead concentrations between the surface soil and 30cm depth soil, and between the 30cm and 60cm depth samples at site 5 (Figure 7; Table 5).

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in lead concentrations between the surface soil and 30cm depth soil, between the surface soil and 60cm depth soil, and between the 30cm and 60cm depth samples at site 6 (Figure 7; Table 5).

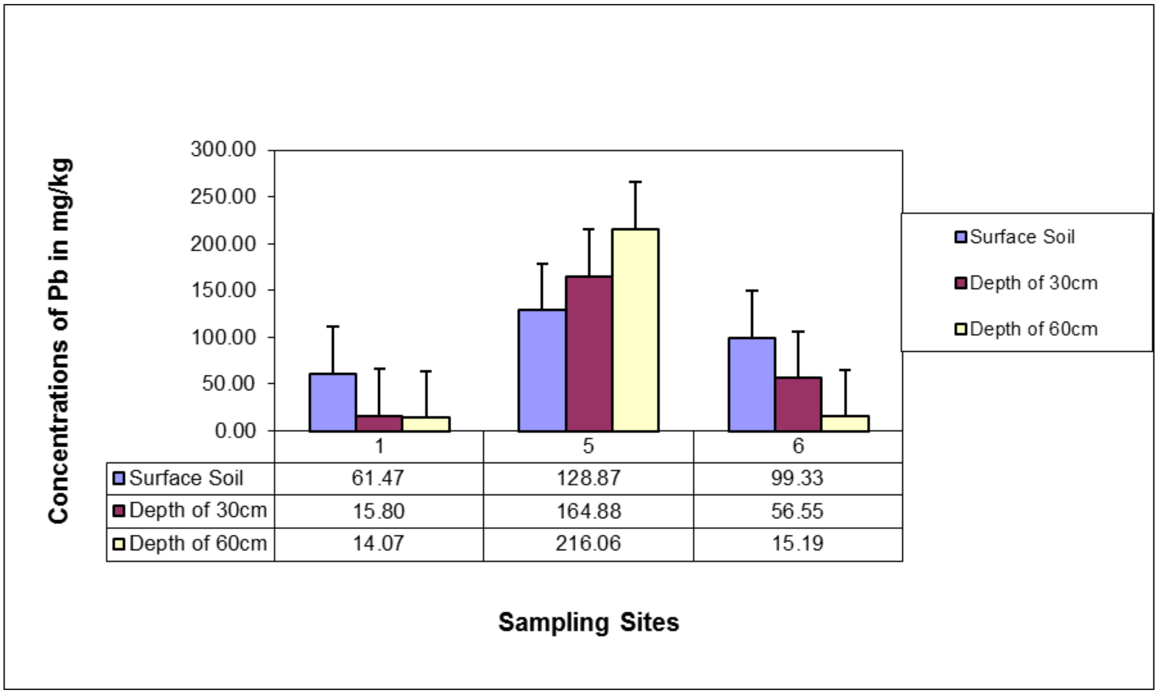
3.2.2) Inbound

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in lead concentrations between the surface soil and 30cm depth soil, between the surface soil and 60cm depth soil, and between the 30cm depth and 60cm depth soil at site 1 (Figure 8; Table 6).

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in lead concentrations between the surface soil and 30cm depth soil, between the surface soil and 60cm depth soil at site 5. No significant differences ($P>0.05$) in pairwise multiple comparisons were found for lead concentrations between 30cm depth soil and 60cm depth soil at site 5 (Figure 8; Table 6).

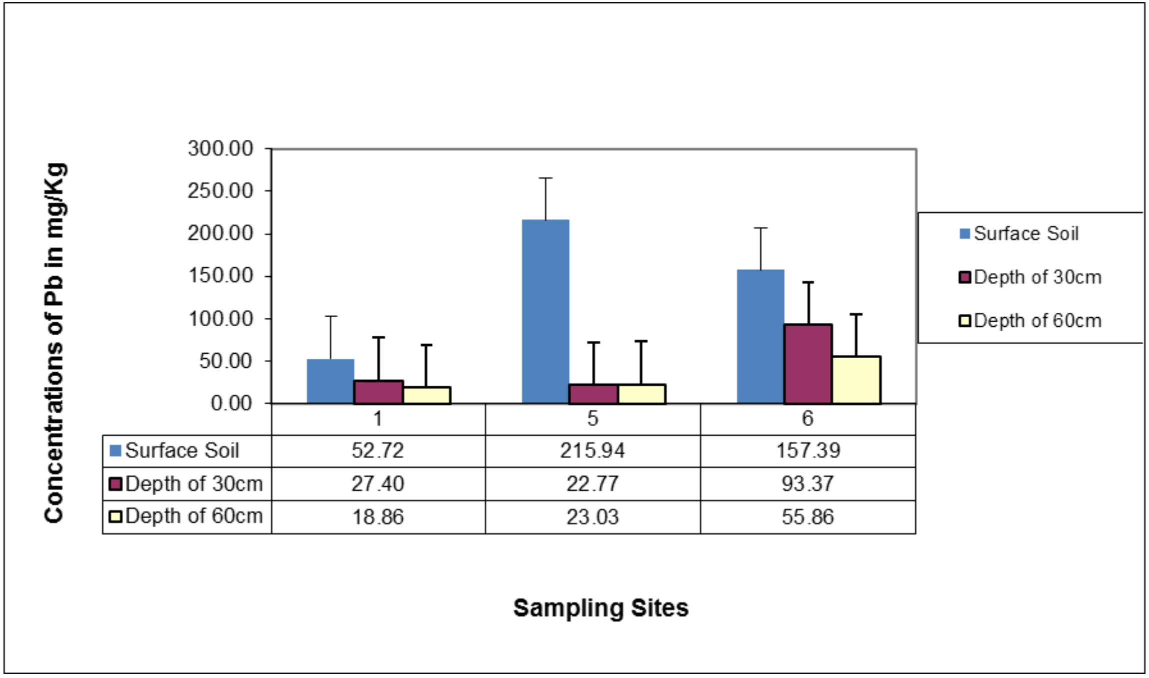
All pairwise multiple comparisons indicated that there were statistically significant differences (P<0.05) in lead concentrations between the surface soil and 30cm depth soil, between the surface soil and 60cm depth soil, and between the 30cm depth and 60cm depth samples at site 6 (Figure 8; Table 6).

Graphs of vertical distribution of lead concentrations in soil samples on the outbound and inbound sides of the N1 highway



	1	5	6
Surface Soil	61.47	128.87	99.33
Depth of 30cm	15.80	164.88	56.55
Depth of 60cm	14.07	216.06	15.19

Figure 7: Vertical distribution of mean lead concentrations (mg/kg) (± SD) as recorded at the respective sites on the outbound side of the N1 highway. N=6.



	1	5	6
Surface Soil	52.72	215.94	157.39
Depth of 30cm	27.40	22.77	93.37
Depth of 60cm	18.86	23.03	55.86

Figure 8: Vertical distribution of mean lead concentrations (mg/kg) (± SD) as recorded at the respective sites on the inbound side of the N1 highway. N=6

Table 5: pH, organic content, Pb concentrations (mg/kg) and soil type of soil samples of the outbound side of the N1 highway

Sites	**Depth**	**pH KCl**	**Organic Content %**	**Pb in mg/kg**	**Soil Type**
1	Surface soil	7.30	0.96	^{a} 61.47	Sand
1	30cm	7.10	0.67	^{b} 15.80	Sand
1	60cm	7.00	0.85	^{b} 14.07	Sand
5	Surface soil	5.98	1.10	^{a} 128.87	Sand
5	30cm	7.30	0.82	^{b} 164.88	Sand
5	60cm	7.10	0.92	^{c} 216.06	Sand
6	Surface soil	7.10	2.52	^{a} 99.33	Sand
6	30cm	7.10	2.50	^{b} 56.55	Sand
6	60cm	7.10	0.99	^{c} 15.19	Sand

Statistically significant differences are indicated with different letters; Superscripts a to c = Comparisons of surface, 30cm and 60cm soil per site.

Table 6: pH, organic content, Pb concentrations (mg/kg) and soil type of soil samples of the inbound side of the N1 highway

Sites	Depth	pH KCl	Organic Content %	Pb in mg/kg	Soil Type
1	Surface soil	7.20	0.99	^{a}52.72	Sand
1	30cm	7.00	0.76	^{b}27.40	Sand
1	60cm	6.90	1.33	^{c}18.86	Sand
5	Surface soil	7.10	2.54	^{a}215.94	Sand
5	30cm	7.10	1.33	^{b}22.77	Sand
5	60cm	7.00	1.97	^{b}23.03	Sand
6	Surface soil	7.10	0.87	^{a}157.39	Sand
6	30cm	7.00	0.90	^{b}93.39	Sand
6	60cm	6.90	1.12	^{c}55.86	Sand

Statistically significant differences are indicated with different letters; Superscripts a to c = Comparisons of surface, 30cm and 60cm soil per site.

3.3. Comparison of lead concentrations in soil along the road verges of the N1 highway before and after the banning of leaded petrol

In this section, a study conducted along the N1 highway before the banning of lead in petrol in South Africa, by Kruger (2008), is considered and the findings thereof are compared with the findings in the current study. The sites from where soil samples were collected before the banning of lead in petrol are the same as in the current study, apart from site 1. In the present study it was not possible to use the same site as site 1 due to recent road construction work. Therefore, site 1 is omitted from the comparisons.

The raw data of the Kruger (2008) were not available, therefore statistical comparisons were not possible between soil samples collected before and after the banning of lead in petrol. The lead concentrations of the Kruger (2008) and the current study are merely compared with each other.

3.3.1) Outbound

The soil samples for the two different studies were both collected for a period of one year, but the samples were not collected in the same months of the year. Thus, for the sake of consistency, the months closest to each other were compared.

Comparing January values (Before lead ban) and February values (After lead ban) for the outbound side

Site 1 was not considered for this comparison because there were no comparable data available between the two studies. Also, see the explanation above. That is why it is indicated on the graph as a zero.

There were higher concentrations of lead found in soil at sites 2, 3, 4, and 5 in the month of February 2011 than in January 2005. There were very little difference in lead concentrations between January 2005 and February 2011 at site 6 (Figure 9).

Comparing March values (Before lead ban) and April values (After lead ban) for the outbound side

There were higher concentrations of lead in soil at sites 2, 3, 4 and 5 in the month of March 2005 than in April 2011. However, lead concentrations in soil in the month of April 2011 were higher than in March 2005 at site 6 (Figure 10).

Comparing May values (Before lead ban) and June values (After lead ban) for the outbound side

Lead concentrations in soil sites 2, 3, 4, and 6 in May 2005 were higher than in the month of June 2011. There were very little difference in lead concentrations in soil in the months of May 2005 and June 2011 at site 5 (Figure 11).

Comparing July values (Before lead ban) and August values (After lead ban) for the outbound side

There were higher concentrations of lead in soil at sites 2, 5 and 6 in July 2005 than in August 2011. However, lead concentrations in soil in August 2011 were higher than in July 2005 at site 3. There were very little differences in lead concentrations in soil at site 4 when July 2005 are compared to August 2011 (Figure 12).

3.3.2) Inbound

Comparing January values (Before lead ban) and February values (After lead ban) for the inbound side

Data collected on lead concentrations from sites 4, 5, and 6 in February 2011 indicated higher concentrations, compared to those of January 2005. However, lead concentrations from sites 2 and 3 in the current study are lower compared to those found in January 2005 (Figure 13).

Comparing March values (Before lead ban) and April values (After lead ban) for the inbound sides

Lead concentrations from site 2 measured in April 2011 were lower than that measured in March 2005. Lead concentrations from sites 3, 4, 5 and 6 were found to be higher in April 2011 that in March 2005 (Figure 14).

Comparing May values (Before lead ban) and June values (After lead ban) for the inbound sides

Lead concentrations from sites 3 and 4 measured in June 2011 were lower than that of May 2005. Lead concentrations from sites 2, 5 and 6 measured in June 2011 were higher than those measured in May 2005 (Figure 15).

Comparing July values (Before lead ban) and August values (After lead ban) for the inbound side

Lead concentrations from sites 2, 3, 5 and 6 measured in August 2011 were lower than that of July 2005. Lead concentrations from site 4 measured in August 2011 were found to be higher than that found in July 2005 (Figure 16).

Graphs of the soil lead concentrations before and after the banning of lead in petrol on the outbound side of the N1 highway

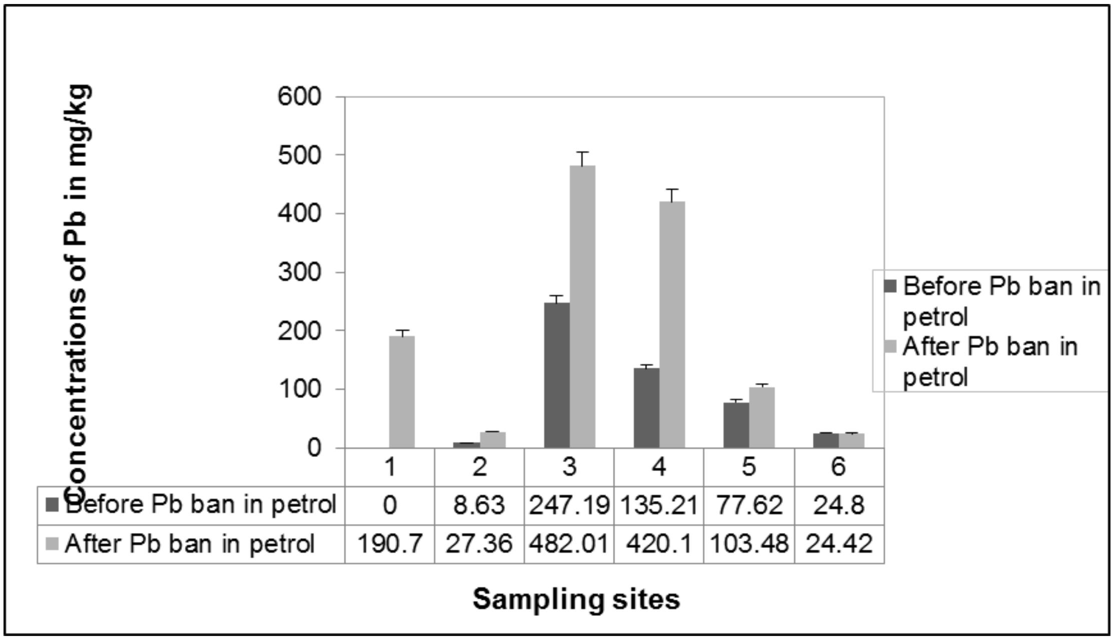
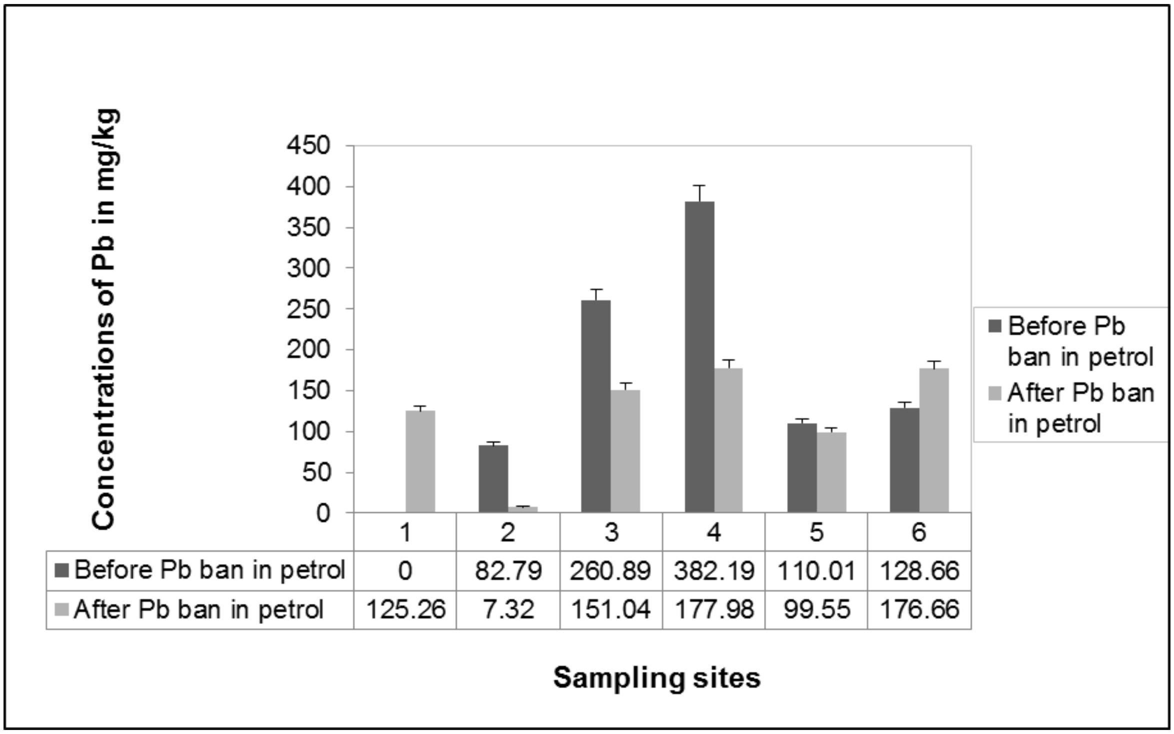


Figure 9: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after the lead ban in petrol for the outbound side of the N1. (January 2005 - before lead ban; February 2011 - after lead ban)



	1	2	3	4	5	6
■ Before Pb ban in petrol	0	82.79	260.89	382.19	110.01	128.66
■ After Pb ban in petrol	125.26	7.32	151.04	177.98	99.55	176.66

Figure 10: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the outbound side of the N1. (March 2005 - before lead ban; April 2011 - after lead ban)

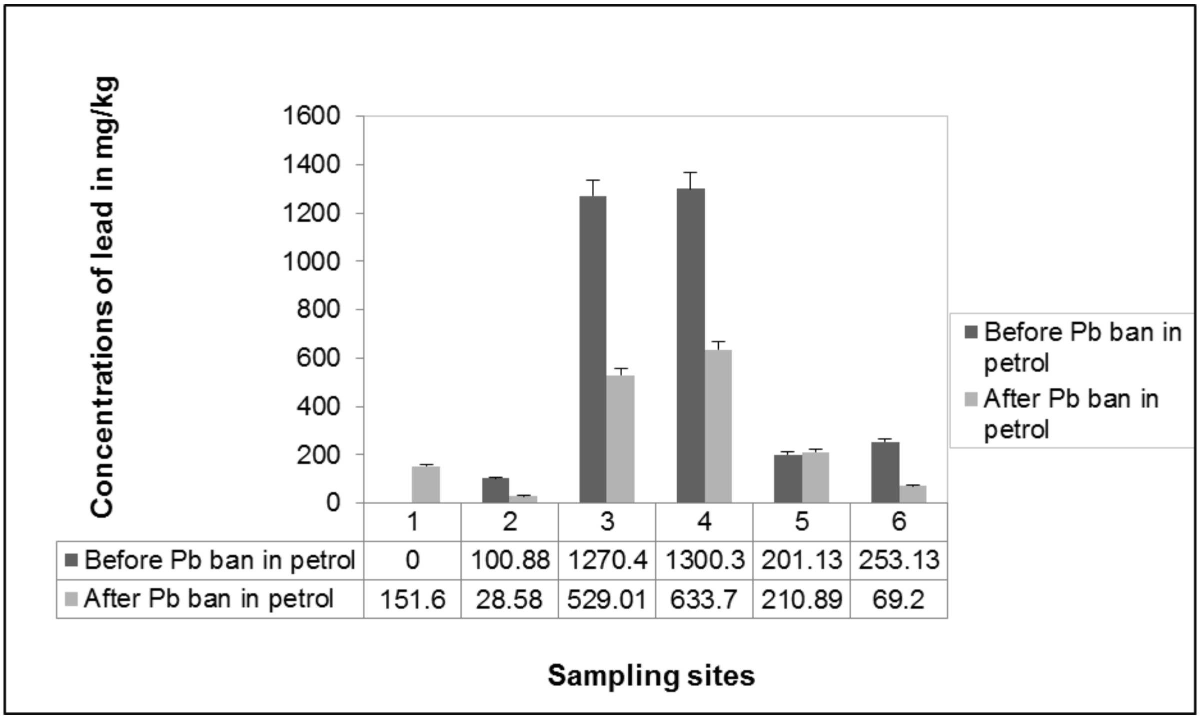
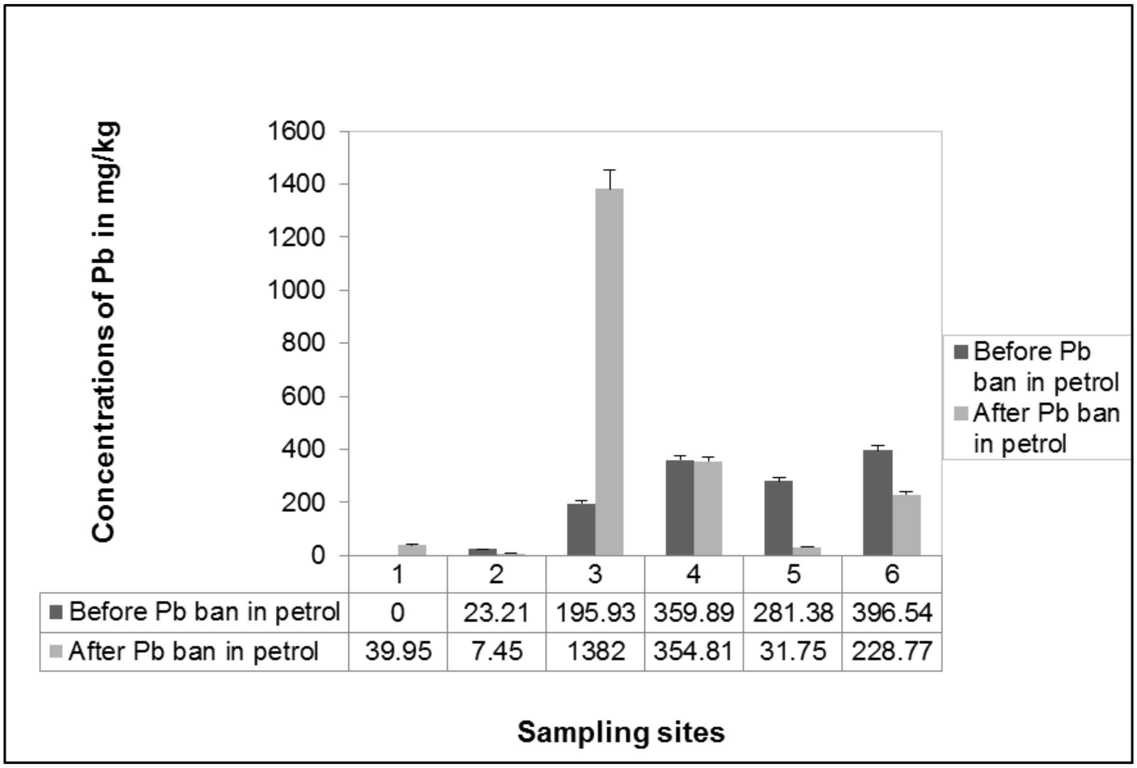


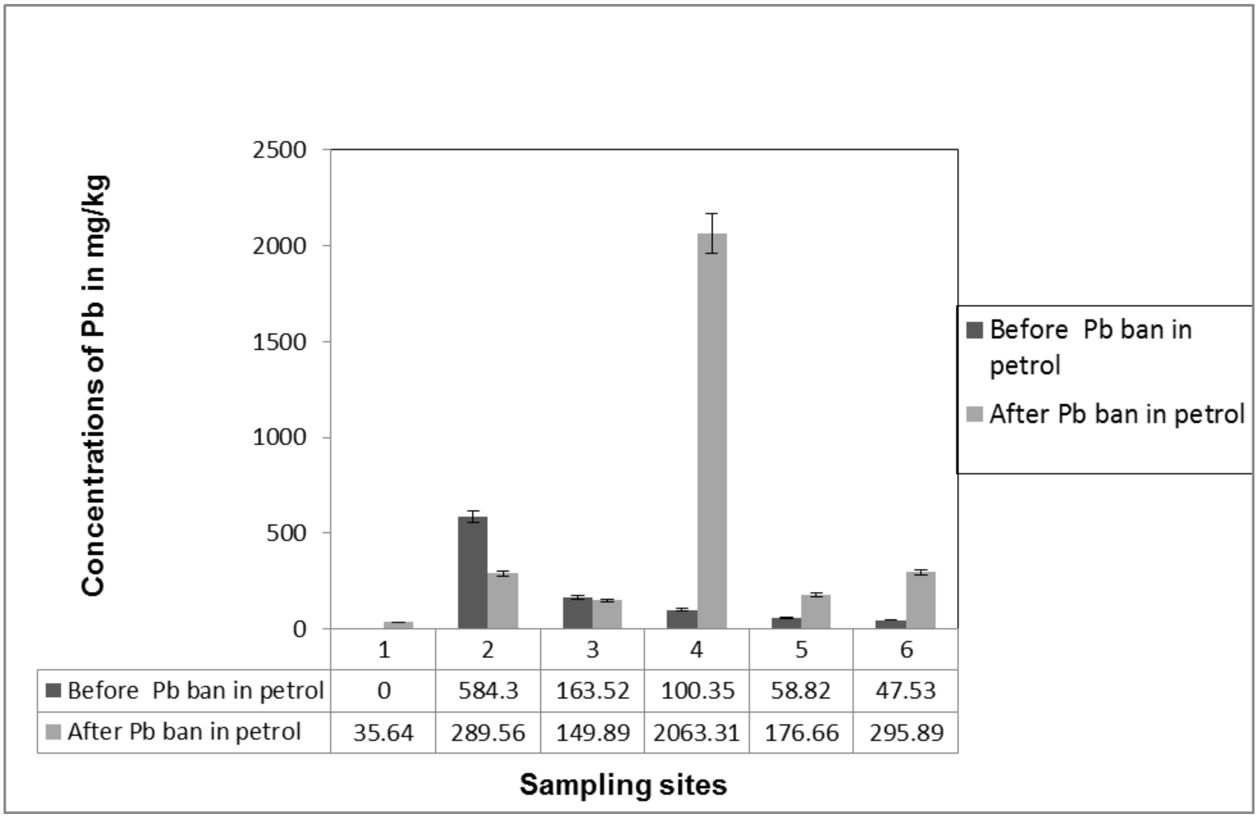
Figure 11: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the outbound side of the N1. (May 2005 - before lead ban; June 2011 - after lead ban)



	1	2	3	4	5	6
■ Before Pb ban in petrol	0	23.21	195.93	359.89	281.38	396.54
■ After Pb ban in petrol	39.95	7.45	1382	354.81	31.75	228.77

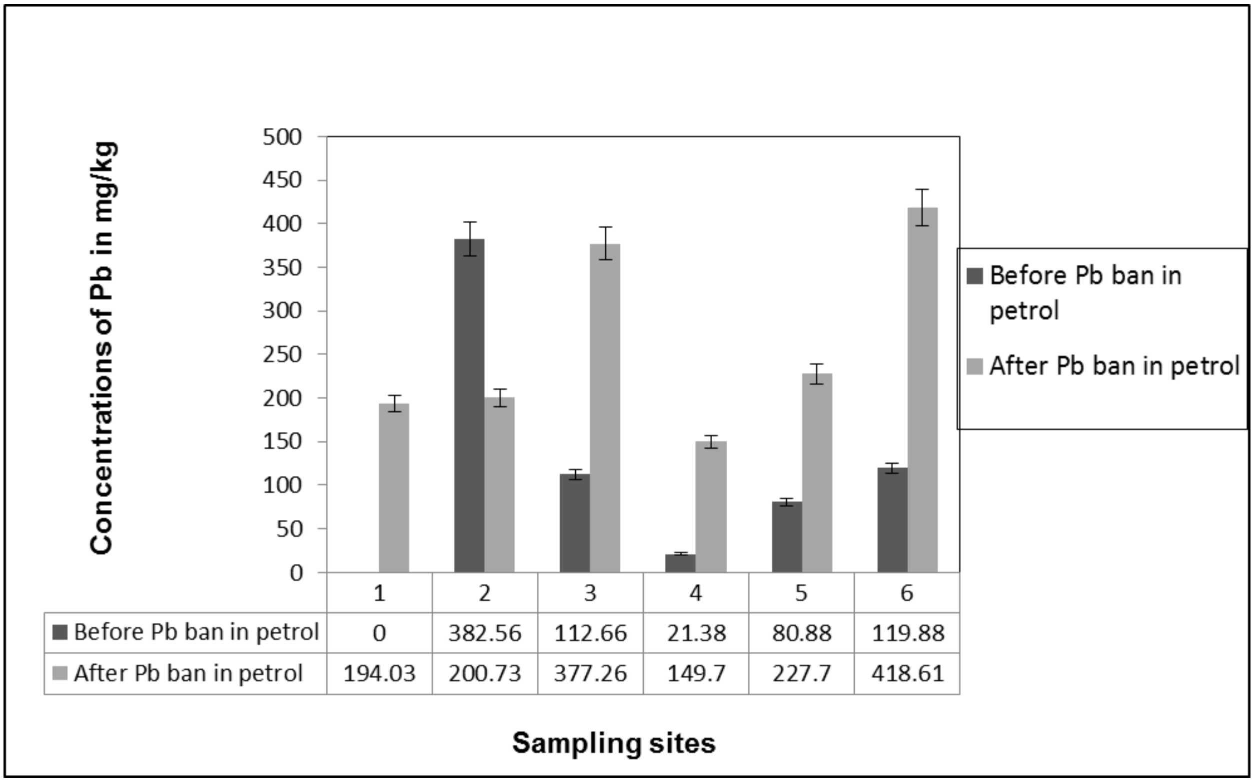
Figure 12: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the outbound side of the N1. (July 2005 - before lead ban; August 2011 - after lead ban)

Graphs of the soil lead concentrations before and after the banning of lead in petrol on the inbound side of the N1 highway



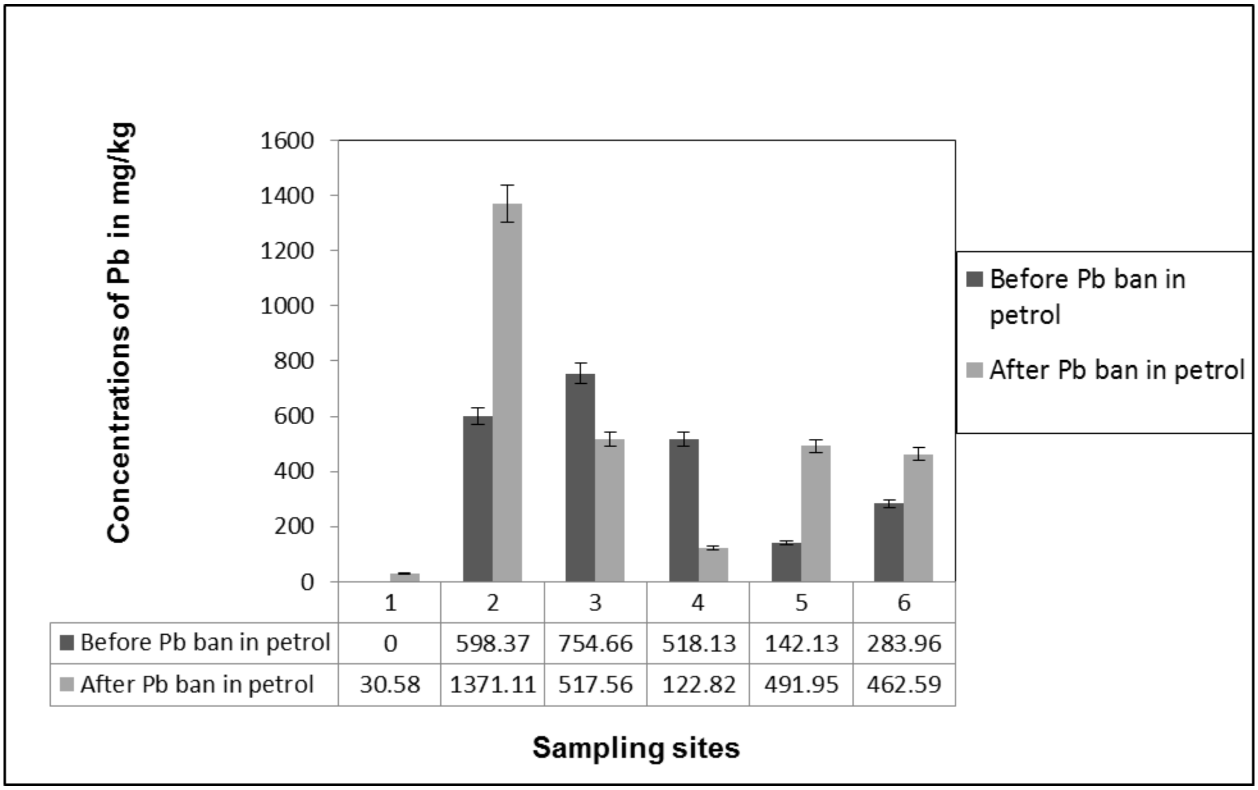
	1	2	3	4	5	6
■ Before Pb ban in petrol	0	584.3	163.52	100.35	58.82	47.53
■ After Pb ban in petrol	35.64	289.56	149.89	2063.31	176.66	295.89

Figure 13: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the inbound side of the N1. (January 2005 - before lead ban; February 2011 - after lead ban)



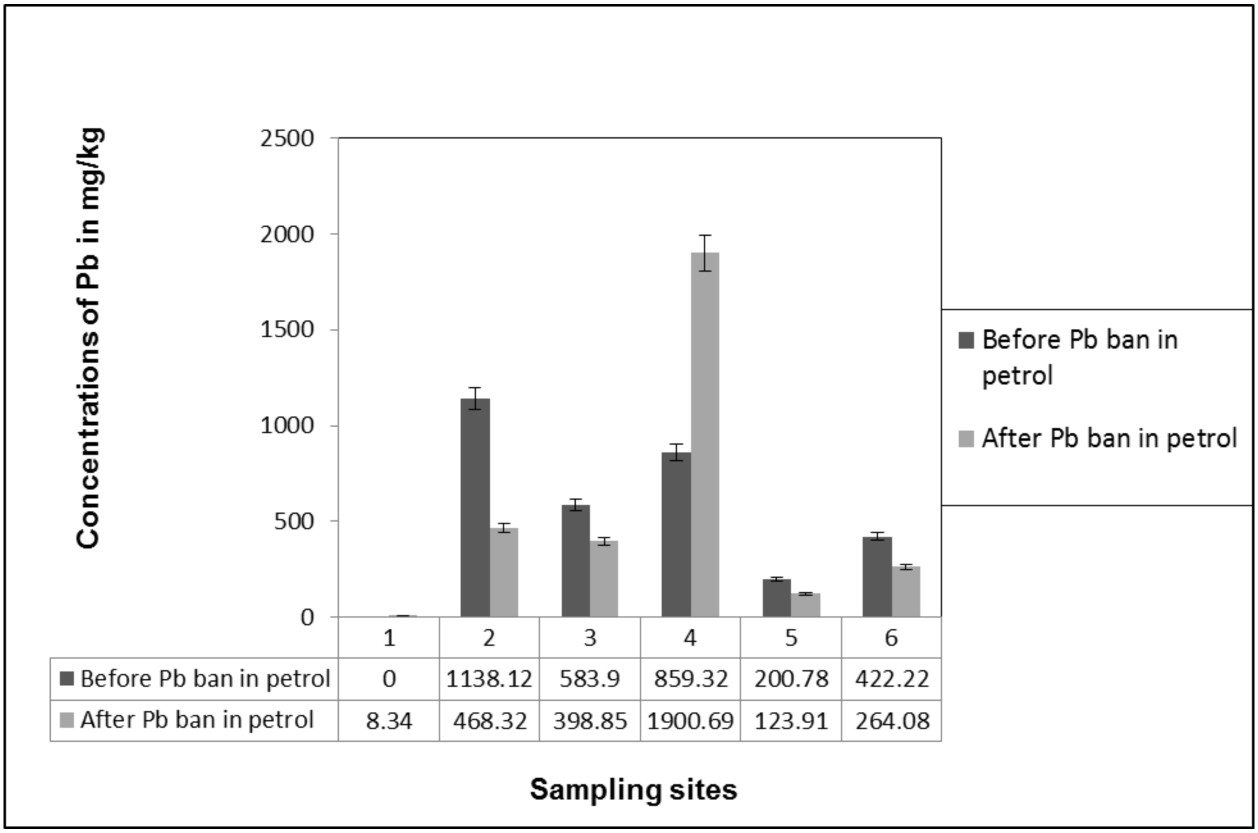
	1	2	3	4	5	6
■ Before Pb ban in petrol	0	382.56	112.66	21.38	80.88	119.88
■ After Pb ban in petrol	194.03	200.73	377.26	149.7	227.7	418.61

Figure 14: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the inbound side of the N1. (March 2005 - before lead ban; April 2011 - after lead ban)



	1	2	3	4	5	6
■ Before Pb ban in petrol	0	598.37	754.66	518.13	142.13	283.96
■ After Pb ban in petrol	30.58	1371.11	517.56	122.82	491.95	462.59

Figure 15: Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the inbound side of the N1. (May 2005 - before lead ban; June 2011 - after lead ban)



	1	2	3	4	5	6
■ Before Pb ban in petrol	0	1138.12	583.9	859.32	200.78	422.22
■ After Pb ban in petrol	8.34	468.32	398.85	1900.69	123.91	264.08

Figure 16 : Mean concentrations of lead (mg/kg) (± SD) in the soil before and after lead ban in petrol for the inbound side of the N1. (July 2005 - before lead ban; August 2011 - after lead ban)

PART 2: DISCUSSION

3.4) Lead in soil along the road verges of the N1 highway over a period of one year

The highest mean lead concentrations of over 1000mg/kg were found at the following sites: the outbound side of site 3 in December 2011 (1018.81mg/kg) and site 3 in August 2011 (1382.04 mg/kg) and the inbound side of site 2 in June 2011 (1371.11mg/kg), site 4 in February 2011 (2063.31mg/kg) and site 4 in August 2011 (1900.69 mg/kg). In a study done in Finland by Peltola et al. (2005) it was found that lead in soil in urban environments at concentrations over 1000 mg/kg is hazardous.

Lead concentrations at 1000 mg/kg or higher were also observed in the soil at sites 3 and 4 of the present study. These sites are located near residential areas where children may be exposed to lead in the soil. This may be a cause for concern as children absorb more lead from the environment than adults as indicated in a report conducted by Ahamed and Siddiqui (2007). Children's behaviour, including the tendency to touch and taste any objects in their surroundings, may increase their risk of exposure to soil lead. Children always have a habit of eating non-food items such as soil and paint and exhited excessive hand-to-mouth behaviour exposing them to lead poisoning. The risk of lead exposure is particularly higher under the age of four years, when children are still at the exploring stages of their lives. Children also retain more lead in their bodies than adults. In the body this lead is distributed to several organs, including the brain, liver and kidneys, and is stored in the teeth and bones, where it accumulates over time (Laidlaw et al., 2005). The rapid development of the nervous system in children makes them more susceptible to lead-induced disturbance (Finkelstein et al., 1998).

A number of studies around the world have reported that urban soils have contributed significantly to child BPb poisoning (Mielke and Reagan, 1998). Several ecological studies have found that there is a correlation between urban soil lead concentrations and children’s BPb. Mielke et al. (1997) reported that there was a significant logarithmic relationship between soil lead concentrations and child BPb in New Orleans. Similar levels of child BPb originating from soil lead may also be found in Cape Town. There is a need for further studies to investigate the impact of lead from soil on children in Cape Town.

The N1 highway is one of the major highways in South Africa and receives high volumes of traffic on a daily basis (Tables 3 and 4). The results of the present study show that sites 3 and 4 recorded the highest concentrations of lead in the soil samples on both sides of the road during the entire sampling period. The case of sites 3 and 4 being more predominant to other sites could be attributed to the fact that these sites are located near turnoffs, experiencing heavy traffic volumes more frequently than the other sites during peak hours. Vehicles are often moving slowly as a result of the heavy traffic in these areas and this may account for the high concentrations of lead in the soil at these sites. This is in line with Francek’s (1992) report that traffic congestion at crossroads and turnoffs result in higher levels of metals, including lead, in the environment.

Although leaded petrol has been phased out in South Africa since January 2006, there is still a danger of lead contamination due to the long decay half-life that lead exhibits (Pirkle et al., 1985). Chen et al. (1997) reported that higher concentrations of metals reaching the soil remain present in the subsoil for many years even after the source of pollution has been removed. This can also explain the high concentrations of lead in the soil at sites 3 and 4. The high concentrations of lead at these sites may also come from the wear of brake linings and rubber tyres. In a study done by the EEA (2007), 3126mg/kg of soil lead concentrations were reported in Sweden from brake linings and 107mg/kg from rubber tyres. This may thus indicate that a similar situation is applicable in South Africa as a result of the fact that the number of vehicles driven in South Africa is at the same level or higher as that observed in Sweden, with most of these vehicles being older in South Africa than in developed countries such as Sweden. In addition, Harper et al. (2003) reported that older vehicles are linked with higher levels of pollutant emissions in the environment. These sources of lead concentrations in the environment could introduce high amounts of lead into the atmosphere (Rodrigues-Flores and Rodrigues-Castellon, 1982), which may cause accumulation of lead in the upper 0 to 5 cm of soil (Harrison et al., 1981).

Mean lead concentrations were found to be relatively low at site 1, compared to other sites throughout the entire sampling period on both sides of the road. The relatively low concentrations of lead in the soil at this site may be due to low organic soil content (between 0.96% and 0.99%) at this site compared to other sites. Turer et al. (2001) reported that the concentrations of metals in soil increase as the amount of organic matter increases and decreases when the amount of organic matter decreases. This may at least partly explain the low concentrations of lead at this site.

The mean concentrations of lead found in the roadside soil of the N1 highway ranged between 7.32mg/kg and 2063.31mg/kg. In a study done in Solonge, France by Lee et al. (1997) mean lead concentrations of 1.456 mg/kg were found in roadside soils. In a study by Sezgin et al. (2003) mean lead concentrations of 185.85mg/kg were found in roadside soil of Istanbul, Turkey. The mean lead concentrations of 319.014mg/kg in roadside surface soils in the present study are much higher than in the aforementioned studies. The higher concentrations of lead in the soil in the present study may be due to the fact that vehicles are on average older in South Africa than in developed countries. Swaileh et al. (2004) found that cars are a source of several pollutants to the environment, particularly lead.

A previous study along the N1 highway conducted before the banning of leaded petrol (Kruger, 2008) recorded mean lead concentrations ranging between 12.96mg/kg and 1990mg/kg. The present study conducted after the banning of lead in petrol found comparable mean lead concentrations when compared to the Kruger (2008) investigation. This may be due to the fact that lead has a long decay half-life in the soil (Pirkle et al., 1985) and means that although a major source of lead pollution (leaded petrol) was removed the contamination of the soil does not necessarily lower in the short to medium term. These potentially toxic lead concentrations in the soil may affect the health of residents and the surrounding environment. The contaminated soil may also cause elevated concentrations of lead in crops, such as vegetables, grown along the highway and thus affect food quality and safety (Ho and Tai, 1988; Garcia and Millan, 1998). Food chain contamination is one of the most important pathways through which toxic pollutants enter into the human body (Ma et al., 2006). Along the N1 highway there are residential areas, shopping malls, and farmlands where crops are grown and livestock were seen grazing. The concern is that these crops that are grown close to this busy highway could contain lead levels that may be dangerous to human and animal health when consumed (Williamson and Evans, 1972; Nabuluo et al., 2006).

3.4.1) Factors influencing the concentrations of lead in soil

Lead concentrations in roadside surface soil are influenced by a number of factors as described by Melaku et al. (2005). Their possible influences in the present study are discussed below.

3.4.1.1) Rainfall and runoff

There was a sharp drop in lead concentrations in the soil at site 4 on the outbound side in February 2011 from 2063 mg/kg to 122.82 mg/kg in June 2011. Average rainfall measurement in February was 18mm and in June 70mm (Table 2). One of the reasons for this sharp drop may be due to the fact that samples were collected during different periods of the year, when the amount of rainfall differs. In a study conducted by Sabin et al. (2005) in Los Angeles it was found that metal concentrations in the environment were significantly lower during periods of heavy rains than periods of low rainfall. They also found that a deposition of 1% of metals was recorded in the environment during periods of heavy rains and 10% during the period of low rains, thus leading to a conclusion that deposition of metals occurs mostly during periods of low rains. This can partly explain the high concentrations of lead of 2063mg/kg in the soil at the outbound side of site 4 in February with average rainfall of 18mm, to lower concentrations of 122.82mg/kg in June with an average rainfall of 70mm (Table 2).

Greenstein et al. (2004) reported that run-off due to rain for long periods may affect the concentrations of metals in the soil. The fluctuating pattern in lead concentrations found in surface soil along the N1 highway confirmed that rainfall and runoff played a contributing role. Lead polluted runoff water may run into storm water pipes and water bodies as reported by Mitsch and Gosselink (1993) and Nabuloa et al. (2006), thus causing toxic effects in aquatic animals when lead bioaccumulates in their body tissues, and may also cause toxic impacts to humans if animals, used as food by humans, are consumed (Schiff et al., 2002). A similar situation may possibly be observed at site 5 of the present study as it is located near a river which may be polluted by lead runoff from the N1 highway.

3.4.1.2) Wind

There were sharp increases and decreases in the mean lead concentrations at most of the sites throughout the sampling period. The prevailing winds in Cape Town are south-easterly in the summer and north-westerly in the winter. Atmospheric particulates containing lead compounds emitted from vehicle exhausts are deposited within 0 to 5 meters from the road's edge on roadside surface soils and can be further carried to longer distances by the wind (Othman et al., 1997). Bakirdere and Yaman (2008) reported that the directions and strength of the wind can remove metal particles from the southern to the northern side of a stretch of the road. The prevailing winds in Cape Town are extremely strong and blow from the Cape Flats over the N1 in the summer. The soil type is sandy as seen in Tables 5 and 6 of the present study, causing soil to blow away from one area and to settle somewhere else (Tong and Che Lam, 2000). The fluctuating pattern in lead concentrations in the soil of the N1 highway of the present study can be partially attributed to wind being another contributing factor. This can be a serious problem as residential homes are constructed close to the N1 highway at many of the sampling sites. Although leaded petrol has been phased out of use in South Africa, there is still a possibility of lead contamination in the soil in areas close to the road, due to the long decay half-life of lead already present in the soil (Pirkle et al., 1985). Cannon and Bowles (1962) found that grasses within 150m from the highway roadside were contaminated with lead, putting residents and animals close to this highway at high risk when these grasses are consumed. In order to minimize the effects of such types of lead contamination to residents and plants, residential homes should be constructed several meters away from highway roadsides (Cannon and Bowles, 1962).

Nabulao et al. (2006) also reported that leaves on roadside crops can accumulate metals at high concentrations from vehicle emissions resulting in a serious health risk to animals and humans when consumed. This can be evident on the N1 highway as agricultural crops were seen to grow next to the N1 highway, even though outside the sampling sites of the present study. These crops may have been exposed to vehicle emissions, due to wind driven transport of contaminants, and can accumulate considerable concentrations of metals (Swaileh et al., 2004). Residents and animals that consume these crops may be under high risk of metal contamination. Othman et al. (1997) found that lead pollution along the roads of Damascus, Syria may be found a distance away from a road's edge and suggested that vegetables be planted at least 200m away from the roadside. This contamination away from the road's edge may be due to wind driven transport of lead containing soil particles.

3.5) Vertical distribution of lead in soil along the road verges of the N1 highway

For the purpose of this study, once-off soil samples were collected at depths of 0-2cm, 30 cm and 60 cm at sites 1, 5 and 6, respectively, on the outbound and the inbound sides of the of N1 highway.

Lead concentrations ranged from 52.72 mg/kg to 215.94 mg/kg for surface soil, from 15.80 mg/kg to 164 mg/kg at a depth of 30 cm and from 14.06 mg/kg to 216.07 mg/kg at a depth of 60 cm (Tables 5 and 6).

In a study conducted by Ramakrishnaiah and Somashekar (2002) it was reported that higher concentrations of lead were present in the top 5 cm of soil and decreased with increasing depth. They also found that at surface level the highest soil lead concentration was 276.26 mg/kg and at a depth of 30 cm the concentration was at 31.02 mg/kg. In the present study, the highest soil lead concentration at surface level was at 215.94 mg/kg and at a depth of 30 cm the highest concentration recorded was 164 mg/kg. It can thus be concluded that the soil of the present study is more contaminated at a depth of 30 cm when compared to the above mentioned study. The reason for this can be in the fact that the soil in the present study is sandy (Tables 5 and 6), and due to its structure cause lead to migrate deeper into the soil. Godin (1986) attempted to evaluate the vertical migration of metals in soil. Samples were taken from boreholes, to a maximum depth of 1 m. The study showed that lead concentrations in the soil decreased with increasing depth. However, the depth reached by the lead was not determined. Godin (1986) concluded that there is a strong link between metal concentrations and the organic matter of the soil. Furthermore, Godin (1986) concluded that downward migration of contaminants are more pronounced in sandy soils. Yassaglou (1987) also found significant lead concentrations at a depth of 160 cm in sandy soil.

The concentrations of lead in the soil were statistically higher at the surface level (0 - 2 cm), when compared to soil collected at depths of 30 cm and 60 cm. These higher concentrations may be as a result of the difference in soil organic content at surface level which is slightly higher than at depths of 30 cm and 60 cm (Table 5). Sharma et al. (2000) reported that there is a positive correlation between lead concentration and the amount of soil organic content. They also concluded that as soil organic content increase lead concentrations also increase.

In a study done in China by Fayun et al. (2009) it was reported that lead was evenly distributed at surface level in the soil, and that lower lead concentrations were found at depths of 40 cm and 60 cm with relatively higher concentrations found at 80 cm and 100 cm depths into the soil. This observation was attributed to long term pollution from leaching due to a low pH value of 5.85 in the top soil. Because of the low pH, the leaching process might have been accelerated down to depths of 80 cm and 100 cm. pH is one of the main factors governing the concentrations of soluble metals like lead; solubility tends to be increased at lower pH values and decreases at higher pH values (Wang and Qin, 2005). This may explain the higher concentrations of lead (216 mg/kg) found at a depth of 60 cm, relative to the surface soil (128 mg/kg), at the outbound side of the N1 highway at site 5 of the present study.

From the results (Tables 5 and 6), it was found that soil pH values were in a range from 5.98 to 7.30 with an average of 7.10, indicating that the pH were generally neutral to weak alkaline. Soil organic content was found to range from 0.69 % to 2.54 % with an average of 1.28 %.

Sheppard and Thibault (1992) reported that soils with organic content ranging from 0.52% to 2.3% often retain most of the lead present within them to a depth of 30 cm. This may explain the relatively high lead concentration of 168.88 mg/kg, at a depth of 30 cm at the outbound side of the N1 highway at site 5, which was found to have a soil organic content of 0.82%. Asami et al. (1995) attributed the low mobility of lead in polluted soils to their affinity to soil organic matter. Marsh and Siccama (1997) reported a decrease in soil lead content with depth consistently correlating this with soil organic matter (which decreases with increasing soil depth). This can explain the general consistent decrease in soil lead concentrations from surface level (0 – 2 cm), to depths of 30 cm and 60 cm at all the sites considered in this study.

Nandram and Verloo (1985) reported a low solubility of lead in the soil with a pH of 6 to 6.5. They also found that lead exhibited weak solubility at slightly alkaline conditions (pH 8), hence concluding that metals are more soluble under extremely acidic conditions than at more alkaline pH values. In the present study, the soil pH ranged from 5.98 to 7.30 with an average pH of 7.10 in a neutral to slightly alkaline condition. This may explain why the concentrations of lead are generally higher in the surface soil samples for all sites of the present study.

3.6) Comparison of lead concentrations in soil along the road verges of the N1 highway before and after the banning of leaded petrol

The results generally show differences in lead concentrations in the soil for most sites before and after the banning of leaded petrol, with few sites showing no significant differences.

The results also showed that there is a fluctuating pattern in lead concentrations in soil along the N1 highway before and after the banning of leaded petrol in South Africa. This may be due to different reasons.

A high concentration of 1300.25mg/kg was found before the banning of leaded petrol at the outbound side of the road at site 4 in the month of May, with a lowest soil lead concentration of 8.63 mg/kg found at the outbound side at site 2 in the month of January.

A high concentration of 1138.12 mg/kg was recorded on the inbound side of site 2 in the month of July before the lead ban in petrol, with the lowest concentration of 21.38 mg/kg recorded at the inbound side of site 4 in the month of March.

The highest concentration of 1382.04mg/kg was recorded at the outbound side in the month of August at site 3 after the banning of leaded petrol. The lowest lead concentration of 7.32mg/kg was recorded at the outbound side of the road at site 2 in the month of April after the banning of leaded petrol.

The highest soil lead concentration of 2063mg/kg was recorded after the banning of leaded petrol at the inbound side at site 4 in the month of February, with the lowest lead concentration of 8.34mg/kg recorded at the outbound side of the road at site 2 in the month of August.

The higher concentration of 2063mg/kg found at site 4 in the month of February after the lead ban, may be due to the fact that this site is located on an incline where traffic intensity has been high over the years (during which leaded petrol was in use). Significant deposits of lead from vehicles had been made at this site as the heavy vehicular traffic left its effects at this site. Metals can remain in the subsoil for years after their source has been removed (Chen et al., 1997). This can explain the high concentration of lead at site 4 after even leaded petrol had been phased out in South Africa.

Lead concentrations in soil coming from traffic activity can be transported through the food chain into the human body and thus be very toxic to humans. In agricultural areas, the intake of metals through the soil-crop system could play a major role in human exposure to metals (Liu et al., 2007).

A study conducted in 2010 in the USA revealed that the BPb during the years of maximum leaded petrol usage (1960 - 1975) was estimated at about 48 µg/dl and possibly even 63 µg/dl. The conclusion is thus that high levels of BPb (estimated at 40µg/dl to 63µg/dl) can lead to clinical and behavioural impairment, which may have serious health implications for adults, who had high levels of lead exposure as children. Lead acquired from leaded petrol emissions was the main source of lead exposure for children during the latter two-thirds of the 20th century (Robbins et al., 2010). In South Africa, a similar situation is applicable to adults at risk of health problems, who had high levels of lead exposure as children during the period of the use of leaded petrol, which spanned from 1960 to when it was totally phased out in 2006.

In a study conducted by Turer et al. (2001) it was found that metals are released into the soil from the weathering of road surface, asphalt, corrosion of batteries and road signs. This may explain the fluctuating pattern and the constant availability of lead in soil along the N1 highway even after the banning of leaded petrol, a reality which points to the fact that there certainly are multiple sources of lead contamination in soil along road verges.

Although the use of unleaded petrol may have led to a subsequent decrease in fuel emissions of lead into the environment, lead may still be deposited into the soil from exhaust gases and worn metal alloys in vehicle engines (Winther and Slento, 2010). Metals are not easily removed from the soil because of their irreversible immobilization within different soil types as reported by Gulser and Erdogan (2008). The above studies may explain why there is a constant availability of lead in the soil at some sites along the N1 highway.

Therefore, lead accumulation and toxicity in soil due to vehicular emission, even after the banning of leaded petrol, will remain a relevant topic for investigation into the future.

CHAPTER FOUR: RESULTS AND DISCUSSION: MANGANESE

PART 1: RESULTS

4.1) Distribution of manganese in soil along the road verges of the N1 highway over a period of one year

The mean manganese concentrations for the outbound and inbound sides of the N1 highway for the sampling period February 2011 to December 2011 are presented in Table 7 and illustrated in Figures 17 to 22. Manganese concentrations are expressed in mg/kg.

4.1.1) Comparisons of soil manganese concentrations between sampling sites per sampling occasion

4.1.1.1) Outbound

On sampling occasion one, statistically significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 1 and 2, sites 2 and 3, and between sites 5 and 6. There were no significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil between sites 3 and 4, sites 4 and 5, and sites 1 and 6.

On sampling occasion two, pairwise multiple comparisons of manganese concentrations in the soil were significantly different ($P<0.05$) between sites 1 and 2, sites 2 and 3, sites 3 and 4, and between 5 and 6. No significant difference ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 4 and 5, and sites 1 and 6.

On sampling occasion three, there were statistically significant differences (P<0.05) in pairwise multiple comparisons of manganese concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 4 and 5, and between sites 1 and 6. No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 3 and 4 and between sites 5 and 6.

On sampling occasion four, statistically significant differences (P<0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 1 and 2, sites 2 and 3, sites 4 and 5, sites 5 and 6, and between sites 1 and 6. Sites 3 and 4 recorded no significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil.

On sampling occasion five, pairwise multiple comparisons of manganese concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, and between sites 1 and 6 indicated significant differences between the pairs (P<0.05). No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 5 and 6.

On sampling occasion six, pairwise multiple comparisons of manganese concentrations in the soil were significantly different (P<0.05) between sites 1 and 2, sites 2 and 3, sites 3 and 4, and between sites 4 and 5. No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 5 and 6 and between sites 1 and 6.

4.1.1.2) Inbound

On sampling occasion one, there were significant differences (P<0.05) in pairwise multiple comparisons of manganese concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, and between sites 4 and 5. No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 5 and 6, and sites 1 and 6.

On sampling occasion two, pairwise multiple comparisons of manganese concentrations in the soil were significantly different ($P<0.05$) between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5. No significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 5 and 6, and sites 1 and 6.

On sampling occasion three, there were significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil between sites 1 and 2, sites 2 and 3, sites 3 and 4, sites 4 and 5, sites 5 and 6, and between sites 1 and 6. No other statistical significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded.

On sampling occasion four, statistically significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentration in the soil were recorded between sites 1 and 2, sites 2 and 3, and between sites 4 and 5. No statistically significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were found between sites 3 and 4, sites 5 and 6, and between sites 1 and 6.

On sampling occasion five, there were significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil at sites 1 and 2, sites 2 and 3, and between sites 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 3 and 4, sites 4 and 5, and between sites 5 and 6.

On sampling occasion six, pairwise multiple comparisons of manganese concentrations in the soil were significantly different ($P<0.05$) at sites 1 and 2, sites 3 and 4, sites 5 and 6, and between sites 1 and 6. No significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between sites 2 and 3, and sites 4 and 5.

4.1.2) Comparison of manganese concentrations over the sampling period per sampling site

4.1.2.1) Outbound

At site 1, pairwise multiple comparisons of manganese concentrations in soil indicate that there were statistically significant differences (P<0.05) between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 2, pairwise multiple comparisons of manganese concentrations in the soil were significantly different (p<0.05) between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, and between occasions 1 and 6. No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 5 and 6.

At site 3, there were no statistically significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 4, no significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6.

At site 5, manganese concentrations in the soil between occasions 2 and 3, 3 and 4, 4 and 5, 5 and 6, and between occasions 1 and 6 were statistically significantly different (P<0.05) in pairwise multiple comparisons. No statistically significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were found between occasions 1 and 6.

At site 6, pairwise multiple comparisons of manganese concentrations in the soil were significantly different (P<0.05) between occasions 2 and 3, 3 and 4, 4 and 5, 5 and 6, and as well as occasions 1 and 6. No significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 1 and 2.

4.1.2.2) Inbound

At site 1, there were statistically significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil between occasions 2 and 3, 3 and 4, 4 and 5, and as well as occasions 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were found between occasions 1 and 2, and between occasions 5 and 6.

At site 2, pairwise multiple comparisons of manganese concentrations in the soil were significantly different ($P<0.05$) between occasions 1 and 2, and 2 and 3. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 3 and 4, 4 and 5, 5 and 6, and as well as occasions 1 and 6.

At site 3, there were statistically significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil between occasions 1 and 2, 2 and 3, 4 and 5, 5 and 6, and as well as occasions 1 and 6. No statistically significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 3 and 4.

At site 4, significant differences ($P<0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 1 and 2, 2 and 3, 3 and 4, 5 and 6, and as well as occasions 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 4 and 5.

At site 5, manganese concentrations in the soil between occasions 1 and 2, 2 and 3, 3 and 4, 4 and 5, as well as occasions 5 and 6 were significantly different ($P<0.05$) in pairwise multiple comparisons. No statistically significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 1 and 6.

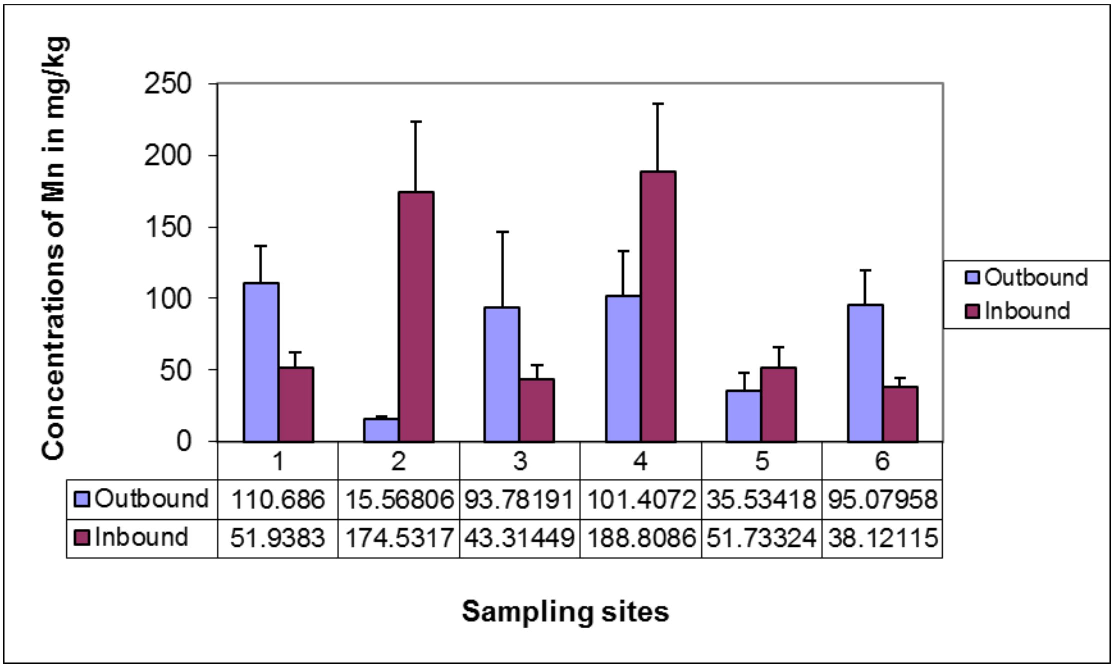
At site 6, pairwise multiple comparisons of manganese concentrations in the soil were significantly different ($P<0.05$) between occasions 1 and 2, 3 and 4, 4 and 5, and as well as occasions 1 and 6. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations in the soil were recorded between occasions 2 and 3, and between occasions 5 and 6.

Table 7: The mean manganese concentrations (mg/kg) (± SD) for the outbound and inbound sides of the N1 highway for the sampling period February 2011 to December 2011. Numbers 1 to 6 in the left column represent the sampling sites

SAMPLING SITE N1		**SAMPLING OCCASION**					
		Feb-2011	**Apr-2011**	**Jun-2011**	**Aug-2011**	**Oct-2011**	**Dec-2011**
1) Out	**Mean**	$^{\mathrm{a}}$**110.68**$^{\mathrm{1}}$	$^{\mathrm{a}}$**79.81**$^{\mathrm{2}}$	$^{\mathrm{a}}$**70.16**$^{\mathrm{2}}$	$^{\mathrm{a}}$**114.87**$^{\mathrm{3}}$	$^{\mathrm{a}}$**46.83**$^{\mathrm{4}}$	$^{\mathrm{a}}$**60.92**$^{\mathrm{4}}$
	SD	25.83	34.86	11.94	46.37	11.84	11.89
1) In	**Mean**	$^{\mathit{a}}$**51.93**$^{\mathit{1}}$	$^{\mathit{a}}$**57.55**$^{\mathit{1}}$	$^{\mathit{a}}$**43.96**$^{\mathit{1}}$	$^{\mathit{a}}$**25.76**$^{\mathit{2}}$	$^{\mathit{a}}$**33.93**$^{\mathit{2}}$	$^{\mathit{a}}$**39.23**$^{\mathit{2}}$
	SD	10.76	6.42	12.22	6.53	10.80	10.46
2) Out	**Mean**	$^{\mathrm{b}}$**15.58**$^{\mathrm{1}}$	$^{\mathrm{b}}$**23.60**$^{\mathrm{1}}$	$^{\mathrm{b}}$**18.38**$^{\mathrm{1}}$	$^{\mathrm{b}}$**14.07**$^{\mathrm{1}}$	$^{\mathrm{b}}$**94.76**$^{\mathrm{2}}$	$^{\mathrm{b}}$**81.68**$^{\mathrm{2}}$
	SD	2.54	4.01	4.29	3.78	17.44	26.70
2) In	**Mean**	$^{\mathit{b}}$**174.53**$^{\mathit{1}}$	$^{\mathit{b}}$**101.96**$^{\mathit{2}}$	$^{\mathit{b}}$**155.89**$^{\mathit{3}}$	$^{\mathit{b}}$**140.26**$^{\mathit{3}}$	$^{\mathit{b}}$**166.48**$^{\mathit{3}}$	$^{\mathit{b}}$**140.60**$^{\mathit{3}}$
	SD	48.62	8.79	48.21	51.31	21.76	22.35
3) Out	**Mean**	$^{\mathrm{c}}$**93.78**$^{\mathrm{1}}$	$^{\mathrm{c}}$**67.85**$^{\mathrm{2}}$	$^{\mathrm{c}}$**221.47**$^{\mathrm{3}}$	$^{\mathrm{c}}$**114.73**$^{\mathrm{4}}$	$^{\mathrm{c}}$**133.30**$^{\mathrm{4}}$	$^{\mathrm{c}}$**139.97**$^{\mathrm{4}}$
	SD	53.01	7.11	32.60	15.07	33.31	19.21
3) In	**Mean**	$^{\mathit{c}}$**43.31**$^{\mathit{1}}$	$^{\mathit{b}}$**120.81**$^{\mathit{2}}$	$^{\mathit{c}}$**87.14**$^{\mathit{3}}$	$^{\mathit{b}}$**158.33**$^{\mathit{4}}$	$^{\mathit{c}}$**73.98**$^{\mathit{4}}$	$^{\mathit{b}}$**132.85**$^{\mathit{5}}$
	SD	10.25	20.96	16.36	172.44	15.65	41.55
4) Out	**Mean**	$^{\mathrm{c}}$**101.40**$^{\mathrm{1}}$	$^{\mathrm{d}}$**33.50**$^{\mathrm{2}}$	$^{\mathrm{d}}$**104.12**$^{\mathrm{3}}$	$^{\mathrm{d}}$**95.68**$^{\mathrm{3}}$	$^{\mathrm{d}}$**66.28**$^{\mathrm{4}}$	$^{\mathrm{d}}$**91.76**$^{\mathrm{5}}$
	SD	31.33	5.48	16.76	10.73	15.67	35.16
4) In	**Mean**	$^{\mathit{d}}$**188.80**$^{\mathit{1}}$	$^{\mathit{c}}$**41.91**$^{\mathit{2}}$	$^{\mathit{d}}$**61.21**$^{\mathit{3}}$	$^{\mathit{c}}$**87.88**$^{\mathit{4}}$	$^{\mathit{d}}$**135.24**$^{\mathit{5}}$	$^{\mathit{d}}$**87.60**$^{\mathit{6}}$
	SD	47.33	4.45	10.52	9.10	120.96	112.07
5) Out	**Mean**	$^{\mathrm{d}}$**35.53**$^{\mathrm{1}}$	$^{\mathrm{d}}$**34.32**$^{\mathrm{1}}$	$^{\mathrm{e}}$**65.38**$^{\mathrm{2}}$	$^{\mathrm{e}}$**12.17**$^{\mathrm{3}}$	$^{\mathrm{e}}$**27.90**$^{\mathrm{4}}$	$^{\mathrm{e}}$**55.10**$^{\mathrm{5}}$
	SD	12.90	16.96	10.30	2.71	8.50	12.79
5) In	**Mean**	$^{\mathit{e}}$**51.73**$^{\mathit{1}}$	$^{\mathit{e}}$**72.87**$^{\mathit{1}}$	$^{\mathit{e}}$**113.27**$^{\mathit{3}}$	$^{\mathit{d}}$**46.53**$^{\mathit{4}}$	$^{\mathit{e}}$**161.87**$^{\mathrm{5}}$	$^{\mathit{e}}$**43.90**$^{\mathit{6}}$
	SD	13.88	19.13	49.85	28.33	226.65	4.64
6) Out	**Mean**	$^{\mathrm{e}}$**95.07**$^{\mathrm{1}}$	$^{\mathrm{e}}$**76.61**$^{\mathrm{2}}$	$^{\mathrm{e}}$**53.65**$^{\mathrm{3}}$	$^{\mathrm{f}}$**74.43**$^{\mathrm{4}}$	$^{\mathrm{e}}$**33.69**$^{\mathrm{5}}$	$^{\mathrm{e}}$**48.79**$^{\mathrm{5}}$
	SD	24.22	20.23	9.93	10.49	4.61	6.65
6) In	**Mean**	$^{\mathit{e}}$**38.12**$^{\mathit{1}}$	$^{\mathit{e}}$**69.86**$^{\mathit{2}}$	$^{\mathit{f}}$**60.94**$^{\mathit{2}}$	$^{\mathit{d}}$**31.71**$^{\mathit{3}}$	$^{\mathit{f}}$**72.92**$^{\mathit{4}}$	$^{\mathit{f}}$**63.32**$^{\mathrm{4}}$
	SD	5.98	14.94	6.58	14.33	16.50	10.48

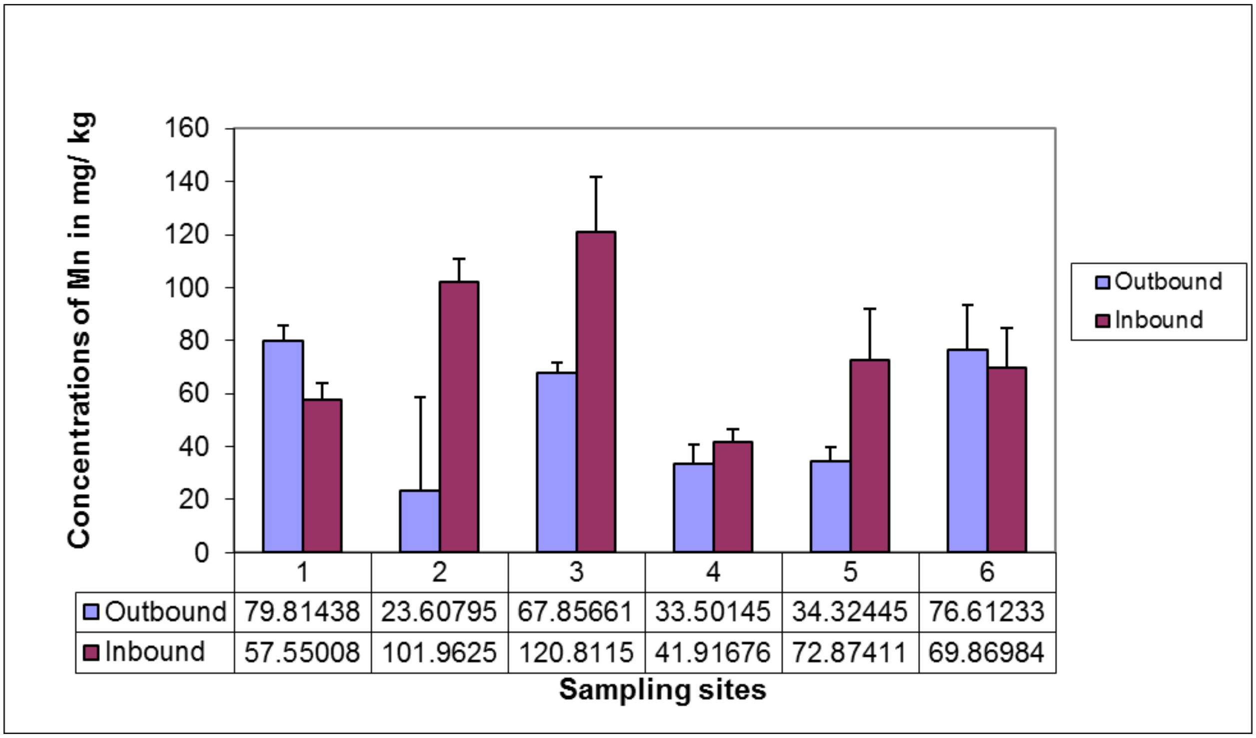
Statistically significant differences are indicated with different letters or numbers. Superscripts a to f (non-italicised) = mean value obtained from soil samples at outbound sides compared with each other for the different sites along the length of the highway; Superscripts a to f (italicised) = mean value obtained from soil samples at inbound sides compared with each other for the different sites along the length of the highway; Superscripts 1 to 6 (non-italicised) = mean value obtained from soil samples at the outbound side of one particular site compared with each other for different sampling occasions; Superscripts 1 to 6 (italicised) = mean value obtained from soil samples at the inbound side of one particular site compared with each other for different sampling occasions.

Graphs of soil manganese concentrations of the N1 highway over the sampling period February 2011 to December 2011



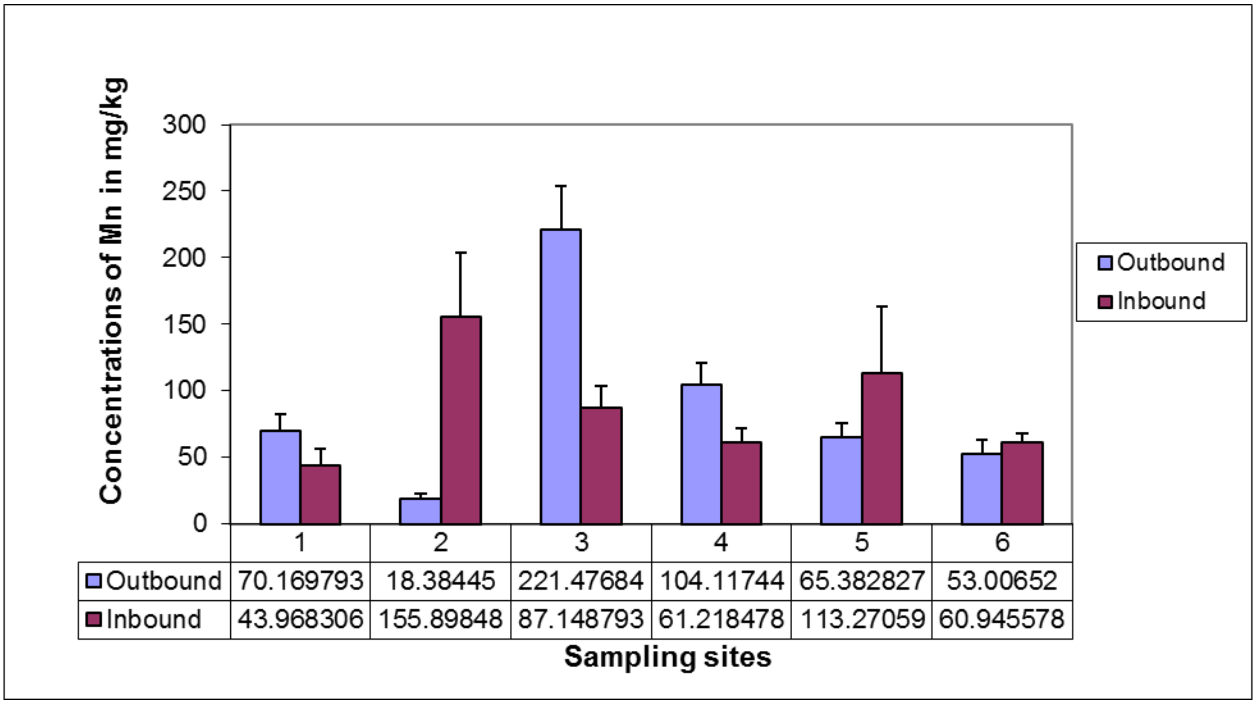
	1	2	3	4	5	6
▨ Outbound	110.686	15.56806	93.78191	101.4072	35.53418	95.07958
■ Inbound	51.9383	174.5317	43.31449	188.8086	51.73324	38.12115

Figure 17: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the February 2011 sampling occasion. N = 6.



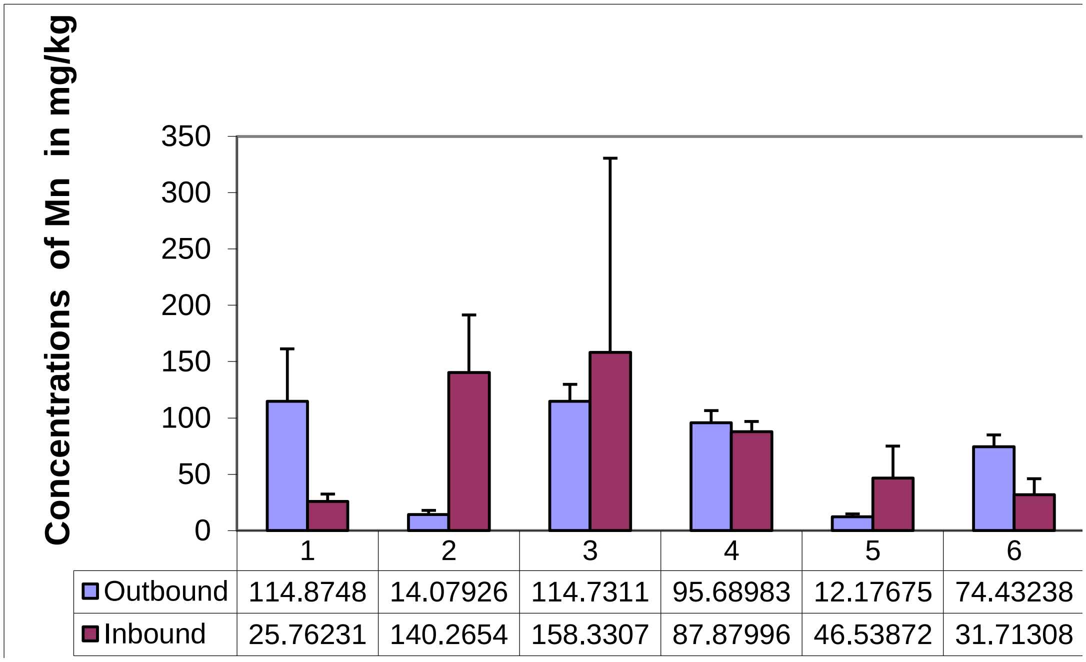
	1	2	3	4	5	6
🟦 Outbound	79.81438	23.60795	67.85661	33.50145	34.32445	76.61233
🟪 Inbound	57.55008	101.9625	120.8115	41.91676	72.87411	69.86984

Figure 18: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the April 2011 sampling occasion. N = 6.



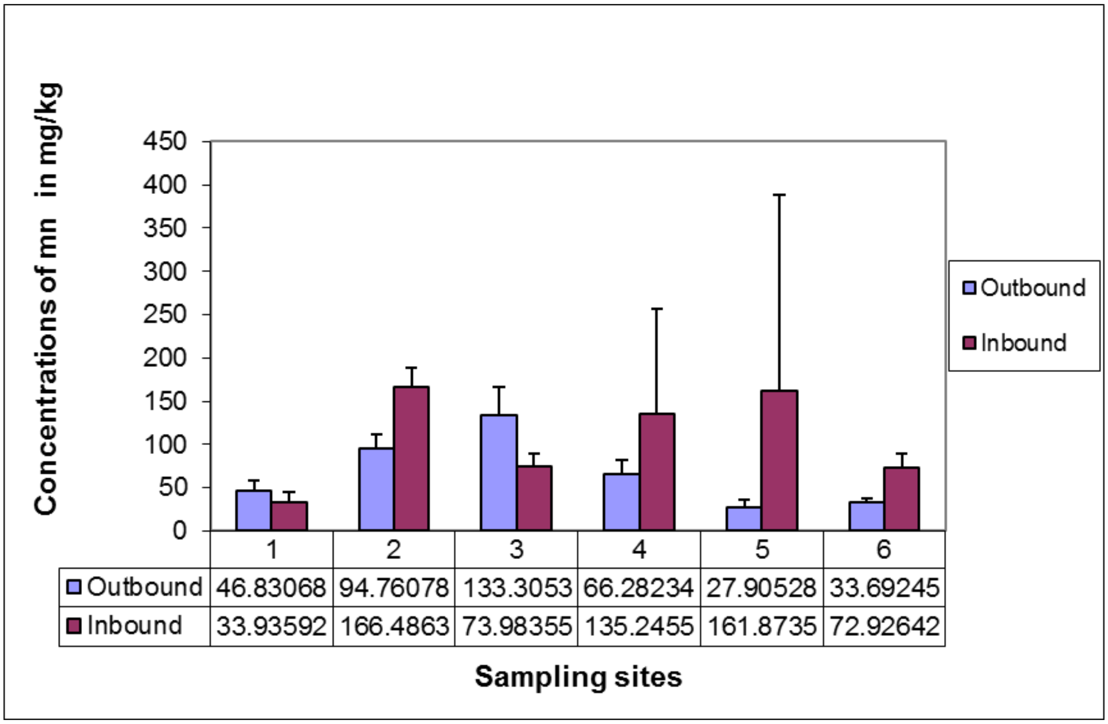
	1	2	3	4	5	6
🟦 Outbound	70.169793	18.38445	221.47684	104.11744	65.382827	53.00652
🟥 Inbound	43.968306	155.89848	87.148793	61.218478	113.27059	60.945578

Figure 19: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the June 2011 sampling occasion. N = 6.



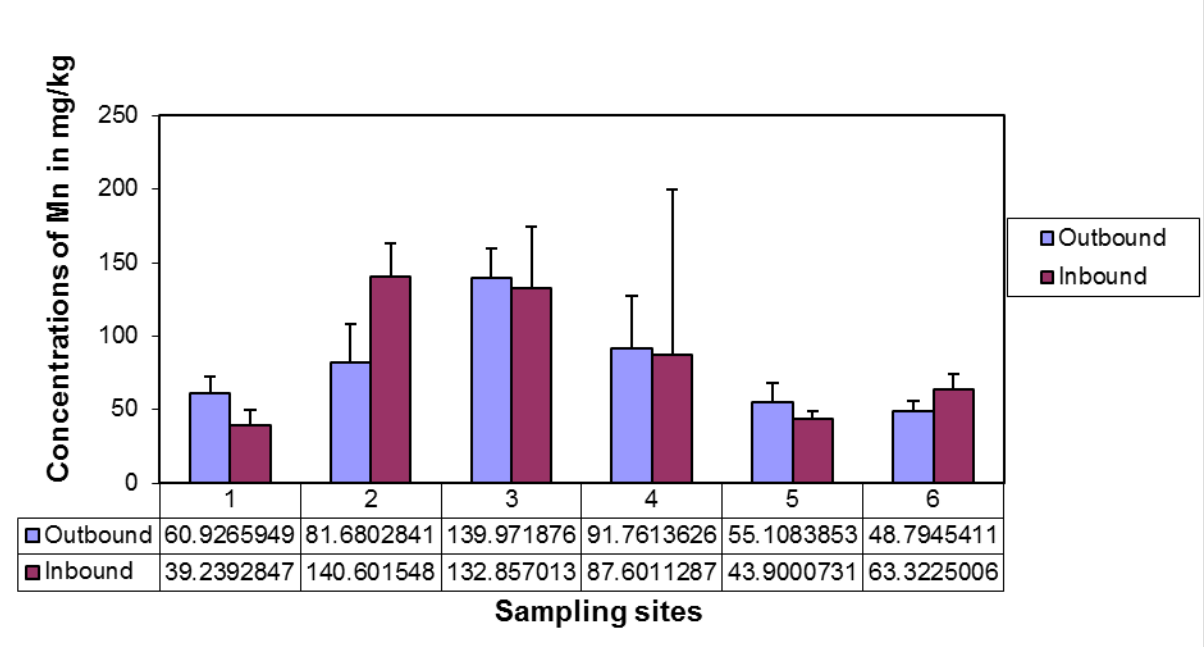
	1	2	3	4	5	6
🟦 Outbound	114.8748	14.07926	114.7311	95.68983	12.17675	74.43238
🟥 Inbound	25.76231	140.2654	158.3307	87.87996	46.53872	31.71308

Figure 20: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the August 2011 sampling occasion. N = 6.



	1	2	3	4	5	6
Outbound	46.83068	94.76078	133.3053	66.28234	27.90528	33.69245
Inbound	33.93592	166.4863	73.98355	135.2455	161.8735	72.92642

Figure 21: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the October 2011 sampling occasion. N = 6.



	1	2	3	4	5	6
🟦 Outbound	60.9265949	81.6802841	139.971876	91.7613626	55.1083853	48.7945411
🟥 Inbound	39.2392847	140.601548	132.857013	87.6011287	43.9000731	63.3225006

Figure 22: Mean manganese concentrations (mg/kg) (± SD) for the N1 highway for the December 2011 sampling occasion. N = 6.

4.2) Vertical distribution of manganese in soil along the road verges of the N1 highway

4.2.1) Outbound

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in manganese concentrations between surface soil and 30 cm depth soil, and between surface soil and 60 cm depth soil at site 1. No significant differences ($P>0.05$) in pairwise multiple comparisons were indicated for manganese concentrations between 30 cm and 60 cm depth soil at site 1 (Figure 23; Table 8).

All pairwise multiple comparisons indicated that there were no statistically significant differences ($P>0.05$) in manganese concentrations between surface soil and 30 cm depth soil, between surface soil and 60 cm depth soil, and between 30 cm and 60 cm depth soil at site 5 (Figure 23; Table 8).

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in manganese concentrations between surface soil and 30 cm depth soil, between surface soil and 60 cm depth soil, and between 30 cm and 60 cm depth soil at site 6 (Figure 23; Table 8).

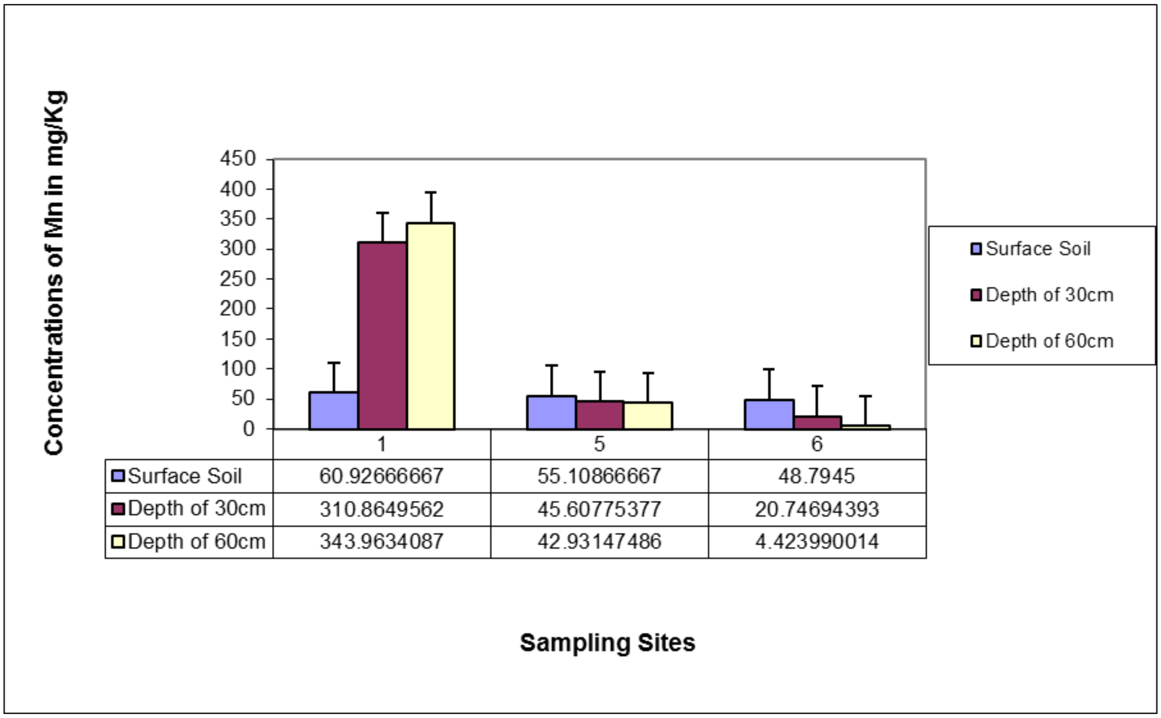
4.2.2) Inbound

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in manganese concentrations between surface soil and 30 cm depth soil, and between 30 cm and 60 cm depth soil at site 1. No significant differences ($P>0.05$) in pairwise multiple comparisons of manganese concentrations were found between surface soil and 60 cm depth soil at site 1 (Figure 24; Table 9).

All pairwise multiple comparisons indicated that there were statistically significant differences ($P<0.05$) in manganese concentrations between surface soil and 30 cm depth soil, and between surface soil and 60 cm depth soil. No statistically significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations were found between 30 cm and 60 cm depth soil at site 5 (Figure 24; Table 9).

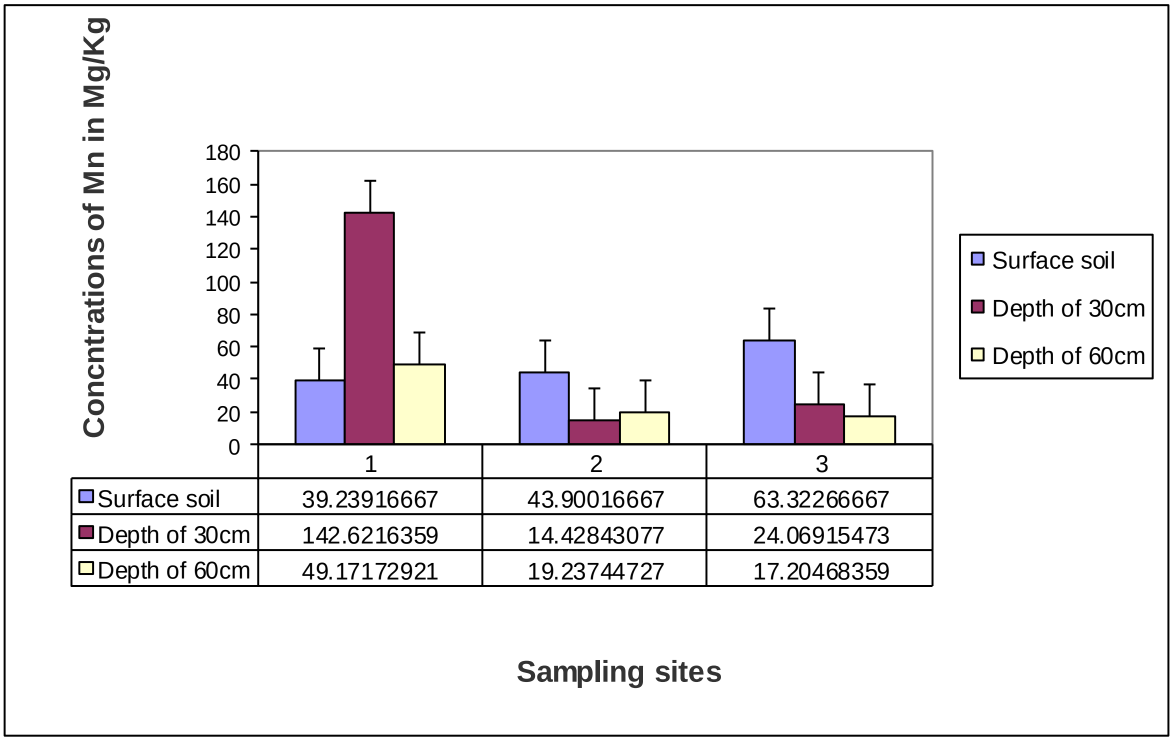
All pairwise multiple comparisons indicated that there were statistically significant differences (P<0.05) in manganese concentrations between surface soil and 30 cm depth soil, and between surface soil and 60 cm depth soil. No statistically significant differences (P>0.05) in pairwise multiple comparisons of manganese concentrations were found between 30 cm and 60 cm depth soil at site 6 (Figure 24; Table 9).

Graphs of vertical distribution of manganese concentrations in soil samples on the outbound and inbound sides of the N1 highway



	1	5	6
Surface Soil	60.92666667	55.10866667	48.7945
Depth of 30cm	310.8649562	45.60775377	20.74694393
Depth of 60cm	343.9634087	42.93147486	4.423990014

Figure 23: Vertical distribution of mean manganese concentrations (mg/kg) (± SD) as recorded at the respective sites on the outbound side of the N1 highway. N=6



	1	2	3
Surface soil	39.23916667	43.90016667	63.32266667
Depth of 30cm	142.6216359	14.42843077	24.06915473
Depth of 60cm	49.17172921	19.23744727	17.20468359

Figure 24: Vertical distribution of mean manganese concentrations (mg/kg) (± SD) as recorded at the respective sites on the inbound side of the N1 highway. N=6

Table 8: pH, organic content, manganese concentrations (mg/kg) and soil type of soil samples of the outbound sides of the N1 highway

Sites	**Depth**	**pH KCL**	**Organic Content %**	**Mn in mg/kg**	**Soil Type**
1	Surface soil	7.30	0.96	^{a}60.9	Sand
1	30cm	7.10	0.67	^{b}310.8	Sand
1	60cm	7.00	0.85	^{b}343.96	Sand
5	Surface soil	7.20	1.10	^{a} 55.10	Sand
5	30cm	7.30	0.82	^{a}45.60	Sand
5	60cm	7.10	0.92	^{a}42.93	Sand
6	Surface soil	7.10	2.52	^{a}48.7	Sand
6	30cm	7.10	2.50	^{b}20.74	Sand
6	60cm	7.10	0.99	^{c}4.42	Sand

Statistically significant differences are indicated with different letters; Superscripts a to c = Comparisons of surface, 30cm and 60cm soil per site.

Table 9: pH, organic content, manganese concentrations (mg/kg) and soil type of soil samples of the inbound sides of the N1 highway

Sites	**Depth**	**pH KCL**	**Organic Content %**	**Mn in mg/kg**	**Soil Type**
1	Surface soil	7.20	0.99	^{a}39.23	Sand
1	30cm	7.00	0.76	^{b}142.62	Sand
1	60cm	6.90	1.33	^{a}48.17	Sand
5	Surface soil	7.10	2.54	^{a}43.90	Sand
5	30cm	7.10	1.33	^{b}14.4	Sand
5	60cm	7.00	1.97	^{b}19.23	Sand
6	Surface soil	7.10	0.87	^{a}63.32	Sand
6	30cm	7.00	0.90	^{b}24.06	Sand
6	60cm	6.90	1.12	^{b}17.20	Sand

Statistically significant differences are indicated with different letters; Superscripts a to c = Comparisons of surface, 30cm and 60cm soil per site.

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4.3) Comparison of manganese concentrations in soil along the road verges of the N1 highway before and after the banning of leaded petrol

This section makes use of data collected in a previous unpublished pilot study conducted by the author of this dissertation before manganese was used as an additive in petrol in South Africa.

The sites from where soil samples were collected before the banning of lead in petrol (August 2005) are the same as in the current study (August 2011), apart from site 1. In the present study it was not possible to use the same site as site 1 due to recent road construction work. Therefore, site 1 is omitted from the comparisons.

Only values for the month of August are used in this analysis because data collected for the study before the banning of leaded petrol were a once-off sampling survey that involved only the month of August.

4.3.1) Outbound

The mean manganese concentrations in soil at site 2 were found to be statistically significantly ($P<0.05$) higher in 2005 (122.94 mg/kg) than in 2011 (114.87 mg/kg) (Figure 25).

No statistically significant differences ($P>0.05$) in mean manganese concentrations in the soil were found at site 3 when the 2005 and 2011 data were compared (Figure 25).

The mean manganese concentrations in soil at site 4 were found to be statistically ($P<0.05$) higher in 2005 (123.05 mg/kg) than in 2011 (95.68 mg/kg) (Figure 25).

The mean manganese concentrations in soil at site 5 were found to be statistically ($P<0.05$) higher in 2005 (73.18 mg/kg) than in 2011 (12.12 mg/kg) (Figure 25).

The mean manganese concentrations in soil at site 6 were found to be statistically ($P<0.05$) lower in 2005 (20.54 mg/kg) than in 2011 (74.43 mg/kg) (Figure 25).

4.3.2) Inbound

The mean manganese concentrations in soil at site 2 were found to be statistically ($P<0.05$) lower in 2005 (91.29 mg/kg) than in 2011 (140.26 mg/kg) (Figure 26).

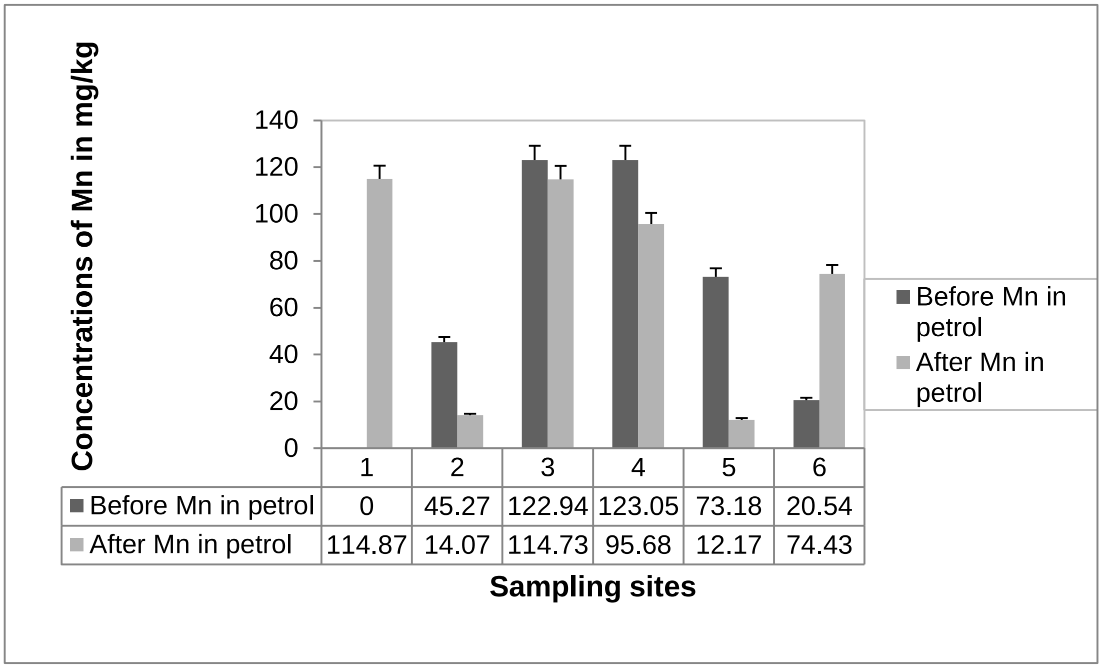
No statistically significant differences ($P>0.05$) in mean manganese concentrations in the soil were found site 3 when the 2005 and 2011 data were compared (Figure 26).

The mean manganese concentrations in soil at site 4 were found to be statistically ($P<0.05$) higher in 2005 (122.6 mg/kg) than in 2011 (87.88 mg/kg) (Figure 26).

No statistically significant differences ($P>0.05$) in mean manganese concentrations in the soil were found site 5 when the 2005 and 2011 data were compared (Figure 26).

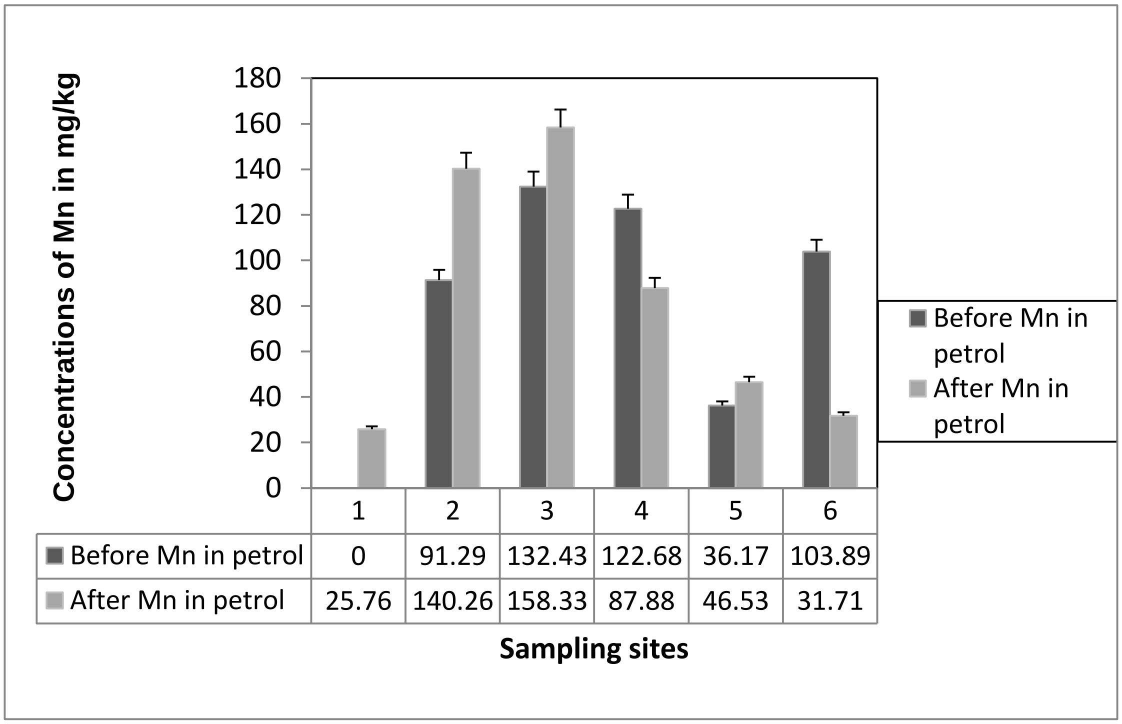
The mean manganese concentrations in soil at site 6 were found to be statistically ($P<0.05$) higher in 2005 (103.89 mg/kg) than in 2011 (31.71 mg/kg) (Figure 26).

Graphs of manganese concentrations in the soil, before and after the addition of manganese in petrol for the outbound and inbound sides of the N1 highway



	1	2	3	4	5	6
■ Before Mn in petrol	0	45.27	122.94	123.05	73.18	20.54
■ After Mn in petrol	114.87	14.07	114.73	95.68	12.17	74.43

Figure 25: Mean concentrations of manganese (mg/kg) (± SD) in the soil before (August 2005) and after (August 2011) the addition of manganese in petrol for the outbound side of the N1 highway.



	1	2	3	4	5	6
■ Before Mn in petrol	0	91.29	132.43	122.68	36.17	103.89
▨ After Mn in petrol	25.76	140.26	158.33	87.88	46.53	31.71

Figure 26: Mean concentrations of manganese (mg/kg) (± SD) in the soil before (August 2005) and after (August 2011) the addition of manganese in petrol for the inbound side of the N1 highway.

PART 2: DISCUSSION

4.4) Manganese concentrations in roadside soils along the road verges of the N1 highway over the period of one year

The natural concentrations of manganese in surface soil ranges from less than 1 mg/kg to more than 7000 mg/kg, with average values reported in surface soil in the range of 500 - 900 mg/kg (Pellezzari et al., 1999). According to Lindsay (1979) soil generally contains 200 - 3000 mg/kg manganese with an average value of 600 mg/kg.

Methylcyclopentadienyl manganese tricarbonyl (MMT) is one of the main sources of inorganic manganese contamination in the urban environment, mainly in areas with high traffic density (Salehi et al., 2003). Exposure to high concentrations of atmospheric manganese can lead to adverse respiratory and neurological health effects. However, little is known about the potential health effects that may result from long term low level manganese exposure of a population (Pal et al., 1999).

The mean manganese concentrations found in the roadside soil of the N1 ranged between 12.17 mg/kg and 221.47 mg/kg for the soil samples collected from all the sites. The highest level of manganese obtained in this study was found at site 3 on the outbound side (221.47mg/kg). The levels of manganese in the soil were found to be relatively low during the entire sampling period compared to 806 mg/kg recorded by Ekmekyapar et al. (2012). The concentrations of manganese obtained from this study is also lower than the 309 mg/kg value reported by Khan et al. (2011). When the highest manganese concentration obtained from this study is compared with the levels in similar studies in other countries, the concentrations of manganese obtained was lower than the concentrations recorded from studies conducted in the United States of America (2532 mg/kg), China (1740 mg/kg), and Poland (1122 mg/kg) (Dudka, 1992; Bradford et al.,1996; Abida et al., 2009). These relatively low levels found in the present study are indicative of mild to low manganese contamination of the sampled soil. Another possible reason for the relatively low concentrations of manganese in soil may be as a result of the fact that manganese particles may have been be deflected back into the atmosphere rather than being deposited on to the surface soil (Bhuie and Roy, 2001).

Although manganese is an essential metal in humans and animals when present in small concentrations (Rollin et al., 2005), it may become more toxic, when humans and animals are exposed to excessive concentrations (Okonkwo and Mothiba, 2005). Many studies have shown that fine particles of manganese can be absorbed into the blood system through the lungs and into the central nervous system and the brain (Archibald and Tyree, 1987). Manganese oxides readily accumulated in rodent brain tissues and the visceral organs resulting to various physiological and neurological toxic effect (Chandra et al., 1979). In a study conducted by Santos-Burgoa et al. (2001) in a manganese mining district, on the general population living in that area, it was revealed that some persons displayed poor motor function as a result of manganese exposure. In another study conducted in Southwest Quebec, Canada, a correlation was established between poor limb movements, poor learning ability and recall, and elevated blood manganese concentrations in residents exposed to manganese from a number of environmental sources (Mergler et al., 1999). A Similar study conducted in the USA found that blood manganese content from children in Newark and New Jersey were higher when compared to children in rural areas, possibly due to combustion of manganese containing fuel (Joselow et al., 1978). A similar situation may also be present among residents in Cape Town who may be exposed to elevated levels of manganese or even relatively low levels over a long time period.

Lytle et al. (1995) found that manganese compounds from motor vehicle exhausts readily accumulate in terrestrial and aquatic environments along heavily travelled roadways. They also found a significant relationship between manganese concentrations in plant species (*Asclepias speciosa* and *Lactura serriola*) and traffic volume. Some of the manganese emitted from motor vehicle exhausts may be deposited and retained on the surface soil and other fractions may leach into layers of soil or absorbed by plants (Schmidt and Sticher, 1991). Although outside the scope of the present study, it may be that natural vegetation along the N1 are potentially exposed to manganese contamination and toxicity.

4.5) Factors influencing the concentrations of manganese in soil

4.5.1) Vehicular density

Manganese may be released into the environment through the use of MMT as a vehicle fuel additive (EPA, 2003).

MMT was introduced in South Africa, particularly in Gauteng and the Western Cape provinces in the year 2000 (DEAT and DME, 2003). The N1 highway is located near residential areas and shopping malls where residents may be exposed to elevated levels of manganese. The EPA (2000) reported that long-term exposure to high levels of manganese, mainly by inhalation may negatively affect the central nervous system, visual reaction time, hand steadiness and coordination in humans.

Other exposures may be by absorption through the skin from accidental spills or the use of manganese based petrol as a solvent cleaner and from misuse such as petrol sniffing (Egyed and Wood, 1996). Those at risk include infants, pregnant women, the elderly, those with iron deficiency, people with Parkinson's disease, and workers exposed to petrol or exhaust fumes (Rollin et al., 2005).

In Canada where the use of MMT has been extensive over the years, it has been estimated that there has been a 10% per year increase in manganese emission rates from MMT in petrol since 1981 (Loranger and Zayed, 1994). A positive correlation between atmospheric manganese concentration and traffic density has also been observed (Loranger and Zayed, 1997).

In a study by Bhuie et al. (2005) where variables such as annual average daily traffic density, distance travelled and manganese content in petrol were taken into consideration, the annual average manganese concentration in the soil from MMT emission was calculated to be 5.73 mg/kg. In the present study, the highest mean manganese concentration in the soil was 221.47 mg/kg at the outbound side of site 3; with the total annual traffic density recorded to be 1156367 (Table 3). These values exceeded the value reported above indicating that the N1 soils may be contaminated with manganese. Lytle et al. (1995) reported that manganese concentrations in the soil were strongly related to the distance from roadways with moderate and high traffic volumes in a study conducted in Utah. The prolonged inhalation of high levels of manganese may negatively affect the central nervous system and hand steadiness (EPA, 2003).

4.5.2) Wind

There were fluctuating patterns in manganese concentrations in the soil along the N1 highway at all sites throughout the sampling period. The prevailing winds in Cape Town are south-eastern in the summer and north-western in the winter. Atmospheric particulates containing manganese compounds emitted from vehicle exhausts are deposited within 0 to 5 meters from the road's edge on roadside surface soils and can be further carried to longer distances by the wind (Othman et al., 1997). The combustion of MMT in an urban area is one of the main sources of airborne manganese, particularly in areas of high traffic density (Sierra et al., 1998). The particle size emitted to the atmosphere varies from 0.1 to 0.45 µm (WHO, 2004). The soil surface retains about 50% of the emitted particles while the other half is reflected back to the air (Bhuie et al., 2005). This airborne manganese can be deposited into water bodies and may adversely affect the health of nearby communities that rely on this source for drinking water and agricultural purposes (WHO, 2004). Bakirdere and Yaman (2008) reported that the directions and strength of the wind can remove metal particles from the southern to the northern side of a stretch of the road. The prevailing winds in Cape Town can be extremely strong at times and blow from the Cape Flats over the N1. The soil type is sandy as seen in Tables 5 and 6 of the present study, causing soil to blow away in one area and settling somewhere else (Tong and Lam, 2000). The fluctuating pattern in manganese concentrations in the soil of the N1 highway of the present study can be attributed to wind being another contributing factor.

4.5.3) Mobility of manganese in the soil

Due to the fact that manganese also naturally occurs in the environment, it has been difficult to ascertain its exact source and hence distinguish between manganese produced by anthropogenic sources and that occurring naturally. However, an important set of factors which come into consideration when assessing the dispersion of manganese in the environment is its physico-chemical properties (Veysseyre et al., 1998). This may explain the fluctuating pattern in the concentrations of manganese in the soil along the N1 highway.

Malm et al. (1988) reported that most of the manganese in South American rivers came from industrial and residential sources in a form in which the metal is found to be bound to suspended particles. The same situation may be observed in the river located near site 5 of the present study and other rivers in and around Cape Town that are located near industrial and residential areas. This manganese may significantly bioaccumulate in animals and plants that occur in these water bodies (WHO, 2004).

Manganese-containing particles are mainly removed from the atmosphere by gravitational settling, with large particles tending to fallout faster than small particles (EPA, 1984). The decay half-life of airborne particles is usually of the order of one day depending on the size of the particles and atmospheric conditions (Nriagu, 1978).

In a study conducted by Fernandez et al. (1992), it was reported that manganese was detected inside gaseous flying ash particles in the form of oxides and chlorides. Veld fires and the burning of bushes in and around Cape Town may lead to the release of manganese particles in the air and their subsequent deposition into the soil by gravitation. When these soluble oxides and chlorides reach environmental media such as soils, they leach out and become mobile. Research evidence elsewhere suggests that manganese has been identified in surface water and ground water samples through the process of leaching (ATSDR, 2008), a situation which might also occur for the river near site 5 of the present study.

4.6) Vertical distribution of manganese in the soil along the road verges of the N1 highway for the outbound and inbound sides of sites 1, 5 and 6

Manganese concentrations in the soil ranged from 39.23 mg/kg to 63.32 mg/kg at surface level, from 14.4 mg/kg to 310.86 mg/kg for depths of 30 cm, and from 4.42 mg/kg to 343.96 mg/kg for depths of 60 cm.

Ramakrishnaiah and Somashekar (2002) reported that manganese concentrations are higher at depths of 5 cm from the surface and decrease with increasing depth. They also found that the highest concentration of manganese in the soil was 188.12 mg/kg at surface level. In the present study, the highest concentration of manganese was 63.32 mg/kg at surface level. The present study also revealed that manganese concentrations generally decrease with increasing depth for all sites, except for site 1. At site 1 the manganese concentrations at depths of 30 cm and 60 cm were found to be higher on both sides of the road compared to the surface soil samples. The soil type found at these sites is sandy. Manganese particles can hence easily move from surface soil down to depths of 30 and 60 cm. Kalavrouziotis et al. (2007) reported in their study that metal accumulation and distribution in the soil depends on a number of factors such as distance of the sample from the highway, the soil type, the chemical and physical properties such as pH, soil organic matter, clay content, wind direction and the duration of exposure. Bakirdere and Yaman (2008) also reported that soil type and soil properties such as texture could influence metal concentrations in the soil.

The soil organic content ranged from 0.69% to 2.54 %. Although the vertical downward mobility of manganese in the present showed a non-statistical correlation with the soil organic content, the trend was not consistent for all the sites.

Nandram and Verloo (1985) reported an increase in the solubility of manganese in soils with a pH value of 2 and a low solubility of manganese in slightly alkaline soils with a pH value of 8. Soil pH values in the present study were found to vary from 6.90 to 7.30, implying the presence of neutral to weak alkaline soils. This may be one of the contributing factors explaining the general decrease in manganese concentrations with increasing depth found in the present study. Manganese may be less vertically mobile in the neutral to slightly alkaline soil of the present study. The vertical mobility of metals may also be influenced by other physico-chemical factors not investigated in this study.

4.7) Comparison of manganese concentrations in soil along the road verges of the N1 highway before and after the banning of leaded petrol

The objective of this study was to compare manganese in the soil before and after the addition of manganese in petrol in 2006 in South Africa. Five different sites were selected along the N1 highway. The samples before manganese addition in petrol were collected in August 2005 and the samples after manganese addition in petrol were collected in August 2011. The samples were both collected at the same sites. Higher levels of manganese concentrations in the soil were expected for soil samples collected after the addition of manganese in petrol.

The concentrations levels of manganese in the soil were found to be fluctuating for all sites for samples collected before and after manganese addition in petrol. These fluctuating manganese concentrations could be due to the natural abundance of manganese in nature as well as other anthropogenic sources causing a compounding of the variation among the sites, indicating that manganese contribution from MMT is very low and does not as yet significantly increase manganese contamination along the N1 highway.

The concentrations of manganese in the soil samples collected before manganese addition in petrol ranged from 20.54 mg/kg to 132.43 mg/kg with the highest concentration found at site 3 of the inbound side of the road. The concentrations in the soil samples collected after the addition of manganese in petrol ranged from 12.17 mg/kg to 158.33 mg/kg, with the highest concentration of 158.33 mg/kg found at site 2 of the inbound side of the road. The fluctuating pattern in concentrations of manganese in the soil samples collected before and after the addition of manganese in petrol could be attributed to the natural abundance of manganese from other naturally occurring crustal material as described by Joselow et al. (1978).

In a study conducted by Bhuie and Roy (2001) surface soil samples of 0–5 cm depth where collected at a distance of 40 m from the roadside in the Greater Toronto area in Canada. These soil samples were analysed for a number of metals, including manganese. In their results it were found that although MMT has been used continuously in petrol for approximately 25 years in Canada, its contribution to the terrestrial environment has been very low and has not significantly increased manganese levels along the highways. This may also explain the generally low levels of manganese in the soil along the N1 highway after the years of MMT usage in South African petrol. It can thus be concluded that significant concentrations of manganese found in the soil along the N1 highway may partially be due to naturally occurring manganese and other man-made pollution sources, and not only from the use of MMT in petrol.

The generally low concentrations of manganese in the soil samples collected before and after the addition of manganese in petrol may also be attributed to the type of soil and the soil organic content at the sites. The predominant soil type at these sites was sand. Kabata-Pendias and Pendias (1984) reported that manganese concentrations in surface soils increase due to the increase in organic content in the soil. The soil organic content was generally low in the present study and may be a contributing factor in the manganese concentration found. A number of other factors also govern the extent of metal accumulation and distribution in the soil. These factors include the distance of the sample from highway, the soil physico-chemical properties such as pH, clay content, wind direction, car density on the road in question, and duration of exposure (Kalavrouziotis et al., 2007).

In a study conducted in South Africa by Rollin et al. (2005) it was found that there were significantly higher concentrations of manganese in the blood of children, in the soil and classroom dust for Johannesburg when compared with Cape Town. They also found a mean value for blood manganese at 9.80 mg/L in Johannesburg children compared with

6.74 mg/L for children from Cape Town. In addition, blood-manganese levels of 4.2% in children in Cape Town and blood-manganese levels of 12.5% in children in Johannesburg was observed and recorded. These recorded blood-manganese levels were found to just exceed 14 mg/L, which is the upper normal reference value specified by the Agency for Toxic Substances Disease Registry (ATSDR, 2000). Rollin et al. (2005) also found that levels of manganese in blood were significantly associated with concentrations of manganese in classroom dust at schools. Although significant differences in manganese concentrations in the soil, in the dust, and in child blood percentage content was observed and recorded for the cities of Johannesburg and Cape Town, the final conclusion was that these differences may have arisen from naturally occurring manganese rather than from manganese coming from the use of MMT in petrol.

In another study conducted by Mielke et al. (2002) it was estimated that the USA highway fuel use (which had a manganese content of 8.3 mg per litre of fuel) yielded about 5000 metric tons of manganese in 1999. An assumption made from the study was that if 13% of manganese was emitted via the exhaust system, 650 tons of manganese will become aerosols annually, while 87% or 4350 tons will remain in vehicles' engines. As was observed with the use of lead-based compounds as a fuel additive, in which case the emissions posed health risks for neonates, the same effect is applicable when manganese is used as a fuel additive (the hepatic clearance for manganese in neonates is not fully functional). Children living in urban environments have been found with elevated levels of manganese in their blood (Joselow et al., 1978). Thus, manganese from the use of MMT in petrol may still potentially present a potential concern to public health.

CHAPTER FIVE: CONCLUSION

Objective 1

- To assess the accumulation of lead and manganese in soil along the N1 highway.

The results obtained from the spatial distribution study of lead showed that lead concentrations in the soil of the present study ranged between 7.32 and 2063.31 mg/kg. This is an indication that although leaded petrol has been phased out in South Africa, there is still a danger of lead contamination, partly due to the long decay half-life that lead exhibits (Pirkle et al., 1985). Various other sources of lead pollution in the study area may also be contributing factors to the lead still occurring at elevated levels. The relatively high lead concentrations in the soil may affect the health of residents and the surrounding environment, including agricultural land (vegetables are grown along the N1 close to sampling site 6). Crops grown on this contaminated soil may take up unacceptable levels of lead and thus affect food quality and safety. Another cause for concern is that children absorb more lead from the environment than adults. Children's behaviour, including their tendency to touch and taste any objects in their surroundings, may increase their risk of exposure to soil lead. Children tend to have the habit of eating non-food items such as soil, exposing them to lead poisoning (Ho and Tai, 1988).

The mean manganese concentrations found in the roadside soil of the N1 ranged between 12.17 mg/kg and 221.47 mg/kg. The highest level of manganese in the present study was found to be much lower than the 806 mg/kg, which was recorded by Ekmekyapar et al. (2012). This is an indication that manganese concentrations in the present study have not yet reached levels that will cause definite harm to human and environmental health. In other studies where manganese concentrations in soil, due to MMT addition in petrol, were investigated similar or slightly higher concentrations were found. Although manganese is an essential metal in humans and animals when present in small concentrations (Rollin et al., 2005), there is a risk of chronic toxic effects due to long term exposure to relatively low concentrations in humans, animals and plants.

Objective 2

- To determine the vertical distribution of lead and manganese in soil along the N1 highway

Ramakrishnaiah and Somashekar (2002) reported that higher concentrations of lead were present in the top 5 cm of soil and decreased with increasing depth. The result from the present vertical distribution study showed that lead concentrations in the soil also generally decreased as the depth increased. They also found that at surface level the highest soil lead concentration was 276.26 mg/kg and at a depth of 30 cm the highest concentration was at 31.02 mg/kg. In the present study, the highest soil lead concentration at surface level was at 215.94 mg/kg and at a depth of 30 cm the highest concentration recorded was 164 mg/kg. The reason for phenomenon may be that the soil in the present study is sandy and due to its structure cause lead to migrate more easily deeper into the soil. This finding of the present study support the finding of Godin (1986) who concluded that downward migration of contaminants are more pronounced in sandy soils. Sheppard and Thibault (1992) reported that soil with organic content ranging from 0.52% to 2.3%, as found in the present study, often retain most of the lead present within them to a depth of 30 cm. Lead tend to exhibit weak solubility, and consequently mobility, at slightly alkaline conditions. In the present study the soil pH ranged from 5.98 to 7.30 with an average pH of 7.10. This may partly explain why the concentrations of lead were generally higher in the surface soil samples of the present study. The risk of lead contamination and toxicity therefore remain in the upper layer and even beneath the surface of the soil. Change is soil pH may trigger the solubility of lead resulting in the potential contamination of groundwater and other environmental resources.

The results from the present vertical distribution study showed that manganese concentrations in the soil generally decreased as the sampling depth increased. Another study’s findings agreed with the present study and reported that manganese concentrations are higher at depths of 5 cm from the surface and decrease with increasing depth. There were however downward migration of manganese found in the present study, and were particularly evident at site 1. pH, soil organic content and soil type seemed to be contributing factors in the downward movement of manganese, like in the case of lead.

Objective 3

- To compare the concentrations of lead and manganese in soil along the N1 highway, before and after the banning of leaded petrol in South Africa

The results showed that there is a fluctuating pattern in lead concentrations in soil along the N1 highway before and after the banning of leaded petrol in South Africa. In some cases lead concentrations were found to be higher after the banning of leaded petrol than before the ban. This may be due to different reasons. Although the use of unleaded petrol may have led to a subsequent decrease in fuel emissions of lead into the environment, lead may still be deposited into the soil from various sources related to motor vehicles and other sources. Lead is also not easily removed from the soil because of its irreversible immobilization within different soil types (Gulser and Erdogan, 2008). Bhuie and Roy (2001) also indicated that lead accumulation in soil was a long term process and the reduction of soil lead levels will probably be a process that will take several years. Therefore, lead accumulation and toxicity in soil, even after the banning of leaded petrol, will remain a relevant topic for investigation into the future.

The concentrations of manganese in the soil were found to be fluctuating for all sites for samples collected before and after manganese addition in petrol. These fluctuating manganese concentrations could be due to the natural abundance of manganese in nature as well as other anthropogenic sources causing a compounding of the variation among the sites, indicating that manganese contribution from MMT may still be very low and does not as yet significantly increase manganese contamination in soil along the N1 highway. A previous study found that athough MMT has been used continuously in petrol for approximately 25 years in Canada, its contribution to the terrestrial environment has been very low and has not significantly contributed to manganese levels along the highways. This may also explain the generally low levels of manganese in the soil along the N1 highway after the years of MMT usage in South African petrol. It can thus be concluded that significant concentrations of manganese found in the soil along the N1 highway may partially be due to naturally occurring manganese as well as other man-made pollution sources, and not only from the use of MMT in petrol.

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