# LONG-TERM EFFECTS OF SEWAGE SLUDGE APPLICATION ON HEAVY METAL DISTRIBUTION IN A LOAM SOIL AND INDIGENOUS VEGETABLES.

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**Abstract**

Heavy metal accumulation in soils could have serious negative effects on soil life, plants, ground water and human health. Tons of sewage sludge, a mixture of activated and anaerobically digested sludges, with high concentration of heavy metals, are produced at Darvill Waste Water Works (DWWW) and irrigated on land as a suspension. The aim of this study was to investigate the spatial and vertical distribution of different heavy metals and their availability in soils and tissue composition of indigenous vegetables after long-term disposal of sewage sludge (more than 50 years) at a dedicated site in Pietermaritzburg. The disposal site has an area of 57 ha. Soil samples were collected from 0-10, 10-20, 20-30, 30-40 and 40-50 cm depths from five transects on the land. A reference transect not treated with sludge was included. Concentrations of Zn, Cu, Ni, Cr, Pb, Cd, Hg and As were determined after extraction with aqua regia, $NH_4NO_3$, DTPA and the TCLP. Indigenous vegetables growing voluntarily on this area were harvested and analysed for heavy metals to determine the risk that the people consuming them are exposed to.

Geo-spatial distribution maps showed that Zn, Cu, Ni, Cr, Pb, Cd, Hg and As were higher than the total investigative level (TIL), total maximum threshold (TMT) and only Zn, Cr, Pb and Cd had exceeded maximum permissible limits (MPL) while the other elements were approaching the MPL, with some transects being more contaminated than others, and with variation between different points within the same transects. Irrigation of sewage sludge results in substantial buildup of heavy metals in soils. Heavy metals such as Zn, Cr, and Cu had not moved much beyond 30 cm, whereas for Pb, Ni, Hg and As had moved up to 50 cm depth from the aqua regia extractions. Arsenic levels in the control were as high as in the disposal land and sometimes even higher than some other transects. Results from DTPA and $NH_4NO_3$ extracts indicated that available heavy metal were also high in the available form indicating a high possibility of metal up take by plants. Indigenous vegetable tissue composition of these metals also exceeded MPL set by FAO. Amaranths took up the greatest amounts of these heavy metals followed by tomato plant, with *Solunum nigrum* and pumpkin lower level, which also exceeded MPL, with less in the fruit. Zn was the most taken up by these indigenous vegetables. The findings of this work suggest that soils and plants on the long-term sewage sludge disposal land are now heavily polluted and that there is an urgent need for remediation of these soils in DWWW.

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Professor P. Muchaonyerwa (Supervisor)

**Acknowledgment**

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**Abbreviations**

DWWW: Darvill waste water works

PMB: Pietermaritzburg

MPL: Maximum permissible limits

TMT: Total maximum threshold

PTME: Potential toxic metal and elements

DTPA: Diethylenetriamine penta acetic acid

TCLP: Toxicity character leaching procedure

IDW: Inverse distance weighting

TIT: Total investigative level in soils

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# 1. INTRODUCTION AND LITERETURE REVIEW

## 1.1 INTRODUCTION

Large quantities of sewage sludge are generated in treatment plants and disposal has become a major environmental concern globally, including in South Africa (Snyman and Van der Waals, 2004; Rohrs et al., 1998). Industrial growth and increased urbanization in developing countries require municipal authorities to handle large volumes of sewage sludge with limited resources (Nyamangara and Mzezewa, 1999). Treatment of sewage sludge is done in three steps, which are preliminary, primary and secondary treatments (Tesfai, 2004). The preliminary step removes large solids and grits through screening, while the primary treatment mixes the incoming sludge, combined with heating to mild temperature to accelerate biological conversion. The secondary treatment allows the mixture to undergo further digestion before it is dewatered and thickened. The major concerns of sewage sludge disposal largely results from heavy metal concentration that may originate from industrial waste, together with pathogenic organisms and endocrine disruptors. Therefore the final sludge being disposed on land requires safe handling.

Electroplating industries, car battery manufactures and leather tanneries have been put under great pressure to reduce the metal concentrations in their effluents (Bahbahanina et al., 2010), through the introduction of cleaner technology and recycling. While it is a legal requirement that industries treat their wastes on site before disposal, the reality is that, due to costs associated with such treatments, these wastes could be disposed of without treatment into the sewage system. Major heavy metals found in industrial waste, and subsequently in sewage sludge, include lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni), among others (Raymond et al., 2011; Snyman and Herselman, 2006) . A number of sewage sludge disposal strategies are used worldwide, including incineration, disposal into water systems (river or sea), composting and/or disposal on agricultural land. Some of these strategies can be used more than others. According to Hue (1988), with the high energy requirements for sewage sludge incineration, scarcity of landfill sites and increasing cost of commercial fertilizers, have made cropland application an attractive means of disposal but with environmental concerns that if heavy metals from sewage sludge enter the soil, will enter the food chain.

While sewage sludge production has increased presenting disposal challenges, soil quality continues to deteriorate (Chale-Matsau, 2005), and application of sewage sludge on agricultural land, as an organic fertilizer, could provide an viable way to dispose of the increasing amounts of sludge generated in the major metropolitan areas of South Africa (Korentajer, 1991). High levels of organic matter, macro elements, including phosphorus, potassium and nitrogen and micro-elements (Tesfai, 2004), in sewage sludge, make agricultural land application a feasible alternative strategy for its disposal (Hu et al., 1996), while also improving quality of South African agricultural soils. The feasibility of land application of sewage sludge as a disposal strategy could be limited by its possible content of heavy metals, pathogenic organisms and endocrine disruptors.

Raw sewage sludge may contains significant amounts of heavy metals, which are not degraded during the treatment process, and leave the treatment works either in the final effluent or sludge produced (Corrondo et al., 1978). In South Africa heavy metals of concern in sewage sludge include Pb, Cd, Zn and Cu (Snyman and Van der Waals, 2004). Where sewage sludge contains lower heavy metal concentrations than critical levels given in the guidelines proposed by the WRC (1997), it can be used for land application in South Africa. As such, land application could provide an opportunity for nutrient cycling from sewage sludge. However, where the sludge contains elevated levels of heavy metals, the practice could result in metal accumulation in the soil (Tesfai, 2004).

The Darvill Waste Water Works (DWWW), in Pietermaritzburg, has disposed of sewage sludge at a dedicated site just outside the plant for over 50 years. Sewage sludge produced at DWWW contains different heavy metals, which could have accumulated in the soil or could have leached to deeper layers of the soil and into ground water. A preliminary study done as part of a BSc Soil Science Honours project, at the University of KwaZulu-Natal, showed that only Zinc had reached maximum permissible limits after over 40 years of application of the sewage sludge (Bekink, 2007). The fate of these heavy metals in soil depend on their interaction with soil constituents (clay minerals, organic matter, and oxihydroxides of Fe and Al), pH, and redox potentials among other factors. The metals can be sorbed on soil colloids (silicates, organic matter, oxihydroxides of Fe and Al), lost through erosion and leaching to surface and ground water, respectively, or be taken up by plants growing on the contaminated site. Soils, surface and ground water, and plants that could accumulate these heavy metals pose risks to animal and human health. It is essential to

determine the spatial and vertical distribution of heavy metals on such sewage disposal lands to assess the effect of long term irrigation of soils with sewage sludge.

The toxicity and mobility of heavy metals depends on their forms and other soil characteristics. Different extraction methods have been used to estimate different forms of heavy metals in soils. These methods include aqua regia, DTPA, TCLP and $NH_4NO_3$. According to the South African guidelines, total and available heavy metals in soils contaminated with sewage sludge should both be extracted and analysed (Snyman et al., 2004). Aqua regia extraction (pseudo-total) gives an indication of pseudo-total heavy metals (not an accurate reflection of total extraction metals), while DTPA and $NH_4NO_3$ extraction are related to plant available fractions. Ammonium nitrate is mostly used by the Department of Environmental Affairs in South Africa, while TCLP estimates the fraction that is potentially leachable. Heavy metal accumulation in plants depends on species (Khan et al., 2008) in addition to the metal concentration and form in the soil. Local communities around DWWW, including Sobantu, Hollingwood and Mkhambathini harvest indigenous vegetables for consumption and for sale in Pietermaritz Street, Ray-stop and in the market in town. According to the rules of DWWW, people are strictly not allowed to enter the area without permission. Harvesting of the vegetables is done in the early hours of the morning, when there is no staff member from DWWW. It is essential to understand uptake of heavy metals by the vegetables growing at sewage disposal sites and the risks they pose to the health of people consuming these vegetables.

1.2 OBJECTIVES

The general objective of this study was to investigate the spatial and vertical distribution of different heavy metals and their availability in soils and tissue composition of indigenous vegetables after long-term disposal of sewage sludge at a dedicated site. The specific objectives were:

(i) To determine spatial and vertical distribution of total heavy metal concentrations in a long-term sewage sludge disposal site.

(ii) To determine the potentially leachable and plant available heavy metal concentration at a long-term sewage disposal site.

(iii) To determine heavy metal concentrations in the tissues of different species of indigenous vegetables growing at the dedicated sewage disposal site

## 2. LITERATURE REVIEW

### 2.1 Solid waste and sewage sludge production in South Africa.

Most environmental problems in cities are related to the production and containment of urban solid waste (Buenrostro and Bocco, 2000). According to DWAF (1997), the average amount of waste generated per person per day in South Africa is 0.7 kg. This amount is closer to the average produced in developed countries (0.73 kg in the UK and 0.87 kg in Singapore), compared to waste of developing countries such as 0.3 kg in Nepal (DWAF, 1997). About 59 million tonnes of waste is produced in South Africa (DEA, 2012), and about 5.9 million tonnes of general waste is being recycled and 53.5 million tonnes is landfilled. Sewage sludge falls under unclassified waste contributing about 1%.
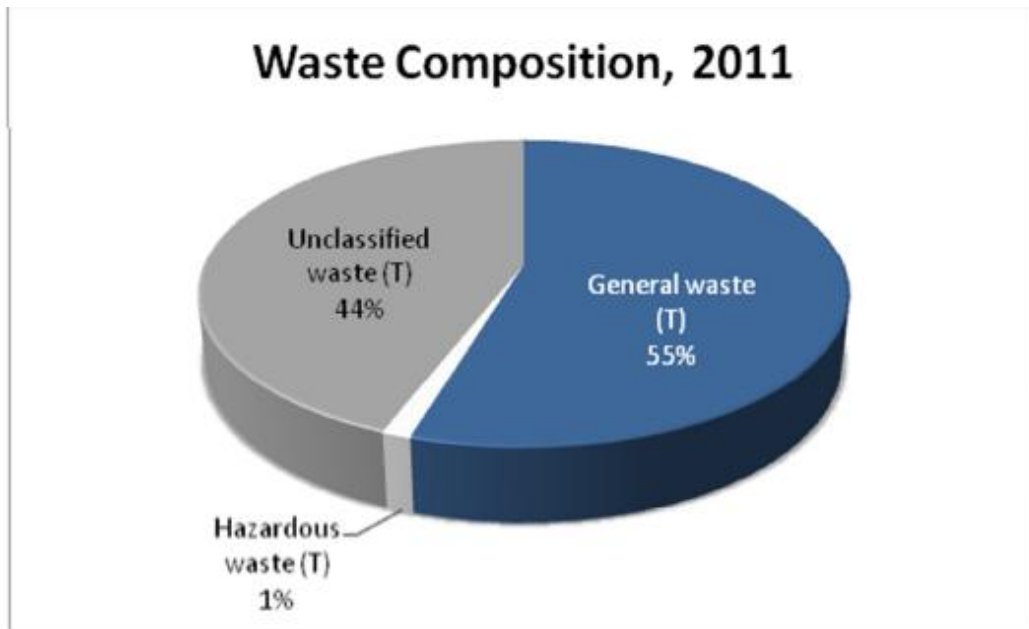


**Figure 2.1**: **National waste generation in South Africa in 2011 (DEA, 2012).**

Gauteng produces the largest proportion of waste (Table 2.1), followed by Western Cape, Northern Cape, then Mpumalanga. More than 5 million cubic metres of hazardous waste high in heavy metals is produced every year in South Africa, mostly in Mpumalanga and KwaZulu-Natal and this is due to the concentration of mining activities and fertiliser production in these two provinces.

**Table 2.1: Percentage municipal waste contribution by province in South Africa in 2011.**

| Province | Kg/capita/annum | Waste generated as % of total waste |
|---|---|---|
| Western Cape | 675 | 20 |
| Eastern Cape | 112 | 4 |
| Northern Cape | 547 | 3 |
| Free State | 199 | 3 |
| KwaZulu Natal | 158 | 9 |
| North West | 68 | 1 |
| Gauteng | 761 | 45 |
| Mpumalanga | 518 | 10 |
| Limpopo | 103 | 3 |

**(Source: DEA, 2012)**

Significant quantities of organic industrial solid waste are generated in some countries (Pipatti et al., 2006). Industrial waste may include cafeteria garbage, scrap metals, trash, oil, chemical, weed grass and trees (SDWF, 2003). This industrial waste may then end up in a sewage treatment works and mixed with sewage sludge causing a major environmental concern when the sludge is applied to land. In South Africa an estimated 28% of the sludge generated at the sewage plants is used beneficially for agricultural purposes (Du Preez et al., 1999).

Rapid growth of urban areas in South Africa is placing a burden on the existing infrastructure (Rohrs et al., 2008), with the plant stations not being able to handle these large volumes. Sewage sludge has to undergo various treatments at sewage works in order to render it for suitable disposal and reuse (Jaganyi et al., 2005). These highly polluted sludge's may contain pathogens like viruses, bacteria, protozoa and eggs of parasitic worms, toxic organic substances and heavy metals (Bruce et al., 1989).

Sewage sludge is a by-product of the treatment of domestic and industrial wastewater. It can also be regarded as a residue from separation of the liquids and solids (Fytili and Zabaniotou, 2008)

and it usually contains paper and plastics which are removed earlier before the separation of faecal material from water. Sewage sludge, generated in large volumes daily not only in South Africa but all around the world, has created environmental problems, when the sludge is not properly treated and also causing an impact on human health (WRC, 2002). In South Africa different types of sludge are produced where about 57% is anaerobic digestion. This is a process by which micro-organisms break down biodegradable material, this is done in the absence of oxygen (Snyman et al., 2004). About 20% comes from the activated sludge, a biological wastewater treatment by which flocs of micro-organisms are formed when wastewater is aerated. Blended sludge, made of more than two types of sludge are blended together to facilitate a higher sludge solids concentration and a more homogenous mixture of sludge prior to dewatering, makes up 12%. About 2% comes from the petro sludge, 1% comes from the aerobic digestion and 0.3% is produced from dams.

Most of the sludge (74% mass) produced in treatment works in South Africa is not treated further than the traditional anaerobic digestion and activated sludge treatment as shown on Figure 2.2 (Chale-Matsau, 2005). Figure 2.2 illustrates the most important tertiary methods or techniques employed in waste water treatment works plants in South Africa (Snyman et al., 2004). According to Snyman et al. (2004) metropolitan city councils and smaller towns compost their sludge while, compressing of material into pellets (pelletisation) is only used by large metropolitan city councils. Aerobic digestion is employed as an additional treatment method after anaerobic digestion.
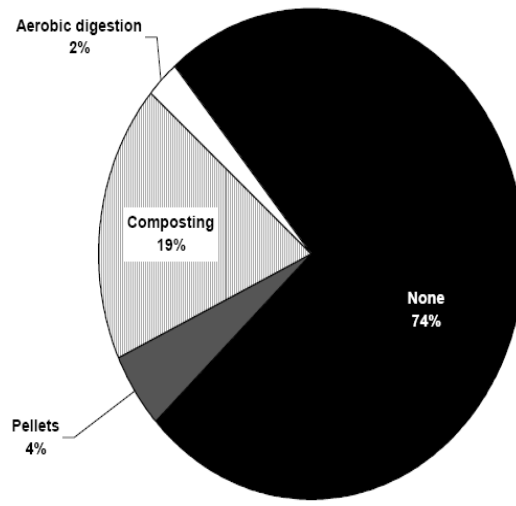
**Figure 2.2: Stabilization technologies employed by the wastewater treatment plants in South Africa on a mass percent basis (Snyman et al., 2004).**

Some sludge produced from treatment plants in South Africa is used for a number of activities including application onto golf courses and some collected by farmers for agricultural use (Jangayi et al., 2005). In many developing countries industrialization and urbanization have impacted the handling of huge volumes of sewage sludge with limited resources within the past 20-30 years (Topcuoglu, 2005; Olley, 1997). Rapid urbanization along with its increasing human activities in metropolitan areas imposes great challenges to urban environmental management of sewage sludge as treatment plant cannot handle the large volumes (Xiao et al., 2006).

**2.2 Soil chemistry of heavy metals.**

Heavy metals most commonly found at contaminated sites are Pb, Cr, As, Zn, Cd, Cu and Hg (USEPA, 1996). These metals pose a risk of bioaccumulation and biomagnification in the food chain (Raymond et al., 2011). Lead (Pb) which belongs to group IV and period 6 of the periodic table, is a naturally occurring, bluish gray metal commonly found as a mineral combined with other elements (USDHHS, 1999). Mean lead concentration on the surface soils ranges from 10 to 67 mg/kg (Raymond, et al 2011). In soil Pb exists principally in the +2 oxidation state in soils. Lead can become very insoluble is reduced soils (McBride, 1994), these is because of its

precipitation by sulfide generated from sulfate reduction. According to Mcbride (1994), Pb under reducing or nonacid condition, is the least mobile heavy metal in soils. In soils treated with sewage sludge Pb levels are considerable higher than natural soils and most of Pb appears to be unavailable to plants. Chromium is a transition metal and is one of the less common elements (Raymond et al., 2011). In soil the major sources of Cr include electroplating processes and the disposal of Cr containing waste (Smith et al., 1995). Chromium can exists in soils as Cr(VI) and can be reduced to Cr(III) by soil organic matter, $Fe^{2+}$ under anaerobic conditions and $S^{2-}$ (Raymond et al., 2011). In soils, Cr mobility depends on sorption characteristics, clay content, iron oxide content and organic matter. Arsenic, a metalloid of group VA and period 4, occurs in a variety of minerals (Raymond, et al., 2011). Arsernic in soils can found in two forms +3 and +5. In soils As can be chemisorbed by Fe and Al oxides, noncrystalline aluminosilicates, and to a smaller extent, layer silicate clays (McBride, 1994). Arsenic can precipitate when metal cations are present as it behaves as a chelates (Bodek, et al., 1988). Mobility of As in soils increases with increasing pH (Raymond et al., 2011), and can also co-precipitate with/or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions. Like Cr, Zn, As is a transition metal and where many As compounds can adsorb strongly to soils and are therefore transported only over a short distance in groundwater and surface water (Raymond et al., 2011). Zinc in soils can only occur in the +2 oxidation state (McBride, 1994). According to Davies et al. (1988), Zn occurs naturally in the soil but its concentrations are rising unnaturally due to anthropogenic additions. In acidic and aerobic soils, Zn has medium mobility, held in exchangeable forms on clay and organic matter. According to McBride, (1994), under acidic, oxidizing conditions, $Zn^{2+}$ is the most soluble and mobile and does not complex tightly with organic matter at low pH. In soils Zn can interrupt the activity of microorganisms together with earthworms, thus retarding the breakdown of organic matter (Raymond et al., 2011). Cadmium is a transition element and in its compounds it occurs as the divalent ion. Cadmium is highly mobile in well drained soils and is soluble in acidic soils (McBride, 1994), this high mobility is attributed to $Cd^{2+}$ being adsorbed weakly on organi matter, silicate clays, and oxides unless the pH is higher than 6. Cadmium in soils with a pH higher than 7 can co-precipitate $CaCO_3$ or precipitate as $CdCO_3$ and solubility may be limited by Cd phosphate. According to Raymond et al. (2011), Hg, Cd and Pb are three big metal poisons and are known for their essential biological functions. Cadmium had chemical similarities to Zn, an essential micronutrient for plants and animals (Campbell et al., 2006). Bio-availability and mobility in

neutral to alkaline soils is low for Cd (McBride, 1994). Application of fertilizers, pesticides, sewage sludge increases the total concentration of Cd in Soils, and the bio-availability of this Cd determines whether plants Cd uptake occurs to a significant degree (Raymond et al., 2011). Copper is also a transition metal and is an essential micronutrient required for growth in both plants and animals (VCI, 2011). Solubility of Cu increases with pH (Raymond et al., 2011) and mobility is low in reduced soils (McBride, 1994). Copper ($Cu^{2+}$) has high affinity for soil colloids and as a results in near-neutral soils its mobility is low. Solubility of Cd is high in soils high in organic matter. Mercury is of the some group as Zn and Cd. Stability of Hg is mostly determined by the redox potential and pH of the system and Hg is most stable under oxidizing conditions (Raymond et al., 2011). Mobility of Hg is probable very sensitive to loading, and with traces of $Hg^{2+}$ being very immobile and at high levels of Hg, mobility is medium (McBride, 1994). According to McBride (1994), accumulation of Hg in soils tends to correlate with the organic matter levels. Nickel occurs to the environment only at low levels and is essential in small doses (Raymond et al., 2011). In low pH, Ni exists as nickelous ion Ni(II) where in neutral solutions it precipitates as nickelous hydro-oxide. Nickel can be dangerous when the maximum tolerant amounts are exceeded. Nickel ($Ni^{2+}$) cation, almost electronegative, this fact and its electronic structure favour the formation of complexes with organic matter that are comparable in stability to those of Cu (McBride, 1994).

## 2.3 Sewage sludge disposal in South Africa.

According to Snyman and Herselman (2006) selection of appropriate disposal methods is based on sludge guidelines where classification is based on the microbiological class (table 2.2) together with stability class (table 2.3) and pollutant class (table 2.4).

**Table 2.2: Preliminary classification: Microbial class.**

| Microbial Class | A | B | | C |
|---|---|---|---|---|
| | All three samples comply with the following standard | Two of the three samples comply with the following standard | The sample that fail does not exceed the following standard | One or more other sample exceed the following concentration |
| Faecal coliforms | < 1000 | < 1 x $10^6$ | < 1x $10^7$ | >1 x$10^7$ |
| Helminth ova (Total viable ova/$g_{dry}$) | < 0.25 (or one visible ova/4$g_{dry}$) | < 1 | 4 | >4 |

**Table 2.3: Preliminary classification: Stability class.**

| Stability class 1 | 1 | 2 | 3 |
|---|---|---|---|
| | Plan/design to comply with one of the options listed below on a 90 percentile basis. | Plan/design to comply with one of the options listed below on a 75 percentile basis. | No stabilisation or vector attraction reduction options required. |
| Vector attraction reduction options (Applicable to Stability class 1 and 2 only) | | | |

Option 1: Reduce the mass of volatile solids by a minimum of 38 %.

Option 2: Demonstrate vector attraction reduction with additional anaerobic digestion in a bench scale unit.

Option 3: Demonstrate vector attraction reduction with additional aerobic digestion in a bench-scale unit.

Option 4: Meet a specific oxygen uptake rate for aerobically treated sludge.

Option 5: Use aerobic processes at a temperature greater than 40 C (average temperature 45 C) for 14 days or longer (e.g during sludge composting).

Option 6: Add alkaline material to raise the pH under specific conditions.

Option 7: Reduce moisture content of sludge that do not contain unstabilised solids (from treatment processes other than primary treatment) to at least 75 % solids.

Option 8: Reduce moisture content of sludge with unstabilised solids to at least 90 % solids.

Option 9: Inject sludge beneath the soil surface within a specified time, depending on the level of pathogen treatment.

Option 10: Incorporate sludge applied to or placed on the surface of the land within specified time periods after application to or placement on the surface of the land.

**Table 2.4: Preliminary classification: Pollutant class.**

| Metal limits for South African Wastewater sludge (mg/kg) | | | |
|---|---|---|---|
| Pollutant Class | a | b | C |
| Arsenic | < 40 | 40 – 75 | >75 |
| Cadmium | < 40 | 40 – 85 | >85 |
| Chromium | < 1200 | 1200 – 3000 | >300 |
| Copper | < 1500 | 1500 – 4300 | >4300 |
| Lead | < 300 | 300 – 840 | >840 |
| Mercury | < 15 | 15 – 55 | >55 |
| Nickel | < 420 | 420 | >420 |
| Zinc | < 2800 | 2800 - 7500 | >7500 |

One could then classify sludge as A2c class. The guidelines will then determine which type of methods will be appropriate for that particular sludge. There are major uses to derive benefits from sludge, including generation of compost, collection by farmers on site, use as a bottom layer for golf course, use on cultivated lawn and use by local municipalities. Figure 2.4 illustrates disposal methods used in South Africa by wastewater treatment plants. Large proportion is used by local municipal garden farms, stockpiled or applied on land. In many treatment plants in South Africa stockpiled sludge decreased in size over time (Snyman et al., 2004).
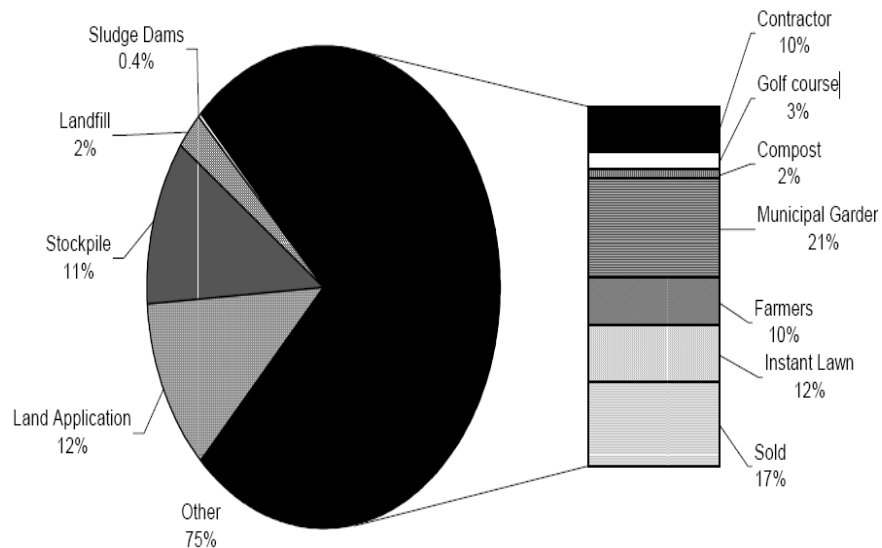
**Figure 2.3: Major disposal methods employed by the wastewater treatment plants surveyed in South Africa on a percent basis (Snyman et al., 2004).**

2.3.1 Incineration

Municipalities in South Africa are faced with a major problem of sustainable disposal of sludge in an environmentally acceptable manner (Botha et al., 2011). Incineration destroys the organic pollutants and reduces the volume of sewage sludge (EPA, 2009). Sewage sludge containing about 20% solids, incinerators can reduce its volume by about 90% on a wet basis. According to the EPA, (2009) sewage sludge to be incinerated has to comply with the proposed rules of the national emission standards for hazardous air pollution for mercury and beryllium. The preferred management option of many sludge treatment plants in South Africa is the thermal treatment. In South Africa sludge incineration has been proposed for power generation has been regarded as an alternative for sewage sludge disposal and also renewable energy generation (Botha et al., 2011). Sewage sludge incineration has advantages of ensuring complete combustion of all organic content in sludge, reduction of sludge volume by 95%, stable ash production and simplified gas clean-up to meet operating requirements. However, the ash produced has very fine dust and the dust is difficult to collect when dry. There are challenges in incineration of sludge, such as high amount

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of ash produced, large particles can be removed from the sludge by upstream processing but fine silts will still be present in the sludge feed (Botha et al., 2011).

2.3.2 Composting

There has been increasing recognition on sludge composting as it provides viable and economical alternation for waste management (Wei et al., 2000). Composting of sewage sludge could lead to an increase in microbial population, causing numerous microbially enhanced physico-chemical changes within mixture. According to Amir et al. (2004), these changes influences metal distribution through release of heavy metals during organic matter decomposition, metal solubilization by the decrease of pH, metal biosorption and metal complexation with the newly formed humic substances. Composting is preferred over landfill and incineration, because of low operational costs, beneficial use of end product, less pollution to the environment, but major concerns are the potential hazards, pathogens, heavy metals and organic contaminants that could be present in compost (Wei et al., 2000).

One of the major limitations of sewage sludge compost being applied on land is the high levels of heavy metals and bioavailability to the soil plant system (Amir et al., 2004). Use of sewage sludge compost on agricultural land suggests that the degree of stability and its content together with its biogeochemical forms of heavy metals are well known (Amir et al., 2004). Tessier et al. (1997) suggests that many studies have been carried out, trying to understand speciation of heavy metals in soils and soils amended with composed sewage sludge, while Petruzzelli et al. (1994) suggested that each heavy metal on sludge compost depends on its initial chemical state, adsorption and precipitation mechanisms in the sludge. Effects of stabilization and also the humification process occur during the composting process (Amir et al., 2004)

2.3.3 Landfills

Landfilling is the deposition of waste on land (DWAF, 2005), and this is done either by filling in of excavations or creation of a landfill above grade. Landfill is regarded as the cheapest and most convenient method of waste disposal. Disposal of sewage sludge by landfill process has to comply with terms and regulations of the Environment Conservation Act of 1989, where the amendment

Act states that *"no person shall establish, provide or operate any disposal site without a permit issued by the Minister of Environmental Affairs and Tourism"*. According to DWAF (2005), disposal of sewage sludge on landfill is determined by the waste type, size of operation and potential for significant leachate generation.

About 95% of the waste generated in South Africa is disposed in landfills, whereas in the world the figure is believed to be in excess of 85% (DWAF, 2005). Disposal of sludge in landfills has environmental impacts which can be divided into short and long term. Short term impact include air pollution, flies, windblown litter and unsightliness while long term impact include problems such as ground water pollution, landfill gas generation and devaluation of land holdings.

2.3.4 Disposal on agricultural land

About 66% of sewage sludge applied to the land is used for improving the nutrient content of the soil and the conditions, and this is done for improved agricultural crop production, feed crops and pastures (EPA, 1993). Application of sewage sludge on agricultural land depends on the physical characteristics of the sludge. According to WRC (1997) two approaches have been used in many countries permitting land application which are precautionary approach and environmental sustainability approach. The precautionary approach prevent pollutants from accumulating in waste receiving soils and the environmental sustainability approach takes into account the soils capacity to assimilate and attenuate and detoxify contaminants. Application of sewage sludge on land should be done at rates which are needed to supply required plant nutrients (WRC, 1997). In Austria the regulations on sewage sludge disposal requires that as from 2004, sewage sludge should be treated before application to land so as to reduce its biological reactivity (EU, 2001). In Italy it is prohibits to use untreated sludge and therefore sludge is regulated before being disposed on land. In Netherlands and France sludge must be treated either by biological, chemical or heat treatment before application according to the directive 86/278/EEC while in Sweden no organic waste will be accepted in landfills. There were certain concerns on sewage sludge application on agricultural land, one being the potential risk to public health and also the environment (EPA, 1993). The EPA base numerical limits for sewage sludge application and these are expressed in terms of limitation on the cumulative loading of 10 metals and an annual pollutant loading of 12 organic pollutants. Sewage sludge would be applied to agricultural land over a period of time from

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repeated application and that no application of sludge would be allowed once the cumulative load has been reached (EPA, 1993).

Environmental effects of heavy metals depend on their forms. In soils the fate and transport of heavy metals depends mostly on the chemical form and speciation of the metals. According to Shiowatana et al. (2001) once these heavy metals enter the soil, they are adsorbed by initial fast reaction then followed by a slow adsorption reaction and then they are redistributed into different chemical forms with varying bioavailability, mobility and toxicity. For these heavy metals to be distributed there are reactions controlling such as mineral precipitation and dissolution, ion exchange, adsorption and desorption, aqueous complexation, biological immobilization and mobilization, and plant uptake (Wuana and Okieimen, 2011).

## 2.4 Determination of heavy metal pools by different extraction methods.

2.4.1 Aqua regia

The aqua regia method uses concentrated $HNO_3$ and HCl in a ratio of 3:1 mixture. The aqua regia method is mostly used by many researchers because of the high relative concentration of $HNO_3$, which is efficient to decompose sulfides, while the total acidity is sufficiently strong to solubilize easily reactive metallic elements. According to Vercoutere et al. (1995), aqua regia digestion procedure is for the analysis of total recoverable heavy metals in soils and the availability to plants. Aqua regia digestion does not recover 100% of all the elements in soil but still have useful applications (Rayment and Lyons, 2011). This is because some metals are bound to silicates. There are residual elements that are not released by aqua regia procedure during the digestion, and these are mostly bound to silicates minerals (Chen and Ma, 2001) but these are considered unimportant for the estimation of mobility and behavior of these elements (Niskavaara et al., 1997). The procedure is used in many countries to estimate the impact of soil amendments such as sewage sludge on the environment (Chen and Ma, 2001) but the procedure is tedious and also time consuming (Siaka et al., 1998).

## 2.4.2 TCLP

Environmental Protection Agency of the USA developed the Toxicity Charateristics Leaching Procedure (TCLP) to measure leachability and hence the risk it poses to ground water. In the USA this procedure plays a major part in classification of waste through determining the concentration based on the exemption criteria. Some hazardous substances do not necessarily leach out (DWAF, 2005), and TCLP and Acid Rain Test (ART) can be used to test mobility of hazardous substances that will leach. The TCLP procedure is known to mimic the type of process that a waste might be exposed to even under natural conditions in a landfill. When a waste is to be landfilled in a site the TCLP procedure would be used especially if the site receives a variety of organic and inorganic waste (DWAF, 2005)

## 2.4.3 Ammonium nitrate

Ammonium nitrate is a non-buffer neutral salt. Ammonium nitrate is used to determine readily soluble trace elements in soils (Gryschko et al., 2004). Extraction with this method has been widely used and successfully applied in studies for nutrient elements deficiency in agricultural crops, animals and environmental pollution analysis (Sabiene and Brazauskiene, 2004). Available metal content in soil is determined by using the $NH_4NO_3$. Extraction of readily available trace elements was described in German DIN19730 (1997) by shaking the soil with 1M $NH_4NO_3$ solution. One of the chemical mechanisms involved when soils are extracted with 1 M $NH_4NO_3$ is the decrease in pH together with an increase in ionic strength (Gryschko et al., 2004) but due to high ionic strength most of the colloids and parts of soluble metal organic complexes are precipitated. $NH_4NO_3$ (1 M) solution predicts heavy metals taken up by plants and also fits well for elements which are mainly bound by low strength electrostatic forces to the soil.

## 2.4.4 Diethylenetriamine penta acetic acid (DTPA)

The Diethylenetriamine penta acetic acid (DTPA) procedure is a rapid simple way for evaluating phytoavailability of heavy metals in soils by unbuffered salts solution, (Beckett 1989). According to Gupta and Atten (1993), other extractants like DTPA were needed to predict phytoavaibility of heavy metals on soils since some salt solution did not reflect the plant available metals. DTPA chelating agents such as (diethylenetriamine penta acetic acid) extracting solution removes

micronutrient cations adsorbed on solid phases together with water soluble constituents. According to Rayment and Lyons (2011) using chelating agents such as DTPA extracting solution removes micronutrient cations adsorbed on solids phases together with water-soluble constituents. Extraction of micronutrients with DTPA has been used to assess soil fertility (Lindsay and Norvell, 1978).

**2.5 Guidelines for treatment and disposal of sewage sludge in South Africa.**

In South Africa a few waste water treatment plants disinfect their sewage sludge. It is necessary to treat sludge before land disposal, for the purpose of reducing soil contamination. Treatment of sludge involves separation of solids from liquids. Types of treatments used include anaerobic digestion of solids, aerobic treatment of wastewater to remove materials (Table 2.5).

**Table 2.5: Different processes for sludge treatment, (Department of the Environment, 1989).**

| Process | Description |
|---|---|
| Sludge pasteurization | Minimum of 30 minutes at 70°C or 4 hours at 55°C , followed in all cases by primary anaerobic digestion |
| Anaerobic digestion | Mean retention period of at least 12 days primary digestion in temperature range 35°C± 3°C or at least 20 days primary digestion in temperature range 25°C± 3°C, followed in each case by a secondary stage which provides a mean retention period of at least 14 days. |
| Aerobic digestion | Mean retention period of at least 7 days digestion. All sludge to be subject to a minimum of 55°C for a period of at least 4 hours. |
| Composting | The compost must be maintained at 40°C for at least 5 days and 4 hours during this period at a minimum of 55°C within the body of the pile followed by a period of maturation adequate to ensure that the compost reaction process is substantially complete |

According to Snyman et al. (2004) little information has been gathered on sludge handling by small treatment plants but it is believed that most of the sludge is accumulated on site.

Reuse of sewage sludge and the effluent from the sludge via land application is a desirable goal because of its beneficial components to the soil (Behabahaninia et al., 2010). Sewage sludge contains the organic and mineral or inorganic nutrients (N, P, K) that makes it a valuable resource to use both in improving marginal lands and also as a supplement to fertilizers and soil conditions

(EPA, 1993). Using sewage sludge for land improvement and productivity are substantial but sewage sludge contains high levels of pathogens, high concentrations of pollutants. According to EPA (1993), reuse of sewage sludge for beneficial purposes is primarily related to farm and home gardens use. Use of sewage sludge to aid in the growth of a final vegetative cap for municipal solid waste landfills is also considered a beneficial use. Continuous application of sludge to the soil may cause the soil to reduce its capacity to retain metals, this can then cause the soil to release heavy metals into the groundwater or soil solution available for plants uptake (Mapanda et al., 2004). One of the most critical long term hazards of heavy metal transfer from sewage sludge is associated with the application of these wastes to soils (MacBride et al., 1997), once these heavy metals enter the soil they do not degrade they only accumulate.

Disposal of sewage sludge continues to be one of the most difficult and expensive problems in the field of wastewater engineering (Snyman et al., 2000), but the major benefit of disposing sludge to the land increases the supply of plant nutrients and also provision of some of the essential micronutrients (Zn, Cu, Mo and Mn). Disposal of sewage sludge on and off-site must meet legal requirements (Guide: Sewage sludge, Utilisation in South Africa) in terms of permissible limits (Herselman and Snyman 2009). Reuse and disposal of sludge in the agricultural sector had to comply with the "Guide for permissible utilization and disposal of sewage sludge" (Snyman et al., 2000). Not all the sludge generated in South Africa can be used in agricultural practices (Synman and Herselman, 2006) because of the high levels of heavy metals in it. For this reason guidelines have been developed for other management options such as disposal in land facility. South Africa introduced these guide-lines in 1991 and these were revised in 1997 with considerable amendments to the heavy metal loading and usage restrictions. According to Snyman et al. (2000), the first edition of the Permissible Utilization and Disposal of Sewage Sludge of 1991 was aimed to assist organizations involved in sewage treatment to promote safe handling, disposal and utilization of sewage sludge.

Table 2.6 shows the comparison between the metal content of the sludge aimed for unrestricted use in 1991 and 1997 sludge guidelines. These guidelines for metals are based on the benchmark values of the typical South African sludge and samples (Snyman, and Herselman, 2005). This means that South African sludge showing higher metal content then the values on table 1 should be investigated and monitored. Guidelines are needed to prevent contamination of soil and uptake

by plants (Snyman and Waals, 2004). The guidelines set in 1991 were subject to consideration debates, where no consensus was reached by the Departments (Department of Health, Department of Water Affairs and Forestry, Department of Agriculture and the Department of Environment Affairs and Tourism). In 1991 the guidelines were used as an interim while talks between departments were on going. The Permissible Utilisation and Disposal of Sewage Sludge Edition 1, was finally published in 1997 and was aimed at assisting organizations involved in sewage treatments to promote safe handling, disposal and utilisation of sewage sludge (WRC, 1997)

**Table 2.6: Guidelines on element permissible limits on the utilization and disposal of sewage sludge of 1991 and 1997.**

| Metal | 1991 Limit (mg/kg dry sludge) | 1997 Limit (mg/kg dry sludge) | TIL (mg/kg) | TMT (mg/kg) | MPL (mg/kg) |
|-------|-------|-------|-------|-------|-------|
| Cd | 20 | 15.7 | 2 | 3 | 5 |
| Co | 100 | 100 | - | - | - |
| Cr | 1750 | 1750 | 80 | 350 | 450 |
| Cu | 750 | 50.5 | 100 | 120 | 375 |
| Hg | 10 | 10 | 0.5 | 1 | 9 |
| Mo | 25 | 25 | - | - | - |
| Ni | 2750 | 200 | 50 | 150 | 200 |
| Pb | 400 | 50.5 | 56 | 100 | 150 |
| Zn | 2750 | 353.5 | 185 | 200 | 700 |
| As | 15 | 15 | 2 | 2 | 20 |
| Se | 15 | 15 | - | - | - |
| B | 80 | 80 | - | - | - |
| F | 400 | 400 | - | - | - |

**Snyman et al., 2000; Herselman and Moodly, 2009;** TIL stands for total investigative level in soil, TMT stands for total maximum threshold in soil, MPL stands for maximum permissible limits in soil.

These guidelines were then compared to the guidelines set by the government for $NH_4NO_3$ extractable metals in soils to protect ground water from pollution (Baden-Wurttemburg, 1993). The guide lines were perceived to be overly restrictive specifically with regard to some of the potential toxic metals and elements (PTME) for sewage sludge. When heavy metals exceed the MPL set by Herselman and Moodly (2009) for aqua regia digestion, then sewage sludge application is not permissible.

**Table 2.7: Maximum permissible total metal content in soil (mg/kg).**

|    | Aqua regia (a) | $NH_4NO_3$ (b) | DTPA (c) | TCLP (d) |
|----|----------------|----------------|----------|----------|
| Cd | 5    | 0.1   | 0.07 | 0.03 |
| Cr | 450  | 0.13  | 0.14 | 1.02 |
| Cu | 375  | 1.2   | 0.5  | 0.43 |
| Hg | 9    | 0.007 | -    | 0.07 |
| Ni | 200  | 1.2   | 0.98 | 0.91 |
| Pb | 150  | 3.5   | 1.53 | 0.08 |
| Zn | 700  | 5.0   | 1.5  | 7.15 |
| As | 20   | 0.14  | -    | 0.07 |

a Herselman and Moodly (2009); Herselman (2009)

b Baden-Wurtternberg (1993)

c Havilin and Suitoupour (1981)

d Snyman et al., (2004)

Heavy metals are ubiquitous and monitoring them is important in various fields because of their effects on ecosystems and living organisms, for an example part of drug quality control is detecting and determining heavy metals (Vukovic et al., 2012). Table 2.4 indicates the maximum permissible limits for heavy metals in soils for different extraction procedures. Trace metals in soils and sediments may exist in different chemical forms or ways of binding (Rauret, 1997). McGrath (1987) found that anomalously high contents of Zn, Cu, Ni, Cd, and Cr, from sewage sludge had persisted in the top soil of a field trial for more than 40 years after application of the sludge. The determination of heavy metals in soils may be carried out for various reasons, including total elementary content (Alloway, 1995), it is more important to be able to estimate the mobile fraction, the readily soluble fraction, the exchangeable fraction, or the plant available fraction of heavy metal content of a soil as a more direct indication of the likelihood of deleterious or toxic effects on the environment (Alloway, 1995). Diverse amounts of heavy metals may be found everywhere in soils, water, sediments and plants (Dube et al., 2000). In soils heavy metals may be bound or sorbed by particular natural substances which may increase or decrease their mobility. In

agriculture accumulation of heavy metals is of interest because they contribute toxic elements into the human food chain and special attention should be paid to the dangerous health elements and to most consumed agricultural crops (Grytsyuk, 2005). Effects of long term pollution depend on total, leachable and plant available forms determined. To assess the potential effects of heavy metal contamination in soils, total concentration of metals is the regulatory criterion used (Roy and McDonald, 2003). According to Vilar et al. (2005) this assumes all chemical forms and phases in which a given metal can occur will produce similar biological effects. Biological and toxicological evidence show chemical form and oxidation state at which an element occurs and introduced into the environment is a critical factor (Roy and McDonald, 2003). Bio-availability and mobility of heavy metals to soil and plants are affected by many factors where soil pH is the most important factor.

## 2.6 Effects of long term pollution with sewage sludge on total, leachable and plant available forms of heavy metals.

Accumulation of heavy metals on vegetable plants depends on environmental conditions, metal species and plant available forms of heavy metals (Mosleh et al., 2013). However accumulation of heavy metals in plants growing on contaminated soils can cause toxicity effects on animals and humans through ingestion (Roy and McDonald, 2003). Uptake of metals by plants is a function of a plant species, concentration of metals in soil, metal concerned and plant tissue (Roy and McDonald, 2013). A study done by Singh and Agarwal, (2006) indicated that cowpea, spinach, chickpea, pea and wheat growing on metal contaminated soils affect plant biomass yield and metal distribution in different parts of the plant. In the environment exchangeable fractions and water-soluble fractions are readily available whereas the residual fractions are immobile under natural conditions (Roy and McDonald, 2003). Leafy vegetables accumulate metals in their tissues and such accumulation may cause health related issues in humans and animals grazing on that land (Chaney et al., 2000; Khan et al., 2008). Different vegetable plants accumulate and translocate variable amounts of heavy metals from soil into their tissue (Molseh et al., 2013).

 In soils major sources of heavy metal accumulation are through wastewater irrigation, solid waste disposal, industrial activities and sewage sludge application (Khan et al., 2008). Heavy metals in

the body have the potential to damage central nervous system (Brevik, 2013). According to Khan et al. (2008) consumption of vegetable contaminated with heavy metals can deplete the human body's essential nutrients, decreasing immunological impacts, retarded growth, malnutrition and increased susceptibility to gastrointestinal cancer. Repeated application of sewage sludge reduces the capacity of the soil to retain heavy metals. This causes heavy metals to leach to ground water, or soil solution available for plant uptake (Mosleh et al., 2013). Crops and vegetable species growing in metal polluted soils are unusable to avoid the adsorption of these metals.

**2.7 Concluding Remarks on the Review.**

Long term application of sewage sludge on soil can lead to contamination of soils with heavy metals and pathogens. Contamination of soil with heavy metals is of serious concern due to their toxicity and persistence in the environment as it affects soil life. There is a greater potential of using sewage sludge as a soil amendment to improve soil fertility as it provides essential nutrients (N, P, and K), and high amounts of organic matter to the soil. There is greater concern of using sewage sludge on soils as it can cause pollution of ground water, accumulation of heavy metals within the soil profile and uptake of heavy metals by plants. Within a soil profile heavy metals have shown greater potential accumulating at the top surface and mobility is determined mostly by pH of the soil. Heavy metal concentration distribution spatially accumulates mainly on the topsoil and extensive mobility within the soil depth. In soils spatial distribution of heavy metals acts as a good aid to assess the possible enrichment and identifying hot spot areas with high metal concentration. This accumulation of heavy metals depends on plant species with the efficiency of different plants absorbing heavy metals evaluated by plants uptake or soil to plant transfer factors of the metals. Vegetable plants growing on heavy metal contaminated soil could accumulate heavy metals. Translocation of heavy metals in vegetable plants growing on contaminated soils is more on the leaves and the edible parts of the plant. Accumulation of heavy metals tends to be on the leaf especially leafy vegetables and also in their tissues and this affects food quality and safety. Consumption of heavy metal contaminated vegetables can cause health related issues and may affect the function of the ecosystem.

# 3 MATERIALS AND METHODS

## 3.1 Site description

The study was carried out at a dedicated sewage sludge disposal site at Darvill Waste Water Works in Pietermaritzburg (from $29.602500^{\circ}$S to $29.61139^{\circ}$S and from $30.433900^{\circ}$E to $30.43861^{\circ}$E), KwaZulu Natal (Figure 3.1). It lies from latitude $29.602500^{\circ}$S to $29.61139^{\circ}$S and from longitude of $30.433900^{\circ}$E to $30.43861^{\circ}$E. Pietermaritzburg normally receives about 695 mm of rain per year and most of its rain comes during the summer season. Average summer temperatures are about $27^{\circ}$C and mean winter temperatures are about $20.5^{\circ}$C. The entire area is on Ecca shale, which is underlined by Dwyka tillite on the downslope slope. On the upslope slope shale is the dominant parent material with some dolerite intrusions.

The Darvill Waste Water Works cover 78 ha and sewage sludge (anaerobically digested and activated) has been applied as a suspension through sprinkler irrigation system for over 50 years on 57 ha of the land. The sewage sludge disposal area is divided into six transects. Transects 1 to 5 have been irrigated with sewage sludge, and Transect 6, where no sludge has been applied, is the control. Transects were different in terms of distance from the source of the sludge, with Transect 1 being the closest and Transect 5 the furthest. Part of Transects 1 and 4 are on lower slope positions than the others, and Transect 4 receives drainage water from Transect 5 and part of Transect 3, and as such it is always wet. Except for the control transect, which had three sampling points, all transects had five sampling points which were taken as replicates (Figure 3.2).

## 3.2 Soil sampling

Using standard sampling procedures, soil samples were collected from the 28 sampling points, at 0-10; 10-20; 20-30, 30-40, and 40-50cm depths. For selected points within each transect, the 50-60 and 60-70 cm depths, were also included. At each sampling depth, two samples were taken around each sampling point, and mixed to get a composite sample. Sampling was done with a bucket auger and kept in well labeled plastic bags before oven drying at a temperature of $38^{\circ}$C for 72 h. The oven-dry samples were ground with a mortar and pestle and sieved to less than 2 mm and stored in plastic containers at room temperature before analysis.
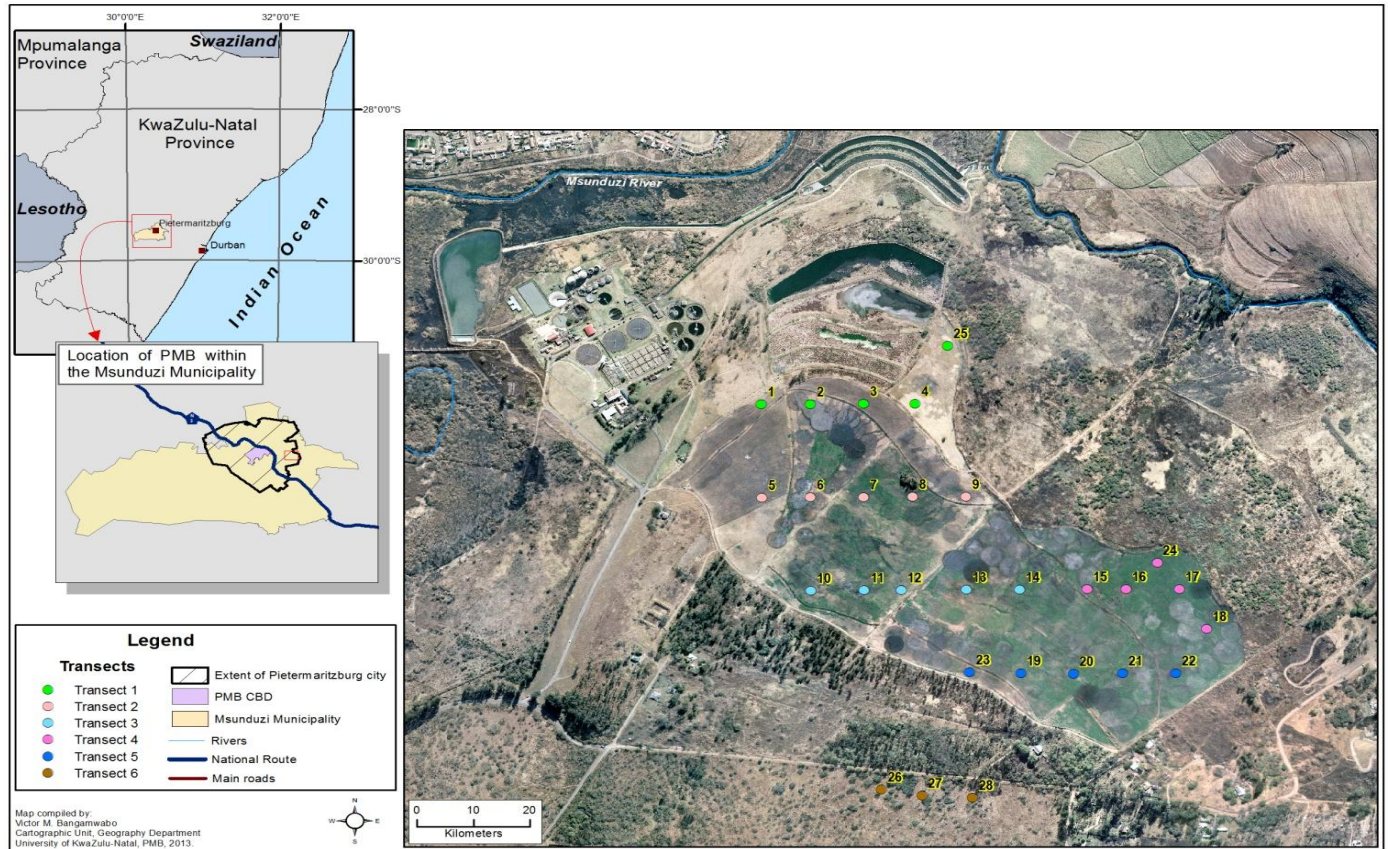
**Figure 3.1: Dedicated disposal site showing sampling points near Darvill Wastewater Treatment Works.**
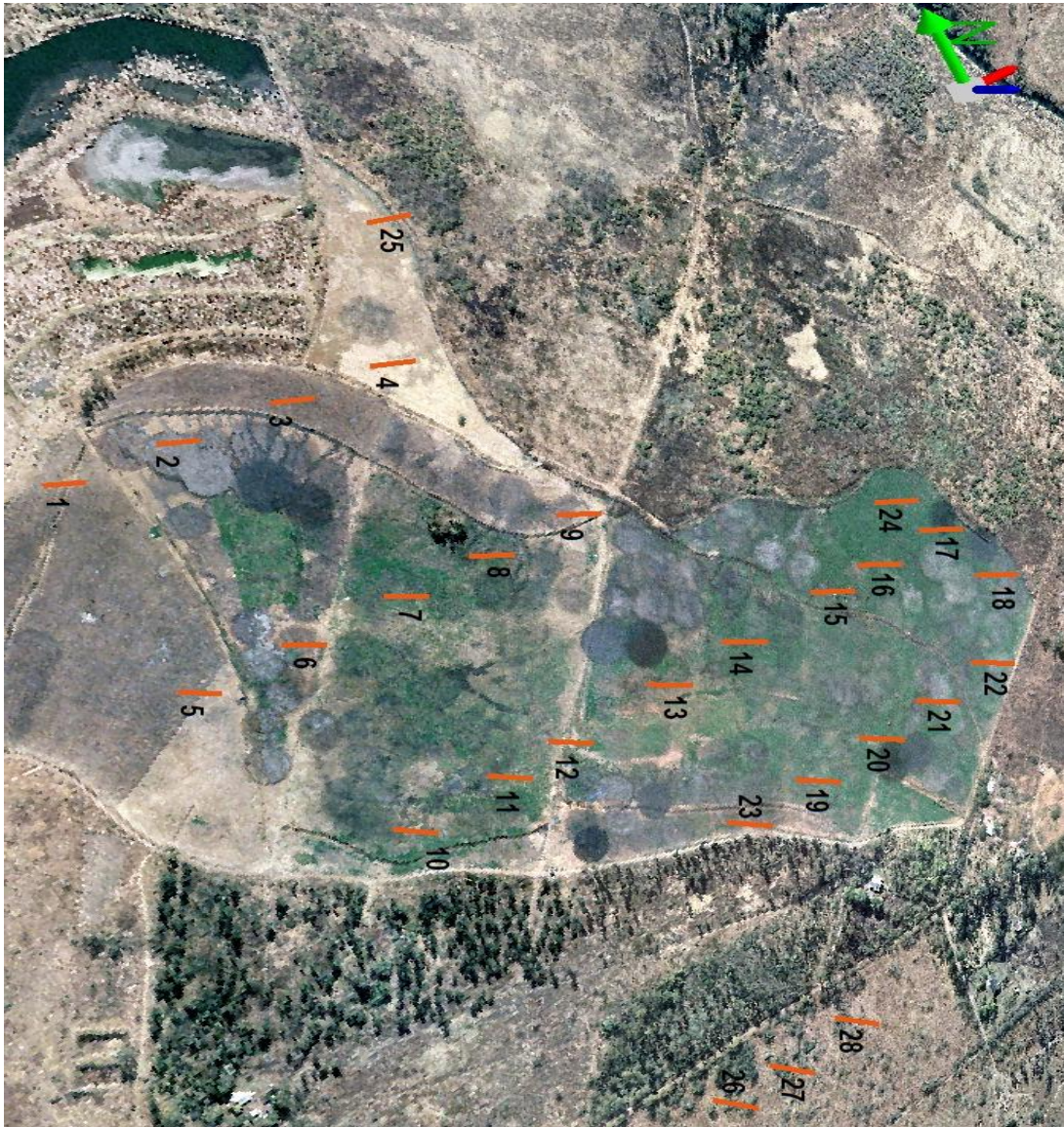
**Figure 3.2: Oblic map showing the different sampling points.**

**3.3 Sample analysis**

*3.3.1 Soil pH and electrical conductivity*

Soil pH was analyzed using 1:5 soil: solution ratio, both $H_2O$ and 0.1M KCl using PHM 210 standard meter. The same water suspensions used for pH analysis were also used for determination of electrical conductivity (EC) using CDM 210 conductivity meter.

*3.3.2 Particle size distribution*

Soils were ground and sieved (<0.2 mm). The soils used for particle size analysis were from the 10-20, 20-30, 30-40 cm depths, from transect one (sampling points 2 and 3), transect two (points 5 and 7), transect three (points 12 and 14), transect four (points 17 and 18), transect five (points 19 and 21) and transect six (point 27). The 0-10 cm depth was not included because most of the material from this depth was mostly sludge. The two samples at each depth, from the same transect, were mixed to get composite sample and 20 g of was treated with 50 ml Calgon solution (35.7 g sodium hexametaphosphate; 7.9 g sodium carbonate and de-ionized water to a 1L) and shaken overnight at a speed of 30 rpm, before further dispersion with ultrasound. The high in organic matter in some of the samples was removed by addition of hydrogen peroxide overnight on sand-bath at 70$^o$C. Sand, silt and clay fractions were then determined following the double pipette procedure as in Gee and Bauder (1986).

*3.3.3 Carbon and nitrogen measurements*

The soils used for C and N measurements were from the 0-10, 10-20, and 20-30 cm depths, from transect one (points 2 and 3), transect two (points 5 and 7), transect three (points 12 and 14), transect four (points 17 and 18), transect five (points 19 and 21) and transect six (point 27). Leco analyser was used for determination of C and N, where 0.2 g of soil was weighed and subjected to furnace temperature (1450 $^o$C) for about 120 seconds. The procedure that was followed is as described in "TruMac CNS/NS Carbon/Nitrogen/Sulfur Determinators Instruction Manual" (Leco Corporation 2012)

### 3.3.4 Total heavy metals concentrations

Total heavy metal concentrations were analysed after extraction with Aqua regia extraction (Chen and Ma, 2001) from the dried, ground and sieved soils (< 0.5 mm). Soil (0.5g) was treated with aqua-regia (12ml concentrated HCl 32% and 4 ml concentrated $HNO_3$ 55%) and digested in a microwave digester (EPA 3051H-HP500) at $175^oC$ for 10 minutes. An aliquot of the digest (5 ml) was diluted to 50 ml in storing bottle with de-ionised water before analysis of Zn, Cu, Ni, Cr, Pb, Cd, As and Hg with an inductively coupled plasma optical emission spectrometry (ICP-OES 720 Varian).

### 3.3.5 Potentially leachable heavy metals

Potential leaching of the heavy metals to ground water was tested using the Toxicity Characteristic Leaching Procedure (TCLP) for samples from sampling points 1, 5, 12 , 17, 21 and 27 for transects 1, 2, 3, 4, 5 and 6 respectively. The samples were from the 0-10, 10-20, 20-30, 30-40, 40-50, 50-60 and 60-70 cm depths. Extraction was done by suspending 1 g soil in 20 ml dilute glacial acetic acid, shaken on an end to end shaker for 20 hours (DWAF, 2005) at a speed of 30 rpm, followed by filtration through Whatman no. 2 filter paper. The pH of the suspension was adjusted to less than pH 2 and stored < $4^oC$ for three days before analysis. Heavy metals (Zn, Cu, Ni, Cr, Pb, Cd, and As ) were measured with inductively coupled plasma optical emission spectrometry (ICP-OES 720 Varian). Hg analysis was not included here due to technical errors on the ICP-OES 720 Varian machine

### 3.3.6 Ammonium nitrate extractable heavy metals

In line with the requirements of the Department of Water Affairs, all the samples were also analysed after extraction with 1M Ammonium Nitrate (80.04 g ammonium nitrate dissolved in 1L with de-ionised water). This procedure gives an estimate of the plant available heavy metals (Snyman and Herselman 2006). Air dry soil samples (20 g) were each suspended in 50 ml Ammonium Nitrate solution, shaken for 2 hours at 25 $^oC$, at a speed of 40 r.p.m, before filtration through Whatman no. 2 filter paper. Extractable Zn, Cu, Ni, Cr, Pb, Cd, As and Hg in the filtrate were analysed with ICP-OES 720 Varian.

### 3.3.7 Diethylenetriaminepentaacetic acid (DTPA) extractable heavy metals

Plant available heavy metals were extracted with diethylenetriaminepentaacetic acid (DTPA). The composite soils, from each transect, used for this extraction were from the 0-10, 10-20, 20-30, 30-40, 40-50, 50-60, and 60-70 cm depths, from sampling points 2 and 3 (transect one), 5 and 7 (transect two), 12 and 14 (transect three), 17 and 18 (transect four), 19 and 21 (transect five) and 27 (transect six). The soils (25 g) were extracted with 50 ml of solution containing 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.10 M triethanalamine (TEA) (1.97 g diethylenetriaminepenta acetic acid, 1.47 g calcium chloride dehydrate, 14.92 g triethanalamine and 6.8 g hydrochloric acid in 1.0 L de-ionised water, pH 7.3). The soil samples were shaken for two hours at $25^oC$, at a speed of 40 rpm, then filtered with Whatman no. 2 filter paper, and the pH measured immediately, before storing the samples at $4^oC$ until analysis. Extractable Zn, Cu, Ni, Cr, Pb, Cd and As in the extracts, were measured with ICP-OES 720 Varian. Hg analysis was not included here due to technical errors on the ICP-OES 720 Varian instrument.

## 3.4 Heavy metal concentration in indigenous vegetable plant tissue.

### 3.4.1 Plant sampling and preparation for analysis

Indigenous vegetable plant samples were collected randomly, in April 2013, from transects 2, 3, 4 and 5 at DWWW using 1m x1m quadrats. Transect 1 and the upper parts of transect of 2, where DUZITURF company produces turf grass, had no indigenous vegetables growing. The vegetables were *Amaranthus hybridus* , *Solunum nigrum* (Solanaceae) also known as *(Black nightshade)*, *Solanum lycopersicum* (plants and fruits) and *Curcubita pepo* (Cucurbitaceae) were collected from transect 5 for comparison with the plant material.

The vegetables were taken to the laboratory within 2 hours of harvesting, where they were washed with tap water, rinsed with distilled water and put into drying bags. The samples were then oven dried at $38^oC$ to constant weight (about 7 days). The plant material was weighed for determination of dry matter, and ground to < 0.5 mm using Fritsch Pulverisette mortar grinder.

*3.4.2 Plant analysis of heavy metals*

The plant samples (0.5 g) were weighed into 50 ml polyvinyl containers suitable for Aqua regia digestion (Chen and Ma. 2001). The samples were treated with 16ml of Aqua regia (12 ml of 32% HCl and 4 ml of 55% $HNO_3$) and digested with a microwave digester (EPA 3051H-HP500) at $175^oC$ for 10 minutes,  for 8 minutes.  An aliquot of the digest (5 ml) was diluted with 45 ml of de-ionised water in a 50 ml polyvinyl tube and analysed for As, Cr, Cu, Hg, Zn, Pb, Cd and Ni with an ICP-OES 720 Varian.

**3.5 Statistical analysis**

All statistical analyses in this study were performed using Genstat 14th edition software. Two way analysis of variance (ANOVA) was used to determine the effects of transect and soil depth for pseudo-total, TCLP, $NH_4NO_3$ and DTPA extractable heavy metal data. For heavy metal concentrations in vegetables, two way ANOVA was used to determine the effects of vegetable type and transect, only for transects where all the vegetables were found. Stepwise regression analysis was done with SAS 11th edition. Correlation analysis was used to relate total soil metal concentration, $NH_4NO_3$ and DTPA extractable concentrations. Geo-spatial maps of heavy metals were obtained using Inverse Distance Weighting (IDW) technique. The technique gives a general view of how the heavy metals were spatially distributed on the area.

# 4. RESULTS

## 4.1 Soil pH

Soil pH ($H_2O$) in transects 1 and 6 was 5.1 or lower at all depths, while it was at least pH 5.3 at all depths for all the other transects, with the surface layers (0-10 cm) having at least pH 6 Table 4.1). The lowest pH was in the 10-20 cm depth in transect 1, 20-30 cm in transects 2 and 4, 30-40 and 40-50 cm depths in transect 5. Soil pH in sludge irrigated soil was 0.3-1.4 units higher than the reference soil. The pH in KCl was lower than that in water and generally followed the same trend. Electrical conductivity ranged 78-98 mS/cm and generally increased with depth for all transects.

## 4.2 Total C & N

Total C was ≥ 9% in the top 30 cm of transects 2, 3, 4 and 5, and in the 0-10 cm depth in transect 1. The control (transect 6) had 2% C in the top 30 cm depth (Table 4.1). Total C in the 0-10 cm depth ranged 12-19% in all the transects except the transect 6 (2.4%) and it decreased with depth to 3.5, 9.1, 14.0, 9.6, 11.0, and 2.0% in the 20-30 cm depth for transects 1, 2, 3, 4, 5 and 6, respectively. Total N was > 1% in transect 5 (top 30cm), transect 2 (top 20 cm), transect 3 (10-20 and 20-30 cm depth) and transect 1 (0-10 cm depth). The control had ≤ 0.2% at all depths measured. Total N also decreased with depth with only transect 4 showing an increase. The C:N ratio was 10:1 with just the surface layers in transect 3 and 4 being higher.

**Table 4.1: Soil chemical composition.**

| transect | Depth (cm) | pH(H$_2$O) | pH(KCl) | EC(ms/cm) | %C | %N |
|---|---|---|---|---|---|---|
| 1 | 0-10 | 5.1 | 4.1 | 90.4 | 11.53 | 1.10 |
|   | 10-20 | 4.6 | 3.8 | 94.1 | 6.13 | 0.56 |
|   | 20-30 | 5.0 | 4.1 | 94.4 | 3.45 | 0.30 |
|   | 30-40 | 5.4 | 4.4 | 96.6 | ND | ND |
|   | 40-50 | 5.4 | 4.5 | 95.6 | ND | ND |
| 2 | 0-10 | 6.0 | 4.7 | 80.0 | 16.7 | 1.60 |
|   | 10-20 | 5.8 | 4.9 | 81.4 | 14.5 | 1.41 |
|   | 20-30 | 5.6 | 4.6 | 82.5 | 9.05 | 0.88 |
|   | 30-40 | 5.7 | 4.8 | 91.1 | ND | ND |
|   | 40-50 | 5.9 | 5.8 | 90.3 | ND | ND |
| 3 | 0-10 | 6.4 | 4.6 | 88.4 | 16.7 | 0.51 |
|   | 10-20 | 6.2 | 5.3 | 82.9 | 16.0 | 1.57 |
|   | 20-30 | 5.5 | 4.6 | 89.5 | 14.0 | 1.42 |
|   | 30-40 | 5.5 | 3.6 | 92.7 | ND | ND |
|   | 40-50 | 5.4 | 4.7 | 78.4 | ND | ND |
| 4 | 0-10 | 6.4 | 5.5 | 80.4 | 18.79 | 0.41 |
|   | 10-20 | 6.0 | 5.1 | 85.0 | 18.33 | 0.52 |
|   | 20-30 | 5.6 | 4.8 | 83.6 | 9.61 | 0.98 |
|   | 30-40 | 5.8 | 4.9 | 88.5 | ND | ND |
|   | 40-50 | 5.8 | 5.2 | 82.5 | ND | ND |
| 5 | 0-10 | 6.7 | 5.8 | 80.6 | 11.84 | 1.16 |
|   | 10-20 | 6.5 | 5.6 | 84.7 | 11.06 | 1.19 |
|   | 20-30 | 5.7 | 4.8 | 81.7 | 10.98 | 1.18 |
|   | 30-40 | 5.3 | 4.4 | 96.4 | ND | ND |
|   | 40-50 | 5.3 | 4.4 | 99.0 | ND | ND |
| 6 | 0-10 | 5.0 | 4.1 | 98.1 | 2.44 | 0.18 |
|   | 10-20 | 4.9 | 4.0 | 98.1 | 2.18 | 0.16 |
|   | 20-30 | 4.9 | 4.0 | 98.2 | 2.02 | 0.15 |
|   | 30-40 | 5.1 | 4.2 | 97.9 | ND | ND |
|   | 40-50 | 5.1 | 4.2 | 96.8 | ND | ND |

ND stands for not determined

## *4.3 Particle size distribution*

The soils in transects 1 to 5 were loamy, with 17-21% clay in transects 2, 3, 4, and 5, while transects 1 had 10% (Table 4.2). Transect 6 (control) had a sandy loam soil with 15.4% clay. The soils had high coarse silt contents ranging from 27 to 38%, while coarse sand ranged from 15 to 29%.

**Table 4.2: Particles size distribution (%) of soils in the different transects.**

| Transect | Depth(cm) | Clay | fiSi | coSi | fiSa | meSa | coSa |
|---|---|---|---|---|---|---|---|
| 1 | 10-20 | 10 | 4.1 | 35.3 | 5.0 | 188 | 24.8 |
|  | 20-30 | 11 | 5.5 | 38.3 | 6.0 | 11.6 | 26.2 |
|  | 30-40 | 11 | 5.9 | 35.6 | 5.2 | 8.3 | 28.8 |
| 2 | 10-20 | 18 | 6.0 | 38.0 | 6.0 | 13.0 | 21.7 |
|  | 20-30 | 14 | 6.1 | 39.0 | 7.0 | 8.9 | 19.0 |
|  | 30-40 | 15 | 6.0 | 36.9 | 6.0 | 8.7 | 18.0 |
| 3 | 10-20 | 19 | 6.1 | 37.0 | 5.1 | 13.1 | 28.0 |
|  | 20-30 | 17 | 6.0 | 39.5 | 6.0 | 11.0 | 21.5 |
|  | 30-40 | 15 | 6.0 | 35.0 | 4.0 | 10.5 | 25.0 |
| 4 | 10-20 | 21 | 5.2 | 35.1 | 8.1 | 11.0 | 16.1 |
|  | 20-30 | 19 | 5.1 | 36.0 | 9.0 | 11.2 | 17.6 |
|  | 30-40 | 19 | 6.1 | 34.5 | 9.4 | 11.0 | 16.6 |
| 5 | 10-20 | 17 | 3.5 | 27.9 | 6.7 | 8.0 | 18.3 |
|  | 20-30 | 14 | 3.3 | 46.8 | 9.5 | 8.1 | 17.9 |
|  | 30-40 | 15 | 2.16 | 30.3 | 7.0 | 8.7 | 19.9 |
| 6 | 10-20 | 15.4 | 7.0 | 9.1 | 20.1 | 22.5 | 24.9 |
|  | 20-30 | 15.1 | 6.1 | 8.0 | 19.8 | 23.0 | 27.0 |
|  | 30-40 | 15 | 6.5 | 8.0 | 20.0 | 23.4 | 26.7 |

fiSi= fine silt, coSi= coarse silt, fiSa= fine sand, meSa= medium sand, coSa= coarse sand

**Table 4.3**: **Regression analysis.**

| Element | Stepwise regression equation | Soil parameter |
|---------|------------------------------|----------------|
| $As_{tot}$ | $Y= 17.17 - 0.66[clay]$ | |
| | $R^2= 0.387$ | Clay |
| $Cd_{tot}$ | $Y= 2.92 - 0.365[\%C]$ | |
| | $R^2= 0.347$ | %C |
| $Pb_{tot}$ | $Y= 227.3 - 13.74[Clay] + 8.033[\%C]$ | |
| | $R^2 = 0.158$ | %C |
| | $R^2 = 0.465$ | Clay |
| $Cr_{tot}$ | $Y = 42.61 - 61.16[\%C]$ | |
| | $R^2 = 0.861$ | %C |
| $Cu_{tot}$ | $Y = -82.26 + 49.83[\%C] + 7.47[pH]$ | |
| | $R^2 = 0.649$ | %C |
| | $R^2 = 0.071$ | pH |
| $Ni_{tot}$ | $Y= 33.86 - 1.48[\%C] + 1.42[Clay]$ | |
| | $R^2 = 0.294$ | %C |
| | $R^2 = 0.146$ | Clay |
| $Zn_{tot}$ | $Y= 419.5 - 28.16[\%C] + 51.73[Clay]$ | |
| | $R^2 = 0.708$ | %C |
| | $R^2 = 0.062$ | Clay |

Hg: no variable met the significance level for entry into the model

$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 \ldots \ldots \beta n X n$

$\beta_o=$ intercept

$\beta_1 \beta_2$ and $\beta_n$ are the coefficient of the predictors (explanatory variable) $X_1$, $X_2$, and $X_n$

### *4.4 Aqua regia extractable heavy metals*

### *4.4.1 Pseudo-total Zn and Cr concentrations in different transects with depth*

Mean Zn concentrations in transect 1 decreased from 0-10 cm to 40-50 cm depth. In transect 2 and 5 mean Zn concentrations increased from 0-10 cm to 10-20 cm depth, then decreased from 20-30 cm depths as shown in Fig. 3.4a. Transect 3 and 4 showed mean Zn concentration to increase from the 10-20 cm to the 20-30 cm depth but decreased in the 30-40 cm depth and increased again in the 40-50 cm depth. In transect 6 mean Zn concentration were lower than MPL and there was little movement within the profile.

Chromium concentrations in transect 1 and 4 decreased with depth down to 40-50 cm depth while the concentration remained constant in the top 20 cm, and declined with depth down to the 40-50

cm depths (Fig 3.1a). In transect 3 mean Cr concentrations decreased with depth from 0-10 cm to 30-40 cm depth, then slightly increased in the 40-50 cm depth. Transect 5 mean Cr concentrations increased from 806 mg/kg in the 0-10 cm depth to 955 mg/kg in the 10-20 cm depth, then decreased from 20-30 cm to 40-50 cm depths. In Transect 6 mean Cr concentrations were lower than 200 mg/kg in all depths except in the 30-40 cm depth, which had a mean Cr concentration of 267 mg/kg.
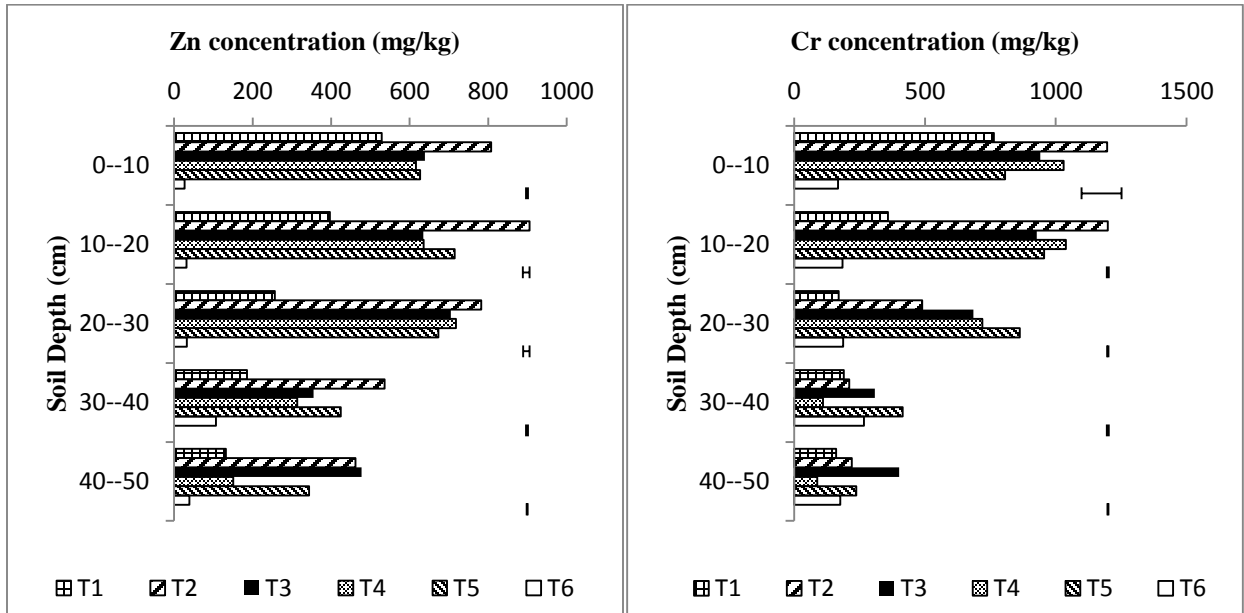


**Figure 4.1a Mean pseudo-total Zn and Cr concentrations in different transects with depth. Error bars represent least significant differences at p<0.05.** *(TIL, TMT and MPL of Zn =185, 200 and 700 mg/kg and for Cr = 80, 350 and 450 mg/kg, respectively).*

*Spatial distribution of Zn and Cr*

Figure 4.1b illustrates Zn concentrations spatially distributed across the study area at 10-20 cm depth. Zinc concentrations were observed to have exceeded MPL across the entire area. In sampling site of all transects, Zn concentrations were higher than 700 mg/kg MPL. As seen in (Fig. 4.1c), Zn has moved down the profile in all transects. Spatially, there was little variation in Zn concentration within transects. In some site Zn concentrations approached 1600 mg/kg, as seen in transect 1 site 4, having 1131.2 mg Zn /kg, transect 2 site 6 in the 0-10 cm depth with 1134.4

mg/kg, 10-20 cm depth with 1134.4 mg/kg and 20-30 cm depth with 1598.9 mg/kg . In Transects 6 Zn concentrations were lower than MPL.

Figure 4.1b demonstrates geo-spatial distribution of Cr in the 0-10 cm and 10-20 cm depth. The mean Cr concentrations in the treated soils exceeded the maximum permissible limit (MPL) of 450 mg/kg set by Water Research Commission of South Africa (Herselman et al., 2005, WRC, 1997 and Snyman and Waals, 2004) in the top 30 cm. Spatial distribution of Cr was even throughout the entire area (Fig. 4.1c) with transect 2, 3, 4 and 5 showing highest concentrations with mean concentrations 1198, 928, 1030 and 955 mg/kg respectively. Transect 2 and 4 showed highest concentrations in the 0-10 cm depth (Fig. 4.1b) and 10-20 cm depths. The results showed clear evidence of long term application of sewage sludge as the concentrations were high. The results showed that transect 4 and some part of transect 5 find to be at a bottom slope had high Cr concentrations on the surface layer mostly because transect 3 and 5 drains to this transect. There were variations among sampling points within the same transect (Fig 4.1c). High Cr concentrations have also been observed moving down the profile with transect 1 and 2 having the highest Cr concentrations in the 0-10 cm depth, transect 4 and 5 high Cr concentrations in the 20-30 cm depth, while transect 5 also shows high Cr concentrations in the 30-40 cm depth and transect 3 had the highest concentrations of Cr in the 40-50 cm depth (Fig. 4.1c)

Zn (mg/kg) in 0-10 cm soil depth
- 6.98 - 196.54
- 196.54 - 386.11
- 386.11 - 575.67
- 575.67 - 765.24
- 765.24 - 954.8
- 954.8 - 1144.37
- 1144.37 - 1333.94

Zn (mg/kg) in 10-20 cm depth
- 8.05 - 197.31
- 197.31 - 386.58
- 386.58 - 575.84
- 575.84 - 765.11
- 765.11 - 954.37
- 954.37 - 1143.64
- 1143.64 - 1332.9

Cr (mg/kg) in the 0-10 cm depth
- 38.805 - 215.779
- 215.779 - 392.753
- 392.753 - 569.727
- 569.727 - 746.701
- 746.701 - 923.675
- 923.675 - 1100.649
- 1100.649 - 1277.623
- 1277.623 - 1454.597
- 1454.597 - 1631.571

Cr (mg/kg) in 10-20 cm depth
- 40.197 - 240.281
- 240.281 - 440.364
- 440.364 - 640.447
- 640.447 - 840.531
- 840.531 - 1040.614
- 1040.614 - 1240.697
- 1240.697 - 1440.781
- 1440.781 - 1640.864
- 1640.864 - 1840.947

**Figure 4.1b: Spatial distribution of pseudo-total Zn and Cr at 0-10 cm and 10-20 cm depth.**

400     0     400     800   Meters

**Figure 4.1c: Spatial distribution of total Zn and Cr at different depth. Layers C, D and E represent the 20-30, 30-40 and 40-50 cm, respectively. Each map has different legends of concentrations. The darker the colour the higher the concentration.**

*4.4.2 Pseudo-total Cu and Ni concentrations in different transects with depth*

In transect 1 and 5 mean Cu concentrations decreased from 0-10 cm to 40-50 cm depth, and slight increase in the 40-50cm depth (Fig. 4.2a). Mean Cu concentrations increased from 0-10 to 10-20 cm depth, then decreased moving down the profile from 20-30 cm to 40-50 cm depths in transect 2. In transect 3 and 4 mean Cu concentrations increased with depth from 0-10 cm to 20-30 cm depths, then decreased from 30-40 cm to 40-50 cm depths of transect 4 and increased in 40-50 cm depth of transect 3 mean Cu concentrations. In transect 6 mean Cu concentrations did not change moving down the profile.

Mean Nickel concentration in transect 1 and 5 increased from the 0-10 cm depth to 10-20 cm depth, then decreased from 20-30 cm to 30-40 cm depth. In transect 2 mean Ni concentrations increased moving down the profile from 0-10 cm to 40-50 cm depth. Transect 3 results showed mean Ni concentrations were constant in the top 20 cm and decreased in the 30-40 cm to 40-50 cm depths, while in transect 4 mean Ni concentrations increased from 0-10 cm to 20-30 cm depth then decreased in the 30-40 cm to 40-50 cm depths (Fig 4.2a).
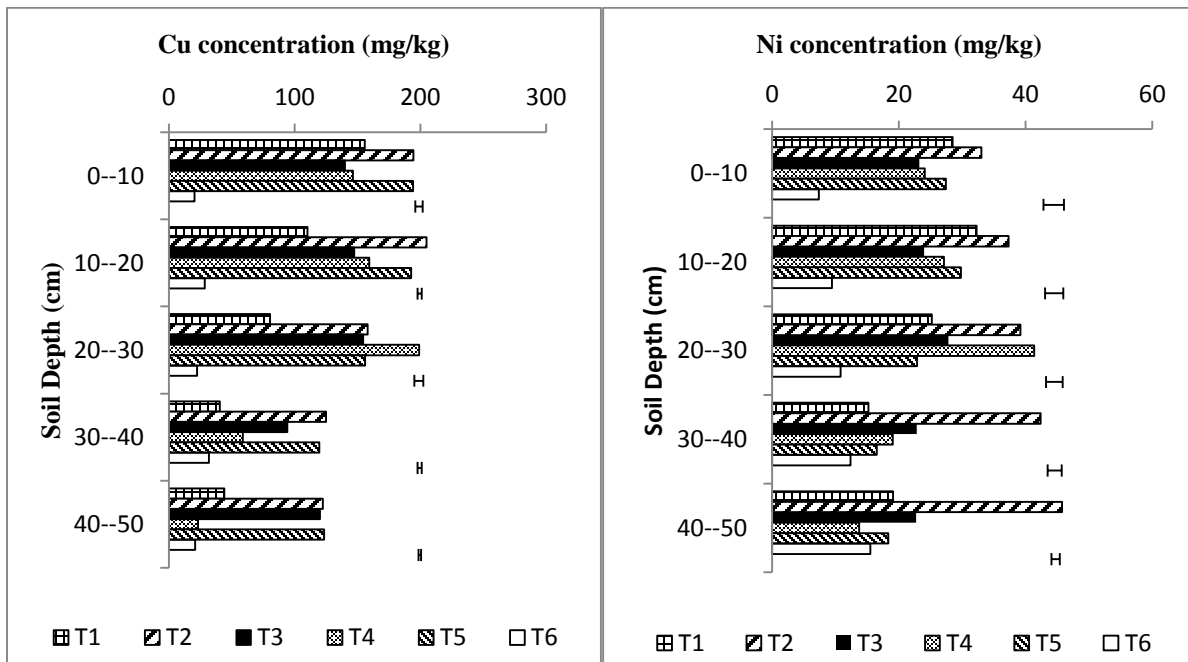


**Figure 4.2a: Mean pseudo-total Cu and Ni concentrations in different transects with depth. Error bars represent least significant differences at p<0.05.** *(TIL, TMT and MPL for Cu =100, 120 and 375 mg/kg; and for Ni =50, 150 and 200 mg/kg, respectively).*

*Spatial distribution of Cu and Ni*

Figure 4.2b illustrates Cu concentrations spatially distributed evenly. Mean Cu concentrations results showed that most accumulation was in top layers with a few sites highly contaminated moving down the profile meaning that Cu moved down the profile. In the 10-20 cm depth a few sites showed Cu accumulations as seen in Fig. 4.2b all Cu concentrations were about 300 mg/kg in these sites. While there concentrations are generally evenly distributed at all the different layers, there are some variations within transects. In transect 5 site 22 showed high concentrations of Cu in the 10-20 cm depth showing that Cu had moved down the profile. In the 30-40 cm depth a few hotspots were observed and site 14, 20 and 22 showed high concentrations as seen in (Fig. 4.2c). In transect 6 showed lower Cu concentration as compared to other transect although the concentration were a bit high.

The concentrations of Ni were far below the 200 mg/kg throughout all transects and sampling points. Figure 4.2b illustrates Ni concentrations spatially distributed throughout the entire area in the 10-20cm depth. Nickel concentrations seem to accumulate in the 0-10 cm depth and 10-20 cm depths and decreased moving down the profile (Fig. 4.2b). Nickel concentration were seen to be higher in specific sites especially site 2, 7, 9, 18 and 22 (Fig. 4.2c). Nickel concentrations accumulated in the 0-10 cm depth but moving down the profile spatial distribution of Ni concentrations decreased (Fig. 4.4c)
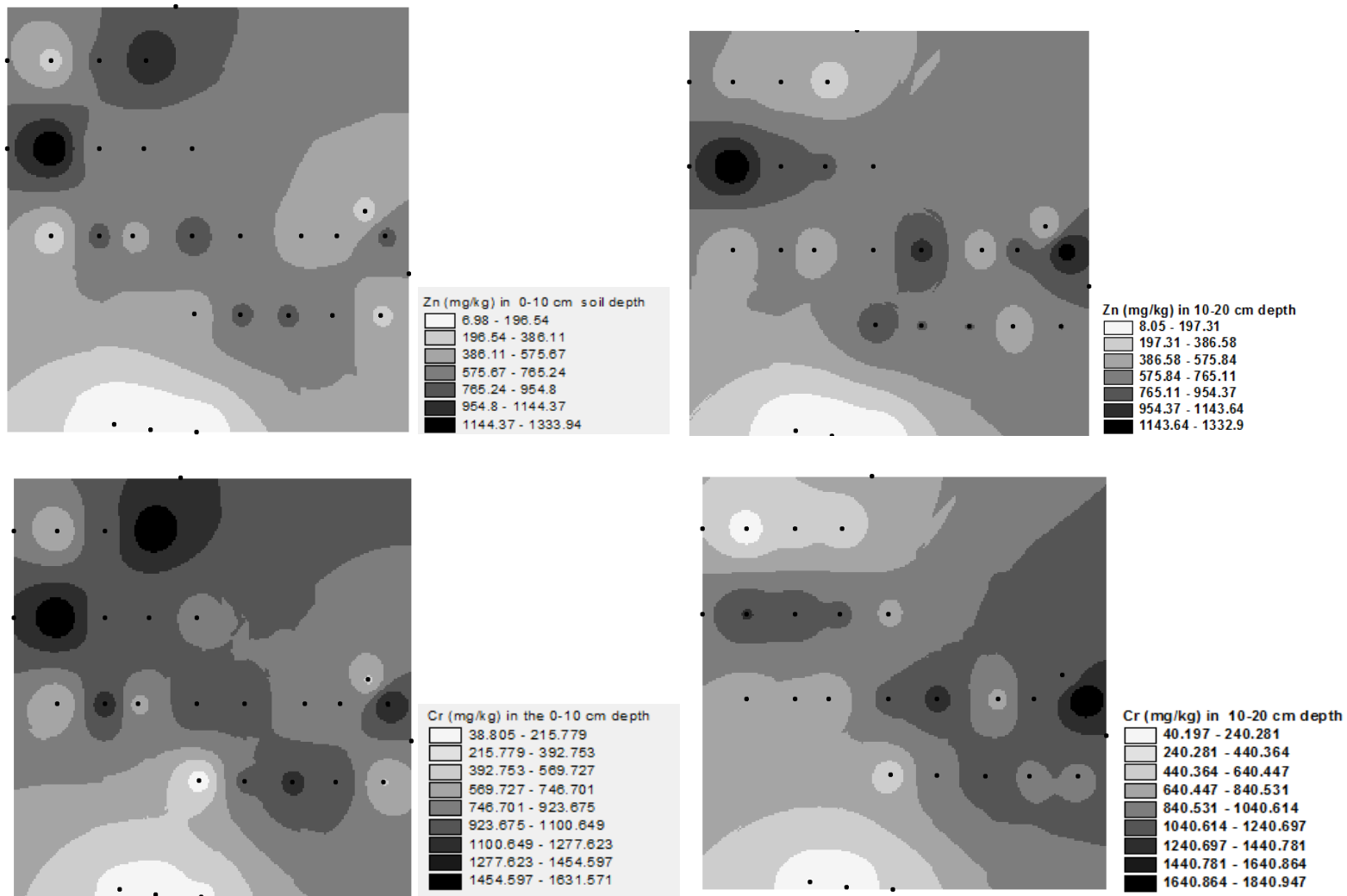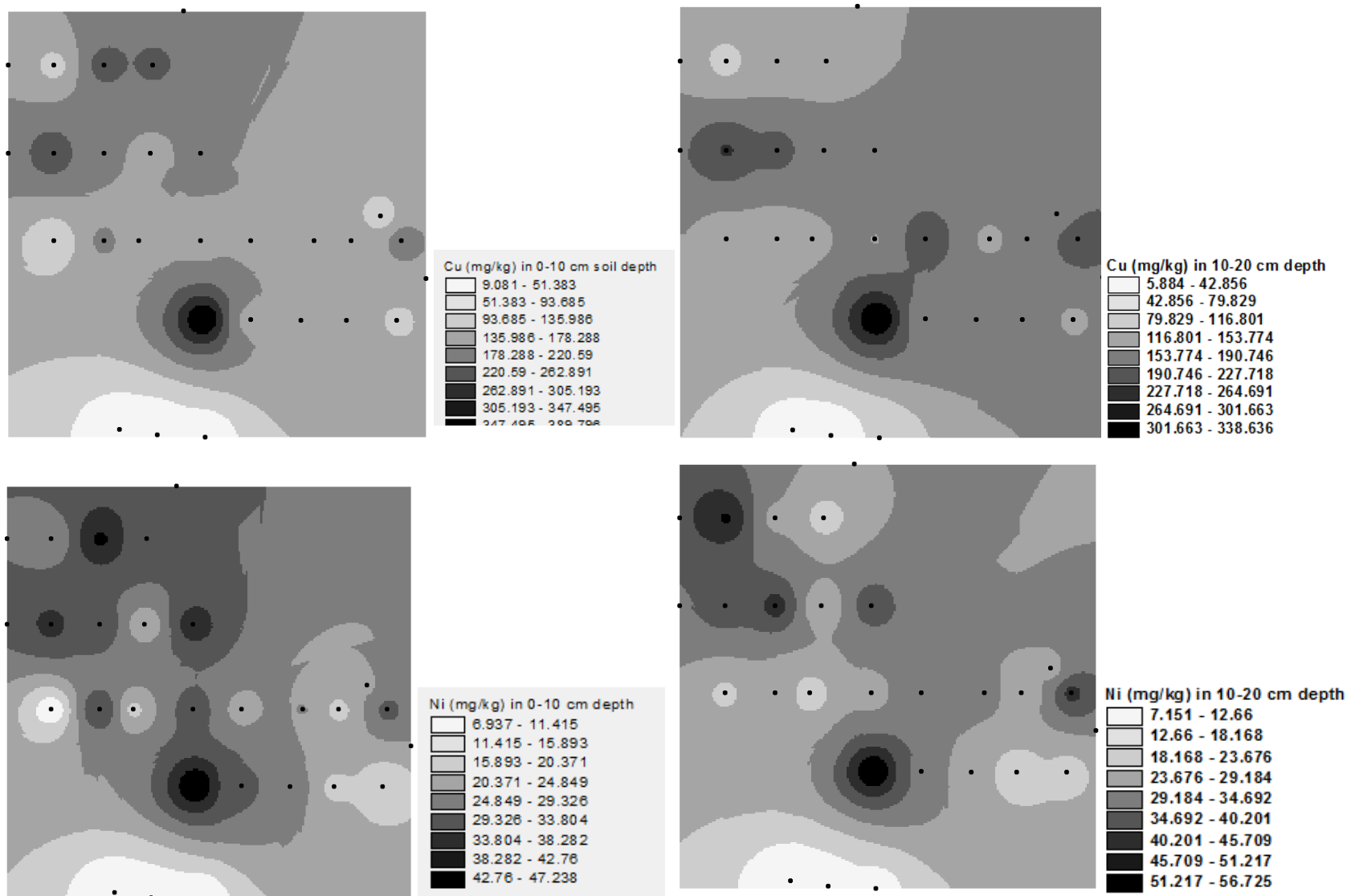
**Figure 4.2b: Spatial distribution of pseudo-total Cu and Ni at 0-10 cm and 10-20 cm depth.**
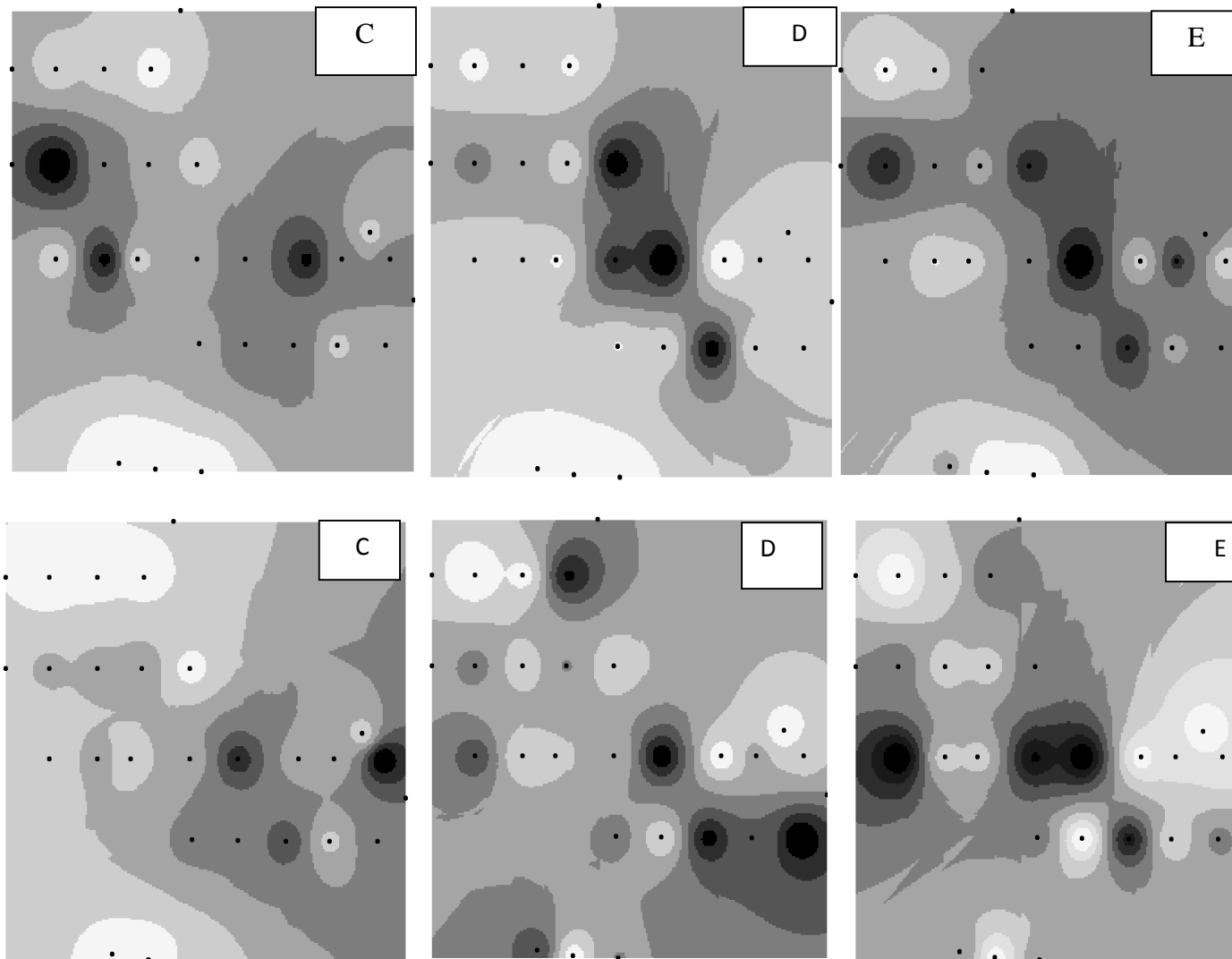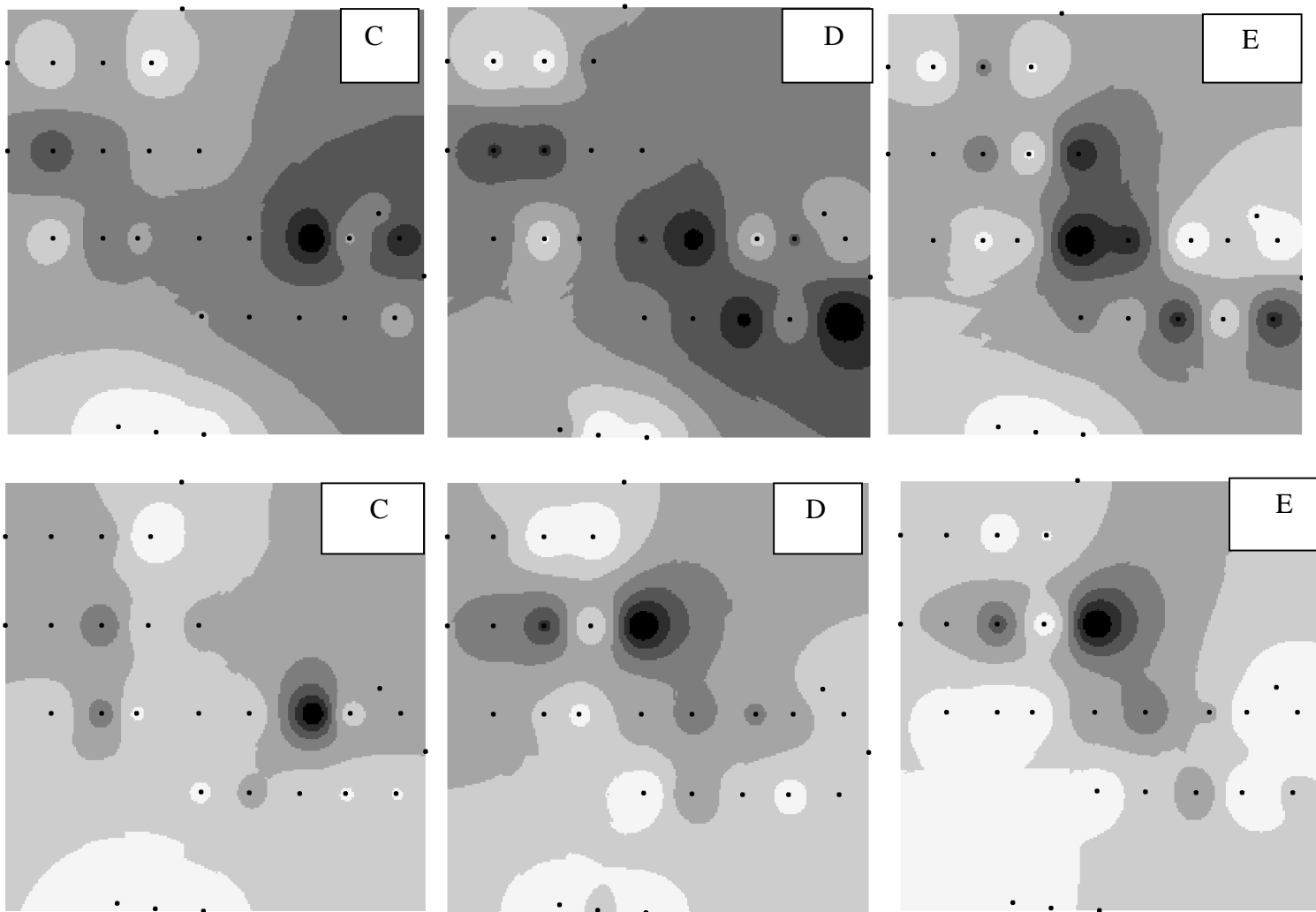
**Figure 4.2c: Spatial distribution of total Cu and Ni at different depth. Layers A, C, D, E represent the 0-10, 20-30, 30-40 and 40-50 cm, respectively. Each map has different legends of concentrations. The darker the colour the higher the concentration.**

### 4.4.3 *Pseudo-total Pb and Cd concentrations in different transects with depth*

Figure 4.3a illustrates mean Pb concentrations with vertical movement down the profile across all transects. Mean Pb concentrations in transect 1 decreased with depth from 0-10 cm to 30-40 cm depth. In transect 2 the mean Pb concentrations increased from 0-10 cm to 10-20 cm, decreased in the 20-30 cm to 30-40 cm depth then decreased in the 40-50 cm depth. In transect 3 mean Pb concentrations increased from 0-10 cm to 20-30 cm depth, then decreased to in the 30-40 cm. In transect 4 mean Pb concentration decreased from 0-10 cm to 10-20 cm, then slight increase in the 20-30 cm to 30-40 cm depth and decreased in the 40-50 cm depth. Mean Pb concentrations in transect 5 increased from 0-10 cm to 10-20 cm depth, decreased from 20-30 cm to 30-40 cm depth then increased in the 40-50 cm depth. In transect 6 there were no changes in movement of Pb within the profile. In the 0-10 cm only transect 1 and 2 exceeded the MPL, while transect 1, 2 and 5 exceeded MPL in the 10-20 cm and transect 2 and 3 exceeded MPL in the 30-40 cm while all the other depths had not exceeded MPL but still approaching the MPL.

Mean Cd concentrations in transect 1 decreased from 0-10 cm to 20-30 cm depth (Fig. 4.3b), then slightly increased in the 30-40 cm to 40-50 cm depth. In transect 2, 4 and 5 mean Cd concentrations increased from 0-10 cm to 20-30 cm depth, then decreased in the 30-40 cm depth while it slightly increased in the 40-50 cm depth (Fig. 4.3c). In transect 3 mean Cd concentration increased from 0-10 cm depth to 10-20 cm depth, then decreased in the 20-30 cm to 30-40 cm depth. There was little movement in transect 6. In all the depths all transects had exceeded the MPL with only the control below the MPL.

**Figure 4.3a Mean pseudo-total Pb and Cd concentrations in different transects with depth. Error bars represent least significant differences at p<0.05.** *(TIL, TMT and MPL for Pb =56, 100 and 150 mg/kg; and for Cd =2, 3 and 5 mg/kg, respectively).*

*Spatial distribution of Pb and Cd*

Figure 4.3b demonstrates spatial distribution of Pb concentrations from 0-10 to10-20 cm depth across transects. Lead concentrations exhibit differences as it moved down the profile with just a few areas showing hotspots where the element is highly concentrated (Fig. 4.3b). Spatially Pb was evenly distributed across the study area with just a few sampling site showed high concentrations as seen in (Fig. 4.3b) then the others. Lead concentrations differed spatially moving down the profile (Fig. 4.3c) high with high contamination in the 20-30 cm depth of site 3 in transect 1 , site 8 in transect 2 and site 13 in transect 3. Moving down the profile site 8 still had high concentration of Pb in the 30-40 cm and 40-50 cm.

Figure 4.3b illustrates geo-spatial distribution for Cd in soil where the levels were seen to be above MPL of 2 mg/kg except for site 3 in transect one where Cd concentration were lower than 1 mg/kg. Spatially Cd was evenly distributed across study area with variations among points within the same

transects. A few samples sites were seen to have high concentrations of Cd, site 2 in transect 1, site 7 and 9 in transect 2 and site 15 and 17 in transect 4 and site 21 in transect 5. In all these sites Cd concentrations were above MPL except in site 3 and in transect 6 the control. Based on the geo-spatial maps, Cd accumulation was on the surface layers but moved down with depth to 20-30 cm to 30-40 cm depth (Fig 4.3c).
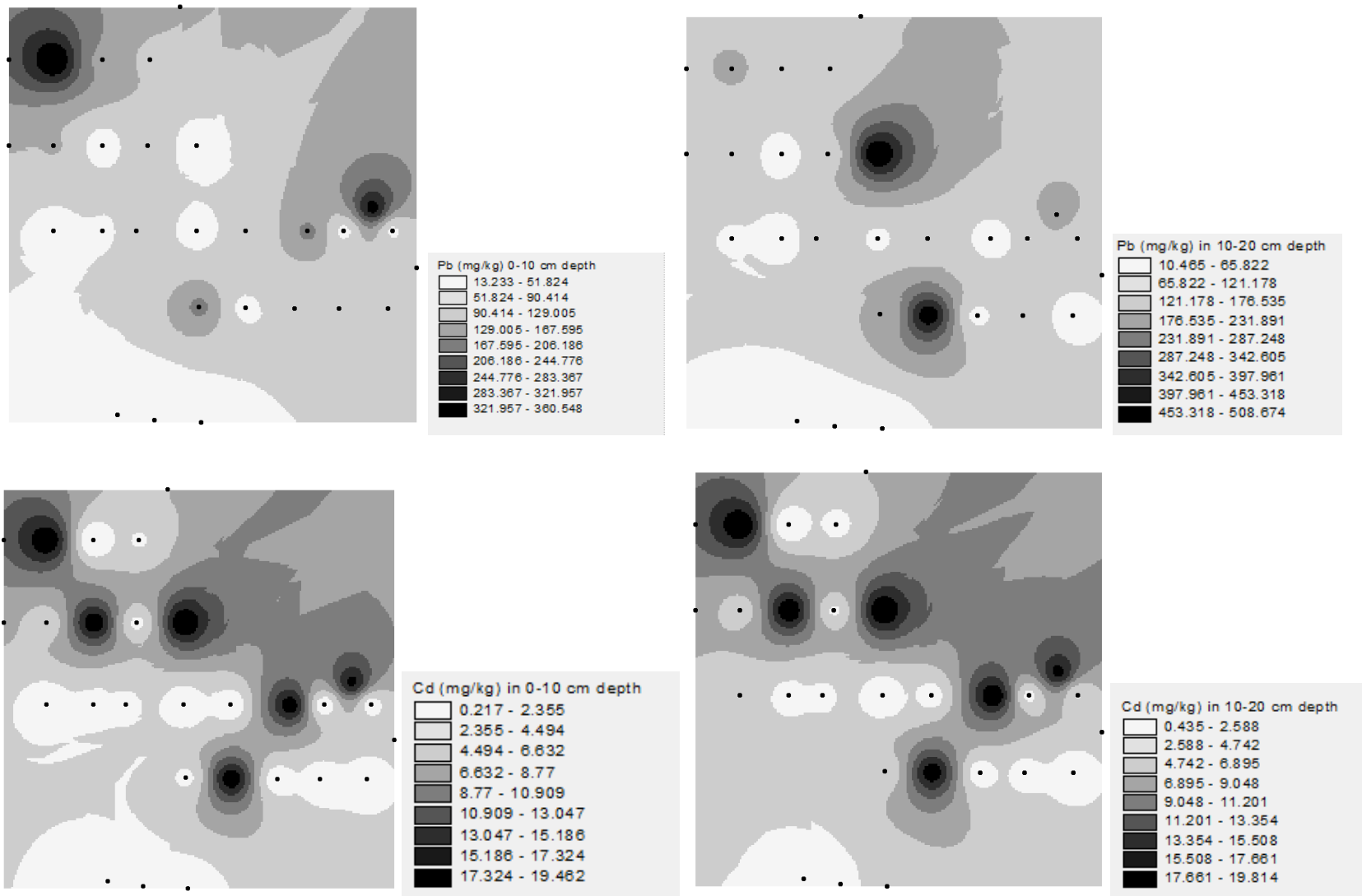
**Figure 4.3b: Spatial distribution of pseudo-total Pb and Cd at 0-10 cm and 10-20 cm depth.**
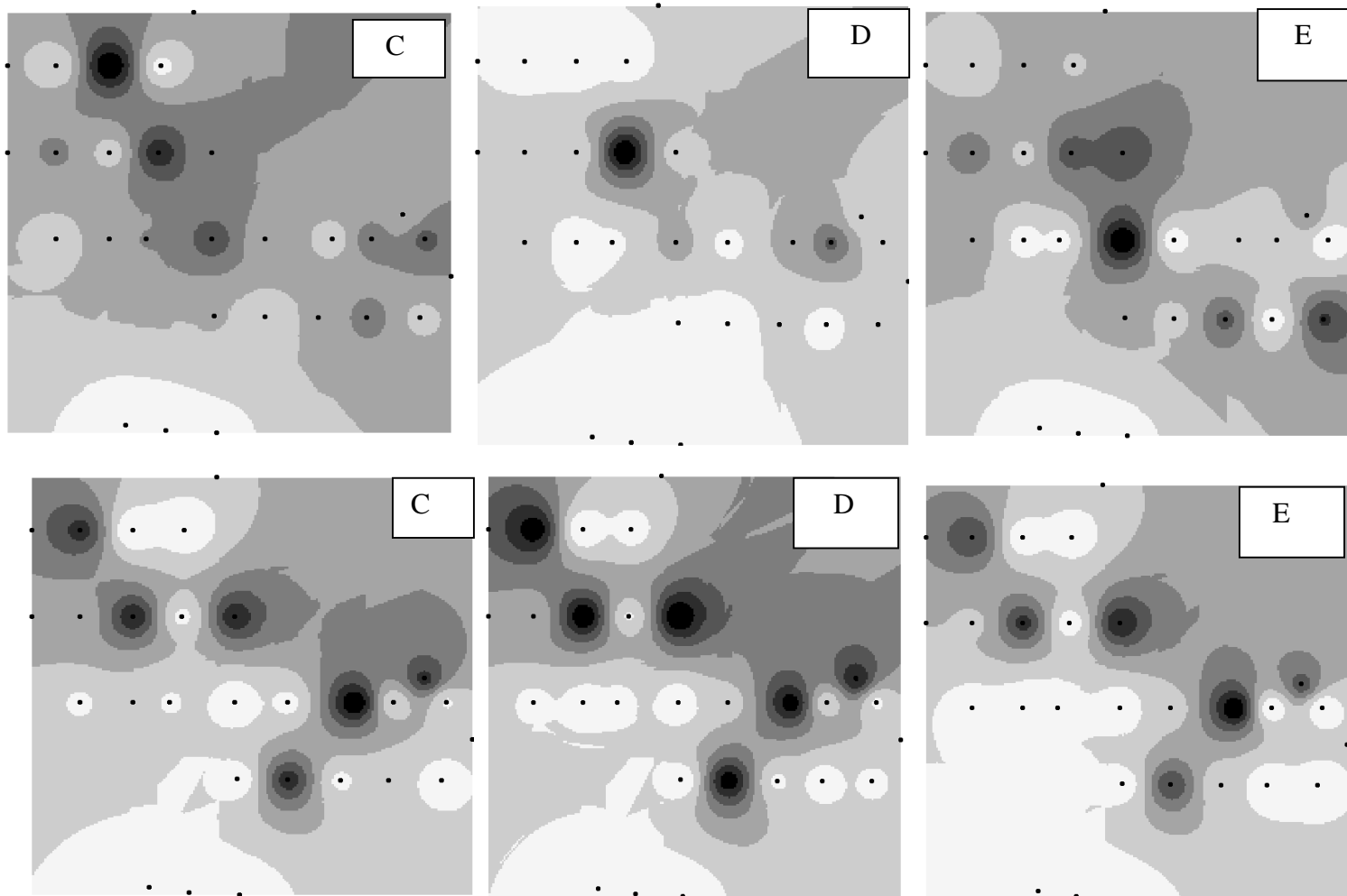
**Figure 4.3c: Spatial distribution of total Pb and Cd at different depth. Layers C, D and E represent the 20-30, 30-40 and 40-50 cm, respectively. Each map has different legends of concentrations. The darker the colour the higher the concentration.**

### 4.4.4 Pseudo-total Hg and As concentrations in different transects with depth

Fig 4.4a results illustrates vertical distribution of Hg concentrations across transects, where the concentrations of Hg exceeded MPL. Mean Hg concentration decreased from 0-10 cm to 30-40 cm depth, then increased in the 40-50 cm depth. In transect 2 mean Hg concentrations increased with from 0-10 cm to 30-40 cm, then slightly decreased in the 40-50 cm depth. In transects 3 and 4 mean Hg concentration increased from 0-10cm to 20-30 cm, decreased in the 30-40 cm, then increased in the 40-50 cm depth. In transect 5 mean Hg concentrations increased from 0-10 cm to 10-20 cm depth, then decreased in the 20-30 cm to 30-40 cm depth.

Mean As concentrations increased from 0-10 cm to 10-20 cm depth, then decreased to 20-30 cm depth then decreased in the 20-30 cm depth and decreased further between the 30-40 cm and the 40-50 cm depths (Figure 4.4a). Transect two shows As levels increases with depth moving down the profile from 0-10cm to 40-50 cm. Transect three also shows the As levels increased with depth with only a decrease on the 30-40 cm depth but increased in the last depth (40-50 cm). Transect four shows that As levels decreased with depth (Fig. 4.4a) spatial distribution maps. Transect five showed no much movement of As levels as there is a slight decrease from 0-10 cm to 30-40 cm depth and a slight increase in the 40-50 cm depth. Transect six showed some contamination with no movement of As.
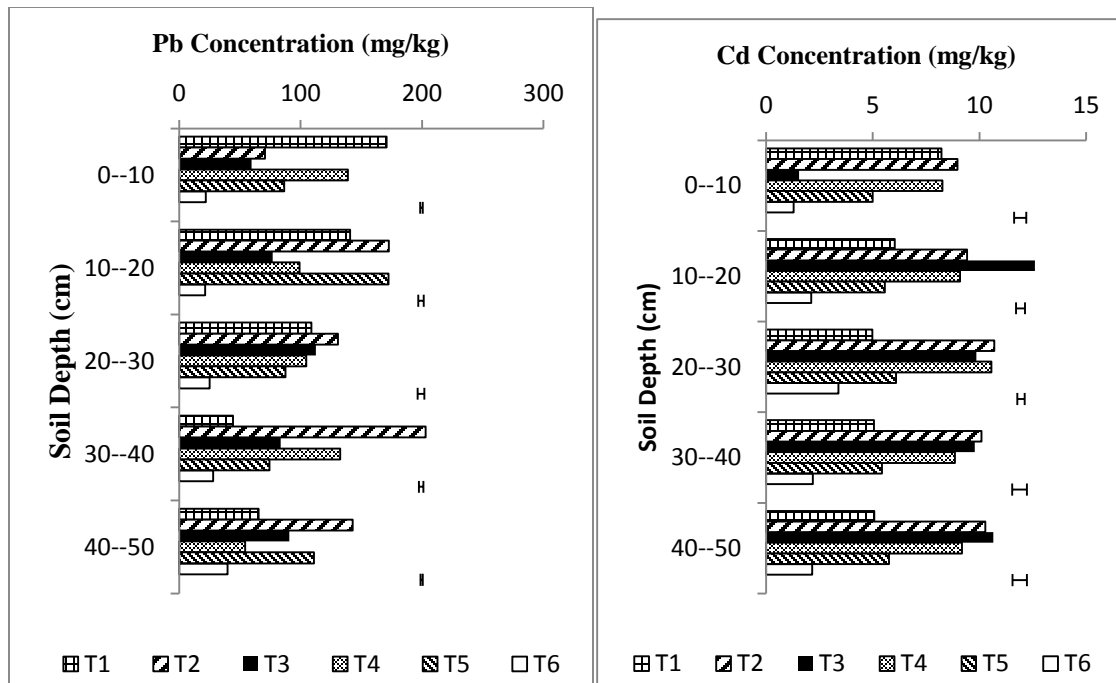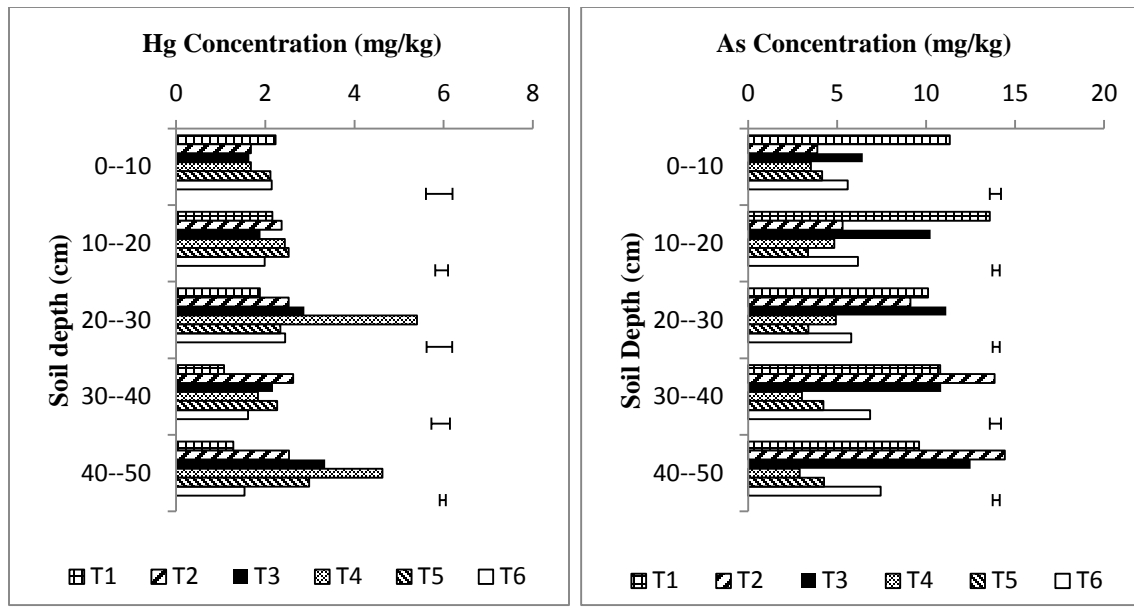
**Figure 4.4a Mean pseudo-total Hg and As concentrations in different transects with depth. Error bars represent least significant differences at p<0.05.** *(TIL, TMT and MPL for Hg = 0.5, 1 and 9 mg/kg and for As = 2, 2 and 20 mg/kg, respectively).*

*Spatial distribution of Hg and As*

Figure 4.4b demonstrates spatial distribution of Hg in the 0-10 cm and 10-20 cm depths and at different depth moving down a soil profile for the entire region (Fig. 4.4c). The results indicate that Hg concentrations were higher than the TIL and TMT levels but did not exceed the MPL although the levels were slowly approaching the MPL. High concentration of Hg were still observed at 10-20 cm depth and this can be seen with hotspots in site 11, 15 and 21, while in the 0-10 cm depth showed contamination almost throughout the entire area and this is shown by the hotspots in site 3, 5, 11, 12, 15 and 21 (Fig.4.4b). In the 20-30 cm depth Hg concentrations showed that concentration were much higher than in the 10-20 cm depth as the sites that were highly contaminated in the 0-10 cm depth were similar to concentrations in the 30-40 cm depth (Fig. 4.4c). In the 40-50 cm depth little of the heavy metal has moved from the 30-40 cm to 40-50 cm depths as only site 12 and 14 have shown to be highly contaminated.

Figure 4.4b illustrates spatial distribution of As concentration is soils characterized by localized hotspots. The entire area was contaminated with As at high concentrations exceeding TIL and TMT and MPL especially for transect 1, 2 and 3. The results indicate that even the control had high levels of As exceeding the MPL. In the 0-10 cm depth contamination is more on the surface particularly on transects 1, 3 and 5 (Fig. 4.4b). Spatially As has been seen to be evenly distributed across the entire area especially transect 1, 2, 3 and 5 with high concentrations of As (Fig. 4.4c). In the 20-30cm, As accumulated in transect 1, 2 and 3 with transect 4 showing no contamination in this depth. Little of As has moved to the 30-40 cm and contamination was observed on transect 1, 2, 3 and the top part of transect 5.  Arsenic moved from the surface layer to 30-40 cm depth, and to the 40-50 cm depth As in transect 3 and 5. Transect 6 also showed some contamination of As as the levels were seen to be higher than 2 mg/kg.
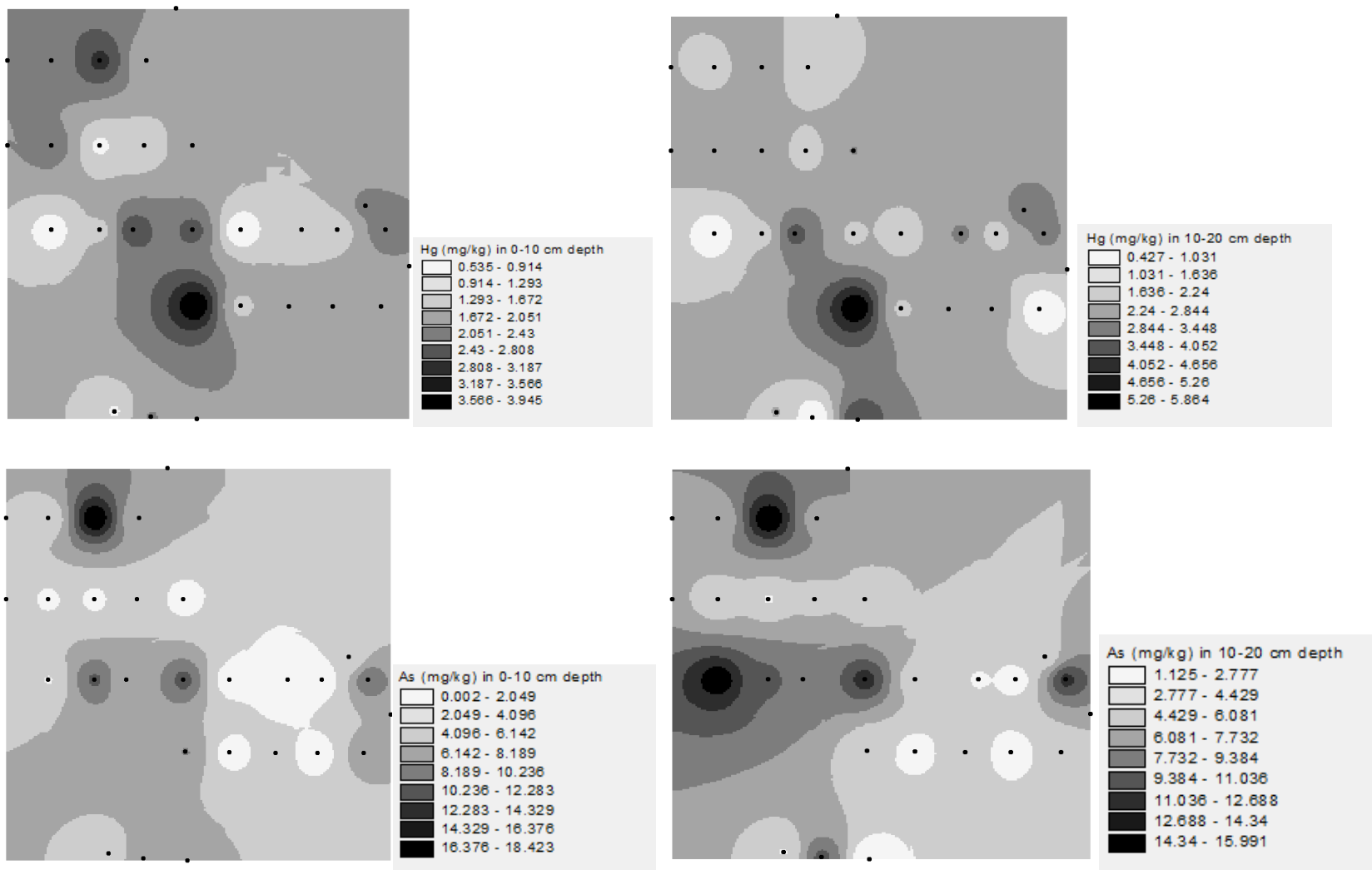
**Figure 4.4b: Spatial distribution of pseudo-total Hg and As at 0-10 cm and 10-20 cm depth.**
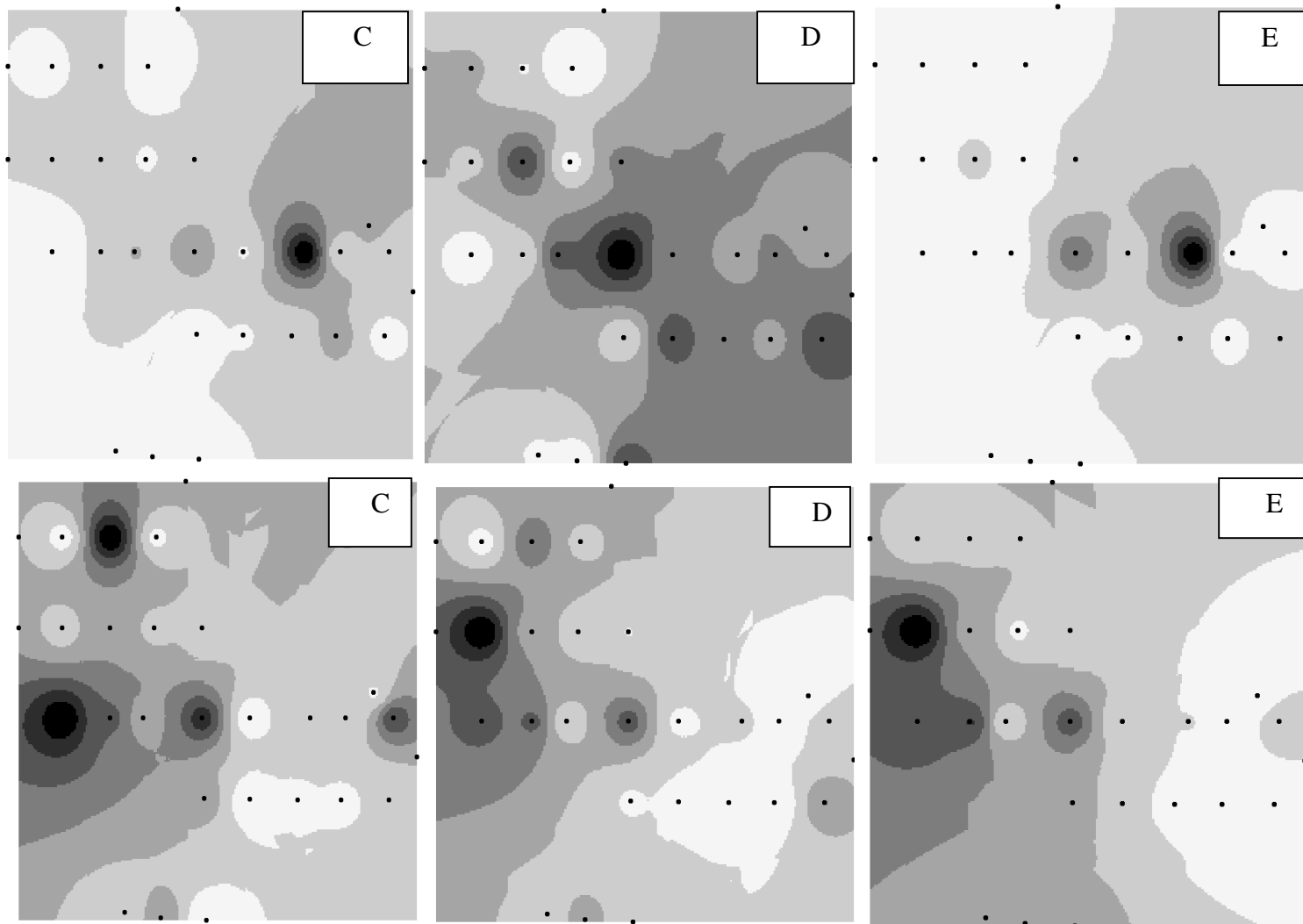
**Figure 4.4c: Spatial distribution of total Hg and As at different depths. Layers C, D and E represent the 20-30, 30-40 and 40-50 cm, respectively. Each map has different legends of concentrations. The darker the colour the higher the concentration.**

*4.5 Potentially leachable and available heavy metals, Ammonium nitrate analysis results are on the appendix section*

*4.5.1 Potentially leachable Cr*

Mean Cr concentrations in transect 1 and 2 showed mean concentrations of 0.60 mg/kg in the 0-10 cm depth, 1.17 mg/kg in the 10-20 cm depth , then 0.61-0.63 mg/kg from the 20-30 cm depth to 60-70 cm depths (Fig. 4.1). Transect 3, mean Cr concentration increased in the 0-10 cm had mean concentration 0.6 mg/kg to 0.7 mg/kg in 10-20cm depth then decreased in the 30-40 cm to 40-50 cm depths, while in transect 4 results showed an increase in mean Cr concentration in the 0-10 cm depth 0.6 mg/kg to 10-20 cm depth 0.7 mg/kg, then decreased up to 60-70 cm depth with a mean concentration 0.50 mg/kg. Transect 5 results indicated an increase from 0-10 to 60-70 cm depth with concentrations increasing from 0.7 to 0.8 mg/kg respectively. MPL was not exceeded in all transects.

 *DTPA extractable Cr*

Figure 4.1 illustrates the mean Cr concentrations extracted with DTPA. In transect 1 mean Cr concentrations showed similar trends in the 0-10 cm and the 10-20 cm depth with mean Cr concentration of 0.3 mg/kg then increased to 0.4 mg/kg in 30-40 cm depth, the decreased up to 60-70cm depth with mean Cr concentrations of 0.3 mg/kg. In transect 3 there was little movement of Cr in the profile. Transects 4 and 5 had higher Cr concentrations than other transects, and were similar, at all depths except the top 20 cm in which transect 5 had higher levels. In transect 6 the mean concentration were the same throughout the depth moving down the profile. The results showed that in all the depths the MPL had been exceeded for all transects except for the control.
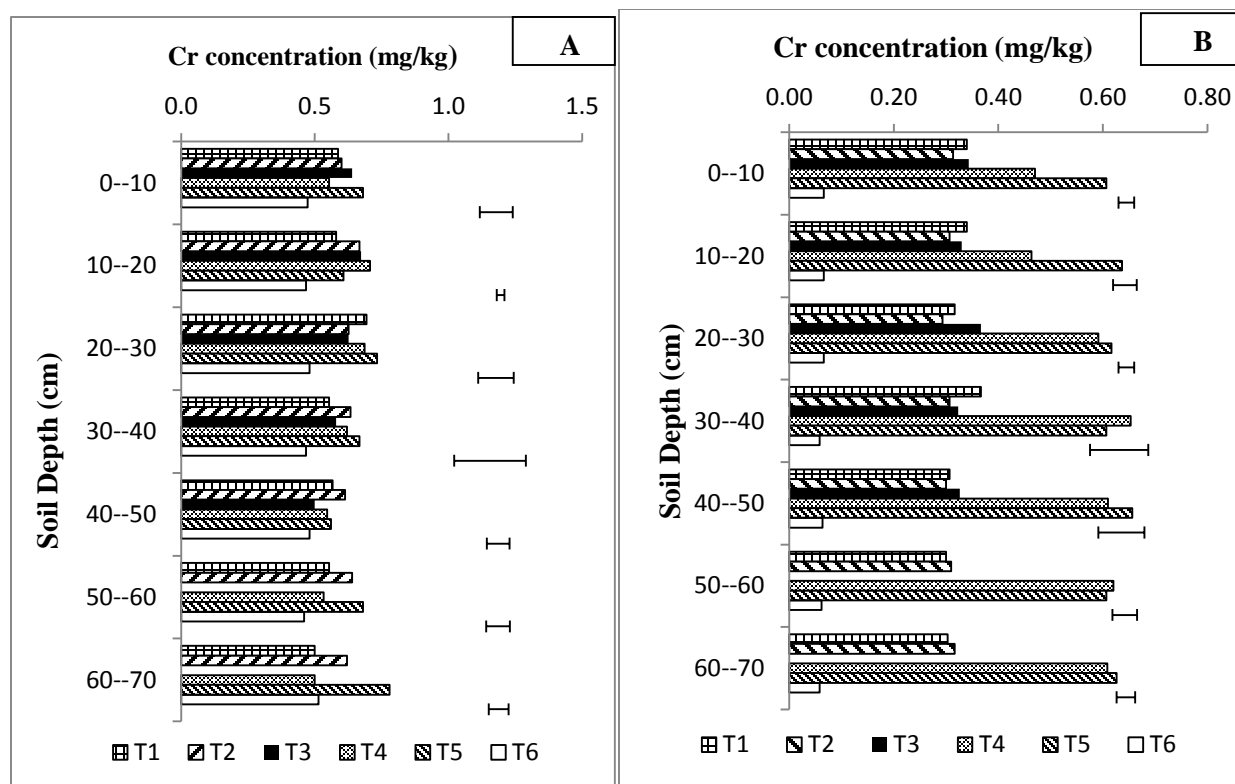
**Figure 4.1: Chromium concentration in soil treated with sludge based on TCLP (A),** *MPL =*
*1.02 mg/kg* **and DTPA (B),** *MPL = 0.14 mg/kg* **extractions. Error bars represent least**
**significant differences at p<0.05.**

*4.5.2 Potentially leachable Copper*

Mean Cu concentrations in all of transects 1-5 were similar and higher than those in transect 6 at
all depths down to the 30-40 cm depth except transects 1 and 2 which had higher concentrations
in the 10-20 and 20-30 cm depths respectively (Figure 4.2). Beyond the 40-50 cm depth Cu
concentrations in transect 4 were similar to the control while transect 5 had the highest, the levels
were higher in these depths than upper layers in the same transect. Leachable Cu concentrations
in transect 1 was highest in the 20-30 cm depth, while that of transect 2 was highest in the 10-20,
20-30 and 30-40 cm depths, with those of transects 3 and 4 being highest in the to 40 cm. Transect
6 results showed no movement of Cu concentrations down the profile. In all transects the MPL
had been exceeded for all the depths except for the control.

*DTPA extractable Copper*

Concentrations of DTPA extractable Cu were highest in the top 40 cm of the soil and showed a general decline with depth (Figure 4.2). In the 0-10 cm depth transects 2, 3, 4 and 5 had similar Cu concentrations which were higher than transect1. Transects 3 and 5 were the top two in terms of DTPA extractable Cu at all depths whereas transect 1 had the least among the contaminated transects, and was only slightly higher than the control beyond the 40-50 cm depth. There were no differences in DTPA extractable Cu among the depths, in transect 6. The results showed that the MPL had been exceeded for all the depth in all transects.



**Figure 4.2: Copper concentration in soil treated with sludge based on TCLP (A),** *MPL = 0.43 mg/kg* **and DTPA (B),** *MPL = 0.5 mg/kg* **extractions. Error bars represent least significant differences at p<0.05.**

*4.5.3 Potentially leachable Ni*

Potentially leachable Ni increased with depth for all transects to the 20-30 cm depth for transect 1, and to 30-40 cm depth for transects 2, 3, 4 (beyond which there was minimal change) and to the 60-70 cm depth for transect 5. Transect 6 results showed low concentrations of Ni, less than 0.29 mg/kg, and did not vary with depth. In all the depths the results showed that the MPL had been exceeded in all transects with only the control that showed low levels the MPL.

*DTPA extractable Ni*

Concentrations of DTPA extractable Ni were highest in the top 40 cm of the soil and showed a general decline with depth; except for transect 4 in which the highest concentrations were in the 30-40 and 40-50 cm depths (Figure 4.3). In the 0-10 cm depth transects 1, 2, 4 and 5 had similar Cu concentrations which were lower than transect 3. Transects 3 and 5 were similar at all other depths in terms of DTPA extractable Ni, and when compared with transect 4, they were higher in the 20-30 cm and lower in the 30-40 and 40.50 cm depths. There were no differences in DTPA extractable Ni among the depths, in transect 6. For all the depths in all transects, the results showed that the MPL had been exceeded except for the control.

**Figure 4.3.: Nickel concentration in soil treated with sludge based on TCLP (A),** *MPL = 0.91 mg/kg* **and DTPA (B),** *MPL 0.98 mg/kg* **extractions. Error bars represent least significant differences at p<0.05.**

## 4.5.4 Potentially leachable Zn

Concentration of TCLP extractable Zn increased with depth in transect 1 from 67 in the 0-10 cm depth to 84 mg/kg in the 20-30 cm depth, and then decreased significantly at lower depths (Figure 4.4). In transects 2, 4 and 5 Zn mean concentrations increased with depth down to the 40-50 cm depth, whereas for transect 3 the concentration was high and did not change with depth down to the 40-50 cm depth. Transect 6 results showed low concentrations of Zn, less than 0.3 mg/kg, and did not vary with depth. The results showed that MPL had been exceeded in all depths, across all transect.

*DTPA extractable Zn*

Concentrations of Zn in transect 1, 2 and 4 were highest in the top 20 cm and decline with depth, except for transect 4 in the 30-40 cm depth where it was high. Transects 3 and 5 remained among the highest with no change in concentration throughout the top 50 cm beyond which there was a decline. Transects 1 and 4 had lower Zn concentrations than the other transects in the 0-10 and 10-20 cm depths respectively. In transect 6 there was little change of Zn concentration. In all the depths and transects the MPL had been exceeded.



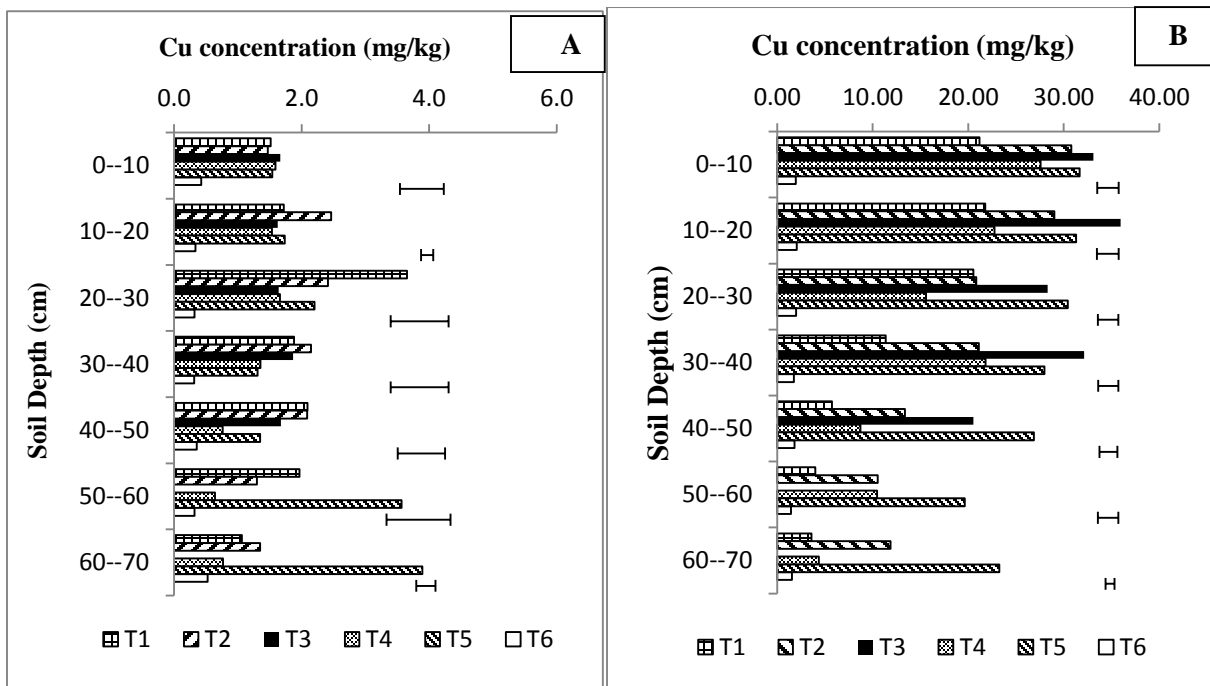**Figure 4.4: Zinc concentration in soil treated with sludge based on TCLP (A), *MPL = 7.15 mg/kg* and DTPA (B), *MPL = 1.5 mg/kg* extractions. Error bars represent least significant differences at p<0.05.**

## 4.5.5 Potentially leachable Pb

Transect 1 had the highest TCLP Pb concentration at all depths while the control showed higher Pb than some of the other transects (Figure 4.5). Only transects 1 and 2 had higher TCLP extractable Pb concentration than the control at all depths. There was minimal variation in Pb concentration with depth in all transects. The results showed that in all the depths and across all transects the MPL had been exceeded.

## DTPA extractable Pb

All other transects had higher DTPA extractable Pb than the control at all depths. Transect 1 had higher Pb concentration in the top 60 cm than the other transects, which were generally similar, except in the 40-50 cm depth, where transect 5 had higher levels (Figure 4.5). The results showed the the MPL had been exceeded for all transects in all depths.
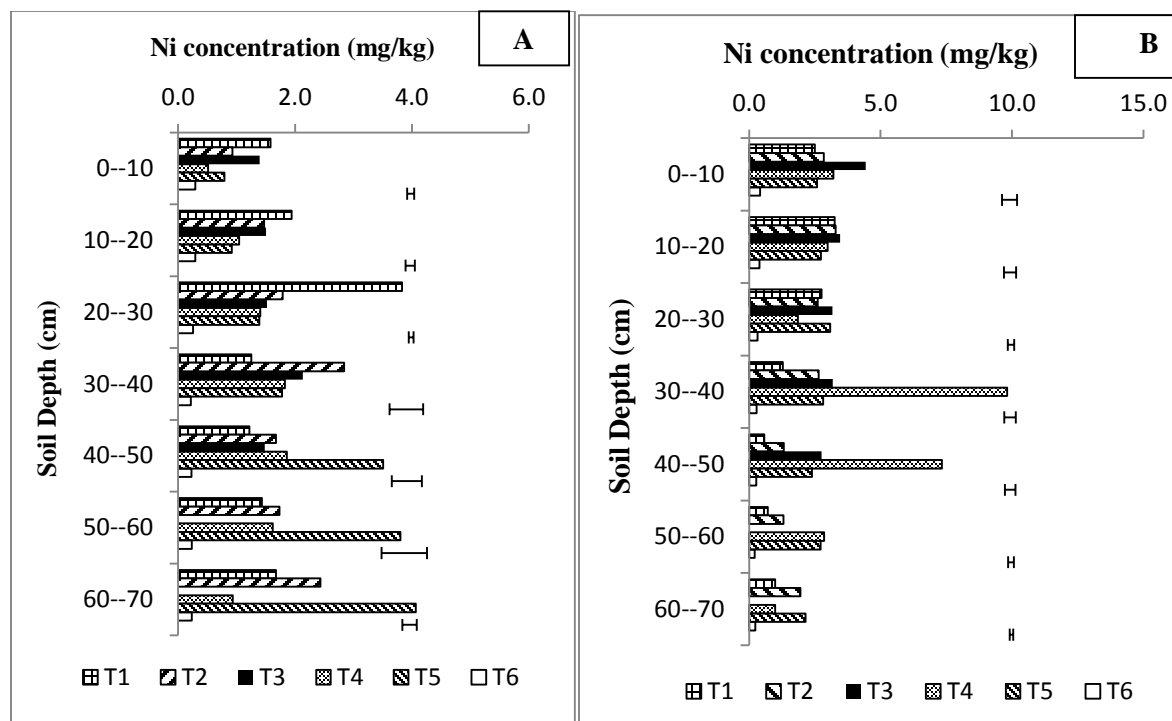


**Figure 4.5: Lead concentration in soil treated with sludge based on TCLP (A), *MPL = 0.08 mg/kg* and DTPA (B), *MPL = 1.53 mg/kg* extractions. Error bars represent least significant differences at p<0.05.**

*4.5.6 Potentially leachable Cd*

Transects 1 and 3 (and 2 and 4 in the 10-20 cm) had higher potentially leachable Cd concentration in the top 30 cm of the soil than the control (Figure 4.6). Beyond 30 cm all the other transects had higher Cd concentration than the control, except transect 4 at 50-60 and 60-70 cm. Except in transect 4, TCLP extractable Cd increased with depth with the highest concentrations in transect 5 beyond 30 cm. Transect 6 showed an increase from 0-10 cm to 20-30 cm depths, then decreased. The MPL had been only exceeded in transects 2, 3 and 5 from 30-40 cm up to 60-70 cm depths.

*DTPA extractable Cd*

All other transects had higher DTPA extractable Cd than the control at all depths. All other transects treated with sludge had the highest concentrations in the top 40 cm except transect 5, which had the lowest Cd concentration in the top 20 cm but had highest beyond 40 cm. Transect 3 had the higher Cd concentration in the top 0-10 cm than transects 1, 2 and 4, whereas all four transects had similar Cd concentrations in the 10-20 and 20-30 cm depths. The MPL had only been exceeded in transects 3, 4 and 5 from 10-20 cm up to 60-70 cm depths.
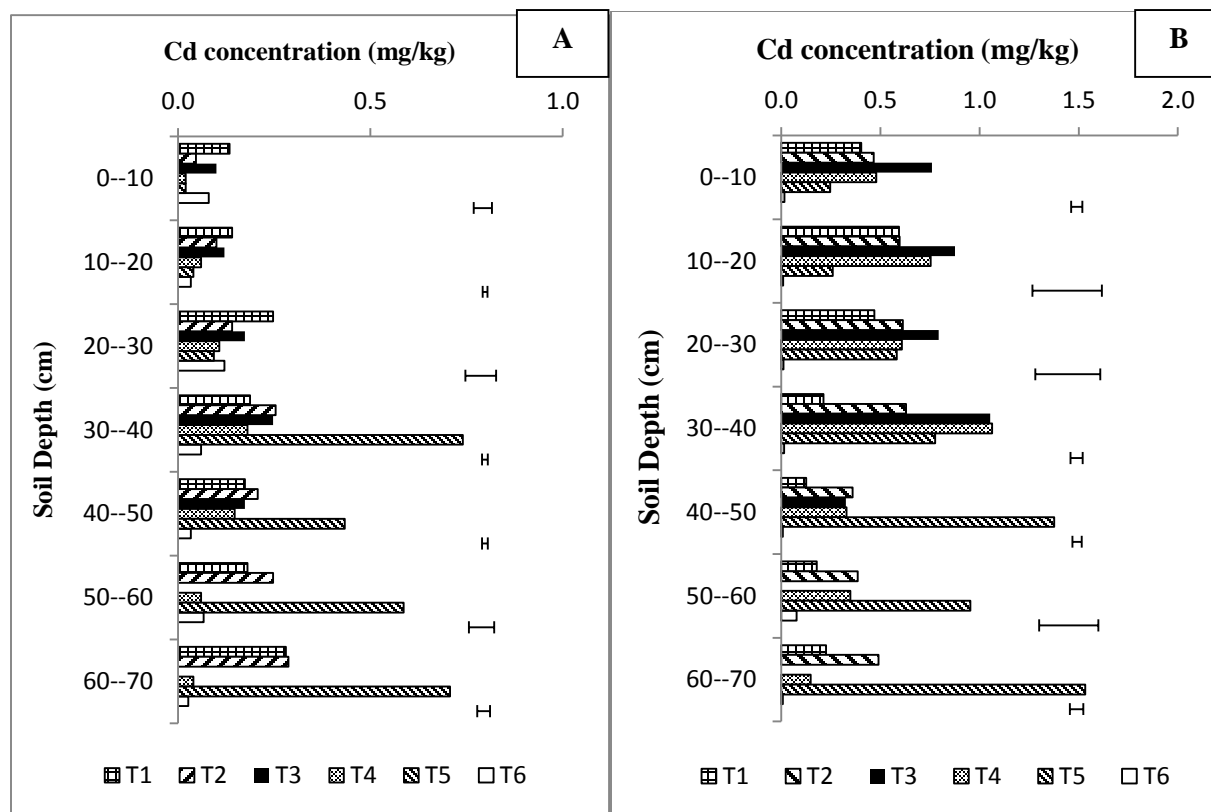
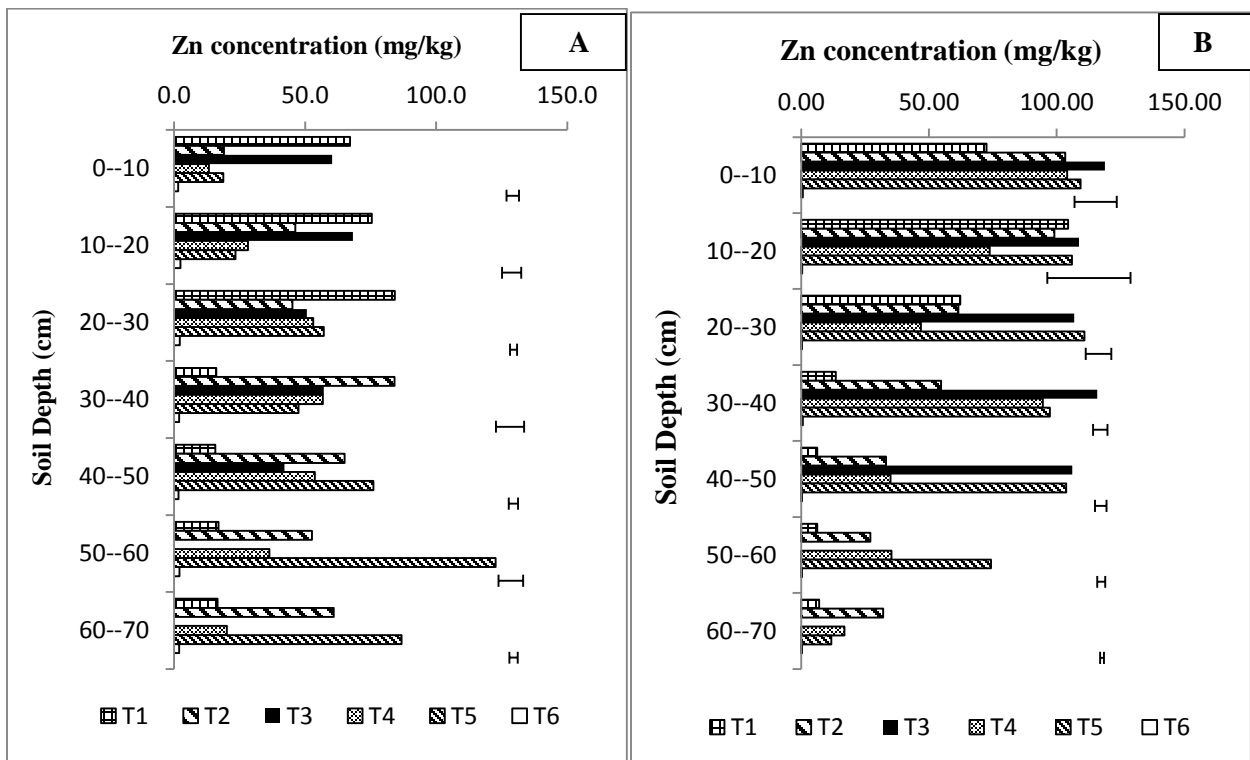**Figure 4.6: Cadmium concentration in soil treated with sludge based on TCLP (A),** *MPL = 0.03 mg/kg* **and DTPA (B),** *MPL = 0.07 mg/kg* **extractions. Error bars represent least significant differences at p<0.05.**

*4.5.7 Potentially leachable As*

Concentrations of TCLP extractable As in all the transects were higher than the control at all depths (Figure 4.7). Transect 2 was among the top two in terms of As concentration at all depths, and these concentrations were similar to those in transect 5 beyond the top 20 cm.. Transect 6 showed little changes in As concentration down the profile. The results showed that the MPL had been exceeded in all transects across all transects.

*DTPA extractable As*

All transects had higher DTPA extractable As concentration than the control at all depths (Figure 7). Transects 1 and 2 had higher As concentrations than the other transects in the top 0-10 cm, while in the 10-20 cm transect 1 had the least (of sludge treated) and transect 2 the highest. In the 20-30 cm depth transect 4 had the highest and transect 1 the least. Beyond 30 cm all transects had similar As concentrations except in the 50-60 cm depth where transect 5 had higher concentrations than the others. Transect 6showed low levels of As as compared to other transects. The MPL was not found for As, could not relate the results to the MPL.



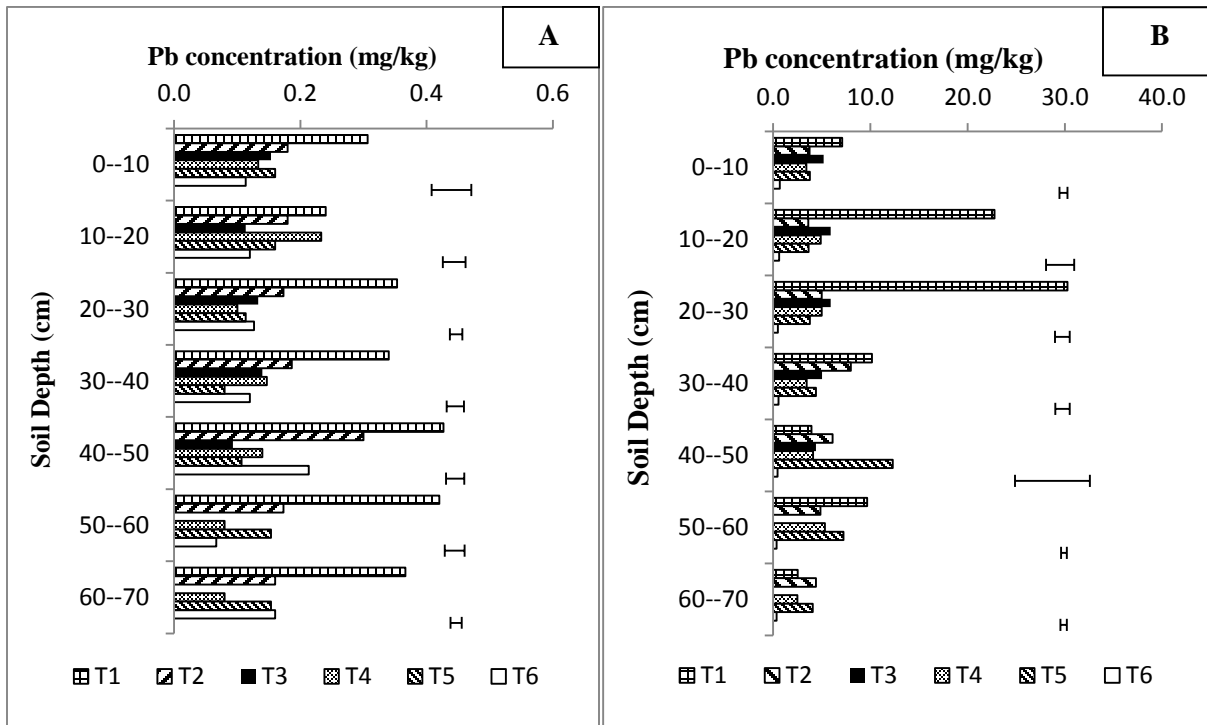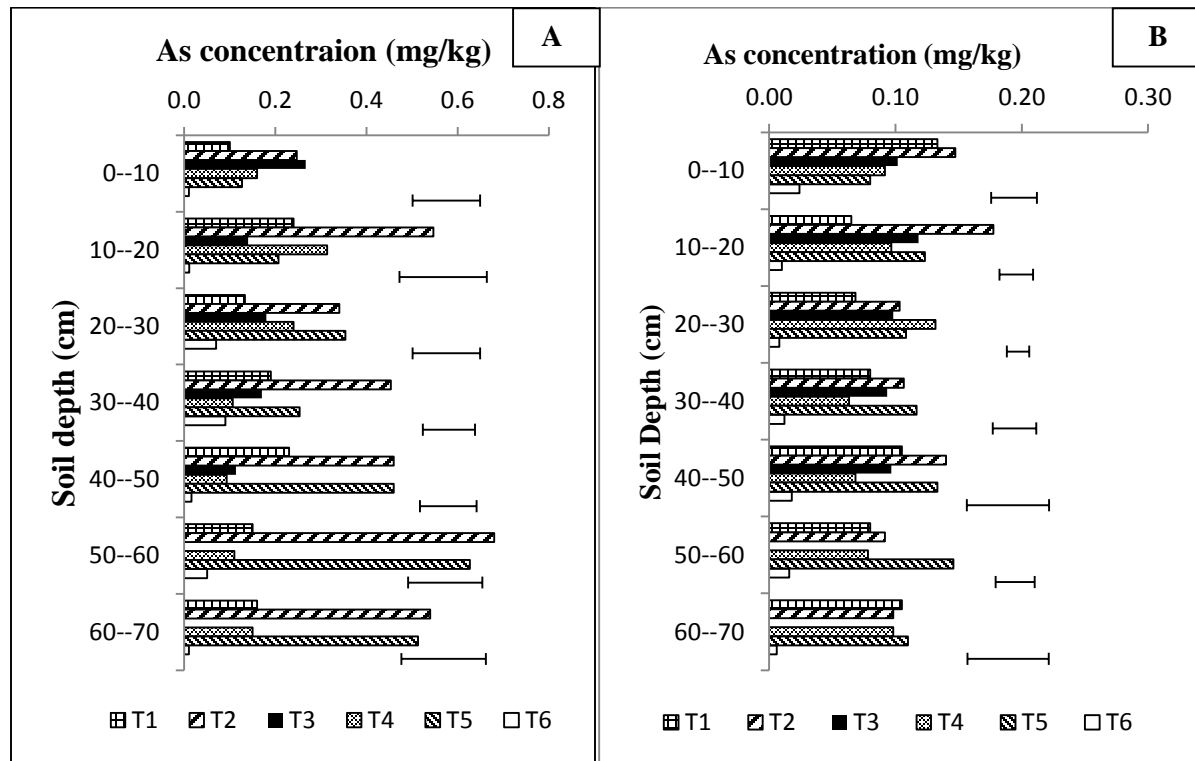**Figure 4.7: Arsenic concentration in soil treated with sludge based on TCLP (A),** *MPL = 0.07 mg/kg a*nd **DTPA (B) extractions. Error bars represent least significant differences at p<0.05.**

*4.6 Heavy metal concentration in indigenous vegetables*

Table 4.3 illustrates dry matter results of the plants collected from the study area. No plants samples were collected from transect 1. *Solunum nigrum* was not found in transect 5 while pumpkin was not found in transect 2 and 4. All the other plants were found in all transects.

**Table 4.4: Average dry matter of vegetables on study site.**

|  | Dry matter | $(g/m^2)$ |  |  |
| --- | --- | --- | --- | --- |
| Vegetable | Transect 2 | Transect 3 | Transect 4 | Transect 5 |
| Amaranths | 28.1 | 26.1 | 29.8 | --- |
| *Solunum nigrum (Black nightshade)* | 151.5 | 107.3 | 85.2 | --- |
| Tomato plant | 154.0 | 243.4 | 198.3 | 421.6 |
| Pumpkin | --- | 122.0 | 193.2 | --- |
| Tomato fruit | ---- | ---- | --- | 67.5 |

**---** no plants were found during sampling

Tissue concentrations of all the heavy metals, except Hg, of all the vegetables were extremely higher than the permissible limits. The As results were not included in the analysis due to ICP 720 Varian machine not detecting any result on As analysis. Metal concentration was dependent both on the plant species and on transect. For example the tomato plant took up more Zn than Amaranth in transects 3 and 4, and yet it took up less in transect 2. Heavy metal concentrations in Amaranth were up to 6, 125, 9, 6 and 43 times the MPL of Zn, Cr, Cu, Cd and Pb, respectively. The concentrations in *Solunum nigrum* were up to 4, 68, 5, 6, and 33 times the MPL of Zn, Cr, Cu, Cd and Pb, respectively. The concentrations in tomato tissue were up to 7, 63, 4, 8, and 36 times the MPL of Zn, Cr, Cu, Cd and Pb, respectively. The concentrations in pumpkin tissue were upto 2, 16, 3, 4, and 43 times the MPL of Zn, Cr, Cu, Cd and Pb, respectively.

The metal concentrations within a specific vegetable varied with transect. The tomato plant had greater heavy metal concentration than the fruit, for all the metals measured.

**Table 4.5: Mean metal concentrations in Amaranths, *Solunum nigrum*, tomato plant, pumpkin and tomato fruit.**

| Vegetable | Transect | Zn | Cr | Cu | Ni | Cd | Hg | Pb |
|---|---|---|---|---|---|---|---|---|
| | | Elementary | | concentration | | | (mg/kg) | |
| Limits | | **60** | **2.3** | **40** | **-** | **0.2** | **10***  | **0.3** |
| Amaranths | 3 | 207.7 | 126.3 | 372.7 | 9.9 | 0.9 | 0.3 | 9.7 |
| | 4 | 368.5 | 288.4 | 201.4 | 12.1 | 1.2 | 0.8 | 12.8 |
| *Solunum nigrum* | 3 | 109.8 | 8.0 | 41.2 | 1.9 | 1.1 | 0.9 | 4.1 |
| | 4 | 88.1 | 13.2 | 47.9 | 1.7 | 0.7 | 0.8 | 4.4 |
| Tomato plant | 3 | 253.3 | 138.5 | 165.9 | 7.5 | 1.5 | 0.9 | 10.9 |
| | 4 | 395.9 | 119.0 | 124.3 | 9.3 | 1.1 | 0.9 | 11.1 |
| Pumpkin | 3 | 99.2 | 37.8 | 131.3 | 6.9 | 0.4 | 0.6 | 8.4 |
| | 4 | 140.4 | 18.0 | 55.8 | 1.8 | 0.8 | 2.5 | 12.8 |
| | LSD | 8.2 | 1.02 | 1.67 | 0.3 | 0.02 | 0.07 | 0.2 |
| Amaranths | 2 | 248.5 | 99.2 | 60.7 | 5.0 | 1.2 | 1.1 | 6.9 |
| *Solunum nigrum* | 2 | 233.0 | 156.4 | 195.1 | 9.28 | 1.2 | 0.9 | 10.0 |
| Tomato plant | 2 | 205.1 | 145.1 | 81.1 | 5.4 | 1.1 | 1.0 | 7.8 |
| | LSD | 2.2 | 4.61 | 1.79 | 0.3 | 0.08 | 0.08 | 1.0 |
| Tomato plant | 5 | 363.2 | 49.7 | 198.6 | 17.4 | 1.5 | 0.9 | 17.0 |
| Tomato fruit | 5 | 87.3 | 11.6 | 71.3 | 2.3 | 0.3 | 0.6 | 13.4 |
| | LSD | 2.0 | 2.4 | 2.2 | 2.7 | 0.05 | 0.03 | 1.1 |

Heavy metal limits, by FAO; 10* mg/kg represents a limit for Hg in spices (Bemph et al., 2012), no limits for Ni could be found

**Table 4.6: Plant uptake of Amaranths, *Solunum nigrum*, tomato plant, pumpkin and tomato fruit in DWWW.**

| | | | | Plant uptake (kg/m$^2$) | | | | |
|---|---|---|---|---|---|---|---|---|
| Vegetables | Transect | Zn | Cr | Cu | Ni | Cd | Hg | Pb |
| Amaranths | 3 | 5.4 | 3.3 | 9.7 | 0.3 | 0.02 | 0.01 | 0.3 |
| | 4 | 10.9 | 8.6 | 6.0 | 0.4 | 0.04 | 0.02 | 0.4 |
| *Solunum nigrum* | 3 | 11.8 | 0.9 | 4.4 | 0.2 | 0.1 | 0.09 | 0.4 |
| | 4 | 7.5 | 1.1 | 4.1 | 0.1 | 0.1 | 0.1 | 0.4 |
| Tomato plant | 3 | 61.6 | 33.7 | 40.4 | 1.8 | 0.4 | 0.2 | 2.7 |
| | 4 | 78.5 | 23.6 | 24.6 | 1.8 | 0.2 | 0.2 | 2.2 |
| Pumpkin | 3 | 12.1 | 4.6 | 16.0 | 0.8 | 0.05 | 0.07 | 1.0 |
| | 4 | 27.1 | 3.5 | 3.8 | 0.1 | 0.05 | 0.2 | 0.9 |
| Amaranths | 2 | 6.98 | 2.8 | 1.7 | 0.1 | 0.03 | 0.03 | 0.19 |
| *Solunum nigrum* | 2 | 35.3 | 23.7 | 29.5 | 1.4 | 0.2 | 0.1 | 1.6 |
| Tomato plant | 2 | 31.6 | 22.3 | 12.5 | 0.8 | 0.2 | 0.2 | 1.2 |
| Tomato plant | 5 | 153.1 | 20.9 | 83.7 | 7.3 | 0.6 | 0.4 | 7.2 |
| Tomato fruit | 5 | 5.9 | 0.8 | 4.8 | 0.2 | 0.02 | 0.04 | 0.9 |

# 5. DISCUSSION

Findings in this study suggest that pH increased with the application of sewage sludge in all treated transects with only transect 1 showing similar levels to the reference site and this was in agreement with findings of Kelly et al. (1984). The lower pH (than control) in transects 1 could increase availability of most of the heavy metals studied. Metals cations are known to favour sorption and precipitation at high pH levels while at low pH they become more available (McBride, 1994). The higher pH in the other transects could therefore reduce availability although it also depends on loading levels.

The thick layers of soils with higher total C in all other transects than transects 1 and 6, indicates that long term application of sewage sludge resulted in accumulation of organic matter. The high accumulation of organic matter could have implications on heavy metal accumulation since the metals are part of the sludge and they can get complexed by organic matter (McBride, 1994). The higher pH in transects with high OM suggested that the sludge could have a liming effect. Research done in South Africa found that sewage sludges have a pH ranging from 6.4- 6.7 (Jaganyi et al., 2005), and as such soils amended with large amounts of such sludge would have an elevated pH, which could affect availability of metal ions. The lower clay content in transect 1 could partly explain the lower total C in that transect compared to others. In sandier soils OM is not protected in aggregates, from decomposition, which could result in release and leaching of metal elements, as there are lower colloids to retain the metals ions.

Aqua regia analysis indicated that sewage sludge disposal on land has increased the heavy metal concentrations in soils which was in agreement with Liu et al. (2005). The high concentrations of heavy metals on the hotspots could be as the transects being either closer to the source of irrigation or being at the lower slope positions. The higher levels of Cr in the sludge treated soils, than the control, suggest that the concentrations are a result of sludge applications and less of the background concentration from the parent material. The Cr levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Cr in the top 20 cm in the past six years. The lower Cr in transect 1, than the other sludge treated soils, could be explained by the lower total C levels in this transect which are limited to the top 0-10 cm. The metal is brought as part of the sludge, and

organic matter has a huge effect on mobility of Cr. The $Cr^{3+}$ ion is easily complexed by organic matter and chemisorbed by silicate clays (McBride, 1994), which explains the concentration of the metal in the top 30 cm, where OM was also high. The higher levels of Cr than the MPL suggest that urgent remediation efforts need to be pursued. The negative effects of such accumulation of Cr, through uptake by plants and leaching to groundwater could depend on the form in which the metal occurs. Based on the TCLP results which were only slightly higher than the control, it can be deduced that only low levels of Cr may leach to ground water, which suggests minimum pollution with this element. The low mobility could be explained by the liming effect of the sludge (raising pH) and complexation by organic matter (McBride, 1994). While there is little potential for Cr leaching, DTPA results suggest that high levels of the metal can be taken up by plants which could lead to elevated tissue Cr composition. This is supported by the results of plant analysis, which indicated that Amaranthus, *Solanum nigram* and tomato took up over 120, 65 and 60 times the acceptable limit for human consumption (Bempah et al., 2012).

Accumulation of heavy metals in plants is a cause of serious concern due to the potential public health impact (Khan et al., 2008). These elevated levels could have serious implications on human health. The Cr(III) form of Cr is more common in soils and Cr(VI) generally occurs at higher pH levels, aerobic conditions, low amounts of organic matter and the presence of Fe and Mn oxides which oxidize Cr(III) (Zayed et al., 2003). The soils from this study area are high in organic matter and slightly acidic suggesting the transformation of Cr(VI) to the trivalent form may have occurred . This contradicts with Zayed et al. (1998) reports, that Cr accumulation in plants occurs when Cr is supplied with Cr(VI) than when supplied with Cr(III). The Cr(VI) form is the most dangerous form of Cr which can cause major health risk concerns such as cancer effect, death, lung function and blood system problems, asthma and nasal sputum ulcers (ATSDR, 1998).

Since there are elevated levels of Cr in the surface layers, which are not that mobile, yet plant available, there is potential for pollution of surface water through erosion, and exposure of larger animals consuming the water and feeding on plants laden with this metal. The variation in metal concentrations across the landscape and within transects implies that remediation strategies should pay special attention to hotspots.

Higher levels of Zn concentrations in the treated soils are an indication of accumulation of Zn from sludge application. The Zn levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Zn in the top 20 cm in the past six years. Under low pH levels, Zn is mostly soluble and mobile because it is not tightly complexed with organic matter (McBride, 1994). Mobility and uptake of Zn in soils is affected by plant species, soil pH, soil sorption surface and properties of metal source (Hooda, 2010). Labile pool of Zn is much higher in acidic soils than alkaline soils (Hooda, 2010) and since the treated soils were slightly acidic more lability could be expected. This is supported by the high levels of Zn, both pseudo-total and plant available form at the deepest layers (70 cm) studied. Based on the DTPA results Zn concentrations declined with depth but all concentrations were higher than the control at all depths, which suggested a high potential for uptake by plants and leaching into ground water. The high levels of available Zn are in agreement with the results of plant tissue concentrations where Amaranthus, *Solanum nigram*, tomato and pumpkin took up over 6, 4, 7 and 2 times the acceptable limit for human consumption, respectively. Zinc availability mostly is due to high organic matter content, and with high in OM in the treated soils, Zn is available for uptake by plants. Possibilities of surface erosion and soil seepage to surface water bodies could result as Zn is not tightly complexed with OM and is mobile. Low levels of Zn in transect 1 could be explained by the low levels of OM, while the high levels in the top 30 cm are due to the high levels of OM in the top 30 cm making Zn more available. The high levels of Zn, that are more than the total investigative level in soils (TIL) and total maximum threshold in soils (TMT) throughout the depths suggests that Zn might have moved to deeper layers. These finding are supported by the TCLP results, which indicated higher levels at deeper layers, suggesting high potential for pollution of ground water while the MPL was only exceeded in transect 2 in the top 30 cm. Elevated Zn has toxic effects on microbial population in soil (Giller et al., 1998), and mineralization rate of nutrients like phosphorus and nitrogen. Studies by Macdonald et al. (2007) indicated that Zn did not have effects on respiration rate while Griffiths et al. (2007) suggested that microbial biomass C decreased in an agricultural sandy loam soil contaminated with lower (than this study) levels of Zn from sludge. Communities consuming plants from the study area may be affected by elevated Zn levels in the plant. Zn in humans results in cell death in the brain (Plum et al., 2010).

The higher Cu levels in the top 30 cm, with high OC, which decreased with depth, could be explained by sorption to organic matter and clay minerals (Bodek et al., 1988; Hooda, 2010). The Cu levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Cu in the top 20 cm in the past six years. Copper in soils can be strongly adsorbed by clay minerals and organic matter and as a result Cu tends to remain in the horizon that has greater organic content (Hooda, 2010). The results of the study indicated an increase in the top 30 cm. Sandy soils, low in pH and OC, like transect 1, have a greater potential of Cu leaching but the TCLP results suggest that transect 5 had high Cu concentrations in the deeper depths. In soils Cu(II) is rated low-mobility element in near-neutral soils and it tends to build up in the surface of contaminated soils because of its high affinity, showing virtually no downward migration (McBride, 1994). Mobility of Cu may be significant under low pH conditions as Gerritse and van Driel (1984) reported that soils low in pH possess a greater potential for Cu leaching. A study by He et al. (2006) indicated that leaching of Cu was at minimum at pH 5–7 and increased at lower pH levels. Solubility of Cu decreases at pH levels about 7 (Bergkvist et al., 1981). The slightly acidic soil pH results from this study could therefore explain the solubility of Cu in these soils. The TCLP results suggest high level of Cu were found moving to depths. The high DTPA extractable Cu concentrations in the deeper layers indicated that Cu is more available even to deeper rooted plants and there is potential for leaching to ground water. Copper is more soluble than Cr and Zn thus its more leachable suggesting greater potential for leaching into ground water. For phytoremediation deep rooted crops would be needed. TCLP and DTPA analysis suggest that Cu has leached to deeper layers and also available at deeper depths, suggesting that high levels of Cu could be taken up by plants. This is supported by the plant analysis results which indicated high levels of Cu being taken up by Amaranthus, *Solunum nigrum* and tomato exceeding the acceptable limits for contaminated plant consumption by human. These high levels of Cu in plants may cause serious effects on the communities consuming these plants, where the Guidelines for Drinking-Water Quality proposed by WHO, (1996) suggested that elevated levels of Cu may cause liver and kidney damage, "pink disease", and cirrhosis to humans. The levels of concentrations in Amaranthus, *Solunum nigrum* and tomato were 9, 5 and 4 times higher than the acceptable limits, respectively (Bempah et al., 2012).

Copper and Ni occur commonly in sewage sludge treated soils and may reach toxic levels (McBride, 1994). The low levels of Ni of less than TIL of 50 mg/kg (and thus MPL of 200 mg/kg) from the aqua regia extraction, suggested that long-term land application of sewage sludge made a low contribution to Ni levels, possibly because Ni could have been low in sewage sludge from Pietermaritzburg. The Ni levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Ni in the top 20 cm in the past six years. In alkaline soils, mobility of Ni becomes low with solubility decreasing at high pH levels and the changes in Ni toxicity due to ageing were high in soil with the highest pH (Hooda, 2010). Available Ni with DTPA analysis suggests that there's a high potential for up take by plants with high concentrations observed from all depths higher than the control and declining with depth. Plant analysis suggests that higher levels of Ni had accumulated in plants harvested from study site, indicating that more of Ni was in the available form. The TCLP analysis also suggests a potential for pollution to ground water although the levels had not exceeded the TIL and the TMT. Although Ni concentrations were low, soil contamination with Ni has a potential negative effect on plants and microorganisms (Hooda, 2010). The toxicity of Ni to plants can cause stunting, cupping and foliar necrosis and may reduce yield in plants like cabbages, lettuce and beets (Temple and Besessar, 1981). According to a study by Akerblom et al. (2007), negative effects of Ni on microorganisms include changes in microbial community, effect on microbial respiration but some microorganisms become tolerant to such conditions.

The high levels of Pb, with levels exceeding the TIL and TMT, in all transects, suggest that the source of the Pb was sewage sludge. The Pb levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Pb in the top 20 cm in the past six years. The accumulation of Pb in the top 30 cm of the soil, in agreement with McBride (1994), could be explained by the organic C levels. Humus rich soils exhibit strong complexation of $Pb^{2+}$ by organic matter making organic matter an important sink for Pb in soils. The high levels of Pb can be attributed to high levels of OM and elevated pH in all transects, except transect 1, when compared to the control. At higher pH Pb may precipitate as hydroxide or carbonate. Soil pH above pH 6 and relatively approaching neutral, suggested that complexation with organic matter, chemisorption on oxides and silicate clays could have all been favored at these relatively high pH levels. While McBride (1994)

reported that soils contaminated with Pb at the surface show little indication of metal leaching, and Camobreco et al. (1996) reported that Pb forms strong complexes with the surface, which tends to make Pb less mobile, and soluble organics, by which provides a good opportunity for facilitated transport by soluble organics when present. The results of TCLP extraction indicated high levels of Pb in deeper depths suggesting a greater potential of leaching to ground water especially in transect 1, which had lower clay than the other transects, suggesting that lower sorption could have contributed.

Plants were harvested in April 2013, and they would have grown in summer, and as such the observed effects were not because the plant grew off season (they are summer crops). High Pb concentrations based on DTPA extraction in all transects, particularly in transect 1 (lowest clay and OM), was in agreement with the levels in tissue of all plants with Amaranthus, *Solunum nigrum*, tomato and pumpkin taking up over 43, 33, 36 and 43 times of the acceptable levels for human consumption, respectively. Contrary to McBride, (1994) who reported that in most soils Pb appears unavailable to plants with little translocation from roots to tops, this study showed that high concentration of Pb can accumulate in plant leaves. Elevated levels of Pb in the human body can cause kidney damage, brain damage, a rise in blood pressure and behavioral disruptions of children such as aggression (ATSDR, 2005). According to Forbes and Sandweson, (1978) Pb could affect enzyme functioning in microorganisms and lead to decreased microbial community.

Pseudo-total Cd concentrations from aqua regia analysis represent a clear evidence of the influence of long term application of sewage sludge on Cd accumulation in soils. The Cd levels in this study were two-to-three times higher than those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has been a significant increase in soil Cd in the top 20 cm in the past six years. Soil pH is considered as a central factor for Cd accumulation and controls the fraction of Cd in soils (Peijun et al., 2009). In acidic soils Cd is boundless strongly allowing more plant uptake (Hooda and Alloway, 1996). According to Pepper et al. (1983), few cases were reported where increasing pH did not reduce plant Cd concentrations. The finding of this study also suggested that with increasing pH Cd levels in plants decreased. However the high levels of Cd form the DTPA analysis suggest that there could be high levels of Cd enough for adsorption and accumulation from the soil matrix into the plant tissues. High mobility of Cd in soils can be attributed to the fact that Cd can be adsorbed rather weakly on organic matter, silicate clays and

oxides unless the pH is high than 7. Findings by Roy et al. (2013) suggest that Cd and Zn are more labile in soils. Logan et al. (1997) reported that Cd uptake by plants would be more on soils treated with high Cd in sewage sludge compare to low Cd in sewage sludge.

The plant analysis results suggest that the levels of Cd in the plant can be attributed to high Cd in sewage sludge and Cd accumulation over time. Interestingly increased Cd levels in plants may have higher bioavailable to animals and humans that ingest the plant (Hood, 2010), but this may not have serious impacts on plants as some plants such as sunflower, flax and wheat may contain high levels of Cd in them (Wolnik et al., 1983). Different plant species accumulate different heavy metals concentrations as the plant analysis indicted that Amaranthus, *Solunum nigrum*, tomato and pumpkin accumulated about 6, 6, 8 and 4 mg/kg respectivily. The Cd: Zn ratio could limit Cd transfer and bioavailability (Hart et al., 2002; Chaney et al., 2001). The recommended limit ratio for Cd: Zn is 0.015 mg/kg for biosolids (Hood, 2010). The lower the Cd: Zn ratio the less likely that increased bioavailable Cd will accumulate in plants, which was supported by the findings of this study.

The findings of soil Hg in this study could be explained by organic matter content. Hooda (2010) reported that in soils Hg accumulation tends to correlate with organic matter levels. The Hg levels in this study were comparable to those determined by Bekink (2007) at the same sludge disposal lands, suggesting that there has not been significant increase in soil Hg in the top 20 cm in the past six years. Although the Hg levels had not exceeded the MPL (9 mg/kg), the concentration exceeded the TIL and the TMT of 0.5 mg/kg and 1 mg/kg, respectively, which suggests that preventive measures and monitoring need to be initiated. Mercury's mobility in soils is more sensitive to loading, with traces of $Hg^{2+}$ being much immobile and higher levels having medium mobility (McBride, 1994).

Findings of this study suggest that increasing clay content brings about an increase in the mobility of As, with only transect 1 indicating levels decreasing with clay content. The high levels of As in both the treated and control suggested that a significant concentration of As originates from the parent rock from which the soils formed. Although TIL and TMT levels of 2 mg/kg were exceeded, the MPL of 20 mg/kg had not been reached, which suggested limited threat posed by As originating from the sewage sludge. The chemical behavior of As is similar to that of phosphate in soils, and

as such, As can be expected to adsorb more strongly on clay, under acidic conditions. According to Hooda, (2010) As can be considered relatively immobile under oxidizing conditions. However studies have indicated that a fraction of As may be bioavailable, depending on soil contamination levels. The high levels of TCLP extractable As at deeper layers of the soil suggested a greater potential of ground water contamination. Mostly the availability of As in soils is controlled by iron and aluminum, with pH also affecting the solubility. In acidic soils with high clay content, As is immobile as it is adsorbed most effectively, whereas in neutral to alkaline soils it may be mobile in the soluble Na arsenate form (McBride, 1994). Contrary to McBride (1994), the results from the study area indicated that As had moved down the profile suggesting a greater potential of leaching to ground water. The high DTPA extractable As concentrations observed throughout the depths, than the control samples, could cause high plant uptake of the As. The plant analysis results suggest that the plants growing from the study area took up high concentrations of As. Humans consuming plants high in As may suffer from stomachache, nausea, vomiting, and diarrhea (Hooda, 2010).

## 6. Conclusion

Application of sewage sludge for over 50 years has led to accumulation of heavy metals in soils and plants, far beyond the MPL in the DWWW soils. The results from the pseudo-total analysis indicated that the majority of the heavy metals had exceeded MPL while the rest approached the limit. These heavy metals pollution varied spatially, across the entire area, and vertically down the profile with some areas and/or depths having greater concentrations than the others. Most of these heavy metals leach down to ground water particularly Zn and As. More of these heavy metals occur in their available forms, and accumulate in plants, especially the amaranths. Accumulations of these metals pose risks of ground and surface water contamination, and human health of those communities consuming vegetables growing on this land. The fact that Amaranthus, *Solunum nigrum*, tomato plant and pumpkin plants managed to grow in such polluted soil could be because they are adapted to such a mix of heavy metals and thus may play an important role in phytoremediation efforts. The high concentration of the metals in plants suggests that phytoremediation could be a viable strategy for rehabilitation of this land. Further studies should test on approaches such as liming and selected plants, single or combination, for remediation of this land. Urgent low cost effective and sustainable methods to remediate the polluted area are required considering the serious levels of concentrations.

REFERENCES

Abdu, A. 2005. Effects of sewage sludge on tree growth, soil properties and groundwater quality. *Master of Science Thesis, University of Malasia*

Agency for Toxic Substances and Disease Registry (ATSDR). 1998. Toxicological Profile for Chromium. *U.S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.*

Agency for Toxic Substances and Disease Registry (ATSDR). 2005. Toxicological profile for lead. Atlanta: *U.S. Department of Health and Human Services, Public Health Service.*

Alloway, B. J. 1995. Heavy metals in soils. Second edition. *Edmundsbury Press Pty Ltd*

Allowy, B. J. 1990. The origins of heavy metals in soils. Heavy metals in soils, B, J. Allowy, ed., John Wiley, *New York, 8-39*

Akerblom, S., Baath, E., Bringmark, L. and Bringmark, E. 2007. Experimental induced effects of heavy metals on microbial activity and community structure of forest mor layers. *Biol. Fertil. Soils 44:79-91*

Aydinalp, C. and Marinova, S. 2003. Distribution and forms of heavy metals in some agricultural soils. Polish Journal of Environmental Studies. *12(5):629-633*

Behbahaninia, A., Mirbagher, S.A. and Nouri J. 2010. Effects of sludge from wastewater treatment plants on heavy transport to soils and groundwater. *Iran. J. Environ. Health. Sci. Eng., 2010, 7: No. 5, pp. 401-406*

Bekink, M. 2007. Investigative heavy metals concentration in soil and turff-grass growing in a sewage sludge disposal site, Darvill Waste Water Works. Unpublished Honors project. University of KwaZulu Natal.

Bergkvist, B., Folkeson, L., Berggren, D. 1981. Fluxes of Cu, Zn, Pb, Cr and Ni in temperate forest ecosystem- a literature review. *Water Air Soil Pollut. 47:217-286*

Bern-Liebefeld H.H. 1993. Heavy metals in sewage sludge and town waste compost. In: Merian E (ed.) Metals and their Compounds in the Environment. *VCH, Weinheim. 357-365.*

Bodek, I., Lyman, W.J., Reehl, W.F. and Rosenblatt. 1988. In environmental inorganic chemistry, processes and estimation methods. *Pergamon Press, Elmsford, NY, USA.*

Camobreco, V.J., Richards, B.K., Steenhuis, T.S., Peverly, J.H., and McBride M.B. 1996. Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Science 161:740-750*

Campbell, P.G.C. 2006. Cadmium-A priority pollutant. *Environmental Chemistry, vol 3, 6:387-388*

Carrondo, M.J.T., Lester J.N., Perry R. and Stoveland S. 1987. Analysis of heavy metals in sewage sludg, sewage and final effluent. Department of the environment for contracts *DGR/480/66 and DGR/480/240. Macaulay institute for soil research.*

Chale-Matsau, J.R.B. 2005. Survival of Microorganisms in Soil Amended with Sewage Sludge, and their Subsequent Persistance in Crops. *University of Pretoria etd*

Chander, K., Dyckmans J., Joergensen R.G., Meyer, B., and Raubuch M. 2001. Different source of heavy metals and their long term effects on soil microbial properties. *Boil fertile soils 34:241-247.*

Chang, A.C., Page, A.L., Warneke, J.E., Resketo, M.R. and Jones, T.E. 1983. Accumulation of cadmium and Zn in barley grown on sludgetreated soils: a longterm field study. *J. Envir. Qual.12,391*

Chao Wang, Xin Hu, Mao-Lin Chen, Yun-Hau Wu. 2005. Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni, and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *Journal of Hazardous Materials B119: 245-249.*

Chen, M. and L.Q. Ma. 2001. Comparison of three aqua regia digestion methods for analyzing 16 elements in soils. *Soil Sci. Soc. Am. J. 65:491-499.*

Correa, S.R., White, R.E., Weatherley, A.J. 1996. Effect of compost treatment of sewage sludge on nitrogen behavior in two soils. *Waste Management 26 (6):614-9*

Chrostowski, P., Durda, J.L., and Edelman K.G. 1991. The use of natural processes for the control of chromium migration. *Remediation, vol. 2: no 3, pp. 341-351*

Davies, B.E. and Jones, L.H.P. 1988. Micronutrients and toxic elements, in Russell's Soil Conditions and Plant Growth. *A Wild, Ed, pp 781-814, John Wiley & Sons; Interscience, New York, NY, USA, 11ᵗʰ edition.*

Department of the Environment. 1989. *Code of Practice for Agricultural Use of Sewage Sludge*. Her Majesty's Stationery Office, London.

Department of Water Affairs and Forestry (DWAF). 2001. *Waste Generation in South Africa*. Water Quality Management Series. Pretoria.

Department of Water Affairs and Forestry Second Edition (DWAF). 1997. *Waste Management Series*. Minimum Requirements for Waste Disposal by Landfill.

Du Preez, L.A., Van Der Merwe, W. and Terblanche, J.S. 1999. Biosolids management at 18 wastewater treatment plants in South Africa - optimisation strategies. Proc. Specialized Conference on Disposal and Utilization of Sewage Sludge: Treatment Methods and Application Modalities. *Athens, Greece. 13-15 October*.

Dube, A., Zbytniewski, R., Kowalkowski, T., Cukrowska, E., Buszewski, B. 2000. Adsorption and migration of heavy metals in soils. *Polish journal of environmental studies 10: No. 1 1-10*

Ekama, G, A. 1993a. Evalution of dual digestion system. *Water SA, 19 (3) 201-208*

Enviromental Protection Agency (EPA). 2009. Technical Bakground Document for the Sewage Sludge Exposyre and Hazard Assessment. U.S. Enviromental Protection Agency. *EPA 822-B-03-001*.

Forbes, R.M. and Sanderson, G.C. 1978. Lead toxicity in domestic animals and wildlife. *Topics Environ. Health 225*

Grritse, R.G. and Van Driel, W. 1984. The relationship between adsorption of trace metals, organic matter, and pH in temperate soils. *J. Environ. Qual. 13:197-204*

Giller, K., Witter, E., and McGrath, S. 1998. Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review. *Soil Biology and Biochemistry, 30:1398–1414.*

Griffiths, B., Díaz-Raviña, M., Ritz, K., McNicol, J., Ebblewhite, N., and Baath, E. 1997. Community dna hybridisation and communities from heavy metal polluted soils. *FEMS Microbiology Ecology, 24:103–112.*

Goa, S., Walker, W.J., Dahlgren, R.A., and Blod J. 1995. Simultaneous sorption of Cd, Cu, Ni, Pb, and Cr on soils treated with sewage sludge supernatant. *Water, Air and Soil Pollution 93: 331-345*

Grytsyuk, N., Arapis, G., Perepelytnikova, L., Ivanova, T. and Vynograds'ka, V. 2005. Heavy metals effects on forage crops yields and estimation of elements accumulation in plants as affected by soil. *Science of the total environment 354: 224-231.*

Hart, J.J., Welch, R.M., Norvell, W.A. and Kochian, L.V. 2002. Transport interactions between cadmium and zinc in roots of bread and durum wheat seedlings. *Physiol. Plant Sci. 82:27-33*

Herselman, J. E. and Snyman H. G. 2009a. *Guidelines for the Utilisation and Disposal of Sludge. Water Research Commission TT 349/09, Pretoria, South Africa*

Hobbelen, P.H.F., Koolhaas, J.E. and Van Gestel, C.A.M. 2006. Effects of heavy metals on the litter concumption by the earthworm lumbricus rubellus in field soils. *Pedobiologia 50:51-60*

Hooda, P.S. 2010. Trace elements in soils. *Blackwell Publishing Ltd. United Kingdom.*

Horwell J, Speir T.W, Van Schaik A.P, 2003. Bio-indicators to assess impacts of heavy metals in the land-applied sewage sludge. *Biol Biochem 35: 1501-5*

Hue, N.V. 1988. Residual effects of sewage-sludge application on plant and soil-profile chemical composition. *Commun. Soil Sci. Plant Anal., 19: 1633-1643*

Hunt, R.P. 1997. Strategic assessment for the disposal of sewage sludge Darvill wastewater treatment works Pietermaritzburg. *Umgeni water, Pietermaritzburg 1997.*

Jabeen, J., Ahmad, A. and Iqbal, M. 2009. Phytoremediation of heavy metals: Physiological and Molecular Mechanisms. Bot. Rev. *75:339–364*

Jaganyi, D., Tesfai, F, K., Southway, C. and Mamabolo, M. 2005. Determination of inorganic pollutants and assessment of the current South African guidelines on permissib le utilization of sewage sludge. *Water SA 31: 3.*

Kelly, W.D., Martens, D.C., Reneau, R.B., and Simpson, T.W. 1984. Agricultural use of sewage sludge: A literature review. Project A-097-VA. *Virginia Water Resource Research Centre, Virginia Polytechic Institute and State University Blacksbury, Virginia 24060-3397*

Keirungi, J. 2006. The design and assessment of an intergrated municipal waste beneficiation facility: towards improved sewage slidge management in developing countries. *MSc thesis Rhodes University.*

Korboulewsky, N., Dupouyet, S. and Bonin, G. 2002. Environmental risk of applying sewage compost to vineyards: Carbon, heavy metals, Nitrogen and phosphorus accumulation. *J. Environ. Qual., 31 (5):1522-7*

Korentajer, L. 1991: A Review of the Agricultural Use of Sewage Sludge: Benefits and potential hazards. *Soil and Irrigation Research Institute.*

Kosobucki, P., Chmarzynski A., Buszewski B. 2000. Sewage sludge composting. *Polish Journal of Enviromental Studies 9: (4), 243-248*

Krishnamurti, G.S.R., Huang, P.M. and Kozak, L.M. 1999. Sorption and desorption kinetics of cadninm frm soils: influence of Phosphate. *Soil Sci. 164: 888-898*

Logan, T.J., Lindsay, B.J., Coins, L.E., Ryan, J.A. 1997. Assessment of sludge metal bioavailability to crops: sludge rate response. *J. Environ.Qual. 26, 534–550.*

Liu,W., Zhao J., Ouyang, Z., Soderlund, L., and Liu, G. 2005. Impacts of sewage irrigation on heavy metals distribution and contamination in Beijing, China. *Enviromental international 31:805-812.*

Macdonald, C., Singh, B., Peck, J., van Schaik, A., Hunter, L., Horswell, J., Campbell, C., and Speir, T. 2007. Long-term exposure to Zn spiked sewage sludge alters soil community structure. *Soil Biology and Biochemistry, 39:2576–2586.*

Mandapa, F., Mangwayana, E.N., Nyamangara, J., Giller, K.E., (2004). The effects of long-term irrigation using wastewater on heavy metal contents of soils under vegetables in Harare, Zimbabwe. *Agriculture, Ecosystems and Environment 107: 151-156*

Maleki, A. and Zarasvand, M.A. 2008. Heavy metals in selected edible vegetables and estimation of their daily intake in Sanandaj, Iran. *Southeast Asian j Trop Med Public Health 39(2):335–340*

Marchioretto, M.M., Bruning, H., Loan N.T.P. and Rulkens W.H. 2002. Heavy Metals Extraction from Anaerobically Digested Sludge. *Water Science and Technology 46(10):1-8*

Marx, C.J., Alexander, W.V., Johannes, W.G. and Steinbach-Kanes, S. 2004. A Technical and Financial Review of Sewage Sludge Treatment Technologies. *Water Research Commission Report No. 1240/1/04. Water Research Commission, Pretoria*

McBride, M.B. 1994. Environmental chemistry of soils. *Oxford University Press, New York.*

McBride, M.B., 1995. Toxic metal accumulation from agricultural use of sewage sludge: are USEPA regulations protective? *Journal of Environmental quality.* 24: 5-8.

McBride, M.B., 2002. Toxic metals in sewage sludge- amended soils: has promotion of beneficial use discounted the risk. *Advances in environmental research xx (2002) xxx-xxx.*

McBride, M.B., Richards, B.K., Stenhuis, T., Russo, J.J., Sauve , S. 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science 162:487–500.*

McGrath, S.P. 1987. Long-term metal transfers following applications of sewage sludge. In Pollutant Transport and Fate in Ecosystems, eds. P. J. Coughtrey, M. H. Martin and M. H. Unsworth, pp. 301±317. *Blackwell Scienti®c Publications, Oxford*.

McLaughlin, M.J, and Singh, B.R. 1999. Cadmium in soil and plant: a global perspective. In: Cadmium in soils and plants. (Eds MJ McLaughlin, BR Singh). *Netherlands: Kluwer academic publishing Pp. 13-21.*

Moor, C., Lymberopoulou, T., and Dietrich, V.J. 2001. Determination of heavy metals in soils, sediments and geological materials by ICP-AES and ICP-MS. *Mikrochim. Acta 136: 123-128*

Muchaweti, M., Birkett, J.W., Chinyanga, E., Zvauya, R., Scrimshaw, M.D. and Lester, J,N. 2006. Heavy metal content vegetables irrigated with mixture of wastewater and sewage sludge in Zimbabwe: Implications for human health. Agriculture. *Ecosystem and Enviroment 112, 41-48*

Muse, J.K., Mitchell, C.C Jnr. and Mullins, G.L. 1991. Land Application of Sludge. Community Resource Development Publications, Auburn University, Auburn. Potential Hazards. *Water SA, 17: No.3, pp 189-196.*

Nyamangara, J. and Mzezewa J. 1999. The effects of long-term sludge application on Zn, Cu, Ni and Pb levels in clay loam soil under pasture grass in Zimbabwe. *Agric. Ecosyst. Environ., 73: 199-204*

Olley, J.E. 1997. Solid waste streams regional and cultural variability. *Enviromental Resource Management (ERM), London, UK*

Patel, S.S. and V.S. Srivasthava. 1999. Impact of textile dying andprinting industrial effluents on soil and ground water quality. A case study. *Indian Journal of Environmental Protection, 19(10):771-773*

Peijun, L., Xin, W., Allinson G, Xiaojun L. and Xianzhe X. 2009. Risk assessment of heavy metals in soils previously irrigated with industrial wasterwater in Shenyang, China. *Journal of Hazardous Material 161:516-521*

Permissible Utilisation and Disposal of Sewage Sludge, 1st edn. (1997*). Water Research*

Petrus, R., and Warchol, J.K. 2005. Heavy metal removal by clinoptilolite. An equilibrium study in multi-component systems. *Water Res*. *39: 819-830*.

Plum, L.M., Rink, L. and Haase, H. 2010. The Essential Toxin: Impact of Zinc on Human Health. *Int. J. Environ. Res. Public Health 2010, 7, 1342-1365*

Quan-Ying, C., Ce-Hui, M., Qi-Tang, W., Qiao-Yum, Z. and Katsoyiannis, A. 2007. Concentration and speciation of heavy metals in six different sewage sludge- composts. *Journal of hazardous Materials 147:1063-1072*.

Rahman, S.H, Khanam, D., Adyel, T.M., Islam, M.S., Ahsan, M.A. and Akbor, M.A. 2012. Assessment of heavy metals contamination of agricultural soil around Dhaka export processing zone, Bangladesh: Implication of Seasonal Variation and Indices. *Applied sciences 2: (2012), 584-601*

Rauret, G. 1998. Extraction procedure for the determination of heavy metals in contaminated soil and sediment. *Talanta 46:449-455*.

Rayment, G.E. and Lyons, D.J. 2010. Soil chemical methods-Australasia. *Csiro publishing*.

Rohrs, L.H., Fourie, A.B. and Blight, G.E. 1998. Effects of sewage sludge and refuse composition on the rate of degradation and leachate quality of co-disposed waste in a water-deficient environment. *Water SA 24: No. 2: 137*

Roy, M., Louis, M. and McDonald, M. 2013. Metal uptake in plants and health risk assessment in metal-contaminated smelter soils. *Land degradation and development, (2013) DOI: 10.1002/dr.2237*

Rudd, T. 1987.  Scope of the problem. In: John NL (ed.) Heavy Metals in Wastewater and Sludge Treatment Processes: Sources, Analysis and Legislation. *CRC Press, Boca Raton. 2-23*.

Rudolfs, W., Frank, L.L. and Ragotzkie, R.A. 1950. Literature Review on the Occurrence and Survival of Enteric Pathogens and Relative Organisms in Soil, Water, Sewage and Sludges and on Vegetation. *Sewage and Industrial Wastes 22:1261-1281*

Safe Drinking Water Foundation, (SDWF). 2003. Industrial & Solid Waste Recycling Technologies.

Samuding, K., Abustan, I., Rahman, M.T.A. and Isa, M.H. 2009. Distribution of heavy metals profile in groundwater system at solid waste disposal site. European Journal of Scientific Research. *37(1):55-62*

Schmidt, J.P. 1997. Understanding phytotoxicity threshold for trace elements in land Applied sewage sludge. *Journal of Environmental Quality 26 4-10.* Sewage Sludge Utilization and Disposal. Water Institute of Southern Africa.

Sherene, T. 2010. Mobility and transport of heavy metals in polluted soil environment. An Internation Journal, *2(2):112-121*

Silviera, D. J. and Sommers, L. E. 1977. Extractability of Copper, Zinc, Cadmium, and Lead in Soils Incubated with Sewage Sludge. *Journa/ of Env/ronmental Quality 6:47-52*.

Snyman, H.G, Alexander, W.V, and Marx, C.J. 2000. Land disposal and agricultural reuse of sewage sludge within the framework of the current South African guidelines. *WISA 2000 Biennial conference, Sun City, South Africa.*

Snyman, H.G. and Van der Waals, J. 2004. Laboratory and field scale evaluation of agricultural use of sewage sludge. *Water Research Commission on the Project*.

Snyman, H.G., and Herselman, J.E. 2009. Guidelines for the utilization and disposal of wastewater sludge. *WRC Project No. K5/1622,* 3 Ekama, G.A., 1993a. Sludge management for land disposal. In Ekama, G.A. (ed): *Wastewater Sludge: Volume 3 of 5: Requirements for the On-site and Off-site Disposal of sewage sludge*

Soldatini, G.F., Riffaldi, R., and Levi-Minzi, R. 1979. *Water, Air Soil pollution, 6:113*

Tchobanoglous, G. and Burton, L,F. 1991. Wastewater engineering treatment, disposal and reuse, *McGraw-Hill, USA*.

Temple, P.J. and Besessar, S. 1981. Uptake and toxicity of nickel and other metals in crops grown on soil contaminated by a nickel refinery. *J. Plant Nutr. 3:473-482*

Topcuoglu, T. 2005. Effects of repeated application of sewage sludge and MSW compost on the bioavailability of heavy metals in greenhouse soil. Polish J. Environment Studies Vol 14, no. 2:317-222

USEPA. 1996. Report: recent Develepment for In Situ Treatment of metals contaminated Soils, U.S. Enviromental Pretection Agency, Office of Solid Waste and Emergency Response,

USDHHS. 1999. Toxicological profile for lead, United States Department of health and Human Services, Atlanta, Ga, USA.

Vanek, A., Boruvka, L., Drabek, O., Mihaljevic, M. and Komarek, M., 2005. Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. *Plant soil environment, 51, (7): 316-321*

Vukovic, J. Avidad, M. A. and Capitan-Vallvey, L.F. 2012. Characterization of disposal optical sensors for heavy metal determination. *Talanta xxx(2012) xxx-xxx.*

Walter, I., Martinez, F. and Cala, V. 2006. Heavy metals speciation and phytotoxic effects of three representative sewage sludge for agricultural uses. *Enviromental pollution 139:507-514*

Williams, C. H. 1980. Soil acidification under clover pasture. *Aust. J. Exp. Agric. Anim. Husb. 20:* 561-7.

Xiao, Y, Bai, X, Ouyang, Z, Zheng, H. and Xing, F. 2006. The composition, trend and impact of urban soild waste in Bejing. *Springer Science.*

Yanez L, Ortiz D, Calderon J, Batres L, Carrizales L. and Mejia J. 2002. Overview of human and chemical mixtures: problems facing developing countries. *Enviromental Health Perspectives 110, 901-9*

**Appendix: Plant available extractable NH₄NO₃ for Cr, Cu, Ni, Zn, Pb, Cd and As heavy metals**
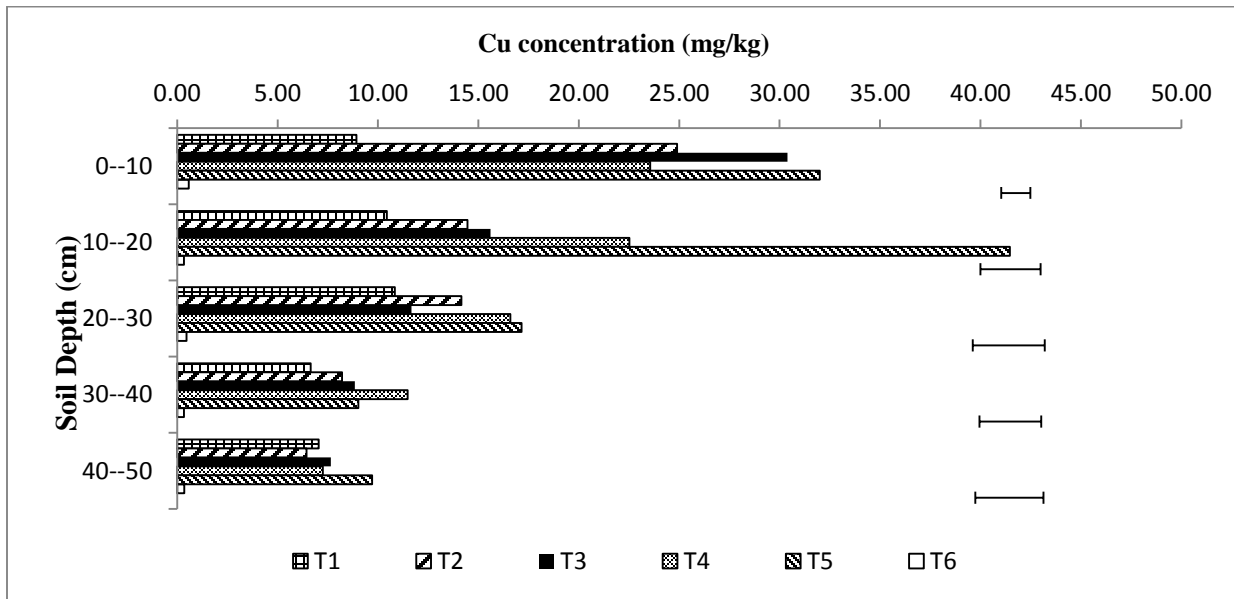
*Ammonium nitrate extractable Cr*

Fig.4.9 illustrates mean Cr concentrations of measured with $NH_4NO_3$ extraction. The results show that mean Cr concentrations exceeded the MAT set by DWAF, (1996) and Snyman and Herselman, (2006c). In transect 1 0-10 cm depth, mean Cr concentrations were higher than MAT with mean concentrations of 0.33 mg/kg, increased in the 10-20 cm depth with mean concentration of 0.43 mg/kg, then increased in the 20-30 cm depth showing mean concentrations of 0.51 mg/kg and in the 30-40cm and 40-50 cm a decline in mean Cr concentrations was observed.. In transect 2 mean Cr concentrations accumulated in the 0-10 cm depth then decreased with depth up to 40-50 cm depth, while transect 3 showed high mean Cr concentrations as compared to other transects with the mean concentration of 0.94 mg/kg in the 0-10 cm depth, then decreases with depth moving down the profile up to 30-40 cm depth with a mean concentration of 0.78 mg/kg. Transect 4 results showed mean Cr concentrations did not move much down the profile as the mean concentrations ranged between 0.72 and 0.64 mg/kg from 0-10 cm to 40-50 cm depth although these concentration were higher than MAT in all depths. In transect 5 mean Cr concentration increased in the 0-10 cm to 40-50 cm depth showing concentrations of 0.65 mg/kg to 2.61 mg/kg. In transect 6 there was little movement within the profile.
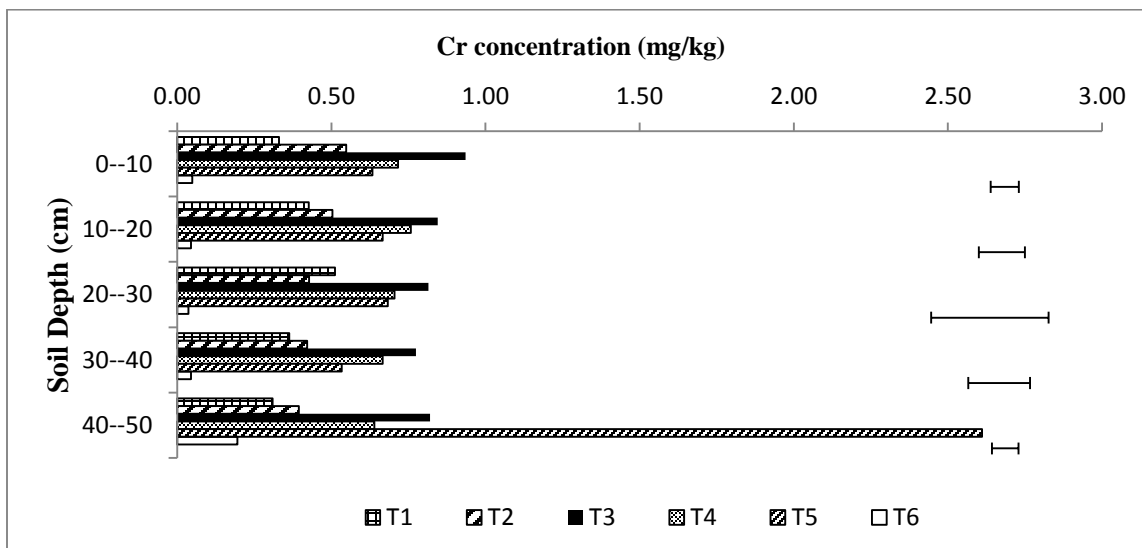
**Appendix 1: Chromium concentration in soil treated with sludge based on NH₄NO₃ extractions Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable Cu*

Mean Cu concentrations in transect 1, 0-10 cm depth increased slightly up to 20-30cm depth with mean concentration of 10.83 mg/kg while transect 2, 3 and 4 mean Cu concentrations decreased moving down the profile from 0-10cm to 4-50cm depth. In transect 5 results mean Cu concentrations increased in the 0-10 cm with 32.00 mg/kg to 10-20 cm depth with 41.46 mg/kg, then decreased from 20-30 cm to 40-50 cm depth. .
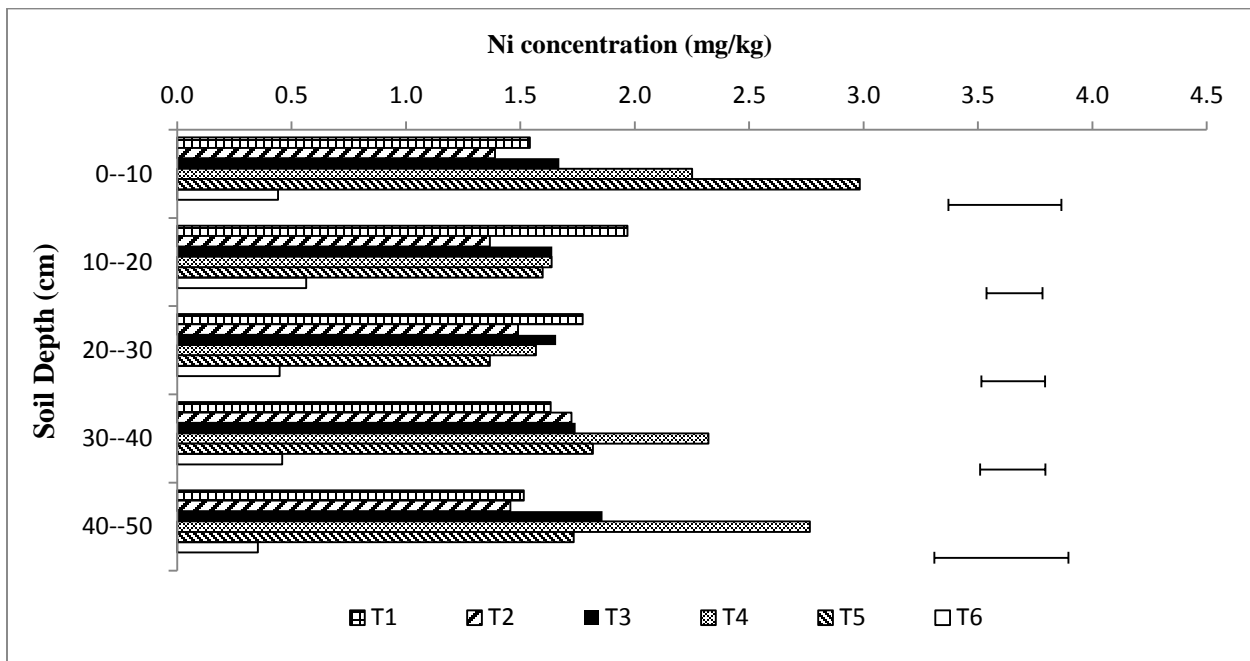


**Appendix 2: Copper concentration in soil treated with sludge based on NH₄NO₃ extractions Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable Ni*

Figure 4.11 illustrates results for Ni where mean Ni concentrations has been observed to increase moving down the profile in transect 1, with concentrations increasing from 1.54 mg/kg in 0-10 cm depth to 1.97 mg/kg in 10-20 cm depth, while in the bottom depths concentrations were observed

to have decreased. In transect 2 results showed that mean Ni concentrations decreased in the 10-20 cm depth with a concentration of 1.64 mg/kg compared to 0.10 cm depth which showed a concentration of 1.67 m /kg, a slight increase in mean Ni concentration was observed in the 20-30 and 30-40 cm depth, then decreased in the 40-50cm depth. Transect 3 showed high mean Ni concentration in the 0.10cm depth then decreased in the 10-20 cm depth from 1.67 mg /kg to 1.64 mg/kg then increased in the 20-30 cm depth to about 1.66 mg/kg. The trend at which Ni was moving down the profile in this transect was similar to transect 1. Transect 4 and 5 showed similar trends in terms of movement of Ni within the depths, where high concentrations where found in 0-10 cm depth then decreased in the 10-20cm then a slight increase in the 20-30 cm depth. Transect 6 showed the lowest mean Ni concentrations.
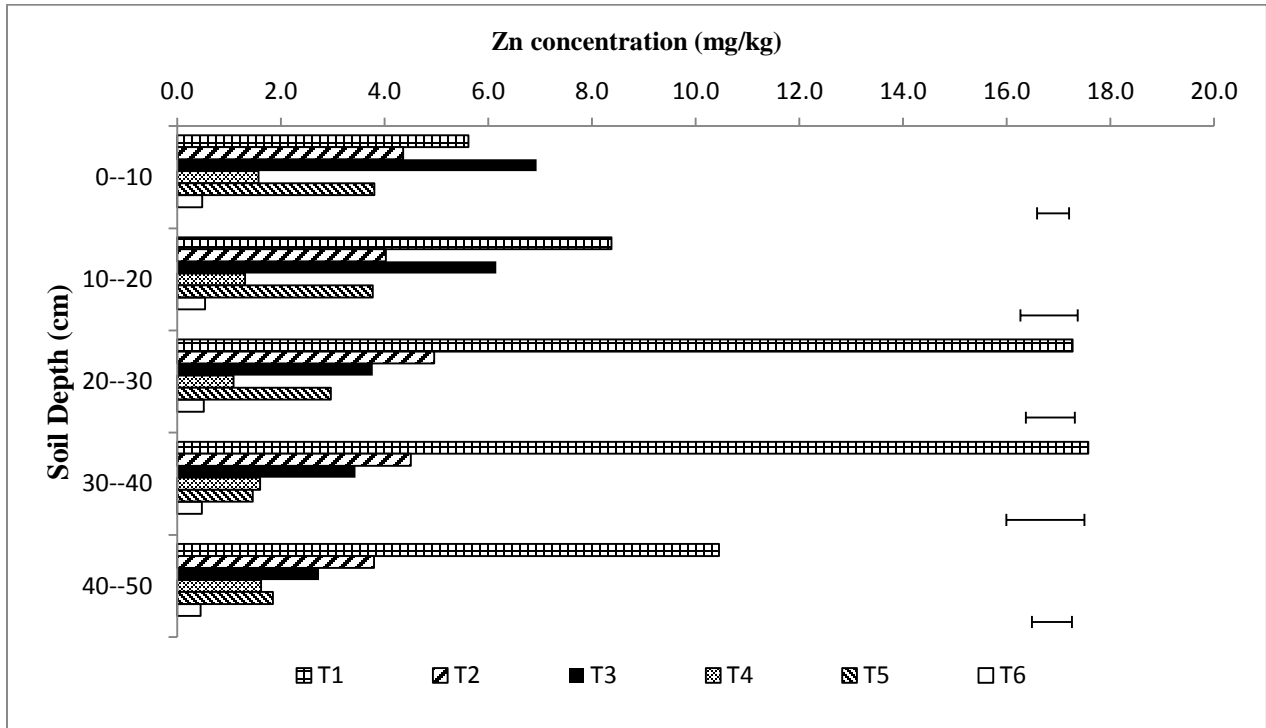


**Appendix 3: Nickel concentration in soil treated with sludge based on NH$_4$NO$_3$ extractions Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable Zn*

Figure 4.11 illustrates results for Zn concentration where transect 1 showed Zn concentrations increasing moving down the profile with 0-10 cm depth having concentrations of about 5.62 mg/kg increasing up to 17.58 mg/kg in the 30-40 cm depth. Transect 2 showed Zn concentration were

high in the 0-10cm depth then decreased in 10-20cm depth then increased in the 20-30 cm depth followed by a decrease in the 30-40 and 40-50cm depths. Transect 3, 4 and 5 results showed that Zn concentrations decreased moving down the profile with 0-10 cm depth showed high concentrations.
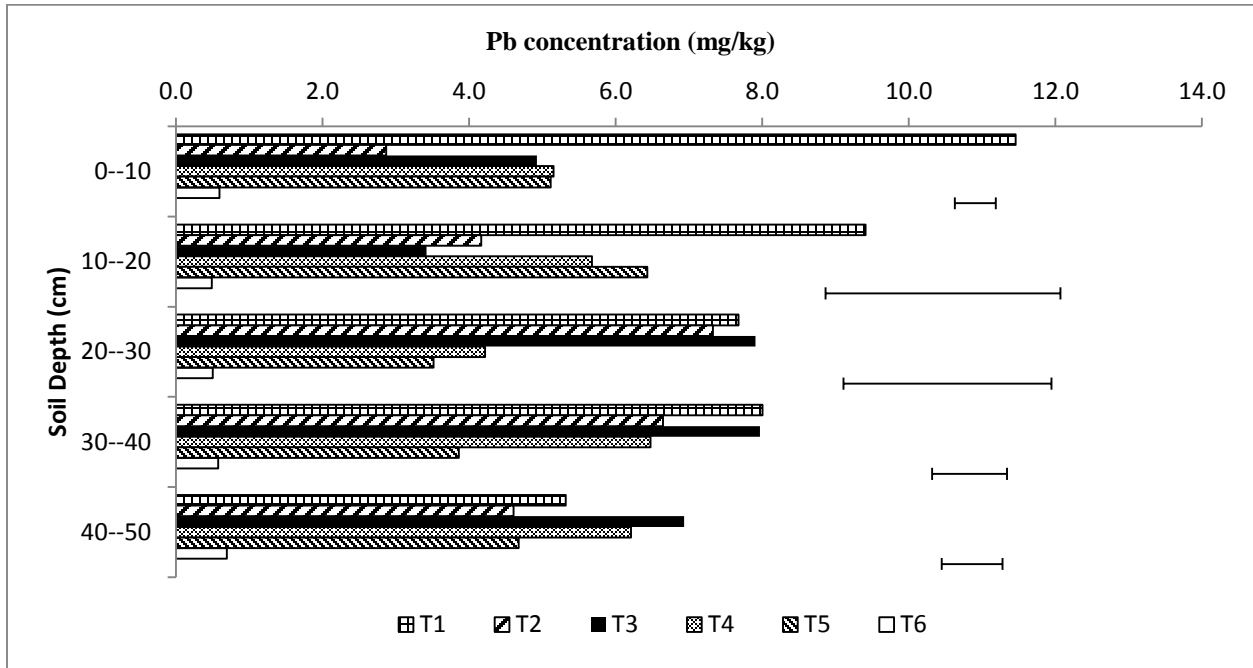


**Appendix 4: Zinc concentration in soil treated with sludge based on NH₄NO₃ extractions**
**Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable Pb*

Fig. 4.12 illustrates Pb concentrations analysed with $NH_4NO_3$ extraction giving the available concentrations of Pb. The concentrations of Pb exceeded the maximum available threshold (MAT) set by DWAF (1996), Snyman and Herselman (2006c). Transect 1 showed high concentrations of Pb at the 0-10 cm depth but moving down the profile it decreases. Transect2 and three behaved the some way with less concentration on 0-10 cm but increasing moving down the profile. Transect 4 showed that concentration of Pb increased in the 10-20 cm but a decrease

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in the 20-30 cm depth and a slight increase in the 30-40 cm depth. Transect 2, 0-10 cm depth was not much contaminated with Pb but moving down the profile availability of Pb increased beyond MAT set at 3.5 mg/kg. Transect 3, 4, 5 indicate a similar behaved, as the trends did not show much differences moving down the profile. In transect 6 there was on contamination as this is the control site.
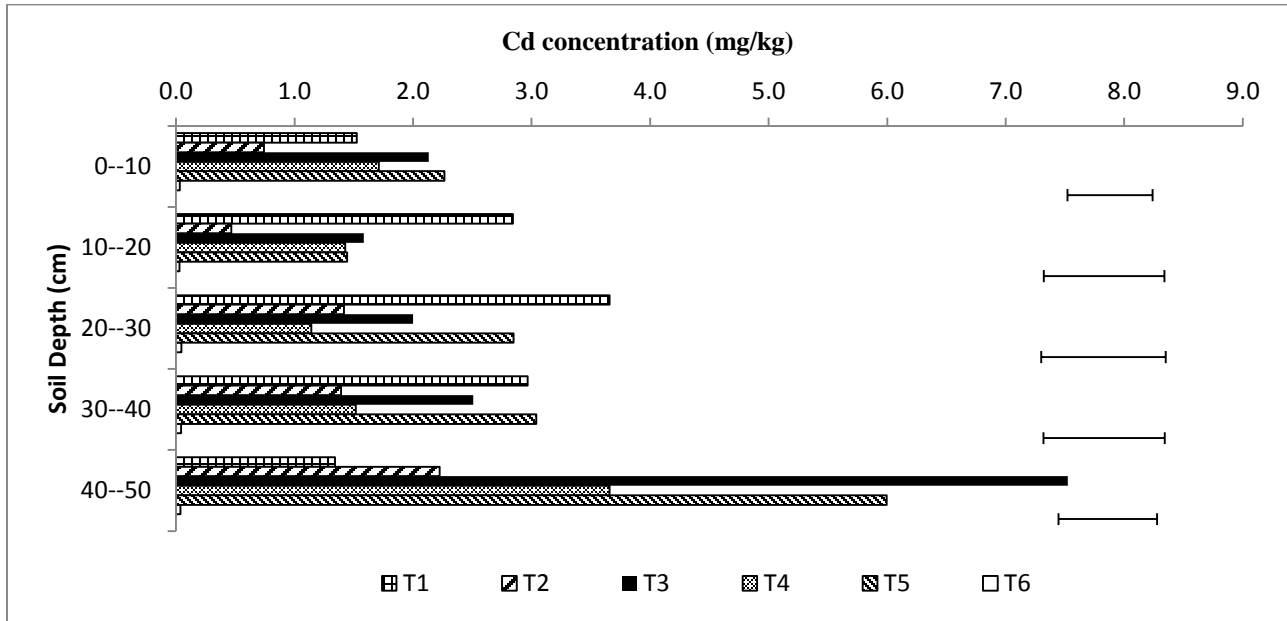


**Appendix 5: Lead concentration in soil treated with sludge based on NH₄NO₃ extractions Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable Cd*

Figure 4.13 illustrates Cd results where transect one and 5 results showed that Cd levels in decreased down the profile. Transect 2 showed an increase from 0-10 cm to 10-20 cm depth then decreased to 30-40 cm depth, then slight increase in 40-50 cm depth, a slight increase in 40-50 cm depth was observed. Transect three results showed that at 0-10 cm depth there has been an increase to 10-20 cm depth, then a slight decrease moving down the profile up to 30-40 cm depth. In 40-50 cm depth an increase in Cd levels in soil was observed. Transect four showed no much movement

Cd in this transects.  In transect 5 a slight increase from 0-10 cm)to 20-30 cm was observed then a decrease in Cd levels was observed at 40-50 cm depth. Transect 6 showed little movement of Cd



**Appendix 6: Cadmium concentration in soil treated with sludge based on NH₄NO₃ extractions Error bars represent least significant differences at p<0.05.**

*Ammonium nitrate extractable As*

Figure 4.14 illustrates results of As where transect one showed that As levels were high in the 0-10cm depth, decreased in the 10-20 cm depth and a slight increase in 20-30 cm depth, then decreases in 30-40cm and 40-50cm depth. Transect 2 results show an increase from 0-10 cm to 10-20 cm depth, then a decrease from 20-30 cm to 30-40 cm depth. In the 40-50 cm depth showed a slight increase indicating that As has moved down the profile. Transect 3 and four results showed that As levels did not move much with depth. Results from transect 5 showed that As levels slightly decrease moving down the profile.
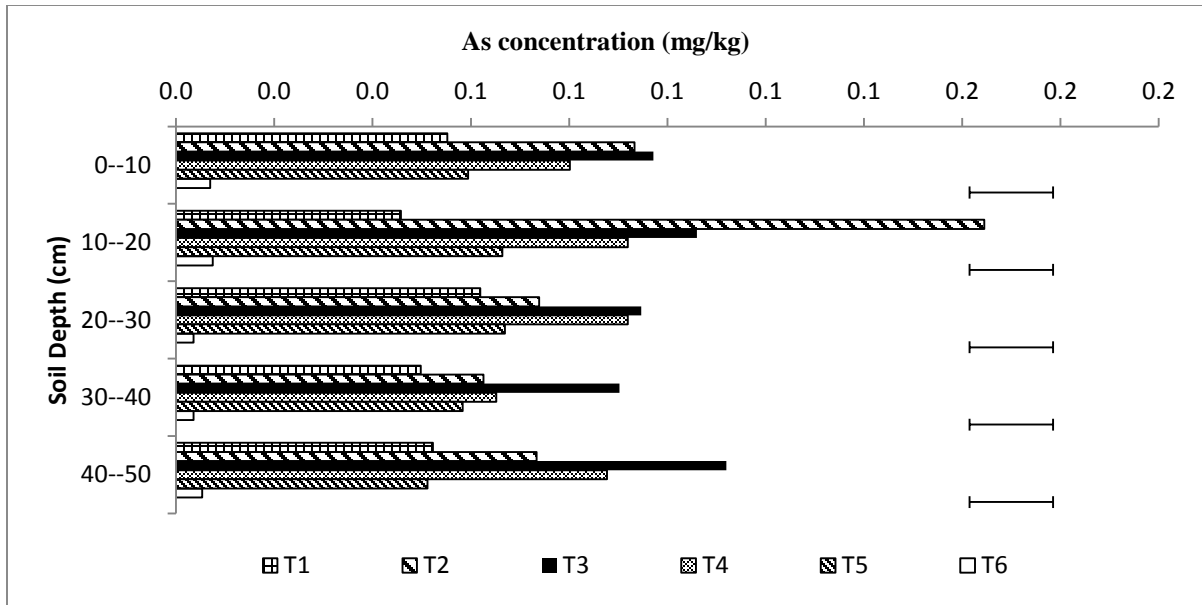
**Appendix 7: Arsenic concentration in soil treated with sludge based on NH₄NO₃ extraction**
**Error bars represent least significant differences at p<0.05.**