QUANTIFICATION OF METHANE AND HEAVY METALS LEVELS IN LEACHATE. A CASE STUDY OF DANDORA DUMPSITE, NAIROBI, KENYA

BY

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DECLARATION

This thesis is my original work except where due references are made. It has not been submitted partially or wholly for the award of degree to this or any other institution of learning.

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This thesis has been submitted with our approval as university supervisors

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DEDICATION

This thesis is dedicated to my dear mother, Mary Awura Panyako, for her consistent encouragement and persistent follow-up, children- Joy, Blair and Marvellous Tsuma, for the constructive criticism they always made and husband Mr. Brown Tsuma.

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those whose names I have not listed, who kept on encouraging me in the course of this study. Thanks to Mrs. Mwangi, Mr. Luvonga and Benjamine for their support.

Last but not least the Almighty God, for giving good health and ability to complete this work.

ABSTRACT

Increased rate of urbanization in Kenya influences solid and liquid waste generation and management and other environmental impacts. This has increased use of landfills to manage wastes and reduce pollution. However, researchers have cited landfills to be one of contributing sources of methane, a greenhouse gas whose level has increased in the atmosphere. It has been noted since 2007 that there is an increase in greenhouse methane attributing to extreme weather and climate change. Methane is a potent environmental pollutant due to its activity as asphyxiate and its explosive nature. Basing on these characteristics and the global concerns about rising levels, the study sought to assess the emission levels of methane from an open landfill at Dandora (dumpsite) in Nairobi County.

Landfills contain leachates which can seep into ground water. Leachate may contain heavy metals that pollute the groundwater supplies. Because of their environmental and health implications, the study also assessed levels of some selected heavy metals i.e. lead, copper, zinc, nickel, chromium and cadmium in the landfill leachate. Sampling was done for six months; during dry, short rain and wet periods. This was mainly to determine the effects of seasons on the levels of analytes. Levels of heavy metals in the leachates were determined using Atomic Absorption Spectrometer (AAS). Gas chromatography with flame ionization detector (FID) was used for methane analysis.

The main aim of this study was to assess levels of methane in landfills and heavy metals in leachate from Dandora dumpsite, in Nairobi Kenya. Leachate was scooped from ten sampling trenches in Dandora dumpsite to analyse level of heavy metals using AAS technique. The findings were that the levels of lead metal ions were highest, 46.49 ppm in November and lowest, 9.58 ppm in April. Levels of copper metal ions were highest, 16.05 ppm in November, 13.2 ppm in February, and lowest, 5.57 ppm in April. Zinc metal ions concentration was highest, 358.4 ppm in November, 340.6 ppm in December, 164.8ppm in

January, 151.9ppm in February, 72.5ppm in March and 46ppm in April. Levels of nickel metal ions ranged from 1.18 ppm in April to 7.92ppm in November. Chromium metal ions levels were between 7.04 ppm in March and 14.27 ppm in November. Cadmium metal ions were found at three sampling points during the month of December only. Their concentration was 0.09 ppm.

Methane was highest at the sampling point where wet waste was disposed. The levels of methane ranged from below detectable level (BDL) at five points to as high as 3779.8717 ppm at point P_{17}. Methane flux ranged from zero to 48869.0515 µg C m^{-2} h^{-1} at point P_{12}. The part of dumpsite covered by vegetation, bear dry ground or/and the inactive site had lowest level of methane or no methane was detected.

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ABBREVIATIONS

AAS   Atomic Absorption Spectroscopy

BDH   British Drug House

BDL   Below detectable level

BOC   British Oxygen Company

BOD   Biological Oxygen Demand

COD   Chemical Oxygen Demand

CTR   Cathode Ray Tube

ECF   European Climate Foundation

EDS/EDX   Energy Dispersive x-ray Spectroscopy

EEA   European Environmental Act

EPA   Environmental Protection Agency

EU   European Union

FID   Flame Ionization Detector

GC   Gas Chromatograph

IPCC   International Panel on Climate Change

ILRI   International Livestock and Research Institute

Kg/day   kilogram's per day

kJ/g   kilo Joule per gram

LDC   Least Developed Countries

LEL   Lower Explosive Limit

M   molar

mA   milli Amperes

mJ   milli Joules

mg/L   milli grams per litre

Mol   mole

NSEM   National System for Environmental Monitoring

MSW   Municipal solid waste

NEMA   National Environmental Management Authority

NIST   National Institute of Standards and Technology

nm   nanometres

nmol   nanomoles

nmol/mol   nanomoles per mole

NOAA   National Oceanic and Atmospheric Administration

^{0}C   degrees celsius

^{0}F   degrees Fahrenheit

%   percent

SPSS   Statistical Package for Social Scientists

kg/day   kilograms per day

TWAS   Today's World Advancement of Sciences

UEL   Upper explosive limit

UK   United Kingdom

VOAs   Volatile Organic Acids

XRF   X-Ray Fluorescence

CHAPTER ONE

INTRODUCTION

1.1 Background

Kenya is urbanization rate has been increasing in the recent years (about 0.6 % per year) (Republic of Kenya, 2009). The yearly city people increase rate has been projected to increase by 5.2%, 4.2% and 3.2% from 2000 to 2010, from 2010 to 2020 and from 2020 to 2030 respectively (TWAS newsletter, 2009).The increase in population in the urban influence solid and liquid waste production and management and other environmental problems (Republic of Kenya, 2009). Dump sites and landfills are good option for waste management and disposal. Currently, no landfill exists in the city of Nairobi (Kavila, 2011), but dumpsites are in use. The main municipal solid waste deposit place serving Nairobi County in Kenya is situated at Dandora, Figure 1. There is an illegal dump site at Kibera to manage MSW in that region (Rotich *et al*, 2005). Fresh air for the urban is growing population is rare due to increased waste generation and poor management which results to environmental impacts (TWAS newsletter, 2009).

Methane is one of the air pollutants found in places where solid and liquid wastes are disposed either in dump sites or landfills (Hurst *et al*., 2005) due to chemical and biological reactions taking place from different substrates (Chandler, 2008). Other environmental contaminants include organic compounds which are specifically in leachates (Schultz and Kjeldsen, 1986) and various metal salts, which originate from cationic and anionic components of leachates (McKay,

1996). Some of heavy metals commonly found in dump site include Zn, Cu, Cd, Pb, Ni, and Cr (Lu, *et al*, 1985).
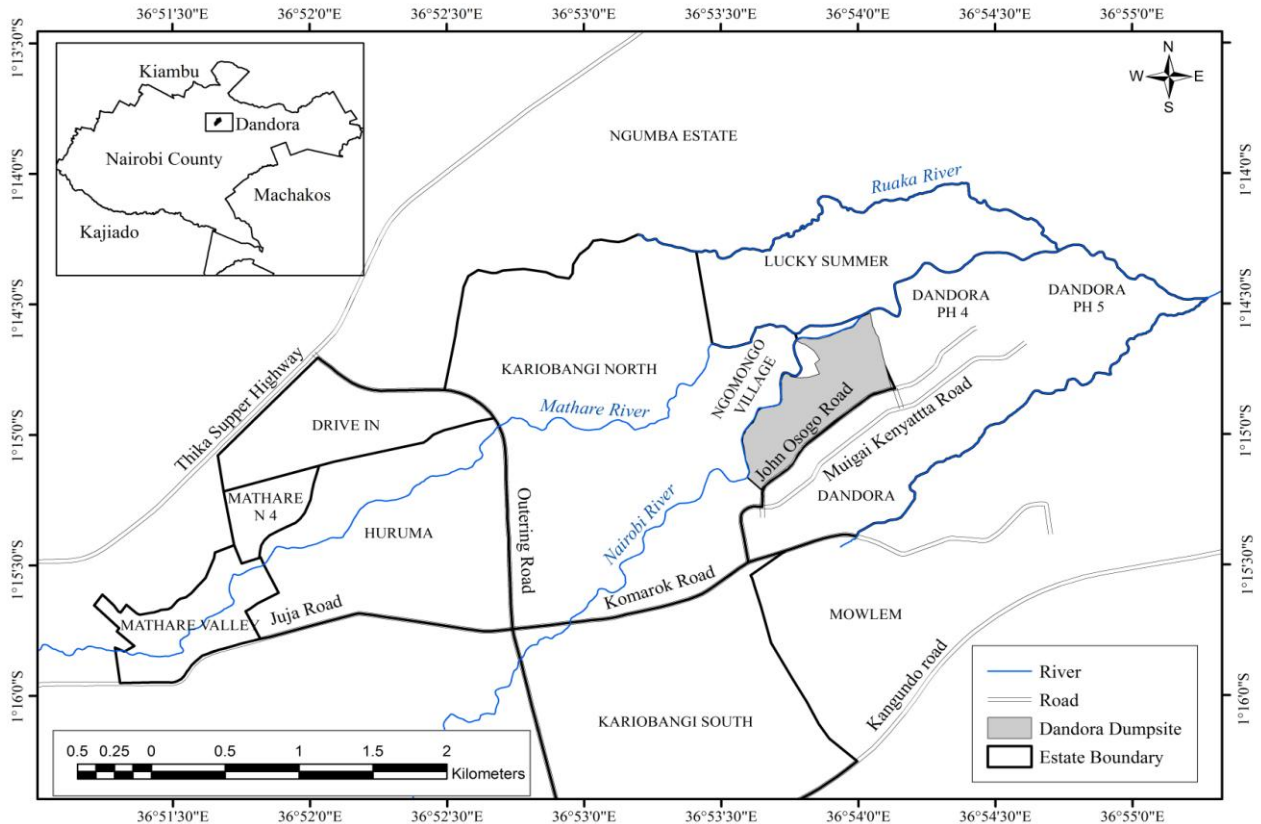
Figure 1: Map showing the location of Dandora dump site and neighbouring estates in Nairobi County, Kenya.

These heavy metals may be in form of a solution causing water pollution (Aucott, 2008). Leachates are a possible harmful waste from dump sites or landfills. If not treated and managed, could be a source of contamination to ground water, generally affect the environment and could be a source of health problems (Kostova, 2006). A study by Kulikowska and Klimiuk, (2008), showed that the effect of leachate composition of heavy metals, dissolved solids, phosphorus (P), chlorine (Cl), calcium (Ca), magnesium (Mg) and sulphate (SO_4^{2-}) depended on time of year of rather than the age of the landfill.

Studies have been done about how to manage increasing waste generation as the population increases. A project about landfills replacing dump sites was to be funded by World Bank to deal with garbage problem and also offer employment to Kenyans (Kavila, 2011).

An experimental bucket was set up at Chiromo campus as a control to quantify levels of heavy metals in leachate. The experimental bucket had features of a landfill. It was important to quantify the level of heavy metals in leachate from the bucket because it had a bottom unlike the dump site which lacks a bottom to separate soil from MSW that is disposed.

A dump site has several adverse effects from its operations. For example; local environment being polluted when ground water and/ or aquifers are contaminated by leakage or sink holes (Tampa 2011) as well as the residual soil; off gassing of methane and other gases such as ammonia, carbon dioxide and hydrogen sulphide which are generated due to the decay of organic wastes (Shindell *et al*, 2009); disease vectors like rats and flies are harboured; injuries to wild life; and simple nuisance problems such as dust during dry season, odour, mud during rainy season, vermin or noise pollution (Tampa 2011). Studies done about waste management were cognitive tool to this study on largest dump site (Dandora) in the capital city of Kenya. The study sought to quantify methane and heavy metals levels from Dandora dump site.

1.2 Statement of problem

Waste management systems such as dump sites and landfills reduce trash and garbage in urban areas of countries. Dump sites and landfills emit gases such as methane and carbon dioxide, which are greenhouse gases (Shindell *et al*, 2009). To reduce the greenhouse gas effect and pollution, methane is combusted to give carbon dioxide which is less potent than methane as shown in equation (1).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad\qquad (1)$$
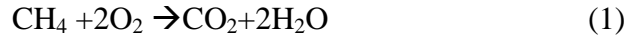
Methane can be collected and used as clean fuel, which minimizes its emission to atmosphere. Since methane can be ignited by hot surface due to its explosiveness (Clay, 2008), its concentration in air can be reduced by trapping and using it as fuel. It was necessary to know the level of methane from the Dandora dump site in order to utilize waste management technique to increase the generation of low-carbon fuel.

Dump sites and landfills also contain leachate (semi-solid) which are potential hazardous waste. Untreated leachate could impact on the environment and cause pollution to ground water (Kostova, 2006). This is mainly because leachate may contain heavy metals such as lead, copper, zinc, nickel, chromium and cadmium. Effects of these heavy metals to human health are known from previous studies (Aucott, 2008). The study sought to quantify the levels of these heavy metals in leachate from the largest dump site in Kenya. The report of the findings would give insights on other dump sites in the country and help advice the policy makers accordingly.

1.3 Main Objective

The main objective was to quantify the level of methane and selected heavy metals in leachate from Dandora dump site.

1.4 Specific Objectives

The specific objectives were to:

1) Quantify the level of methane from Dandora dumpsite.

2) Quantify the levels of heavy metals Pb, Cu, Zn, Ni, Cr and Cd in the leachate from Dandora dumpsite as well as from experimental bucket at Chiromo Campus.

3) Determine the spatial variation of the levels of heavy metals in the leachate from Dandora dump site to the seasonal variation.

1.5 Justification of Research

Whereas dump sites are solution to waste management in several Countries, they are great source of environmental pollution besides climate change. Waste generation increases as the population grow and also as a Country develops. Generated waste has to be disposed to minimise environmental impacts. A heap of waste in oxygen-free conditions provided by a dump site, decay producing gases, organic and inorganic compounds. The rate at which levels of the green gas methane has been increasing in the atmosphere is alarming, especially to the researchers (Chandler, 2008). It has been noticed that dump sites and landfills contribute to increased level of atmospheric methane (Kaluli *et al*, 2011). Concerns due to high concentrations of methane in the atmosphere was a reason for searching some of the sources of the gas and ways which could be used to minimise its levels. Methane can be trapped and used as clean fuel, hence assist in both reducing its rise in level in the atmosphere and providing renewable fuel. Leachate from dumpsites and landfills contains heavy metals, which are likely to be ground water contaminants, if it seeps underground (Aibaiges *et al*, 1986). Dumpsites have no bottoms, therefore there are high chances of heavy metals seeping underground to cause pollution to ground water. Some residents of Dandora, Luckysummer and Kariobangi Estates depend on water supplies from wells and boreholes in these areas. Because of these it was important to quantify levels of heavy metals in leachate to enable policy makers to be aware of the risk posed by the Dandora dump site, hence act accordingly.

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1.6 Limitations

The study aimed at quantifying methane and selected heavy metal ions levels in air and leachate from Dandora dump site. Methane samplers limited duration for sampling to less than six months because it is generated within fourteen days when organic wastes degrade. Methane could not be kept in the freezer for a long time because it could escape. Due to this it was to be analysed in two days after its collection. Methane from the experimental bucket at Chiromo campus was not analysed because other organic compounds form after fourteen days of decaying waste, also the tank allowed escape of the gas.

Leachate is semi-solid substance formed when liquid from waste or another source comes in contact with solid matter. Changes in seasons could affect the amount produced and might have led to dilution especially during rainy season.

CHAPTER TWO

LITERATURE REVIEW

2.1 Waste management

Methane is one of the dumpsite and landfill gases that are relatively potent greenhouse gases (NOAA, 2008). It is the main component of natural gas accounting for 23% of the world's energy consumption. Other sources of methane are burning biomass and agriculture (Thilo, 2009). Human-related activities (Anthropogenic) give about 50% of methane (Butterbach-Bahl *et al,* 1997). Natural sources of methane other than dump sites and landfills include; wetlands, gas hydrates, permafrost, termites, lakes, non-wet land soils and wild fires (Thilo, 2009). Climate, manufacturing and farming production characteristics, waste management practices, power types and usage are some of the factors that determine methane emission levels (Bloom *et al,* 2010). Temperature and moisture significantly affect digestion process in an oxygen-free condition which results to methane emission in both human-related and natural sources (Chen *et al,* 2010).

The current climate change that is being experienced is due to the previous methane emissions of the developed countries as shown in Table 1, whereas the 50 least developed countries (LDCs), emit only 1 % of the worldwide carbon emissions, such as methane, carbon dioxide and carbon monoxide.

Table 1: Estimates of worldwide methane emmission from MVs (mty[-1]) to the atmosphere (Source: Chen *et al*, 2010).

	Flux to atmosphere Quiescent degassing	Quiescent and eruptions	Flux to atmosphere & oceans
Dimitrov (2002)	0.33-2.64	10.3-12.6	_
Etiope and Klusman (2002)[a]	>1-2[b]	5-10[c]	_
Kopf (2002)	_	_	0.08-1.4
Milkov and others (2003)	2.9	6	3.3
Kopf (2003)[d]		0.00005-0.328	0.2-12.3
Dimitrov (2003)		5	
The study (Environmental Geology, 2004)	>3-4.5	>6-9	

a- On shore MV only.

b- flux from vents

c- flux from vents and flank micro seepage

d- Estimate not reliable; significant arithmetic mistakes are made during calculations and data manipulations.

The world's poorest population, who often depend on peasant farming to survive are in danger because of the climate change. Global Humanitarian Forum report estimates that 300,000 deaths occur annually and 325 million persons are negatively affected by extreme climate conditions (TWAS newsletter, 2009).

Developing countries are the most affected by climate change. About 99 % of deaths and more than 90 % of the financial losses, such as loss of homes and property are due to extreme weather and climate change, yet their law-makers often do not have knowledge of the skill with regard to their issues (TWAS newsletter, 2009). The European Climate Foundation (ECF) whose main objective is to support climate and energy laws to minimize Europe's greenhouse gas production and to help Europe mitigate climate change globally. ECF has provided four major sections to act upon within Europe in order to achieve its aims. These are: Energy competence in construction and manufacturing, low-carbon energy generation, transportation; and EU climate laws and international relations. Kenya may also seek to improve in areas of Energy efficiency and low-carbon power generation from wastes.

The levels of methane in environment in the year 1998, was 1.745 ppm (parts per million), up from 0.700 ppm in the year 1750 (increased at a rate of about 0.241% in 248 years). The level of methane remained the same since 1998, but by 2008, it rose to 1.800 ppm (increased at the rate of 0.306% in ten years) (NOAA, 2008). In 2010, methane levels in the Arctic had risen to 1.850 ppm (increased at the rate of 1.351% in two years). The likely of global warming by methane is high than CO_2 (IPCC, 2012).

Methane acts as asphyxiate since it reduces oxygen levels in a poorly ventilated atmosphere. Methane at 7 % concentration reduces oxygen to 19.5 %, while at 71 % concentration reduces oxygen to fatally low 6 % (Doyle, 2001).

Leachate is semi-solid mixture of any fluid that pass through matter, extracts solutes, suspended solids and/or any other component of the material through which it has passed (Kostova, 2006). Leachate from municipal solid waste (MSW) dumpsites and landfills varies in strength as a result of the biological activity occurring as the solid waste breaks down (Reinhart, 1998).

2.2 Dumpsites and landfills outside Kenya

Municipal and other Wastes management is a challenge to many countries in terms of getting appropriate dumping site and concern for the health of the people due to increase in domestic and industrial waste production (Pastor *et al*, 1993). Landfills are used in many countries for MSW disposal. Water penetrate through wastes dissolving organic and inorganic matter, hence producing polluted leachates finally get to shallow streams. A study conducted in Spain on siliceous soils on plants and animals in central about effects of leachates from landfills. The results of their study showed that synthetic leachate was the most toxic (Pastor *et al*., 1993).

National System for Environmental Monitoring (NSEM) has registered about 5135 dumpsites and 275 landfills in Bulgaria (Kostova, 2006). The study done by Kostova (2006), categorised landfills into 3 classes. Class 1 – landfills were for industrial wastes, class 2 – landfills were for municipal wastes and class 3 – landfills were for hazardous wastes. The findings of her study about leachate from sanitary landfills were that when biodegradable waste, like newspaper, card and fritter away food, was disposed of the anaerobic conditions of a landfill, gases and soluble chemicals were formed due to action of bacteria.

A study by Kulikowska and klimiuk (2008), indicated that even with the short duration of landfills some parameter like moderately alkiline pH of 7.84, low heavy metal levels, low chemical oxygen demand concentration of less than 2000 ppm and less than 0.4 BOD/COD ratio the landfill are characterized by methanogen contamination.

Baun (2004), studied specifically less than 30 landfill leachate samples. In spite of the few data and the different definition of the dissolved fraction (<0.45 mm or <0.0001 mm) his studies consistently showed that colloids as well as organic and inorganic compounds were important for all heavy metals in landfill leachate .The free metal ion constituted less than 30 % typically less than 10 %, of the total metal concentration (Baun, 2004).

A study about evaluation of urban waste manure as daily cover for bad odour control at landfill place was done in UK by Hurst and Longhurst. Daily compost cover was to be solution to environmental pollution (Hurst *et al.*, 2005). Use of landfills in United Kingdom (UK) changed in recent years to meet the challenges of the European Landfill Directive (ELD). The UK imposed landfill tax upon disposal of waste which generate gases due to their decomposition into landfills.

Landfills in the United States (US) are regulated by the Environmental Protection Agency whose guidelines are mandatory. The principles were set by the United States Environmental Protection Agency (USEPA).

Landfills in Canada are regulated by Provincial Environmental Agencies (PEA) and Environmental Protection Acts (EPA). The fate of heavy metals in landfills in New York, showed that metals in landfills could be found in aqueous, elementary or combined forms

depending on the landfill environment and wastes (Townsend *et al*, 1998). Engineered landfills were found mainly in South Africa, Botswana and Zimbabwe (Rotich *et al*, 2005).

Metals such as Pb, Cd, Cu, Zn, Ni, Cr and other heavy metals are rare earth metals. The metals have effect on both biological oxygen demand (BOD), and chemical oxygen demand (COD), of microorganisms in dump sites and landfills. Heavy metals escape from a landfill or dump site in solution form through leachate or run off that is not successfully captured by the leachate collection system (Aucott, 2008).

2.3 Dump sites in Kenya

It was established by a study entitled, summary of management practices of solid waste disposal sites in African urban and rural municipalities, that most countries in Africa practice open dumping method. There are no landfills in Kenya. The old Nakuru town landfill was on the shores of Lake Nakuru and was abandoned without proper sealing. Heavy metals leached into the lake, and the wild animals such as deer that graze the site have symptoms of lead poisoning. Further, the water quality testing station and an education centre were constructed on the old dump (Hutchinson *et al*, 1987). Inappropriate land use for contaminated area, the old Nakuru town dump, is an illustration of how difficult landfill sites could be managed.

Dandora dump site, is the legal one serving the Nairobi City. Other dump sites have no identity and they serve in various regions in the country.

A study on MSW in the City of Nairobi indicated the following waste production statistics (Kaluli *et al*., 2011): hotels (6.79kg/day), other business-related (1.39kg/day), high income

households (0.65kg/day), middle income household (0.60kg/day), slum dwellers (0.55kg/day), markets (2.43kg/day) and road maintenance (48.30kg/day) in Table 2.

Table 2: Sources and statistics of generated waste in the City of Nairobi (Source: Kaluli *et al*, 2011)

Source of waste	Amount (in kg/day)	Density	CV (kcal/ kg)
Restaurants	6.79	0.28	1630
Other commercial	1.39	0.26	1692
High income household	0.65	0.30	1233
Middle income household	0.60	0.26	1349
Low income household	0.55	0.28	630
Markets	2.43	0.38	1427
Road sweepings	48.30 per kM	0.23	n/a
Average		0.28	1032

Kaluli's (2011) study noticed the difference between low and higher income households.

Table 3, indicates MSW which was to be produced in the City of Nairobi in the year 2011. Shops and restaurants (94000 kg/day), houses (1285000 kg/day), markets (82000 kg/day) and road sweepings (69000 kg/day).The oil industry estimated 27,000 tonnes of oil waste which were produced from motor vehicles. About 6,000 tonnes were recycled and more was used as fuel (Kaluli *et al*, 2011).

Table 3: Projected MSW in the City of Nairobi (Source: Kaluli *et al* 2011)

Shops and restaurants	94000 kg /day
Houses	1285000 kg/day
Markets	82000 kg/day
Road sweepings	69000 kg/day

Table 4 shows components of MSW in the City of Nairobi. Food, paper, textile/clothing, plastic, grass/wood, leather, rubber, glass, cans/tins, other metals and other materials constituted MSW. It was noticed that most beverages were sold in returnable bottles which accounted for the low proportion of glass and cans/tins. In many MSW samples, the proportion of dust and fines (ash) was substantially greater than that indicated in the analysis, which was treated with caution (Kaluli *et al,* 2011).

Table 4: Waste composition of MSW in the City of Nairobi (Source: Kaluli *et al*, 2011)

Component	Average %	High income %	Low income %
Food	51.5	50	57
Paper	17.3	17	16
Textile	2.7	3	2
Plastic	11.8	14	12
Grass /wood	6.7	8	2
Leather	0.9	1	1
Rubber	1.5	1	2
Glass	2.3	2	2
Cans/tins	1.7	2	1
Other metal	0.9	1	0
Other materials	2.7	7	4

Table 5 Shows percentage composition of specific constituents of MSW in the City of Nairobi. Substances considered were; moisture, ash, substances that could burn, carbon, hydrogen, nitrogen, sulphur, chlorine and oxygen (Kaluli *et al,* 2011).

Table 5: Percentage composition of specific constituents of MSW in the City of Nairobi (Source: Kaluli *et al* 2011)

Substance	Percentage (%)
Moisture	64.2
Ash	8.9
Combustible	26.8
Carbon	49.33
Hydrogen	5.45
Nitrogen	1.22
Sulphur	0.14
Chlorine	0.21
Oxygen	43.75

Dumpsite currently located along Kisumu-Nairobi road in Kisumu was to be relocated to along Kisumu-Bondo road, but residents resisted. They were told that the dumpsite was to be a sanitary landfill (Kavila, 2011). In the City of Eldoret, most waste is incinerated. Mwakirunge landfill in the City of Mombasa is located along old Nandi road (Kaluli *et al*, 2011). According to National Environmental Management Authority (NEMA), Mombasa is the first City in Kenya to have a modern landfill.

2.4 Methane formation and characteristics

Methane has a boiling point of -161^0 C (-257.8^0 F) at a pressure of one atmosphere (760 mmHg), according to NIST chemistry web book (2012). Methane is combustible over a very narrow range of concentrations (5-15 %) in air. A 5 % level of methane in air is referred to as the lower explosive limit, (LEL) and the 15 % level is the upper explosive limit, (UEL). A combustible

level of methane can be ignited by a weak spark (electrical, frictional, or static), which generates very high temperature for a very short time. The minimum spark energy needed for methane ignition is only 0.30 mJ (Kuchta, 1985). A combustible level of methane can also be ignited by a hot surface or an open flame (Lide, 1996). There is therefore need for emitted methane by degrading solid wastes to be trapped and be used as clean fuel in the country. Unexpected and unexplained flames in some estates may be minimized or eradicated if explosive methane is not allowed in air.

High levels of methane is expected from dump sites and landfills due to biological and chemical reaction taking place (Chandler, 2008).

Equations for some reactions that lead to methane formation from various substrates:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \hspace{4cm} (2)$$

$$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O \hspace{3cm} (3)$$

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \hspace{3.5cm} (4)$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \hspace{3cm} (5)$$

$$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O \hspace{2cm} (6)$$

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2 \hspace{3.5cm} (7)$$

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O \hspace{3cm} (8)$$

$$4CH_3NH_3^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+ \hspace{2cm} (9)$$

$$2(CH_3)_2NH_2 + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_4^+ \hspace{1.5cm} (10)$$

$$2(CH_3)_2NCH_2CH_3H + 2H_2O \rightarrow 3CH_4 + CO_2 + 2\ H_3NCH_2CH_3 \qquad (11)$$

$$4(CH_3)_3NH^- + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_4^+ \qquad (12)$$
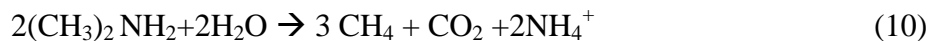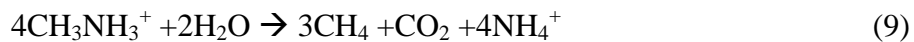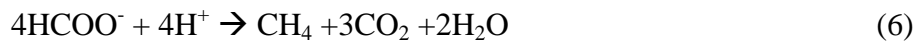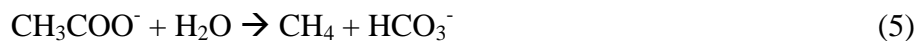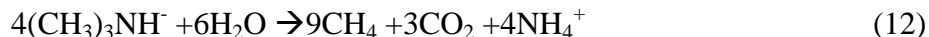
Contaminated air is found where solid and liquid wastes are disposed, in landfills and dump sites.

Methane produces more energy per mass unit (55.7kJ/g) than other large hydrocarbons. It produces little carbon dioxide per unit heat produced compared to other hydrocarbon fuels. Methane as a fuel does not produce smoke unlike fossil fuels such as kerosene, petrol and diesel (Clay, 2008).

2.5 Leachate

Leachate is generated as a result of interaction of solid waste and water (Townsend *et al*, 1998). Leachate may contain dissolved or hanging substances connected with home and other wastes management of in the dump site or landfill, and many by-products of chemical and natural reactions (Kostova, 2006). Leachate from MSW landfills and dump sites have different pH values, organic and inorganic matter concentrations and moisture as a result of the biological activity occurring when the solid waste degrades (Townsend *et al*, 1998). Leachate from young landfills constitute both high dissolved solids content as well as high concentration of organic matter compared to domestic waste water (Hurst *et al* 2005). Leachate also may contain some hazardous components found in waste flow (Kostova, 2006).

The class of organic compounds found at highest concentration in leachates is generally volatile organic acids (VOAs) produced during the decomposition of lipids, proteins, and carbohydrates (Schultz and Kjeldsen, 1986). Organic contaminants of leachate are primarily soluble refuse

components or decomposition products of biodegradable fractions of waste (Ogundiran and Afolabi, 2008). Organic compounds detected in MSW landfill leachates or contaminated ground water plumes originating from landfills include organic acids, ketones, aromatic compounds, chlorinated aromatic compounds, ethers, phthalates, halogenated aliphatic compounds, alcohols, amino aromatic compounds, nitro-aromatic compounds, phenols, heterocyclic compounds, pesticides, sulphur substituted aromatic compounds, poly-aromatic hydrocarbons, poly-chlorinated bi-phenyls and Organo-Phosphates (Albaiges and Ventura, 1986).

2.6 Inorganic pollutants

Other environmental pollutants found in the leachate are mainly metal salts, which originate from different anionic and cationic constituents of leachates (Mckay, 1996). Common heavy metals found in dump site and landfill leachates include zinc (Zn), copper (Cu), cadmium (Cd), lead (Pb), nickel (Ni) and chromium (Cr) (Lu *et al.,* 1985; Ogundiran *et al.,* 2007).

2.6.1 Zinc

Effects of heavy metals to human health are as follows: Too little zinc (below 0.3 mg/kg/day) causes loss of appetite, decreased sense of taste and smell, sluggish healing of skin injury. Zinc shortage can cause birth abnormalities (Wayne, 2010). Too much zinc in the body can cause stomach cramps, skin irritation, vomiting, nausea and anaemia. Very high levels of zinc can harm pancreas, cause arteriosclerosis and disturb the protein metabolism. long exposure to zinc chloride can cause respiratory disorders. Presence of zinc negatively influences the activity of microorganisms and earthworms. This slows down breakdown of organic matter, which lowers the level of methane to be generated (Wayne, 2010).

2.6.2 Copper

Long term contact with Cu can cause irritation of the nose, mouth and eyes and it causes headache, stomach aches, dizziness, vomiting and diarrhoea. Effects of copper are manifested at fairly low concentrations (Baun, 2004). Copper also negatively influences the activity of microorganisms. This slows down decomposition of organic matter, hence lowers level of methane to be produced. Copper absorption is depressed when zinc is given in high excess over copper, i.e. 1mg/kg copper and 5mg/kg zinc or up to 36mg/kg copper together with 180mg/kg zinc (Wayne, 2010).

2.6.3 Cadmium

Cadmium is one of the most poisonous elements which may be released to in the atmosphere. It is toxic to kidney, can cause bone demineralization as a result of renal dysfunction, and also cancer (Indian, 2008; Benard, 2008). Breathing of cadmium- polluted air can cause breathing problems, lung diseases and pneumonia (Hutchinson and Meema, 1987). Cd-contaminated food causes acute gastrointestinal effects. Low dosages of cadmium cause ovarian progesterone biosynthesis, while high dosages inhibit it (Godt, 2006).

2.6.4 Nickel

Nickel is deposited in kidneys, lungs, liver, heart and testes symptoms nickel poisoning include; headache, vertigo, nausea, vomiting, irritability and insomnia (Das *et al.,* 2008).

2.6.5 Lead

Lead accumulates in bone, kidney and liver. It has gastrointestinal absorption of 10 % and biological half-life of about 20 years. Higher levels of lead reduce synthesis of haemoglobin and causes anaemia. It also affects nervous system and impairs renal system (Hutchinson and Meema, 1987).

2.6.6 Chromium

Chromium can cause allergic reactions such as skin rash, nose irritations and nose bleeds, upset stomach and ulcers, weakened immune systems, kidney and liver damage and respiratory problems. Chromium ends up in air through coal combustion and in soils through waste disposal (Baun, 2004).

CHAPTER THREE

METHODOLOGY

3.0 Study area

Dandora dumpsite was the study area. The dumpsite has irregular shape (Figure 2), with an area of about 265,000 m^2. It lies between latitude $1^0 15.108'$ S to $1^0 14.640'$ S and longitude $35^0 53.704'$ E to $36^0 54.033'$ E. It is an open dumpsite surrounded by Dandora, Kariobangi and Luckysummer Estates (Figure 1).

3.1 Methane

3.1.1 Chemicals

Chemicals used were nitrogen gas (by nitrogen generator 2081 HC, ILRI), hydrogen gas (by hydrogen generator LNI schmildlin SA 18040, ILRI) and methane standard (comprising of 401.7 ppm CO_2, 4020 ppm N_2O and 4.282 ppm CH_4, which translated to 0.097% methane). The purity of methane was 99.9%. Manufacturer of the gases was Air liquide, UK.

3.1.2 Instruments and sample points

Instruments used were head space chambers (Figure 13, appendix B), SRI 8610C Gas Chromatograph machine (manual injection machine with FID column supelco hayesep D chromatographic column, 2.2mm long and diameter 1.0 mm). Single level standard calibration was used. Carrier gases, N_2:H_2, for FID were 99.9 % pure.

There were twenty sampling points as shown in Figure 2.
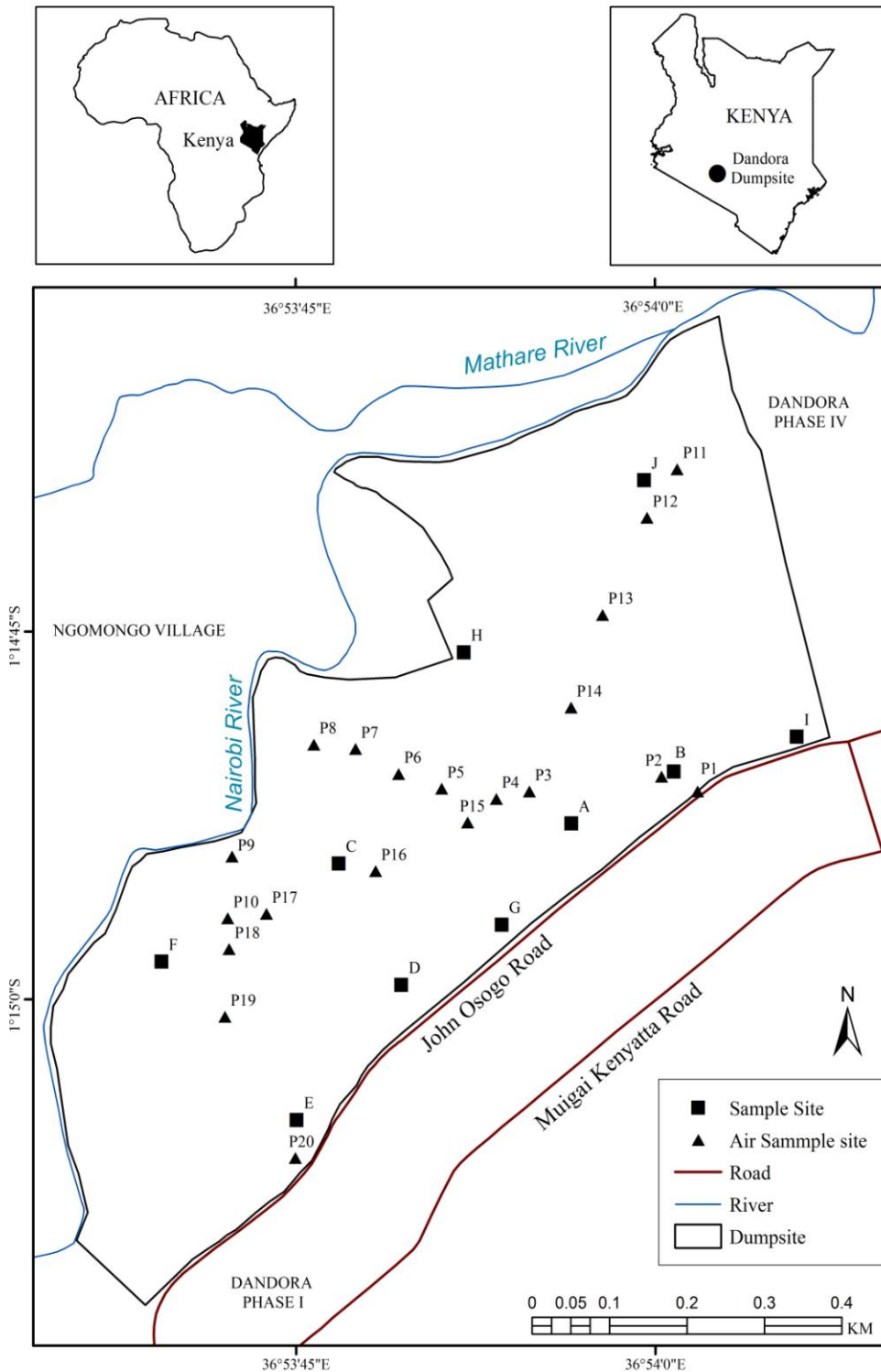
Figure 2: Map of Dandora dumpsite showing the sample sites for leachate and air sampling sites for methane.

The closed Chamber technique (Bruggemann *et al*, 2009) was used in collecting methane from the dumpsite. Flux measurement with dynamic chambers or flow-through chambers refers to a system where the headspace air of a chamber is constantly exchanged at a specific flow rate (Denmead, 2008).

3.1.3 Measuring methane emissions from Dandora dump site

Standard gas sampling by pressurized vials or syringe was done by injection of 20 ml gas volume in a 10 ml vial. Headspace gas was mixed in the syringe before sampling was to avoid pressure perturbation and/or excess dilution of gas in the chamber by entry of outside air through the vent tube (Hutchinson and Mosier, 1998). The resulting dilution was considered if the gas sampling volume to chamber volume ratio was >0.01. Quality control samples were taken as gas samples from a calibration standard to the field. The control sample was treated and stored in the same manner as other headspace gas samples (Rochette and Erickson-Hennel, 2008). Gas samples were analysed within 24-hours after sampling.

Sampling time was another critical issue. CH_4 fluxes change diurnally and seasonally when environmental conditions, such as temperature, soil moisture, groundwater level, and substrate supply vary. Sampling considered variation in time. For estimating cumulative seasonal CH_4 fluxes from rice paddies, Buenda et al, (1997) suggested that sampling at 06:00, 12:00 and 18:00 hour was sufficient to capture most of the diurnal variation observed throughout the growing season and that sampling was most important where fluxes were most variable, between flowering and harvest. The case of Dandora dumpsite CH_4 fluxes were measured after every seven minutes, starting with zero minutes (as soon as headspace chamber was installed), as in Tables 7 and 8 for the results. The sampling started at 9:00 to 17:20 hours. A total of 80 samples were collected from twenty sampling points.

3.1.4 Methane flux calculation

The CH_4 flux at the soil surface occurs simultaneously during microbial production and consumption process (Conen *et al*, 1998) as well as gas diffusion (e.g., thermo-osmosis), so that any major variation in the headspace gas concentrations could give feedback on diffusion gradients as well as soil processes and hence, net fluxes at the biosphere-atmosphere interface. Fluxes were calculated from the temporal change in gas levels in the chambers' headspace. The change could be linear or non-linear. Non-linearity resulted as the headspace CH_4 levels varied with time where by the slope between soil-air-CH_4 level and headspace concentration decreased. There was decreased flux either due to the diminishing gas-level gradient (Davidson *et al*, 2002) or because of stimulated microbial CH_4 uptake (for alkaline soil). For sites where the soils were net sinks for atmospheric CH_4, decreasing headspace CH_4 level reduced the diffusion flux of CH_4 into the soil, hence affected the rate of CH_4 uptake (Butterbach-Bahl *et al*, 2002).

The validity of using a linear approach for the calculation of CH_4 fluxes was tested using the goodness of fit R^2 values while comparing different calculation methods. It was clear that use of lin ear fits as bases of flux calculations resulted in an underestimation of real fluxes, so that the use of non-linear regression for temporal variation in headspace levels deviated from assumed linearity (Bloom *et al*, 2010).

Linear or non-linear regression estimated the gradient of headspace level variations over time. CH_4 fluxes from Dandora dumpsite were calculated using linear approach and tested by the goodness of fit R^2. Methane standard calibration curve, $Y = 0.0804x - 12.895$ equation (14)

Where Y was the level of methane (ppm) and x was the peak area. $R^2 = 0.9993$ for the curve.

Table 6: Rating of closed chamber measurements based on design of chambers, calculation of fluxes, quality control measures, and gas sampling strategy (Source: Shindell *et al*, 2009)

Chamber characteristics	Unit	Poor	Good	Recommendation
Type of chamber		Push-in		Base &chamber
Insulation		No	Yes	
Vent		No	Yes	
Pressurized sample (fixed volume containers only)		No	Yes	
Quality control sample		No	Yes	
Time zero sample		No	Yes	
Nonlinear model considered		No	Yes	
Zero slope tested		No	Yes	
Temperature corrections		No	Yes	
Pressure corrections		No	Yes	
Type of sample vial		Plastic syringe< glass syringe< other vials Extainers, Vacutainers, on side analysis		
Height of chamber (depend on type of	Cm	<10	10-40	Flexible height

vegetation)				
Chamber base insertion depth	Cm	<5	5-20	(depend on soil type, roots)
Area /perimeter ratio	Cm	<2.5	2.5-10	>10
Number of samples for calculating fluxes		1	4	>4
Duration of deployment	Min	>60	20-60	<20
Temporal resolution of measurement	days	>14	3-10	Sub daily
Duration of sample storage prior to analysis				
Plastic syringes	days	>2	1	<0.5
Glass syringes	days	>2	2	<1
Others	days	>30	5-30	<5

The rating was based on a detailed evaluation of the importance of each characteristic in the measurement error and on the authors' own judgment based on long-term experiments in closed chamber measurements (table modified following Rochette and Erickson Hannel, 2008)

Head space chambers were installed into the ground to trap generated gas at that point as in Figure 13, appendix B (Bruggemann, *et al*, 2009). Three head space chambers were installed at a distance of five metres from each other, in triangular set up, at Dandora dumpsite. Twenty cubic centimetres of air samples was removed from each of the three chambers using a needle fitted to syringe (Figure e). The samples were collected in a pool whose volume was 60 cm^3 from the

three head space chambers in same syringe (Figure f). A labelled vial was cleaned using 40 cm^3 of the collected sample while remaining amount, 20 cm^3, in the syringe was transferred into the vial. (Figure g, appendix B). Vials were placed in a box (Figure h) and transported to the laboratory at ILRI for analysis (Butterbach-Bahl *et al*, 2002). The samples were analysed within two days after collection.

The samples were removed from vials using a needle fitted onto syringe and injected into SRI 8610C Gas chromatograph machine. FID carrier gas was nitrogen/hydrogen (99.9 % pure), ECD make up gas CO_2:N_2 (5:95 v/v) was used. Software used was peak simple USB-7189. Flow rate was ECD 3m/s per 1.5ml FID (Butterbach-Bahl, *et al*, 2002).

3.2 Leachate

3.2.1 Sampling sites.

 Ten sampling trenches (in figure 2) marked as A, B, C, D, E, F, G, H, J and K were made about four metres from John Osogo road (Figure 2). The trenches were forty centimetres deep, forty centimetres wide and forty centimetres long, which gives leachate/0.064m^3.

Leachates were collected from the ten sampling sites for six months, from November 2012 to April 2013. About 50g leachate samples were scooped from each sampling site using a stainless steel shovel. The sample leachates were mixed well and placed in self-seal polythene bags. The bags were labelled and transferred into another labelled self-seal polythene bag for transport to the laboratory and kept in the freezer at Chiromo campus waiting for analysis. Samples collected in the months of November and December 2012, represented the short rains season. Samples collected in January and February 2013 were to represent sampling in the dry season. For long rainy season, samples were collected in March and April 2013.

3.2.2 Chemicals

Chemicals required for analysis of heavy metals in the leachate were: nitric acid 69 % manufactured and supplied by uni-chem® chemical reagents while the following standard stock solutions were of 99.9% purity and were obtained from British Drug House ltd, England. These were; copper (made by dissolving 1mg of pure copper metal in hot 20/80 nitric acid/water (v/v) per litre solution), nickel (from nickel sulphate batch number 29329. 1mg of the salt was dissolved in 1 litre of acidified water), cadmium (from cadmium chloride batch number 14057. 1 mg of the salt was dissolved in 1 litre of acidified water), lead (made by dissolving 1mg pure lead metal in hot 20/80 nitric acid/water (v/v) per litre solution), zinc (from zinc sulphate batch number 36092. 1 mg of the salt dissolved in 1 litre of acidified water), and chromium (from potassium dichromate salt. 1 mg of the salt was dissolved in 50/50 nitric acid/water (v/v) per litre solution). All stock solutions were 1000ppm. Acetylene (by Sigma-Aldride) and oxygen (by BOC, Kenya) were used for AAS analysis of copper, nickel, lead, cadmium and zinc. Nitrous oxide-acetylene gas (by BOC, Kenya and Sigma-Aldride) was used for the AAS analysis of chromium. The gases were of 99.9% purity.

3.2.3 Instruments

Instruments used were analytical balance (in the pesticide analytical chemistry laboratory, Chiromo campus), hot magnetic stirrer (34532, with heat control nob and stirrer nob), AAS machine (at Mines and Geology; Spectre AA.10, Varian 8061176) and Gallenkamp oven model OV-160 for drying glassware. Apparatus used were self-seal polythene bags, heavy duty gloves, measuring cylinder (10 ml), volumetric flask (50 ml), conical flasks (250 ml), beakers, filter funnel, stainless steel shovel, spatulas, plastic water tank (sky plast), filter papers (whatman cat no. 1001 125) and polypropylene bottles.

3.2.4 Pre-treatment and digestion of leachate

The leachates were transferred from polythene bags into acid washed beakers and then oven dried for 12 hours. Large undigested residues were removed, leaving fine particles. For analysis, 5.000 ± 0.001g of the leachate samples were weighed into labelled conical flasks. 20ml of concentrated nitric acid (69%) was measured using a measuring cylinder and poured drop by drop into the sample in the conical flask. The acid was added drop wise to prevent frothing. The samples were digested at a temperature of 105^0C for 30 minutes (Das *et al.,* 2008). The temperature of the hot magnetic stirrer was increased to 120^0C and the sample digested for one hour. One ml of hydrogen peroxide was added to the sample, which was then heated for 20 minutes at 105^0C [Hurst *et al*., 2005). The digests were then allowed to cool and filtered into a 50 ml volumetric flask, through double whatman (cat No. 1001 125) filter papers wetted using acid (10% v/v nitric acid).

Filter papers were used in place of glass wool or cotton wool because they were more efficient and no fine particles escaped into the filtrate. After filtering, the digests were made to volume using triply distilled water. The filtered digest were transferred and stored in pre conditioned polypropylene bottles ready for AAS analysis (Goldstein, 2003).

3.2.5 Quantitative analysis of heavy metal ions in the Leachate

This was done by atomic absorption spectrometer model spectr-AA.10 (Varian serial no. 8061176) which uses a hollow cathode lamp (current range of 3-10 mA) with wavelength range of (217-357.9) nm. The model was made up of the spectrophotometer, graphic printer, the gas control unit and the colour graphic cathode ray tube (CTR).

Parameters analysed were, Cu, Zn, Cr, Cd, Ni and Pb from the samples in three seasons.

3.3 Experimental bucket at Chiromo campus

An experimental bucket was set up at Chiromo campus to represent a landfill in November 2012. It measured 1.5 m by 1.0 m and was 1.5 m deep. A plastic water tank (sky plast, 210 L) was placed in a hole, then wet/dry wastes from cafeteria, which consisted mainly food and peels from tack shop were placed inside, waste papers from the Department of Chemistry were also added into the tank.

The plastic water tank was tightly closed using its cover. Materials for constructing landfill are usually bricks and clay lining at the bottom. This prevents methane from being absorbed by OH radical found in the soil to form mainly carbon dioxide and water (Chandler, 2008) as shown in equation (13)

$$CH_4 + 8OH \rightarrow CO_2 + 6H_2O \qquad (13)$$
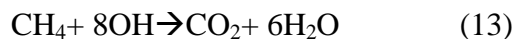
Plastic water tank was used as a representative of bricks and clay lining. The tank was also used because leachate was collected to quantify levels of heavy metals then compare with that from Dandora dumpsite. Experimental control bucket at Chiromo campus was close to the School of Physical Sciences and the School of Mathematics.

3.4 Data analysis and interpretation

Results of the analytes for both methane and the heavy metals were presented using bar graphs, the mean and standard deviation (excel). The data was handled using statistical package for social scientists (SPSS) using Pearson correlation coefficient and two way ANOVA.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Methane

Air in Dandora dumpsite was collected using head space chambers (37.3 cm long, 26.7 cm wide and 12 cm high) Figure d, a volume of about 0.012 m^3, at an interval of seven minutes for twenty one minutes per sample (Davidson, et al, 2002). There were twenty sampling points: P_1 (at $1^0$14.859'S, $36^0$54.033'E), P_2 (at $1^0$14.849'S, $36^0$53.008'E), P_3 (at $1^0$14.859'S, $36^0$53.916'E), P_4 (at $1^0$14.864'S, $36^0$53.893'E), P_5 (at $1^0$14.857'S, $36^0$53.855'E), P_6 (at $1^0$14.847'S, $36^0$53.825'E), P_7 (at $1^0$14.830'S, $36^0$53.795'E), P_8 (at $1^0$14.827'S, $36^0$53.766'E), P_9 (at $1^0$14.903'S, $36^0$53.709'E), P_{10} (at $1^0$14.945'S, $36^0$53.706'E), P_{11} (at $1^0$14.640'S, $36^0$54.019'E), P_{12} (at $1^0$14.673'S, $36^0$53.998'E), P_{13} (at $1^0$14.739'S, $36^0$53.967'E), P_{14} (at $1^0$14.802'S, $36^0$53.945'E), P_{15} (at $1^0$14.880'S, $36^0$53.873'E), P_{16} (at $1^0$14.913'S, $36^0$53.809'E), P_{17} (at $1^0$14.942'S, $36^0$53.733'E), P_{18} (at $1^0$14.966'S, $36^0$53.707'E), P_{19} (at $1^0$15.012'S, $36^0$53.704'E) and P_{20} (at $1^0$15.108'S, $36^0$53.753'E). The samples were collected between 9:00 and 17:20 hour local time in Kenya. Levels of methane were obtained at 0, 7, 14 and 21 minutes interval while flux was after twenty one minutes.

The analysis of methane from the Dandora dumpsite gave the following results (Tables 7 and 8). The concentration or level of methane was given in parts per million (ppm). Methane flux is a flow. It is change in concentration of methane per square metre per unit time (hours), and was calculated using the formula in equation (14).

Table 7: Concentration or level and fluxes of methane from Dandora dumpsite in week 1

Sampling point	Duration (minutes)	CH_4 Concentration (ppm)	CH_4 fluxes ($\mu gCm^{-2}h^{-1}$)	Sampling point	Duration (minutes)	CH_4 Concentration (ppm)	CH_4 fluxes ($\mu gCm^{-2}h^{-1}$)
P_1	0	196.86		P_6	0	27.30	
	7	203.70			7	79.54	
	14	277.07			14	113.01	
	21	280.65	1744.03		21	174.07	2544.47
P_2	0	244.29		P_7	0	BDL	
	7	1634.41			7	BDL	
	14	1309.24			14	BDL	
	21	1685.49	21473.75		21	BDL	0
P_3	0	75.58		P_8	0	BDL	
	7	228.64			7	BDL	
	14	94.51			14	BDL	
	21	74.73	0		21	BDL	65.51
P_4	0	BDL		P_9	0	1953.52	
	7	36.61			7	2411.31	
	14	15.54			14	2279.82	
	21	25.47	319.21		21	1343.64	0
P_5	0	BDL		P_{10}	0	987.69	
	7	BDL			7	1666.63	
	14	BDL			14	618.73	
	21	BDL	57.72		21	BDL	0

Table 8: Concentration or level and fluxes of methane from Dandora dumpsite in week 2

Sampling point	Duration (minutes)	CH_4 Concentration (ppm)	CH_4 fluxes ($\mu gCm^{-2}h^{-1}$)	Sampling point	Duration (minutes)	CH_4 Concentration (ppm)	CH_4 fluxes ($\mu gCm^{-2}h^{-1}$)
P_{11}	0	730.42		P_{16}	0	BDL	
	7	2184.90			7	BDL	
	14	2700.07			14	BDL	
	21	2829.56	36587.28		21	BDL	0
P_{12}	0	544.17		P_{17}	0	1242.80	
	7	1630.19			7	817.19	
	14	1890.17			14	795.32	
	21	3490.66	48869.05		21	3779.87	40758.99
P_{13}	0	1423.12		P_{18}	0	649.65	
	7	2662.92			7	648.54	
	14	658.74			14	966.40	
	21	2742.10	10487.33		21	1411.26	13977.94
P_{14}	0	80.96		P_{19}	0	114.16	
	7	327.25			7	250.66	
	14	277.27			14	154.46	
	21	319.52	3575.12		21	166.07	319.67
P_{15}	0	BDL		P_{20}	0	1031.30	
	7	BDL			7	436.06	
	14	BDL			14	2978.57	
	21	BDL	0		21	1781.25	25737.57

Methane standard calibration curve, $Y = 0.0804x - 12.895$ equation (14)

Where Y was the level of methane (ppm) and x was the peak area. $R^2 = 0.9993$ for the curve.

From the concentration difference of CH_4 in the incoming air and in the outflowing air, the gas exchange rate, and the area covered by the chamber, the methane flux was calculated:

The slope was used in the following formula to calculate the flux rate:

Formula for calculating CH_4 Flux (15)

$$\text{Flux } (\mu g \text{ Cm}^{-2} \text{ h}^{-1}) = \frac{\text{Chamber volume } (m^3) * \text{ Mole weight } (g \text{ mol}^{-1}) * \text{slope } (ppmv \text{ min}^{-1}) * 60 * 10^6}{\text{Chamber area } (m^2) * \text{Mole volume of } CH_4 \ (m^3 \text{ mol}^{-1})}$$

60 and 10^6 were constants used for converting minutes into hours and grams into micrograms, respectively (Buendia, *et al*, 1997). Another parameter used for interpretation of flux data was site characteristics (bear dry/wet ground or fresh waste or ground covered by vegetation) for all chamber positions.

Methane concentration was highest at point P_{12}, with flux of 48869.05 µg C m^{-2} h^{-1}, followed by point P_{17}, with flux of 40758.99 µg C m^{-2} h^{-1}. Five points P_5, P_7, P_8, P_{15} and P_{16} had below detectable level (BDL) concentration. At point P_4, the concentration of methane was BDL ($0 \geq$ level of CH_4) at time T_1 (0 minutes), when the headspace chamber had just been installed in the ground. There was flow of methane at points P_5 and P_8 though the level was BDL ($0 \geq$ level of CH_4) due to probably the presence of OH in the soil (alkaline soil).

Sites P_3, P_9 and P_{10} had zero flux, yet methane levels were recorded because of probably the sites were characterised by methanogen conditions. There was a lot of vegetation and wetness at these

sites. Methane produced remains in the headspace without flowing. At P_9, the level remained higher even after twenty one minute because of the grass on the site. The level of the gas at P_{10} was highest (1666.63 ppm) at seven minute after which it reduced to BDL ($0 \geq$ level of CH_4) due to the presence of OH.

At points P_7, P_{15} and P_{16}, the level was BDL ($0 \geq$ level of CH_4) as well as zero flux because they were bear dry ground.

The sites where the soils are net sinks for atmospheric methane (contain OH, which reacts with methane to form water as in equation 13), decreasing headspace CH_4 concentration, hence reducing the diffusion flux of CH_4 into the soil. Morning and afternoon timings did not affect the concentration or flux of methane.

Comparing methane emission from Dandora dumpsite with estimates of global methane flux from mud volcanoes (MVs), 0.08-1.4 µg C m^{-2} h^{-1} were from Kopf in the year 2002, 3.3 µg C m^{-2} h^{-1} were from Milkov in the year 2003 and 0.2-12.3 µg C m^{-2} h^{-1} were from Kopf in the year 2003 to the atmosphere. The dump site emits   than the MVs (Table 1). The lowest CH_4 flux was 57.72 µg C m^{-2} h^{-1} in Dandora dumpsite lower is within range of flux (0.2-123 µg C m^{-2} h^{-1}) to atmosphere and oceans from MVs.

4.2 Heavy Metals

4.2.1 Lead

Lead metal ions in leachate were detected in the concentration range of BDL ($0 \geq$ level of metal ions) to 7.62±0.62 ppm. The highest concentration was recorded at site D during the month of December, this was followed by site G that had a concentration of 6.39±0.39 ppm (Table 5) in

the Appendix A. Figure 3 shows the concentration levels of lead metal ions from all the sites. Months of December and November showed higher mean levels (4.65 ppm and 4.57 ppm) of lead as compared to the other four months.
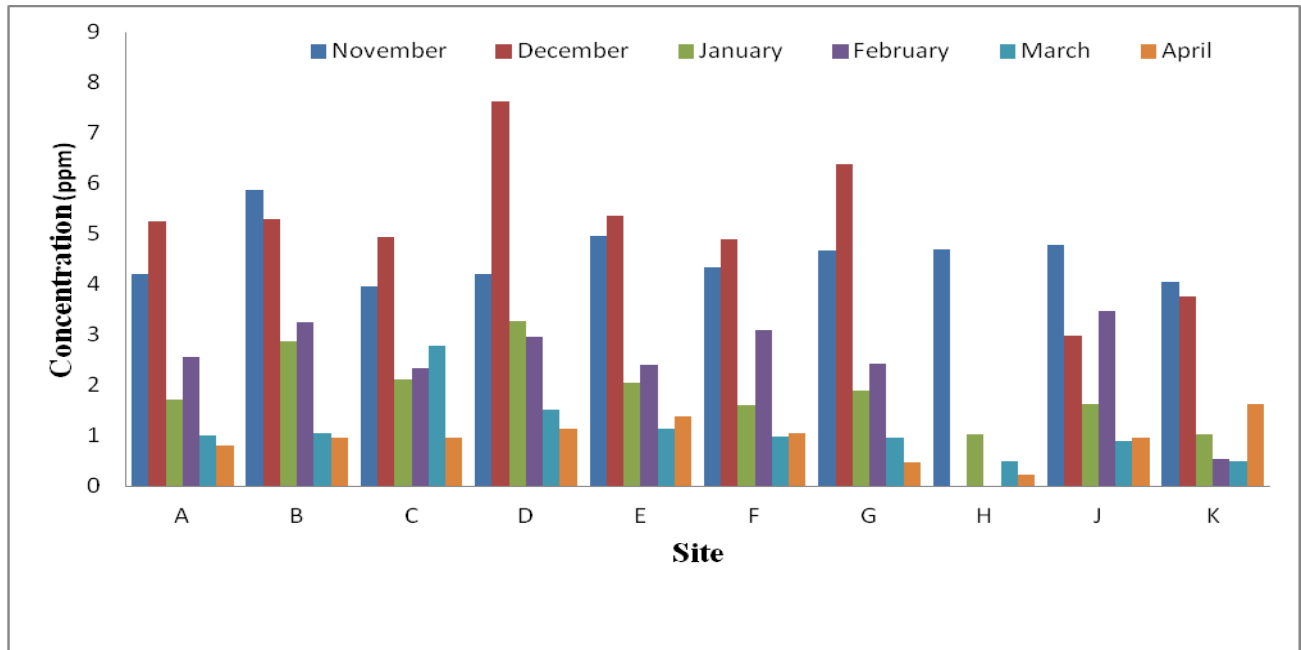
Figure 3: Level of Lead metal ions in leachate from Dandora dumpsite

This could have been because of minimal leaching into the ground since the trenches were about one foot deep, and the rains were not continuous during this season. Mean levels (1.13 ppm and 0.96 ppm) of lead were lower in March and April as compared to other four months. This could have been due to run-off of surface water as it rained. Table   below gives levels of heavy metals in drinking water.

Table 9: Maximum admissible limits set by international organisations.

Table 1. Drinking water contaminants and maximum admissible limit set by different national and international organizations. (For health risk and aesthetic value)

| | EC (µS/cm) | TDS (mg/L) | pH | Turbidity (NTU) | Heavy Metals (µg/L) | | | | | | | | | |
					As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
USEPA, 2008	NM*	500	6.5 - 8.5	0.5- 1	10	5	100	100	1300	300	50	100	15	5000
EU, 1998	2500	NM	6.5 – 9.5	NM	10	5	NM	50	2000	200	50	20	10	NM
WHO, 2008	250	NGL**	NGL**	NGL^a	10	3	NM	50	2000	NGL***	400	70	10	NGL**
Iranian, 1997	NM	500	6.5 - 8.5	25	50	10	NM	50	1000	1000	500	NM	50	NM
Australian, 1996	NM	500^c	6.5 - 8.5	5.0	7	2	NM	50^c	2000	300^c	500	20	10	3000^b
Indian, 2005	NG	1500	6.5 – 9.2	10	50	10	NM	50^c	1500	300	100	20	100	5000
New Zealand, 2008	NM	1000	7.0 – 8.5	2.5	10	4	1000	50	2000	200	400	80	10	1500

*NM = Not mentioned,

** NGL= No Guideline, because it occurs in drinking-water at concentrations well below those at which toxic effects may occur,

*** No Guideline, because it is not of health concern at concentrations normally observed in drinking water, but may affect the acceptability of water at concentration above 300 µg/L,

NGL^a No Guideline but desirable less than 5 NTU,

^{b} based on quality (Aesthetic) not safety (Health risk),

^{c} Chromium as Cr^{+6} not total Cr.

Major sources of lead poisoning include lead in paint, unleaded petrol and diesel, water pipes, food and lead used in tableware such as ceramic dishes, bean pots, toys, decorate drinking glasses. Table 15, in appendix A shows drinking water contaminants and maximum admissible limit set by different national and international organisations.

Maximum limit for lead is 0.015 ppm (15 µg/L), in drinking water which is much lower than the concentration detected in the leachate. Table 16, which gives guideline on the specification limits for residues of metal catalyst sets a range of 0.10 ppm (100 µg/L) to 10 ppm for permitted daily exposure (PDE) of lead metal (European Medicines Agency, 2007).Upper limit is slightly above the highest (7.00 ppm) concentration detected in the leachate while lower limit is below the lowest level (0.96 ppm).

Table 10: Class exposure and concentration limits for individual metal catalyst and metal reagents.

	Oral exposure		Parental exposure	
Classification	PDE (μg/day)	Concentration (ppm)	PDE	Concentration (ppm)
Class 1A: Pt, Pd	100	10	10[*]	1[*]
Class 1B: Ir, Rh, Ru, Os	100[**]	10[**]	10[**]	1[**]
Class C: Mo, Ni, Cr, metals of significance safety concern.	300	30	30[*]	3[*]
Class 2: Cu, Mn metals with low safety concentration	2500	250	250	25
Class 3: Fe, Zn metals with minimal safety concentration	13000	1300	1300	130

[*] Specific limits have been set for inhalation exposure to Pt, Cr and Ni.

[**]Subclass limit the total amount of listed metals should not exceed the indicated limit.

4.2.2 Copper

The copper metal ions in leachate were detected in the concentration range of BDL ($0 \geq$ level of metal ions) to 6.25 ± 0.17ppm. The highest concentration was recorded at site J during the month of February this was followed by site C with concentration of 3.18 ± 0.17 ppm in the month of November (Table 6). Figure 4 shows the concentration of copper metal ions in all the sites. The

months of November and February showed higher levels (1.61 ppm and 1.32 ppm) of copper than the other four months.
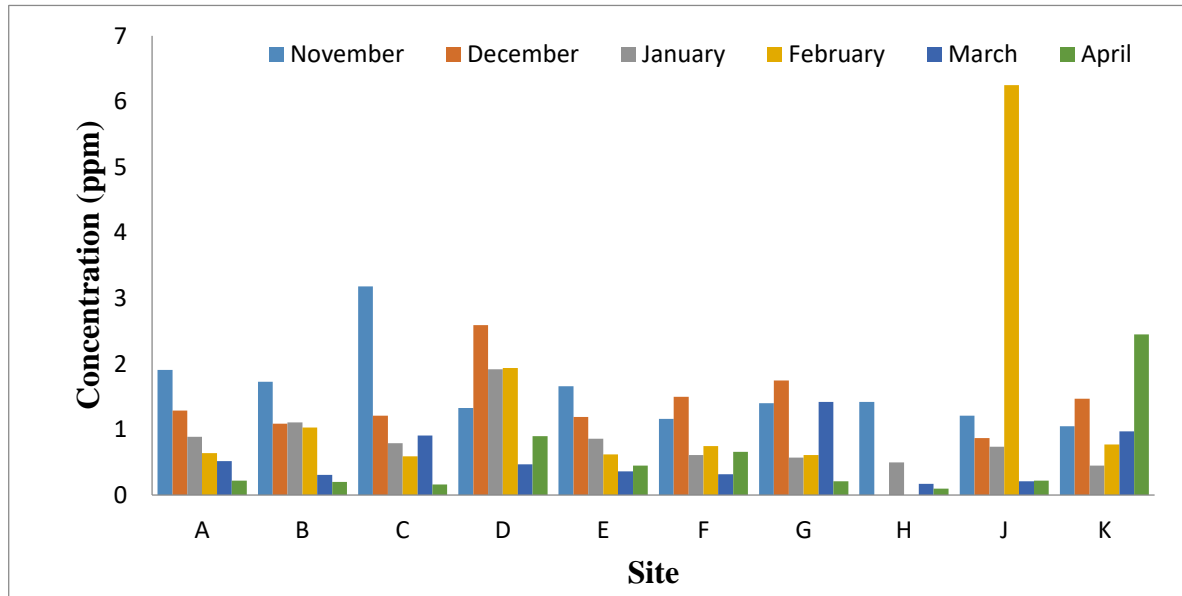

Figure 4: Levels of copper metal ions in leachates from Dandora dumpsite

The months of November and February showed higher total levels (16.05 ppm and 13.2 ppm) of copper than the other four months. Sources of copper to environment include copper pipes, copper wires for connections, brass and bronze faucets (USEPA, 1987). The months of March and April showed lower total levels (5.66 ppm and 5.57 ppm) of copper as compared to other four, but higher than concentration level (1.3mg/L or 1.3 ppm) set by U.S.E.P.A. This may be due to use of copper pipes to replace lead, bronze and brass faucets.

Some of the uses of copper are: soldering instruments, making coins and ornaments, making electrical wires and contacts in switches, plugs and sockets, making brass, bronze and German silver which have diverse uses. Since all MSW is disposed at Dandora dumpsite, we expect high level of the metal, considering the many uses of copper.

4.2.3 Zinc

The zinc metal ions in leachate were detected in the concentration range of BDL (0≥level of metal ions) to 64.80±0.22 ppm. The highest concentration was recorded at site D during the month of December; this was followed by site G with concentration of 51.40±0.40 ppm in the months of November (Table 7). Figure 5 shows the concentration of Zinc metal ions in all the sites. The months of December and November showed higher mean levels (34.06 ppm and 35.84 ppm) of zinc than the other four months.
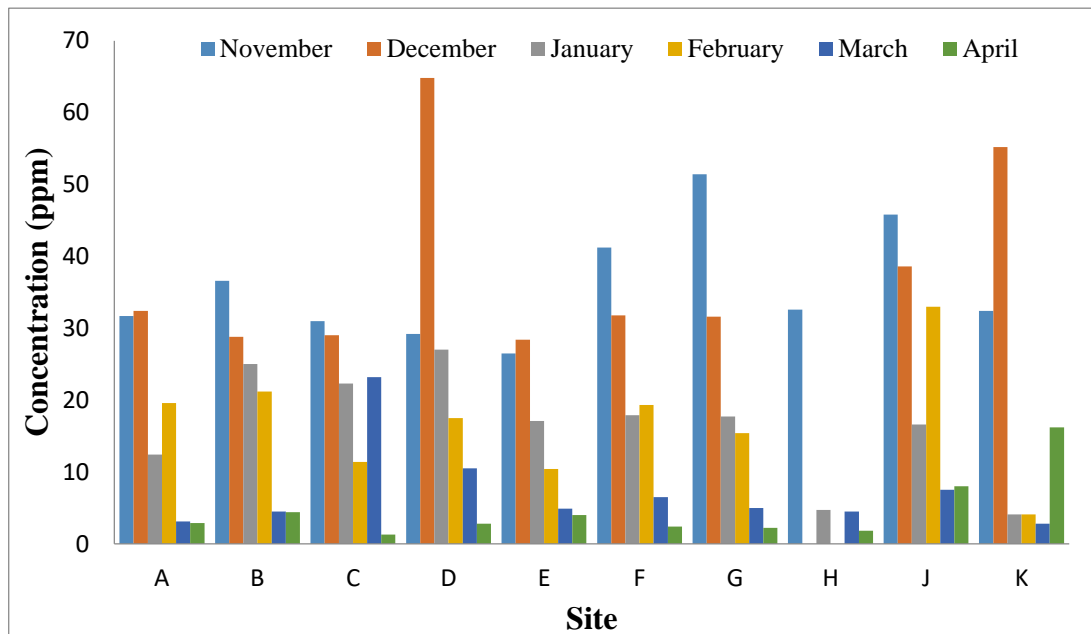

Figure 5: Levels of Zinc metal ions in leachates from Dandora dumpsite

The months of December and November showed high total levels (340.6 ppm and 358.4 ppm) of zinc than the other four months. The levels (72.5 ppm and 46 ppm) are lower for the months of March and April, but higher than maximum admissible limit which is 5mg/L (or 5 ppm). Zinc is found naturally in environment as the salt, zinc sulphide. The salts are widely used in industry. Zinc oxide is used to make white paints and ceramics, in producing rubber. Many uses of zinc and its salts make it available in high concentration in the environment and specifically in waste.

4.2.4 Nickel

The nickel metal ions in leachate were detected in the concentration range of 0.03±0.02 ppm to 1.25±0.25 ppm. The highest concentration was recorded at site A during the month of November, followed by site B with concentration of 0.89±0.07 ppm (Table 8). Figure 6 shows the mean concentration of Nickel metal ions in all the sites. The months of November and December showed higher mean levels (0.79 ppm and 0.49 ppm) of nickel than the other four months.

Figure 6: Levels of Nickel metal ions in leachates from Dandora dumpsite

The months of November and December showed higher total mean levels (7.92 ppm and 4.89 ppm) of nickel than the other four months. Maximum admissible limit set by USEPA (2008) for nickel is 100 µg /L (0.1 ppm) which is much lower than the level found in the leachate.

4.2.5 Chromium

The Chromium metal ions in leachate were detected in the concentration range of 0.08±0.07 ppm to 2.97±0.97 ppm. The highest concentration was recorded at site F during the month of

November; this was followed by site G with concentration of 2.25±0.25 ppm (Table 9). Figure 7 shows the mean concentration level of Chromium metal ions in all the sites. The months of November and December showed higher mean levels (1.43 ppm and 1.07 ppm) of chromium metal ions than the other four months.
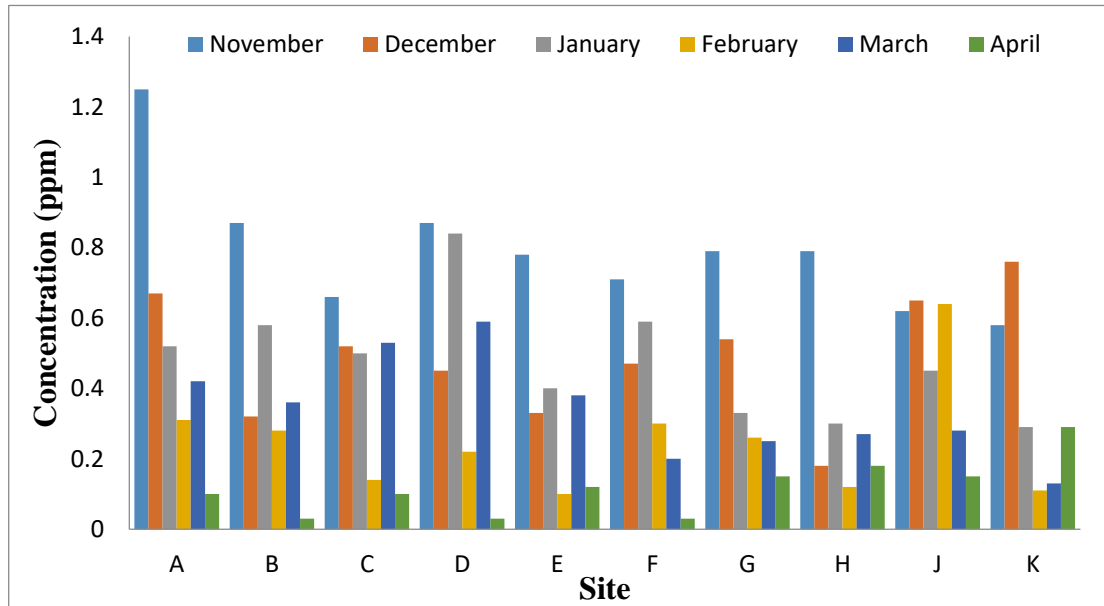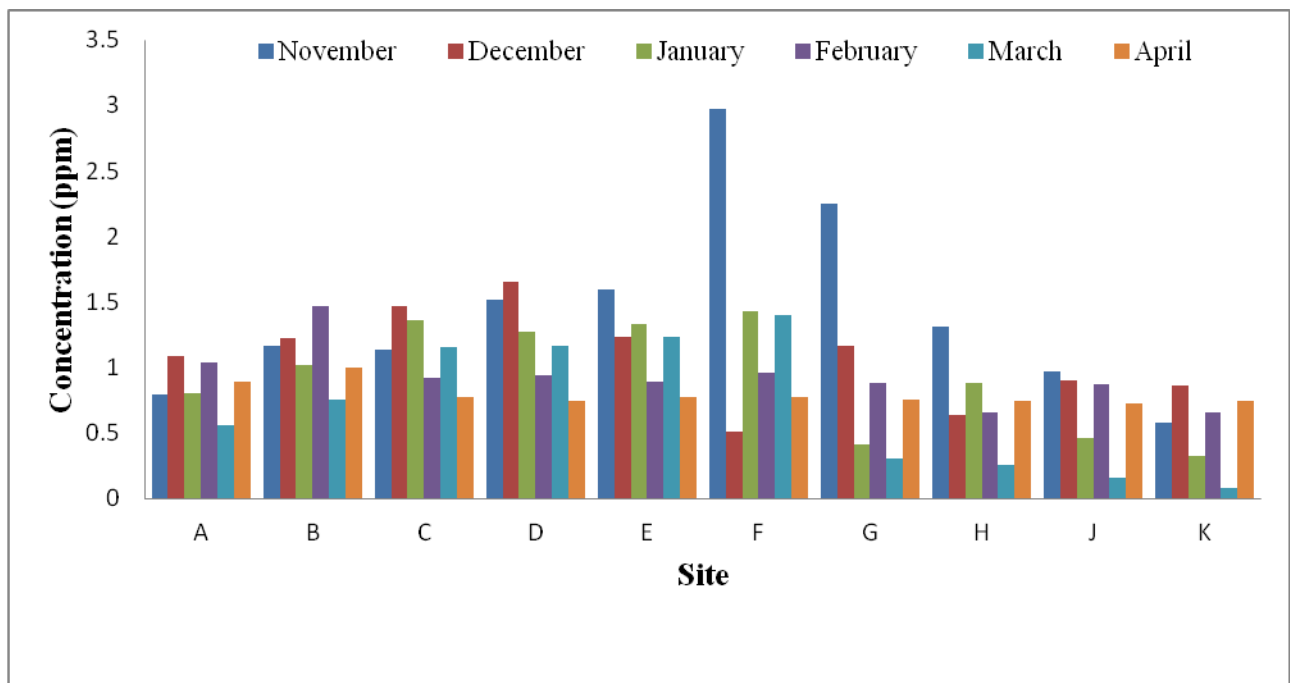

Figure 7: Levels of Chromium metal ions in leachates from Dandora dumpsite

The months of November and December showed higher total mean levels (14.27 ppm and 10.73 ppm) of chromium metal ions than the other four months. This level is very high compared to the maximum admissible limit by USEPA (2008) which is 0.1 ppm (100 μg /L).

4.2.6 Cadmium

The Cadmium metal ions in leachate were detected in the concentration range of BDL ($0 \geq$ level of metal ions) to 0.07 ± 0.06 ppm. The highest concentration was recorded at site A during the month of December; this was followed by site B with concentration 0.01 ± 0.006 ppm. The metal was not detected in most of the sites (Table 10). Figure 8 shows the mean concentration of cadmium metal ions in all the sites. Cadmium was only detected during the month of December with mean concentration 0.009 ± 0.007 ppm.
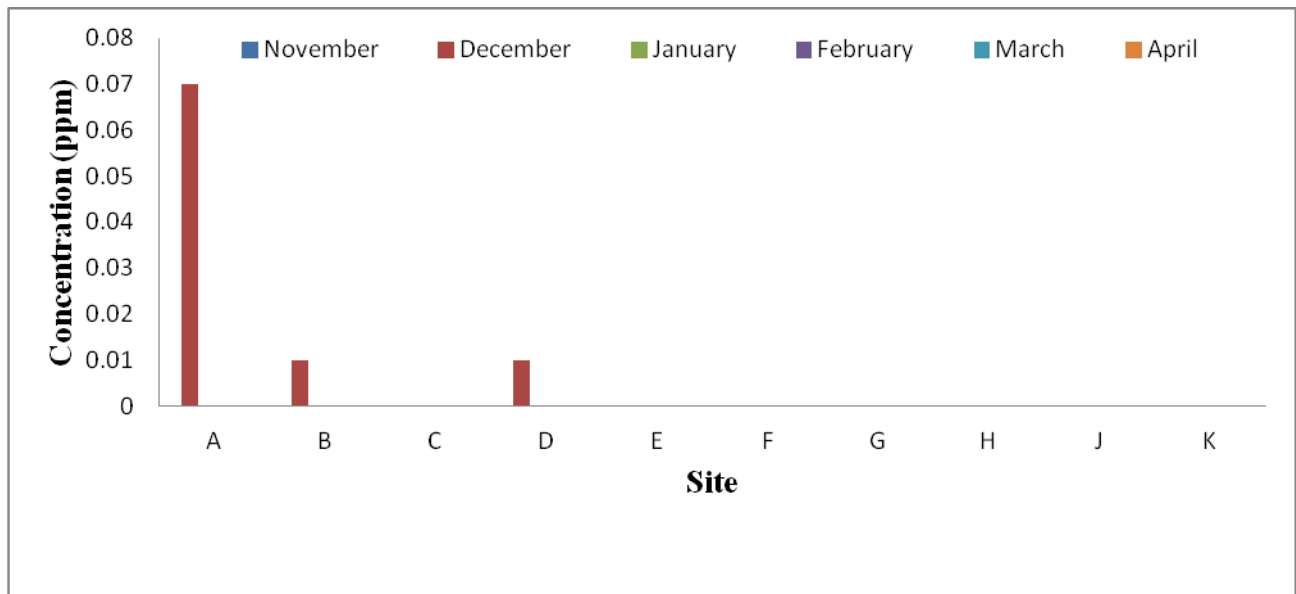
Figure 8: levels of Cadmium metal ions in leachates from Dandora dumpsite

Cadmium was only detected during the month of December with total mean concentration 0.09 ± 0.073 ppm. It was detected in only three sites, A, B and D. The concentration is higher than the maximum admissible limit set by USEPA (2008) which is 5µg /L (0.05 ppm). This could have been because Cd is emitted into the air from burning of fossil fuels, burning of waste and burning of Zn, Pb and Cu (Calabrese and Kenyon, 1991). Smoking is another source of cadmium exposure. Cadmium concentration in smoker's body is twice as much as do non-smokers. Cd phosphate fertilizers or sewage sludge can release Cd to firm fields (IRIS, 1999).

The study analysed leachate and not air. This might have been the reason why many sample sites did not contain Cd. The sites A, B and D in Dandora where Cd was detected in December could be because MSW containing Cd-in-food was disposed.

4.2.7 Spatial Variation of Heavy Metal ion levels in the Leachate from each sampling site

Figure 9 shows the mean spatial variation of heavy metal ion levels in leachate samples collected at the ten sampling sites. The results showed that the highest mean level detected in the samples were Zinc metal ions at 25.30ppm, this was followed by Lead at 3.45 ppm. The high levels of the heavy metal ions indicate the use of these metals in the urban centre (Merck Index, 1983).
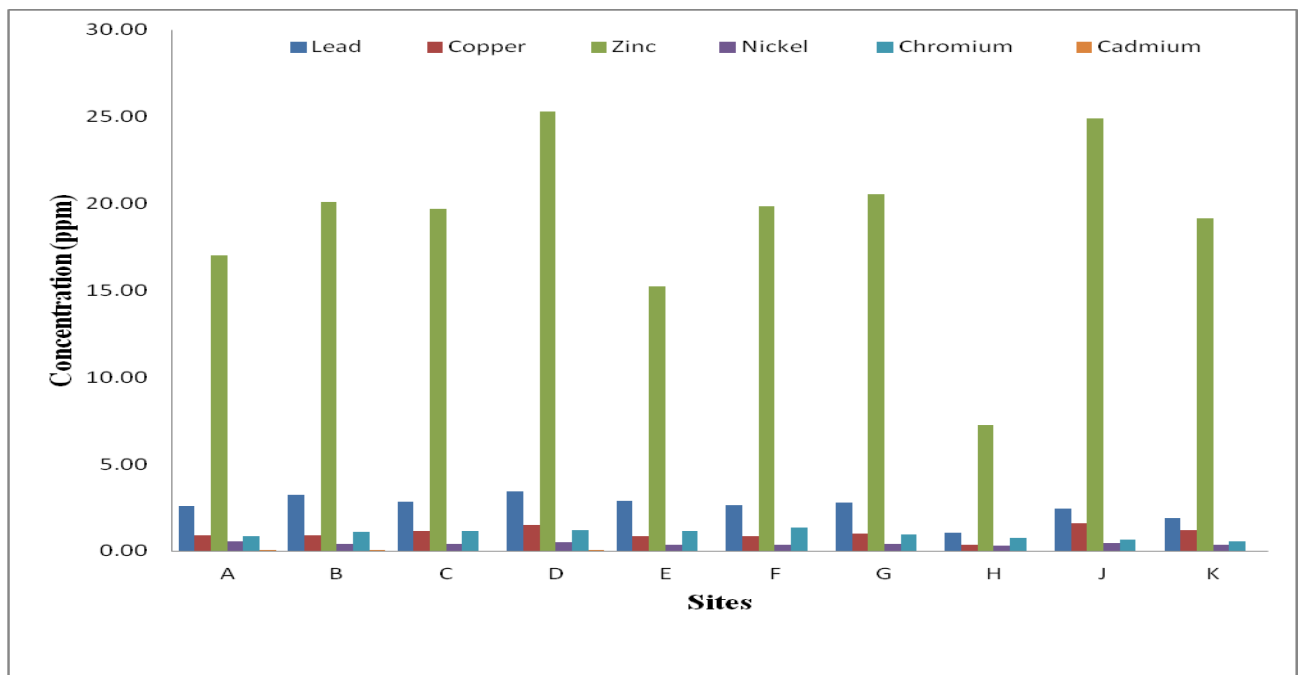
Figure 9: Spatial variation of heavy metal ions in leachates from each sampling site.

4.1.8 Spatial variation of heavy metal ion levels in leachate for all sampling periods

The spatial variation of heavy metal ion levels in the leachate was relatively high in all the sampling seasons as shown in Figure 10.

Figure 10: Spatial variation of heavy metal ions levels in the samples in each sampling period.

4.2.7 Summary of metal ion levels

The results showed that the highest mean level detected in the samples were Zinc metal ions at 25.30ppm, this was followed by Lead at 3.45 ppm. The high levels of the heavy metal ions indicate the use of these metals in the urban centre (Merck Index, 1983). Metallic zinc is mixed with other metals to form alloys such as brass and bronze (Kirk-Othmer, 1978). Door and window locks are made from brass. Zinc can combine with other chemicals to form salts. Zinc

sulphide and zinc oxide are used to make white paints, ceramics, and other products. Zinc oxide is also used in producing rubber. Zinc salts, such as zinc sulphate and zinc chloride are used in preserving wood and manufacturing and dyeing fabrics (Kirk-Othmer, 1978).

Zinc is used as protective coating for metals to prevent corrosion, for electrical apparatus, household utensils, castings, printing plates, building materials, rail-road, car linings, automotive equipment, reducing agent in organ-chemistry; deoxidizing bronze, extracting gold, purifying fats for soaps, bleaching bone glue, insulin zinc salts, reagents in analytical chemistry (Merck Index, 1983).

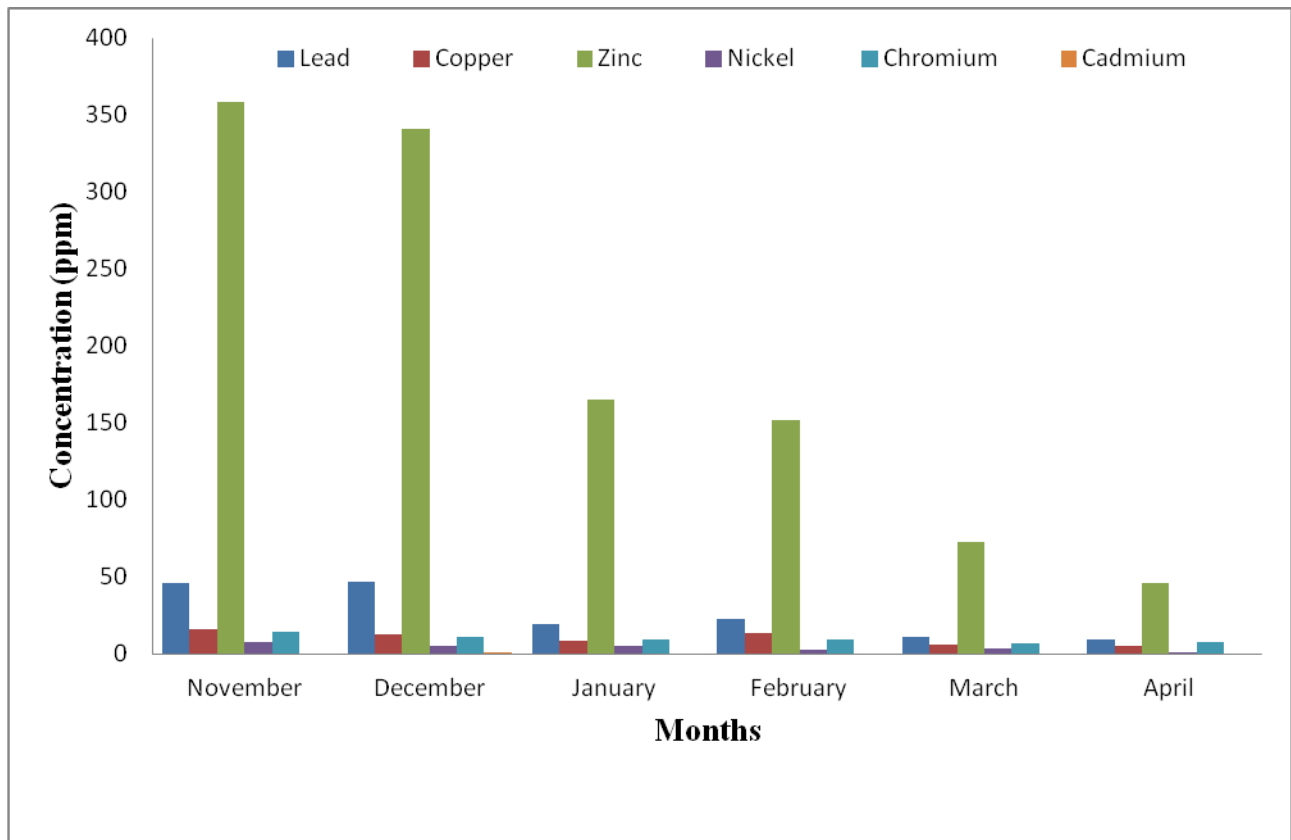The spatial variation of heavy metal ion levels in the leachate was relatively high in all the sampling seasons. This could be because metals in the MSW were either as compounds or elements which when the leachate was digested metal ions were obtained. MSW is continually disposed throughout the year. It is expected more MSW to be disposed with increasing population.

From the sum of heavy metal ion levels in the leachate samples in all sampling periods, levels of zinc ions were highest followed by lead. This could have been because of frequent use of items and compounds containing zinc and /or lead.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This study found out that the concentration of zinc was highest in the leachate from both Dandora and Chiromo. The levels of metals were lowest during rainy season (in March and April 2013) and highest during short rain, i.e. month of November and December 2012. The reason for low levels could have been seeping into ground due to heavy rains in March and April.

The level of heavy metals analysed was above the recommended level in drinking water (Table 14) and also PDE for pharmaceutical substances (Table 16). There is need to:

i) Treat water from wells and boreholes in the surrounding Estates of Dandora dumpsite before distribution to houses.

ii) Treat leachate before using as manure in order to reduce amount of heavy metals it contain.

The concentration of methane was highest where there was wet waste without or minimal sinks for atmospheric methane. Soils which are sinks, (contain OH) decrease headspace methane concentration and results to reduced diffusion flux. Methane is generated and absorbed by OH in the soil to form carbon dioxide and water (in equation 13), that's why there were low levels of methane on bear ground or where the ground was covered by vegetation. Methane is generated within fourteen days of waste decomposition under anaerobic conditions. The gas can be trapped if the waste is in closed dumpsite and used as clean fuel.

6.2 Recommendations

The findings of this study enable to recommend the following:

The Dandora dumpsite be controlled, restrict people to live closer to the site. This will reduce effects of metals such as chromium, which ends up in air through waste disposal (Table from EPA).

Borehole water and other sources of water supply to Dandora and its neighboring estates to be examined for levels of heavy metals to meet the WHO standards for drinking water.

Generated methane be trapped and used as fuel. This will reduce dependence on charcoal or/and kerosene by residents.

CHAPTER SIX

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