# ASSESSMENT OF THE LEVEL OF ENVIRONMENTAL POLLUTION DUE TO LEACHATE MIGRATION FROM THE CLOSED MALLAM SCC WASTE DISPOSAL SITE, ACCRA - GHANA

This thesis is submitted to the

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# DECLARATION

This is to certify that the work presented in this thesis was carried out entirely by myself, and all assistance have been duly acknowledged. This thesis has never been presented either in part or in whole for a degree in any other University.

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# DEDICATION

This research is dedicated to the Almighty God for His unmerited favour and to Mrs. Rosemond Toloo Addai for her support.

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## TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# ABSTRACT

The closed Mallam State Construction Corporation (SCC) waste disposal site is one of the many unengineered and improperly decommissioned municipal solid waste (MSW) landfills in Accra, Ghana. The site served as a landfill site for the Accra Metropolitan Assembly (A.M.A) for 7 years and received variety of solid waste from the A.M.A and other neighbouring municipal assemblies. Leachate management plans were, however, not implemented. Untreated leachate from the waste disposal site flows through the human settlements around the waste disposal site and enter into nearby surface water (Bawere Stream). The site was closed in 2001 after several agitations from the people living around, coupled with the fact that it was full to its maximum. The waste disposal site was not properly decommissioned prior to its closure. As a result, untreated leachate from the site still flows through the human settlements and enter the Bawere Stream. The research was carried out to assess the level of contamination of surface water, soil and groundwater due to leachate migration from the closed waste disposal site with emphasis on major ions ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $HCO_3^-$ , $SO_4^{2-}$, $NO_3^-$, and $PO_4^{3-}$ ) and trace elements (Fe, Pb, Cd, Cr, Mn, As, Zn, Hg, Cu and Co). Major ions were measured using conventional methods. Trace element concentrations were determined using Atomic Absorption Spectrometry. Stable isotopic composition ($\delta\ ^{18}O$ and $\delta\ ^{2}H$) of the surface water, soil and groundwater were determined using the Liquid-Water Stable Isotope Analyzer (Off - Axis Integrated Cavity Output Spectroscopy via laser absorption). Results showed high level of contamination of the surface water. The mean concentrations of $Na^+$, $K^+$, Fe, Pb, Cd and Mn (388 mg/L, 53 mg/L, 0.046 mg/L, 0.229 mg/L and 0.234 mg/L respectively) in the surface water were above the maximum permissible limit of the WHO (1996) guideline for drinking water. The mean $\delta\ ^{18}O$ and $\delta\ ^{2}H$ values of the surface water were -1.59 $^{o}/_{oo}$ vrs VSMOW and -10.79 $^{o}/_{oo}$ vrs VSMOW respectively. Porosity of the soil in and around the closed waste disposal site decreased with depth while the volumetric water content increased with depth. Trace element contamination of the soil was low. However, elevated concentrations of most of the trace elements were observed near the ground surface between 0 and 60 cm depths of the profiles. The level of contamination of the groundwater was high. The mean concentrations of $Na^+$, Fe, Cd and Mn (330 mg/L, 1.178 mg/L, 0.040 mg/L and 0.157 mg/L respectively) in the groundwater were above the maximum permissible limit of the WHO (1996) guideline for drinking water. It is recommended that the closed Mallam SCC waste disposal site should be properly decommissioned and future waste disposal sites in Ghana should be properly engineered to minimize surface water and groundwater contamination due to leachate migration.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background

The closed Mallam State Construction Corporation (SCC) waste disposal site is one of the many unengineered and improperly decommissioned municipal solid waste (MSW) landfills in Accra and for that matter, Ghana. Prior to its usage as municipal dumpsite, the site served as a quarry for the State Construction Company (SCC) and hence its name. The closed Mallam SCC waste disposal site operated for 7 years as a landfill site for the Accra Metropolitan Assembly (AMA) and was closed in 2001 after several agitations from the people living around, coupled with the fact that it was full to its maximum.

Landfills or dumpsites are not benign repository of discarded materials; they are biochemically active units where toxic substances are created or leached from combinations of non-toxic precursors and gradually released into the surrounding environment over a period of decades (Papadopoulou *et al.*, 2006). Thus, poorly engineered and uncontrolled landfillls or dumpsites may pose serious public health and environmental risks, particularly to the people living near them (USEPA, 1984; Fatta *et al.*, 1999). One major source of these threats is from leachate (Hughes *et al.*, 2008).

The term “leachate” refers to liquids that flow from waste, carrying dissolved or suspended contaminants. Therefore, once leachate is formed, it may migrate into nearby surface water or through the unsaturated zone and contaminate the underlying aquifer (Mor *et al.*, 2006). The degree of groundwater contamination depends on the concentration and toxicity of contaminants in the leachate, type and permeability of the geological strata, depth of water table and the direction of groundwater flow (Al-khaldi, 2006). Leachate is an environmental hazard when not properly managed (Chian and DeWalle, 1976; Kelley, 1976; Lo, 1996; Masters, 1998; Kumar and Alappat, 2002).

Generally, the area between the aquifer and the surface, termed as the vadose or unsaturated zone, works like a giant sponge, soaking up water and contaminants. Groundwater contamination is common in highly developed industrialized areas, where urbanization, transportation, industrial and agricultural as well as landfill site activities affects surface and subsurface soil layers.

Among others, a study carried out by Njoroge in cooperation with UNEP in 2007 on the Dandora municipal waste dumping site in Nairobi, Kenya, showed high contamination of the surrounding soil with heavy metals, particularly, lead, mercury, cadmium, copper and chromium, mainly due to leachate migration from the dumpsite. The results also showed that, children and adolescents living and schooling near the dumpsite had high incidence of diseases that were associated with high exposure levels to these metal pollutants.

A study conducted by Denutsui *et al.*, in 2009 on the Oblogo municipal solid waste landfill site in Accra, Ghana, also revealed contamination of the unsaturated zone water with heavy metals and major anions due to leachate migration from the dumpsite. These components may adversely affect groundwater quality in the area when they finally end up in the aquifer.

Apart from the potential impact on groundwater and surface water quality for domestic water supply use, municipal landfill leachate may also pose threats to aquatic life and other beneficial uses when it migrates into surface water (Lee and Jones-lee, 1994).

## 1.2 Statement of the problem

In Ghana, most of the municipal solid waste is disposed of in landfills or dumpsites that are neither properly engineered nor effectively monitored during its operation and after its closure. They are also not properly decommissioned prior to their closure, hence there may be high potential of the untreated leachate contaminating the surrounding soil and polluting the underlying groundwater and nearby surface water.

The closed Mallam SCC waste disposal site is therefore no exception. While in operation, the dumpsite received all forms of solid wastes ranging from domestic, commercial and industrial waste from the Accra Metropolitan Assembly as well as the Ga South and West Municipal Assemblies. These wastes were not segregated at source and there were no pre-treatment of the hazardous waste forms before disposal. Hazardous waste disposal cells were also not created and as such all the various categories of municipal solid waste were lumped up in the dumpsite and compacted daily.

Additionally, leachate management plans were not implemented; no impermeable liners were used to control leachate migration into groundwater and there were no leachate collection and treatment systems. Untreated leachate or runoffs from the dumpsite flows through the human settlements around the dumpsite and enter into the nearby surface water (Bawere stream) (Figure 3.0), which is a source of fish for some of the people in Mallam.

The dumpsite was not properly decommissioned prior to its closure; therefore there was no final capping of the dumpsite and drains were still not constructed to control leachate or runoffs from the dumpsite. Due to this, leachate or runoffs from the dumpsite still flows through the human settlements around the dumpsite and enter into the Bawere stream.

There may be a high potential for surface water, soil and groundwater contamination due to leachate migration from the closed waste disposal site. This may pose public health risk to the people around the dumpsite and needs to be investigated.

## 1.3 Research Objectives

Due to the problems outlined, this research is to assess the level of contamination of surface water, soil and groundwater due to leachate migration from the closed waste disposal site.

### 1.3.1 Specific Objectives

The Specific objectives of this research work are,

- To determine the variation of porosity and volumetric water content along the soil profile.

- To determine and quantify the concentration of major ions and trace elements in the leachate from the closed Mallam SCC waste disposal site.
- To determine if there is natural attenuation in profiles of the trace elements through analysis of soil samples at various depths near the dumpsite.
- To determine the variation of stable isotopic composition along the profiles.
- To study the effect of leachate migration on surface water and groundwater quality in Mallam, using major ions, trace elements and stable isotopes.

## 1.4 Relevance and Justification

- The Accra Metropolitan Assembly has secured some funds from the World Bank to transform the closed waste disposal site into green recreational center. The research will therefore provide information to the Accra Metropolitan Assembly, the Ghana Environmental Protection Agency and other relevant bodies on the pollution level of the surrounding environment due to leachate migration from the closed waste disposal site. This will go a long way to facilitate the development of mitigation or remedial measures where necessary.
- Some of the people in Mallam use groundwater in meeting their domestic water needs. The results of the research will help reveal whether it is safe to harness groundwater for domestic purposes in Mallam, particularly areas close to the waste disposal site.
- The results of the research will help to predict the public health risk of the increasing population of people settling very close to the waste disposal site.

### 1.5 Scope of the Study

The research will mainly deal with analysis of the physico-chemical parameters of surface water, soil and hand-dug wells in the study area. This will be followed by discussion of results, conclusion and recommendations.

# CHAPTER TWO

# LITERATURE REVIEW

## 2.1 Landfill Leachate

Landfilling is an indispensible method employed globally for the management of solid waste. It ranges from simple dumping of solid waste into any available depression on land to controlled disposal in a well designed or engineered site. A wide variety of wastes from industries, residences and municipalities had been and will continue to be disposed of through this method with the primary aim of eliminating or minimizing the public health and environmental risks associated with waste materials.

In landfills, physical, chemical and biological processes interact simultaneously to bring about the decomposition of wastes. One of the by-products of all these processes is leachate.

Municipal solid waste (MSW) leachate may contain a wide variety of conventional and non-conventional contaminants at concentrations where small amounts in both groundwater and surface water may render the water unsafe for domestic water supply and many other purposes (Lee and Jones-Lee, 1993). Formation and eventual migration of leachate into the surrounding environment is one of the main environmental problems associated with landfills. In view of this, modern sanitary landfills have leachate collection and treatment systems as well as bottom liners which serve as means of managing the migration of leachate (Lee and Jones-Lee, 1993).

The adverse environmental effects associated with leachate migration will obviously be more pronounced in unengineered and poorly managed landfills such as the Mallam SCC landfill. These landfills have no leachate management plans and operate on the principle that, the leachate generated will slowly migrate into the underlying geology and in so doing any contaminant present would be attenuated through physical, chemical and biological processes.

### 2.1.1 Formation of Landfill leachate

Rain falling on a landfill site may infiltrate the site, become runoff or return to the atmosphere via evaporation and transpiration. The rain water that infiltrates the site, in addition to moisture contained in the waste and water produced from waste decomposition, leach organic and inorganic contaminants from the waste as they migrate to the bottom of the site. The resulting solution or liquid is termed leachate.

Mechanisms regulating mass transfer of organic and inorganic contaminants from wastes into leaching water of which leachate is generated, can be divided into three main groups:

- Hydrolysis of solid waste and biological degradation
- Solubilisation of soluble salts contained in the waste
- Suspension of particulate matter

Leachate composition may greatly be influenced by the first two processes (Taylor and Allen, 2006).

Municipal Solid Waste (MSW) landfills usually have high percentage of organic materials which undergo natural decomposition. Biodegradation of these organic materials can be categorized into two main phases, the aerobic and the anaerobic phase (Kjeldsen *et al*., 2002)

During the aerobic process, the organic component of the waste is oxidized, through a series of hydrolytic reactions, to form carbon dioxide, water, nitrates and sulphates (Kjeldsen *et al*., 2002). There may be increase in temperature of the landfill due to the exothermic nature of the reactions (Taylor and Allen, 2006).The water formed flows towards the base of the landfill and is enriched with solubilized or suspended organic matter and inorganic ions from the solid phase (Taylor and Allen, 2006).The carbon dioxide formed is released as a gas or is dissolved in the water to form carbonic acid ($H_2CO_3$) which subsequently dissociates to yield bicarbonate anion ($HCO_3^-$) at near neutral pH (Aucott, 2006). Generally, the aerobic decomposition stage is short and it is subsequently replaced by the anaerobic decomposition phase when the oxygen within the waste profile is depleted (Taylor and Allen, 2006).

The anaerobic phase is sub-divided into three main stages; acetogenic (acid), initial methanogenic and stable methanogenic stage (Christensen and Kjeldsen, 1995 ). These stages can occur simultaneously in different parts of the landfill since waste is buried over many years in a series of cells and lifts. The anaerobic phase generates carbon dioxide and methane (Kjeldsen *et al*., 2002). In the acetogenic stage, the hydrolytic, fermentative and acetogenic bacteria dominate, resulting in an accumulation of organic acids (carboxylic acids) (Kjeldsen *et al*., 2002).

Acetogenic fermentation results in a decrease in leachate pH due to the production of volatile fatty acids (VFAs) (Kjeldsen *et al*., 2002). The leachate contains considerable concentrations of dissolved metals and inorganic ions and are characterized by high values of biological oxygen demand (BOD) (commonly >10,000 mg/l), high BOD/COD ratios (commonly > 0.7), acidic pH values (typically 5 - 6) and ammonia ($NH_3$) (Taylor and Allen, 2006).

The initial methanogenic stage is characterized by the rise to dominance of the methane producing bacteria (methanogens) (Barlaz and Ham, 1993). These bacteria convert the organic acids produced in the acetogenic stage to methane and carbon dioxide (Christensen and Kjeldsen, 1989, Barlaz *et al*., 1989a). A highly reducing chemical environment develops, resulting in the reduction of sulphates ($SO_4^{-2}$) to sulphides ($S^{-2}$) (Taylor and Allen, 2006). The pH rises as $NH_3$ neutralizes hydrogen ions ($H^+$), leading to the depletion of volatile organic acids (VOAs) and increasing presence of ammonium ions ($NH_4^+$). The pH is maintained in the neutral range, however, by bicarbonates ($HCO_3^-$) and this supports the continued flourishing of the methanogens. The presence of sulphides and hydroxides favours the precipitation of metals (Taylor and Allen, 2006).

In the stable methanogenic stage, the methane production rate reaches its maximum and decreases thereafter, as the pool of soluble substrate (carboxylic acids) decreases(Taylor and Allen, 2006). In this stage, the rate of methane ($CH_4$) production is dependent on the rate of cellulose and hemicellulose hydrolysis (Aucott, 2006). The pH continues to increase to steady state pool concentrations that are of the order of a few mg/L (Belevi and Baccini, 1989). The leachate produced in the methanogenic stages are characterized by almost neutral pH and low concentrations of volatile acids and TDS, indicating that solubilisation of majority of the organic components of the waste is almost complete, although waste stabilization may continue for several decades (Christensen and Kjeldsen, 1995).

The rate of waste degradation is a function of moisture content or amount of rainfall, temperature, waste density, waste age, waste composition, waste particle size, substrate availability, pH, microbial population, and microbial nutrient availability (Demenico and Schwarts, 1998). These may in turn affect the quality and quantity of leachate produced. However, the factor which has most consistently been shown to affect the rate of waste degradation and to a greater extent, the quality and quantity of the leachate produced, is the moisture content (Al-khadi, 2006).

Leachate formation may continue for several years after the closure of a landfill or dumpsite (Ghana EPA, 2002). This may, however, be reduced by capping the surface of the landfill with low permeability material such as clay or high density polyethylene (Ghana EPA, 2002).The capping will reduce infiltration of rainwater and thus delay the waste decomposition process which contributes to leachate formation (Ghana EPA, 2002).

### 2.1.2 Composition of Landfill Leachate

The composition of leachate varies greatly from site to site, and can even vary within a particular site. Some of the factors affecting leachate composition include:

- Age of the waste or landfill
- Type and chemical composition of the wastes
- Site hydrology
- Climate and moisture regime including seasonal effects
- Degree of decomposition that has taken place

- Operational and management strategies of the landfill

Generally, municipal landfill leachate contain four groups of contaminants; namely, dissolved organic matter (such as alcohols, pesticides, acids, aldehydes and short chain sugars); inorganic macro components (such as chloride, sulphate, and nitrate); heavy metals (such as cadmium, chromium, copper, lead and nickel ) and; xenobiotic organic compounds (such as halogenated organics like PCBs and dioxins) (Lee and Jones-Lee, 1993; Christensen *et al.*, 2001,). New landfills may produce highly concentrated leachate than older ones (Lee and Jones-Lee, 1993).Thus, leachate from old or closed landfills may have low polluting potential than leachate from new or operational landfills.

### 2.1.3 Migration and Attenuation of Landfill Leachate

Leachate migration is basically the phenomenal movement of leachate from a landfill or dumpsite after its formation. Under normal conditions, all the leachate formed in a landfill or dumpsite accumulates to the bottom due to gravity (Al-khadi, 2006). From there, it may migrate through the following pathways;

- Horizontally at the ground surface or at shallow depth to a surface receptor, such as stream or river.
- Vertically to an aquifer and then horizontally in the aquifer to a receptor, such as spring or stream (Al-Khadi, 2006).

Thus, the observation of leachate discharge from a landfill or dumpsite and the decline in the quality of nearby surface water and groundwater, are indicators that leachate is being formed and migrating (Freeze and Cherry, 1979, Taylor and Allen, 2006). Groundwater contaminated by leachate is comparatively enriched with $\delta\ ^{18}O$ than uncontaminated groundwater nearby because leachate is enriched with $\delta\ ^{18}O$ as result of isotopic fractionation in landfills (Fritz and Fontes, 1986, Panno *et al.*, 2001). High values of total dissolved solids (TDS) in nearby or surrounding surface water may also indicate leachate migration (Panno *et al.*, 2001).

As leachate migrates from the landfill, its quality is renovated by a process referred to as natural attenuation. This is simply the reduction in concentration of contaminants in leachate as it migrates through the various pathways due to physical, chemical, and biological processes. The degree of natural attenuation is dependent on many site-specific factors including the bacteria population, clay content, organic content, permeability of the soil, flow rates, temperature, pH and redox conditions (O' Leary and Walsh, 1995).

The mechanisms of attenuation include: adsorption, biological uptake, cation and anion exchange reactions, dilution, filtration, and chemical precipitation reactions (Lee and Jones, 1991). Through these mechanisms most of the constituents of leachate are attenuated as they migrate. For example, trace metal components of leachate are easily attenuated as they migrate through the unsaturated zone (O'Leary and Walsh, 1995). Chlorides can however be used to trace leachate migration from a landfill site because its concentration is less affected by the mechanisms of attenuation (McMahon and Thomas, 1974).

### 2.1.4 Effects of Landfill Leachate

Leachate, as mentioned earlier, is a host of deleterious or toxic substances which can pose threats to human health and the environment when directly exposed to surface water and groundwater. Apart from degrading the quality of surface water and groundwater for domestic water supply and use, leachate may destroy aquatic life and adversely impact bio-diversity (Lee and Jones-Lee, 1994).

The toxic chemicals in leachate, especially the heavy metals and the xenobiotic organics, may also accumulate in the biota (Lee and Jones-Lee, 1994). This may impact negatively on humans and other living organisms that depend on aquatic life. The major potential effects of a leachate release to surface water are expected to be oxygen depletion in part of the surface waterbody, changes in stream bottom fauna and flora as well as ammonia toxicity (Lee and Jones-Lee, 1994).

Leachate contaminated groundwater can adversely affect industrial and agricultural activities that depend on groundwater. For certain industries, contaminated water may affect quality of their products, decrease equipment lifetime, or require pre-treatment of the water supply, all of which results in additional financial burdens (O'Leary and Walsh, 1995).

The use of leachate contaminated water for irrigation may also lead to decrease soil productivity, bioaccumulation and biomagnification of toxicants and its attendant problems (Lee and Jones-Lee1994). The effects of leachate are mainly dependent on its composition since there are significant variations in the composition of leachate from different landfills (Flyhammar, 1995).

### 2.1.5 Heavy Metals in Ladfill Leachate

The term “heavy metal” is not uniformly defined in literature in terms of its specific gravity and atomic weight. However, in this context, heavy metals are taken to mean metals of the periodic table with atomic numbers greater than 20 (excluding the alkali metals and the alkali earths) or metals having specific gravities greater than 5 g/cm$^3$ or metals with high atomic masses.

Despite the toxicological significance of heavy metals, some heavy metals including lead, cadmium and mercury are incorporated in certain consumer and industrial products (such as batteries, switches, circuit board and certain pigments) due to their useful physical and chemical properties (Aucott, 2006). These products ultimately end up in the municipal waste stream at the end of their cycle and are most often disposed of in landfills. Depending on the landfill management strategies, most of these heavy metals escape to the environment primarily through the landfill leachate (Aucott, 2006).

There have been a number of studies on full scale landfills and test cells in which researchers indicated the presence of heavy metals in leachates (Christensen et al., 1994; Robinson, 1995; Reinhart and Grosh, 1998; Revans et al., 1999; Kjeldsen and Christophersen, 2001, Denutsui *et al.*, 2011). Most of these studies reported that the concentration of heavy metals in leachates were at or below the drinking water standards and may not necessarily be a major environmental concern. However, the situation may be different in non-engineered and poorly managed landfills, such as that of the closed Mallam SCC waste disposal site.

### 2.1.6 Processes Affecting Heavy Metal Concentrations in Landfill Leacahte

Physico-chemical conditions in landfills may affect the concentration of heavy metals in the leachate generated or released (Kjeldsen *et al.*, 2002). For example, the low concentration of heavy metals in methanogenic leachate may not only be ascribed to low heavy metal content in the waste but also to some physico-chemical processes prevailing in the landfill. Heavy metal balances for landfills have shown that less than 0.02 % of heavy metals received at landfills are leached from the landfill after 30 years (Flyhammer, 1995; Aulin and Neretnieks, 1995; Belevi and Baccini, 1989). Many authors (Flyhammer, 1995; Aulin and Neretnieks, 1995; Belevi and Baccini, 1989) have mentioned sorption, precipitation and redox processes as affecting the concentration of heavy metals in lanfill leachate.

#### 2.1.6.1 Sorption

Sorption is a physical and chemical phenomenon in which one substance becomes attached to another. It is defined to include adsorption, absorption, ion exchange and surface complexation (Christensen *et al*., 1994). Heavy metal cations, such as $Pb^{2+}$ and $Hg^{2+}$ have high affinity to organic matter, clay minerals, calcites and oxides of Fe, Mn, Al and Si (Aucott, 2006). Well developed humus, for example, is reported to have a cation exchange capacity in the range of 1.5 to 3.0 meq/g (Aucott, 2006). Generally, landfills with higher organic matter and clay content and with neutral to a high pH values have higher sorptive capacity (Bozkurt *et al*., 1999). The greater the sorptive capacity of a landfill environment, the more heavy metals are immobilised and the lower the concentration of heavy metals in the leachate produced (Bozkurt *et al*., 1999).

#### 2.1.6.2 Precipitation

Precipitation occurs when dissolved metal species falls out of solution as insoluble compound. Sulphides and carbonates are capable of precipitating many heavy metals (including Cd, Ni, Zn, Cu, and Pb) and are typically present in landfills (Kjeldsen *et al*., 2002). Sulphide precipitation has often been cited as an explanation for low concentration of heavy metals in landfill leachate (Christensen *et al*., 1994;

Christensen *et al.*, 2001). Cr is, however, an exception since it does not form insoluble precipitate with sulphides (Christensen *et al.*, 2001). Occasionally, phosphates and hydroxides precipitate heavy metals in a landfill (Christensen *et al.*, 1994). For example, Cr tends to form insoluble precipitates with hydroxides at neutral to higher pH values (Christensen et al., 1994; Reinhart and Grosh, 1998).

### 2.1.6.3 Redox Reactions

Theoretically, once the waste in a landfill is well decomposed under anaerobic conditions, the rate of oxygen intrusion may exceed the rate of microbial oxygen depletion (Kjeldsen *et al.*, 2002). Hence, with time, the landfill becomes aerobic and facilitates oxidative reactions. Generally, landfill conditions that favour the formation of oxidized compounds would lead to some, perhaps significant, mobilisation of heavy metals in the leachate produced (Reinhart and Grosh, 1999; Martensson *et al.*, 1999).

Heavy metal mobilisation in leachate from aerobic landfills may result from the following;

- Oxidation of metal sulphide precipitates, produced under anaerobic conditions, into metal sulphates, which are generally soluble (Christensen *et al.*, 2001).
- Reduction of the pH of the landfill due to the oxidation of reduced sulphur, nitrogen and iron as well as production of $CO_2$ (Calmano *et al.*, 1993)
- Increased complexation capacity of oxidized humic acids relative to reduced humic acids (Martensson *et al.*, 1999)

## 2.2 The Unsaturated Zone

The unsaturated zone, sometimes called the vadose zone or zone of aeration, is the portion of the subsurface above the groundwater table and above the capillary fringe (Freeze and Cherry, 1979). In some places it is absent, as is common where there are lakes and marshes, and in some places it is hundreds of meters thick, as is common in very arid regions (USGS, 2001).

The soil pores in this zone are only partially filled with water and the water content is less than the porosity (Freeze and Cherry, 1979). The unsaturated zone plays several critical hydrologic roles; it provides water and nutrients that are vital to the biosphere and is intensively used for the cultivation of plants, it serves as a buffer for runoff and erosion through its potential to absorb water infiltrating from rainfall (USGS, 2001). The unsaturated zone also serves as a conduit and often the main factor controlling the transport of water and contaminants from the land surface to the groundwater or surface water system (USGS, 2001). Thus, a better understanding of the unsaturated zone and its processes are essential when assessing the level of environmental pollution due to leachate migration from waste disposal sites. Considerable information on water and pollutant transport through the unsaturated zone can be gleaned from physical measurements made on cuttings and core materials from the zone (Wood, 1975).

### 2.2.1 Movement of Water through the Unsaturated Zone

Contaminant solute transport through the unsaturated zone is closely linked to the water flux through the zone (Nielsen *et al*., 1986). Thus, in assessing the level of environmental pollution due to leachate migration, it is important to know the mechanisms involved in water movement through the unsaturated zone. In terms of water infiltration, the unsaturated zone may be categorized into four main zones; saturation zone, transmission zone, wetting zone and the wetting front (Figure 2.1).

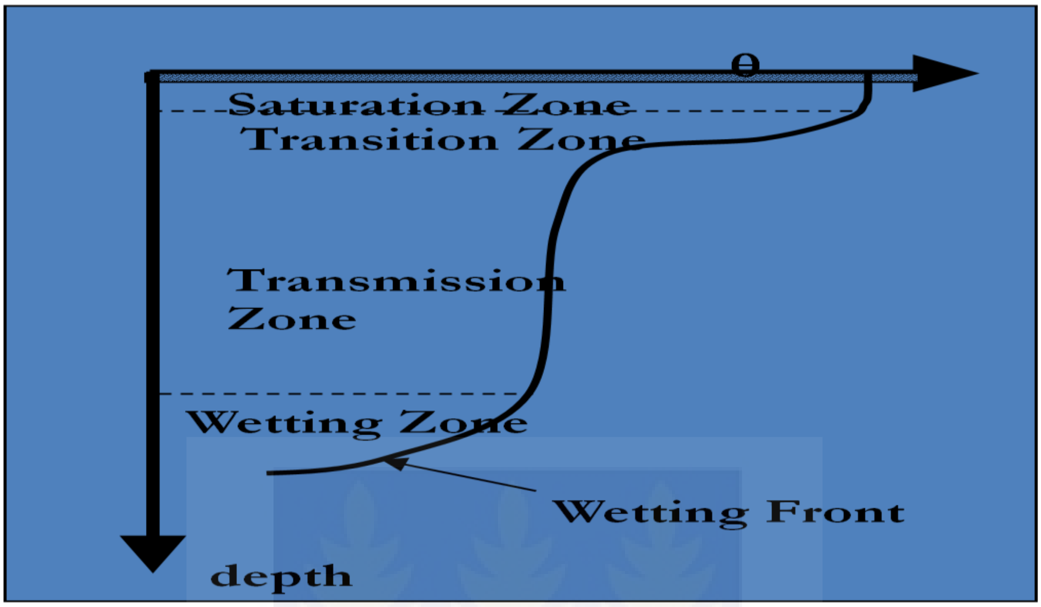


Figure 2.1 Categorization of the unsaturated zone in terms of water infiltration

Downward infiltration into an initially unsaturated soil generally occurs under the combined influence of suction and gravity gradients (Nimmo, 2005). Water is pushed by pressure gradients from the point of its application where it is saturated locally, and pulled by capillary action due to adhesion force of water to the soil solids, producing a suction gradient from wet towards drier soil. As the water penetrates deeper, the wetted part of the profile (wetting zone) lengthens and the average suction gradient decreases, since the overall difference in pressure head (between the saturated soil surface and the transmission zone) divides itself along an ever-increasing distance (Edlefson and Anderson, 1943). This trend continues until eventually the suction gradient in the upper part of the profile becomes negligible, leaving the constant gravitational gradient in effect as the only remaining force moving water downward. Since the gravitational head gradient has the value of unity (the gravitational head decreasing at the rate of 1 cm with each centimeter of vertical depth below the surface), it follows that the flux tends to approach the hydraulic conductivity as a limiting value (Edlefson and Anderson, 1943). In a uniform soil under prolonged ponding, the water content of the wetting zone approaches saturation (Feddes *et al*., 1988). Once the soil is completely wetted, any more water will move downward and join the water table towards the aquifer (Edlefson and Anderson, 1943).

Movement of water from the ground surface to the sub-surface depends on factors such as intensity of rainfall or irrigation application rate, soil surface conditions, soil properties, water content and hydraulic conductivity. Major or intense recharge events normally occur during the rainy season (Nimmo, 2005).

Unsaturated flow can be expressed mathematically using the Richards equation (Richards, 1931) which is defined as;

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial \psi}{\partial z} + 1\right)\right] \qquad \textbf{2.1}$$

where,

$K$ is the hydraulic conductivity,

$\psi$ is the pressure head,

$z$ is the elevation above a vertical datum,

$\theta$ is the water content, and $t$ is time.

### 2.2.2 Processes that Govern the Transport and Fate of Contaminant Solute in the Unsaturated Zone

Transport of contaminant solute through the unsaturated to the saturated zone depends on factors such as water flow velocity, water content, soil properties, solute species, solute reactions and degree of saturation (Nimmo, 2005). Depending on the above factors, the transport of contaminant solute may range from being nearly instantaneous to several hundreds of years (Nielsen *et al*. 1986). The processes that govern the transport and fate of contaminant solute in the unsaturated zone are diffusion, dispersion, advection, sorption and biological degradation (Nimmo, 2005).

#### 2.2.2.1 Diffusion

Diffusion in solution is the process whereby ionic or molecular constituents move under the influence of their kinetic activity in the direction of their concentration gradient (Šimu˚nek *et al*., 2006). This process causes a solute to move from a location with a higher concentration to a location with a lower concentration. It ceases when the concentration gradient is zero (Freeze and Cherry, 1979). Diffusive transport in the unsaturated zone mainly occurs in the absence of any bulk hydraulic movement of the solution. For instance, in a low permeability environment, diffusion is the main process by which contaminant solutes reach the saturated zone (Boulding and Gin, 2004). Diffusive transport can be described using Fick’s first Law, which states that, the mass of a diffusing substance passing through a given cross-section per unit time is directly proportional to the concentration gradient (Close, 2010).

$$\mathbf{F= -D}\left(\frac{d_c}{d_x}\right) \qquad \mathbf{2.2}$$

where,

F = mass of solute per unit area per time (M/L$^2$T),

D = diffusion coefficient (L$^2$/T)

C = solute concentration in (M/L $^3$).

$\left(\frac{d_c}{d_x}\right)$ = concentration gradient which is a negative quantity in the direction of diffusion

#### 2.2.2.2 Dispersion

Dispersive transport of solutes results from the uneven distribution of water flow velocities within and between different soil pores (Nielsen *et al*., 1986). Dispersion can be derived from Newton's law of viscosity which states that velocities within a single capillary tube follow a parabolic distribution, with the largest velocity in the middle of the pore and zero velocities at the walls (Šimu˚nek *et al.*, 2006). Solutes in the middle of a pore, for this reason, will travel faster than solutes that are farther from the center (Nielsen *et al*., 1986). Additionally, the distribution of solute ions within a pore depends on their charge, as well as on the charge of pore walls (Nielsen *et al*., 1986). Thus some solutes may move significantly faster than others.

#### 2.2.2.3 Advection and Adsorption

Advective transport occurs when contaminant solutes are transported through the unsaturated zone with the moving fluid or due to the fluids bulk motion (Walter and Masterson, 2003). However, adsorption occurs when contaminant solutes being transported through the unsaturated zone attach themselves to the soil particles (Close, 2010). Adsorption is one of the main processes that reduces or slows down contaminant solute transport through the unsaturated zone (Šimu˚nek*et al*., 2006). The adsorptive process is significant in soils that have high organic matter and clay content (Close, 2010).

#### 2.2.2.4 Biological degradation

Biological degradation occur when micro-organisms degrade or breakdown contaminant solutes as they migrate through the unsaturated zone (EPA, 1994). The process reduces some toxic degradable organic solutes in the unsaturated zone, hence reducing their potential to adversely impact groundwater (EPA, 1994).

### 2.2.3 Soil Physical Parameters that Influence Unsaturated Flow

Migration of leachate through the unsaturated zone is greatly influenced by the soil physical parameters (Šimu˚nek *et al.*, 2006). Thus, a knowledge of the physical parameters of the soil underlying and in the immediate environ of a waste disposal site is essential when assessing the transport and fate of some leachate contaminants through the unsaturated zone. Some of the soil physical parameters include; texture, structure, bulk density, porosity and water content.

#### 2.2.3.1 Texture

Soil texture is determined by the relative proportion of the three kinds of soil particles; sand, silt, and clay. Soil texture affects soil behaviour, in particular its retention capacity for water and nutrients (Graham-Bryce, 1963). Sand and silt are the products of physical and chemical weathering; clay, on the other hand, is a product of chemical weathering but often forms as a secondary mineral precipitated from dissolved minerals (Grossman and Reinsch, 2002). It is the specific surface area of soil particles and the unbalanced ionic charges within them that determine their role in the cation exchange capacity of soil (Barone *et al.*, 1989). Sand is least active, followed by silt; clay is the most active. Sand resists compaction and increases porosity (Schaap *et al.*, 2001). Silt is mineralogically like sand but with its higher specific surface area and it is more chemically active than sand (Bruce and Klute, 1956). Clay has very high specific surface area and generally large number of negative charges that gives a soil its high retention capacity for water and nutrients (Baron *et al.*, 1989). In medium-textured soils, clay is often washed downward through the soil profile and accumulates in the subsoil.

Particle size data can be used to predict soil hydraulic properties and hence the transport and fate of contaminant solute through the unsaturated zone (Schaap, 2001).

#### 2.2.3.2 Bulk Density

Bulk density is the ratio of the dry mass of a soil to its volume. It is usually expressed in $gcm^{-3}$. Bulk density is influenced by factors such as organic matter content, porosity, structure and depth in profile (Bruce and Klute, 1956). Bulk density data can be used to predict or ascertain the degree of soil aeration, compactness, water content and infiltration rate. Most soil bulk densities range from 1 to 2 $gcm^{-3}$, with particle density of 2.65 $gcm^{-3}$ (Grossman and Reinsch, 2002). Generally, the bulk density of clays and loams varies from 1.1 to 1.5 $gcm^{-3}$; those of sandy soils from 1.4 to 1.8 $gcm^{-3}$ and that of organic soils is as low as 0.5 $gcm^{-3}$ (Grossman and Reinsch, 2002).

#### 2.2.3.3 Porosity

The porosity of a rock or soil is defined as the ratio of the volume of void space to the total volume of the given medium. It is mathematically represented as;

$$\mathbf{n} = \left(\frac{\mathbf{V_V}}{\mathbf{V_T}}\right) \qquad \mathbf{2.3}$$

where, n is the porosity, $V_v$ and $V_T$ are the volume of void space and the total volume respectively.

It is usually expressed in decimal fractions or percentages. Porosity can be an important controlling influence on the hydraulic conductivity. Within deposits of well-sorted sand or in fractured rock formations, hydraulic conductivity increases with increasing porosity (Freeze and cherry, 1979). However, this relationship does not hold for all rocks and soil types.

Clay-rich soils, for example, usually have higher porosities than sandy or gravelly soils but lower hydraulic conductivities (Freeze and cherry, 1979).

Porosity can be mathematically expressed in relation to bulk density as;

$$\mathbf{n\ \% = \left(1 - \frac{B_d}{P_d}\right) \times 100} \qquad \mathbf{2.4}$$

where, n % is the porosity expressed in percentage, $B_d$ is the bulk density and $P_d$ is the particle size density of the soil.

#### 2.2.3.4 Water Content

Water content is the measure of the quantity of water in a given soil medium. It may be expressed in volumetric or mass basis (gravimetric). However, volumetric water content is mostly used because its range has a clearly defined maximum at the medium's porosity and it relates easily to visualizations of intrapore geometry (Close, 2010). Volumetric water ($\theta$ or $\theta_w$) is defined as the volume of water per bulk or total volume of the soil medium (Egbi, 2011).

$$\boldsymbol{\theta_V} = \left(\frac{V_w}{V_T}\right) \qquad \mathbf{2.5}$$

where, $\theta_w$ is the volumetric water content, $V_w$ is the volume of water and $V_T$ is the bulk or total volume of the given soil medium.

Gravimetric water content ($\boldsymbol{\theta}_g$) is also defined as the ratio of the mass of water to the bulk or total mass of the given soil medium.

$$\boldsymbol{\theta}_g = \left(\frac{M_W}{M_T}\right) \qquad \mathbf{2.6}$$

where, $\theta_g$ is the gravimetric water content, $M_w$ is the mass of water in the soil medium and $M_T$ is the bulk or total mass of the given soil medium.

Volumetric and gravimetric water content is related by the formula;

$$\theta_v = \left(\frac{\rho_b}{\rho_w}\right) \theta_g \qquad \mathbf{2.7}$$

where, $\rho_b$ is the bulk density and $\rho_w$ is the density of water

The hydraulic conductivity in a given soil medium is directly proportional to the water content (Nimmo, 2005).

## 2.3 Water Quality Parameters

The quality of water is ascertained based on its physical, chemical and biological characteristics with reference to appropriate standards and use. The commonest standards usually relates to drinking water, safety of human contact and health of ecosystems (Pandey *et al.*, 1993). The quality of natural water is degraded due to the introduction of certain physical, chemical and biological substances into it. Introduction of these substances, are mostly due to anthropogenic activities such as waste disposal and agricultural practices (Kodarkar, 1992).

The physical and chemical characteristics of water and hence its quality can be determined by measuring parameters such as pH, Electrical Conductivity(EC), Temperature, Total Dissolved Solids (TDS), Chemical Oxygen Demand (COD) , Salinity, Alkalinity, Major ions, Trace elements etc.

### 2.3.1 pH

pH is the measure of hydrogen ion activity or concentration in water. It is measured on a logarithmic scale of 0 to 14 (with 7 being neutral) and mathematically represented by the relation;

$$\mathbf{pH = -\log [H^+]} \qquad \mathbf{2.8}$$

where $[H^+]$ is the hydrogen ion concentration

pH value more than 7.0 indicates basic conditions while pH less than 7.0 indicates acidic conditions. The pH of water is usually influenced by geology, organic acids (decaying leaves and other matter), temperature and human-induced acids such as acid rain. One of the most important reactions that contribute to the pH of natural water system is the dissolution of carbon dioxide in water. It is represented by the steps below;

i. $CO_{2\,(g)} + H_2O_{\,(l)} \longrightarrow H_2CO_{3(aq)}$

ii. $H_2CO_{3\,(aq)} \longrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$

iii. $HCO_3^-{}_{(aq)} \longrightarrow H^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$

The second and the third reactions both produce $H^+$ which may influence the pH of the solution (Hem, 1985). Pure water at temperature of 25 °C has a neutral pH (pH 7.0) while the pH of most groundwater range from 6 to about 8.5. pH measurements are normally done in-situ using portable pH meters.

### 2.3.2 Electrical Conductivity (EC)

Electrical conductivity of water is the measure of the ability of the water to conduct electric current. It has SI unit of Siemens per metre but it is usually expressed in microsiemens per centimetre (µS/cm). Electrical conductivity indirectly measures the presence of dissolved inorganic ions such as carbonate, sulphate, phosphate, chloride, calcium, sodium, magnesium, iron and potassium. The electrical conductivity of water is a function of temperature, type of ions present, and concentration of various ions. Very high conductivity value is an indication of some level of contamination and the water may not be safe for some domestic purposes. World Health Organization (WHO) (1996) guideline value for drinking water for example, prescribed a maximum permissible limit of 1000 µS/cm.

### 2.3.3 Total Dissolve Solids (TDS)

Total Dissolved Solids (TDS) measures the total amount of mobile charged ions, including minerals, salts or metals dissolved in a given volume of water. It is usually measured using the conductivity/TDS meters or the standard gravimetric techniques and expressed in units of milligram per litre (mg/L) or gram per litre (g/L) of water. High TDS values in surface and groundwater are indications of some level of contamination. Generally, water with Total Dissolved Solids below 500 mg/L may be safe for drinking purposes. Water with TDS values above 500 mg/L may not be recommended for domestic and industrial purposes (WHO, 1996).

### 2.3.4 Alkalinity

Alkalinity is the total measure of substances in water that have acid-neutralizing ability. These substances are mainly carbonates, bicarbonates and hydroxides. The main sources of natural alkalinity are rocks (which contain carbonate, bicarbonate, and hydroxide compounds) and atmospheric carbon dioxide. In order to ensure accuracy, alkalinity must be ascertained in-situ (Trivedy, 1990).

### 2.3.5 Major Ions

Concentrations of major ions (such as nitrates, sulphates, phosphates, chlorides, sodium, calcium, potassium, magnesium etc) in water may be used to indicate the quality of water (U.S. EPA, 2009). These ions are naturally present in relatively low concentrations in surface and groundwater systems. However, due to anthropogenic activities such as waste disposal, agricultural practices and industrialisation, their concentrations may increase to toxic levels in some water bodies (Romanelli *et al.*, 2011).

Additionally, higher concentrations of some major ions (concentrations exceeding the recommended standards) in water bodies have been associated with adverse human health and ecological effects (Thompson *et al.*, 2007). Nitrate concentrations exceeding 45 mg/L (similar to 10mg/L of Nitrate-N) in drinking water, for example, causes methemoglobinemia (‘blue-baby syndrome’) in bottle-fed infants below 6 months (De Roos *et al.*, 2003).

### 2.3.6 Trace Elements

In relation to water quality analysis, trace elements are elements that are found in concentrations below 100 mg/L. At relatively low concentrations some trace elements (such as Zn, Cr, Fe, Zn, Cu, Co, etc.) are essential for human and/or animal health but may become toxic at higher concentrations. Others, including Pb, Hg, As and Cd may be toxic even at lower concentrations (U.S. EPA, 1991). Concentration of trace elements in natural water systems is generally low (ranging from nanogram to microgram levels per litre) and their origin is mainly from weathering or dissolution of minerals and rocks containing the said elements.

The trace elemental composition and concentration of water due to natural phenomena may not necessarily pose adverse environmental impacts (Garbarino *et al.*, 1995). However, due to anthropogenic activities such as waste disposal, agricultural practices and industrialisation, their composition and concentration in some natural water bodies have increased steadily and are of great environmental concern (Zubair, 1998).

## 2.4 Solway Weighted Water Quality Index

The Solway Weighted Water Quality Index developed by Bolton *et al.*, 1978 for the Solway River Purification Board (RPB), was adapted and modified by Ansa- Asare (1998) for use as a water quality index for Ghana (Water Resource Commission, Ghana, 2003). It has been used by the Water Resource Commission to classify the quality of all the Basins in Ghana (Water Resource Commission, Ghana, 2003).

The water quality index is founded on three factors involving the measurement of the attainment of water quality objectives. The factors measure the following:

- Number of objectives that are not met
- Frequency with which objectives are not met, and
- Amount by which objectives are not met

These three factors are combined to form the index which can fall into one of the following four classifications: good, fair good, poor quality and grossly polluted. These rankings describe the state of water quality compared to its desirable or natural state (Water Resource Commission, Ghana, 2003).

## 2.5 Environmental Stable Isotopes

Environmental isotopes are naturally occurring isotopes of elements that are found in abundance in the environment. These include isotopes of H, C, N, O and S which are principal elements of hydrological, geological and biological systems. Environmental isotopes can be employed to obtain critical hydrological information such as;

- Origin of groundwater
- Mechanisms of groundwater recharge
- Age and dynamics of groundwater
- Interconnections between different aquifers
- Inter-relationship between surface water and groundwater
- Groundwater and surface water pollution

Some of the environmental isotopes are stable while others are radioactive (Butler and Verhagen, 1997). Environmental stable isotopes can serve as tracers of water, carbon, nutrient and solute cycling. The commonest environmental isotopes used in the field of hydrology are those of oxygen and hydrogen (Clark and Fritz, 1997).Variation in the stable isotope ratios is governed by chemical reactions and phase changes because of the energy difference between the chemical bonds involving different isotopes of an element. Such energy differences are caused by the relative mass difference between isotopes (fractionation). The stable isotopes of light elements show greater variations because they have larger relative mass differences. Thus, imparting measurable fractionation during physical and chemical reactions (Chery *et al.*, 2000).

Stable isotope ratios in hydrology are conventionally reported as per mil (‰) deviation from those of a standard using the delta (δ) notation

$$\delta\ (‰) = \left[\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right] x \ \ 1000 \qquad 2.9$$

where, R is the isotope concentration ratio ($H^2/H^1$, $O^{18}/O^{16}$) of a sample or a standard. The isotopic standard used for H and O isotopes is the Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961; Craig and Gordon, 1965). The $O^{18}$ and $H^2$ content of precipitation at a given locality at a particular time, generally depend on the location within the continental landmass and more specifically on the condensation-precipitation history of the atmospheric vapour (Freeze and Cherry, 1979).

Meteoric processes modify the stable isotopic composition of water and hence the recharge waters in a particular environment will have a characteristic isotopic signature (Dansgaard, 1964). This may be use to distinguish waters from different environments. Most authors (including Clark and Fritz, 1997) have shown that, meteoric waters retain their distinctive stable isotopic fingerprints until they mix with waters of different origin and composition or dissolve species.

Among researchers, Denutsui (2009) used the stable isotopes of water to assess the source of pollution of the Densu Delta Wetland, Ghana. Similarly, Castenada *et al*. (2012 ) used stable isotopes of water to investigate surface water and groundwater contamination with landfill leachate from a municipal landfill in Metro Manila, Philippines. Therefore, stable isotopes of water can be used to assess groundwater and surface water contamination due to leachate migration from the closed Mallam SCC waste disposal site.

## 2.6 Soil Pore Water Extraction for Stable Isotopic Analysis

The composition and reactivity of the soil liquid phase is dependent on the properties of the incoming water and fluxes of matter and energy originating from the local (neighbouring) soil solid phase, biological system, and atmosphere (Di Bonito, 2005). Analysis of the composition of pore water along the soil profile may be used to predict the state and concentrations of chemicals that may reach ground and surface water through transport from the soil environment (pollutant fate) ( Gazis and Feng, 2004). Tang and Feng (2001) and Gazis and Feng (2004) all used the stable isotopic composition of extracted pore water to investigate the fate of contaminant transport in the soil environment.

In order to obtain accurate isotopic signature of the pore water, the extraction technique must be very efficient and also minimize fractionation as much as possible. Fractionation effects appear to be more pronounced for the more strongly bound water, which is produced towards the end of the extraction period (Di Bonito, 2005). The effect is greater for soils with a large fraction of small pores (i.e. high specific surface area), such as clays and clayey soils (Di Bonito, 2005). It is therefore important to extract the residual water as completely as possible to minimize this effect. The commonly used extraction techniques are cryogenic vacuum distillation, azeotropic distillation, micro-distillation with Zn and immiscible displacement using centrifugation techniques (Walker *et al*., 1994).

# CHAPTER THREE

# STUDY AREA, MATERIALS AND METHODS

This chapter describes the study area, mode of sampling and data collection as well as the analytical methods.

Primary and secondary data was used in this study. Primary data, which is the main source of information for the study, was obtained through field and laboratory analysis. The secondary data was obtained through desk study.

## 3.1 Description of the Study Area

### 3.1.1 Location

The study area is the closed Mallam SCC waste disposal site located at Mallam in the Ga South District Assembly. The site is situated in an abandoned quarry formerly operated by the State Construction Company (SCC) and covers about 5 acres of land. It is on latitude 05$^{o}$34.291 N and longitude 000$^{o}$17.486 W and is 40 m above sea level. The location map is shown in Figure 3.1.

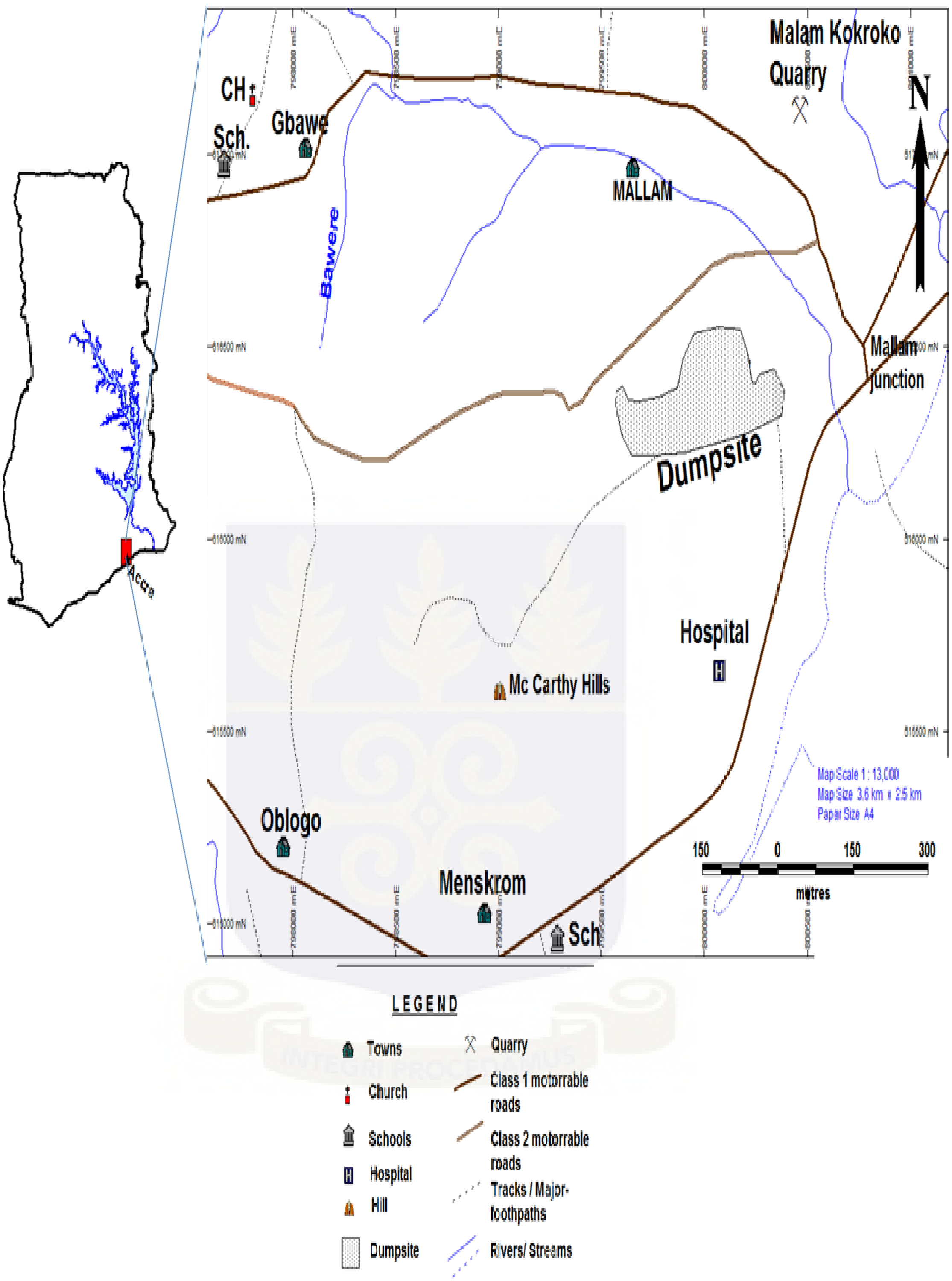


Figure 3.1 Map showing the location of the study area

### 3.1.2 Climate

The study area is located in a tropical coastal savanna climate. Rainfall is bi-modal with average annual rainfall being 730 mm (Denutsui, 2009). The first rainy season occurs between March and June while the second occur between September and October. Rain usually falls in short intensive storms and gives rise to local flooding where drainage channels are obstructed.

There is very little variation in temperature throughout the year. The mean monthly temperature ranges from 24.7 °C (76.5 °F) in August (the coolest) to 28 °C (82.4 °F) in March (the hottest), with an annual average of 26.8 °C (80.2 °F) (Denutsui, 2009). Relative humidity is generally high, varying from 65 % in the mid-afternoon to 95% at night (Teley, 2001). The predominant wind direction is from the WSW to NNE with wind speed normally ranging between 8 to 16 km/h (Denutsui, 2009).

### 3.1.3 Vegetation, Land Use and General Geology

The dominant vegetation in the study area is shrub and grassland (Teley, 2011). Grasses and occasional patches of shrub characterized the landfill area. Land in the study area is mainly used for residential purposes.

The geology is mainly of the Togo structural units comprising mica schist, minor quartzite, quarzite and minor mica schist. The rocks which are metamorphosed sedimentary rocks are incompetent and susceptible to fracturing upon stress. The rocks form the range of mountains and hills known as the Akwapim- Togo range. Kesse (1985) indicated that the Akwapim Togo beds have been subjected to intense directional metamorphism and pressure resulting in intense folding, fracturing and faulting. Geological map of the study area is shown in Figure 3.2.

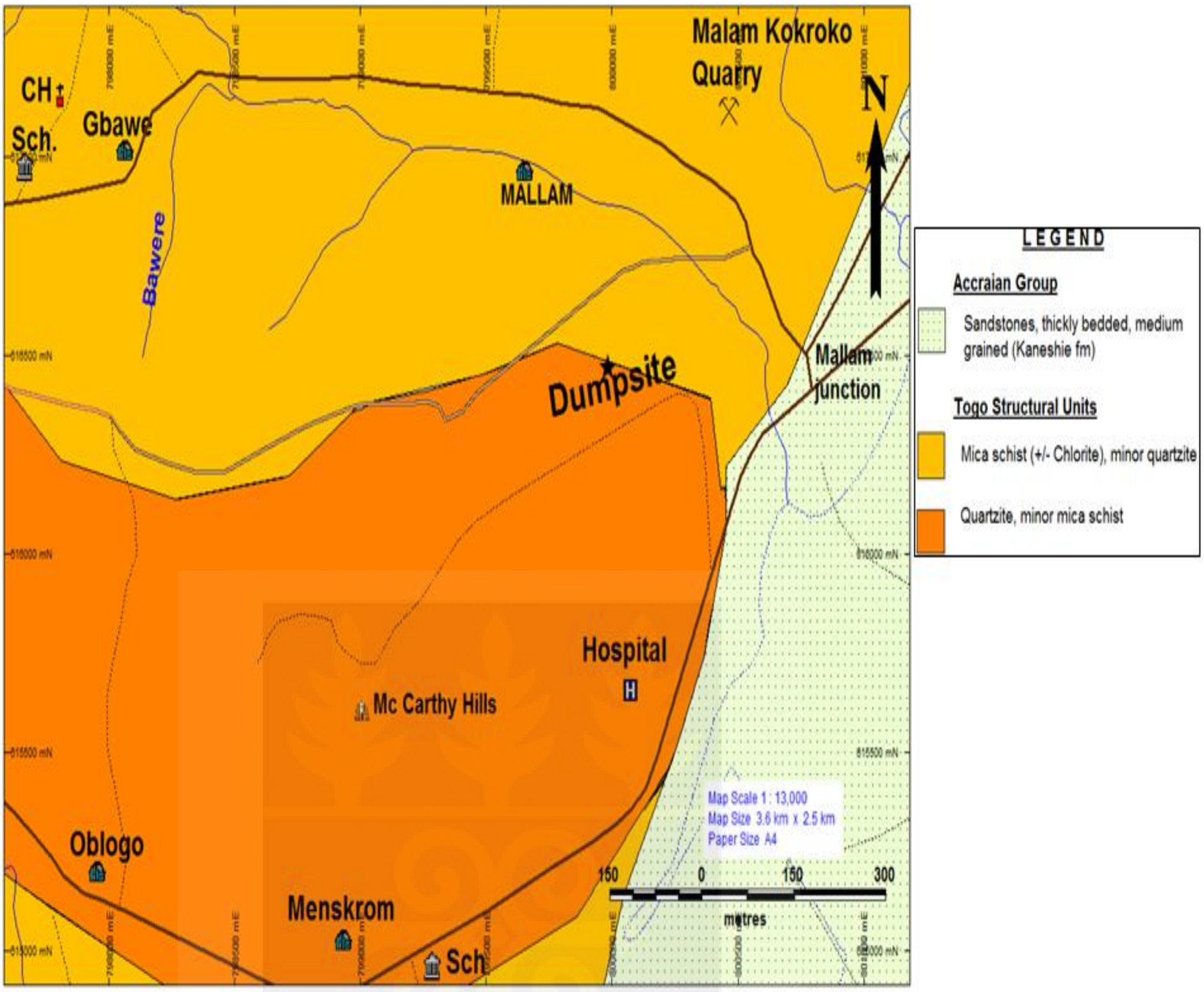


Figure 3.2 Geological map of the study area

## 3.2 Data Collection

Prior to the fieldwork, a desk study was carried out to, among other things, study the general physiography of the area and site map of the main study area and to review literature on leachate, the unsaturated zone, protocols for sampling, sample preservation and quality assurance. Site reconnaissance surveys were also carried out.

### 3.3 Waste Characterization

As indicated earlier, the composition and toxicological significance of landfill leachate depends on the waste stream. In the 7- year operation as a municipal waste disposal site, the closed Mallam SCC waste disposal site received variety of waste.

A secondary data on the percentage composition of the waste stream is shown in Table 3.1.

Table 3.1 Percentage composition of the waste stream in the Mallam SCC waste disposal site

| **Type of Waste** | Organic* | Paper | Textile | Plastic | Glass | Metals | Inert | Others |
|---|---|---|---|---|---|---|---|---|
| **%Composition** | 65 | 6 | 1.7 | 3.5 | 3 | 2.5 | 17.1 | 1.2 |

*(food and plant components)

Source : Waste Management Department, Accra Metropolitan Assembly(1999)

### 3.4 Fieldwork

This involved sampling of surface water, soil from drilled profiles, water from hand-dug wells and leachate as well as measurement of physico-chemical parameters (pH, Temperature, Electrical Conductivity, Total Dissolved Solids, Salinity and Alkalinity) of water and leachate samples.

### 3.5 Sample Collection and Quality Assurance

Samples were collected from four surface water points, five soil drilled profile points, four hand-dug wells and four leachate points. A total of four surface water, twenty-five soil, four hand-dug wells and four leachate samples were used for the study.

The water and leachate were sampled in October, 2012 and January, 2013 while soils from the drilled profiles were sampled in November, 2012.

The leachate and water samples were all collected in pre-conditioned high density polyethylene bottles. The bottles were conditioned by washing initially with detergent, then with ten percent (10 %) nitric acid, and finally rinsing with distilled water. This was done to avoid contamination. The water samples were taken in triplicate (samples for major ions, trace metals and stable isotope analyses) while the leachate samples were in duplicate (samples for major ions and trace metals analyses).

The samples for trace metals analysis were preserved with three drops of concentrated nitric acid at about pH of 2. This was done to prevent the trace metals from adsorping to the walls of the sampling bottles.

The samples for stable isotopes analysis were collected in 60 ml pre-conditioned bottles without acidification or filtration. The bottles were filled to the brim and tightly capped to prevent evaporation. The samples were all well labelled.

All the samples, except that for the stable isotopes analysis, were kept in thermo-insulated container with ice cubes to as much as possible preserve them in their natural state. Samples for the isotope analysis were, however, not ice packed to prevent condensation.

Five soil profiles were drilled (in areas around the waste disposal site) to a depth ranging from 100 to 200 cm, using the hand auger. Five soil samples at 20 cm intervals were taken from each profile. At least 500.0 g of fresh soil sample was collected at each interval. The samples were collected using plastic trowel into aluminium foils and then packaged in clean polyethylene bags with emetic seal. The samples were well labelled and kept in thermo-insulated container with ice cubes to protect the samples from physical and chemical changes (such as drying and oxidation) as much as possible.

The samples were all transported to the Ghana Atomic Energy Commission laboratories for preparations and analyses. Detail descriptions of the sampling points are shown in Table 3.2 and Figure 3.3.

Table 3.2 Description of the sampling points

| **Sample ID** | **Sample Site** | **GPS Location** | **Remarks** |
|---|---|---|---|
| L1 | 1 m from northern part of the dumpsite | N05.57189$^0$<br>W000.29137$^0$ | Leachate sampled. Dark brown colouration |
| L2 | 2 m from the northeastern part of the dumpsite | N05.57213$^0$<br>W000.29104$^0$ | Leachate sampled. Dark brown colouration |
| L3 | 15 m from the northeastern part of the dumpsite | N05.57312$^0$<br>W000.29063$^0$ | Leachate sampled. Dark brown colouration |
| L4 | 2 m from the western part of the dumpsite | N05.57189$^0$<br>W000.29671$^0$ | Leachate sampled. Dark brown colouration |
| SW1 | 20 m from the northeastern part of the dumpsite. | N05.57300$^0$<br>W000.28925$^0$ | Surface water sampled. Leachate flows horizontally from the dumpsite to the point |
| SW2 | 30 m southeastern of SW1 | N05.56867$^0$<br>W000.28646 | Surface water sampled. |
| SW3 | 50 m southeastern of SW1 | N05.56734$^0$<br>W000.28627$^0$ | Surface water Sampled. |
| SW4 | 300 m north of SW1 | N05.57764$^0$<br>W000.30576$^0$ | Surface water sampled |
| G1 | 70 m from the northwestern part of the dumpsite. House number 200. | N05.57601$^0$<br>W000.29462$^0$ | Groundwater sampled. Hand-dug well located close to a cesspit |
| G2 | 60 m from the northern part of the dumpsite. House number 6. | N05.57462$^0$<br>W000.29193$^0$ | Groundwater sampled. Hand-dug well |
| G3 | 60 m from the northern part of the dumpsite. House number 4. | N05.57454$^0$<br>W000.29181$^0$ | Groundwater sampled. Hand-dug well |

Table 3.2 Continued

| Sample ID | Sample Site | GPS Location | Remarks |
|---|---|---|---|
| G4 | 65 m from the northeastern part of the dumpsite. House number 8. | $N05.57458^0$<br>$W000.29092^0$ | Groundwater sampled. Hand-dug well located close to a septic tank |
| SPA | 10 m from the northeastern part of the dumpsite. House number 35 | $N05^0 34.359$<br>$W000^0 17.460$ | Soil sampled |
| SPB | 30 m from the northern part of the dumpsite. House number 10 | $N05^0 34.370$<br>$W000^0 17.617$ | Soil sampled |
| SPC | About 40 m northwestern part of the dumpsite. House number 102 | $N05^0 34.357$<br>$W000^0 17.719$ | Soil sampled |
| SPD | About 65 m from the northwestern part of the dumpsite. House number 200. | $N05^0 34.546$<br>$W000^0 17.672$ | Soil sampled |
| SPE | About 200 m from the northeastern part of dumpsite. New Life School | $N05^0 34.560$<br>$W000^0 17.410$ | Soil sampled |

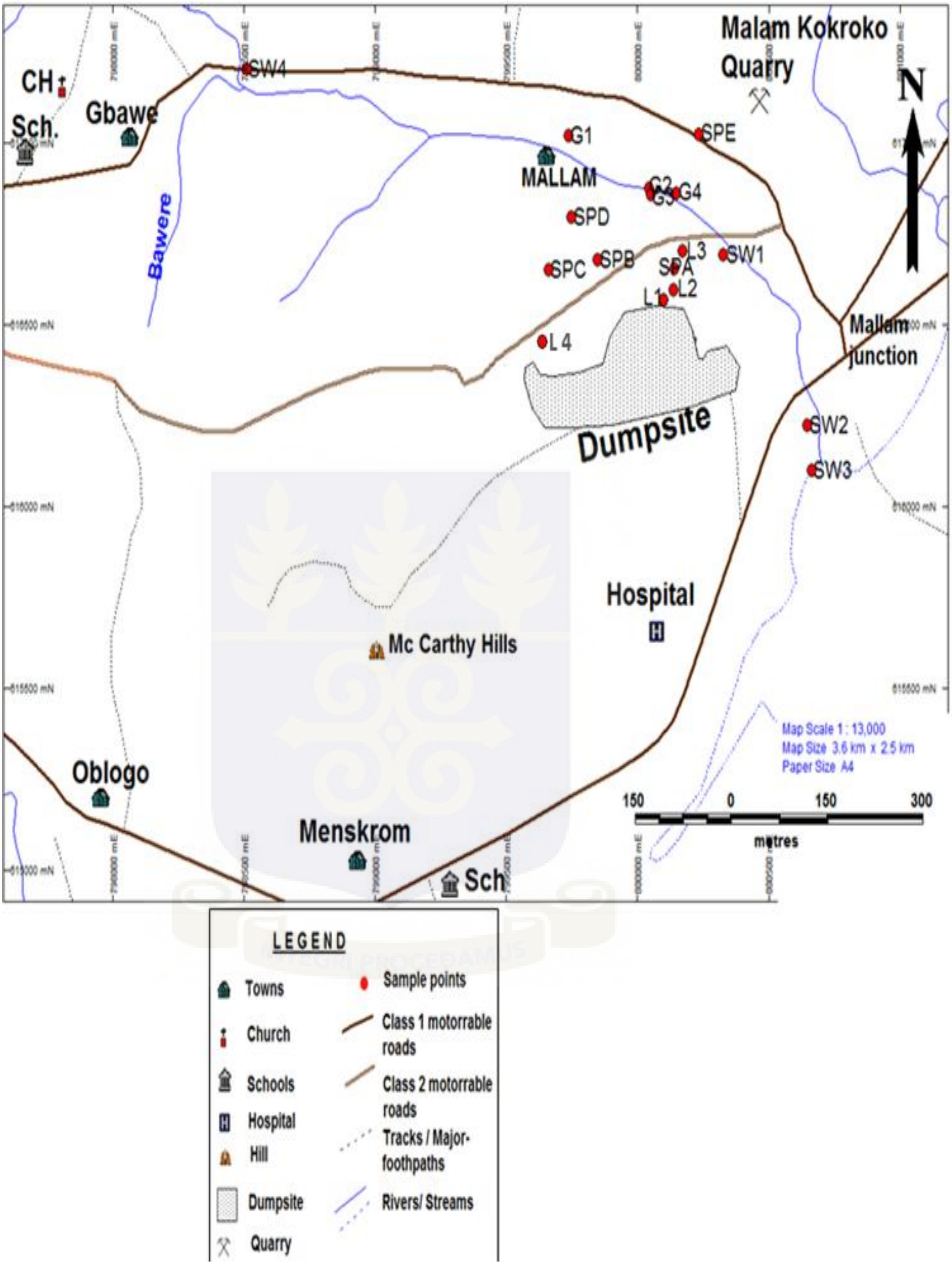


Figure 3.3 Map of the study area showing the location of the sampling points

## 3.6 In-Situ Measurements

The water and leachate samples were subjected to the following in-situ measurements using the appropriate methods or instruments.

### 3.6.1 pH, Temperature, Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

A multi-function HACH Sension 5 portable pH meter was used to measure pH and temperature while electrical conductivity (EC) and total dissolved solids (TDS) measurements were made using a multi-function HACH Sension 5 conductivity meter. Prior to their usage, the meters were both calibrated. The pH meter was calibrated with standard pH buffers 4.01, 7.0 and 9.21, respectively. The conductivity meter was calibrated using the following standard solutions; 0.01 M KCl (Conductivity: 1413 $\mu$Scm$^{-1}$) and 0.1 M KCl (Conductivity: 12880 $\mu$Scm$^{-1}$).

The pH and conductivity meters were placed simultaneously in a beaker containing each sample. The readings were taken each time the meters stabilized. After each reading, the electrodes were rinsed with double distilled water and small portion of the next sample to be determined.

### 3.6.2 Determination of Alkalinity and Bicarbonate

Alkalinity can be determined by either the potentiometric method or methyl orange indicator method. The choice of a method is dependent on the pH of the sample. The methyl orange indicator method is used for samples with pH < 4.5 while the potentiometric method is used for samples with pH > 4.5 (Eaton *et al*., 1995)

In this work, the potentiometric method was employed since pH of the samples was greater than 4.5. 25 mL aliquot of each sample was measured with a measuring cylinder and transferred into 250 mL conical flask and titrated against 0.02 M HCl solution till a pH of 4.5 is obtained. Three replicate titrations were done and the mean (titre) value calculated. The volume of sample, HCl (average titre) and the molarity of the acid were used to compute the alkalinity using the equation 3.1 (Eaton *et al.*, 1995)

$$\boldsymbol{Alkalinity}\left(\boldsymbol{mg}\frac{\boldsymbol{CaCO_3}}{\boldsymbol{L}}\right) = \frac{\boldsymbol{A \times M \times 50000}}{\boldsymbol{Volume\ (V) of\ sample}} \qquad \textbf{3.1}$$

where,

A = the averaged titre value in mL

M = the molarity of the acid (HCl solution)

The bicarbonate concentration was calculated using equation 3.2 (Eaton *et al.*, 1995).

$$[\boldsymbol{HCO_3^-}] = (\mathbf{1.2191817}) \times \boldsymbol{Alkalinity} \qquad \textbf{3.2}$$

## 3.7 Laboratory Analysis

This describes the sample preparations and analytical techniques employed in the laboratories for the determination of major ions, trace metals, soil physical parameters and stable isotopic composition of the samples.

### 3.7.1 Analysis of Major Ions in Water and Leachate Samples

This describes the analytical techniques used in the determination of the concentrations $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $PO_4^{3-}$ in the samples.

#### 3.7.1.1 Analysis of $Na^+$ and $K^+$

The levels of $Na^+$ and $K^+$ in the samples were determined by the flame emission photometric method, using the Sherwood 420 Flame Photometer (Sherwood, UK).

**Calibration**

2 mL of the suppressor solution was added to 5 mL of the mixed Na and K standard and thoroughly mixed by swirling. The combined solution was aspirated into the liquefied petroleum gas (LPG) – fed flame of the Sherwood 420 Flame photometer. The concentrations of Na and K were read at their respective wavelengths (K: 766.5 nm; and Na: 589 nm).

**Analysis**

A blank solution made of thoroughly mixed double -distilled water and suppressor solution (5:2), was aspirated into the (LPG) fed flame of the Sherwood 420 Flame Photometer. After analysis of the blank, the Na and K content of the water and leachate samples were determined. The procedure is as follows: 5 mL of the each sample was transferred into 10 mL test tube followed by addition of 2 mL of suppressor solution. The mixture was homogenized by shaking for about 1 minute. The homogenized solution was aspirated into the flame of the photometer. The contents of Na and K were read and recorded.

#### 3.7.1.2 Analysis of $Ca^{2+}$

The most widely used method for the determination of $Ca^{2+}$ is by complexometric titration involving ethylene diamine tetra-acetic acid (EDTA) with ammonium purpurate (murexide) powder as an indicator. Murexide at a pH 11 is purple in colour in the absence of $Ca^{2+}$ but in the presence of $Ca^{2+}$ ions it forms pink complex.

**Analysis**

For the purpose of this study blank solutions were first titrated to serve as correction for the samples. 25 mL of each sample was measured into a 250 ml conical flask, followed by 1.5 mL of NaOH solution and approximately 50 mg of murexide indicator powder was added to the sample solution before titration. The solution was titrated against 0.01 M EDTA solution till the colour changes from purple to pink. In the final stage of the titration, EDTA solution was added drop-wise as the colour change is not instantaneous and the end point was compared to the blank solution. The concentrations of Ca was calculated by using equation 3.3

$$mg\ of\ \frac{Ca}{L} = \frac{(A\ x\ B)\ x\ 400.8}{ml\ of\ sample} \qquad 3.3$$

where,

A = titre value

B = mg/CaCo$_3$ equivalent to 1ml of EDTA titrant at the Ca indicator end point

### 3.7.1.3 Analysis of Mg$^{2+}$

The concentrations of Mg$^{2+}$was determined using Atomic Absorption Spectrometry (AAS). The concentration of Mg$^{2+}$ was then calculated from equation 3.4 (Eaton *et al*., 1995).

$$\textbf{Final Concentration} = Absorbance\ \ x\ Dilution\ factor \qquad 3.4$$

### 3.7.1.4 Analysis of Chloride (Cl$^-$)

Chloride ($Cl^-$) was determined by titrimetry using the argentometric method. A blank solution was prepared by measuring 25 mL of double-distilled water and titrated against AgNO$_3$ using potassium chromate (K$_2$Cr$_2$O$_4$) solution as indicator.

The chloride content of the samples was determined as follows:

25 mL of each sample was measured using a measured into a conical flask and titrated with 0.0141 M $AgNO_3$ using $K_2Cr_2O_4$ till the greenish yellow colour of the solution changed to brick-red. Three replicate titrations were done and the mean titre calculated. The chloride content was calculated from equation 3.5 (Eaton *et al.*, 1995)

$$mg/L = \frac{(A-B) \times M \times 35.45 \times 1000}{ml\ of\ sample} \qquad 3.5$$

where,
A = average titre
B = titre value for the blank solution
M = molarity of $AgNO_3$.

#### 3.7.1.5 Analysis of Nitrate ($NO_3^-$), Sulphate ($SO_4^{2-}$) and Phosphate ($PO_4^{3-}$)

The nitrate, sulphate and phosphate concentrations in the samples were determined according to the official methods in the Association of Official Analytical Chemists. Nitrate was determined using the Association of Official Analytical Chemists (AOAC) Official method 973.50 (AOAC, 1995). The Official method 4500 - $SO_4^{2-}$ E (Turbidimetric method) was used for the determination of sulphate. Phosphate was determined by Official method 4500 - P E (Ascorbic acid method) (AOAC, 1995).

##### 3.7.1.5.1 Analysis of Nitrate ($NO_3^-$)

**Principle**

The method is based on the reaction of nitrate ion with brucine sulphate in $H_2SO_4$ solution at a temperature of 100 °C. The yellow colour of the resulting complex is measured at a wavelength of 410 nm.

**Calibration**

5 mL of each of the calibrant solution was pipetted into separate 20 mL test tube. To each test tube, 1 mL of 30 % of NaCl was added, followed by addition of 5 mL of 6.5 M $H_2SO_4$. The test tube was shaken to ensure thoroughly mixing of the reagents.

0.5 mL of the brucine - sulphanilic acid was added to the content of each test tube except the blank. The test tube was then packed on a rack and lowered into a water bath at 95 °C for 25 minutes. At the end of the 25 minutes, the rack together with the test tube was removed from the water bath and immersed in ice. An appropriate aliquot of the yellow coloured calibrant solutions was transferred into 1 cm cell. The cell was placed into the spectrophotometer and the absorbance of the solution measured at a wavelength of 410 nm. A standard graph of absorbance of standards against concentration of standards was plotted (Appendix H).

**Analysis**

5 mL aliquot of each water and leachate samples were transferred into separate 20 mL test tube and the same procedure used for the establishment of the calibration graph was followed to obtain the absorbance of each of the samples at a wavelength of 410 nm on the UV - Visible Spectrophotometer. The concentration of $NO_3^-$ in the sample was deduced from the calibration graph. The concentration was calculated from the relation:

$$\boldsymbol{C_{NO_3^-} = C_{calibration} \times D_f} \qquad \mathbf{3.6}$$

where,

$C_{NO_3^-}$ = nitrate concentration

$C_{calibration}$ = concentration from the calibration graph

$D_f$ = dilution factor

### 3.7.1.5.2 Analysis of Sulphate ($SO_4^{2-}$)

**Principle**

The method is based on the reaction of $SO_4^{2-}$ with barium chloride ($BaCl_2$) under acidic conditions to precipitate barium sulphate ($BaSO_4$). The absorbance of white

$BaSO_4$ suspension is measured at a wavelength of 420 nm on the UV – Visible Spectrophotometer.

**Calibration**

10 mL of the standard $SO_4^{2-}$ calibrants solutions were quantitatively transferred into separate test tubes. To each test tube, 1 mL of the acid salt solution, 0.5 mL glycerol solution (conc.) and 0.5 g of $BaCl_2$ were added. The resulting cloudy solution was shaken for 50 seconds and left to stand for 5 minutes. Appropriate aliquot of the cloudy solution was transferred into 1 cm cell and the absorbance of the coloured solution measured at a wavelength of 420 nm on the UV – Visible Spectrophotometer. The absorbance of each calibrant solution was plotted against concentration of the calibrants (Appendix H). A straight line graph was obtained. The concentrations of the water and leachate samples were deduced from the graph after measurement of the absorbance for each sample at a wavelength of 420 nm on the UV - Visible Spectrophotometer.

**Analysis**

10 mL aliquot of each sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to obtain the absorbance at a wavelength of 420 nm on the UV - Visible Spectrophotometer. The concentration of $SO_4^{2-}$ in each of the water and leachate samples was obtained from the calibration graph.

#### 3.7.1.5.3 Analysis of Phosphate ($PO_4^{3-}$)

**Principle**

Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form an antimonyl - phosphomolybdate complex, which is reduced to intensely coloured molybdenum blue by ascorbic acid. The absorbance of the molybdenum blue is measured at a wavelength of 880 nm on a UV - Visible Spectrophotometer.

### Calibration of UV-Visible Spectrophotometer

In order to construct a calibration curve, 10 mL aliquot of the calibrant solutions were transferred into separate 20 mL test tubes. To each test tube, 2 mL of the combined reagent was added to each test tube and left to stand for about 5 minutes. During this period, the blue colour of antimonyl - phosphomolybdate complex was developed in each test tube. Appropriate aliquot of each blue – coloured calibrant solution was transferred into a 1 mL cuvette; the cuvette was inserted into the spectrophotometer and the absorbance measured at a wavelength of 880 nm against a reagent blank. A calibration graph of absorbance against concentration of $PO_4^{3-}$ in each calibrant solution was plotted (Appendix H). The concentration of $PO_4^{3-}$ in the sample was deduced from the calibration graph.

### Analysis

10 mL aliquot of the each sample was transferred into a 20 mL test tube and the same procedure as used for the establishment of the calibration graph was followed to obtain the absorbance of each sample at a wavelength of 880 nm on the UV -Visible Spectrophotometer. The concentration of $PO_4^{3-}$ in the water samples was obtained from the calibration graph.

## 3.8 Analysis of Trace elements

The trace elements were determined using the Atomic Absorption Spectrometry (AAS). Atomic absorption spectrometry operates on the principle that the atom in the ground state absorbs the light of wavelengths that are characteristic to each element when light is passed through the atoms in the vapour state. Since the light absorbed depends on the concentration of atoms in the vapour, the concentration of the target element can be determined from the measured absorbance (USEPA, 1991). Flame Atomic Absorption Spectrometry (FAAS) and Cold Vapour Atomic Absorption Spectrometry were employed in the analysis of the trace elements. Prior to the analysis the samples were acid digested.

### 3.8.1 Digestion of Water and Leachate Samples

5 ml of each raw sample was measured in three replicates into TFM Teflon vessels of microwave digester (ETHOS 900). 6 mL of 65 % of concentrated $HNO_3$, 3 ml of 35 % HCl and 0.25 % $H_2O_2$ was added to each vessel containing the sample. The vessels were swirled gently to mix well and fitted vertically into the microwave digester and digested for 20 minutes. Once digestion was completed, the solution containing the sample were cooled in water bath for twenty (20) minutes to reduce high temperature and pressure build-up within the vessels. The mixture was then transferred quantitatively into volumetric flask and diluted to 20 ml using deionised distilled water. All the samples were analysed using VARIAN AA 250FS Atomic Absorption Spectrometer. To ensure the reliability of the analytical method during digestion and sample preparation, blank samples were also digested along with each set of samples and subsequently analysed for appropriate elements through the same procedure.

### 3.8.2 Digestion of Soil Samples

1.5 g of each air dried, crushed, pulverished and sieved soil sample was measured weighed into a pre-prepared 45 mL Teflon beakers of a microwave acid digestion bomb. 6 ml of concentrated $HNO_3$, 3 mL $H_2SO4$ and 0.25 mL $H_2O_2$ were added to the sediment samples. The Teflon beakers with the bomb were closed tightly. The bomb was placed at the center of a microwave oven (ETHOS 900 Microwave Labstation) and digested for 43 minutes. Once digesting time elapsed, the bomb was removed and placed in a vent for 5 minutes and the vessels with their contents were cooled in a water bath for 25 minutes to reduce high temperature and pressure that may have built-up within the vessels. The mixture was then transferred quantitatively into a volumetric flask and diluted to 20 mL using deionised water. Quality assurance and quality control included the preparation of reagent blank in a similar manner as the samples without the analyte along with each set of samples and subsequently analysed for the elements of interest.

### 3.8.3 Atomic Absorption Measurements

Fast Sequential Atomic Absorptions Spectrometer (VARIAN, AA 250 FS, Australia) was used for atomic absorption measurements. Fe, Pb, Cd, Cr, Mn, As, Zn, Cu and Co were measured using Flame Absorption Atomic Spectrometry (FAAS) while Hg was measured using Cold Vapour Atomic Absorption Spectrometry.

#### 3.8.3.1. Calibration of Atomic Absorption Spectrometer

The Atomic Absorption Spectrometer was calibrated with the calibration standards for the element being determined. The absorbances obtained were used to plot calibration graphs for each element. Three standard solutions (of the same element) of increasing concentrations were used to establish the reliability of readings since the equipment is already fixed to a programmable computer that reads out concentration and absorbance directly. The calibration function was established by plotting absorbance (% absorption) for a set of calibration solutions against the concentration analyte

(Appendix G). Linearity of the calibration curves were checked before samples were aspirated. “Resloping” was carried out with standards during readings to account for instrumental drift. After the calibration, each element was determined by measurement of the absorbances of the samples aspirated into the absorption cell.

#### 3.8.3.2 Calculation of the Final Concentrations of the Analysed Trace Elements

The final concentration of each analysed element was calculated from the relation:

$$\boldsymbol{Final\ Concentration} = \frac{\boldsymbol{Conc(DF)\ x\ \ Nominal\ Volume}}{\boldsymbol{Sample\ Weight}} \tag{3.7}$$

where, Conc = AAS reading

DF = dilution factor

Nominal volume = the final volume after the reagent and water was added

## 3.9 Determination of the Solway Weighted Water Quality Index of the Surface Water and Groundwater Samples

The mean values of the measured pH, $NO_3^-$ , $PO_4^{3-}$ , EC and temperature of the surface water and groundwater samples were each assigned water quality ratings (weightings) from a statistically calculated rating table generated by Bolten *et al*.(1978) (Appendix F). The Weighted Water Quality Index (Solway Index) was then calculated from the relation below;

$$\textbf{Solway Index (weighted)} = \frac{1}{x}\left(\sum_{i=}^{n} q_i\, w_i\right)^2 \tag{3.8}$$

where ,

x = the sum of the maximum weightings of the parameters being considered

$q_i$ and $w_i$ = the quality and weighting, respectively, of the $n^{th}$

Based on the value of the calculated Water Quality Index, the quality of the water is classified into one of the four classes indicated in Table 3.3.

Table 3.3 Solway water quality classifications

| **Class** | **Range** | **Description** |
|---|---|---|
| I | > 80 | Good* |
| II | > 50 – 80 | Fairly good** |
| III | 25 – 50 | Poor quality*** |
| IV | < 25 | Grossly polluted **** |

Source ; Water Resource Commission, Ghana (2003)

* (Water unpolluted and/or is recovering from pollution; all uses are protected with only a minor degree of threat or impairment; no uses are ever interrupted and conditions rarely depart from natural or desirable levels).

** (Most uses of the water are protected but a few are threatened or impaired; a single use may be temporarily interrupted and conditions sometimes depart from natural or desirable levels).

*** (Several uses of water are threatened or impaired; more than one use may be temporarily interrupted and conditions often depart from natural or desirable levels).

**** (Most uses of water are threatened or impaired; several uses may be temporarily interrupted and conditions usually depart from natural or desirable levels).

## 3.10 Determination of Soil Physical Parameters

Water content, bulk density, porosity and particle size distribution of the drilled profiles were determined using the methods described below.

### 3.10.1 Determination of Soil Water Content

The gravimetric and volumetric water contents of each soil sample were determined as describe below.

10 g of the wet soil sample was weighed into an aluminium can of known weight and oven dried at a temperature of 105 °C for 48 hours to obtain an average constant weight (Egbi, 2011). The gravimetric (Ɵg) and volumetric (Ɵv) water contents were then calculated from equation 3.9 and 3.10 respectively (Egbi, 2011).

$$\Theta \qquad \Theta g = \frac{Ww - Wd}{Wd} \text{ x } 100 \qquad 3.9$$

$$\Theta \qquad \Theta v = \Theta g \text{ x } Bd \qquad 3.10$$

where,

Ww = Weight of the wet soil
Wd = Weight of the oven dried soil
Bd = Bulk density of the soil

### 3.10.2 Determination of bulk density

The bulk density of each soil sample was determined using the clod method (Egbi, 2011). A firm representative clod of about 2 cm in diameter was weighed precisely up to 0.01 g from each soil sample. About 25 cm long thread (wax) of known weight was tied to the clod firmly on one end. The clod was then carefully immersed in a graduated measuring cylinder filled with water. The volume of water displaced equals the volume of clod and the wax. With the specific gravity or density of wax being 0.86 g/cm$^3$ and its known weight, the volume of the wax was determined. The volume of the clod (soil sample) was obtained by subtracting the volume of the wax from the volume of the water displaced on immersion of the clod. The dry mass of the sample was also determined after oven drying the soil at a temperature of 105 °C for 48 hours to obtain an average constant weight. The bulk density was then determined from the equation 3.11.

$$Bd = \frac{Oven\ Dried\ Weight\ of\ soil(clod)}{Volume\ of\ Clod} \qquad 3.11$$

### 3.10.3 Porosity

Porosity of the soil was determined from equation 3.12 below (Egbi, 2011);

$$\mathbf{n\ \% = \left(1 - \frac{B_d}{P_d}\right) \times 100} \qquad 3.12$$

where,

n % = percentage porosity

$B_d$ = bulk density

$P_d$ = particle size density (2.65 g/cm)

### 3.10.4 Particle Size Analysis

In particle size analysis, the mineral part of the soil was separated into various size fractions and the proportions of these fractions determined. The soil samples were pretreated to remove organic matter and the different fractions separated as follows.

#### 3.10.4.1 Pre-treatment of soil sample for particle size analysis

Approximately 20 g of homogenized soil sample was placed into a 1liter beaker; 100 ml acetate buffer (1 M) was added and heated on a water bath (100 °C) until it gives off no effervescence. About 25 ml of the buffer was then added to the mixture successively until effervescence reoccurred. The mixture was then centrifuged and decanted. About 250 ml of deionised water was added to the residue, centrifuged and decanted. About 15 ml each of deionised water and 30 % Hydrogen Peroxide were then added to residue in a beaker; covered with a watch glass and allowed to stand overnight. The beaker with the residues was placed in a water bath (80 °C) and 5 to 10 ml $H_2O_2$ (30 %) added successively until decomposition of organic matter was completed as supernatant becomes clear. Water was then added up to 300 ml and boiled on a hot plate for about an hour to remove any remaining $H_2O_2$. The sample was cool, centrifuged and decanted. Approximately 300 ml of water was then added to disperse the soil residues. The suspension formed was quantitatively transferred into a 1liter polythene bottle where 20 ml of a dispersing agent (Sodium hexametaphosphate 4 % and soda 1 % solution) and 400 ml of water were added. It was shaken for 16 hours on a shaker at speed of about 30 revolutions per minute.

#### 3.10.4.2 Separation of fractions

The suspension was passed through a 50 µm sieve which was placed in a funnel positioned above a 1 liter sedimentation cylinder with a stand and clamp. The filtrate was then topped up with water to the 1liter mark and this was used for the clay silt fraction determination. The sand fraction which remained on the sieve was quantitatively washed into a porcelain dish, evaporated on the water bath and dried for at least an hour.

#### 3.10.4.3 Determination of sand fraction

The dried sand was transferred into the top sieve of a stacked set of the following mesh sizes; 250 µm, 100 µm and 50 µm. It was sieved for 10 minutes on the sieving machine at amplitude of 7 and intervals of 4. Each of the sieves was then emptied into a weighing dish and accurately weighed.

#### 3.10.4.4 Determination of silt and clay by hydrometer

The suspension obtained from the separation of fractions was allowed to equilibrate thermally and temperature recorded. The sedimentation cylinder was covered and shaken after which a drop of amyl alcohol was added. The hydrometer was carefully lowered into the suspension and readings recorded. The hydrometer was removed, rinsed and wiped to dryness. The hydrometer was reinserted into the suspension and readings recorded at the following minutes; 5, 120 and 960. This was also repeated for a blank sample.

## 3.11 Extraction of Soil Pore Water

A vacuum extraction line consisting of four parallel units with cryogenic collection of the extracted soil water was used to extract water from the soil samples (Appendix A). 250 g of each soil sample was extracted. The extraction was performed under static vacuum, after a brief outgassing of the system at the beginning of each extraction run. The maximum extraction time used was around 7 hours, with temperature maintained at about 95$^o$C (Araguás-Araguás *et al.*, 1995). The extracted soil water was poured into 300 ml glass bottle and tightly sealed to avoid evaporation. The extracted soil pore samples were labelled and made ready for the determination of their stable isotopic composition. For quality control purposes, the performance of the extraction system was checked prior to the extraction of the samples. This was done by adding water of known isotopic composition ($\delta\ ^{18}O$) to dry soil samples and extracting these soil samples using the extraction system. The isotopic content of the extracted water was then compared with those of the original water. The results were reproducible and well within the acceptable error limits.

## 3.12 Determination of the Stable Isotopes of Water

### Instrumentation

Determination of the composition of the isotopes ($\delta\ ^{18}O$ and $\delta\ ^{2}H$) in the water samples was accomplished using the Los Gatos DLT - 100 Liquid - water Stable Isotope Analyzer (off - axis integrated cavity output spectroscopy (OA - ICOS) via laser absorption). The equipment is made up of laser analysis system, an internal computer, a CTC LC - PAL liquid auto-sampler, a small membrane vacuum pump and a room air intake line that passes air through a Drierite column for moisture removal. The auto-sampler and the DLT - 100 are connected by ~ 1 m long polytetrafluoroethylene (PTFE) transfer line. A 1.2 $\mu$L microliter syringe (Model 7701.2N, Hamilton) is used to inject 0.75 $\mu$L of sample through PTFE septum in the auto-sampler.

### Reference Material

The validity of the isotopic composition analysis ($\delta^2 H$ and $\delta^{18} O$) using the liquid - water stable isotope analyzer was checked by International Atomic Energy Agency (IAEA) reference material, GISP [(Water) ($\delta^2 H_{VSMOW}$ and $\delta^{18} O_{VSMOW}$)]. This reference material is also known as NIST RM 8536 and was developed by the IAEA in cooperation with the US National Institute of Standards and Technology (NIST).

### Standard

Three secondary standards were used for the analysis: two calibration standards [prepared from IAEA reference material, GISP ([(Water) ($\delta^2 H_{VSMOW}$ and $\delta^{18} O_{VSMOW}$)], and a control standard (in - house prepared).

Calibration standard 1: STD$_1$ (WS$_1$) - enriched: $\delta^2 H = 2.10 \pm 0.3\ Hg$ and $\delta^{18} O = 0.24 \pm 0.03$

Calibration standard 2: STD$_2$ (WS$_2$) – depleted: $\delta^2 H = -117.00 \pm 1.0$ and $\delta^{18} O = -15.55 \pm 0.1$

Calibration standard 1: STD$_1$ (WS$_1$) – control: $\delta^2 H = -68.78 \pm 0.6$ and $\delta^{18} O = -9.6 \pm 0.8$

**Experimental procedure**

The experimental procedure was according to the methods prescribed in the International Atomic Energy Agency (IAEA) Training Course Series 35 [IAEA laser spectroscopic analysis of liquid samples for stable hydrogen and oxygen isotopes], (IAEA, 2009). The procedure is as follows:

1 mL aliquot of each standard (in - house, working and control) and 1 mL aliquot of the water sample were quantitatively transferred into 1.5 mL auto - sampler glass using the 1000 $\mu$L Eppendorf disposable tip pipette. The 1.5 mL auto - sampler glass vial were then capped with PTFE septum caps. This was followed by the arrangement of the samples on the CTC LC PAL auto - sampler. The arrangement of the samples and the standards is also according the procedure described below (IAEA, 2009): A dummy sample (de - ionized water) was place in the first position to prime the flow line. The dummy vial was followed by the three secondary standards (two calibration standards and a control standard); five water samples, followed by another set of three standards. This array of standards and water samples were repeated up to a maximum six times (30 water samples) for a single run. Each standard and water sample was individually measured six injections lasting for 25 minutes. Measurement for each batch of 30 samples lasted for 20 hours. The measurement results for the last four of the six injections from each vial were averaged. The measured and the known δ

values of calibration standards before and after each batch of five water samples were used for a linear regression to convert absolute isotope ratios to δ values.

Since the instrument is prone to give erratic results during the start of a run, the dummy sample used allowed the system to stabilize before the first standards were run on the liquid - water analyzer (IAEA, 2009). The arrangement of the vials in the CTC LC PAL auto - sampler was designed to overcome the effects of instrumental drift which can be significant during a daily run (IAEA, 2009). The first two injections were disregarded because they are often less stable and the injections with the most potential for carrying a memory effect of the previous sample (IAEA, 2009).

# CHAPTER FOUR

# RESULTS AND DISCUSSIONS

## 4.1 Physico-Chemical Parameters of Leachate, Surface Water and Groudwater Samples

The physico-chemical paramaters of leachate, surface water and groundwater samples are presented in Table 4.1.

Table 4.1 Physico-chemical parameters of leachate (L), surface water (SW) and groundwater(G) samples

| Sample ID | Date of Sampling | Temp | pH | EC(µS/cm) | TDS(mg/L) | T. Alk(mg/L) |
|---|---|---|---|---|---|---|
| L1 | 25/10/2012 | 25.1 | 8.82 | 13700 | 6860 | 3780 |
| L2 | 25/10/2012 | 25.3 | 8.51 | 14270 | 7120 | 5400 |
| L3 | 25/10/2012 | 25.1 | 8.73 | 12740 | 6310 | 4600 |
| L4 | 25/10/2012 | 25.3 | 8.89 | 12070 | 6040 | 3900 |
| L1 | 27/ 01/ 2013 | 25.3 | 8.39 | 15390 | 7700 | 2900 |
| L2 | 27/ 01/ 2013 | 25.0 | 8.22 | 14260 | 7110 | 3100 |
| L3 | 27/ 01/ 2013 | 25.0 | 8.47 | 12490 | 6250 | 2500 |
| L4 | 27/ 01/ 2013 | 24.7 | 9.03 | 20800 | 10350 | 2800 |
| Min |  | 24.7 | 8.22 | 12070 | 6040 | 2500 |
| Max |  | 25.3 | 9.03 | 20800 | 10350 | 5400 |
| Mean |  | 25.1 | 8.63 | 14465 | 7218 | 3623 |
| StDev |  | 0.2 | 0.28 | 2784 | 1380 | 996 |
| SW1 | 25/10/2012 | 27.9 | 7.76 | 1061 | 534 | 400 |
| SW2 | 25/10/2012 | 28 | 7.66 | 1025 | 512 | 176 |
| SW3 | 25/10/2012 | 28.3 | 7.50 | 1036 | 518 | 188 |
| SW4 | 25/10/2012 | 27.7 | 7.40 | 1043 | 522 | 156 |
| SW1 | 27/ 01/ 2013 | 24.6 | 7.51 | 1206 | 600 | 1700 |
| SW2 | 27/ 01/ 2013 | 24.9 | 7.56 | 1171 | 583 | 600 |
| SW3 | 27/ 01/ 2013 | 25.1 | 7.65 | 1167 | 581 | 200 |
| SW4 | 27/ 01/ 2013 | 25.1 | 8.02 | 1124 | 561 | 600 |
| Min |  | 24.6 | 7.40 | 1025 | 512 | 156 |
| Max |  | 28.3 | 8.02 | 1206 | 600 | 1700 |
| Mean |  | 26.5 | 7.65 | 1106 | 552 | 588 |
| StDev |  | 1.6 | 0.19 | 71 | 34 | 518 |

Table 4.1 Continued

| **Sample ID** | **Date of Sampling** | **Temp** | **pH** | **EC(µS/cm)** | **TDS(mg/L)** | **T. Alk(mg/L)** |
|---|---|---|---|---|---|---|
| G1 | 25/10/2012 | 24.6 | 6.88 | 1106 | 555 | 244 |
| G2 | 25/10/2012 | 26.6 | 6.99 | 932 | 467 | 208 |
| G3 | 25/10/2012 | 26.1 | 7.03 | 992 | 498 | 284 |
| G4 | 25/10/2012 | 24.8 | 7.16 | 1106 | 553 | 140 |
| G1 | 27/ 01/ 2013 | 24.3 | 6.8 | 1203 | 600 | 390 |
| G2 | 27/ 01/ 2013 | 25.6 | 6.77 | 946 | 470 | 242 |
| G3 | 27/ 01/ 2013 | 24.4 | 6.94 | 912 | 454 | 298 |
| G4 | 27/ 01/ 2013 | 24.8 | 7.45 | 1423 | 708 | 246 |
| Min | | 24.3 | 6.77 | 912 | 454 | 140 |
| Max | | 26.6 | 7.45 | 1423 | 708 | 390 |
| Mean | | 25.2 | 7.02 | 1096 | 547 | 258 |
| StDev | | 0.8 | 0.22 | 173 | 86 | 72 |
| **WHO (1996) | | 22-29 | 6 – 9 | 1000 | 500 | 400 |

The temperature of the leachate ranged from 24.7 to 25.3 °C with a mean value of 25.1 °C. The observed temperature of the leachate could be attributed to microbial activity in the landfill and the ambient air temperature during sampling.

Temperature of the surface water samples varied from 24.6 to 28.3 °C with a mean value of 26.5 °C. The measured temperature of the surface water samples may be attributed to the ambient air temperature as well as the temperature of the migrating leachate and domestic effluents from the surrounding houses. Sinokrat and Stefen (1993) indicated that temperature of water may be influenced by ambient air temperature and anthropogenic activities such as the introduction of liquids with different temperature conditions.

The temperature of the groundwater samples ranged from 24.3 to 26.6 °C with a mean value of 25.2 °C. The measured temperature of the groundwater samples may be attributed to the ambient air temperature during sampling.

The pH of leachate varied from 8.22 to 9.03 with a mean value of 8.63. The alkaline nature of the leachate samples suggests that the closed dumpsite is in the methanogenic stage of decomposition. Christensen et al. (1999) observed that methanogenic landfills produce alkaline leachate due to the continuous production of $HCO_3^-$ , $NH_3$ and $OH^-$ from the decomposing waste.

The pH of the surface water samples ranged from 7.40 to 8.02 with a mean value of 7.63. Drever (1982) observed that liquids with different pH conditions discharged into water may influence the pH of the water. The slightly alkaline condition of the surface water samples could be attributed to mixing with the alkaline leachate and domestic effluents with alkaline properties from the surrounding houses. Maximum pH value of 8.02 was observed at sampling point SW1 (Table 4.1) because of higher leachate effect due to its close proximity to the dumpsite (Table 3.2).

The pH of the groundwater samples ranged from 6.77 to 7.45 with a mean value of 7.00. The slightly neutral to alkaline pH of the groundwater could be attributed to dissolution of minerals in the rocks of the aquifer as well as mixing of the recharge water (rain water) with akaline liquids (which may possibly be leachate) as it migrates through the unsaturated zone.

Comparing the pH of the surface water to that of the groundwater, it is observed that the pH of the surface water was higher than that of the groundwater due to higher anthropogenic effects.

The electrical conductivity (EC) values of the leachate samples ranged from 12,070 to 20,800 µS/cm with a mean value of 14,465 µS/cm while the TDS value ranged from 6,040 to 10,350 mg/L with a mean value of 7,218 mg/L. The relatively high EC and TDS values of the leachate may be due to leaching of dissolved inorganic ions from the decomposing waste in the dumpsite.

The electrical conductivity values of the surface water samples ranged from 1,025 to 1,206 µS/cm with a mean value of 1,106 µS/cm while the TDS varied from 512 to 600 mg/L with a mean value of 552 mg/L. Fritz and Fontes (1986) observed that leachate migration into water may generally increase the electrical conductivity and total dissolve solids values of the water due to the presence of inorganic ions in the leachate. The observed EC and TDS values of the surface water samples could be attributed to contributions from leachate and domestic effluents from the surrounding houses. The influence of leachate on the measured EC and TDS values of the surface water samples is suggested by the observation of maximum EC and TDS values at the sampling point SW1 (Table 4.1) which is in close proximity to the dumpsite.

In the groundwater samples, the EC values ranged from 912 to 1,423 µS/cm with a mean value of 1,096 µS/cm while the TDS values varied from 454 to 708 mg/L with a mean value of 547 mg/L. The measured EC and TDS values of the groundwater samples could be attributed to factors such as dissolution of minerals in the rocks of the aquifer and mixing of the recharge water with possibly leachate from the dumpsite.

Comparing the EC and TDS values of the two sampling periods (Table 4.1), it is observed that low values were recorded during the first sampling period which coincided with some rainfall, suggesting dilution as the main factor.

In the leachate samples, the total alkalinity values ranged from 2,500 to 5,400 mg/L with a mean value of 3,623 mg/L. The relatively high total alkalinity values of the leachate may be attributed to leaching of carbonates and bicarbonates from the decomposing organic waste in the dumpsite. Kjeldsen *et al*. (2002) observed that methanogenic leachate had high concentrations of carbonates and bicarbonates due to the methanogenic decomposition of organic waste in landfills.

The total alkalinity values of the surface water samples varied from156 to 1,700 mg/L with a mean value of 588 mg/L. Chapman (1996) indicated that total alkalinity in water is primarily due to the presence dissolved carbon dioxide species, bicarbonate and carbonate ions. Total alkalinity in water may, however, be influenced by leachate due to its carbonate and bicarbonate components (Mor *et al*., 2006). The measured total alkalinity values of the surface water samples could be attributed to contributions from leachate and domestic effluents from the surrounding houses. Maximum total alkalinity values were recorded at the sampling point SW1 (Table 4.1) because of higher leachate effect due to its closeness to the dumpsite.

In the groundwater samples, the total alkalinity values ranged from 140 to 390 mg/L with a mean value of 258 mg/L. The observed total alkalinity values of the groundwater samples could be attributed to factors such as dissolution of carbonate minerals in the rocks of the aquifer and mixing with possibly leachate from the closed dumpsite.

The observed physico-chemical parameters of the leachate samples generally suggests that leachate from the closed dumpsite may be a source of contamination of the surface water (Bawere Stream) and groundwater.

The measured physico-chemical parameters of the surface water samples show some level of contamination of the surface water (Bawere stream) mainly due to leachate migration from the closed dumpsite. The EC, TDS and total alkalinity values of the surface water samples were above the maximum permissible limit of the WHO (1996) guideline for drinking water.

The observed physico-chemical parameters of the groundwater samples generally shows some level of contamination of the groundwater possibly, due to leachate migration from the closed dumpsite. The EC and TDS values of the groundwater samples were above the maximum permissible limit of the WHO (1996) guideline for drinking water.

## 4.2 Major Ions in Leachate, Surface Water and Groundwater Samples

The major ions in leachate, surface water and groundwater samples are presented in Table 4.2 and Figure 4.1.

Table 4.2 Results of the concentration (mg/L) of major ions in leachate (L), surface water (SW) and groundwater (G) samples

| Sample ID | Date of Sampling | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Cl^-$ | $HCO_3^-$ | $NO_3^-$ | $SO_4^{2-}$ | $PO_4^{3-}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| L1 | 25/10/12 | 4010 | 6482 | 401 | 74 | 2460 | 4609 | 5.85 | 387 | 13.14 |
| L2 | 25/10/12 | 3255 | 6143 | 240 | 64 | 2350 | 6584 | 7.21 | 352 | 16.32 |
| L3 | 25/10/12 | 2789 | 4622 | 160 | 63 | 2128 | 5608 | 6.61 | 345 | 12.79 |
| L4 | 25/10/12 | 7892 | 10450 | 321 | 106 | 3228 | 4755 | 5.27 | 305 | 4.82 |
| L1 | 27/01/13 | 4150 | 6520 | 420 | 74 | 2749 | 3536 | 8.85 | 649 | 20.80 |
| L2 | 27/01/13 | 3460 | 6200 | 243 | 64 | 2249 | 3779 | 15.73 | 368 | 17.67 |
| L3 | 27/01/13 | 2850 | 4790 | 173 | 64 | 2149 | 3048 | 19.49 | 362 | 18.73 |
| L4 | 27/01/13 | 8420 | 12300 | 368 | 96 | 5048 | 3414 | 12.82 | 771 | 4.36 |
| Min | | 2789 | 4622 | 160 | 63 | 2128 | 3048 | 5.27 | 305 | 4.36 |
| Max | | 8420 | 12300 | 420 | 106 | 5048 | 6584 | 19.49 | 771 | 20.80 |
| Mean | | 4603 | 7188 | 291 | 75 | 2795 | 4417 | 10.23 | 442 | 13.58 |
| StDev | | 2250 | 2729 | 101 | 16 | 981 | 1215 | 5.22 | 170 | 6.16 |
| SW1 | 25/10/12 | 400 | 70 | 55 | 52 | 215 | 488 | 0.73 | 52 | 0.71 |
| SW2 | 25/10/12 | 379 | 61 | 51 | 52 | 213 | 229 | 0.50 | 49 | 0.48 |
| SW3 | 25/10/12 | 380 | 63 | 48 | 42 | 206 | 215 | 0.34 | 47 | 0.47 |
| SW4 | 25/10/12 | 389 | 16 | 38 | 42 | 203 | 190 | 0.18 | 41 | 0.15 |
| SW1 | 27/01/13 | 402 | 70 | 56 | 53 | 238 | 2073 | 0.86 | 69 | 0.72 |
| SW2 | 27/01/13 | 385 | 62 | 52 | 53 | 222 | 732 | 0.55 | 65 | 0.66 |
| SW3 | 27/01/13 | 381 | 64 | 50 | 42 | 206 | 244 | 1.22 | 49 | 0.65 |
| SW4 | 27/01/13 | 391 | 17 | 46 | 42 | 234 | 613 | 1.11 | 47 | 0.07 |
| Min | | 379 | 16 | 38 | 42 | 203 | 190 | 0.18 | 41 | 0.07 |
| Max | | 402 | 70 | 56 | 53 | 238 | 2073 | 1.22 | 69 | 0.72 |
| Mean | | 388 | 53 | 50 | 47 | 217 | 613 | 0.69 | 52 | 0.49 |
| StDev | | 9 | 23 | 6 | 6 | 13 | 632 | 0.36 | 10 | 0.25 |
| G1 | 25/10/12 | 348 | 27 | 64 | 53 | 128 | 297 | 0.24 | 50 | <0.001 |
| G2 | 25/10/12 | 257 | 3 | 64 | 53 | 106 | 254 | 0.19 | 83 | 0.06 |
| G3 | 25/10/12 | 270 | 4 | 66 | 53 | 100 | 346 | 0.12 | 76 | 0.03 |
| G4 | 25/10/12 | 428 | 20 | 42 | 42 | 142 | 171 | 0.28 | 67 | 0.14 |
| G1 | 27/01/13 | 351 | 28 | 69 | 44 | 134 | 475 | 0.30 | 95 | 0.02 |
| G2 | 27/01/13 | 278 | 4 | 67 | 43 | 122 | 295 | 0.55 | 84 | 0.05 |
| G3 | 27/01/13 | 268 | 5 | 65 | 53 | 102 | 363 | 0.72 | 69 | <0.001 |
| G4 | 27/01/13 | 439 | 20 | 52 | 52 | 218 | 300 | 0.55 | 95 | 0.08 |
| Min | | 257 | 3 | 42 | 42 | 100 | 171 | 0.12 | 50 | 0.02 |
| Max | | 439 | 28 | 69 | 53 | 218 | 475 | 0.72 | 95 | 0.14 |
| Mean | | 330 | 14 | 61 | 49 | 131 | 313 | 0.37 | 77 | 0.06 |
| StDev | | 73 | 11 | 9 | 5 | 38 | 88 | 0.21 | 15 | 0.04 |
| **WHO (1996) | | 200 | 30 | 200 | 150 | 250 | - | 10 | 200 | <0.3 |

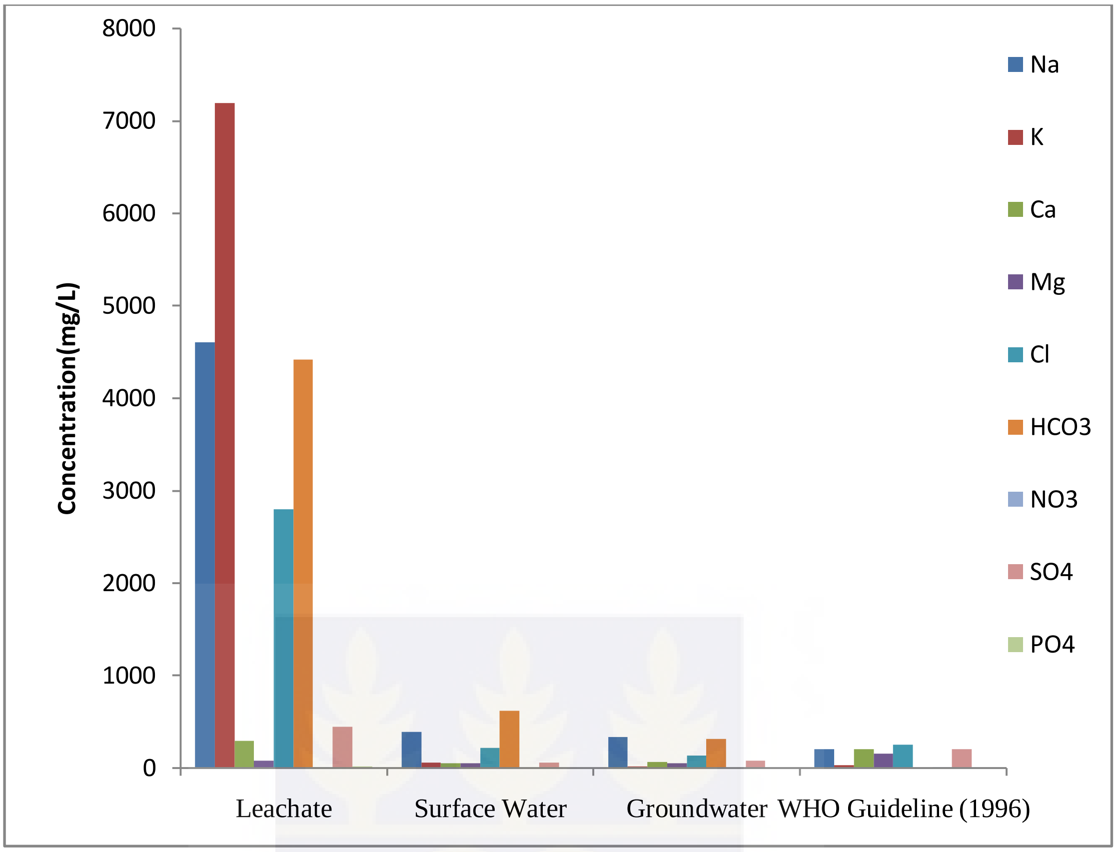


Figure 4.1 Variation in the mean concentration of major ions in leachate, surface water and groundwater samples

In the leachate samples, the concentration of $Na^+$ varied from 2,789 to 8,420 mg/L with a mean value of 4,603 mg/L while that of $K^+$ ranged from 4,622 to 12,300 mg/L with a mean value of 7,188 mg/L. The high concentrations of $Na^+$ and $K^+$ may be attributed to leaching from the organic waste materials present in the waste stream.

In the surface water samples, the concentration of $Na^+$ varied from 379 to 402 mg/L with a mean value of 388 mg/L while that of $K^+$ ranged from 16 to 70 mg/L with a mean value of 53 mg/L. The observed concentration of $Na^+$ and $K^+$ in the surface water may be due to contributions from leachate. Maximum $Na^+$ and $K^+$ concentrations were recorded at the sampling point SW1 (Table 4.2) because of higher leachate effect due to its close proximity to the dumpsite.

In the groundwater, the concentration of $Na^+$ varied from 257 to 439 mg/L with a mean value 330 mg/L while that of $K^+$ ranged from 3 to 28 mg/L with a mean value of 14 mg/L. Nova Scotia Environment (2008) reported that, sources of $Na^+$ and $K^+$ in groundwater may include dissolution of Na and K bearing minerals in the rocks of the aquifer, landfill leachate and sea spray aerosols in coastal areas. The observed concentration of $Na^+$ and $K^+$ in groundwater could mainly be attributed to contributions from leachate.

Comparing the concentrations of $Na^+$ and $K^+$ in the groundwater samples, it is observed that the concentration of $K^+$ is low (Figure 4.1). This may be due to the fact that $K^+$ is geochemically immobile and non-reactive (Hem, 1985).

In the leachate samples, the concentration of $Ca^{2+}$ recorded varied from 160 to 420 mg/L with a mean value of 291 mg/L while that of $Mg^{2+}$ ranged from 63 to 106 mg/L with a mean value of 75 mg/L. The relatively high concentrations of $Ca^{2+}$ and $Mg^{2+}$ in the leachate may be attributed to the dissolution and leaching of carbonate compounds in the waste stream. Waste materials such as food, plants, plastics and batteries may have contributed to the observed $Ca^{2+}$ and $Mg^{2}$ concentrations in the leachate.

In the surface water samples, the concentration of $Ca^{2+}$ varied from 38 to 56 mg/L with a mean value of 50 mg/L while that of $Mg^{2+}$ ranged from 42 to 53 mg/L with a mean value of 47 mg/L. The measured concentrations of $Ca^{2+}$ and $Mg^{2+}$in the surface water samples may be attributed to contributions from leachate. The contribution of leachate to the measured $Ca^{2+}$ and $Mg^{2+}$ concentrations of the surface water samples is suggested by the maximum $Ca^{2+}$ and $Mg^{2+}$concentrations recorded at the sampling point SW1(Table 4.2), which is in close proximity to the dumpsite.

The concentration of $Ca^{2+}$ in the groundwater samples varied from 42 to 69 mg/L with a mean value 61 mg/L while that of $Mg^{2+}$ ranged from 42 to 53 mg/L with a mean value of 49 mg/L. The recorded concentrations of $Ca^{2+}$ and $Mg^{2+}$ in the groundwater samples may be attributed to dissolution of $Ca^{2+}$ and $Mg^{2+}$ bearing minerals in the rocks of the aquifer or possible mixing of the recharge water with leachate from the dumpsite.

Chloride concentration in the leachate ranged from 2,128 to 5,048 mg/L with a mean value 2,795 mg/L. The high concentration of $Cl^-$ in the leachate could be attributed to the dissolution and leaching of chloride and chloride containing compounds from the decomposing waste materials in the dumpsite. These waste materials may include food, plants, textiles, paper and synthetic products (Taylor and Allen, 2006).

Chloride concentration in the surface water samples varied from 206 to 238 mg/L with a mean value of 217 mg/L. The observed concentration of chloride in the surface water may be due to contributions from leachate and domestic effluents from the surrounding houses. Maximum $Cl^-$ concentrations were recorded at the sampling point SW1 (Table 4.2) because of higher leachate effect due to its closeness to the dumpsite.

The concentration of $Cl^-$ in the groundwater samples ranged from 100 to 218 mg/L with a mean value of 131 mg/L. Panno *et al*. (2001) indicated that sources of $Cl^-$ in groundwater may include weathering and leaching of sedimentary rocks and soils, dissolution of salt deposits, landfill leachate, sewage and sea spray aerosols in coastal areas. The measured concentration of $Cl^-$ in the groundwater samples could mainly be attributed to contributions from leachate, sea spray aerosols and sewage from septic tank and cesspit sited close to some of the hand-dug wells sampled (Table 3.2).

Comparing the mean concentration of $Cl^-$ in the surface water samples to that of the groundwater samples (Figure 4.1), it is observed that the concentration in the surface water was high, possibly due to higher leachate effect.

Bicarbonate concentration in the leachate samples ranged from 3,048 to 6,584 mg/L with a mean value of 4,417 mg/L. The high concentration of $HCO_3^-$ in the leachate may be due to leaching from the organic and inert waste materials present in the dumpsite.

The concentration of $HCO_3^-$ in the surface water samples varied from 190 to 2,072 mg/L with a mean value of 613 mg/L. The measured concentration $HCO_3^-$ in the surface water could be attributed to contributions from leachate and domestic effluents from the surrounding houses. Maximum $HCO_3^-$ concentrations were recorded at the sampling point SW1 (Table 4.2) because of higher leachate effect due to the closeness of SW1 to the dumpsite.

Bicarbonate concentration in the groundwater samples ranged from 171 to 475 mg/L with a mean value of 313 mg/L. The observed $HCO_3^-$ concentration in the groundwater samples may be due to mixing of the recharge water with leachate from the dumpsite.

Comparing the mean concentration of $HCO_3^-$ in the surface water samples to that of the groundwater samples (Figure 4.1), it is observed that the concentration in the surface water was high, possibly due to higher leachate effect.

Nitrate concentration in the leachate samples ranged from 5 to19 mg/L with a mean value of 10 mg/L. The measured concentration of $NO_3^-$ in the leachate may be due to leaching from disposed waste materials in the dumpsite. These waste materials may include food, plants and animal wastes.

In the surface water samples, the concentration of nitrate ($NO_3^-$) varied from 0.18 to 1.22 mg/L with a mean value of 0.69 mg/L. The observed concentration of $NO_3^-$ in the surface water could be due to contributions from leachate and domestic effluents from the surrounding houses. Maximum $NO_3^-$concentration of 1.22 mg/L was observed at the sampling point SW1 (Table 4.2) because of higher leachate effect due to its close proximity to the dumpsite.

The concentration of $NO_3^-$ in the groundwater ranged from 0.12 to 0.72 mg/L with a mean value of 0.37 mg/L. Moore *et al*. (2006) reported that sources of nitrate in water may include deposition from the atmosphere, decomposition of plant and animal materials, sewage, manures, chemical fertilizers, landfill leachate, domestic and industrial effluents. The observed concentration of $NO_3^-$ in the groundwater samples may be attributed to contributions from atmospheric deposition, leachate from the dumpsite and sewage from septic tank and cesspits sited close to some of the hand-dug wells sampled.

Comparing the mean concentration of $NO_3^-$ in the surface water to that of the groundwater, it was observed that the concentration in the surface water was higher due to variation in the transit time of $NO_3^-$ into surface water and groundwater. Additionally, higher leachate effect may have contributed to the comparatively high concentration of $NO_3^-$ in the surface water.

Sulphate ($SO_4^{2-}$) concentration in the leachate varied from 305 to771 mg/L with a mean value 442 mg/L. The relatively high concentration of $SO_4^{2-}$ in the leachate may be attributed to the leaching of $SO_4^{2-}$ from the decomposing organic waste in the dumpsite.

The concentration of $SO_4^{2-}$ recorded in the surface water samples varied from 41 to 69 mg/L with a mean value of 52 mg/L. Leachate from the dumpsite and domestic effluents from the surrounding houses may have contributed to the measured $SO_4^{2-}$ concentrations in the surface water samples. Maximum $SO_4^{2-}$ concentration was observed at the sampling point SW1 (Table 4.2) because of higher leachate effect due to its closeness to the dumpsite

$SO_4^{2-}$ concentrations in the groundwater samples ranged from 50 to 95 mg/L with a mean value of 77 mg/L. The sources of $SO_4^{2-}$ in groundwater may include dissolution of minerals (such as gypsum and anhydrite), atmospheric deposition, decomposition of organic matter, industrial effluents, landfill leachate, saltwater intrusion and sea spray aerosols in coastal areas (Minnesota Pollution Control Agency, 1999). The observed concentration of $SO_4^{2-}$ in the surface water samples may be attributed to contributions from leachate and sea spray aerosols.

Phosphate ($PO_4^{-3}$) concentration in the leachate samples ranged from 4 to 21 mg/L with a mean value of 14 mg/L. The measured concentration of $PO_4^{-3}$ in the leachate may be due to leaching from the decomposing organic waste materials in the dumpsite.

The concentration of $PO_4^{-3}$ in surface water samples varied from 0.07 to 0.72 mg/L with a mean value of 0.49 mg/L. The observed concentration of phosphate in the surface water may be attributed to contributions from leachate and domestic effluents from the surrounding houses. Maximum $PO_4^{-3}$ concentration of 0.72 mg/L was recorded at the sampling point SW1 (Table 4.2) because of higher leachate effect due to the closeness of SW1 to the dumpsite.

$PO_4^{-3}$ concentration in the groundwater samples ranged from < 0.001 to 0.14 mg/L with a mean value of 0.06 mg/L. The sources of $PO_4^{-3}$ in groundwater may include leaching from soils and rocks, decaying biomass, fertilizers, landfill leachate, industrial and septic system effluents (Minnesota Pollution Control Agency, 1999).

The observed concentration of $PO_4^{-3}$ in the groundwater samples could be attributed to contributions from leachate as well as leaching from soils and rocks.

Comparing the concentration of $PO_4^{-3}$ in the groundwater samples to that of the surface water samples, it is observed that the concentration in the groundwater is low. This could be attributed to the lower mobility and longer transit time of phosphorus in the unsaturated zone.

The measured concentrations of major ions in the leachate were relatively high suggesting that leachate from the dumpsite may be a source of contamination of the surface water and groundwater with major ions.

The observed concentrations of major ions in the surface water samples suggest some level of contamination of the surface water with major ions. Leachate from the dumpsite is one of the main sources of contamination. $Na^+$ and $K^+$ concentrations in the surface water were above the maximum permissible limit of the WHO (1996) guideline for drinking water.

The observed concentrations of major ions in the groundwater samples suggest some level of contamination of the groundwater with major ions. Leachate from the dumpsite is one of the main sources of contamination. $Na^+$ concentration in the groundwater was above the maximum permissible limit of the WHO (1996) guideline for drinking water.

### 4.3 Trace Metals in Leachate, Surface Water and Groundwater Samples

The concentrations of the trace elements (Fe, Pb, Cd, Cr, Mn, As, Zn, Hg, Cu and Co) measured in the leachate, surface water and groundwater samples are presented in Table 4.3 and Figure 4.2.

Table 4.3 Results of the concentration (mg/L) of trace elements in leachate (L), surface water (SW) and groundwater samples (G)

| **Sample ID** | **Date of Sampling** | **Fe** | **Pb** | **Cd** | **Cr** | **Mn** | **As** | **Zn** | **Hg** | **Cu** | **Co** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| L1 | 25/10/12 | 2.872 | <0.001 | 0.060 | 0.112 | <0.002 | <0.001 | 0.012 | <0.001 | 0.036 | <0.005 |
| L2 | 25/10/12 | 4.04 | <0.001 | 0.104 | 0.140 | <0.002 | <0.001 | 0.008 | <0.001 | 0.024 | <0.005 |
| L3 | 25/10/12 | 3.536 | <0.001 | 0.040 | 0.104 | <0.002 | <0.001 | 0.016 | <0.001 | 0.032 | <0.005 |
| L4 | 25/10/12 | 2.068 | <0.001 | 0.056 | 0.068 | <0.002 | <0.001 | 0.028 | <0.001 | <0.003 | <0.005 |
| L1 | 27/01/13 | 1.524 | 0.100 | 0.020 | 0.080 | 0.100 | 0.020 | <0.001 | 0.008 | <0.003 | <0.005 |
| L2 | 27/01/13 | 2.660 | <0.001 | 0.028 | 0.016 | 0.052 | 0.020 | <0.001 | 0.008 | <0.003 | <0.005 |
| L3 | 27/01/13 | 2.064 | 0.044 | 0.032 | 0.024 | 0.124 | 0.016 | <0.001 | 0.008 | <0.003 | <0.005 |
| L4 | 27/01/13 | 1.402 | 0.142 | 0.032 | 0.034 | 0.160 | 0.020 | <0.001 | 0.012 | 0.986 | <0.005 |
| Min | | 1.402 | <0.001 | 0.020 | 0.016 | <0.002 | <0.001 | <0.001 | <0.001 | <0.003 | <0.005 |
| Max | | 4.040 | 0.142 | 0.104 | 0.140 | 0.160 | 0.020 | 0.028 | 0.012 | 0.986 | <0.005 |
| Mean | | 2.521 | 0.036 | 0.047 | 0.072 | 0.055 | 0.010 | 0.008 | 0.005 | 0.135 | <0.005 |
| StDev | | 0.937 | 0.056 | 0.027 | 0.045 | 0.065 | 0.010 | 0.010 | 0.005 | 0.344 | - |
| SW1 | 25/10/12 | 1.780 | <0.001 | 0.084 | 0.120 | <0.002 | < 0.001 | 0.012 | < 0.001 | 0.024 | 0.068 |
| SW2 | 25/10/12 | 1.356 | <0.001 | 0.044 | 0.088 | <0.002 | < 0.001 | 0.008 | < 0.001 | <0.003 | 0.072 |
| SW3 | 25/10/12 | 3.028 | <0.001 | 0.064 | 0.132 | 0.188 | < 0.001 | < 0.001 | < 0.001 | <0.003 | 0.680 |
| SW4 | 25/10/12 | 0.740 | <0.001 | 0.032 | 0.048 | <0.002 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| SW1 | 27/01/13 | 1.132 | 0.140 | 0.028 | <0.001 | 0.324 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| SW2 | 27/01/13 | 0.792 | <0.001 | 0.024 | <0.001 | 0.272 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| SW3 | 27/01/13 | 1.052 | 0.224 | 0.024 | 0.028 | 0.352 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| SW4 | 27/01/13 | 0.624 | <0.001 | 0.020 | <0.001 | 0.116 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| Min | | 0.624 | <0.001 | 0.020 | <0.001 | <0.002 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| Max | | 3.028 | 0.224 | 0.084 | 0.132 | 0.352 | < 0.001 | 0.012 | < 0.001 | 0.024 | 0.680 |
| Mean | | 1.313 | 0.046 | 0.040 | 0.052 | 0.157 | <0.001 | 0.003 | <0.001 | 0.003 | 0.103 |
| StDev | | 0.787 | 0.087 | 0.023 | 0.055 | 0.149 | - | - | - | 0.008 | 0.235 |
| G1 | 25/10/12 | 1.396 | <0.001 | 0.112 | 0.068 | 0.220 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G2 | 25/10/12 | 0.916 | <0.001 | 0.060 | 0.060 | 0.040 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G3 | 25/10/12 | 0.532 | <0.001 | 0.760 | 0.120 | <0.002 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G4 | 25/10/12 | 0.956 | <0.001 | 0.760 | 0.092 | <0.002 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G1 | 27/01/13 | 0.748 | <0.001 | 0.044 | 0.084 | 0.888 | 0.012 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G2 | 27/01/13 | 0.704 | <0.001 | 0.040 | 0.044 | 0.288 | 0.012 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G3 | 27/01/13 | 2.148 | <0.001 | 0.028 | 0.024 | 0.044 | 0.004 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| G4 | 27/01/13 | 2.020 | <0.001 | 0.024 | < 0.001 | 0.388 | 0.008 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| Min | | 0.532 | <0.001 | 0.024 | 0.024 | <0.002 | < 0.001 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| Max | | 2.148 | <0.001 | 0.760 | 0.120 | 0.888 | 0.012 | < 0.001 | < 0.001 | <0.003 | <0.005 |
| Mean | | 1.178 | < 0.001 | 0.229 | 0.062 | 0.234 | 0.005 | < 0.001 | <0.001 | <0.003 | <0.005 |
| StDev | | 0.614 | - | 0.329 | 0.032 | 0.302 | 0.005 | - | - | - | <0.005 |
| **WHO (1996) | | 0.3 | 0.01 | 0.003 | 0.05 | 0.05 | 0.01 | 0.001 | 0.005 | 1 | - |

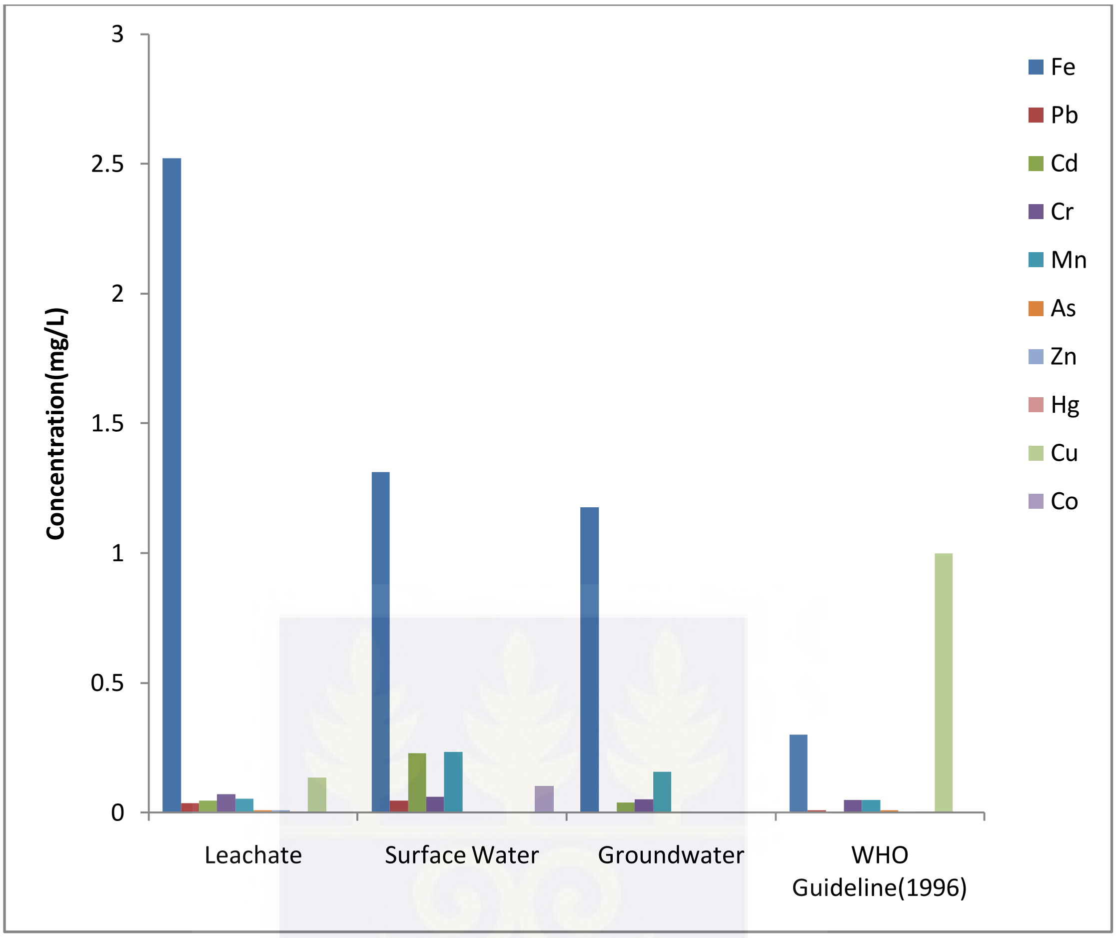


Figure 4.2 Variation in the mean concentration of trace elements in leachate, surface water and groundwater samples

In the leachate samples, the concentrations of Fe ranged from1.40 to 4.04 mg/L with a mean value of 2.52 mg/L. The measured concentration of Fe the leachate could be due to leaching from Fe-containing waste materials in the dumpsite. These waste materials may include electrical-waste, iron and steel scraps. The dark brown of colouration of the leachate confirms the presence of Fe. The dark brown colour is due to the oxidation of ferrous to ferric forms and the formation of ferric hydroxide colloids and complexes with fulvic / humic substances (Chu *et al*., 1994).

The concentration of Fe in the surface water samples varied from 0.624 to 3.028 mg/L with a mean value of 1.313 mg/L. The observed concentrations of Fe in the surface water samples could be attributed to contributions from runoff, leachate from the dumpsite and domestic effluents from the surrounding houses. The contribution of leachate to the measured concentrations of Fe in the surface water samples is further supported by the maximum Fe concentrations recorded at the sampling point SW1 (Table 4.3) which is in closed proximity to the dumpsite.

Fe concentration in the groundwater samples varied from 0.532 to 2.148 mg/L with a mean value of 1.178 mg/L. The sources of Fe in groundwater may include dissolution of iron bearing minerals in the rocks of aquifer, industrial effluents, acid mine-drainage, landfill leachate and sewage from septic tanks (Minnesota Pollution Control Agency, 1999). The measured concentration of Fe in the groundwater samples could mainly be attributed to contributions from leachate, iron bearing minerals in the rocks of the aquifer and sewage from septic tank and cesspits sited closed to some of the hand-dug wells.

Comparing the mean concentration of Fe in the surface water to that of the groundwater (Figure 4.2), it is observed that the concentration in the surface water was high due to higher leachate effect.

The concentration of Pb in the leachate samples varied from <0.001 to 0.142mg/L with a mean value of 0.036 mg/L. The concentration of Pb in some of the samples may be due to leaching from Pb-containing waste materials in the dumpsite. These waste materials may include batteries, leaded solder, lead-based paints, leaded-PVC, ceramics, optical and electrical glasses.

The concentrations of Pb in the surface water samples ranged from <0.001 to 0.22 mg/L with a mean value of 0.18 mg/L. The sources of Pb in surface water may include atmospheric deposition, industrial effluents and landfill leachates (Naja and Volesky, 2009). The measured concentration of Pb in the surface water samples could mainly be attributed to leachate from the dumpsite. Maximum Pb concentration of 0.22 mg/L was observed at the sampling point SW1 (Table 4.3) because of higher leachate effect due to its closeness to the dumpsite.

In the groundwater samples Pb was below detection. This could be attributed to adsorption by clay minerals and organic matter in the unsaturated zone and the aquifer.

In the leachate samples, the concentration of Cd varied from 0.020 to 0.104 mg/L with a mean value of 0.047 mg/L. The presence of Cd in the leachate may be due to leaching from Cd containing waste materials in the dumpsite. These waste materials may include Cd-based batteries, electroplated iron and steel scraps, plastics, textiles and electrical-waste (Ackah *et al*., 2011).

The concentrations of Cd in the surface water samples varied from 0.024 to 0.760 mg/L with a mean value of 0.229 mg/L. Domestic effluents from the surrounding houses and leachate from the dumpsite may have contributed to the measured concentration of Cd in the surface water samples. Maximum Cd concentrations were recorded at the sampling point SW1 (Table 4.3) because of higher leachate effect due to its closeness to the dumpsite.

The measured concentration of Cd in the groundwater samples ranged from 0.020 to 0.084 mg/L with a mean value of 0.040 mg/L. The Sources of Cd in groundwater may include atmospheric depositions, sea spray aerosols, fertilizers, industrial effluent, septic tanks and landfill leachate (Minnesota Pollution Control Agency, 1999).

The measured concentration of Cd in the groundwater samples is mainly attributed to contributions from leachate, sea spray aerosols and sewage from septic tank and cesspit sited close to some of the hand-dug wells.

Cr concentration in leachate samples varied from 0.016 to 0.140 mg/L with a mean value of 0.072 mg/L. The presence of Cr in the leachate samples may be due to leaching from Cr containing waste materials in the dumpsite. These waste materials may include paints, textiles, Cr-plated iron and steel scraps (Nriagu, 1988).

The concentration of Cr in the surface water samples varied from <0.001 to 0.120 mg/L with a mean value of 0.062 mg/L. Leachate migration from the dumpsite may have contributed to the measured Cr concentrations in the surface water samples. This is suggested by the observation of maximum concentrations of Cr at the sampling SW1 (Table 4.3) which is in close proximity to the dumpsite.

The measured concentration of Cr in the groundwater samples ranged from <0.001 to

0.132 mg/ L with a mean value of 0.052 mg/L. Comparing the concentrations of Cr in the groundwater to that of the surface water, it is observed that the concentration in the groundwater is lower. This could be attributed to some degree of adsorption by clay minerals and organic matter in the unsaturated zone.

In the leachate samples, the concentration of Mn varied from <0.002 to 0.160 mg/L with a mean value of 0.55 mg/L. The measured concentration of Mn in the leachate samples may be due to leaching from Mn-containing waste materials in the dumpsite. These waste materials may include Mn-incorporated metal scraps, dry cells, textiles, paints, ceramics and electronic- waste.

In the surface water samples, the concentration of Mn varied from <0.002 to 0.888 mg/L with a mean value of 0.234 mg/L. Lenntech (2011) indicated that the sources of Mn in surface water include atmospheric depositions, industrial effluents, landfill leachates and fertilizers. The measured concentration of Mn in the surface water samples could mainly be attributed to atmospheric depositions and leachate migration from the dumpsite. Maximum Mn concentrations were observed at the sampling point SW1 (Table 4.3) because of higher leachate effects due to the closeness of SW1 to the dumpsite.

In the groundwater samples, the concentration of Mn ranged from <0.002 to 0.352 mg/L with a mean value of 0.157 mg/L. Atmospheric depositions and leachate migration from the dumpsite could have contributed to the measured concentration of Mn in the groundwater.

Comparing the mean concentrations of Mn in the groundwater samples to that of the surface water samples, it is observed that the concentration in the groundwater is low (Figure 4.2). Adsorption by clay minerals and organic matter in the unsaturated zone may have contributed to the lower concentration of Mn in the groundwater samples.

In the leachate samples, arsenic (As) concentration ranged from < 0.001 to 0.020 mg/L with a mean value of 0.01 mg/l. The measured concentration of As in some of the leachate samples may be due to leaching from waste materials in the dumpsite. These waste materials may include pesticide residues, electronic-waste, glasses and paints.

The concentration of As in the surface water samples varied from <0.001 to 0.012 mg/L with a mean value of 0.005 mg/L. Leachate migration from the dumpsite may have contributed to the measured concentration of As in the surface water since leachate from the dumpsite contains relatively high concentration of As. The contributions of leachate to the measured concentration of As in the surface water is further supported by the observation of maximum As concentration of 0.012 mg/L at SW1 (Table 4.3) which is in close proximity to the dumpsite.

As was below detection in the groundwater samples. This may be attributed to adsorption by clay minerals and organic matter in the unsaturated zone and the aquifer.

In the leachate samples, the concentration of Zn varied from <0.001 to 0.028 mg/L with a mean value of 0.008 mg/L. The concentration of Zn in some of the leachate samples may be due to leaching from Zn-containing waste materials in the dumpsite. These waste materials may include batteries, flourescent lamps and Zn-incorporated steel and iron scraps.

The concentration of Zn in surface water samples varied from <0.001 to 0.012 mg/L with a mean value of 0.003 mg/L. Ritter *et al*. (2002) reported that the sources of Zn in water may include weathering and leaching of Zn bearing minerals and rocks, industrial effluents, fertilizers, landfill leachate and sewage systems. The measured concentration of Zn in the surface water could mainly be attributed to contributions from leachate and domestic effluents from the surrounding houses. Maximum Zn concentration of 0.012 mg/L was recorded at the sampling point SW1 (Table 4.3) because of higher leachate effect due to its closeness to the dumpsite.

Zn was below detection in the groundwater samples. This may be attributed to adsorption by clay minerals and organic matter in the unsaturated zone and the aquifer.

The concentration of mercury (Hg) in the leachate samples ranged from <0.001 to 0.012 mg/L with a mean value 0.005 mg/l. The measured concentration of Hg in some of the leachate samples may be due to leaching from Hg-containing waste materials in the dumpsite. These waste materials may include electrical-waste and pesticide residues.

In the surface water samples Hg was below detection. This could be attributed to adsorption by suspended particles or organic matter surfaces in the surface water and subsequent migration to the sediments.

Hg was below detection in the groundwater samples. This may be attributed to adsorption by clay minerals and organic matter in the unsaturated zone as well as the aquifer.

In the leachate samples, the concentration of copper (Cu) varied from <0.003 to 0.986 mg/L with a mean value of 0.135 mg/L. The measured concentration of Cu in some of the leachate samples may be explained as due to leaching from Cu-containing waste materials in the dumpsite. These waste materials may include Cu-plated metals, E- waste, paints and pesticide residues (Ackah *et al*., 2011).

In the surface water samples, the concentration of Cu ranged from <0.001 to with a mean value of 0.003 mg/L. The sources of Cu in surface water may include weathering and leaching of Cu bearing minerals and rocks, industrial effluents, landfill leachate, sewage sludge and pesticides (Minnesota Pollution Control Agency, 1999). The observed concentration of Cu in the surface water samples could mainly be attributed to contributions from leachate and domestic effluents from the surrounding houses.

The concentration of Cu in the groundwater samples was below detection. This could be attributed to adsorption by clay minerals and organic matter in the unsaturated zone as well as the aquifer.

The concentration of cobalt (Co) in the leachate was below detection (<0.005) mainly due to the sorptive capacity of the inert (soil) and organic matter components of the waste in the dumpsite. Bozkurt *et al*. (1999) in their study of the long-term fate of organics in waste deposits and its effect on metal releases, indicated that sorption of metals by clay minerals and organic matter in the waste deposits significantly affect the concentration of metals in the leachate produced.

In the surface water samples, the concentration of Co varied from <0.005 to 0.680 mg/L with a mean value of 0.103 mg/L. The sources of Co in surface water may include atmospheric deposition, sea spray aerosols, industrial effluents, urban run-off and agricultural run-off (Nagpal, 2004).The measured concentration of Co in the surface water samples could mainly be attributed to contributions from run-off and atmospheric deposition.

The concentration of Co in the groundwater samples was below detection. This could be attributed to adsoption by clay minerals in the aquifer.

The measured concentrations of trace elements in the leachate suggest that leachate from the dumpsite may be a source of contamination of the surface water and groundwater with trace elements.

The measured concentrations of trace elements in the surface water samples shows that the surface water (Bawere stream) is contaminated with some trace elements due to leachate migration from the dumpsite. Fe, Pb, Cd, Cr, Mn and Zn concentrations in the surface water were above the maximum permissible limits of the WHO (1996) guideline for drinking water, suggesting that the surface water may not be safe for drinking purposes.

The measured concentrations of trace elements in the groundwater samples show contamination of the groundwater with some trace elements. Fe, Cd and Mn concentrations were above the maximum permissible limits of the WHO (1996) guideline for drinking water, suggesting that the groundwater may not be safe for drinking purposes.

## 4.4 Classification of the Quality of the Surface Water and Groundwater using the Adapted Solway Water Quality Index

### 4.4.1 Classification of the Surface Water Quality

The mean value of the measured pH, $NO_3^-$, $PO_4^{3-}$, EC and Temperature were used in the calculation of the Solway Weighted Water Quality Index (Table 4.4 ) of the surface water samples, since data was not available for dissolved oxygen, ammonium-N, faecal coliform and suspended solids.

Table 4.4 Calculation of the Solway Water Quality Index (WQI) of the surface water samples

| **Parameter** | **Mean Value** | **Water Quality Rating** | **Maximum Weighted Water Quality Rating** |
|---|---|---|---|
| Dissolved Oxygen (% Saturation.) | | | 18 |
| BOD (mg/l) | | | 15 |
| Amm-N (mg/l) | | | 12 |
| pH | 7.63 | 9 | 9 |
| $NO_3$-N (mg/l as N) | 0.69 | 7 | 8 |
| Faecal Coliform (Counts/100ml) | | | 12 |
| $PO_4$-P (mg/l as P) | 0.49 | 0 | 8 |
| Suspended Solids (mg/l) | | | 7 |
| Electrical Conductivity (µS/cm) | 1104 | 0 | 6 |
| Temperature (°C) | 26.5 | 5 | 5 |
| Percentage Total Score (%) | | 21 | 100 |

The weighted maximum water quality rating (score) was out of 36, since data was not available for dissolved oxygen, ammonium-N, faecal coliform and suspended solids.

$$\text{Solway Weighted Water Quality Index} = \frac{1}{36} \text{ x } (21)^2 = 12.25$$

The calculated Solway water Quality index of 12.25 suggests that the surface water may belong to Class IV and may therefore be grossly polluted.

### 4.4.2 Classification of the Groundwater Quality

The mean value of the measured pH, $NO_3^-$, $PO_4^{3-}$, EC and Temperature were used in the calculation of the Solway Weighted Water Quality Index (Table 4.5 ) of the groundwater samples, since data were not available for dissolved oxygen, ammonium-N, faecal coliform and suspended solids.

Table 4.5 Calculation of the Solway Water Quality Index (WQI) of the groundwater samples

| **Parameter** | **Mean Value** | **Water Quality Rating** | **Maximum Weighted Water Quality** |
|---|---|---|---|
| Dissolved Oxygen (% Saturation.) | | | 18 |
| BOD (mg/l) | | | 15 |
| Amm-N (mg/l) | | | 12 |
| pH | 7.63 | 9 | 9 |
| $NO_3$-N (mg/l as N) | 0.69 | 8 | 8 |
| Faecal Coliform (Counts/100ml) | | | 12 |
| $PO_4$-P (mg/l as P) | 0.49 | 6 | 8 |
| Suspended Solids (mg/l) | | | 7 |
| Electrical Conductivity (µS/cm) | 1104 | 0 | 6 |
| Temperature (°C) | 26.5 | 5 | 5 |
| Percentage Total Score (%) | | 28 | 100 |

The maximum weighted water quality rating was out of 36, since data were not available for dissolved oxygen, ammonium-N, faecal coliform and suspended solids.

$$\text{Solway weighted Water Quality Index} = \frac{1}{36} \text{ x } (28)^2 = 21.77$$

The calculated Solway water Quality index of 21.77 suggests that the groundwater may belong to Class IV and may therefore be grossly polluted.

## 4.5 Soil Analysis Results

### 4.5.1 Particle Size Distribution of the Soil Profiles

The particle size distribution of the profiles is presented in Table 4.6 and Appendix B.

Table 4.6 Particle size distribution of the soil profiles using Robinson's Pipette Method

| **Profile** | **Depth(cm)** | **%Sand** | **% Silt** | **%Clay** | **Textural Class (USDA)** |
|---|---|---|---|---|---|
| SPA | 20 | 79.43 | 15.42 | 4.59 | Loamy sand |
| | 40 | 76.24 | 17.56 | 6.15 | Loamy sand |
| | 60 | 59.44 | 20.23 | 20.27 | Sandy loam |
| | 80 | 57.08 | 22.86 | 19.97 | Sandy loam |
| | 100 | 58.33 | 21.22 | 19.98 | Sandy loam |
| | | 66 | 19 | 14 | Sandy loam |
| SPB | 20 | 76.44 | 18.53 | 4.68 | Loamy sand |
| | 40 | 75.21 | 19.02 | 5.31 | Loamy sand |
| | 60 | 59.19 | 20.84 | 19.96 | Sandy loam |
| | 80 | 60.12 | 19.94 | 19.92 | Sandy loam |
| | 100 | 59.95 | 20.12 | 19.92 | Sandy loam |
| | | 66 | 20 | 14 | Sandy loam |
| SPC | 20 | 80.97 | 17.45 | 1.56 | Loamy sand |
| | 40 | 79.79 | 18.55 | 1.65 | Loamy sand |
| | 60 | 70.54 | 20.15 | 9.3 | Loamy sand |
| | 80 | 69.79 | 21.18 | 9.01 | Loamy sand |
| | 100 | 68.99 | 22.89 | 8.09 | Loamy sand |
| | | 74 | 20 | 6 | Loamy sand |
| SPD | 20 | 20.11 | 35.33 | 44.54 | Clay |
| | 40 | 18.41 | 36.42 | 45.15 | Clay |
| | 60 | 17. 39 | 36.27 | 46.32 | Clay |
| | 80 | 17.14 | 36.18 | 46.66 | Clay |
| | 100 | 17.05 | 35.11 | 47.82 | Clay |
| | | 18 | 36 | 46 | Clay |
| SPE | 20 | 75.15 | 18.93 | 5.91 | Loamy sand |
| | 40 | 73.25 | 19.45 | 7.29 | Loamy sand |
| | 60 | 70.54 | 19.22 | 10.23 | Sandy loam |
| | 80 | 70.23 | 19.55 | 10.19 | Sandy loam |
| | 100 | 69.99 | 20.12 | 9.88 | Sandy loam |
| | | 72 | 19 | 9 | Sandy loam |

The particle size distribution of profile SPA shows the soil is homogeneous with depth. Approximately 66 % consisted of sand, 19 % of silt and 14 % clay (Table 4.6). This suggests that the textural class of profile SPA is sandy loam (based on the United States Department of Agriculture (USDA) Soil Textural Triangle). The high percentage sand and low percentage clay content of the profile suggest that profile SPA may be relatively porous and thus enhance leachate migration into surface and groundwater. Maximum percentage clay content of 22.27 % was recorded at the 60 cm depth of the profile (Table 4.6). This suggests that at the 60 cm depth of profile SPA, adsorption of the trace elemental components of leachate by clay minerals may be relatively high.

The soil in profile SPB is homogeneous with depth. Approximately 66 % consisted of sand, 20 % of silt and 14 % clay (Table 4.6). This suggests that the textural class of profile SPB is sandy loam (based on the USDA Soil Textural Triangle).The high percentage sand and low percentage clay content of the profile suggest that the profile may be relatively porous and thus enhance leachate migration into surface and groundwater. The maximum percentage clay content of the profile was observed at 60 cm depth (Table 4.6). This suggests that at the 60 cm depth of profile SPB, adsorption of the trace elemental components of leachate by clay minerals may be relatively high.

The particle size distribution of profile SPC shows the soil is homogeneous with depth. Approximately 74 % consisted of sand, 20 % of silt and 6 % clay (Table 4.6). This suggests that the textural class of profile SPC is loamy sand (based on the USDA Soil Textural Triangle). The maximum percentage clay content of the profile was 9.30 % and recorded at 60 cm depth (Table 4.6).

Compared with profiles SPA and SPB, profile SPC may be more porous and easily facilitate leachate migration into surface water and groundwater due to the high percentage sand and low percentage clay content. Besides, adsorption of the trace elemental components of leachate by clay minerals may be reduced considerably in profile SPC due to the lower percentage clay content.

In profile SPD, the soil is homogeneous with depth. Approximately 18 % consisted of sand, 36 % of silt and 46 % clay (Table 4.6). This suggests that the textural class of profile SPB is clay (based on the USDA Soil Textural Triangle).The maximum percentage clay content of the profile was 47.82 % and this value was recorded at the 100 cm depth (Table 4.6).

Compared with profiles SPA and SPB, profile SPD may be less porous due to its high percentage clay and low percentage sand. In addition, adsorption of trace elements in leachate may be high in profile SPD due to the relatively high percentage clay content.

The soil in profile SPE is homogeneous with depth. Approximately 72 % consisted of sand, 19 % of silt and 9 % clay (Table 4.6). This suggests that the textural class of profile SPE is sandy loam (based on the USDA Soil Textural Triangle).The maximum clay content in the profile was 10.23 % and recorded at the 60 cm depth (Table 4.6).

Compared with profile SPD, profile SPE may easily facilitate leachate migration into surface water and groundwater due to its low percentage clay content.

The particle size distribution of the profiles shows that the soil is homogeneous with depth. Sand particles dominate the profiles, followed by silt and then clay. The high percentage sand and low percentage clay content of the profiles suggest that the soil in and around the dumpsite may relatively be porous and thus enhance the migration of leachate into surface water and groundwater. The relatively high percentage clay content at the 60 cm depth of most of the profiles suggest that, adsorption of the trace elemental components of leachate may be relatively high at the 60 cm depth of the soil in and around the closed dumpsite.

### 4.5.2 Porosity and Moisture Content of the Profiles

The porosity and moisture content of the profiles are presented in Figure 4.3, 4.4, 4.5, 4.6 and 4.7.

The porosity of profile SPA decreased from 53.6 % at the 20 cm depth to a minimum value of 48.3 % at the 60 cm depth. From the 60 cm depth, the porosity increased to 54 % and 49.8 % at the 80 cm and 100 cm depths respectively (Figure 4.3). The minimum porosity recorded at the 60 cm depth could be attributed to the sharp increase in the clay content at that depth.

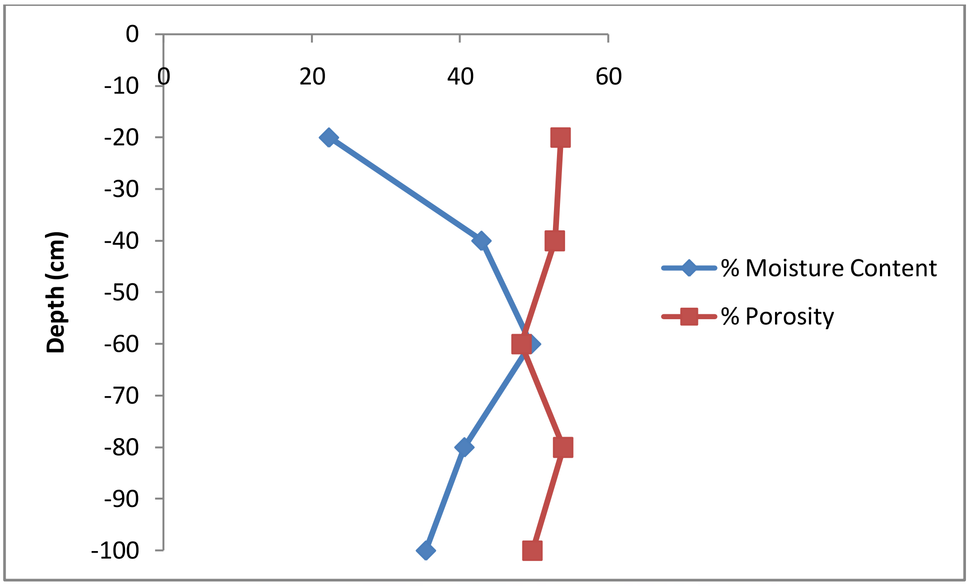


Figure 4.3 Variation of porosity and moisture content with depth of profile (SPA)

The water content also increased from 22.3 % at the 20 cm depth to a peak value of 49.6 % at 60 cm depth. From the 60 cm depth the water content decreased to 40.6 % and 35.4 % at the 80 cm and 100 cm depth respectively (Figure 4.3). The maximum water content recorded at the 60 cm depth could be attributed to the sharp increase in the clay content at 60 cm depth.

Comparing porosity to moisture content of the profile, it is observed that as porosity decreased to its minimum value at the 60 cm depth, the moisture content increases to its peak value with the percentage clay content serving as the main determining factor. This suggests that porosity is inversely proportional to the moisture content of the profile.

In profile SPB, the porosity decreased from 50.6 % at the 20 cm depth to a minimum value of 47.9 % at the 60 cm depth. From the 60 cm depth, the porosity increased to 53.6 % and 49.8 % at the 80 cm and 100 cm depths respectively (Figure 4.4). The minimum porosity recorded at the 60 cm depth of the profile could be attributed to the sharp increase in the clay content at the 60 cm depth.

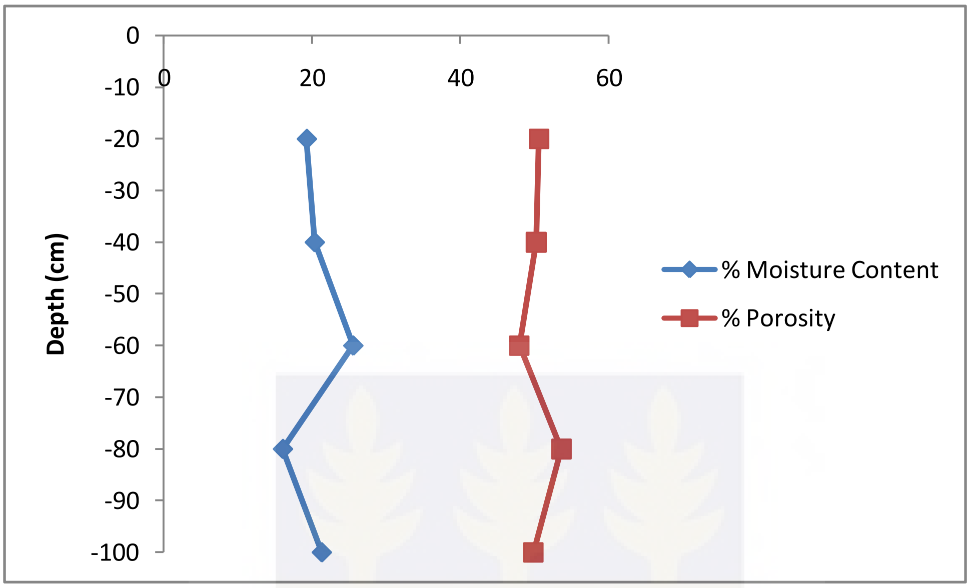


Figure 4.4 Variation of porosity and moisture content with depth of profile (SPB)

The water content also increased from 19.26 % at 20 cm depth to a peak value of 25.53 % at 60 cm depth. From the 60 cm depth, the water content decreased to 16.03 % and 21.28 % at the 80 cm and 100 cm depth respectively (Figure 4.4). The maximum water content recorded at the 60 cm depth could be attributed to the sharp increase in the clay content at 60 cm depth.

Comparing porosity to moisture content of the profile, it is observed that as porosity decreases to its minimum value at the 60 cm depth, the moisture content increases to its peak value with the percentage clay content serving as the main determining factor. This indicates that porosity is inversely proportional to the moisture content of the profile.

For profile SPC, the porosity decreased from 49.8 % at the 20 cm depth to 49.1 % at the 60 cm depth. The minimum porosity (47.9 %) was recorded at the 40 cm depth (Figure 4.5). From the 60 cm depth, the porosity increased to 49.8 % at both the 80 cm and 100 cm depths. The observed porosity could mainly be attributed to the high percentage sand and low percentage clay content of the profile.

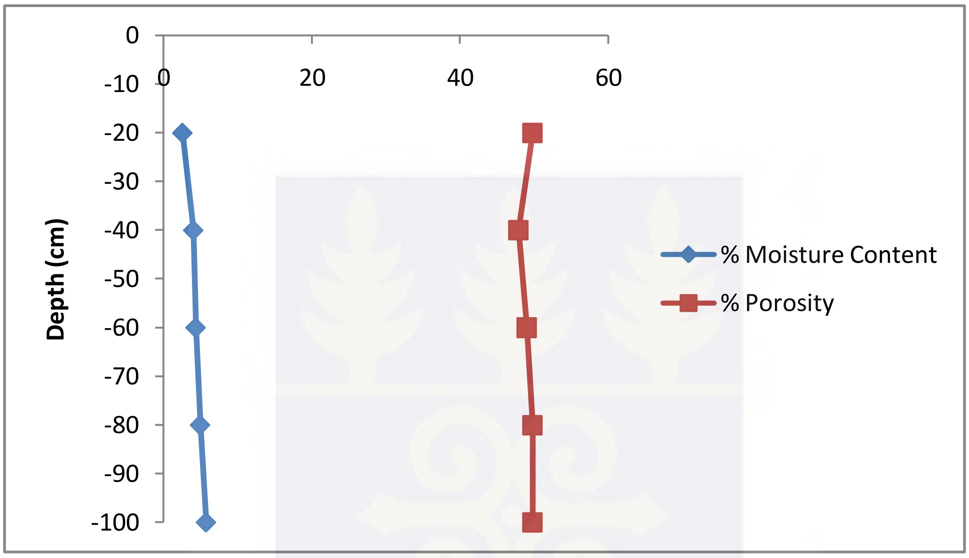


Figure 4.5 Variation of porosity and moisture content with depth of profile (SPC)

The water content on the other hand, increased from 2.53 % at the 20 cm depth to a maximum value of 5.7 % at the 100 cm depth (Figure 4.5). This could also be attributed to the to the high percentage sand and low percentage clay content of the profile.

Comparing porosity to the moisture content of the profile, it is observed that both increased with depth of the profile mainly due to the high percentage sand and low percentage clay content of the profile.

In profile SPD, the porosity increased from 51.7 % at the 20 cm depth to 53.6 % at the 40 cm depth. From the 40 cm depth, the porosity decreased to a minimum value 49.1 % at the 60 cm depth and then increased to 54 % and 51.3 % at the 80 cm and 100 cm depths respectively (Figure 4.6).

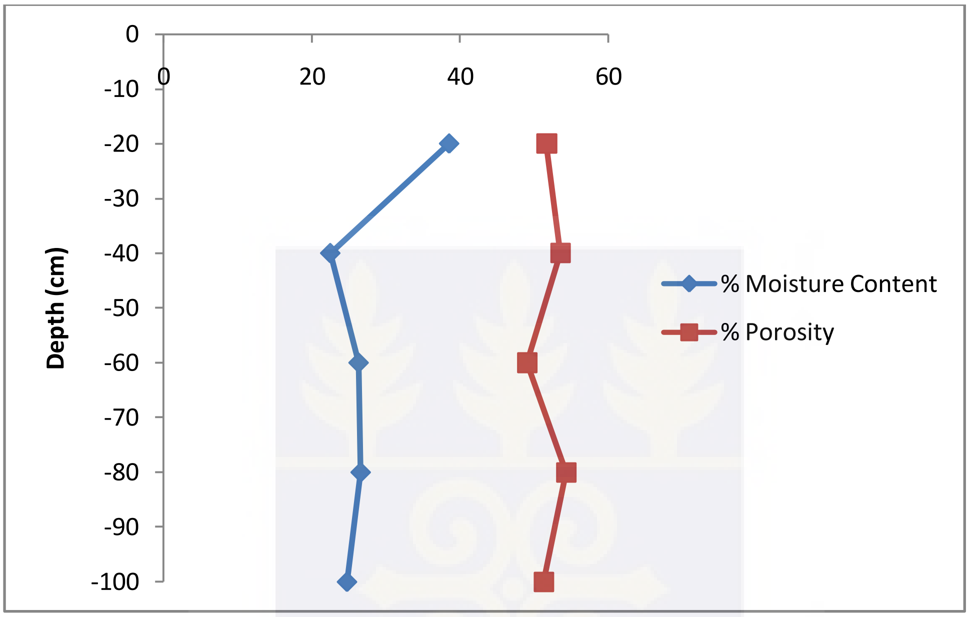


Figure 4.6 Variation of porosity and moisture content with depth of profile (SPD)

Comparing the porosity of profile SPD to that of profiles SPA, SPB and SPC, it is observed that profile SPD is less porous due to the its higher percentage clay content.

The water content decreased from a peak value of 38.53 % at 20 cm depth to 26.33 % at 60 cm depth. From the 60 cm depth, the water content increased to 26.61 % at 80 cm depth and decreased to 24.77 % at 100 cm depth (Figure 4.6).

Comparing porosity to the moisture content of the profile, it is generally observed that porosity is inversely proportional to the moisture content with the percentage clay content serving as the main determining factor.

In profile SPE, porosity decreased from 48.7 % at the 20 cm depth to a minimum value 47.9 % at the 60 cm depth. From the 60 cm depth, the porosity increased to 51.3 % and 49.1 % at the 80 cm and 100 cm depths respectively (Figure 4.7). The minimum porosity observed at the 60 cm depth is mainly attributed to the sharp increase in the clay content at the 60 cm depth.

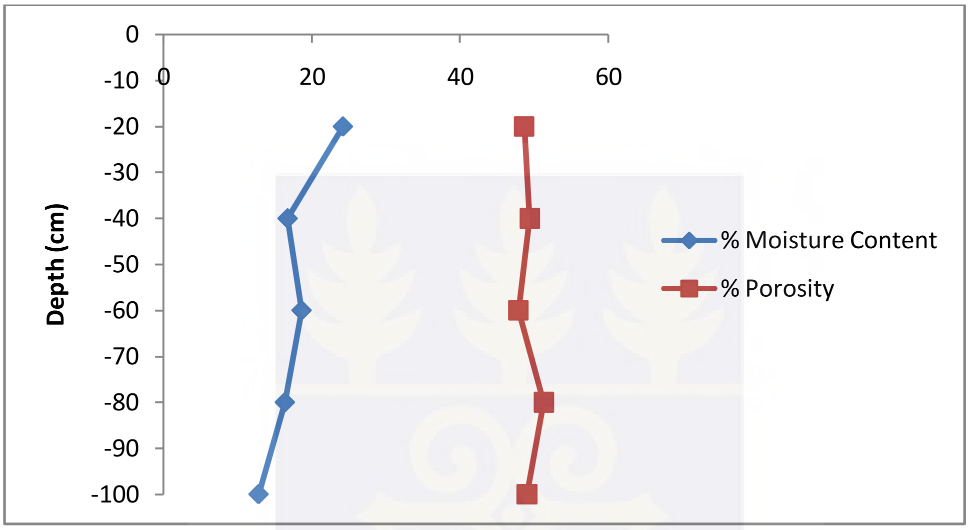


Figure 4.7 Variation of porosity and moisture content with depth of profile (SPE)

The water content also decreased from a peak value of 24.21 % at 20 cm depth to 18.63 % at 60 cm depth. From the 60 cm depth, the water content decreased to 16.68 % and 12.83 % at 80 cm and 100 cm depths, respectively (Figure 4.7). The decreasing water content with the depth of the profile could be explained as mainly due to the high percentage sand and low percentage clay content of the profile.

Comparing the porosity to the moisture content, it is generally observed that porosity is inversely proportional to the moisture content and the main determining factor is the percentage clay content of the profile.

Generally, porosity decreases with depth of the profiles and if this trend persists through and beyond the unsaturated zone, leachate may migrate slowly to groundwater and thus contamination of the groundwater may be reduced.

Generally, moisture content increases with depth of the profiles and if this trend continues through and beyond the unsaturated zone, the possibility of groundwater contamination with leachate may be high. This is because hydraulic conductivity of soil media is directly proportional to the moisture content.

### 4.5.3 Trace Metals in the Soil Profiles

The trace metals analysed include Fe, Pb, Cd, Cr, Mn, As, Hg, Zn and Cu. Figure 4.8, 4.9, 4.10, 4.11 and 4.12 show the trace metal concentrations in the soil profiles.

In profile SPA, the maximum concentrations of all the elements analysed, except As and Zn, were found between 0 and 60cm depths of the profile (Figure 4.8 and Appendix C). The elevated concentrations of most of the trace elements observed near the ground surface (between 0 and 60 cm) may be due to contributions from anthropogenic sources, mainly leachate from the closed dumpsite. Hafez (2004) also observed that anthropogenic activities contributed to elevated concentrations of trace elements at the surface horizon. The concentrations of Pb, Cd, Cr, Mn, Hg and Cu were generally attenuated beneath the 60 cm depth (Figure 4.8 and Appendix C). This may be due to the comparatively high clay content at the 60 cm depth.

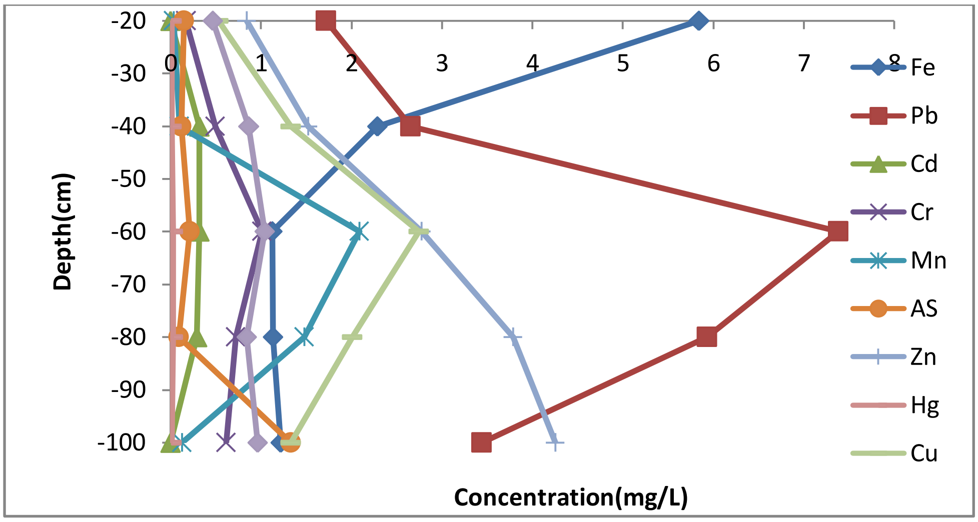


Figure 4.8 Variation of trace elemental concentrations with depth of profile (SPA)

In profile SPB, maximum concentrations of all the trace elements analysed, except Cd and Hg, were recorded between 0 and 60 cm depths of the profile (Figure 4.9 and Appendix C). The concentrations of Fe, Pb, Cr and Zn were generally attenuated beneath the 60 cm depth (Figure 4.9 and Appendix C).

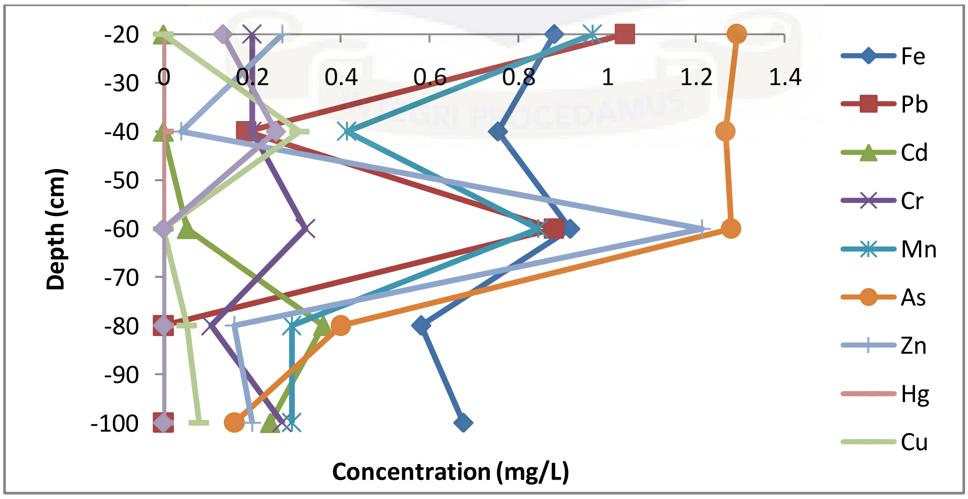


Figure 4.9 Variation of trace elemental concentrations with depth of profile (SPB)

Comparing the concentrations of trace elements in profile SPA with profile SPB, it was observed that the concentrations in profile SPB were generally lower due to the relatively lower clay content at the 60 cm depth of profile SPB as well as the location of profile SPB from the dumpsite. Profile SPB is located 30 m from the dumpsite while profile SPA is located 10 m from the dumpsite. Thus, contributions due to the horizontal flow of leachate from the dumpsite may be reduced in profile SPB.

In Profile SPC, the maximum concentrations of Pb, Cd, Cr, As and Cu were recorded between 0 and 60 cm depths (Figure 4.10 and Appendix C). Hg was below detection and Pb was the only element attenuated beneath the 60 cm depth of the profile (Figure 4.10 and Appendix C). The maximum concentration of Mn observed at the 100 cm depth could be attributed to leaching of the metal with the infiltrating water. The attenuative effect of profile SPC is comparatively lower than that of profile SPA and SPB due to its comparatively lower percentage clay and higher percentage sand content.

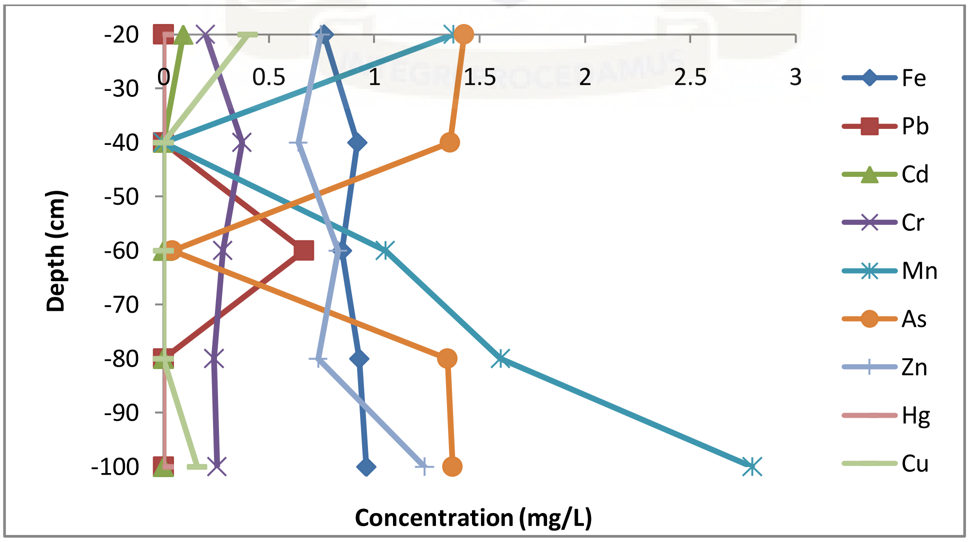


Figure 4.10 Variation of trace elemental concentrations with depth of profile (SPC)

In profile SPD, maximum concentrations of all the elements except Cr and Mn were recorded between 0 and 60 cm (Figure 4.11 and Appendix C). Hg was below detection and Fe, Pb, Cd, Zn and Cu were generally attenuated below the 20 cm depth (Figure 4.11 and Appendix C). The maximum concentration of Mn observed at the100 cm depth could be attributed to leaching of the metal with infiltrating water.

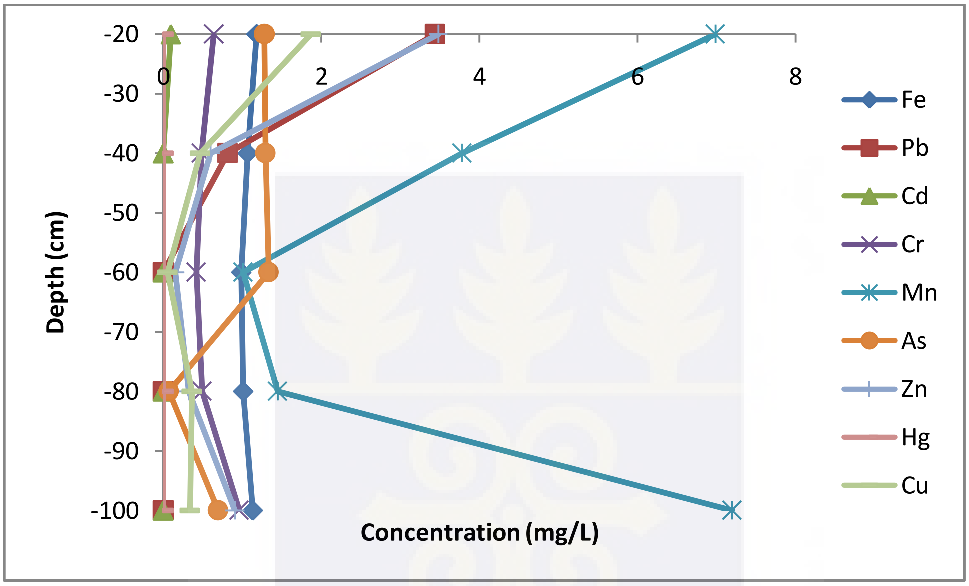


Figure 4.11 Variation of trace elemental concentrations with depth of profile (SPD)

Comparing profile SPD to profiles SPA and SPB, it was observed that the depths below which attenuation of most of the trace elements occurred in profile SPD was nearer to the ground surface (20 cm depth) than in profiles SPA and SPD (60 cm depth). This could be attributed to the comparatively higher clay content near the ground surface in profile SPD.

In Profile SPE, maximum concentrations of Fe, Cr, As and Cu were also measured below the 60 cm depth (Figure 4.12 and Appendix C). This may be explained as due to leaching of the metals with infiltrating water. Pb, Cd and Hg were below detection mainly due to reduced horizontal flow effects of leachate on the profile because of its location from the dumpsite. Profile SPE, as indicated earlier, is about150 m from the dumpsite.

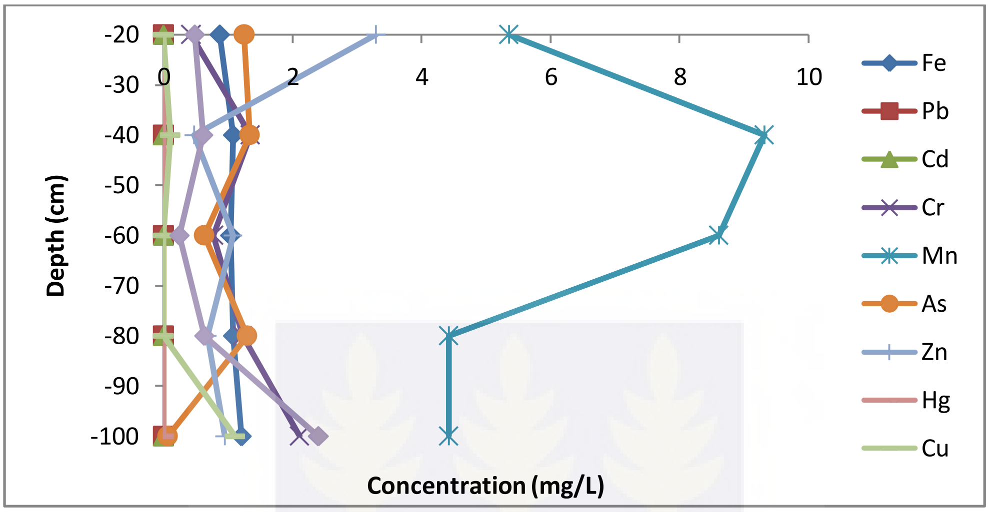


Figure 4.12 Variation of trace elemental concentrations with depth of profile (SPE)

The concentration of Mn in the profile was comparatively higher due to contributions from car exhaust fumes since the profile is located very close to a Class 2 motorable road and also the main Mallam lorry station. The concentrations of Zn and Mn were attenuated beneath 20 cm depth and 40 cm depths respectively.

The attenuative effect of profile SPE was lower than that of profiles SPA and SPB mainly due to the comparatively lower percentage clay content of profile SPE.

Generally, elevated concentrations of most of the trace elements measured were observed near the surface horizon between 0 and 60cm depths of the profiles. This suggests some degree of attenuation and also indicates that the trace elements in the leachate are migrating slowly to the groundwater.

## 4.6 Stable Isotope Analyses ($^{18}O$ and $^{2}H$)

### 4.6.1 Isotopic Content of Surface Water and Groundwater Samples

The $\delta\ ^{18}O$ value of the surface water samples ranged from -2.33 $^{o}/_{oo}$ to -0.21 $^{o}/_{oo}$ vrs VSMOW with a mean value of -1.59$^{o}/_{oo}$ vrs VSMOW (Appendix D). The sampling point SW1 was comparatively enriched with $\delta\ ^{18}O$ mainly due to higher leachate effect. Panno *et al*. (2004) observed that landfill leachate is enriched with $\delta^{18}O$ due to isotopic fractionation in landfills.

In the groundwater samples the $\delta\ ^{18}O$ value ranged from -2.38 $^{o}/_{oo}$ to -0.68 $^{o}/_{oo}$ vrs VSMOW with a mean value of -1.70 $^{o}/_{oo}$ vrs VSMOW (Appendix D). There is enrichment in the $\delta\ ^{18}O$ value of the groundwater samples since the average $\delta\ ^{18}O$ value of groundwater in Accra is -3.5 $^{o}/_{oo}$ vrs VSMOW (Akiti, 1980). The enrichment could be attributed to factors such as evaporation and mixing with possibly leachate from the dumpsite.

The measured $\delta\ ^{18}O$ value of the surface water samples suggest mixing of the surface water with leachate from the closed dumpsite.

The measured $\delta\ ^{18}O$ value of the groundwater samples suggest mixing of the groundwater with possibly, leachate from the dumpsite.

### 4.6.2 Deuterium ($^{2}H$ ) and Oxygen-18 ($^{18}O$) Relationship in Surface Water, Extracted Soil Pore Water and Groundwater Samples

The $^{2}H$ and $^{18}O$ relationship in the surface water, extracted soil pore water and groundwater samples are presented in Figure 4.13.

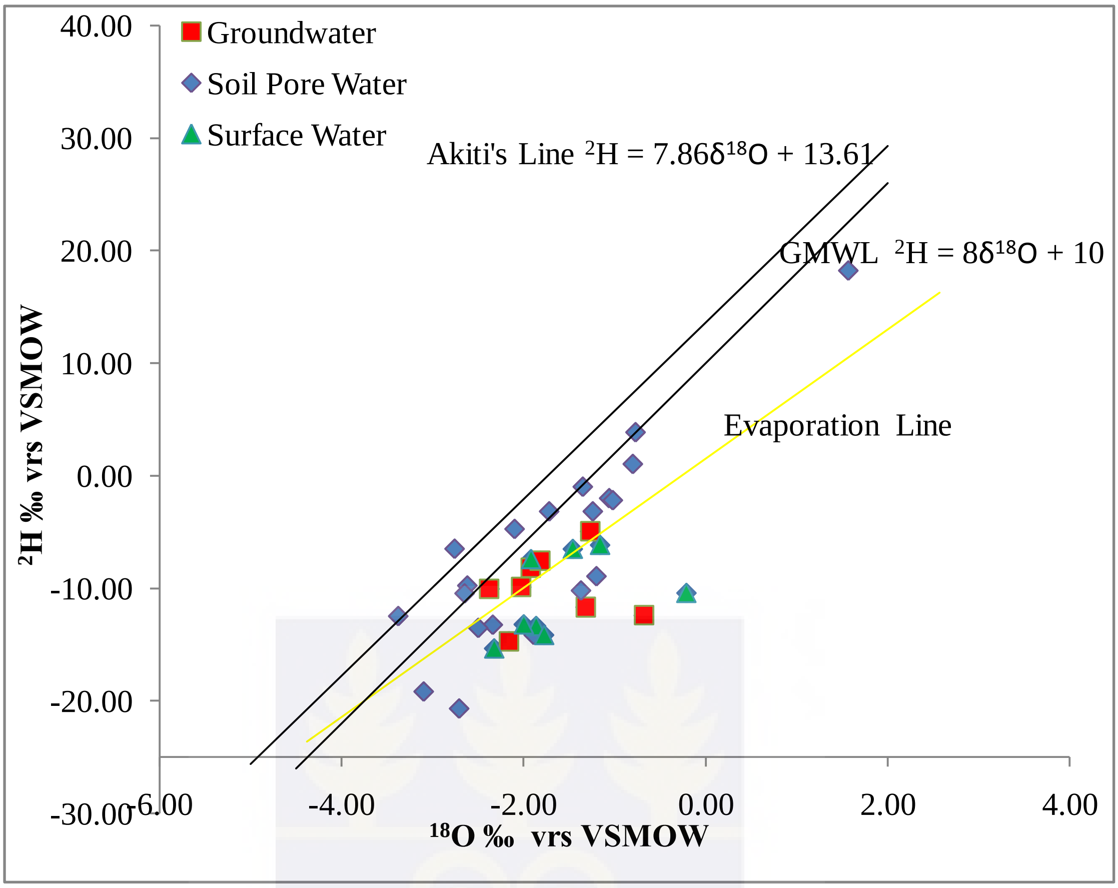


Figure 4.13 δ $^{2}$H $^{o}/_{oo}$ vrs VSMOW and δ $^{18}$O $^{o}/_{oo}$ vrs VSMOW in surface water, soil pore water and groundwater samples

The surface water samples were all distributed below the Global Meteoric Water Line and the Local Meteoric Water Line (Akiti's Line) and shows evaporation. This suggests that evaporation is contributing to the enrichment of the δ $^{18}$O value of the surface water samples.

Most of the extracted soil pore water samples were distributed below and between the Local Metoric Water Line (Akiti's Line) and Global Meteoric Water Line and shows evaporation.

All the groundwater samples plotted below the Local Meteoric Water Line and Global Meteoric Water Line and shows evaporation. This suggests that evaporation is contributing to the enrichment of the $\delta\ ^{18}O$ value of the groundwater samples.

### 4.6.3 Variation of $\delta\ ^{18}O$ with Depth of the Soil Profiles

Variation of $\delta\ ^{18}O$ value with depth of the profiles is presented in Figure 4.14.

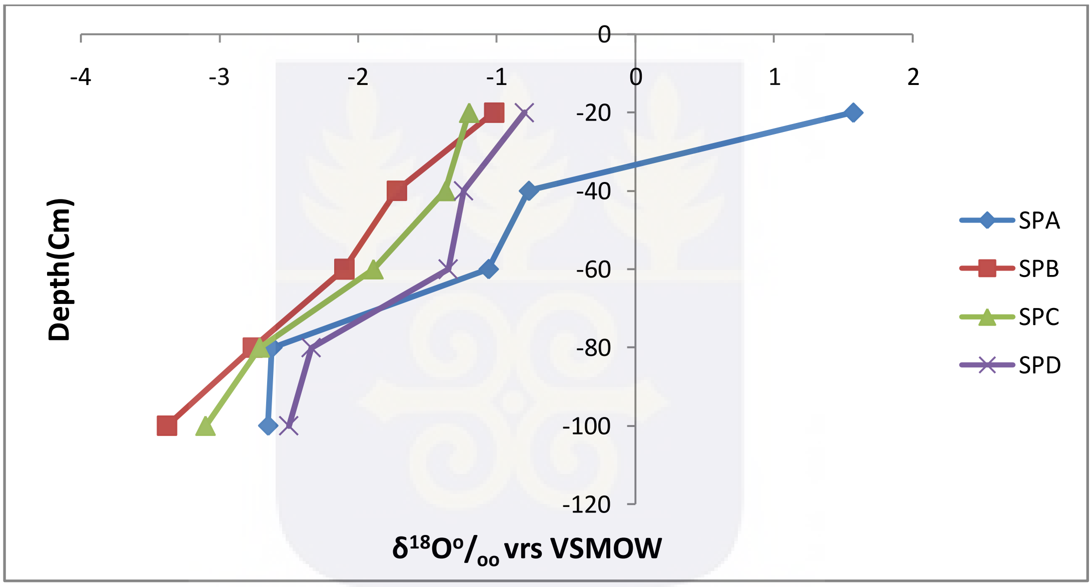


Figure 4.14 Variation of $\delta\ ^{18}O$ ($^{o}/_{oo}$) vrs VSMOW of extracted soil pore water with depth of the profiles

In profile SPA, the $\delta\ ^{18}O$ value of the extracted soil pore water showed depletion with depth of the profile. It ranged from -2.65 $^{o}/_{oo}$ vrs VSMOW at 20 cm depth to 1.57 $^{o}/_{oo}$ vrs VSMOW at the 100 cm depth with a mean value of -1.11 $^{o}/_{oo}$ vrs VSMOW (Appendix E). Evaporation and leachate migration from the dumpsite could have accounted for the enrichment near the ground surface. The observed depletion of $\delta\ ^{18}O$ with depth of the profile suggests that leachate from the dumpsite is migrating slowly to the groundwater.

In profile SPB, the δ $^{18}$O values showed depletion from -3.38 $^{o}/_{oo}$ vrs VSMOW at the 20 cm depth to -1.02 $^{o}/_{oo}$ vrs VSMOW at 100 cm depth with a mean value of -2.20 $^{o}/_{oo}$ vrs VSMOW (Appendix E). The enrichment near the ground surface is attributed to evaporation and leachate migration from the dumpsite. The observed depletion of δ $^{18}$O with depth of the profile suggests that leachate from the dumpsite is migrating slowly to the groundwater.

In profile SPC, the δ $^{18}$O was depleted with depth of the profile. The δ $^{18}$O value varied from -3.1 $^{o}/_{oo}$ vrs VSMOW at the 20 cm depth to -1.2 $^{o}/_{oo}$ vrs VSMOW at 100 cm depth with a mean value of -2.05 $^{o}/_{oo}$ vrs VSMOW**.** Evaporation and leachate migration from the dumpsite may have accounted for the enrichment near the ground surface. The observed depletion of δ $^{18}$O with depth of the profile suggests that leachate from the dumpsite is migrating slowly to the groundwater.

Profile SPD also showed depletion of δ $^{18}$O with depth of the profile. The δ $^{18}$O value ranged from -0.8 $^{o}/_{oo}$ vrs VSMOW at the 20 cm depth to -2.5 $^{o}/_{oo}$ vrs VSMOW at 100 cm depth with a mean value of -1.65 $^{o}/_{oo}$ vrs VSMOW. The enrichment near the ground surface is attributed to evaporation and leachate migration from the dumpsite. The observed depletion of δ $^{18}$O with depth of the profile suggests that leachate from the dumpsite is migrating slowly to the groundwater.

Depletion of δ $^{18}$O value of the extracted pore water with depth of each profile suggest that leachate from the closed dumpsite is migrating slowly to the groundwater.

# CHAPTER FIVE

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

Leachate from the closed Mallam SCC waste disposal site contains relatively high concentrations of major ions ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $HCO_3^-$ $SO_4^{2-}$, $NO_3^-$ and $PO_4^{3-}$) and trace elements (Fe, Pb, Cd, Cr, Mn, As, Zn, Hg and Cu) and may be a source of contamination of surface water, soil and groundwater in Mallam.

The surface water (Bawere stream) is contaminated with major ions ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $HCO_3^-$, $SO_4^{2-}$, $NO_3^-$ and $PO_4^{3-}$) and trace elements (Fe, Pb, Cd, Cr, Mn, As, Zn and Cu) due to leachate migration from the closed dumpsite. The observed values of EC, TDS, total alkalinity as well as the concentrations of $Na^+$, $K^+$, Fe, Pb, Cd, Cr, Mn and Zn in the Bawere stream were above the maximum permissible limit of the WHO (1996)guideline for drinking water, suggesting that the Bawere stream may not be safe for drinking and some domestic purposes.

The stable isotopic composition ($^{18}O$ and $^{2}H$) of the surface water (Bawere stream) are enriched. This enrichment is continuous with leachate flow to the surface water suggesting mixing of the surface water with leachate from the closed dumpsite.

Generally, porosity of the soil in and around the closed dumpsite decreased with depth while the volumetric water content increased with depth. If the trend of decreasing porosity with depth of the soil persists through and beyond the unsaturated zone, leachate may migrate slowly to the groundwater.

Elevated concentrations of most of the trace elements measured (Fe, Pb, Cd, Cr, Mn, As, Zn, Hg and Cu) were observed near the surface horizon between 0 and 60 cm depths of the profiles. This suggests some degree of attenuation and also indicates that the trace elements in the leachate are migrating slowly to the groundwater.

The stable isotopic composition ($^{18}O$ and $^{2}H$) of the extracted soil pore shows enrichment due to evaporation and possible mixing of the infiltrating water with leachate. The depletion of $\delta\ ^{18}O$ of the extracted pore water with depth of the profiles, however, suggests that leachate is migrating slowly to the groundwater.

The groundwater is contaminated with major ions ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $HCO_3^-$, $SO_4^{2-}$, $NO_3^-$ and $PO_4^{3-}$) and trace elements (Fe, Cd, Cr and Mn) due to the contributions of leachate from the closed dumpsite. The observed values of EC, TDS, as well as the concentrations of $Na^+$, Fe, Cd and Mn in the groundwater were above the maximum permissible limit of the WHO (1996) guideline for drinking water, suggesting that the groundwater in Mallam may not be safe for drinking purposes.

The stable isotopic composition ($^{18}O$ and $^{2}H$) of the groundwater shows enrichment due to evaporation and possible mixing of the recharge water with leachate from the closed dumpsite.

There is therefore high level of environmental pollution due to leachate migration from the closed Mallam SCC waste disposal site.

## 5.2 Recommendations

In the light of the above, the following are recommmended:

- The dumpsite should be properly decommissioned.
- Assessment of the level of xenobiotic organic compounds and microbial population in the surface water and groundwater should be conducted.
- An extended study of the unsaturated zone should be conducted to include the determination of the hydraulic conductivity.
- The study should be replicated in all the closed landfill sites in Ghana.
- Dumpsites in Ghana should be properly engineered to minimize environmental pollution due to leachate migration.

## REFERENCES

Abu-Rukah, Y., Al-Kafahi, O. (2001). The assessment of the effect of landfill leachate on groundwater quality – a case study. El-Akader landfill site – North Jordan, J. Arid Environ., 49 (3), 615 – 630.

Ackah, M., Carboo, D., Yeboah, P. O., Pwamang, J., and Agyemang, O. (2011). Determination of Metal Ion Concentrations in Components of Household Solid Waste in the Akwapim South Municipality of Ghana.Research Journal of Environmental and Earth Sciences 3(5): 508-511, 2011.

Akiti, T. T. (1980). Étude géochimique et isotopique de Quelques aquifers du Ghana. (Dr. Ing. Thesis) Université Paris, Sud. Pp 232.

Akiti ,T. T. (1987). Environmental isotope study of groundwater in crystalline rocks of the Accra Plains (Ghana). In: Wand U., Strauch G. (eds) Isotopes in nature, Academy of Sciences of the GDR, Central Institute of Isotope and Radiation Research, Leipzig: 107-121.

Al-Khadi S. (2006), Assessment of groundwater contamination vulnerability in the vicinity of Abqaiq landfill-A GIS Approach, Dissertation, King Fahd University of Petroleum and Mines, Saudi Arabia.

Andreottola, G., and Cannas, P. (1992), Chemical and biological characteristics of landfill leachate, in *Landfilling of waste: Leachate*, Christensen, T.H., Cossu, R., and Stegmann, R., Eds., Elsevier Applied Science, London, UK, 1992, 65

Ansa-Asare, O. D. (1998), Do diurnal dissolved oxygen cycles have diagnostic value for assessing pollution status in lakes, (PhD Thesis), Department of Chemistry, University of Aberdeen, Scotland. UK.

Araguas-Araguas, L., Rozanski, K., Gofiantini R., Louvat., D.J. (1995). Journal of Hydrolology, pp. 168: 159.

Aucott, M. (2006). The fate of heavy metals in landfills: A Review; Prepared for The “Industrial Ecology, Pollution Prevention and the NY-NJ Harbor” Project of the New York Academy of Sciences.

Aulin, C. and Neretnieks, I., (1995). Material balance for an industrial landfill, in *SARDINIA '95, Fifth International Landfill Symposium, Proceedings, Volume III*, Christensen, T.H., Cossu, R., and Stegmann, R., Eds., CISA. Cagliari, Italy, 173, 1995.

Barone, F. S., Yanful, E. K., Quigley, R. M and Rowe, R. K (1989). Effect of Multiple Contaminant migration on diffusion and adsorption of some domestic waste contaminants in natural clayey soils, *Can. Geotech J.,26(2) 189-198.*

Barlaz, M. A., Schaefer, D. M., and Ham, R. K. (1989). Bacterial Population Development and Chemical Characteristics of Refuse Decomposition in a Simulated Sanitary Landfill, *Appl. Environ. Microhiol., 55,* 55, 1989a

Barlaz, M. A. and Ham, R. K. (1993). Leachate and gas generation, in *Geotechnical Practice for Waste Disposal,* D. E. Daniel, Ed., Chapman and Hall, London, 1993, 113.

Belevi, H. and Baccini, P. (1989). Long-term behavior of municipal solid waste landfills, *Waste Manag., Res.*, 7, 43.

Bianchi, V., Zantedeschi, A., Montaldi, A., and Majone, F. (1984), Trivalent Chromium is Neither Cytotoxic nor Mutagenic in Permealized Hamster Fibroblasts, Toxicological Letters, 23: 51-59.

Bolton, P. W., Currie, J. C., Tervet, D. J. and Welsh, W.T., (1978). An index to improve water quality classification, *Wat. Pollut. Control*, **6**: 271-285.

Boulding, J.R., Ginn, J.S. (2004). Practical handbook of soil, vadose zone and ground water contamination: assessment, prevention and remediation, CRC Press.

Bozkurt, S., Moreno, L., and Neretnieks, I. (1999). Long-term fate of organics in waste deposits and its effect on metal release, *Sci. Total Environi.*, 228, 135.

Bruce, R. R., and Klute, A. (1956). The measurement of soil-water diffusivity. Soil Sci Soc Am Proc 20:458562.

Butler, M. J. and Verhagen, B. T. (1997). Environmental isotope tracing of water in the urban environment of Pretoria, South Africa. In: *Groundwater in the Urban Environment, Vol 1:Problems, processes and Management*, J. Chilton *et al.* (Eds.), Balkema, Rotterdam, The Netherlands. 101–106.

Calmano, W., Hong, **J.,** and Forstner, U., (1993). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential, *Water Sci. Techi.*, 28(8-9), 223, 1993.

Castañeda S. S, Sucgang, R. J.,Almoneda, R.V., Mendoza, N. D. S., David, C. P. C. (2012). Environmental isotopes and major ions for tracing leachate contamination from a municipal landfill in Metro Manila, Philippines; Journal of Environmental Radioactivity 110: 30-37.

Chian E. S. K., and DeWalle F. B. (1976). "Sanitary Landfill Leachates and Their Treatment" ASCE, Journal of Environmental Engineering Division, Vol. 102, No. EE2, pp. 411-431.

Chapman, (1996). Water Quality Assessments - A Guide to Use of Biota, Sediments and Water in Environmental Monitoring, Second Edition Great Britain at the University Press, Cambridge pp.74-112.

Chery, L., Michelot, J. L., Blavoux, B. and Dray, M., (2000). Project of French isotopic data base, In: *Isotope Techniques in Water Resources Development and Management*, IAEA, Vienna, Austria. Poster Session 2, 9–11.

Christensen, T. H. and Kjeldsen, P., (1989). Basic biochemical processes in landfills. Chapter 2.1 in *Sanitary Landfilling: Process, Technology and Environimental Impact,* Christensen, T.H., Cossu, R.,and Stegmann, R., Eds., Academic Press, London, UK, 1989, 29.

Christensen, T. H., Kjeldsen, P., Albrechtsen, H. J., Heron, G., Nielsen, P. H., Bjerg, P. L., and Holm, P. E.,(1994), Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Environ. Sci. Technol.*, 24, 119, 1994.

Christensen, T. H. and Kjeldsen, P., (1995). Landfill emissions and environmental impact: An introduction. in*SARDINIA '95, Fifth Internatioial Landfill Symposium, Proceedings, Volume lll,* Christensen, T.H., Cossu, R., and Stegmann, R., Eds., CISA, Cagliari, Italy.

Christensen T. H, Kjeldsen P., Bjerg P. L, Jensen D. L., Christensen J. B., Baun A (2001). Biogeochemistry of landfill leachate plumes. Appl. Geochem., 16:659–718.

Chu, L. M., Cheung, K. C., and Wong, M. H. (1994). Variations in the chemical properties of landfill leachate. Environ. Manage., 18: 105-117.

Clark, I.D. and Fritz, P., (1997), *Environmental Isotopes in Hydrogeology*, 328 pp New York, Boca Raton: Lewis Publishers.

Close, M. (2010). Critical Review of Contaminant Transport Time through the Vadose Zone. Institute of Environmental Science and Research (ESR) Report No. R10/113 ISBN 978-1-927137-54-3

Craig, H. (1961), Isotopic variations in meteoric waters, Science, 133, 1702–1703, doi:10.1126/science.133.3465.1702.

Craig, H., and L. I. Gordon (1965). Deuterium and oxygen 18 variations in the ocean and the marine atmosphere, in Stable Isotopes in Oceanographic Studies and Paleotemperatures, Spoleto 1965, edited by E. Tongiorgi, pp. 9–130, Cons. Naz. Della Ric, Pisa, Italy

Dansgaard, W. (1964). Stable isotopes in precipitation, Tellus, 16, 436– 468, doi:10.1111/j.2153-3490.1964.tb00181.x.

De Laune, R. D. and Reddy, K. R (2005), Redox Potential, Elsevier.

De Roos, A. J., Ward, M. H., Lynch, C. F. and Cantor, K. P. (2003), Nitrate in public water supplies and risk of colon and rectum cancers. Epidemiology, **14(6),** 640-649.

Demenico and Schwarts (1998), Physical and chemical hydrology, John Wiley and Sons Inc, 2nd edition.

Denutsui, D. (2009), Assessment of Pollution in the Densu Wetland Using Hydrochemistry and Isotopic Techniques (Mphil Thesis) Graduate School of Nuclear and Allied Science, University of Ghana, Legon, Accra: pp 66-67

Denutsui D., T. T. Akiti, S. Osae, A. O. Tutu, S. Blankson-Arthur, J.E. Ayivor, F.N. Adu-Kwame and C. Egbi (2012). Leachate Characterization and Assessment of Unsaturated Zone Pollution near Municipal Solid Waste Landfill Site at Oblogo, Accra-Ghana; Research Journal of Environmental and Earth Sciences 4(1): 134-141, 2012.

Drever, J. I., (1982), The Geochemistry of Natural Waters. Prentice-Hall, Inc., Englewood Cliffs, NJ, 388p.

Eaton, A. D., Clesceri, L. S., Greenberg, A. E., and Franson, A. H. (1995). Standard methods for the examination of water and waste water, 19th edition, American Public Health Association fifteenth street 1015 NW. Washington DC, 20005.

Edlefson, N. E. and Anderson, A. B. C. (1943), "Thermodynamics of Soil Moisture", Hilgardia, Volume15, 1943, pp. 31-298.

Edmunds, W. M., (1996), Indicators in the Groundwater Environment of Rapid Environmental Change. In: Berger, A.R. and W.J. Iams, (Eds.), Geoindicators: Assessing Rapid Environmental Changes in Earth Systems. A.A. Balkema, Rotterdam, pp: 121-136.

Egbi, D. C. (2011). Assessment of groundwater quality through the partitioning of ions and trace elements due to migration of leachate from Abloradjei waste disposal site, Ghana, to water in the unsaturated zone**.** (Mphil Thesis) Graduate School of Nuclear and Allied Science, University of Ghana, Legon, Accra.

EPA, (2009). United States Environmental Protection Agency, National primary drinking water regulations, United States EPA, Washington, D.C.

EPA (1994). Symposium on Natural Attenuation of Ground-Water, EPA/ 600/R-94/162.

Fatta, D., Papadopoulos, A., Loizidou, M. (1999). A study on the landfill leachate and its impact on the groundwater quality of the greater area, Environ. Geochem. Health, 21(2): 175-190.

Feddes, R. A., Kabat, P., Van Bakel, P. J. T., Bronswijk, J. J. B., and Halbertsma, J. (1988). "Modelling Soil Water Dynamics in the Unsaturated Zone - State of the Art", Journal of Hydrology, Vol. 100, pp. 69-111.

Flyhammar, P. (1995). Leachate quality and environmental effects at active Swedish municipal landfill, in: R. Cossu, H. T. Christensen and R. Stegmann (eds) Regulations, Environmental Impact and Aftercare. Proceedings Sardinia ’95, Fifth International Landfill Symposium. Vol. III, Sardinia, Italy, pp. 549–557.

Freeze, R., and Cherry, A. (1979). Groundwater, Prentice Hall, Edgewood Cliffs, NJ.

Fritz, I., and Fontes, B. (1986). Handbook of Environmental Isotope Geochemistry, The Terrestrial Environment B, Vol. 2, 557 pp. Amsterdam: Elsevier. (A comprehensive reference book on isotope techniques in hydrology)

Gabarino, J. R., Antwieiler, R. C, Brinton, T. I., Roth, D.A., and Taylor, H. E. (1995). Concentration and transport data for selected dissolved inorganic constituents and dissolved organic carbon in water collected from the Mississippi River and some tributaries, July 1991-May 1992. U.S. Geological survey Open- File Report (95-149).

Gazis, C., and Feng, X.H. (2004). A stable isotope study of soil water: evidence for mixing and preferential flow paths. *Geoderma*, **119(1-2)**, 97-111.

Ghana EPA (2002), Ghana Landfill Guidelines: Best Practice Environmental Series, Pp: 15.

Naja ,G. M. and Volesky, B. (2009), Toxicity and Sources of Pb, Cd, Hg, Cr, As, and Radionuclides in the Environment.

Graham- Bryce, I. J. (1963). “Effect of moisture content and soil type on self diffusion of $^{86}$Rb in soils”. *J. Agric. Sci., 60,239-244.*

Grossman R. B., Reinsch, T. G. (2002). SSSA Book Series: 5 Methods of Soil Analysis Ch2, Ed. Dane J.H, Clarke Topp G. Soil Science Society of America, Inc. Madison, Wisconsin, USA.

Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper 2254.263 pp.

Hughes K., Christy A., and Heimlich J. (2008). Landfill Types and Liner Systems. Ohio State University Extension Fact Sheet CDFS - 138 - 05.

Kelley, W. E. (1976). “Ground-Water Pollution near a Landfill” ASCE, Journal of Environmental Engineering Division, Vol. 102: No. EE6: Pp 1189-1199.

Kesse, G.O., (1985). The Mineral and Rock Resources of Ghana, Balkema, Rotterdam, pp: 25-26.

Kjeldsen, P., Christensen,T. H., Albrechtsen, P., Heron, H. J., Nielsen, G., Bjerg, P. H., and Holm P. E (1994). Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Environ. Sci. Technol.,* 24, 119.

Kjeldsen, P. and Christophersen, M. (2001). Composition of leachate from old landfills in Denmark, *Waste Manag. Res.,* 19, 249-256.

Kjeldsen, P., Barlaz, M., Rooker, A. Baun, A., Ledin, A., and Christensen,T. (2002). Present and long term composition of MSW landfill leachate: A Review, Critical Reviews in Environmental Science and Technology, 32, 297-336.

Kodarkar M. S. (1992). Methodology for water analysis, physicochemical, Biological and Microbiological Indian Association of Aquatic Biologists Hyderbad; Pub., **2,** 50.

Kowalski1, M. Siepak, L. Boszke (2007). Mercury Contamination of Surface and Ground Waters of Poznań, Poland ;*Polish J. of Environ. Stud. Vol. 16, No. 1, 67-74.*

Kumar, D., and Alappat, B.J. (2003). “A Technique to Quantify Landfill Leachate Pollution”, Ninth International Landfill Symposium, October 2003, Cagliari, Italy (2003a, in Press).

Kylefors, K., Ecke, H., and Lagerkvist, A. (1999). Relevancy of discharge limit of COD for landfill leachates,in*Sardinia 99, Seventh International Waste Management and Landfill Symposium, 4-8 October,S. Margherita di Pula, Cagliari, Sardinia, Italy. Proceedings, Vol. IV*

Lee, G. F., and Jones, A. R. (1991). "Groundwater Pollution by Municipal Landfills: Leachate Composition, Detection and Its Water Quality Significance." Proceedings of the National Water Well Association Fifth National Outdoor Action Conference, Las Vegas, NV, 1991.

Lee, G. F., and Jones-Lee, A. (1993). Groundwater Quality Protection: A Suggested Approach for Water Utilities. Report to the CA/NV AWWA Section Source Water Quality Committee, Aug, pp. 8.

Lee, G. F. and Jones-Lee, A. (1994). 'Impact of Municipal and Industrial Non-Hazardous Waste Landfills on Public Health and the Environment: An Overview', prepared for California EPA Comparative Risk Project, Sacramento, CA.

Lenntech, Y. (2011). Manganese (Mn) – *Chemical properties, health and Environmental effects*. Retrieved 9/17/2011 from http: //www.lenntech.com/periodic/elements/mn.htm

Lo, I. M. C (1996). "Characteristics and Treatment of Leachates from Domestic Landfills" Environment International, Vol. 22: No. 4: Pp 433-442.

Lovei, M., and Lev B. S. (1997). "Lead Exposure and Health in Central and Eastern Europe: Evidence from Hungary, Poland and Bulgaria." In Magda Lovei, ed., *Phasing Out Lead from Gasoline in Central and Eastern Europe: Health Issues, Feasibility, and Policies.*Washington, D.C.: World Bank.

Di Bonito, M. (2005). Trace Elements in Soil Pore Water: A Comparison of Sampling Methods, Doctorial Thesis, University of Nottingham.

Martensson, A. M., Aulin, C., Wahlberg, O., and Argen, S. (1999). Effect of humic substances on the mobility of toxic metals in a mature landfill, *Waste Manag. Res.*, 17, 296.

Masters, G. M. (1998). "Introduction to Environmental Engineering and Science" Prentice-Hall of India Private Limited, New Delhi, India.

McBride, M. B. (1994). Environmental chemistry of soils, 1st Edition; Oxford University Press, 416 p.

McMahon, M. A., and Thomas, G.W. (1974). Chloride and initiated water flow in disturbed and undisturbed soil cores, Soil Sci. Soc. Am.Proc. 38 :727.

Minnesota Pollution Control Agency (1999). Environmental Outcome Division Groundwater Monitoring and Assessment Programme.

Moore, K., Ekwurzel, B. E., Esser, B. K., Hudson, G. B., and Moran, J. E. (2006). Sources of groundwater nitrate revealed using residence time and isotope methods. Appl. Geochem., 21(6): 1016-1029.

Mor S, Ravindra K., Dahiya R. P., Chandra, A. (2006). Leachate Characterization and Assessment of Groundwater Pollution near Municipal Solid Waste Landfill Site. Environ. Monit.Assess., 4: 325-334.

Nielsen, D. R., van Genuchten M. T., and Biggar J. W (1986). Water flow and solute transport processes in the unsaturated zone. Water Resour Res 22(9):89–108

Nimmo, J.R., (2005). Unsaturated Zone Flow Processes, in Anderson, M.G., and Bear, J., eds., Encyclopedia of Hydrological Sciences: Part 13--Groundwater: Chichester, UK, Wiley, v. 4, p. 2299-2322, doi:10.1002/0470848944.hsa161

Nova Scotia Environment (2008). At 1-877-9 ENVIRO.www.gov.ns.ca/nse/water/

Nriagu, J. O., (1988). Historical Perspectives. IN: Chromium in the Natural and Human Environments, Vol. 20 (J.O. Nriagu and E. Nieboer, editors). John Wiley & Sons, New York: 1-20.

O' Leary, P., and Walsh, R. (1995). Decision makers guide line to solid waste management, volume II, solid and hazardous waste education center, University of Wisconsin.

Palmer, C. D. and P. R. Wittbrodt, (1990). Geochemical Characterization of the United Chrome Products Site, Final Report. IN: Stage 2 Deep Aquifer Drilling Technical Report, United Chrome Products Site, Corvallis, OR, September 28, 1990, CH2M Hill, Corvallis, OR.

Pandey, A. K., Siddiqi S. Z., and Rama R. (1993). Physico-chemical and biological characteristics of Husain sagar, an industrially polluted lake, Hyderabad. Proc. Acad. Environ. Biol. 2(2), 161-167.

Panno S. V .C, Hackley, K. C., Hwang, H. H., Greenberg, S., Krapac, I.G., Landsberger, S., and O'Kelly D. J. (2001). Source Identification Of Sodium And Chloride Contamination In Natural Waters: Preliminary Results.

Papadopoulou, M., Karatzas, G., and Bougioukou, G. (2006). Numerical modelling of the environmental impact of landfill leachate leakage on groundwater quality – a field application. Greece.

Reinhart, D. R. and Grosh, C. J. (1998). Analysis of Florida MSW landfill leachate quality, Florida Center for Solid and Hazardous Management, Gainesville.

Revans, A., Ross D., Gregory, B., Meadows, M., Harries, C., and Gronow, J. (1999). Long-term fate of metals in landfill, *in Sardinia '99, Seventh Inter-national Waste Management and Landfill Symposium, Volume 1,* , Christensen, T. H., Cossu, R., and Stegmann, R., Eds., CISA. Cagliari, Italy.

Richards, L. A. (1931), "Capillary Conduction of Liquids through Porous Mediums", Physics, Vol. 1, pp. 318-333

Ritter, L., Keith S., Sibley, P. (2002). Sources, Pathways, and Relative Risks of Contaminants in Surface Water and Groundwater: A Perspective Prepared for the Walkerton Inquiry; Journal of Toxicology and Environmental Health, Part A, 65:1–142, 2002.

Robinson, H. D. (1995). The technical aspects of controlled waste management, A review of the composition of leachates from domestic wastes in landfill sites. Report for the UK Department of the Environment. Waste Science and Research, Aspinwall & Company, Ltd., London, UK.

Romanelli, A., Massone, H. E. and Qutrozl, O. M. (2011). Integrated Hydrogeological Study of Surface & Ground Water Resources in the Southeastern Buenos Aires Province, Argentina. Int. J. Environ. Res., **5 (4)**, 1053-1064.

Schaap, M. G., Leij, F. J., and van Genuchten, M. T., Rosetta, B. (2001). A computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions. *J. Hydrol.* 251, 163–176, 2001.

Šimu˚nek J. , Van Genuchten M.T. and *Brown Jr. G. E. (2006).* Contaminant Transport in the Unsaturated Zone Theory and Modeling.The Handbook of Groundwater engineering. pp.1-16

Sinokrat, B. A., and H. G. Stefan (1993). Stream temperature dynamics: Measurement and modeling, *Water Resour. Res*., *29*(7), 2299–2312.

Tang, K.L., and Feng, X.H. (2001). The effect of soil hydrology on the oxygen and hydrogen isotopic compositions of plants' source water. *Earth and Planetary Science Letters*, **185(3-4)**, 355-367.

Taylor, R., and Allen A. (2006). Waste disposal and landfill: Potential hazards and information needs, London, UK.

Teley, A. H., (2001). The impact of Waste disposal on the surface and groundwater environment: A case study of the Mallam landfill site, Accra. M.Phil. Thesis, In Environmental Science, University of Ghana, Legon.

Thompson, T., Fawel, J., Kunikane. S., Jackson, D., Appleyard, S., Callan, P., Bartram, J., and Kingston, P. (2007). Chemical safety of drinking water: assessing priorities for risk management. pp. 160.World Health Organization Publication, Geneva, Switzerland.

Trivedy, R. K. (1990). Physico-Chemical Characteristics and Phytoplankton of the River Panchgang Near Kolhapur, Maharastra, River Pollution in India, *Ashish Publishing House*, New Delhi, (1990) 159.

United States Environmental Protection Agency (USEPA) (1984). Office of Drinking Water, A Groundwater Protection Strategy for the Environmental Protection Agency, 11.

U. S. Environmental Protection Agency (1991). Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, revision 3.3, EPA 600 4-91/010.

USGS, (2001), Unsaturated- zone flow: Definitions and Details, USGS.

Walker, G. R., Woods, P. H., and Allison, G. B. (1994). Inter-laboratory comparison of methods to determine the stable- isotope composition of soil-water. *Chemical Geology*, **111(1-4)**, 297-306.

Walter, D.A., Masterson, J. P. (2003). Simulation of Advective Flow under Steady-State and Transient Recharge Conditions, Camp Edwards, Massachusetts Military Reservation, Cape Cod, Massachusetts, Water-Resources Investigations Report 03-4053, USGS.

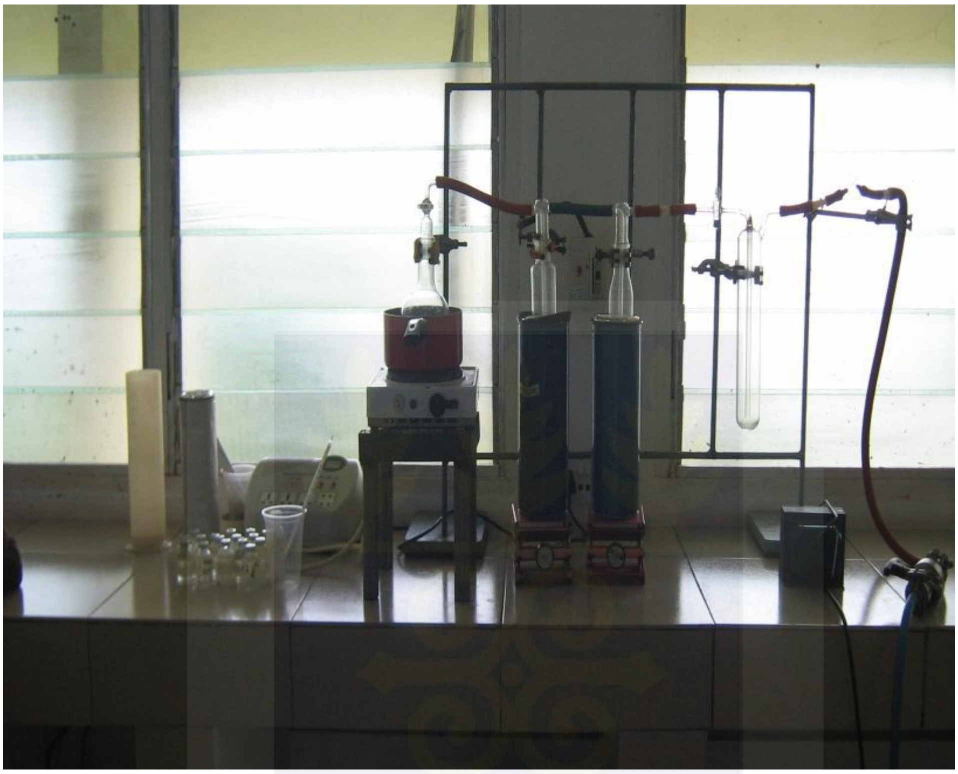
Water Resource Commission, Ghana (2003). Ghana Raw Water Quality Criteria and Guidelines, 1st Edition; CSIR-Water Research Institute, Accra, Ghana.

WHO, (1996). Guidelines for Drinking Water, vol. 2, Recommendations, World Health Organisation, Geneva.

Wood, W.W., and Signor, D. C. (1975), Geochemical Factors affecting artificial groundwater recharge in the unsaturated zone: Transitions, American Society of Agricultural Engineers, v. 18.p.677-683.

Zubair, A. (1998). "Groundwater Pollution and its Environmental Impact on Health in Karachi Region, Pakistan". Ph.D. Thesis, University of Ulster: Northern Ireland, UK.

# APPENDICES



Appendix A: Soil Pore Water Vacuum Extraction System

## Appendix B: Results of the Soil Physical Properties

BDg/cm = Bulk Density % n = Porosity ϴg = Gravimetric water Content

ϴv = Volumetric Water Content

| **Profile** | **Depth(cm)** | **BDg/cm$^3$** | **% n** | **% ϴg** | **% ϴv** | **%Sand** | **% silt** | **%Clay** | **Textural Class (USDA)** |
|---|---|---|---|---|---|---|---|---|---|
| SPA | 20 | 1.23 | 53.6 | 18.1 | 22.3 | 79.43 | 15.42 | 4.59 | Loamy sand |
| | 40 | 1.25 | 52.8 | 34.3 | 42.9 | 76.24 | 17.56 | 6.15 | Loamy sand |
| | 60 | 1.37 | 48.3 | 36.2 | 49.6 | 59.44 | 20.23 | 20.27 | Sandy loam |
| | 80 | 1.22 | 54.0 | 33.3 | 40.6 | 57.08 | 22.86 | 19.97 | Sandy loam |
| | 100 | 1.33 | 49.8 | 26.6 | 35.4 | 58.33 | 21.22 | 19.98 | Sandy loam |
| SPB | 20 | 1.31 | 50.6 | 14.7 | 19.26 | 76.44 | 18.53 | 4.68 | Loamy sand |
| | 40 | 1.32 | 50.2 | 15.4 | 20.33 | 75.21 | 19.02 | 5.31 | Loamy sand |
| | 60 | 1.38 | 47.9 | 18.5 | 25.53 | 59.19 | 20.84 | 19.96 | Sandy loam |
| | 80 | 1.23 | 53.6 | 14.8 | 16.03 | 60.12 | 19.94 | 19.92 | Sandy loam |
| | 100 | 1.33 | 49.8 | 16 | 21.28 | 59.95 | 20.12 | 19.92 | Sandy loam |
| SPC | 20 | 1.33 | 49.8 | 1.9 | 2.53 | 80.97 | 17.45 | 1.56 | Loamy sand |
| | 40 | 1.38 | 47.9 | 2.9 | 4 | 79.79 | 18.55 | 1.65 | Loamy sand |
| | 60 | 1.35 | 49.1 | 3.2 | 4.32 | 70.54 | 20.15 | 9.3 | Loamy sand |
| | 80 | 1.33 | 49.8 | 3.7 | 4.92 | 69.79 | 21.18 | 9.01 | Loamy sand |
| | 100 | 1.33 | 49.8 | 4.3 | 5.72 | 68.99 | 22.89 | 8.09 | Loamy sand |
| SPD | 20 | 1.28 | 51.7 | 30.1 | 38.53 | 20.11 | 35.33 | 44.54 | Clay |
| | 40 | 1.23 | 53.6 | 18.3 | 22.51 | 18.41 | 36.42 | 45.15 | Clay |
| | 60 | 1.35 | 49.1 | 19.5 | 26.33 | 17. 39 | 36.27 | 46.32 | Clay |
| | 80 | 1.21 | 54.3 | 25.4 | 26.61 | 17.14 | 36.18 | 46.66 | Clay |
| | 100 | 1.29 | 51.3 | 19.2 | 24.77 | 17.05 | 35.11 | 47.82 | Clay |
| SPE | 20 | 1.36 | 48.7 | 17.8 | 24.21 | 75.15 | 18.93 | 5.91 | Loamy sand |
| | 40 | 1.34 | 49.4 | 12.5 | 16.75 | 73.25 | 19.45 | 7.29 | Loamy sand |
| | 60 | 1.38 | 47.9 | 13.5 | 18.63 | 70.54 | 19.22 | 10.23 | Sandy loam |
| | 80 | 1.29 | 51.3 | 12.7 | 16.38 | 70.23 | 19.55 | 10.19 | Sandy loam |
| | 100 | 1.35 | 49.1 | 9.5 | 12.83 | 69.99 | 20.12 | 9.88 | Sandy loam |

## Appendix C: Results of the analysis of concentrations (mg/L) of trace elements along the profiles

| Profile | Depth | Fe | Pb | Cd | Cr | Mn | AS | Zn | Hg | Cu | Co |
|---|---|---|---|---|---|---|---|---|---|---|---|
| SPA | 20 | 5.845 | 1.72 | <0.002 | 0.173 | 0.036 | 0.146 | 0.84 | 0.0133 | 0.533 | 0.467 |
|  | 40 | 2.284 | 2.653 | 0.32 | 0.493 | 0.101 | 0.12 | 1.52 | 0.0133 | 1.333 | 0.867 |
|  | 60 | 1.124 | 7.387 | 0.32 | 1.013 | 2.09 | 0.213 | 2.773 | 0.0267 | 2.747 | 1.04 |
|  | 80 | 1.132 | 5.933 | 0.293 | 0.72 | 1.48 | 0.093 | 3.787 | 0.0267 | 2.013 | 0.84 |
|  | 100 | 1.22 | 3.44 | <0.002 | 0.613 | 0.126 | 1.333 | 4.253 | 0.0133 | 1.333 | 0.96 |
| SPB | 20 | 0.88 | 1.04 | <0.002 | 0.2 | 0.967 | 1.293 | 0.267 | <0.001 | <0.003 | 0.133 |
|  | 40 | 0.753 | 0.187 | <0.002 | 0.2 | 0.413 | 1.267 | 0.04 | <0.001 | 0.307 | 0.253 |
|  | 60 | 0.917 | 0.88 | 0.053 | 0.32 | 0.845 | 1.28 | 1.213 | <0.001 | <0.003 | <0.005 |
|  | 80 | 0.581 | <0.001 | 0.36 | 0.107 | 0.289 | 0.4 | 0.16 | <0.001 | 0.053 | <0.005 |
|  | 100 | 0.676 | <0.001 | 0.24 | 0.267 | 0.289 | 0.16 | 0.2 | <0.001 | 0.08 | <0.005 |
| SPC | 20 | 0.761 | <0.001 | 0.093 | 0.2 | 1.376 | 1.427 | 0.747 | <0.001 | 0.4 | <0.005 |
|  | 40 | 0.919 | <0.001 | <0.002 | 0.373 | <0.014 | 1.36 | 0.64 | <0.001 | <0.003 | 0.52 |
|  | 60 | 0.847 | 0.667 | <0.002 | 0.28 | 1.052 | 0.04 | 0.827 | <0.001 | <0.003 | 0.187 |
|  | 80 | 0.928 | <0.001 | <0.002 | 0.24 | 1.599 | 1.347 | 0.733 | <0.001 | <0.003 | <0.005 |
|  | 100 | 0.963 | <0.001 | <0.002 | 0.253 | 2.796 | 1.373 | 1.24 | <0.001 | 0.16 | <0.005 |
| SPD | 20 | 1.183 | 3.44 | 0.373 | 0.64 | 6.993 | 1.28 | 3.48 | <0.001 | 1.867 | 0.6 |
|  | 40 | 1.064 | 0.813 | 0.213 | 0.48 | 3.779 | 1.293 | 0.6 | <0.001 | 0.467 | 0.147 |
|  | 60 | 0.984 | <0.001 | 0.267 | 0.42 | 1.011 | 1.333 | 0.147 | <0.001 | 0.053 | <0.005 |
|  | 80 | 1.008 | <0.001 | 0.187 | 0.493 | 1.443 | 0.067 | 0.32 | <0.001 | 0.36 | <0.005 |
|  | 100 | 1.131 | <0.001 | 0.173 | 0.96 | 7.197 | 0.693 | 0.907 | <0.001 | 0.333 | 0.36 |
| SPE | 20 | 0.869 | <0.001 | <0.002 | 0.427 | 5.352 | 1.25 | 3.293 | <0.001 | <0.003 | 0.48 |
|  | 40 | 1.08 | <0.001 | <0.002 | 1.347 | 9.313 | 1.333 | 0.467 | <0.001 | 0.107 | 0.613 |
|  | 60 | 1.041 | <0.001 | <0.002 | 0.773 | 8.603 | 0.633 | 1.08 | <0.001 | <0.003 | 0.24 |
|  | 80 | 1.072 | <0.001 | <0.002 | 1.227 | 4.417 | 1.293 | 0.68 | <0.001 | <0.003 | 0.627 |
|  | 100 | 1.201 | <0.001 | <0.002 | 2.107 | 4.417 | 0.067 | 0.946 | <0.001 | 1.107 | 2.4 |

Appendix D: Results of stable isotopic composition ($^{18}$O and $^{2}$H) of surface water (SW) and groundwater samples (G)

| **Sample ID** | **Date of Sampling** | **δ $^{18}$O** | **δ $^{2}$H** |
|---|---|---|---|
| SW1 | 25/10/2012 | -1.86 | -13.32 |
| SW2 | 25/10/2012 | -1.78 | -14.12 |
| SW3 | 25/10/2012 | -2.00 | -13.18 |
| SW4 | 25/10/2012 | -2.33 | -15.31 |
| SW1 | 27/01/2013 | -0.21 | -10.39 |
| SW2 | 27/01/2013 | -1.46 | -6.48 |
| SW3 | 27/01/2013 | -1.16 | -6.13 |
| SW4 | 27/01/2013 | -1.92 | -7.39 |
| Mean | | -1.59 | -10.79 |
| G1 | 25/10/2012 | -1.92 | -8.17 |
| G2 | 25/10/2012 | -2.38 | -10.02 |
| G3 | 25/10/2012 | -2.03 | -9.87 |
| G4 | 25/10/2012 | -2.16 | -14.68 |
| G1 | 27/01/2013 | -1.27 | -4.92 |
| G2 | 27/01/2013 | -0.68 | -12.38 |
| G3 | 27/01/2013 | -1.32 | -11.65 |
| G4 | 27/01/2013 | -1.82 | -7.53 |
| Mean | | -1.70 | -9.90 |

Appendix E: Results of stable isotopic composition ($^{18}O$ and $^{2}H$) of the extracted soil pore water

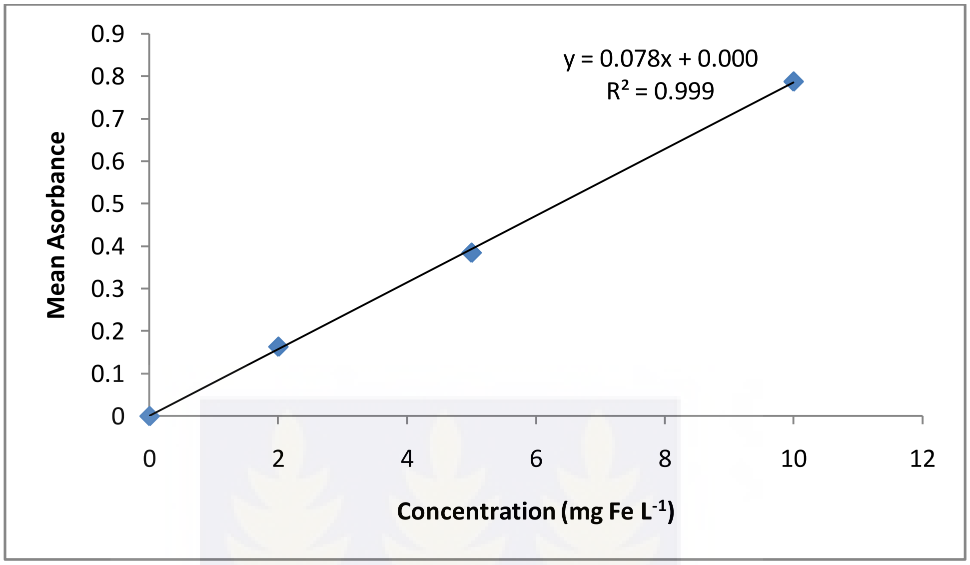
| **Profile** | **Depth (cm)** | **$\delta\ ^{18}O$ ( ‰)** | **$\delta\ ^{2}H$ ( ‰)** |
|---|---|---|---|
| SPA | 20 | 1.57 | 18.25 |
| | 40 | -0.77 | 3.89 |
| | 60 | -1.06 | -1.97 |
| | 80 | -2.62 | -9.73 |
| | 100 | -2.65 | -10.42 |
| Mean | | -1.11 | 0.004 |
| SPB | 20 | -1.02 | -2.15 |
| | 40 | -1.72 | -3.14 |
| | 60 | -2.1 | -4.7 |
| | 80 | -2.76 | -6.64 |
| | 100 | -3.38 | -12.44 |
| Mean | | -2.20 | -5.814 |
| SPC | 20 | -1.2 | -8.9 |
| | 40 | -1.37 | -10.17 |
| | 60 | -1.89 | -14.11 |
| | 80 | -2.71 | -20.65 |
| | 100 | -3.1 | -19.14 |
| Mean | | -2.05 | -14.594 |
| SPD | 20 | -0.8 | 1.07 |
| | 40 | -1.24 | -3.14 |
| | 60 | -1.35 | -4.95 |
| | 80 | -2.34 | -13.21 |
| | 100 | -2.5 | -13.49 |
| Mean | | -1.65 | -6.744 |

## Appendix F: Rating table for weighted arithmetic and weighted Solway Water Quality Index

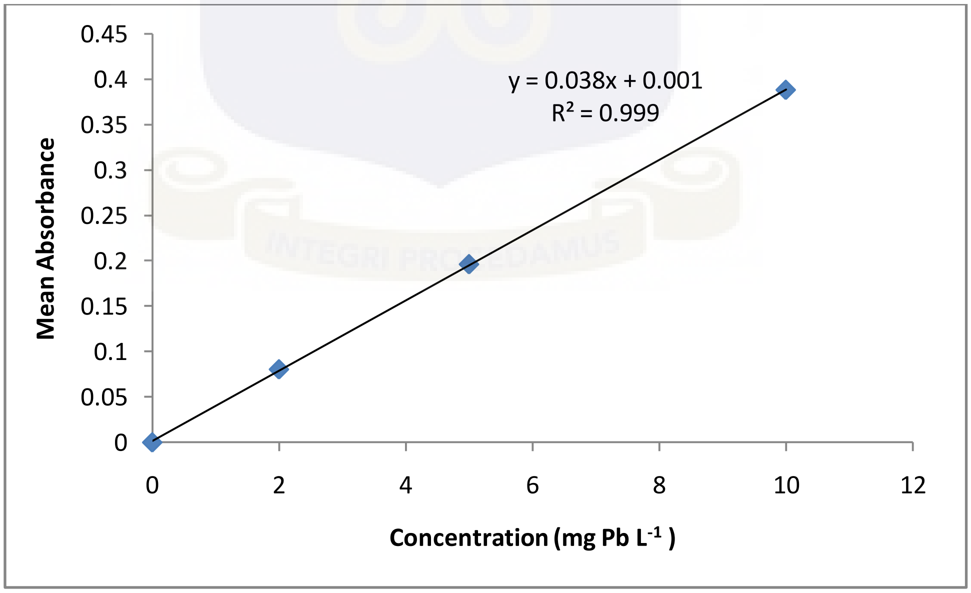
| Weighted Water Quality Rating ($q_i$ x $w_i$) | DO (per cent saturation) | BOD (mg/l) | Amm-N (mg/l as N) | Faecal Coliform (Counts/100ml) | pH | $NO_3$-N (mg/l as N) | $PO_4$-P (mg/l as P) | SS (mg/l) | Conductivity (µS/cm) | T (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| 18 | 93-109 | | | | | | | | | |
| 17 | 88-92 110-119 | | | | | | | | | |
| 16 | 85-87 120-129 | | | | | | | | | |
| 15 | 81-84 130-134 | 0-0.9 | | | | | | | | |
| 14 | 78-80 135-139 | 1.0-1.9 | | | | | | | | |
| 13 | 75-77 140-144 | 2.0-2.4 | | | | | | | | |
| 12 | 72-74 145-154 | 2.5-2.9 | 0-0.09 | 0-249 | | | | | | |
| 11 | 69-71 155-164 | 3.0-3.4 | 0.10-0.14 | 250-999 | | | | | | |
| 10 | 66-68 165-179 | 3.5-3.9 | 0.15-0.19 | 1 000-3 999 | | | | | | |
| 9 | 63-65 $180^+$ | 4.0-4.4 | 0.20-0.24 | 4 000-7 999 | 6.5-7.9 | | | | | |
| 8 | 59-62 | 4.5-4.9 | 0.25-0.29 | 8 000-14 999 | 6.0-6.4 8.0-8.4 | 0-0.49 | 0-0.029 | | | |
| 7 | 55-58 | 5.0-5.4 | 0.30-0.39 | 15 000-24 999 | 5.8-5.9 8.5-8.7 | 0.50-1.49 | 0.030-0.059 | 0-9 | | |
| 6 | 50-54 | 5.5-6.1 | 0.40-0.49 | 25 000-44999 | 5.6-5.7 8.8-8.9 | 1.50-2.49 | 0.060-0.099 | 10-14 | 50-180 | |
| 5 | 45-49 | 6.2-6.9 | 0.50-0.59 | 45 000-79 999 | 5.4-5.5 9.0-9.1 | 2.50-3.49 | 0.100-0.129 | 15-19 | 0-49 190-239 | $25^+$ |
| 4 | 40-44 | 7.0-7.9 | 0.60-0.99 | 80 000-139 999 | 5.2-5.3 9.2-9.4 | 3.50-4.49 | 0.130-0.179 | 20-29 | 240-289 | 23.0-24.9 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **3** | **35-39** | **8.0-8.9** | **1.00-1.99** | **140 000-249 999** | **5.0-5.1 9.5-9.9** | **4.50-5.49** | **0.180-0.219** | **30-44** | **190-379** | **21.5-22.9** |
| **2** | **25-34** | **9.0-9.9** | **2.00-3.99** | **250 000-429 999** | **4.5-4.9 10.0-10.4** | **5.50-6.99** | **0.220-0.279** | **45-64** | **380-539** | **19.5-21.4** |
| **1** | **10-24** | **10.0-14.9** | **4.00-9.99** | **430 000-749 999** | **3.5-4.4 10.5-11.4** | **7.00-9.99** | **0.280-0.369** | **65-119** | **540-839** | **17.5-19.4** |
| **0** | **0-9** | **$15.0^{+}$** | **$10.00^{+}$** | **$750\ 000^{+}$** | **0-.3.4 11.5-14** | **$10.00^{+}$** | **$0.370^{+}$** | **$120^{+}$** | **$840^{+}$** | **0-17.4** |

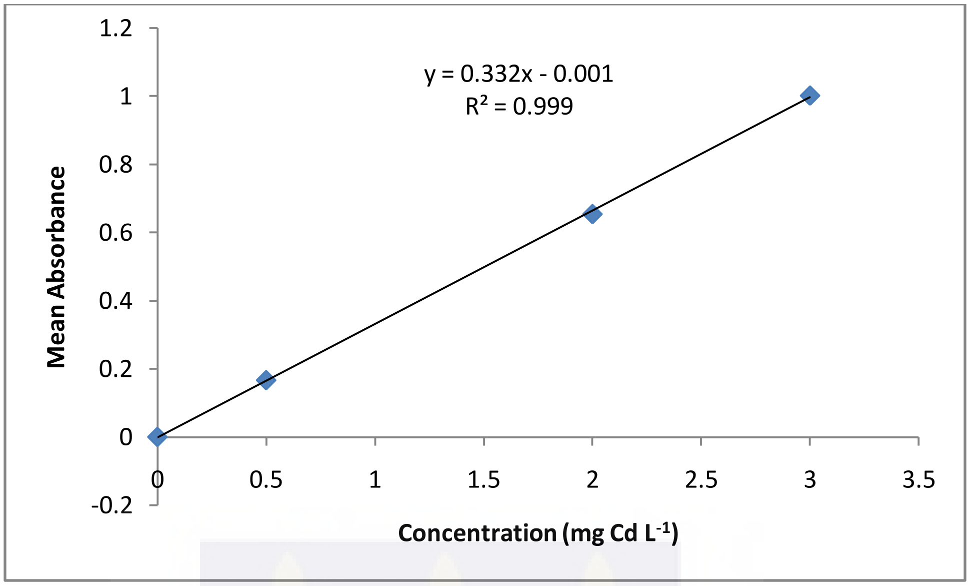
Appendix G: Calibration graphs for the analysis of trace metals using the Atomic Absorption Spectrometer



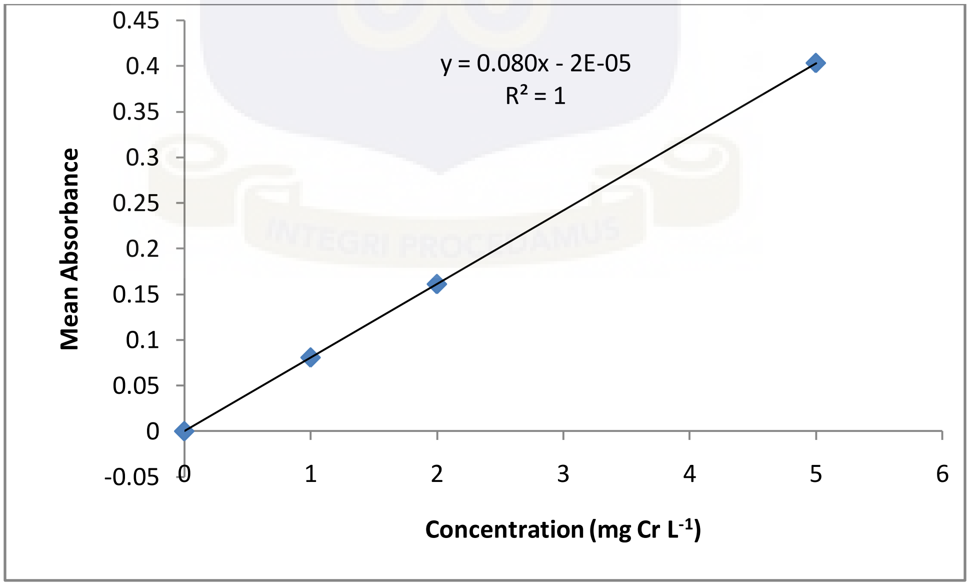
Calibration graph for the analysis of Fe



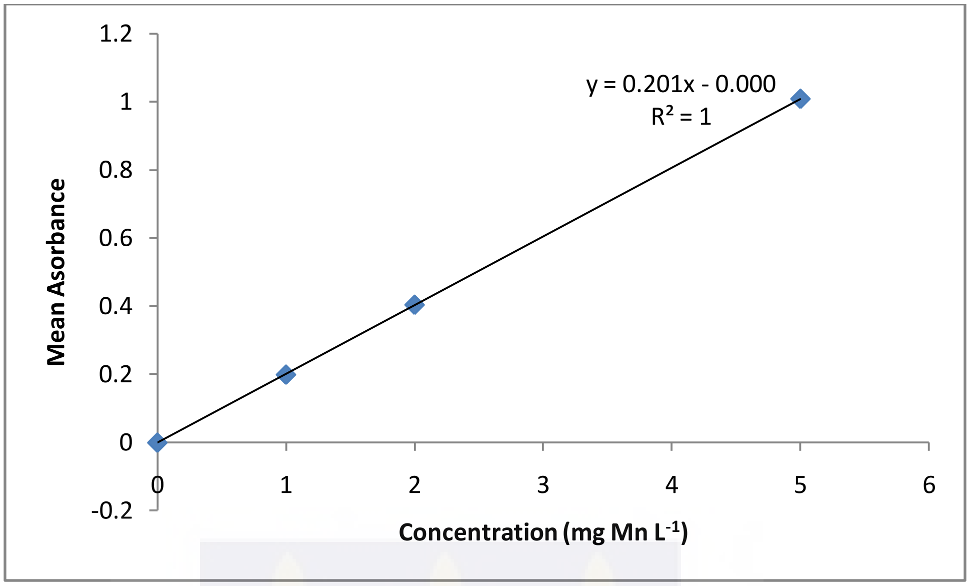
Calibration graph for the analysis of Pb



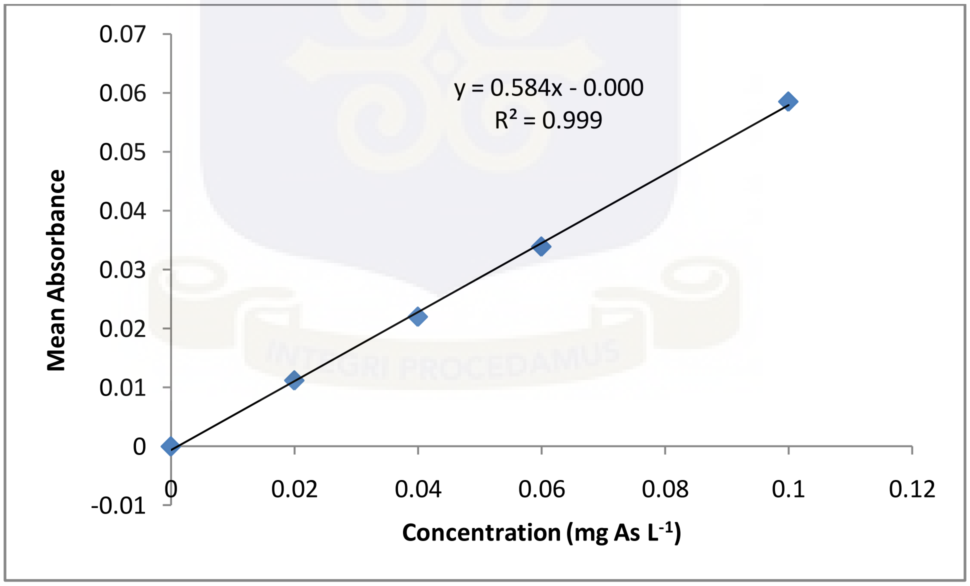
Calibration graph for the analysis of Cd



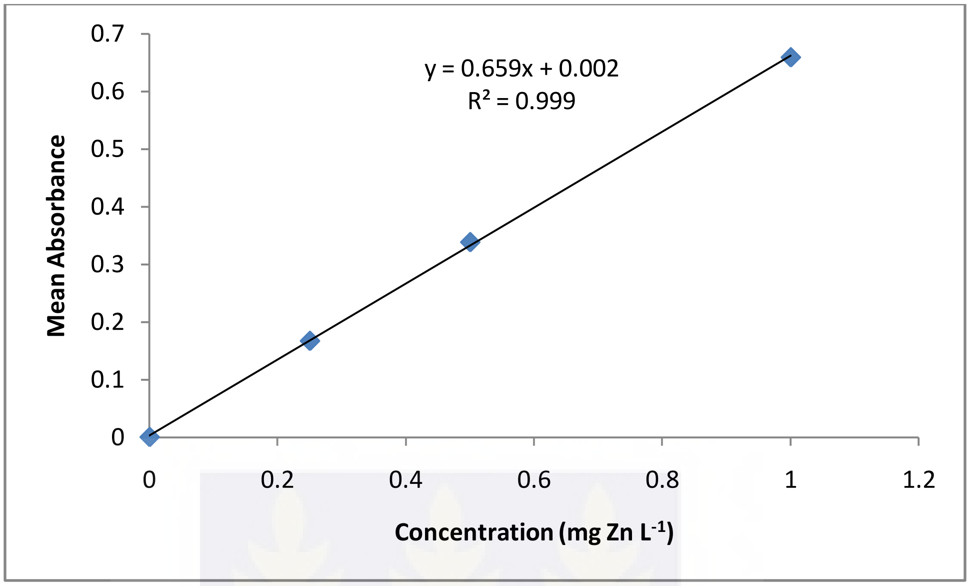
Calibration graph for the analysis of Cr



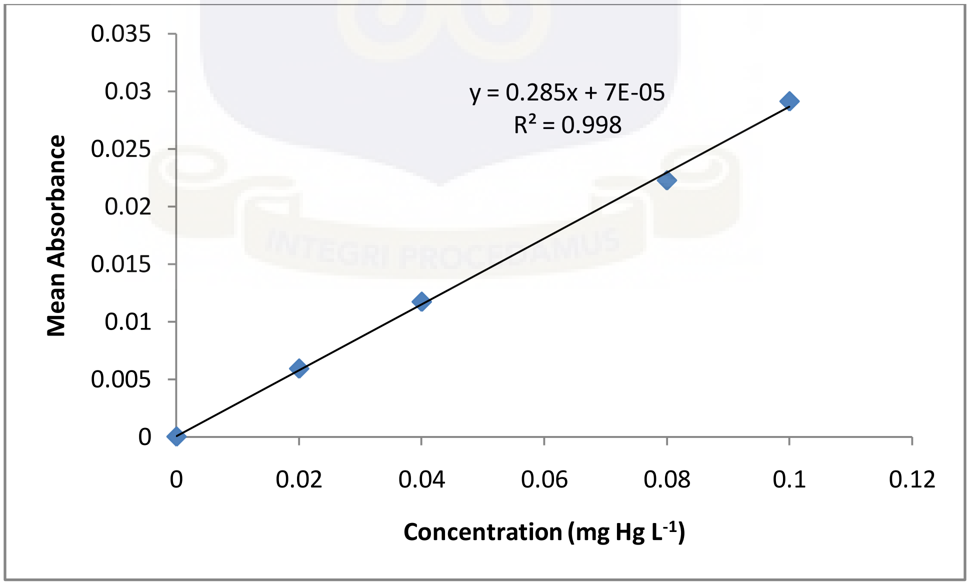
Calibration graph for the analysis Mn



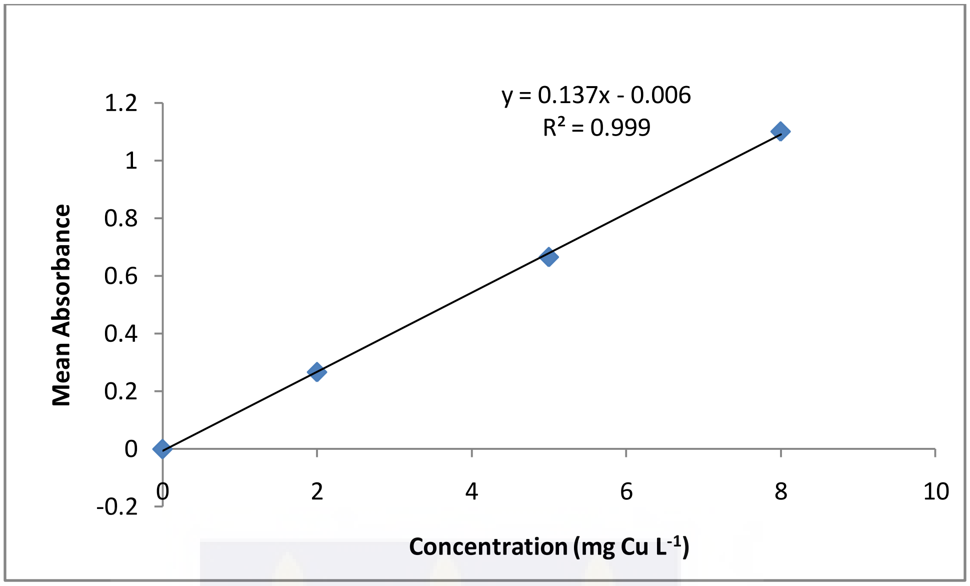
Calibration graph for the analysis of As



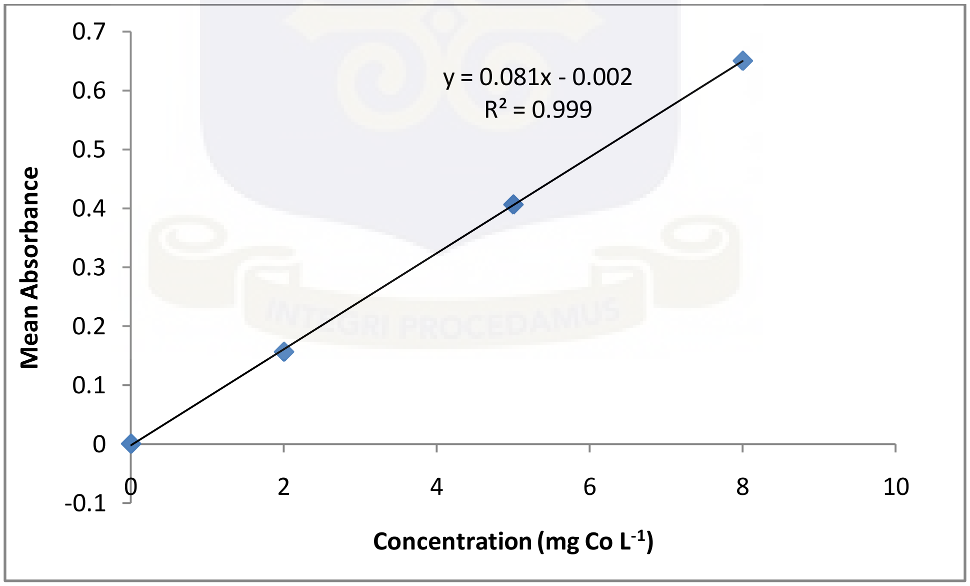
Calibration graph for the analysis Zn



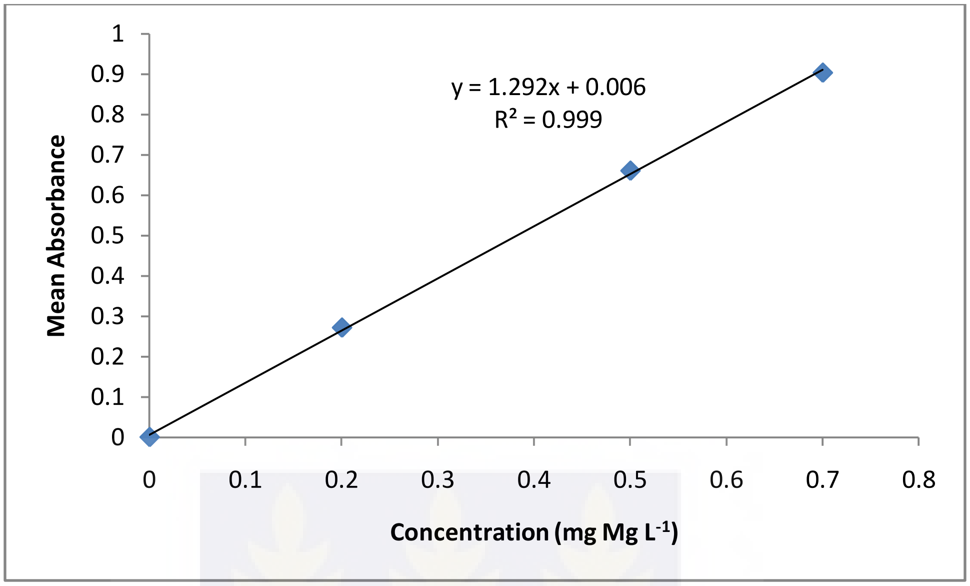
Calibration graph for the analysis Hg



Calibration graph for the analysis Cu

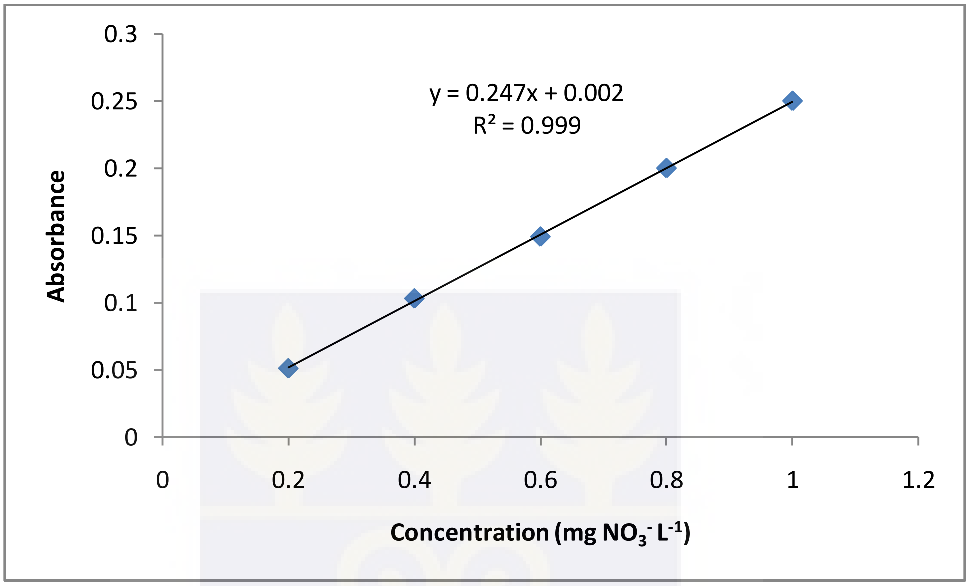


Calibration graph for the analysis of Co

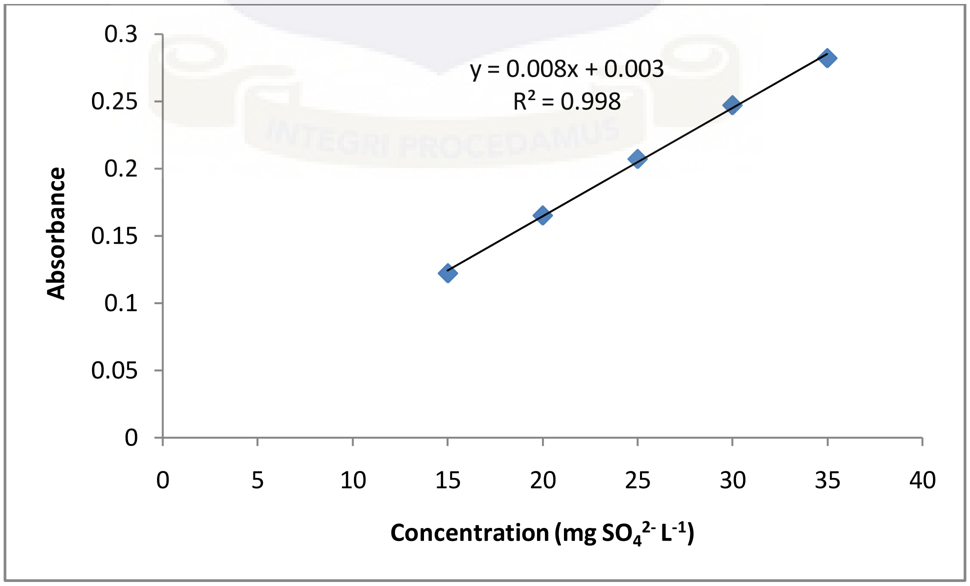


Calibration graph for the analysis Mg

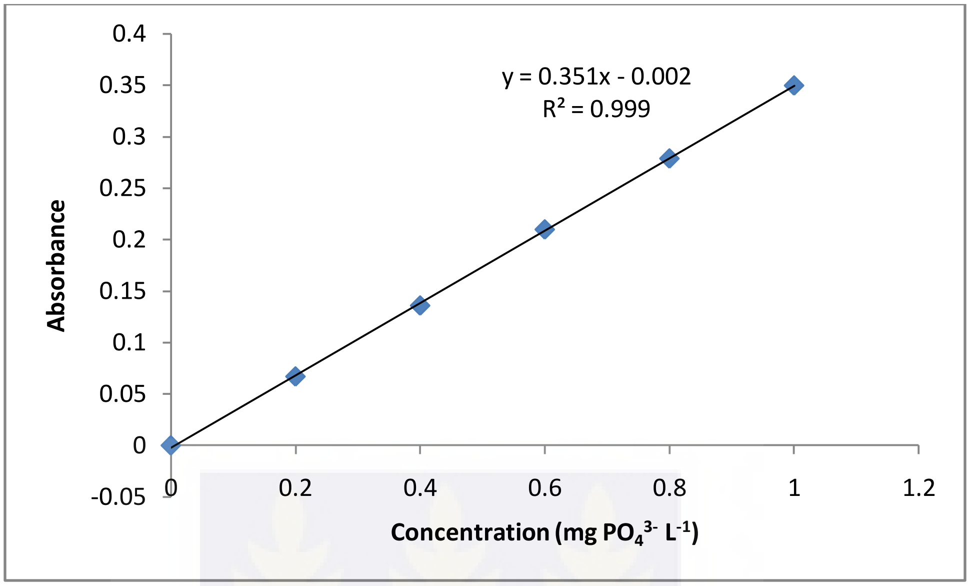
Appendix H: Calibration graphs for the analysis of $NO_3^-$, $SO_4^{2-}$ and $PO_4^{3-}$ using the UV-Visible Spectrophotometer



Calibration graph for the analysis $NO_3^-$



Calibration graph for the analysis $SO_4^{2-}$



Calibration graph for the analysis $PO_4^{3-}$