ASSESSMENT OF PHYSICO-CHEMICAL PARAMETERS, NUTRIENTS, FLUORIDES, PESTICIDES AND SELECTED HEAVY METALS CONTAMINATION IN LAKE ELEMENTAITA DRAINAGE BASIN

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DECLARATION

This thesis is my original work and has never been submitted for the award of degree to this or any other institution of learning.

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DEDICATION

This thesis is dedicated to my dear parents Mr. and Mrs. Daniel Kimoni, my husband Beavon Anyona, my siblings Rachel, Lillian, Evelyn, Evans, Milkah, Denis, Ruth and Samuel and friends for their honorable financial support.

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ABSTRACT

This study aimed at assessing physio-chemical parameters, nutrients, fluoride, pesticides and selected heavy metals contamination in Lake Elementaita drainage basin. Water pollution has been identified globally as one of the most serious problems in environmental conservation. Pesticides, heavy metals and nutrients are of concern in the world waters and have been considered as long-term worldwide water pollutants since they cause deterioration of water quality and cause adverse effects on the lake ecosystem.

Water, sediments and soil were collected from seven sites within Lake Elementaita drainage basin and analysed for physico-chemical parameters, nutrients, fluoride, heavy metals and organochlorine pesticides (OCP) residues. The sampling strategy covered dry (October 2014) and wet (April 2015) season. Analysis of the 17 OCPs was done using gas chromatograph equipped with electron capture detector (GC-ECD), whereas for heavy metals analysis atomic absorption spectrometer was used. Physico-chemical parameters analysed included electrical conductivity, pH, TDS, TSS and temperature.

Nitrate and phosphate concentrations were below WHO maximum limits with dry season recording higher values. Phosphates concentrations ranged from 0.02±0.00 to 0.38±0.07 mg/L, 0.45±0.02 to 10.04±0.10 mg/kg and 0.78±0.00 to 4.47±0.03 mg/Kg in water, sediment and soil, respectively. Nitrates ranged from 0.43±0.04 to 3.00±0.36 mg/L, 0.36±0.06 to 2.21.02±0.18 mg/kg and 0.65±0.05 to 4.90±0.29 mg/kg in water, sediment and soil, respectively.

All the 17 OCPs were detected with concentrations below WHO maximum limits. The OCPS residues ranged from BDL to 0.49±0.09 µg/L, BDL to 762.27±91.70 µg/kg and BDL to 615.93±119.21 µg/kg in water, sediment and soil samples, respectively in dry season and BDL to

0.16±0.00 µg/l, BDL to 42.97±1.00 µg/kg and BDL to 13.92±0.21 µg/kg in water, sediment and soil samples, respectively in wet season. Endosulphan sulphate recorded high concentration in soil and sediment samples in both seasons.

Concentrations of cadmium, copper, zinc and lead were above WHO maximum limits for water in some samples analysed with the wet season recording high values. Cadmium values ranged between 0.04±0.00 and 0.35±0.02 mg/L, 2.06±0.42 and 16.07±0.02 mg/kg, 2.78±0.08 and 29.75±0.14 mg/kg in water, sediment and soil, respectively. Copper concentrations ranged between 0.07±0.04 and 8.49±0.40 mg/L, 2.93±0.66 and 861.76±80.58 mg/kg, 2.96±0.39 and 865.83±5.76 mg/kg in water, sediment and soil, respectively. Lead concentrations ranged between BDL to 9.28±0.9 mg/L, BDL to 475.75±16.61mg/kg, 10.38±0.99 and 502.18±20.76 mg/kg in water, sediment and soil, respectively. Zinc concentration ranged between 0.14±0.00 and 0.41±0.02 mg/L, 45.73±9.44 and 106.28±2.89 mg/kg, 57.95±6.68 and 86.95±5.55 mg/kg in water, sediment and soil, respectively. Fluoride concentration in water ranged between 1.70±0.28 to 977.80±0.01 mg/L in Mbaruk River and Lake Elementaita North, respectively.

The results revealed high levels of heavy metals in water, soil and sediments which exceeded WHO maximum limits, whereas the concentrations of pesticides were below the maximum limits. Therefore heavy metal contamination was of concern for sustainable management of the lake water quality and biodiversity. Pesticide levels measured could also cause longer-term concern due to potential bioaccumulation and biomagnifications in the food chain. Further studies are recommended to establish the effect of measured contaminants on the lake ecosystems and flamingoes.

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LIST OF ABBREVIATIONS

BDL	Below Detection Limit
CWQA	Canadian Water Quality Assurance
DDT	Dichloro Diphenyl Trichloroethane
DDE	Dichloro Diphenyl Ethane
ECD	Electron Capture Detector
GC	Gas Chromatography
HCH	Hexachlorocyclohexane
OCPs	Organochlorine Pesticides
PCPB	Pest Control Products Board
POPs	Persistent Organic Pollutants
QA	Quality Assurance
QC	Quality Control
SPSS	Statistical Programme for Social Scientists
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
UNEP	United Nations Environment Programme
WHO	World Health Organization

UNITS OF MEASUREMENT

µg	Microgram
µS	Micro Siemen
G	Gram
Kg	Kilogram
L	Litre
ml	Millilitre
^{o}C	Dégrée Celsius
Ppm	Parts per million

CHAPTER ONE

1. INTRODUCTION

1.1 Background of the study

In Africa water has been placed as a very important resource which without it there is no life. Research from United Nations shows that around 1.1 billion people find it hard to access uncontaminated drinking water (UNEP, 2003). The research also states that 5 million deaths occur every year majorly from sub-Sahara Africa as a result of unclean water (UNEP, 2003).

The World Health Organization defines water pollution as inclusion of any external material either from anthropogenic or natural sources in a water body that changes its natural qualities and intended purposes (WHO, 2007). Despite the stiff population growth and industrialization, there is a high demand for drinking water while the available clean water is becoming more polluted in the world (Schindler, 2001).

The most common contaminants in surface and groundwater include: agrochemicals and microorganisms (Ongley, 1996). The agrochemical pollutants cause deterioration of water quality by chemical runoff and soil erosion together with percolation. They are mainly from animal wastes, fertilizers and pesticides.

1.1.1 Nutrients

Nitrates and phosphates are the most common known nutrients from fertilizers that have potential to pollute water. Rapid population growth in most parts of the world has led to agricultural intensification associated with application of higher amounts of external inputs in order to boost agricultural production to cater for the population growth. However, these nutrients once in the water sources lead to eutrophication (Maher *et al.*, 2002), associated with growth of biomass in aquatic ecosystems (Hanrahan *et al.*, 2001). This causes toxic algal blooms and finally destruction of habitat, making the water not safe for human consumption and recreational activities (Hendrik and Killebrew, 2010).

1.1.2 Pesticides

A pesticide is a substance intended to prevent, destroy, or repel pests which include diseases, vectors, insects and weeds (Radcliffe *et al*., 2009). Based on the intended use, pesticides can be categorised into: insecticides, nematocides, fungicides and herbicides, among others. They can also be classified according to their chemical structure for instance, organochlorines, organophosphates, pyrethroids, triazines, and carbamates (Wasswa, 2008).

Pesticides can contaminate water through direct application, runoff, and atmospheric deposition (Barlas, 2002). In the environment, they can poison fish and wildlife, contaminate food sources, and destroy animal protective cover- habitat. Synthetic organic pesticides are applied to control insects, weeds, and other organisms in extensive agricultural settings.

Pesticides health effects on birds and animals

The use of pesticides especially in agriculture has enhanced food production globally (Guo *et al.*, 2008). However, this has also raised worries on potential adverse effects on human health and the environment in general (Li *et al*., 2006). Pesticides have a potential to move from one area to another through hydrological systems which are sources of water for both natural ecosystems and humans (Barbash and Resek, 1996). In high doses, pesticides are known to cause reproductive failure or even death in livestock and birds (Arias-Estevez *et al.*, 2008).

1.1.3 Heavy metals

Heavy metals are elements whose specific gravity is greater than 4.0 and with large atomic weights varying from 63.5 g/mol to 200.5 g/mol (Garbarino *et al.*, 1995). They occur in surface waters in dissolved phases, colloidal and particulate form (Muinde, 2012).

Heavy metals originate from minerals, chemical weathering and also soil leaching (Mohamed *et al.*, 2010). The anthropogenic sources are related especially with industrial and domestic effluents, landfills, coal and mineral ores mining and runoff by water during rainy seasons (Zarazua *et al.*, 2006).

Heavy metals are majorly taken as common pollutants in the environment; their existence in aquatic environments has raised serious problems about their effects on ecosystems (Yahaya *et al.*, 2009). Living organisms need minimum amount of heavy metals like cobalt, zinc, vanadium and copper whose nutrition necessity vary significantly between species. However, excess levels of essential metals can lead to health risk to humans since they can antagonize each other or become toxic in the body (Mwamburi, 2003). Non-essential and essential heavy metals of actual concern are cadmium, copper, chromium, mercury, lead, arsenic and zinc. Some have no physiological role in the body like lead, mercury, arsenic, cadmium and chromium (Authman, 2008).

1.1.4 Description of Lake Elementaita

Lake Elementaita is a shallow alkaline lake (<1.5 meters deep) with a total surface area of 20 km^2 (Adeka *et al.*, 2008). The lake lies on the Kenyan Great Rift Valley floor at 1776 m altitude above sea level with coordinates of $36^o14'23.92''$E and $0^o26'33.47''$S (KLS, 2010). It is fed by inflows from two streams: Rivers Kariandusi, Mbaruk (being the main water source) feeding it from the south and Kariandusi hot springs which feed the lake from the eastern plateaus. Lake Elementaita basin is 630 km^2 (KLS, 2010). It has a subsurface flow from Lake Naivasha (Mumo, 2002) and it is preserved by Soysambu and Tutu conservancy (KLS, 2010). The lake levels are prone to frequent fluctuations and in some cases the lake and its feeders dry up (Murimi *et al.*, 1993).

1.2 Problem statement

Lake Elementaita was identified as a Ramsar site in 2005, a wild heritage site in 2011 and bird sanctuary in 1999 by UNESCO (KLS, 2010). Currently, the lake resources are threatened by natural and anthropogenic activities which include; hot springs discharges, overgrazing, and discharges from industries and hotels (Adeka *et al.*, 2008). Overgrazing occurs in ranches during dry periods, particularly in the southern part, hence accelerates erosion during heavy rains. This leads to increase in nutrients concentrations as reported by Njenga, 2004. From 2004 to 2008, nitrates concentration increased by 0.15 to 10.29 mg/L while phosphates concentration increased by 0.47 to 0.90 mg/L (Njenga, 2004).

Pesticides imports and usage in sub-Sahara African countries accounts for 3% of the world pesticides imports. Several researches on pesticide residues in water, sediment and soil in Kenya appear to indicate continuous application of already banned OCPs. Research conducted in

Riftvalley lakes for instance Lake Naivasha (Gitahi *et al.,* 200) and Nakuru show presence of organochlorine and organophosphate pesticides although in low concentrations. Lake Elementaita being part of the three great lakes in the region, with flower farming and livestock keeping pose a threat to the drainage basin (Jaetzold *et al.*, 2010).

Commercial activities around the lake include timber pole treatment yard by Cabro East African Ltd, mainly to reduce moisture in electrical poles and impregnation with protective copper chromium arsenate (CCA) (Mwaura, 1999). However, the effluent from these industries and commercial activities could get their way into the lake and affect the water quality.

The birds' population has decreased rapidly in the recent years (KLS, 2010). According to Kenya lakes system, there has been a wide variation in the number of birds in Lake Elementaita. For instance, in 2000 about 600,000 birds were recorded but the number decreased to >200,000 by 2009 (KLS, 2010). The decrease in birds' population has been attributed to water pollution although little information is available to confirm the allegation (KLS, 2010).

Cases of high levels of fluorosis in children in Riftvalley have been reported. Research conducted by (Kahama *et al*, 1997) indicated high levels of dental fluorosis in children. The high levels have been attributed to the rift formation around the area. This study was established to give informative data that can be used to advance management of Lake Elementaita water quality.

1.3 Objectives

1.3.1 Overall Objective

To assess physio-chemical Parameters, nutrients, fluorides, pesticides and selected heavy metals contamination in Lake Elementaita drainage basin.

1.3.2 Specific objectives

1. To determine the physico-chemical characteristics of water, soil, and sediments from Lake Elementaita drainage basin.
2. To identify and quantify pesticides residues in water, soil and sediment from Lake Elementaita drainage basin.
3. To determine the concentration of nutrients, selected heavy metals and fluoride in water, sediment and soil from Lake Elementaita drainage basin.
4. To determine effect of seasonal variations on the levels of nutrients, selected heavy metals, fluoride and pesticides in Lake Elementaita drainage basin.
5. To compare the levels of nutrients, selected heavy metals, fluoride and pesticides in the lake, River Mbaruk and Kekopey hot spring.

1.4 Justification and Significance of the Study

Lake Elementaita is among the three lakes (L. Nakuru and L. Bogoria) which are currently nominated in the Kenya lake system within Great Rift Valley as ecologically, geologically and hydrologically interlinked (KLS, 2010). A lot of research has been done by different researchers on the lake which is evident that the lake is slowly losing its integrity. According to Adeka *et al*. (2008), the lake faces threats from natural and anthropogenic activities. Other studies have reported increase in nutrient levels (Njenga, 2004) and heavy metal contamination (Mwaura, 1999). Additional studies have reported gradual decrease in birds' population (KLS, 2010) which is clear evidence that much has to be done on Lake Elementaita to preserve its ecosystem.

Pollution may lead to extinction of the important plant and animal species such as the flamingoes which earn the country revenue through tourism. To achieve Kenya's vision 2030 it is of essence to observe closely natural systems and conserve them for future generation and for sustenance of an incessant flow of income. There exists inadequate mechanism for monitoring and assessing biodiversity and water quality of Lake Elementaita. However, this is important to ensure implementation of laws and regulations pertaining to sustainable use of the lake resources.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Nutrients in the Environment

High population growth in Rift Valley region together with increased urbanization and industrialization has led to the over-exploitation and contamination of the aquifers resources. Major sources of contamination include industrial and municipal solid wastes and wastewater, and agrochemicals.

The closest town to Lake Elementaita is Gilgil, which has various industries such as Kerio Valley mining fluorspar and Cabro East Africa Company for pole treatment and hotels like Serena Camp, Elementaita Lodge among others that are close to the lake. The close proximity of the industries and hotels to the lake could be attributed to access to potable water supplies. However, mishandling of pesticides and fertilizers from various application areas have led to pollution of the scarce water resources (Al-Jayyousi and Shatnawi, 1995).

Agriculture has been classified as one of the main sectors contributing to sediment and nutrient pollution of water sources mostly through diffuse pollution (Ulen *et al*., 2007; Wood *et al*., 2005). In addition, sediments act as new nutrients sources to the overlying water once they are adsorbed to the sediments (Masunaga *et al*., 1993; Abrams and Jarrell, 1995).

Agricultural activities like poorly managed animal feeding operations; overgrazing; improper ploughing; mishandling of pesticides during application, irrigation water, and fertilizer leads to nutrients pollution (Hendrik and Killebrew, 2010). Overgrazing exposes soils and increases runoff from poorly managed farms hence leading to nutrients contamination in ground and surface waters. Nutrients and oxygen-demanding organics and solids wastes contaminate water resources by destroying fish habitat, increase growth of undesirable plants and algal blooms and alter the water quality (Hendrik and Killebrew, 2010).

Manure contains high amounts of nitrogen and phosphorous. These nutrients directly enter the nearby streams directly or indirectly through percolation or runoff when livestock are grazed at the river banks. For instance, in China, Thailand and Vietnam waste from the industrial swine contributed to pollution in South China Sea compared to waste sources from domestic activities. High nutrient levels in water leads to increase in algal and bacterial growth leading to disappearance of native plant and fish (Daniels *et al.*, 2008). In the year 2010, about 238,000 working farms and ranches in the United States generated 500 million tons of manure through animal feeding operations (Hendrik and Killebrew, 2010).

In Lake Elementaita, agriculture contributes a high percentage of nutrients. In the year 2001, total nitrogen recorded was 2 mg/L and by 2002 it increased to 2.4 mg/L. Total phosphorus recorded was 0.02 mg/L in 2001 and 0.04 mg/L by 2002 .The high nutrients levels were alleged to be due to application of fertilizer in local farms to improve on crop yield and also due to waste water, sewage and detergents (Kitaka, 2001).

2.1.1 Nitrates

Nitrate is a highly soluble, stable and negatively charged ion in water. Due to its low potential for adsorption, it is difficult to be removed from water (Luk and Au-Yeung, 2002). Nitrate is the most oxidized and abundant form of inorganic nitrogen found in water (Luk and Au-Yeung, 2002). Some of the anthropogenic sources of nitrate include commercial and industrial waste water, fertilizers, acid rain, septic tanks effluent and leaching (Bleifuss *et al.*, 2003).

High nitrate concentration in water and consumption leads to gastric cancer and methaemoglobinaemia. Methaemoglobinaemia is the conversion of nitrate to nitrite in the stomach whereby nitrite combines with haemoglobin to form methemoglobin, hence reducing the ability of the blood to transport oxygen leading to blue baby syndrome, which in extremes can damage brain and finally lead to death in human (Levalloisa *et al.*, 1998). In animals high nitrates can lead to damages in the reproductive system (Luk and Au-Yeung, 2002; McCasland *et al.*, 1998).

2.1.2 Phosphates

Phosphate is a nutrient with a negative charge ion, measured as a growth limiting factor for plants and microorganisms (Muñoz *et al.*, 1997). It is responsible for controlling freshwater and terrestrial ecosystems productivity (Zhang *et al.*, 1998). Agriculture has been considered to be the main source of phosphates. The major sources of phosphate include soil run-off from agricultural areas, poorly treated sewage, fertilizers and atmospheric deposition (Kiely, 1997). Other phosphates sources in the environment include cleaning products such as detergents, fire extinguishers, toothpaste, human excrements, textile processing and food wastes (Weiner *et al.*, 2001). Detergent phosphates have been estimated to contribute 3-7% of total phosphate contributions to surface waters (CEEP, 2007).

In natural water bodies, phosphates concentration exceeding 1mg/l will lead to eutrophication (Reeve and Barnes 1994). Health effects as a result of excess phosphates especially inorganic orthophosphates include development of acute oral and renal effects, mainly calcification of the kidneys at high concentrations (Weiner *et al.*, 2001). WHO has provided a maximum 'safe' level of about 5 mg/L but high levels (above 100 mg/L) can affect water treatment processes.

2.2 Pesticides in the Environment

Usage of POPs has been banned in most of the countries especially in the USA. Despite the ban, some POPs like DDT still found their way into the environment majorly in the developing countries (Wandiga, 2001; Mandavilli, 2006). Lindane and DDT are still applied in public health sector to control head lice and malaria, respectively (Getenga *et al*., 2004).

Pesticide use in Africa has been estimated to be 1.23 kg per hectare (Williamson *et al.*, 2008). This value is low compared to Latin America and Asia whose estimates are 7.17 and 3.12 kg, respectively. However, harmful environmental effects are increased by the application of banned or illegal products and mishandling of chemicals (Williamson *et al.*, 2008). Despite banning DDT worldwide for agricultural purposes, in Ethiopia maize farmers still use it by mixing malathion with DDT to increase their crops yields and in malaria control program (Williamson *et al.*, 2008). In Uganda, there has been a gradual increase in pesticide use over the past half century (Kasozi *et al*., 2006), while Lake Victoria basin is singled out as the region with activities that apply pesticides (NEMA, 2000).

Efficiency of pesticide application has been found to be lower compared to that of fertilizer; of the pesticides applied to crops, more than 0.1% reach the intended pest whereas the remaining accumulates in soils, later leaches into the water sources hence toxic to micro-organisms, aquatic animals, and humans. Once in the soil, accumulated pesticides may harm organisms that play an important role in soil functioning and structure. Also increase pesticide usage may make weeds, viruses, and pests to be resistant to pesticides hence a constant need to develop new products. This after some time may lead to farmers using higher concentration or more frequent pesticide applications, raising the risk of negative impacts on animal and human health (Wilson and Tisdell, 2001).

Poor access to pesticides information, unavailable protective equipment and farmer illiteracy has contributed to adverse health risks to farmers (Wood *et al.,* 2000). Health impacts from exposure to or mishandling of pesticides include acute pesticide poisoning symptoms, including skin irritation, eye irritation, and stomach poisoning (Maumbe *et al.*, 2003).

2.2.1 Classification of Pesticides

Pesticides are divided into organic and inorganic. Inorganic pesticides are naturally occurring non-carbon elements, generally stable, non-volatile and soluble in water. Most of them contain arsenic, cyanide, mercury and thallium, but the presence of such metals make pesticides persistent and bio accumulative (Hassall, 1990).

Organic pesticides are mainly synthetic compounds containing either aliphatic or aromatic hydrocarbon chains. They consist of organochlorines, organophosphorus, organosulfates, carbamates and pyrethroids depending on the element bonded to the hydrocarbon system (Wasswa, 2008). Once pesticides enter an ecosystem, they may persist for long periods. Organochlorines insecticides such as DDT, for instance, were detected in surface waters in the USA 20 years after their use had been banned (Arias-Estevez *et al.*, 2008). Likewise, pesticides undergo biomagnification once they enter the food chain, whereby there is more accumulation in tissue of organisms than in the surrounding environment (Arias -Estevez *et al.*, 2008).

2.2.1.1 Organochlorines

Organochlorine pesticides (OCPs) are insecticides which contain carbon, hydrogen and chlorine. They are generally effective, nonbiodegradable hence pose a major environmental challenge. They consist mainly of DDT, DDD, methoxychlor, aldrin, dieldrin, heptachlor, lindane, endosulfan, isodrin, isobenzan, endrin, chlordane, toxaphene, mirex, and Kepone (Darko *et al.*, 2008). OCPs have been used widely in agriculture, as well as, in mosquito, termite and tsetse fly control programs (Guo *et al.*, 2008).

Organochlorine pesticides are known to have low polarity and lipophilic (high lipid solubility). As a consequence, they have a potential for bioaccumulation in the food chain posing a great threat to human health and the environment globally (Afful *et al.*, 2010). They are also known to be volatile and resist photo degradation and hydrolysis. In East Africa, OC pesticides have been in use since the 1940s and have tended to accumulate in soil (Madadi *et al.*, 2006; Ssebugere, 2010) and sediment (Werimo *et al.*, 2009). Due to leaching from sediment, OC pesticides and their residues find their way into edible fish (Ssebugere *et al.*, 2009). Organochlorine pesticides can be divided into three groups: DDTs, Cychlodienes and hexachlorocyclodienes.

Engel *et al*. (2000) established health risks related to organochlorine pesticides and its metabolites; fourteen out of twenty three POPs are OC pesticides which were ear-marked for phase-out and elimination. They include DDT, aldrin, endrin, dieldrin, chlordane, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, alpha - hexachlorocyclohexane, beta - hexachlorocyclohexane chlordecone, lindane, endosulphan, and pentachlorobenzene (Stockholm UNEP, 2009).

2.2.1.2 Organophosphates

These are insecticides which contain phosphorus as a derivative of orthophosphoric acid. They are known to be unstable, non-persistent and toxic to vertebrate animals as opposed to organochlorines, and they include Malathion, parathion, dimethoate, fenitrothion among others.

2.2.1.3 Carbamates

These are insecticide derivatives of carbonic acid. Generally they have low mammalian oral and dermal toxicity and broad spectrum insect control. They include carbaryl and carbofuran.

2.3 Heavy Metals

Inorganic and organic complexation, oxidation-reduction reactions, precipitation/dissolution reactions, and adsorption/desorption reactions processes govern the metal concentration in the soil at a given time (Muinde, 2012). Aquatic sediments constitute the most important reservoir of metals and other pollutants in the aquatic systems which later through biogeochemical processes, the metals and other pollutants remobilize and are released back to the overlying water causing water pollution (Simpson *et al*., 2002).

Metal solubilisation depends on various reactions involving water, sediment and specific metal of interest (Simpson *et al*., 2002). Adsorption is the process whereby metals are removed from the water column and stored in the substrate, while desorption returns the metal to the water column, where recirculation and bioassimilation may take place (Simpson *et al*., 2002). Metals maybe desorbed from the sediment if the water salinity increases, redox potential decreases, or the pH decreases (Bartram and Balance, 1996).

***Salinity increase*:** high salt concentrations create increased competition between cations and metals for binding sites. Often, metals will be driven off into the overlying water (Simpson *et al*., 2002).

***Redox potential decrease*:** a decreased redox potential, as is often seen under oxygen deficient conditions, will change the states of metal ions ($Mn^{n+)}$ and release the metal ions into the overlying water (Simpson *et al*., 2002).

***pH decrease*:** a lower pH increases the competition between metal and hydrogen ions for binding sites. A reduction in pH may also dissolve metal- carbonate complexes, discharging free metal ions into the water sources (Connell *et al*., 1984; Muinde, 2012).

According to Saeed and Shakes, (2008), pollution of the aquatic environment by inorganic chemicals is a main risk to the aquatic organisms including fish. The agricultural drainage water comprising of pesticides, fertilizers, effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge amounts of inorganic anions and heavy metals (ECDG, 2002). The most common anthropogenic sources of metals are industrial discharges, petroleum contamination and sewage disposal (Santos *et al*., 2005).

2.3.1 Cadmium

Cadmium is a group 12 metal in the periodic table along with zinc and Hg and with atomic number of 48 and one main oxidation state (+2). It is persistent and low-abundance, chalcophile element that normally exists as a substitute for Hg, Cu, Pb and Zn in sulphide minerals, especially sphalerite ZnS, and, to a lesser extent, in other Zn minerals such as smithsonite, $ZnCO_3$. High cadmium values usually indicate mineralization of sulphide.

Sources of Cadmium

Cadmium is found in the environment through natural or anthropogenic processes. In the surface environment, Cd is most mobile under oxidizing conditions at pH levels below 8. It readily forms complexes in solution with halides, cyanides and ammonium species, and has a strong affinity for organic matter. Humic substances bind Cd^{2+} to a greater extent than the major inorganic ligands, especially at high pH levels (Lawler and Tippings, 2003). At elevated temperatures, cadmium tends to volatilize hence giving a mechanism for it to enter into the hydrological cycle through atmospheric deposition downwind of industrial regions. In the aquatic systems, sources of cadmium can be through runoff from agricultural sites especially where there is application of phosphate fertilizer (Huang and Zhang, 2004), industrial processes involving electroplating and battery manufacturing processes, paint, ink and plastic manufacture whereby wastes from processes may leach-out and have an impact on surface water chemistry (Morrow, 2001).

Cadmium solubility in soil is strongly affected by pH whereby at low pH conditions cadmium solubility increases and very little adsorption of cadmium by soil colloids, hydrous oxides, and organic matter occurs (ECB, 2005). In high soil pH values, cadmium is moderately immobile and precipitation of cadmium compounds occurs hence high mobility of Cd (weak in binding to soily sediment) (Lawler and Tippings, 2003) resulting to most of it being leached out. Both toxicity and bioavailability of cadmium are influenced by soil characteristics (ECB, 2005).

Global mean of cadmium for surface soil has been estimated to be 0.53 mg/kg with mean cadmium in soil ranging from 0.06 to 1.1 mg kg^{-1}. The high concentrations reflect anthropogenic influence (Kabata and Pendias, 2001). Concern has been raised in industrialised countries over anthropogenic accumulations of cadmium in the environment leading to it being classified as a potential harmful element with respect to soil biological activity, plant metabolism and the health of humans and animals (Kabata and Pendias, 2001).

Cadmium tends to accumulate in plants and aquatic biota despite it being not essential in body functioning hence has problems of toxicity through inhalation of dust which damages lungs and long term exposure may cause cancer (WHO, 1996). The maximum tolerable intake of Cd is 7 µg kg^{-1} of body weight (WHO, 1996). Uptake by some invertebrates may show a complicated relationship with pH, showing a maximum in bioaccumulation at pH 5.5 (Vesely, 1994).

2.3.2 Copper

Copper is an essential element required by humans and animals for carbohydrate metabolism and functioning of enzymes together with the formation of haemoglobin in blood for transport of haemoglobin in vertebrates and shellfish (Heike Bradl, 2005). It is not magnified in the body nor accumulated in food chain. At high doses copper can be toxic to humans and at low concentration it can be biocidal to microorganisms like algae and mosses. Copper is not biodegradable, hence, it accumulates in the environment and may eventually reach hazardous concentrations levels (ECB, 2005)

Copper is found in chalcophile/chalcopyrite deposits along with Pb, Cd, and Zn which is used in the manufacture of several important alloys and other industries. It is released from plumbing system (Gustavo, 2007). Copper can cause various types of acute and chronic disorders and health hazards in flora, fauna and human beings when ingested beyond the permissible level of 1.3 ppm. In human beings it causes Wilson’s disease (ECB, 2005).

Sources of Copper

Copper enters into the environment through natural and anthropogenic sources. In water, sources of copper are extensive. In addition to natural levels originating from rocks weathering and atmospheric deposition, anthropogenic release can be through factories effluents and sewages or diffuse runoffs from land, roads and roofs (TDC, 2004).

The contamination of air and water, by copper is contributed by mining, milling, concentrating, refining of copper ores, electroplating industries, and petroleum refining. Copper can be used in many fields including: transportation, manufacturing, currency, transmission of electricity, construction (roofing, decoration) and agriculture (as fungicide and herbicide).

2.3.3 Lead

Sources of lead in the environment can be through anthropogenic or natural sources (weathering of soil and volcanoes) with the anthropogenic sources being the main contributors. In water, little is transferred through natural's ores with much of lead coming from atmospheric fallout, runoff or wastewater. At the beginning of the 20th century, motor vehicles were invented which lead to use of lead in petrol hence a significant increase in environmental lead contamination and community exposure (GA, 1991; CAGPSA, 1994). Between the year 1965 and 1990, world lead consumption increased to about 5.6 million tones (OECD, 1993). These and human activities contribute to increase in lead circulation in soil, water and air globally. Despite of more efforts being done to control lead by phasing it out, still massive reservoirs of the metal exist in soil, dust and house paint. These sources will continue to affect populations for many years (Nriagu, 1988).

Metallic lead is attacked by pure water in the presence of oxygen; further attack can be prevented by use of water containing carbonates and silicates which acts by forming a protective films and ligands (GA, 1991). Lead can be moved from the water column to the sediment by adsorption (predominant) to organic matter and clay minerals, precipitation as insoluble salt, and reaction with hydrous iron and manganese oxide.

Lake benthic microorganisms are able to directly methylate certain inorganic lead compounds. Under appropriate conditions, dissolution due to anaerobic microbial action may be significant in subsurface environments (CAGPSA, 1994). The most stable form of lead in natural water is dependent on ions present, the pH, and the redox potential. The least soluble forms mostly include the carbonate, hydroxycarbonate and hydroxide in oxidizing reactions and PbS is the most stable solid where sulfur is present in reduced reaction (CAGPSA, 1994). Pb (0) and Pb (+2) can be methylated in the presence of oxygen by methyl glycine and methyl iodine which can lead to dissolution of the previous lead bound to the particulate matter and sediment. Lead will be retained in the upper 2-5 cm of soil, especially soils with at least 5% organic matter or a pH 5 or above (CAGPSA, 1994).

Lead can cause various adverse health effects in humans whereby acute exposure is linked to interference with red blood cell chemistry, interruptions of regular physical and mental growth in babies and young children, slight deficits in the attention span, hearing, and learning abilities of children, and slight increases in the blood pressure of some adults. Chronic exposure has been connected to cerebrovascular and kidney disease in humans and for lifetime exposure it can cause cancer (Sharma and Pervez, 2003).

2.3.4 Chromium

Chromium is an important element in human and animal balanced diet especially in its trivalent form and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals. Hexavalent in contrast is carcinogenic and at large doses can cause death (Murray *et al*., 2005). Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation and pulp and paper production.

In water, chromium occurs in two oxidation states, +3 and +6. Under salt water conditions with a pH of approximately 8, cation Cr^{4+} may also be present (Chattopadhyay *et al.*, 2010). Anionic Cr^{6+}, is unstable, readily bioaccumutive and is found in the upper layers of the water. In the natural aqueous environment, chromium is relatively unstable in the dissolved state and undergoes precipitation in the form of a suspension as well as undergoing bioaccumulation (Chattopadhyay *et al.*, 2010).

In soil, chromium is generally dependent on the bedrock content of which the greatest amounts occur in soils from ultra-alkaline rock and some of the metamorphic rocks. Hexavalent and trivalent chromium are the most stable of all due to its orbital stability for instance, Cr (VI) being filled and Cr (III) being half-filled. Cr (VI) is extremely labile in the biological system and it can easily pass through cell membranes, often via sulphate transport system (Costa, 2003).

2.3.5 Zinc

Zinc is an essential element required by the body which in high levels can be harmful to health (WHO, 2001). In aquatic environment, zinc sources can be from fertilizers, sewage sludge, industrial wastes and mining. Zinc metal does not exist in the natural environment. It is present only in the divalent state Zn (II) and in its ionic form; it is subject to solvation and solubility which is pH and anion dependent. Zinc is a transition element and is able to form complexes with various organic ligands.

Zinc is extensively used as metals protective coat, in dye casting and in the construction industry, and for alloys (Akan *et al.,* 2010). Its organic and inorganic compounds can be applied as fungicides, topical antibiotics, lubricants and in medical and household applications, automotive equipment, storage and dry cell batteries, and dental applications (Akan *et al.,* 2010).

Sources of Zinc

Sources of zinc in the environment can be through anthropogenic and natural sources with natural inputs released through igneous emissions and forest fires and mining (Garrett, 2000), zinc production facilities, iron and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and incineration, and the use of zinc-containing fertilizers and pesticides being the main anthropogenic sources (Garrett, 2000). The solubility of zinc is mostly determined by pH whereby at low pH values, zinc becomes ionic in aqueous phase. Also at pH greater than 8.0, zinc precipitates and might also form stable organic complexes which can increase the mobility or solubility of the metal.

Zinc's adsorption to clay and organic matter makes it unlikely to be leached from soil. Sandy soils with low organic content at low pH have a reduced capacity for zinc adsorption. Zinc is not biomagnified and only dissolved zinc tends to be bioavailable, and bioavailability depends on the physical and chemical characteristics of the environment and biological processes. Natural background of total zinc concentrations are usually < 0.1–50 µg/litre in fresh water, 0.002−0.1 µg/litre in seawater, 10–300 mg/kg dry weight in soils, up to 100 mg/kg in sediments, and 300 ng/m^3 in air (WHO, 2001).

2.4 Fluoride

Fluoride (F^-) is the most reactive electronegative element present in the environment. In nature, fluoride occurs in a combined state especially in minerals like topaz. The principal source of fluoride is either natural by emission from volcanic activities or through man-made additives like fluoride in toothpaste (NaF, SnF_2, Na_2PO_3F) and water fluoridation (addition of fluoride in the form of NaF to drinking water) (Fouskaki *et al.*, 2003). The variation in fluoride contents is determined by volcanic activity due to rift formation and residence time i.e., chemical reactions involving Ca^{2+} and F^-. The Rift valley in the world has volcanic rocks which are rich in Na and F and it is mostly affected by climatic conditions which favour chemical weathering (Fouskaki *et al.*, 2003).

Once in the environment, it directly or through intermediate steps passes into water body systems, food chain and finally to the human body through ingestion. In the human body, fluoride deposit itself to the targeted organ especially where there is presence of calcium (Konieczka *et al.*, 2000).

According to WHO the recommended level of fluoride in drinking water is 1.5 mg/L (WHO, 2004). Intake of fluoride of about 1 ppm in drinking water is essential in the human body and animals for the formation of healthy bones and teeth. When the amount is too low it leads to dental caries and malformation of bones and when it’s too high > 1.5 it leads to dental fluorosis and mottled enamel (KEBS, 2010).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of the study area

Lake Elementaita

Lake Elementaita was initially identified as a bird sanctuary due to the huge flamingo population and over 450 other species of birds, which make a rare ornithological spectacle in east Africa (KLS, 2010). It is also rich in other birdlife species such as ducts, pelicans, African jacanas, Egyptian gees, grebes and rare purple swamp hen (Adeka *et al.*, 2008).

The Lake is threatened by silting as a result of vegetation destruction, overgrazing which causes wind and water erosion, charcoal burning and deforestation (SAL, 2008). This has led to sedimentation, eutrophication and livestock waste, toxic chemicals from agricultural pesticides and acaricides threatening the lakes' delicate ecosystem (SAL, 2008). Soils in the area are volcanic with a small portion of fertile, deep soil in the higher, eastern area of Gilgil, while the major part of the area is saline, strongly weathered and acidic (Alamirew *et al*., 2007).

The vegetation around Lake Elementaita is made up of Acacia and Euphorbia tree species and various bush land (i.e. *Rhus natalensis*) and grassland (i.e. *Cynodon dactylon*) (GoK, 2010). A high amount of former woodland has been cleared or turned into bush and grasslands as a result of farming, grazing and fires. The natural vegetation is at risk of getting even more diminished due to its use as firewood and for charcoal production (SAL, 2008).

Considering climatic conditions in the area, only 30 % of land is considered arable and 50 % agro-ecological zones (SAL, 2008). Farmers also grow beans and maize and use irrigation for vegetable plantation (SAL, 2008).

There are a few ranches and large scale farms which produce a high quantity of flowers and plants using irrigation as well as milk and meat (Elementaita and Kekopey), which is of high importance to the local population and the national economy (Jaetzold *et al*., 2010). Some activities like charcoal production, sand and salt harvesting from Lake Elementaita for commercial purposes, livestock grazing are also practised. Overgrazing is a common problem due to a high demand of forage for both livestock by nomadic Maasai and wildlife and often leads to soil erosion after periods of drought (SAL, 2008).

Lake Elementaita and its riparian are characterized by volcanic soils in the eastern part of the area and saline, intensively weathered and acidic soil in the remaining part of the area (Alamirew *et al*., 2007). The rain pattern in the area is bimodal; April to June (long rain) and from October to November (short rains) (SAL, 2008). The Lake is used for breeding the pink backed pelican and lesser flamingoes (Adeka *et al.*, 2008), salt harvesting on the east, small scale peasant farming on the west and north and livestock rearing on the southern part of the lake. The area is characterised by rocky rupture lines, volcanic exposures and craters (GoK, 2010). Figure 3.1 shows the map of the study area.

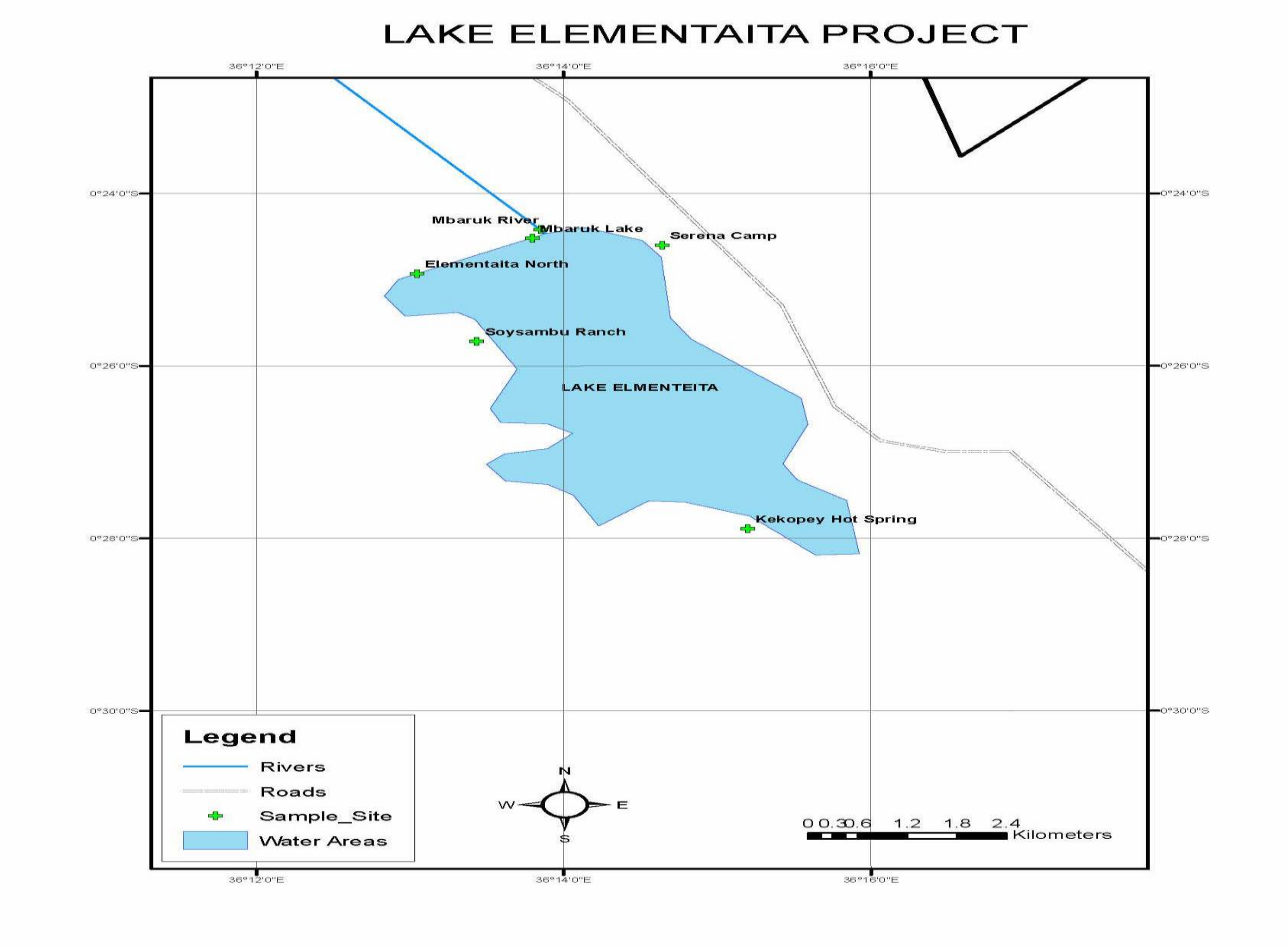


Figure 3.1.Map of Lake Elementaita basin

3.2 Sampling sites with the global positioning system (GPS) coordinates.

The GPS coordinates and altitudes of the sampling sites are summarised in Table 3.1.

Table 3.1 GPS coordinates of sampling sites

Site	**GPS Location**	**Altitude**
Mbaruk River (MR)	00^{0}28’22’’S and 036^{0}15’06’’E	1785 m
Mbaruk Lake (ML)	00^{o}24’37’’S and 036^{o}13’25’’E	1787 m
Kekopey Spring (KS)	00^{o}28’22’’S and 036^{o}15’06’’E	1781 m
Kekopey Lake (KL)	00^{o}28’22’’S and 036^{o}13’06’’E	1784 m
Lake Elementaita North (EN)	00^{o}24’37’’S and 036^{o}13’06’’E	1786 m
Serena Camp (SC)	00^{o}24’38’’S and 036^{o}14’25’’E	1782 m
Soysambu Ranch (SR)	00^{o}25’23’’S and 036^{o}12’31’’E	1783 m

3.3 Sampling

Water, soil and sediment samples were collected between October 2014 and April 2015 capturing the dry and wet seasons for seven sites selected to represent the lake and the main drainage systems of the Lake and the major human activities taking place within the drainage basin.

Water samples were collected by grab method into 2.5 L amber bottles for pesticides and nutrients analysis and in 1L polyethylene plastic bottles for heavy metals and fluoride analysis. The containers had been pre-washed with tap water, liquid detergent, rinsed with distilled water and dried overnight. Each water sample was labelled and treated with 100 g sodium chloride to dehydrate microorganisms that could degrade the pesticides.

Soil samples were collected from farms closer to the lake where water and sediments were collected. Soil samples were dug using a pre-cleaned hoe and scooped using stainless steel shovels down to the depth of 15-30 cm from three different spots within the sites. Three composted samples were mixed and a 500g representative sample packed and wrapped in aluminium foil, labelled and packed in self-sealing bags.

Sediment samples were collected from the lake and river where water was collected. They were scooped using a pre-cleaned stainless steel shovel from three different spots within the sites. The three composites were mixed and a 500g representative sample was packed and wrapped in aluminium foil, labelled and packed in self-sealing bags. All the samples were transported to the laboratory in cooler boxes and stored in a freezer at $^{-}20\ ^{o}C$ for soil and sediment and fridge at $4\ ^{o}C$ for water samples prior to laboratory analysis.

3.4 Pesticides Analysis

3.4.1 Equipment and Apparatus

Fractional distiller was used for triple distillation of all general purpose solvents. Soxhlet set up comprising of heating mantles, Soxhlet extractors and condensers was used for soil and sediment samples extraction while the water was extracted by solvent-solvent extraction method using 2.0 litre separatory funnel. Sample extracts were concentrated using LABCONCO rotary evaporator. Glass columns of length 20 cm and 2 cm internal diameter were used in alumina clean-up of the samples for pesticide analysis.

Total Dissolved Solids and electrical conductivities were measured using scientific Martin instruments model MI 306. The pH of water, soil and sediment samples was measured using pH meter model IQ 150. All samples weights were measured using Fisher scientific A-160 weighing balance calibrated using 1.0 g. Moisture content in soil and sediments was determined by gravimetric method using BINDER E28#04-71528 oven, whereas drying of glassware was carried out in MAMMOTH laboratory oven.

A lab-line explosion proof refrigerator was used for temporal storage of sample extracts before analysis and deep freezer was used for temporal storage of samples before extraction. HP Agilent GC system 6890N equipped with a micro electron capture detector (ECD) was used for qualitative and quantitative determination of organochlorine pesticides (OCPs) residues in the sample extracts.

Other glassware used included: measuring cylinders (1000 ml, 100 ml), beakers, glass vials (10 ml), auto sampler vials (1.5 ml), desiccators, Pasteur pipettes, syringes (10, 25, 50, 100 micro litre) and Whatman filter papers (No.1 and No. 42).

3.4.2 Chemicals and Reagents Used

General Purpose Grade n-hexane, acetone, dichloromethane (DCM) were triple distilled before use and HPLC grade iso-octane were purchased from local suppliers such as SCIELAB Ltd, Nairobi. Analytical grade chemicals were from different manufacturers for instance aluminium oxide from Central Drug House Ltd, anhydrous sodium sulphate from Central Drug House Ltd, sodium chloride from SCIELAB and activated charcoal from Lobe Chemie Pvt Ltd, disodium hydrogen phosphate from Central Drug House Ltd and analytical grade hydrochloric acid from Panreac Ltd.

High purity white spot nitrogen (99%) used for reducing samples was bought from Gas labs Ltd, while high purity helium used for chromatography was purchased from BOC Kenya Ltd. High purity pesticide standard mixture was purchased from Sigma Aldrich, Germany Ltd. Distilled water used to prepare solutions and rinse glassware was prepared at the department of chemistry laboratories, University of Nairobi.

3.4.3 Preparation of reagents

Aluminium oxide (Al_2O_3) was dried overnight at 200 ^oC for activation, followed by deactivation with 8% water by adding 8 ml of HPLC grade water to 92 g of activated Al_2O_3 in 250 ml round bottomed flask. The mixture was shaken thoroughly to eliminate all lumps and left over night to condition.

Anhydrous sodium sulphate (Na_2SO_4) was prepared by baking out for 16 hours at 200 ^oC to remove all the impurities. The phosphate buffer for pH 7 was prepared by mixing 29.6 mL 0.2 N HCl and 50 mL 0.2 M dipotassium hydrogen phosphate.

3.4.4 Sample preparation

3.4.4.1 Extraction of water, soil and sediment samples.

Soxhlet extraction of soil and sediment was done following EPA method 3540. Soil and sediment samples were thawed for about 6 hours prior to extraction. Triplicate samples of about 20 g samples were dried with baked out anhydrous Na_2SO_4 for about 6 hours then transferred to the Soxhlet thimble and 100 µl of 0.1 ppm isodrin solution was added as a recovery standard. This was extracted with 200 ml of hexane: acetone in the ratio (3:1 v/v) in round bottomed flasks for at least 16 hours at a rate of 8 cycles per hour. The extracts were then concentrated to 2 ml in isooctane using a LABCONCO rotary evaporator, transferred into 10 ml glass vials with caps and stored in the refrigerator at a temperature of 4 ^{o}C prior to cleanup.

Water samples were extracted by Solvent-solvent extraction following EPA method 3510. 1.5 L of water sample was transferred into a 2 litre separatory funnel and pH adjusted to neutral by adding 50 ml of buffer solution. This was followed by an addition of 100 g sodium chloride to aid in salting out the OCPs from the aqueous phase. 60 ml of triple distilled DCM was added into the separatory funnel extracted 3 times by shaking vigorously for two minutes (with venting intervals) and collecting the extracts. The combined extracts were eluted into conical flasks followed by drying using anhydrous sodium sulphate, 2 mL isooctane was added and concentrated in the LABCONCO rotary evaporator to 1 m L. The extracts were transferred into 10 ml glass vials with screw caps and stored in the fridge at 4 ^{o}C prior to cleanup.

3.4.4.2 Cleanup with Aluminium Oxide

The concentrated water, soil and sediment extracts were purified by passing through the 25 cm long x 2 cm multilayered glass columns with sintered glass at the bottom. The column was packed with a 1 cm layer baked out Na_2SO_4 followed by a layer of deactivated alumina (15 g per sample) and another 1 cm layer of baked out Na_2SO_4 at the top. The column was first conditioned by passing 15 ml triple distilled n- hexane before introduction of the concentrated extract and eluted the OCPs with 165 ml n-hexane. The eluates were further concentrated to 1 ml in isooctane using a rotary evaporator.

Sulphur in soil and sediment extracts was removed by addition of a small amount of copper metal following EPA method 3660.

All water, soil and sediment extracts were concentrated to 0.5 ml under a stream flow of white spot nitrogen. The extracts were transferred into vials for automated GC-ECD analysis. The ECD was calibrated using a standard mixture containing 17 organochlorine pesticides. Confirmatory analysis was carried out using GC-MS.

3.4.4.3 GC-ECD Analysis

A gas chromatograph model Agilent 6890N equipped with an auto sampler model Agilent 7683 series injector and an electron capture detector (µECD) was used for the analysis of the OCPs in the water, soil and sediment. The injector and detector temperatures were maintained at 250 ^{o}C and 300 ^{o}C, respectively. Nitrogen was used as the carrier gas and make-up gas with a constant flow rate of 1 ml/min. The injection volume was 1 µl with a pulsed split less injection mode. The column was a high performance capillary column, HP5 (5% phenyl methyl siloxane) with dimensions of 30 m long, internal diameter of 0.25 mm and film thickness of 0.25 µm. Chemstation software version 1990-2002 was used for instrument control and data handling.

3.4.4.4 Preparation of Calibration Curves

Calibration standard curves were prepared from pesticide standard stock solutions containing the OCPs. 9 level calibration standard solutions were prepared. Concentration range covered low, middle and high levels of the calibration window. Sample analysis was carried out by injecting 1µl sample size into the GC in split less mode. The resulting chromatograms were analyzed for OCPs following external standard method. Retention times of sample peaks were matched with those of the reference standards to identify the specific congeners while standard calibration curves were used for quantitative analysis.

3.4.4.5 Multilevel Calibration Curves

Calibration of the gas chromatogram was done by analysing nine calibration standard solutions of OCPs 17 mixture. The standard solutions were prepared in iso-octane. Standard curve for each of the pesticides was constructed by plotting from the relative response factor, that is, ratio of instrument response (peak area) normalized with syringe standard (Isodrin) peak area, against the analyte concentration.

3.5 Heavy Metal Analysis

3.5.1 Sample Preparation and Chemical Analysis

Soil and sediment samples were thawed to room temperature and oven-dried at 105 ^{o}C. The dry samples were ground using mortar and pestle and sieved through 2 mm sieve. 1 g samples were taken in triplicate and digested at 90 ^{o}C for 60 minutes, using 10 ml of analytical grade concentrated 11.9 M hydrochloric and 14 M nitric acids, in the ratio of 3:1v/v, (Aqua regia reagent mixture) so as to leach out the metals from the matrices. 1 ml of analytical grade perchloric acid was added to the mixture in the digestion tubes to aid in digestion of organic matter. After total digestion and subsequent cooling, the sample solutions were filtered through Whatman filter paper no. I then qualitatively transferred to 50 ml volumetric flasks and finally topped to the mark using distilled water.

For water samples, 100 ml of triplicate samples were digested following the aqua regia and perchloric acid method as described above. Acid blanks were subjected to the same digestion procedures for quality control of both sediments and soils.

Atomic Absorption Spectrophotometer (AAS) model AA-6300 Shimadzu was used for analysis of metals after calibration using standard solutions. Appropriate hollow cathode lamps were used for each element (Kennedy, 1990). The targeted metals were cadmium (Cd), lead (Pb), zinc (Zn), chromium (Cr) and copper (Cu). The following formula was used to quantify heavy metals in soil and sediments:

Concentration in mg/kg = c*v/m

Where c = concentration of metal in the extract (ug/mL)

v = volume of extract (mL)

m = weight of sample (g)

On the other hand, the formula used to quantify heavy metals in water was;

[Metal] mg/l in sample = c*v1/v2

Where c = concentration in mg/L of the metal in the final extract

V1 = volume of the final extract (50mL)

V2 = volume of the original sample (100mL)

3.6 Analysis of nutrients

3.6.1 Nitrates

3.6.1.1 Preparation of reagents for nitrates analysis

Coloring reagent: To 250 ml of distilled water, 105 ml of conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N-(1-naphthyl) ethylenediamine dihydrochloride was added. The mixture was stirred to dissolution, after which 136 g of sodium acetate ($C_2H_3NaO_2$) was added and the mixture stirred to dissolve before diluting to 500 ml with distilled water.

2 M KCl; 150 g of KCl was made to 1 Litre of solution in a volumetric flask.

Nitrate stock; To 100 mL volumetric flask, 0.163 g KNO_3 was added and dissolved and made up to the mark with distilled water to make a concentration of 100 ppm.

Nitrate Standard solution; To 100 mL volumetric flask, 10 ml of the nitrate stock solution was diluted with distilled water and topped up to the mark to make a concentration of 10 ppm.

Nitrite stock; To 100 mL volumetric flask, 0.15 g $NaNO_2$ was dissolved and topped up with distilled water to the mark to make a concentration of 100 ppm.

Nitrite standard solution; To 100 mL volumetric flask, 10 mL of nitrite stock solution was diluted with distilled water and topped up to the mark to make 10 ppm concentration solution.

3.6.1.2 Sample preparation for chemical analysis

Air-dried soil and sediments were ground and sieved through 2 mm sieve. 1.00 g was weighed in triplicate into a 125 mL Erlenmeyer flask. 10 mL of the 2 *M* KCl extractant was added. The solution was shaken for 15 minutes on a reciprocating shaker at 200 revolutions per minute. The soils and sediment suspensions were filtered using Whatman filter paper No.1.

A series of standard solutions were prepared in 10 mL Nessler tubes. 10 ml of each sample were also prepared and together with the standards were held with a rag holder. 2 ml of buffer-color reagent was added to each standard and sample, mixed and allowed to develop the color for at least 15 minutes.

The absorbances for all samples were read in the UV -vis spectrophotometer at 540 nm for NO_2-N and 534 for NO_3-N against the blank and the concentration of nitrites and nitrates plotted against absorbance.

3.6.2 Phosphates

3.6.2.1 Preparation of chemicals and reagents for phosphates analysis

Bray and Kurtz P-1 Extracting Solution (0.025 M HCl in 0.03 M NH_4F) was prepared by dissolving 1.11 g of reagent-grade ammonium fluoride (NH_4F) in about 0.9 L of distilled water. 25 mL of previously standardized 1M HCl was added and made to 1 L volume with distilled water and mixed thoroughly for five minutes.

5 N sulfuric acid solution was prepared by diluting 70 ml of concentrated H_2SO_4 with distilled water to 500 ml. Antimony potassium tartrate solution was prepared by dissolving 1.3715 g of potassium antimony tartrate ($K_2Sb_2(C_4H_2O_6)_2 \cdot 3\ H_2O$) in 400 ml distilled water in a 500 ml volumetric flask and diluted to volume (stored in a dark, glass-stoppered bottle). Ammonium molybdate solution was prepared by dissolving 20 g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 ml of distilled

water. Ascorbic acid was prepared by dissolving 1.76 g of ascorbic acid in 100 ml of distilled water. Combined reagent was freshly prepared by mixing 50 ml of 5N H_2SO_4, 5 ml of antimony potassium tartrate solution, 15 ml of ammonium molybdate solution and 30 ml of ascorbic acid solution.

100 ppm Stock phosphorus solution was prepared by dissolving 0.144 g of oven dried potassium dihydrogen phosphate, KH_2PO_4 in distilled water and diluted to 100 m L. 10 ml of the solution was pipetted from the stock solution to 100 m L and diluted to the mark with distilled water to make the 10 ppm working standard solution for phosphorus.

3.6.2.3 Preparation of soil and sediments for analysis

2 g of soil and sediment samples were weighed into a 50 mL Erlenmeyer flask, 20 mL of extracting solution was added to each flask and shaken at 200 epm for five minutes at room temperature (25 ^{o}C). The extracts were filtered through Whatman filter paper No. 2.

To 10 mL of the standards, 1.6 mL combined reagent was added for calibration and the same amount of the combined reagent was added to the samples and the color absorbance of each sample measured at 880 nm with the UV-Vis spectrophotometer using the reagent blank as reference solution.

Phosphate in soil and sediment was converted to mg/kg using the equation below:

Bray and Kurtz p-1extractable P (mg P/ kg soil) = CP x [0.020 L extract] /0.002 kg soil

Where CP = Concentration of P in Bray and Kurtz P-1 extract, in mg/L.

3.7 Moisture content determination

Moisture content in soil and sediment was determined by heating 5 g triplicate samples at 105 ^{o}C to a constant weight. The BINDER oven model E28#04-71528 was used for moisture content determination. The weight of each vial was determined while empty (W_1), after addition of the wet sample (W_2) and finally after heating in the oven to a constant weight (W_3).

Moisture content in the soil was calculated using the formula:

% Moisture content $= \mathbf{[W_2\text{-}W_3/W_2] \times 100}$

The moisture content in the wet soils was used to correct the dry weight of the soil and sediment samples taken for extraction at the analysis.

3.8 Total suspended solids (TSS)

The water samples were mixed thoroughly by shaking for 2 minutes before TSS determination. 100 ml of the mixed sample was filtered through a pre-weighed standard Whatman filter paper number 1. The residue retained on the filter paper was dried to a constant weight at 105 ^{o}C for 1 hour and cooled to room temperature in the desiccator. The final weight of the paper was weighed using analytical balance model Fisher 160A. The TSS was calculated using the formula:

mg TSS/L = (A-B)*1000/sample volume, mL

Where:

A=weight of paper + dried residue, (mg)

B=weight of dry filter paper (mg) before experiment.

3.9 Determination of fluoride

The fluoride analysis was performed using a Jenway 3040 model ion-meter equipped with fluoride electrode from Accumet ltd.

Fluoride stock solution (1000 ppm) was prepared from sodium fluoride and stored in polyethylene bottle.

Total Ionic Strength Buffer (TISAB) solution- TISAB II was prepared by mixing 58g sodium chloride, 57 ml of glacial acetic acid, 4g of 1,2-cyclohexanediamine-N,N,N’,N’-tetraacetic acid (CDTA) and 150 ml of 6N NaOH in volume of 1L (pH 5.0-5.5).

Water samples and fluoride standard solutions each in 10 ml were diluted in the ratio of 1:1 with TISAB solution, mixed with a magnetic stirrer for 3 minutes. Using the fluoride electrode-ion meter, electrode potentials of the sample solutions were directly determined and the values compared with those of fluoride standard solutions.

3.10 Determination of pH and Conductivity

pH, conductivity and Total Dissolved Solids (TDS) measurements were carried out using a calibrated portable meter model ExStikR11. Calibration for conductivity measurement was carried out using standards solutions of conductivity 84 µS, 1,413 µS and 12,880 µS. TDS was determined directly by the meter using internal calibration following the relationship between TDS and conductivity. pH meter was calibrated using pH buffer solution and adjusted with known pH of buffer solutions 7.0 4.0 and 10.0.

20g of soil and sediment samples were each weighed in triplicates and transferred into separate 100ml beakers. It was followed by an addition of 40 ml distilled water, stirred well with a glass rod and the solution allowed to stand for half an hour with intermitted stirring.

To the soil-water suspension in the beaker, the electrode was immersed and the pH value determined from automatic display of the pH meter.

3.11 Determination of Temperature

Water temperature measurements were made in degrees Celsius, using a digital thermometer by directly dipping the thermometer in the natural body of water being studied. The temperature was read and reported to 1 decimal place.

3.12 QA and QC

Method validation was carried out prior to all sample extractions and involved subjecting field blanks (distilled water and anhydrous sodium sulphate) to the same condition as samples and determining the recoveries. The recoveries were determined for all blank samples by spiking with the internal standard (isodrin) for pesticides. Also clean glassware soaked in 10% HNO_3 (v/v) were used to ensure that no cross contamination of samples occurred (Mwamburi, 2009).

3.13 Statistical Data Analysis

Microsoft excel was used to analyse data. The Statistical Package for Social Scientists (SPSS) was applied to determine the correlation between seasonal variations and the levels of pesticides residues detected. Graphs and statistical tables were used to represent results obtained and to show the interrelationships of various variables such as pH, TSS, TDS, electrical conductivity, sample type and the levels of pesticide residue in the lake.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Results of physico-chemical characteristics of water, soil and sediments

4.1.1 Physico-chemical characteristics of water

The physico-chemical properties of water determined included temperature, pH, conductivity, TSS and TDS. Table 4.1 below shows the summary of results of physico-chemical characteristics of water samples from seven sampling sites collected during the wet and dry seasons.

Table 4.1: Physico-chemical characteristics of water for dry and wet season.

SITE	**TDS (g/L)**		**EC (mS/cm)**		**TEMP(^{O}C)**	**TSS (mg/L)**		pH
	DRY	WET	DRY	WET		DRY	WET	
MBARUK RIVER	0.07	0.31	0.14	0.62	20.0	0.01±0.00	0.01±0.00	6.94
MBARUK LAKE	4.05	5.62	8.12	11.18	35.6	0.01±0.00	0.23±0.04	10.84
KEKOPEY SPRING	2.97	2.33	5.91	4.65	48.9	0.01±0.00	0.00±0.00	8.24
KEKOPEY LAKE	3.97	3.39	7.93	6.78	40.0	0.07±0.00	0.07±0.00	10.33
SERENA CAMP	3.85	5.60	7.68	11.20	34.4	0.05±0.00	0.86±0.04	10.36
SOYSAMBU RANCH	4.21	5.70	8.40	11.53	32.2	0.05±0.01	0.18±0.07	10.74
ELEMENTAITA NORTH	3.85	5.70	7.65	11.50	32.2^{o}C	0.06±0.00	0.09±0.00	10.55

Temperature of the lake water ranged between 20 °C and 48.9 ºC. The high temperature observed could be attributed to the shallow nature of the lake. Kekopey Spring site recorded the highest temperature (48.9 ºC) which could be attributed to the hot underground water discharged directly into the lake.

The pH of the lake water ranged between 6.94 and 10.84. This was relatively high compared to WHO recommended limit of 6.5 to 8.5 for drinking water (WHO, 2004). The high pH could be attributed to the fact that Lake Elementaita originates from carbonaceous volcanic rocks (Chernet *et al.,* 2001). The low pH values (8.24 and 6.94) at the mouths of the Kekopey Spring and Mbaruk River respectively were attributed to the high inflow of fresh water from the hot spring and River Mbaruk. The relatively more acidity of water from Mbaruk River can be attributed to the high phosphates concentration obtained during analysis.

The levels of TDS during the dry season ranged between 0.071g/l and 4.21 g/L at Mbaruk River and Elementaita North, respectively. In the wet season, it ranged from 0.31 g/L to 5.7 g/L at Mbaruk River and Soysambu Ranch, respectively. The high concentrations of TDS at some sites such as Elementaita North (5.7 g/L) could be associated with high concentration of dissolved minerals as a result of volcanic activities, coupled with high tropical temperatures and elevated evaporation rates experienced in shallow lakes (Ayenew, 2005). The Mbaruk River (0.071 g/L), Mbaruk Lake (4.05 g/L), Kekopey Spring (2.97 g/L), Kekopey Lake (3.97 g/L), Elementaita North (3.85 g/L), Serena Camp (3.85 g/L) and Soysambu Ranch (4.21 g/L) sites recorded TDS values above WHO maximum limits value of 0.5 g/L for drinking water (WHO, 2004).

TSS ranged from 0.01±0.00 to 0.07±0.00 mg/L during dry season at Mbaruk River and Kekopey Lake, respectively. On the other hand, the wet season recorded higher TSS values compared to the dry season, with levels ranging from 0.01±0.00 to 0.86±0.04 mg/L at Mbaruk River and Serena Camp, respectively. The high TSS recorded during the wet season (especially at Serena Camp) could be attributed to the effect of surface runoff from the agricultural activities and discharge from the hotels around the site.

Electrical conductivity ranged from 0.62 mS/cm to 11.53 mS/cm in wet season for Mbaruk River and Soysambu Ranch, respectively. During the dry season, EC ranged from 0.14 mS/cm to 8.40 mS/cm for Mbaruk River and Soysambu Ranch, respectively. The values obtained were above WHO maximum guideline for drinking water which is 0.90 mS/cm (WHO, 2004).

Comparing with other studies that have been conducted on physiochemical parameters for Lake Elementaita; Njenga *et al. (*2004) recorded pH between 9.6 and 9.7, whereas the EC ranged between 58.50 and 61.50 (mS/cm). Therefore, the current results for pH agreed with the previous reported data while EC was lower than the reported.

4.1.2 Sediment physico-chemical properties

Soil and sediment characterization was done using Avery and Bascomb, (1982) method to determine the properties of the soil from the seven sites. It was done at the National Agricultural Laboratory (NAL) based at Kenya Agricultural Research Institute (KARI).

Sediment samples from Lake Elementaita drainage basin had pH ranging from 6.45-9.88 with low pH measured at Mbaruk River and high at Serena camp. Most of the sites recorded pH levels higher than 9. Organic carbon ranged between 0.33-1.84 at Kekopey Spring and Elementaita North, respectively. There were high levels of potassium, calcium and magnesium. Table 4. 2

below illustrate composition of different sediments properties in Lake Elementaita drainage basin.

Table 4. 2: Composition of sediments from different sites in Lake Elementaita basin (dry wt)

SITES	pH	TOTAL N %	TOTAL ORG C %	P mg/Kg	K me %	C me %	Mg me %	Mn me %	Cu ppm	Fe ppm	Zn ppm	Na me %	E. Cond. mS/cm
Mbaruk River	6.45	0.13	1.08	55	2.75	24.6	1.74	1.97	3.15	601.2	14.01	2.47	1.64
Mbaruk Lake site	6.48	0.15	1.05	53	2.78	24.2	1.7	1.93	3.12	601.6	14.04	2.43	1.67
Kekopey Spring	9.71	0.05	0.33	4.68	1.7	9.1	2.8	0.62	3.32	236.9	14.64	3.59	1.75
Kekopey Lake site	9.68	0.07	0.36	4.63	1.5	9.3	2.6	0.64	3.33	236.7	14.58	3.55	1.79
Soysambu Ranch	9.39	0.08	0.66	8.2	3.95	30.9	0.09	1.04	2.86	302.5	8.1	3.94	1.69
Serena Camp	9.88	0.06	0.58	7.5	2.56	26.4	2.9	1.23	3.12	316.7	14.34	3.56	1.62
Elementaita North	10.3	0.13	1.84	19	1.09	8	0.34	0.12	2.45	198.9	13.67	3.57	1.73

me% = percent mill equivalent

4.1.3 Soil physico-chemical properties

Soil pH ranged between 8.41-11.1 for Kekopey Lake site and Elementaita North, respectively. Low total nitrogen and phosphorus levels were measured in all soils. The low carbon levels for instance ranging from 0.37 - 1.93 at Soysambu Ranch and Elementaita North, respectively makes the soil to have low ability to retain organic contents hence more pollution during heavy soil runoff. Potassium, calcium and magnesium levels were high. Sodium content in soil was high (2.75-3.97) with low electrical conductivity. Iron was measured in high levels compared to metals followed by zinc. Table 4.3 below indicates composition of different soil properties in Lake Elementaita drainage basin.

Table 4. 3: Composition of soils for different sites in Lake Elementaita drainage basin (dry wt)

SITES	PH	TOTAL N %	TOTAL ORG C %	P Mg/Kg	K me%	C me%	Mg me%	Mn me%	Cu ppm	Fe ppm	Zn ppm	Na me%	E.Cond mS/cm
Mbaruk River	9.36	0.13	1.12	39	3.83	35.7	3.48	1.98	1	402.2	4.6	3.94	3.26
Mbaruk Lake site	9.45	0.15	1.09	37	3.57	34.5	3.31	1.87	1.2	404.6	4.8	3.78	3.21
Kekopey Spring	8.57	0.05	0.38	6	3.11	15.6	4.07	0.75	1.11	439.1	4.91	3.94	0.8
Kekopey Lake site	8.41	0.04	0.41	6	3.16	15.3	4.01	0.77	1.06	438.8	4.86	3.97	0.75
Soysambu Ranch	9.01	0.05	0.37	5	2.75	13.3	0.73	0.66	2.63	137.2	5.46	2.75	0.33
Serena Camp	9.96	0.08	0.64	5	3.63	17.4	2.73	0.86	1.02	361.8	4.35	3.9	1.7
Elementaita North	11.1	0.16	1.93	21	2.95	8.7	0.48	0.14	1.12	204.7	4.74	3.89	6.68

me% = percent mill equivalent

The soil was 64% sandy, 18% clay and 18% silt with sandy loam texture. From the data obtained, texture obtained revealed high levels of sand followed by clay and silt. The high composition of sand implies low levels of organic matter, hence low ability to retain organic contaminants such as pesticides (Cerrillo *et al*., 2004).

4.2 Nutrients analysis

4.2.1 Phosphates

4.2.1.1 Phosphates in water.

The results of phosphate levels in water during wet and dry season are shown in Figure 4.1 below and Table A1.1 in Appendix I. Comparing both seasons, phosphate concentration was higher during dry season than in wet season. Wet season recorded concentration ranging between 0.02±0.00 and 0.24±0.02 mg/L at Kekopey Lake and Mbaruk Lake, respectively. Dry season recorded concentration ranging between 0.10±0.01 and 0.38±0.07 mg/L for Kekopey Spring and Mbaruk Lake, respectively.

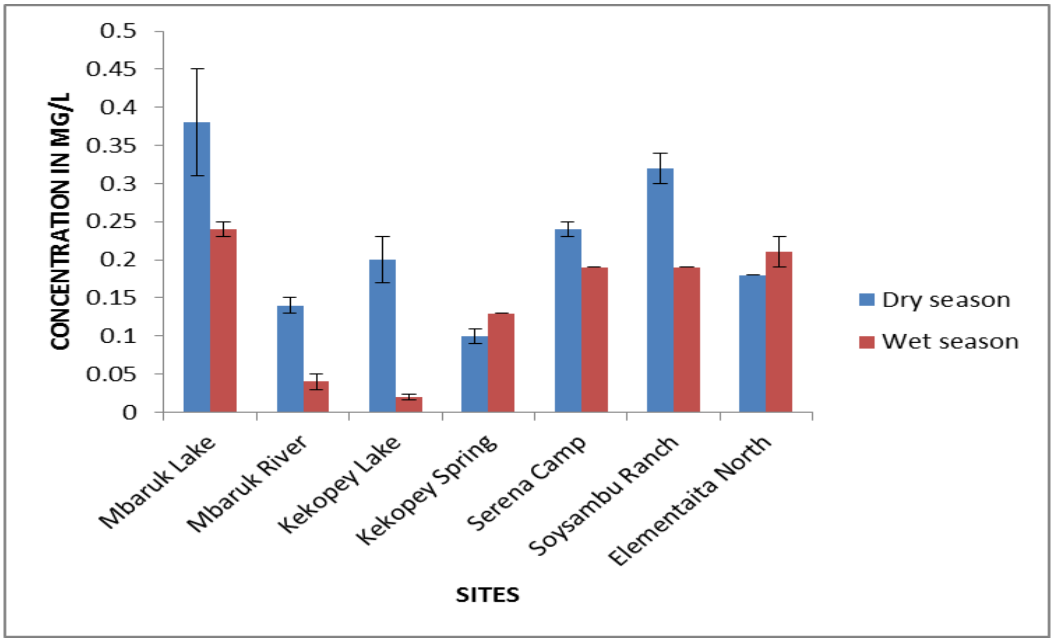


Figure 4.1: Average phosphate concentrations in water during wet and dry seasons

4.2.1.2 Phosphate levels in sediments during wet and dry season

Figure 4.2 below shows phosphate concentrations in sediments in both wet and dry seasons. Additional data is given in Table A1.2 in Appendix I. Phosphate concentration ranged between 0.45±0.02 and 10.04±0.10 mg/kg during wet season for Mbaruk River and Mbaruk lake, respectively. In the dry season, concentrations ranged from 0.52±0.00 to 6.27±0.02 mg/kg for Mbaruk Lake and Kekopey Spring, respectively.

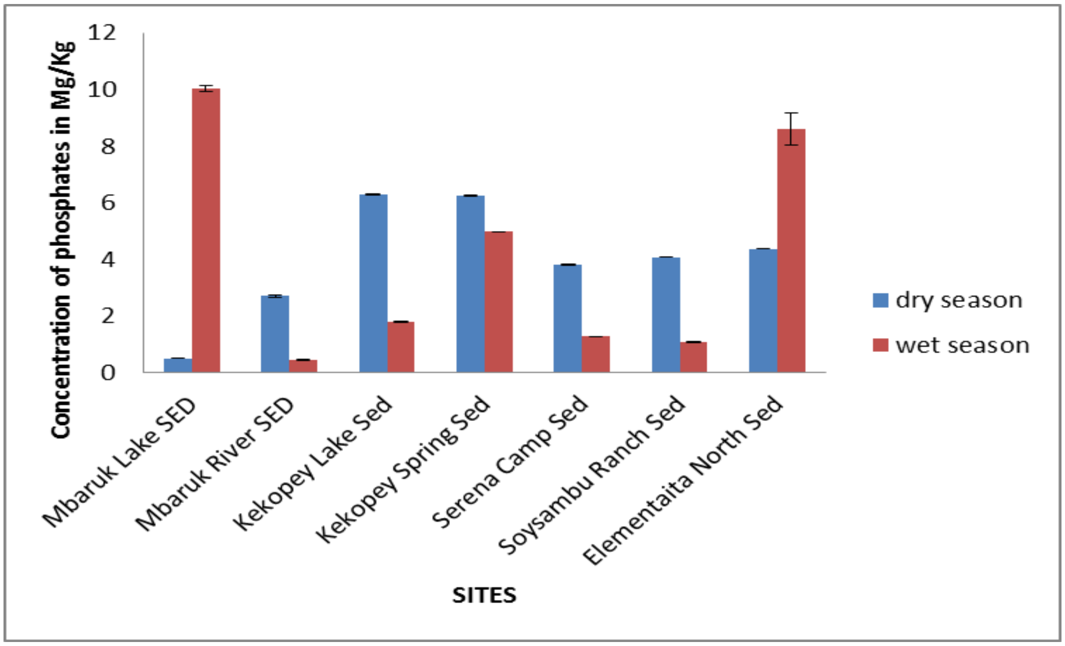


Figure 4. 2: Average phosphate concentration in sediment for both wet and dry season

4.2.1.3 Phosphate levels in soil during wet and dry season

Figure 4.3 below shows phosphate concentrations in soils in both wet and dry seasons. Additional data is given in Table A1.3 in Appendix I. Concentration ranged from 0.78±0.00 to 3.11±0.08 mg/kg during wet season for Kekopey spring and Serena Camp, respectively. Dry season ranged from 1.41±0.01 to 4.47±0.03 mg/kg at Soysambu ranch and Serena camp site, respectively. Comparing the two seasons, phosphates concentrations was found to be much higher in dry season than in the wet season.

Concentration of phosphates in Lake Elementaita was found to be below WHO maximum guidelines of 5 mg/L for water, but the concentration can lead to eutrophication. The sources might have been attributed by run-off from agricultural sites and fertilizers and livestock keeping especially at Soysambu Ranch site where cattle, sheep and goats had access to the lake (Kiely, 1997).

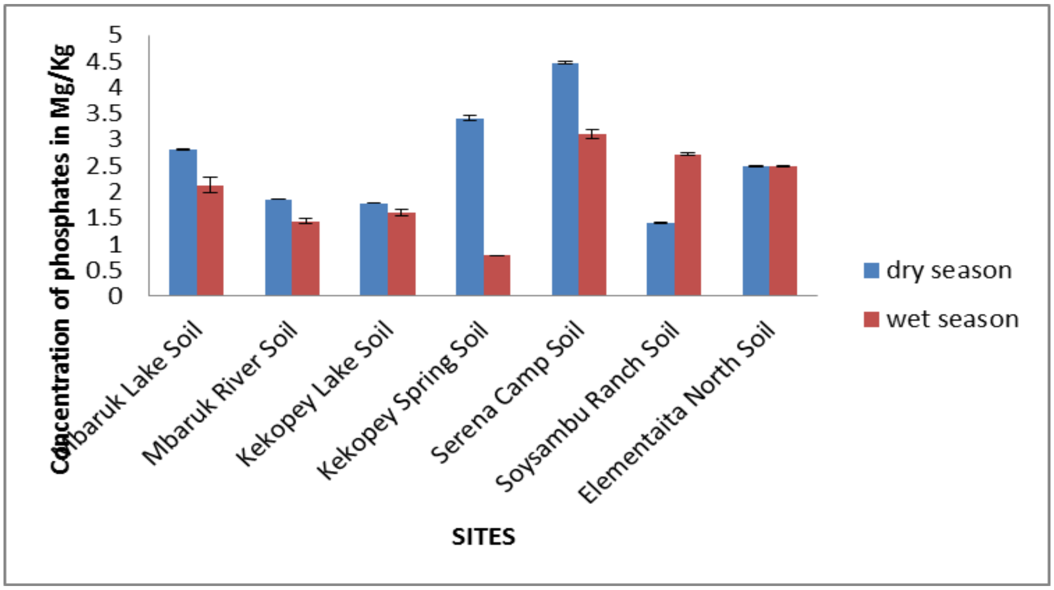


Figure 4. 3: Average phosphate concentration in soil for both wet and dry season

High phosphate concentrations in the lake could also be attributed to poorly treated sewage, cleaning products such as soaps and detergents and toothpaste from various hotels situated near the lake (Weiner *et al.,* 2001). Domestic activities like cleaning of cloths and bathing (hot spring water is believed to have medicinal value) at Kekopey Spring contributes to increase in inorganic phosphates at the sites (Adeka *et al.,* 2008).

4.2.2 Nitrates

Nitrates in the environment can be either from natural or anthropogenic activities which include fertilizer application, commercial and industrial wastewater, septic tank effluents and atmospheric deposition (Bleifuss, 2003). WHO recommended safe level for nitrates at10 mg/L.

4.2.2.1 Nitrate levels in water during wet and dry season

Figure 4.4 below shows nitrate concentrations in water in both wet and dry seasons. Additional data is provided in Table A1.4 in Appendix I. Nitrates concentration ranged between 0.69±0.05 and 3.00±0.36 mg/L in wet season at Mbaruk River and Elementaita North, respectively. During the dry season, the concentration of nitrates ranged from 0.43±0.02 to 0.91±0.26 mg/L at Serena camp and Mbaruk River, respectively. Comparing both seasons, concentration of nitrates was highest during wet season. Nitrates levels in Lake Elementaita water were found to be below the WHO maximum limit of 10 mg/L.

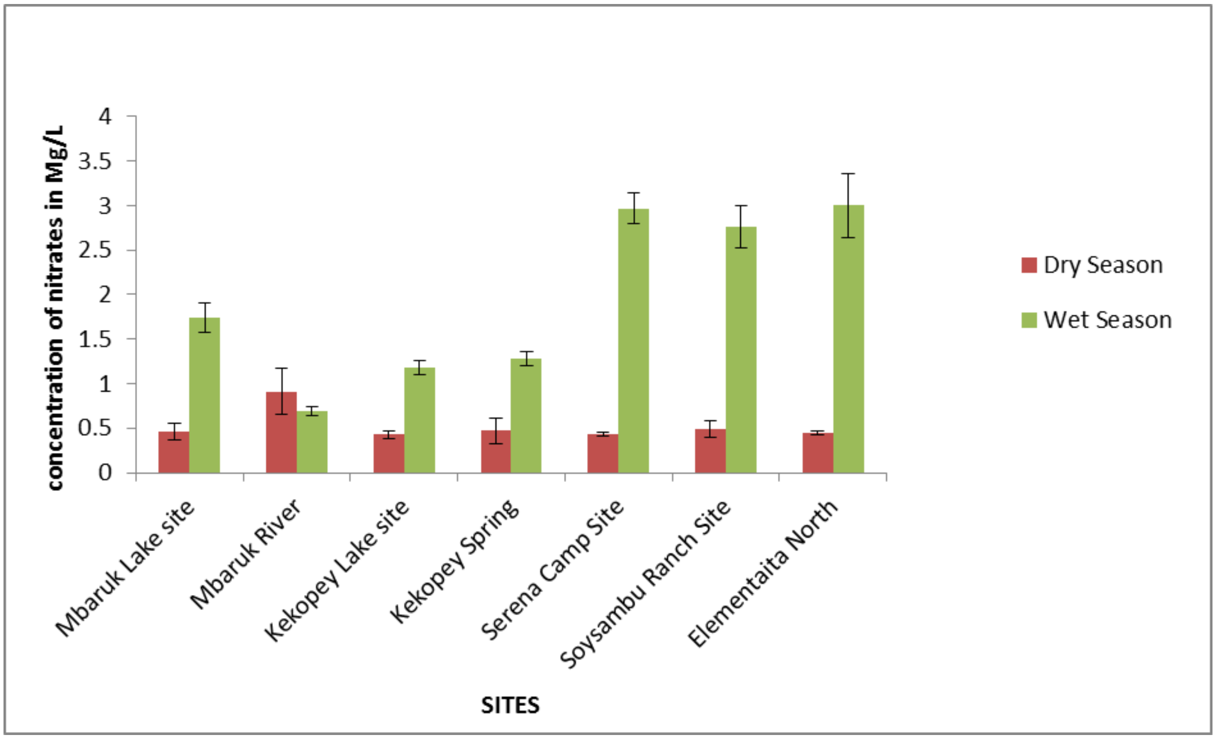


Figure 4.4: Average nitrate concentration in water for both wet and dry season

Study by Njenga *et al*. (2004) reported nitrates concentration in Lake Elementaita ranging between 0.12 and 0.15 mg/L. From these analyses, the current results suggest that there has been an increase in the concentration of nitrates in the lake water samples.

4.2.2.2 Nitrate levels in sediments during wet and dry season

Nitrates concentration in sediments ranged between 0.36± 0.06 to 2.01±0.05 mg/kg during the dry season for Elementaita North and Mbaruk River, respectively. During the wet season, the concentration ranged between 1.02±0.01 and 2.21±0.18 mg/kg for Serena camp and Kekopey Spring, respectively. Comparing both seasons, the dry season recorded higher concentration than the wet season. Figure 4.5 below shows nitrate concentrations in both wet and dry season in sediment and its concentrations illustrated in Table A1.5 in Appendix I.

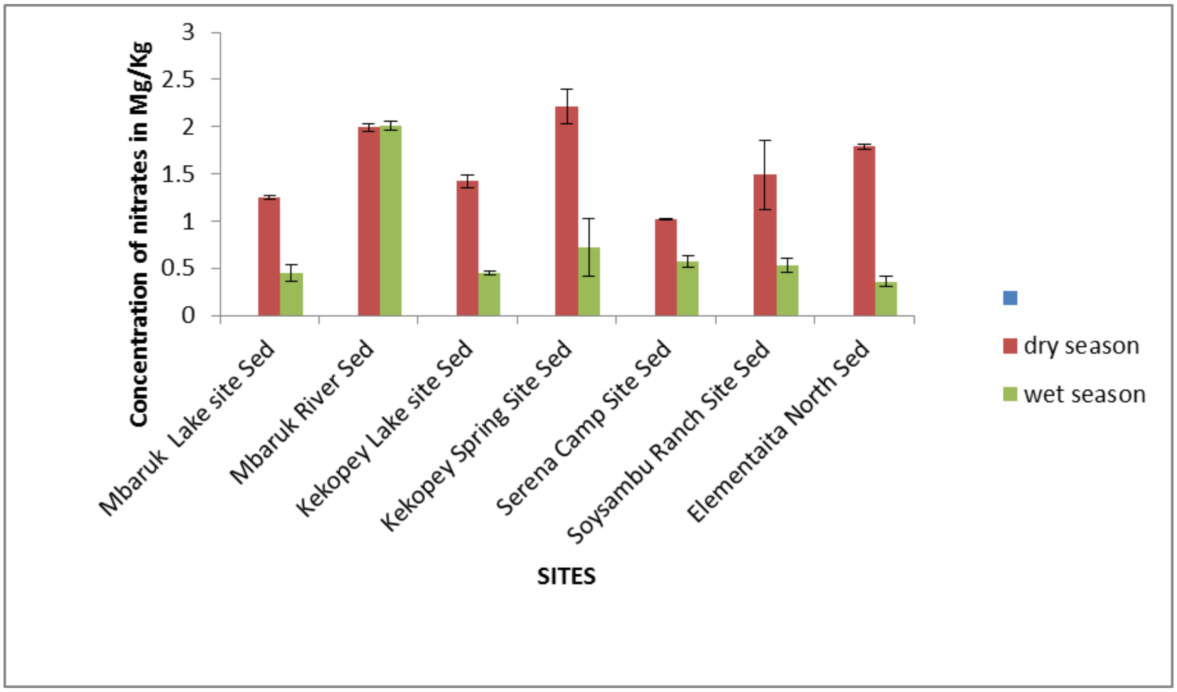


Figure 4.5 Average nitrate concentration in sediment during both wet and dry seasons

4.2.2.3 Nitrate levels in soil during wet and dry season

Nitrates concentration in soils ranged between 0.65±0.05 to 2.60±0.08 mg/kg during wet season at Elementaita North and Mbaruk Lake, respectively. During dry season, the concentration ranged from 1.46±0.07 to 4.90±0.29 mg/kg for Kekopey Spring and Soysambu Ranch, respectively. The high concentration of nitrates might have been attributed to agricultural activities around the site whereby farmers applied fertilizer in order to boost their crop yields.

Figure 4.6 below shows nitrate concentrations in soils in both wet and dry seasons. Additional data is provided in Table A1.6 in Appendix 1.

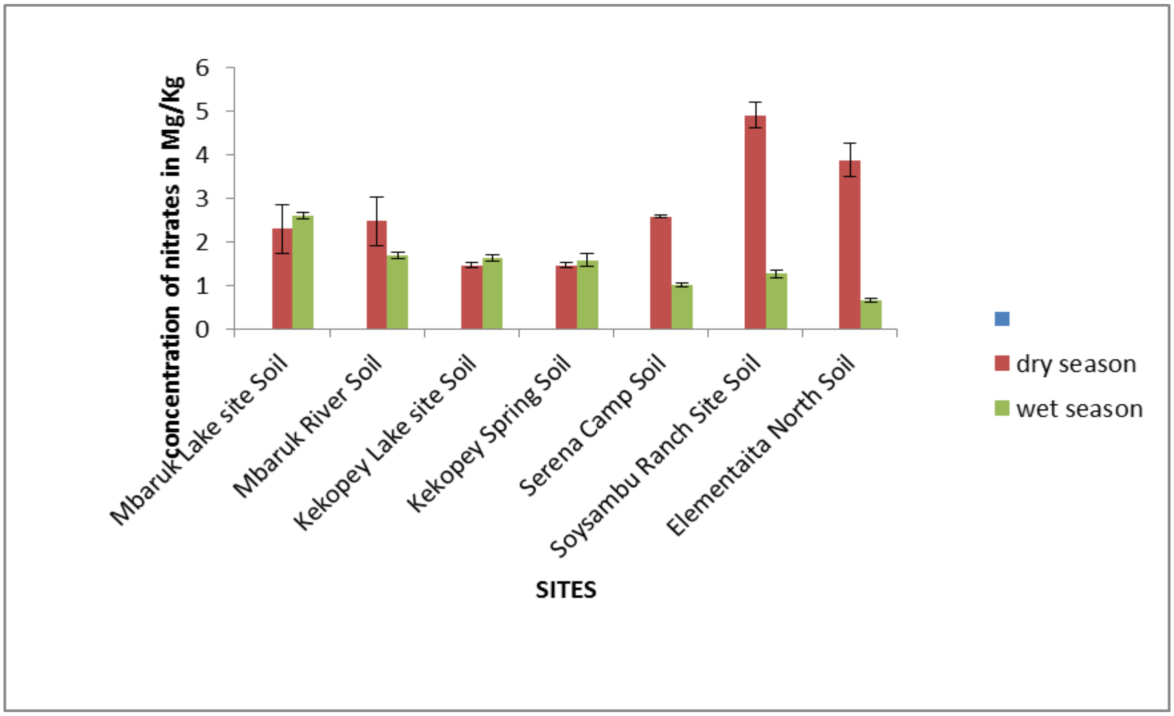


Figure 4.6: Average nitrate concentration in soil for both wet and dry season

Comparing both seasons, the dry season recorded higher concentration of nitrate levels in Lake Elementaita water were below the WHO maximum limit of 10 mg/L, hence suitable for consumption.

4.3 Results of pesticides analysis

4.3.1 Limits of Detection

The LOD of each of the OCPs was calculated based on the lowest concentration of the calibration standards injected and the corresponding signals of noise using the following equation by Miller and Miller, (1993) as shown below:

$$\textbf{LOD} = \frac{\text{3 X Noise Peak Area X Concentration of the lowest standard injected (ng/L)}}{\text{Analyte response in the lowest calibration point}}.$$

The limits of detection for OC pesticides ranged from 1.10 ng/L for α HCH to 3.60 ng/L for aldrin (Table 4.4). Compounds detected below the LOD were reported as below detection limit (BDL).

Table 4.4:Limit of detection values for various pesticides Average= mean± S.D

Pesticides	LOD (ng/L)	Pesticides	LOD (ng/L)
α HCH	1.1±0.1	Endosulfan sulfate	2.1±0.1
β HCH	1.6±0.1	Aldrin	3.6±0.1
γ HCH	1.6± 0.1	Dieldrin	3.1±0.1
δ HCH		Endrin	2.2±0.1
p,p,'- DDT	1.7± 0.1	Endrin aldehyde.	2.2±0.1
p,p,'- DDE	1.8± 0.1	Heptachlor	1.1±0.1
p,p, '- DDD	1.6±0.1	Heptachlor epoxide	1.1± 0.1
α- endosulfan	1.1±0.1	Methoxychlor	1.6±0.1

4.3.2 Multi-level Calibration Curves

Pesticide calibration curves were developed using nine different concentrations of 17 OCPs standard solution mixture. The calibration curves were linear and gave a correlation factor of R^2 above 0.99 indicating a high linearity between instrument response and analyte concentration. A sample calibration curve is illustrated in Figure 4.7 below. Additional calibration curves are attached in Appendix IV.

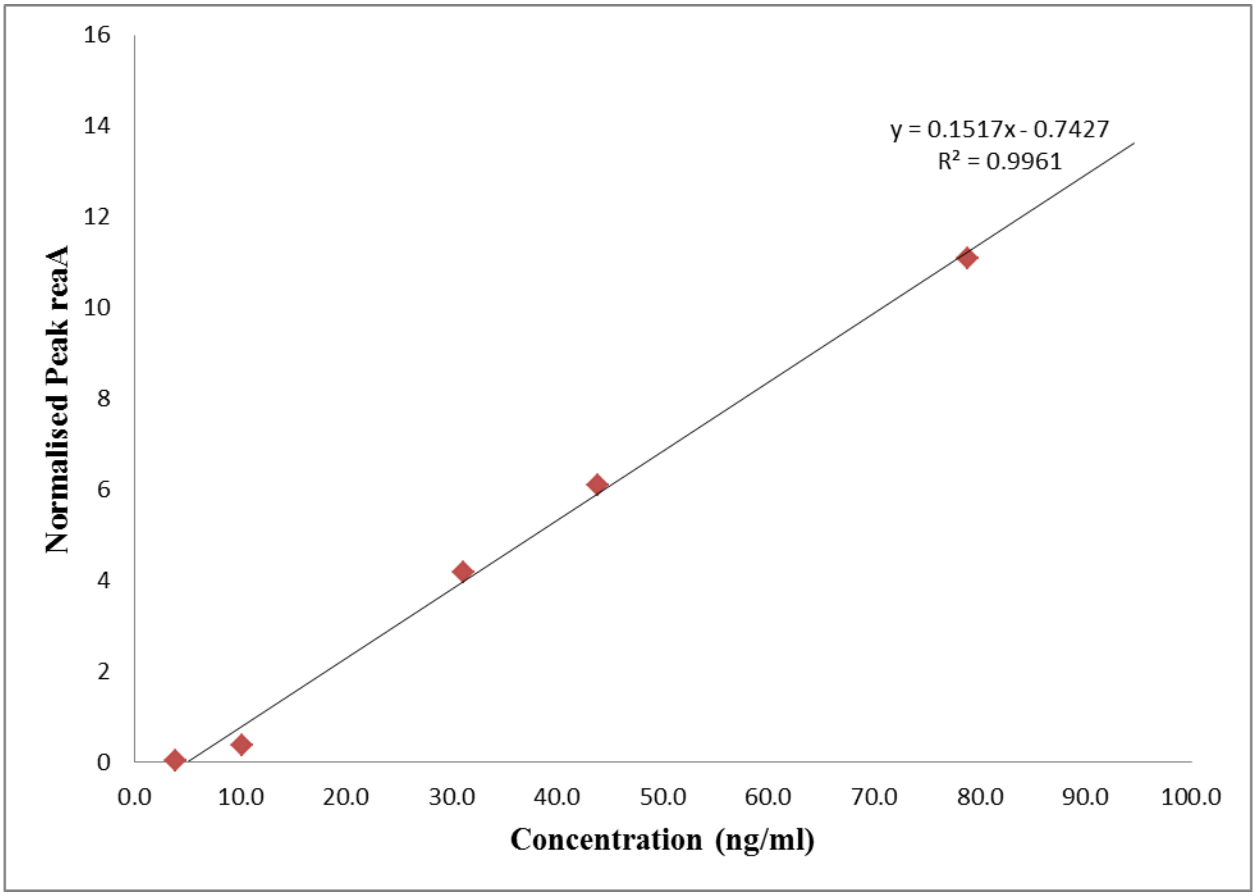


Figure 4.7: Sample calibration curve for γ-HCH

4.3.3 OCPs recoveries

The mean recoveries for the 17 OCPs ranged from 70% and 114%. This was found to be within the acceptable range of 70% and 120%, hence the results were not corrected (UNEP, 2007). The recoveries for the pesticides analyzed are summarized in Table 4.5 below.

Table 4.5: Average recoveries for various OC pesticides (mean± S.D)

Pesticide	**%Recovery(mean±S.D)**	**Pesticide**	**%Recovery(mean±S.D)**
α-HCH	94.82±8.31	Endosulfan sulfate	78.25±10.56
β-HCH	87.52±4.09	Aldrin	94.26±5.23
γ-HCH	92.06±9.58	Dieldrin	114.83±3.33
δ-HCH	82.54±6.95	Endrin	70.01±4.21
***p,p'*- DDT**	99.89±3.41	Endrin aldehyde	77.81±8.63
***p,p'*- DDE**	78.35± 5.12	Heptachlor	92.08±4.56
***p,p'*-DDD**	99.31±2.84	Heptachlor epoxide	98.35±2.45
α- endosulfan	102.58±4.95	Methoxychlor	88.23±6.86
β- endosulfan	93.23±7.13		

4.3.4 Organochlorine pesticides in water

Water, sediments and soil samples collected from the seven sites in Lake Elementaita drainage basin recorded the presence of OCPs. Pesticides residues in soil and sediment were higher in samples collected during dry season than in samples collected in the wet season. Higher concentrations of OCPs were recorded in water during the wet season compared to the levels measured in samples collected in the dry season (Appendix II, Table A2.1).

All the 17 OCPs were detected in Lake Elementaita. Dry season recorded concentrations ranging from BDL to 0.49±0.09 μg/L.

Hexachlorocyclohexane (HCH) isomers were generally low during both seasons with concentrations ranging from BDL to 0.49±0.09 µg/L with α- HCH recording highest (0.49±0.09 µg/L) for Mbaruk River. Heptachlor and heptachlor epoxide concentrations ranged from BDL to 0.06±0.00 µg/L and BDL to 0.02±0.00 µg/L at Mbaruk River and Serena Camp, respectively. Aldrin and dieldrin concentrations ranged from BDL to 0.31±0.09 µg/L and BDL to 0.04±0.01 µg/L, respectively with high concentrations recorded at Serena Camp site.

DDT and metabolites residue levels ranged from BDL to 0.12±0.03 µg/L with DDT recording the highest concentrations of 0.12±0.00 µg/L at Serena Camp. *p,p'*-DDE recorded lowest concentration values of all the metabolites. Endosulphan sulphate recorded highest residue levels ranging from BDL to 0.07±0.00 µg/L compared to the parent compounds Endosulphan 1 and Endosulphan 2 whose concentrations ranged from BDL to 0.06±0.01 µg/L. Endrin and endrin aldehyde concentrations ranged from BDL to 0.01±0.00 µg/L and BDL to 0.05±0.00 µg/L, respectively with high concentrations recorded at Serena Camp. Methoxychlor concentrations ranged between BDL to 0.07±0.01 µg/L at Serena Camp.

Figure 4.8 below and Table A2.1 in Appendix II present 17 OCPs from the seven sampling sites for dry seasons.

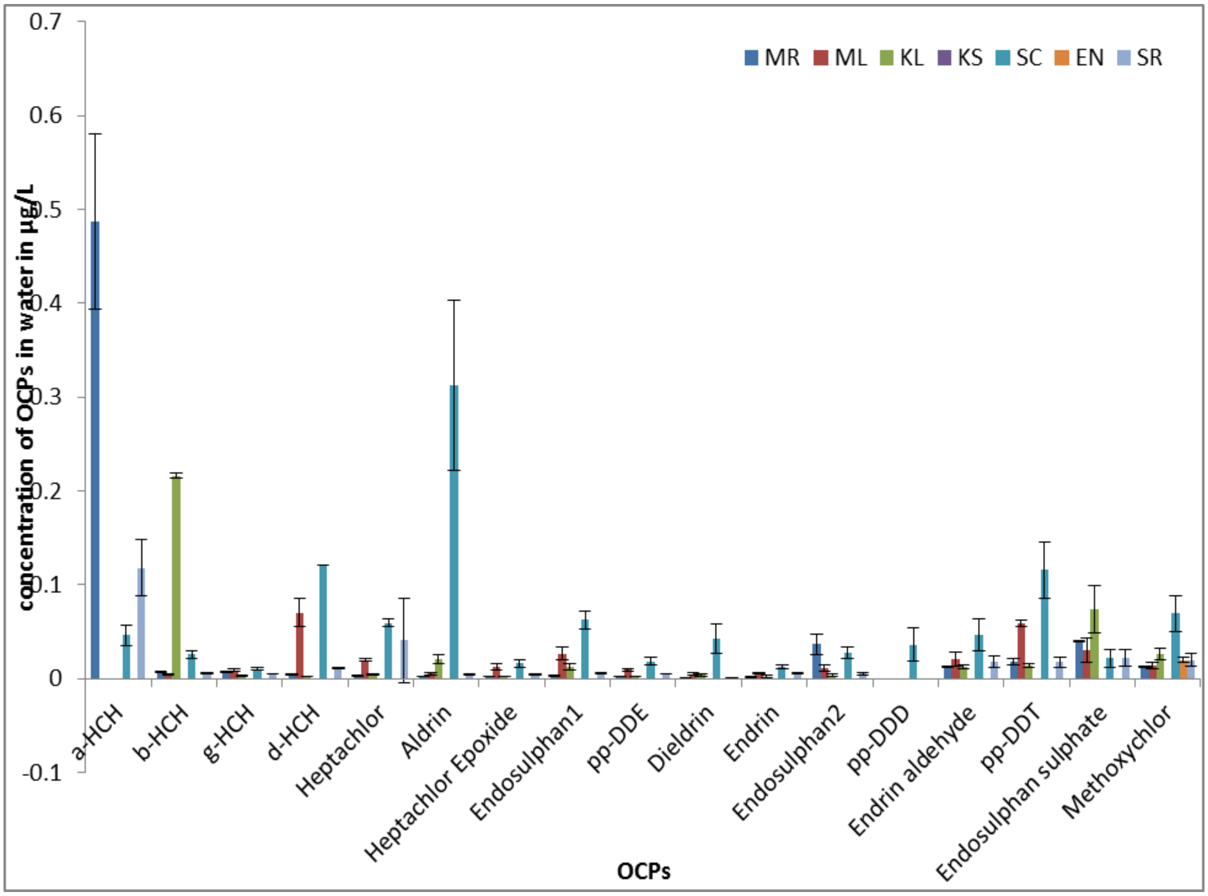


Figure 4.8: Mean concentrations of OCPs in water during dry season.

The wet season recorded concentrations ranging from BDL to 0.16±0.00 µg/L in water. HCHs recorded concentrations ranging from BDL to 0.04±0.00 µg/L with α- HCH giving the highest value at Elementaita North. Aldrin and dieldrin concentrations ranged from BDL to 0.06±0.00 µg/L and BDL to 0.02±0.00 µg/L, respectively with high concentrations recorded at Elementaita North. DDT recorded highest value amongst its metabolites with concentrations ranging from BDL to 0.09±0.00 µg/L at Elementaita North. Figure 4.9 below and Table A2.2 in Appendix II present 17 OCPs from the seven sampling sites for wet season.

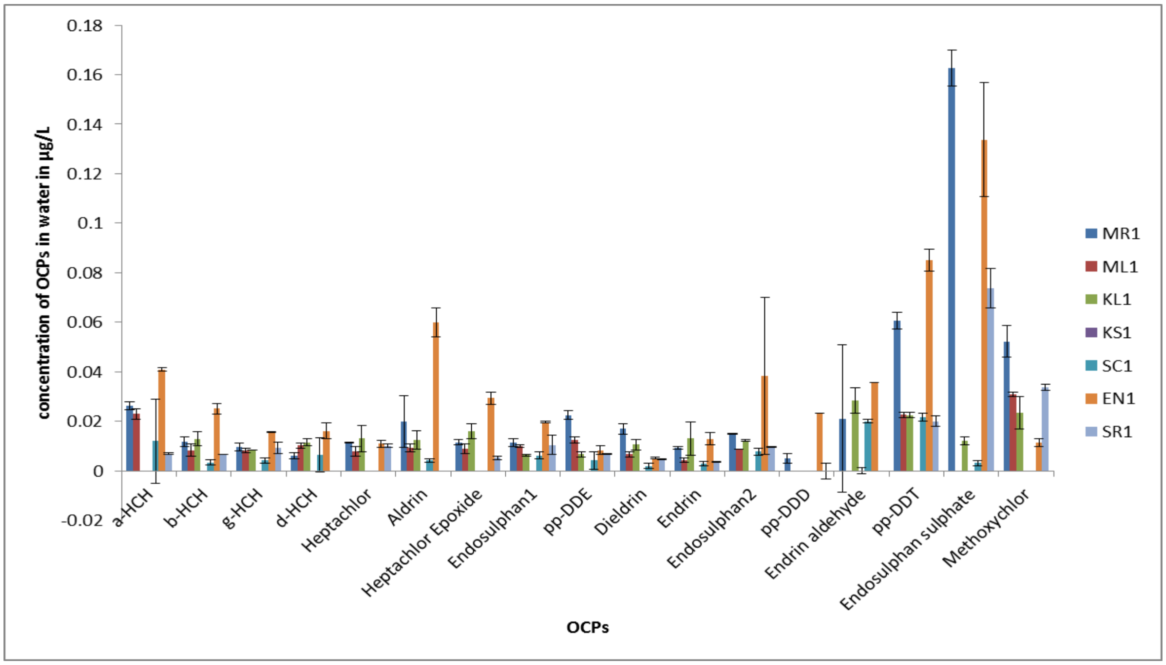


Figure 4.9: Mean concentrations of OCPs during wet season

Kekopey Spring recorded values BDL. Sum of HCHs ranged from 0.05 to 0.37 with α -HCH recording the highest values and γ -HCH recording the least. Heptachlor recorded highest ∑0.09 µ g/L compared to its isomer heptachlor epoxide. DDT and its metabolites recorded values ranging from ∑0.03 to 0.23 µ g/L with DDT giving the highest value. Endosulphan sulphate had the highest sum value of 0.25 µg/L compared to its parent endosulphan 1(0.08 µ g/L) and endosulphan II (0.07 µ g/L). The high levels of OCPs detected in the Lake water during wet season could have been attributed to runoff, desorption from sediments and wet deposition. In the environment, aldrin breaks down slowly by oxidation to dieldrin with the metabolite having equally slow degradation rate. This explains the large amount of aldrin in water compared to its metabolite.

However, OCPs residues in water in both dry and wet seasons were below the World Health Organization (WHO) permissible maximum limits for drinking water in all samples signifying low risks to the end users (IUPAC, 2003).

4.3.5 Concentrations of organochlorine pesticides residues in sediments

The concentration of OCPs in sediment samples collected during the dry season ranged from BDL to 762.27±91.70 µg/kg at Soysambu Ranch.

Hexachlorocyclohexane isomers had concentrations ranging from 23.90±0.29 to 198.17±2.46 µg/kg. δ - HCH recorded the highest values of all the isomers with the high value recorded at Kekopey Lake (198.17±2.46 µg/kg) and γ -HCH recording the least (23.90±0.29 µg/kg). Heptachlor and heptachlor epoxide recorded concentration values ranging from 36.29±9.55 (Soysambu Ranch) to 146.76±13.66 µg/kg at Kekopey Lake and 25.15±1.02 µg/kg (Serena Camp) to 70.99±10.35 µg/kg (Elementaita North), respectively. Aldrin and dieldrin had concentration values ranging from 26.05±0.61 (Serena Camp) to 89.96±7.80 µg/kg (Mbaruk Lake) and 7.89±1.45 (Mbaruk Lake) to 33.83±2.91 µg/kg (Soysambu Ranch), respectively. Endrin and endrin aldehyde recorded concentrations ranging from 16.44±0.17 (Kekopey Spring) to 45.86±6.11 µg/kg (Mbaruk Lake) and 123.32±3.47 (Soysambu Ranch) to 153.76±2.59 µg/kg (Kekopey Spring). Endosulphan sulphate recorded high concentration values compared to its parent isomer endosulphan 1 and endosulphan 2. The concentrations ranged from BDL to 762.27±91.70 µg/kg with the highest concentration recorded at Soysambu Ranch. Among the DDT and its metabolites, *p,p'*-DDT recorded the highest while *p,p'*-DDD recorded the lowest. The highest concentration (193.78±27.2 µg/kg) was detected at Kekopey Spring. Methoxychlor recorded concentration ranging from 102.09±4.01 to 178.87±24.65 µg/kg with the highest concentration recorded at Kekopey Spring.

Figure 4.10 below and Table A2.3 in Appendix II presents 17 OCPs from the seven sampling sites for both during dry and wet seasons, respectively.

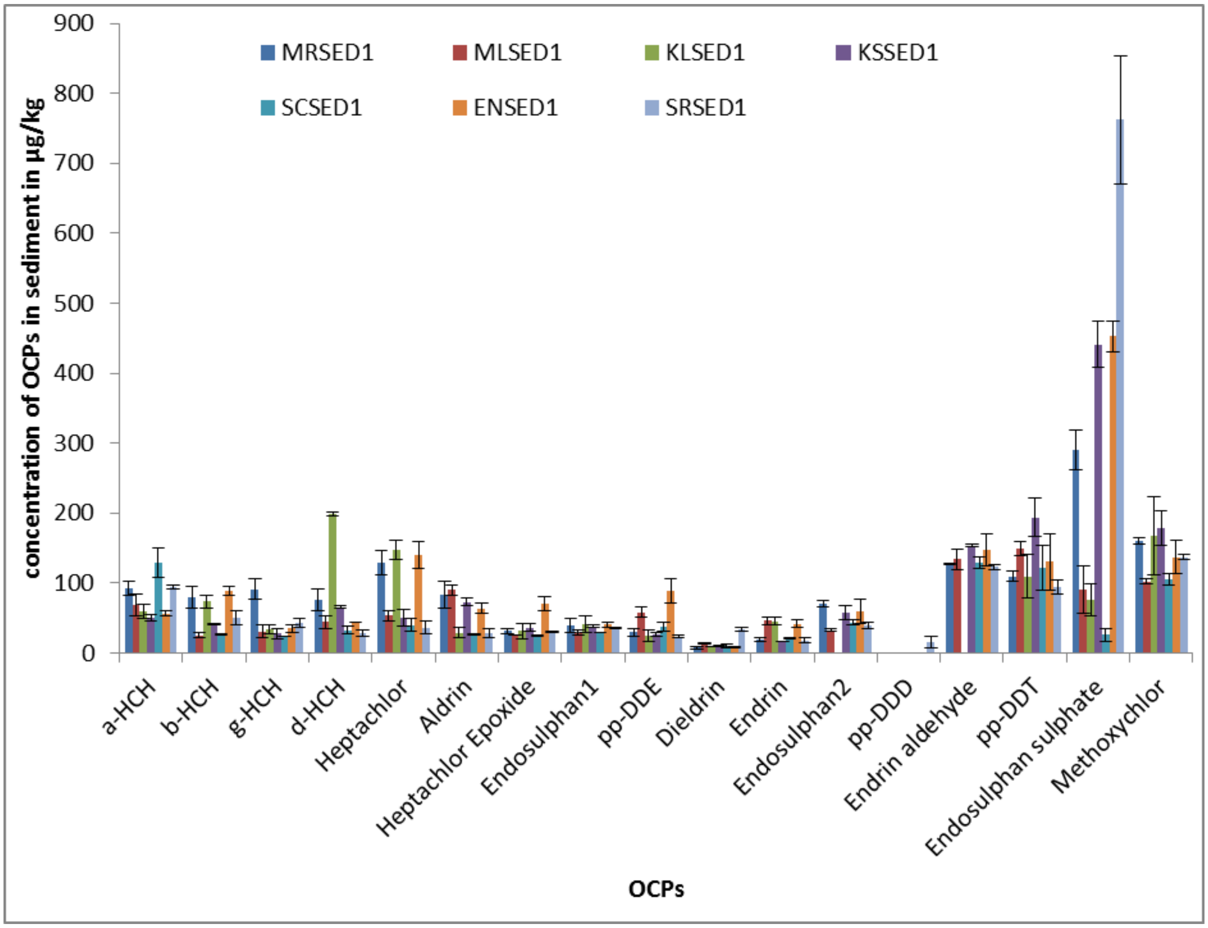


Figure 4.10: Mean concentrations of OCPs in sediment during dry season.

The wet season recorded concentrations values ranging from BDL to 42.97±1.00 µg/kg at Elementaita North. HCHs recorded concentration values ranging from BDL to 8.02±0.62 µg/kg with δ-HCH recording the highest value at Mbaruk Lake. Heptachlor epoxide recorded highest concentrations amongst its isomer with concentrations ranging from 0.79±0.11 to 5.99±0.19

µg/kg at Kekopey Lake and Elementaita North, respectively. Endosulphan had concentrations value ranging from 0.99±0.03 to 42.97±1.00 µg/kg. DDT and its isomers had concentrations ranging from BDL to 16.49±0.13 µg/kg with DDT recording the highest values. Methoxychlor had concentration values ranging from BDL to7.39±0.41 µg/kg with the highest concentration recorded at Mbaruk River. Figure 4.11and Table A2.4 in Appendix II presents 17 OCPs from the seven sampling sites for wet season.

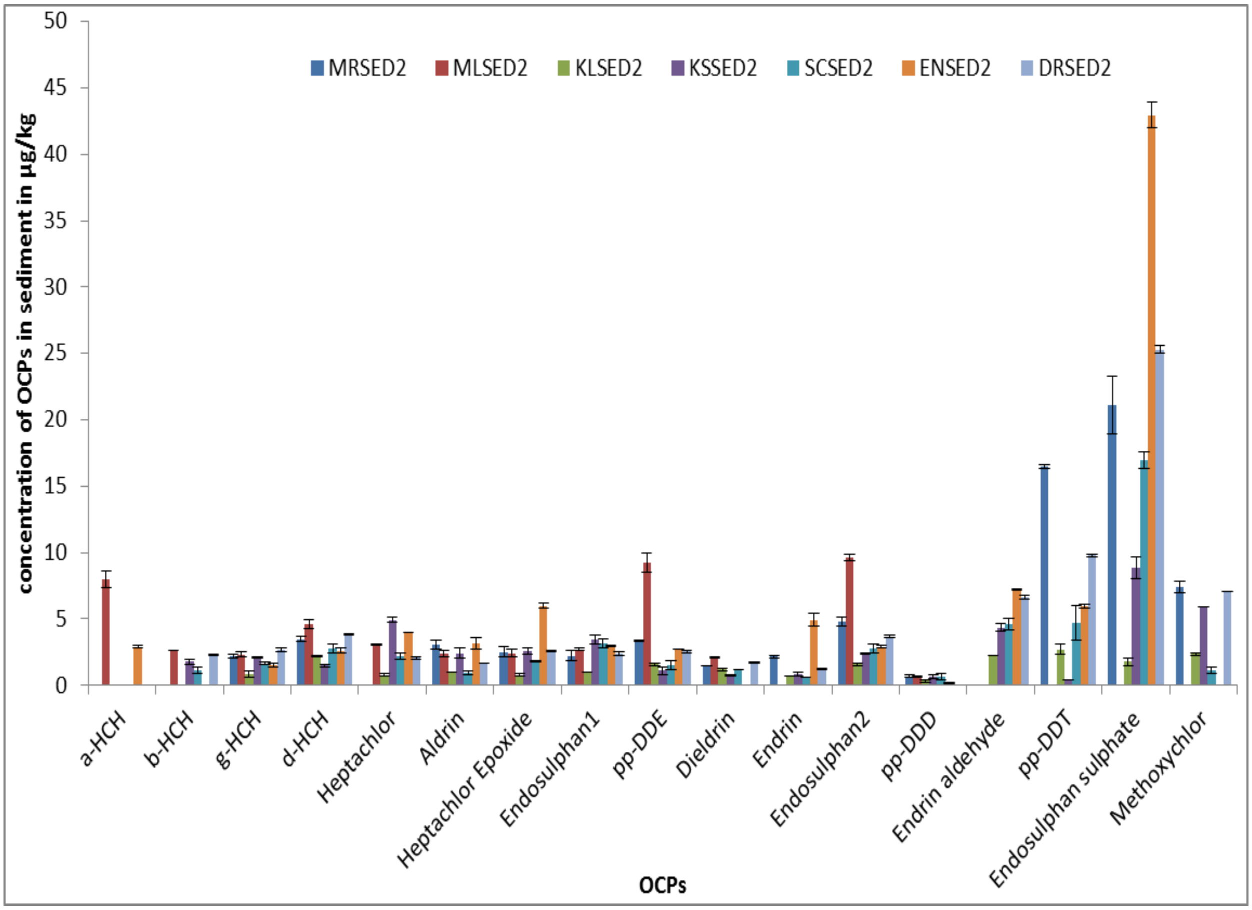


Figure 4.11: Mean concentrations of OCPs in sediment during wet season.

HCHs had sum values ranging between 149.99 to 277.09 µg/kg with α -HCH recording the highest and γ -HCH the least value. *p,p'*-DDT recorded higher value of 483.23 µg/kg compared to its metabolites *p,p'*-DDE and *p,p'*-DDD. Endosulphan sulphate recorded sum value of 1,128.2 µg/kg which was higher than Endosulphan 1 and Endosulphan II. Endrin had a higher sum value of 420.31 compared to its parent endrin (90.66 µg/kg).

Comparing both seasons, OCPs levels were highest during dry season than in wet season.

The higher concentrations of endosulphan sulphate detected compared to the parent compounds could be explained by environmental degradation where endosulphan sulphate is known to be more persistent in sediments than in water (Wan *et al*., 2005).

The presence of endosulphan sulphate in higher concentration and heptachlor in the area indicates that these insecticides are still being applied illegally despite their banning as an insecticide (PCPB, 1998).

4.3.6 Concentrations of organochlorine pesticides residues in soil

Organic carbon content and heterogeneousity of soil makes it susceptible to accumulation of hydrophobic chemicals such as organochlorine pesticides compared to water media. During the dry season, the concentration of OCPs ranged from BDL to 615.93±119.21 µg/kg at Kekopey Spring. α-HCH recorded high concentration values of all the isomers of HCH with concentrations ranging from 17.76±0.73 (Soysambu Ranch) to 46.83±2.59 µg/kg with the highest value recorded at Elementaita north. Heptachlor recorded high concentrations compared to heptachlor epoxide with concentrations ranging from 20.56±1.73 to 27.40±7.49 µg/kg at Serena camp site. Aldrin and dieldrin had concentrations ranging from 16.92±1.16 (Kekopey Lake) to 50.24±2.29 µg/kg (Elementaita North) and 6.26±0.1 (Kekopey Lake) to17.16±4.97 µg/kg Serena Camp, respectively. Endrin aldehyde had high concentration values as compared to the parent compound endrin. Endrin aldehyde had values ranging from BDL to 128.38±35.94 µg/kg with the high value recorded at Serena Camp site.

Concentration of the 17 OCPs in soil for the seven sites are as illustrated in Figure 4.12 below and in Table A2.5 in Appendix II.

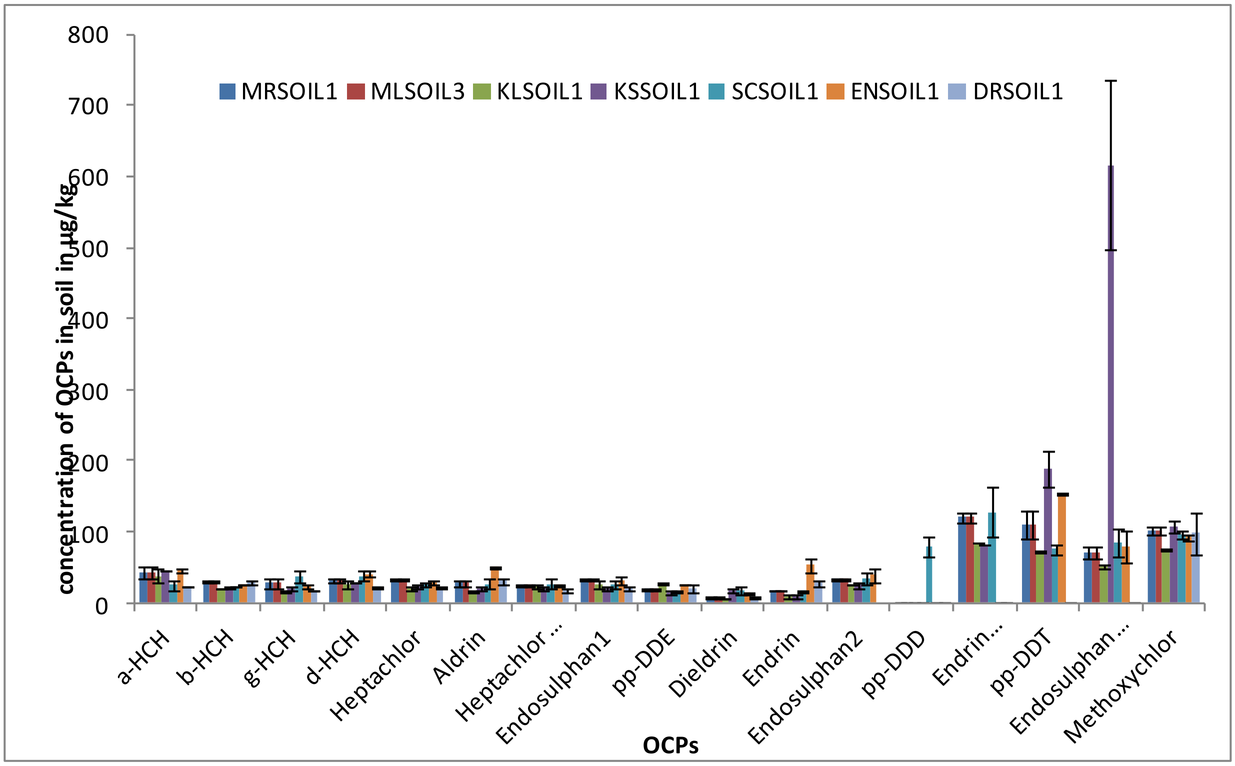


Figure 4.12: Concentrations of OCPs in soils during dry season

p,p'-DDT and its metabolites were the highest with concentration values ranging from BDL to 188.39±24.77 µg/kg at Kekopey Spring followed by *p,p'*-DDE. Endosulphan sulphate content was highest compared to the parent metabolite with concentration values ranging from BDL to 615.93±119.21 µg/kg at Kekopey Spring. The wet season recorded concentrations ranging from BDL and 13.92±0.21 µg/kg at Soysambu Ranch. Among the HCHs, β-HCH recorded highest values with concentrations ranging from BDL to 1.61±0.1 µg/kg. Almost all sites recorded values below detection limits for HCHs. Heptachlor epoxide recorded highest concentration values compared to heptachlor with concentrations ranging from BDL to 2.47±0.24 µg/kg at Mbaruk Lake. Endosulphan had concentration values ranging from BDL to 13.92±0.21 µg/kg with endosulphan sulphate recording highest values. DDT recorded highest concentration values amongst its isomers with concentrations ranging from BDL to 3.55±0.04 µg/kg at Elementaita North. Concentration of the 17 OCPs in soil for the seven sites are as illustrated in Figure 4.13 below and Table A2.6 in Appendix II.

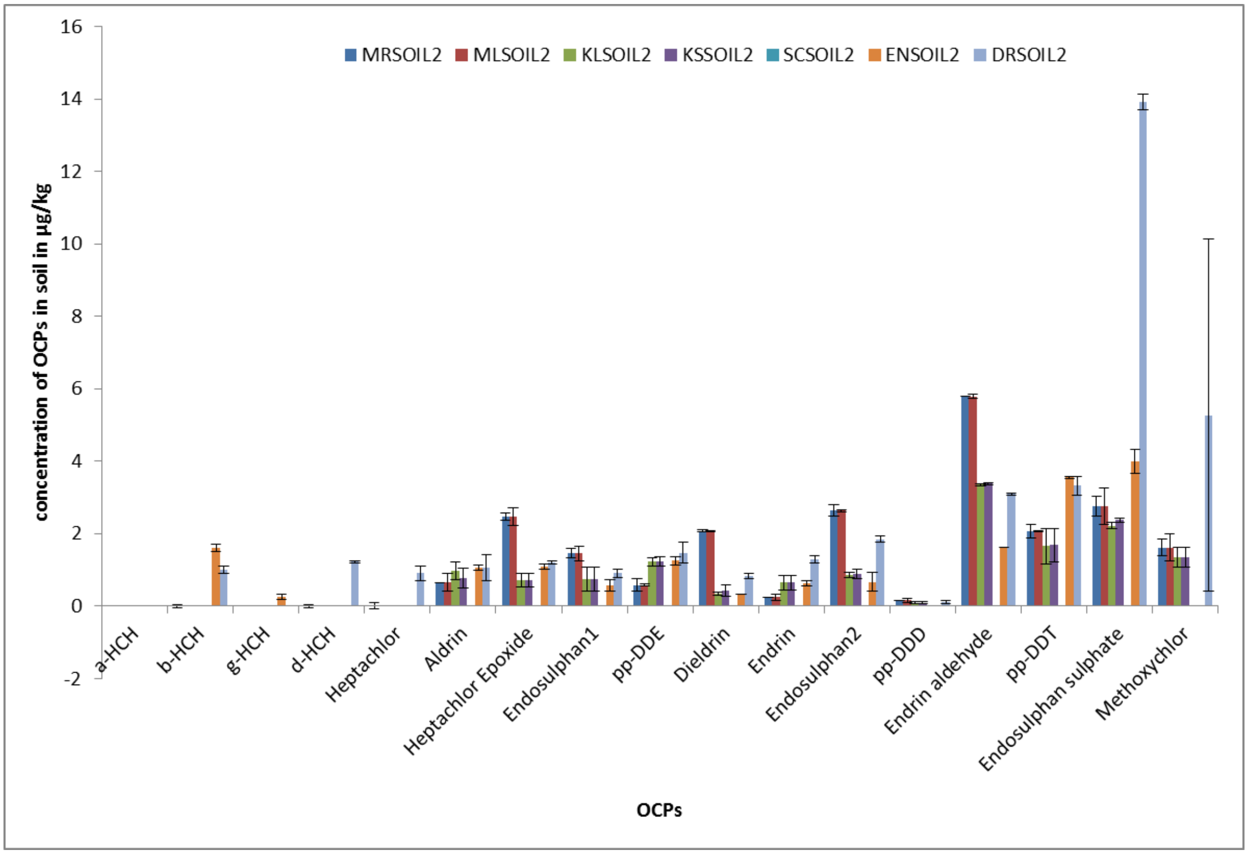


Figure 4.13: Concentrations of OCPs in soils during wet season

The sum of HCHs ranged between 90.73 to132.01 µg/kg with α-HCH recording the highest value and β -HCH recording the least value. Sum of DDT and its metabolites ranged from 39.49 to 360.76 µg/kg with DDT recording the highest value followed by DDE. Endosulphan recorded sum values ranging from 97.34 to 499.08 µg/kg with endosulphan sulphate recording the highest value. Heptachlor epoxide recorded higher value ∑87.03 µg/kg compared to its parent heptachlor ∑93.51 µg/kg.

Endosulphan sulphate is the major degradation product of technical endosulphan which is a mixture of two isomers (α and β) (Montgomery, 2000) and its presence in the area indicates that it is still in use illegally (PCPB, 1999).

The concentrations of α-HCH and its isomers remained generally low and almost constant during both seasons. This could be linked to their degradation in the environment and their solubility in water (Derek *et al.*, 2009).

Compared with HCHs, concentrations of endosulfan isomers and metabolite in the soils were higher and this might be because β-endosulfan and endosulfan sulfate persist in soil for over two years (Harris *et al.*, 2000).

High concentration of methoxychlor in soil and sediment samples compared to water samples was attributed to the poor solubility of the compound in water.

Since most of the OCPs were banned by Stockholm convection, their presence in the soil could be attributed to previous use and volatilization from the previous applied surfaces.

Endrin is persistent in soil and less susceptible to biodegradation and hydrolysis reactions hence high amounts in the soil. It is also affected by volatilization, photo degradation and heat transformation which transform it to endrin aldehyde hence accounting to the high concentration of endrin aldehyde as compared to its parent compound endrin.

Comparing both seasons, OCPs concentration was highest during dry season than in wet season, the low concentration during wet season could be because the OCPs were washed away into rivers by surface run-off and leaching (UNEP, 2003). Mbaruk River, Mbaruk Lake and Soysambu Ranch recorded significantly high concentration of OCPs in their soils. Despite the banning of most of them and restriction, it seems farmers are still applying them illegally as insecticides (PCPB, 1998). The presence of the industries around treating their products with insecticides (pole treatment) could have contributed to some of the OCPs detected. The OCPs residue in the soil was found to be below EPA maximum limits for soil as indicated in Appendix V Table A5.2. Lake Elementaita has no outlet and therefore any incoming organochlorines are likely to build up in the lake.

Comparing with other research done on OCPs in other regions, Musa *et al.* (2011) also detected OCPs in Lake Victoria whereby the concentration of OCPs in soil and sediment were found to be notably below EPA guidelines for soil and sediments. Okoya *et al.* (2013) reported OCPs levels in water and sediment that were significantly ($P < 0.05$) higher in dry season than wet season among the rivers of southwestern Nigeria. Other researchers who have reported OCPs residue in the environment include Getenga *et al.*, 2004; Wandiga *et al.*, 2002 and Gitahi *et al.*, 2002.

4.4 Heavy metal analysis

Heavy metals are among the most common environmental pollutants. Their existence and potential ecological effects on human health and environment has led to serious concerns. Living organisms require trace amounts of some heavy metals and slight changes either due to natural or anthropogenic factors in the concentration of these trace elements above the acceptable levels can pose a health risk (Mwamburi, 2003). The concentrations of copper, cadmium, zinc and lead were analyzed in surface water, soil and sediments collected from seven sites.

4.4.1 Heavy metals level in water

During dry season, heavy metal concentration ranged from 0.04±0.00 to 0.08±0.01mg/L Cd, 0.16±0.00 to 0.24±0.09 mg/L Pb, 0.08±0.05 to 3.13±0.56 mg/L Cu and 0.14±0.00 to 0.41±0.02 mg/L Zn. Concentration of heavy metals for the seven sites are as illustrated in Figure 4.14 below and in Table A3.1 in Appendix III.

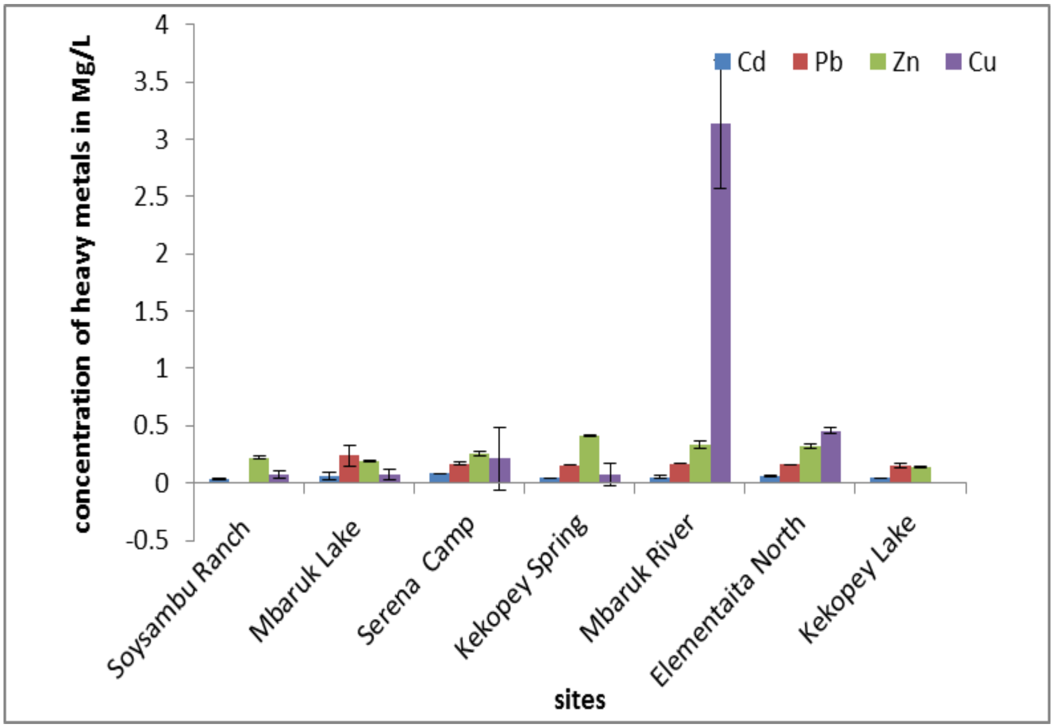


Figure 4.14: Average levels of heavy metals in water for dry season.

During wet season, heavy metal concentration ranged from 0.32±0.00 to 0.35±0.02 mg/L for Cd, 4.23±0.33 to 9.28±0.90 mg/L for Pb, and 4.66±0.06 to 8.49±0.40 mg/L for Cu. Concentration of heavy metals for the seven sites are as illustrated in Figure 4.15 and in Table A3.2 in Appendix III.

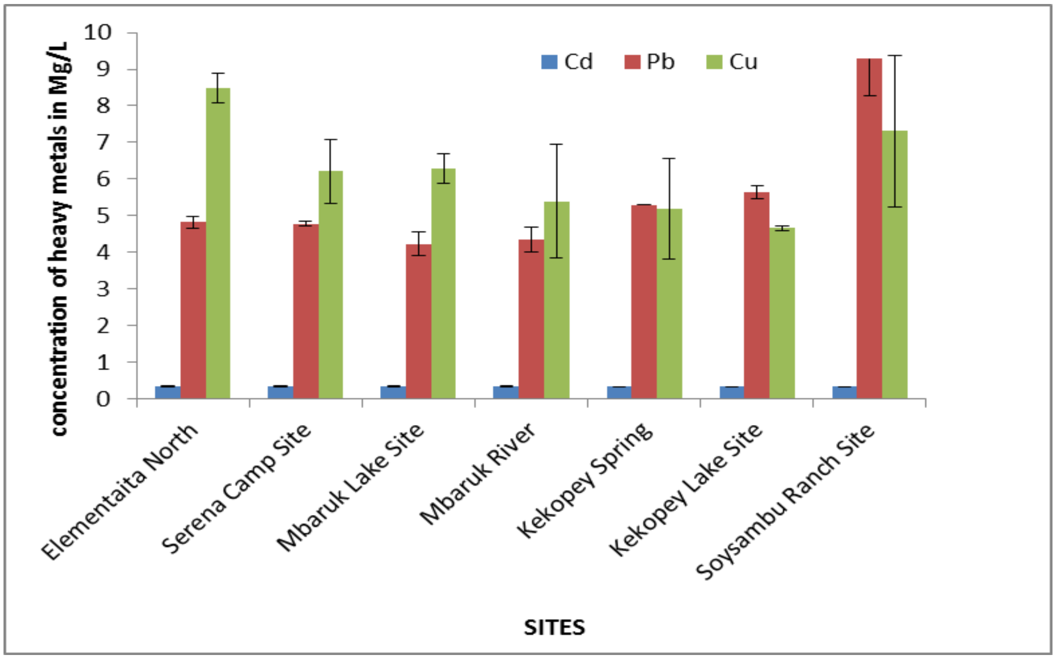


Figure 4.15: Average levels of heavy metals in water for wet season.

4.4.1.1 Cadmium

In aquatic system, sources of cadmium can include runoff from agricultural areas where phosphate fertilizer containing cadmium was applied (Huang *et al.*, 2004). The highest concentration of cadmium in water was recorded at Serena Camp (0.08±0.01 mg/L), while Kekopey Spring recorded concentration values BDL. Cadmium concentration at Mbaruk River ranged between 0.05±0.01 and 0.34±0.01 mg/L, Mbaruk Lake (0.06±0.03 and 0.34±0.01 mg/L), Kekopey Spring (0.04±0 and 0.32±0.0 mg/L), Kekopey Lake (0.05±0.01 and 0.32±0.01 mg/L), Serena Camp (0.08±0.01 and 0.338±0.01 mg/L), Soysambu Ranch (0.04±0.0 and 0.33±0.01 mg/L) and Lake Elementaita North (0.06±0.01 and 0.35±0.02 mg/L). The presence of cadmium could have been attributed to high mobility of Cd (weak in binding to soil and sediment) (Lawler and Tippings, 2003) which could also result to increased leaching. From the results obtained cadmium in water samples was found to be above CWQGs maximum guideline value of 0.005 mg/L recommended for the protection of aquatic life (CWQGs, 2002).

4.4.1.2 Copper

Mean concentration of copper ranged from 3.13 ± 0.55 mg/L to 8.48 ± 0.40 mg/L. The concentration of copper at Mbaruk River ranged between 3.13±0.56 and 5.39±1.55 mg/L, Mbaruk Lake (0.08±0.05 and 6.29±0.40 mg/L), Kekopey Spring (0.08±0.09 and 5.19±1.38 mg/L), Kekopey Lake (0.14±0.01 and 4.66±0.06 mg/L), Serena Camp (0.21±0.28 and 6.21±0.86 mg/L), Soysambu Ranch (0.07±0.04 and 7.30±2.07 mg/L) and Lake Elementaita North (0.46±0.02 and 8.49±0.40 mg/L).

Copper can enter the aquatic ecosystems from different sources including; Copper compounds used in fungicides, algaecides, insecticides, wood preservatives, electroplating and azo dye manufacture (Akan *et al.*, 2010). High concentration of Copper was recorded at Elementaita North and could be attributed to agricultural activities and the presence of Cabro Ltd which treats poles with preservatives for fungicides and insecticides, and the use of fertilizers. The mean concentrations of Cu were above CWQG guideline (CWQG, 2002).

4.4.1.3 Lead

The concentration of lead in water samples was highest at Kekopey Lake (5.639±0.17 mg/L) and lowest at Elementaita North (0.16±0.02 mg/L). Lead concentrations at Mbaruk River ranged between 0.17±0.01 and 4.346±0.33 mg/L, Mbaruk Lake (0.24±0.09 and 4.23±0.33 mg/L), Kekopey Spring (0.16±0.01 and 5.29±0 mg/L), Kekopey Lake (0.16±0.02 and 5.64±0.17 mg/L), Serena Camp (0.17±0.01 and 4.78±0.07 mg/L), Soysambu Ranch (0±0 and 9.28±0.9 mg/L) and Lake Elementaita North (0.161±0 and 4.816±0.17 mg/L). The concentrations recorded were above CWQGs guideline limits (CWQGs, 2002).

4.3.1.4 Zinc

The concentration of zinc in water was highest at Kekopey Spring (0.41±0.02 mg/L) and lowest at Kekopey Lake (0.14±0.00 mg/L). The mean concentration at Mbaruk River was 0.337±0.03 mg/L, Mbaruk Lake (0.19±0.01 mg/L), Kekopey Spring (0.41±0.02 mg/L), Kekopey Lake (0.14±0.00 mg/L), Serena Camp (0.26±0.02 mg/L), Soysambu Ranch (0.22±0.02 mg/L), and Lake Elementaita North (0.33±0.02 mg/L). From the results the concentrations were below the CWQGs maximum guideline limits (CWQGs, 2002).

4.4.2 Heavy metals level in sediment

During dry season, concentration of heavy metals ranged from 2.06±0.42 to 2.89±0.59 mg/kg for Cd, BDL to 3.14±0.49 mg/kg for Pb, 2.93±0.66 to 134.07±27.05 mg/kg for Cu, and 45.73±9.44 to 106.28±2.89 mg/kg for Zn. The concentrations of heavy metals measured in sediments from the seven sites are as illustrated in Figure 4.16 below and in Table A3.3 in Appendix III.

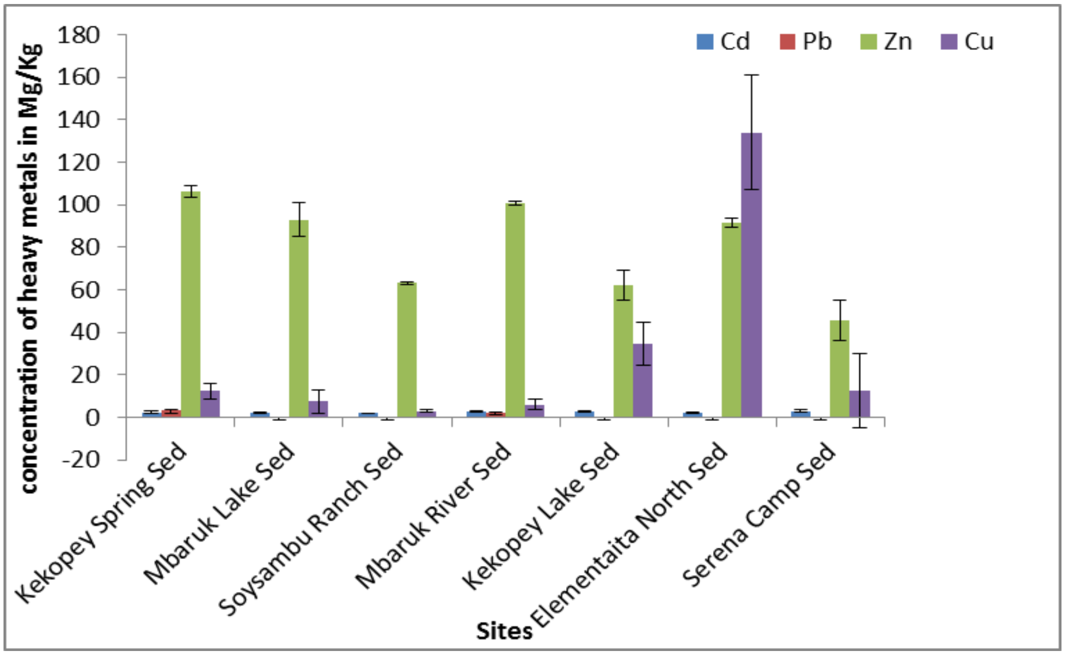


Figure 4.16: Average levels of heavy metals in sediment for dry season.

During wet season, concentration of heavy metals ranged from 14.97±0.01 to16.07±0.017 for Cd, 343.60±4.20 to 48.75±16.61 for Pb and 15.04±1.15 to 861.76±80.58 mg/kg for Cu. The concentrations of heavy metals in the seven sites are as illustrated in Figure 4.17 below and in Table A3.4 at Appendix III.

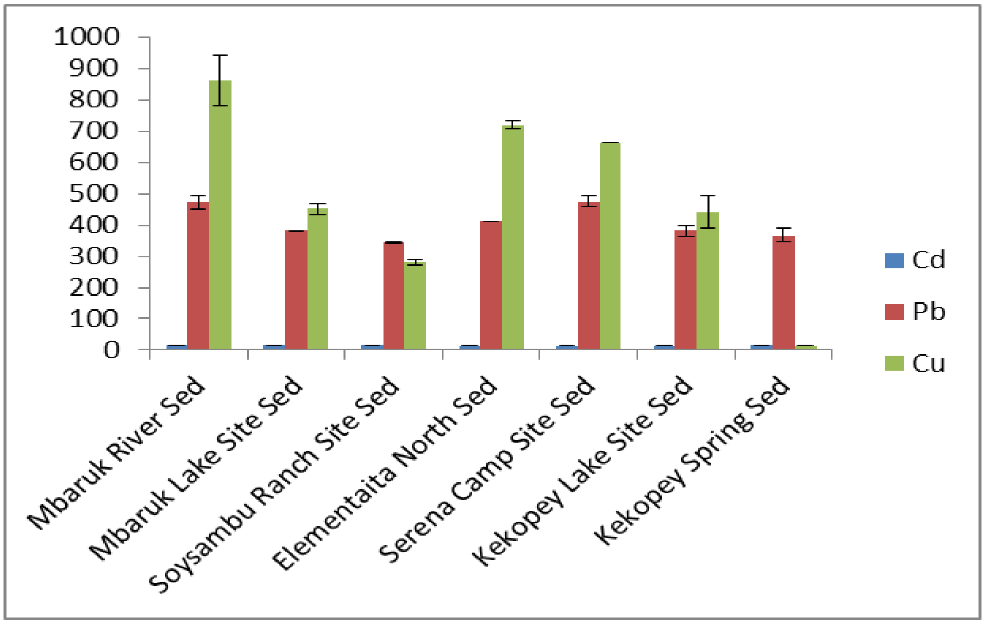


Figure 4.17: Average levels of heavy metals in sediment for wet season.

4.4.2.1 Cadmium

The highest concentration of cadmium was recorded in samples from Kekopey Spring (16.07±0.02 mg/kg), whereas the lowest was 2.06±0.42 mg/ kg recorded in sediments from lake Elementaita North. The concentration of cadmium at Mbaruk River ranged between 2.72±0.17 mg/kg and 14.99±0.01 mg/kg, Mbaruk Lake (2.24±0.17 and 15.53±0.01 mg/kg), Kekopey Spring (2.36±0.50 and 16.07±0.17 mg/kg), Kekopey Lake site (2.89±0.42 and 15.04±0.00 mg/kg), Serena Camp (2.89±0.59 and 15.28±0.01 mg/kg), Soysambu Ranch (2.07±0.08 and 15.11±0.01 mg/kg), and Lake Elementaita North (2.06±0.42 and 14.97±0.01 mg/kg).

4.4.2.2 Copper

The concentration of copper in sediment ranged between 2.92±0.66 mg/kg and 861.76±80.58 mg/kg measured in samples from Soysambu Ranch and Kekopey Spring, respectively. The concentration of copper at Mbaruk River ranged between 719.31±11.51 and 5.915±2.51 mg/kg, Mbaruk Lake (7.43±5.44 and 450.69±17.27 mg/kg), Kekopey Spring (861.76±80.58 and 12.4±3.56), Kekopey Lake (34.70±10.29 and 662.33±0.00), Serena Camp (12.74±0.17 and 15.04±1.15), Soysambu Ranch (2.93±0.66 and 281.78±8.63), and Lake Elementaita North (134.07±27.05 and 440.85±50.76), respectively.

The presence of copper in sediment could be attributed to the overlying water and leaching from the soil as a result of runoff and wet and dry deposition. The high concentration of copper in Mbaruk River could be attributed to agricultural activities from the upper side of the area especially the use of fertilizers, fungicides and insecticides. Whereas several studies have been done locally and internationally on the levels of copper in sediments from different regions, no particular trends have been evident due to mixed results of low and high levels in different studies (Oyoo-Okoth *et al*., 2010). For instance, Ochieng *et al*. (2008) reported concentrations of copper in Lake Victoria Winam gulf ranging from 3.90 – 150.20 mg/kg , whereas in the Northern Delta Lakes the concentration ranged from 36.77 – 315.36 mg/kg was found (Saeed and Shaker, 2008).

4.4.2.3 Lead

Lead concentration in sediment ranged between BDL and 475.75±6.61 mg/kg. Most of the sites recorded values below detection limit (0.0005) during dry season. Lead concentration at Mbaruk River ranged between (2.29±0.23 and 472.82±20.76 mg/kg), Mbaruk Lake (0.00±0.00 and 381.78±0.00 mg/kg), Kekopey Spring (3.14±0.49 and 367.09±20.76 mg/kg), Kekopey Lake (0.00±0.00 and 475.75±16.61 mg/kg), Serena Camp (0.00±0.00 and 362.09±2.76 mg/kg), Soysambu Ranch (0.00±0.00 and 343.6±4.2 mg/kg), and Elementaita North (0.00±0.00 and 381.78±16.61 mg/kg).

The high concentration of lead in the lake sediment indicated potential anthropogenic sources of contamination. There are high chances that since the lake is situated along the busy Nairobi-Nakuru highway, the vehicle emissions could be one of the most probable sources of lead contamination.

The mean lead concentrations ranged from 2.29 ± 0.49 to 475 ± 16.61 mg/kg in Kekopey Spring and Lake Elementaita Serena camp, respectively. Sources of lead in sediments may possibly include industrial wastes and from water pipes, lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors and plastic stabilizers (WHO, 2004; Akan *et al*., 2010).

4.4.2.4 Zinc

The highest mean zinc concentrations were recorded at Kekopey Spring (106.27 ± 2.89 mg/kg), whereas the lowest concentration values at Serena Camp (45.72 ± 9.43 mg/kg). Zinc concentration at Mbaruk River was 100.56±0.94, Mbaruk Lake site (93.08±8.09), Kekopey

Spring (106.28±2.89 mg/kg), Kekopey Lake (61.91±7.02 mg/kg), Serena Camp (45.73±9.44 mg/kg), Soysambu Ranch (63.13±0.42 mg/kg) and Lake Elementaita North (91.35±2.12 mg/kg).

The source of zinc concentrations in sediments could be from zinc carbonates used as pesticides (Anglin-Brown *et al.*, 1995). Compared to other studies, mean zinc levels in the current study area were lower than 96.2 - 229.6 mg/kg recorded in five Rift Valley lakes in Kenya (Ochieng *et al.*, 2007). Concentration of heavy metals in sediments was found to be higher during wet seasons than in dry season. The high concentration of heavy metals in the sediment might have been due to leaching from soil and input from runoff.

4.4.3 Heavy metal levels in soils.

During the dry season, the concentration of heavy metals ranged from 2.78±0.08 to 6.86±0.17 mg/kg for Cd, 10.38±0.99 to 17.97±0.47 mg/kg for Pb, 2.96±0.39 to 35.79±8.87 mg/kg for Cu, and 57.95±6.68 to 86.95±5.55 mg/kg for Zn. The concentrations of heavy metals in the seven sites are shown in Figure 4.18 below and in Table A3.5 in Appendix III.

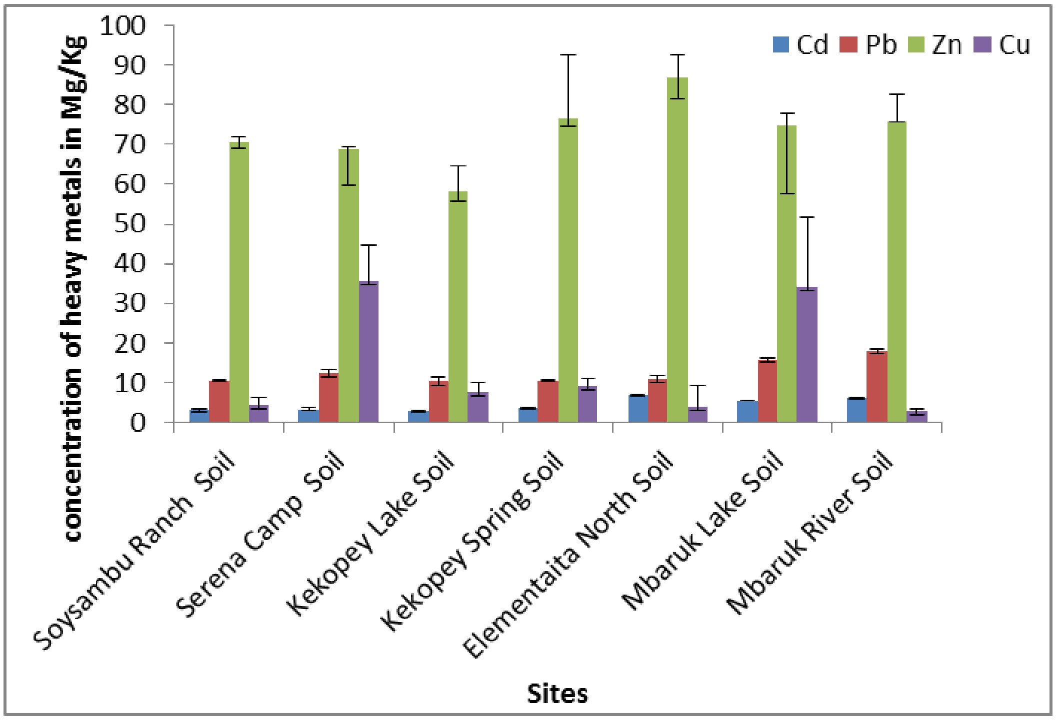


Figure 4.18: Average levels of heavy metals in soil for dry season.

During wet season, concentration of heavy metals ranged from 15.60±0.75 to 29.75±0.14 mg/kg for Cd, 308.36±29.07 to 502.18±20.76 mg/kg for Pb and 249.22±60.44 to 865.83±5.76 mg/kg for Cu. The concentrations of the heavy metal for the seven sites are shown in Figure 4.19 below and in Table A3.6 at Appendix III.

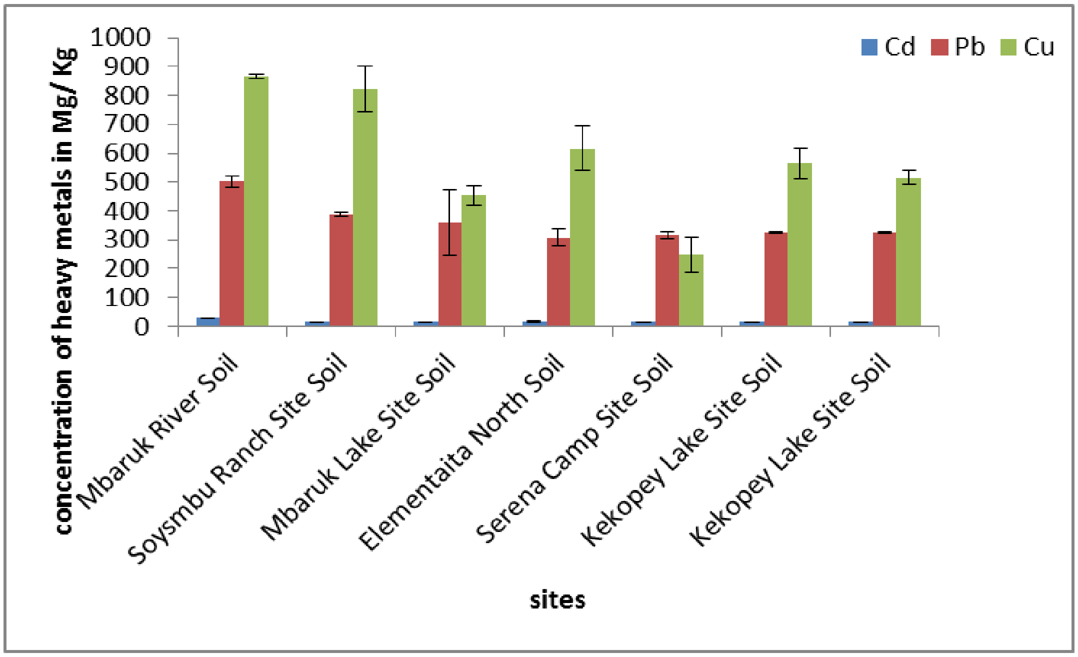


Figure 4.19: Average levels of heavy metals in soil for wet season.

4.4.3.1 Cadmium

Cadmium concentration in soil ranged between 2.78±0.08 mg/kg and 29.75±0.14 mg/kg dry weight. Cadmium concentration in Mbaruk River ranged between 6.09±0.25 and 29.75±0.14 mg/kg, followed by Mbaruk Lake site (5.56±0.00 and 16.09±0.36 mg/kg), Kekopey Spring (3.43±0.17 and 15.91±0.29 mg/kg), Kekopey Lake (2.78±0.08 and 15.60±0.75 mg/kg), Serena Camp (3.25±0.42 and16±0.08 mg/kg), Soysambu ranch (3.01±0.25 and 16.52±0.11 mg/kg), and Lake Elementaita North (6.86±0.17 and 16.39±0.48 mg/kg). The high cadmium mean level may have been contributed by cadmium-containing fertilizers and sewage sludge (Jensen and Bro-Rasmussen, 1992). Cadmium is widely used in paints and plastics and therefore there is also possibility of some of it entering the Lake in the form of industrial or municipal effluent. Cadmium is much less mobile in soils than in water and its solubility, adsorption and distribution is governed by soil pH, soluble organic matter and competition from other metal ions (Lawler and Tippings, 2003).

4.4.3.2 Copper

Copper concentration in soil at Mbaruk River ranged between 2.96±0.39 and 865.83±5.76 mg/kg, Mbaruk Lake (34.26±17.26 and 454.76±34.58 mg/kg), Kekopey Spring (9.21±2.08 and 515.81±23.02 mg/kg), Kekopey Lake (7.73±2.11 and 564.65±51.80 mg/kg), Serena Camp (35.795±8.87and 249.22±60.44 mg/kg), Soysambu Ranch (4.305±1.88 and 821.06±80.58 mg/kg), and Lake Elementaita North (4.03±5.38 and 615.52±77.71 mg/kg), respectively. The highest mean concentration was recorded at Mbaruk River (865.83±5.80 mg/kg). This might have been attributed to the discharge from the nearby industries using copper in its processes and agricultural effluents. Although copper is classified as an essential element required in trace amounts, high levels >25 mg/kg may lead to health effects. The mean copper concentrations in the study area were above the WHO standard values of 100 mg/kg for the survival of aquatic organisms (WHO, 2004).

4.4.3.3 Lead

Lead is insignificantly important in physiological role in living organisms and at a concentration above 50-400 ppm (35 mg/kg) in soil is toxic (Mwamburi, 2003). Lead concentration was found to range from 10.37±0.99 mg/kg to 502.18±20.76 mg/kg weight in the soil at Lake Elementaita Kekopey and Mbaruk River, respectively. Lead concentration at Mbaruk River ranged between (17.97±0.47 and 502.18±20.76 mg/kg), Mbaruk Lake (15.77±0.69 and 358.28±112.13), Kekopey Spring (10.59±0.19 and 325.98±4.2 mg/kg), Kekopey Lake (10.377±0.99 and 325.98±4.2 mg/kg), Serena Camp (12.36±0.99 and 314.23±12.46 mg/kg), Soysambu Ranch (10.49±0.19 and

387.65±8.31 mg/kg), and Lake Elementaita North (11.04±0.88 and 308.36±29.07 mg/kg), respectively.

Most of the sites recorded concentration higher than WHO maximum guideline value for lead in soil (35 mg/kg) (WHO, 2004). The high concentration of lead at Mbaruk River might have been due to slightly lower pH. At low pH the heavy metal concentrations are known to be higher and toxic (Connell *et al*., 1984; Muinde, 2012). Since the river flow cuts along the busy road this could also lead to spillage of leaded gasoline from cars especially when there is high traffic along the Nakuru-Nairobi highway. Wet deposition, industrial and agricultural discharge entering the river also can contribute. Lead is non-essential element and excess of it in the human body can produce a damaging effect on the kidney, liver and nervous system, as well as effects on blood vessels and other tissues (Sharma and Pervez, 2003).

4.4.3.4 Zinc

Zinc concentration in soil ranged between 57.95±6.68 and 86.95±5.6 mg/kg for Kekopey Lake and Lake Elementaita North, respectively. The concentration in soil samples at Mbaruk River was 75.86±6.81 mg/kg, Mbaruk Lake (74.84±3.16 mg/kg), Kekopey Spring (76.66±16.03 mg/kg), Kekopey Lake site (57.95±6.68 mg/kg), Serena Camp (68.713±0.72 mg/kg), Soysambu Ranch (70.76±1.04 mg/kg) and Lake Elementaita North (86.95±5.55 mg/kg), respectively. The results on zinc concentrations in all the sampling sites did not exceed the WHO recommended limit of 123 mg/kg (WHO, 2008). Zinc concentrations in soil for wet season were not analyzed.

In general, there was higher concentration of heavy metals during wet season than it was in dry season. Rainfall lowers the pH of the soil hence metal concentration in the soil becomes high.

Heavy metals are neither created nor destroyed but are redistributed. This distribution is not even, hence, heavy metals levels in soils vary in amounts from either natural processes or pollution factors. These consequently distribute into the environment through human activities which include manufacturing, farming, mining and uses of leaded gasoline.

Comparing this data with other researchers, Ochieng *et al.* (2007) recorded high concentration levels of heavy metals in the three great lakes of Riftvalley. Nzeve *et al.* (2014) also recorded heavy metal concentrations in sediment below WHO maximum limits in Masinga reservoir.

4.5 Fluoride

Fluoride concentration in Lake Elementaita ranged between 1.70±0.28 mg/L and 977.80±0.01 mg/L at Lake Elementaita North and Mbaruk River sites, respectively for dry season. Seasonal variation was not determined. The concentration at Lake Elementaita was relatively high in all sites except for Mbaruk River. The low concentration at Mbaruk River was due to high flows of the water which dilutes the fluoride concentration. The high concentrations in the lake and other site could have been attributed by the volcanic rocks due to rift formation within the area. The values obtained were extremely above the USEPA recommended limits of 1.5 ppm (USEPA, 1976). Table 4.5 below illustrates average fluoride concentration in Lake Elementaita water.

Table 4.6: Average fluoride concentration in Lake Elementaita water.

Sites	**Concentration (mg/L)**
Soysambu Ranch	646.3±0.00
Kekopey Spring	100±0.01
kekopey lake site	104.2±0.03
mbaruk lake site	622.90±0.00
Serena Camp	654.30±0.01
Lake Elmentaita North	977.80±0.01
Mbaruk River	1.70±0.28

N=3 mean± standard deviation

Comparison of fluoride concentrations in water from different sites

The highest fluoride levels were detected in water from the Lake with Lake Elementaita North taking the lead, followed by Soysambu, Serena Camp and Mbaruk lake sites. Figure 4.20 shows the comparison of fluoride levels in different sites.

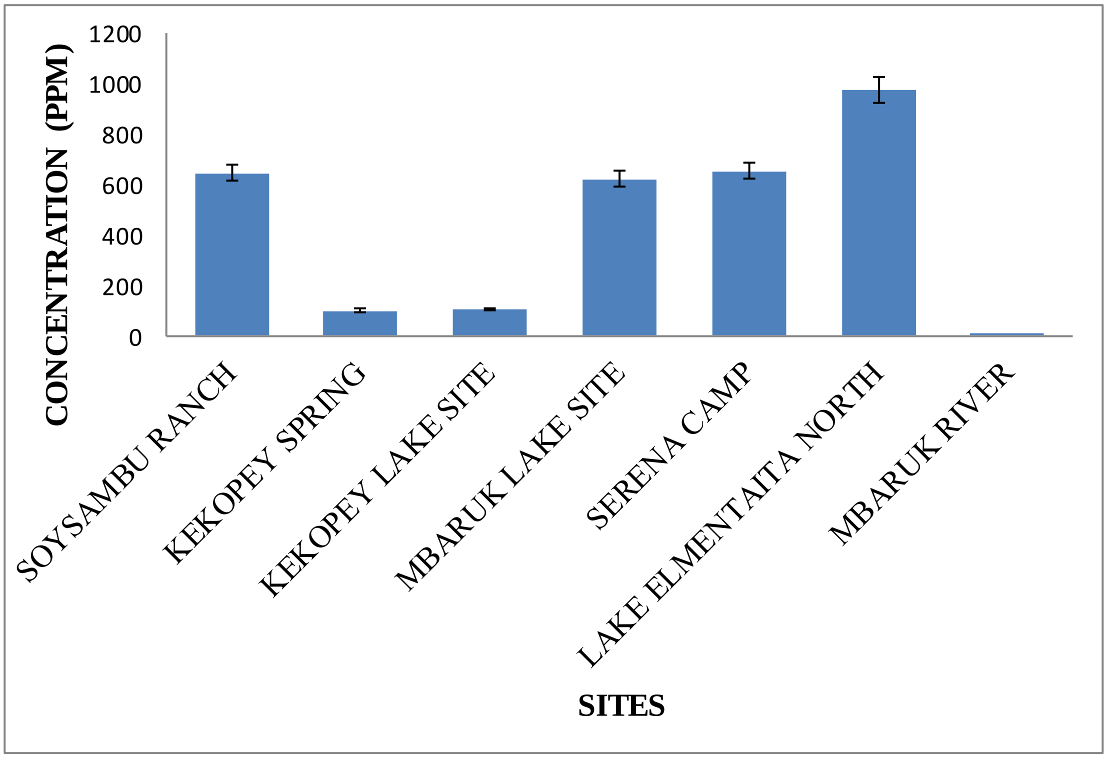


Figure 4.20 Average fluoride concentration in water

4.6 Correlation analysis

SPSS was applied for determination of Pearson's correlation coefficients which have numerical values (r) ranging between -1.000 to +1.000. These values represent the linear relationship between two data sets (Situma, 2010). Positive values indicate direct relationship in variables while negative values indicate inverse variation relationship. The strength of the linear correlation of the variables is determined by the numerical value of r, whereby zero values implies no correlation between the data sets, below 0.5 are considered to be weak, while those above 0.5 are strong. The significance of the correlations is indicated by the p value. Correlations are significant if $p<0.005$ and are not significant if $p >0.005$ (APA, 2001).

4.6.1 Correlation of pesticides in different seasons per matrix

OCPs in soil in dry season indicated a negative correlation with those in water and sediment in both seasons. OCPs in soil for wet season recorded a strong positive correlation in both seasons.

A positive correlation of OCPs during wet season indicates that at high concentration, OCPs are released from the soil to sediment by leaching and surface runoff. They are also released from sediment to water by desorption, redistribution and resuspension (Table A5.1 Appendix V).

4.6.2 Correlation of pesticides across matrices

The correlation coefficient values (p) of OCPs in water were positive with those in sediment (0.692) and soil (0.242) as illustrated in (Table A5.2 in Appendix V). A positive relation can be attributed to desorption to overlying water by sediments when they have been redistributed at high concentration or adsorption on sediments' organic carbon since OCPs are hydrophobic. Similarly, since OCPs have high affinity to organic matter, they could be released from the soil to sediment by leaching and surface runoff at high concentration or evaporation due to high volatility.

4.6.3 Correlation of heavy metals in different seasons per matrix

The correlation coefficient values (*p*) for heavy metals in water were positive with those in sediment and soil during both seasons. Most significant correlation occurred during the wet season which could be attributed to heavy metals being released from soil to sediment by leaching and surface runoff. From sediment, heavy metals can be released to water by desorption and solubilizing.

During wet season, there is high concentration and flow of heavy metals into the water phase and heavy metal resuspension and desorption in the sediment phase (Milenkovic *et al.*, 2005; Dallas and Day, 1998) (Table A5.3 Appendix V).

4.6.4 Correlation of heavy metals across matrices

Heavy metals in soil had a strong positive correlation with those in sediment except those in water. This could be attributed to the fact that heavy metals get to the sediment through leaching, desorption and resuspension. They can also be released from sediment to water phase through desorption (Milenkovic *et al.*, 2005) (Table A5.4 Appendix V).

4.6.5 Correlation of nutrients in different seasons per matrix

Nitrates in water during wet season had a positive correlation with those in sediment in the dry season (0.155) and soil in dry season (0.98). During wet season, there was significant runoff from the agricultural area. Due to high mobility of nitrate in water, it is leached or percolated from the soil to the sediments then to the water by sorption. Nitrates also get to water phase by surface runoff during wet season (Neitsch, 2002) (Table A5.5 Appendix V).

Phosphates in water had a positive correlation with those in soil and sediment in both dry and wet seasons. Due to the low mobility of phosphate in soil, it gets to the sediment by diffusion and leaching during wet season and by leaching and surface runoff to water phase (Neitsch, 2002) (Table A5.6 Appendix V).

4.6.6 Correlation of nutrients across matrices

Nitrates in water had a positive correlation with those in sediment (0.509) and negative correlation with those in soil (-0.542). In water, nitrates get to the sediment by absorption and sedimentation hence a positive correlation (Table A5.7 Appendix V).

Phosphates in water had a positive correlation with those in sediment and soil with r values (0.168) and (0.481), respectively. Phosphates moves from soil to sediment by diffusion and to the water by surface runoff (Table A5.8 Appendix V).

4.6.7 Correlation of pesticides and selected physico-chemical properties per matrix

There was a negative correlation between OCPs in water with those of TDS, pH and electrical conductivity as indicated by the negative Pearson's correlation(r) values. A direct relationship was shown by TSS with r value of 0.439. OCPs tend to adsorb to the organic particles in water hence the positive correlation of OCPs with TSS.

In sediment, no significant effect between the physicochemical properties and OCPs were observed. This could be attributed to the hydrophobic behavior of most OCPs hence not likely to be affected by pH and electrical conductivity.

Total organic carbon, total nitrogen and pH showed a positive correlation with OCPs in soil ($p<0.05$). But electrical conductivity did not have a significant effect. The r values were 0.337, 0.048 and 0.240 for total organic carbon, total nitrogen and pH, respectively as illustrated in table A5.11. Table A5.9, A5.10, A5.11 in Appendix v illustrates correlations of levels of ∑OCPs with physico-chemical parameters in water, sediment and soil.

4.6.8 Correlation of heavy metals and selected physico-chemical properties per matrix

Heavy metals in water had a weak positive correlation towards TDS except for zinc and copper . Electrical conductivity had a significant relationship with heavy metals in water except for zinc and copper. There was a significant relationship between heavy metals and pH and TSS except for lead which had a negative correlation. At high pH some metals like cadmium and lead precipitate forming complexation products which influence metal toxicity by chemical speciation in water and sediment. During dry season, heavy metal concentrations are reduced from water to sediment through precipitation and sedimentation (Rashed, 2001).

In sediment, a positive correlation was revealed between heavy metals and those of pH except for lead and copper which had a negative correlation. Total nitrogen and phosphorus had a negative correlation with the heavy metals while total organic carbon had a weak positive correlation towards heavy metals. Electrical conductivity had a negative correlation towards heavy metals except for copper which had a positive correlation.

Heavy metals in soil had weak positive correlation with pH and a strong positive correlation with total nitrogen and total organic carbon. pH had a strong positive correlation towards total nitrogen and total organic carbon and a weak correlation towards electrical conductivity. Table A5.12, A5.13, A5.14 at Appendix V shows the results of correlation of levels of ∑heavy metals with physico-chemical parameters in water, sediment and soil.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

All the 17 Organochlorine pesticide residues analyzed were detected in water, sediment and soil samples from Lake Elementaita drainage basin. The concentrations of OCPs were highest in soils and sediments during dry season, whereas in water, the residues were highest during wet season.

Pesticide residues in water samples were below the WHO maximum guideline limits suggesting no significant concern to cause immediate health effects with respect to the 17 analysed pesticides.

Heavy metals cadmium, copper, zinc and lead were detected in water, sediment and soil samples from Lake Elementaita drainage basin at different concentrations. There was higher concentration of heavy metals during wet season than in dry season. Copper and lead concentrations were above the WHO maximum limit for water, while zinc and cadmium were below WHO maximum limits.

Phosphates and nitrates levels were below WHO maximum limits for aquatic life. The concentrations were higher during dry season compared to the wet season.

Nutrients concentrations in water, sediment and soil were found to be higher in the lake compared to Mbaruk River and Kekopey Spring. Sediments and soils recorded high values for nitrates in Mbaruk River followed by Kekopey Spring.

The 17 Organo chlorine pesticides residues analyzed recorded high values in the lake compared to Mbaruk River and Kekopey Spring, respectively. Soil samples recorded high concentrations of OCPs.

Heavy metal concentrations were found to be high in the river followed by the Kekopey Spring then the lake itself.

The physico-chemical parameters TDS, TSS, EC, temperature and pH were found to be above WHO maximum limits for aquatic life. No much variation was recorded for temperature in all sites whereas Kekopey Spring recorded PH below the WHO maximum limits.

Fluoride concentration was found to be extremely high – exceeding WHO maximum limits for water samples with the lake recording the least values.

5.2 Recommendations

1) Research should be carried out to determine the levels of other pesticides such as organophosphates, pyrethroids commonly used at present.
2) Studies should be conducted to determine the levels of OCPs in river fish and flamingoes.
3) There is need to find out if the nearby pole treatment company has any influence on high copper values in water, sediment and soil samples.
4) Research should be done to show the extent at which the river and the spring influence the concentration of heavy metals in the lake.
5) Continuous monitoring of OCPs in the lake.
6) Results from physico-chemical parameters revealed values above WHO maximum limits for TDS, TSS, EC, pH and temperature for water. Since the influence is due to the carbonative

nature and high vaporization rates of the lake drainage basin, alternative use of Lake Elementaita waters should be studied for instance for tourist attraction activities, whereas the river water can be explored for domestic and agricultural purposes. Also TSS can be reduced by ensuring the vegetation cover around the area is intact by introducing even livestock grazing.

7) Alternative water sources to be used by residents such as rain water, surface water and low fluoride ground water to prevent dental and skeletal fluorosis.
8) Policy makers should put in place an environmental monitoring program and mitigation strategies of reducing the heavy metal pollutants and hence manage the water quality status within the lake basin.

REFERENCES

Abrams, M.M. and Jarrell, W.M., (1995) Soil phosphorus as a potential nonpoint source for elevated stream phosphorus levels. *Journal of Environmental Quality*, 24; 132-138.

Adeka, J.E., Strobl, R.O. and Becht, R., (2008) *An environmental system analysis of lake Elmentaita, Kenya with reference to water quality.* The 12th world lake conference 1365-1372 pp. Institute of environment and sustainability unit H05, 7 P 272, 1-2012 Ispran (VA) Italy.

Afful, S., Anim, A.K. and Serfor-Armah,Y., (2010) Spectrum of organochlorine pesticide Residues in fish samples from the Densu Basin. Res. J. *Environ .Earth Sci*., 2(3): 133-138.

Akan, J.C., Abdulrahman, F.I., Sodipo, O.A., Ochanya, A.E. and Askira, Y.K., (2010) Heavy metals in sediments from river Ngada, Maiduguri Metropolis, Borno state, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*. 2((9); 131-140.

Alamirew, D., Korme, T., Olago, D. and Barongo, J., (2007) Geology, Hydrogeology and Hydrochemistry of the Nakuru-Elmenteita-Naivasha watershed, Kenyan Rift.University of Nairobi, Department of Geology/ Geological Survey of Ethiopia, Lecture.

Al-Jayyousi, O. and Shatnawi, M., (1995) Evaluating future water policies in Jordan using decision support systems, *International Journal of Water Resource Development*. 11(3); 315-330.

Anglin-Brown, B., Armour-Brown, A and Lalor, G.C., (1995) Heavy metal pollution in Jamaica: Survey of cadmium, lead and zinc concentrations in the Kintyre and hope flat districts. DOI: 10.1007/DF00146708. *Environ. Geochem. Health*, 17:51-56.

American Psychological Association, (2001) Publication manual of the American Psychological Association (5th ed.). Washington, DC.

Arias-Estevez, M., Lopez-Periago, E., Martinez-Carballo, E., Simal-Gandara, J., Mejuto, J. C. and Garcia-Rio, L., (2008) The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agriculture, Ecosystems and Environment, 123;* 247-260.

Authman, M.M.N., (2008) *Oreochromis niloticus* as a biomonitor of heavy metal pollution with emphasis on potential risk and relation to some biological aspects. *Global veteria* **2** (3):104-109.

Avery, B.W. and Bascomb, C.L., (1982) Soil Survey Laboratory Mathods Harpenden, UK.

Ayenew, T. , (2005) Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. *SINET: Ethiopian Journal of Science* **28**; 171-188.

Barbash, J.E. and Resek E.A., (1996) Pesticides in ground water: Distribution, trends and governing factors. Michigan: *Ann Arbor Press*.

Barlas N. E., (2002) Determination of Organochlorine Pesticide Residues in Water and Sediment Samples in Inner Anatolia in Turkey. Bull. Environ. Contam. Toxicol. (**2002) 69**:236–242 © 2002 Springer-Verlag New York Inc.

Bartram J., and Balance R., (1996) *Water quality monitoring*. A practical guide to the design and implementation of fresh water quality studies and monitoring programmes. Chapman & Hall, London,United Kingdom.

Bleifuss P.S., Hanson G.N. and Schoonen M.A.A., (2003) *Tracing sources of nitrate in the Long Island Aquifer system.* Access from the World Wide Web on May 2006 from http:www.geo.sunysb.edu/reports/bleisfuss/.

CCME (Canadian Council of Ministers of the Environment), (2003) Canadian water quality guidelines for the protection of aquatic life: summary tables.updated.In : Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg.1-16.

Canberra, Australian Government Publishing Service (CAGPSA), (1994) Reducing lead exposure in Australia,: risk assessment and analysis of economic, social and environmental impacts.

CEEP, (2007) *Phosphates: a good environmental solution for detergents*, pp 1-3.http:www.ceep-phosphates. (accessed November 20,2015).

Centers for Disease Control and Prevention. Atlanta, (1991) *Preventing lead poisoning in young children:* a statement by the, GA, Centers for Disease Control and Prevention.

Cerrillo, I., Granada, A., Espinosa, M., Olmos, B., Jimec nez, M., Cano, A and Olea-Serrano, M., (2004) Endosulfan and its metabolites in fertile women placenta, cord blood and human milk. *Environmental Research* **98;** 233-239.

Chattopadhyay, B., Roy, U. and Mukhopadhyay, K., (2010) Mobility and Bioavailability of Chromium in the Environment: Physico-Chemical and Microbial Oxidation of Cr (III) to Cr (VI). *Sci. Environ.* 14 (2) 97 – 101.

Chernet, T., Travi, Y. and Valles, V., (2001) Mechanism of degradation of the quality of natural water in the lakes region of the Ethiopian rift valley. *Water Research* **35**; 2819-2832.

Connell B.S., Cox M. and Singer I., (1984) Nickel and Chromium in Brunner, F. and Coburn,J.W.(eds):Disorders of minerals metabolism. *Academic press*, New York USA. 472-532.

Costa, M. H., Botta, A. and Cardille, J. A., (2003) Effects of large-scale changes in land cover on the discharge of the Tocantins River, Southeastern Amazonia. *Journal of Hydrology*, 283**,** 206-217.

Dallas, H.F. and Day, J.A., (1993) The effect of water quality variables on riverine ecosystems: A review. *Fresh Water Unit*. University of Cape Town. Rondebosch. South Africa: 240.

Daniels, M., Daniel, T. and van Devender, K., (2008) *Soil phosphorus levels: concern and recommendations.* The University of Arkansas Cooperative Extension Services. USDA and County Governments Cooperating. FSA1029-4M-6-98M.

Darko, G., Akoto, O. and Oppong, C., (2008) Persistent organochlorine pesticide residues in fish, sediment and water from lake Bosomtwi, Ghana. *Chemo*.,72(1)21-24.

Derek, C.G., Muir, C. and Wit, A., (2009) Trends of legacy and new persistent organic pollutants in the circumpolar arctic: Overview, conclusions, and recommendations. *Science of the Total Environment* **408** (2010); 3044–3051

ECDG, (2002) European Commission DG ENV. E3 Project ENV. E.3/ETU/0058. Heavy metals in waste. Final report.Edition. ISBN 9966-23-983-9.

Engel, L.S., O'Meera, E.S. and Schwartz, S.M., (2000) Maternal occupation in agriculture and risk of defects in Washington State, 1980–1993. Scand. J. *Work Environ. Health* 26; 193–198.

European Chemicals Bureau, (2005) Existing chemicals.http://ecb.jrc.it/existing-chemicals/(accessed July 28,2005).

Fouskaki, M. S., Koci, S. M. and Chaniotakis, N.A., (2003) Morpholinoethanesulfonic acid-based buffer system for improved detection limit and stability of the fluoride ion selective electrode. *Anal. Chim.* Acta, 478; 77-84.

Garbarino, J. R., Hayes, H., Roth, D., Antweider, R., Brinton, T. I. and Taylor, H., (1995) Contaminants in the Mississipi River, U. S. Geological Survey Circular 1133, Virginia.

Garrett, J.L., (2000) 'Overview' in J.L.Garrett and M.T.Ruel (eds)'Achieving Urban Food and Nutrition Security in the Developing World',2020 Vision for Food, Agriculture, and the Environment Focus No.3, Brief 1 of 10, International Food Policy Research Institute, Washington, DC.

Getenga, Z. M., Kengara, F. O. and Wandiga, S. O., (2004) Determination of organochlorine pesticides in soil and water from river Nyando Drainage System within Lake Victoria Basin, Kenya. *Bull. Environ. Contam. Toxicol,* **72** (2): 335-342.

Gitahi, S.M., Harper, D.M., Muchiri, S.M., Tolo, M.P. and Nga'nga, R.N., (2002) Organochlorine and organophosphorus pesticide concentrations in water, sediment, and selected organisms in lake Naivasha(Kenya).*hydrobiologia*.488;123-128.

Government of Kenya, (2010) *Agricultural Sector Development Strategy* 2010-2020.ministry of Agriculture, Nairobi, Kenya.

Guo, Y., Meng, X. Z., Tang, H. L. and Zeng, E.Y., (2008) Tissue distribution of organochlorine pesticides in fish collected from the Pearl River delta, China: Implications for fishery input source and bioaccumulation. *Environ. Pollut.*, 155: 150-156.

Gustavo, R., (2007) Enhanced copper release from pipes by alternating stagnation and flow events. *Env. Sci Tech*., 41, 7430-7436.

Hanrahan, G., Gledhill, M., Fletcher P. J. and Worsfold P. J., (2001) High temporal resolution field monitoring of phosphate in the River Frome using flow injection with diode array detection. *Analytica Chimica*; 55-62.

Harris, M., Van den H, M., Rouse, J., Martin, P.A., Struger, J., Bishop, C. and Takacs, P., (2000) Pesticides in Ontario; A critical assessment of potential toxicity of agricultural products to wildlife with consideration for Endocrine disruption. Volume 1: Technical Report series No. 340; *Canadian Wildlife Service*, Ontario Region.

Hassall, A. K., (1990) The Biochemistry and Uses of Pesticides – Structures Metabolism, Mode of Action and Use in Crop Protection. Macmillan press Ltd, London, United Kingdom.

Hendrik W. and Killebrew, K., (2010) *Environmental Impacts of Agricultural Technologie*s. Evans School Policy Analysis and Research (EPAR) of the Bill & Melinda Gates Foundation .Washington University.1-18.

Huang, M. and Zhang, L., (2004) Hydrological responses to conservation practices in a catchment of the Loess Plateau, China. *Hydrological Processes,* 18**,** 1885-1898.

IUPAC, (2003) Regulatory Limits for pesticides in water. *Pure Appl.chem*.,75(8);1123-1156.

Jaetzold, R., Schmidt, H., Hornet, Z. B. and Shisanya, C. A., (2010) Farm Management Handbook of Kenya, Volume II, Part B: *Natural Conditions and Farm Management Information, Central Kenya (Rift Valley and Central Provinces)*, Nairobi, Ministry of Agriculture, Kenya, in Cooperation with the German Agency for International Cooperation (GIZ).

Jensen, A. and Bro-Rasmussen, F., (1992) *Environmental cadmium in Europe*. Reviews in Environmental Contamination and Toxicology, 125: 101–181.

Kabata-Pendias, A. and Pendias, H., (2001) *Trace Elements in Soils and Plants,* CRC Press LLC, Boca Raton, Florida, USA.

Kahama, R.W., Kariuki, D.N., Kariuki, H.N. and Njenga, L.W., (1997) Fluorosis in children and sources of fluoride around Lake Elementaita, Kenya. Fluoride.30; (1)19-25.

Kasozi, G.N., Kiremire, B.T., Bugenyi, F.W.B., Kirsch, N.H. and Nkedi-Kizza, P. , (2006).Organochlorine residues in fish and water samples from Lake Victoria, Published online on 1 March 2006 .

Kenya Bureau of Standards (KEBS) , (2010) KS 05-459-1: 2007: Drinking water – Specification Part 1: *The requirements for drinking water (ICS 13.060.20), KBS Nairobi*. Third

Kenya Lakes System (KLS) in the Great Rift Valley (Elmentaita, Nakuru and Bogoria) (2010) *Nomination Proposal, Republic of Kenya.*

Kiely, G., (1997) *Environmental Engineering*. McGraw-Hill.

Kitaka, N., (2001) *Phosphorus Dynamics and Sediment-water Interchange in Lake Naivasha, Kenya*. PhD Thesis, University of Leicester, Leicester, United Kingdom.

Konieczka, P. P., Zygmunt, B. and Namiesnik, J., (2000) Comparison of Fluoride Ion-Selective Electrode Based Potentiometric Methods of Fluoride Determination in Human Urine *Toxicol. Environ. Chem.,* 74, 125-130.

Lawler, A. J. and Tipping, E., (2003) Metals in bulks deposition and surface waters at two upland locations in northern England. *Envir. Pollut.,* 121;153–167.

Levalloisa, P., Thériault, M., Rouffignat, J., Tessier, S., Landry, R., Ayotte, P., Girard, M., Gingras, S., Gauvin, D., and Chiasson, C., (1998) *The Science of the Total Environment* 217 91-101.

Li, J., Zhu, T., Wang, F., Qiu, X.H. and Lin, W.L., (2006) Observation of organochlorine pesticides in the air of the Mount Everest region. *Ecotoxicol Environ Saf*, 63; 33-41

Luk, G. and Au-Yeung, W., (2002) Experimental Investigation on the Chemical Reduction of Nitrate from Groundwater. Advances in Environmental Research 6; 441-453.

Madadi, O.V., Wandiga S.O. and Jumba I.O., (2006) The status of persistent organic pollutants in Lake Victoria catchment. In: Odada, Eric O., Daniel, O. (Eds.), *Proceedings of the 11th World Lakes Conference*, 2; 107–112.

Maher W., Frikowa F., Wruck D., Louie H., Nguyen T. and Huang W.Y., (2002) Determination of total phosphorous and nitrogen in turbid waters by oxidation with alkaline potassium peroxodisulfate and low pressure microwave digestion, autoclave heating or the use of closed vessels in a hot water bath: comparison with Kjeldahl digestion. *Analytica Chimica* 283-293.

Mandavilli, A., (2006). DDT Returns. Nature Medicine 2006, (12), 870-871. http://dx.doi.org/10.1038/nm0806-870.(accessed December 7,2015).

Maumbe, M. and Swinton, S. M., (2003) Hidden health costs of pesticide use in Zimbabwe's smallholder cotton growers. *Social Science & Medicine*, 57; 1559-1571.

Masunaga, S., Wolfe, N.L. and Carriera, L., (1993) Transformation of para-substituted benzonitriles in sediment and in sediment extract. *Water Sci. Technol*. 28: 123-132

McCasland, M., Trautmann, N.M., Porter, K. S. and Wagenet, R. J., (1998) *Nitrate: Health Effects in Drinking Water.* Cornell University.

Milenkovic, N.M., Damjanovic, M. and Ristic, M., (2005) Study of heavy metal pollution in sediments from the Iron Gate (Danube, River), Serbia and Montenegro. Pakistan. *Journal of Environmental Studies*. 14: 781- 787.

Mohamed, M. E., Mohamed, M. Y. and Eman, A. M., (2010) Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt. Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center (NWRC), Cairo, Egypt.

Montgomery, J.H., (2000) Ground water Chemicals Desk Reference, third ed. Lewis Publishers and CRC Press, Boca Raton, FL.

Morrow, H., (2001) Cadmium and Cadmium Alloys. In: Kirk-Othmer Encyclopedia of Chemical Technology, 5Th ed., Vol. 4. New York: John Wiley & Sons, 471–507. [online edition]

Muinde, M.V. , (2012) Heavy metal effects on types and levels of omega-3 polyunsaturated fatty acids (PUFAs) in tilapia fish (oreochromis niloticus) in Winam Gulf of Lake Victoria. M.Sc. Thesis. Department of Chemistry, University of Nairobi.

Mumo, F.A., (2002) Water balance of the southern Kenya rift valley lakes, international institute of Geo information science and earth observation, *ITC, Enschede* 114.

Muñoz, A., Mas, T. F., Estela, J.M. and Cerda, V., (1997) Evaluation of spectrophotometric methods for determination of orthophosphates by sequential injection analysis. *Analytica Chimica*; 21-29.

Murimi, S.K., Gachuki, F.N., Mungai, D.N., Gachuru, C.K.K. and Thomas, D.B., (1993) The drying Up of East Africa rift valley Lakes in recent times with special reference to Lake Elementaita Land and water management in Kenya: towards sustainable land use, proceedings of the fourth National workshop, Kikuyu, Kenya.

Murray, K.J., Mozafarzadeh, M.L. and Tebo, B.M., (2005) Cr (III) oxidation and Cr toxicity in cultures of the Manganese (II)-oxidizing Pseudomonas putida strain GB-1. *Geomicrobiol*. J. 22: 151-159.

Musa, A., Oladiran, J.A., Ezenwa, M.I.S., Akanya, H.O. and Ogbadoyi, E.O., (2011) Effect of heading on some micronutrients, anti-nutrients and toxic substances in Amaranthus cruentus grown in Minna, Niger State, Nigeria. *American Journal of Food and Nutrition*. 1(2): 147-154.

Mwamburi, J., (2003) Variations in trace elements in bottom sediments of major rivers, in Lake Victoria's basin, Kenya. *Lakes and reservoirs: research and management*, **8**(1): 5-13.

Mwamburi, J., (2009) Trace metal concentration in water and sediments of satellite lakes within Lake Victoria (Kenya) basin. *Lakes and Reservoirs*: Research and Management 14: 203-219.

Mwaura, F., (1999). A spartio chemical survey of the hydrogeothermal springs in L.Elementaita Kenya. *International Journal of salt Lake Research*. Department of Geography, University of Nairobi. 8 (2): 127-138.

Neitsch. S. L. E. A., (2002) Soil and Water Assessment tool. *Theoretical Documentation*.Texas, Texas Water Resource Institute,College Station.

NEMA – National Environment Management Authority, Uganda, (2000) Status of Organochlorine residues in fish and water samples from Lake Victoria. Uganda J. Persistent Organic Pollutant Pesticides in Uganda: *A Historical Overview*. NEMA Secretariat, Kampala.

Njenga, J.W., (2004) Comparative Studies of Water Chemistry of Four Tropical Lakes in Kenya and India. *Asian Journal of Water, Environment and Pollution*, 1(1 & 2); 87-97.

Nriagu, J.O. and Pacnya, J.M., (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333: 134–139.

Nzeve, J.K., Kitur, E.C. and Njuguna, S,G., (2014)Determination of heavy metals in sediments of Masinga Reservoir, Kenya. *Journal of Envirinment and Earth Science*.4(20).

Ochieng, E. Z., Lalah, J.O. and Wandiga, S.O., (2007) Analysis of heavy metals in water and surface sediments in five Rift Valley lakes in Kenya for assessment of recent increase in anthropogenic activities. Bull. *Environ. Contam. Toxicol*.79: 570 -576 (15).

Ochieng, E. Z., Lalah, J.O. and Wandiga, S.O., (2008). Water quality and trace metal distribution in a pristine lake in the lake Basin in Kenya. *Bull. Environ. Contam. Toxicol*. 80: 362 – 366.

Okoya, A.A., Ogunfowokan, A.O., Asubiojo, O.I. and Torto, N., (2013) OCP Residues in sediments and waters from cocoa producing Areas of Ondo state South- Western Nigeria. International scholarly Research Network(ISRN).*Soil science*.1-12.

Ongley, E.D., (1996)-Control of water pollution from Agriculture. FAO irrigation and Drainage paper no.55 FA, Rome.

Organisation for Economic Co-operation and Development(OECD), (1993) Lead background and national experiences with reducing risk. Paris.

Oyoo-Okoth, E., Wim, A., Osano, O., Kraak, M.H.S., Ngure, V., Makwali, J. and Orina, P.S., (2010) Use of the fish endoparasite Ligula intestinalis(L., 1758) in an intermediate cyprinid host (Restreneobola argentea) for biomonitoring heavy metal contamination in Lake Victoria, Kenya. *Lakes & Reservoirs: Research and Management*, 15: 63 – 73.

PCPB, (1998) List of Pest Control Products Provisionally Registered by the Pest Control Products Board for use in Kenya (Revised June, 1998). PCPB, Nairobi, p. 86.

Radcliffe, E.B., Hutchison, W.D. and Cancelado, R.E., (2009) *Integrated Pest Management, Concepts, Tactics, Strategies and Case Study, Cambridge University press*.

Rashed, M.N., (2001) Monitoring of environmental heavy metals in fish from Nasser Lake. *Environmental International*. 69: 27-33.

Reeve, R. N. and Barnes, J. D., (1994) *Environmental Analysis*, John Wiley & Sons.

Saeed, M.S. and Shaker, M. I., (2008) Assessment of heavy metals pollution in water and sediments and their effect on oreochromis niloticus in the northern delta lakes, Egypt**.** Central Lab for Aquaculture Research, Agricultural Research Center. *Limnology;*475-491.

Santos, I. R., Silva-Filho, E. V., Schaefer, C. E., Albuquerque- Filho, M. R. and Campos, L. S., (2005) Heavy metals contamination in coastal sediments and soils near the Brazilian Antarctic Station, King George Island. Mar. *Poll. Bull*., 50: 85-194.

Schindler, D.W., (2001) The cumulative effects of climate warming and other human stresses on Canadian freshwaters in the new millennium. Can. J. Fish *Aquat. Sci*.58: 18-29.

Sharma, R. and Pervez, S., (2003) Enrichment and exposure of particulate lead in a traffic environment in India.*Environ. Geochem.Health,* 25: 297 – 306

Simpson, S.I., Rochford, S.I. and Birch, G.F., (2002) Geochemical influences on meta partitioning in contaminated estuarine sediments. Mar. *Freshwat. Res*., 53; 9 – 17.

Situma, D., (2010*) Assessment of Polycyclic Aromatic Hydrocarbons in Air and Soil from Selected Sites in Nairobi*. Msc Thesis. Department of chemistry. University of Nairobi, Kenya

Sparvs Agency Ltd (SAL), (2008) A final report on Threat Reduction Assessment.Stockholm, Sweden.

Ssebugere, P., Kiremire, B.T., Kishimba, M., Wandiga, S.O., Nyanzi, S.A., and Wasswa, J., (2009) DDT and metabolites in fish from Lake Edward, Uganda. *Chemosphere* 76, 212–215.

Ssebugere, P., Wasswa, J., Mbabazi, J., Nyanzi, S.A., Kiremire, B.T., and Marco, J.A.M., (2010) Organochlorine pesticides in soils from South-western Uganda. *Chemosphere* 78, 1250–1255.

Stockholm Environment Institute and United Nation Environment Programme, (2009)*Rain water harvesting*: A lifeline for human well-being. Nairobi, United Nations Environment Programme.

TDC environmental report, (2004).Copper sources in urban runoff and shoreline activities, 72p.

http://www.tdcenvironmental.com/CuSourcesReportCEP-T-4Ver2.pdf

Ulen, B., Bechmann, M., Folster, J., Jarvie,H.P. and Tunney, H., (2007) Agriculture as a phosphorus source for eutrophication in the north-west European countries, Norway, Sweden, United Kingdom and Ireland: a review Soil. *Use Manage.*, 23,; 5–15.

UNEP chemicals, (2007) POPs Training Project. Practical Training Course in Nairobi, Kenya at University of Nairobi, Department of Chemistry.

United Nations Environment Programme-UNEP, (2003) *Regionally based assessment of persistent toxic substances, Global Report*. UNEP Chemicals; Chatelaine, Switzerland. http://www.chem.unep.ch/pts/ [accessed 2 April 2007].

US Environmental Protection Agency (US EPA), (1976) Guidelines for state and Areawide Water Quality Management Programme Development. USEPA, Washington DC.

Vesely, J., Havlicek, L., Strnad, M., Blow, J.J., Donella-Deana, A., Pinna, L., Letham, D.S., Kato, J., Detivaud, L., Leclerc, S. and Meijer, L., (1994) Inhibition of Cyclin-dependent Kinases by Purine Analogues. *European Journa of Biochememistry*, 224(2), 771-786, ISSN 0014-2956.

Wan, M.T., Kuo, J.-n., Buday, C., Schroeder, G., Aggelen, G.V. and Pasternak,J., (2005) Toxicity of alpha-,beta-,and(alpha+beta)-endosulfan and their formulated and degradation and biological implications in streams. *Environ.Toxicol.Chem.*,24:1146-1154.

Wandiga, S.O., (2001) Use and distribution of organochlorine pesticides. The future in Africa. *Pure Apple. Chem*,73,(7);1147-1155.

Waswa, J., (2008) Characterization of Selected Pesticides Residues in Sediments of the Ugandan side of Lake Victoria. PhD Thesis, Department of Chemistry, Makerere University, Uganda.

Weiner, M.L., Salminen, W.F., Larson, P.R., Barter, R.A., Kranetz, J.L and Simon, G.S., (2001) Toxicological review of inorganic phosphates. *Food and Chemical Toxicology*. 759-786.

Werimo, K., Bergwerff, A.A. and Seinen, W., (2009) Residue levels of organochlorines and organophosphates in water, fish and sediments from Lake Victoria – Kenyan portion. *Aquat. Ecosyst*. Health Manage. 12; 337–341.

WHO , (1996) Participatory Hygiene and Sanitation Transformation (PHAST): a new approach to working with communities. Geneva,WHO.

www.who.int/water_sanitation_health/hygiene/envsan/phast.

WHO, (2001) Depleted uranium: Sources, Exposure and Health Effects.

WHO, (2004) Guidelines for drinking water quality: Recommendations 3rd Edn. World Health Organization, Geneva, 1,; 516.Williamson, M.M. 1953 *Endemic dental fluorosis*.

WHO, (2007a) Combating waterborne disease at the household level: International Network to Promote Household Water Treatment and Safe Storage. Geneva: WHO. www.who.int/household_water/advocacy/combating_disease/en/.

Williamson, S., Ball, A. and Pretty, J., (2008) Trends in pesticide use and drivers for safer pest management in four African countries. *Crop Protection, 27,* 1327-1334.

Wilson, C. and Tisdell, C., (2001) why farmers continue to use pesticides despite environmental, health and sustainability costs. *Ecological Economics,* 39, 449-462.

Wood,S., Sebastian, K. and Scherr, S. J., (2000) *Pilot analysis of global ecosystems: agroecosystems.* Washington, DC: World Resources Institute and International Food Policy Research Institute.

Wood, F.L., Heathwaite, A.L., and Haygarth, P.M., (2005) Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the taw catchment, Devon, UK. J. *Hydrol*., 304 (1–4),; 118–138.

World Health Organization, (WHO)/UN Child. Fund (UNICEF), (2008) *Progress on Drinking-Water and Sanitation: Special Focus on Sanitation. Geneva*, Switz. /New York: WHO/UNICEF. 5 8 pp.ss., Washington, DC.

www.who.int/water_sanitation_health/hygiene/envsan/phast.

Yahaya, M.I., Mohammad, S. and Abdullahi, B. K., (2009) Seasonal Variations of Heavy Metals Concentration in Abattoir Dumping Site Soil in Nigeria. *Sci. Environ*. Manage. December, 2009 13,(4) ;9 – 13.

Zarazua, G., Ávila-Pérez, P., Tejeda, S., Barcelo-Quintal, I. and Martínez, T., (2006). Analysis of total and dissolved heavy metals in surface water of a Mexican polluted river by Total Reflection X-ray Fluorescence Spectrometry, Spectrochimica Acta Part B: *Atomic Spectroscopy*, 61, 1180-1184.

Zhang, H., Davison, W., Gadi, R. and Kobayashi, T., (1998) In situ measurement of dissolved phosphorous in natural waters using DGT.*Analytica Chimica* 29-38.

APPENDIX I

Table A1.1: Phosphate concentration in water in mg/l in dry and wet seasons.

SITE	Dry season	Wet season
Mbaruk Lake	0.38±0.07	0.24±0.01
Mbaruk River	0.14±0.01	0.04±0.01
Kekopey Lake	0.20±0.03	0.02±0.00
Kekopey Spring	0.10±0.01	0.13±0.00
Serena Camp	0.24±0.01	0.19±0.00
Soysambu Ranch	0.32±0.02	0.19±0.00
Elementaita North	0.18±0.00	0.21±0.02

Table A 1.2: Phosphate concentration in sediment in mg/kg in dry and wet seasons

Sites	dry season	wet season
Mbaruk Lake SED	0.52±0.00	10.04±0.1
Mbaruk River SED	2.71±0.03	0.45±0.02
Kekopey Lake SED	6.29±0.01	1.80±0.03
Kekopey Spring SED	6.27±0.02	4.99±0.00
Serena Camp SED	3.81±0.01	1.28±0.00
Soysambu Ranch SED	4.08±0.01	1.08±0.03
Elementaita North SED	4.37±0.00	8.61±0.58

Table A1.3: Phosphate concentration in soil in mg/kg in dry and wet seasons.

Sites	dry season	wet season
Mbaruk lake site	2.81±0.02	2.13±0.14
Mbaruk river Soil	1.85±0.00	1.44±0.06
Kekopey lake Soil	1.78±0.00	1.59±0.06
Kekopey Spring Soil	3.41±0.04	0.78±0.00
Serena Camp Soil	4.47±0.03	3.11±0.08
Soysambu Ranch Soil	1.41±0.01	2.72±0.03
Elementaita North Soil	2.49±0.02	2.48±0.01

Table A1.4: Nitrates concentration in water in mg/L in dry and wet seasons

Sites	dry season	wet season
Mbaruk Lake	0.46±0.09	1.74±0.17
Mbaruk River	0.91±0.26	0.69±0.05
Kekopey Lake	0.43±0.04	1.18±.08
Kekopey Spring	0.47±0.15	1.28±0.08
Serena Camp	0.43±0.02	2.97±0.17
Soysambu Ranch	0.49±0.09	2.76±0.24
Elementaita North	0.47±0.03	3.00±0.36

Table A1.5: Nitrates concentration in sediment in mg/kg in dry and wet seasons.

Sites	dry season	wet season
Mbaruk Lake	0.45±0.09	1.25±0.02
Mbaruk River	2.01±0.05	1.99 ±0.05
Kekopey Lake	0.45±0.02	1.42±0.07
Kekopey Spring	0.72±0.30	2.21±0.18
Serena Camp	0.57±0.06	1.02±0.01
Soysambu Ranch	0.53±0.08	1.49±0.36
Elementaita North	0.36±0.06	1.79±0.03

Table A1.6:Nitrates concentration in soil in mg/kg in dry and wet seasons.

Sites	dry season	wet season
Mbaruk Lake	2.29±0.55	2.6±0.08
Mbaruk River	2.29±0.55	1.68±0.08
Kekopey Lake	1.46±0.07	1.62±0.08
Kekopey Spring	1.46±0.07	1.58±0.16
Serena Camp	2.58±0.04	1.02±0.04
Soysambu Ranch	4.90±0.29	1.26±0.09
Elementaita North	3.87±0.37	0.65±0.05

APPENDIX II

Table A2.1: OCPs in water for seven sites for dry season in µg/L

OCPs	Mbaruk River	Mbaruk Lake	Kekopey Lake	Kekopey Spring	Serena Camp	Elementaita North	Soysambu Ranch
a-HCH	0.49±0.09	BDL	BDL	BDL	BDL	BDL	0.12±0.03
b-HCH	0.01±0.00	BDL	0.22±0.00	BDL	0.03±0.00	BDL	0.01±0.00
g-HCH	0.01±0.00	0.01±0.00	BDL	BDL	0.01±0.00	BDL	0.01±0.00
d-HCH	BDL	0.07±0.02	BDL	BDL	0.12±0.00	BDL	0.01±0.00
Heptachlor	BDL	0.02±0.00	BDL	BDL	0.06±0.00	BDL	0.04±0.05
Aldrin	BDL	0.01±0.00	0.02±0.00	BDL	0.31±0.09	BDL	0.00±0.00
Heptachlor Epoxide	BDL	0.01±0.00	BDL	BDL	0.02±0.00	BDL	0.00±0.00
Endosulphan 1	BDL	0.03±0.01	0.01±0.00	BDL	0.06±0.01	BDL	0.01±0.00
p,p'-DDE	BDL	0.01±0.00	BDL	BDL	0.02±0.00	BDL	BDL
Dieldrin	BDL	0.01±0.00	BDL	BDL	0.04±0.01	BDL	BDL
Endrin	BDL	0.01±0.00	BDL	BDL	0.01±0.00	BDL	0.01±0.00
Endosulphan 2	0.04±0.01	0.01±0.00	BDL	BDL	0.03±0.00	BDL	0.01±0.00
p,p'-DDD	BDL	BDL	BDL	BDL	BDL	0.04±0.01	BDL
Endrin aldehyde	0.01±0.00	0.02±0.00	0.01±0.00	BDL	0.05±0.00	BDL	0.02±0.00
p,p'-DDT	0.02±0.00	0.06±0.00	0.01±0.00	BDL	0.12±0.03	BDL	0.02±0.00
Endosulphan sulphate	0.04±0.00	0.03±0.01	0.07±0.00	BDL	0.02±0.00	BDL	0.02±0.00
Methoxychlor	0.01±0.00	0.01±0.00	0.03±0.00	BDL	0.07±0.01	0.02±0.00	0.02±0.00

Table A2.2: OCPs in water for wet season in μg/L

OCPs	**Mbaruk River**	**Mbaruk Lake**	**Kekopey Lake**	**Kekopey Spring**	**Serena Camp**	**Elementaita North**	**Soysambu Ranch**
a-HCH	0.03±0.00	0.02±0.00	BDL	BDL	0.01±0.00	0.04±0.00	0.01±0.00
b-HCH	0.01±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.03±0.00	0.01±0.00
g-HCH	0.01±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.02±0.00	0.01±0.00
d-HCH	0.01±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.01±0.00	0.01±0.00
Heptachlor	0.01±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.01±0.00	0.01±0.00
Aldrin	0.02±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.06±0.00	BDL
Heptachlor Epoxide	0.01±0.00	0.01±0.00	0.02±0.00	BDL	BDL	0.03±0.00	0.01±0.00
Endosulphan 1	0.01±0.00	0.01±0.00	0.01±0.00	BDL	0.01±0.00	0.02±0.00	0.01±0.00
p,p'-DDE	0.02±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.01±0.00	0.01±0.00
Dieldrin	0.02±0.00	0.01±0.00	0.01±0.00	BDL	BDL	0.01±0.00	BDL
Endrin	0.01±0.00	BDL	0.01±0.00	BDL	BDL	0.01±0.00	BDL
Endosulphan 2	0.02±0.00	0.01±0.00	0.01±0.01	BDL	0.01±0.00	0.04±0.00	0.01±0.00
p,p'-DDD	0.01±0.00	BDL	BDL	BDL	BDL	0.02±0.00	BDL
Endrin aldehyde	BDL	BDL	0.03±0.00	BDL	0.02±0.00	0.03±0.00	BDL
p,p'-DDT	0.06±0.00	0.02±0.00	0.02±0.00	BDL	0.02±0.00	0.09±0.00	0.02±0.00
Endosulphan sulphate	0.16±0.00	BDL	0.01±0.00	BDL	BDL	0.13±0.00	0.07±0.01
Methoxychlor	0.05±0.00	0.03±0.00	0.02±0.00	BDL	BDL	0.01±0.00	0.03±0.00

Table A2.3: OCPs in sediment for dry season in µg/kg

OCPs	Mbaruk River	Mbaruk Lake site	Kekopey Lake	Kekopey Spring	Serena Camp	Elementaita North	Soysambu Ranch
a-HCH	91.71±10.00	69.17±15.35	59.69±10.74	50.75±4.49	129.04±21.09	56.49±3.22	94.41±1.98
b-HCH	80.07±15.55	25.50±3.21	73.50±9.17	41.41±1.25	27.07±0.89	88.16±6.39	50.48±10.53
g-HCH	90.81±14.65	31.17±8.39	34.69±6.24	27.74±6.79	23.90±0.29	35.10±5.78	42.84±6.95
d-HCH	76.25±16.15	44.06±8.57	198.17±2.46	65.57±1.66	32.84±5.12	44.59±0.34	28.65±5.21
Heptachlor	129.26±17.81	53.44±7.85	146.76±13.66	49.94±11.59	40.05±9.12	139.95±19.17	36.29±9.55
Aldrin	83.60±18.69	89.96±7.80	29.02±7.57	73.31±5.72	26.05±0.61	64.16±6.52	28.49±6.23
Heptachlor Epoxide	31.99±3.79	25.51±0.34	31.51±11.47	36.25±5.09	25.15±1.02	70.99±10.35	29.56±0.99
Endosulphan 1	39.98±10.03	29.17±3.02	41.06±11.29	37.77±1.84	29.86±0.21	40.85±3.98	35.79±0.31
p,p'-DDE	29.86±5.91	58.08±7.39	24.71±8.57	26.48±2.59	37.47±6.30	89.28±17.63	23.41±2.09
Dieldrin	7.89±1.45	14.44±1.03	9.30±0.73	10.27±1.54	10.87±2.67	8.63±1.49	33.83±2.91
Endrin	19.59±3.34	45.86±6.11	45.22±5.40	16.44±0.17	21.25±0.54	42.11±5.03	18.34±3.29
Endosulphan 2	70.19±4.84	32.85±1.35	BDL	57.92±9.45	43.98±3.27	59.64±16.69	39.29±4.49
p,p'-DDD	BDL	BDL	BDL	BDL	BDL	BDL	15.86±8.73
Endrin aldehyde	127.09±0.95	134.29±14.89		153.76±2.59	129.39±8.09	147.69±23.11	123.32±3.47
p,p'-DDT	109.56±6.89	149.93±9.83	109.77±31.17	193.78±27.28	121.83±32.03	130.44±39.96	94.56±10.14
Endosulphan sulphate	289.93±28.76	90.69±34.25	76.13±23.66	441.32±33.68	26.25±9.36	452.79±21.55	762.27±91.70
Methoxychlor	160.62±4.62	102.09±4.01	168.21±56.16	178.87±24.65	106.0608.19	136.95±23.98	137.16±4.19

Table A2.4: OCPs in sediment for wet season in µg/kg

OCPs	**Mbaruk River**	**Mbaruk Lake**	**Kekopey Lake**	**Kekopey Spring**	**Serena Camp**	**Elementaita North**	**Soysambu Ranch**
a-HCH	BDL	8.02±0.62	BDL	BDL	BDL	2.92±0.14	BDL
b-HCH	BDL	2.65±0.01	BDL	1.77±0.17	1.17±0.25	BDL	2.3±0.02
g-HCH	2.23±0.16	2.32±0.2	0.83±0.23	2.11±0.02	1.66±0.09	1.55±0.13	2.66±0.15
d-HCH	3.49±0.17	4.61±0.32	2.24±0.05	1.51±0.11	2.78±0.33	2.61±0.17	3.82±0.05
Heptachlor	BDL	3.07±0.03	0.76±0.09	4.93±0.19	2.17±0.23	3.99±0.01	2.09±0.11
Aldrin	3.07±0.38	2.38±0.25	0.95±0.00	2.43±0.36	0.95±0.12	3.18±0.41	1.69±0.00
Heptachlor Epoxide	2.53±0.35	2.43±0.29	0.79±0.11	2.59±0.23	1.79±0.05	5.99±0.19	2.55±0.06
Endosulphan 1	2.24±0.38	2.71±0.07	0.99±0.03	3.45±0.34	3.19±0.35	3.01±0.04	2.36±0.13
p,p'-DDE	3.34±0.02	9.24±0.73	1.58±0.09	1.1±0.32	1.51±0.32	2.69±0.00	2.55±0.13
Dieldrin	1.48±0.04	2.09±0.02	1.19±0.06	0.75±0.03	1.2±0.03	BDL	1.73±0.07
Endrin	2.16±0.12	BDL	0.74±0.00	0.83±0.13	0.62±0.03	4.95±0.51	1.23±0.04
Endosulphan 2	4.8±0.36	9.63±0.21	1.58±0.06	2.43±0.04	2.77±0.31	2.89±0.09	3.69±0.13
p,p'-DDD	0.67±0.09	0.61±0.05	0.32±0.06	0.66±0.11	0.68±0.24	0.18±0.08	BDL
Endrin aldehyde	BDL	BDL	2.25±0.03	4.34±0.29	4.61±0.43	7.24±0.03	6.65±0.17
p,p'-DDT	16.49±0.13	BDL	2.73±0.37	0.42±0.04	4.71±1.34	5.95±0.16	9.81±0.1
Endosulphan sulphate	21.13±2.19	BDL	1.8±0.28	8.86±0.82	16.98±0.62	42.97±1.00	25.29±0.27
Methoxychlor	7.39±0.41	BDL	2.36±0.98	5.93±0.08	1.13±0.23	BDL	7.09±0.00

Table A2.5: Average OCPs in soil for dry season in μg/kg

OCPs	Mbaruk River	Mbaruk Lake site	Kekopey Lake	Kekopey Spring	Serena Camp	Elementaita North	Soysambu Ranch
a-HCH	42.10±8.52	42.10±8.52	38.21±9.17	46.20±0.04	25.72±6.76	46.83±2.59	22.86±0.35
b-HCH	29.27±1.18	29.27±1.18	20.33±8.34	21.60±0.93	22.73±0.15	26.12±0.94	29.55±2.79
g-HCH	27.79±6.28	27.79±6.28	16.32±1.37	20.75±3.54	37.23±7.09	23.68±1.94	17.76±0.73
d-HCH	31.47±3.19	31.47±3.19	25.66±5.69	28.01±0.26	38.52±7.66	41.36±3.35	21.92±1.89
Heptachlor	33.02±0.97	33.02±0.97	20.56±1.73	22.83±1.84	26.24±3.52	28.96±1.98	21.48±0.54
Aldrin	27.51±3.24	27.51±3.24	16.92±1.16	21.19±2.88	26.45±7.36	50.24±2.29	30.58±4.12
Heptachlor Epoxide	25.44±1.68	25.44±1.68	24.07±2.33	20.57±1.77	27.40±7.49	24.92±1.01	17.56±2.01
Endosulphan 1	32.59±2.29	32.59±2.29	25.49±5.58	21.23±3.05	25.11±5.22	31.96±5.82	19.83±2.14
p,p'-DDE	19.91±0.98	19.91±0.98	26.13±1.39	13.99±2.83	16.03±0.79	25.38±0.63	19.96±5.67
Dieldrin	7.61±0.39	7.61±0.39	6.26±0.11	16.67±2.56	17.16±4.97	13.39±1.29	7.51±1.7
Endrin	17.27±0.48	17.27±0.48	8.74±2.50	8.56±2.39	16.37±1.61	53.34±9.11	28.03±3.46
Endosulphan 2	33.42±1.64	33.42±1.64	25.65±0.2	25.36±4.67	34.51±7.74	39.08±9.48	BDL
p,p'-DDD	BDL	BDL	BDL	BDL	78.37±14.09	BDL	BDL
Endrin aldehyde	120.81±7.59	120.81±7.59	85.51±0.77	81.82±1.09	128.38±35.94	BDL	BDL
p,p'-DDT	109.09±19.64	109.09±19.64	71.55±1.50	188.39±24.77	76.08±6.84	153.02±0.89	BDL
Endosulphan sulphate	69.78±8.26	69.78±8.26	51.13±3.51	615.93±119.21	84.50±19.71	79.01±21.52	BDL
Methoxychlor	101.72±5.44	101.72±5.44	75.70±1.39	107.79±8.95	95.43±6.27	92.77±3.73	97.71±30.57

Table A2.6: Average OCPs in soil for wet season in μg/kg

OCPs	**Mbaruk River**	**Mbaruk Lake**	**Kekopey Lake**	**Kekopey Spring**	**Serena Camp**	**Elementaita North**	**Soysambu Ranch**
a-HCH	BDL	BDL	BDL	BDL	BDL	BDL	BDL
b-HCH	BDL	BDL	BDL	BDL	BDL	1.61±0.1	1.01±0.1
g-HCH	BDL	BDL	BDL	BDL	BDL	0.25±0.08	BDL
d-HCH	BDL	BDL	BDL	BDL	BDL	BDL	1.23±0.03
Heptachlor	BDL	BDL	BDL	BDL	BDL	BDL	0.91±0.2
Aldrin	0.65±0.25	0.65±0.25	0.97±0.00	0.78±0.27	BDL	1.07±0.07	1.06±0.37
Heptachlor Epoxide	2.47±0.1	2.47±0.24	0.72±0.19	0.72±0.19	BDL	1.09 ±0.06	1.21±0.04
Endosulphan 1	1.45±0.13	1.45±0.21	0.74±0.32	0.75±0.33	BDL	0.57±0.15	0.91±0.12
p,p'-DDE	0.58±0.17	0.58±0.03	1.22±0.12	1.23±0.12	BDL	1.25±0.11	1.47±0.29
Dieldrin	2.07±0.03	2.07±0.01	0.33±0.04	0.42±0.16	BDL	0.33±0.01	0.83±0.08
Endrin	0.25±0.00	0.25±0.09	0.65±0.2	0.65±0.2	BDL	0.64±0.07	1.29±0.1
Endosulphan 2	2.63±0.16	2.63±0.02	0.85±0.07	0.89±0.12	BDL	0.66±0.26	1.85±0.09
p,p'-DDD	0.16±0.00	0.16±0.06	0.09±0.03	0.09±0.03	BDL	BDL	0.12±0.04
Endrin aldehyde	5.78±0.00	5.78±0.00	3.35±0.03	3.38±0.03	BDL	1.63±0.00	3.09±0.04
p,p'-DDT	2.06±0.19	2.06±0.02	1.66±0.49	1.68±0.47	BDL	3.55±0.04	3.32±0.26
Endosulphan sulphate	2.75±0.28	2.75±0.51	2.22±0.08	2.38±0.06	BDL	3.99±0.34	13.92±0.21
Methoxychlor	1.62±0.24	1.62±0.38	1.34±0.27	1.34±0.27	BDL	BDL	5.26±0.49

Table A2.7: Sum of OCPs in water, sediment and soil of lake Elementaita drainage basin

Sites	**Sum of OCPs in water in μg/L**	**sum of OCPs in sediments μg/kg**	**sum of OCPs in soil in μg/kg**
Mbaruk River	0.52	754.71	375.65
Mbaruk Lake	0.24	524.59	375.65
Kekopey Lake	0.30	535.39	276.19
Kekopey Spring	0	753.17	637.59
Serena Camp	0.54	439.49	406.74
Elementaita North	0.29	848.97	373.50
Soysambu ranch	0.25	835.03	194.99

APPENDIX III

Table A3.1:mean ±standard deviations for heavy metals levels in water for dry season in mg/L

Site	Cd	Pb	Cu	Zn
Soysambu Ranch	0.039±0.0	0±0	0.074±0.04	0.224±0.02
Mbaruk Lake	0.060±0.03	0.241±0.09	0.075±0.05	0.196±0.01
Serena Camp	0.082±0.01	0.171±0.01	0.213±0.28	0.257±0.02
Kekopey Spring	0.043±0	0.158±0.01	0.075±0.09	0.412±0.02
Mbaruk River	0.053±0.01	0.17±0.01	3.134±0.56	0.337±0.03
Elementaita North	0.061±0.01	0.161±0	0.457±0.02	0.326±0.02
L.Elementaita Kekopey Lake	0.046±0.01	0.155±0.02	0.139±0.01	0.139±0.001

Table A3.2.mean ±standard deviations for heavy metals levels in water for wet season in mg/l

SITE	Cd	Pb	Cu
Elementaita North	0.348±0.02	4.816±0.17	8.485±0.40
Serena Camp	0.338±0.01	4.777±0.07	6.205±0.86
Mbaruk Lake	0.343±0.01	4.229±0.33	6.287±0.40
Mbaruk River	0.339±0.01	4.346±0.33	5.391±1.55
Kekopey Spring	0.321±0.0	5.286±0	5.1879±1.38
Kekopey Lake	0.323±0.01	5.639±0.17	4.659±0.06
Soysambu Ranch	0.325±0.01	9.280±0.9	7.304±2.07

Table A3.3:mean ±standard deviations for heavy metals levels in sediment for dry season in mg/kg

Site	Cd	Pb	Cu	Zn
Kekopey Spring Sed	2.36±0.50	3.138±0.49	12.4±3.56	106.275±2.89
Mbaruk Lake Sed	2.243±0.17	0±0	7.43±5.44	93.075±8.09
Soysambu Ranch Sed	2.065±0.08	0±0	2.928±0.66	63.125±0.42
Mbaruk River Sed	2.715±0.17	2.29±0.23	5.915±2.51	100.563±0.94
Kekopey Lake Sed	2.893±0.42	0±0	34.703±10.29	61.913±7.02
Elementaita North Sed	2.063±0.42	0±0	134.073±27.05	91.35±2.12
Serena Camp Sed	2.895±0.59	0±0	12.74±0.17	45.725±9.44

Table A3.4:mean ±standard deviations for heavy metals levels in sediment for wet season in mg/kg

Site	Cd	Pb	Cu
Kekopey Spring Sed	16.07±0.017	472.818±20.76	861.76±80.58
Mbaruk Lake Sed	15.533±0.01	381.775±0	450.685±17.27
Soysambu Ranch Sed	15.113±0.01	343.6±4.2	281.78±8.63
Mbaruk River Sed	14.996±0.01	411.145±0	719.31±11.51
Kekopey Lake Sed	15.043±0.00	475.753±16.61	662.33±0
Elementaita North Sed	14.973±0.01	381.778±16.61	440.8475±50.76
Serena Camp Sed	15.277±0.01	367.093±20.76	15.0374±1.15

Table A3.5:mean ±standard deviations for heavy metals levels in soil for dry season in mg/kg

Site	Cd	Pb	Cu	Zn
Soysambu Ranch Soil	3.013±0.25	10.487±0.19	4.305±1.88	70.763±1.04
Serena Camp Soil	3.248±0.42	12.36±0.99	35.795±8.87	68.713±0.72
Kekopey Lake Soil	2.775±0.08	10.377±0.99	7.733±2.11	57.95±6.68
Kekopey Spring Soil	3.428±0.17	10.598±0.19	9.205±2.08	76.663±16.03
Elementaita North Soil	6.863±0.17	11.038±0.88	4.028±5.38	86.95±5.55
Mbaruk Lake Soil	5.56±0	15.77±0.69	34.258±17.26	74.838±3.16
Mbaruk River Soil	6.093±0.25	17.97±0.47	2.96±0.39	75.863±6.81

Table A3.6: mean ±standard deviations for heavy metals levels in soil for wet season in mg/kg

Wet	Cd	Pb	Cu
Mbaruk River Soil	29.753±0.14	502.183±20.76	865.83±5.76
Soysambu Soil	16.518±0.11	387.65±8.31	821.06±80.58
Mbaruk Lake Soil	16.095±0.36	358.283±112.13	454.755±34.58
Elementaita North Soil	16.387±0.48	308.358±29.07	615.523±77.71
L.Elementaita Serena Camp Soil	16±0.08	314.23±12.46	249.218±60.44
Kekopey Lake Soil	15.603±0.75	325.978±4.2	564.645±51.80
Kekopey Spring Soil	15.907±0.29	325.978±4.2	515.805±23.02

APPENDIX 1V

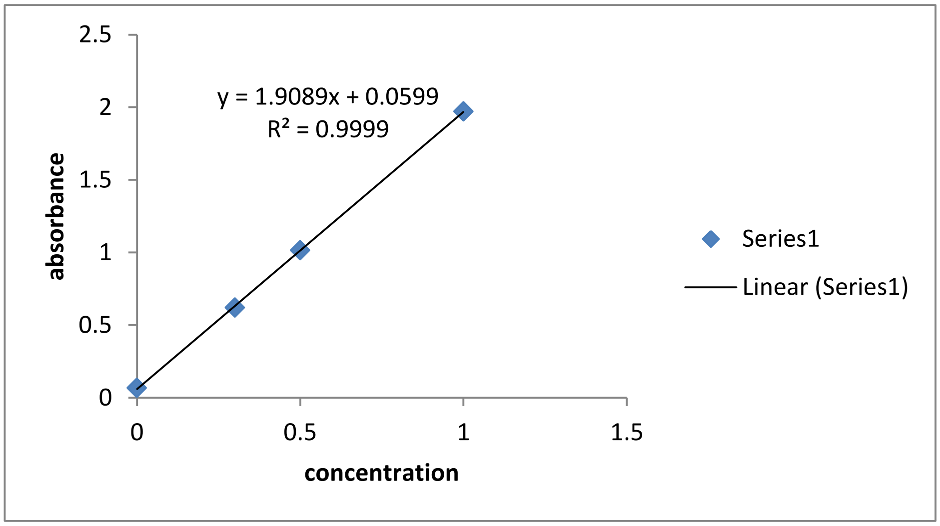


Figure A4.1: Calibration curve for phosphates

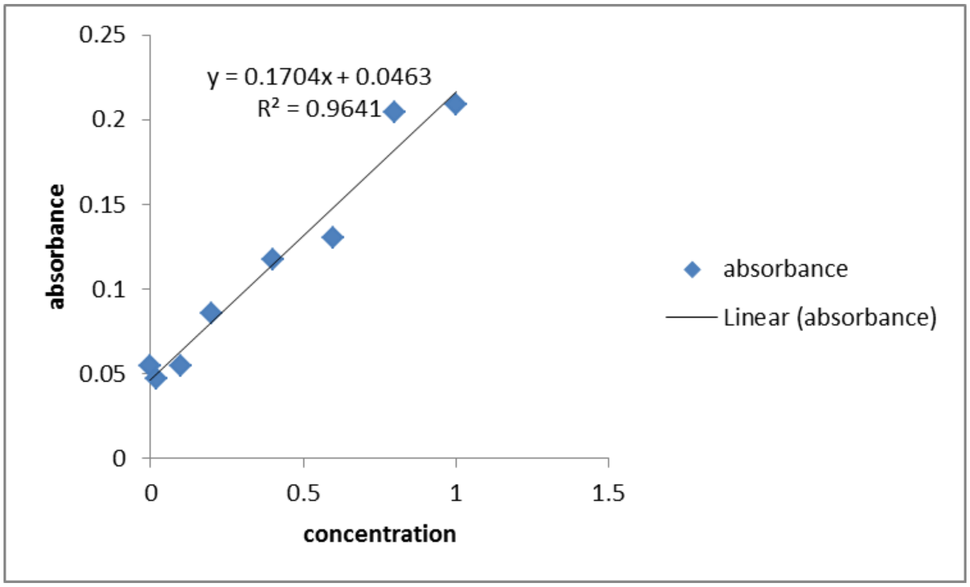


Figure A4.1B: Calibration curve for nitrates

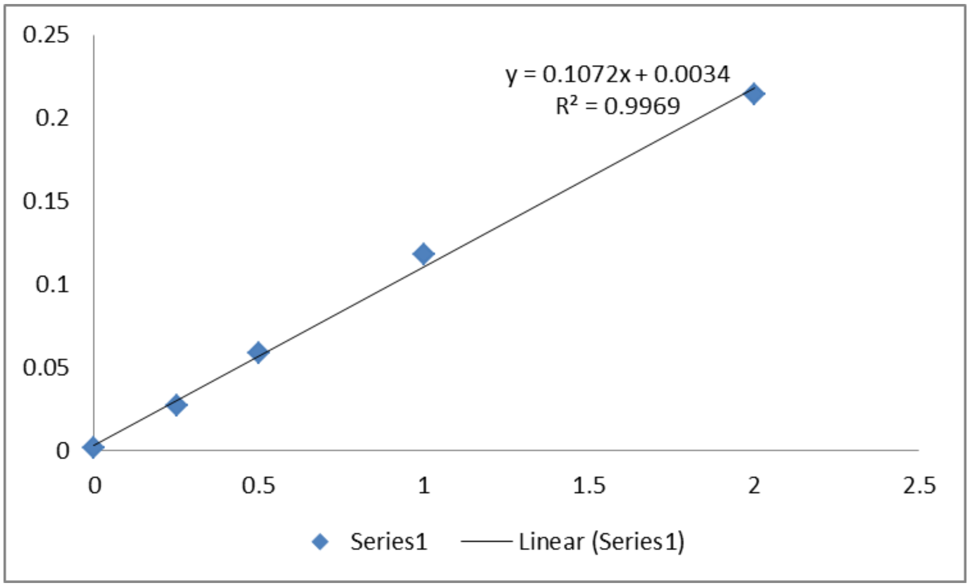


Figure A4.2 Calibration curve for copper

Figure A4.3: multi-level calibration curves for analyzed OC pesticides

Figure A4.4:Sample calibration standard chromatograms

Figure A4.5:Chromatograms of samples

APPENDIX V

Table A5.1: Correlation of levels of ∑OCPs in water, sediment and soil in dry and wet season

		OCP in Soil Dry Season	OCP in Soil Wet Season	OCP in Sediment Dry Season	OCP in Sediment Wet Season	OCP in Water Dry Season	OCP in Water Wet Season	
OCP in Soil Dry Season	Pearson Correlation	1	-.508	-.007	-.196	-.287	-.322	
	Sig. (2-tailed)		.244	.987	.673	.532	.482	
	N	7	7	7	7	7	7	
OCP in Soil Wet Season	Pearson Correlation	-.508	1	.623	.440	-.314	.240	
	Sig. (2-tailed)	.244		.135	.323	.493	.604	
	N	7	7	7	7	7	7	
OCP in Sediment Dry Season	Pearson Correlation	-.007	.623	1	.705	-.549	.487	
	Sig. (2-tailed)	.987	.135		.077	.202	.267	
	N	7	7	7	7	7	7	
OCP in Sediment Wet Season	Pearson Correlation	-.196	.440	.705	1	-.071	.699	
	Sig. (2-tailed)	.673	.323	.077		.879	.080	
	N	7	7	7	7	7	7	
OCP in Water Dry Season	Pearson Correlation	-.287	-.314	-.549	-.071	1	-.232	
	Sig. (2-tailed)	.532	.493	.202	.879		.617	
	N	7	7	7	7	7	7	
OCP in Water Wet Season	Pearson Correlation	-.322	.240	.487	.699	-.232	1	
	Sig. (2-tailed)	.482	.604	.267	.080	.617		
	N	7	7	7	7	7	7	

Table A5.2: Correlation of levels of ∑OCPs in water, sediment and soil

		OCPs in Water	OCPs in Sediment	OCPs in Soil	
OCPs in Water	Pearson Correlation	1	.692	.242	
	Sig. (2-tailed)		.085	.601	
	N	7	7	7	
OCPs in Sediment	Pearson Correlation	.692	1	.435	
	Sig. (2-tailed)	.085		.329	
	N	7	7	7	
OCPs in Soil	Pearson Correlation	.242	.435	1	
	Sig. (2-tailed)	.601	.329		
	N	7	7	7	

Table A5.3: Correlation of levels of ∑heavy metals in water, sediment and soil in dry and wet season

		Heavy Metals Soil Dry Season	Heavy Metals Sediment Dry Season	Heavy Metals Water Dry Season	Heavy Metals Water Wet Season	Heavy Metals Sediment Wet Season	Heavy Metals Soil Wet Season
Heavy Metals Soil Dry Season	Pearson Correlation	1	.952	.120	.681	.861	.719
	Sig. (2-tailed)		.048	.880	.524	.340	.489
	N	4	4	4	3	3	3
Heavy Metals Sediment Dry Season	Pearson Correlation	.952	1	.372	.581	.788	.624
	Sig. (2-tailed)	.048		.628	.605	.422	.571
	N	4	4	4	3	3	3
Heavy Metals Water Dry Season	Pearson Correlation	.120	.372	1	.891	.983	.915
	Sig. (2-tailed)	.880	.628		.300	.116	.265
	N	4	4	4	3	3	3
Heavy Metals Water Wet Season	Pearson Correlation	.681	.581	.891	1	.959	.999
	Sig. (2-tailed)	.524	.605	.300		.183	.035
	N	3	3	3	3	3	3
Heavy Metals Sediment Wet Season	Pearson Correlation	.861	.788	.983	.959	1	.973
	Sig. (2-tailed)	.340	.422	.116	.183		.149
	N	3	3	3	3	3	3
Heavy Metals Soil Wet Season	Pearson Correlation	.719	.624	.915	.999	.973	1
	Sig. (2-tailed)	.489	.571	.265	.035	.149	
	N	3	3	3	3	3	3

Table A5.4 Correlation of levels of ∑heavy metals in water, sediment and soil samples

		Cd in Water	Pb in Water	Zn in Water	Cu in Water	Cd in Sedime	Pb in Sedime	Cu in Sedime	Zn in Sedimen	Cd in Soil	Pb in Soil	Zn in Soil	Cu in Soil
Cd in Water	Pearson Corr	1	-0.6192728	0.00195941	0.03953494	0.11868123	0.69543941	0.03953494	-0.13470582	0.209559067	-0.11025563	0.371722371	-0.47099807
	Sig. (2-tailed)		0.13808146	0.99667361	0.93293584	0.79993643	0.08276301	0.93293584	0.773385439	0.652001317	0.813959838	0.411624189	0.28606442
	N	7	7	7	7	7	7	7	7	7	7	7	7
Pb in Water	Pearson Corr	-0.6192728	1	-0.2473678	0.01610978	-0.5085405	-0.6250821	0.01610978	-0.3941844	-0.37396998	-0.0083448	-0.25634632	0.428095625
	Sig. (2-tailed)	0.13808146		0.59278503	0.97265475	0.24383343	0.13334935	0.97265475	0.381566225	0.40857585	0.985833918	0.578969724	0.337964295
	N	7	7	7	7	7	7	7	7	7	7	7	7
Zn in Water	Pearson Corr	0.00195941	-0.2473678	1	-0.3542887	0.06577924	0.2324495	-0.3542887	0.644739918	0.366093253	0.145319641	0.701510087	0.122253874
	Sig. (2-tailed)	0.99667361	0.59278503		0.43556677	0.88857113	0.61595566	0.43556677	0.117960305	0.419297592	0.755894347	0.078985896	0.794002876
	N	7	7	7	7	7	7	7	7	7	7	7	7
Cu in Water	Pearson Corr	0.03953494	0.01610978	-0.3542887	1	0.07030318	0.15657167	1	-0.14169376	0.342420887	0.208196843	-0.11938897	0.469711605
	Sig. (2-tailed)	0.93293584	0.97265475	0.43556677		0.88094434	0.73744172	0	0.761860654	0.45216019	0.654164216	0.798760379	0.287565339
	N	7	7	7	7	7	7	7	7	7	7	7	7
Cd in Sedime	Pearson Corr	0.11868123	-0.5085405	0.06577924	0.07030318	1	0.66647073	0.07030318	0.151157174	0.680742067	0.689253722	-0.2756291	0.115450574
	Sig. (2-tailed)	0.79993643	0.24383343	0.88857113	0.88094434		0.10207726	0.88094434	0.74630914	0.092295832	0.086708156	0.549647444	0.805308594
	N	7	7	7	7	7	7	7	7	7	7	7	7
Pb in Sedime	Pearson Corr	0.69543941	-0.6250821	0.2324495	0.15657167	0.66647073	1	0.15657167	-0.09445662	0.587971006	0.330999686	0.10922222	-0.18215593
	Sig. (2-tailed)	0.08276301	0.13334935	0.61595566	0.73744172	0.10207726		0.73744172	0.840359846	0.165009165	0.46834712	0.81568261	0.695867228
	N	7	7	7	7	7	7	7	7	7	7	7	7
Cu in Sedime	Pearson Corr	0.03953494	0.01610978	-0.3542887	1	0.07030318	0.15657167	1	-0.14169376	0.342420887	0.208196843	-0.11938897	0.469711605
	Sig. (2-tailed)	0.93293584	0.97265475	0.43556677	0	0.88094434	0.73744172		0.761860654	0.45216019	0.654164216	0.798760379	0.287565339
	N	7	7	7	7	7	7	7	7	7	7	7	7
Zn in Sedime	Pearson Corr	-0.1347058	-0.3941844	0.64473992	-0.1416938	0.15115717	-0.0944566	-0.1416938	1	0.499973899	0.337292692	0.648076786	0.353596576
	Sig. (2-tailed)	0.77338544	0.38156623	0.11796031	0.76186065	0.74630914	0.84035985	0.76186065		0.253198777	0.459402161	0.115444095	0.436528056
	N	7	7	7	7	7	7	7	7	7	7	7	7
Cd in Soil	Pearson Corr	0.20955907	-0.37397	0.36609325	0.34242089	0.68074207	0.58797101	0.34242089	0.499973899	1	0.870692646	0.362978821	0.596333191
	Sig. (2-tailed)	0.65200132	0.40857585	0.41929759	0.45216019	0.09229583	0.16500917	0.45216019	0.253198777		0.010758324	0.423566738	0.157580854
	N	7	7	7	7	7	7	7	7	7	7	7	7
Pb in Soil	Pearson Corr	-0.1102556	-0.0083448	0.14531964	0.20819684	0.68925372	0.33099969	0.20819684	0.337292692	0.870692646	1	0.062962362	0.733780359
	Sig. (2-tailed)	0.81395984	0.98583392	0.75589435	0.65416422	0.08670816	0.46834712	0.65416422	0.459402161	0.010758324		0.893323514	0.060482491
	N	7	7	7	7	7	7	7	7	7	7	7	7
Zn in Soil	Pearson Corr	0.37172237	-0.2563463	0.70151009	-0.119389	-0.2756291	0.10922222	-0.119389	0.648076786	0.362978821	0.062962362	1	0.171671956
	Sig. (2-tailed)	0.41162419	0.57896972	0.0789859	0.79876038	0.54964744	0.81568261	0.79876038	0.115444095	0.423566738	0.893323514		0.712836126
	N	7	7	7	7	7	7	7	7	7	7	7	7
Cu in Soil	Pearson Corr	-0.4709981	0.42809563	0.12225387	0.46971161	0.11545057	-0.1821559	0.46971161	0.353596576	0.596333191	0.733780359	0.171671956	1
	Sig. (2-tailed)	0.28606442	0.3379643	0.79400288	0.28756534	0.80530859	0.69586723	0.28756534	0.436528056	0.157580854	0.060482491	0.712836126	
	N	7	7	7	7	7	7	7	7	7	7	7	7
**	Correlation is significant at the 0.01 level (2-tailed).												
*	Correlation is significant at the 0.05 level (2-tailed).												

Table A5.5: Correlation of levels of ∑nitrates in water, sediment and soil in dry and wet season

		Nitrates in Water Wet Season	Nitrates in Water Dry Season	Nitrates in Sediment Wet Season	Nitrates in Sediment Dry Season	Nitrates in Soil Wet Season	Nitrates in Soil Dry Season
Nitrates in Water Wet Season	Pearson Correlation	1	-.570	-.022	.155	.459	.980
	Sig. (2-tailed)		.182	.963	.740	.300	.000
	N	7	7	7	7	7	7
Nitrates in Water Dry Season	Pearson Correlation	-.570	1	.700	-.618	-.485	-.619
	Sig. (2-tailed)	.182		.080	.139	.270	.139
	N	7	7	7	7	7	7
Nitrates in Sediment Wet Season	Pearson Correlation	-.022	.700	1	-.474	-.135	-.154
	Sig. (2-tailed)	.963	.080		.283	.773	.741
	N	7	7	7	7	7	7
Nitrates in Sediment Dry Season	Pearson Correlation	.155	-.618	-.474	1	-.093	.153
	Sig. (2-tailed)	.740	.139	.283		.843	.742
	N	7	7	7	7	7	7
Nitrates in Soil Wet Season	Pearson Correlation	.459	-.485	-.135	-.093	1	.471
	Sig. (2-tailed)	.300	.270	.773	.843		.287
	N	7	7	7	7	7	7
Nitrates in Soil Dry Season	Pearson Correlation	.980	-.619	-.154	.153	.471	1
	Sig. (2-tailed)	.000	.139	.741	.742	.287	
	N	7	7	7	7	7	7

Table A5.6: Correlation of levels of ∑phosphates in water, sediment and soil in dry and wet season

		Phosphates in Water Dry Season	Phosphates in Water Wet Season	Phosphates in Sediments Dry Season	Phosphates in Sediment Wet Season	Phosphates in Soil Dry Season	Phosphates in Soil Wet Season
Phosphates in Water Dry Season	Pearson Correlation	1	.602	-.654	.277	-.102	.611
	Sig. (2-tailed)		.152	.111	.548	.829	.145
	N	7	7	7	7	7	7
Phosphates in Water Wet Season	Pearson Correlation	.602	1	-.479	.621	.386	.608
	Sig. (2-tailed)	.152		.277	.137	.392	.148
	N	7	7	7	7	7	7
Phosphates in Sediments Dry Season	Pearson Correlation	-.654	-.479	1	-.364	-.023	-.348
	Sig. (2-tailed)	.111	.277		.422	.961	.444
	N	7	7	7	7	7	7
Phosphates in Sediment Wet Season	Pearson Correlation	.277	.621	-.364	1	.176	-.024
	Sig. (2-tailed)	.548	.137	.422		.706	.960
	N	7	7	7	7	7	7
Phosphates in Soil Dry Season	Pearson Correlation	-.102	.386	-.023	.176	1	.184
	Sig. (2-tailed)	.829	.392	.961	.706		.692
	N	7	7	7	7	7	7
Phosphates in Soil Wet Season	Pearson Correlation	.611	.608	-.348	-.024	.184	1
	Sig. (2-tailed)	.145	.148	.444	.960	.692	
	N	7	7	7	7	7	7

Table A5.7: Correlation of levels of ∑nitrates in water, sediment and soil

		Nitrates in Water	Nitrates in Sediment	Nitrates in Soil
Nitrates in Water	Pearson Correlation	1	.509	-.542
	Sig. (2-tailed)		.243	.209
	N	7	7	7
Nitrates in Sediment	Pearson Correlation	.509	1	-.161
	Sig. (2-tailed)	.243		.731
	N	7	7	7
Nitrates s in Soil	Pearson Correlation	-.542	-.161	1
	Sig. (2-tailed)	.209	.731	
	N	7	7	7

Table A5.8: Correlation of levels of ∑phosphates in water, sediment and soil

		Phosphates in Water	Phosphates in Sediment	Phosphates in Soil
Phosphates in Water	Pearson Correlation	1	0.17	0.48
	Sig. (2-tailed)		.72	.27
	N	7	7	7
Phosphates in Sediment	Pearson Correlation	.17	1	.01
	Sig. (2-tailed)	.72		0.99
	N	7	7	7
Phosphates in Soil	Pearson Correlation	.48	.01	1
	Sig. (2-tailed)	.27	.99	
	N	7	7	7

Table A5.9: correlations of levels of ∑OCPs with physico-chemical parameters in water

Correlations

		Summation of OCPs in Water	TDS	Electrical Conductivity	TSS	pH
Summation of OCPs in Water	Pearson Correlation	1	-.339	-.339	.439	-.483
	Sig. (2-tailed)		.457	.457	.324	.273
	N	8	7	7	7	7
TDS	Pearson Correlation	-.339	1	1.000**	.492	.980**
	Sig. (2-tailed)	.457		.000	.262	.000
	N	7	7	7	7	7
Electrical Conductivity	Pearson Correlation	-.339	1.000**	1	.490	.980**
	Sig. (2-tailed)	.457	.000		.264	.000
	N	7	7	7	7	7
TSS	Pearson Correlation	.439	.492	.490	1	.432
	Sig. (2-tailed)	.324	.262	.264		.333
	N	7	7	7	7	7
pH	Pearson Correlation	-.483	.980**	.980**	.432	1
	Sig. (2-tailed)	.273	.000	.000	.333	
	N	7	7	7	7	7

**. Correlation is significant at the 0.01 level (2-tailed).

Table A5.10: correlations of levels of ∑OCPs with physico-chemical parameters in sediment

Correlations

		Summation of OCPs in Sediment	pH	Total Nitrogen	Total Organic Carbon	Phosphorous	K	C	Mg	Mn	Cu	Fe	Zn	Na	Elevtrical Conductivity
Summation of OCPs in Sediment	Pearson Correlation	1	-.662	-.548	-.589	-.226	.086	.120	.446	.199	.063	.344	.132	-.049	-.607
	Sig. (2-tailed)		.105	.203	.164	.627	.855	.798	.315	.669	.893	.450	.777	.916	.148
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
pH	Pearson Correlation	-.662	1	.756*	.865*	.294	.043	-.165	-.661	-.263	-.179	-.480	-.404	.137	.871*
	Sig. (2-tailed)	.105		.049	.012	.523	.927	.723	.106	.570	.700	.276	.369	.770	.011
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Nitrogen	Pearson Correlation	-.548	.756*	1	.921**	.832*	.383	.431	-.281	.327	-.341	-.112	-.401	.291	.904**
	Sig. (2-tailed)	.203	.049		.003	.020	.397	.334	.542	.474	.455	.811	.372	.526	.005
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Organic Carbon	Pearson Correlation	-.589	.865*	.921**	1	.626	.128	.093	-.450	-.019	-.337	-.266	-.357	.311	.997**
	Sig. (2-tailed)	.164	.012	.003		.133	.784	.843	.311	.968	.460	.564	.432	.498	.000
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Phosphorous	Pearson Correlation	-.226	.294	.832*	.626	1	.598	.815*	.103	.748	-.316	.189	-.286	.271	.588
	Sig. (2-tailed)	.627	.523	.020	.133		.157	.026	.826	.053	.490	.685	.534	.557	.165
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
K	Pearson Correlation	.086	.043	.383	.128	.598	1	.812*	.564	.799*	-.627	.641	-.771*	.565	.117
	Sig. (2-tailed)	.855	.927	.397	.784	.157		.026	.187	.031	.132	.121	.042	.186	.803
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
C	Pearson Correlation	.120	-.165	.431	.093	.815*	.812*	1	.495	.993**	-.276	.499	-.299	.224	.052
	Sig. (2-tailed)	.798	.723	.334	.843	.026	.026		.259	.000	.549	.254	.515	.629	.912
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mg	Pearson Correlation	.446	-.661	-.281	-.450	.103	.564	.495	1	.536	-.588	.974**	-.362	.603	-.433
	Sig. (2-tailed)	.315	.106	.542	.311	.826	.187	.259		.215	.165	.000	.424	.152	.332
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mn	Pearson Correlation	.199	-.263	.327	-.019	.748	.799*	.993**	.536	1	-.227	.517	-.253	.176	-.061
	Sig. (2-tailed)	.669	.570	.474	.968	.053	.031	.000	.215		.625	.234	.584	.705	.896
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cu	Pearson Correlation	.063	-.179	-.341	-.337	-.316	-.627	-.276	-.588	-.227	1	-.749	.865*	-.996**	-.378
	Sig. (2-tailed)	.893	.700	.455	.460	.490	.132	.549	.165	.625		.053	.012	.000	.404
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Fe	Pearson Correlation	.344	-.480	-.112	-.266	.189	.641	.499	.974**	.517	-.749	1	-.532	.757*	-.242
	Sig. (2-tailed)	.450	.276	.811	.564	.685	.121	.254	.000	.234	.053		.219	.049	.601
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn	Pearson Correlation	.132	-.404	-.401	-.357	-.286	-.771*	-.299	-.362	-.253	.865*	-.532	1	-.821*	-.385
	Sig. (2-tailed)	.777	.369	.372	.432	.534	.042	.515	.424	.584	.012	.219		.024	.393
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Na	Pearson Correlation	-.049	.137	.291	.311	.271	.565	.224	.603	.176	-.996**	.757*	-.821*	1	.354
	Sig. (2-tailed)	.916	.770	.526	.498	.557	.186	.629	.152	.705	.000	.049	.024		.436
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Elevtrical Conductivity	Pearson Correlation	-.607	.871*	.904**	.997**	.588	.117	.052	-.433	-.061	-.378	-.242	-.385	.354	1
	Sig. (2-tailed)	.148	.011	.005	.000	.165	.803	.912	.332	.896	.404	.601	.393	.436	
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table A5.11: correlations of levels of ∑OCPs with physico-chemical parameters in soil

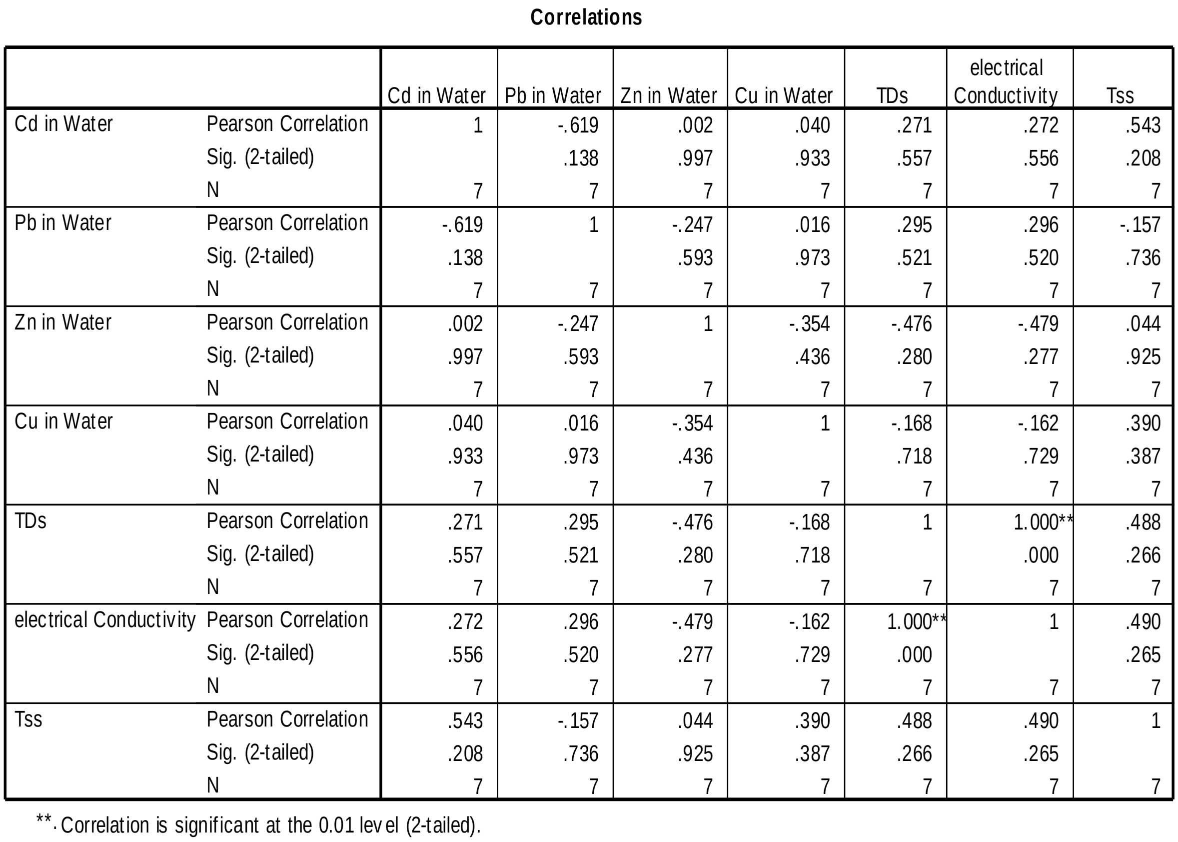
Correlations

		Summation of OCPs in Sediment	pH	Total Nitrogen	Total Organic Carbon	Phosphorous	K	C	Mg	Mn	Cu	Fe	Zn	Na	Elevtrical Conductivity
Summation of OCPs in Sediment	Pearson Correlation	1	.240	.048	.337	-.033	-.568	-.308	.255	-.211	-.187	-.172	.569	-.031	-.115
	Sig. (2-tailed)		.604	.918	.460	.945	.184	.501	.581	.650	.687	.713	.183	.947	.806
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
pH	Pearson Correlation	.240	1	-.677	-.157	-.936**	-.415	-.460	-.001	-.904**	-.277	-.981**	-.106	.935**	.477
	Sig. (2-tailed)	.604		.095	.736	.002	.354	.299	.999	.005	.547	.000	.821	.002	.279
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Nitrogen	Pearson Correlation	.048	-.677	1	.799*	.865*	.055	.149	-.496	.431	-.440	.657	.049	-.736	-.289
	Sig. (2-tailed)	.918	.095		.031	.012	.907	.750	.258	.334	.324	.109	.916	.059	.529
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Organic Carbon	Pearson Correlation	.337	-.157	.799*	1	.484	-.218	-.094	-.648	-.070	-.834*	.166	.008	-.295	-.189
	Sig. (2-tailed)	.460	.736	.031		.271	.638	.841	.116	.882	.020	.722	.986	.520	.686
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Phosphorous	Pearson Correlation	-.033	-.936**	.865*	.484	1	.236	.339	-.157	.775*	-.016	.926**	.179	-.953**	-.498
	Sig. (2-tailed)	.945	.002	.012	.271		.610	.457	.737	.041	.973	.003	.701	.001	.255
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
K	Pearson Correlation	-.568	-.415	.055	-.218	.236	1	.944**	-.309	.637	.069	.484	-.728	-.106	-.606
	Sig. (2-tailed)	.184	.354	.907	.638	.610		.001	.500	.124	.884	.271	.064	.822	.149
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
C	Pearson Correlation	-.308	-.460	.149	-.094	.339	.944**	1	-.220	.729	.022	.576	-.558	-.226	-.812*
	Sig. (2-tailed)	.501	.299	.750	.841	.457	.001		.636	.063	.963	.176	.193	.625	.027
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mg	Pearson Correlation	.255	-.001	-.496	-.648	-.157	-.309	-.220	1	.144	.831*	.020	.732	-.140	.032
	Sig. (2-tailed)	.581	.999	.258	.116	.737	.500	.636		.758	.020	.966	.062	.765	.946
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mn	Pearson Correlation	-.211	-.904**	.431	-.070	.775*	.637	.729	.144	1	.388	.954**	.009	-.794*	-.717
	Sig. (2-tailed)	.650	.005	.334	.882	.041	.124	.063	.758		.389	.001	.984	.033	.070
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cu	Pearson Correlation	-.187	-.277	-.440	-.834*	-.016	.069	.022	.831*	.388	1	.245	.390	-.237	.079
	Sig. (2-tailed)	.687	.547	.324	.020	.973	.884	.963	.020	.389		.596	.387	.609	.867
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Fe	Pearson Correlation	-.172	-.981**	.657	.166	.926**	.484	.576	.020	.954**	.245	1	.092	-.921**	-.629
	Sig. (2-tailed)	.713	.000	.109	.722	.003	.271	.176	.966	.001	.596		.844	.003	.130
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn	Pearson Correlation	.569	-.106	.049	.008	.179	-.728	-.558	.732	.009	.390	.092	1	-.416	.114
	Sig. (2-tailed)	.183	.821	.916	.986	.701	.064	.193	.062	.984	.387	.844		.353	.808
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Na	Pearson Correlation	-.031	.935**	-.736	-.295	-.953**	-.106	-.226	-.140	-.794*	-.237	-.921**	-.416	1	.427
	Sig. (2-tailed)	.947	.002	.059	.520	.001	.822	.625	.765	.033	.609	.003	.353		.339
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Elevtrical Conductivity	Pearson Correlation	-.115	.477	-.289	-.189	-.498	-.606	-.812*	.032	-.717	.079	-.629	.114	.427	1
	Sig. (2-tailed)	.806	.279	.529	.686	.255	.149	.027	.946	.070	.867	.130	.808	.339	
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table A5.12: correlations of levels of ∑heavy metals with physico-chemical parameters in water



Correlations

		Cd in Water	Pb in Water	Zn in Water	Cu in Water	TDs	electrical Conductivity	Tss
Cd in Water	Pearson Correlation	1	-.619	.002	.040	.271	.272	.543
	Sig. (2-tailed)		.138	.997	.933	.557	.556	.208
	N	7	7	7	7	7	7	7
Pb in Water	Pearson Correlation	-.619	1	-.247	.016	.295	.296	-.157
	Sig. (2-tailed)	.138		.593	.973	.521	.520	.736
	N	7	7	7	7	7	7	7
Zn in Water	Pearson Correlation	.002	-.247	1	-.354	-.476	-.479	.044
	Sig. (2-tailed)	.997	.593		.436	.280	.277	.925
	N	7	7	7	7	7	7	7
Cu in Water	Pearson Correlation	.040	.016	-.354	1	-.168	-.162	.390
	Sig. (2-tailed)	.933	.973	.436		.718	.729	.387
	N	7	7	7	7	7	7	7
TDs	Pearson Correlation	.271	.295	-.476	-.168	1	1.000**	.488
	Sig. (2-tailed)	.557	.521	.280	.718		.000	.266
	N	7	7	7	7	7	7	7
electrical Conductivity	Pearson Correlation	.272	.296	-.479	-.162	1.000**	1	.490
	Sig. (2-tailed)	.556	.520	.277	.729	.000		.265
	N	7	7	7	7	7	7	7
Tss	Pearson Correlation	.543	-.157	.044	.390	.488	.490	1
	Sig. (2-tailed)	.208	.736	.925	.387	.266	.265	
	N	7	7	7	7	7	7	7

**. Correlation is significant at the 0.01 level (2-tailed).

Table A5.13: correlations of levels of ∑heavy metals with physico-chemical parameters in sediment

Correlations

		Cd in Sediment	Pb in Sediment	Zn in Sediment	Cu in Sediment	pH	Total Nitrogen	Total Organic carbon	P	K	Mg	Mn	Cu	Fe	Zn	Na	electrical Conductivity
Cd in Sediment	Pearson Correlation	1	.666	.151	-.633	.173	-.133	.564	.016	.162	.546	.657	.567	.646	.543	-.703	-.400
	Sig. (2-tailed)		.102	.746	.127	.710	.777	.187	.972	.728	.204	.109	.184	.117	.207	.078	.374
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Pb in Sediment	Pearson Correlation	.666	1	-.094	-.343	-.113	-.244	.239	.539	.701	.287	.645	.316	.467	-.035	-.260	-.785*
	Sig. (2-tailed)	.102		.840	.451	.809	.599	.606	.212	.079	.533	.118	.490	.291	.941	.574	.037
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn in Sediment	Pearson Correlation	.151	-.094	1	-.554	.207	-.096	.426	.329	.123	-.145	.375	.248	.447	-.200	-.381	.022
	Sig. (2-tailed)	.746	.840		.197	.656	.838	.340	.471	.793	.756	.407	.592	.314	.668	.399	.963
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cu in Sediment	Pearson Correlation	-.633	-.343	-.554	1	-.677	-.157	-.936**	-.415	-.460	-.001	-.904**	-.277	-.981**	-.106	.935**	.477
	Sig. (2-tailed)	.127	.451	.197		.095	.736	.002	.354	.299	.999	.005	.547	.000	.821	.002	.279
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
pH	Pearson Correlation	.173	-.113	.207	-.677	1	.799*	.865*	.055	.149	-.496	.431	-.440	.657	.049	-.736	-.289
	Sig. (2-tailed)	.710	.809	.656	.095		.031	.012	.907	.750	.258	.334	.324	.109	.916	.059	.529
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Nitrogen	Pearson Correlation	-.133	-.244	-.096	-.157	.799*	1	.484	-.218	-.094	-.648	-.070	-.834*	.166	.008	-.295	-.189
	Sig. (2-tailed)	.777	.599	.838	.736	.031		.271	.638	.841	.116	.882	.020	.722	.986	.520	.686
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Organic carbon	Pearson Correlation	.564	.239	.426	-.936**	.865*	.484	1	.236	.339	-.157	.775*	-.016	.926**	.179	-.953**	-.498
	Sig. (2-tailed)	.187	.606	.340	.002	.012	.271		.610	.457	.737	.041	.973	.003	.701	.001	.255
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
P	Pearson Correlation	.016	.539	.329	-.415	.055	-.218	.236	1	.944**	-.309	.637	.069	.484	-.728	-.106	-.606
	Sig. (2-tailed)	.972	.212	.471	.354	.907	.638	.610		.001	.500	.124	.884	.271	.064	.822	.149
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
K	Pearson Correlation	.162	.701	.123	-.460	.149	-.094	.339	.944**	1	-.220	.729	.022	.576	-.558	-.226	-.812*
	Sig. (2-tailed)	.728	.079	.793	.299	.750	.841	.457	.001		.636	.063	.963	.176	.193	.625	.027
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mg	Pearson Correlation	.546	.287	-.145	-.001	-.496	-.648	-.157	-.309	-.220	1	.144	.831*	.020	.732	-.140	.032
	Sig. (2-tailed)	.204	.533	.756	.999	.258	.116	.737	.500	.636		.758	.020	.966	.062	.765	.946
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mn	Pearson Correlation	.657	.645	.375	-.904**	.431	-.070	.775*	.637	.729	.144	1	.388	.954**	.009	-.794*	-.717
	Sig. (2-tailed)	.109	.118	.407	.005	.334	.882	.041	.124	.063	.758		.389	.001	.984	.033	.070
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cu	Pearson Correlation	.567	.316	.248	-.277	-.440	-.834*	-.016	.069	.022	.831*	.388	1	.245	.390	-.237	.079
	Sig. (2-tailed)	.184	.490	.592	.547	.324	.020	.973	.884	.963	.020	.389		.596	.387	.609	.867
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Fe	Pearson Correlation	.646	.467	.447	-.981**	.657	.166	.926**	.484	.576	.020	.954**	.245	1	.092	-.921**	-.629
	Sig. (2-tailed)	.117	.291	.314	.000	.109	.722	.003	.271	.176	.966	.001	.596		.844	.003	.130
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn	Pearson Correlation	.543	-.035	-.200	-.106	.049	.008	.179	-.728	-.558	.732	.009	.390	.092	1	-.416	.114
	Sig. (2-tailed)	.207	.941	.668	.821	.916	.986	.701	.064	.193	.062	.984	.387	.844		.353	.808
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Na	Pearson Correlation	-.703	-.260	-.381	.935**	-.736	-.295	-.953**	-.106	-.226	-.140	-.794*	-.237	-.921**	-.416	1	.427
	Sig. (2-tailed)	.078	.574	.399	.002	.059	.520	.001	.822	.625	.765	.033	.609	.003	.353		.339
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
electrical Conductivity	Pearson Correlation	-.400	-.785*	.022	.477	-.289	-.189	-.498	-.606	-.812*	.032	-.717	.079	-.629	.114	.427	1
	Sig. (2-tailed)	.374	.037	.963	.279	.529	.686	.255	.149	.027	.946	.070	.867	.130	.808	.339	
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table A5.14: correlations of levels of ∑heavy metals with physico-chemical parameters in soil

Correlations

		Cu in Soil	pH	Total Nitrogen	Total Organic carbon	P	K	Mg	Mn	Cu	Fe	Zn	Na	electrical Conductivity	Cd in Soil	Pb in Soil	Zn in Soil
Cu in Soil	Pearson Correlation	1	.247	.432	.568	.499	-.133	.095	-.304	.044	.035	-.288	.190	-.015	.596	.734	.172
	Sig. (2-tailed)	.000	.593	.332	.183	.254	.777	.840	.508	.925	.940	.530	.684	.974	.158	.060	.713
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
pH	Pearson Correlation	.247	1	.756*	.865*	.294	.043	-.165	-.661	-.263	-.179	-.480	-.404	.137	-.030	.253	.004
	Sig. (2-tailed)	.593		.049	.012	.523	.927	.723	.106	.570	.700	.276	.369	.770	.948	.584	.994
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Nitrogen	Pearson Correlation	.432	.756*	1	.921**	.832*	.383	.431	-.281	.327	-.341	-.112	-.401	.291	.324	.626	.057
	Sig. (2-tailed)	.332	.049		.003	.020	.397	.334	.542	.474	.455	.811	.372	.526	.478	.133	.903
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Total Organic carbon	Pearson Correlation	.568	.865*	.921**	1	.626	.128	.093	-.450	-.019	-.337	-.266	-.357	.311	.180	.557	-.069
	Sig. (2-tailed)	.183	.012	.003		.133	.784	.843	.311	.968	.460	.564	.432	.498	.699	.194	.884
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
P	Pearson Correlation	.499	.294	.832*	.626	1	.598	.815*	.103	.748	-.316	.189	-.286	.271	.660	.819*	.122
	Sig. (2-tailed)	.254	.523	.020	.133		.157	.026	.826	.053	.490	.685	.534	.557	.107	.024	.794
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
K	Pearson Correlation	-.133	.043	.383	.128	.598	1	.812*	.564	.799*	-.627	.641	-.771*	.565	.519	.569	-.232
	Sig. (2-tailed)	.777	.927	.397	.784	.157		.026	.187	.031	.132	.121	.042	.186	.232	.182	.617
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mg	Pearson Correlation	.095	-.165	.431	.093	.815*	.812*	1	.495	.993**	-.276	.499	-.299	.224	.684	.633	.123
	Sig. (2-tailed)	.840	.723	.334	.843	.026	.026		.259	.000	.549	.254	.515	.629	.090	.127	.793
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mn	Pearson Correlation	-.304	-.661	-.281	-.450	.103	.564	.495	1	.536	-.588	.974**	-.362	.603	.094	.104	-.429
	Sig. (2-tailed)	.508	.106	.542	.311	.826	.187	.259		.215	.165	.000	.424	.152	.841	.824	.337
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cu	Pearson Correlation	.044	-.263	.327	-.019	.748	.799*	.993**	.536	1	-.227	.517	-.253	.176	.681	.582	.133
	Sig. (2-tailed)	.925	.570	.474	.968	.053	.031	.000	.215		.625	.234	.584	.705	.092	.171	.777
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Fe	Pearson Correlation	.035	-.179	-.341	-.337	-.316	-.627	-.276	-.588	-.227	1	-.749	.865*	-.996**	.005	-.366	.706
	Sig. (2-tailed)	.940	.700	.455	.460	.490	.132	.549	.165	.625		.053	.012	.000	.991	.419	.076
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn	Pearson Correlation	-.288	-.480	-.112	-.266	.189	.641	.499	.974**	.517	-.749	1	-.532	.757*	.053	.165	-.538
	Sig. (2-tailed)	.530	.276	.811	.564	.685	.121	.254	.000	.234	.053		.219	.049	.911	.724	.213
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Na	Pearson Correlation	.190	-.404	-.401	-.357	-.286	-.771*	-.299	-.362	-.253	.865*	-.532	1	-.821*	-.090	-.358	.564
	Sig. (2-tailed)	.684	.369	.372	.432	.534	.042	.515	.424	.584	.012	.219		.024	.848	.431	.187
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
electrical Conductivity	Pearson Correlation	-.015	.137	.291	.311	.271	.565	.224	.603	.176	-.996**	.757*	-.821*	1	-.040	.338	-.724
	Sig. (2-tailed)	.974	.770	.526	.498	.557	.186	.629	.152	.705	.000	.049	.024		.931	.458	.066
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Cd in Soil	Pearson Correlation	.596	-.030	.324	.180	.660	.519	.684	.094	.681	.005	.053	-.090	-.040	1	.871*	.363
	Sig. (2-tailed)	.158	.948	.478	.699	.107	.232	.090	.841	.092	.991	.911	.848	.931		.011	.424
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Pb in Soil	Pearson Correlation	.734	.253	.626	.557	.819*	.569	.633	.104	.582	-.366	.165	-.358	.338	.871*	1	.063
	Sig. (2-tailed)	.060	.584	.133	.194	.024	.182	.127	.824	.171	.419	.724	.431	.458	.011		.893
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Zn in Soil	Pearson Correlation	.172	.004	.057	-.069	.122	-.232	.123	-.429	.133	.706	-.538	.564	-.724	.363	.063	1
	Sig. (2-tailed)	.713	.994	.903	.884	.794	.617	.793	.337	.777	.076	.213	.187	.066	.424	.893	
	N	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

APPENDIX VI

Table A6.2: Drinking Water Pesticide Guideline for some Organizations (ug/L) (IUPAC, 2003)

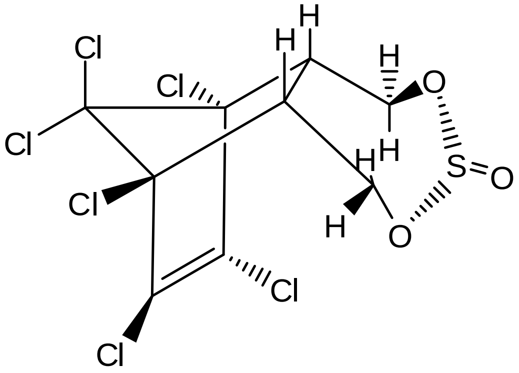
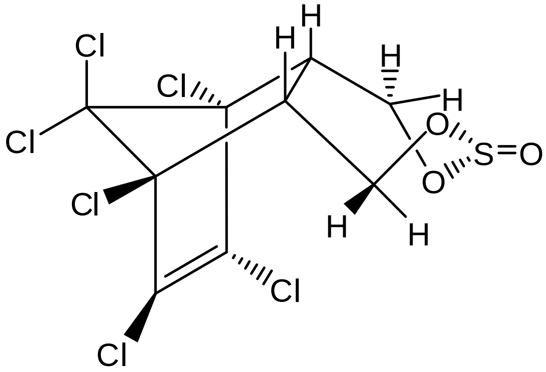
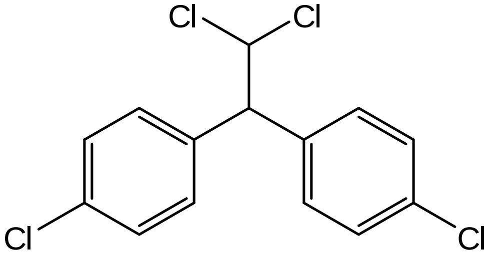
PESTICIDE	**WHO**	**EPA**	**AUSTRALIA**
Aldrin	0.03	-	0.01
Dieldrin	0.03	-	-
DDT	2	0.02	0.06
Lindane	2	0.02	0.05
Methoxychlor	20	40	0.02
Endrin	-	2	-
Heptachlor	0.03	0.4	0.05
Heptachlor epoxide	0.03	0.2	0.05

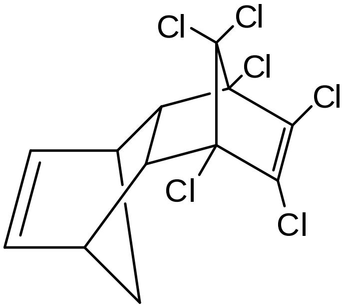
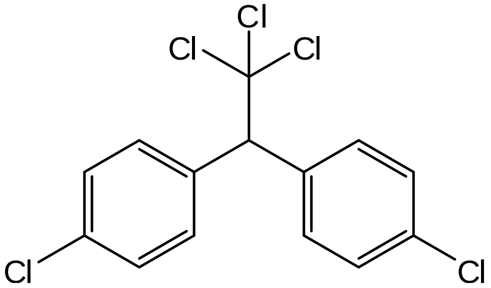
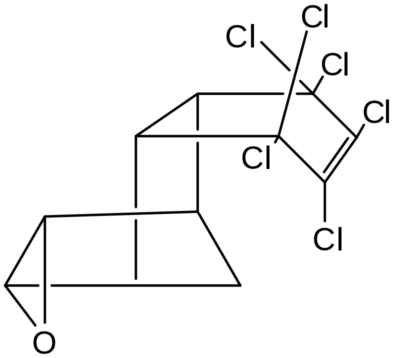
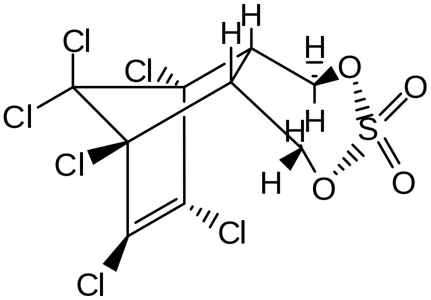
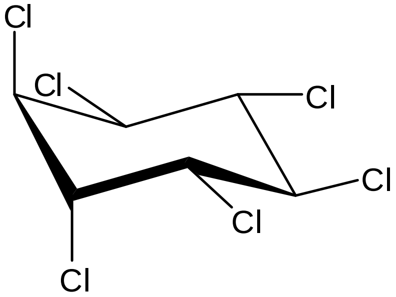
Table A6.3: EPA guidelines for OCPs in soil .

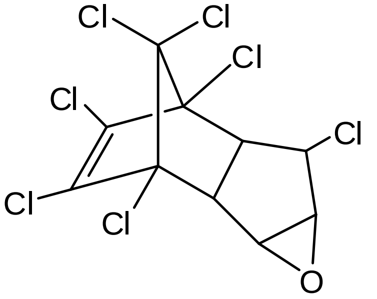
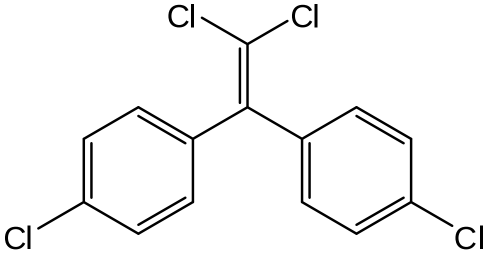
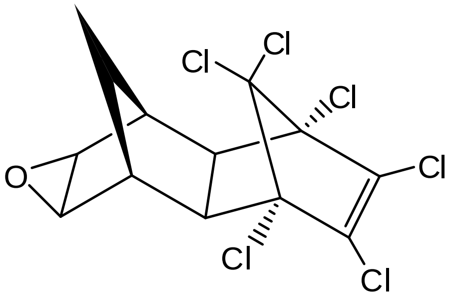
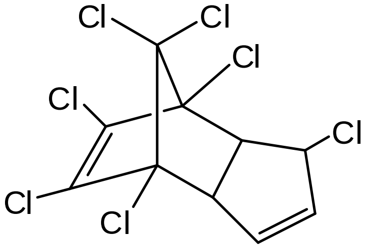
PESTICIDES	EPA (mg/kg)
Aldrin	0.04
Dieldrin	0.04
DDT	7 CSQG(1999)
Lindane	0.010 CSQG(1999)
Methoxychlor	
Endrin	20
Heptachlor	0.2
Heptachlor epoxide	

APPENDIX VII

Figure A7.1:Chemical Structures of Pesticides

SN	Name	Structures
	α−Endosulphan	
	β−Endosulphan	
	Aldrin	

	(1,1-dichloro-2,2-bis (4-chlorophenyl) ethane) p,p DDD	
	dichloro-diphenyl-trichloro-ethane (DDT)	
	Dieldrin	
	EndosulphanSulf ate	
	hexachlorocyclohexane (HCH),	

	Heptachlor epoxide	
	2,2-bis p-chlorophenyl1, 1-dichloroethylene- p,p'-DDE	
	Endrin	
	Heptachlor	
	Methoxychlor