ASSESSMENT OF POLLUTION AND PREDICTION OF ENVIRONMENTAL RISKS OF ORGANOCHLORINE PESTICIDE RESIDUES ON AQUATIC COMMUNITIES IN LAKE NAIVASHA, KENYA

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Assessment of Pollution and Prediction of Environmental Risks of Organochlorine Pesticide Residues on Aquatic Communities in Lake Naivasha, Kenya

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A Thesis submitted in fulfillment for the Degree of Doctor Philosophy in Environmental Technology in the Jomo Kenyatta University of Agriculture and Technology

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DECLARATION

This Thesis is my original work and has not been presented for a degree in any other university.

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This Thesis has been submitted for examination with our approval as University Supervisors.

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Dr. Ruth N. Wanjau,

KU, Kenya.

DEDICATION

This work is dedicated to my son, my daughter and all my nephews and nieces to serve as an inspiration for hard work and a testimony that with God all things are possible.

ACKNOWLEDGEMENTS

Special thanks go to my supervisors; Prof. Joseph M. Keriko, Dr. Ruth N. Wanjau and Prof. Jackson J. Kitetu for their tireless efforts to see this work completed, the encouragement, contribution and confidence they put in this work drove the study to copmletion. Acknowledgement is made on the contributions of Prof. Khamisi M. Tsanuo, and Dr. Eric R. Okong'o without whose support the study would be incomplete.

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LIST OFABBREVIATIONS AND ACRONYMS

AI	Artificial Intelligence
AAS	Atomic Absorption Spectrophotometer
ADI	Acceptable Daily Intake
ANOVA	Analysis of Variance
BAF	Bioaccumulation Factor
BDL	Below Detection Limit
BOD	Biological Oxygen Demand
CAAC	Catchment Area Advisory Committees
CAS	Chemical Abstract Service
CBR	Case Based Reasoning
CCME	Council of Canadian Ministers for Environment
$\mathbf{C_d}$	Degree of Contamination
CF	Contamination Factor
COD	Chemical Oxygen Demand
DDA	2, 2 bis - (4-Chlorophenyl) Acetic Acid
DDE	Dichloro-diphenyl trichoro-ethylene
DDT	Dichloro-diphenyl tichoro-ethane
DO	Dissolved Oxygen
$\mathbf{DT_{50}}$	50% Dissipation Time
DW	Dry Weight
EAWS	East Africa Wildlife Society

EC_{50}	Effective Concentration that Kill 50% of the Population
ECD	Electron Capture Detector
EEC	European Economic Commission
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
EPBA	Environmental Protection of Biodiversity Act
GEF	Global Environmental Fund
GPS	Global Positioning System
GoK	Government of Kenya
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High Pressure Liquid Chromatography
I**GAD**	Inter Governmental Authority on Development
IMCE	Inter-ministerial Committee for Environment
ITCZ	Inter-Tropical Convergence Zone
IUCN	International Union for Conservation of Nature
KEMFRI	Kenya Marine and Fisheries Research Institute
KWS	Kenya Wildlife Society
LC_{50}	Lethal Concentration at which 50% of Test Population Dies
LNROA	Lake Naivasha Riparian Owners' Association
MEA	Millennium Ecosystem Assessment
N	Number of Cases Evaluated in PERPEST

NEMA	National Environment Management Authority
NGO	Non Governmental Organization
NPS	Non-Point Sources
NWSC	National Wetlands Standing Committee
o	*Ortho*
OCP	Organochlorine Pesticides
OP	Organophosphorous
p	*Para*
PCB	Polychlorinated Biphenyls
PCPB	Pesticide Control and Products Board
PDA	Personal Data Assistant
PERPEST	Prediction of Ecological Risks of Pesticides
PLI	Pollution Load Index
RCW	Ramsar Convention of Wetlands
SD	Secchi Depth
SS	Sampling Site
TRV	Toxicity Reference Value
UNEP	United Nations Environment Programme
WAP	Weighted Analogies Prediction
WHO	World Health Organization
WAB	Water Appeal Boards
WASREB	Water Services Regulatory Board

WMI	Ministry of Water and Irrigation
WRMA	Water Resources Management Authority
WRUA	Water Resources Users Associations
WSB	Water Services Boards
WSTF	Water Services Trust Fund
WW	Wet Weight

ABSTRACT

Anthropogenic activities in the Lake Naivasha catchments pose serious environmental threats to sustainable freshwater ecosystem management. The future of the lake hangs on the balance of economic exploitation and sustainable watershed conservation. The current growth experienced in the chemical intensive flower industry, human settlements and power generation have led to chemical pollution, wetland reclamation and increased water abstraction volumes, which threaten the existence of the water body. Chemical drift during spray and washing of agrochemicals during the rainy season add the chemicals to water bodies. This study reports the findings of an environmental pollution assessment and environmental risks assessment posed by organochlorine pesticide residues and their metabolites in the Lake Naivasha basin during the period between 2008 and 2009. The objective of the study was to assess environmental pollution in reference to heavy metals, organochlorine pesticides in Lake Naivasha basin and to predict environmental risks of organochlorine pesticides on aquatic communities. Primary data was acquired through interviews, observations and sample whereas secondary data was obtained from published information. The data was analyzed statistically at $p = 0.05$ confidence level using significant T-Test, ANOVA and Dixon's test. The concentrations of lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu), *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, heptachlor, heptachlor epoxide, lindane, aldrin, dieldrin, endosulfan and methoxychlor in water column and three fish species; Tilapia, *(Oreochromis leucosticus)*, Common carp, *(Cyprinus carpio)* and Mirror carp, *(Cuprinus spectacularlus)* from Lake Naivasha, Kenya were determined. The contaminants were chosen due to their toxicity to aquatic life and persistence. Lake bed

sediments were also analyzed for the concentrations of Pb, Cd, Zn, Ni and Cu. Fishnet caught fish samples were bought from fishermen while still alive and identified by the Kenya Marine and Fisheries Research Institute (KEMFRI) staff whereas sediment and water samples were collected from 10 sampling sites in the basin. Water, fish and sediment samples for heavy metal analysis were wet oxidized and the concentrations determined using Flame Atomic Absorption Spectrophotometry (AAS). Edible portions of fish were homogenized and extracted with High Pressure Liquid Chromatography (HPLC) grade dichloromethane and cleanup with Florisil, the concentrations were determined using Varian CP 3800 Gas Chromatograph equipped with Electron Capture Detector. The mean heavy metal concentrations in sediments (in µg/g) ranged within 38.81 - 118.42 (Ni), 34.58 - 70.22 (Zn), 18.18 - 60.25 (Pb), 1.13 - 2.66 (Cu) and 0.74 - 3.66 (Cd) respectively these were higher than those found in fish. The mean heavy metal concentrations in fish (µg/g) ranged between 13.39 – 14.63 (Ni), 7.31 – 9.32 (Zn), 1.49 – 1.56 (Pb), 0.27 – 0.36 (Cu) and 0.13 – 0.44 (Cd) respectively. The order of bio-concentration of the metals in fish are *C. spectacularlus>C. carpio>O. leucosticus* respectively. The heavy metal concentrations in the water column (total content, mg/L) ranged between 0.81 - 1.92 (Zn), 0.08 - 0.45 (Ni), 0.01 - 0.36 (Pb), 0.004 - 0.04 (Cd), and 0.001 - 0.01 (Cu) respectively. The study shows that the Lake bed is contaminated with Cd, moderately contaminated with Ni and Pb, but not contaminated with Zn and Cu. Pearson's correlation coefficient at p = 0.05 revealed negative correlation between heavy metals and Secchi depth indicating that the metals are adsorbed on suspended particulate matter. Naivasha Town, River Malewa and Flower farms were found to be important sources of heavy metal contamination in the Lake. Organochlorine pesticides were

detected in fish (wet weight, µg/Kg); methoxychlor was most predominant ranging within Below Detection Limit (BDL) - 28.87, BDL - 7.26 for *p, p'*- DDT, 0.14 - 6.69 for *p, p'*- DDE, BDL - 21.13 for *p, p'*- DDD, 0.41 - 4.19 heptachlor and BDL - 0.22 for heptachlor epoxide. Low concentrations (ng/L) were detected in the water column; heptachlor ranged within 455.5 - 6762.23, 33.95 - 100.11 for heptachlor epoxide, 42.55 - 305.97 for aldrin, 48.93 - 11.58 for dieldrin, 6.13 - 405.57 for *p, p'*- DDT, 37.82 - 498.03 for *p, p'*- DDE, 26.72 - 42.9 for *p, p'*- DDD, 10.12 - 69.89 for lindane, 16.15 - 1932.1 for methoxychlor, 16.02 - 1025.25 for endosulfan sulfate, 34.84 - 271.7 for endosulfan II and 20.1 - 77.28 for endosulfan I. The measured exposure concentrations of endosulfan and methoxychlor in the water column were analyzed with a modified version of the PERPEST model version 2.0 to predict the environmental risks of methoxychlor on aquatic communities in the Lake. The modified PERPEST model predictions were consistent with experimental data for concentrations of 0.3 – 50 µg/L and 2.0 – 75 µg/L for methoxychlor and endosulfan respectively. The modified model could not be applied on the measured exposure concentrations of endosulfan which fell below the optimal range. The prediction shows that the most affected aquatic communities are insects, microcrustacea and rotifers. The research findings indicate that; (i). The lake bed is contaminated with cadmium, nickel and lead (ii). The heavy metal and pesticide concentrations in the water column and fish are within those recommended by WHO/FAO for freshwaters, (iii). Consumption of fish from the lake does not pose any risk to the consumers with respect to methoxychlor, *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, heptachlor and heptachlor epoxide, Cd, Pb, Cu Zn and Ni (iv). Flower farms, River Malewa and the Naivasha Municipal Council are important sources of contaminants, (v).

Though organochlorine insecticides are only targeted to insects, they were found to have adverse effects on other aquatic communities, (vi). Formulated endosulfan was the most used organochlorine pesticide in the catchment, (vii). Endosulfan was found to pose environmental risks on insects, rotifers, macrocrustacea and microcrustacea. (vii). Water abstraction was unregulated and unsustainable (vii). Geochemical processes are important sources of heavy metals in the lake (viii). The current ecological changes experienced in the lake today are due to human activities in the lake. The study recommends that the economic activities in the catchment area be controlled and regular surveillance/monitoring of the pesticides and other contaminants can be carried out.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Lake Naivasha lies between 0° 08' to 0° 55' S and 36° 00' to 36° 45' E altitude 1,890 masl on the floor of Africa's Eastern Rift Valley, covering approximately 140 Km ^{2} (Gitahi, 1999; Becht *et al*., 2005). It is the largest freshwater lake in Kenya (Hartley, 1985). The overall climate of the Eastern Rift Valley is semi-arid (Harper *et al.*, 1992; Becht *et al*., 2005). The lake provides one of the most important wetlands in the floor of the Rift Valley. The location of site is indicated in Plate 1.1 and Plate 1.2. The Lake is a shallow endorheic freshwater Lake system on the Eastern Rift Valley which includes a deeper Crater Lake (Crescent Lake) and a partially-separated soda (Lake Oloidien) extension as well as a separate soda Crater Lake (Sonachi).

Plate 1.1. Aerial View of the Lake Naivasha Basin

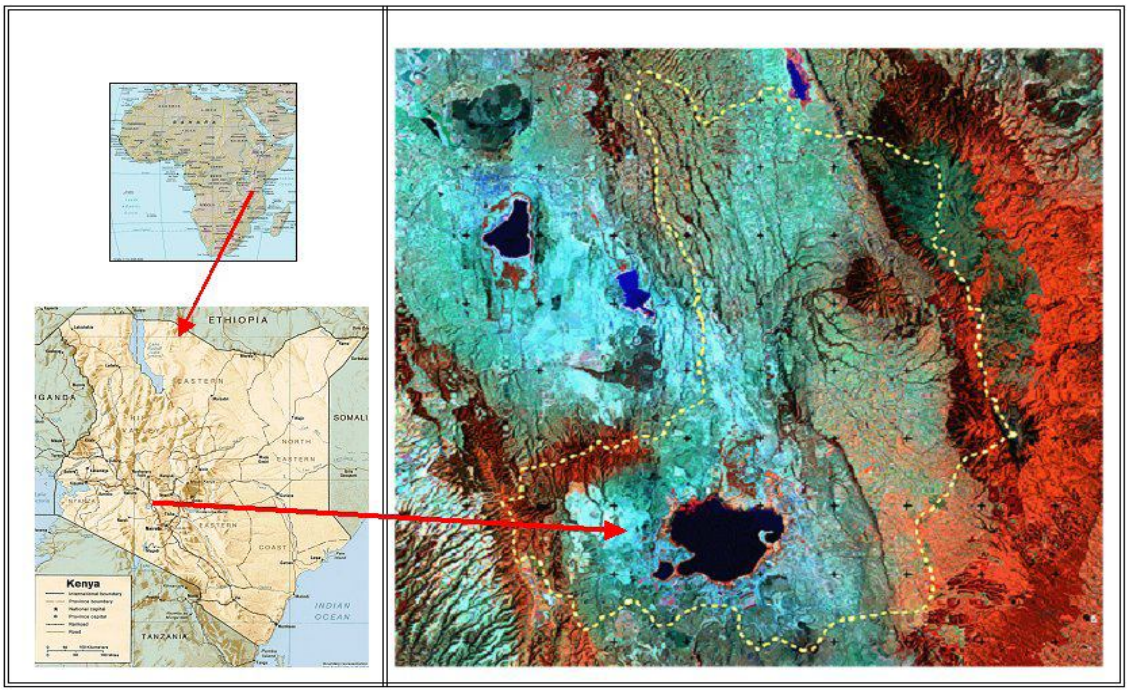


Plate 1.2. Location of the Lake Naivasha Basin

The larger Lake system (main lake) has fringing swamps and submerged vegetation and an attendant riverine floodplain with a delta into the Lake (Harper, 1993). The drainage basin lies within the range of the Inter-Tropical Convergence Zone (ITCZ) (Becht *et al.*, 2005). Mount Kenya and the Nyandarua Ranges capture moisture from the monsoon winds, casting a significant rain shadow over the Lake Naivasha basin. The rainfall distribution is of the bi-modal character, with long rains during April - June and short rains during October - November (Birdlife International, 2007).

The long-term spatial distribution varies from about 600 mm at Naivasha town to some 1,700 mm on the slopes of the Nyandarua ranges. The Kinangop plateau experiences an annual

rainfall of between 1,000 - 1,300 mm. The open surface evaporation of Lake Naivasha is approximately 1,729 metric tons/year (Becht *et al*., 2005; Birdlife International, 2007).

1.2 Aquatic and Terrestrial Life in the Catchment

The main Lake is a freshwater lacustrine wetland with fringing shoreline vegetation dominated by papyrus (*Cyperus papyrus)* with many other emergent plants, floating-leaved wetland plants and submerged species of *Ceratopyllum demersum*, *Potamogeton* and *Najas pectinata* (Gitahi, 2005). The soda Crater Lake (Oloidien) is dominated by microscopic blue-green algae with soda-tolerant *Cyperus laevigatus* in the shoreline (Harper, 1993). All the wetland areas are dominated by fringing woodland of *Acacia xanthophloea* including the floodplains of the rivers which run into the Lake through a delta-like area which is dominated by papyrus. The edges of the main Lake have a complex vegetation of terrestrial, water-tolerant and wetland plants due to the frequent changes in water level. The surrounding areas are mainly dry scrub with horticulture and planted shade and ornamental trees in some places (Harper, 1993; LNROA, 1993).

The most common fish in Lake Naivasha is Tilapia species, including *Tilapia nigra* (introduced in 1925); *Tilapia zillii* (introduced in 1965) and *Tilapia leucosticta* (introduced in 1954). Another common fish is the largemouth Black Bass (*Micropterus salmoides*) introduced in 1929, 1940 and 1951 (Bennum, 1993). Other species present are Tilapia, *Oreochromis leucostictus, Barbus amphigramma* and *Lebistes reticulata*. There has been a sharp decline in fish population in the lake especially Tilappine species.

With a shoreline of approximately 80 Km, lake Naivasha supports a much diverse population of fish-eating and other water birds (Plate 1.3), these include three grebe species, *Podicipedidae, Phalacrocorax,* darter, *Anhinga rufa,* two pelican species *Pelecanus spp,* at least twelve resident and migrant ducks and geese, *Anatidae spp*. of herons and egrets, *Ardeidae,* storks, spoonbills, ibises, Ciconiidae spp., Threskiornithidae spp., many rails, crakes, jacanas, Rallidae spp. and Jacanidae spp. (Bennun, 1993).

Plate 1.3. Avian Fauna in Lake Naivasha

In winter, the resident species are augmented by numerous waders, Charadriidae, Scolopacidae spp. and four species of kingfisher and Alcedinidae spp. About ninety pairs of fish eagles exist, *Heliectus vocifers,* forming one of the densest known populations of this species. Of the about 350 species recorded in the catchment area 60 - 80 species are basically aquatic at some time of the year (Birdlife International, 2007).

1.3 Land Use and Tenure/Ownership

The waters of the Lake and the riparian lands are the property of the state. The surrounding land is mainly privately owned with access to the riparian land and Lake granted to the owners (LNROA, 1993). The surrounding area is a complex of private land, state land, local authority land and some forest reserves higher in the catchments (LNROA, 1993; Gitahi *et al*., 2002; Gitahi, 2005). The site is dominated by agriculture, mainly irrigated horticulture involving flowers, vegetables, fruits and cereals, rearing of cattle, sheep, goats and donkeys, fisheries in the Lake, residence in the riparian areas, tourism involving water sports and hotels, lodges, camping as well as wildlife tourism and private conservation areas and the Naivasha urban area and light industrial area (Harper, 1993; LNROA, 1993; Gitahi, 2005).

1.4 Environmental Issues in the Lake Naivasha Ecosystem

The lake is of international significance as a bird breeding and feeding site and was awarded Ramsar status in 1995 by the Ramsar Convention of Wetlands (RCW, 2010). However the lake has undergone significant ecological changes which led it to be listed in the Montreux record 2009 as an endangered Ramsar site requiring urgent attention (Mireri, 2005; EAWS, 2009; RCW, 2010). The lake has lost most of its aquatic organisms to pollution. There has also been encroachment of the riparian land leading to loss of the Lake's buffering capacity. The introduction of intensive flower farming and geothermal power generation in the catchment has led to excessive water abstraction which exceed lake's safe yield leading to shrinkage of the Lake.

Human population growth in the catchment has been described as the single most important driver of pressure on the resources. The need for human settlements, food and services has led to the reclamation of the papyrus belts and over harvesting of fish and papyrus for domestic purposes. The ecological footprint and water footprints in the catchment area reveal that the lake is not able to regenerate itself and is at a risk of extinction if urgent conservation measures and wise use of the catchment resources are not introduced.

1.5 Chemical Pollution

Chemical pollution has been described as one of the single most drivers of ecological changes in the lake (Food and Waterwatch, 2008). The larger catchment has experienced a steady growth of irrigation agriculture and supports one of the largest cut flower industries in Africa (Gray, 2000). The growth of these flowers requires large volumes of fertilizers, agrochemicals and growth altering hormones for increased productivity and quality. The Lake has experienced increased primary productivity due to inflow of plant nutrients from the catchment, booms of water hyacinth have been reported (Plate 1.4). There are wide variations in the physicochemical parameters which impact directly on the environmental health of the Lake as indicated in Table 1.1.

Plate 1.4. Booms of Water hyacinth November, 2009

Table 1.1 Physicochemical Parameters in Lake Naivasha

Parameter	**Range**	**Parameter**	**Range**
Ph	82.2 – 8.9	Phosphates	0.8 - 2.6
Conductivity	220 – 1480	Fluorides	0.1 – 25.1
Dissolved oxygen	5.8 – 10.5	Chlorides	69 – 797
Nitrates	15.9 – 25.8	Carbonates	305 – 470
Potassium	15 – 146	Magnesium	2.0 – 10.1
Sodium	101 – 256	Calcium	2.8 – 7.9

(Source; Njenga, 2004) all parameters are in mg/L except pH and conductivity (µS/cm)

Deaths of thousands of aquatic organisms especially fish and fish eating birds have been reported (Food and Waterwatch, 2008). Food and Waterwatch (2008) reports that thousands

of fish and fish eating birds died after large amounts of chemicals were discharged into the lake from flower farms. A similar episode was observed in March 2010 but this was largely blamed of oxygen depletion by the National Environmental Management Authority (Plate 1.5). Wastewater from the flower farms is released to the lake without prior treatment, thus posing a great danger to aquatic organisms. The use of constructed wetlands in the flower farms is inefficient and do not allow enough time for the contaminants to be removed and maintenance lacking.

Plate 1.5. Fish Floating in Lake Naivasha after Chemical Pollution in March 2010

The use of organochlorine pesticides which are effective and persist for a long time is rampant, these chemicals have the potential to accumulate in fish tissues and also change the ecological character of a freshwater lake. Chemicals wash into the lake through discharge canals that connect the lake to the farms (Plate 1.6 and 1.7).

Plate 1.6. Discharge Canal connecting the Lake to a Flower Farm

Gitahi (1999) reported the presence of some organochlorine pesticides in water and fish from the Lake.

Plate 1.7. Water Abstraction Canal connecting the Lake to a Flower Farm

The cultivated areas in the basin have been studied for pesticide loading; Plate 1.8 illustrates the estimated pesticide loads in the soils adjacent to the Lake.

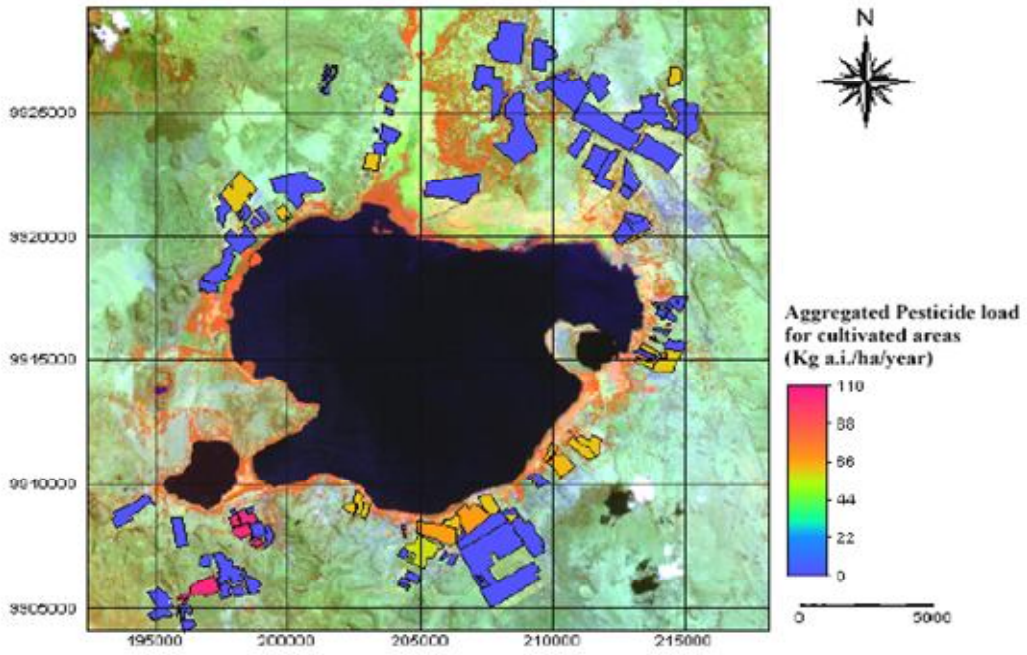


Plate 1.8. Pesticide Load for Cultivated Areas around Lake Naivasha

Waste handling in the basin is another big issue; most flower farms have heaps of wastes left in the open. The chemicals in the wastes are leached and find their way into the lake during the rainy season. Some flower farms burn their wastes thus transferring the pollutants to the atmosphere and transforming them. Used chemical containers are also poorly handled and can be seen in most farms in open areas and get washed during downpour. Plate 1.9 shows an example of a spent chemical containers and polythene dump.

Plate 1.9. Used Agrochemical Containers and other Wastes in the Open

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Pesticides

Pesticides are any substances or mixtures intended for preventing, destroying, or killing animals causing harm during, or otherwise interfering with production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animals feedstuffs, or which may be administered to animals for the control of insects, arachnids, or other pests in or on their bodies (FAO, 1990). Currently there are over 500 compounds registered worldwide as pesticides or metabolites of pesticides (Muhammad, 2006). Pesticides can be classified based on functional groups in their molecular structures (such as organo-halogen, organo-sulphur, organo-nitrogen, botanicals and inorganic) or their specific biological activities or target species such as insecticides, fungicides, herbicides, arcaricides etc. Herbicides are by far the most commonly used chemicals in the agricultural field followed by insecticides, fungicides and others (Muhammad, 2006).

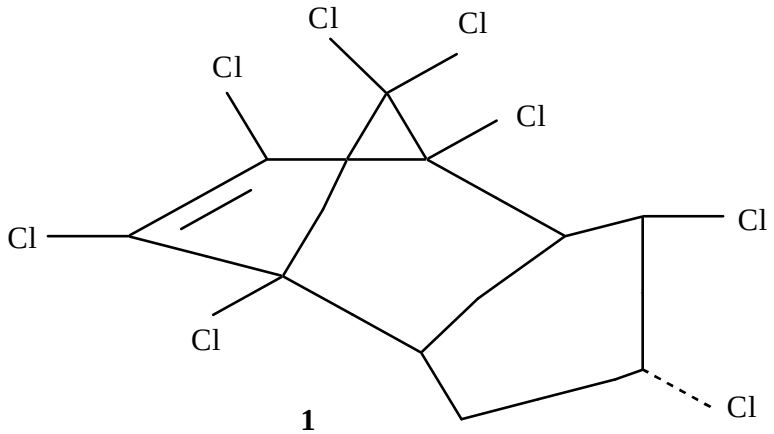
2.1.1 Organochlorine Pesticides

Organochlorine pesticides consist of two different major groups based on their molecular structures, namely, the cyclodiene or diene and the DDT groups (Alfred *et al*., 2000). Organochlorine pesticides are considered to be eco-toxic and have long term effect on the environment and human health. These chemicals exhibit characteristics of environmental persistence so that long term exposures might result and effects may be felt some distance from the point of production or release. Under the Stockholm Convention of 2001, there are

12 designated persistent organic pollutants or better known as “Stockholm POPs” which are given priorities in the assessment of pollutants in the environment and out of the 12 pollutants, 9 are pesticides. However, it is crucial to recognize that the exclusion of certain chemicals from worldwide assessment does not imply that other persistent toxic substances are not important (UNEP, 2008). Aldrin (CAS 309-00-2), dieldrin (CAS 60-57-1), endrin (CAS 72-20-8), heptachlor (CAS 76-44-8) and DDT (50-29-3) are all included in the 12 “Stockholm POPs” while HCHs and endosulfan were omitted even though they are considered as priority pollutants by US EPA (UNEP, 2008). However in most POP monitoring studies, these compounds were also assessed.

2.1.2 Cyclodiene Insecticides

Cyclodiene insecticides are cyclic compounds possessing the characteristic “endo-methylene bridged” structure. With one exception, all the cyclodiene insecticides are the Diels-Alder reaction products of hexa-chloropentadiene and a suitable unsaturated compound. Chlordane (**1**), heptachlor (**2**) and aldrin (**3**) are products of Diels-Alder reactions; dieldrin (**4**), heptachlor epoxide (**5**), and endrin are prepared by the epoxidation of aldrin, heptachlor and isodrin respectively.



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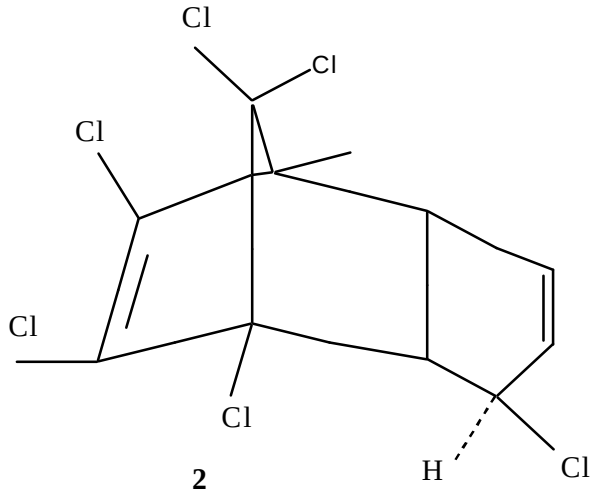

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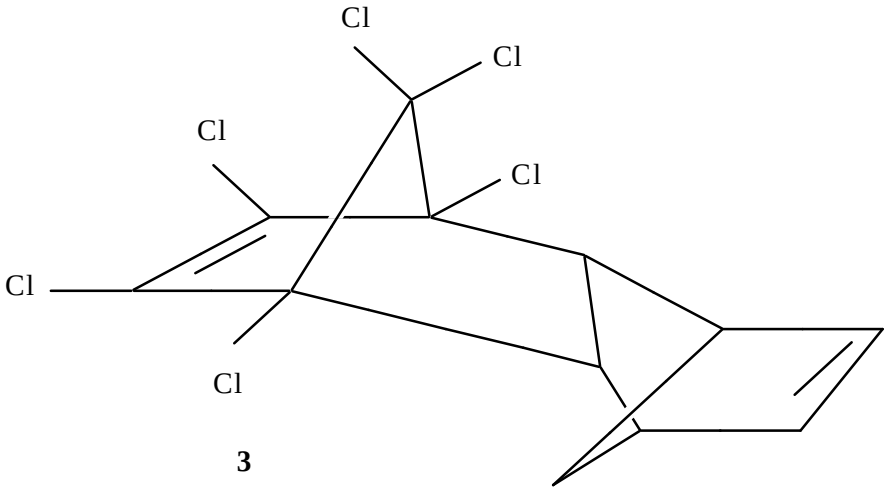

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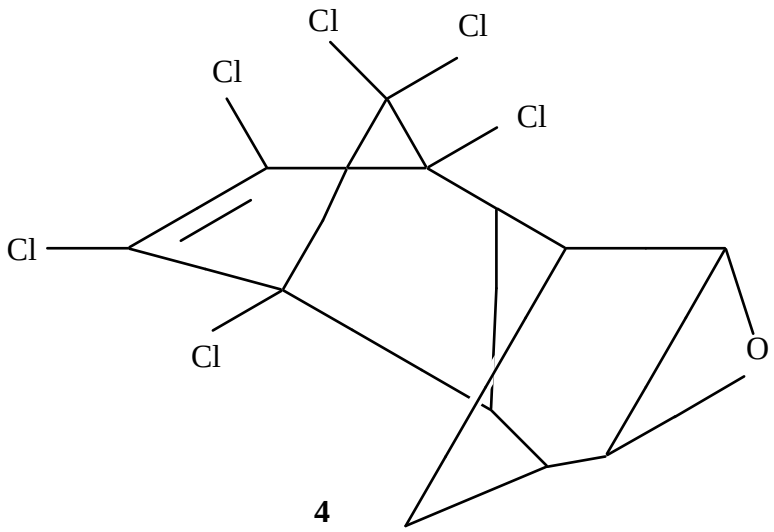

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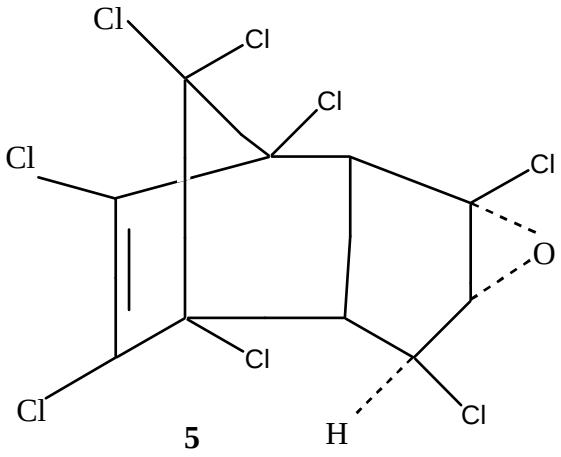

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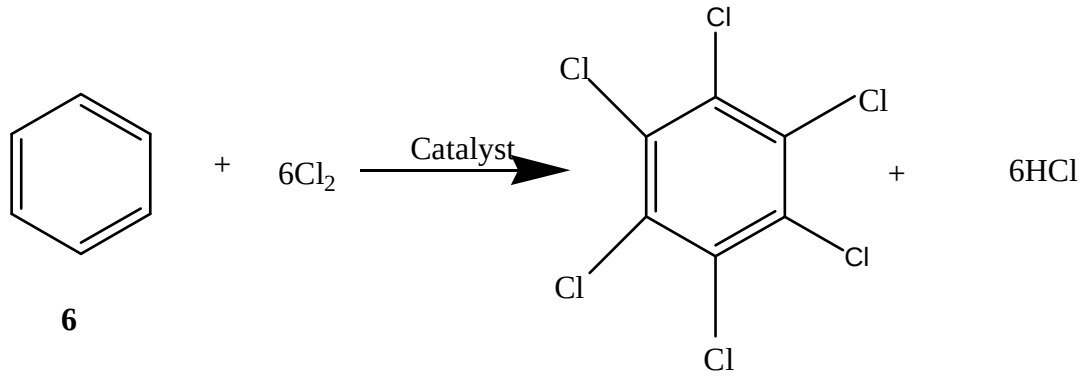
2.1.3 Hexachlorobenzene (HCB) Pesticides

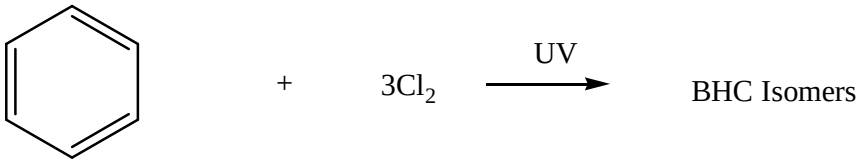
Hexachlorobenzene (**7**) pesticides are prepared through the chlorination of benzene (**6**) in the presence of a catalyst.



6 **7**

2.1.4 Benzenehexachlorides (BHC) Pesticides

Benzenehexachloride (BHC) (**8, 9**) isomers and hexachlorobenzene (HCB) are important examples. BHC is a misnomer, BHCs are hexachlorocyclohexane isomers prepared from chlorination of benzene in the presence of ultraviolet light. “Technical HCH”, which is a mixture of various isomers, including α-HCH (55 - 80%), β-HCH (5 - 14%) and γ-HCH (8 - 15) and lindane (CAS 58 - 89 - 9), which is essentially pure γ-HCH. Pure (99%) isomers can be obtained by selective re-crystallization from crude BHC.



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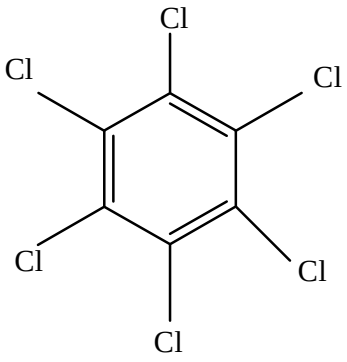

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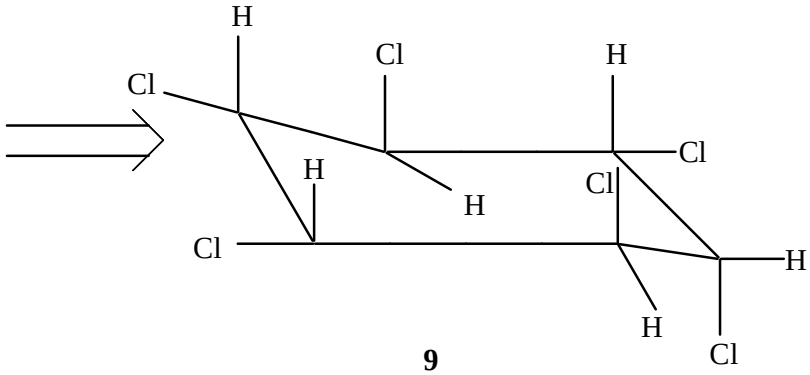

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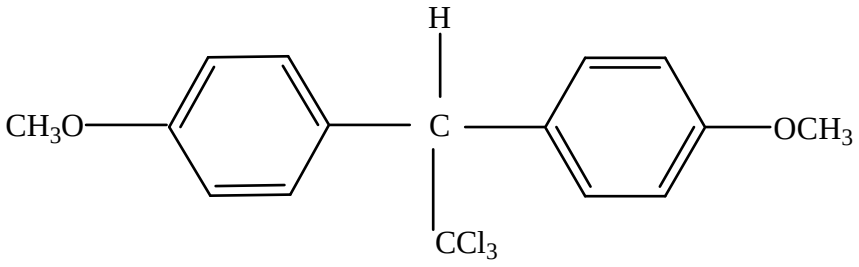
2.1.5 DDT and its Analogs

The DDT and its analogs contain two aromatic rings and represent the major group in OCPs. Methoxychlor (CAS 72-43-5) (**10**), *p, p'* - DDT (**11**), *o, p* - DDT (**12**), *p, p'* - DDD (**13**), and DDE (**14**) are some examples of this group. Technical grade DDT as a mixture of about 85% *p, p'* - DDT and 15% *o, p'* - DDT. This compound is metabolized mainly to *p, p'* - DDD and *p, p'*- DDE in the environment, which unfortunately are more toxic than parent compound (Murty, 1986).



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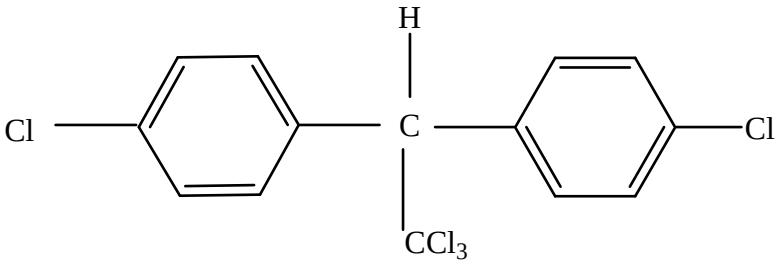

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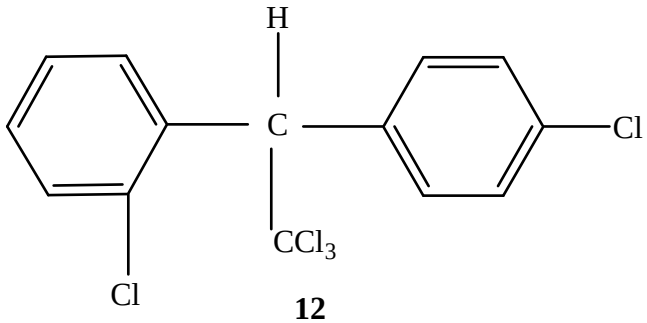

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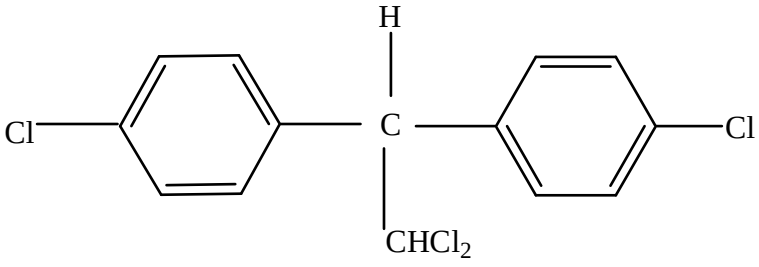

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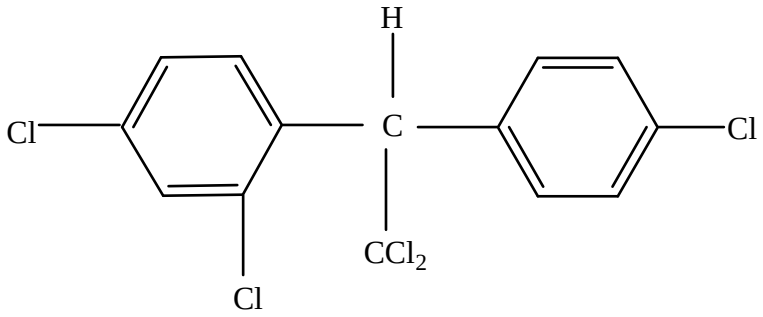

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2.1.5.1 Mechanism of DDT Action

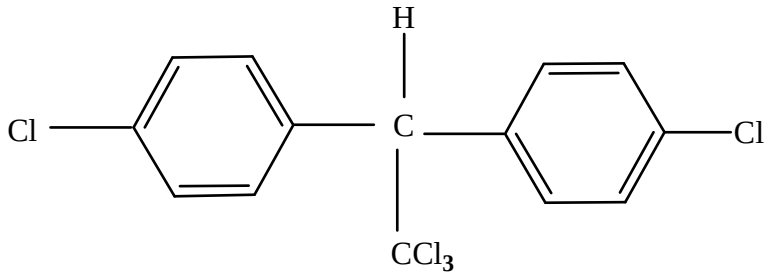
DDT is a very effective insecticide also used in public health for the eradication of mosquitoes. Insects sprayed with DDT exhibit hyperactivity and convolutions consistent with the interaction of the DDT with the nervous system. DDT molecules are trapped in the pores of the nervous membranes. This distorts the membrane and sodium ion leak through and depolarizes the nervous cells so that it can no longer transmit impulses. The toxicity of DDT thus is not due to its chemistry but size and geometry that allows for the blockage of the pores of the nerve membranes. Insects are especially susceptible to DDT because it is readily absorbed through the insect cuticle.

DDT is not appreciably absorbed through the skin of mammals. Introduction of $-NO_2$, $-CO_2H$, $-CO_2CH_3$ and -OH constituents into the aromatic ring lead to loss of the toxicity of DDT. This partly is due to decreased absorption through the cuticle and impart to decreased adsorption on the non-polar nerve membrane.

2.1.5.2 Environmental Degradation of DDT

In the environment *p, p'* - DDT (**11**) undergoes relative degradation of the HCl group to yield dichloro-diphenyl drichoro-ethylene (DDE) when heated in water. Subsequent hydrolysis of

the DDE (**15**) to 2, 2 bis - (4-chlorophenyl) acetic acid (DDA) (**16**) is extremely slow. There are only uncreative vinyl and aryl chlorides in DDE. As a consequence DDE is the principal DDT degradation product in the environment.



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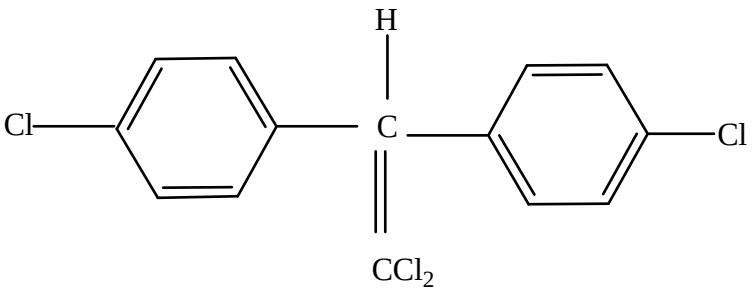
Fast



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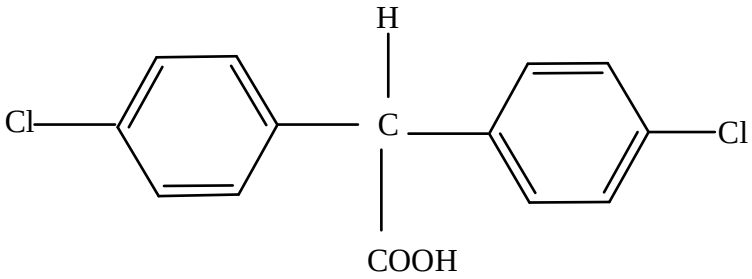
Slow



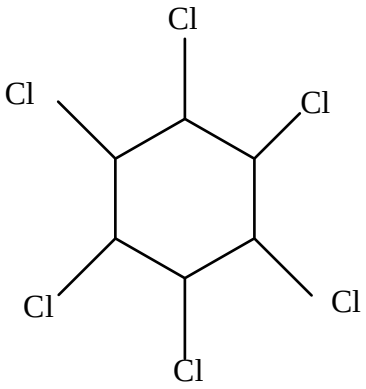
16

Methoxychlor (**10**) and other DDT analogs do not have the *p, p'* - chloro group have been

much less persistent in the environment. This is due to their metabolism by soil micro-organisms to phenols that are readily degraded further to acetate. The enzyme involved in the oxidation is the cytochrome *p*-450 similar to enzymes found in insects thus the reason for less effectiveness of Methoxychlor.

2.1.6 Lindane

Lindane (**17**) is another organochlorine pesticide often encountered in environmental analysis. Lindane was one of the most widely used insecticides in the world in controlling a wide range of sucking and chewing insects (Muhammad, 2006). Lindane tends to accumulate in the fatty tissue. It is used in the control of insects such as insect borers, beetles and hornets. It is also used in flea collar (in dogs).



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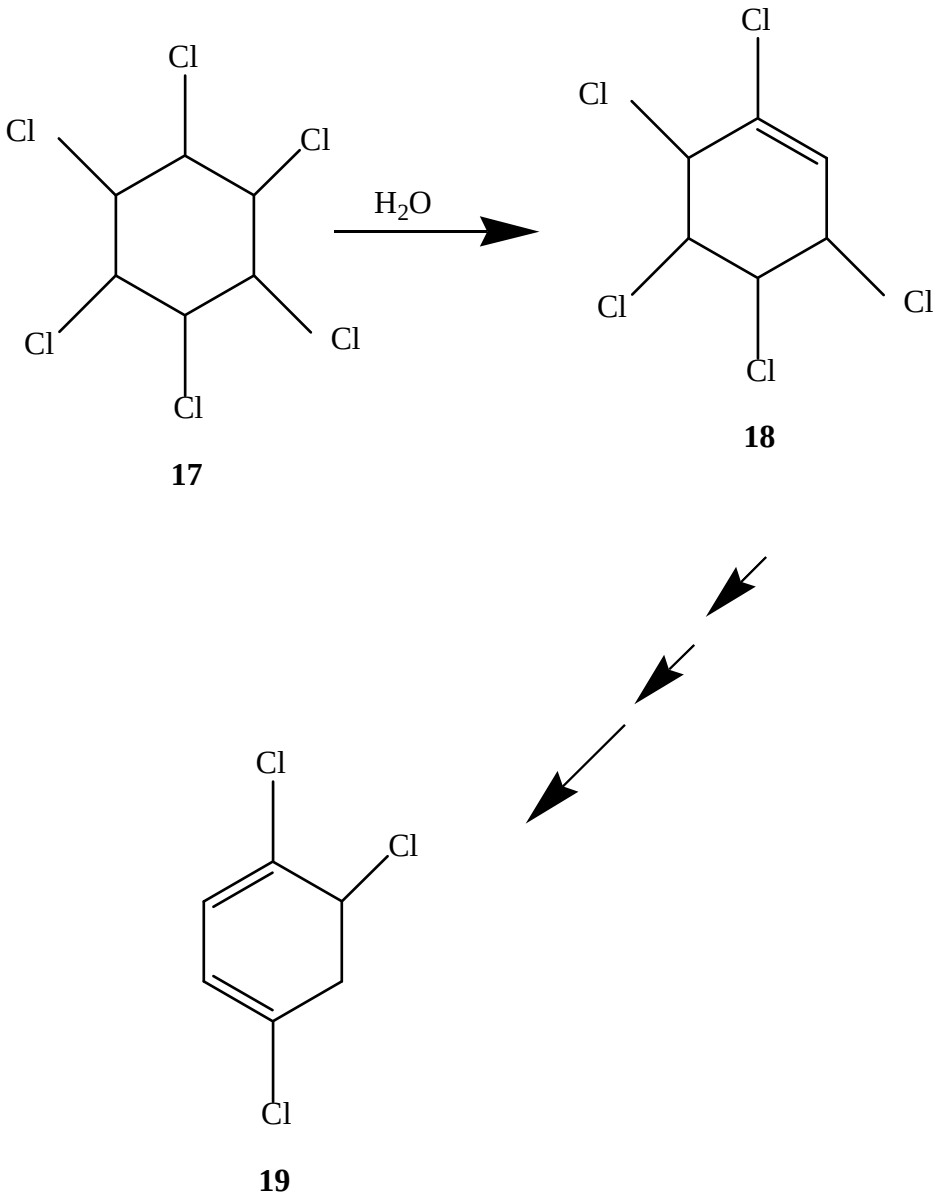
Lindane undergoes slow environmental degradation by the elimination of the HCl group in the aqueous phase

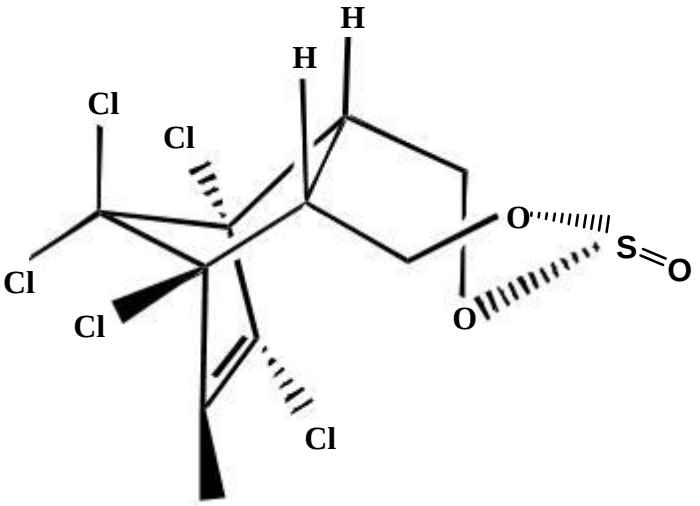


17 **18** **19**

2.1.7 Endosulfan

Endosulfan (CAS 115-29-7) was introduced in 1954 and used as a contact and stomach insecticide and arcaricide in a great number of food and non food crops. This compound has been formulated to be used in commercial agriculture, home gardening and wood

preservation. The technical grade endosulfan contains at least 94% of two isomers α endosulfan (**20**) and β-endosulfan (**21**).



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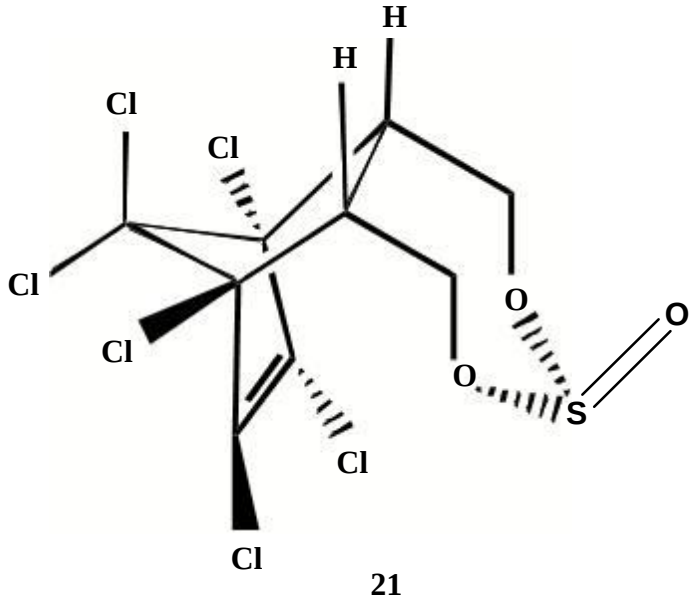

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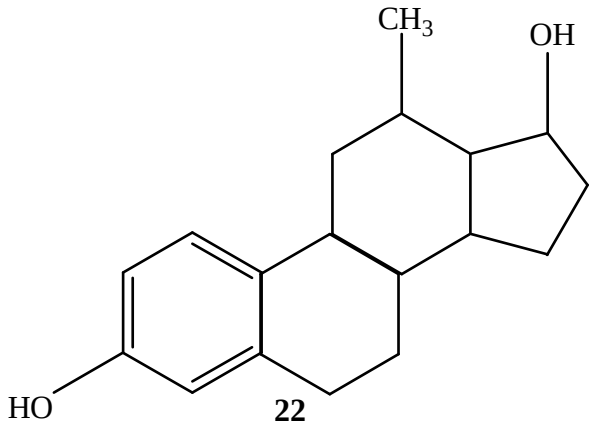
2.1.8 Long Term Effects of Organochlorine Pesticides

In pesticide residue analysis for environmental studies cyclodiene and DDT type insecticides together with Lindane (γ-BHC) are often encountered (Alfred *et al*., 2000). This is due partly to their widespread application and toxicity and partly to their persistence in the environment. Although many OCPs are now curtailed or drastically restricted in their use, they are still found because of their resistance to chemical and biological degradation. Organochlorine pesticides cause both chronic and acute toxicity. Acute poisoning of these compounds involves the central nervous system causing excitement, tremors, sudden loss of consciousness, and convulsions. These may be preceded by headaches, irritability, loss of memory and nausea.

In the body organochlorine pesticides accumulate in meat and are soluble in fats. Organochlorine pesticides have been blamed for the deaths and reduced populations of fish eating birds. This has been due to the interruption of the reproductive cycle in birds. The presence of these compounds in birds leads to enhanced levels of cytochrome *p*-450 oxidase enzymes in the liver (Tyagi and Mehra, 1990). Elevated levels of the oxidase enzyme lead to reduced levels of estradiol (**22**) in birds. Birds mate if a certain level of estradiol is present (Tyagi and Mehra, 1990). If breeding gets delayed, then the offspring hatch at a time when there is less food available for their growth. Food is an especially important factor with large birds that require a full season for the young to develop.



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Organochlorine residues also lead to small egg-shells due to estradiol levels, which regulate the levels of calcium necessary for shell formation. Low levels of estradiol results in low levels of calcium thus low levels of calcium available for shell formation (Tyagi and Mehra, 1990).

It has been observed that some pesticides inhibit the formation of eggshells even in the presence of adequate supply of calcium. Presumably these pesticides interfere with the enzyme carbonic anhydrase that is responsible for the conversion of carbon dioxide to carbonate. The carbonate is required to combine with calcium to form calcium carbonate of the shell (Tyagi and Mehra, 1990). It has been established that DDE (**16**) but not DDT interfere with the formation of the shell in this way.

2.2 Environmental Fate and Dissipation of Pesticides

When a pesticide is applied to a field, certain reactions follow. Foliar-applied pesticides stick to leaves, where they are absorbed. But rainfall inevitably washes some of the chemical off the leaf surface onto the soil below and some may be transformed by sunlight. Soil-applied pesticides generally interact first with moisture around and between soil particles, influencing

the ultimate chemical reaction in the environment (Tyagi and Mehra, 1990). Thus, a 'soil solution' can be viewed as a chemical staging area for most reactions controlling environmental fate. For instance, sorption processes (transfer), degradation by microbial and chemical reactions (transformation), volatilization to the atmosphere, leaching into deeper soil profiles, and overland flow (transport) all occur predominantly from soil solution (Landner, 1989; Springer *et al*., 2002).

2.2.1 Sorption

Sorption is a transfer process by which pesticides are dispersed between solid matter and water in soil. It is important in regulating the concentration of pesticides in soil water. One important environmental sink (retention or storage site) for many pesticides is organic matter. The transfer called 'partitioning' for a pesticide into organic matter in soil is a somewhat non-specific mechanism.

Much organic matter (humus) is made up of a series of organic polymers (long chains or mats of molecules) and generally consists of two systems; a hydrophilic (water loving) surface and a hydrophobic (water hating) interior. The convention of 'like dissolves like' holds for pesticide interactions with organic matter in soil. Non-ionic (non-charged or neutral) pesticides escape from soil solution into the hydrophobic interior and as a result, pesticide equilibrium is set up between organic matter and soil solution. Pesticides move between organic matter and water in soil. Also, pesticides may undergo an aging process, over time, whereby the chemical moves deeper into organic matter and becomes unavailable to move back into soil solution. Pesticides that are water soluble tend to remain at the surface

of soil organic matter, while those that are insoluble will penetrate to the hydrophobic interior (Landner, 1989; Springer *et al*., 2002).

The amount of pesticide sorbed is largely a function of the total amount of organic matter (sorption regions) in the soil. Sorption to clay mineral particles also occurs but usually is less significant than sorption to organic matter in determining environmental fate, unless the soil has very low organic matter content (Bailey and Strong, 1978). Many pesticides develop a charge as the result of soil solution pH (a measure of acidity) i.e. neutral pesticide molecules can become ionic (charged) and more reactive. If the pH induced charge is positive, the pesticide can bind to negatively charged soil. If the induced charge is negative, the pesticide may actually be repelled from the negatively charged surfaces of soil solids (Landner, 1989).

Sorption to soil particles is also dependent on soil water content because water is necessary for chemical movement and water molecules will compete with pesticide molecules for attachment sites on clay and organic matter. Therefore, pesticide sorption tends to be greater in dry soils than in wet soils. Decreased soil water content forces the pesticide to interact with soil surfaces. However, the amount of sorption also depends on the type of clay and organic matter content (Aufbau and Afghan, 1990).

The bond between a pesticide molecule and a soil particle determines, to a large degree, the environmental fate of the pesticide. For instance, pesticides that are tightly sorbed to soil particles have decreased mobility and are less likely to contaminate ground water. The bond may decrease the rate at which the pesticide is degraded by soil microbes, leading to longer environmental persistence. Pesticides strongly sorbed to soil particles may travel primarily

with eroded soil and enter surface water, while weakly sorbed pesticides that are more water soluble may be released into soil water solution and enter surface water as runoff (Landner, 1989; Springer *et al*., 2002).

2.2.2 Microbial Degradation

Communities of soil micro-organisms are very diverse. For example, researchers have estimated that between 5,000 and 7,000 different bacterial species may exist in a single gram of fertile soil (Bailey and Strong, 1978). Populations of bacteria can often exceed one hundred million individuals in one gram of soil, and populations of fungal colonies can exceed ten thousand. Microbial degradation is a transformation process that results when soil micro-organisms (bacteria and fungi) either partially or completely metabolize (break down) a pesticide. Micro-organisms can cause changes in a pesticide when this activity occurs in the presence of oxygen. It is termed aerobic metabolism and in the absence of oxygen, anaerobic metabolism. Most micro-organisms inhabiting the soil profile where oxygen is plentiful degrade pesticides via aerobic metabolism. As a pesticide undergoes aerobic metabolism, it is normally transformed into carbon dioxide and water (Landner, 1989; Springer *et al*., 2002).

Under anaerobic metabolic conditions micro-organism degradation may produce additional end products such as methane. Those micro-organisms using anaerobic metabolism for breaking down pesticides are typical of the microbes inhabiting waterlogged soils in terrestrial systems or living in the bottom sediments of ponds, lakes and rivers. These organisms are also present in ground water and to some extent in the soil profile. Pesticides, along with many other naturally occurring organic molecules, may serve as a source of food

or energy for soil microbes. It is unlikely that their capacity to serve as a food source is adequate to sustain high numbers of microbes. Pesticides are more apt to serve as incidental food sources for microbes also drawing from other food sources. Most soil microbes are associated in colonies on the soil surface and not free in soil solution. A pesticide in soil solution has to move to these microbial colonies and cross the microbial cell membrane into the cell to metabolize. Some microbes produce enzymes which are exported from the cell to predigest pesticides that are poorly transported. Once inside an organism, a pesticide can metabolize via internal enzyme systems (Wandiga *et al*., 2002).

Any energy derived from the breakdown of the chemical can be used for growth and reproduction. Any portion not fully degraded to carbon dioxide or incorporated into cells is released back into soil solution as intermediate chemical metabolites. Recent studies have revealed that multiple organisms often are involved in the degradation phenomenon. Previous notions that single species are solely responsible for microbial degradation of a pesticide probably are not correct (Springer *et al*., 2002). Different species have different capabilities, and together they can form a 'pool of talent' resulting in degradation of the pesticide. The likelihood that the chemical will be completely degraded is decreased if any of the microbes are missing from the pool. The ability of microbes to degrade a pesticide is related to their metabolic capacity and the complexity of the molecule and to environmental factors that regulate microbial activity (water content, temperature, aeration, nutrients) (Landner, 1989; Springer *et al*., 2002).

2.2.3 Abiotic Degradation

Abiotic (chemical) degradation is the breakdown of pesticides by non-biological reactions without the involvement of living organisms) occurring in soil solution and on the soil surface. Factors which affect abiotic degradation include the chemical nature of the pesticide as well as its temperature, water content and pH. Hydrolysis (reaction with water) is important for the degradation of many pesticides, as is photo-degradation (reaction with sunlight). These two processes generally are the most important abiotic mechanisms involved (Alfred *et al*., 2000).

Abiotic degradation results in less transformation of a molecule than does biological degradation. Hydrolysis is a common chemical reaction a process by which a pesticide reacts with a water molecule. Hydrolysis reactions generally substitute a hydroxyl (-OH) group from water into the structure of the pesticide, displacing another group. Reaction with water breaks apart the molecule, and the extent of breakdown is pH dependent (Landner, 1989; Springer *et al*., 2002).

2.2.4 Photo-degradation

Photo-degradation (photolysis) involves the breakdown of organic pesticides by direct or indirect energy from sunlight. Light energy can be absorbed by the pesticide or by secondary materials (such as organic matter) which become ‘activated’ and in turn, transfer energy to the pesticide. In either case, pesticides absorb energy from sunlight become unstable or reactive and degrade. Photolysis can occur in water, in air or on surfaces such as soil or a plant leaf. Photolytic reactions occur near the surface of the ground (in the top few

hundredths of an inch) or near water surfaces, where light can penetrate (Bailey and Strong, 1978).

2.2.5 Volatilization

Volatilization is the process whereby a solid or liquid evaporates into the atmosphere as a gas. The process provides a significant pathway of transfer for some pesticides. In principle, volatilization is an escape mechanism. Compounds with high vapor pressure and low water solubility have a tendency to volatilize. The tendency of a pesticide to volatilize from water is approximated by the ratio of its vapor pressure to its aqueous solubility. The same is partially true for soils, but the tendency for a pesticide to volatilize from soil also can be inversely proportional to its potential to bind to soil (Landner, 1989).

Specific environmental factors that tend to increase volatilization include high temperature, low relative humidity, and air movement. A pesticide that is tightly sorbed to soil will have a lower solution concentration and be less likely to volatilize. That is, less volatilization occurs from drier soils because the lack of water allows the pesticide to adsorb onto soil particles. Volatile pesticides usually are incorporated (plowed into the soil) after application to reduce loss into the atmosphere (Jaws, 2006).

However, it has also been shown that pesticide volatilization from soil is complex and highly dependent on the movement of water to and from the soil surface. Once a pesticide enters the atmosphere as a gas, it can become ‘diluted’ in water droplets and as a result, highly susceptible to long-range transport from the application site. Within the atmosphere, the

pesticide may undergo reactions with light (photolysis) and water (hydrolysis) and adsorb to suspended materials such as dust particles. Pesticides in a gaseous state may dissolve in atmospheric water and be transferred back to the soil surface during rainfall.

2.2.6 Leaching

Leaching is the term for the transport process of downward movement (infiltration) of pesticides in water (Tyagi and Mehra, 1990). Two kinds of phenomena are associated with leaching: preferential flow, and matrix flow. Preferential flow allows pesticide molecules to move rapidly through a section of the soil profile, with reduced likelihood that the molecules will be retained by soil particles or degraded by microbes. Preferential flow is characterized by water that flows rapidly through worm holes, root channels, cracks, and large structural voids in soil (Plate 2.1).

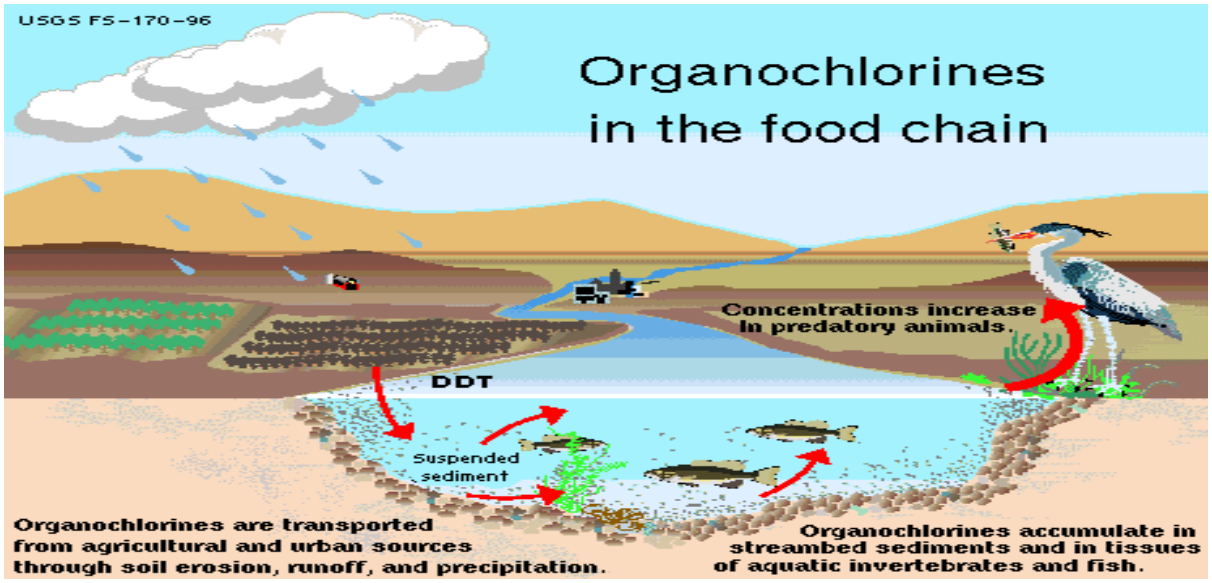


Plate 2.1. Flow of Pesticides in the Food Chain

Matrix flow results in a slower migration of water and chemicals through the soil structure; the pesticide moves slowly with water into small pores in soil and has more time to contact soil particles.

The potential for volatilization and photolysis diminishes considerably as the pesticide infiltrates the first few hundredths of an inch of soil. As the pesticide moves lower into the root zone, there is generally less organic matter, more compaction, and lower biotic activity. Once the pesticide leaches past the root zone, abiotic degradation reactions frequently become more important than biotic reactions because microbial populations generally are smaller below the root zone. In fact, microbes in deeper soils operate under 'starvation' and are less energetic due to a lack of carbon and nitrogen.

In addition, pesticides rarely reach deep into the soil profile so microbes therefore, are not adapted to degrade them quickly. The most important factors in determining whether a pesticide will leach are its degradation (persistence) capabilities, its sorption characteristics and its inclination to release rapidly into soil solution once it is sorbed. Pesticides that are weakly sorbed by soil and resist degradation are more likely to leach to ground water than are those that remain bound to soil. Factors such as soil type, topography, and rainfall also may impact the leaching potential of a pesticide and factors such as; application rate, frequency, and type (foliar, pre- and post-emergence) need to be considered (Springer *et al*., 2002).

The fate of pesticides in aquifers is unclear. Studies have shown that degradation will occur in the capillary fringe (the region above the aquifer) and in ground water. Sub-surface rates of degradation tend to be lower than those in surface soils, perhaps reflecting smaller

microbial populations, limitations in essential secondary nutrients or lack of adaptation (of microbial populations) to use the compound.

2.2.7 Runoff and Erosion

Runoff, the movement of water across the soil surface occurs when water collects (due to rainfall, irrigation or melting snow) at a rate faster than it can infiltrate the soil. As rain falls, small soil particles become dislodged and are carried laterally by water in a process known as erosion. Because pesticides are applied directly to the soil, large amounts eventually end up there and as water runs off and soils erode, dissolved and sorbed pesticides go along. Runoff and erosion have the potential to move more pesticide off site than leaching, due to the fact that runoff is a surface phenomenon. Surface runoff and erosion move pesticides and other pollutants laterally from points of higher elevations to collection points (streams, rivers, ponds, lakes) at lower elevations (Alfred *et al*., 2000).

Climatic factors such as rainfall timing, duration, intensity and surface features such as slope length and grade, soil permeability and surface cover greatly influence the degree to which pesticides are mobilized by runoff and erosion. Similarly, pesticide management factors may significantly affect runoff. For example, a soil-incorporated pesticide is less likely to run off site than the same compound applied to the soil surface.

2.3 Environmental Risks of Pesticides on Aquatic Communities

Aquatic organisms are of wide diversity in terms of size, weight and susceptibility to pesticide dose. Plate 2.2 indicates aquatic organisms such as, water flea, reproduction cycles of fish, blue green algae and water worms.

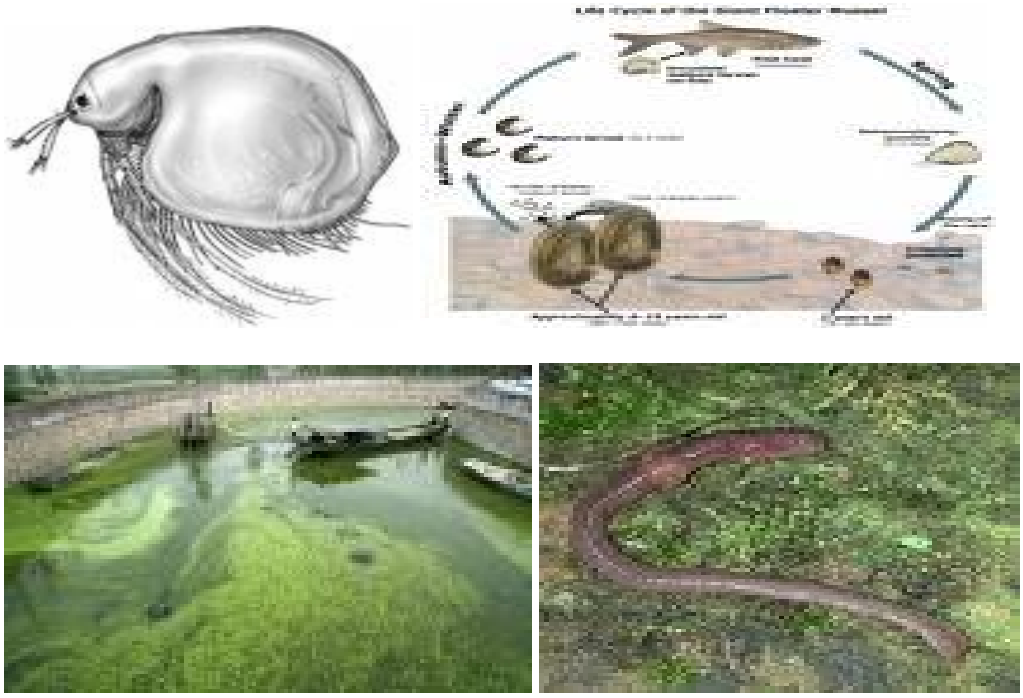


Plate 2.2 Aquatic Organisms

2.3.1 Environmental Risks of Pesticides on Fish

Fish species are sensitive to enzymatic and hormone disruptors (Bishop, 1992). Chronic exposure to low levels of pesticides may have a more significant effect on fish populations than acute poisoning (Bishop, 1992). Doses of pesticides that are not high enough to kill fish are associated with subtle changes in behavior and physiology that impair both survival and reproduction (Kegley *et al*., 1999). Biochemical changes induced by pesticidal stress lead to metabolic disturbances, inhibition of important enzymes, retardation of growth and reduction in the fecundity and longevity of the organism (Murty, 1986). Liver, kidney, brain and gills are the most vulnerable organs of a fish exposed to the medium containing any type of toxicant (Jana and Bandyopadhyaya, 1987). The fish show restlessness, rapid body

movement, convulsions, difficulty in respiration, excess mucous secretion, change in color, and loss of balance when exposed to pesticides. Similar changes in behavior are also observed in several fishes exposed to different pesticides (Haider and Inbaraj, 1986).

The Great Lakes fish are contaminated with chlorinated organic compounds such as PolyChlorinated Biphenyls (PCB) and dichlorodiphenyl trichloroethane (DDT), pesticides such as mirex and dieldrin and trace amounts of metals such as lead and mercury (Susan *et al.*, 2001). Lake trout which became extinct in the Great Lakes in the 1950s have been shown to be very sensitive to dioxins and PCBs when exposed as embryos (Shirose *et al.*, 1995). Several species of salmon introduced into the Great Lakes have severely enlarged thyroid glands which is strong evidence of hormone disruption (Shirose *et al.*, 1995). Salmon in the Lake Erie show a variety of reproductive and developmental problems (Shirose *et al.*, 1995). For example, early sexual development and a loss of the typical male secondary sexual characteristics, such as heavy protruding jaws and red coloration on the flanks have been reported (Henriksen *et al.*, 2000).

2.3.2 Environmental Risks of Pesticides on Amphibians

Amphibians are important components of aquatic habitats, especially in tropical regions of the world (McDiarmid, 1992). The mechanisms responsible for the decline of amphibian populations include chemical pollution from pesticides, fertilizers and global climate change (Lips, 1998). The health of amphibians can suffer from exposure to pesticides (Harfenist, 1989). Because of their semi-permeable skin, the development of eggs and larvae in water, and the position in the food web, amphibians are prone to adverse effects of waterborne and

airborne pollutants in their breeding and foraging habitats (Bishop, 1992). Pesticides may affect amphibian populations in a number of ways (Carey and Bryant, 1995) they may kill individual amphibians directly (Kirk, 1988) or indirectly through alterations in immune or neurological function (Cooke, 1971). Pesticides may also affect recruitment in amphibian populations by disrupting normal growth and development of the young or by impairing adult reproduction (Carey and Bryant, 1995; DVM, 2010). An extensive research study conducted in Quebec, Canada, shows that hind limb deformities are commonly observed in transformed bullfrogs, green frogs, northern leopard frogs and American toads (Quellet *et al*., 1997). Deformity rates tend to be higher at agricultural areas, suggesting that herbicides and pesticides are the likely causes.

In one study, the interactions of gonadal steroids and pesticides (DDT, DDE) on gonoduct growth in larval tiger salamanders, *Mbystoma tigrinum* were examined. The salamanders were immersed in a solution of DDE, DDT or injected with estradiol or di-hydrotestosterone. Essentially all the compounds tested had some adverse effect on the gonoduct growth in this species of salamanders (Clark *et al*., 1998).

Very rapidly deteriorating status of freshwater turtles and tortoises in Southeast Asia has resulted in an increasing number of these species being listed as threatened in the IUCN Red List. Globally, 42% of turtle and tortoise species are threatened (Baillie *et al*., 2004). The decline in the population of alligator in the Lake Apopka, Florida (USA) is contaminated by organochlorine pesticides that emanate from a chemical spill (Baillie *et al*., 2004). A number of disturbing abnormalities were recorded in hatchlings and juvenile alligators including

modifications of enzyme activity, concentrations of sex hormones, abnormal ovarian morphology and unusually small phalluses (Guillette *et al*., 1994, 1999). Because these chemicals are known to be weak androgen receptors, the hypothesis that the individual and the population level effects observed in the alligators are due to chemical disruption of endocrine function seems reasonable (Ankey and Giesy, 1998).

The common snapping turtle (*Chelydra serpentina*) is the largest freshwater turtle occurring in Canada. Snapping turtle eggs from the Great Lakes contain high concentrations of fat-soluble contaminants which are absorbed while food is being digested. These include PCBs, dioxins, furans and organochlorine pesticides. Abnormal development, such as incidence of un-hatched eggs or deformed animals, occurs at the highest rates in the sites which are the most contaminated (Shirose *et al*., 1995). In addition, a correlation between contaminated eggs and reduced developmental success has also been indicated (Bishop *et al*., 1991).

The anti-cholinesterase effects of the phyto-pesticide, biosal (neem based formulation), on Indian garden lizard (*Calotes versicolor*) have been observed in the kidney and liver. About 13.6 – 18% and 39.52 - 52.61% of the cholinesterase activities in the kidney and liver are reduced following low exposure to biosal (Khan *et al*., 2003). Amphibians Pesticides are absorbed and accumulated by algae.

2.3.3 Environmental Risks of Pesticides on Algae and Plankton

The effects of pesticides on algae and plankton have been demonstrated (Rice and Sikka, 2000). Herbicides are formulated to kill plankton by photosynthetic inhibition and other

modes of action (Rice and Sikka, 2000). However, insecticides also show adverse effects on algae and plankton. MacFarlane *et al*. (2004) investigated the effects of *p, p'*- DDT on photosynthesis and chlorophyll *a* content in the marine diatom, *Nitzschia delicatissima* at four light intensities. MacFarlane *et al*. (2004) reported a consistent reduction in carbon fixation and chlorophyll *a* per cell over controls in a 24 hr period with DDT concentration between 9.4 ppb and 1000 ppb. The maximum reductions of carbon uptake, chlorophyll *a* and carbon/chlorophyll *a* uptake per cell occurred at the highest light intensities. Carbon fixation per cell was reduced by as much as 94% in water containing an initial DDT concentration of 100 ppb, and chlorophyll *a* per cell by as much as 86% in 220 ppb DDT. Above 100 ppb, further decreases of carbon fixation and chlorophyll *a* per cell were not observed. Distortion of the chloroplasts in the cells exposed to DDT was also observed at the lowest concentration of DDT used. At 1000 ppb, chloroplasts were totally destroyed within 24 hr.

Lee *et al*. (2004) reported the effect of DDT on green algae (*Selanastrum capricormutum),* the study showed that concentrations of 3.6 and 36 ppb were inhibitory to the photosynthetic CO_2 fixation and the longer the exposure to DDT the greater the inhibition. Kinetic studies of CO_2 fixations indicate that DDT stimulated the incorporation of ^{14}C into glycolic acid, a major compound of photorespiration and caused the concomitant suppression of flow of ^{14}C into aspartic acid, a major component of the C_4-di-carboxylic acid pathway. The shift from an efficient pathway by DDT was interpreted to be through interruption of cyclic photophosphorylation.

Mitra and Raghu (1989) investigated the effects of DDT on the germination and growth of plants. Of the species tested, oil-rich seeds of plants such as peanut (*Arachis hypogaea*) and mustard (*Brassica juncea*), were more prone to DDT induced inhibition of germination and subsequent plant growth than cereals, pulses and fiber crops, like rice (*Oryza sativa*), barley (*Hordeum vulgare*), mung bean (*Vigna radiata*), pigeon pea (*Cajanus cajan*) and cotton (*Gossypium hirsutum*). Studies with ^{14}C labeled DDT showed that insecticide uptake by seeds were directly proportional to seed size. However, there was no direct relationship between DDT uptake by the seeds and its subsequent translocation to the growing regions or the degree of growth inhibition (Capel *et al*., 2001). Data suggest that oil content of the seeds has a bearing on the susceptibility or tolerance of a plant to DDT. It is suggested that lipids of the plant cell solubilize and disperse DDT in the cytoplasm which in turn affects normal metabolism within the cell.

2.3.4 Environmental Risks of Pesticides on Disolved Oxygen and pH

Dissolved oxygen is a basic requirement for a healthy aquatic ecosystem. Most fish and beneficial aquatic insects "breathe" oxygen dissolved in the water column. Some fish and aquatic organisms (such as carp and sludge worms) are adapted to low oxygen conditions, but most desirable fish species (such as trout and salmon) suffer if dissolved oxygen concentrations fall below 3 - 4 mg/L (Carey and Bryant, 1995). Larvae and juvenile fish are more sensitive and require even higher concentrations of dissolved oxygen. Many fish and other aquatic organisms can recover from short periods of low dissolved oxygen availability. Prolonged episodes of depressed dissolved oxygen concentrations of 2 mg/L or less can result in "dead" water bodies (Carey and Bryant, 1995).

Dissolved oxygen concentrations in the water column fluctuate under natural conditions, but severe depletion usually results from human activities that introduce large quantities of biodegradable organic materials into surface waters. In polluted waters, bacterial degradation of organic materials can result in a net decline in oxygen concentrations in the water. Oxygen depletion can also result from chemical reactions place a chemical oxygen demand on receiving waters. Other factors (such as temperature and salinity) influence the amount of oxygen dissolved in water. Prolonged hot weather will depress oxygen concentrations and may cause fish kills even in clean waters because warm water cannot hold as much oxygen as cold water.

The degradation (mono-dechlorination) of organochlorine insecticides leads to the release of HCl, a molecule that is highly acidic in water upsetting the water pH. Photochemical reactions via ultra violet (UV) irradiation of aldrin and dieldrin either in dry films or in aqueous solutions yield photo-aldrin and photo-dieldrin (Alfred *et al*., 2000). Double bonds in aldrin can also be oxidized giving dieldrin making use of oxygen (Aufbau and Afghan, 1990).

Aquatic plants provide as much as 80% of the dissolved oxygen necessary for aquatic life in ponds and lakes (Carey and Bryant, 1995). Spraying herbicides to kill aquatic plants can result in severely low oxygen levels and the suffocation of fish. As the aquatic organisms die due to low oxygen levels more materials will be decaying using up more oxygen and releasing acidic materials which offset important biochemical processes.

2.4 Heavy Metals

'Heavy metals' is a collective term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm^3 (Alloways, 1990). Although it is a loosely defined term, it is widely recognized and usually applied to the elements such as Cd, Cr, Cu, Hg, Ni, Pb and Zn which are commonly associated with pollution and toxicity problems. Unlike most organic pollutants, such as organo-halides, heavy metals occur naturally in rock-forming and ore minerals and so there is a range of normal background concentrations of these elements in soil, water, sediments and living organisms (Hambridge, 1971; Page *et al*., 1987). Pollution gives rise to anomalously high concentrations of the metals relative to the normal background levels. Therefore, presence of the metal is insufficient evidence of pollution, the relative concentration is all important.

Apart from aerosols in the atmosphere and direct effluent discharges into waters, the concentrations of heavy metals available to terrestrial, aquatic and marine organisms (that is bio-availability) is determined by the solubilization and releases from rock forming minerals and the adsorption and precipitation reactions which occur in soils and sediments. The extent to which metals are absorbed depends on the properties of the metal concerned (valency, radius, degree of hydration and coordination with oxygen), the physicochemical environment (pH and redox status), and presence of soluble ligands in the surrounding fluids (Kabata and Alina, 1984).

Heavy metals find wide applications in; industry, electronics, machines and the artifacts of everyday life. Consequently they tend to reach the environment from a vast array of

anthropogenic sources as well as natural geochemical processes, some of the oldest environmental pollution in the World are due to metal use such as Cu, Hg and Pb mining, smelting and utilization by ancient civilizations such as the Romans and the Phoenicians (Hambridge, 1971).

2.4.1 Sources of Heavy Metals

2.4.1.1 Geochemical Sources

In geological terms heavy metals are included in the group of elements referred to as 'trace elements' which together constitute 1% of the rocks in the earth's crust, the macro-nutrients (O, Si, Fe, Ca, Na, K, Mg, N, P and S) comprise 99% of the earth's crust (Alloways, 1990). These 'trace elements occur as 'impurities' isomorphously' substituted for various macro-nutrient constituents of the crystal lattice of many primary minerals. Primary minerals are thus found in igneous rocks which originally crystallized from molten magma. In sedimentary rocks trace elements occur sorbed to the secondary minerals which are products of the weathering (physical degradation and chemical decomposition) of primary minerals.

Due to the background heavy metals concentration it is therefore important to determine the local background concentrations of heavy metals in order to determine whether the concentrations in the soil and sediments under investigation are significantly higher than those of the area. The normal procedure is to determine the mean metal content and its standard deviation in an area for the range of elements being investigated. Anomalously high (or low) concentrations will lay outside the value for the mean ± 3 SDs, but values of ± 2

SDs above the mean are regarded as ‘threshold’ values (Alloways, 1990; Alloways and Arynes, 1993).

2.4.1.2 Metalliferous Mining

Metals are obtained from mining or recycling of scrap metal originally derived from geological sources. The disposal of large amount of tailing from mining and continued weathering (chemical alteration) of ore minerals in historical and abandoned mining sites is an important source of heavy metals in the environment. Frequently, bacteria such as *Thiobacillus thiooxidants* help to catalyze the oxidation reactions in tailings deposits and in weathering ore bodies (Alloways, 1990; Alloways and Arynes, 1993). Another feature is that most of the major ore minerals often have several other metals associated with them. Many of these metals will have contaminated the environment in the vicinity of mines and smelters.

2.4.1.3 Agrochemicals

Agriculture constitutes one of the very important Non-Point Sources (NPS) of metal pollutants. The main sources include; impurities in fertilizers (Cd, Cr, Mo, Pb, U, V, Zn), pesticides (Cu, As, Hg, Pb, Mn, Zn), desiccants (As for cotton), wastes from intensive pig and poultry production (Cu, As), composts and manures (Cd, Cu, Ni, Pb, Zn, As), sewage sludge, (Cd, Ni, Cu, Pb, Zn) and corrosion of metal objects (such as galvanized metal roofs and wire fences: Zn, Cd) (Alloways and Arynes, 1993).

2.4.1.4 Fossil Fuel Combustion

A wide range of heavy metals are found in fossil fuels which are either emitted into the environment as particles during combustion or accumulate in ash which may itself be transported and contaminate soils or waters, or may be leached *in situ*. Some of the metals arising from fossil fuel combustion are Pb, Zn, As, Sb, Se, Ba, Cu, Mn and V (Alloways and Arynes, 1993).

2.4.1.5 Metallurgical Industries

Many metals are used in specialist alloys and steel: V, Mn, Pb, W, Mo, Cr, Co, Ni, Cu, Zn Sn, Si, Ti, Te, Ir, Ge, Tl, Sb, In, Cd, Be, Bi, Li, As, Ag, Sb, Pr, Os, Nb, Nd and Gd. Hence both the manufacture and disposal, or recycling, of these alloys in scrap metal can lead to environmental pollution of a wide range of metals. Steel manufacture usually involves a lot of recycling of scrap and so steel works are often point sources of atmospheric aerosols of metals (Alloways and Arynes, 1993). Non-ferrous metal production causes environmental pollution not only of the metal being manufactured, but also of other minor associated metals such as, As, Cd, Cr, Cu, Co, Ni, Pb, Sb, Tl, Te, U, V, Zn and Se (Alloways and Arynes, 1993).

2.4.1.6 Electronics

A large number of trace elements including the heavy metals are used in the manufacture of semi-conductors and other electrical components. These include Cu, Zn, Au, Ag, Pb, Y, W, Cr, Se, Sn, Ir, In, Ga, Ge, Re, Sn, Tb, Co, Hg, Sb, As and Gd. Environmental pollution can

occur from the manufacture of the components and their disposal in waste. Electronic wastes (e-wastes) also contain PCBs (Alloways, 1990; Alloways and Arynes, 1993).

2.4.1.7 Other Sources

Other significant sources of heavy metals pollution in manufacture and disposal include; Batteries (Pb, Sb, Zn, Cd, Ni, Hg, Pm), pigments and paints (Pb, Cr, As, Sb, Se, Mo, Cd, Ba, Zn, Co, I, Ti), catalysts (Pt, Sm, Sb, Ru, Co, Rh, Re, Pd, Os, Ni, Mo, I), polymer stabilizers (Cd, Zn, Sn, Pb), printing and graphics (Se, Pb, Cd, Zn, Cr, Ba), medical uses (Ag, Sn, Hg, Cu, and Zn), drugs/medicinal preparations (As, Bi, Sb, Se, Ba, Ta, Li, Pt), and additives in fuels and lubricants (Se, Te, Pb, Mo, Li).

2.4.2 Environmental Toxicity and Biochemical Behavior of Heavy Metals

Some heavy metals are required by most living organisms in small but critical concentrations for normally healthy growth (referred as “micronutrients” or ‘essential trace elements’) but excess concentrations cause toxicity. Those metals which are unequivocally essential, whose deficiency causes diseases under normal living conditions include Cu, Mn, Fe and Zn for both plants and animals, Co, Cr, Se and I for animals and B, Mo for plants. Most micro-nutrients owe their essentiality to being constituents of enzymes and other important proteins involved in key metabolic pathways. Hence, a deficient supply of the micro-nutrients will result in the shortage of the enzyme which leads to metabolic dysfunction causing disease.

Elements with no known essential biochemical functions are called ‘non-essential elements’. These include As, Cd, Hg, Pb, Pu, Sb, Tl and U, cause toxicity at concentrations which

exceed the tolerance of the organism but do not cause deficiency disorders at low concentrations like micro-nutrients. These are clearly shown by the typical dose response curve in the Fig. 2.1.

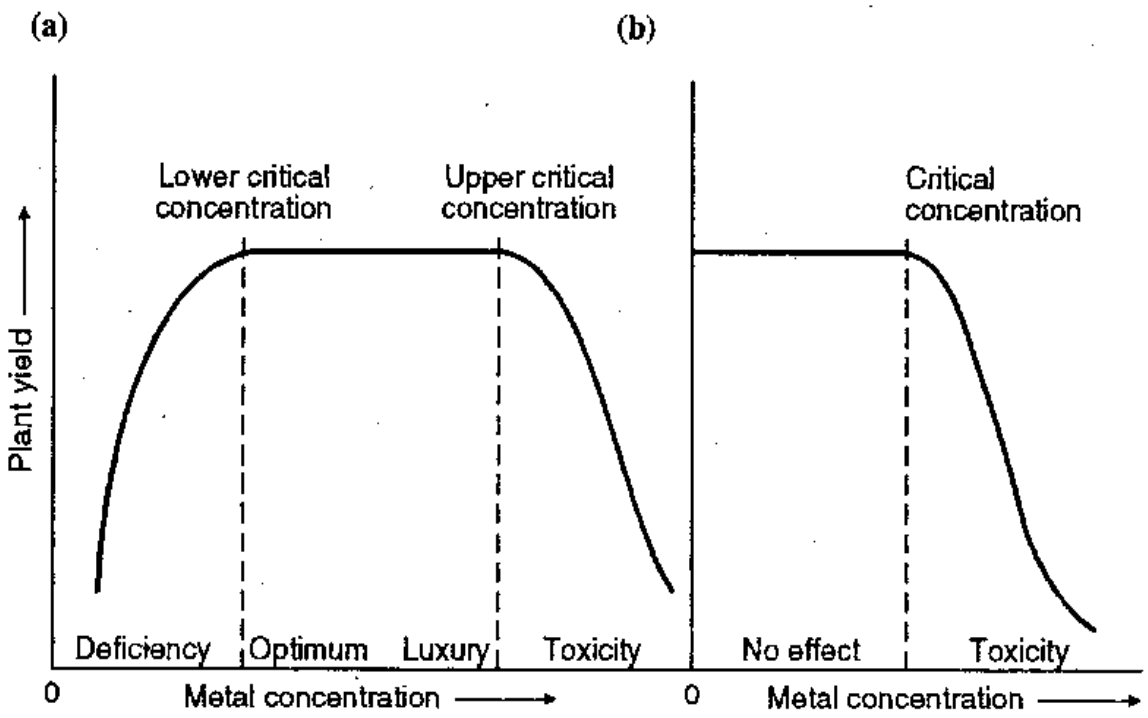


Figure 2.1. Typical dose-response curves for (a) micro-nutrients and (b) non-essential trace elements (Source; Alloway, 1990)

At the biochemical level, the toxic effects caused by excess concentration of these metals include competition for sites with essential metabolites, replacement of essential ions, reactions with –SH groups, damage to cell membranes, and reactions with the phosphate group of ADP and ATP. Organisms have homeostatic metabolisms which enable them to tolerate small fluctuations in the supply of most elements but prolonged excesses eventually

exceed the capacity of the homeostatic system to cope and toxicity occurs, which if severe can cause the death of organisms. An example of homeostasis in animals and the control of excess metals is the formation of metallothionein proteins containing - SH groups which bind to metals, such as Cd and Zn and enable them to be excreted without causing biochemical dysfunction. In plants, similar compounds called phytochelatins carry out the same function binding divalent metals, such as cadmium in physiologically inactive forms.

2.4.3 Environmental Fate of Heavy Metals

Atmospheric aerosol particles remain suspended for varying lengths of time determined by the particle size, the wind speed, relative humidity and precipitation. Aerosols particles range in diameter from 5 nm - 20 μm but most are in the size range 0.1 - 10 μm. Particles > 10 μm tend to settle out under gravity relatively rapidly but those less than < 10 μm remain in the atmosphere for 10 - 30 days being removed by washout, settlement, impaction and in the case of very small particles < 0.3 μm by diffusive deposition. Under some circumstances such as humidity smaller particles may sometimes cluster and form larger particles which are deposited more rapidly. In the 10 - 30 day period during which aerosol particles may remain suspended in the atmosphere they can be transported thousands of kilometers depending on the circulation of air masses (Alloways and Arynes, 1993).

While suspended in the air, metal aerosols can be inhaled by humans and animals and subsequently absorbed into the bloodstream through the alveoli of the lungs. Particles falling on the foliage may also enter plant tissues by absorption through cuticle but this depends on the presence of moisture and its pH, type of plant and other parameters. The particles on the

foliage may also be consumed with the plants. Most particles eventually reach the soil and may be ingested with incompletely washed vegetables, by children eating soil intentionally (pica), or accidentally from unwashed hands after gardening or playing with contaminated soil.

In aqueous and marine environments aerosol particles deposited in water, either directly or washed off surfaces into water courses, either react with the constituents of the water or settle to the bottom where they react with the sediments. The solubility of metal ions in solution will depend on the concentrations of anions and chelating ligands, present in water, its pH, redox status and presence of adsorbent sediments. Several metal ions are adsorbed and co-precipitated with oxides of Fe, Mn and Al in both sediments and soils, for example Fe oxides co-precipitate V, Mn, Ni, Cu, Zn, Mo. Mn co-precipitates Fe, Co, Ni, Zn, Pb. Metal ions in solution can be absorbed into aquatic plants and animals and can cause toxicity if the concentration is sufficiently high (Alloways, 1990).

2.5 Application of Computer Models in Environmental Analysis

The tiered ecological risk assessment of pesticides consists of a conservative first tier and more realistic higher tiers. These higher tiers can include the use of laboratory tests using more realistic exposure regimes, testing of indigenous species, the use of a variety of models (population, food-web, landscape) and conducting experiments in model ecosystems (Ansara *et al*., 2003). To this end many experiments performed with micro-cosms and meso-cosms are performed during the last 20 years and published in the open literature (EXTOXNET, 2004).

Brock *et al.* (2000; 2006) reviewed the open literature for micro-cosm and meso-cosm experiments on the effects of herbicides and insecticides. This review was performed to establish ecological threshold values for pesticides in surface waters and to evaluate current standard setting methodologies. In order to predict effects of pesticides on aquatic communities and ecosystems, large simulation models like for instance food-web models can be used (Traas *et al*., 1998; Koelmans *et al*., 2001). Ecological models, however, are either incomplete or have many uncertain parameters, so experts may predict effects of toxicants better.

2.5.1 The PERPEST Model

The PERPEST model is a model for the **P**rediction of **E**cological **R**isks of **PEST**icides in freshwater ecosystems. PERPEST is based on Case Based Reasoning (CBR) (Van den Brink *et al*., 2002; Van den Brink *et al*., 2003; Avramenko and Kraslawski, 2008; Ani *et al*., 2009). The model has been applied in many parts of the World to predict ecological risks of pesticides and results published widely (Van den Brink *et al*., 2002). The prediction of the effects of a certain concentration of a pesticide on a defined aquatic ecosystem is based on published information on effects of pesticides on the structure and function of aquatic ecosystems as observed in semi field experiments.

The Weighted Analogies Prediction (WAP) searches for most analogous cases in the database (Egbert *et al*., 2003). Based on the most analogous cases predictions are made. The model can be used in ecological risk assessment of a new pesticide to determine the areas that need more experimental data where uncertainties are large. The model can also be used

to translate spatially and temporal distributed concentration data into effect environmental risk studies.

2.5.2 Case Based Reasoning (CBR)

Case-based reasoning is a field in artificial intelligence system for solving problems that is able to utilize the specific knowledge of previously experienced, concrete analogous situations/cases for solving new problems. It enables incremental, sustained learning since new experience is retained, making it immediately available for future problems (Aamodt and Plaza, 1994; Van den Brink *et al*., 2003).

2.5.3 Prediction Methods

The PERPEST model searches for analogous cases based on available information in the data base. The question case is characterized using several variables (Table 2.1). Based on the most analogous case prediction is done. The goodness of fit is evaluated as a measure of accuracy of the prediction.

2.5.4 The PERPEST Database

The database (case base) consist of two different data sets, one containing results of the effects of pesticides on several endpoints observed in semi-field experiments and another set on the fate and effect characteristics of pesticide (Van den Brink *et al*., 2003; Brock *et al*., 2000, 2006).

Table 2.1. Variables in the PERPEST Database

Variable	**Description**
DT_{50}	Field dissipation DT_{50} (days)
EC_{50}	EC_{50} of the most sensitive standard test species according to OECD guidelines (μg/L)
Full Name	Name of the substance
Henry's constant	Air-water partition coefficient (Pa m^3/mol)
K_{ow}	Water-organic matter partition coefficient K_{ow} (L/kg)
Toxicity mode of action	Toxicity mode of action
Molecule	Molecule group
Type_sub	Type of substance
Conc	Exposure concentration of substance (μg/L)
Expos	Exposure regime
Hydrology	Hydrology during experiment
ToxUnit	Concentration as toxic unit

(Source; Egbert *et al*., 2003)

The first data set comprises case studies in which the effect of a certain concentration of a pesticide is evaluated in a semi field experiment simulating freshwater ecosystems. The exposure regimes are classified either as single/pulse or multiple/constant based on the frequency of dosage application frequencies. The hydrology are categorized either flow through lentic systems (rivers) or as stagnant/recirculating for lotic systems (lakes, dams,

ponds). Each evaluated concentration in the experiment is presented as a separate case in the data base.

Aquatic communities are classified community metabolism, algae and macrophytes, microcrustacea, rotifers, macrocrustacea, macrocrustacea, insects and other macro-invertebrates for insecticides. Community metabolism, phytoplankton, vertebrates, macrophytes, zooplankton, macrocrustacea, insects, other macro-invertebrates and periphyton are considered for herbicides (Table 2.2). The responses observed for various groups are classified as; no effects, sight effects and clear effects. Each case is described in terms of; pesticide name, concentration, reference, exposure regime, hydrology and effect on each groups of aquatic organisms.

Table 2.2. Grouped Endpoints used in PERPEST

Herbicides	**Insecticides**
Community metabolism	Community metabolism
Phytoplankton	Algae and macrophytes
Periphyton	Microcrustacea
Macrophytes	Rotifers
Zooplankton	Macrocrustacea
Macrocrustacea & Insects	Insects
Other macro-invertebrates	Other macro-invertebrates

(Source; Egbert *et al*., 2003)

The second data set consists of effects of different pesticides on test species. During the prediction the exposure concentration is converted to Toxic Units (TU) by dividing the concentration by EC_{50} of the most sensitive standard test species; *Daphnia magna* for insecticides and *Scenedesmus subspicatus* or *Selenastrum capricornutum* for herbicides (Egbert *et al*., 2003; Brock *et al*. 2000; 2006).

2.5.5 Analogous Cases Search Routine

The order of sequence followed in finding similar cases in PERPEST is given in Fig. 2.2. The various steps are explained in sections to section 2.5.6 to 2.5.11.

2.5.6 Description of the Question Case

In PERPEST the minimum information for a question case is the pesticide name and its concentration. If the pesticide is not available in the database its Chemical Abstract Service (CAS) number, toxicity mode of action (TMoA), molecule group, substance type and effective concentration (EC_{50}) for standard test organisms must be entered (Egbert *et al*., 2003).

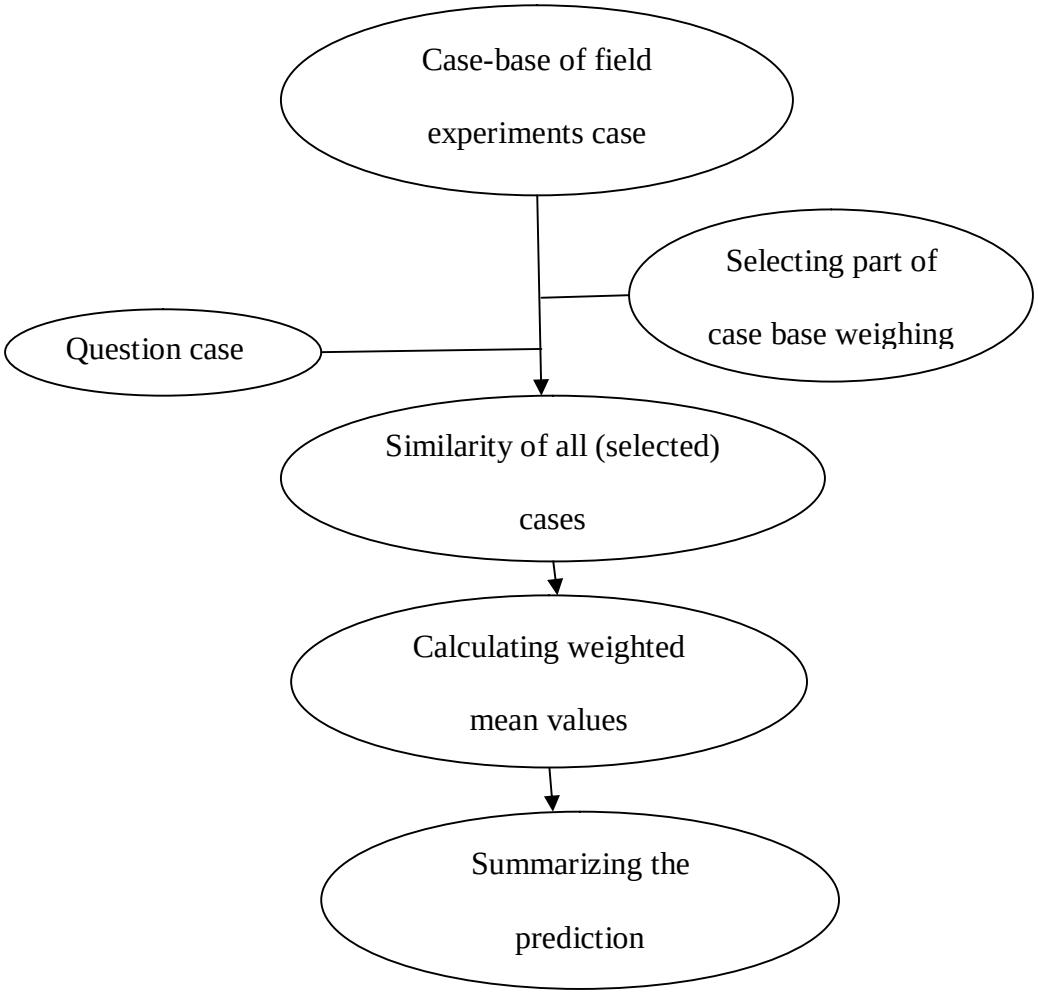


Figure 2.2. Method used in PERPEST (Source; Egbert *et al.*, 2003)

2.5.7 Selection of Conditional and Response Variables

The next step in CBR is to select variables that are to be used in the analysis. Selection of conditional and response variables help to retrieve the most analogous cases in the database. (Egbert *et al.*, 2003). The conditional variables used in PERPEST can be selected based on similarity in; DT_{50}, EC_{50}, name, Henry's constant, pesticides' water organic matter partition

coefficient, K_{ow}, toxicity mode of action, molecule type, type of substance, exposure concentration, exposure regime, hydrology and closeness to toxic unit of the question case.

2.5.8 Transformation, Standardization and Weighing of Variables

To narrow the prediction to the most analogous cases standardization and transformation can be done on some variables to shrink certain parts of the database. Weighting is done to assign more weight to key parameters in the prediction (Egbert *et al*., 2003). The model has an inbuilt way of doing this.

2.5.9 Results of the Prediction

After optimization of the run, results are displayed in pie charts showing the percentages for each effect cases and the number of cases in database used to make the prediction. The references of the most analogous cases used in the prediction in open literature are also given. The summarized results can be copied and pasted to Micro soft word. A summary of the results can also be copied from a table of results which also shows the confidence intervals for each prediction. A plot of concentration versus response can also be generated and copied and pasted to Microsoft word in colored line graphs. The accuracy of the prediction is indicated as log(likelihood in cross validation), convergence and distance from most analogous case with the corresponding confidence intervals.

2.5.10 Procedures in Making a PERPEST Prediction

The following procedure can be used while making a prediction using the PERPEST model;

1. Download and install the PERPEST model in a computer.
2. Select the model by double clicking and click on ‘Run as’, this displays the PERPEST model window.
3. Click on the ‘Select predict effect of toxicant’.
4. The PERPEST data window (Pesticide data) that is needed to describe the question case is displayed.
5. Click on ‘Experimental features’ by clicking to input data.
6. Then click on ‘Weighting variables’ to select weights and conditional variables.
7. Click on ‘Options menu’ to select desired conditions for the prediction.
8. Click on ‘Bootstrap’ to input bootstrap method and desired confidence limits.
9. Click on the ‘Optimize icon’ to input/select optimization parameters and desired ranges.
10. Click on the ‘PERPEST icon’ to select/input the desired weights and mode of transformations.
11. Click on the ‘Optimization icon’ at the bottom to optimize the prediction.
12. Click ‘OK’ to display Predicted effects after optimization is complete.
13. Click on ‘Gradient icon’ to view graphs and ‘confidence limits’ to view the confidence limits of each prediction.

2.6 Environmental Legislation, Management and Governance

Environmental management in Kenya is vested to lead agencies to govern by Acts of parliament and other legislations. The following section describes some of the important legal and institutional frameworks that relate to Lake Naivasha.

2.6.1 The Environmental Management and Coordination Act (EMCA), 1999

The Environmental Management and Coordination Act (EMCA), 1999 is the legislation that governs environmental management in Kenya (GoK, 2000; Wamukoya *et al*, 2007, GoK, 2010). Under the act of parliament of 1999 the National Environment Management Authority was created. The objective and purpose for which the Authority was established was to exercise general supervision and co-ordination over all matters relating to the environment and to be the principal instrument of Government in the implementation of all policies relating to the environment. The authority was mandated to;

i. Co-ordinate the various environmental management activities being undertaken by the lead agencies and promote the integration of environmental considerations into development policies, plans, programs and projects with a view to ensuring the proper management and rational utilization of environmental resources on a sustainable yield basis for the improvement of the quality of human life in Kenya.
ii. Take stock of the natural resources in Kenya and their utilization and conservation.
iii. Establish and review in consultation with the relevant lead agencies, land use guidelines.

iv. Examine land use patterns to determine their impact on the quality and quantity of natural resources.

v. Carry out surveys which will assist in the proper management and conservation of the environment.

vi. Advise the Government on legislative and other measures for the management of the environment or the implementation of relevant international conventions, treaties and agreements in the field of environment, as the case may be.

vii. Advise the Government on regional and international environmental conventions, treaties and agreements to which Kenya should be a party and follow up the implementation of such agreements where Kenya is a party.

viii. Undertake and co-ordinate research, investigation and surveys in the field of environment and collect, collate and disseminate information about the findings of such research, investigation or survey.

ix. Mobilize and monitor the use of financial and human resources for environmental management.

The above responsibilities therefore make NEMA the key body that is supposed to ensure sustainable exploitation of the lake and other resources in the basin.

2.6.2 The Water Act, 2002

The Water Act 2002 relates to the management of wetlands and water sources. Lake Naivasha is a freshwater lake and the provisions of the Water Act 2002 provides for its management. The Act is main legislation that regulates the water sector in Kenya, this

therefore means that all policies, regulations and by-laws, directives and administrative actions from the ministry, strategic plans and all activities by water sector institutions must be done in accordance with and be consistent with the provisions and content of the Water Act 2002.

The Water Act which came into force in 2003 was passed with various objectives;

i. The Act was meant to clearly differentiate the roles of various actors in water sector i.e. the government, local government, the private sector and the public into two main areas, water resources management and water services and supply

ii. The Act also had the intention of entrenching public participation and involvement in water services and water resources management.

iii. The Act also intended to clearly define water rights and legislate ways in which water resources can be utilized.

The Water Act introduced new water management institutions to govern water and sanitation. The Water Services Regulatory Board (WASREB) to set standards and regulate the sub-sector; the Water Appeal Boards (WABs) to be responsible for the management of efficient and economical provision of water and sewerage services; Water Services Boards (WSBs) in the actual provision of water and sewerage services; the Water Services Trust Fund (WSTF) to finance pro-poor investments; and the Water Resources Management Authority (WRMA) to manage and protect Kenya's water resources. Catchment Area Advisory Committees (CAAC) support the WRMAs at the regional level. Water Resources

Users Associations (WRUAs) were established as a medium for cooperative management of water resources and conflict resolution at sub-catchment level. The Ministry of Water and Irrigation (WMI) is vested with the responsibility for overall sector oversight including policy formulation, coordination and resource mobilization.

2.6.2.1 State Ownership of all Water Resources

The Act vests all water resources in the state and the water resources are to be managed and utilized in accordance with the Act. This means that the state has ownership of all water resources in Kenya. The Act provides that exploitation of water resources require authority granted through the issuance of a water permit.

2.6.2.2 Protection of the Quality of Water Resources

The Act provides for the protection of the quality of water resources through the following provisions;

i. The Act created the WRMA and specified one of the functions to be the regulation and protection of water resources quality from adverse impact.
ii. The Act also provides for the classification of water resources quality objectives in order to preserve the water quality of each resource.
iii. The Act makes it an offence for a person to in any way cause pollution in a water course or water resource by throwing, conveying or permitting to be thrown any rubbish, dirt, refuse, trade waste or other offensive material into the river or water resources and ensuring effective disincentives and penalties for pollution.

iv. The Act further provides that a licensee may construct and maintain drains, sewers and other works for intercepting, treating or disposing of any foul water arising or flowing upon such land otherwise for preventing water from being polluted.

v. WRUAs and CAACs are mandated to monitor the pollution of water resources in their areas.

2.6.3 The Public Health Act, 1984

The Public Health Act (Cap 242) regulates activities detrimental to the human health. The owner(s) of the premises responsible for environmental nuisance such as effluents, noise and air emissions at levels that can affect human health are liable to prosecution under this Act. An environmental nuisance is one that causes danger, discomfort or annoyance to the local inhabitants or which is hazardous to human health. The Act prohibits drainage of surface water into foul water sewers, discharge into sewers matters which may interfere with the free flow of the sewage and enforces treatment of effluent before discharge into sewers or water bodies and ensure effluent standard. The Act make provisions for protecting sources of drinking water supply from pollutions. Section 126 of the Public Health Act empowers the Minister to make rules on *inter alia;* the standard of purity of any liquid, which after treatment in any purification works may be discharged as effluent. The section prohibits draining of waste water into foul water sewers, and discharge into sewers matters.

The Public Health Act pertains to the issues concerning Lake Naivasha as an act that can control the discharge of effluents from the flower farms and the Naivasha Town all of which

affect the quality of water. The act allows the public health officers to close or order firms that are causing adverse effects to the human health to close or to mitigate the impacts by treating or proper waste handling.

2.6.4 Lake Naivasha Riparian Owners Association

The Lake Naivasha Riparian Owners Association in collaboration with the Government has prepared a management plan for the Lake and its environs (Harper *et al*., 1992). While the management plan was a community initiative, the Government has participated in the formulation of the plan and in its implementation in order to ensure that the plan represents the interests of all stakeholders *inter alia*. The mandate of LNROA includes the conservation of Lake Naivasha biodiversity, assessment of the Lake's hydrological system in order to establish the water balance and exchange of data and information on the Lake's ecosystem. Water management including review of water abstraction rights in relation to the available water in order to ensure sustainable agricultural and urban development, which takes into account the need to protect the Lake and its biodiversity and provision of access corridors to the Lake and creation of a buffer zone around it. Another mandate is monitoring the Lake's ecosystem, including the adherence by the riparian farmers to the agro-chemicals code of conduct and the application of Environmental Impact Assessment on land use around the lake to ensure protection of water quality.

2.6.5 The Environmental Management and Coordination (Water Quality) Regulations, 2006

The Water Quality Regulations, 2006 are meant to provide guidelines for water quality management. The Act applies to Lake Naivasha as a freshwater lake that serves as a source of domestic water, irrigation, fisheries, and recreation. The Act set to among other things protect of sources of water through;

i. *Prevention of Water Pollution;* under the regulations every person shall refrain from any act which directly or indirectly causes, or may cause immediate or subsequent water pollution, and it shall be immaterial whether or not the water resource was polluted before the enactment of the Act. No person shall throw or cause to flow into or near a water resource any liquid, solid or gaseous substance or deposit any such substance in or near it, as to cause pollution.

ii. *Set standards for Sources of Domestic water;* All sources of water for domestic uses shall comply with the standards set out in First Schedule of these Regulations.

iii. *Protection of Lakes, Rivers, Streams, Springs, Wells and other water sources;* No person shall: (a) discharge, any effluent from sewage treatment works, industry or other point sources into the aquatic environment without a valid effluent discharge license issued in accordance with the provisions of the Act. (b) abstract ground water or carry out any activity near any lakes, rivers, streams, springs and wells that is likely to have any adverse impact on the quantity and quality of the water, without an Environmental Impact Assessment license issued in accordance with the provisions of the Act; or (c) cultivate or undertake any development activity within a minimum of

six meters and a maximum of thirty meters from the highest ever recorded flood level, on either side of a river or stream, and as may be determined by the Authority from time to time.

iv. *Bans, Restrictions, etc on use of Water Sourc*es; The Authority in consultation with the relevant lead agency may impose bans and restrictions and other measures on the use of sources of water for domestic use in order to prevent and control their degradation.

v. *Compliance with Water Quality Standards;* All operators and suppliers of treated water, containerized water and all water vendors shall comply with the relevant quality standards in force as promulgated by the relevant lead agencies.

vi. *Water Quality Monitoring;* The Authority in consultation with the relevant lead agency, shall maintain water quality monitoring records for sources of domestic water at least twice every calendar year and such monitoring records shall be in the prescribed form as set out in the Second Schedule to these Regulations.

vii. *Discharge into Aquatic Environment;* No person shall discharge or apply any poison, toxic, noxious or obstructing matter, radioactive waste or other pollutants or permit any person to dump or discharge such matter into the aquatic environment unless such discharge, poison, toxic, noxious or obstructing matter, radioactive waste or pollutant complies with the standards set out in the Third Schedule of these Regulations.

viii. *Discharge into the Environment;* Every local authority or person operating a sewage system or owner or operator of any trade or industrial undertaking issued with an

effluent discharge license as stipulated under the Act shall comply with the standards set out in Third Schedule to these Regulations. Every local authority or person operating a sewage system or owner or operator of any trade or industrial undertaking shall be guided by the monitoring guide for discharge into the environment as set out in the Fourth Schedule to these Regulations or as the Authority may prescribe.

Under the act the water quality issues of a lake such as Lake Naivasha pertains and thus reference to the act is very important if sustainable management of the Lake is to be achieved.

2.6.6 The Stockholm Convention, 2001

The Stockholm Convention, 2001 deal with 12 designated persistent organic pollutants (POPs) or "Stockholm POPs". POPs persist and remain un-degraded in the environment for long periods after application. They accumulate in the fatty tissues of organisms and lead to the damage of the nervous system, cause cancer and damage the reproductive system and the immune systems. Under the convention global treaty was negotiated aiming at protecting human health and the environment from POPs. The convention focuses on pesticides (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex and toxaphene), industrial chemicals; polychlorinated biphenyls (PCBs) and by-products such as dioxins and furans. Parties/signatories are obliged to take measures to eliminate production, restrict use, identify sources and reduce release of POPs by-products.

The Stockholm Convention, 2001 deals POPs 12 of which are organochlorine pesticides that are normally encountered in environmental analysis some of which have been detected in Lake Naivasha before.

2.6.7 Ramsar Convention of Wetlands

Lake Naivasha is a Ramsar wetland and the rules that govern the management of Ramsar sites apply. The protection of Ramsar wetlands is well spelt out in the Environmental Protection and Biodiversity Act (EPBA) (UNEP, 2008). Under the Act, Ramsar Wetlands are recognized as a matter of national environmental significance (RCW, 2002). A person must not take an action that has, will have, or is likely to have, a significant impact on the ecological character of a Ramsar Wetland, without approval (RCW, 2002; UNEP, 2008). To obtain approval, the action must undergo a rig environmental assessment and approval process (RCW, 2002). The ecological character of a Ramsar Wetland is the combination of the ecosystem components, processes and benefits/services that characterize the wetland at a given point in time. Within this context, ecosystem benefits are defined in accordance with the Millennium Ecosystem Assessment (MEA) definition of ecosystem services as 'the benefits that people receive from ecosystems (RCW, 2002; UNEP, 2008).

Under its biodiversity conservation provisions, the Act establishes an improved framework for managing Ramsar wetlands in the form that are intended to promote national standards of management, planning, environmental impact assessment, community involvement, and monitoring, for all Ramsar wetlands. A management plan for a Ramsar wetland cannot be

accredited unless it will promote the management of the wetland in accordance with such principles (Database, 1995; RCW, 2002; UNEP, 2008).

The United Nations Environmental Programme (UNEP) recognizes the vulnerability of water systems and what it means for people who are dependent on them is essential so policy makers can develop and implement effective local and trans-boundary important policies (UNEP, 2008). UNEP calls for sustainable agriculture and sustainable fisheries in the management of freshwater ecosystems in order to achieve sustainable ecosystem management (UNEP, 2008). The sustainable management of water resources calls for the establishment of water and ecological footprints in order to guide policy formulation (Tole and Shitsama, 2000; Hoesktra and Chapagain, 2007; Hoesktra and Chapagain, 2008).

This study was carried out to assess the human activities that pose a threat to the ecological character of Lake Naivasha and its catchment. The study sought to document some of the significant impacts resulting from current human activities in the basin making use of physicochemical parameters, pollution load indices and micro-organism population as indicators of Lakes water quality.

2.7 Literature Gaps in Lake Naivasha

Though a lot of work has been done on pesticides and heavy metals in the lake most studies have addressed DDT, lindane and dieldrin and some fish species. No studies have linked the pollution in the lake to sources. The studies did not compare the concentrations of the pesticides and heavy metals in discharges from the flower farms, inflowing rivers and the Oloidien Lake. Survey of the published work show no pollution load indices determination.

The application of expert computer model in environmental risks and dietary risk assessments have not been carried out.

A study on the water abstraction volumes, aquatic organisms' populations in relation to contaminants exposure concentrations and human activities in the basin have not been carried out. There is also luck of an inventory of pesticides used in the basin. There is no data on the concentrations of endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide and methoxychlor in the waters and fish species of the Lake Naivasha basin.

No studies have applied pesticide models in the analysis of the environmental health of the Lake which this study intends to do.

2.8 Problem Statement

DDT, endrin, heptachlor, aldrin, dieldrin and lindane are all banned and have been classified as human carcinogens and are believed to cause serious adverse effects on aquatic organisms. Being a freshwater ecosystem the quality of the water and aquatic life require regular monitoring to inform policy on the emerging issues. Methoxychlor and endosulfan are still widely used though the use of endosulfan is being phased out. Cd and Pb are also classified as carcinogens and have no known beneficial importance to the human body. Though Zn, Ni and Cu are considered essential to the human body, high concentrations lead to adverse effects. The inflow of these organochlorine pesticides and heavy metal contaminants in the lake could lead to the bio-concentration of the toxicants into the food chain. The lake serves as a source of drinking water and food inform of fish to the local communities. This can

further lead to the exposure of humans and other aquatic organisms to the introduction of the contaminants in the food. The purpose of the study therefore was to assess chemical contamination of water, sediments and fish in the lake. The study was extended to the catchment areas to establish concentrations, spatial distribution and sources of the contaminants. Dietary risks assessments were done undertaken for the consumption of fish with respect to heavy metals and pesticides. The environmental risks of the measured exposure of pesticides to aquatic communities were predicted using a modified version of the PERPEST model.

2.9 Hypotheses

2.9.1 Null Hypotheses

i. There are no changes in the human activities in the Lake Naivasha basin for the period from 1983 to 2008.

ii. The distribution of population densities of selected aquatic organisms in the lake bed does not vary with the pesticide exposure concentration.

iii. There is no difference between the levels of Cd, Cu, Zn, Ni and Pb in the waters from the Lake Naivasha and the allowable concentrations in freshwater lakes.

iv. There is no difference between the concentrations of Cd, Cu, Zn, Ni and Pb in the surface sediments of Lake Naivasha and those found in World shale.

v. There is no difference between the concentrations of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde,

heptachlor, heptachlor epoxide, aldrin, dieldrin, methoxychlor and lindane in the waters of Lake Naivasha basin and the limits given for freshwater lakes.

vi. There is no difference between the concentrations of *p, p'*- DDT, p, p'- DDE, *p, p'*- DDD, heptachlor, heptachlor epoxide and methoxychlor in fish from Lake Naivasha and those set by WHO and EEC.

vii. The measured exposure concentrations of endosulfan and methoxychlor do not pose any ecological risks to insects, algae and macrophytes, community metabolism, fish, rotifers, microcrustacea, microcrustacea and Non-anthropod.

2.10 Study Objectives

2.10.1 Main Objective

To assess environmental pollution in reference to heavy metals, organochlorine pesticides in Lake Naivasha basin and to predict environmental risks of organochlorine pesticides on aquatic communities.

2.10.2 Specific Objectives

i. To determine physicochemical water quality parameters in the lake Naivasha.

ii. To establish changes in human activities in the Lake Naivasha basin from 1983 to 2008.

iii. To assess water abstraction volumes in the Lake Naivasha basin.

iv. To establish the pesticides used in the Lake Naivasha basin.

v. To determine the population density of selected aquatic organisms in the lake bed.

vi. To determine the concentration of Cd, Cu, Zn, Ni and Pb in the water from the Lake Naivasha Basin.

vii. To determine the concentration of Cd, Cu, Zn, Ni and Pb in surface sediments from the Lake Naivasha basin.

viii. To determine the concentrations of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, aldrin, dieldrin, methoxychlor and lindane in the waters from the Lake Naivasha basin.

ix. To determine the concentrations of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, methoxychlor, heptachlor and heptachlor epoxide in fish (*O. leucosticus, C. carpio* and *C. spectacularlus*) from Lake Naivasha.

x. To determine environmental risks posed by the measured exposure concentrations of endosulfan and endosulfan on insects, fish, rotifer, algae and macrophytes, microcrustacea, macrocrustacea and Non-anthropod using a modified version of the PERPEST model.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Experimental Design

The study was broken up into the following broad areas;

i. Determination of limnology parameters (dissolved oxygen, Secchi depth and water temperature).

ii. Establishing a pesticides inventory used in the basin.

iii. Evaluation of secondary data on water abstraction.

iv. Assessment of changes in anthropogenic activities in the Lake Naivasha basin from 1983 to 2008.

v. Determination of the population densities of selected aquatic organisms in the lake bed of Lake Naivasha.

vi. Analysis of lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni) and copper (Cu) in water from the catchment.

vii. Analysis of lead, cadmium, zinc, nickel and copper in surface sediments from the Lake bed.

viii. Analysis of lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni) and copper (Cu) in fish from the catchment.

ix. Analysis of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, aldrin, dieldrin, methoxychlor and Lindane in water from the Catchment.

x. Analysis of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, methoxychlor, heptachlor and heptachlor epoxide in fish (*O. leucosticus*, *C. carpio* and *C. spectacularlus*.) from Lake Naivasha.

xi. Modification and application of PERPEST Model in ecological risks assessment of measured exposure concentrations of endosulfan and methoxychlor on insects, fish, rotifer, algae and macrophytes, community metabolism, microcrustacea, macrocrustacea and Non-anthropod invertebrates.

3.2 Acquisition of Limnology Data

3.2.1 Measurements of Dissolved Oxygen and Temperature

Dissolved oxygen concentrations were measured in mg/L in triplicates using a Clark Type oxygen ion selective electrode (APHA, 1995) available at the LNROA laboratories. Water temperatures were measured along side with dissolved oxygen using the Clark Type Oxygen ion selective electrode with an inbuilt thermometer. The two readings were recorded in triplicates for each site.

3.2.2 Secchi Depth Measurements

Secchi depth was measured in triplicates using a 20 cm Secchi disc with white and black quadrants available at the LNROA laboratories. The Secchi disk was lowered into the water till the disk just disappears from view (Michael, 1990). The depth was recorded. The disk was lowered a little further and then gradually raised until it reappears and the depth recorded. The mean Secchi disk depth was calculated for three measurements.

3.3 Determination of Pesticides Used in the Catchment

The pesticides used in the Lake Naivasha basin were determined through use of interviews with small scale farmers, agricultural extension officers and agrochemicals sales outlets in the basin. Lists of pesticides used in the flower farms were also obtained from two flower farms.

3.4 Acquisition of Water Abstraction Volumes and Google Images

Existing water abstraction data was acquired from flower farms alongside allocated abstraction volumes. Consultations were also done with Water Resources Management staff at the Naivasha office. Satellite images were acquired from *World Wide Web* (*www*) and were classified according to the dates of capture.

3.5 Determination of Aquatic Organisms Population Density

The population of aquatic organisms was determined using Oligoceates and Chironomidae as indicator organisms in the Lake bed. The population density was determined by capturing the organisms with sediments by using an Ekman dredge sampler as described by Michael (1990). The Ekman dredge sampler was lowered to the lake bed with jaws open. On reaching the Lake bottom a weight (messenger) was sent down. This released the springs which hold the jaws apart. The jaws closed shut and during the process the bottom material was scooped up by the jaws. The bottom materials were transported to the LNROA laboratories for analysis. The materials were washed in a net to trap the organisms. The organisms were identified and the number for each sample determined manually through physical hand count.

3.6 Materials and Apparatus

3.6.1 Chemicals, Solvents and Reagents

All chemicals and reagents used in the study were analytical grade reagents and triple distilled organic solvents for pesticides analysis as described by APHA (1995). The reagents were sourced from PDH Poole, Ultra scientific USA and Sigma Aldrich. Distilled water for pesticide analysis was purified by extraction twice with pesticide grade hexane in an Erlenmeyer flask. Before use the purified water was heated to boiling for ten minutes to remove traces of hexane. Pesticide grade solvents were used in the analysis; solvents were triple distilled in all glass bottles where pesticide grade solvents were not available. Florisil and anhydrous sodium sulfate were dried by heating overnight at 650 ºC in the oven.

3.6.2 Cleaning of Sample Containers and Glassware

Sample containers and glassware used in the study were soaked with a dilute nitric acid solution overnight then cleaned with detergent and rinsed with distilled water. Apparatus for pesticide analysis were cleaned by washing with soap and water, rinsing with hot water, distilled water, twice with analytical grade acetone, twice with pesticide grade ethyl acetate and finally with pesticide grade hexane. The glassware and containers were then baked at 400 ºC for 45 min. in an oven to remove traces of organic solvents. These were stored in a closed cupboard to avoid dust deposits.

3.6.3 Sample Weighing, Length Measurements and Drying

All weightings were done using a digital analytical balance GR-200 series with an accuracy of 0.001 g available at the JKUAT Chemistry research laboratories. Lengths of the fish specimens were measured for each specimen from mouth to tail using a graduated ruler. Fish muscles were extracted and dried in an oven as described in APHA (1995). A Salvis Model oven available at the JKUAT Chemistry research laboratory was used at a temperature of 105 ^{0}C for 48 hours.

3.6.4 Sample Concentration and Shaking

Sample concentrations were done using a Rotary evaporator, Buchi Rotavapor GR-200 Series (available at the JKUAT Chemistry research laboratories) by evaporating in a water bath at a temperature of 40 ^{o}C as described by Alfred *et al*. (2000) and APHA (1995). The specimens were shaken with organic solvents during extraction as described by Alfred *et al*. (2000) and APHA (1995) using an orbital shaker, Heildoph Nimax 1010 DT Model (available at the JKUAT Chemistry research laboratories).

3.7 Sample Sites

Sampling sites were mapped out using an iPAQ Business Navigator from Helwet Packard Personal Data Assistant (PDA) available during the Field Information Technology Field course at LNROA, 2009. The approximate locations recorded using Global Positioning System (GPS). The sites were named from SS1 - SS10 and are shown in Fig. 3.1 and their location on the globe is presented in Table 3.1.

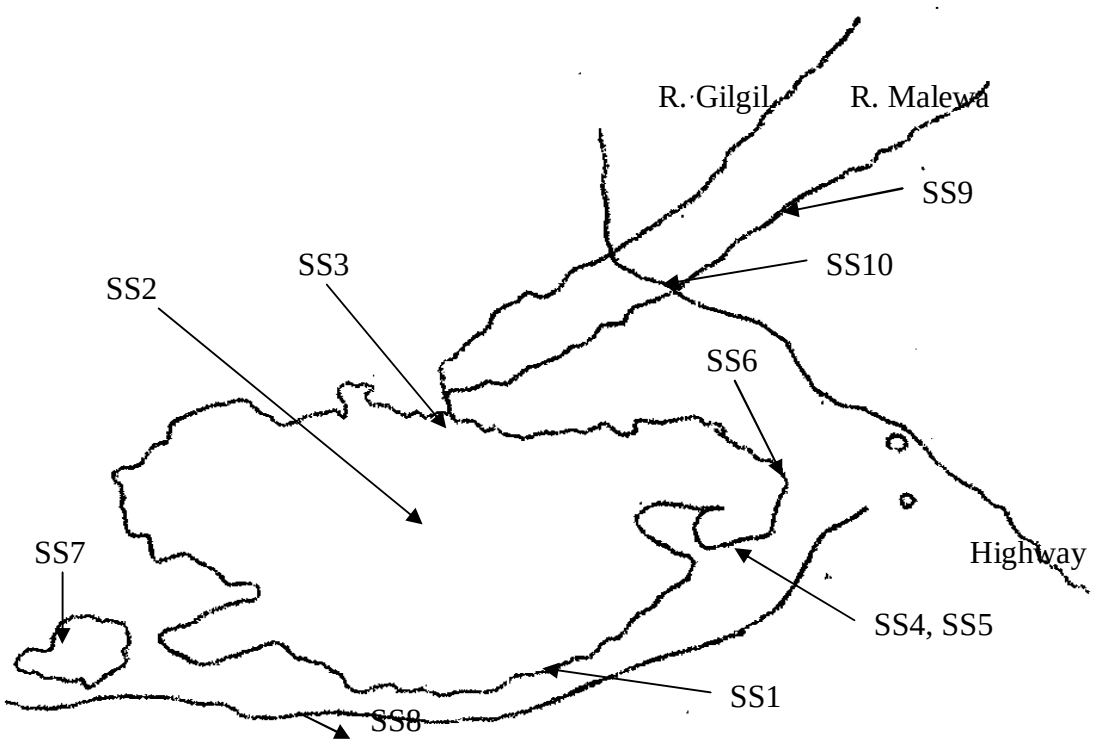


Figure 3.1. Sampling Sites in the Lake Naivasha Basin

Key: SS1 - Oserian Bay, SS2 - Mid Main Lake, SS3 - Karati Delta, SS4 - Crescent shore, SS5 - Crescent Mid, SS6 - Kihoto Sewer Point, SS7 - Oloidien, SS8 - Sher Canal, SS9 - River Malewa Turasha Bridge, SS10 - River Malewa Highway Bridge.

The locations of the sampling points on the globe are presented in Table 3.1.

Table 3.1. Global Positioning Coordinates of Sampling Sites

	Site Description	**Latitude**	**Longitude**
SS1	Oserian Bay	$0^0$44’42.49’’S	$36^0$21’13.38’’E
SS2	Mid Main Lake	$0^0$46’08.87’’S	$36^0$21’02.54’’E
SS3	Karati	$0^0$43’49.05’’S	$36^0$21’06.82’’E
SS4	Crescent shore	$0^0$46’05.27’’S	$36^0$24’35.59’’E
SS5	Crescent Mid	$0^0$46’15.57’’S	$36^0$24’50.79’’E
SS6	Kihoto	$0^0$44’17.28’’S	$36^0$24’46.70’’E
SS7	Oloidien	$0^0$48’57.01’’S	$36^0$15’53.27’’E
SS8	Discharge Canal	$0^0$50’15.26’’S	$36^0$21’08.01’’E
SS9	R. Malewa Turasha Bridge	$0^0$39’30.10’’S	$36^0$24’24.48’’E
SS10	R. Malewa Bridge	$0^0$40’09.41’’S	$36^0$23’11.99’’E

3.8 Sampling

3.8.1 Water Samples

Water samples were collected at random from the Lake Naivasha basin as described in APHA (1995). Samples were collected in triplicates from 10 sampling sites along River Malewa, Main Lake, Lake Oloidien, discharge canals and Crescent Lake.

3.8.2 Fish Samples Collection

Fishnet caught fish were bought from fishermen while still alive and identification done by officials from the Kenya Marine and Fisheries Research Institute (KEMFRI). Fish specimens were bought from various landing beaches in the lake. The fish specimens included; *C. spectacularlus, C. carpio,* and *O. leucostictus*. Sampling consisted of collecting two fish composites per site. Each composite contained 5 adult fish of the same species and of similar size (so that the smallest individual within the composite is no less than 75% of the total length of the largest individual) as described by EPA (2000, 2002) by The samples were labeled and stored in a Coleman cooler box under ice and transported to the JKUAT Chemistry research laboratory for analysis.

3.8.3 Sediment Samples Collection

Sediments were sampled from the lake bed using the procedure described by Michael (1990). Samples were collected in triplicates from 10 sites using an Ekman dredge grab sampler. Samples were wrapped with pre-cleaned polythene bags and transported to the laboratory under ice.

3.9 Sample Pre -Treatment and Treatment

3.9.1 Water Sample for Heavy Metal Analysis

Samples were collected in triplicates in pre-cleaned plastic bottles from all sites. Sample pH was adjusted to 4.0 by addition of approximately 2.0 mL analytical grade HNO_3 per liter (APHA, 1995). Samples were transported to the laboratory under ice in Coleman cooler

boxes and stored in the refrigerator. Samples were thoroughly mixed before laboratory samples were drawn.

3.9.2 Water Sample for Pesticide Analysis

Water samples were collected at random from the Lake Naivasha basin as described by APHA (1995), Alfred *et al*. (2000) and Aufbau and Afghan (1990). Samples were collected in triplicates from 10 sampling sites (Fig. 3.1) along River Malewa, Main Lake, Lake Oloidien, Crescent Lake and discharge canals. 1 L water samples were collected in amber glass bottles in triplicate from each sampling point and immediately preserved with mercuric chloride solution. The samples were stored in Coleman cooler boxes while in the field and during transportation to the laboratory in Nairobi for analysis. Once in the laboratory, the samples were immediately extracted into organic solvent and stored for cleanup and analysis.

3.10 Analysis of Secondary Data

Satellite images were analyzed manually by visual assessments. The areas with different activities were characterized by their spectral reflectance. These activities were ground truthed through site visits and consultation with experts. The water abstraction data was analyzed through computation and comparison with recently published data.

3.11 Analytical Procedures

3.11.1 Homogenization of Fish Muscle

Fish specimens were washed with distilled water and muscle cut. The muscles were homogenized using a blender for pesticide analysis and mortar and pestle for heavy metal analysis as described by APHA (1995) Alfred *et al*. (2000) and Aufbau and Afghan (1990).

3.11.2 Determination of Moisture Content in Fish

The moisture content in fish specimens were determined using the methods described by Wasswa and Kiremire (2004). Three 10 g portions of the homogenate fish samples were weighed in pre-weighed beakers and dried in the oven overnight at 105 ºC. The weight of the dry sample was calculated by difference and the moisture content taken as the weight loss, the mean percentage moisture content was calculated and the standard deviation calculated.

3.11.3 Determination of Lipid Content in Fish

The moisture content in fish specimens were determined using the methods described by Wasswa and Kiremire (2004) APHA (1995) EPA (2000) and EPA (2002). Three 10 g portions of the homogenate fish samples were weighed out in pre-weighed beakers and extracted thrice with 50 ml chloroform. A 20 g portion of anhydrous sodium sulfate was added to each sample and shaken in an orbital shaker for 30 minutes to remove moisture. The extracts were stored in the fume-hood to allow the solvents to volatilize. The extracts were combined and left until only the lipid portion was left. The weight of the lipid was calculated by difference and the mean lipid content calculated.

3.11.4 Heavy Metal Analysis

3.11.4.1 Digestion of Water Samples

Water samples were wet digested using mixtures of acids as described by APHA (1995). Samples were mixed thoroughly and aliquots of 100 ml taken in triplicates. These were acid digested with a mixture of analytical grade nitric acid and perchloric acid (3:1) for 90 min. at 90 ºC to near dryness. The digests were filtered through Whatman No. 41 filter paper and made to 50 ml using de-ionized water. The digests were transferred to pre-cleaned plastic bottles and stored in a refrigerator in plastic bottles to avoid changes in volume.

3.11.4.2 Digestion of Fish Samples for Heavy Metal Analysis

Fish muscles were homogenized using mortar and pestle as describe by Wandiga *et al*. (2002) and Wasswa and Kiremire (2004). Ten grams of homogenized fish muscle were weighed out and digested with mixtures of analytical grade nitric and perchloric acid (1:3 v/v) at 90 ºC for 2 hr until clear solutions were formed. The digests were filtered and topped up with de-ionized water and stored in plastic bottles in a refrigerator prior to analysis.

3.11.4.3 Sediment Digestion for Heavy Metal Analysis

Sediments were dried to a constant mass in the oven at 105 ºC and crushed using mortar and pestle into fine powder and later sieved to remove debris and rock particles as described by APHA (1995). Samples were digested with a mixture of analytical grade nitric and perchloric acid at 90 ºC for 2 hr. The digests were filtered and topped up with distilled de-ionized water and stored in plastic bottles in a refrigerator.

3.11.4 Pesticide Analysis

3.11.5.1 Extraction and Removal of Co-extractives of Water Extracts

Sample extraction was done by solvent-solvent extraction using dichloromethane as described by Aufbau and Afghan (1990) and APHA (1995). One liter water samples were transferred into 2 L separatory funnel and treated with 50 mL of phosphate buffer of pH 7. Then analytical grade sodium chloride (100 g) was added to the water and mixed thoroughly to salt out pesticides (Herlich, 1990). Extraction was effected by shaking the sample with three portions 60 ml High Pressure Liquid Chromatography (HPLC) grade dichloromethane and collecting the organic layer. The combined extracts for each sample was concentrated to 1 ml using rotary evaporator at 40 ºC and cleaned by eluting through 20 g Florisil, packed in 25 cm long and 1.5 cm internal diameter chromatographic column packed (at a flow rate of 2 ml/min.) with activated anhydrous sodium sulfate both at the bottom of the column and on top of Florisil layer to remove any moisture present (Muhammad, 2006).

3.11.5.2 Extraction and Clean-up of Lipid Fraction in Fish

Fish lipids were extracted using solvent extraction method with HPLC grade dichloromethane as described by Herlich (1990), APHA (1993) and Alfred *et al*. (2000). Twenty grams homogenate fish samples were taken in triplicates and mixed with 20 g analytical grade anhydrous sodium sulfate in a mortar and crushed with a pestle to give a homogeneous dry mixture (Herlich, 1990; APHA, 1993; Alfred *et al*., 2000). The mixture was transferred into an Ernmeyer flask and shaken for about 45 min. in an orbital shaker with dichloromethane. The extract was filtered through a glass wool plug into an evaporating

flask. The extraction was then repeated three times, each with 50 mL of dichloromethane. The extracts were pooled and evaporated completely at 40 ºC with a rotor vapor leaving only the lipid portion.

The fats were transferred into separatory funnel and dissolved in HPLC grade petroleum ether and diluted with 650 ml distilled water, 20 ml phosphate buffer pH 7.0 and shaken with hexane. A 500 ml distilled water aliquot and 50 ml saturated sodium sulfate was then added and shaken vigorously (Herlich, 1990). The aqueous layer was discarded and the hexane extract concentrated in rotary vapor.

The combined extracts for each sample was concentrated using rotary evaporator at 40 ºC and cleaned by eluting through 20 g Florisil, packed in 25 cm long and 1.5 cm internal diameter chromatographic column (at a flow rate of 2 ml/min.) packed with activated anhydrous sodium sulfate both at the bottom of the column and on top of Florisil layer to remove any moisture present. The cleaned samples were concentrated to 0.5 ml and stored in glass vials before analysis.

3.12 Sample Analysis

3.12.1 Pesticide Concentration and Measurements

Sample analysis was done using Varian CP 3800 Gas Chromatograph equipped with Electron Capture Detector (ECD) available at University of Nairobi, pesticides laboratory. Separation was done using BPX 5 capillary column of dimensions 30 m x 0.25 mm x 0.25 µm film thickness. Confirmatory analysis was done using BPX 35 capillary column of dimensions 50

m x 0.25 mm x 0.25 µm film thickness. A temperature program was used starting from 90 ºC (with hold time of 3 min.), increased to 215 ºC at 8 ºC/min. (with hold time of 25 min.), then increased to 270 ºC at 5 ºC/min. (with hold time of 5.37 min.), and finally ramped to 275 ºC at 5 ºC/min. (with hold time of 18.63 min.). The carrier gas was high purity helium (99.9995%) with white spot nitrogen as the makeup gas. Quantification followed external calibration method using high purity pesticide reference standards mixture obtained from Ultra Scientific USA.

3.12.1.1 Quality Assurance

All sampling, extraction and analysis were done in triplicate to allow verification of the detected pesticide residues (WNDR, 1996). Recovery tests were carried out using the reference pesticide standards to determine performance of the methodology. Quantification of pesticide residues was carried out using high purity pesticide reference standards. Field blanks and method blanks were also incorporated to check contamination during sampling, transportation and laboratory preparation procedures (UNEP, 1993).

3.13 Heavy Metals Measurements

The atomic absorption spectrophotometer (AAS - Buck Scientific VGP 210 Model available at the JKUAT Chemistry research laboratory) was used for the analysis of all samples. The concentrations of the metals were assayed in triplicates. A series of standards were prepared for instrumental calibration from stock solution analytical grade AAS standard solutions

from BDH Poole and Sigma Aldrich. A standard and blank sample was run after every seven samples to check instrumental drift (Miller and Miller, 1988).

3.14 Quality Control

To ensure quality and validity of the analytical procedure the instrument was calibrated using standards prepared from analytical standards grade stock solutions, the standards were prepared in the linear working range as described in the instruments manual. To check precision of measurements concentrations were read in triplicates. A blank sample was included in the calibration curve as the first point. The instrumental parameters were optimized as described in the instrument manufacturer's manual. The instrument detection limit were determined by reading a blank sample seven times and calculated as 3 times the standard deviation of the measurements at $p = 0.001$ (Skoog and Leary, 1992).

The method percentage recoveries were determined for all metals by spiking with a known amount standard (Miller and Miller, 1988; WDNR, 1996). The samples were taken through all steps in analysis and measurements taken. Representative samples were sent to Geology and Mines Laboratories in Nairobi for comparison. Results indicate that there is no significant difference between results obtained from the two laboratories at $\boldsymbol{p = 0.05, n = 5,}$ $\mathbf{t_{(n-1)}}$ and $\mathbf{n_1 + n_2 - 2}$ degrees of freedom ($\boldsymbol{\upsilon}$).

3.15 Application of Modified PERPEST Model

The PERPEST model was modified, calibrated and validated with experimental data as described by DEQ (2003). The experiments employed endosulfan as the test pesticide, C.

carpio and *Tilapine spp*. as indicator species simulating. Aquarium tanks were set up using sediments and water from Lake Naivasha. Juvenile fish were exposed to endosulfan at various concentrations and the mortality of fish recorded with time for each concentration as described by Henry *et al*. (2003). The experiments simulated lotic freshwater ecosystems, dissipations of the pesticides were also studied. The results of the study accurately estimated the EC_{50} and the toxicity reference values for testing aquatic biota reported by the pesticide registrant. The data from the experiment were chosen because the prevailing conditions replicated those of Lake Naivasha. Juvenile Tilappine *spp*. and C. *Carpio* from Lake Naivasha were also used in the study.

Key parameters were altered to reflect tropical climatic conditions and dissipation of the pesticide. Conditional variables were weighted and optimized at 95 5% confidence level. The accuracy of the prediction was tested through comparison of toxicity reference values for testing aquatic biota, EC_{50} values and response at specified concentrations as described by DEV (2001) and Ani *et al*. (2009). The modified PERPEST model was used to predict the effects of the measured exposure concentrations of methoxychlor and endosulfan eight aquatic communities.

3.16 Hypotheses Testing

Hypotheses were tested by comparing the means of the measured concentrations with those of acceptable limits. Comparisons of sites were done using site SS2 middle lake as the control point. T significant test were all done at 95% confidence level with $\mathbf{n_1 + n_2 - 2}$ degrees

of freedom where $\mathbf{n_1}$ and $\mathbf{n_2}$ are the number of replicates taken for each mean. For sediments the Hypotheses were tested using the Tomlinson's Pollution Load Index (PLI). The null hypotheses was used in the analysis, the hypotheses was rejected if the calculated value of T was greater than the Critical values ($\mathbf{T_{cal} > T_{critical}}$) at 95% confidence level.

3 .17 Data Analysis and Presentation

The resultant data was analyzed statistically using ANOVA, T - test, F - test, arithmetic mean, range, standard deviation, Pearson's correlation coefficient and regression analysis. All tests were done at 95% confidence limits. The data was presented in tables, bar charts, pie charts and line graphs. T significant test at 95% confidence level was used to test hypotheses.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Limnology Data for Sampling Sites

The Limnological parameters of Lake Naivasha were determined and are presented in Table 4.1 and Fig. 4.1. Dissolved oxygen levels ranged within 6.9 to 20 mg/L, temperature 22 to 26 ^{o}C and Secchi disc depth 10 to 110 cm.

Table 4.1. Limnology Parameters of Water in the Sampling Sites (n = 3)

Sites	**Temperature (^{o}C)**	**Dissolved Oxygen (mg/L)**	**Secchi Depth (cm)**
SS1	24 ± 2.5	7.9 ± 1.1	55 ± 1.5
SS2	24 ± 1.5	8.45 ± 1.1	65 ± 2.0
SS3	23 ± 1.0	7.9 ± 1.1	30 ± 1.5
SS4	26 ± 1.2	6.9 ± 1.2	45 ± 2.5
SS5	22 ± 1.3	7.9 ± 1.0	110 ± 2.5
SS6	25 ± 1.2	8.5 ± 1.1	53 ± 1.1
SS7	23 ±1.5	20.0 ± 1.2	10 ± 1.5
SS8	ND	ND	ND
SS9	22.3 ± 1.0	7.9 ± 1.0	45 ± 2.5
SS10	24.2 ± 1.0	ND	35 ± 2.0

(Mean ± standard deviation, n = 9, ND – Not Determined)

The Secchi disc depth which is a measure of water clarity varied widely from 10 - 110 cm in the basin. The highest Secchi depth was observed at site SS5 which is the deepest point in the lake and with no inflows. Site SS3 where most inflowing rivers enter the lake show a Secchi depth of 30 cm indicating inflow of suspended matter. The low SD at site SS7 was due to blue green algae in the Lake Oloidien.

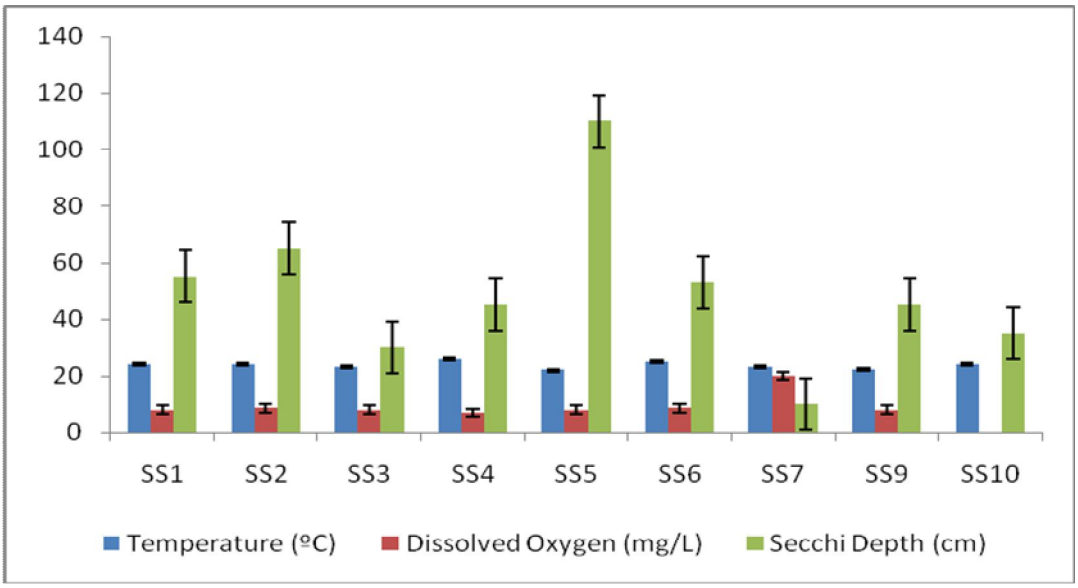


Figure 4.1. Spatial Variations of Temperature, Dissolved oxygen and Secchi depth

The concentrations of dissolved oxygen also varied widely from 6.9 to 20 mg/L. The highest dissolved oxygen levels were found at site SS7 a site with high photosynthetic activity caused by the blue green algae. The lowest dissolved oxygen concentration was observed at site SS1 indicating anoxic condition this could be due to the decaying materials that are deposited along the shoreline as the winds blow. The temperature ranged between 22 - 26 ºC, the highest temperature was observed at site SS4; at the shoreline and the high water

temperatures could be due to heat exchange between the rock surface and water, this could also affect the dissolved oxygen. The dissolved oxygen levels are highest at low temperature regions and the vice versa. The lowest temperature is found at site SS5 at the middle of the Lake. This could be due to vertical mixing of the waters.

4.1.1 Statistical Tests Data

The $T_{calculated}$ values for T significant tests for (temperature, dissolved oxygen and Secchi depth) the sample sites with the Mid Lake (SS2) values at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 4, $\mathbf{t_{critical}}$ = 2.78) are presented in the Table 4.2. The data indicates all sites have no significant difference with respect to temperature. Dissolved oxygen concentrations are not significantly different apart from SS7 which is significantly different from that found at SS2. The sites are significantly different with respect to Secchi depth.

Table 4.2. $T_{calculated}$ for Temperature, Dissolved Oxygen and Secchi Depth

Sampling Sites	**Temperature**	**Dissolved oxygen**	**Secchi depth**
SS1	0.0	0.75	8.48
SS3	1.18	0.75	29.70
SS4	2.21	2.019	16.97
SS5	2.14	0.79	29.82
SS6	1.10	0.068	11.15
SS7	1.00	15.05	46.67
SS8	---	----	-----
SS9	2.00	0.76	13.25
SS10	0.23	----	22.2

The underlined values show sites with significantly different concentrations from those found at SS2

4.2 Pesticides Used in the Lake Naivasha Basin

Common pesticides used in the Lake Naivasha basin are presented in Table 4.3a and 4.3b. The study indicates that all classes of pesticides are used in the basin. The most noticeably used organochlorine pesticide is endosulfan under various trade names (Thiofanex, Phase Plus, Callsulfan, and Thiodane).

Table 4.3a. Common Pesticides used in the Lake Naivasha Basin and Classification

Pesticide	**Type**	**Ingredients**	**Category**	**Class**	**Toxicity**
Folio gold	---	Mefenoxam & Chlorothalonil	DT	Class III	SH
Polytrin	---	Profenofos Q + Cypermethrin	PY + OP	Class II	HH
Score	---	Difenoconazole	---	Class IV	NH
Oshothane	-----	Macozeb	DT	Class IV	NH
Ortiva	Fungicide	Azoxystrobin	----	Class III	SH
Oshothane	Fungicide	Mancozeb	DT	Class III	SH
Ridomil	Fungicide	Metalaxyl-m+mancozeb	DT	Class III	SH
Dictator-plus	Miticide	Propargate + Tetradifon-	----	Class IV	NH
Karate	Pyrethroid	Lamda-cyhalothvin	PY	Class II	HH
Actava	Insecticide	Thiamethoxam	----	Class III	SH
Thiovit	Fungicide	Sulphur	IO	Class III	SH
Thionex	Insecticide	Endosulfan	OC	Class II	HH

Table 4.3b. Common Pesticides used in the Lake Naivasha Basin and their Classification

Danadim	Insecticide	Dimethoate	OP	Class II	HH
Duduzol	Insecticide	Diazinon	OP	Class II	HH
Farsban	----------	Chlorpyrifos	OP	Class II	HH
Farm-X	Insecticide	Deltamethrin	PY	Class II	HH
Cuprocaffaro	Fungicide	Copper	IO	Class III	SH
Copper	Fungicide	Copper	IO	Class III	SH
Marathon	Insecticide	Malathion	OP	Class II	HH
Farmcozeb	-------	Mancozeb	OP	Class IV	NH
Thiofanex	Insecticide	Endosulfan	OC	Class II	HH
Phaser plus	Insecticide	Endosulfan	OC	Class II	HH
Callisulfan	Insecticide	Endosulfan	OC	Class II	HH
Thiodane	Insecticide	Endosulfan	OC	Class II	HH
Sumithion	Insecticide	----	OP	Class II	HH

Key; Extremely hazardous (EH), Highly hazardous (HH), Slightly hazardous (SH), Not hazardous (NH), Organophosphorous (OP), Pyrethroids (PY), Organochlorine (OC), Dithiocarbamate (DT), Inorganic (IO).

Most of the pesticides are highly hazardous to aquatic life as indicated in the labels in the WHO classification. Some of the organochlorine pesticides are banned, restricted use whereas others like endosulfan are being phased out gradually.

4.2.1 Banned Pesticide

Some banned pesticide by Pest Control and Produce board, Kenya. Some banned pesticides were detected and are presented in Table 4.4.

Table 4.4 Some Banned Pesticides in Kenya detected in Lake Naivasha

Common name	**Use**	**Date Banned**
Aldrin	Insecticide	2004
DDT (Dichlorodiphenyl Trichloroethane)	Agriculture	1986
Dieldrin	Insecticide	2004
Endrin	Insecticide	1986
Heptachlor	Insecticide	1986
Hexachlorobenzene (HCB)	Fungicide	2004

(Source; PCPB, 2009)

4.3 Water Abstraction Volumes

The water abstraction data is presented in Table 4.5 and Fig. 4.2. The data reveal that the flower farm abstracts an average of 79,309.3 m^3 of water per month. The farm abstracts in excess of 18,258.57 m^3 per month over and above the allocated volume indicating that the farm does not stick to the allocated volumes. Based on the data, abstraction increases during the dry season, periods when the Lake levels are also very low and thus expose the lake to fluctuations in water volumes leading to seasonal shrinkage of the lake.

Table 4.5. Average Water Use per Month in One Flower Farm in Naivasha (m^3)

Month	**Meter Reading**	**Allocated Amount**	**Amount in excess**	**Total Water Used**
June 2009	4,524,211.00	62,000	12,289.10	72,199.10
July 2009	4,608,851.20	62,000	22,733.20	84,640.20
August 2009	4,695,968.60	62,000	25,210.40	87,117.40
September 2009	4,764,984.40	62,000	9,105.80	69,015.80
October 2009	4,830,924.10	62,000	4,032.70	65,939.70
November 2009	4,900,014.80	62,000	9,180.70	69,090.70
December 2009	5,007,180.40	62,000	45,258.60	107,165.60

Meter reading as at 31st May = 4,452,011.90

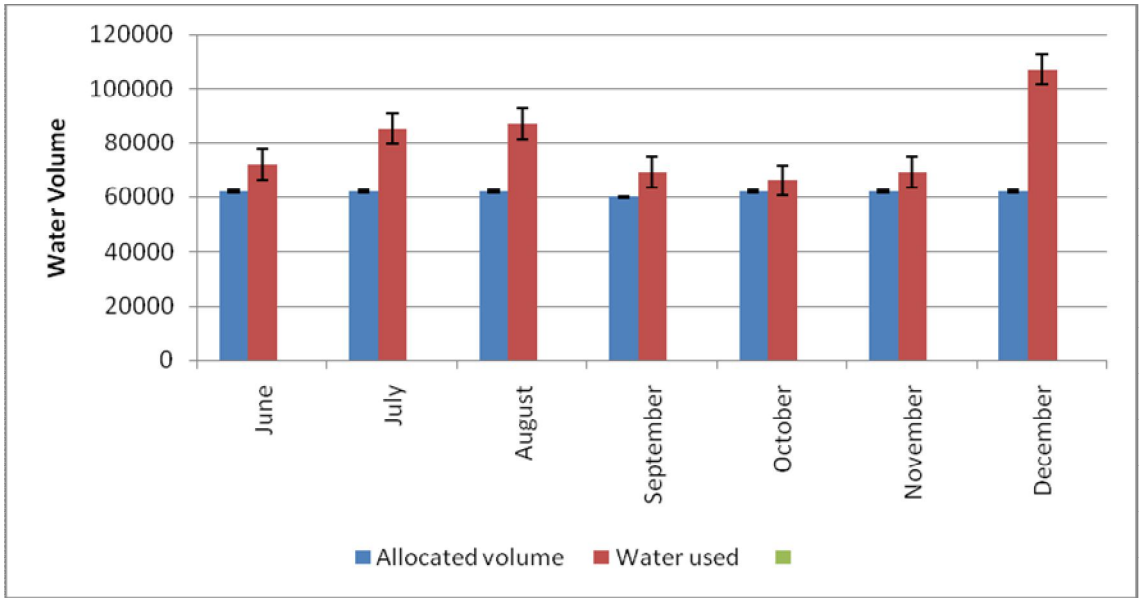


Figure 4.2. Allocated Water Volumes (m^3) and Monthly Consumption

Based on the data flower farms draw approximately 2.4 x 10^6 m^3 per month and 2.88 x 10^7 m^3 each year. These figures exceed safe yields indicating serious assault to the Lake. Harper and Mavuti (2004) reported the water balance for the lake from 1934 – 1983; 95 m^3/month from rain water, 220 m^3/month from river inflow, whereas removal by evaporation accounts for 260 m^3/month and ground water outflow by 55 m^3/month.

The Lake supports the largest Geothermal Power Generation plant in Africa; the Olkaria Geothermal plant, the plant uses water both directly and indirectly during drilling and during power generation. It is estimated that 100,000 m^3 of water are required for the drilling of one well (Nyakundi, 2004). Harper and Mavuti (2004) reported the geothermal power generation plant extracts 1.5 x 10^6 m^3/year. The above figures give a total abstraction volume of 3.03 x 10^7 m^3 /year against a safe yield of 1.65 x 10^7 m^3 /year, leaving a shortfall of 1.38 x 10^7 m^3 /year, meaning the lake cannot regenerate itself. The data reveals an unsustainable exploitation of Lake Naivasha. The current average volume of the lake is 5.6 x 10^8 m^3 is ten times lower than that reported earlier (Campbel *et al*., 2003).

Kenya exports approximately 88,000 metric tons of cut flowers annually, 70% (61,600 tons) of this come from the Lake Naivasha cluster (Food and Waterwatch, 2008). The crop water requirement for a rose plant in Naivasha is 830 mm/year and 1000 mm/year in Thika, roses constitute 70% of Kenya flower export (Food and Waterwatch, 2008). The average virtual or embedded water of Kenyan roses is 90 m^3/ton, the drainage from the Rose farm is 66%, the non-evaporative virtual water content in greenhouses in Kenya is 190 m^3/ton, hydroponics

improve water use efficiency by 65% (Hoekstra and Chapagain, 2007; Hoekstra, *et al*., 2009; Hoekstra and Chapagain, 2008).

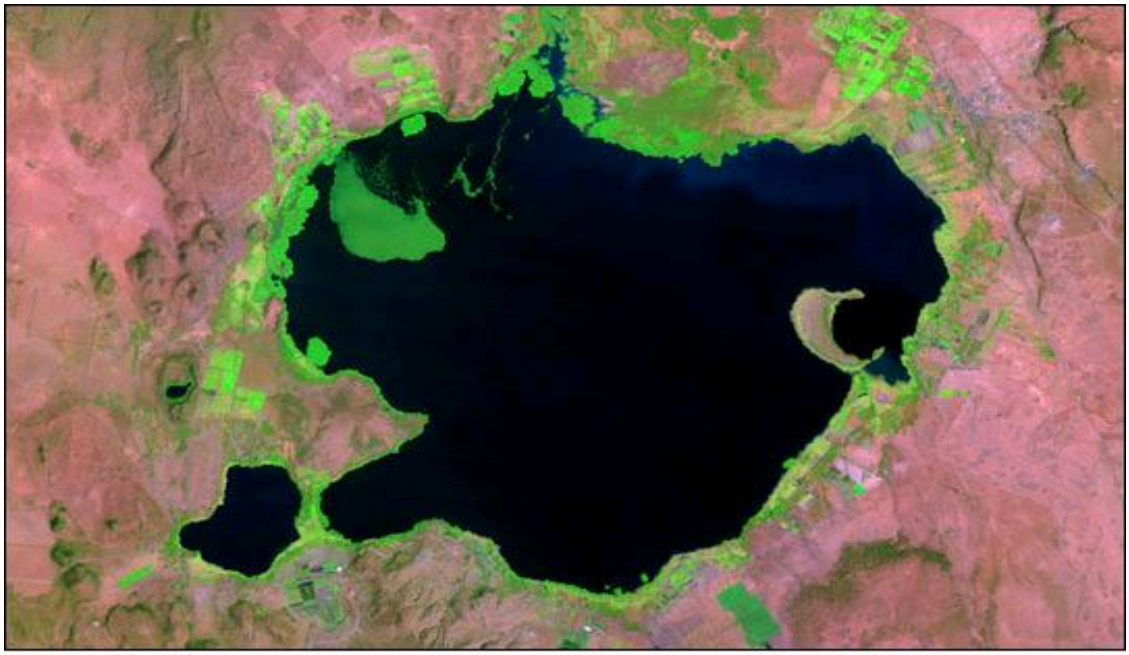
Hoekstra and Chapagain (2008) reported that Kenya exports 88,000 tons of flowers annually. By doing this Kenya is exporting 1.67 x 10^7 m^3 of her water annually as embedded or virtual water to Europe. This spares the countries that receive the Roses and Carnation from mobilization of 1.67 x 10^7 m^3 of their water resources annually thus reducing economic, political and environmental stresses in their countries. The biggest market for Kenyan flowers is in Holland, United Kingdom, Germany and France some of the water rich nations in the world. Kenya is therefore exporting her water to Europe yet she remains a nation with acute water scarcity. Naivasha residents get supplies from boreholes which yield saline waters.

4.4 Changes in Human Activities in the Lake Naivasha Basin from 1983 to 2008

Analysis of satellite images taken in 28th January 1986 and 27th January 2000 shows increased human development in the catchment area (Plate 4.1). Vegetation appears green, bare ground or low vegetation appears in shades of pink (http://earthobservatory.nasa.gov/IOTD/view.php). Urban development appears purple, and water appears deep blue (http://earthobservatory.nasa.gov/IOTD/view.php). The increase in the size of the city of Naivasha to the Northeast of the lake is apparent. New development has sprung up in the South and Southeast edges as well, where bright, reflective greenhouse rooftops glimmer in the sun in the 27th January 2000 image which is visibly absent in the 28th January 1986 image. The decrease in vegetations (greenness) around the lake shores in the

27th January 2000 image may be linked to reduced area covered by papyrus and other aquatic plants which can be attributed to seasonal variations in weather patterns.

Analysis of the 2nd February 2008 image shows a marked increase in greenhouse canopies in the South and Southeast edges of the lake as compared to the 27th January 2000 image (Plate 4.2). This indicates a rapid growth in both open farming and greenhouses in the area which results into an increased use of agrochemicals and irrigation water. The Google image taken in 2nd February 2008 image shows the introduction of greenhouse flower farming in the Northern edge of the lake which are visibly absent in the 28th January 1986 and 27th January 2000 satellite images.



January 28, 1986

January 27, 2000

Plate 4.1. Earth Observatory Satellite Images for Lake Naivasha (1986 and 2000) (Source; http://earthobservatory.nasa.gov/IOTD/view.php?id=4341)

Plate 4.2. Earth Observatory Image for Lake Naivasha February, 2nd 2008 (Source; http://earthobservatory.nasa.gov/IOTD/view.php?id=8599).

Due to the fact that flowers are not held to the same standards for chemical residues as food products, strong pesticides can be used on the flowers to produce the perfect, pest-free bloom, and this could pose a health risk to workers and local wildlife, including hippos (FAO, 2002). Water quality analysis using satellite images reveals a decline in water quality (Lillesand and Keifer, 1979). The deep blue color indicates clear waters or deep water whereas the light blue indicates presence of suspended solids or shallow waters (http://earthobservatory.nasa.gov/IOTD/view.php).

4.4.1 Water Quality

The 28th January 1986 image (Plate 4.1) has the deepest blue color indicating water clarity or deep waters; compared to the 27th January 2000 image which shows a decline in clarity as observed represented by a sharp decline in the blue color especially in the area neighboring

Naivasha town. The 2nd February 2008 image (Plate 4.2) show an increase in turbidity at the Oserian bay an area which has the highest density of flower farms, this is a big shift compared to the observations made on the 28th January 1986 and 27th January 2000 images. The 27th January 2000 image (Plate 4.3) show a rather deep blue color in most parts of the lake which could be due to increased water clarity or water depth however the area neighboring Naivasha town shows a sharp decline in the deep color indicating presence of suspended solids.

4.5 Aquatic Organisms in Lake Naivasha

The population of benthic communities (Oligoceates and Chironomidae**)** in the lake bed was calculated per unit area and is presented in Table 4.6 and Fig. 4.3. The population of the assessed organisms varied widely between sites and ranged between 25 – 775 organisms/m^2.

Table 4.6. Population of Benthic Communities from the Lake (organisms/m^2)

Sites	**Chironomidae**	**Oligoceates**	**Total**
SS1	75 ± 10.2	25 ± 19.2	100
SS2	250 ± 20.2	275 ± 22.2	525
SS5	250 ± 19.2	250 ± 24.2	500
SS7	350 ± 13.2	425 ± 15.2	775

The sampling sites were chosen due to their importance in terms of receiving inflows from the catchment. Site SS1 (Oserian bay) had the lowest population of the benthos compared to other sites. This is a site that has the highest number of discharge canals emptying into the

lake. The low populations indicate an inflow of materials that have the potential of altering the organisms' population. The turbidity at the bay is higher than that found in other sites which can also affect the organisms' population. Site SS7 at Lake Oloidien had the highest population of aquatic organisms. The dissolved oxygen concentration at the site was highest and the site also had high turbidity attributed to high algae population.

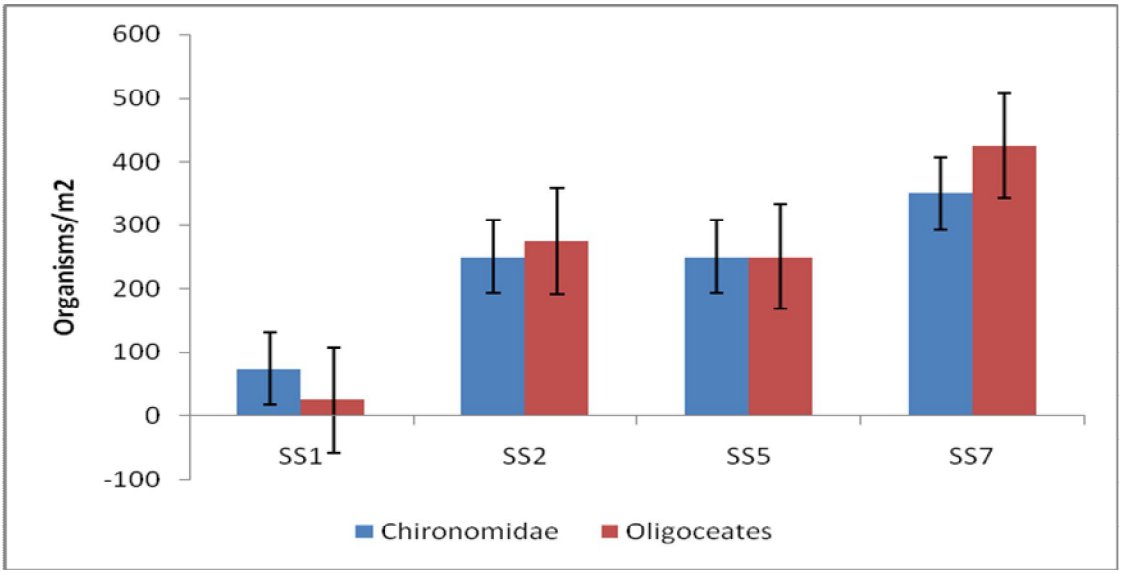


Figure 4.3. Spatial Variations of Aquatic organisms' population

The high population of aquatic organisms in SS7 was thought to be due to high dissolved oxygen concentration essential for life and high algae population which serve as food for the organisms. The site is described as being highly eutrophic (Mavuti and Harper, 2004). Sites SS2 and SS5 show high populations compared to SS1, the sites are found at the deepest points in the lake are have low turbidity and are thought to be less polluted due to dilution by the large water volumes.

4.5.1 Statistical Tests

The $T_{calculated}$ values for T significant tests for the population density of aquatic communities in Lake Naivasha for the sampling sites with the Mid Lake (SS2) values at p $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 4, $\mathbf{t_{critical}}$ = 2.78) are presented in the Table 4.7.

Table 4.7. $T_{calculated}$ Values for the Population Density of Aquatic Communities

Sampling Sites	**Oligocheates**	**Chironomidae**
SS1	18.07	16.41
SS5	1.30	0.0
SS7	11.83	8.79

The underlined values show sites with significantly different organisms' population from those found at SS2

Statistical tests at 95% confidence level the aquatic organisms' populations were significantly different for site SS1 and SS7 for both species with the population found at SS2. However the populations recorded at SS5 are similar to those found at SS2.

4.6 Heavy Metals Concentrations in Water from Different Sites in Lake Naivasha

The concentrations of heavy metals analyzed in the water samples from the 10 sites of study are presented in Table 4.8 and Fig. 4.4.

Table 4.8. Mean Heavy Metals Concentrations in Water of Lake Naivasha Basin (n = 9)

	Copper (µg/L)	**Lead (µg/L)**	**Cadmium (µg/L)**	**Zinc (mg/L)**	**Nickel (mg/L)**
SS1	2.42 ± 0.5	26.21 ± 0.5	12.58 ± 0.7	1.03 ± 0.1	0.08 ± 0.01
SS2	1.06 ± 0.1	9.12 ± 0.7	4.65 ± 1.2	0.97 ± 0.7	0.13 ± 0.07
SS3	1.88 ± 0.1	11.23 ± 0.8	16.77 ± 2.4	0.80 ± 0.1	0.17 ± 0.01
SS4	4.29 ± 0.6	5.33 ± 0.2	11.18 ± 1.2	1.33 ± 0.1	0.13 ± 0.05
SS5	5.23 ± 0.7	23.41 ± 1.2	3.73 ± 0.9	1.34 ± 0.6	0.18 ± 0.05
SS6	4.69 ± 0.6	1.21 ± 0.2	6.52 ± 0.3	1.02 ± 0.1	0.21 ± 0.11
SS7	4.69 ± 0.1	11.23 ± 0.8	38.21 ± 2.3	1.41 ± 0.5	0.45 ± 0.07
SS8	13.56 ± 1.0	36.16 ± 0.6	2.79 ± 0.3	1.90 ± 0.1	0.24 ± 0.11
SS9	4.03 ± 0.1	18.55 ± 0.7	11.77 ± 2.4	1.53 ± 0.7	0.13 ± 0.07
SS10	11.01 ± 0.9	14.56 ± 0.6	14.92 ± 1.1	1.38 ± 0.4	0.13 ± 0.06

Mean ± standard deviation

The results indicate that concentrations of heavy metals follow the order of zinc > nickel > lead > cadmium > copper. The values in Table 4.8 show wide variations between sites (Fig. 4.4), which may be due to the proximity of some sites to point sources.

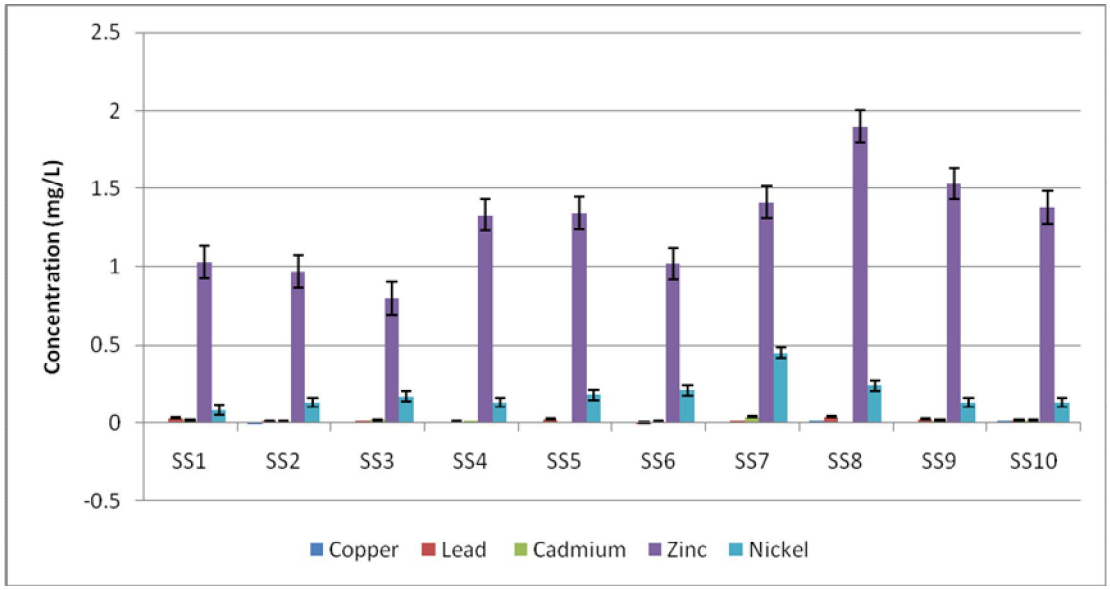


Figure 4.4. Bar Graph for Spatial Variability of Heavy Metals within Sampling Sites

4.6.1 Concentration of Zinc (Zn) in Water of Lake Naivasha

The concentrations of zinc ranged between 0.8 - 1.9 mg/L with a wide variation between sites. The highest concentration was found at site SS8 (1.9 ± 0.1mg/L), a canal draining wastewater into the Lake from flower farms along the Moi South Lake road. Other sites with high concentrations were sites SS7, SS9, SS5, SS4 and SS10 (Fig. 4.5). Site SS10 was along the main Nakuru - Nairobi highway and thus shows the significance of traffic pollution in the basin. The high concentrations observed at SS7 could be due to the bio-concentration of the metal by the blue green algae.

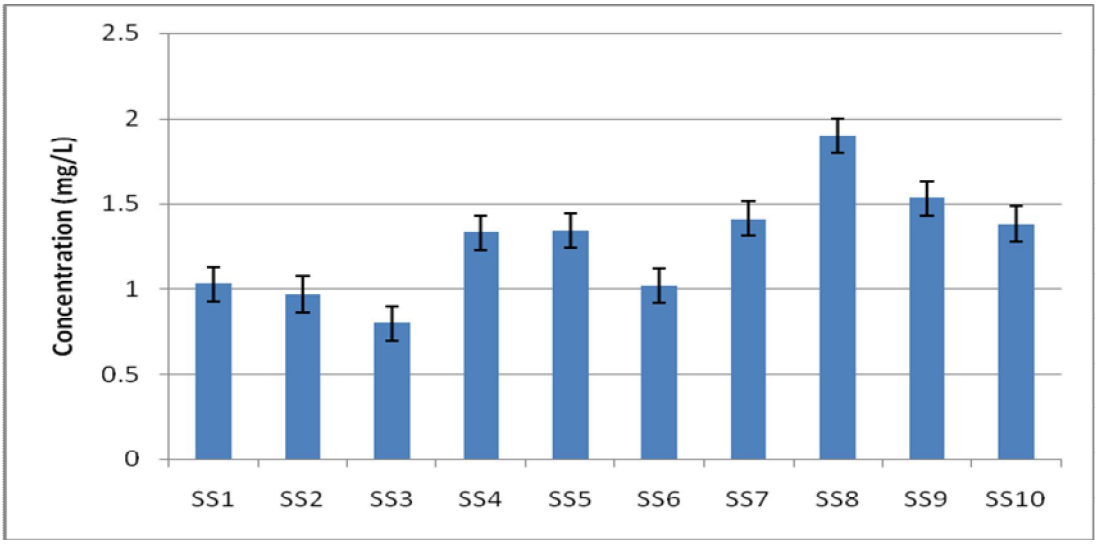


Figure 4.5. Concentrations of Zinc in Water Samples from Lake Naivasha

The zinc concentrations in water are above the toxicity reference value (120 µg/L) for screening contaminants of potential concern for effects on aquatic biota (Suter and Tsao, 1996). This indicates that the measured concentrations pose potential risks to aquatic biota. However they are below the maximum permissible limits for irrigation water of 2 mg/L and below the maximum allowable limits for sources of domestic water of 1.5 mg/L (GOK, 2006). However zinc concentration at site SS8 is higher than maximum allowable limits for effluent discharge into the environment. This calls for removal of the metal before discharge of the wastewater at that point (GOK, 2006). The measured zinc concentrations falls within the ranges of zinc allowed in freshwater ecosystems (Alloways and Arynes, 1993) and also below the maximum allowable levels in drinking water (WHO, 1984; CCME, 1991; Manahan, 1991; Murley, 1992). Results of the present study are lower than those reported

earlier in the Lake Victoria Basin (Kisamo, 2003) and in Lake Naivasha (Kamau *et al*., 2007).

4.6.2 Concentration of Nickel (Ni) in Water Samples from Lake Naivasha

The concentrations of nickel in water ranged between 0.08 - 0.45 mg/L. The highest concentration was found at site SS7 at Lake Oloidien (Fig. 4.6). The high levels of nickel at site SS7 could be due to the bio-concentration of the metal by blue green algae which form a large biomass. Inflows from the flower farms upstream could be another source. Site SS8, a wastewater canal had the next highest concentration of nickel followed by site SS6, sewer entry point, sites SS5 and SS3 where Rivers Malewa, Karati and Gilgil enter the Lake respectively.

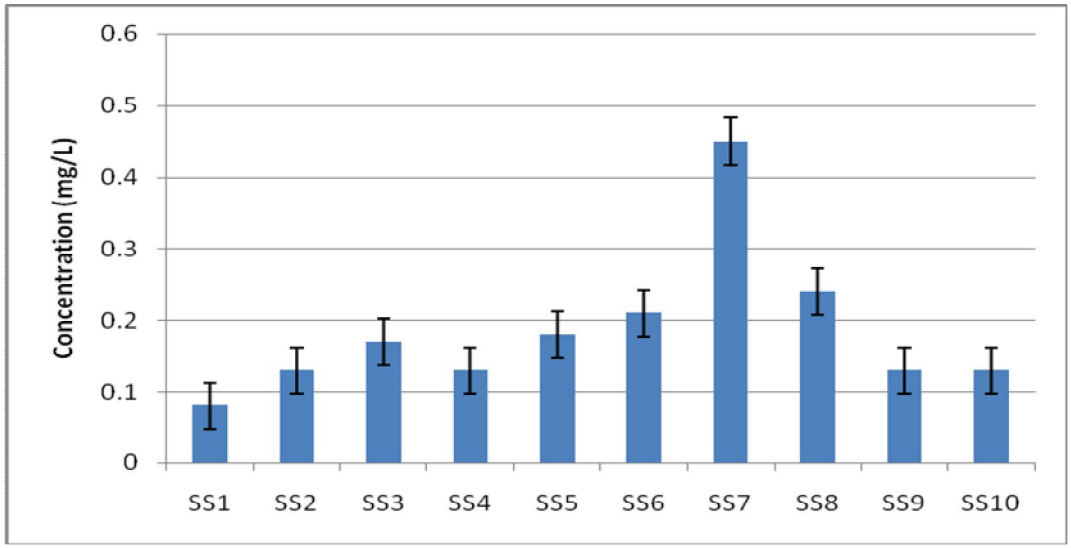


Figure 4.6. Mean Concentrations of Nickel in Water Samples from Lake Naivasha

Site SS1, next to where the wastewater canal discharges into the Lake shows the lowest nickel concentration (0.08 ± 0.01 mg/L). This could be due to uptake of nickel by water

hyacinth which is thriving at the site. The nickel content in the canals is lower than the maximum allowable concentration for nickel in effluent discharge of 0.3 mg/L (GOK, 2006). However, all sites had concentrations of nickel higher than the toxicity reference value (87.71 µg/L) for screening contaminants of potential concerns for effects on aquatic biota reported by Suter and Tsao (1996). The measured concentrations indicate that nickel pose a potential environmental risks to aquatic biota.

The findings of the present study correlate with the relatively high nickel concentrations in the geological formations in the catchment and is thought to come mainly from geochemical processes (Alloways and Arynes, 1993; Tarras *et al*., 2002; Kamau *et al*., 2007; 2008). The results of the present study are significantly higher than those reported earlier (Simiyu and Tole, 2000; Kubo, 2004) indicating increased input of nickel in the catchment. These concentrations fall within the allowable ranges of nickel in freshwater ecosystems (Alloway and Arynes, 1993) and are below the maximum allowable levels in drinking water by various researchers and bodies (WHO, 1984; CCME, 1991; Manahan, 1991; Murley, 1992).

4.6.3 Concentration of Copper (Cu) in Water from Lake Naivasha

The concentration of copper found in this study ranged between 1.06 - 13.56 µg/L. The highest copper concentration was found at site SS8 (13.56 ± 1.0 µg/L) indicating inflows of copper from the flower farm (Fig. 4.7). The second largest concentration is found at the site SS10 (11.01 ± 0.9 µg/L) along the Nairobi – Nakuru highway. This could be as a result of traffic pollution or wastewater discharge from the Delamere Estates upstream. Site SS1 despite having several canals, show low copper content in the water, this could be due to the

uptake of the labile copper fraction by the thriving water hyacinth and other aquatic plants growing in this region, dilution by the large volumes could also be in play.

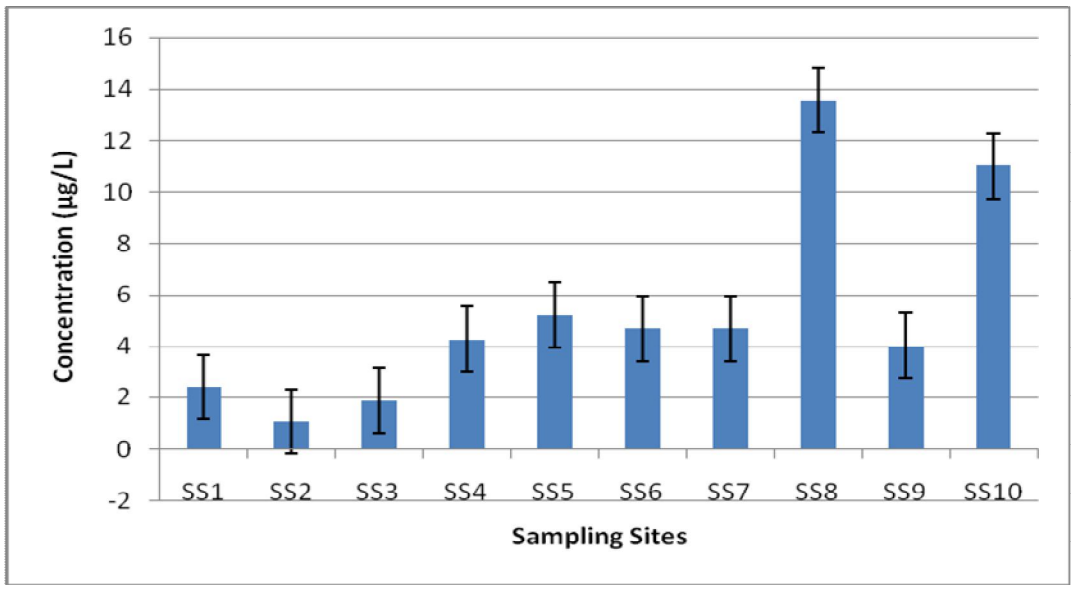


Figure 4.7. Mean Concentrations of Copper in Water Samples from Lake Naivasha

Site SS3, a site where the rivers enter the Lake show low copper content compared to the amounts recorded at site SS10. This could be as a result of dilution by the water from River Gilgil or removal of copper through natural processes as the river flows downstream. The concentrations of copper in the lake are higher than the toxicity reference values for screening contaminants of potential concern (6.54 µg/L) to aquatic biota reported by Suter and Tsao (1996). This indicates that the concentrations pose potential adverse effects to aquatic biota. The concentration of copper in the present study compare with those reported by (Simiyu and Tole, 2000; Kubo, 2004). The levels of copper in the lake are within the limits for freshwater ecosystems (Alloways and Arynes, 1993) and lower than maximum

acceptable limits in drinking water (WHO, 1984; CCME, 1991; Manahan, 1991; Murley, 1992).

4.6.4 Concentration of Cadmium (Cd) in Water from Lake Naivasha

The concentration of cadmium fell between 2.79 - 38.32 µg/L (Fig. 4.8). The highest concentration of cadmium is found at site SS7 (38.21 ± 2.3 µg/L), Lake Oloidien possibly due to bio-accumulation by blue green algae. Sites SS10 (14.92 ± 0.6 µg/L) and SS9 (11.77 ± 2.4 µg/L) along River Malewa had high cadmium levels indicating inflow from upper catchment (Fig. 4.7). Site SS3 (16.77 ± 2.4 µg/L) a site where the rivers enter the Lake also indicated high cadmium emphasizing the fact that River Malewa is an important source, unlike copper cadmium doesn't appear to be removed as rivers flow downstream.

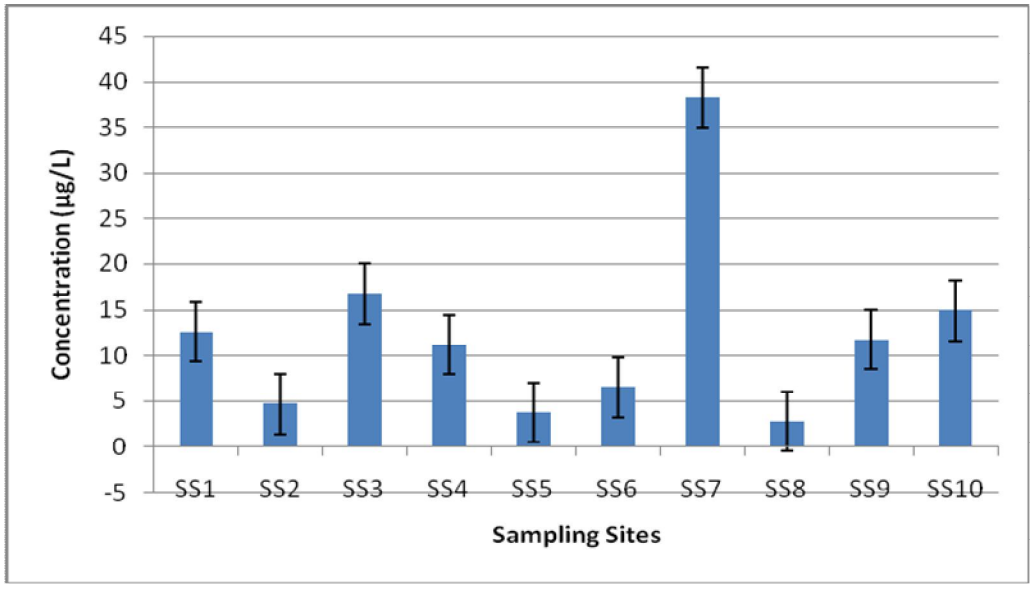


Figure 4.8. Concentrations of Cadmium in Water from Lake Naivasha

The measured concentrations are all above the toxicity reference value (0.66 µg/L) for screening contaminants of potential concern to aquatic biota as reported by Suter and Tsao (1996). This indicates that the measured concentrations pose environmental risks to aquatic biota. However the concentrations of cadmium in water agree with levels reported earlier by Simiyu and Tole (2000) and Kubo (2004). The concentrations fall within the range of freshwater ecosystems (Alloways and Arynes, 1993) and are below the maximum WHO acceptable levels in drinking water (WHO, 1984; CCME, 1991; Manahan, 1991; Murley, 1992). Results of the present study agree with those reported at the Lake Victoria basin by Kisamo (2003).

4.6.5 Concentration of Lead (Pb) in Water from Lake Naivasha

Concentrations of lead ranged between 0.01 - 0.36 µg/L (Fig. 4.9). This shows wide variation between samples from different sampling sites. The highest lead concentration was found at site SS8 (36.16 ± 0.6 µg/L) followed by sites SS1 (26.21 ± 0.5 µg/L), SS5 (23.41 ± 1.2 µg/L), SS9 (18.55 ± 0.7 µg/L) and SS10 (14.56 ± 0.6 µg/L) respectively. These show similar trends as recorded for other metals above and further emphasize the importance of flower farms and River Malewa as sources of heavy metals in the Lake. Site SS5 at crescent Lake next to a discharge canal also shows high levels of lead.

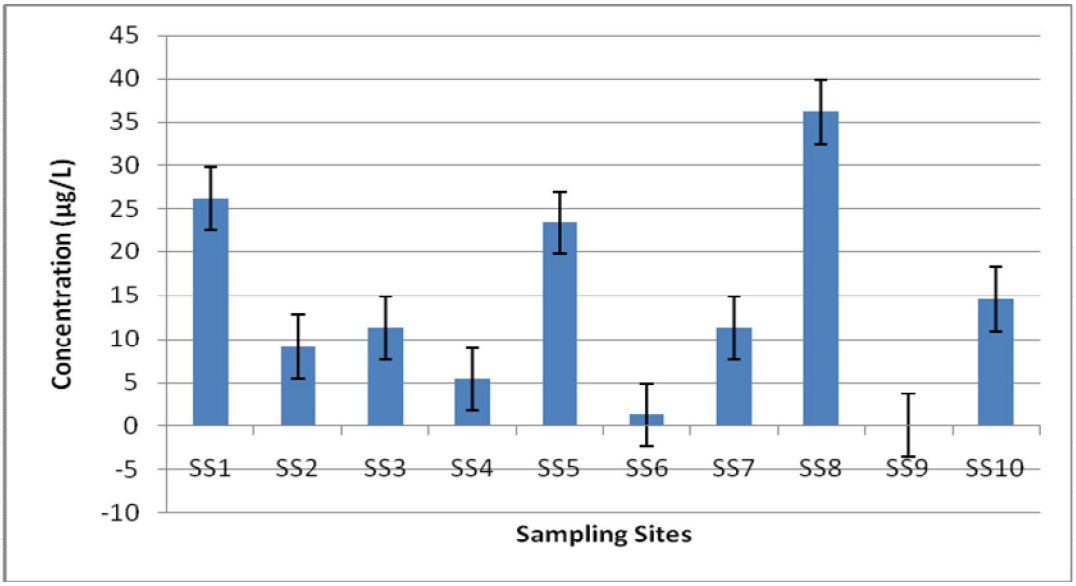


Figure 4.9. Concentrations of Lead in Water from Lake Naivasha

Concentrations of lead in water are higher than the toxicity reference values (1.32 µg/L) for screening contaminants of potential concern to aquatic biota (ERD, 1999). This indicates potential adverse effects to the aquatic biota. However the measured concentrations agree with those reported by Simiyu and Tole (2000) and Kubo (2004) and is lower than those reported by Kamau *et al*. (2007, 2008) and Kisamo (2003). The concentrations fall within the range of freshwater ecosystems (Alloways and Arynes, 1993) and are below the maximum acceptable levels in drinking water (WHO, 1984; CCNE, 1991; Manahan, 1991; Murley, 1992).

4.6.6 Comparison of Heavy Metal Concentrations in Water and Limnology Data

The Pearson's correlation coefficient for checking correlations between two variables was used to check correlation between pairs of metals and water quality parameters. Pearson's

correlation coefficient (p = 0.05) at 95% confidence interval revealed significant correlation between Secchi depth and concentrations of heavy metals in water. The correlation coefficients ($\mathbf{r^2}$) values were Pb (-0.26), Cu (-0.27), Zn (-0.41), Ni (-0.50), and Cd (-0.70) respectively. Negative correlations between heavy metal concentrations and Secchi depth show an inverse relationship which suggests that most of the metals are adsorbed on suspended particulate matter.

Statistical analysis of inter-metallic relationship using Pearson's correlation coefficient (p < 0.05) at 95% confidence interval revealed a degree of correlation and significant regression relation among the metals. This indicates identical behavior of metals in the water column and could indicate origin from similar sources. The correlation coefficients ($\mathbf{r^2}$) with p < 0.05 were; Cu - Pb (0.51), Cu - Zn (0.78), Cu - Ni (0.18), Pb - Zn (0.58) and Cd - Ni (0.67). There was however inverse relationships between Pb - Cd (-0.25), Cu - Cd (-0.15), Ni - Pb (-0.06), Cd - Zn (-0.04) and Ni - Zn (-0.29), which could be due to origin from different sources or antagonism. The Pearson's product mean for water and sediments indicate an interesting pattern at p < 0.05, the correlation coefficients ($\mathbf{r^2}$) were positive for Cu (0.12), Zn (0.11), and negative for Pb (-0.31), Cd (-0.03) and Ni (-0.33). The positive correlation could signal exchange between sediments and the water column maintaining a state of equilibrium whereas the inverse relationship indicates removal of metals from either sediments to the water column and vice versa.

4.6.1 Statistical Tests

The $T_{calculated}$ values for T significant tests for heavy metal concentrations in water samples from various sampling sites with the Mid Lake (SS2) values at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 16, $\mathbf{t_{critical}}$ = 2.12) are presented in the Table 4.9. Statistical analysis of data using T test at 95% confidence level shows that most sites have concentrations that are significantly different from those found at SS2. The concentrations of zinc and nickel were found to be similar in most sites studies. However there were significant differences between the heavy metals concentrations found in various sites for copper, lead and cadmium.

Table 4.9. $T_{calculated}$ Values for T Significant Tests for Heavy Metal Concentrations in Water Samples

Sampling Sites	**Copper**	**Lead**	**Cadmium**	**Zinc**	**Nickel**
SS1	8.41	12.79	18.16	0.27	2.25
SS3	18.15	6.24	14.37	0.77	1.8
SS4	16.89	16.56	12.24	1.62	0.0
SS5	18.76	32.36	1.95	0.17	1.85
SS6	18.42	34.57	4.81	1.28	1.95
SS7	81.67	6.31	41.21	0.28	10.29
SS8	39.15	93.11	4.78	1.67	2.68
SS9	66.32	8.52	8.44	4.18	0.0
SS10	34.21	18.77	20.07	1.62	0.0

The underlined values show sites with significantly different concentrations from those found at SS2.

4.7 Heavy Metals Concentrations in Sediments from Lake Naivasha

The heavy metal contents in sediments are presented in Table 4.10 and Fig. 4.10.

Table 4.10. Mean Heavy Metals Concentrations (n = 9) in Sediments (µg/g)

	Copper	**Lead**	**Zinc**	**Cadmium**	**Nickel**
SS1	1.49 ± 0.3	28.03 ± 2.1	48.01 ± 2.1	1.68 ± 0.5	55.71 ± 1.5
SS2	1.84 ± 0.3	26.14 ± 1.5	34.86 ± 3.2	1.63 ± 0.5	46.71 ± 2.1
SS3	2.46 ± 0.1	43.94 ± 0.7	63.62 ± 3.6	0.74 ± 0.1	100.31 ± 3.7
SS4	3.22 ± 0.3	43.18 ± 2.0	70.22 ± 3.2	2.53 ± 0.5	118.42 ± 5.2
SS5	1.13 ± 0.1	31.82 ± 1.5	37.97 ± 2.5	2.47 ± 0.6	38.81 ± 2.8
SS6	2.21 ± 0.1	57.38 ± 3.5	62.38 ± 2.5	3.26 ± 0.6	57.89 ± 2.2
SS7	2.21 ± 0.1	22.73 ± 1.0	62.38 ± 2.5	2.55 ± 0.7	46.71 ± 2.1
SS8	2.66 ± 0.5	26.13 ± 1.1	65.28 ± 1.5	3.66 ± 0.5	73.68 ± 2.3
SS9	1.84 ± 0.5	60.23 ± 2.2	62.38 ± 2.5	3.35 ± 0.4	101.31 ± 3.8
SS10	2.31 ± 0.3	18.18 ± 1.2	45.56 ± 3.2	2.87 ± 0.7	68.42 ± 3.2

Mean ± Standard Deviation.

Nickel is the most predominant metal followed by zinc, lead, copper and cadmium respectively. From Table 4.10 and Fig. 4.10 it can be seen that there are wide variability in the concentrations of the metals between sites in the lake Naivasha basin. Peak concentrations of Pb, Zn and Ni were found at sites SS9, SS6, SS4, SS3 and SSI respectively.

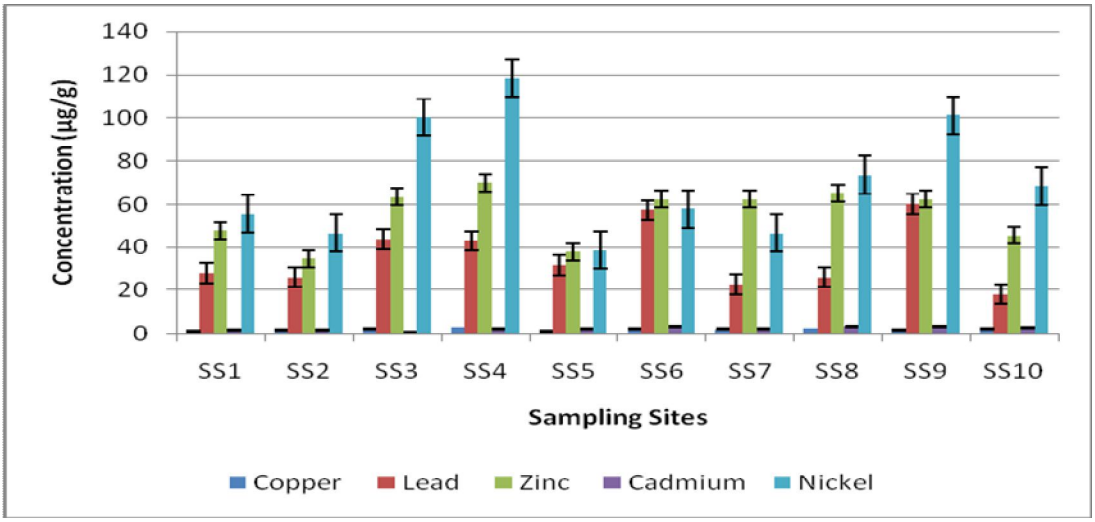


Figure 4.10 Mean Heavy Metals Concentrations (n = 9) in Sediments (µg/g)

It shows that these sites are thought to be important entry points for the contaminants. Therefore sediments from River Malewa, Naivasha Municipal Council and the Flower farms are important sources of Pb, Zn and Ni.

4.7.1 Concentration of Nickel in Sediments from Lake Naivasha

As can be seen from Table 4.10 the concentrations of nickel ranged between 38.81 - 118.42 µg/g with the highest levels found at site SS4 (118.42 ± 5.2 µg/g) which is at Crescent shoreline next to a discharge canal (Fig. 4.11). Other sites with relatively higher levels of nickel in sediments are SS9 (along River Malewa) SS3, (River entry point) and SS10 (along River Malewa). This emphasize the point that river Malewa is an important source of sediment inputs in the Lake.

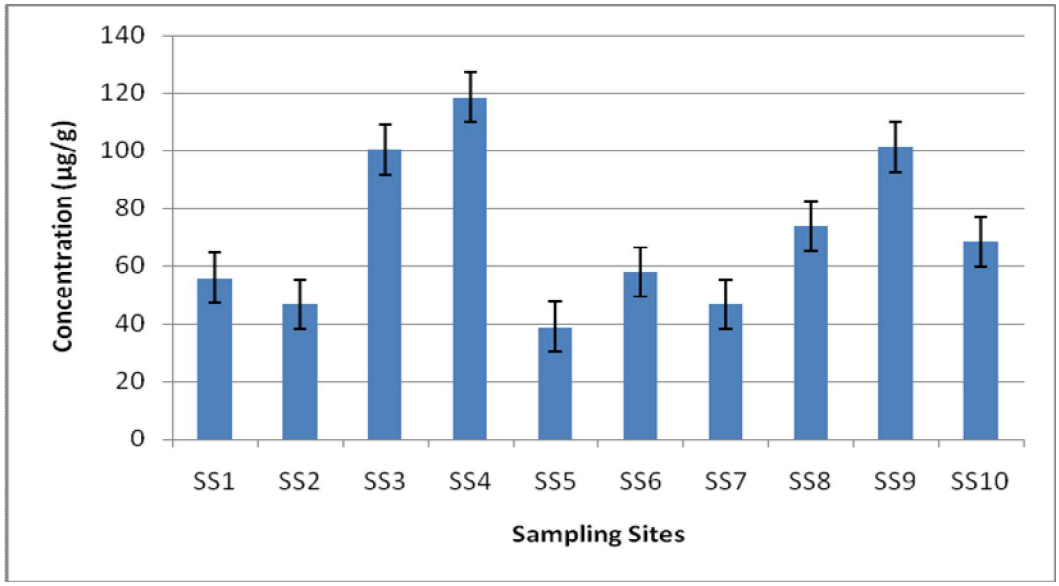


Figure 4.11. Bar Graph for the Mean Concentrations of Nickel (Ni) in Water from Lake Naivasha

All sites in the lake bed have nickel concentrations higher than the toxicity reference value (20.9 µg/g) for screening contaminants of potential concerns to aquatic biota in sediments reported by Jones and Turki (1997). This indicates that the concentration of nickel at the sites pose potential adverse effects to aquatic biota.

4.7.2 Concentration of Copper (Cu) in Sediments from Lake Naivasha

The concentrations of copper in sediments in Lake Naivasha are presented in Table 4.10 and Fig. 4.12. From Table 4.10 the highest concentration of copper was found at site SS4.

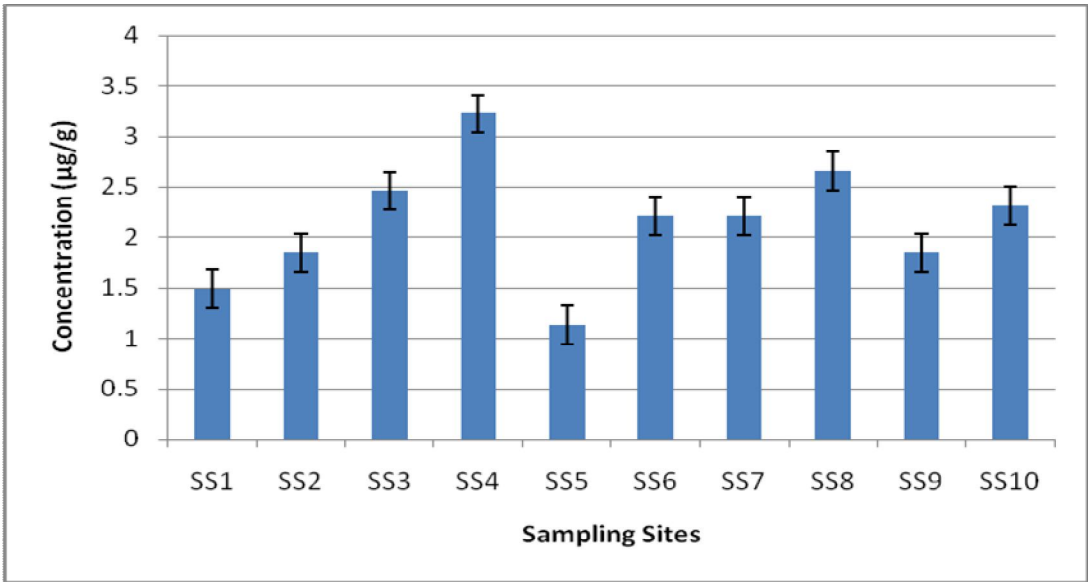


Figure 4.12. Bar Graph for the Mean Concentrations of Copper in Sediments

Sites SS4, SS8, SS3, and SS6 also had relatively high concentrations of copper in sediments. Flower farms, inflowing rivers and the Naivasha Municipal council were found to be important sources of copper in the basin. The measured exposure concentrations in the lake's surface are lower than the toxicity reference values (TRV) (34 µg/g) for screening contaminants of potential concern for effects on aquatic biota reported by Jones and Turki (1997) however the important sources in the basin should be monitored continuously. Thus indicating that copper concentrations in the lake's bed does not pose any environmental risks on aquatic biota.

4.7.3 Concentration of Cadmium (Cd) in Sediments from Lake Naivasha

The concentrations of Cd in various sites are presented in Table 4.10 and Fig. 4.13. Cadmium was detected in all samples from the lake, with concentration levels ranging between 0.74 -

3.66 µg/g. The highest concentration was found at site SS8 (3.66 ± 0.5), a discharge canal from flower farms along the Moi South Lake road followed by sites SS9, SS6, SS10 SS5 and SS4. This further stresses the argument that River Malewa, Naivasha Municipal Council and flower farms are important sources of metals in the sediments.

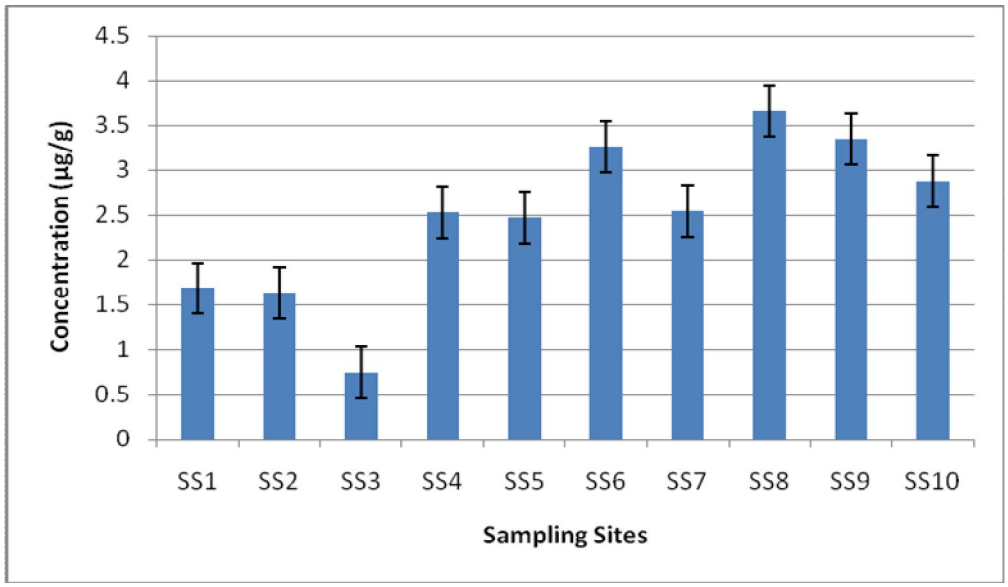


Figure 4.13. Bar Graph for the Mean Concentrations of Cadmium in Sediments

The measured exposure concentrations of cadmium are higher than the toxicity reference values (1.2 µg/g) for screening contaminants of potential concern on aquatic biota in most sites than those reported by Jones and Turki (1997). However site SS3 has cadmium concentrations lower than the TRV value indicating no potential environmental risks to aquatic biota.

4.7.4 Concentration of Zinc (Zn) in Sediments from Lake Naivasha

Zinc was detected in all sites within the lake basin sediments; the data is presented in Table 4.10 and Fig. 4.14). The levels ranged from 34.86 - 65.28 µg/g. There were no wide variations between sites as observed for other metals in the Lake's bed. The highest concentration was found at site SS4 (70.22 ± 3.2 µg/g), a strong indicator of most recent inflows from the flower farms. Other sites with high levels were sites SS8, SS3, SS7, SS6 and SS9. This also indicates that the important sources of heavy metals in the basin are River Malewa, Flower farms and the Naivasha Municipal Council.

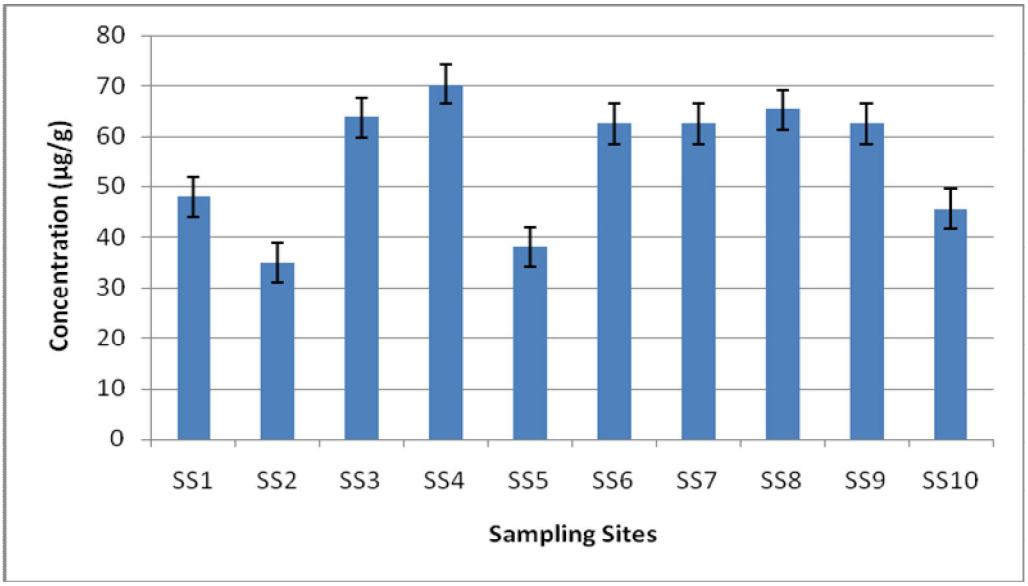


Figure 4.14. Bar Graph for the Mean Concentrations of Zinc in Sediments

The measured concentrations of zinc in the lake surface are lower than the toxicity reference values (TRV) (150 µg/g) for screening contaminants of concern on aquatic biota reported by Jones and Turki (1997). Thus indicating that zinc concentrations in the lake's bed does not pose any environmental risks on aquatic biota.

4.7.5 Concentration of Lead (Pb) in Sediments from Lake Naivasha

Lead was detected in sediments from all sites and ranged between 18.18 - 60.23 µg/g with the highest concentrations being found at site SS9 (60.23 ± 2.2 µg/g) along a River Malewa tributary in an area with intensive small scale farming along the river banks. The data is presented in Table 4.10 and Fig.4.15. This is followed by site SS6 (sewerage entry point from the Naivasha Municipal Council) suggesting inflows from the town. However, the lead concentrations were low at site SS10 (18.18 ± 1.2 µg/g) unlike in other cases. The high concentrations at site SS3 indicate inflowing rivers are important sources of sediments.

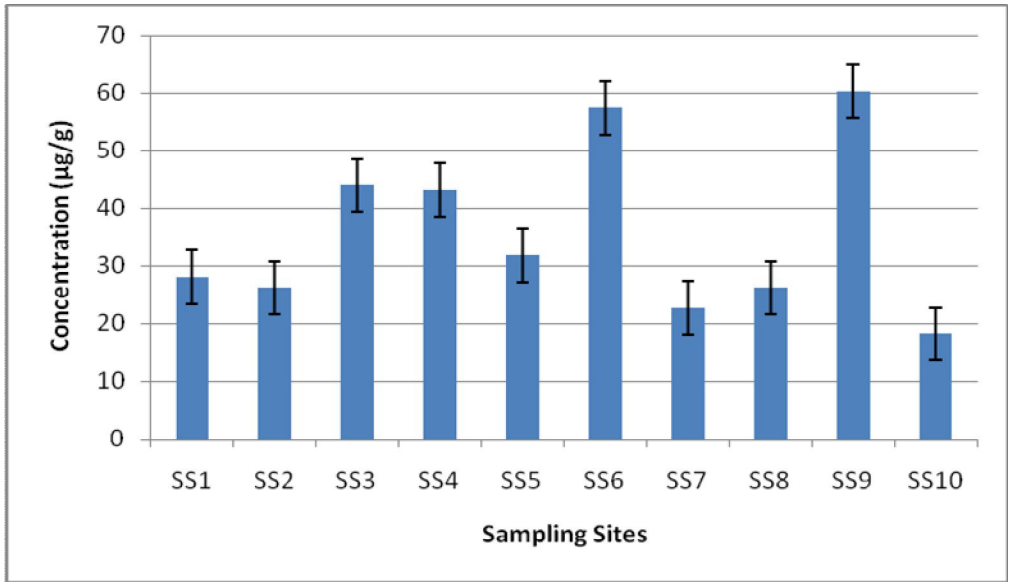


Figure 4.15. Bar Graph for the Mean Concentrations of Lead in Sediments

The measured exposure concentrations of lead are lower than the toxicity reference value (46.7 µg/g) for screening contaminants of potential concerns in sediments on aquatic biota reported by Jones and Turki (1997). However sites SS9 and SS6 have higher concentration

values than TRV indicating that the concentrations at the sites pose potential adverse effects to aquatic biota.

4.7.6 Statistical Tests

The $T_{calculated}$ values for T significant tests for heavy metal concentrations in various Lake bed sediments from various sampling sites with the Mid Lake (SS2) values at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 16, $\mathbf{t_{critical}}$ = 2.12) are presented in the Table 4.11. Significant differences at 95% confidence levels between the heavy metal concentrations in sediments from various sites and those found at SS2 were recorded. The highest differences were record for Zn, Ni and Pb in most sites

Table 4.11. $T_{calculated}$ Values for Heavy Metal Concentrations in Various Lake Bed Sediments

Sample Sites	**Copper**	**Lead**	**Cadmium**	**Zinc**	**Nickel**
SS1	2.63	2.33	0.23	**10.93**	**11.09**
SS3	0.0	34.22	5.55	18.99	39.86
SS4	6.24	21.68	4.05	24.86	40.68
SS5	10.35	8.52	3.42	2.44	7.18
SS6	7.14	26.11	6.64	21.56	11.69
SS7	3.72	7.22	3.42	21.56	0.0
SS8	8.25	0.10	10.09	23.84	27.55
SS9	0.0	40.74	8.55	21.56	39.86
SS10	3.53	13.18	4.59	7.52	18.05

Underlined values indicates sites whose concentrations are significantly different from those found at SS2

4.7.7 The Pearson's Coefficients

Statistical analysis of inter-metallic relationship using Pearson's correlation coefficient at p = 0.05 at 95% confidence interval reveal positive correlation and significant regression relation among the metals. The correlation coefficients ($\mathbf{r^2}$) with $p < 0.05$ were: Pb - Cu (0.1), Pb - Zn (0.49), Cu - Zn (0.73), Cu - Cd (0.16), Cu - Ni (0.68), Pb - Cd (0.16), Pb - Ni (0.52), Zn - Cd (0.29), Zn - Ni (0.69) and Cd - Ni (0.69) in sediments. The highest positive correlation was found between Cu - Zn (0.73) and the lowest was between Pb - Cu (0.1). The positive correlations between heavy metal concentrations suggested either a common source or a similar geochemical origin. The low positive correlations between lead and copper could mean that they are coming from different sources or have different chemical behavior in the lake bed.

4.7.8 Contamination Factor

Contamination factors and degree of contamination values are important in the assessment of pollution of sites. The contamination factors are calculated using Equation 4.1.

$$\boldsymbol{CF}_{\mathbf{metal}} = \boldsymbol{C}_{\mathbf{metal}} / \boldsymbol{C}_{\mathbf{background}} \quad \text{---------- 4.1}$$

Where CF is Contamination Factor of the metal, C_{metal} is concentration of the metal in the sample and $C_{\text{background}}$ is concentration of metal in the background. The average shale values (Pb: 20, Cu: 45, Zn: 95, Ni: 68, Cd: 0.3 mg/kg) (Turekian and Wedepohl, 1961) are commonly used as background values in sediment studies (Lopez-Sanchez *et al*., 1996; Jones and Turki, 1997; Datta and Subramanian, 1998; Morillo *et al*., 2002; Kucuksezgin *et al*., 2004).

The degree of contamination (C_d) was defined as the sum of all contamination factors. The following terminology is suggested for describing the contamination factor (CF values), (Hakanson, 1980). CF < 1: low contamination factor; 1 ≤ CF < 3: moderate contamination factor; 3 ≤ CF < 6: considerable contamination factor; CF ≥ 6: very high contamination factor. The CF values for copper and zinc are < 1, lead between 1 and 3, whereas 50% of the CF values for nickel are < 1 and the rest between 1 and 3. This shows that the sites are not contaminated with copper and zinc but are moderately contaminated with lead and nickel. The CF values for cadmium are all > 6 indicating that most sites are contaminated with cadmium indicating serious anthropogenic pollution. This agrees with results reported earlier by Moturi *et al*. (2005) and Tarras *et al*. (2002).

4.7.9 Degree of Contamination

The following terminology is adopted to describe the degree of contamination (C_d values). C_d < 6: low degree of contamination; 6 ≤ C_d < 12: moderate of contamination; 12 ≤ C_d < 24: considerable degree of contamination; C_d ≥ 24: very high degree of contamination indicating serious anthropogenic pollution. Considering the degree of contamination, the C_d values lie within 9.31 - 27.53. Most sites have C_d values range within 12 - 24 indicating contamination. However sites SS9, SS6 all along Malewa River had C_d values > 24 indicating high degree of contamination an indication of serious anthropogenic pollution.

4.7.10 Tomlinson's Pollution Load Index (PLI)

Tomlinson's Pollution Load Index (PLI) (Tomilson *et al*., 1980) of the sediment is obtained as a concentration factor (CF) of each metal with respect to the background value in the sediment (Kucuksezgin *et al*., 2004), by applying the following Equation 4.1;

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times \ldots \times CF_n)} \text{ ---------- } 4.1$$

Where n is number of sites and CF_n are the contamination factors in each sites. PLI represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The concentration factor and pollution load index are given in Table 4.12.

The PLI values of lake sediments at the various sampling points are presented in Table 4.7. The PLI values for all sediments are high and ranged between 0.89 and 1.01. PLI values greater than one were registered at sites SS4 and SS9 other relatively high values were observed at sites; SS6, SS3, SS10 and SS7. The trend of PLI values in the sediments indicates that the effluent discharge from the Municipal Council and inflowing rivers are the main source of contamination in the Lake.

Table 4.12. Contamination Factors and Degree of Contamination of Sites

	Copper	**Lead**	**Zinc**	**Cadmium**	**Nickel**	**Degree of Contamination**	**Pollution Load Index**
SS1	0.03	1.40	0.50	5.63	0.82	13.95	0.89
SS2	0.04	1.30	0.37	5.43	0.69	13.25	0.88
SS3	0.05	2.19	0.67	2.46	1.48	9.31	0.94
SS4	0.07	2.15	0.74	8.43	1.74	21.56	1.02
SS5	0.03	1.59	0.40	8.23	0.57	19.04	0.88
SS6	0.05	2.86	0.66	10.86	0.85	26.14	0.99
SS7	0.05	1.13	0.66	8.51	0.69	19.52	0.93
SS8	0.06	1.30	0.69	12.22	1.08	27.53	0.98
SS9	0.04	3.01	0.66	11.16	1.49	27.52	1.01
SS10	0.05	0.90	0.48	9.56	1.01	21.56	0.93

The underlined values represent sites with high degree of contamination an indication of serious anthropogenic pollution.

4.8 Heavy Metal Concentrations in Fish

The concentrations (µg/g) of copper, lead, zinc, cadmium and nickel were determined in edible portions of fish (fillet) in three fish species from Lake Naivasha namely; Tilapia, *O. leucostictus*, Mirror carp, *C. Spectacularlus* and Common carp, *C. carpio*. The heavy metal concentrations (µg/g,) are presented in Table 4.13 and Fig. 4.16. Statistical analysis using Pearson's correlation coefficient at 95% confidence interval reveal high degree of correlation

and significant regression relation between weight and length (r = 0.99), this indicates that the two can be related to age of fish. Significant positive correlation exists between weight and Cu, Pb, Zn and Ni. However, there is negative correlation for Cd, at 0.51, 0.78, 0.98, 0.25 and -0.36 for Cu, Pb, Zn, Ni, and Cd respectively. Though Ni has the lowest correlation coefficient it is the most predominant metal in fish followed by zinc, lead, copper and cadmium respectively.

Table 4.13. Mean Heavy Metal Concentrations (µg/g) in Fish of Lake Naivasha (n = 11)

	O. leucostictus	***C. carpio***	***C. spectacularlus***
Copper	0.27 ± 0.1	0.28 ± 0.1	0.36 ± 0.1
Lead	1.49 ± 0.1	1.56 ± 0.2	1.51 ± 0.1
Zinc	7.31 ± 0.9	8.87 ± 1.1	9.32 ± 1.5
Cadmium	0.36 ± 0.8	0.13 ± 0.1	0.44 ± 0.1
Nickel	13.62 ± 1.5	13.39 ± 1.1	14.63 ± 1.5

Mean ± standard deviation.

As can be seen from Table 4.8 the highest concentration of nickel (14.63 ± 1.5 µg/g) was found in Mirror carp *(Cyprinus Spectacularlus)* and the lowest (13.39 ± 1.1 µg/g) in Common carp (C*uprinus carpio)*. Results indicate that *C. Spectacularlus* has the highest accumulation potential for metals followed by *C. carpio* and Tilapia (*Oreochromis leucostictus)* respectively. This can be attributed to the position of the fish species in the food chain. *C. Spectacularlus* and *C. carpio* are omnivorous, they can eat a vegetarian diet of

water plants, but prefers to scavenge the bottom for insects, crustaceans (including zooplankton), and benthic worms whereas *O. leucostictus* eat algae and plants.

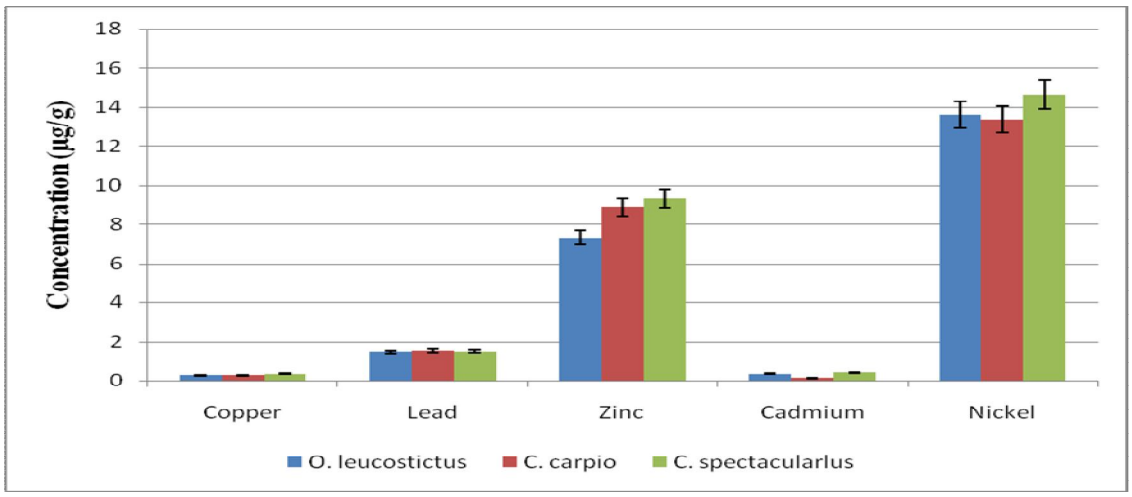


Figure 4.16. Bar Graph for the Mean Heavy Metal Concentrations in Fish

4.10.2.3 Human Risk Assessment of Consumption of Fish from Lake Naivasha

Dietary risk assessments were conducted for the consumption of *O. leucostictus, C. carpio* and *C. spectaculurus* from Lake Naivasha with respect to concentrations of copper, lead, zinc, cadmium and nickel in edible portions of fish (fillet). The average daily intakes were found to be lower than the Acceptable Daily Intake (ADI) for Pb, Cd, Cu, Zn and Ni respectively. The study shows that the consumption of 1 Kg of fish fillet per day for a healthy 60 Kg adult does not pose any risks with respect to Pb, Cd, Ni, Cu and Zn (Table 4.14).

Table 4.14. Dietary Risk Assessment for the Consumption of Fish (mg/Kg bodyweight) from Lake Naivasha

Metals	***O. leucostictus***	***C. carpio***	***C. spectacularlus***		**Source**
Copper	4.5×10^{-3}	4.67×10^{-3}	6.0×10^{-3}		Macrae *et al.*, 1993
Lead	2.48×10^{-2}	2.6×10^{-2}	2.52×10^{-2}		
Zinc	1.22×10^{-1}	1.48×10^{-1}	1.55×10^{-1}		
Cadmium	6.0×10^{-2}	2.17×10^{-2}	7.33×10^{-2}		
Nickel	2.27×10^{-1}	2.23×10^{-1}	2.44×10^{-1}		

Key; ADI - Acceptable daily intake

4.8.1 Statistical Tests

The $T_{calculated}$ values for T significant tests for heavy metal concentrations in various fish specimens from Lake Naivasha at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 4, $\mathbf{t_{critical}}$ = 20) are presented in the Table 4.15. Statistical analysis of the data indicates that there is no significant difference between the Pb, Zn and Cu concentrations in *C. spectacularlus and C. carpio*. There are no significant differences between the Pb, Cd, Cu and Ni concentrations in *O. leucostictus and C. carpio*. However there is significant difference between the concentrations of Cu and Zn concentrations in *C. spectacularlus* /*O. Leucostictus*.

Table 4.15. $T_{calculated}$ Values for Heavy Metal Concentrations in Various Fish Species of Lake Naivasha

Metal	***O. leucostictus*/*C. carpio***	***C. spectacularlus* /*O. Leucostictus***	***C. spectacularlus*/ *C. carpio***
Copper	0.25	<u>2.21</u>	0.84
Lead	1.09	0.49	0.52
Zinc	<u>3.82</u>	<u>3.99</u>	1.02
Cadmium	0.76	0.84	<u>4.61</u>

The underline values show species that were significantly different at 95% confidence level

4.8.2 Bio-accumulation Factor

Bio-accumulation of metals in the fish species were quantified by a bio-accumulation factor (BAF), which is the ratio of particular metal concentration in the specimen to the concentration of that metal in the water column. The values of bio-accumulation factors were calculated using Equation 4.2:

BAF = µg per Kg in dry weight / µg per Kg in water ……. 4.2

The concentrations of metals in fish were converted to dry weight using the average percent moisture content of 80%, and then converted from µg/g to µg/Kg. The mean concentrations of Cu, Pb, Cd, Zn and Ni (µg/Kg) used in the calculation of BAF were derived from sites: SS1, SS2, SS3, SS4, SS5 and SS6 which are inside the main Lake. These were recorded as 3.26, 12.5, 9.23, 1080 and 150 for Cu, Pb, Cd, Zn and Ni respectively.

The BAF values were in the range of 414 - 552 (Cu), 596 - 624 (Pb), 33 - 43 (Zn), 70 - 238 (Cd) and 446 - 487 (Ni). These are low compared to BAF values reported in other studies (Fig. 4.17). This can be explained by the fact that the present study determined total metal content in the water column and most of the metals were not bio-available for accumulation due to adsorption on particulate matter and dissolved carbon. However, the study shows that the bio-concentration of Ni, Cu, Cd and Zn is highest in *C. spectacularus.* However, accumulation of lead is not different from that recorded in *C. carpio*.

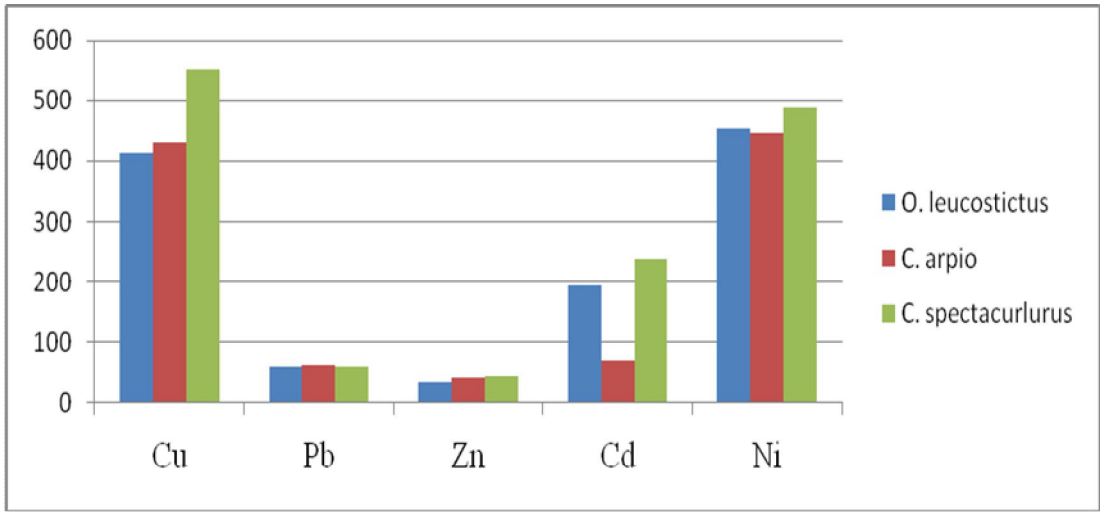


Figure 4.17. Bar Graph for BAF Values in Fish

The order of accumulation of the metals in fish is *C. Spectacularlus* > *C. carpio* > *O. leucostictus.*

4.9 Pesticide Residues and their Metabolites in Water from Lake Naivasha

The limit of detection was lowest for heptachlor and highest for *p, p'*- DDT, mean percent recovery ranged within 70.1 - 78.5%, 8.5 - 13.2% and 79.8 - 91.4% for relative standard

deviation and accuracy respectively. The pesticides data are presented in Table 4.16a, Table 4.16b and Fig. 4.18 respectively.

Table 4.16a. Pesticide Residues Concentrations (ng/L) in Water from Lake Naivasha (n = 6)

Site	**Heptachlor**	**Heptachlor Epoxide**	**Dieldrin**	***p, p′*- DDT**	***p, p′*- DDE**	***p, p′*- DDD**
SS1	1732.2 ± 42.2	48.6 ± 2.3	54.4 ± 3.4	6.1 ± 1.1	55.3 ± 4.5	31.9 ± 4.3
SS2	475.2 ± 12.4	69.9 ± 4.3	48.9 ± 4.5	22.5 ± 2.2	39.8 ± 4.5	37.3 ± 5.4
SS3	3701.1 ± 100.2	44.9 ± 3.3	170.2 ± 7.5	35.3 ± 4.3	41.9 ± 4.3	37.3 ± 3.2
SS4	5581.9 ± 67.3	100.1 ± 5.3	160.3 ± 8.7	184.3 ± 6.7	37.8 ± 3.4	39.4 ± 8.3
SS5	1678.6 ± 59.1	33.9 ± 2.1	56.1 ± 3.5	49.1 ± 7.3	110.3 ± 10.2	37.6 ± 3.4
SS6	455.6 ± 30.5	74.5 ± 3.6	108.1 ± 6.2	25.2 ± 2.3	29.0 ± 4.3	37.6 ± 4.3
SS7	703.5 ± 89.3	57.8 ± 4.2	71.9 ± 5.4	38.7 ± 4.5	95.7 ± 8.9	26.7 ± 3.2
SS8	5099.7 ± 120.2	90.1 ± 5.4	1158.5 ± 10	405.6 ± 9.2	498.1 ± 10.1	42.9 ± 4.5
SS9	6762.2 ± 432.3	73.4 ± 3.3	830.4 ± 8.9	52.1 ± 5.5	114.4 ± 9.8	39.3 ± 4.5
SS10	628.1 ± 23.2	42.7 ± 5.4	56.2 ± 4.3	81.8 ± 6.7	77.9 ± 7.5	45.7 ± 5.6

Mean ± standard deviation, n = 6

Table 4.16b. Mean Pesticides Residues Concentrations (ng/L) in Water in Lake Naivasha (n = 6)

	Methoxychlor	**Lindane**	**Endosulfan I**	**Endosulfan - II**	**Endosulfan sulfate**	**Aldrin**
SS1	629.2 ± 12.1	39.2 ± 1.2	23.0 ± 2.3	41.7 ± 2.4	16.2 ± 1.2	42.6 ± 4.6
SS2	23.6 ± 2.3	34.2 ± 2.1	20.1 ± 2.1	44.2 ± 3.1	78.4 ± 4.3	51.3 ± 3.6
SS3	450.3 ± 13.2	35.5 ± 3.4	46.1 ± 3.4	51.1 ± 4.3	133.0 ± 4.2	77.4 ± 5.4
SS4	239.7 ± 5.4	51.6 ± 2.1	57.9 ± 4.5	92.8 ± 5.1	195.5 ± 9.2	127.6 ± 8.2
SS5	96.8 ± 5.2	10.1 ± 1.3	21.2 ± 1.9	84.3 ± 6.5	60.2 ± 3.2	115.5 ± 7.8
SS6	21.8 ± 2.1	48.6 ± 1.9	42.9 ± 3.1	61.9 ± 5.5	345.2 ± 6.7	88.3 ± 6.6
SS7	16.1 ± 3.2	51.1 ± 4.2	28.6 ± 1.8	48.2 ± 3.3	88.2 ± 5.6	62.8 ± 5.4
SS8	1932.1 ± 56.4	69.7 ± 5.1	50.0 ± 4.1	271.7 ± 5.4	795.9 ± 7.7	305.9 ± 10.2
SS9	496.8 ± 11.2	33.2 ± 1.2	77.3 ± 5.2	129.4 ± 7.8	1025.2 ± 12.2	192.4 ± 6.4
SS10	291.8 ± 6.5	69.9 ± 3.1	30.9 ± 1.4	34.8 ± 1.7	12.1 ± 1.2	67.4 ± 5.4

Mean ± standard deviation, n = 6

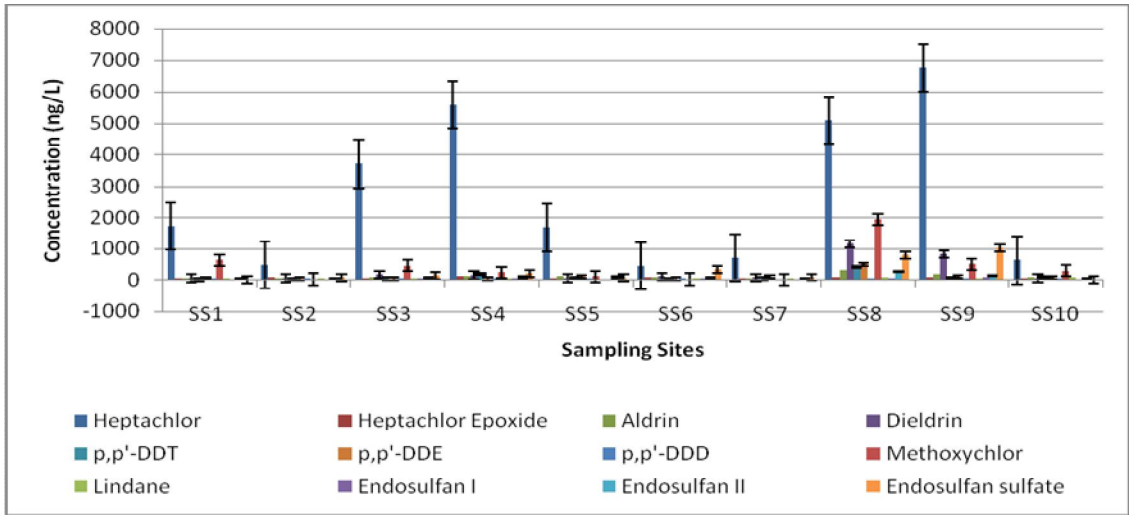


Figure 4.18. Mean Pesticides Residues Concentrations (ng/L) in Water in Lake Naivasha

4.9.1 Levels of Heptachlor and Heptachlor Epoxide in Water from Lake Naivasha

Among the screened pesticides, heptachlor was the most frequently encountered and recorded the highest concentration in the catchment. The concentration of heptachlor was in the range of 455.85 - 6762.23 ng/L, the highest concentration was found at site SS9 with a mean concentration of 6762.23 ± 43.2 ng/L and the lowest at site SS6 of 455.58 ± 30.5 (Table 4.16 and Fig. 4.19). Sites SS3 and SS8 are adjacent to flower farms. While site SS9 is along River Malewa due to intensive carrot farming activities in the area. Metabolite heptachlor epoxide was also detectable in the catchment in the range of 33.95 - 100.1 ng/L. Compared to its main metabolite heptachlor epoxide; heptachlor concentrations were 10 to 100 times higher for most of the sites indicating slow degradation or recent use of the pesticide in the catchment. The fact that high concentrations of heptachlor were detected at the sites close to intense agricultural activities signifies the possibility of the sites being non point sources of the pesticide.

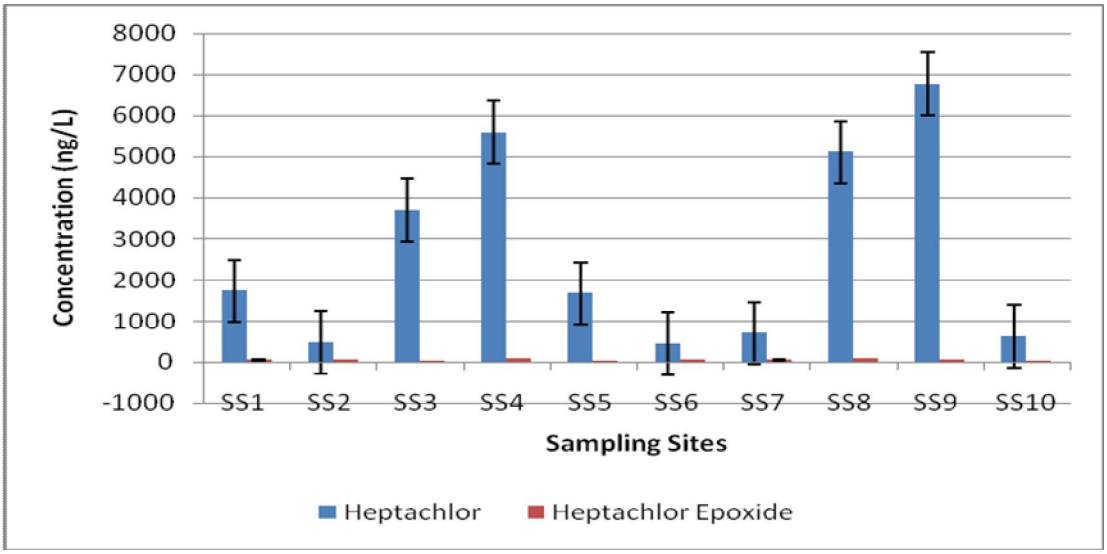


Figure 4.19. Bar Graph for Heptachlor and Heptachlor Epoxide in Lake Naivasha Water

Although the previous studies conducted on Lake Naivasha did not assess/report levels of heptachlor, the findings from this study revealed interesting results that need monitoring to establish the trend and actual sources of the compound. In addition, the high levels of heptachlor compared to heptachlor epoxide imply the possibility of recent use of heptachlor. But from the national pesticide records, the agricultural use of heptachlor was banned in 1986 (PCPB, 2009). The only possible source of these compounds therefore, could be through unscrupulous business activities or undeclared pesticide formulations and calls for increased surveillance on pesticides use in Kenya.

The measured heptachlor and heptachlor epoxide concentrations are significantly higher than the toxicity reference values (0.0036 µg/L) for screening contaminants of potential concern to aquatic biota reported by EPA (1992) in all sites. The high concentrations reveal that the

heptachlor and heptachlor epoxide concentrations in the water column pose serious environmental risks to aquatic biota.

4.9.2 Levels of Aldrin and Diedrin in Water from Lake Naivasha

Both aldrin and dieldrin were detected in the water from the catchment. Results are presented in Tables 4.16a, 4.16b and Fig. 4.20. Aldrin and dieldrin were detected in the Lake with aldrin residues ranging between 42.55 - 305.97 ng/L and dieldrin between 48.93 - 1158.46 ng/L. The highest concentrations of dieldrin were detected at site SS8 (1158.45 ± 10.2 ng/L) followed by site SS9 (830.41 ± 8.9 ng/L) while aldrin was detected at lower concentrations of 305.97 ± 10.2 and 192.37 ± 6.4 ng/l respectively. Site SS8 is a discharge canal from the flower farms and site SS9 along a tributary of River Malewa, is in an area with intensive small scale farming.

The study shows that dieldrin concentrations were higher than those of aldrin in most sites apart from sites SS4 and SS10. The higher levels of dieldrin compared to aldrin suggests contamination previous use of dieldrin. The detection of dieldrin in the basin calls for increased surveillance since dieldrin use was banned in 2004 (PCPB, 2009). In the soil, aldrin is converted by epoxidation to dieldrin, which is more stable and highly persistent in the environment. Both aldrin and dieldrin are known to strongly adsorb to soil with high organic matter, it is thus possible that aldrin and dieldrin enter the Lake from the catchments as particulate bound.

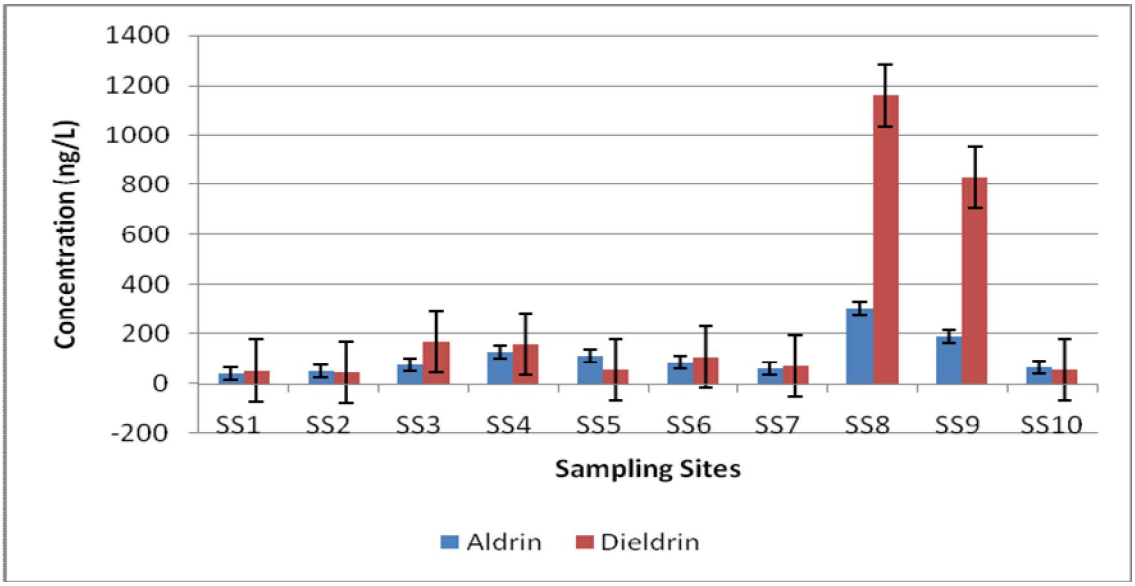


Figure 4.20. Bar Graph for Residue levels of Aldrin and Dieldrin

4.9.3 Levels of DDTs in Water from Lake Naivasha

The DDTs analyzed in this study included *p, p'*- DDT and its metabolites, *p, p'*- DDE and *p, p'*- DDD residues. The results are presented in Table 4.16a and Fig. 4.21. The highest concentrations of DDT were detected at sites SS8 (405.57 ± 9.2 ng/L), SS4 (184.26 ± 6.7 ng/L), SS10 (81.81 ± 6.7 ng/L). Site SS8 is along a discharge canal. The concentrations of p, p'- DDE were highest among the three in most cases followed by *p, p'*- DDT and *p, p'*- DDD respectively. The high levels of *p, p'*- DDE compared to *p, p'*- DDT imply contamination due to previous use of *p, p'*- DDT. Site SS8 had the highest level of *p, p'*- DDE, *o, p'*- DDD, *p, p'*- DDT suggesting that flower farms are an important source of DDT and its metabolites. Site SS9 also recorded high levels of *p, p'*- DDE while site SS6, the site where Municipal wastes enter the Lake show low concentrations of the DDTs indicating low contribution. Sites SS10 and SS9 along River Malewa also show high concentrations. However, the

concentrations detected at SS3 entry points of the river show low concentrations indicating removal of the pesticides as the River flows downstream.

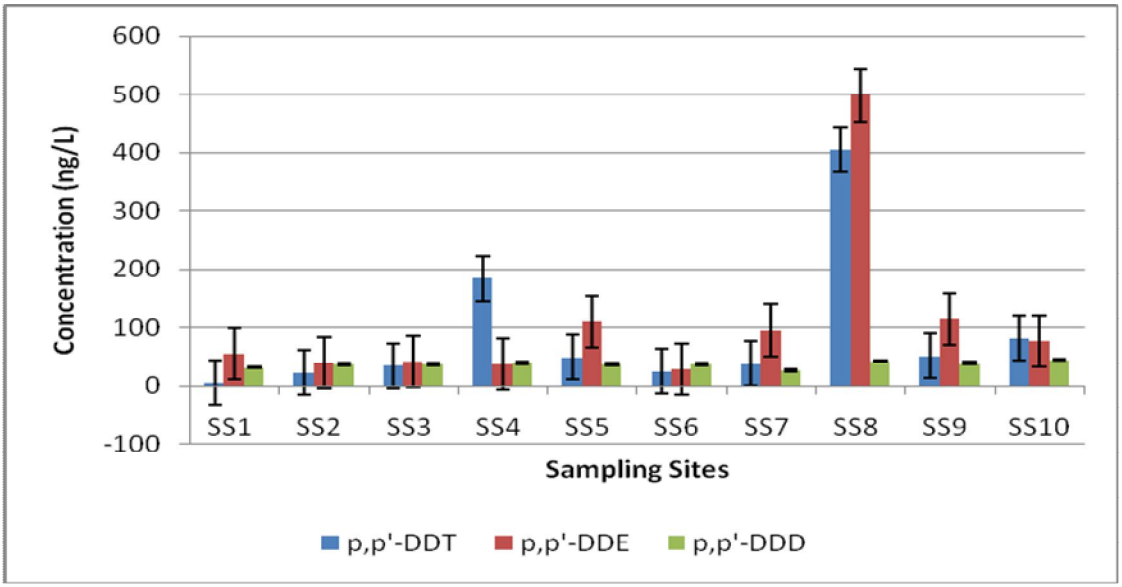


Figure 4.21. Bar Graph for Residue levels of DDTs in Lake Naivasha Water

A trend similar to most of the other pesticides was noted in the case of DDTs whereby areas with intense agricultural activities were found to have higher residues compared to areas with limited activities. Calculation of DDE/DDT rations gave 91% of the samples with the ration greater than 1 implying that most of the DDTs detected was due to previous use of the pesticide in the catchment. Nationally, the agricultural use of DDT was banned in 1986 (PCPB, 2009). Currently DDT use is restricted to emergency control of mosquitoes under incidences of malaria epidemics only.

4.9.4 Levels of Methoxychlor in Water from Lake Naivasha

The levels of Methoxychlor were within the range of 16.1 - 629.2 ng/L. The data is presented in Table 4.16b and Fig. 4.22. The concentrations are below the 40 µg/L maximum permissible level (US-EPA, 1989). However, concentrations at sites SS8, SS1, SS9, SS3, SS10, SS4 and SS5 registered values higher than the 30 ng/L (toxicity reference value (TRV) for testing aquatic biota) (Suter and Tsao, 1996). The highest concentrations of methoxychlor were found at sites SS8 (1932.1 ± 56.4 ng/L) and SS1 (629.2 ± 12.1 ng/L) adjacent to flower farms, indicating inflows from the farms (Fig. 4.23). Site SS3 where inflowing rivers enter the lake had a concentration of 450.3 ± 13.2 ng/L indicating inflows from upper catchment. Site SS6 next to the Naivasha Municipal wastewater discharge show a low concentration of 21.8 ± 2.1 ng/L compared to other sites. This indicates low contribution from the municipal. Low levels of methoxychlor were however detected at sites SS2 and SS4 inside the lake. Low concentrations were thought to be due to settling of particulates/sedimentation and dilution. These levels show wide variability between sites. This was due to the proximity of some sites to agricultural activities and from inflows which appeared to be major sources of methoxychlor. The detection of methoxychlor in the basin was expected since its being used as an alternative for DDT and it use is not restricted or banned.

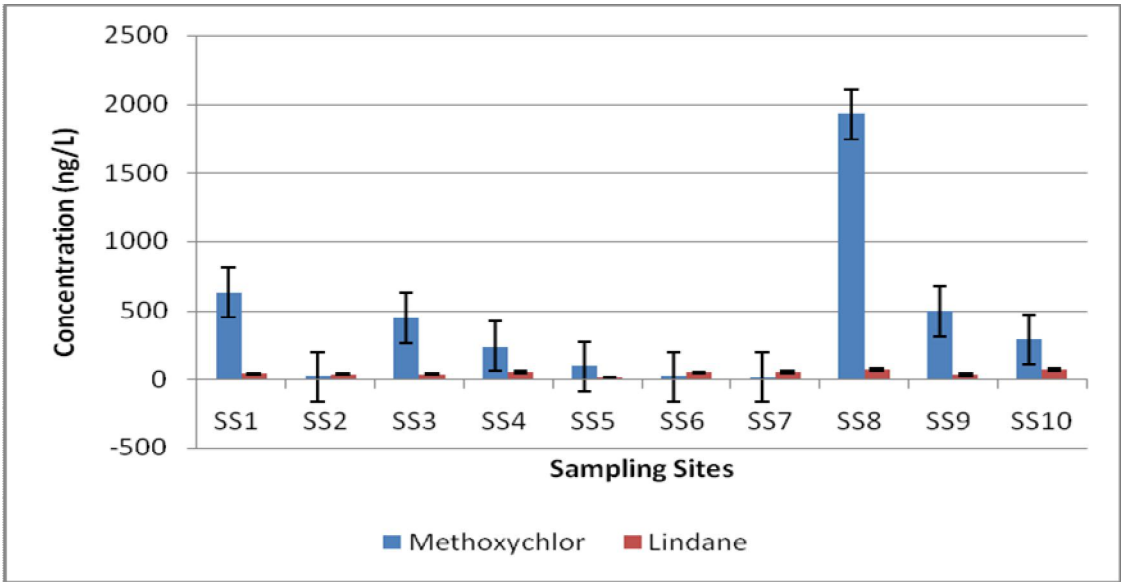


Figure 4.22. Bar Graph for Residue levels of Methoxychlor and Lindane in Lake Naivasha Water

4.9.5 Levels of Lindane in Water from Lake Naivasha

The levels of Lindane in the basin are presented in Table 4.16b and Fig. 22. Lindane was within the range of 10.12 - 69.89 ng/L and was detected in most sites where high concentrations were found at sites SS10, SS8, SS5, SS7 and SS1. This indicates that flower farms, River Malewa and the Naivasha Municipal Council are important sources of lindane. The detection of lindane in most sites implies it recent use in the catchment area and lindane has been classified as toxic to aquatic life forms. Lindane belongs to the class of hexachlorobenzene and its use was banned in 2004 (PCPB, 2009). Its detection calls for further monitoring to establish source.

4.9.6 Levels of Endosulfan and its Metabolites in Water from Lake Naivasha

Endosulfan isomers (endosulfan I and endosulfan II) and its metabolite, endosulfan sulfate, were determined and detected in samples from all sites in the basin. Results are presented in Table 4.16b and Fig. 4.23. These results indicate that metabolite endosulfan sulfate was predominant in most sites with a range of 12.12 - 1025.25 ng/L followed by endosulfan II (34.84 - 271.7 ng/L), and endosulfan I (20.1 - 77.28 ng/L) respectively. There were wide variations between samples with sites SS9 showing the highest concentrations of the three metabolites followed by site; SS8, SS6, SS4, SS3 and SS2. Site SS9 is a site along a tributary of River Malewa with high intensity of intensive vegetable farming especially carrots. Site SS3 is the River entry point into the lake while sites SS8 and SS2 are along discharge canals from the flower farms, whereas site SS6 is located at a site where wastewater discharges from the Naivasha Municipality enter the Lake. The high concentrations of endosulfan found in these sites indicate that flower farms, River Malewa and the Naivasha Municipal Council are important sources of endosulfan and its metabolites.

The results of water analysis agree with findings made on the endosulfan usage in the catchment (Table 4.3). A survey on insecticides use in the catchment indicated that Thionex, Thiofanex, Phaser plus, Callisulfan and Thiodane, pesticides formulated with endosulfan as the active ingredient are widely used. Endosulfan is also added to other insecticides to increase their efficacy. The concentrations of endosulfan sulfate were generally higher than those of *alpha* (I) and *beta* (II) isomers in most of the cases which indicated rapid transformation of the isomers to the metabolite. The USEPA is terminating uses of

endosulfan gradually to address its unacceptable risks to agricultural workers and wildlife (USEPA, 2010).

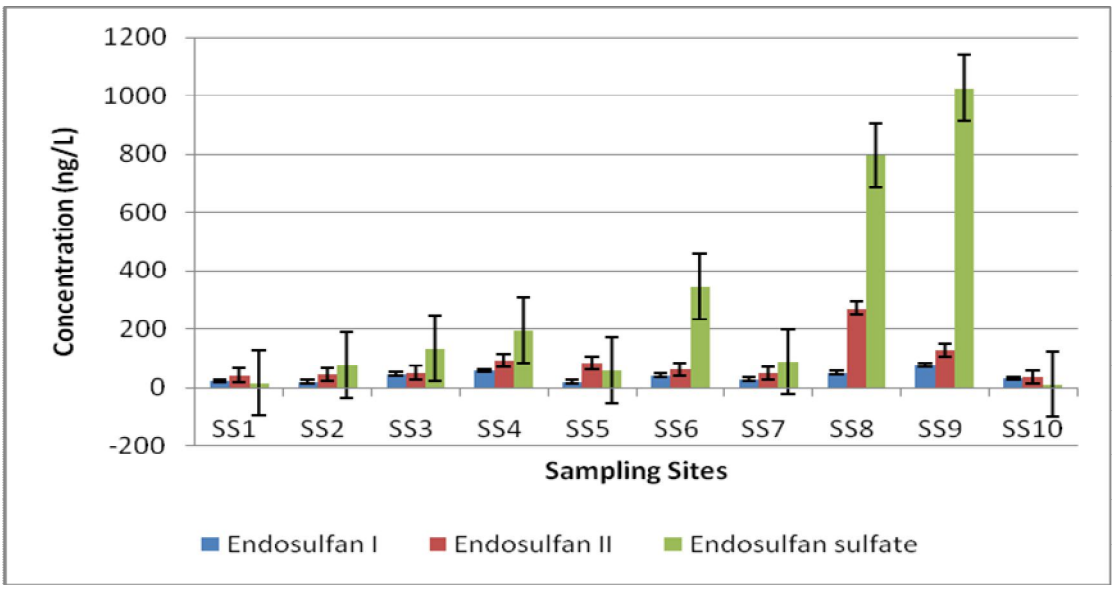


Figure 4.23. Residue Levels of Endosulfan and its Metabolites in Lake Naivasha Water

Technical endosulfan is a 2:1 to 7:3 mixtures of α- and the β-isomers. In the environment, endosulfan is oxidized in plants and in soils to form primarily endosulfan sulfate and endosulfan-diol (Jalili *et al.*, 2007). The formation of endosulfan sulfate is mediated essentially by micro-organisms and endosulfan-diol is essentially the major hydrolysis product. Microbial mineralization is generally slow. The detection of endosulfan sulfate in larger quantities compared to endosulfan I and II implies contamination due to previous use in areas of intense agricultural activities and these could be acting as point sources of the compounds into the drainage basin of the lake.

4.9.7 Statistical Tests

The $T_{calculated}$ values for T significant tests for organochlorine pesticide residues in water from Lake Naivasha and Mid Lake Values (SS2) at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 10, $\mathbf{t_{critical}}$ = 2.23) are presented in the Table 4.17a and Table 4.17b.

Table 4.17a. $T_{calculated}$ Values for Organochlorine Pesticides in Waters of Lake Naivasha

Sampling Site	**Heptachlor**	**Heptachlor epoxide**	**Dieldrin**	***p, p'*-DDT**	***p, p'* - DDE**	***p, p'*- DDE**
SS1	79.91	24.62	6.36	38.45	9.22	0.27
SS3	86.56	20.35	43.29	7.97	1.31	0.37
SS4	203.6	15.21	34.24	64.73	1.57	0.14
SS5	54.64	45.49	5.50	9.77	18.46	0.35
SS6	1.72	3.41	25.45	3.12	3.26	0.27
SS7	6.84	7.71	11.41	9.64	16.84	0.37
SS8	103.22	9.97	297.45	304.53	121.67	0.26
SS9	39.02	2.83	235.35	243.3	20.42	0.26
SS10	17.67	13.49	13.16	20.97	13.62	0.21

The underlined values indicate sites whose concentrations of pesticides are significantly different form SS2 at 95% confidence level.

Statistical analysis of pesticides shows significant differences between sites apart from a few sites. However the concentration of *p, p'*- DDE is similar to that at SS2 for all sites.

Table 4.17b. $T_{calculated}$ Values for Organochlorine Pesticide Residues in Water of Lake Naivasha with SS2 Values

Sample sites	**Methoxychlor**	**Lindane**	**Endosulfan I**	**Endosulfan II**	**Endosulfan Sulphate**	**Aldrin**
SS1	143.25	10.81	3.35	2.77	134.49	5.06
SS3	86.65	0.86	20.35	4.29	34.78	16.24
SS4	107.19	21.99	22.48	25.63	34.13	24.95
SS5	37.70	48.33	1.39	16.53	3.35	22.07
SS6	2.27	20.06	19.63	8.67	106.65	15.03
SS7	2.26	10.77	12.48	3.24	4.59	5.71
SS8	90.79	18.65	19.51	112.51	249.86	66.95
SS9	113.13	93.19	29.31	29.29	208.13	59.04
SS10	110.59	66.93	20.38	14.59	143.36	7.98

The underlined values indicate sites whose concentrations of pesticides are significantly different form SS2 at 95% confidence level.

4.10 Pesticide Analysis in Fish from Lake Naivasha

4.10.1 Biological Prameters of the Fish from Lake Naivasha

The total lipid content, moisture content, weight and length of specimens were determined and are presented in Table 4.18. Percentage recoveries of pesticides in fish were in the range of 75.52 - 96.02% and were relatively high compared to those found in water.

Table 4.18. Mean Lipid Content, Length, Moisture, and Weight of Fish of Lake Naivasha (n = 11)

Parameters	***O. leucostictus***	***C. carpio***	***C. spectacularlus***
Lipid content (%)	1.87 ± 1.0	0.78 ± 0.1	0.92 ± 0.2
Moisture content (%)	81.89 ± 3.1	79.22 ± 3.8	79.78 ± 1.3
Weight (g)	202.69 ± 33.1	829.96 ± 196.7	765.13 ± 29.8
Length (cm)	22.57 ± 1.2	41.1 ± 4.0	41.66 ± 0.8

Mean ± Standard Deviation, n = 11

The highest lipid content was recorded in *O. leucostictus* followed by *C. spectacurlus* and *C. carpio* respectively. The moisture content was not significantly different between species. The weight and length of specimens varied widely, *O. leucostictus* recorded the lowest weight and length. However *C. carpio* recorded the highest weights while *C. spectacurlus* recording the highest lengths.

4.10.1 Statistical Tests

The $T_{calculated}$ values for T significant tests for lipid fractions, moisture, length and weight of fish specimens from Lake Naivasha at $\boldsymbol{p = 0.05}$, degrees of freedom (υ) ($\mathbf{n_1 + n_2 - 2}$) = 20, $\mathbf{t_{critical}}$ = 20) are presented in the Table 4.19.

Table 4.19. $T_{calculated}$ values for lipid fractions, moisture, length and weight of fish specimens from Lake Naivasha

	O. leucostictus/ C. carpio	***C. spectacularlus / O. Leucostictus***	***C. spectacularlus/ C. carpio***
Lipid fraction	11.43	8.83	1.31
Moisture content	2.44	5.49	1.4
Weight	11.09	65.62	7.56
Length	16.06	77.19	2.26

The underlined values indicate species that are significantly different at 95%.

Statistical analysis of the mean lipid fraction, moistures weight and length shows that *O. leucostictus/C. carpio* and *C. spectacularlus* / *O. Leucostictus* are significantly different at 95% confidence level. However the moisture content and lipid fraction content are same for *C. spectacularlus/ C. carpio* whereas the weight and length of the two species are significantly different.

4.10.2 Pesticide Concentrations in Fish from Lake Naivasha

The pesticide concentrations in *O. leucostictus, C. carpio* and *C. spectacularlus* are presented in Table 4.20. Pesticides were below the instrument/method detection limit for some fish specimen analyzed. The concentrations in ascending order are *O. leucostictus,* followed by *C. carpio* and *C. spectacularlus* respectively.

Table 4.20. Pesticide Concentrations (µg/Kg) in Fish of Lake Naivasha (n = 6)

Pesticides	***O. leucostictus***	***C. carpio***	***C. spectacularlus***
p, p'- DDT	BDL - 1.91	BDL - 7.26	BDL - O.72
p, p' – DDE	0.21 - 0.46	0.14 - 0.51	0.21 - 6.69
p, p' – DDD	BDL - 21.13	BDL - 27.15	0.23 - 4.33
Methoxychlor	BDL - 28.87	0.17 - 10.07	BDL - 2.43
Heptachlor	0.41 - 1.01	0.42 - 4.19	0.81 - 1.58
Heptachlor epoxide	BDL - 0.03	BDL - 0.14	0.14 - 0.22

Mean ± Standard Deviation, n = 11, BDL - Below detection limit

4.10.2.1 Levels of Heptachlor and its Metabolite in Fish from Lake Naivasha

Among the screened pesticides, heptachlor was detected in all specimens, this was recorded in the range of 0.41 - 4.19 and BDL - 0.22 µg/Kg for the metabolite heptachlor epoxide. The highest concentration of heptachlor was found in *C. carpio,* (4.19 ± 0.6 µg/Kg) whereas the lowest (BDL) was found in *O. leucostictus* (Table 4.20). Heptachlor epoxide concentrations in the specimens were relatively low compared to heptachlor which indicate slow transformation to the metabolite. The low concentrations of the metabolite in specimens could also mean low bio-concentration of the metabolite. The fact that heptachlor was detected in fish samples indicate recent use of the pesticide in the catchment. Although the previous studies conducted on Lake Naivasha did not report levels of heptachlor, the findings from this study revealed interesting results especially in water that need monitoring to

establish the trend and actual sources of the compound. In addition, the high levels of heptachlor compared to heptachlor epoxide imply the possibility of recent use of heptachlor. Moreover, from the national pesticide records, since the agricultural use of heptachlor was banned in 1986 (PCPB, 2009), the only possible source of these compounds could be through unscrupulous business activities or undeclared pesticide formulations.

4.10.2.2 Levels of DDTs in Fish from Lake Naivasha

The *p, p'*- DDT and its metabolites *p, p'*- DDE and *p, p'*- DDD were determined in fish specimens from the lake, results presented in Table 4.20. *p, p'*- DDE was detected in all specimens analyzed whereas *p, p'*- DDD and *p, p'*- DDT was not detected in all specimens. *p, p'*- DDD showed relatively high concentrations in most species followed by *p, p'*- DDT and *p, p'*- DDE respectively. The highest concentrations of DDT were detected in *C. carpio*, (7.26 ± 0.4 µg/Kg), whereas the lowest concentrations were detected in *O. leucostictus*. The levels of *p, p'* - DDE were in the range of 0.14 - 6.69 µg/Kg, the highest was found in *C. spectacularlus*, (6.69 ± 1.2 µg/Kg) and the lowest concentrations in *O. leucostictus* (BDL). The high levels of *p, p'*- DDD compared to *p, p'*- DDT implied degradation of DDT to the DDD metabolite. Nationally, the agricultural use of DDT was banned in 1986 (PCPB, 2009) and this could partly explain the high ratio of DDE to DDT. Currently, the use of alternatives such as pyrethroids are strongly encouraged in the country, while DDT use is restricted to emergency control of mosquitoes under incidences of malaria epidemics only.

4.10.2.3 Levels of Methoxychlor (CAS No. 72-43-5) in Fish from Lake Naivasha

Methoxychlor was detected in most specimens and the data is presented in Table 4.20. Methoxychlor was in the range of BDL - 28.87 µg/Kg. The highest concentrations were registered in *O. leucostictus,* (28.87 ± 3.2 µg/Kg), followed by *C. carpio* (10.07 ± 1.1 µg/Kg) and *C. spectacurlus* (2.43 ± 1.1 µg/Kg). The pesticide was detected in all samples of *C. carpio.* Concentrations detected in *O. leucostictus* indicate the highest concentrations in pesticides found in all specimens. The presence of methoxychlor in fish indicates bio-concentration from the water column which shows recent use of the pesticides in the catchment.

4.10.2.3 Human Risk Assessment of Consumption of Fish from Lake Naivasha

Dietary risk assessments were conducted for the consumption of *O. leucostictus, C. carpio* and *C. spectaculurus* from Lake Naivasha with respect to concentrations of *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, methoxychlor, heptachlor and heptachlor epoxide in edible portions of fish (fillet). The average daily intakes are 27.27 – 275, 27.27 430, 7.2 – 45, 3.45 – 40.99, 7.16 – 29.76 and 136.24 – 1000 times lower than the Acceptable Daily Intake (ADI) for *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, methoxychlor, heptachlor and heptachlor epoxide respectively (FAO/WHO, 1977; ICPS, 1982; WHO, 1984). The study shows that the consumption of 1 Kg fish fillet per day for a healthy 60 Kg adult does not pose any risks with respect to pesticide contents (Table 4.21).

Table 4.21. Dietary Risk Assessment for the Consumption of Fish (mg/Kg bodyweight)

Pesticides	***O. leucostictus***	***C. carpio***	***C. spectacularlus***	**ADI**	**Source**
p, p'- DDT	3.18×10^{-5}	1.21×10^{-4}	1.2×10^{-5}	3.3×10^{-3}	ICPS, 1982
p, p'- DDE	7.67×10^{-6}	8.5×10^{-6}	1.12×10^{-4}	3.3×10^{-3}	ICPS, 1982
p, p'- DDD	3.52×10^{-4}	4.53×10^{-4}	7.22×10^{-5}	3.3×10^{-3}	ICPS, 1982
Methoxychlor	4.81×10^{-4}	1.68×10^{-4}	4.05×10^{-5}	1.66×10^{-3}	FAO/WHO 1977
Heptachlor	1.68×10^{-5}	6.98×10^{-5}	2.63×10^{-5}	5.0×10^{-4}	WHO, 1982
Heptachlor epoxide	5.0×10^{-7}	2.33×10^{-6}	3.67×10^{-6}	5.0×10^{-4}	WHO, 1982

Key; ADI - Acceptable daily intake

4.11 Results of Recent Research in Lake Naivasha

Recent studies on Lake Naivasha include investigation of geochemical and physical characteristics of rivers and lake sediments and sediment stratography in an attempt to obtain information for better management of the lake (Håkan *et al*., 2002). Previous studies have also reported heavy metals such as mercury in fish from Lake Naivasha with concentrations ranging from 4.8 - 81.1 ng/g. The concentrations varied from one fish species to the other with *Micropterus salmoides* recording concentration of 52 ng/g, *Barbus paludinosus*, 81.1 ng/g, *Haplochromine spp.*,5.6 ng/g; *Tilapia zilli*, 9.3 ng/g; *Oreochromis leucostictus*, 4.8 ng/g; and *Procambarus clarkii*, 11.7 ng/g (Campbell *et al*., 2003). Gitahi *et al*, 2003 reported some pesticides in Water, sediments, red swamp crayfish (*Procambarus clarkii*) and black bass (*Micropterus salmoides*) from Lake Naivasha. The mean *p, p'*- DDT, *o, p'* - DDT and *p,*

p' - DDE residue levels recorded in black bass 28.3 ± 30.0, 34.2 ± 54.0 and 16.1 ± 16.1 μgKg^{-1}, respectively and crayfish 4.6 ± 5.1, 3.2 ± 2.8 and 1.4 ± 1.1 μgKg^{-1}, respectively, were higher than previously recorded (Gitahi *et al.*, 2003). This indicated recent usage of technical DDT in the lake's catchment. Levels of *p, p*'- DDT, higher than those of *p, p*'- DDE further emphasized this. Mean lindane, dieldrin, β -endosulfan and aldrin concentrations in black bass were 100.5, 34.6, 21.6 and 16.7 μgKg^{-1}, respectively. The same residues were detected at lower concentrations in crayfish at 2.0, 2.0, 2.0 and 1.9 μgKg^{-1}, respectively (Gitahi *et al.*, 2003). Mugachia *et al*, 1992 also reported the concentrations of DDT, lindane and dieldrin in water and fish from Lake Naivasha and River Tana.

4.12 Modification of the PERPEST Model

The PERPEST model was calibrated and validated using local (Kenyan) conditions. The DT_{50}, K_{oc}, Henry's constant and LC_{50} were adjusted to values at 25^0C. The exposure regime and hydrology were reset to reflect the conditions at the lake. The model was optimized; weighting and transformation were done as indicated in Table 4.21. Results of the best values after optimization are indicated in Table 4.21. The goodness of fit on cross validation was -1050, log(likelihood) -851.2 with a convergence of 0.0321 at 95% confidence level. The model was validated using experimental data The study shows that the modified model works optimally between a concentration range of 0.3 – 50 µg/L. TRVs, LC_{50} and responses at specific concentrations were correlated and were found to be statistically similar at 95% confidence levels.

Table 4.22 Parameters Used in the Modification of the PERPEST Model

Parameter	Weight on parameter	Transformation	Optimization value
CAS	5	Logarithmic	2.39
Toxic units	9	No transformation	6.979
Toxicity mode of action	5	No transformation	6.867
Molecule group	5	No transformation	5.45
Hydrology	4	No transformation	8.543
Exposure regime	5	No transformation	9.952
Dt50	5	Logarithmic	7.205
Henry's constant	5	No transformation	8.711
Koc	6	No transformation	8.588
Minimum distance	3	No transformation	0.04895

The modified PERPEST model was used to predict the ecological effects of the measured exposure concentrations of methoxychlor.

4.13 Prediction of Environmental Risks of Methoxychlor using the Modified PERPEST Model

Results of the prediction for ecological risks of pesticides (PERPEST 2.0) are presented in Table 4.22, a summary of results for 0.63 µg/L is presented in Fig. 4.24.

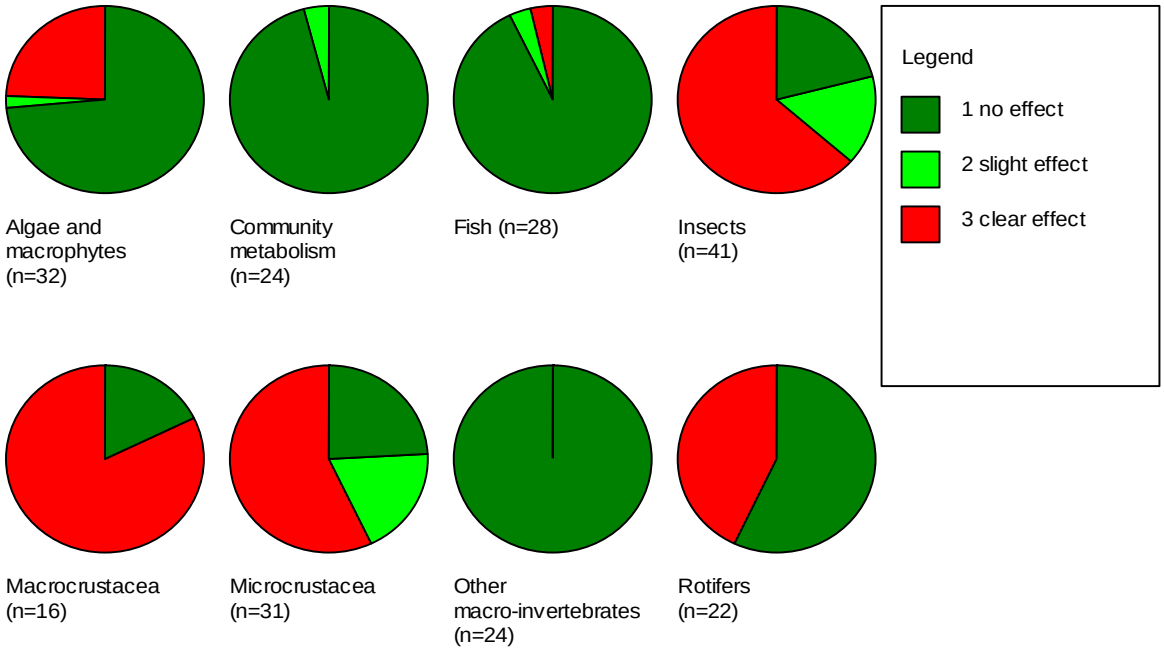


Figure 4.24. PERPEST predictions for 0.63 µg/L of Methoxychlor on Aquatic Communities (n is the number of analogous cases considered in the Prediction)

Seven aquatic communities were considered namely; insects, microcrustacea, algae and macrophytes, macrocrustacea, macro-invertebrates, rotifers and community metabolism. A positive correlation between occurrence of risks and concentration of methoxychlor is observed for insects, microcrustacea, macrocrustacea and rotifers. However, no clear trend was observed for algae and macrophytes and community metabolism over the measured pesticide exposure concentration range and was thought to be due to indirect effects. Macro-invertebrates were not however affected across the measured exposure concentrations.

Table 4.23. PERPEST result for Measured Methoxychlor Concentrations

	0.01	**0.04**	**0.08**	**0.1**	**0.2**	**0.4**	**0.6**	**0.63**
Algae and Macrophytes = 1	1	1	1	1	0.85	0.75	0.75	0.75
Algae and Macrophytes = 2	0	0	0	0	0	0.02	0.03	0.04
Algae and Macrophytes = 3	0	0	0	0	0.14	0.21	0.21	0.21
Community metabolism = 1	1	1	1	1	1	0.95	0.95	0.95
Community metabolism = 2	0	0	0	0	0	0.04	0.04	0.042
Community metabolism = 3	0	0	0	0	0	0	0	0
Fish = 1	1	1	1	1	1	0.95	0.90	0.91
Fish = 2	0	0	0	0	0	0	0.04	0.05
Fish = 3	0	0	0	0	0	0.04	0.05	0.05
Insects = 1	0.66	0.47	0.5	0.52	0.42	0.28	0.24	0.26
Insects = 2	0.33	0.41	0.36	0.34	0.20	0.17	0.18	0.18
Insects = 3	0	0.11	0.13	0.13	0.37	0.54	0.56	0.56
Macrocrustacea = 1	1	1	0.90	0.90	0.56	0.26	0.25	0.25
Macrocrustacea = 2	0	0	0	0	0	0	0	0
Macrocrustacea = 3	0	0	0.09	0.09	0.43	0.73	0.75	0.75
Microcrustacea = 1	0.49	0.57	0.54	0.54	0.30	0.29	0.26	0.26
Microcrustacea = 2	0.50	0.28	0.27	0.27	0.30	0.23	0.19	0.19
Microcrustacea = 3	0	0.14	0.18	0.18	0.39	0.46	0.53	0.53
Macro-invertebrates = 1	1	1	1	1	1	1	1	1
Macro-invertebrates = 2	0	0	0	0	0	0	0	0
Macro-invertebrates = 3	0	0	0	0	0	0	0	0
Rotifers = 1		1	0.83	0.83	0.91	0.73	0.73	0.73
Rotifers = 2		0	0	0	0	0	0	0
Rotifers = 3		0	0.16	0.167	0.08	0.27	0.26	0.26

Key; 1 - no effect class, 2 - slight effects and 3 - clear effects.

4.13.1 Environmental Risks of Methoxychlor on Algae and Macrophytes in Lake Naivasha

Primary producers (algae and macrophytes) are non-target organisms for methoxychlor, increased probability of ecological risks was observed with increased methoxychlor concentration (Fig. 4.25). The no effect factor changes from 100% - 75.2%. Clear effect factor increases from 14.6% - 21.2% over the measured exposure concentration range 0.2 - 0.63 µg/L. The slight effect increases from 0.4 - 0.63 µg/L. The observable effect concentration is 0.2 µg/L this value is higher than the toxicity reference value of 0.03 µg/L for testing aquatic biota (Suter and Tsao, 1996). Pesticides are absorbed and accumulated by aquatic organisms (Rice and Sikka, 2000).

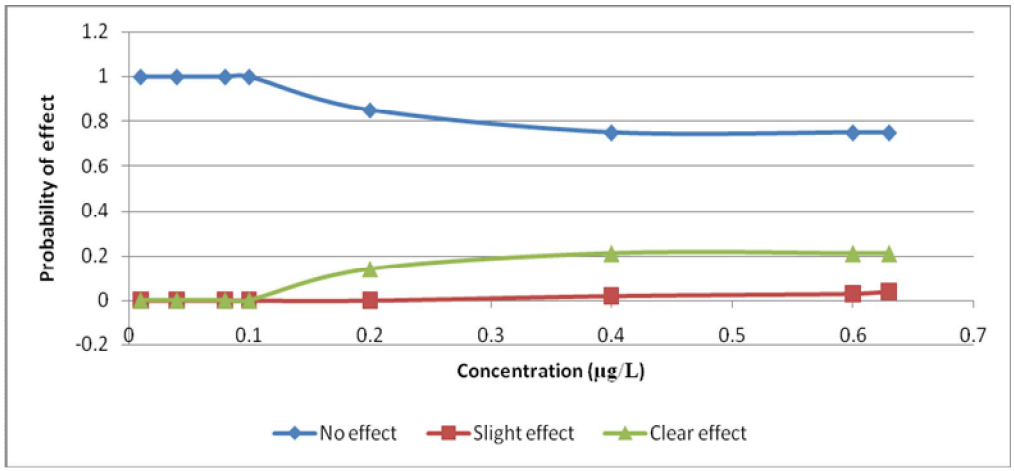


Figure 4.25. Concentrations of Methoxychlor versus Response of Algae and Macrophytes

The study shows that the measured nominal concentration has a 20% probability of causing observable reduction in the population of algae and macrophytes.

4.13.2 Environmental Risks of Methoxychlor on Community Metabolism in Lake Naivasha

The effects of methoxychlor on dissolved oxygen levels and pH were assessed and are presented in Fig. 4.26. The prediction shows that the measured range of concentrations has no observable ecological effects on community metabolism and remains constant at 0%. The slight effects predicted could be due to indirect effects.

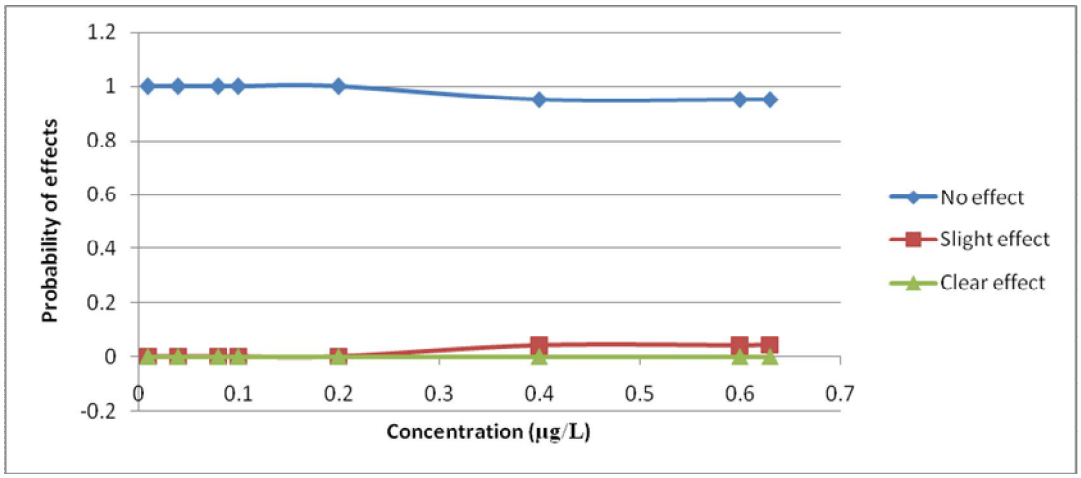


Figure 4.26. Concentrations of Methoxychlor versus Response of Community Metabolism

4.13.3 Environmental Risks of Methoxychlor on Fish in Lake Naivasha

The predictions of ecological risks of methoxychlor on fish are presented in Fig. 4.27. A clear trend of increased risk with increasing concentration is observed. The observable effect concentration from this prediction is 0.2 µg/L. This value is higher than the toxicity reference value (0.03 µg/L) for testing aquatic biota, illustrating accuracy of the prediction (Suter and Tsao, 1996). The no effect factor varies from 100% to 90.9% whereas the clear effect factors changes from 0% to 4.55% over the concentration ranges within 0.2 - 0.63 µg/L. The study shows that the pesticide though not targeted on the fish has a 4.5% probability of causing observable ecological effect of fish population.

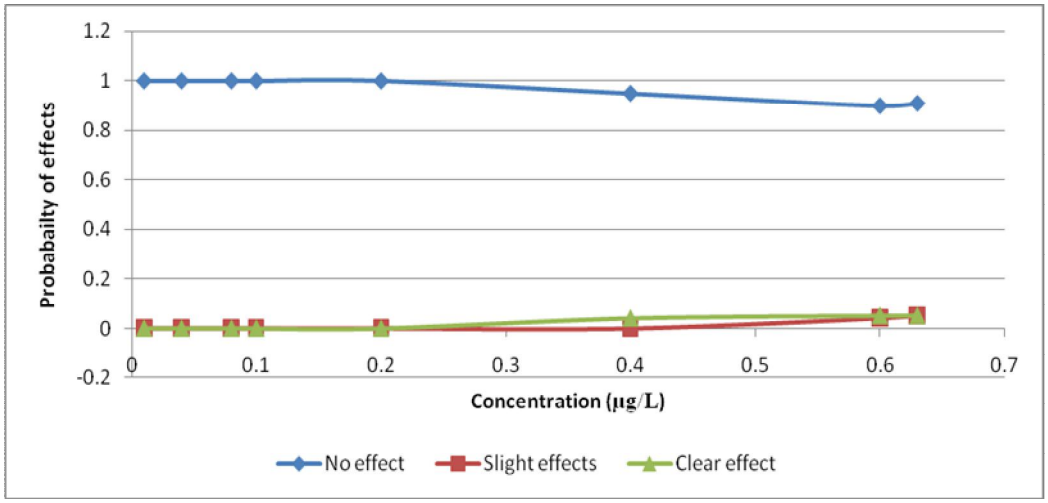


Figure 4.27. Concentrations of Methoxychlor versus Response of Fish

4.13.4 Environmental Risks of Methoxychlor on Insects in Lake Naivasha

Methoxychlor is a pesticide that is targeted to insects and is described as effective in the control of insects, a plot of likelihood of adverse effects occurring versus concentrations are presented (Fig. 4.28). The prediction shows that there is an increase in ecological risks as concentration increases. The increase in clear effects is observed from 0.04 - 0.08 µg/L which is followed by a decline from 0.08 - 0.1 µg/L, this then rises from 0.1 - 0.6 µg/L and remain constant up to 0.63 µg/L. The no effect and slight effect factors also decrease with increase in concentration. The clear effect factor rises to reach a maximum value at 0.60 and 0.63 µg/L.

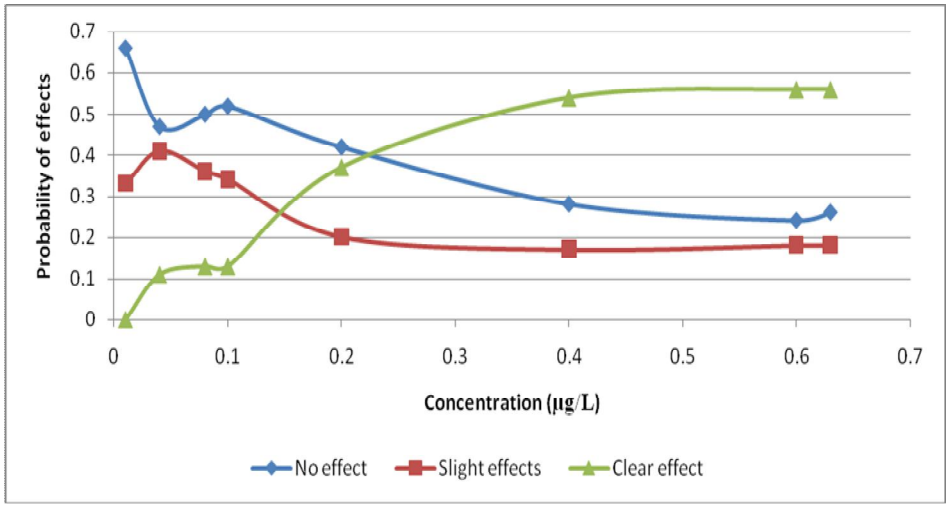


Figure 4.28. Concentrations of Methoxychlor versus Response of Insects

The study shows that the measured nominal concentration has a 56% probability of inducing clear reduction in insect population. The observed variations between the concentrations of 0.02 to 0.1 indicate uncertainties in the prediction.

4.13.5 Environmental Risks of Methoxychlor on Macrocrustacea and Microcrustacea in Lake Naivasha

The PERPEST prediction for macrocrustacea and microcrustacea show a similar trend (Fig. 4.29 and Fig. 4.30), micro-crustaceans show the highest sensitivity to the pesticide at low concentrations compared to macrocrustacea, the clear effects emerge at 0.04 µg/L and 0.08 µg/L microcrustacea for and macrocrustacea respectively. However, the high concentrations appear to have more marked clear effects on macrocrustacea compared to microcrustacea, the clear effect factors changes from 9.9 - 75% and 14.2 - 53.4% for microcrustacea and

macrocrustacea respectively. The observable effect concentrations for macrocrustacea and microcrustacea are between 0.2 - 0.4 µg/L and 0.4 - 0.6 µg/L respectively.

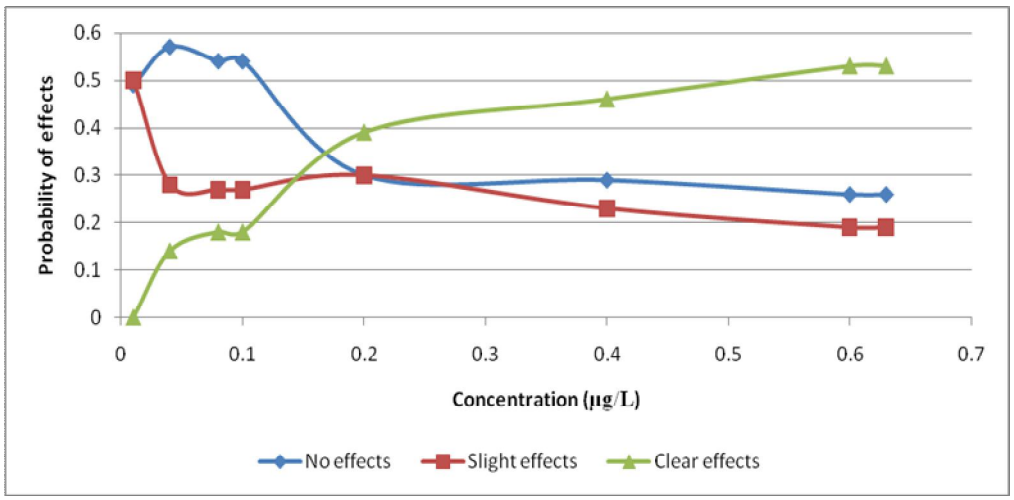


Figure 4.29. Concentrations of Methoxychlor versus Response of Microcrustacea

The study shows that though the pesticide is not targeted on crustaceans there is a high probability of causing a severe reduction in crustacean populations. Macrocrustacea and microcrustacea accumulated pesticides in their bodies orally and dermal. Increased dermal absorption is observed in this class of organisms due to the semi-permeable nature of the skin (Murty, 1986). Chronic exposure to low pesticide concentrations is associated with subtle changes in behavior and physiology that impair both survival and reproduction (Kegley *et al.*, 1999).

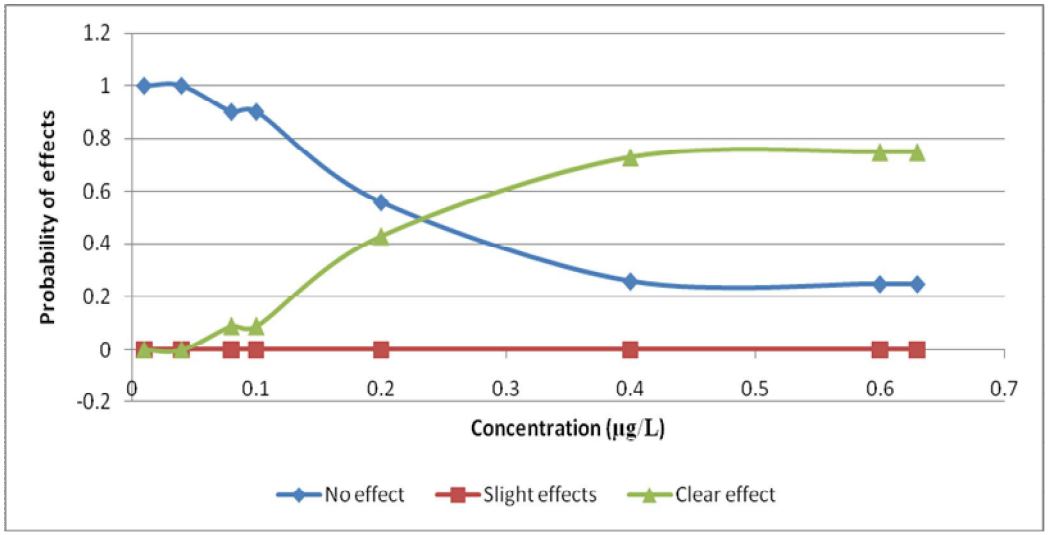


Figure 4.30. Concentrations of Methoxychlor versus Response of Macrocrustacea

4.13.6 Environmental Risks of Methoxychlor on Rotifers in Lake Naivasha

Methoxychlor is a pesticide that is not targeted to rotifers but is described as toxic to aquatic organisms. The likelihood to cause adverse effects versus concentrations is presented (Fig. 4.31). The plot shows that there is an increase in the probability of clear ecological risks occurring as concentration increases. The increase in clear effects is observed from 0.08 - 0.1 µg/L which is followed by a decline from 0.1 - 0.2 µg/L, this then rises from 0.2 - 0.4 µg/L the falls at 0.6 µg/L and remain constant up to 0.63 µg/L. The measured nominal concentration has a 26% probability of causing observable effects on rotifers lasting for 8 weeks.

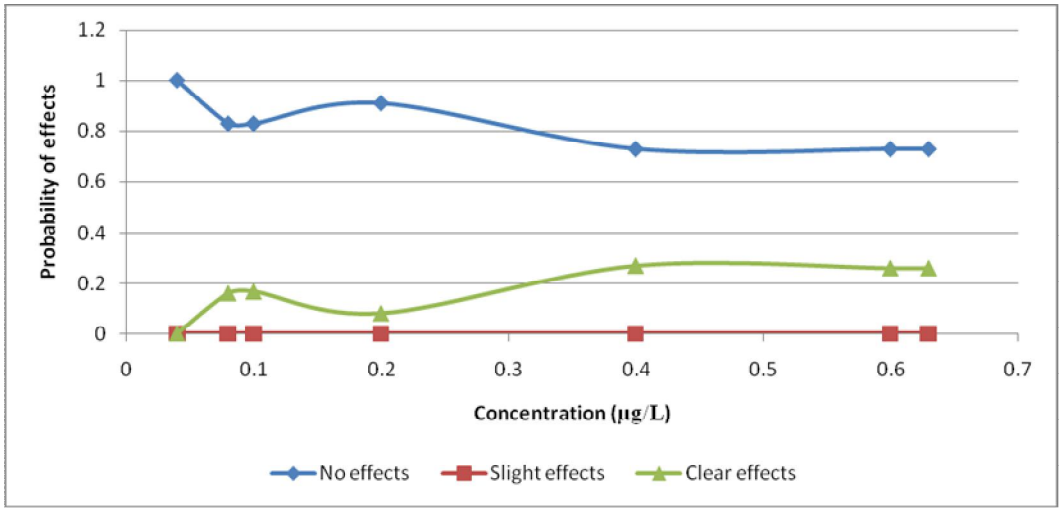


Figure 4.31. Concentrations of Methoxychlor versus Response of Rotifers

4.13.7 Environmental Risks of Methoxychlor on Macro-invertebrates in Lake Naivasha

The PERPEST prediction shows that the measured exposure concentrations have no effects on macro-invertebrates (Fig. 4.32) the no effect, slight effect and clear effect factors remain constant at 100%, 0% and 0% respectively over the 0.01 - 0.63 µg/L concentration range. The measured concentration has no potential of causing observable adverse effects on macro-invertebrates.

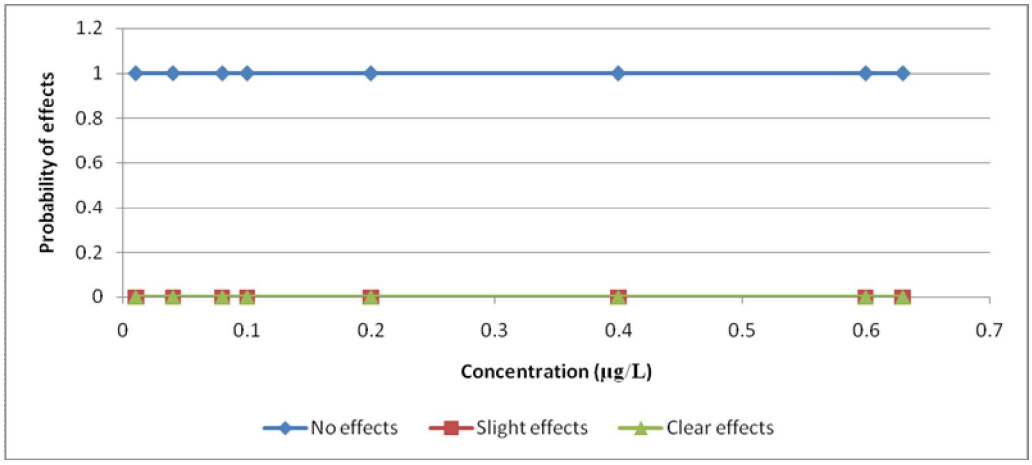


Figure 4.32. Concentrations of Methoxychlor versus Response of Macro-invertebrates

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study revealed some trends and the following conclusions were drawn.

5.1.1 Limnology Parameters in Lake Naivasha

A wide variability in the limnology parameters including dissolved oxygen, water temperature and clarity was observed. The study shows an increase in water temperature and an improved clarity and dissolved oxygen levels compared to one reported earlier by Campbell *et al*. (2003) and Njenga (2004). The turbidity measured in the main Lake was due to inflow of suspended solids from the upper catchment whereas in Lake Oloidien was due to the blue green algae bloom. Areas with high dissolved oxygen show a high population of aquatic organisms.

5.1.2 Pesticides Use in the Lake Naivasha Basin

A wide range of pesticides are used in the basin, these include organochlorine, organophosphorus, botanicals, inorganic and carbamates. Some of the most important organochlorine used in the basin was endosulfan in several formulations which is currently being phased out due to its toxicity to humans and wildlife. Most of the pesticides used in the sediment had labels indicating serious toxicity to aquatic organisms and wildlife and were classified as slightly hazardous, moderately hazardous of highly hazardous.

Poor storage, handling and disposal of agricultural wastes and agrochemical containers were observed in several farms in open dumps (Plate 1.9).

5.1.3 Water Abstraction in the Lake Naivasha Basin

The available data reveal that some flower farms exceed abstraction volumes allocated by the Ministry of Water. Crude methods of abstraction were observed where some flower farms dug trenches allowing water to flow from the lake to the farms (Plate 1.7). The abstraction is unregulated and farms exceed abstraction volumes allocated. Water abstraction pumps are visible inside the Lake for most flower farms and the Olkaria Geothermal plant. Abstraction of water from Rivers Malewa and Gilgil which recharge were also noted. Inter basin water transfer is also present leading to increased pressure on the feeder rivers. The frequent fluctuations in water levels in the lake were blamed to abstraction.

5.1.4 Changes in Human Activities in the Lake Naivasha Basin

Assessment of Landsat satellite images capture between 1986 - 2008 reveal an increase in the area covered by green houses, Naivasha town and open farms. The study also reveals a decline in the vegetation along the Lake's shores. A decline is water quality was also observed and based on the intensity of the blue color. The area occupied by the lake was found to shrink during the study period.

5.1.5 Aquatic Organisms in Lake Naivasha

A clear pattern of reduction in aquatic life population with increasing concentration of contaminants is observed. This indicates that the chemicals have adverse effects on the well being of the organisms. Low densities of aquatic organisms were also recorded in sites receiving discharges from the flower farms. Areas of high turbidity also recorded low

population densities. The highest population of the organisms was found in Lake Oloidien which had the highest dissolved oxygen and an algal boom.

5.1.6 Heavy Metals Concentrations in Water and Sediments of Lake Naivasha

Heavy metals were detected in most samples collected in the lake. Sediments were found to contain high levels of cadmium. The inflow of the metals was thought to originate from geochemical processes in the catchment and human activities. Traffic pollution along inflowing rivers, municipal council and flower farms all contribute to the heavy metal loads in the lake. The most important source was thought to be geochemical processes due to inflow of sediments and other suspended materials from upper catchment. Bio-concentration and bio-magnifications of the metals was observed in fish though this was low compared to levels reported elsewhere due to the fact that the metals were in most cases particulate bound thus not bio-available.

The study shows that the Lake bed is contaminated with cadmium, moderately contaminated with Ni and Pb, but not contaminated with Zn and Cu. Tomlinson's Pollution Load Index (PLI) values indicate that the effluent discharge from the Naivasha Municipal council and River Malewa are important sources of heavy metal contamination in the Lake.

5.1.7 Heavy Metals Concentrations in Fish of Lake Naivasha

Heavy metals were detected in all the three fish species analyzed. There was no clear pattern in the order of increase in the various species. However Nickel was most predominant followed by zinc, lead copper and cadmium respectively. The species were significant

differences in the heavy metal contents between fish species. The order of accumulation of the metals in fish is *C. Spectacularlus* > *C. carpio* > *O. leucostictus.*

5.1.8 Pesticides Residues in Lake Naivasha

The study shows that most pesticides were detected in water and fish samples from the lake. The measured concentrations were however low and compared to the acceptable levels in food and freshwater ecosystems respectively. There is need however to treat wastewaters before discharge into the canals to remove the pesticides. The occurrences of the pesticides indicate recent use in the catchment. Some banned organochlorine pesticides such as aldrin, dieldrin, endrin, heptachlor, lindane and DDT were detected in the basin, this calls for increased monitoring and surveillance to determine the actual sources. The mean values and ranges of residues found in fish ware below the FAO / WHO maximum acceptable limits in fish and sea food however increased monitoring is recommended to detect any changes.

5.1.9 Dietary Risks Assessment of Consumption of Fish from Lake Naivasha

Dietary risk assessment conducted in the lake from the consumption of fish from the lake reveal that fish is safe for consumption and does not pose any risks to the consumer with respect to *p, p'*- DDT, *p, p'*- DDE, *p, p'*- DDD, methoxychlor, heptachlor and heptachlor epoxide. The water is however, not safe for drinking due to water quality issues such as suspended solids and chemical concentration especially at sites next to discharge canals thus require treatment before use.

5.1.10 Environmental Risks Assessments of Pesticide Residues in Lake Naivasha

The study shows that a modified version of PERPEST can predict the environmental risks of a pesticide accurately. The measured concentrations o methoxychlor have a potential of altering the biodiversity by selectively eliminating some organisms. This is in accordance with the findings of other organochlorine pesticides like endosulfan and lindane. A loss of biodiversity is likely since some organisms are more sensitive to the insecticide than others under the same exposure conditions. Each organism has a specific role in the ecosystem and elimination will lead to loss of functionalities of ecological niche. The study show that crusteceans and insects the groups most at risk. It is thus important that use of such chemicals in the catchment is controlled in order to reduce episodes of washdown into the lake. The current reductions in aquatic organism populations in the lake can be explained through such studies.

The study reveal that fish are less senstive to the measured exposure concentrations compared to other organisms. Massive death of fish during pollution episodes are, however, reported. The study shows that fish deaths will be accompanied by a big loss of lesser organisms which go unnoticed due to their small size or lack of interest in such taxa.

5.2 Recommendations

5.2.1 General Recommendation

The study recommends regular monitoring and surveillance of the pollutants in the basin in order to establish usage and applications of the contaminants in the basin. This will help in detecting pollution episodes before the pollutants enter the lake.

The Naivasha town wastewater treatment plant should also be assessed to determine efficiency in correction of water quality before discharge. Samples should be collected at the discharge point to check compliance with the wastewater discharge quality standards set by NEMA (GoK, 2006).

To check the inflow of pollutants from the catchment area, the papyrus belt and the adjacent areas along the lake and inflowing rivers.

i. Stop farming in the riparian areas of the lake and inflowing rivers.
ii. Regulation of the flower farm sector.
iii. Establishment of water treatment plants in the flower farms and the Municipal council to help correct effluent quality standards.
iv. Introduce integrated pest management to reduce reliance of agrochemicals.
v. To introduce measures to counter the inflow of pollutants.

5.2.2 Recommendation for Further Research

Areas recommended for further research are;

i. Analysis of PCBs in water, fish and sediments in the Lake.
ii. Determination of sources, distribution and concentration plant nutrients nitrogen and phosphates.
iii. Determination of bio-diversity.
iv. Aquarium experiments simulating Lake Naivasha to help understand the fate and dissipation of pollutants in the Lake.
v. Study of pesticides and heavy metals concentrations in fish eating birds.

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