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Organochlorine Pesticides Residues in Lake Naivasha Catchment Water

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ABSTRACT

Lake Naivasha, Kenya, hangs precariously in balance between economic exploitation and biodiversity conservation. There is increasing intensity of horticultural activities around the lake, believed to result in excessive water abstraction and heavy use of agrochemicals. This paper reports the findings of an investigation conducted to determine the extent environmental contamination of 17 organochlorine pesticides including metabolites namely p,p'-DDT, p,p'-DDE, p,p'-DDD, endosulfan I, endosulphan II, endosulphan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, aldrin, dieldrin, methoxychlor, α-HCH, β-HCH, γ-HCH and δ-HCH in 36 water samples collected from Lake Naivasha catchment. Residues of varying magnitude and spatial distribution were detected in the samples. The concentrations of α-HCH varied from 0.013-0.776 µg/l, γ-HCH (0.033-0.419 µg/l), β-HCH (0.004-0.059 µg/l), δ-HCH (<0.010-0.059 µg/l), heptachlor (0.571-7.000 µg/l), heptachlor epoxide (0.005-0.177 µg/l), aldrin (0.0050-0.597 µg/l), dieldrin (0.004-0.765 µg/l), endrin (0.005-0.195 µg/l), endrin aldehyde (0.020-0.256 µg/l) endosulphan I (0.020-0.124 µg/l), endosulphan II (<0.002-0.267 µg/l), endosulphan sulphate (<0.008-0.735 µg/l), p,p'-DDT (0.006-0.197 µg/l), p,p'-DDE (0.030-0.588 µg/l), p,p'-DDD (0.018-0.050 µg/l) and methoxychlor (<0.002-0.891 µg/l), with heptachlor giving the highest overall concentration in most of the sites. The concentration showed wide variations from one sampling site to the other reflecting the socioeconomic diversity around the lake. Total pesticide concentrations in the catchment was in the following order Σheptachlors>Σmethoxychlor>Σaldrins> Σendosulphans>ΣHCHs >ΣDDTs>Σendrins. These results suggest that the occurrence is as a result of use of organoclorine pesticides in the catchment. Concern is therefore raised regarding the possible deleterious effects including endocrine disruption not only in livestock and human population but also wildlife, thus constituting a threat to the ecosystem health around the lake.

Keywords : Lake Naivasha, Organochlorine pesticides residues, water pollution; tropical ecosystems degradation.

I. INTRODUCTION

Lake Naivasha is the second largest fresh water lake in Kenya with an approximate surface area of 100 km2. The lake is next to Naivasha municipality, which is approximately 941 km2. Naivasha is one of Kenya's fastest growing municipalities with a population of about 350,000 people. Lake Naivasha is a shallow basin (mean depth in 2009 < 2 m) with an underground outlet. Its catchments lie in a high altitude of the Gregory Rift Valley with Nyandarua range to the East (4,000 m) and the Mau Escarpment to the West (3,100 m). Mt. Longonot (2,700 m) forms the southern edge of the drainage basin, whereas Eburu (2,700 m) lies on the North-Western edge. The total catchment area is approximately 3,000 km2. The surrounding soils are mainly sediments of the former larger lake and are influenced by the volcanic origins of the basin rocks.

Lake Naivasha is world famous for its rich but uneven biodiversity, with hundreds of bird and plant species, but no native fish.1 Commercial fishery in the lake is basically dependant on exotic species and is currently in severe decline due to overfishing. Exotic fish, such as crayfish introduced in 1970 to diversify the fishery, and carp which appeared in 1999, have completely re-

structured the lake's ecology.2 The lake wetlands formed of papyrus swamps formerly had great significance to the hydrological regime, as habitat for wildlife, stabilizer of the lake's water balance and an important source of raw material for the local economy of the area. Currently papyrus is extinct as an ecosystem service. The lake supports diverse economic activities ranging from floriculture, agriculture to commercial fishery. In addition, the lake water is used for Olkaria geothermal energy generation plant, which is the biggest geothermal power generation plant in Africa.

Lake Naivasha ecosystem is highly sensitive to climatic change. The water level has changed by over 12 meters in the past 100 years,3 fluctuating from one year to the other and within years.4 The main sources of surface inflow are two perennial rivers, the Malewa River and Gilgil River (Figure 1) discharging 80% and 20% respectively. Both rivers have a floodplain and a delta where they enter the lake from the North. The lake waters are fresh, indicative of an outlet, otherwise the sodic influence of the Rift Valley soils would have caused a soda lake as in the case of the nearby lakes such as Elementaita and Nakuru.

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.5 Previous studies on Lake Naivasha have also reported contamination by heavy metals such as mercury in fish with concentrations ranging from 4.8 to 81.1 ng/g. The levels 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.[6]

Despite the socio-economic and geographical significance of Lake Naivasha, its ecosystem is currently under serious threat due to intensive irrigation, farming, land subdivision, increasing use of agrochemicals and deforestation activities. The growth of the township has also led to increased runoff, siltation and increased nutrients discharge into the lake through inflowing rivers and drainage channels. In addition, the southern part of the lake has intensive agricultural practices which are concentrated on the riparian land ranging from large horticultural, floricultural and vegetable farms. These draw enormous quantities of water from the lake for irrigation. The actual amount of water abstracted is not properly regulated nor documented. A conglomeration of all these factors constitute the main challenges facing the Lake Naivasha management authority in trying to balance between economic exploitation and biodiversity conservation. This paper reports the findings of an investigation carried out to determine the occurrence and distribution of organochlorine pesticide residues in Lake Naivasha drainage basin, in an attempt to delineate chemical challenges facing the Lake Naivasha ecosystem.

II. MATERIALS AND METHODS

A. Study Area

Water samples were collected from sites within Lake Naivasha, Crescent Lake, Oloidien Lake and along River Malewa, Turasha River and effluent discharge channels draining the flower farms. A total of twelve sites were considered namely: site 1 (Middle of Crescent Lake), site 2 (Water canal at Crescent Lake), site 3 (Crescent Lake Public Beach), site 4 (River Malewa Bridge), site 5 (River Turasha Bridge), site 6 (Flower farms effluent drain), site 7 (Lake Oloidien), site 8 (Naivasha Municipal sewage discharge point), site 9 (Lake Naivasha western shoreline), site 10 (River Malewa discharge area), site 11 (Middle of Lake Naivasha) and site 12 (Effluent discharge point for flower farms). Figure 1 below shows the location of different sampling sites.

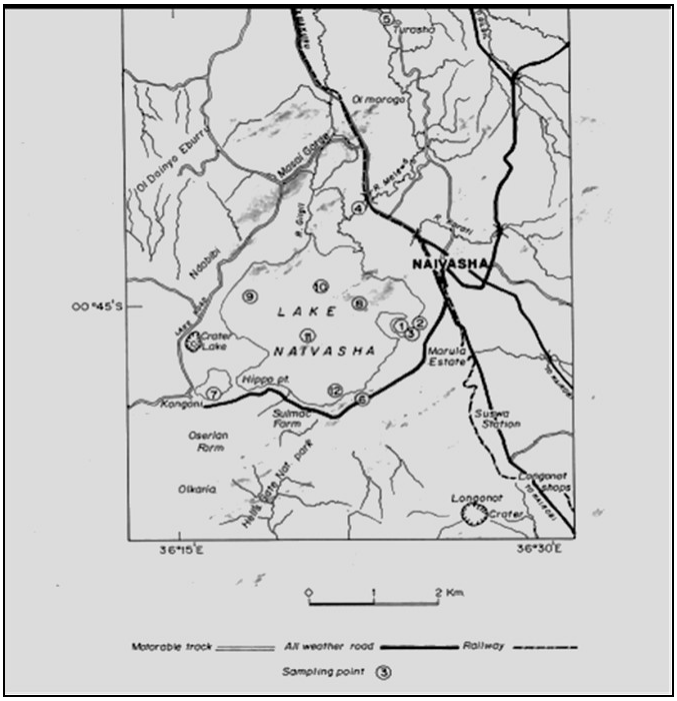

Figure 1: Map of sampling sites

B. Field Sampling

Water samples were collected by grab method in amber glass bottles, in triplicate from each sampling site. Each sample was preserved by spiking with mercuric chloride solution. The samples were labelled according to the sites and replicate number and placed in Coleman cooler boxes containing ice cubes for transportation to the laboratory where they were immediately extracted into organic solvent and stored in a refrigerator at 4 ^{0}C prior to cleanup and analysis.

C. Sample extraction and cleanup:

Solvent-solvent extraction was applied to all water samples. Dichloromethane was used as extracting solvent. 1 L of sample was transferred into 2 L separatory funnel and treated with 50 ml of phosphate buffer (pH 7) and mixed. pH was adjusted to neutral using drops of 0.1 N HCl or 0.1 N NaOH. Analytical grade sodium chloride (100 g) was added to the water and mixed thoroughly to salt out pesticides, after which extraction was effected by shaking the sample with three 60 ml portions of HPLC grade dichloromethane. The organic layer was collected and extraction repeated three times with 60 ml portions of dichloromethane and the extracts combined. The combined extract for each sample was treated with 2 ml HPLC isooctane as a keeper and concentrated to 3 ml using LABCONCO rotary evaporator at 40 ^{0}C. The extract was further reduced to 1 ml under a stream of white spot nitrogen and cleaned by eluting through 15 g deactivated alumina, packed in 25 cm long x 1.5 cm internal diameter glass column laced with 1 cm of activated anhydrous sodium sulphate at the bottom and top of alumina layer to retain any moisture present. The column was conditioned by eluting through 15 ml of n-hexane before transferring sample. The sample was eluted with 165 ml of n-hexane, concentrated to 3 ml using a rotary evaporator and reduced further to 0.5 ml under a stream of nitrogen. The reduced sample was spiked with 100 µl of PCB 198 as reference standard before analysis.

D. Sample Analysis

Sample analysis was done using Aglent 6890N equipped with micro Electron Capture Detector. 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 programme was used starting from 90 ^{0}C (hold time of 3 minutes), increased to 215 ^{0}C at 8 ^{0}C/min (hold time of 25 min), then increased to 270 ^{0}C at 5 ^{0}C/min (hold time of 5.37 min) and finally ramped to 275 ^{0}C at 5 ^{0}C/min (hold time of 18.63 min). The carrier gas was high purity helium (99.995%), while white spot nitrogen was used as a makeup gas. Quantification followed external calibration method using high purity pesticide reference standards mixture purchased from Ultra Scientific USA.

E. QA and QC

The QA&QC parameters followed analysis of replicate samples, blank samples, spike recoveries, syringe standards and reference analytic standards. All sampling, extraction and analyses were conducted in triplicate. The samples were spiked with PCB 155 prior to extraction and PCB 198 as a syringe standard at the time of analysis to correct for detector fluctuations in responses. Recovery tests were carried out using the reference pesticide standards to determine the performance of the method. Field blanks and method blanks were incorporated to check for contamination during sampling, transportation and laboratory preparation procedures.

II. RESULTS AND DISCUSSION

A. Pesticide Residue Levels

The results of pesticides and metabolites analyzed showed that the sites strongly influenced by diverse socio-economic activities and environmental factors in the area. The mean concentrations of each pesticide detected at 12 sites are summarized in Table 1. Heptachlor had the highest concentrations in most of the sites compared to all other pesticides. Other compounds detected at high concentrations include aldrin, *p,p'*-DDE, γ-HCH, methoxychlor, endrin aldehyde, endosulphan sulphate and *p,p'*-DDT. δ-HCH was the least frequent compared to the other 15 compounds analysed.

Table 1: Mean concentrations of pesticide residues in water from different sites along the Lake Naivasha catchment (µg/L) (mean±standard deviation)

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12
alpha HCH	0.78±0.12	0.41±0.01	0.038±0.01	0.10±0.03	0.09±0.03	0.12±0.03	0.15±0.04	0.03±0.02	0.03±0.02	0.03±0.01	0.06±0.02	0.14±0.01
gamma HCH	0.42±0.03	0.18±0.08	0.06±0.01	0.07±0.02	0.03±0.01	0.07±0.01	0.05±0.01	0.05±0.01	0.04±0.01	0.05±0.01	0.05±0.02	0.03±0.01
beta HCH	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.06±0.04	<0.002	<0.002	<0.002	<0.002	<0.002
delta HCH	<0.005	0.03±0.00	0.04±0.02	0.03±0.01	0.03±0.02	0.04±0.01	0.02±0.01	0.03±0.01	0.03±0.01	0.03±0.02	0.02±0.00	0.03±0.02
Heptachlor	7.00±1.41	4.10±0.85	4.55±0.16	0.84±0.05	5.88±1.25	1.23±0.05	1.14±0.19	0.46±0.05	0.83±0.35	1.86±0.05	0.74±0.08	0.57±0.04
Heptachlor epoxide	0.10±0.08	0.100±0.01	0.08±0.01	0.16±0.02	0.09±0.01	0.09±0.01	0.06±0.02	0.09±0.03	0.05±0.01	0.05±0.00	0.18±0.10	0.05±0.02
Aldrin	0.60±0.14	0.17±0.05	0.23±0.11	0.13±0.10	0.19±0.01	0.18±0.09	0.06±0.02	0.09±0.02	0.06±0.03	0.05±0.01	0.12±0.079	0.51±0.06
Dieldrin	0.22±0.03	0.16±0.04	0.08±0.01	0.06±0.03	0.77±0.09	0.75±0.21	0.07±0.02	0.11±0.02	0.05±0.01	0.05±0.01	0.06±0.02	0.04±0.00
Endrin	0.20±0.01	0.20±0.12	0.09±0.01	0.08±0.05	0.13±0.01	0.14±0.06	0.06±0.02	0.08±0.01	0.05±0.01	0.05±0.00	0.11±0.07	0.06±0.04
Endrin aldehyde	0.11±0.02	0.04±0.01	4.52±0.02	0.03±0.01	0.05±0.01	0.26±0.05	0.02±0.01	0.03±0.01	0.02±0.00	0.02±0.01	0.04±0.02	0.02±0.01
Endosulpha I	0.12±0.03	0.06±0.01	0.05±0.01	0.03±0.01	0.08±0.02	0.05±0.01	0.03±0.01	0.04±0.01	0.02±0.01	0.02 ±0.01	0.02±0.00	0.02±0.00
Endosulphan II	<0.002	0.09±0.03	0.06±0.02	0.03±0.02	0.15±0.03	0.27±0.08	0.05±0.01	0.06±0.02	0.04±0.01	0.05±0.00	0.12±0.02	0.03±0.01
Endosulphan sulphate	<0.002	0.19±0.06	0.04±0.02	0.01±0.00	1.01±0.02	0.74±0.13	0.09±0.04	0.44±0.27	0.02±0.01	0.17±0.07	0.06±0.02	0.05±0.04
p,p'-DDT	0.20±0.02	0.05±0.03	0.19±0.07	0.08± 0.04	0.05± 0.02	0.02±0.01	0.04±0.03	0.03±0.02	<0.002	0.02±0.01	0.03±0.01	0.02±0.01
p,p'-DDE	0.59±0.02	0.05±0.01	0.24±0.09	0.08±0.06	0.11±0.02	0.23±0.10	0.10±0.05	0.03±0.01	0.06±0.02	0.04±0.02	0.04±0.01	0.03±0.00
p,p'-DDD	0.05±0.01	0.04±0.01	0.04±0.02	0.02±0.01	0.05±0.01	0.04±0.01	0.03±0.01	0.03±0.02	0.02±0.00	0.02±0.01	0.04±0.02	0.02±0.00
Methoxyclor	<0.002	0.03±0.01	0.02±0.01	0.30±0.06	0.50±0.01	1.92±0.10	0.02±0.01	0.03±0.02	0.89±0.08	0.45±0.20	0.23±0.05	0.02±0.01

Site 1: Middle of Crescent Lake; **Site 2**: Water canal at Crescent Lake; **Site 3**: Crescent Lake Public Beach; **Site 4**: River Malewa Bridge; **Site 5**: River Turusha Bridge; **Site 6**: Flower farms effluent drain; **Site 7**: Lake Oloidien; **Site 8**: Naivasha Municipal sewage discharge point; **Site 9**: Lake Naivasha western shoreline; **Site 10**: River Malewa discharge area; **Site 11**: Middle of Lake Naivasha; **Site 12**: Effluent discharge canal for flower farms.

Hexachlorocyclohexane isomers:

γ-HCH and α-HCH were the most dominant HCH isomers detected in the samples in this study. The mean concentrations of HCHs ranged from <0.002-0.776 µg/l, with the highest concentration of γ-HCH (0.419 µg/l) detected at site 1 followed by site 2 (0.176 µg/l) which is a canal serving as both the water intake and discharge from the flower farms on the eastern side of the lake. Other sites with high concentrations of γ-HCH were 4 (0.069 µg/l), 6 (0.065 µg/l), 3 (0.060 µg/l) and 7 (0.051 µg/l). On the other hand, the highest concentrations of α-HCH were detected at sites 1 (0.777 µg/l), followed by 7 (0.147 µg/l) and 6 (0.117 µg/l). β-HCH had concentrations ranging from <0.002 µg/l to 0.059 µg/l detected at site 7, All other sites had concentrations of β-HCH <0.002 µg/l. δ-HCH concentrations varied from <0.005 to 0.041 µg/l detected in water from site 6.

Heptachlor and heptachlor epoxide:

Heptachlor was one of the most frequent compounds (with 100% presence) and the leading in concentration in most of the sites. The highest concentrations were recorded at sites 1 (7.000 µg/l), 3 (4.553 µg/l) and 2 (4.104 µg/l). Although heptachlor is expected to transform very fast in aqueous media into heptachlor epoxide, the concentrations of this compound were 10 to 100 times higher than the metabolite in most of the sites. Heptachlor epoxide concentrations varied from 0.045.16-0.177µg/l with the highest detected at site 11 followed by sites 4 (0.157 µg/l), 2 (0.100 µg/l) and 1 (0.099 µg/l). Like heptachlor, the metabolite was also detected in 100% of the samples, although sites 10 and 9 showed lower concentrations.

Aldrin and Diedrin:

The concentrations of aldrin in water ranged from 0.063-0.597 µg/l, whereas dieldrin had levels between 0.043 and 0.765 µg/l. The highest concentrations of aldrin were measured at sites 1 (0.579 µg/l), 3 (0.219 µg/l), 5 (0.192 µg/l) and 6 (0.177 µg/l), whereas sites sites 6 (0.765 µg/l) and 5 (0.751 µg/l) had the leading concentrations of dieldrin.

Endrin and endrin aldehyde:

Endrin recorded mean concentrations ranging from 0.047-0.195 µg/l, while endrin aldehyde levels varied from 0.019-0.256 µg/l with the highest concentrations measured at sites 6 and 1 respectively. Over 91% of the sites contained higher concentrations of endrin than endrin aldehyde. The sum endrins measured in the samples was highest at site 6 with concentration of 0.393 µg/l, whereas the lowest concentration was measured at site 12 (0.086 µg/l). Both compounds registered 100% frequency in all the sites investigated. However, the use of this product was banned in Kenya over two decades ago[7] suggesting that presence in environment could be attributed environmental persistence.

Endosulphans:

The concentrations of endosulphan isomers were among the highest in the samples with mean concentrations ranging from <0.002 µg/l-1.013 µg/l. Endosulphan sulphate had the leading concentration in most of the sites followed by endosulphan II and I. Individual isomers had concentrations ranging from 0.021-0.124 µg/l for endosulphan I, <0.002 µg/l -0.267.26 µg/l for endosulphan II, whereas endosulphan sulphate registered concentrations between <0.002 µg/l-1.013 µg/l for endosulphan sulphate. Sites 5 and 6 showed the highest sum endosulphans with concentrations of 1.238 and 1.054 µg/l respectively, showing the possible hot spots contributing to the input of these compounds.

DDTs:

High concentrations of *p,p'*-DDT were detected at sites 1 (0.197 µg/l), 3 (0.191 µg/l) and 4 (0.081 µg/l), whereas the lowest was measured at site 9 situated on the western shoreline on the lake where the impacts of human activities are minimal. Sites 1 and 3 had the highest levels of *p,p'*-DDE, whereas 1 and 11 were leading in *p,p'*-DDD. The results revealed that the eastern edge of Lake Naivasha has the highest input of DDTs with ΣDDTs amounting 0.836 µg/l. Compared to other pesticides, DDTs were the second lowest detected residues in the catchment after the endrins. The high levels of *p,p'*-DDE compared to *p,p'*-DDT implied contamination due to previous use of *p,p'*-DDT. Concentrations of *p,p'*-DDD were generally lower than *p,p'*-DDE except at sites 8 and 11. The mean concentrations of *p,p'*-DDD ranged from 0.022 µg/l to 0.051 µg/l, with the highest measured at site 5 (0.051 µg/l) and 1 (0.051 µg/l) followed by sites 6 and 11 with concentrations of 0.041 µg/l and 0.040 µg/l, respectively. Similar to most of the other pesticides, the levels of DDTs were higher in areas with intense agricultural activities. Calculation of *p,p'*-DDE/*p,p'*-DDT ratios gave 91% of the samples with the ratio greater than 1 implying that most of the DDT detected was due to previous use of the pesticide.

Methoxychlor:

However, the levels of methoxychlor were significantly high in several sites, with site 6 (1.915 µg/l) showing the highest concentration, followed by sites 9 (0.891 µg/l) and 5 (0.499 µg/l). The contrast was observed at sites 1, 2, 3, 7 and 8 where the levels were quite low (with mean concentrations ranging from <0.002 µg/l-0.031 µg/l). Σmethoxychlor ranked the second highest in residue levels compared to other compounds measured in the catchment.

B. Discussion:

Lake Naivasha is facing challenges associated with unsustainable extraction of water for agriculture, horticulture, power generation and urban and domestic water supplies. The ultimate effect is the contribution to the decline in lake water quality as well as the lake levels. The lake is progressively becoming smaller and shallower and at the same time the lake's biodiversity is declining. There are chances of the lake water warming up leading to change in the micro-climate of the lake and encouraging enhanced growth of microscopic algae.

Pesticide residues in lake water samples:

The presence of pesticide residues in the Lake Naivasha water is in agreement with previous studies which reported γ-HCH with concentrations as high as 2 ng/g in fish samples collected from the lake.[8] Detection of pesticides at site 7 situated along Lake Olodien, a salt water lake previously part of Lake Naivasha but cut off due to decreasing lake levels, confirms its high potential of receiving run off from the horticultural areas especially during the long rain season. A similar case was observed in the case of sites 1 situated in the middle of the Crescent Lake and site 3 situated near the horticultural farms on eastern side of Lake Naivasha. The other sites such as 1, 8, 9, 10 and 11 were within the lake and residue levels were characteristically low, with HCH isomers ranging between 0.013-0.116 µg/l, possibly due to dilution by the large masses of water.

Contamination of pesticides residues has been a acandidate of suspecion in Lake Naivasha ecosystem for over a decade, but limited data is avaialble to delineate

this issue. While explaining the potential causes of the decline observed in the pairs of *Haliaeetus vocifer* from 11 to 7 over a period from 1970 to 1997. Some studies attributed the effect to contamination of the lake by agrochemicals leading to breeding failure and decline in availability of prey – coot or fish and loss of feeding opportunity – as the lake became infested with floating alien weeds such as *Salvinia* and *Eichhornia* and the decrease in transparency of lake water caused by eutrophication.[2]

Pesticides residues in the lake samples were generally lower than those detected in samples collected from canals draining the flower farms and the river samples. Of all the pesticides, heptachlor was found to lead in concentration across all the lake sites with the highest detected at sites 1 (7.000 µg/l) and 10 (1.732 µg/l) among the lake sites. Although the residues measured were significantly low and in most of cases below WHO permissible maximum residue levels for drinking water,[9] their longterm impact may be of significance due to high potential of biomagnification through the food chain.

Earlier studies using organisms at higher trophic levels such as birds reported presence of 12 organochlorine pesticide residues namely α-HCH, γ-HCH, β-HCH, aldrin, heptachlor, heptachlorepoxide, endrin, dieldrin, *p,p'*-DDD, *p,p'*-DDE and *p,p'*-DDT in varying concentrations[10] in three different birds species from Lake Nakuru, within the Rift Valley. High prevelance of *p,p'*-DDE (95.5%) and α-HCH (66.4%) was reported. But data for Lake Naivasha is missing.

Pesticide residues in river water samples:

Most of the pesticides detected in the river samples have been reported in other rivers within the country, although at significantly different concentrations than the ones reported in this study. For instance as study on pesticide residues in the drainage basin Lake Victoria reported 10 different organochlorine pesticides namely; α-BHC, β-BHC, lindane, endosulfan, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin and methoxychlor.[11] The levels higher than concentrations measured in the rivers in this study.

Pesticide residues in effluent water samples:

Our investigation reveals high concentrations of most pesticides in canals draining the horticultural farms into the lake. However, analyses of pesticide residues in effluents discharged into the lakes are very rare in the country. Most of the studies in the country have concentrated on parameters related to nutrients such as phosphates, nitrates, BOD and COD levels in effluents.[12,13,14] Heavy metals such as mercury have been considered.[6]

OCPs reported here have high potential of bioaccumulation effects in biota. Further investigation of pesticide residues is required to determine the trend and sources of these pesticides in the catchment. In addition there is need to consider chemicals management issues related to agricultural activities within the lake Naivasha reparian land. The findings of this study, therefore, show the need to regulate and monitor effluents discharged into the lake, and the impacts of socio-economic activities within the catchment.

Sum pesticide residues:

Calculation of the total pesticide concentrations based on related isomer ranked pesticides measured per site and overall in the lake catchment. Heptachlor was the leading in overall concentration with Σheptachlors>Σmethoxychlor>Σaldrins>Σendosulphans > ΣHCHs> ΣDDTs>Σendrins. Although heptachlor was leading in overall pesticide residues in the catchment, analysis of site specific data revealed that this did not apply to all sites. Site 6 and 9 had Σmethoxychlor as the leading compound, whereas Σendoslphans was the highest in site 8 (Table 2). Out of all the sites investigated heptachlor was highest in 75% of sites, followed by methoxychlor with 17% and finally endosulphan leading in 8% of the sites.

Table 2: Sum Concentrations of Parent And Metabolites Residues In Water From Different Sites Within Lake Naivasha Catchments (µg/L) (Sum Conc. ±Standard Deviation)

	ΣHCH	ΣHeptachlors	ΣAldrins	ΣEndrins	ΣEndosulphans	ΣDDTs	Methoxyclor
Site 1	1.20±0.37	7.10±4.88	0.82±0.27	0.31±0.06	0.12±0.07	0.84±0.29	<0.01
Site 2	0.26±0.08	4.20±2.83	0.32±0.01	0.23±0.11	0.34±0.07	0.14±0.01	0.03±0.01
Site 3	0.14±0.02	4.63±3.16	0.30±0.09	0.13±0.03	0.15±0.01	0.47±0.11	0.02±0.00

Site 4	0.20±0.04	0.99±0.48	0.19±0.05	0.11±0.04	0.07±0.01	0.18±0.03	0.30±0.06
Site 5	0.16±0.04	5.97±4.10	0.96±0.41	0.18±0.05	1.24±0.52	0.22±0.04	0.50±0.00
Site 6	0.22±0.05	1.32±0.81	0.93±0.41	0.39±0.08	1.05±0.35	0.35±0.14	1.92±0.10
Site 7	0.28±0.05	1.19±0.76	0.14±0.01	0.08±0.03	0.17±0.03	0.16±0.04	0.02±0.00
Site 8	0.11±0.02	0.55±0.26	0.20±0.01	0.11±0.04	0.55±0.23	0.08±0.01	0.03±0.01
Site 9	0.11±0.02	0.88±0.05	0.12±0.01	0.08±0.02	0.08±0.01	0.08±0.01	0.89±0.09
Site 10	0.10±0.02	1.90±1.28	0.10±0.01	0.07±0.02	0.24±0.08	0.09±0.01	0.45±0.20
Site 11	0.14±0.03	0.92±0.40	0.17±0.04	0.15±0.05	0.20±0.05	0.10±0.01	0.23±0.05
Site 12	0.08±0.01	0.62±0.37	0.11±0.02	0.09±0.03	0.10±0.07	0.07±0.01	0.22±0.02

site 1*: Middle of Crescent Lake;* ***Site 2****: Water canal at Crescent Lake;* ***Site 3****: Crescent Lake Public Beach;* ***Site 4****: River Malewa Bridge;* ***Site 5****: River Turusha Bridge;* ***Site 6****: Flower farms effluent drain;* ***Site 7****: Lake Oloidien;* ***Site 8****: Naivasha Municipal sewage discharge point;* ***Site 9****: Lake Naivasha western shoreline;* ***Site 10****: River Malewa discharge area;* ***Site 11****: Middle of Lake Naivasha;* ***Site 12****: Effluent discharge canal for flower farms.*

ΣHCH = α-HCH + β-HCH + γ-HCH + δ-HCH; ΣHeptachlors = Heptachlor + Heptachlor epoxide; ΣAldrins = Aldrin + Dieldrin; ΣEndrins = Endrin + endrin aldehyde; ΣEndosulphans = Endosulphan I +Endosulphan II + Endosulphan sulphate; ΣDTTs = pp-DDT + pp-DDE+pp-DDD

Frequency of Pesticides Detected:

Despite the low concentrations of most of the compounds investigated in the catchment, high frequencies were recorded for most pesticides including the metabolites. Out of the 16 compounds detected, 100% frequecy was recorded for heptachlor, α-HCH, γ-HCH, heptachlor epoxide, aldrin, dieldrin, endrin, endrin aldehyde, endosulphan I, *p,p'*-DDT and *p,p'*-DDD. On the other hand, *p,p'*-DDT, methoxychlor, endosulphan II, δ-HCH and endosulphan sulphate were detected in 91.6% of the samples. β–HCH was the least frequent with 8.3% detection in all the samples screened. Variation in frequencies of different compounds was attributed to environmental factors controlling transpformation and transport processes as well as the extent of use.

Persistence implications of residue levels in the catchment:

Calculation of the ratio of the parent compound/metabolite has been used in the past to explain whether the residues detected are attributable to current or previous use of pesticides[15]. Usually ratios >1 would imply resent application whereas ratios <1 are attributed to previous use. Similar calculations using residues measured in this study showed that the ratio of *p,p'*-DDT/*p,p'*-DDE >1 occured in one site only, hence the presence of this compound was mainly attributed to previous use. Lindane, on the other hand, is known to undergo transformation into a more environmentally stable isomer α-HCH or β-HCH which is more bio-accumulative. But it can also be transformed into more volatile compounds such as γ-pentachlorocyclohex-1-ene, γ-3,4,5,6 -tetrachlorocyclohex-1-ene, α-HCH, β-HCH and δ-HCH.[16,17,18] Therefore, the ration of γ-HCH/α-HCH (one of the main transformation products) can be used to predict recent application of lindane which is associated with γ -HCH>α-HCH. The study revealed γ -HCH/ α -HCH >1 in 50% of the sites, which could be attributed to previous use of lindane (since lindane constitutes >90% γ-HCH), except sites 2 and 12 which had values γ -HCH/α-HCH >2. Similarly, occurrence of aldrin/dieldrin>1 was found in 66.67% of the sites, endrin/endrin aldehyde>1 (91%) and endosulphan I/endosulphan sulphate>1 (33.3%) (Table 3).

Table 3: Ratios of parent compound against metabolite (parent compound/metabolite)

Ratios	Site1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12
γ-HCH/α-HCH	0.54	4.33	1.61	0.66	0.37	0.56	0.35	1.60	1.14	1.04	0.82	2.43
Aldrin/dieldrin	2.74	1.05	2.62	2.22	0.25	0.24	0.87	0.82	1.15	1.05	2.05	1.48
DDT/DDE	0.34	0.87	0.80	1.05	0.47	0.08	0.40	0.87	0.11	0.56	0.66	0.38
Heptachlor/Heptachlor epoxide	4.95	4.83	2.83	15.79	4.72	26.46	5.88	9.74	2.38	3.49	9.39	14.10

Endrin/Endrin aldehyde	1.69	5.07	1.98	2.80	2.52	0.54	2.92	2.57	2.31	2.46	2.80	2.54
EndosulphanI/Endosulphan sulphate	x	0.31	1.07	2.74	0.08	0.07	0.32	0.10	1.45	0.12	0.34	0.42

***Site 1**: Middle of Crescent Lake; **Site 2**: Water canal at Crescent Lake; **Site 3**: Crescent Lake Public Beach; **Site 4**: River Malewa Bridge; **Site 5**: River Turusha Bridge; **Site 6**: Flower farms effluent drain; **Site 7**: Lake Oloidien; **Site 8**: Naivasha Municipal sewage discharge point; **Site 9**: Lake Naivasha western shoreline; **Site 10**: River Malewa discharge area; **Site 11**: Middle of Lake Naivasha; **Site 12**: Effluent discharge canal for flower farms*

This study has shown that several peristent organic pollutant pesticides occur in detectable quantities in Lake Naivasha catchment. The actual source could not be predicted conclusively due to the fact that samples were collected within a short period of time. However, several pesticides showed higher concentrations in the sites close to areas with intense agricultural activities on the reparian land around the lake and rivers.

Although the pesticide residues detected in water samples from Lake Naivasha had considerably low concentration compared to others lakes, rivers and marine waters previously reported[19,20,21,22] the bioaccumulative properties of these chemicals allow them to build up in the higher trophic levels and causing high risk to human and other animals. Therefore consideration of other matrices such as fish, prey birds, sediments and benthic organisms can provide further information on the levels of these pesticides in the food chain.

A number of additional matrices such as sediment, fish, and birds of prey around the lake, for example, African fish eagles (*Haliaeetus vocifer*) could be sampled for anaysis of pesticide residues. Birds being at the top of the trophic level can be used as good indicators of the environmental health due to amplication of the contaminants through biomagnification. A number of studies have used prey birds in the past as indicators of pollution.[23] Around Lake Naivasha there are over 100 families of *Haliaeetus vocifer*[2] that directly depend on the lake fisheries for daily food and would make suitable indicators of pesticide pollution especially the hydrophobic and peristent organic pesticides. Some of the pesticides such as *p,p'*-DDT, *p,p'*-DDE, γ-HCH, endosulfan, dieldrin and aldrin have been reported before in fish samples from the lake,[8] no data exists about organisms higher in the trophic level.

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