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Spatial Distribution and Temporal Trend in Concentration of Carbofuran, Diazinon and Chlorpyrifos Ethyl Residues in Sediment and Water in Lake Naivasha, Kenya

Peter O. Otieno · Karl-Werner Schramm · Gerd Pfister · Joseph O. Lalah · Stephen O. Ojwach · Munir Virani

Abstract Chlorpyrifos ethyl was found to be widely distributed in water and sediment in Lake Naivasha. Higher levels were reported in sediment (11.2–30.0 ng g^{-1} dry weight (dw) in wet season than in dry season (4.7–17.4 ng g^{-1} dw). The mean concentration of chlorpyrifos ethyl in water in wet season ranged between 8.8 and 26.6 µg L^{-1} and decreased to between below detection limit to 14.0 µg L^{-1} in dry season. On average, higher concentrations of chlorpyrifos ethyl were observed in sediment than water samples. Statistical analysis revealed a significant difference in concentration between the seasons, and a significant interaction between seasons and mean concentrations at $p \leq 0.05$. However, levels of diazinon and carbofuran were below the detection limit in all the samples analyzed. Notably, levels of chlorpyrifos ethyl were higher than the maximum allowable limits (0.1 µg L^{-1}) recommended by European Union for drinking water and general water quality criterion for protection of freshwater water organisms (0.083 µg L^{-1}).

Keywords Lake Naivasha · Pesticides · Horticultural farming · Water · Sediment

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Pesticides are useful in the agricultural production and their application is reported to increase agricultural output as they protect crops from a variety of pests. Studies report that horticultural farms located in Lake Naivasha basin apply huge amounts of pesticides in the farms to raise their yields (Mitoko-Ohayo 1997). Organophosphates (OPs) and carbamates (CBs) are more often used especially, the moderately persistent and acutely toxic carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranylmethylcarbamates), diazinon (O,O-diethyl-O-(2-isopropyl-6-methyl-4-pyrimidinyl)phosphate) and chlorpyrifos ethyl (O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate (Gitahi et al. 2002; Mitoko-Ohayo 1997). Pesticides generally enter the environment through application as an insecticide/acaricide and through a range of transport mechanism and agricultural run-off, the residues find their way into ground and surface waters, and in sediment (Byer et al. 2011). Discharge of agrochemical effluent into the lake through drainage water and agricultural runoff is often documented as a pathway for chemical pollution to surface waters (Huber et al. 2000). Such processes results into increased contaminants exposure to human and aquatic life as well as reduction in water quality (Byer et al. 2011). In general, the contamination is compounded by the rainfall intensity and pattern, which have significant influence on the

distribution, fate, and bioavailability as well as toxicity of chemical contaminants in the environment (Noyes et al. 2009). Based on the partition coefficient of the pesticide, the residues generally remain dissolved in the water column or are adsorbed onto the suspended particulate matter, and ultimately settle as sediment at the bottom of the lake (Tomlin 2006). Consequently, sediment becomes a sink to the acutely toxic pesticide residues from where they remain a potential risk to the aquatic life, human and wildlife through direct toxicity. Scientific evidence has showed that extensive use of chlorpyrifos ethyl and diazinon adjacent to surface waters as observed in the area of study can cause acute toxicity to aquatic organism and other sensitive invertebrates at a nominal water concentration range of 0.035–1.1 $\mu g\ L^{-1}$ (Odenkirchen and Eisler 1988). The concern is worsened by the varied half life of these pesticides in water and sediment that ranges between 14 and 120 days but can last as many as 365 days depending on climatic conditions and other parameters (Howard 1991). Chlorpyrifos ethyl for example, has been detected in different sediment samples in tropical marine environment resulting into its inclusion in different priority list of compounds to be determined in water (Readman et al. 1992). In California for example, widespread detection of chlorpyrifos ethyl and diazinon in the surface waters and its associated toxicity to aquatic microinverterbrates *Ceriodaphnia dubia* have been reported and necessitated continuous monitoring program (Sullivan et al. 2007). Recent studies have also documented that humans are similarly affected by OPs and CBs and cases of impaired neurological development, loss

of memory and parkinson's disease due to low dose chronic exposure have been cited (Dhillon 2008).

Lake Naivasha which is located on the floor of Eastern Rift Valley and lies between 0°42′–0°50′S and 36°16′–36°26′E is a shallow basin served by three perennial inflowing rivers namely River Karati, Malewa and Gilgil (Fig. 1) (Gitahi et al. 2002). The lake has a catchment area that stretches to about 4,200 km^2 that is dominantly used for intensive horticultural farming that requires intensive usage of pesticides. The average annual rainfall is 600 mm with a bimodal character in rainfall distribution where long rains come between April and July and short rains between October and December (Harper and Mavuti 2004). However, the pattern is now erratic and long rains have become short and intense leading to raised agricultural runoff that drains enormous amounts of pesticide residues to the lake. The lake's ecological challenges are exacerbated by the rapid expansion of horticultural farms as well as heavy use of agrochemicals.

Despite the reported acute toxicity of OPs and CBs, and extensive usage of these pesticides in Lake Naivasha basin there is lack of quantitative data on their level of contamination in aquatic system. Our study therefore, aimed at determining the spatial distribution and temporal trend in concentration of selected OPs and CBs residues in Lake Naivasha for strict surveillance and as a monitoring strategy. Though levels of organochlorine in aquatic ecosystem of Lake Naivasha have been reported in previous studies (Gitahi et al. 2002), there is no data available on the levels of commonly used chlorpyrifos ethyl, diazinon and

Fig. 1 Study area and sampling sites
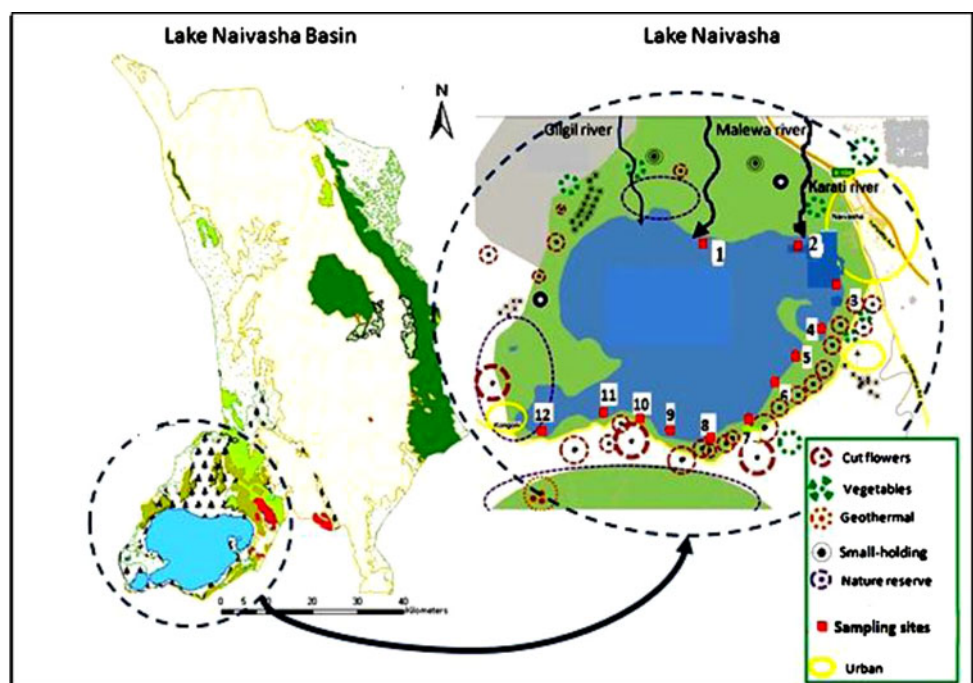
carbofuran in the lake and that was the rationale for this scientific investigation. The other objective was to provide data on relationship between climate-induced ecological changes and aquatic chemical pollution with a view to provide data for ecological risk assessment and recommend sustainable environmental management policies.

Materials and Methods

Water and sediment samples for this study were collected from 12 different sampling sites in Lake Naivasha (see Fig. 1) using targeted-systematic sampling design. Three replicates of both water and sediment samples were collected from the 12 sampling sites during the rainy (June and July, 2010) and dry season (November and December, 2010). Samples were collect twice a month and composited to give single monthly sample for analysis for the 4 months investigated. Sediment samples were collected 5 cm below the lake bed after which unrepresentative materials were removed from the sediment. Samples were then homogenized, wrapped with aluminum foil and kept in a pre-cleaned high density polyethylene plastic. All the samples were frozen in a cool box at 4°C and transported to the Institute of Ecological Chemistry laboratory, Germany for analysis.

Pesticide-grade (>99% purity) chlorpyrifos ethyl, diazinon and carbofuran standard were purchased from Dr Ehrenstorfer, Germany. Additionally, pesticide-grade organic solvents; acetonitrile super gradient HPLC grade from Alfa Aesar, Karlsruhe and analytical grade methanol, n-hexane, ethyl acetate, dichloromethane and anhydrous sodium sulfate from Promochem (Wessel, Germany) were purchased. Bond Elut[TM] and Stata[®] Solid Phase Extraction (SPE) disposable cartridge columns were purchased from Agilent Technologies and Phenomenex, respectively in the USA.

Extraction of water samples was done by first adjusting the pH of 100 mL water samples to 5 with the addition of 0.6 mL acetic acid. Terbuthylazine, chlorpyrifos and propiophenone were introduced into water and sediment samples as internal standards for the extraction and analysis of chlorpyrifos ethyl, diazinon and carbofuran, respectively. Bond-Elut SPE cartridge column fixed with Acrodisc[®] glass fiber prefilter (1 μm glass fiber membrane) and mounted on Supelco Visiprep 12—place vacuum manifold was conditioned before samples were loaded onto to it.

After all samples had run out the column was postwashed by 1 mL solvent mixture of deionized water and methanol (1:1). It was then dried under vacuum for 15 min and analytes eluted twice with 1.5 mL ethyl acetate at a flow rate of 2 mL min^{−1}. The extract was reduced to near dryness in a stream of nitrogen gas before it was re-constituted under vortex in 1 mL acetonitrile–water mixture (7:3) and analyzed by HPLC DAD. For recoveries assays, 100 mL deionized water was fortified with standards and extracted in the same way as the samples. This extraction was performed according modified method used by Schramm et al. (2008).

Air-dried sediment samples (10 g) were placed in Erlenmeyer flask where internal standards were introduced. Afterwards, 50 mL of solvent mixture dichloromethane and n-hexane; (7:3) was added before it was sealed and placed horizontally on an Orbital shaker (280 oscillations min^{−1}) for 1 h. The dichloromethane/n-hexane mixture was suction-filtered through Teflon[®] polytetrafluoroethylene (PTFE) filter and anhydrous sodium sulphate. The sediment was extracted twice more by shaking for 15 min with 50 mL of dichloromethane/n-hexane; (4:1) mixture. The three extracts were pooled in a round-bottomed flask, and reduced to near dryness in the rotary evaporator. The extract was then re-dissolved in 5 mL acetonitrile for clean up. For recovery experiment, 10 g of air-dried samples were fortified with standard then extracted through the same procedure.

Clean up was performed by loading the extract onto a conditioned Strata[TM] SPE cartridge column. The analyte was eluted by 3 mL of ethyl acetate and then reduced to near dryness in a gentle stream of nitrogen gas. The extract was re-dissolved in 1 mL of acetonitrile/water (8:2) mixture and analysed by HPLC DAD.

Analysis was performed by use of Water[®] CapLC[TM] system (Waters Milipore, MA) equipped with autosampler, and UV Photodiode-array detector, linked to PC running Mass Lynx software. The Atlantis D C$_{18}$ (3 μm particle size) analytical column was used with dimensions (150 mm × 0.3 mm i.d) and fitted with a guard column (2.1 mm × 1.8 μm i.d. The analytes was eluted with a gradient solvent system of acetonitrile:water. Qualitative determination was done at 205, 230, and 246 nm for carbofuran, chlorpyrifos ethyl and diazinon, respectively. The analytes were identified by comparing their retention times with the spectra of the standard solutions and quantification was done by use of the response of internal standard. The limit of detection for chlorpyrifos ethyl was 0.11 μg L^{−1}. For carbofuran and diazinon, the LOD was 0.22 μg L^{−1} and 0.30 ng g^{−1}, respectively. In addition, satisfactory mean percent recoveries of between 95.8–112.0% and coefficient of variation of below 13.7% were obtained for both samples.

Statistical analysis was performed using Analyse-it software. All the means were expressed within standard deviation limits. Statistical significant difference between the seasons, and testing of hypothesis was determined by two-way ANOVA at $p \leq 0.05$ (Table 1).

Results and Discussion

Chlorpyrifos ethyl residues were found to be widely distributed in the sediments and water samples in Lake

Naivasha during both wet and dry season (Table 2). However, levels of the residues in sediment were found to be higher during the wet season (11.2–30.1 ng/g dw) than it was in dry season (4.7–17.4 ng/g dw). Significant and consistent decrease in the concentration in sediment matrix was observed from June to December as the intensity of rainfall diminished from an average of 105 mm per month in June to 28 mm per month in December, 2010. Chlorpyrifos ethyl which is among the commonly applied pesticides in the catchment area, generally persist in the soil surface from between 2 weeks to several weeks after application and is often available for run-off for several months after application in the farms due to its low vapor pressure of 1.87×10^{-5} mm Hg at 25°C (Howard 1991). It is expected that during wet seasons the residues are drained to the lake either through water runoff or erosion of soil-bound particles. Since chlorpyrifos ethyl has a moderately higher tendency to adsorb on sediment (log K_{oc} 3.7–4.5) it

will persist in the sediment and may account for the relatively higher levels in sediment than water as observed in this study. Additionally, the pesticides residues in the water column will partition to the suspended organic particulate matter, and ultimately settle as sediment due to its moderately high octanol–water partition coefficient (log K_{ow} 4.7–5.3). Part of the residues will degrade into metabolites through hydrolysis or biotransformation and this can explain the general decrease in concentration in water and sediment observed in Tables 2 and 3. Moreover, high adsorption of chlorpyrifos ethyl in sediment, its relatively low solubility as well as its hydrolysis in the water may further explain the higher levels of chlorpyrifos ethyl in sediment compared to water matrix as seen in Tables 2 and 3.

Owing to the above factors, sediment acts as a sink to chlorpyrifos ethyl, and at the same time provides a source for residual concentration in the water column (Wu and Laird 2004) during dry season when there is no inflow of

Table 1 Percentage mean recoveries in deionized water and control sediment samples

Spiked concentration	Water samples			Sediment samples		
	Mean concentration[a]	% Recovery	% CV	Mean concentration[b]	% Recovery	% CV
0.5	0.48 ± 0.03	95.8 ± 6.2	6.3	0.56 ± 0.03	112.0	5.36
0.8	0.80 ± 0.09	100.4 ± 14.6	11.2	0.86 ± 0.03	106.3	3.48
1.0	1.08 ± 0.09	108.5 ± 9.3	8.3	1.04 ± 0.07	104.0	6.73
2.0	1.95 ± 0.23	97.5 ± 4.6	11.8	2.19 ± 0.07	109.5	13.7
Mean		101.1 ± 7.3	9.4		108.0 ± 3.4	7.32

[a] Concentration in $\mu g \ L^{-1}$

[b] Concentration (ng g^{-1}) ± standard deviation of sediment samples (dry weight). % CV represents percentage coefficient of variation, n = 4

Table 2 Concentration (mean ± SD) of chlorpyrifos ethyl in sediment samples during rainy and dry season

	Sediment samples			
	Wet season		Dry season	
Sites	105 mm month^{-1} June, 2010	92 mm month^{-1} July, 2010	23 mm month^{-1} November, 2010	18 mm month^{-1} December, 2010
1	30.1 ± 3.1	28.8 ± 2.2	9.6 ± 2.0	12.5 ± 0.6
2	27.2 ± 2.4	28.0 ± 2.1	17.4 ± 1.3	16.0 ± 1.3
3	28.7 ± 2.8	30.0 ± 0.6	16.8 ± 0.9	12.4 ± 0.1
4	24.3 ± 1.6	19.5 ± 1.3	4.7 ± 0.8	7.1 ± 1.4
5	22.3 ± 2.3	21.1 ± 1.0	13.0 ± 1.6	11.7 ± 0.3
6	26.6 ± 1.1	21.3 ± 1.2	14.2 ± 2.1	11.5 ± 1.8
7	18.9 ± 1.6	22.4 ± 1.3	7.2 ± 0.4	6.6 ± 0.9
8	13.8 ± 1.1	11.5 ± 0.6	11.9 ± 1.3	9.8 ± 1.1
9	13.6 ± 1.9	11.2 ± 1.0	9.2 ± 1.3	8.3 ± 0.4
10	21.1 ± 2.2	18.7 ± 2.1	13.8 ± 2.1	7.9 ± 0.4
11	22.2 ± 3.4	19.4 ± 0.5	13.2 ± 2.2	9.6 ± 0.9
12	18.0 ± 2.6	17.5 ± 0.6	14.1 ± 2.4	9.6 ± 0.1
Mean	22.2 ± 5.5	21.0 ± 6.2	12.1 ± 4.4	10.3 ± 2.7
Mean for seasons	21.6		11.2	
LSD ($p \leq 0.05$)	0.6		0.8	

LSD least significant difference between concentrations in wet and dry season, *sd* standard deviation, n = 3

Carbofuran and diazinon were bdl (LOD = 0. 22 $\mu g \ L^{-1}$ and 0.30 ng g^{-1})

Significant difference between seasons; F = 38.44, $p < 0.0001$ at $p \leq 0.05$

Significant interaction between seasons and concentrations; F = 58.67, $p < 0.0001$ at $p \leq 0.05$

runoff. Consequently, monitoring levels is important since the presence of chlorpyrifos ethyl in sediment is a potential risk to aquatic biota especially the sensitive invertebrates through direct toxicity and bioaccumulation.

Incidentally, the highest concentration of chlorpyrifos ethyl was found at the mouth of River Malewa, which could be due to inflow of soil-bound chlorpyrifos ethyl residues from upstream. The residue levels obtained from other sampling sites in the study area had no consistent trend or relationship to one another which could be due to haphazard entry of surface runoff to the lake at different points.

The results of this study were found to be consistent with earlier results obtained by Bailey et al. (2000), where chlorpyrifos ethyl was detected in a range of between 21.0 and 85.0 ng g^{-1} dw in muddy bank during wet season and lower levels of between 2.4 and 47.5 ng g^{-1} dw in dry period.

More importantly, statistical analysis revealed a significant difference at $p \leq 0.05$ between levels in the two seasons, which is a demonstration that climate-induced rainfall had an influence on chlorpyrifos ethyl residue contamination. The observation is further supported by significant interaction between the concentration and seasons (F = 58.67) at $p \leq 0.05$ obtained from the statistical analysis. The higher concentration recorded during rainy season may have been due to increased agricultural runoff, which discharged huge amounts of applied pesticides residues into the lake. On the contrary, lower mean concentration of pesticides was observed in November and December when there was low rainfall levels and runoff.

Decrease in concentration could have been due to reduced pesticide loses to surface waters and sediment.

For water samples, the average concentration of chlorpyrifos ethyl residues ranged between 8.8 an 26.6 µg L^{-1} in the wet season but decreased significantly to between bdl and 14.0 µg L^{-1} in the dry season (Table 3). Higher concentration of chlorpyrifos ethyl was reported in the wet season (Table 3) possibly due to the influence of climate-induced ecological changes, particularly increase in average rainfall. This resulted into raised volume of run-off during this period and the drainage of lowly soluble chlorpyrifos ethyl residues into the lake. Although chlorpyrifos ethyl is slightly soluble in water, it was evident from this study that an increased amount of rainfall significantly elevated chlorpyrifos ethyl residue contamination in water (Table 3). Despite reported low solubility of chlorpyrifos ethyl in water, it has been suggested that certain amount of it is generally lost into surface water through erosion of pesticide-bound soil particles (Bloomfield et al. 2006) during intense rainfall. Therefore, loss through runoff and soil erosion is the most likely route of transport of the residues from the agricultural field to the surface waters.

Results obtained in this study suggest that considerable amount of chlorpyrifos ethyl was drained into the lake during the wet season, and were subsequently adsorbed on the suspended particulate matter which ultimately settled to the bottom of the lake as sediment. This observation is consistent with a study conducted by Vu et al. (2006) which reported that an increase in rainfall greater than 10 mm per day is enough to increase the levels of pesticide

Table 3 Concentration (mean ± SD) of chlorpyrifos ethyl in water samples during rainy and dry season

| Sites | Water samples | | | |
| | Wet season | | Dry season | |
	105 mm month^{-1} June, 2010	92 mm month^{-1} July, 2010	23 mm month^{-1} November, 2010	18 mm month^{-1} December, 2010
1	25.7 ± 1.1	20.1 ± 1.7	14.0 ± 2.1	11.0 ± 1.2
2	19.0 ± 1.3	17.1 ± 0.2	12.3 ± 0.9	11.5 ± 0.6
3	21.4 ± 2.1	16.8 ± 0.1	8.8 ± 1.8	9.9 ± 0.6
4	11.2 ± 1.9	14.9 ± 0.2	8.9 ± 2.0	6.6 ± 0.7
5	21.6 ± 1.3	12.4 ± 0.8	11.7 ± 1.9	7.6 ± 1.3
6	14.4 ± 0.9	11.1 ± 0.1	10.3 ± 0.8	9.7 ± 0.2
7	13.9 ± 2.2	7.0 ± 0.8	6.0 ± 0.5	4.3 ± 0.5
8	12.5 ± 1.7	7.6 ± 0.1	5.6 ± 0.3	7.5 ± 0.8
9	8.8 ± 1.6	12.8 ± 0.7	9.1 ± 0.8	bdl
11	18.2 ± 1.3	13.6 ± 1.5	8.9 ± 1.6	5.2 ± 1.0
10	26.6 ± 2.7	13.1 ± 1.3	6.7 ± 1.1	8.0 ± 0.7
12	17.7 ± 1.9	13.9 ± 1.1	8.8 ± 1.2	6.1 ± 0.7
Mean	17.6 ± 5.6	14.8 ± 4.0	9.3 ± 2.5	7.9 ± 2.4
Mean for seasons	16.2		8.7	
LSD ($p \leq 0.05$)	1.26		1.2	

LSD least significant difference between concentrations in wet and dry season, n = 3

Carbofuran and diazinon were bdl (LOD = 0. 22 µg L^{-1} and 0.30 ng g^{-1})

Significant difference between seasons; F = 64.29, $p < 0.0001$ at $p \leq 0.05$

Significant interaction between seasons and concentrations; F = 32.42, $p < 0.0001$ at $p \leq 0.05$

residues in the watershed through runoff. This observation is consistent with studies reported by Huber et al. (2000) report, which suggests that surface run-off is often the dominant nonpoint source pathway for pesticide input to surface waters. An extensive monitoring data by USEPA (2011) found chlorpyrifos ethyl at concentration range of between 3.96 and 24 µg L^{-1} in surface water which is consistent to the results obtained in this study. Moreover, Ollevier and Coene (2001) detected chlorpyrifos ethyl in 37.5% of the water samples that was obtained from Lake Victoria in Kenya. In another related study, Moore et al. (2002) observed during a strong rainfall an increase in chlorpyrifos ethyl concentration of 84 ng g^{-1} dw which steadily decreased to 2.6 ng g^{-1} within a period of one and half months. Elevated concentration of the acutely toxic pesticides in aquatic system has the potential to adversely affect aquatic organisms and humans if not properly monitored. Fish kills caused by pesticides residues carried to the pond, streams by runoff have been reported by Kanekar et al. (2004).

Statistical analysis showed that there was significant difference between the two sampling seasons (F = 64.29, $p < 0.0001$ at $p \le 0.05$) with a consistent decrease in concentration from June to December, 2010. A significant interaction was similarly observed between the different sampling seasons and the concentration of the chlorpyrifos ethyl residues which demonstrated the considerable influence of the climate-related ecological changes on residues concentration in water.

In a related study on spatial distribution of OPs on surface water, a similar trend was observed where higher concentrations of OPs in surface water were found is areas which are dominantly agricultural and experience higher rainfall (Gao et al. 2009).

On the contrary, diazinon and carbofuran were found to be below detection limit in all the samples analyzed despite reported heavy application of these pesticides in the study area. Meanwhile, previous studies by Anderson et al. (2003) and Ensminger et al. (2011) detected diazinon in sediment between the range of 0.1–13.1 ng g^{-1} dw in an exclusively agriculture areas. Elsewhere, carbofuran and its metabolites were detected in water sampled from surface waters adjacent to agricultural farms where mean levels of carbofuran of 11–59.2 µg L^{-1} (3-ketocarbofuran) and 11.8–68.0 µg L^{-1} (3-hydrocarbofuran) were reported (Otieno et al. 2010). Levels were below detection limit in the analyzed matrices could be attributed to their volatilization, degradation, hydrolysis, and photolysis in the environmental medium before our sampling.

In conclusion, the study has established that the level of chlorpyrifos ethyl in water and sediment was found to be higher than the maximum allowable limit (0.1 µg L^{-1}) set by European Union and above the water quality criterion for protection of aquatic life (0.083 µg L^{-1}; USA and

0.0035 µg L^{-1} Canada) (USEPA 2011). This is a clear demonstration of the level of contamination and potential risk to aquatic organism and humans who are directly exposed to the contaminated waters. The higher level of chlorpyrifos ethyl contamination could be attributed to the intensive application rate of application of pesticides in the horticultural farms and subsequent high intensity rainfall, which came soon after application. Based on the expected changes in rainfall pattern and frequency as predicted by the IPCC (2007) report, continuous monitoring of the water quality is imperative for purposes of ecological risk assessment and conservation of the surface waters. Chlorpyrifos ethyl is lipophilic in nature based on its partition coefficient and has the potential to partition through the skin of aquatic organism and bioconcentrate in the tissues. Consequently, inadequate screening and monitoring strategies for these pesticides residues in aquatic system may present possible risks to aquatic organisms. Although diazinon and carbofuran were found below detection limits, continuous monitoring is advised as these pesticides are acutely toxic and past studies have revealed that sub chronic and chronic exposure to low concentrations may have adverse effects to non target organisms.

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