



Toxicological & Environmental Chemistry

ISSN: 0277-2248 (Print) 1029-0486 (Online) Journal homepage: https://www.tandfonline.com/loi/gtec20

Monitoring the occurrence and distribution of selected organophosphates and carbamate pesticide residues in the ecosystem of Lake Naivasha, Kenya

P. Otieno, P. Okinda Owuor, J.O. Lalah, G. Pfister & K.-W. Schramm

To cite this article: P. Otieno, P. Okinda Owuor, J.O. Lalah, G. Pfister & K.-W. Schramm (2015) Monitoring the occurrence and distribution of selected organophosphates and carbamate pesticide residues in the ecosystem of Lake Naivasha, Kenya, Toxicological & Environmental Chemistry, 97:1, 51-61, DOI: 10.1080/02772248.2014.942309

To link to this article: https://doi.org/10.1080/02772248.2014.942309



Published online: 07 Aug 2014.

|--|

Submit your article to this journal 🗹

<u>.ht</u>	Article views: 2	218

View related articles



View Crossmark data



Citing articles: 8 View citing articles 🕑



Monitoring the occurrence and distribution of selected organophosphates and carbamate pesticide residues in the ecosystem of Lake Naivasha, Kenya

P. Otieno^{a,b}*, P. Okinda Owuor^a, J.O. Lalah^c, G. Pfister^b and K.-W. Schramm^{b,d}

^aDepartment of Chemistry, Maseno University, Maseno, Kenya; ^bHelmholtz Center Munich -German Research Center for Environmental Health (GmbH), Molecular EXposomics (MEX), Neuherberg, Germany; ^cDepartment of Chemical Sciences and Technology, Technical University of Kenya, Nairobi, Kenya; ^dLandnutzung Department fuer Biowissenschaften, Wissenschaftszentrum Weihenstephan fuer Ernaehrung, TUM, Freising, Germany

(Received 21 February 2014; accepted 3 June 2014)

Although use of pesticides is critical in agricultural production, their residues present a potential risk to non-target organisms and lower the quality of surface water. In Kenya for instance, widespread use of pesticides in the catchment of Lake Naivasha, has raised concern over the years due to possible pollution of the lake through discharge of runoff from agricultural fields. In this study, sediment, water, and fish samples were analyzed for selected pesticide residue contamination. Chlorpyrifos-ethyl (CPF) was detected in the range of 2.6-24.9 ng/ml and 6.8-35.8 ng/g dry weight (dw) in water and sediment, respectively. Meanwhile, diazinon was detected in the range of below detection limit (bdl) to 33.3 ng/ml and bdl to 9.3 ng/g dw in water and sediment, respectively. CPF was detected in fish tissues (*Niloticus leucosticus*) in the range of bdl to 8.9 ng/g dw with diazinon and carbofuran not detected in any fish sample. A significant difference was observed between different seasons with wet season recording higher levels. Concentrations detected varied seasonally and on average exceeded the maximum criterion set by European Union. Therefore, data generated in this study are useful in environmental risk assessment and as a baseline in formulation of mitigation measures to protect the lake from pesticides residues pollution.

Keywords: pollution; pesticide; Lake Naivasha; sediment; fish; water column

1. Introduction

Lake Naivasha is located on the floor of the Eastern Rift Valley and is approximately 160 km² in area. Due to factors related to climate change, the nature of agriculture in the lake basin has substantially changed from stockrearing, ranching, and sisal-cultivation to irrigated horticulture that is steadily on the rise at the rate of 2 km² per year (Becht, Odada, and Higgins 2005). The observed change in land use pattern has seen emergence of long period of drought and erratic rainfall pattern and subsequent increase in pest population, distribution and resistance, and intensive application of pesticides (Pesticide Products Control Board (PCPB) 2010).

Following the ban on most organochlorines pesticides due to their toxicity and persistence in the environment, agro-industry world over and especially in Lake Naivasha

^{*}Corresponding author. Email: tudor20082000@yahoo.com

catchment have increasingly relied on organophosphate (OP) and carbamates (CB) which are relatively safe (Mitoko-Ohayo 1997; Orlando, Smalling, and Kuivila 2008). In Lake Naivasha basin, farmers have widely used acutely toxic and moderately persistent OPs and CB particularly carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamates), diazinon (*O*,*O*-diethyl-*O*-(2-isopropyl-6-methyl-pyrimidine-4-yl) phosphate), and chlorpyrifos-ethyl (*O*,*O*-diethyl-*O* (3,5,6-trichloro-2-pyridyl) phosphorothioate) (Mitoko-Ohayo 1997) to manage pests in vegetable and flower farms. However, discharge of waste water from greenhouses and runoff from the adjacent agricultural fields into the lake may contribute to pollution of the lake. Huber, Bach, and Frede (2000) demonstrated in his study that application of these pesticides may result in consistent detection of pesticide residues in ground water, natural surface water, sediment, and marine as well as fresh water organisms. Such levels may pose risk to the environment.

As a result of the magnitude of the application of these pesticides in the catchment of Lake Naivasha and their moderate persistence in the environment, a potential exists for a considerable quantity of these pesticides to flow into lake through uncontrolled discharge of waste water and agricultural runoff. Pesticide pollution of the surface waters poses a significant hazard to aquatic organism, wildlife, and humans if they are exposed to levels of active ingredients that exceed permissible limits (Huber, Bach, and Frede 2000). Chlorpyrifos-ethyl (CPF) for example, is known to be potential endocrine disruptor and easily bioconcentrate in different groups of non-target fish and other aquatic organisms (Tomlin 2006). The objective of the study was to monitor the occurrence of carbofuran, diazinon, and CPF and their levels in sediment water and fish tissues during different seasons. The other objective was to determine if the levels of residues in aquatic ecosystem exceed the set criterion for water quality and protection of aquatic life.

2. Material and methods

2.1. Choice and description of the study area

Lake Naivasha is a shallow basin on the floor of Rift Valley and lies between $0^{\circ}42'$ and $0^{\circ}50'S/36^{\circ}16'$ and $36^{\circ}26'$ E at an altitude of 1890 m above the sea level. The lake has a catchment area that stretches to about 4200 km² and is dominantly used for intensive farming that requires intensive use of pesticides (Becht, Odada, and Higgins 2005). The location of the lake predisposes it to the inflow of pesticide-laden surface runoff from the adjacent agricultural fields thus presenting the risk of pollution.

Water and sediment samples were obtained from 12 sampling sites (Figure 1) in Lake Naivasha using targeted-systematic sampling design. Sampling sites were primarily located 20 m from the lake shore, where runoff drainage from the adjacent agricultural fields enters the lake. Three replicates of water and sediment samples were collected from the same sampling sites, in rainy and in dry season (n = 144) within two years. Sediment samples (100 g) were collected 5 cm below the lake bed from the shallow waters along the shore by use of grab sampler. Seven fish samples (*Niloticus leucosticus*) were also collected from each of the three landing sites namely, Kasarani, Oserian, Sher Karuturi during wet and dry seasons for the two years in order to determine the level of bioconcentration of pesticides (n = 84). All the sample matrices were obtained during the same sampling period. The samples were then kept in a cool box at 4 °C, and transported to the Department of Molecular EXposomics (MEX), German Research Center for Environmental Health (GmbH), Germany, for analysis.

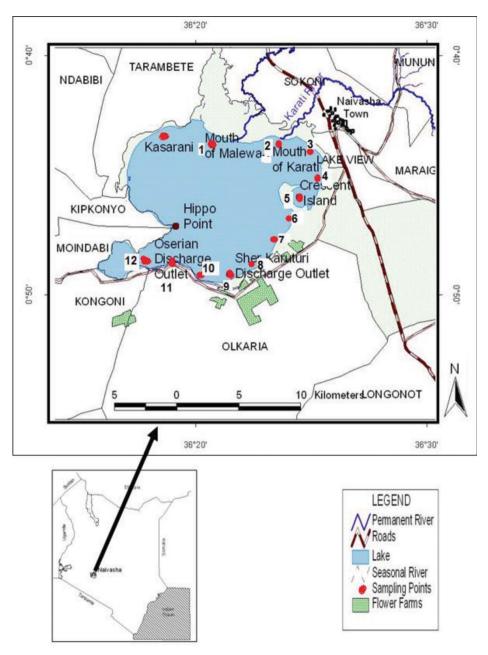


Figure 1. Lake Naivasha: its catchment area and sampling sites.

2.2. Extraction of water samples for high-performance liquid chromatography (HPLC) analysis

Water samples were degassed using ultrasonicator for 5 min and extracted using Solid-Phase Extraction (SPE) cartridge (Bond-ElutTM PPL 200 mg Varian from Agilent Technologies, USA). Afterwards, the cartridge was conditioned by 2 ml ethyl acetate, 2 ml of methanol, and finally by 0.6 ml acidified deionized water in that sequence. The cartridge

was equilibrated by 1.5 ml acidified water before loading samples to the column at a flow rate of 20 ml/min using a vacuum pump. Thereafter, the column was post-washed by 1 ml solvent mixture of deionized water and methanol (1:1) and then dried under vacuum for 15 min. The analyte was eluted with 1.5 ml ethyl acetate twice at a flow rate of 2 ml/min followed by evaporation in a stream of nitrogen gas at 40 °C to near dryness before re-constituted under vortex in 1 ml acetonitrile-water mixture (8:2) for analysis by micro-HPLC diode-array detector (DAD). Extraction was performed according to the method used by Schramm et al. (2008).

2.3. Extraction of sediment samples for HPLC analysis

Sediments samples were air-dried in the laboratory till a constant weight was achieved, then samples were homogenized. Afterwards, 50 ml of solvent mixture dichloromethane and n-hexane (7:3) volume was added before sealing the flask and placing it horizontally on an orbital shaker (280 oscillations/min) for 1 h. The sediment was extracted twice more by shaking for 15 min with 50 ml of dichloromethane and n-hexane; (4:1 volume) mixture. The dichloromethane/n-hexane mixture was suction-filtered through polytetra-fluoroethylene (PTFE) filter and anhydrous sodium sulfate in a Buchner funnel mounted on a round bottomed flask. The three extracts were pooled in a round bottom flask and reduced to near dryness in the rotary evaporator. The residue was re-dissolved in 5 ml acetonitrile. Clean-up was done by use of the StrataTM SPE cartridge obtained from phenomenex, USA followed by micro-HPLC-DAD analysis. Extraction and analysis was done according to the modified method used by Konda and Pásztor (2001).

2.4. Extraction of fish tissues for HPLC analysis

Edible fish muscle and gills were collected from Lake Naivasha during the rainy and dry season and homogenized using a grinder before extracted by the use of matrix solid phase dispersion method. Two grams of C₁₈ bonded-phase solid support from Macherey-Nagel, Germany was placed in a glass mortar and 2.0 g of fish muscles added on it. Additional 2 g of anhydrous sodium sulfate was placed on the mixture followed by addition of terbuthylazine as internal standard. The mixture was allowed to stand for 5 min before blending manually for 3 min. The resultant homogeneous C_{18} and tissue matrix was transferred into previously prepared 10 ml syringe barrel that contained a filter disk. Two additional filter paper discs were placed on top of the column head on top of the sample and the column compressed with a syringe plunger. Ten ml solvent mixture of dichloromethane and n-hexane (1:1) was added to elute the analyte. The extract was re-dissolved in a 5 ml dichloromethane/ n-hexane (1:1) mixture, and the clean-up was performed by the use of 2 g silica as a solidphase extraction sorbent. Silica gel conditioned with 10% water has the capacity to retain fat than florisil or alumina thereby eliminating fat as potential interference matrix (Barker 2007). The analyte was eluted using 10 ml of ethyl acetate and then evaporated to dryness under a mild stream of nitrogen at 40 °C. The residue was re-constituted in 1 ml acetonitrile and transferred to HPLC vial for analysis by micro-HPLC DAD at 230 nm wavelength. The extraction was done according to the method used by Barker (2007).

2.5. Quality assurance and quality control

Pesticides concentrations were validated against a comprehensive set of performancebased quality control criteria including field and laboratory blanks, replicate samples, and matrix spikes.

Item	Matrix	CPF	Diazinon	Carbofuran
MDL	Sediment (ng/g dw)	0.15	0.19	0.14
	Water (ng/ml)	0.07	0.10	0.07
	Fish (ng/g dw)	0.43	0.54	0.63
LOD	Sediment (ng/g dw)	0.23	0.30	0.22
	Water (ng/ml)	0.11	0.14	0.11
	Fish (ng/g dw)	0.66	0.83	0.97
LOQ	Sediment(ng/g dw)	0.77	1.01	0.73
-	Water (ng/ml)	0.37	0.46	0.37
	Fish(ng/g dw)	2.21	2.82	3.24

Table 1. Method detection limit (MDL), LOD, and LOQ for pesticide residues in water and sediment.

Limit of detection (LOD) for analytes ranged between 0.11 and 0.14 ng/ml, 0.16 and 0.31 ng/g, and 0.51 and 0.91 ng/g for water, sediment, and fish samples in HPLC-DAD analysis (Table 1). Meanwhile, limit of quantification (LOQ) was calculated at 10 times the standard deviation, s, at either zero (blank) or the lowest level of measurement. Thus, 10 times standard deviation was used and results tabulated (Table 1).

The accuracy of the method was determined by evaluating percentage recovery where field and laboratory matrices were spiked, extracted, and analyzed at varied concentrations to check the method of extraction (Table 1). Percentage recovery values within acceptable limits between 75% and 120% were accepted and results of this study show that percentage recovery ranged between 95.8% and 108.5%, and 104.0% and 112.0% for water and sediment samples, respectively (Table 2). Percentage recovery for fish extracts was between 84.8% and 117.8% (Table 2).

The precision of the analytical procedure was established by extracting and analyzing samples in three replicates during accuracy studies. Precision was acceptable for the values of replicate with a relative coefficient of variation of less than 20%.

The selectivity of the method was verified by the comparison of the chromatograms of samples that have no target pesticides standards. Blank samples did not present peaks at retention time of the standards. Moreover, the chromatograms of the standards presented satisfactory chromatographic resolution. Field and laboratory blank samples were also analyzed regularly after 10 samples in order to evaluate and monitor the potential introduction of contaminants into the samples during processing. Control water sediment samples were obtained upstream where there were no agricultural activities, while fish control samples were obtained from the nearby fish pond.

Statistical analysis was performed using statistical analysis system (SAS) statistical software (Duncan's multiple-range test) for analysis of variance (ANOVA) and descriptive statistics (mean value, standard deviation, coefficient of variation). All the means were expressed within standard deviation limits. Statistically, significant difference between the season and matrices was determined at p < 0.05.

56 *P. Otieno* et al.

	^a Water sam	ples	^b Sediment sa	mples	Fish samp	oles
Spiked concentration	% Recovery	% CV	% Recovery	% CV	% Recovery	% CV
0.5	95.8 ± 6.2	6.5	112.0 ± 5.0	4.4	89.4 ± 11.2	12.5
0.8	100.4 ± 14.6	14.5	106.3 ± 8.8	8.3	95.7 ± 9.9	10.3
1.0	108.5 ± 9.3	8.6	104.0 ± 9.3	8.9	117.8 ± 14.3	12.2
2.0	97.5 ± 4.6	4.7	109.5 ± 12.2	11.1	84.8 ± 7.7	9.1
Mean	101.1	8.6	108.0	7.1	96.9	11.0

Table 2. Percentage mean recoveries in control water, sediment, and fish samples.

^aMean concentration in ng/g.

^bMean concentration $(ng/g) \pm$ standard deviation of sediment samples (dry weight).

% CV represents percentage coefficient of variation, n = 4.

Note: Bold value indicates the difference between mean and other values.

2.6. Conditions of micro-HPLC

Analysis was done using Water[®] CapLCTM system (Waters Milipore, MA) equipped with autosampler, and UV photodiode-array detector, linked to personal computer (PC) running Mass Lynx 4.0 software. The Atlantis D C₁₈ (3 μ m particle size) analytical column with dimensions (150 mm × 0.3 mm I.D) and at temperature of 30 °C was used.

3. Results and discussion

3.1. Concentration of chlorpyrifos-ethyl residues in sediment and water

Chlorpyrifos-ethyl (CPF) residues were detected in the sediments and water samples obtained from Lake Naivasha during wet and dry seasons (Table 3). However, mean levels of the CPF residues in sediment were significantly higher during the wet season than it was in dry season. It is possible that during wet seasons the residues were drained into the lake either through water runoff or erosion of soil-bound particles where the residues were adsorbed on the sediment.

CPF, which is among the currently applied pesticides in the catchment area, persists in the soil surface from between two weeks to several weeks after application. It is often available for runoff for several months after application in the farms due to its low vapor pressure of 1.87×10^{-5} mm Hg at 25 °C (Tomlin 2006). Additionally, CPF has a moderately higher tendency to adsorb on sediment (log *Koc* 3.7–4.5) (Tomlin 2006). This explains why CPF persists in sediment and may also account for the significantly higher levels in sediment than water as observed in this study (Table 3).

Water sample analysis recorded higher mean concentration level of CPF during wet season than dry season (Table 3). Although CPF is slightly soluble in water, it was evident from this study that an increased amount of rainfall in the wet season significantly elevated CPF residue contamination in water. This could probably be due to increased wash off of soil-bound pesticide residues into Lake Naivasha. Bloomfield et al. (2006) suggested that certain amount of CPF residues is generally lost into surface water through erosion of pesticide-bound soil particles during intense rainfall, an observation which supports our finding.

The results of this study were consistent with earlier results obtained by Bailey et al. (2000), where CPF was detected in a range between 21.0 and 85.0 ng/g dry weight (dw) in muddy bank during wet season and lower levels between 2.4 and 47.5 ng/g dw in dry period. Levels of CPF in water are comparable to results obtained by Schiff and Sutula

)	Chlorpyrifos ethyl	yl					Diazinon		
	Sediment	ment	Water	tter		Sediment	nent	Water	ter	
Site	Wet	Dry	Wet	Dry	Mean	Wet	Dry	Wet	Dry	Mean
Control site	bdl	lbdl	lpdl	lbd	lbdl	lbdl	lbdl	bdl	lbdl	bdl
1	35.8 ± 4.6	14.4 ± 2.9	24.9 ± 4.4	14.9 ± 3.1	22.5^{A}	9.3 ± 2.7	5.7 ± 1.2	26.7 ± 4.3	8.2 ± 2.1	12.5^{A}
2	28.9 ± 3.8	14.9 ± 3.3	18.3 ± 3.2	10.7 ± 1.9	18.2 ^B	8.0 ± 2.1	5.0 ± 2.0	33.3 ± 3.7	8.1 ± 1.2	13.7^{A}
3	29.0 ± 3.3	14.6 ± 2.7	20.2 ± 2.5	7.9 ± 1.2	17.9 ^B	6.3 ± 1.3	5.2 ± 1.7	22.6 ± 3.2	5.2 ± 1.2	9.8^{AB}
4	23.1 ± 3.1	7.5 ± 1.8	16.2 ± 3.1	8.1 ± 2.3	13.7 ^C	5.1 ± 1.4	bdl	17.5 ± 2.8	1.9 ± 0.9	$6.3^{\rm BC}$
5	16.8 ± 2.3	12.1 ± 1.8	13.5 ± 1.9	9.5 ± 1.5	13.0 ^C	5.7 ± 1.2	bdl	6.2 ± 2.3	2.4 ± 0.8	$3.7^{\rm C}$
6	20.8 ± 3.7	10.3 ± 1.6	11.7 ± 2.0	9.9 ± 1.6	13.2 ^C	3.0 ± 1.0	2.0 ± 1.1	12.0 ± 2.5	3.6 ± 1.5	10.4^{A}
7	18.5 ± 1.9	7.9 ± 1.1	9.2 ± 1.4	4.1 ± 1.1	9.9 ^D	3.4 ± 1.2	3.2 ± 1.4	11.7 ± 2.1	5.2 ± 1.7	5.9^{BC}
8	11.6 ± 2.5	8.9 ± 1.2	9.2 ± 1.7	8.2 ± 1.8	9.5 ^D	3.1 ± 1.1	1.8 ± 1.1	6.1 ± 1.2	5.3 ± 1.3	4.1 ^C
6	11.2 ± 2.7	8.0 ± 1.3	8.9 ± 1.1	2.6 ± 1.0	$7.7^{\rm F}$	2.1 ± 1.1	3.3 ± 1.3	2.5 ± 1.1	2.0 ± 0.7	2.5 ^C
10	17.5 ± 2.0	7.1 ± 1.1	11.2 ± 1.3	3.9 ± 1.1	9.9 ^D	2.4 ± 1.0	bdl	6.4 ± 1.2	lbd	$2.6^{\rm C}$
11	13.9 ± 1.8	6.8 ± 1.0	13.7 ± 1.7	5.4 ± 1.4	10.0^{D}	2.0 ± 1.0	bdl	6.2 ± 1.4	lbd	2.4 ^C
12	11.4 ± 1.1	7.3 ± 1.4	11.4 ± 1.2	6.3 ± 1.8	8.5 ^E	1.7 ± 1.3	bdl	lbdl	lbdl	$2.3^{\rm C}$
Mean	19.9^{A}	10.0^{B}	$14.0^{\rm C}$	7.4 ^D	12.8^{E}	6.0^{Λ}	2.6^{B}	12.6 ^C	3.5^{D}	$6.4^{\rm E}$
Sediment and water	14.	14.9 ^A	10.	10.7 ^B		4.3 ^A	34	8.1 ^B	8	
Note: concentration in ng/g and ng/ml ; $LOD = 0.11 ng/g$ dw and 0.3 lng/g dw sediment for CPF and diazinon, respectively, and 0.14 ng/ml for water samples. Data with same characters in the same column or row are not statistically different ($p < 0.05$). Bold value indicates the difference between mean and other values.	/g and ng/ml; LO s in the same colu lifference between	D = 0.11 mg/g dw mm or row are no n mean and other	= 0.11 ng/g dw and 0.3 lng/g dw sediment for C or row are not statistically different ($p < 0.05$) ean and other values.	sediment for CPI stent $(p < 0.05)$.	f and diazinc	n, respectively,	and 0.14 ng/ml	for water samples	ŵ	

Table 3. Concentration of CPF and diazinon in sediment and water during the wet and dry seasons (n = 3).

Toxicological & Environmental Chemistry 57 (2004), where CPF was detected in range of between 10.0 and 100 ng/ml. Monitoring concentration levels is therefore, important since the presence of CPF in sediment is a potential risk to aquatic biota especially the sensitive bottom dwelling invertebrates through direct toxicity and bioaccumulation.

In general, the range of CPF detected in this study in sediment and in water was above the set maximum allowable limit (0.1 ng/ml) set by European Union and above the water quality criterion for protection of aquatic life (0.083 ng/ml; USA and 0.0035 ng/ml Canada) (US Environmental Protection Agency, USEPA 2011). Such elevated concentration of the acutely toxic pesticides in aquatic system has the potential to adversely affect aquatic organisms and humans if not properly monitored.

3.2. Concentration of diazinon in sediment and water

Diazinon levels were detected in higher levels in water in wet season, although a significant decrease in mean concentration was observed in dry season (Table 3). Higher concentration of diazinon in wet season could be due to increased rainfall recorded in this period and its higher solubility (0.04 g/l at 20 °C) in water (Tomlin 2006). These results are consistent to a study, where a range of below detection limit (bdl)-3.2 ng/ml diazinon was detected in surface waters located adjacent to agricultural farms (Orlando, Smalling, and Kuivila 2008). The observed low levels of diazinon compared to CPF may be due to the increased volatilization of the residues in farms and/or increased hydrolysis in the aquatic ecosystem owing to the increased solubility (log *Kow* 3.3–3.81) of diazinon in water.

3.3. Bioconcentration of pesticides residues in tilapia fish (Niloticus leucosticus) tissues

Lipophilic pesticides have the potential to bioconcentrate in exposed organisms in aquatic ecosystem. In this study, CPF, one of the most commonly used lipophilic pesticides in Lake Naivasha catchment was detected in fish tissues. Specifically, pesticides residues were determined in gills and lateral muscles of fish obtained from Kasarani, Oserian, and Sher Karuturi along the shores of Lake Naivasha. Mean levels of CPF in the gills of fish samples were significantly higher in wet season than in dry season (Table 4) probably due to the exposure to increased levels of pesticide residues in water. Meanwhile, higher mean level of CPF in lateral muscles in the wet season was higher than levels in dry season probably due to an increase in percentage lipid content, a component that has the potential to accumulate lipophilic pesticides residues. Overall, CPF detected in fish sampled from the three sampling sites did not vary significantly. This could be attributed to uncontrolled fish movement in the lake and the possibility that fish exposed to pollutants at one point would easily relocate and be caught in another site.

Similarly, pesticides residues were determined in wet and dry seasons where the average levels detected in wet season was significantly higher than dry season (Table 4). This observation could be attributed to increase in phytoplankton during wet season resulting into good nutrition and lipid accumulation as opposed to dry season.

Additionally, studies have demonstrated that bioaccumulation of pesticide residues in fish species is a function of concentration, time of exposure, and the age/size of fish and lipid content (Varo et al. 2002).

For this reason, it is possible to speculate that exposure to high concentration of pesticides residues in wet season during the period of higher discharge of agricultural runoff

Table 4. Seasonal mean concentration (r	nean concent	ration (ng/g	$ng/g \; dw) \; of \; CPF \; residues in fish tissues in different sampling sites.$	dues in fisł	tissues in d	ifferent sam	pling sites.				
			Gills					Mu	Muscles		
Sites	Wet	Dry	Mean concentration	Mean lipid	Mean size	Wet	Dry	Mean concentration	Mean lipid	Mean size	Combined concentration
Control	bdl	lbd	bdl	lbd	Bdl	bdl	bdl	bdl	bdl	lbd	bdl
sample	3.2 ± 0.8 1.7 ± 0.8	1.7 ± 0.2	2.5	0.9	177.5	2.5 ± 0.5	0.7 ± 0.1	1.6	3.1	177.5	2.1^{Λ}
Kasarani			bdl-8.9	bdl-2.1	101 - 250			bdl-6.7	0.4 - 9.3	101 - 250	
Oserian	4.0 ± 0.8 1.2 ± 0.4	1.2 ± 0.1	2.6	0.4	169.8	2.5 ± 0.7	1.2 ± 0.1	1.8	5.1	169.8	2.2 ^A
			bdl-8.4	bdl - 1.2	105 - 250			bdl-8.7	bdl-11.7	105 - 250	
Sher Karuturi	2.8 ± 0.5 0.9 ± 0.5	0.9 ± 0.1	1.8	0.7	161.4	3.2 ± 1.1	1.1 ± 0.3	2.2	5.4	161.4	2.0^{A}
			bdl-5.2	bdl-2.2	100 - 250			bdl-8.7	0 - 11.7	100 - 250	
Mean SD ($p < 0.05$) 3.3	3.3	1.3	2.3^{A}	0.7^{A}		2.7	1.0	1.9^{A}	4.5 ^B		0.23
Note: Data with same characters in the same column or row are not statistically different ($p < 0.05$). LOD = 0.66 ng/g dw; $n = 7$; size was in mm.	haracters in the $\tau = 7$; size was	e same colum in mm.	n or row are not st	atistically di	fferent $(p < 0)$.05).					

	80	
	5	
	S	
	ы)
•	Η	
ī	0	
	E	
	Я	
	õ	
1	H	
	5	
	H	
ç	4	
	Ξ	
Ĩ	s in dif	
	Е	
	2	
	õ	
	2	
	SS	
•	₽	
	q	
,	S	
ç	H	
	Ξ	
	5	
	õ	
	⊒	
•	2	
	ŝ	
	ň	
Ę	Τ.	
Ê	Ļ	
	5	
500	C C	
500	otCF	
f()	V) of CP	
	dw) of CP	
	g dw) of CP	
	g dw) of C	
	g dw) of C	
	(ng/g dw) of CP	
	g dw) of C	
	g dw) of C	
	g dw) of C	ر د د
	g dw) of C)))
	g dw) of C)))
	g dw) of C	
	g dw) of C)))
	incentration (ng/g dw) of C)))
	incentration (ng/g dw) of C	~)
	incentration (ng/g dw) of C	
	g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	incentration (ng/g dw) of C	
	. Seasonal mean concentration (ng/g dw) of C	
	e 4. Seasonal mean concentration (ng/g dw) of C	
	4. Seasonal mean concentration (ng/g dw) of C	

59

into the lake may have significantly influenced higher mean levels of CPF residues in fish tissues in wet season. This factor is compounded by CPF's moderately high partition coefficient (Kow = 4.7-5.3) (Tomlin 2006) that would enhance biological uptake of CPF through the skin and gills of fish and bioconcentrate in the lipid layer of the tissues.

This study is consistent with the results obtained by Kammerbauer and Moncada (1998), where CPF residues were detected in fish tissues raised in aquatic ecosystem located in agricultural areas.

3.4. Diazinon and carbofuran in fish tissues (Niloticus leucosticus)

Diazinon and carbofuran have relatively low octanol-water-partition coefficient (log *Kow* of 3.3 - diazinon) (Trotter, Kent, and Wong 1991) which may account for non-detectable levels in all fish samples analyzed. Another reason could be the potential of fish to metabolize xenobiotic contaminants and its ability to depurate the residues faster than it can uptake (Serrano et al. 1997). While studies report that diazinon is highly toxic to fish, there is evidence that it does not bioconcentrate significantly in fish (Scholz and Collier 2000). However, range of 290–1130 ng/g dw of diazinon and carbofuran residues were detected in shrimp and white fish (Prodhan et al. 2010).

4. Conclusion

Sediment and water are basic components of aquatic ecosystems that provide habitat and food sources for aquatic life. Results demonstrated that analysis of these matrices for pesticide residues is critical in assessment of surface water quality and survival of aquatic life. This is compounded by the fact that maximum concentrations of CPF and diazinon residues detected in water and sediment of Lake Naivasha exceeded aquatic life benchmarks established by US Environmental Protection Agency for pesticides. Since pesticides residues control samples from non-agricultural area were below detection limit, it is possible that contamination by pesticides residues observed in Lake Naivasha was dependent on the land use and the drainage of contaminated surface runoff and erosion of pesticide-laden soil from adjacent agricultural fields into the lake. It can also be concluded that seasonal variation had significant influence on the application of pesticides and subsequent contamination levels observed in Lake Naivasha ecosystem. Out of the commonly applied pesticides, CPF was detected in lateral muscles and gills while carbofuran and diazinon were below detection limit. Although observed concentration of CPF in fish were below acute toxicity levels and may have been too low to significantly present adverse health risk to consumers, there is a need to continuously monitor the levels for risk assessment.

Acknowledgments

We wish to thank the Alexander von Humboldt foundation and National Commission for Science, Technology and Innovation (NACOSTI) for their financial support.

References

Bailey, H.C., L.A. Deanovic, E. Reyes, T. Kimball, K. Larson, K. Cortright, V. Connor, and D.E. Hinton. 2000. "Diazinon and Chlorpyrifos in Urban Waterways in Northern California, USA." *Environmental Toxicology and Chemistry* 19: 82–87.

- Barker, S.A. 2007. "Matrix Solid Phase Dispersion (MSPD) A Review." Journal of Biochemistry Biophysical Methods 70: 151–162.
- Becht, R., E.O. Odada, and S. Higgins. 2005. "Lake Naivasha." In Lake Basin Management Initiative: Experience and Lessons Learned Briefs Including the Final Report: Managing Lakes and Basins for Sustainable Use, A Report for Lake Basin Managers and Stakeholders, 277–298. Kusatsu: International Lake Environment Committee Foundation (ILEC).
- Bloomfield, J.P., R.J. Williams, D.C. Gooddy, J.N. Cape, and P. Guha. 2006. "Impacts of Climate Change on the Fate and Behavior of Pesticides in Surface Groundwater. A UK perspective." *Science of Total Environment* 369: 166–177.
- Huber, A., M. Bach, and H.G. Frede. 2000. "Pollution of Surface Waters with Pesticides in Germany: Modeling Non-Point Sources Inputs." *Agricultural Ecosystem and Environment* 80: 191–204.
- Kammerbauer, J., and J. Moncada. 1998. "Pesticide Assessment in Three Selected Agricultural Production Systems in the Cholutea River Basin of Honduras." *Environmental Pollution* 103: 171–181.
- Konda, L.N., and Z. Pásztor. 2001. "Environmental Distribution of Acetochlor, Atriazine, Chlorpyrifos and Propisochlor Under Field Conditions." *Journal of Agricultural and Food Chemistry* 49: 3859–3863.
- Mitoko-Ohayo, C.J. 1997. "Occupational Pesticide Exposure Among Kenyan Agricultural workers: An Epidemiological and Public Health Perspective." PhD diss., Wageningen Agricultural University, the Netherlands.
- Orlando, J.L., K.L. Smalling, and K.M. Kuivila. 2008. Pesticides in Water and Suspended Sediment of Alamo and New Rivers, Imperial Valley/Salton Sea Basin, California, 2006–2007. US Geological Survey Data Series 365: 32–35.
- Pesticide Products Control Board (PCPB). 2010. Annual Report July 2010–June 2011. Trend in Pesticide Imports from 2003/2004–2008/2009. Kenya: Pest Control Products Board.
- Prodhan, M.D.H, M.A. Rahman, M.S. Ahmed, and K.H. Kabor. 2010. "Pesticide Residues in Fish Samples Collected from Different Fish Cultivation Regions of Bangladesh." SAARC Journal of Agriculture 8: 54–64.
- Scholz, N.L., and T.K. Collier. 2000. "Endangered Salmon and Probabilistic Risk Assessment for Organophopshates Pesticides." SETAC Globe 1: 32–53.
- Schramm, K.W., W. Jaser, G. Welzl, G. Pfister, G.F. Wohler-Moorhoff, and B. Hense. 2008. "Impact of 17 α-ethinylestradiol on the Plankton in Freshwater Microcosms-I: Response of Zooplankton and Abiotic Variables." *Ecotoxicolgy and Environmental Safety* 69: 437–452.
- Schiff, K., and M. Sutula. 2004. "Organophosphorus Pesticides in Storm Run-Off From Southern California (USA)." *Environmental Toxicology and Chemistry* 23: 1815–1821.
- Serrano, R., F. Hernández, J.B. Pená, V. Dosdá, and J. Canales. 1997. "Bioconcentration Depuration and Chronic Toxicity of the Organophosphorus Pesticide Chlorpyrifos in the Marine Mollusc." Archives of Environmental Contamination and Toxicology 33: 47–52.
- Tomlin, C.D.S. 2006. *The Pesticides Manual: A World Compendium*. 14th ed. Hampshire: British Crop Protection Council.
- Trotter, B.M., R.A. Kent, and M.P. Wong. 1991. "Aquatic Fate and Effect of Carbofuran." *Critical Reviews in Environmental Control* 21: 137–176.
- US Environmental Protection Agency, USEPA. 2011. Report on Revised Chlorpyrifos Preliminary Registration Review for Drinking Water Assessment. PC code 059101; Dp Barcode 368388, 389480. Washington DC: Office of Pesticide Programs EPA.
- Varo, R., E. Serrano, F. Pitarch, F.J. Amat, and J.C. Navaro. 2002. "Bioaccumulation of Chlorpyrifos Through An Experimental Food Chain: Study of Protein HSP70 as A Biomarker of Sublethal Stress in Fish." Archives of Environmental Contamination and Toxicology 42: 229–235.