

## **Determination of Organochlorine Pesticide Residues in Soil and Water from River Nyando Drainage System Within Lake Victoria Basin, Kenya**

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A more recent development related to the international action to protect human health and the environment, is the convention on 12 persistent organic pollutants (POPs) reached in Durban, South Africa in 2000. The targeted POPs were DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, hexachlorobenzene (BHC), mirex, toxaphene, polychlorinated biphenyls, dioxins and furans. Data and evidence on their ill effects have mostly been gathered in the temperate lands but very little in the tropical regions (Wandiga 2001). Despite the official ban of these pesticides in Kenya, they are still available in the market, and are being detected in the environment (Wandiga et al. 2000). Currently, some organochlorine compounds are allowed for purposes other than for soil application and are therefore still purchased. Heptachlor is allowed for the treatment of power and telephone pedestals or wire posts to prevent termite damage. Lindane is a traditional component of lotions, creams, and shampoos for the control of lice and mites in humans and in veterinarian products for ectoparasites (Sparovek et al. 2001). However, the environmental fate of these pesticides has become an issue in Kenya and has been receiving more attention than ever before due to international residue limit requirements in food, drinking water supplies as well as in export products such as fish, fruits and horticultural produce (Wandiga et al. 2001). Everaats et al. (1996) analyzed sediments from the Kenyan coast and found  $\alpha$ -BHC,  $\gamma$ -BHC and dieldrin in concentrations of 7.1–62.2 ng/g, 7.3–53.2 ng/g and 37 ng/g of organic carbon (OC), respectively. DDT,  $\beta$ -BHC, dieldrin and heptachlor epoxide have been detected in breast milk of Kenyan women (Wandiga and Mutere 1988). The main route of exposure to the respondents was attributed to oral intake through vegetables, beef, contaminated water, and dairy milk containing the residues (Kanja 1988). DDT and other organochlorine pesticides have been shown to affect reproduction of various test animals (Hayes 1982).

Due to the illegal continued use of the banned compounds and, the environmental and health implications of their use in Kenya, there is a strong need to carry out studies regularly on the residue levels of these compounds at designated sites where they are heavily used. This study was undertaken to analyze soil and water from the Sugar belt in Kenya, where 2260 hectares of land have been devoted to the cultivation of sugarcane for over 40 years. All kinds of pesticides are used on

this land to control all sorts of pests (termites, rodents, insects and weeds). In this study organochlorine compounds were particularly targeted because they are banned and due to their illegal use, there is no proper documentation of the quantities imported into the country. Soil and water samples were collected from designated sites within the Sugar belt and analyzed for the presence of organochlorine compounds. All the pesticides are assumed to have been applied to the fields at label rates.

## **MATERIALS AND METHODS**

The location of the area on which the study was carried out lies within 34° 50' 49" E - 35° 35' 41" E longitude and 0° 4' 55" N – 0° 20' 11" S latitude. Fields in the sugar belt with 2260 hectares devoted to sugarcane cultivation, where pesticides are heavily used for the control of many different pests were selected according to the time when the pesticides were last applied. Four fields were identified and designated as having received pesticide applications 2 months, 6 months, 12 months and 60 months ago, respectively. Three different sampling points were randomly selected within each field. A soil core was dug and soil scooped down to the depth of 30cm, mixed thoroughly before a sub-sample of approximately 500g was taken in a black polythene bag. The soil samples were air-dried, homogenized and crushed in a mortar with a pestle and then sieved through a 2-mm pore sieve in the laboratory. A sub-sample of the soils was taken and characterized.

Water samples were taken from the rivers, which drain the Sugar belt and were considered to be directly receiving the surface run-offs from the sugar belt and from other adjacent farming areas. Water samples were collected in 2.5l amber bottles by taking several composites across the rivers. Where rivers were deep, a grab sample was taken from a strategic position and considered to be representative sample. Sampling from the fields was done twice, in May and October 2002. Rainfall in the area was well distributed throughout the year. Sampling from the river was done once, in the month of October. All samples awaiting analysis were kept in the refrigerator at -4°C. General-purpose reagent (GPR) grade diethyl ether, hexane, acetone, methanol and dichloromethane solvents were all triple-distilled in all-glass apparatus before use. Florisil and Na<sub>2</sub>SO<sub>4</sub> used were heated up to 100°C before they were kept in desiccators to cool. The Whatman #1 filter papers used for extraction of soil samples were pre-soxhlet extracted in extraction solvent for 24 hours and kept in desiccators. All glassware was soaked in detergent for at least 24 hours, washed and rinsed in tap water followed by distilled water before being dried in an oven at 100°C for 24 hours. The dry glassware was stored in a dust-free cabinet. Prior to use the glassware was rinsed with the appropriate solvent.

A sub-sample of 30g of air-dried and homogenized sieved soil was taken in replicas of three and mixed with equivalent weight of Na<sub>2</sub>SO<sub>4</sub> to dry the soil. The dried soil was placed in a pre-extracted filter paper and soxhlet-extracted for 24 hours in 150ml of triple distilled acetone:hexane(1:1) mixture. The extract was

rotary evaporated to 10ml. The 10-ml extract was cleaned up by eluting the extract through a column packed with 10g of activated florisil and topped with  $\text{Na}_2\text{SO}_4$  to a height of 2 cm. The extract was eluted through the column at a rate of 5ml/min. Elution was done using 200ml of 6%, 15% and 50% of diethyl ether in hexane in that order. The extract was reduced to just dryness and then reconstituted in 5ml of HPLC grade hexane.

2 litres of the water sample was measured by measuring cylinder and transferred into a 2.5-litre separatory funnel. 100ml of triple distilled methylene chloride was added to the water sample in the separatory funnel. 50g of  $\text{Na}_2\text{SO}_4$  was added to the separatory funnel to salt out the pesticide into the organic phase. The separatory funnel was tightly corked and vigorously shaken for three minutes with periodic venting to prevent pressure build up by methylene chloride. The contents in the funnel were allowed to stand for ten minutes so that the two phases could separate. The organic phase was passed through a  $\text{Na}_2\text{SO}_4$  column to remove water and then collected in a round-bottomed flask. Another portion of 100ml of methylene chloride was added to the extracted water in the separatory funnel and the process repeated. The extraction was done three times. The dry organic phase was rotary evaporated to dryness, reconstituted in 5ml of HPLC grade hexane before it was analyzed by GC. 1 $\mu$ l was taken from the 5ml extract and injected into the Varian Chrompack CP-3800 GC under the conditions specified. Column: CP-SIL 8CB-15m, 0.25mm (ID), 0.25 $\mu$ m film; sample size: 1 $\mu$ l split 1:20; detector: ECD at 300°C; column temp: 150°C held for one minute changed to 200°C at 4°C/min then to 300°C at 4.5°C/min, flow pressure was 30Psi of the nitrogen gas as the carrier gas and injector temperature at 250°C. External standard calibration was used to determine peak areas from the samples. The following organochlorine pesticides were analyzed in both water and soil samples heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, lindane, endosulfan,  $\alpha$ -BHC and  $\beta$ -BHC. Recovery studies were carried out by spiking soil and water standard samples with 0.01ppm of the pesticide standards. The percentage recoveries for the pesticides ranged from 84-119% and 84-94% from soil and water, respectively. The concentrations in the samples were corrected according to the percentage recovery for each pesticide. The residue concentrations in water and soil samples were expressed in ppm.

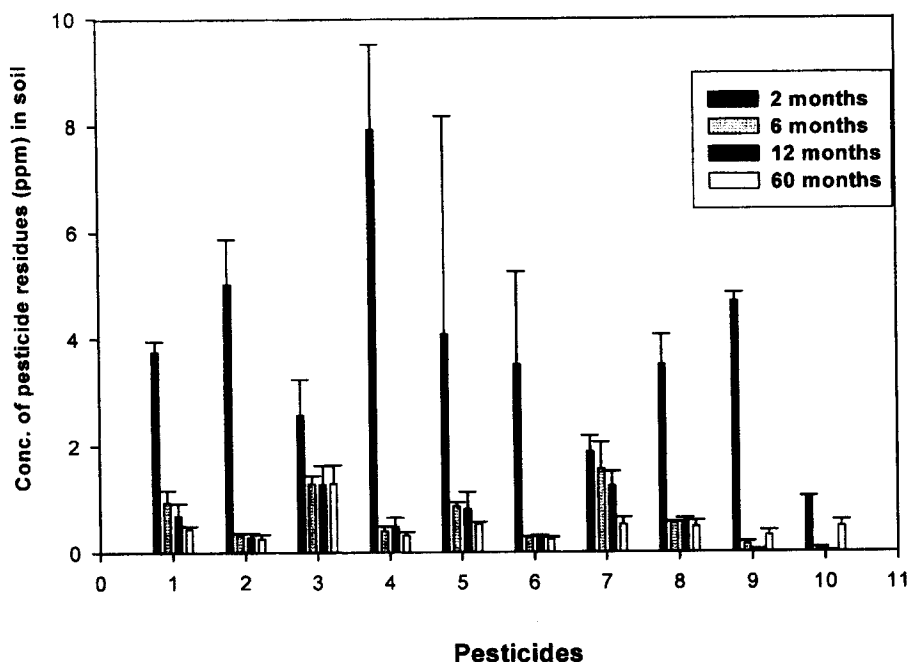
## RESULTS AND DISCUSSION

The soil was characterized as clay with the following properties, organic carbon (OC) 2.07%, pH 6.08, clay content 68%, sand content 28%, silt content 12%, N 0.19%, P 80ppm, Na 0.95%, K 1.85%, Ca 10.5%, Mg 4.95%, Mn 0.51%, Fe 226.96% and electrical conductivity (EC) 0.62 $\mu$ S/cm.

All the compounds which were analyzed in this study were banned in Kenya in 1986 except aldrin and dieldrin, whose use is restricted to the control of termites in the building industry (Pests Control Board 1992). However, the present study revealed high concentrations of the compounds in the soil samples from different fields in the sugar belt (figure 1). Even in the field where the pesticides were

applied five years ago, high concentrations of the compounds were detected (figure 1). Their continued use in the agricultural sector although illegal as far as the Kenya Government policy is concerned, has been attributed to their availability at low costs, low mammalian toxicity and their broad-spectrum bioactivity for a long duration (Wandiga et al. 2002a). Two months after application of the pesticides, the highest concentration of  $7.924 \pm 1.592$  ppm was found for heptachlor and the lowest concentration of  $1.026 \pm 0.118$  ppm for methoxychlor. Concentrations of aldrin and dieldrin, which is an epoxide of aldrin were  $4.088 \pm 0.760$  ppm and  $3.512 \pm 0.559$  ppm, respectively. Sunlight and bacteria in the soil changed Aldrin to dieldrin, which in soil and water degrades slowly (ATSDR 2002).  $\alpha$ -BHC,  $\beta$ -BHC and lindane ( $\gamma$ -BHC) are isomers. Lindane is normally converted to  $\alpha$ -BHC on exposure to sunlight. Of the three isomers,  $\beta$ -BHC was still highest in concentration, after two months in the soil. All the compounds in the soil rapidly dissipated after six months but thereafter, the dissipation rate was low, having attained a steady state in the soil (figure 1). This two-phase dissipation pattern of pesticides from soil has been observed in many studies (Wandiga et al. 2001). All the ten compounds were still in the soil after five years with the highest concentration of endosulfan ( $0.513 \pm 0.139$  ppm) followed by lindane ( $1.294 \pm 0.346$  ppm). Heptachlor concentration was the least ( $0.243 \pm 0.032$  ppm) in the soil after five years. The high concentration of endosulfan in soil is of great concern because of its extreme toxicity to fish and aquatic invertebrates (Gonzalez et al. 2003). Studies have shown that organochlorine pesticides such as the cyclodiene, heptachlor, aldrin, endrin, and dieldrin are the most persistent and were found to persist in field crop soils for long periods of time, with long half-lives of disappearance ranging from 0.3-2.8 years in temperate soils (Wandiga 1995). The adsorption of the compounds by soil, which was influenced by diverse factors such as organic matter content, soil type, and physical-chemical properties of pesticides, that is, vapor pressure, water solubility, and the n-octanol-water partition coefficient ( $K_{ow}$ ), played a role in the persistence of the compounds in soil (Cheng 1990).

The results (figure 1) showed that aldrin and heptachlor were in higher concentrations than their metabolically formed analogues, dieldrin and heptachlor epoxide, respectively. Studies by other researchers have also shown that aldrin and heptachlor were in higher concentrations than their converted products (Barlas 2002; Barlas 1999; Ayas et al. 1997). Ratios of DDE/DDT,  $\alpha$ -BHC/lindane, dieldrin/aldrin and heptachlor e/heptachlor in soil are often used as indicators of recent DDT, lindane ( $\gamma$ -BHC), aldrin and heptachlor inputs into the environment, with low ratios, particularly  $<1$ , indicating recent input (Gonzalez et al. 2003). The hypothesis of recent pesticides input was applied to the ratios of the compounds in this study. The ratios for  $\alpha$ -BHC/lindane after 2, 6, 12 and 60 months were 1.46, 0.73, 0.54 and 0.34, respectively, which did not conform to the hypothesis since the ratio decreased in fields where the compounds were said to have been applied long ago. For heptachlor/heptachlor e ratio the values were 0.45, 0.72, 0.52 and 0.77, after 2, 6, 12 and 60 months. The ratios increased as the pesticides' residence in soil increased except for the period "after 6 months". Dieldrin/adrin ratios were 0.86, 0.63, 0.70 and 0.89 after 2, 6, 12 and 60 months.

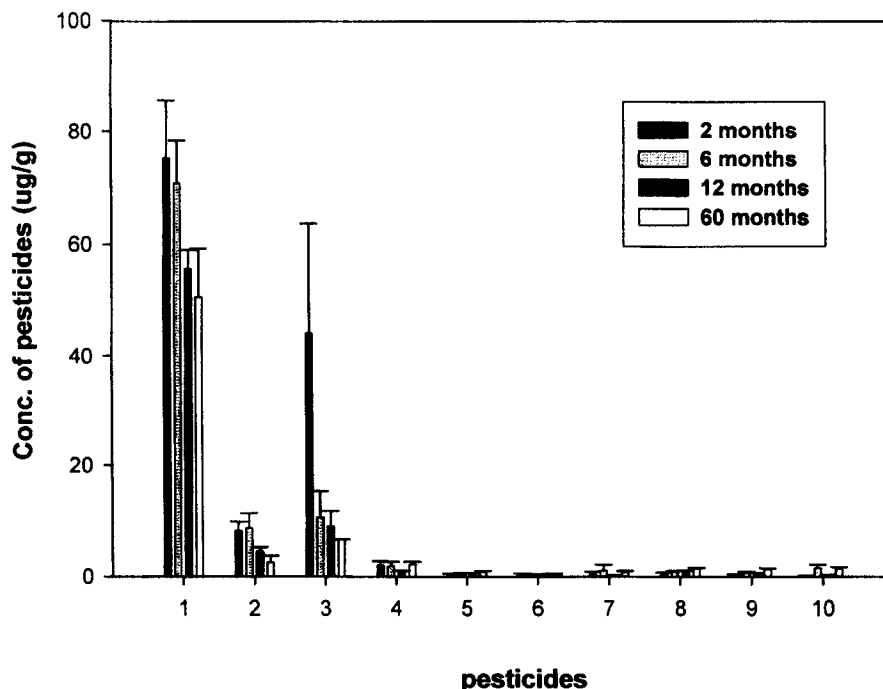


**Figure 1.** Variation of pesticide concentrations in soil from fields in May 2002.

Key: 1. α-BHC; 2. β-BHC; 3. lindane; 4. heptachlor; 5. aldrin; 6. heptachlor e; 7. endosulfan; 8. dieldrin; 9. endrin; 10. methoxychlor.

Apart from the period “after 2 months”, the ratios reflected the period the pesticides have been in the soil and therefore, confirmed the hypothesis. For α-BHC, it appears the compound is applied directly in the soil and does not necessarily originate from the degradation of lindane. This is further supported by the data presented in figure 2, where the concentration of α-BHC was abnormally high.

Figure 2 shows results of soil analysis from the fields five months after the previous sampling. It was revealed that pesticides had just been applied to the fields a month before. The pesticides, which are commonly applied, were herbicides, which were not analyzed in this study. However, the identity of the pesticides, which had been applied to the fields was not disclosed. Comparing the data with one obtained from the previous sampling (figure 1), it was clear that α-BHC had been applied to all fields, including the one which had not received pesticides in the last five years and was still idle and overgrown with vegetation during the second sampling. The other compounds, which were applied to all fields but in lower quantities than α-BHC, were β-BHC and lindane. The remaining compounds heptachlor, aldrin, heptachlor epoxide, endosulfan, dieldrin, endrin and methoxychlor did not seem to have been applied especially to the field designated as “2 months” in the previous sampling. This was supported



**Figure 2.** Variation of pesticide concentrations in soil from fields in October 2002.

Key: 1.  $\alpha$ -BHC; 2.  $\beta$ -BHC; 3. lindane; 4. heptachlor; 5. aldrin; 6. heptachlor;  
7. endosulfan; 8. dieldrin; 9. endrin; 10. methoxychlor.

by concentrations of these compounds, which were lower than concentrations obtained in the previous sampling. In the five months after the previous sampling, rain could have influenced the dissipation of the compounds from soil through surface run-off, leaching and evaporation, resulting in lower concentrations than those obtained in the previous sampling. Concentrations of these compounds were generally higher than in the previous sampling from other fields, implying that these compounds could have been applied to the fields prior to second sampling.

Table 1 shows results of analysis of water samples from different sampling sites. The sites, which directly received surface run-offs from the fields in the Sugar belt, were identified on rivers Mbogo, Nyando at Ogilo, Nyando at Muhoroni and Nyando at Ahero bridge. Other sites on rivers Kedowa, Nyando at Ainamotua and Ahero channel received surface run-offs directly from coffee, tea and rice growing areas, respectively. The samples were taken from rivers at the same time when soil samples were taken from the fields. Most of the pesticides were detected in all the sampling sites except endosulfan, which was only detected on river Nyando at Muhoroni and Methoxychlor on Ahero channel and river Mbogo. High concentrations of  $\alpha$ -BHC were recorded in all the samples from the seven sites. With exception of the sample from river Kedowa with a high concentration

**Table 1.** Variation in concentration of pesticides along the rivers draining the Sugarcane fields in October 2002.

Pesticide	Concentration (ppm) at different sampling points along the rivers						
	A	B	C	D	E	F	G
$\alpha$ -BHC	0.379	0.211	0.182	0.176	0.691	0.251	0.113
$\beta$ -BHC	0.046	0.011	0.010	0.009	0.035	0.014	0.007
Lindane	1.240	0.043	0.039	0.034	0.095	0.104	0.027
Heptachlor	0.070	0.010	0.009	0.006	0.070	0.011	0.006
Aldrin	0.089	0.008	0.005	0.003	0.089	0.006	0.003
Heptachlor e	0.005	0.003	0.003	0.002	0.005	0.004	0.003
Endosulfan	N/D	0.010	N/D	N/D	N/D	N/D	N/D
Dieldrin	0.096	0.005	0.002	0.001	0.096	0.096	0.002
Endrin	0.031	0.001	0.001	N/D	0.031	0.031	0.001
Methoxychlor	0.022	N/D	N/D	N/D	N/D	0.040	N/D

Key: A=River Mbogo; B=River Nyando at Muhoroni; C=River Nyando at Ogilo; D=River Nyando at Ahero bridge; E=River Kedowa; F=Ahero Channel; G=River Nyando at Ainamotua; N/D = Not detectable.

of 0.691ppm, the other six sites had an average concentration of  $0.219 \pm 0.091$  ppm. River Mbogo recorded the highest concentration of lindane (1.240ppm). There was good correlation between the concentrations of the three isomers  $\alpha$ -BHC,  $\beta$ -BHC and lindane in the soil and in the surface water (figure 2 and table 1). The pesticides reached the surface water through the surface run-offs. Although high concentrations of the  $\alpha$ -BHC,  $\beta$ -BHC and lindane were detected in the fields when the surface waters were analyzed, the corresponding concentrations of pesticides detected in water were low due to their low water solubility and their high values of  $\log K_{ow}$  and  $\log K_{oc}$ . These factors, coupled with high clay content (60%) and OC (2.07%) in the soil increased the adsorption of the pesticides in the soil thus reducing their rate of transportation through surface run-offs (Diaz Diaz et al. 1995). The concentrations of the compounds such as  $\alpha$ -BHC,  $\beta$ -BHC and lindane were still above the Environmental protection agency (EPA) limits in drinking water of between 0.001 and 0.002 ppm (ATSDR 2002). The four sampling sites on rivers Mbogo, Nyando at Muhoroni, Nyando at Ogilo and Nyando at Ahero bridge received surface run-offs from the Sugar belt fields. The distance between the fields and the various sampling sites along the rivers increased from river Mbogo to river Nyando at Ahero bridge. The concentrations of the pesticides at these sites also decreased as one moved farther away from the fields (table 1). The first four sampling sites in table 1 are those associated with the Sugar belt fields and follow one another. The concentrations of all the pesticides in samples from the four rivers clearly decreased as the distance of the rivers increased from the Sugar belt fields, which were the source of the pesticides in water. The decrease in concentrations of the pesticides in water as the distance of sampling sites increased from the fields was due to the adsorption of the pesticides by soil,

which reduced the movement of the pesticides to the surface water. For the other three sampling sites on river Kedowa, Ahero channel and river Nyando at Ainamotua, the site at river Kedowa, which receives surface run-offs from coffee farms, had high concentrations of  $\alpha$ -BHC, lindane and  $\beta$ -BHC. Ahero channel also had high concentrations of  $\alpha$ -BHC, lindane and aldrin. River Nyando at Ainamotua, which receives surface run-offs from the tea farms, showed high concentrations of  $\alpha$ -BHC and lindane.  $\alpha$ -BHC was found in all the water samples sampled from the rivers. These compounds have also been detected in sediment samples collected from inland lakes of Baringo, Naivasha, Nakuru and Victoria in Kenya in previous studies (Wandiga et al. 2002b).

The present study has shown that the banned organochlorine pesticide compounds are still in use. There were high concentrations of the compounds in soil where they are directly applied. They were also detected in water from rivers which drain through the farming areas, and that their concentration in water was influenced by their concentration in soil. Rain played a major role in the transportation process through surface run-offs. Their presence in the soil after five years since last application, shows that the pesticides also persist in tropical soil conditions.

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