

Pesticide Residue Levels in Nzoia River Catchment Area

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Abstract

A lot of pesticides are often used to control and manage pests in agricultural areas leading to their accumulation in various matrices and thus polluting the environment. Some of the applied pesticides are biodegradable while others convert to other forms which are even more lethal than the original compounds. The Nzoia River catchment zone being a sugarcane growing region has serious mosquito infestations forcing public health officials to use DDT for mosquito control. A study of pesticide residue levels in the Nzoia catchment area has been done by stratified sampling of water, soils and sediments from eight (8) different sites along the river. The samples were collected in two seasons (during dry and rainy seasons) and were extracted by liquid-liquid extraction method. The extracted samples were then screened and determined qualitatively for pesticides using GC/MS. Quantitative analysis of organochlorines and pyrethroids were done using GC/ECD. The results show a variation of pesticide residue levels with season. Some organochlorines (lindane and endosulfan sulphate) and pyrethroids were within the WHO's MRL (Maximum Residue Limits) while op-DDE in Webuye [0.0794 ± 0.0017 ppm] exceeded the WHO MRL value of 0.04 ppm for op'DDE. The Nzoia River catchment zone is polluted from some of the pesticides studied and unless their use is checked, a serious environmental degradation is likely to ensue. To reduce consumer health concerns, routine monitoring of pesticide residues in water, soil, and sediments is advised. Farmers must be educated on the usage of organic fertilisers and integrated pest management.

Keywords: Pesticide, residue, catchment, soil, pollution, effluent, sediments

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Competing interests:

The authors have declared that no competing interests exist

Introduction

The River Nzoia is important to Western Kenya, flowing through a region estimated to be populated by over 3.2 million people (Le & Pricope, 2017; Odwori, 2021; Kanda *et al.*, 2016; Opere, 2013). Its waters provide irrigation all year round, while the annual floods around the lowland area of Budalangi deposit sediments that contribute to the area's good agricultural production (Omungu, 2014; Ketter, 2018; Ombogo, 2016). Around the industrial region centered at Webuye, the river absorbs a lot of effluent from the paper and sugar factories in the area (Lalah *et al.*, 2018; Omondi, 2017; Kanda *et al.*, 2015; Kanda *et al.*, 2017; Nyakeya *et al.*, 2018;

Welinga, 2016; Twesigye *et al.*, 2011). The river has a number of spectacular waterfalls, and is thought to possess a good hydroelectricity generation potential (Nzoia river basin management initiative, 2006; Chepkania, 2019). The economy of the region is still largely rural and more than 90% of the population earns its living from agriculture and livestock (Mbaisi *et al.*, 2016; Wegulo & Kwamboka, 2019; Nadir *et al.*, 2019). The main food crops include maize, sorghum, millet, bananas, groundnuts, beans, potatoes, and cassava while the cash crops consist of coffee, sugar cane, tea, wheat, rice, sunflower and horticultural crops (Mbaisi *et al.*, 2016; Odwori & Munyendo, 2020). Dairy farming is also practiced together with traditional livestock keeping (Mbaisi

et al., 2016). The River Basin is of great economic importance at local as well as national levels especially in such sectors as agriculture, tourism, fishing, forestry, mining and transport (Odwori, 2021). It is also the main source of water for domestic, (rural and urban water supply), agriculture and commercial sectors (Odwori, 2020; Basweti *et al.*, 2018). The main challenges in the basin include soil erosion and sedimentation, deforestation, flooding, wetland degradation, pollution and solid waste, river bank cultivation, sand harvesting, brick making, human-wildlife conflict and poorly developed infrastructure (Nzoia river basin management initiative, 2006; Moses, 2017; Kogo *et al.*, 2020; Mutua *et al.*, 2016; Mirenga, 2018; Nadir *et al.*, 2019).

Organochlorines (OC's) and pyrethroid pesticides are ubiquitous environmental organic micro-pollutants (Méjanelle *et al.*, 2020; Kumar *et al.*, 2020; Mahdavian & Somashekar, 2013; Jayaraj *et al.*, 2016; Saravi & Dehpour, 2016). Although their production, usage and disposal to the environment has been regulated or prohibited in most western countries since the 1970's, these pesticides are still very important and used in many developing countries especially South Asia, Middle Asia, South America and Africa (Sharm *et al.*, 2019; Keswani *et al.*, 2022; Bradman *et al.*, 2007). In recent decades, many investigation reports have been documented that these contaminants might be transported widely through the atmosphere and eventually pollute all over the world (Carvalho, 2017; Tanabe, 2006). Such a worldwide spread and transition is expected to affect the current status of global contamination and pose a threat to human beings and wildlife, particularly marine mammals (Getenga, 1999; Nabi *et al.*, 2022; Bossart, 2011; Schiavone *et al.*, 2009; García-Fernández *et al.*, 2020).

It is well recognized that pest control through chemicals is a cost- and time- effective measure (Ngowi *et al.*, 2007). Consequently, modern agricultural systems rely heavily on chemical means of pest control (Legros *et al.*, 2021; Chandler *et al.*, 2011; Shetty, 2004; Mengistie *et al.*, 2017). Agricultural systems and agronomic practices in the region have undergone major changes, particularly in the last 10-15 years, leading to even greater dependence on the chemical methods of pest control (Kookana & Simpson, 2000). Global problems such as soil erosion, other forms of land degradation and eutrophication are posing serious threats to the sustainability of the modern agricultural system (Eswaran *et al.*, 2019; Khan *et al.*, 2014). There has, therefore, been a shift towards the use of

reduced tillage practices in the region's agriculture in order to reduce loss in soil structure, erosion of soil particles to minimize nutrient runoffs and subsequent eutrophication of surface waters (Baulch *et al.*, 2019; Zhang *et al.*, 2009; Xu *et al.*, 2010). The use of herbicides facilitates the practice of minimum tillage or no till which together with crop rotation, contributes directly to environmental protection through reduction of soil degradation and runoff losses of nutrient and other contaminants (Holland, 2004; Soane *et al.*, 2012; Somasundaram *et al.*, 2020; Derpsch & Friedrich, 2009). Appropriate use of pesticides based on recommendation is generally expected to cause little adverse impact on the environment. However, trace levels of pesticide residues, have been detected in soil and water (Arora *et al.*, 2014; Székács *et al.*, 2015; Mazlan *et al.*, 2017; Khan *et al.*, 2020; Mawussi *et al.*, 2014; Prado-Lu & Leilanie, 2015). Consequently, community concerns regarding the potential effects of pesticides on non-target organisms have increased immensely (Getenga *et al.*, 2000; Richardson *et al.*, 2019; Dubey & Prakash, 2021; Galhano *et al.*, 2011). Getenga (1999) reports that there is data paucity on pesticide residue levels in areas where they are heavily used in Kenya. Consequently, side effects such as toxicities to non-target species including humans and the formation of persistent pesticide residues in soil and water has been reported (Anonymous, 1993).

In Kenya, the heavy dependency on pesticides use for food production in this catchment area has led to reported cases of unmediated and suicide deaths. Recently, fish were allegedly harvested by use of endosulfan in Lake Victoria. This resulted in the stoppage of fish exports to the European Union which affected fishing and consequently the economy of the riparian countries. The total loss of income due to this ban is estimated to be more than US\$ 300 million (Kengara, 2003).

Materials and methods

Sampling

Water, soil and sediment samples were collected from eight different sites across six districts namely; Kitale East, Uasin Gishu, Kitale West, Lugari, Bungoma and Butere Mumias which are a representative of the region. These sites were selected on the basis of the different agricultural and industrial activities.

Sampling was done during dry season (Nov-March) and wet season (April-June). For soil samples, three field points were selected

randomly near river banks at which soil cores were dug to depth of 30 cm using a 2 cm internal diameter soil corer. The samples were then mixed thoroughly and divided into three replicates of about 500 g then kept in hexane-acetone rinsed containers.

Water samples were collected (sub-surface and $\frac{3}{4}$ below surface) and mixed thoroughly then divided into three replicates and stored in clean (acetone-hexane) rinsed 2 litre amber bottles.

Sediment samples were collected using an Ekman sampler and placed in hexane-acetone rinsed 250 mL glass bottles. All the samples were transported in ice to the laboratory for extraction.

Water Samples Extraction

The sample bottles were shaken to ensure that all particulate matter is suspended and exactly 2 litres of the sample was measured with a clean measuring cylinder, and the excess discarded. The measured sample was then returned into the sampling bottle.

A 100 mL of 50:50 v/v of dichloromethane: n-hexane HPLC grade was added to the sampling bottle, stoppered and shaken for about 3 minutes and the contents transferred to the separating funnel. The separating funnel was then shaken vigorously; the pressure vented regularly at intervals into fume cupboard. The layers were allowed to separate and the lower aqueous layer run into the sample bottle while the organic layer was collected in a 250 mL conical flask. The emulsion formed was broken by centrifugation spun at 400 rpm for about 5 minutes and the aqueous layer pipetted off. The aqueous solution in the sample bottle and further extracted using 50 mL 50:50 v/v n-hexane: dichloromethane, and allowed to separate. The aqueous layer was then poured into a measuring cylinder. To the combined extracts, 3 g of anhydrous sodium sulphate was added and shaken for 30 seconds. The sodium sulphate was allowed to settle and the dried extract decanted into pre-cleaned flask. The sodium sulphate was then rinsed out with 20 mL of diethyl ether.

Sediments and Soil Extraction

Any supernatant water was removed from the sediment sample with a pasture pipette and 30 g of sample (for both soil and sediments) was weighed out to an accuracy of 0.01 g and placed in a water glass then transferred to the mortar. The sediment and soil samples were ground with enough anhydrous sodium sulphate until a dry free flowing powder was produced then transferred to the soxhlet thimble and placed in

the extraction apparatus charged with 250 mL acetonitrile:hexane: dichloromethane at 100 : 50 : 100 v/v. The sample was allowed to extract for at least 10 cycles which took around 3 hours and heating maintained at approximately 70° C.

Cleanup procedures

The extract was cleaned by open column chromatography. A chromatography tube was clamped onto a stand and then glass wool was inserted into the tube to prevent packing materials from passing through. The column was then packed as follows; 10 g of activated florisil was poured followed by 5 g of anhydrous sodium sulphate. The column was tapped gently to achieve an even distribution. The column was then eluted using 20 mL of 50:50 v/v of dichloromethane: hexane. The extract was filtered with No.42 Whatman filter paper into a clean 250 mL conical flask.

Using a rotary evaporator under vacuum, the volume of the hexane extract was reduced to 10 mL. This volume was then transferred with rinsing to a 10 mL graduated test tube and reduced using nitrogen (blowing on the surface) to about 1 mL. This volume was kept in a vial and put in a freezer for pesticide analysis with GC-MS and GC-ECD.

Standards and apparatus

Mixed standards of OC's, and pyrethroids were prepared at Kenya plant health inspectorate services (KEPHIS) including endrin, endosulfan sulphate, heptachlor, pp' DDE, dieldrin, pp' DDD, lindane, op DDE and aldrin for OC's while for pyrethroids the standards included alpha cypermethrin, deltamethrin and lambda cyhalo. Pure pesticide standards (99%) were used for the identification of the pesticide residues in the sample extracts. The standard mixture comprising nine organochlorines and three pyrethroids was prepared. This involved pipetting 2 mL of each of the standards separately for organochlorines, into a 20 mL volumetric flask and topping up to the mark with n-hexane, to make 100 ppm of 9 organochlorines. The 100ppm mixture was then serially diluted to the appropriate concentration by a factor of 10. All solvents were analytical grade and redistilled before use. All glassware was thoroughly cleaned and rinsed with acetone, methanol then hexane before use. The extracts were analyzed using a Claurus 500, PE Auto system gas chromatograph with built in auto sampler equipped with an electron capture detector. The column was 30 m x 0.25 mm with 0.25 μ m thickness. A Varian Chroma pack CP-3800 gas chromatograph and mass spectrometer was used

to identify the OC's and pyrethroids with column of CP-SIL 8 CB 15 m x 0.25 mm x 0.25 um film thickness.

Chemical analysis

From the 1 mL sample extract, 1 μ L was injected into the GC under the following conditions; the sample size was 1 μ L split 1:2; at 300° C. The column oven was set at 150° C for 2 minutes, increasing by 4.0° C/min to 200° C, then to 300° C at 4.5° C/min; flow pressure: 30 psi; injector: 250° C; carrier gas nitrogen flow rate: 40 mL/min; hydrogen: 20 mL/min. The gas chromatographic conditions of GC-MS were same as GC-ECD, except that the carrier gas was helium. Effluents from the GC column were transferred via a transfer line kept at 230° C and fed into a 70-eV electron impact source held at 250 °C. The mass spectrometry was operated under full scan acquisition mode with mass range 50-500.

Various concentrations of standards were also injected. External standard calibrations were used to determine peak areas of samples.

Quality control and method evaluation

Procedure blanks were obtained by extracting distilled water with the same process as the real samples for OC's and pyrethroids. A 200 mL hexane was concentrated to 0.2 mL and used as a solvent blank to check the contamination from the solvent.

For soil and sediments, six 30 g samples were spiked while for water 1500 mL of three samples were spiked with 0.05 ppm, 0.5 ppm, and 1.0 ppm of 3 pyrethroids while for OC's, samples were spiked with 0.1 ppm, 0.5 ppm, and 1.0 ppm of 9 OC pesticides for recoveries correction.

Gas chromatography peak identification was conducted by comparing gas chromatographic retention times (in GC-ECD chromatogram) and mass spectra (in GC-MS) with those of authentic standard. Data was corrected basing on recoveries from the blank and the spiked samples.

Results and discussion

Spatial variations in concentration of the selected pesticides in water, soil and sediments

Organochlorines

Results of the organochlorine pesticides concentration in water during the study period in the eight sampled sites; Kitale (1), Cherangani (2), Uasin Gishu (3), Moi's Bridge (4), Lugari (5), Webuye (6), Pan-Paper (7) and Mumias (8) are shown in Figure 1.

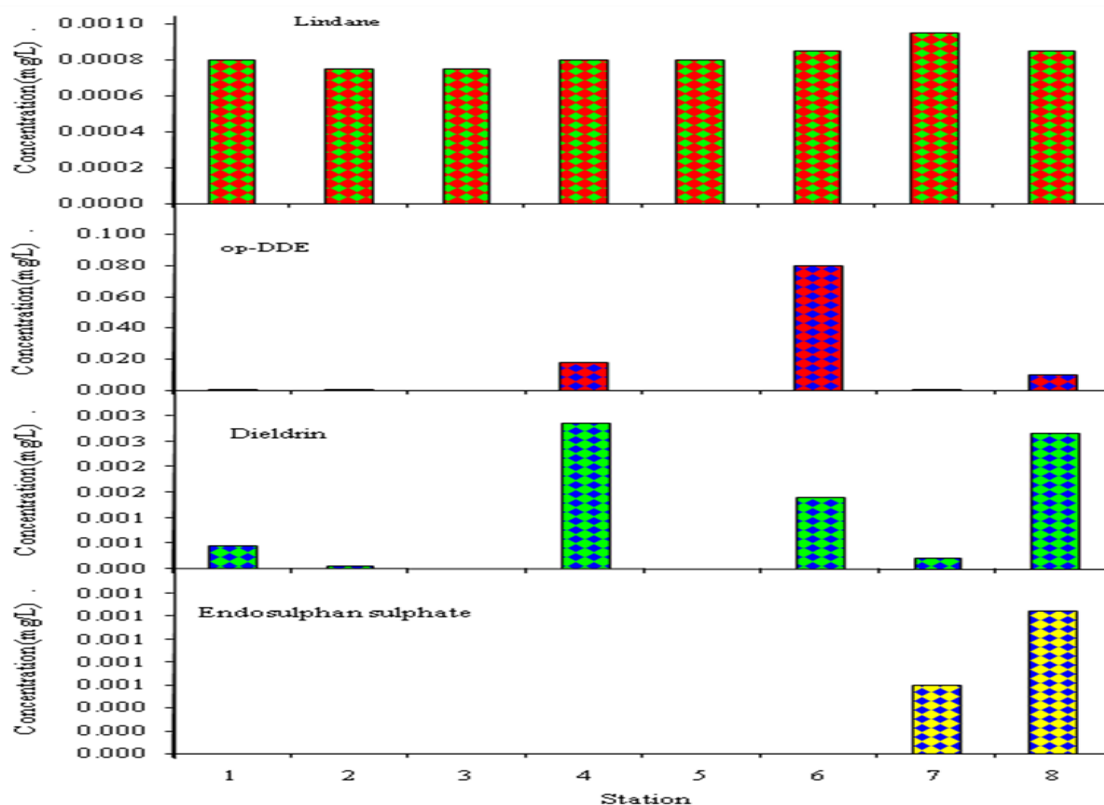


Figure 1: Organochlorine pesticides concentration in water during the study period

Using One-Way ANOVA, differences in the concentration of lindane in water among the sampled stations were not significant; $F = 0.161$, $df = 7$, $P = 0.994$) while those of op-DDE; $F = 3.447$, $df = 7$, $P = 0.0129$), dieldrin; $F = 11.556$, $df = 7$, $P = 0.017$) and endosulphan sulphate; $F = 11.5222$, $df = 7$, $P = 0.018$) were significant. Highest concentration of lindane was recorded in Pan-Paper and lowest in Uasin Gishu and Cherangani. This could possibly be explained by the build-up of this pesticide through accumulation as the river progresses towards Pan-Paper.

The MRL of lindane in water is 0.001 ppm (WHO, 1986), hence, apart from Pan-Paper the rest of the stations had values that were within the recommended values. This means that lindane maybe in significant use in the river's catchment area despite the fact that lindane in Kenya is restricted for seed dressing only.

The highest concentration of op-DDE in water was detected in Webuye followed by Mumias and Moi's Bridge. No op-DDE was detected in the rest of the sampled stations. This could be due to runoff from the flower farms in Moi's Bridge, which may be using this pesticide though it is banned. In Webuye and Mumias there's a lot of agricultural runoffs from sugarcane where DDT is sometimes used to eradicate mosquitoes alongside other agricultural insect pests. Figure 1 shows organochlorine pesticide levels in water during the study period.

The MRL of op'DDE is 0.04 ppm (WHO, 1996), which was exceeded in Webuye, hence, illustrating recent use of functional DDT in the area. Currently the use of DDT in Kenya is banned, except in the control of mosquitoes by public health authorities (PCPB, 1998; Wandiga *et al.*, 1998), but based on findings of the present study, it is apparent that agricultural DDT is being used in the area.

Dieldrin was not detected in waters of Uasin Gishu and Lugari. These regions have little large-scale farming activities, hence, the probability that dieldrin is not being used. Highest concentration was detected in Moi's Bridge and Mumias while intermediate concentrations occurred in Webuye, which were significantly higher ($p < 0.05$) than in Kitale and Pan-Paper. The lowest concentration in water was recorded in Cherangani implying little use of the insecticide in the area. Again, the high concentration of dieldrin in Moi's Bridge could be contributed to by runoff from the rose flower, farms which still indiscriminately use this banned pesticide. In Mumias there's the possibility of accumulation down the river combined with agricultural runoff

from sugarcane farms in the area. Dieldrin in Kenya is restricted to termite control in the building industry (PCPB, 1998) but results from this study indicate it's being used widely for other agricultural purposes. The MRL of dieldrin in water is 0.006 ppm (WHO, 1996), hence, all the stations recorded values within the recommended river water range.

Endosulphan sulphate was detected only in Pan-Paper and Mumias. The MRL of endosulfan sulphate (thiodan) in water is 0.004 ppm (WHO, 1996), which was not exceeded in any of the stations. It can therefore, be concluded that pollution from this pesticide does not pose any threat in the water of River Nzoia. Results of the pesticides concentration in soil during the study period in the eight sampling sites are shown in Figure 2.

The concentrations of lindane among the sampled stations were significantly different (One-Way ANOVA; $F = 7.254$, $df = 7$, $P = 0.029$). Its highest concentration among the stations was recorded in Pan-Paper and Mumias, which was higher than that in Kitale, Cherangani, and Lugari. However, Uasin Gishu, Moi's Bridge and Webuye recorded the lowest concentration of Lindane, which were all statistically dissimilar in concentration levels. The concentration of lindane was generally higher in soil than in water. This could be due to binding capacity to soil particles than water molecules.

The concentrations of op-DDE in soil were significantly different (One-Way ANOVA; $F = 14.307$, $df = 7$, $P = 0.007$) but was only detected in Webuye and very low concentrations in Pan-Paper. In the rest of the stations op-DDE was undetectable. This suggests recent use of functional DDT around Webuye.

Dieldrin (One-way ANOVA; $F = 10.255$, $df = 7$, $P = 0.015$) was detected in soils from all the sampled stations except Uasin Gishu and Moi's Bridge and highest concentration was detected in Webuye. Intermediate concentrations occurred in Kitale, Cherangani, Lugari and Pan-Paper, which were significantly ($p < 0.05$) lower than the levels

recorded in Mumias. This trend suggests current considerable use of the pesticide especially around Webuye for agricultural and wood preservation purposes despite it being restricted for termite control only. The Pan-Paper area recorded much lower values of dieldrin suggesting that although a lot of timber handling goes on in this region, amounts of this pesticide as timber preservative causes negligible threat to soil contamination.

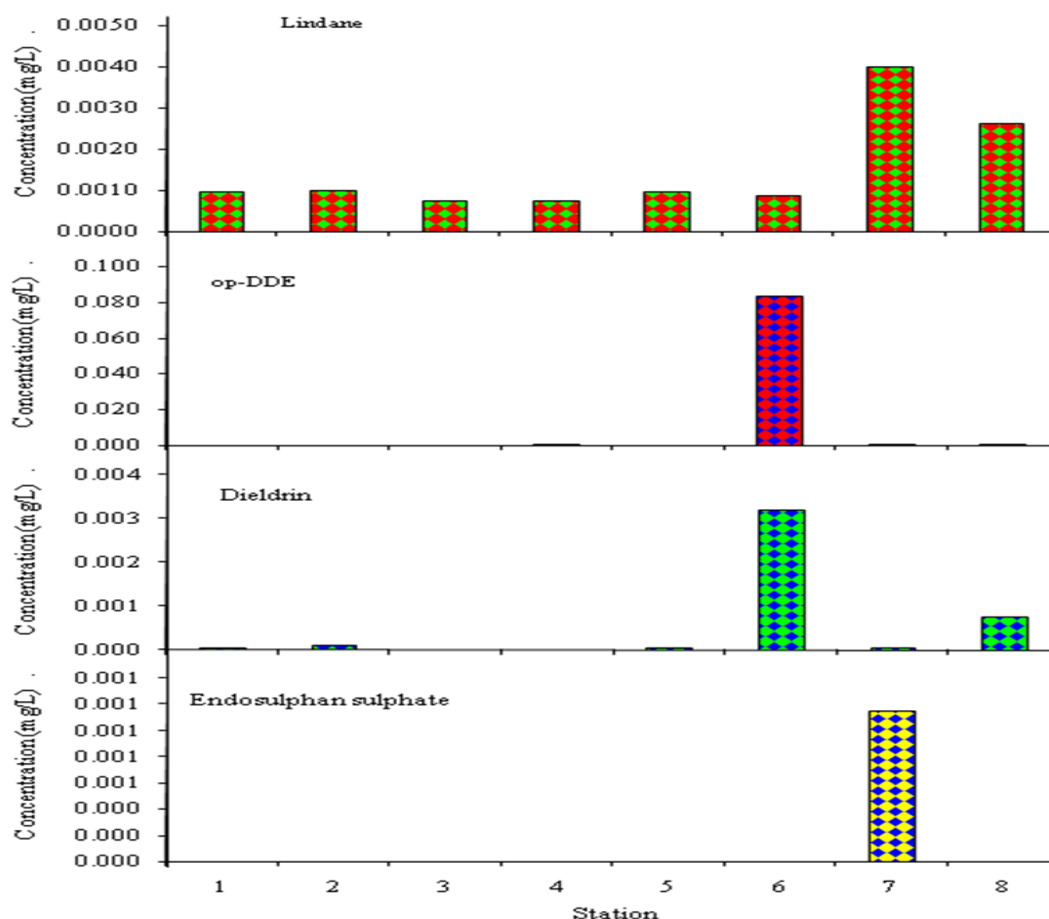


Figure 2: Organochlorine pesticides concentration in soil during the study period

Endosulphan sulphate in soil showed significant differences in concentration among the sampled stations (One-way ANOVA; $F = 10.530$, $df = 7$, $P = 0.016$). No detections of this pesticide occurred in all the stations except in Pan-Paper, which recorded a highly significantly different concentration. From 1980's use of endosulfan sulphate has grown as an alternative to DDT, especially in cotton and sugarcane growing areas because cotton and sugarcane pests had grown resistant to DDT (Wandiga *et al.*, 1998). This explains the high incidence of the pesticide in the soils of Webuye, which is home to large scale sugarcane growing.

Results of the pesticides concentration in sediments during the study period in the eight sampling sites are shown in Figure 3.

Concentrations of lindane, op-DDE, dieldrin and endosulphan sulphate using One-Way ANOVA were significantly different ($F = 8.250$, $df = 7$, $P = 0.025$), ($F = 11.500$, $df = 7$, $P = 0.007$), ($F = 10.433$, $df = 7$, $P = 0.023$) and $F = 9.877$, $df = 7$, $P = 0.024$), respectively among the sampled stations.

Highest concentration of lindane was recorded in Moi's Bridge, followed by Mumias and Pan-Paper, which was still significantly higher than concentrations in the rest of the stations while Kitale recorded lowest. These concentrations were much higher than those of water probably because of accumulation in the sediments with time. This, therefore, suggests continuous use of this pesticide for other agricultural purposes apart from seed dressing.

Dieldrin was undetectable in sediments from Uasin Gishu and Pan-Paper while highest concentration was detected in Moi's Bridge. Intermediate concentrations occurred in Webuye and Mumias while lower levels were recorded in Kitale, Cherangani and Lugari. This suggests extensive use of dieldrin probably in the rose flower farms around Moi's Bridge despite its restriction to termite control only by the Kenyan government. Again, in the Moi's Bridge site, the river is settled (not fast flowing) hence the extensive deposit of dieldrin in the sediments is facilitated.

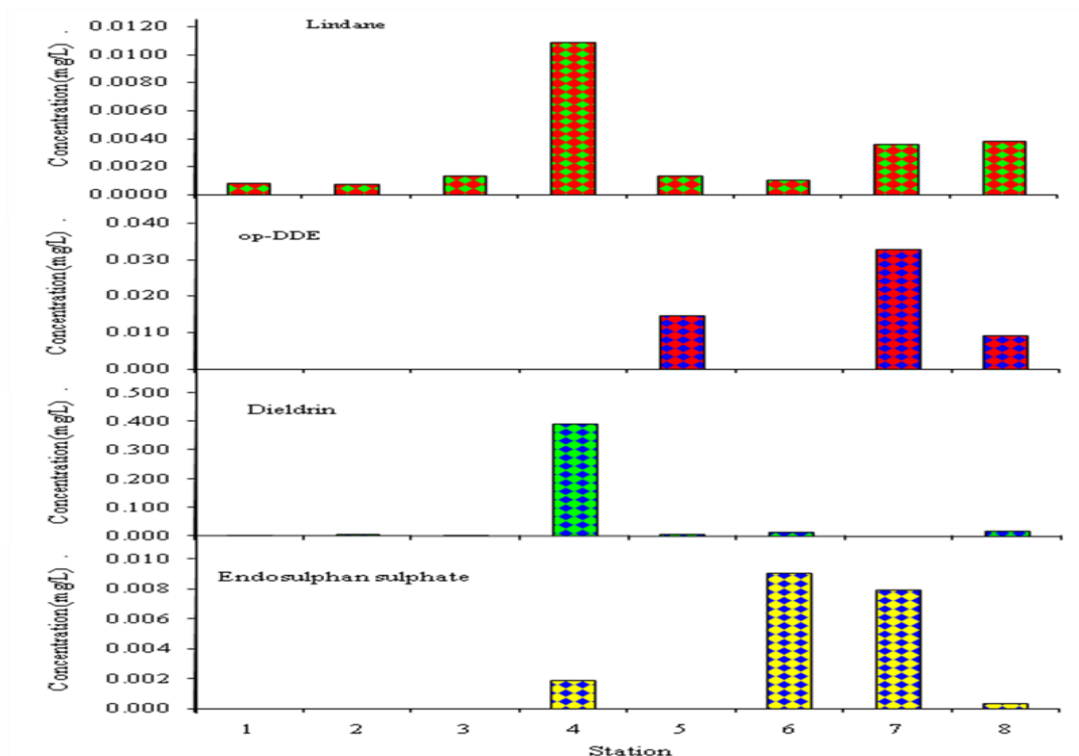


Figure 3: Organochlorine pesticides concentration in sediments during the study period

Similarly, endosulphan sulphate was undetectable in sediment samples for Kitale, Cherangani, Uasin Gishu and Lugari. Significantly higher ($p < 0.05$) concentrations of this pesticide occurred in Webuye and Pan-Paper, which were all significantly higher than the levels recorded in Moi’s Bridge and Mumias. Again this suggests possible use of endosulphan sulphate probably in sugar sugarcane farming.

Pyrethroids

The mean concentrations of the pyrethroid pesticides analyzed in the three environmental media are presented in Table 1.

The concentrations of lambda cyhalo, alpha cypermethrin and deltamethin using One-Way ANOVA were significantly different ($F = 2.3332, df = 2, P = 0.0456$), ($F = 3.1112, df = 2, P = 0.0322$) and ($F = 2.9833, df = 2, P = 0.0472$), respectively. Among the three media sampled Post-hoc comparisons indicated that concentration of lambda cyhalo was significantly ($P < 0.05$) lower in water than in soils and sediments; this is probably because lambda cyhalo has a high affinity for soil but extremely low water solubility and is tightly bound to soil (Haug and Hoffman, 1990).

Table 1: Mean of pyrethroid pesticide concentrations (mg/l) in the soil, water, and sediments in Nzoia

	Soil	Water	Sediments
Lambda cyhalo	0.0038 ± 0.0015	0.0017 ± 0.0007	0.0037 ± 0.0151
Alpha cypermethrin	0.0004 ± 0.0002	0.0011 ± 0.0040	0.0009 ± 0.0004
Deltamethrin	0.0065 ± 0.0019	0.0108 ± 0.0029	0.0059 ± 0.0025

It’s also not appreciably mobile in most soils, hence, higher concentration. Levels of alpha cypermethrin in water and sediments were significantly higher than concentration of this pyrethroid in soils. This is probably because alpha cypermethrin does not attach itself much to sandy soil which is mostly evident in the area. Sediments and soils recorded lower levels of deltamethrin compared to their concentrations in water. Again, this can be explained using the binding capacity of deltamethrin, which is similar to that of alpha cypermethrin.

Results of the pyrethroid pesticides concentration in water during the study period in the eight sampling sites are shown in Figure 4. Differences in the concentration of lambda cyhalo among the sampled stations were significant (One-Way ANOVA; $F = 3.400, df = 7, P = 0.044$).

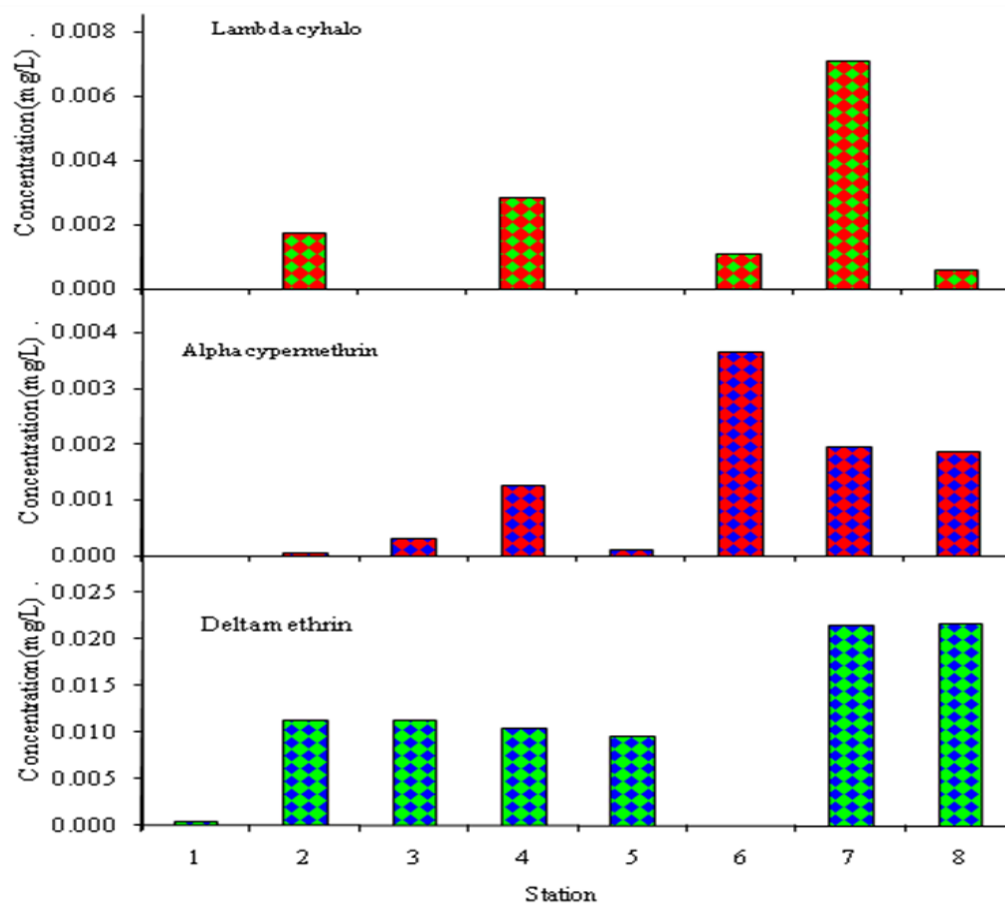


Figure 4: Pyrethroid pesticides concentration in water during the study period

Highest concentration was recorded in Pan-Paper. Intermediate concentrations were recorded in Cherangani and Moi's Bridge, which were significantly ($p < 0.05$) higher than the concentrations in Webuye and Mumias. The lowest concentration of lambda cyhalo was recorded in Uasin Gishu and was also detected in Kitale and Lugari probably because the river around the Lugari sampled site is well covered with flora hence the filter effect. The land

along the river here is not steep hence little agricultural runoff. The MRL of lambda cyhalo in water is 0.05 ppm (FAO/WHO, 1993). All the stations recorded values way below this limit.

There were significant differences in the concentrations of alpha cypermethrin in water among the stations sampled (One-Way ANOVA; $F = 5.337$, $df = 7$, $P = 0.0131$). This pesticide was not detected in Kitale. The highest concentration was, however, detected in Webuye while intermediate values were recorded in Moi's Bridge, Pan-Paper and Mumias. Significantly ($p < 0.05$) lower values of alpha cypermethrin were recorded in Uasin Gishu while Lugari and Cherangani recorded the lowest values in the collected water samples.

All the stations recorded values way below the MRL of alpha cypermethrin (0.05 ppm), (FAO/WHO, 1993). Significant differences in concentration of deltamethrin in water were recorded among the sampled stations (One-way ANOVA; $F = 10.506$, $df = 7$, $P = 0.019$). The highest concentrations of deltamethrin were detected in Mumias and Pan-Paper. Intermediate concentrations occurred in Cherangani, Uasin Gishu, Moi's Bridge and Lugari while lower levels of the pesticide were recorded in Kitale with Webuye recording the least level. Since the MRL of deltamethrin in water is 0.05 ppm, however, all the stations recorded values way below this limit. Deltamethrin is currently used for both agricultural purposes and for malarial control in the area. Since it poses little threat to environmental pollution then it's a better pesticide for malarial control purposes than the DDT group.

Results of pyrethroid concentrations in soil during the study period in the eight sampling sites are shown in Figure 5. Concentration of lambda cyhalo, alpha cypermethrin and deltamethrin using One-Way ANOVA were significantly different ($F = 2.974$, $df = 7$, $P = 0.0482$), ($F = 4.722$, $df = 7$, $P = 0.0371$) and (F

=4.003, df = 7, P = 0.035), respectively in soil among the sampled stations. Highest concentration of lambda cyhalo were recorded in Moi's Bridge and Mumias, which was significantly (p<0.05) higher than concentration in Lugari and

Webuye. Cherangani and Pan-Paper had the lowest concentration of lambda cyhalo, while none of this pesticide was detected in Kitale and Uasin Gishu.

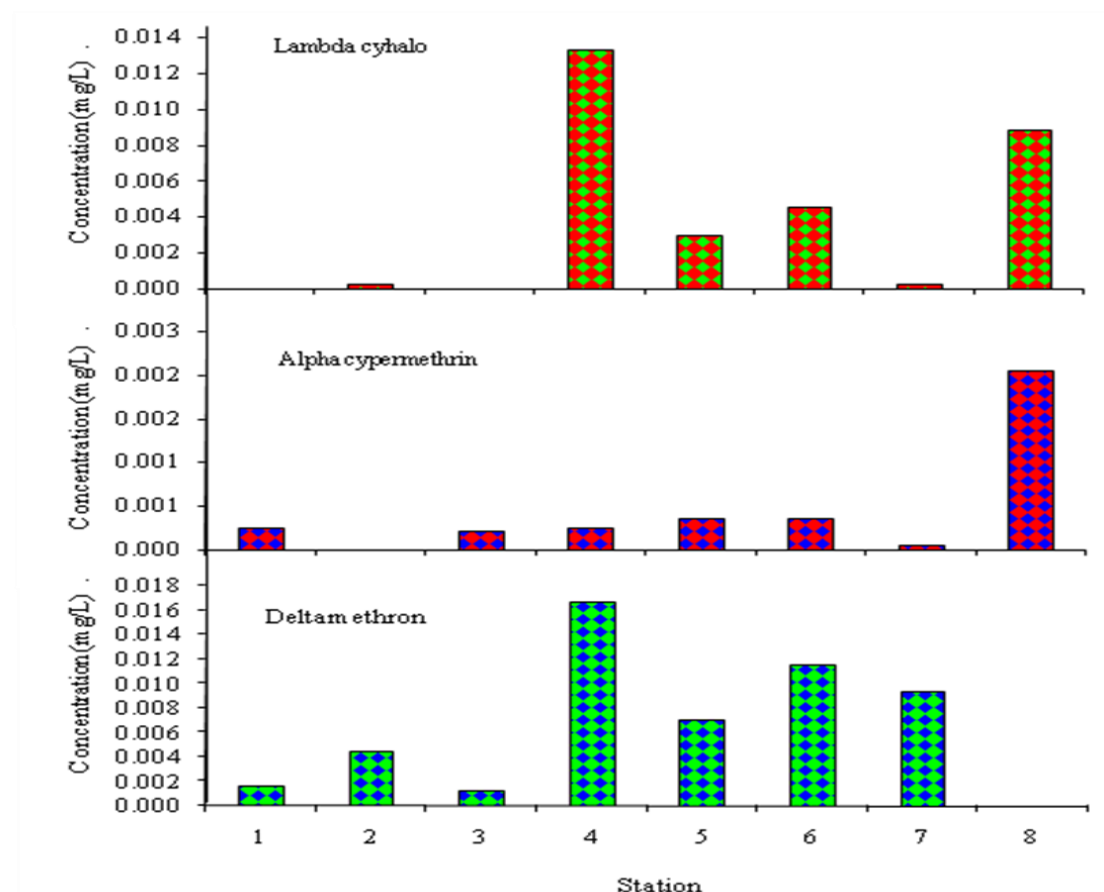


Figure 5: Pyrethroid pesticides concentration in soil during the study period

These concentrations indicate little use of the pesticide in the area. No alpha cypermethrin pesticide was detected in soils of Cherangani. Significantly lower values of this pesticide were recorded in Pan-Paper, which were lower than values from Kitale, Uasin Gishu, Moi's Bridge, Lugari and Webuye. The highest value was, however, recorded in Mumias. Again these concentrations indicate little use of the pesticide in the area. The fact that the concentrations went up gradually down the river where there is a lot of sugarcane farming activities also suggests extensive use of the pesticide.

The highest concentration of deltamethrin in soil was detected in Moi's Bridge, followed by Webuye, Pan-Paper then Lugari. Intermediate concentrations of deltamethrin in soil occurred in Cherangani while the lowest levels of the pesticide were recorded in Kitale and Uasin Gishu. These results suggest extensive use of the

pesticide in the flower farms around Moi's Bridge although it's not hazardous in soil since the soils around the area are sandy, hence, binding capacity is low.

Results of pyrethroids concentration in sediments in the eight sampling sites are shown in Figure 6. Differences in the concentration of lambda cyhalo among the sampled stations were significant, (One-Way ANOVA; F = 3.144, df = 7, P = 0.045). Highest concentration of among the stations was recorded in Mumias which was higher than concentration in Lugari, Webuye, and Pan-Paper.

Kitale, Uasin Gishu, Cherangani and Moi's Bridge had lowest concentrations of this pesticide, which were all statistically disimilar in concentration levels. Since all the sites recorded values lower than the MRL values then there is no threat in the environment of River Nzoia's catchment area from lambda cyhalo.

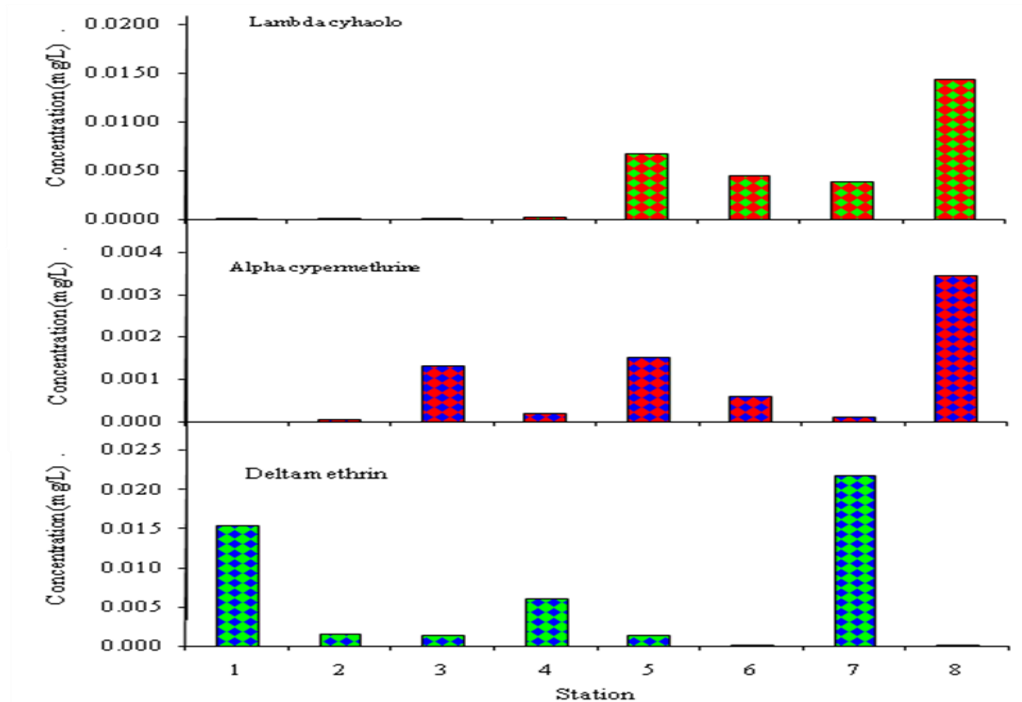


Figure 6: Pyrethroid pesticides concentration in sediments during the study period

There were significant differences in the concentrations of alpha cypermethrin in sediments among the stations sampled (One-Way ANOVA; $F = 3.222$, $df = 7$, $P = 0.046$). It was not detected in Kitale and significantly lower values were recorded in Cherangani, Moi’s Bridge Pan-Paper.

Intermediate values were recorded in Uasin Gishu, Lugari and Webuye while the highest values were recorded in Mumias. Mumias being the last station down-river, it is possible that the contribution came from wash down from upstream. This builds up as the water body moves downstream and accumulates, hence, the higher concentration downstream.

Concentration of deltamethrin in sediments were significantly different among the sampled stations (One-way ANOVA; $F = 4.536$, $df = 7$, $P = 0.039$). Though there were no detection of

this pesticide in Webuye and Mumias, highest concentrations were detected in Kitale and Pan-Paper.

Intermediate concentrations of deltamethrin occurred in Cherangani, Uasin Gishu and Lugari, which were significantly lower ($p < 0.05$) than values recorded in Moi’s Bridge. The high concentration in Kitale could be from the municipal use of it (Power Tab) for mosquito control in the populated town of Kitale.

Temporal variations in concentration of the selected pesticides in water, soil and sediments

Organochlorines

The results of the mean temporal variations in concentration of organochlorine pesticides during the entire study period are shown in Figure 7.

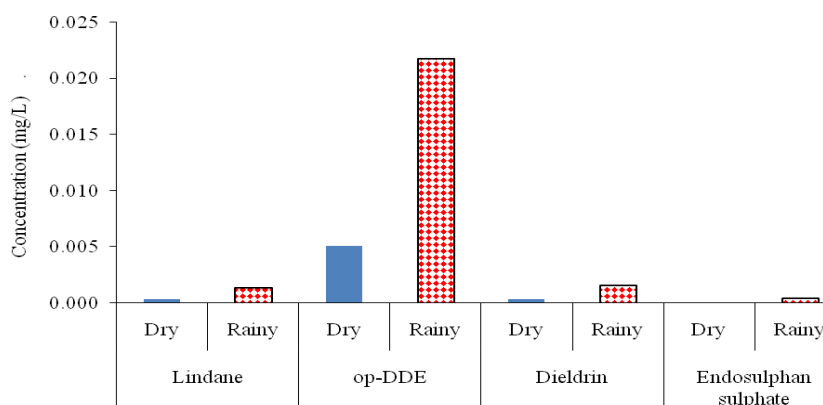


Figure 7: Organochlorine pesticides concentration during the dry and rainy seasons

Differences in concentration of all the organochlorine pesticides among the seasons were significant ($p < 0.05$), with the rainy season recording an increase in the concentration of all those detected pesticides. This is probably because these pesticides are usually applied in farm fields at the beginning of rainy seasons when crops are planted, compared to dry season where

most farms in the area lie fallow or have very little activity.

Pyrethroids

The results of the overall temporal variations in concentration of pyrethroid pesticides during the entire study period are shown in Figure 8.

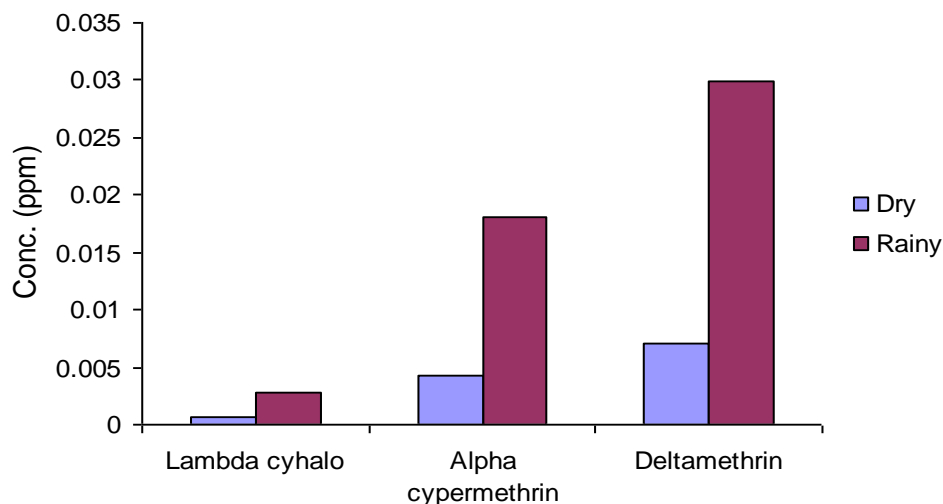


Figure 8: Pyrethroid pesticides concentration in soil, sediments and water during the dry and rainy seasons

Differences in the concentration of all the pyrethroid pesticides detected among the seasons were significant ($p < 0.05$). The rainy season recorded an increase in the concentration of all the detected pyrethroid pesticides because this is the season when these pesticides are applied in farms. Those that are used in mosquito control are also applied in larger quantities in the rainy season since this is the time the insects breed due to the available moisture.

Conclusion and recommendation

The results show that there's danger of pollution of the drinking water of Nzoia from some organochlorines (lindane and op-DDE) specifically in Pan-Paper and Webuye, respectively. There was a general increasing trend of the concentrations of the pollutants as the river progresses to Lake Victoria. The large-scale cash crop areas (rose flowers, sugar cane and tea) were the most polluted. To reduce consumer health concerns, routine monitoring of pesticide residues in water, soil, and sediments is advised. Farmers must be educated on the usage of organic fertilisers and integrated pest management.

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