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## Assessment of organochlorine pesticides (OCPs) contamination in relation to physico-chemical parameters in the Upper River Kuja Catchment, Kenya (East Africa)

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### Abstract

Concentrations of 17 organochlorine pesticides residues (alpha-HCH, beta-HCH, gamma-HCH, delta-HCH, Heptachlor, Aldrin, Endrin, Endosulfan I, Dieldrin, *p,p'*-DDT, Endosulfan II, *p,p'*-DDD, Endrin aldehyde, *p,p'*-DDE, Endosulfan sulfate, Heptachlor epoxide and Methoxychlor) were analysed in water and sediment from Upper River Kuja catchment, Kenya, between January-October 2015, using Gas-Chromatography (GC) with (GC-ECD) equipment. Nutrient levels and water quality parameters: pH ( $7.57 \pm 0.354$ ), secchi disk ( $0.05 \pm 0.019$ ), dissolved oxygen (DO) ( $6.96 \pm 0.897$ ), temperature ( $25.39 \pm 2.201$ ), conductivity ( $62.03 \pm 23.123$ ) and hardness ( $26.39 \pm 6.063$ ) contributed to significant variations in organochlorine pesticide residue levels observed. Statistical significance differences ( $p < 0.05$ ) between water quality parameters in the sampling stations occurred. Pesticide concentrations ranged within BDL –  $0.263 \mu\text{g l}^{-1}$ , for Heptachlor, BDL –  $0.506 \mu\text{g l}^{-1}$  Heptachlor epoxide, BDL –  $0.506$  Aldrin, BDL –  $0.014$  Dieldrin, *p,p'*-DDT, BDL –  $0.644$  *p,p'*-DDE, BDL –  $0.176$  *p,p'*-DDD, and BDL –  $2.220$  methoxychlor. Sediment pesticide residues were higher during rainy period. Results indicate persistent organic pollutants (POPs) exist in our environment, and recent use in sampled area. Increased aquatic monitoring is recommended to detect persistency and changes in target environment.

**Keywords:** water quality, organochlorines, River Kuja catchment, Lake Victoria

### 1. Introduction

Freshwater ecosystems have suffered the most intense human related intervention of all ecosystems over the past 100 years of human history on both national and global scale (Collares-Pereira *et al*, 2002) [5]. According to Jewwit (2002) [20], humans rely on renewable freshwater for drinking, irrigation of crops, industrial use, production of fish and waterfowl, transportation, recreation and waste disposal. As rivers act as drains to the surrounding landscapes, catchments become sinks for accumulating organic and inorganic pollution materials, such as pesticides and heavy metals respectively, severely degrading the environment (Hecky, 1993; Honnen *et al*, 2001; Dallas and Day, 2004; Babu *et al*, 2015) [18, 7, 3]. Pesticide contamination of surface waters have been well documented worldwide and cause a major issue that gives rise to concerns at local, regional, national and global scales due their adverse effects on the environment. At the Stockholm Convention on Persistent Organic Pollutants in 2001, the international community discussed harmful effects of pesticides on human health and the environment and with intention to eliminate or severely restrict their production. Previous studies have shown that increased anthropogenic activities and population growth within the Lake basin catchment has led to pollution and degradation of its aquatic ecosystem (Africa atlas, 2006; Sitoki *et al.*, 2010). River Kuja catchment lies in the South Western region of Kenya, one of the most heavily populated lake regions in the world, with an area of approximately  $184,200 \text{ km}^2$  and is not an exception to environmental degradation from organic and inorganic pollutants. River Kuja is used as source of water for domestic use and animal watering thereby making its quality very critical for the riparian population. However, along this river exists several land-use activities such as agriculture (tea and coffee), agro-based industries such as coffee, deforestation, and urbanization. These activities have the potential to compromise the water quality of the river which may affect

human health as well. Currently, Kenya is at a cross-roads in balancing between best and cost effective agricultural practices to feed its bulging population as well as answer to demands for environmental protection and sustainability (Osoro *et al.*, 2016) [26].

Previous documented studies indicate the presence of pesticides in the market as well as their residues within Lake Victoria Basin environment (Wandiga *et al.*, 2002; Getenga *et al.*, 2004) [35, 14]. Studies carried out by Osoro *et al.*, (2016) [26] showed the presence of DDT,  $\alpha$ -HCH,  $\beta$ -HCH and endrin aldehyde pesticides in water samples collected along main beaches at Rusinga Island in Lake Victoria, Kenya. Samples collected during the long rain season contained the highest amount of pesticide residues while the short dry seasons had lowest concentrations and this was attributed to the runoff from the farms where the pesticides were previously applied. Like in many other developing countries, pesticides are used extensively in Kenya's South Western arable and highly populated highlands region to increase crop yield, as agro-chemical products and for livestock production. Agriculture is the main economic backbone of Kenya, which contributes about one-third (30.2%) to the country's gross domestic product (GDP), and over 80% of the people depend on agriculture related activities for their livelihood. In addition, the proliferation of green-houses in the South Western region of Kenya is also due to demand for higher agricultural output and calls for active use of agricultural chemicals such as pesticides in order to attain maximum economic returns leading to declining water quality (eutrophication), and changes in the freshwater balance in those areas (UNEP, 2003; Himmelein *et al.*, 2011) [32, 19]. Overall, pesticide use in Kenya is already one of the highest in sub-Saharan Africa with a market share of approximately USD 40.4 million by 2003. In addition, about 8,749 tonnes of different types of pesticides were imported into the country in 2006 (PCPB, 2008) [27], hence the aquatic ecosystem of the densely populated areas of South Western Kenya has not been spared either. Currently, inadequate data exist that show levels and exact quantities of organic pollutants such as pesticides residues in water and substrates in Kenya's major rivers such as River Kuja. There is thus an urgent need to carry out regular assessment of surface water quality in order to assess riverine pollution loads as part of inland aquatic environmental sustainable management in order to guide in policy formulations and understand exposure levels to aquatic life and potential risks to humans, hence this study.

## 2. Materials and Methods

### 2.1 Study Area

River Kuja and its catchment has its source in Nyamira County in the Kisii highlands. Many permanent streams drain these South Western highlands, in an area of deeply dissected terrain with an altitude of between 2,000 and 2,350 metres. The river passes through the heart of Kisii County, a rich agricultural county, running west through Migori County where it is joined by the Migori River and flows as the Kuja-Migori River into Lake Victoria (Fig. 1). Ten stations were selected objectively, in the upstream upper reaches, mid reaches and those targeting areas after major agricultural farms, agro-based industries and urban influence to represent the target area. The geology of Kisii highlands base structure consists of the Bukoban, Granitic, Nyanzian and Kavirondian (Ablun series) rocks. Information on the general status of this river is scanty and old and therefore need to be collected and

updated to help in decision making and sustainable utilization. Regular monitoring of water quality is a key requirement for any natural water body due their immense value to man. The overall objective of this study is to assess seasonal variations of organochlorine pesticide residue levels in relation to water quality.

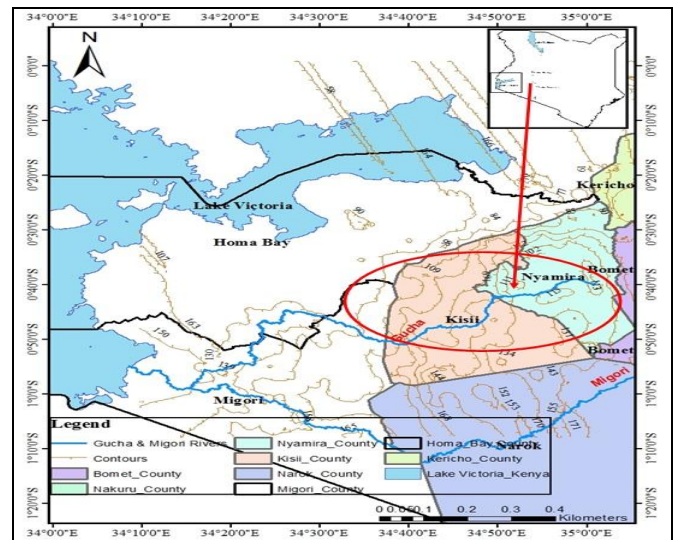


Fig 2.1: Location of River Kuja/Gucha catchment and the related study stations.

### 2.2 Sampling and sample collection

Sampling was done in 10 randomly selected sites (Figure 2.1) along the river whereby purposeful sampling method was adopted on target stations along Upper River Kuja drainage system. Samples were collected in triplicate: in the dry season and in the wet season. Water was obtained by use of grab method into polyethylene and 2.5 L amber bottles, which had been pre-washed with distilled water and dried. For organic residues analysis, each water sample was treated with 1 g mercuric chloride, and mixed for 5 minutes in order to kill pesticide degrading microorganisms.

#### 2.2.1 Physico-chemical parameters

Water samples were obtained on site (YSI Portable system) for physico-chemical determinants; Temperature ( $^{\circ}\text{C}$ ), Dissolved Oxygen ( $\text{mgL}^{-1}$ ), pH, Conductivity ( $\mu\text{Scm}^{-1}$ ). Standard methods were used for *insitu* data collection and sampling (APHA, 2005) [2]. Sites for measurements of physical and chemical water quality parameters were selected by stratified strategy. These sampling stations were determined at unperturbed but accessible points along the main and tributary rivers within the catchment. Sampling stations were marked using a hand held GPS Magellan Global Positioning System, 315 Meridian, as waypoints and salient attributes of the sampling stations recorded prior to sampling. Portable electronic water quality profiler, YSI 650 MDS system was used to log physico-chemical water quality data. The main physical and chemical parameters measured electronically were; temperature ( $^{\circ}\text{C}$ ), dissolved oxygen (DO) ( $\text{mg/L}$ ), conductivity ( $\mu\text{S/cm}$ ), pH and Total Dissolved Solids (TDS). Secchi depth was measured with a standard Secchi disk of 20 cm diameter, with quadrants painted in black and white. The Secchi depth is derived as the average of the depth at disappearance and that of reappearance of the disk in water. General environmental observations about the stations such as sampling site, time of sampling, weather conditions and station features, were noted.

### 2.2.2 Sampling for pesticides

Water and sediment samples for pesticides data was taken from ten sampling stations on a quarterly basis, between March 2015 –December 2015 in the catchment of River Kuja (Figure 1) in order to coincide with the long (April-May) and the dry (July) and short (September) rain seasons. Composites water samples, were obtained by grab method (APHA, 2005) [2] and transferred into 2.5 L amber glass bottles that had been pre-washed with distilled water and dried. 1.0 g mercuric chloride was thoroughly mixed with the water sample for 5 minutes. This was used as a treatment option to avoid degradation of the pesticides by microorganisms. Prior to extraction, all the water samples were temporarily stored in an ice box with wet ice, transported to the laboratory and kept in a standard fridge at 4 °C. Solvent-phase extraction (SPE) method (Thurman *et al*, 1998) [30] was used in extraction of all the samples.

From the same site where water samples were obtained, a pre-cleaned stainless steel shovel (Poner Grab) was used to scoop the sediment in triplicate, thoroughly mixed on a clean piece of aluminum foil then a representative sample of 500 g was then packed in zip lock plastic bags, kept in ice-boxes with wet ice, later transported to the laboratory, kept in a -20 °C deep freezer before extraction, clean-up and analysis, as mentioned for water samples. The rest of the water sample was stored at 4 °C in the dark. Samples stored at 4 °C were used within 2 days after collection.

### 2.3 Quality assurance

For quality control, all samples were picked in composite, extracted and cleaned up before GC-MS procedures. Water samples were spied with 1L distilled water with respective pesticides standards to obtain 0.1 µg l<sup>-1</sup> final concentration of the target pesticides samples. The detection limit of each pesticide under investigation was determined by use of external standards and pure distilled water as available as blanks. Specific pesticide standards were available at the University of Nairobi chemistry laboratories.

### 2.4 Materials and Chemicals

Identification and quantification of pesticide residues in the samples obtained was done by use of high quality pesticide standards mixture of over 99% purity. The pesticide standards were obtained from Dr EHRENSTORFER GmbH, (Ausburg, Germany). Solvents such as Dichloromethane (DCM), acetone, isooctane and hexane were sourced from Fisher Scientific (USA). Other consumable chemicals such as hydrochloric acid (HCL), methanol, sodium chloride (NaCl), aluminum oxide (AlO), sodium hydroxide (NaOH), copper and anhydrous sodium sulphate (NaSO<sub>4</sub>), all of analytical grade, were also obtained from Fisher Scientific (USA). General purpose reagents (GPR) were triple distilled in all-glass apparatus before use.

### 2.5 Sample Extraction and Clean-Up

Used glassware was soaked in detergent for 24 hours, washed and rinsed in distilled water before being dried in an oven at 100 °C for 24 hours. Solvent-phase extraction (SPE) method was used in extraction of water samples. 50 ml of 0.2 M dipotassium hydrogen phosphate buffer was added to a water sample of 2.0 litres, later transferred into a separatory funnel and its pH adjusted to 7.0 by adding drops of 0.1 N sodium hydroxide and 0.1M HCl solutions to neutralize the sample. 100 g sodium chloride was then added to salt out the

pesticides from the aqueous phase. While slowly releasing pressure, 60 ml triple distilled dichloromethane (DCM) was added to this solution and shaken for two minutes. Separation of the phases was achieved after allowing the sample to settle for 30 minutes. A 250 ml Erlenmeyer flask was used to collect the organic layer and extraction twice repeated using 60 ml portions of dichloromethane. After storage in refrigerator at 4 °C, the extracts were combined and cleaned by passing it through Al<sub>2</sub>O<sub>3</sub> chromatographic column topped with anhydrous sodium sulphate. Pesticide residues were sequentially eluted with 175 ml n-hexane. It was necessary to concentrate the elutes to 1 ml using a rotary evaporator at 40 °C, and to reconstitute them in 0.5 ml HPLC grade isooctane for GC analyses.

Prior to mixing, the wet sediment samples were allowed to thaw for 4 hours in the laboratory then EPA method 3540 Soxhlet extraction of sediments applied. Before transferring the sediment sample to the Soxhlet thimble, triplicates of 20 g samples were dried overnight with activated anhydrous sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) then extracted with 200 ml of hexane to acetone (3:1v/v) in a 250 ml round bottomed flasks for a minimum of 16 hours. After storage in refrigerator at 4 °C, the extracts were combined and cleaned by passing it through Al<sub>2</sub>O<sub>3</sub> chromatographic column topped with anhydrous sodium sulphate. The elutes were concentrated to 1ml using a rotary evaporator at 40 °C, and reconstituted in 0.5 ml HPLC grade isooctane for GC analyses. The final samples were analysed by a Varian Chrompack CP-3800 GC equipped with electron capture detector (GC-ECD), under the conditions specified. The following organochlorine pesticide residues were identified: α-HCH, β-HCH, γ-HCH, δ-HCH, p,p-DDD, p,p-DDE, p,p-DDT, aldrin, endrin, dieldrin, endrin aldehyde, endosulphan I, endosulphan II, endosulphan sulphate, heptachlor, heptachlor epoxide, and metoxychlor.

In data analysis, Microsoft excel sheet was used to obtain frequency tables, range, means, standard deviations and error margins (± SE) of the pesticides between stations were obtained for comparisons with WHO/NEMA threshold levels in natural environments. Two-way ANOVA, at p < 0.05, was used to show variations among individual pesticides and within seasons.

### 2.6 Statistical analysis

Statistically significant differences were confirmed by using one-way analysis of variance (ANOVA). Variation in data among sampling sites (spatial, representing different effluent and runoff mixtures) and months (temporal, with different preceding rainfall regimes) collected in, were assessed by using two-way analysis of variance (ANOVA) and a multiple-comparison test procedure (Holm-Sidak test). Data were tested for homogeneity of variation and normality prior to the ANOVA. Two-way analysis of variation was conducted to see weather season had an effect on site variation. In the case of nonparametric conditions, analysis of variance by ranks, Kruskal-Wallis test along with the Newman-Keuls multi-comparison test.

## 3. Results

### 3.1 Water quality parameters

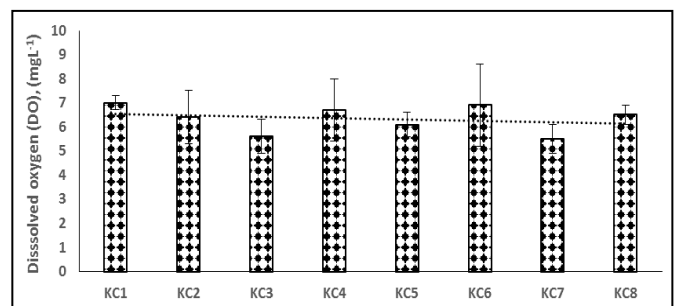
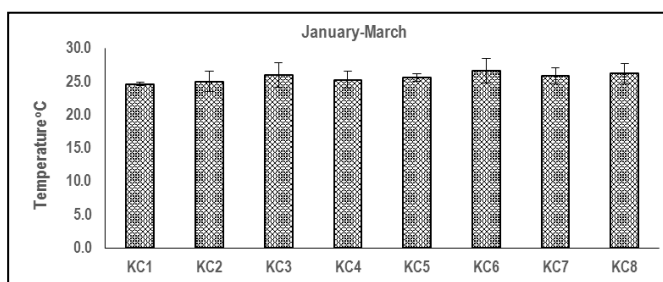
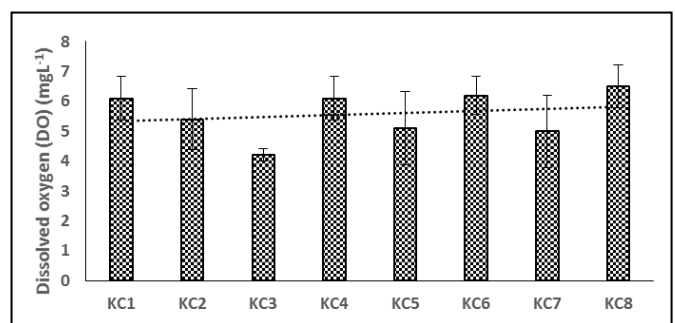
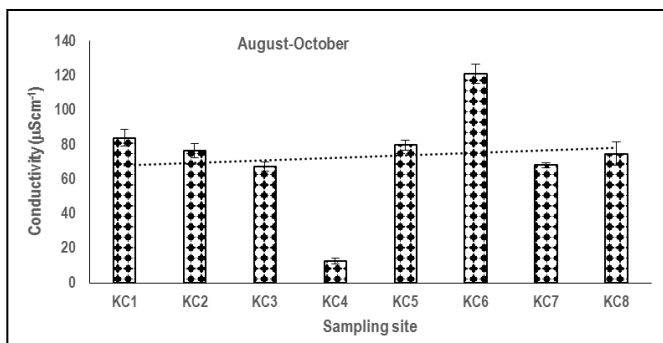
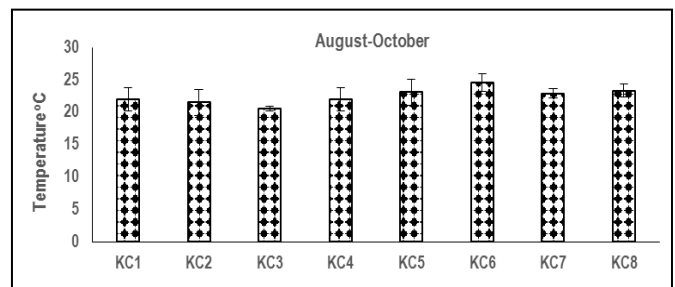
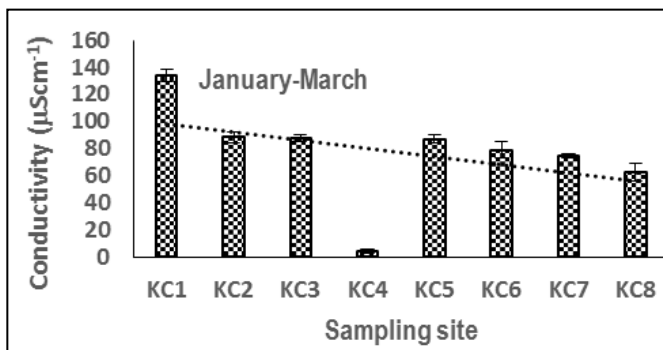
The mean values of physical-chemical measurements of the upper River Kuja catchment system for two different sampling seasons (January-March and August-October) depicting dry and wet seasons are presented in Table 3.1 below. Similarly, the mean values of five selected water

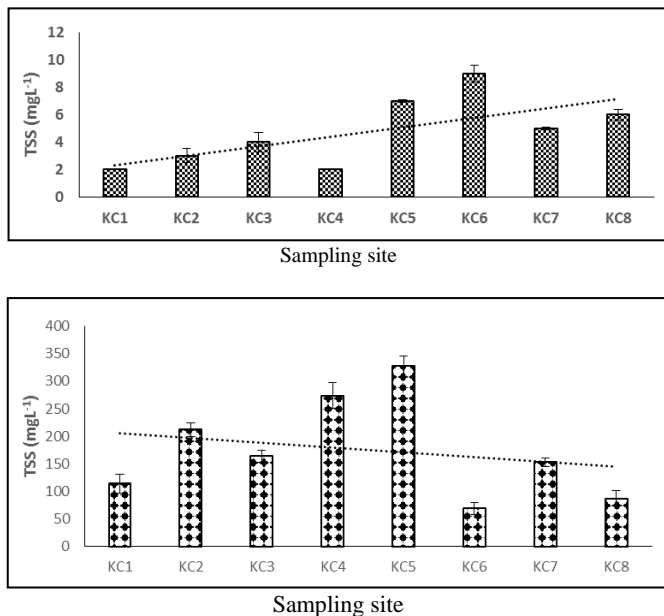
quality parameters (temperature, dissolved oxygen (DO), Total Suspended Solids (TSS), pH and conductivity) is presented in Figure 3.2 indicating high concentration

variations. These analytical results in Figure 3.2 also depict seasonal variance for the selected parameters at the various sampling sites.

**Table 3.1:** Water quality measurements for seasons January- March and August-October 2015. Both sites are summarised according to site and physico-chemical measurements.

| Sample Date: January-March (dry), 2015  |                   |      |      |      |      |      |       |      |      |
|---|-------------------|------|------|------|------|------|-------|------|------|
| Parameter                               | Unit              | KC1  | KC2  | KC3  | KC4  | KC5  | KC6   | KC7  | KC8  |
| Physical-chemical measurements          |                   |      |      |      |      |      |       |      |      |
| Temperature                             | °C                | 26.3 | 25.2 | 26.5 | 25.1 | 23.4 | 24.7  | 26.7 | 24.1 |
| Dissolved Oxygen (DO)                   | mgL <sup>-1</sup> | 4.2  | 5.4  | 4.2  | 6.3  | 5.8  | 5.4   | 5.0  | 5.5  |
| Total Suspended Solids                  | mgL <sup>-1</sup> | 2    | 3    | 4    | 2    | 7    | 9     | 5    | 6    |
| pH                                      |                   | 8.6  | 9.1  | 4.1  | 9.9  | 8.3  | 9.3   | 9.3  | 8.2  |
| Conductivity                            | µS/cm             | 134  | 88.4 | 87.5 | 4.1  | 86.9 | 79.1  | 74.3 | 62.7 |
| Sample Date: August-October (wet), 2015 |                   |      |      |      |      |      |       |      |      |
| Parameter                               | Unit              | KC1  | KC2  | KC3  | KC4  | KC5  | KC6   | KC7  | KC8  |
| Temperature                             | °C                | 23.3 | 26.2 | 24.5 | 23.8 | 22.4 | 24.7  | 25.4 | 24.1 |
| Dissolved Oxygen (DO)                   | mgL <sup>-1</sup> | 6.1  | 5.4  | 4.2  | 6.1  | 5.1  | 6.2   | 5.0  | 6.5  |
| Total Suspended Solids                  | mgL <sup>-1</sup> | 114  | 212  | 164  | 274  | 327  | 69    | 153  | 87   |
| pH                                      |                   | 6.6  | 8.2  | 7.1  | 6.9  | 8.0  | 8.3   | 7.3  | 6.2  |
| Conductivity                            | µS/cm             | 84   | 76.4 | 67.3 | 12.6 | 79.8 | 121.1 | 68.2 | 74.7 |





**Fig 3.2:** Physical-chemical parameters as measured for sites KC1 to KC8 for the Kuja River Catchment System. Selected parameters of Temperature ( $^{\circ}\text{C}$ ), dissolved oxygen (DO) ( $\text{mgL}^{-1}$ ) and Total Suspended Solids (TSS) ( $\text{mgL}^{-1}$ ) for sampling periods of January-March and August-October 2015 whereby results revealed high variation levels. Hatched bars indicate moving averages. Scaling varies for each parameter.

The data obtained from the laboratory tests were compared based on the standard or recommended values. The mean dissolved oxygen (DO) levels were  $5.5\text{--}6.3\text{mgL}^{-1}$  indicating that the difference was not significantly lower than the standard value of DO ( $4\text{--}5\text{mgL}^{-1}$ ). The mean conductivity level of 2 places (KC1,  $134 \pm 4.7\mu\text{Scm}^{-1}$  in the dry and KC6,  $121.1 \pm 9.5\mu\text{Scm}^{-1}$  in the wet season) showed significant variation from the standard value of  $150\mu\text{Scm}^{-1}$ .

About 50% of the sites sampled during the dry period indicated significantly higher mean pH values ( $> 8.5$ ) than the standard value of  $6.5\text{--}8.5$  recommended in natural water samples. Similarly, it was observed that mean pH recorded for all sampled stations except one (KC8) during the wet period was between the recommended standard value of  $6.5\text{--}8.5$  indicating an almost neutral state in the natural waters. At a  $p$  value of 0.05, pH did not vary significantly between stations. No significant seasonal variance was recorded for the sampling seasons of July and October (ANOVA:  $p = 0.304$  ( $P > 0.05$ )).

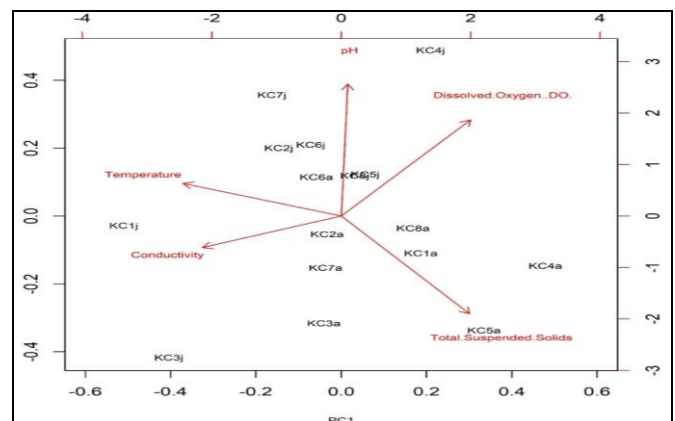
### 3.1.2 Physico-chemical measurements

**Temperature:** Temperature on average varied significantly between the two sampling periods, January-March (an average of  $25.7 \pm 0.64^{\circ}\text{C}$ ) and August-October (an average of  $22.5 \pm 1.26^{\circ}\text{C}$ ) (ANOVA;  $p < 0.05$ ), but did not vary significantly among sites along the catchment system (ANOVA;  $p > 0.05$ ). The highest water temperature recorded in the entire study was at site KC7 ( $26.7 \pm 1.84^{\circ}\text{C}$ ) during January-March 2015 (Figure 3.2) and the lowest at KC3 ( $20.5 \pm 0.34^{\circ}\text{C}$ ) during the August-October period. The overall mean water temperature was recorded as at  $24 \pm 2.24^{\circ}\text{C}$  indicating a slightly lower level than the recommended standard temperature level of  $25.3\text{--}26.7$  in natural waters.

**Total Suspended Solids (TSS):** Significant temporal variation (ANOVA:  $p < 0.05$ ) was recorded between the

January-March and August-October sampling periods. TSS range for January-March varied between levels of  $2\text{--}9 \pm 0.31\text{mgL}^{-1}$  compared to August-October range values of  $69\text{--}327 \pm 14.5\text{mgL}^{-1}$  (Table 3.1). Although no significant difference was recorded for TSS among site variations (ANOVA:  $p = 0.399$  ( $p > 0.05$ )), TSS at site KC5 during August-October, recorded highest levels  $327 \pm 19.0\text{mgL}^{-1}$ . TSS concentration in the wet period was observed to be in a low of  $2 \pm 0.04\text{mgL}^{-1}$  to a higher value of  $327 \pm 19.0\text{mgL}^{-1}$  in water samples during the dry period showing an equally significant variation from the standard value of  $450\text{mgL}^{-1}$  in KC1 to KC5, respectively.

**Conductivity (EC):** Conductivity values for both sampling seasons (January-March and August-October) were recorded within acceptable health limits of  $150\mu\text{Scm}^{-1}$  (Figure 3.2). No significant temporal variation was recorded between January-March and August-October (ANOVA:  $p = 0.634$  ( $p > 0.05$ )). A significant difference was recorded within site variations (ANOVA:  $p < 0.05$ ). Multiple comparison procedures indicated significant variance within each sampling period for sites KC1, KC4 and KC6. All sites exceeded the no effect range during both sampling periods.



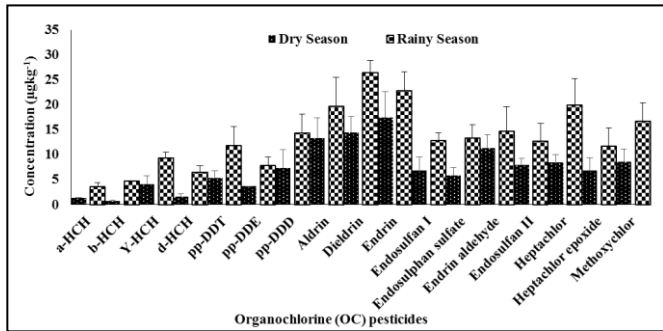
**Fig 3.3:** Principal component analyses (PCA) for sampling stations (KCs) and environmental variables (arrows) in Upper River Kuja catchment between January–November 2015. (Note: j for January and a for August)

## 3.2 Pesticides

### 3.2.1 Spatial variations in organochlorines (OCPs)

Figure 3.3 below shows the mean concentrations for organochlorine residues within the sampled sites in both dry and wet seasons (January-March and August-October) of 2015. The minimum and maximum OCP levels in water samples analysed in all the sampling sites combined were  $0.01 \pm 0.002$  and  $0.03 \pm 0.007\mu\text{gL}^{-1}$  in the dry season and a minimum of  $0.006 \pm 0.001$  to a maximum of  $0.023 \pm 0.004\mu\text{gL}^{-1}$  in the wet season respectively. The residue levels detected in sediments collected in specific target area were higher than those detected in the water in the same sampled points. In addition, the minimum and maximum OCP levels in sediment in all the sampling sites combined were  $0.73 \pm 0.162$  and  $17.431 \pm 5.173\mu\text{kgL}^{-1}$  in the dry season, to a minimum of  $3.634 \pm 0.731$  and a maximum of  $26.47 \pm 2.361\mu\text{kgL}^{-1}$  in the wet season respectively. Stations KC3, KC5 and KC7 recorded highest levels at  $1.5 \pm 0.06\mu\text{gL}^{-1}$ ,  $0.11 \pm 0.01\mu\text{gL}^{-1}$  and  $0.75 \pm \mu\text{gL}^{-1}$  in water samples respectively, and was lowest at KC1, recorded as below detection limit (BDL). There was no significant difference in HCHs, DDTs or the

cyclodienes pesticide group levels between different sampling sites but this was visible within different seasons compared.



**Fig 3.3:** Seasonal variation in the concentration of organochlorine residues in sediment samples from the River Kuja Catchment (KC) system (2015).

Organochlorine pesticide (OCPs) levels in water were ranging from below detection limit (BDL) to levels close to  $1.0 \mu\text{gL}^{-1}$  in water in sampling sites KC5, KC7 and KC8 (Figure 3.3). Analysis of water samples for OCPs at the KC3 and at the KC5 urban area values detected were  $0.01 \pm 0.002 \mu\text{gL}^{-1}$  to  $0.11 \pm 0.001 \mu\text{gL}^{-1}$  and between  $0.03 \pm 0.023 \mu\text{gL}^{-1}$  to  $0.01 \pm 0.63 \mu\text{gL}^{-1}$ . Organochlorine pesticide residue concentrations detected in sediments collected during the sampling period (wet and dry) exhibited higher concentration levels as compared to those detected in water samples. OCPs concentrations in sediment samples ranged between  $1.90 \pm 0.162 \mu\text{gKg}^{-1}$  to  $28.0 \pm 6.773 \mu\text{gKg}^{-1}$  when all sampling stations during the survey are compared. POPs residue levels detected in water samples collected during the survey in the dry period ranged from  $0.013 \pm 0.002 \mu\text{gL}^{-1}$  in KC4 to that of  $1.520 \pm 0.501 \mu\text{gL}^{-1}$  collected in water at KC7 in the same area during the dry period respectively. At an alpha level of  $p < 0.05$ , the results proved to be statistically significant between different stations. However,  $\beta$ -HCH and endrin had values that recorded below detection limit (BDL) in water samples in KC1, KC2 and KC4. The pesticide residue levels detected in water collected upstream (KC1 and KC2) area ranged from BDL to  $0.004 \pm 0.006 \mu\text{gL}^{-1}$  for water at KC6 (during wet season) and BDL to  $2.02 \pm 0.003 \mu\text{gKg}^{-1}$  for sediment samples at KC6 (Figure 3.4). Sediment samples collected from KC5 and KC7 during wet period showed higher values than those obtained at the KC4 and KC8 for methoxychlor, aldrin and DDT compounds. At  $p < 0.05$  alpha level, it was observed that the results were statistically significant between different seasons targeted.

Looking at results of the cyclodiene group compounds, endosulfan I and  $p,p'$ -DDD were of significant values when compared to results obtained of the aldrin, heptachlor epoxide, and dieldrin in the sampled area in both seasons. The hexachlorocyclohexanes (HCH) values and their isomers were observed to be slightly lower than the results of the cyclodienes in KC1, KC2 and KC4 sampled areas when compared. At an alpha level of  $p < 0.05$ , it was observed that the results were statistically significant between stations that were sampled in the survey.

## 4. Discussions and Conclusions

### 4.1 Water quality parameters

Variations in environmental factors such as water quality and physico-chemical parameters during the wet and dry period were noted in the study area and could be due to both natural

causes, underlying anthropogenic factors or human influence (Giuliano *et al*, 2006) [17]. During the study, it was observed that the state of most water samples were highly turbid downstream, especially after the urban areas (KC4, KC5). The dissolved oxygen (DO) levels were well within recommendable levels ( $4-5 \text{ mg L}^{-1}$ ). The DO range was between  $4.2$  to  $6.3 \text{ mg L}^{-1}$  during the dry period indicating that even during period of low rainfall, the mean dissolved oxygen levels in the study area were within the recommended thresholds. The cause for the low DO would be attributed to the reduced water velocity or other biological activities in the aquatic system (Gichuki *et al*, 2006) [15] as well as proliferation of algae blooms which can also lead to oxygen depletion in sampled areas (KC3, KC5, KC7). The presence of fairly warm temperatures and high levels of total suspended solids enhance capture of solar radiation in the water column (Wetzel, 2001) [36], especially during the dry period. Due to low water inflows from springs and run-offs in the dry season as well as time of sampling could be attributed to significant temperature variations recorded during the study. Other studies in the region indicate that water temperatures can influence the amount of oxygen dissolved in a water column with low oxygen levels experienced in warmer waters.

In addition, it seems that water quality data for the Upper Kuja River catchment system could have been influenced by agricultural and storm water runoff, humans and anthropogenic non-point pollution sources activities causing changes in the aquatic system (Jonnalagadda and Mhere, 2001) [21]. Physico-chemical parameters sampled for the sites of the Upper Kuja River catchment system included conductivity and total suspended solids. However, results indicated that at some stations (KC2, KC3, KC4, KC5) the TSS levels fell below the standard recommended level of  $150 \mu\text{Scm}^{-1}$  for recreational and domestic use (DWAf, 1996) [9] except for conductivity whose mean levels were within acceptable range.

This study involved a measure of organic contaminants, water quality and nutrients (physico-chemical parameters) units that are known to cause eutrophication in aquatic systems. Eutrophication supports a dense plant (aquatic) population, of which the decomposition kills animal life by depriving it of critical oxygen. It has also been reported that eutrophication-related problems increase in warmer water systems (Fatoki *et al.*, 2001) [12]. Eutrophication in the Upper Kuja River system is considered moderate (Jan-March, mean =  $5.6 \text{ mgL}^{-1}$ , Aug-Oct, mean =  $6.3 \text{ mgL}^{-1}$  DO), temperature (Jan-March, mean =  $24.3 \text{ }^\circ\text{C}$ , Aug-Oct, mean  $23.0 \text{ }^\circ\text{C}$ ) and mean conductivity during the year (Jan-March, mean =  $77.1 \mu\text{Scm}^{-1}$ , Aug-Oct  $73.0 \mu\text{Scm}^{-1}$ ) levels that were noted to be below the recommended critical standard temperature of  $25.3-26.7 \text{ }^\circ\text{C}$  and  $150 \mu\text{Scm}^{-1}$  for conductivity, hence it can be concluded that conditions that favour eutrophication and proliferation of blue-green algae, unsightly and malodorous scum and the associated release of toxic substances impairing the domestic and recreational use of the river (Fatoki *et al.*, 2001; Cape Metropolitan Council, 2003) [12, 4] were not favourable in the target area during the sampling period. One of the more obvious characteristics of water quality to an observer lies within the visual clarity of the water, defined as the conductivity (electrical conductance) of the water or light penetration ability.

Conductivity, along with Total Dissolved Solids (TDS), is a way to measure the presence of all "anions" and "cations"

drinking water. Most of these compounds are harmless, but in very large quantities may cause potential issues. TSS recordings for the Kuja River River catchment system indicated a clear seasonal trend coinciding the mean in the dry season (January-March) as at  $4.75 \text{ mgL}^{-1}$  increasing to a mean of  $175 \text{ mgL}^{-1}$  during the wet season (August-October) as water flow increased. KC5 marked the highest level ( $327 \text{ mgL}^{-1}$ ) during October, due to probably increased organic and human pollutants originating from the surrounding rural community establishments. Analysis on the organochlorine pesticides residues produced mean residues that were estimated at about  $0.02 \mu\text{gL}^{-1}$  respectively in water samples, which is lower than the recommended value of  $2.0 \mu\text{g}^{-1}$  in drinking water. However, these values were noted to be much lower than the WHO/FAO recommended guidelines limit in drinking water. These results tend to agree with those obtained by Madadi *et al* (2002) <sup>[35]</sup> whose values were as well lower than the recommended WHO thresholds in drinking water. The mean residue levels reported in this study during the two dry (January-March) and wet (August-October) seasons show strong distribution (KCI-KC8) and variability in both seasons than those reported in other areas such as that of the marine environment (Wandiga *et al.* 2002) <sup>[35]</sup>, and Getenga *et al.* (2004) <sup>[14]</sup>. The summary of the analysed organochlorines (OC) residues gives interesting results when the three groups of the compounds are compared. Mean seasonal DDTs show markedly higher concentrations followed by that of the cyclodienes and least that of the HCHs. These results tend to show a similarity to that of Wandiga *et al.* 2002 <sup>[35]</sup> which discussed dry and short rain seasons results from the Kavirondo Gulf of Lake Victoria basin. Although some of these compounds have now been banned from use, the results indicate that they are still in our environment due, to probably, previous uses in the catchment (Mbabazi S.B, 1998) <sup>[23]</sup>. For the cyclodienes group compounds detected, endosulfan is of environmental importance because of its apparent persistence and toxicity to many non-target organisms such as fish (Shetty, *et al.* 2000) whereas heptachlor is an insecticide mostly used to kill termites in homes.

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