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Full Length Research Paper

Occurrence, quantities and probable human health risks of indicatory polychlorinated biphenyls in processed *Lates niloticus* (L.) products from Lake Victoria in Tanzania

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A study was conducted in Lake Victoria to assess the occurrence, levels and risks of indicator polychlorinated biphenyls (PCBs) in four processed *Lates niloticus* (L.) products (salted-sundried, trims, smoked and deep-fried). Samples extractions were done using QuEChERS method while detection and quantification of congeners was done using a GC- ECD and GC- MS. Six PCBs (CB 28, CB 52, CB 118, CB 138, CB 153 and CB 180) were detected at measurable quantities in fish products. The PCBs; CB 138, CB 153 and CB 180 dominated the loading due to their structures and high degree of chlorination. However, the mean concentration of ΣPCBs in this study were below MRL of 75 µg/kg set for fish by European Commission, implying that the fish products were safe for human consumption in regard to indicator PCBs. Similarly, indicator PCBs, CB 138, CB 153 and CB 180 were more prevalent (20 to 80%) in all fish products than other congeners. For both adults and children the cancer risks were low-to-moderate (ranging from 2.0E-04 to 3.0E-04 for adults and 2.0E-04 to 1.0E-03 for children) while the non-cancer risks were insignificant as the Hazard Indices were less than one.

Key words: Polychlorinated biphenyls (PCBs), kayabo, trims, smoked products, deep-fried products, extracting solvent.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic organic compounds that are characterized by their lipophilicity (Cok et al., 2007; Bordajandi et al., 2008; Bjermo et al., 2013), persistence in the environment (due to longer half-lives), toxicity, long range atmospheric transport (LRAT) (Liu et al., 2007), accumulation in biota and increase in concentration with time at higher trophic levels (Polder et al., 2014; Ssebugere et al., 2014; Oluoch-Otiego et al., 2016). The compounds are also regarded as endocrine disruptors (EDs) (Bell, 2014) as they alter the normal functioning of the endocrine system and are difficult to degrade in the environment (Field and Sierra- Alvarez, 2008; Frouin et al., 2013). Most are reported as potential carcinogens being responsible for breast, liver and testicular cancers. They also have negative reproductive effects such as low birth weights, small head circumferences, miscarriages, poor sperm quality and low sperm counts (Bell, 2014).

In recent years Lake Victoria fisheries sector has had an abusive history as in 1998, fish exports from Lake Victoria to the European Union were temporarily banned following observations of tainted fish, which were later proved to have been harvested using endosulfan (Henry and Kishimba, 2006). There are also unsubstantiated claims that in order to extent the shelf life of products in the markets some unfaithful fish sellers store their fish products using chemicals such as pesticides and other unknown repellents which might be potential sources of PCBs in fish products along the fish value chain from fishing to consumption. It is also suspected that some processors use transformer oils for fish frying and consumption of smoked fish products is common in the area. Both transformer oil and smoke are good sources of PCBs in the environment and environmental compartments (Wenaty et al., 2019a; Witczak, 2012).

A study carried out in Poland revealed that smoking fish increases the levels of PCBs specifically; CB 101, CB 118, CB 138, CB 153 and CB 180. The reason for this was found to be due to a decrease in co- distillation with steam and the consequence of their penetration with smoke to the fish meat tissue (Witczak and Ciereszko, 2006, 2012). There is therefore a need to investigate the impacts of smoking on fish products from Lake Victoria. Another study which was done on fried fish products revealed that deep frying reduces the levels of PCBs in fish due to the fact that; (i) deep frying process creates unique cooking conditions that accelerates drying of the fillets (ii) evaporation of water and PCBs from the fillets as a result of high temperature of the cooking oil and by transfer of PCBs to the cooking oil which itself could be acting as an extraction solvent (Witczak and Ciereszko, 2012), though the same compounds are likely to be reintroduced into fish muscles as the cooking oil is reused in subsequent fish processing. Such studies have not been undertaken in Africa and in Lake Victoria in particular thus it is necessary that a study be designed to reveal the prevalence of PCBs and how safe the fish products are. Being lipophilic in nature, high levels of PCBs could be anticipated in fish products such as fish trims that are mainly the fatty tissues of the fish mass. We could also expect high prevalence and levels of PCBs in smoked products due to the reason that the process takes place in closed system and therefore there is no room for escape of PCBs together with water vapour. PCBs are likely to stick in the walls of smoking chambers and go back to surfaces of the fish tissues being processed (Witczak, 2012).

This study therefore was designed to assess the prevalence, levels and risks of indicator PCBs in four processed *L. niloticus* products sold such as salted-sundried, fish trims, smoked fish and deep-fried. The products are mainly consumed by the low and middle income communities in the domestic and regional markets and that to our knowledge no studies regarding the prevalence, levels and risks of PCBs in such products (salted-sundried and trims) have been reported anywhere around the globe and limited studies on smoked and deep fried fish have been reported in developed nations. Studies of such kind have mainly been undertaken for fish products intended for export markets such as fish fillets. Similar studies need to be done for products that are processed for domestic and regional markets as they are consumed by the majority of the low income population and that the safety of such products in terms of chemical hazards particularly PCBs is still unknown. This study focused on only indicatory PCBs because they are known to be more persistent and bio accumulative in food chain compared to other congeners. They are therefore assumed to be a suitable representative for all PCBs.

MATERIALS AND METHODS

Description of the study area

The study was conducted at the Kirumba International Fish Market in Mwanza between April and August 2018. The Kirumba International Fish Market was purposively selected out of other markets in Lake Victoria because it is the largest fish market in the zone that collects fish products from all other regions making up the Tanzanian side of Lake Victoria. Fish folks and other processors bring their already processed fish products at the market and sell them to buyers who then deliver the products to different markets located within and outside the country, such as Uganda, DRC, Burundi, Rwanda, Zambia, Kenya and Malawi where they are used as source of protein as well as income (LVFO, 2013).

Fish samples collection and extraction

Four processed products of *L. niloticus* samples namely; salted-sundried commonly referred to as *Kayabo*, trims commonly known as *Chips*, smoked and deep fried products were collected from randomly selected fish processors and sellers at Kirumba fish Market in Mwanza between April and August 2018. A total of 120 samples (30 samples of each product) were collected for analysis.

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Fish samples extraction and clean-up for determination of indicator PCBs was effected using a quick, easy, cheap, effective, rugged and safe (QuEChERS) procedure with some modifications at the National Fish Quality Control Laboratory in Mwanza, Tanzania. Thirty grams of each sample was measured in triplicates and blended to homogenize. Thirty grams of the composite samples were transferred into 200 ml centrifuge tubes. Thereafter, 2.5 g of sodium bicarbonate ($NaHCO_3$), 60 ml of ethyl acetate and 15 g of anhydrous Na_2SO_4 were added and placed in a shaking machine to homogenize for 20 min. The supernatants were transferred into 15 ml centrifuge tubes containing 0.125 g of Primary Secondary Amine (PSA) and 0.75 g of anhydrous $MgSO_4$ (Anastassiades et al., 2003; Wenaty et al., 2019a, b). The mixture was centrifuged at 2500 rpm for 10 min and left to separate for further 5 min. The supernatants were transferred into vials ready for GC analysis.

Recoveries and analytical quality control

Recovery tests were done for six indicator PCBs of interest. Blank samples were spiked with standards and were subsequently extracted and analysed in the same way as other samples. To maintain the quality of analytical results blanks and standards were run every after five samples.

Chemical analysis

Chemical analysis was performed at the National Fish Quality Control Laboratory in Mwanza. The samples of fish collected were analysed for Polychlorinated biphenyls (Σ-7PCBs); with IUPAC numbers: CB- 28, 52, 101, 118, 138, 153 and 180. The seven indicator PCB congeners were chosen based on their persistence in food web and their tendency to increase in concentration at higher trophic levels. The studied compounds are listed in the Stockholm Convention on POPs for initial elimination and reduction in use because of their effects on environment as well as living organisms.

Gas chromatographic analysis of samples

The determination of the PCBs in the fish samples was carried out using gas chromatography (GC). A gas chromatograph (GC-2010, Shimadzu) equipped with ^{63}Ni Electron Capture Detector (ECD) and a non-polar (HP-5MS) capillary column of 30 m length × 0.25 mm i.d. × 0.25 μm film thickness was used. Nitrogen was used as both a carrier and make-up gas at a flow rate of 23.7 ml min^{-1}. The temperature programme was: initial temperature of 120°C held for 2 min, then increased at a rate of 10°C min^{-1} to 270°C held for 1 min, and at a rate of 2°C min^{-1} to the final temperature of 290°C held for 3 min. The injector and detector temperatures were 220 and 290°C, respectively. The GC was operated in a splitless mode with an injection volume of 1 μL. The standard mixture was injected in the beginning and after every five samples. Samples were injected in duplicate. The confirmation of the findings was done using gas chromatography- mass spectrometry (Shimadzu GC-MS QP 2010 Ultra equipped with a mass selective detector-MSD, fused silica capillary column Rtx-5MS of 30 m length×0.25 mm i.d×0.25 μm film and an autosampler) applying the procedures described by Mahugija et al. (2018). The GC-MS was performed in splitless injection mode and the mass spectrometer was operated in electron impact (EI) ionization and full scan mode. The calibration/working standard solutions were prepared by dissolving portions of the stock solutions in the same solvents as used for the samples. Calibration curves were prepared by running series of mixtures of standard solutions and plotting the peak areas against concentrations. Identification of the compounds involved checking the matching of the retention times and the mass spectra of the PCBs in samples to those of external reference standards that were prepared and run at the same conditions as for the samples. Quantification was carried out by linear integration of the standards and sample data based on peak areas.

Data analysis

Statistical analysis used for data analysis includes subjecting the measured PCBs data to descriptive statistics for the deduction of minimum, maximum, mean concentrations and standard deviations of the detected PCBs. Data was further subjected to SPSS, Version 16.0. Data on PCB concentration were presented as mean ± SD. One-way ANOVA was used to compare concentrations between products. In data processing, the concentrations of PCBs in samples below the limit of detection (<LOD) were treated as zero. Separation of means was done using Duncan's Multiple Range Test. Significance was declared different at $p<0.05$ for all analyses.

Risk assessment model

The estimated dose (CDI) received through consumption of fish products was calculated using Equation 1 and the cancer risk (C_R) using Equation 2, which were adopted from the Environmental Protection Agency of the United States (USEPA, 1997, 2009; Man et al., 2013).

$$CDI = \frac{C * IR * EF * ED}{BW * AT} \quad (1)$$

$$C_R = SF * CDI \quad (2)$$

For non-carcinogenic risks, the hazard quotients (HQ) of each congener PCBs measured were calculated by using Equation 3 and overall non-cancer risk using Equation 4.

$$HQ = \frac{CDI}{RfD} \quad (3)$$

$$HI = \Sigma HQs \quad (4)$$

Where; CDI (mg/kg-day) is the estimated chronic daily intake, C_R is the cancer risk via consumption of fish products contaminated with PCBs, C (mg/kg) is the measured concentration of indicator PCBs in fish products, IR (kg/day) is the fish consumption rate; for this study 0.37 kg/day was used (Wenaty et al., 2018), HI (mg/kg-day) is the hazard index (overall non- cancer risk via consumption of contaminated fish products, HQ (mg/kg-day) is the hazard quotient (individual compound non- cancer risk via consumption of contaminated fish products), EF is the exposure frequency, 365 days/year (USEPA, 2009), ED is the exposure duration, 60 years for adults and 12 years for children USEPA, 2009), SF is the cancer slope factor, in this study, 2 $(mg/kg\text{-}day)^{-1}$ (Ge et al., 2013) for all indicator PCBs detected. RfD is the Reference Dose (mg/kg-day), in this study, 0.02 mg/kg-day for all PCBs, BW is the hypothetical average body weight, in this study, 70 kg for adults and 29 kg for children (USEPA, 2001). AT is the averaging time, 60 years* 365 days/year= 21900 days for adults and 12 years* 365 days/year= 4380 days for children (Ge et al., 2013; USEPA, 2001).

Qualitative descriptions of lifetime cancer risks of PCBs were based on ATSDR standards as follows; very low when the estimated value is ≤10E-06, low: 10E-06<value≤10E-04, moderate:

Table 1. Results of the percentage recoveries for PCBs extraction procedure.

PCBs	Amount spiked (μg/kg)	Amount calculated (μg/kg)	Recoveries (%)
CB 28	75	69.36±0.23	92.48±0.31
CB 52	50	40.90±0.46	81.79±0.93
CB 118	200	166.87±0.46	83.44±0.23
CB 138	260	202.80±0.35	78.00±0.13
CB 153	280	209.43±0.48	74.80±0.17
CB 180	390	278.54±0.82	71.42±0.21

Table 2. Mean concentrations (μg/kg) of individual PCBs and ∑PCBs in processed fish products from Lake Victoria in Tanzania.

PCBs	Samples			
	Kayabo	Trims	Smoked products	Deep fried products
CB 28	6.08±1.95	4.92±1.38	5.20±1.58	1.75±0.35
CB 52	3.04±3.00	3.72±0.87	3.62±0.77	1.25±0.21
CB 101	ND	ND	ND	ND
CB 118	4.24±3.04	1.88±0.76	5.50±0.98	3.40±0.57
CB 138	5.43±3.58	7.13±3.48	5.81±1.86	3.00±1.84
CB 153	5.74±5.18	7.83±4.65	6.46±4.05	3.30±0.14
CB 180	3.93±3.37	6.07±5.15	4.08±2.55	3.35±0.07
∑PCBs	28.46±9.35	31.55±16.66	30.67±6.23	16.05±3.04

10E-04<value≤10E-03, high: 10E-03<value≤10E-01 and very high when the estimated value is ≥10E-01 (Man et al., 2013; Ge et al., 2013; ATSDR, 1995). For non- carcinogenic risks, hazard index (HI) greater than one was considered risky while HI less than one was considered no risk associated with consumption of fish products (Wenaty et al., 2019a, b).

RESULTS AND DISCUSSION

Recovery experiment for PCBs extraction procedure

The results for the recovery experiment are shown in Table 1. The mean percentage recoveries for PCBs extraction procedure ranged from 71.42±0.21% to 92.48±0.31% based on triplicate determinations. Studies have indicated that recoveries ranging between 70 and 120%, the extraction procedure is considered perfect (Afful et al., 2013a, b). Results herein suggest a perfect extraction method that is recommended for use in further PCBs studies, hence needing no corrections for the recoveries.

Concentrations of PCBs in *L. niloticus* fish products from Lake Victoria

Table 2 shows the concentrations (μg/kg) of individual indicator PCBs and the sum (∑PCBs) measured in processed *L. niloticus* products collected at Kirumba International Fish Market. Six indicator PCBs (CB 28, CB 52, CB 118, CB 138, CB 153 and CB 180) were detected at measurable quantities in different fish products whereas CB 101 was not detected (ND) in any of the four fish products.

The mean levels of individual indicator PCBs in different fish products were in the following ranges: 1.75±0.35 μg/kg (deep fried products) to 6.08±1.95 μg/kg (salted-sundried products) for CB 28, 1.25±0.21 μg/kg (deep fried products) to 3.72±0.87 μg/kg (trims) for CB 52, 1.88±0.76 μg/kg (trims) to 5.50±0.98 μg/kg (smoked products) for CB 118, 3.00±1.84 μg/kg (deep fried products) to 7.13±3.48 μg/kg (trims) for CB 138, 3.30±0.14 μg/kg (deep fried products) to 7.83±4.65 μg/kg (trims) for CB 153 and 3.35±0.07 μg/kg (deep fried products) to 6.07±5.15 μg/kg (trims) for CB 180.

Analysis of Variance (Mean separation by using Duncan's Multiple Range Test) showed significant differences for individual indicator PCBs between fish products with trims, smoked products and salted-sundried products having higher levels than deep fried products (Table 3). The total PCBs loading were 28.46±9.35 μg/kg (salted- sundried products), 31.55±16.66 μg/kg (trims), 30.67±6.23 μg/kg (smoked products) and 16.05±3.04 μg/kg for deep fried products.

Table 3. Analysis of Variance for the detected PCBs in processed fish products from Lake Victoria.

PCBs	Sources of variation		
	DF	F	P
CB 28	3	3.54	0.045**
CB 52	3	3.34	0.043**
CB 118	3	10.69	0.001**
CB 138	3	1.91	0.022**
CB 153	3	0.66	0.036**
CB 180	3	0.53	0.665

** Means are significantly different at 0.05 level. DF: Degree of freedom, F: F -Value and P: P –Value.

The pattern of the total PCBs loading was Deep-fried products<Salted-sundried products<Smoked products< Trims. The loading for deep fried products was significantly different (DF = 3.00, F = 1.53 and P = 0.038) from the rest of the products. The total PCBs loading for other investigated products were quite similar. Low levels of PCBs in deep fried products could be attributed to the fact that at high temperatures the cooking oil acts as an extracting solvent, thus high levels of PCBs are expected to be left with the oil (Witczak, 2009a, b).

The trims are the fatty parts of fish, thus PCBs being highly lipophilic are mainly concentrated in fatty tissues (Bjermo et al., 2013; Polder et al., 2014). For smoked products, high concentrations of PCBs could be due to the reason that there is reduced co-distillation of the components with water vapour (Witczak and Ciereszko, 2006) and removal of water from the product as the PCBs are soluble in fat and lipids. Similarly, studies have shown that smoke consist certain amounts of PCBs (Witczak, 2012) and therefore acting as sources of these persistent organochlorine compounds in foods.

For all fish products considered in this study, the PCBs loading was dominated by CB 138, CB 153 followed by CB 180. Comparable results are also reported in previous studies (Polder et al., 2014; Ssebugere et al., 2014; Oluoch- Otiego et al., 2016). The domination tendency of CB 138, CB 153 and CB 180 are also reported in other previous studies (Polder et al., 2014; Oluoch- Otiego et al., 2016). This is due to the fact that CB 138, CB 153 and CB 180 are not metabolized by certain organisms compared to the rest of congeners (Ssebugere et al., 2014). Boon et al. (1997) also reported that the rate of metabolisms of PCBs depends mainly on structure and the degree of chlorination of the molecule. Being highly chlorinated, CB 138, CB 153 and CB 180 tend to have longer half-lives, persistent to biodegradation and therefore easily detected in environmental samples. The contribution of the three congener PCBs to total loading was 53.1% for salted and sundried products, 66.7% for trims, 53.3% for smoked products and 60.1% for deep fried products.

However, the mean concentration of ΣPCBs in this study were within the limit of 75 µg/kg set for fish by European Commission (EC, 2011), implying that the fish products were safe for human consumption in regard to indicator PCBs. Furthermore the total loading as per this study are far higher than that found by Polder et al. (2014) (0.57 µg/kg) from Lake Tanganyika for fresh *Oreochromis niloticus* samples, higher than those detected by Ssebugere et al. (2014) (0.229 to 0.716 µg/kg) in fresh *L. niloticus* from the Ugandan side of Lake Victoria. This indicates that processed products have higher levels than fresh fish. It is therefore suggested that some fish processing technologies such as smoking are main sources of PCBs in food products.

Prevalence of the detected indicator PCBs in different processed *L. niloticus* fishery products

The prevalence (%) of the indicator PCBs detected in different *L. niloticus* processed products are shown in Figure 1. For the six indicator PCBs that were detected in four fish products, all were less prevalent in deep fried products being detected in only 20% of all samples considered in this study. Generally, for the rest of the products the prevalence was in the following ranges: 40 to 60% for salted- sundried fish products, 50 to 70% for trims and 40 to 80% for smoked products. The mean percentage prevalence followed this trend: Deep fried products<Salted-sundried products<Trims<Smoked products. Indicator PCBs, CB 138, CB 153 and CB 180 were more prevalent (20 to 80%) in all fish products than other congeners. This is attributed to their structures and high degree of chlorination.

Human health risk assessment

Human health risk assessment for the indicator PCBs measured in four processed fish products considered in this study was evaluated using Equations 1 to 4 and ATSDR standard for adults and children. As shown in Table 4, the cancer risks based on indicator PCBs

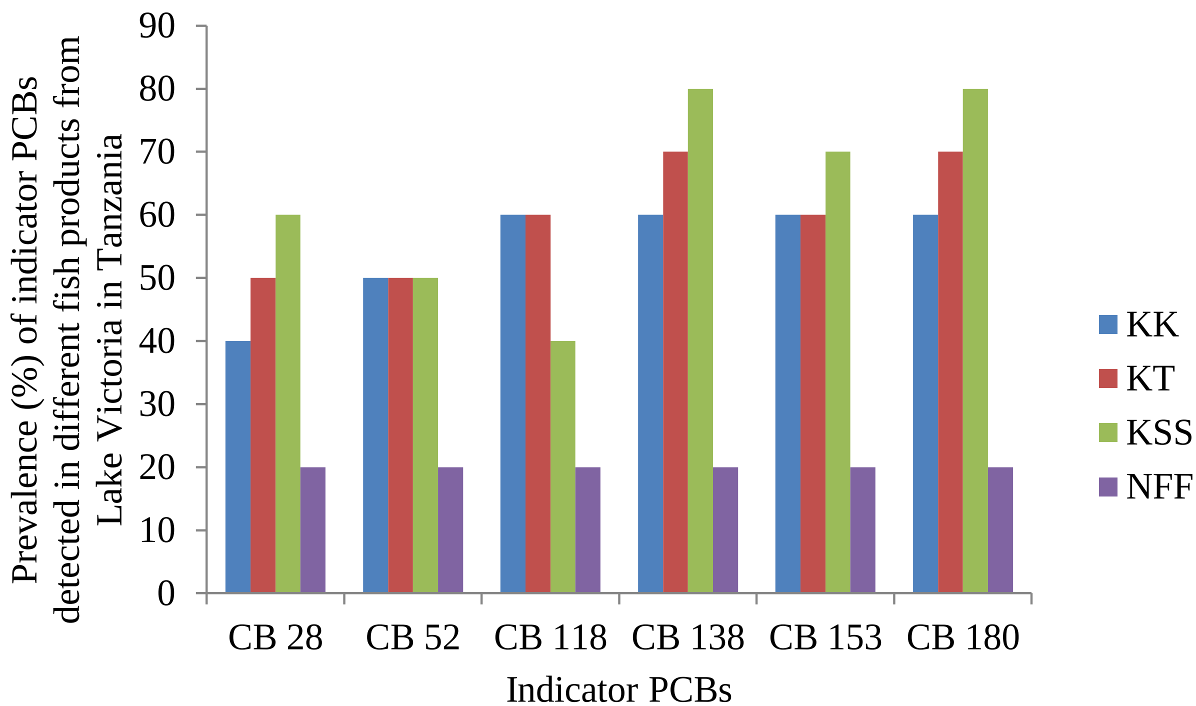

Figure 1. Prevalence (%) of indicator PCBs in fish products (KK- Kayabo, KT- Trims, KSS- Smoked products and NFF- Deep fried products).

loading for adults were in a range between 2.0E-04 and 3.0E-04 while for children were between 2.0E-04 and 1.0E-03. These values are within the range 1.0E-04≤value<1.0E-03 and classified as low to moderate risk (ATSDR, 2007; Man et al., 2013; Wenaty et al., 2019a, b). This observation suggests that there are only few cancer risks of indicator PCBs associated with consumption of *L. niloticus* products from Lake Victoria. Based on ATSDR standard, the cancer risks for PCBs in this study are between low to moderate.

Table 5 shows the hazard quotients (HQs) and hazard indices (HI) defining the non- cancer risks of indicator PCBs associated with consumption of *L. niloticus* products from Lake Victoria. The Hazard Indices (HI)(sum of Hazard Quotients (HQs)) ranged between 8.5E-03 and 1.8E-02 for adults and between 1.0E-02 and 2.0E-02 for children. In both cases, the HI values were very low (less than one). The United States Environmental Protection Agency (USEPA, 2009), recommends that HI values less than one indicates no risk. Therefore results from this study suggest that the risks associated with consumption of the analysed fish products from Lake Victoria are insignificant for both adults and children in regards to indicator PCBs (Table 4).

CONCLUSION AND RECOMMENDATIONS

This study analysed the occurrence, levels and risks of indicator PCBs in processed *L. niloticus* products from Lake Victoria in Tanzania. The levels of the detected PCBs were below the maximum recommended limits for fish and fishery products. The investigated fish products are therefore safe for human consumptions in regards to indicator PCB residues. Human health risk assessment indicated low cancer risks and insignificant non-cancer risks suggesting that the fish products do not present a health risk. However, follow up studies to assess the cooking oil and the influence of fish processing such as deep-frying and smoking on levels of indicator PCBs in fish products are hereby recommended.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Table 4. Lifetime cancer risks for the indicator PCBs detected in processed *L. niloticus* products from Lake Victoria.

PCBs \ Samples	Kayabo		Trims		Smoked products		Deep fried products	
	AD	CHI	AD	CHI	AD	CHI	AD	CHI
	CR	CR	CR	CR	CR	CR	CR	CR
CB 28	6.4E-05	1.6E-04	5.2E-05	1.3E-04	5.5E-05	1.3E-04	1.9E-05	4.5E-05
CB 52	3.2E-05	7.8E-05	3.9E-05	9.5E-05	3.9E-05	9.5E-05	1.3E-05	3.2E-05
CB 101	ND	ND	ND	ND	ND	ND	ND	ND
CB 118	4.5E-05	1.1E-04	2.0E-05	4.8E-05	5.8E-05	1.4E-04	3.6E-05	8.7E-05
CB 138	5.7E-05	1.4E-04	7.5E-05	1.8E-04	6.1E-05	1.5E-04	3.2E-05	7.7E-05
CB 153	6.1E-05	1.5E-04	8.3E-05	2.0E-04	6.8E-05	1.7E-04	3.5E-05	8.4E-05
CB 180	4.2E-05	1.0E-04	6.4E-05	1.6E-04	4.3E-05	1.0E-04	3.5E-05	8.6E-05
∑PCBs	3.0E-04	7.3E-04	3.3E-04	1.6E-04	3.2E-04	7.8E-04	1.7E-04	4.1E-04

AD stands for adults, CHI for children, CR for lifetime cancer risk and ND for Not Determined as the concentration was <LOD.

Table 5. Non- carcinogenic risks of the indicator PCBs measured in processed *L. niloticus* products from Lake Victoria.

PCBs \ Samples	Kayabo		Trims		Smoked products		Deep fried products	
	AD	CHI	AD	CHI	AD	CHI	AD	CHI
	HQ	HQ	HQ	HQ	HQ	HQ	HQ	HQ
CB 28	3.2E-03	3.9E-03	2.6E-03	3.1E-03	2.8E-03	3.3E-03	9.3E-04	1.1E-03
CB 52	1.6E-03	1.9E-03	2.0E-03	2.4E-03	2.0E-03	2.4E-03	6.6E-04	8.0E-04
CB 101	ND	ND	ND	ND	ND	ND	ND	ND
CB 118	2.2E-03	2.7E-03	9.9E-04	1.2E-03	2.9E-03	3.5E-03	1.8E-03	2.2E-03
CB 138	2.9E-03	3.5E-03	3.8E-03	4.6E-03	3.1E-03	3.7E-03	1.6E-03	1.9E-03
CB 153	3.0E-03	3.7E-03	4.1E-03	5.0E-03	3.4E-03	4.1E-03	1.7E-03	2.1E-03
CB 180	2.1E-03	2.5E-03	3.2E-03	3.9E-03	2.2E-03	2.6E-03	1.8E-03	2.1E-03
HI =∑HQs	1.5E-02	1.8E-02	1.7E-02	2.0E-02	1.6E-02	2.0E-02	8.5E-03	1.0E-02

AD stands for adults, CHI for children, HQ for hazard quotient, HI for hazard index and ND for not determined.

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Seasonal variations of some physico-chemical properties of water sources that feed Rivers Wouri and Meme of Cameroon

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Rivers Wouri and Meme are surrounded by streams and wells and serve for irrigation, fishing, domestic purposes and transportation. Water samples were collected from the rivers in February (dry season) and August (wet season) of 2012 at different sites and at different depths and analyzed for some physicochemical properties. This was to study the effect of seasonal changes on the properties and also infer the possible sources of pollution. Water from the other sources was also analyzed. All analyses were done using standard methods. The properties were generally higher during the dry season. Both rivers were acidic. The Electrical conductivities (E.Cs) of River Wouri were generally much lower than those of River Meme with mean values of 2943.0 and 5703.0 µS/cm respectively during the dry season. Ca^{2+}/Mg^{2+} ratios for upstream in River Meme were greater than 3 during the dry season. During the dry season, in Wouri at site WO1, Cations and anions decreased with depth, while at site WO7, the same properties increased with depth. For River Meme at site ME1, there was no significant ($p<0.01$) variation of cations and anions with depth. On the contrary, at site ME8, the anions increased with depth while the cations decreased significantly ($p<0.01$) with depth. The streams were weakly basic with average pH of 8.3 for those of Wouri and 9.0 for those around River Meme. The streams around River Wouri generally had higher physicochemical properties. Physicochemical properties of the wells of Wouri were generally higher than those of the streams during both seasons. There was a very significant correlation ($p < 0.01$) between nitrate and choride ions in both rivers during the dry season. Most of the properties were within the levels set by World Health Organization and Environmental Protection Agency (EPA). The water sources are exposed to increases in anthropogenic activities, such as industrial and municipal waste disposal and farming practices. A more stringent legislation about water management, as well as studies about the biological content of the water sources is recommended.

Key words: Physicochemical, properties, Meme, Wouri, rivers, dry season, wet season.

INTRODUCTION

Water is primordial among the needs of living things and man's most urgent need is good water. The former could not survive in a few days if deprived of it but could do so in as many days without food (Faniran, 1991). Its importance cannot be overemphasized in industries, agriculture, economic activities, health etc. Unfortunately, water scarcity is a global problem affecting close to 2.8 billion people (Mbua, 2013). According to the latter, the situation is alarming in developing countries. While improved water sources were accessible to more than 2 billion people from 1990 to 2010, Sub-Saharan Africa had the lowest drinking-water coverage compared to the other regions of the world (UNICEF/WHO, 2012). The role of good water as engine of socioeconomic development makes its management of pivotal importance. Cameroon's record in this respect falls below expectation. Statistics on the number of persons with access to quality water in the country vary. The figure is estimated to be between 42 and 74% (Otto, 2014) of the population. In Sub-Saharan Africa, including Cameroon about 58% of the population has no access to portable water (Fonjong and Fokum, 2017). There is therefore an increasing need for greater access to portable water.

There is an increased dependence on ground water along the coast of the Gulf of Guinea (Eneke et al., 2011) and Cameroon in particular. This dependence is prominent in agriculture, domestic activities, health etc. The Geology and anthropogenic activities of a region influence the water quality (Eneke et al., 2011). It is evident that although water is highly important, it is often impaired by human and natural activities. Many water diseases are abound; cholera, typhoid, dysentery etc. Water safety is necessary (Nwankwoala and Udom, 2011). Cameroon is endowed with many water sources, which could contribute to the economy of the country. The country has as a long-term plan to emerge by 2035. Water quality is one of the indicators of developed/ emerging countries. Hence, the need for more studies on water quality.

One of the reasons associated to scarcity of drinking water is contamination or pollution. Among the various types of pollution, water pollution is second undesirable only after air pollution, in terms of effects (Milani et al. 1992). Pollution is either natural or anthropogenic. In sub-Saharan Africa, almost all communities in coastal areas depend on groundwater for drinking and domestic purposes (Edet, 2008). This is because it is readily available and is relatively cleaner than surface water sources, which are exposed to pollution from domestic wastes and runoff especially during the rainy season. Groundwater does not need extensive treatment before use (Yidana, 2010). Water quality is therefore an environmental and health issue that needs urgent attention. One of the technologies to monitor water quality is the determination of some of its physicochemical properties. Some of the physicochemical properties of water of great concern are cations, anions and pH. They affect the health of both plants animals. Heavy metals are soluble at low pH and can easily find themselves into waterways. Calcium and magnesium, although necessary for health, cause great health disorders when in excess or when they are not in appropriate ratios.

Douala harbours most of the industries in Cameroon. In the area, there are numerous water bodies of diverse uses by the 2.943 million inhabitants (CDP, 2018). Some of the water bodies are streams, wells and rivers. Conspicuous on the list of rivers is River Wouri lined by the Wouri mangroves. It is hypothesized that the diversity of industrial activities in the area and their effluents constitute a potential threat to water and the mangroves. Many towns in Meme harbour major agricultural establishments. The Meme River is prominent in these towns. It is the largest river in Meme Division. Many other water bodies drain into this river that in turn, empties into the Atlantic Ocean. Agricultural runoffs into these water bodies could carry or contain chemical substances, which would be dangerous at high concentrations. The inhabitants use these water bodies for various purposes. Whereas River Wouri feeds the Wouri Mangrove, River Meme feeds the Rio del Rey Mangrove. The probability that they could be contaminated from the human activities that take place around them could therefore be high. Hence, the dire need to study the quality of the water sources in the area.

There is a great need for good portable and clean water for sustainability, survival of industries and above all, good health of the inhabitants. The increasing indiscriminate disposal of domestic, industrial and agricultural wastes on water and soil is a cause for concern as the latter are exposed to contamination or pollution. Seasonal variations could also affect the quality of the water sources. Water pollution is therefore receiving great attention as an area of research. This work is therefore, aimed at investigating some physicochemical properties water sources that feed certain mangroves of Cameroon and relating them to natural and/or anthropogenic activities within this sub-region. It is also aimed at comparing the effect of seasonal changes and the relative threats on the mangroves from the quality of the water sources and make concrete recommendations.

MATERIALS AND METHODS

Description of sites

Location

One of the areas of study is around River Wouri. The river takes its rise from River Nkam and empties at the Wouri estuary. The region

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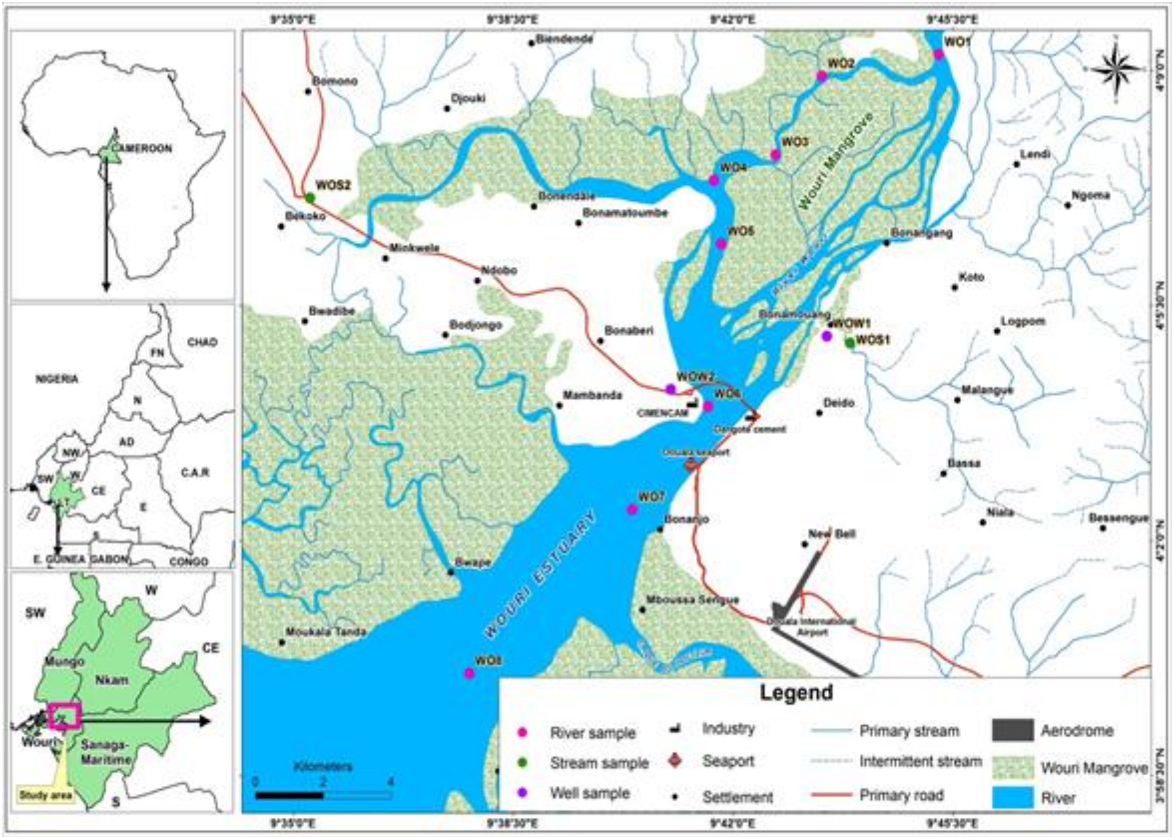

Figure 1. Map showing River Wouri, Water sampling sites and Drainage.

lies between latitudes 3 38 30N and 04 09 34 N and longitudes 9 35 0E and 9 45 30 E (Figure 1). In this area are found the Bassa and the Bonaberi Industrial Zones of Douala. The zones are located within the Douala Basin. The two industrial zones account for the bulk of industrial activities in the country, but depict contrasting features in terms of physical landscape (Dumont, 1968; Regnoult, 1986).The other site is around River Meme. The region lies in the Rio del Rey Basin. It lies between latitudes 04° 29.000 N and 04° 37.019N and longitudes 009° 02.000E and 009° 08.000E (Figure 2).

Topography, geology and drainage

The Bonaberi Industrial Zone evolved almost entirely on the aquatic terrain located on lagoon marginal depressions. This necessitated extensive land reclamation to obtain space on which industrial activities had to be built. The Bassa Industrial Zone terminates into estuarine creek formation of the Dibamba River to the East of the city. The Bonaberi Industrial Zone complex has encroached into the Wouri River and this most likely provokes increased discharge of effluents into it (Tening et al., 2013). The river is fed by streams and passes through the Wouri Mangrove and terminates at the Atlantic Ocean with the formation of the Wouri Estuary (Figure 1).

The basin around River Meme is part of the Douala sedimentary basin. From south to north the sedimentary basin is symmetrically divided by the Cameroon volcanic line (CVL) in two geomorphological settings: the Douala basin (7,000 km^2) to the South and the Rio del Rey basin to the North (2,500 km^2). Within the Rio del Rey basin, isobaths lie up to 80 km from the beach (Tening et al., 2014). Figure 2 is a map of sampling points and drainage around River Meme.

Rock type and soils

The Douala basin consists mainly of sandstone with a few intercalations of limestone and shale. The Mpundu Formation consists of poorly consolidated grits and sandstones that occasionally display bedding (Tening et al., 2013). However, the Douala metropolis lies on the Wouri member of the Mpundu Formation, which is dominantly made up of gravely sandstone with clay matrix. The soils of this area are alluvial resulting from the decomposition of sedimentary rocks. They are essentially sandy and commonly rich in quartz and clay minerals. These soils are very permeable in some areas. However, in other areas, the soils are very rich in clays to the extent that percolation of rainwater takes quite a long time (Tening et al., 2013). The soils around River Meme are ferallitic (Gavaud and Muller, 1980), yellowish in colour and varying from clayey, silty, sandy to lateritic clay sub soils (Tening et al., 2014).

Human activities

The human activities in the Douala city are presented in Table 1. The main activities around River Meme are agricultural with two agro-industrial complexes: the CDC Rubber Plantation and the PAMOL Plantation. Few farmers also cultivate crops like plantains,

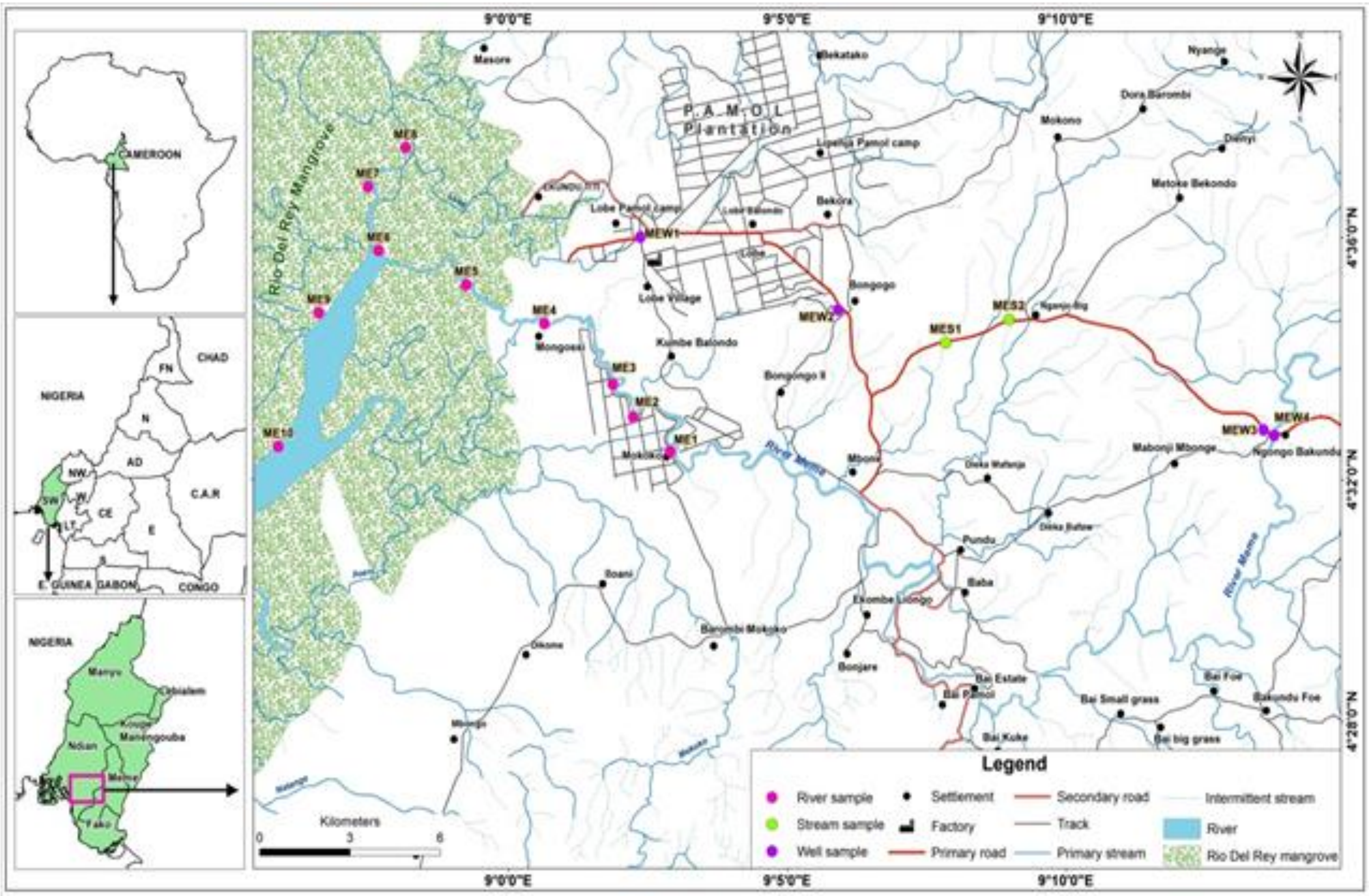

Figure 2. Map showing River Meme, Water sampling sites and Drainage.

Table 1. Major activities in the Douala metropolis.

Activity	Company	Product	Chemical entity
Agro-industry and food processing	Guinness Cameroon SA. Brasseries, La PASTA, ISEBERG, SIC CACAO.	Drinks/processed foods	NO_3^- NO_2^-, PO_4^{3-}, organic substances
Chemical/pulp	CIMENCAM, CEP, SAPCAM, UNALOR, SOPARCA, SIPCA, CCC, PILCAM, PLASTICAM. SOCAME, SCTB	Cement, oils, paints, detergents, vanish, soap, butter, plastics, matches, batteries, fertilizers	NO_3^-, acids, Hg, Cu, Pb, PO_4^{3-}, SO_4^{2-}, NO_2^-
Textiles	CICAM, SACC.	Cloths	Acids, Hg, organic compounds
Petroleum	SCDP, TEXACO, BOCOM, etc.	Aviation fuels, petrol, diesel fuel, wax.	Hydrocarbons, Pb, NO_3^-, PO_4^{3-}
Metallurgy alloys	ALLUCAM, SOCAAFERE,	Metals of various types.	As, Be, Bi, Cd, Cu, Pb, Hg, Ni, Zn.
Glass	SOCAVERE	Bottles	As, Be, Bi, Cd, Cu, Pb, Hg, Ni, Zn.

Adapted from Horan (1990) and Montgomery (1992) by Tening et al. (2013).

cocoyams, Cassava etc. Both the Agro-industrial complexes and the local farmers use fertilizers and other agrochemicals that are likely to impact the water quality in the area.

Sampling

Water samples were collected in the areas from rivers, wells and

Figure 3. Depth sampler before sampling.

Figure 4. Water sampling with a depth sampler.

streams. This was done during the month of February (peak of dry season) and August (peak of rainy season). In the rivers, the sampling points were located at the tributaries. In rivers and wells, the samples were collected at the surface, 1m, 3m and 5m respectively using a 1litre depth sampler (The Science Source: WIFFLE BALL KING, Reg. No. 1149044, USA) (Figure 3). The collection points were geo-referenced. The sampler was placed into the water after assemblage and water collected (Figure 4).The water samples were filtered using Whatman 40 filter papers placed across a funnel. They were filtered into 250ml plastic bottles to the brim and corked. It is worth noting that before filling, the bottles were rinsed several times with water from the point to be collected.

Prior to filtration, temperature, pH and EC were measured using a CE108380 TRACER Pocket Tester™ field meter. The collected samples were rapidly put into a cooler containing ice blocks to restrict microbial activity. They were then transported to the laboratory where they were stored at temperature of -4 ^{0}c before laboratory analysis. Water from wells and streams were collected using small buckets and filtered into 250 ml bottles.

Water analysis

Analysis for ions was done using ion chromatography. This was done at the Biogeochemistry Laboratory, University of Bristol, United Kingdom. Water samples were analysed for the cations

Table 2. Physicochemical properties of water from River Wouri and River Meme during the dry and wet seasons

Code	Name	pH		SO_4^{2-}		$NO_3^-{}_{(aq)}$		$K^+(aq)$		$Na^+{}_{(aq)}$		$Ca^{2+}(aq)$		Mg^{2+}		Ca^{2+}/Mg^{2+}	
				mg L^{-1}													
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
WO1	Quartier Eloka	7.4	7.2	0.7	0.5	2.0	0.0	2.9	0.9	8.6	3.4	5.7	2.9	5.0	1.4	1.14	2.07
WO2	Beange	8.1	7.2	1.9	0.2	n.d.	0.0	2.7	1.3	7.9	2.6	4.4	2.4	2.1	1.1	2.10	2.18
WO3	Beange1	8.2	7.2	2.5	0.7	n.d.	0.0	3.8	0.7	15.6	2.5	5.3	2.8	4.7	1.5	1.13	1.87
WO4	Todo Njebale	7.8	7.2	27.0	0.2	n.d.	0.0	24.2	1.0	123.8	2.8	19.4	3.2	10.5	1.5	1.85	2.13
WO5	Ekongolo	7.8	7.2	38.0	0.6	n.d.	1.0	26.1	1.0	148.3	2.7	16.4	3.5	10.8	1.6	1.52	2.19
WO6	Wouri bridge	7.5	7.2	85.0	0.6	n.d.	0.5	45.7	0.8	300.9	3.3	24.1	3.6	16.8	1.8	1.43	2.00
WO7	Wouri Wharf	7.3	7.2	201.0	0.8	3.7	0.7	137.0	1.0	1022.0	3.6	53.0	3.5	43.0	1.7	1.23	2.06
WO8	Steamer R	7.6	7.2	587.0	2.6	12.0	0.0	337.0	2.8	2604.0	19.0	114.0	3.7	101.0	3.7	1.13	1.00
ME1	CDC Pump,	9.5	7.2	3.0	1.9	0.4	0.9	10.5	5.4	15.8	5.2	13.0	5.4	3.5	n.d.	3.71	-
ME2	Mokoko Be	8.0	7.2	1.6	2.1	4.4	0.4	12.0	5.2	27.2	6.4	13.7	5.6	4.0	n.d.	3.43	-
ME3	Kumbe Be	9.1	7.2	3.0	0.7	n.d.	0.7	11.2	4.4	16.9	0.7	13.7	4.8	4.3	n.d.	3.19	-
ME4	Mongossi B.	8.2	7.2	1.5	1.9	4.7	0.3	10.8	4.8	17.2	0.3	13.1	5.0	3.3	n.d.	3.97	-
ME5	One Man H	8.1	7.1	64.0	0.9	n.d.	0.9	44.0	4.8	246.0	0.9	29.0	5.1	17.0	n.d.	1.71	-
ME6	Matutu	7.6	7.1	340.0	0.7	7.1	0.7	228.0	4.7	1682.0	0.7	82.0	4.8	71.0	n.d.	1.16	-
ME7	Via Masore J	7.4	7.1	317.0	n.d	7.2	n.d	234.0	6.0	1736.0	n.d	82.0	2.5	70.0	n.d.	1.17	-
ME8	Masore Junc	7.4	7.2	296.0	n.d	5.9	n.d	212.0	5.2	1584.0	n.d.	76.0	2.0	65.0	n.d.	1.17	-
ME9	Matutu 2	7.9	7.2	433.0	n.d	9.1	n.d.	445.0	6.5	3454.0	n.d	152.0	3.3	135.0	n.d.	1.13	-
ME10	Big Belly	7.5	7.2	553.0	n.d	11.3	n.d	335.0	8.1	2554.0	n.d	113.0	3.7	97.0	n.d.	1.17	-

n.d. = not determined D = dry season W = wet season WO = Wouri River ME = Meme River.

(Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+) and anions (Cl^-, SO_4^{2-} and NO_3^-) by ion chromatography. Cation analysis was performed by suppressed conductivity ion chromatography using a Dionex ICS-90 equipped with an Ion Pac CS16 column (5 x 250 mm) and an AS40 Autosampler. The eluant was 0.04 N methanosulfonic acid at a flow rate of 0.5 ml/min. The sample injection volume was 25 µl. The cation standards used for calibration were purchased from Fisher Scientific, UK. Saline samples were diluted 10- and 100- fold with de-ionized water. Suppressed conductivity detection ion chromatography using a Dionex IC25 equipped with an ASR Ultra II 4 mm column and AS3500 autosampler performed anion analysis. The eluent was NaOH at 1 ml/min and the sample injection volume was 25 µl. Anion standards used for calibration were purchased from Fisher Scientific, UK. Saline samples were diluted 10- and 100-fold when required with de-ionised water. The relative precisions of both the cation and anion analyses methods were typically better than 5% once samples were corrected for instrument drift. Experimental data was analysed with the statistical package SPSS11.0 and EXCEL 2010 for Windows. Correlation and regression analyses were performed on the various data to evaluate the relationships.

RESULTS AND DISCUSSION

Physicochemical properties of Rivers Wouri and Meme during the seasons

During the dry season, there were variations in physicochemical properties from upstream to downstream (Table 2 and Figure 5). This may have been caused by changes in quantity and/or composition of freshwater discharges. This can

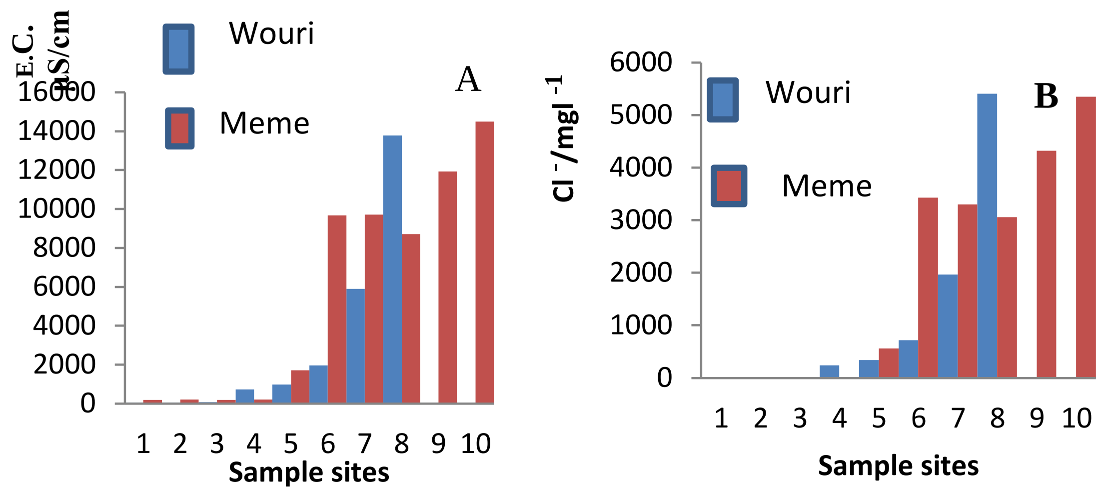

Figure 5. Variation of E.C. (A) and Cl^- (B) from upstream to downstream during the dry season.

Table 3. Comparison of the means of the physicochemical properties of water from Rivers Wouri and Meme during the dry and wet seasons.

River	pH		E.C.		$Cl^-_{(aq)}$		$SO_4^{2-}{}_{(aq)}$		$NO_3^-{}_{(aq)}$		$Na^+_{(aq)}$		$Mg^{2+}_{(aq)}$		$K^+_{(aq)}$		$Ca^{2+}_{(aq)}$	
	µS/cm		mg L^{-1}															
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
Wouri	7.7	7.2	2943.0	56.7	1085.8	3.8	117.8	0.8	5.9	0.3	528.9	5.0	24.2	1.8	72.4	1.2	30.2	3.2
Meme	8.0	7.2	5703.0	109.3	2005.2	15.8	201.2	1.40	6.3	0.7	1133.4	13.4	47.0	n.d.	154.2	5.5	58.7	4.2
WHO	**6.5-8.5**		**1000**		**250**		**250**		**50**		**200**		**30**		**100**		**75**	

n.d. = not determined. W = Wet season D = Dry season.

alter the Chemistry of the environment, such as hydrogeology and temperature not suitable for the mangrove ecosystem as was reported by Tening et al. (2013). Nutrients from fresh water inflow not only affect water quality but equally species diversity as was reported by Doering (1996). All the mean values of River Meme were higher than those of River Wouri (Table 3). The degree of acidity of water is inferred from its pH. The mean pH of 7.7 for Wouri and 8.0 for Meme respectively were within the permissible range of 6.5-8.5 (WHO, 2008; EPA, 2018). pH of a water body is very important in determination of water quality since it affects other chemical reactions such as solubility and metal toxicity as was reported by Fakayode (2005). They indicated that the rivers were slightly alkaline and not polluted (Fakayode, 2005). In a similar study, Tening et al. (2013) found the pH of River Wouri to be 7.4.

Electrical conductivity is a measure of the amount of ions in solution. The Electrical conductivities (E.Cs) of River Wouri were generally much lower than those of River Meme with mean values of 2943.0 and 5703.0 µS/cm respectively. These values were much higher than the maximum allowable value of 1000 µS/cm set by WHO (2008). Mean concentrations of the cations stood at $Na^{+}_{(aq)}$ >$K^{+}_{(aq)}$ > $Ca^{2+}_{(aq)}$ > $Mg^{2+}_{(aq)}$ for both rivers. Anions showed a trend of $Cl^{-}_{(aq)}$ > $SO_4^{2-}{}_{(aq)}$ > $NO_3^{-}{}_{(aq)}$. There was a significant difference ($p<0.01$) between the means of both rivers. This could be an indication that from River Wouri the sampling scenario had no effect on the statistical detection of temporal trends in physicochemical properties of water samples as was reported by Tening et al. (2013) and that the higher values of River Meme could be attributed to the nature of activities and the soils of the area.

The concentration of most ions in water is measured in mg/L. It is a measure of the amount of the respective ions present in water one litre of solution. The means for Ca^{2+} for River Wouri and River Meme, 30.2 and 58.7 mg L^{-1} respectively were below the WHO limit for domestic and industrial use. Too much calcium prevents the uptake of magnesium, and hence the optimum balance of these two minerals in the water which we drink is vital to our health as was reported by Rosborg (2015). Magnesium concentrations were generally higher in Meme than in Wouri. Clay minerals have low concentration of Mg^{2+} according to Todd (1980). If the concentration of Mg^{2+} were from clay mineral alone, it would have been low. Hence the high concentration could be attributed to natural and anthropogenic sources. Potassium had an average concentration of 72.4 in Wouri and 154.2 mg L^{-1} in Meme. The high concentrations of potassium in these rivers could partly be from industrial sources in the area such as the salt producing industry, Sel camerounaise (SELCAM)) in Douala for Wouri and the CDC for Meme.

The mean concentration of Sodium in River Wouri was 528.9 while in River Meme; it was 1133.4 mg L^{-1}. These values are much greater than the maximum allowable limit of 200 mg L^{-1} set by WHO (2008). High Na levels may contribute to elevated blood pressure according to Rosborg (2015). Long term discharge of these ions which function as dispersants into the mangrove environment can change the structural properties of the swamp land and lead to stress events. This could lead to regression of the mangrove land surface and species that grow on them.

During the wet season**,** the composition of anions and cations varied at different sites of both rivers (Table 2). Unlike during the dry season where the differences were significant ($p<0.05$), the differences during the wet season were not very significant. Both rivers were acidic (Table 3). The physicochemical properties of River Meme were much higher than those of River Wouri. Similar results were obtained during the dry season. However, these properties were far below the acceptable limits formulated by WHO (2008).

The normal Ca^{2+}/Mg^{2+} ratio is 2-3/1 as set by Rosborg (2015). Ca^{2+}/Mg^{2+} ratios for upstream in River Meme were greater than 3 during the dry season. This is an indication that inhabitants of this region are exposed to the effects of excess Calcium. Excess calcium is associated with prostate cancer and also inhibits production of Vitamin D3 according to Treadwell (2011).

Variation of physicochemical properties of water from the Rivers Wouri and Meme with depth during the seasons

During the dry season, in Wouri at site WO1, located at upsteam, Cations and anions decreased with depth, while at site WO7, located at downstream, the same properties increased with depth (Table 4). Where the cations increased with depth could be an indication that one of the major sources of cations is the breakdown of bedrock materials and where they decreased with depth could be an indication that one of the major sources of the cations was anthropogenic. The increase in cations and anions were reflected in the corresponding increase in conductivity with depth (Table 4). This increase in conductivity with depth was prominent at site WO7 (Table 4).

For River Meme at site ME1, there was no significant ($p<0.01$) variation of cations and anions with depth (Table 4). This is shown in the conductivity which remained the same (190.0 µS/cm) with depth (Table 4). On the contrary, at site ME8, the anions increased with depth while the cations decreased significantly ($p<0.01$) with depth. This could be an indication that at this site, the cations had anthropogenic sources. It is also an indication that downstream, the anions had as source weathering of bedrocks. It can be seen that in both rivers, one of the major sources of cations was anthropogenic probably from the industries around the Wouri River and the CDC and agricultural establishments around River Meme.

During the wet season, for Wouri at site WO1, there were no significant ($p<0.05$) changes in pH and electrical conductivity with depth (Table 4). This could be an indication that natural and anthropogenic factors did not influence these parameters as depth increases. At site WO1, nitrate was only present (0.4 mg L^{-1}) at depth of 5 m. The anions did not show any trend with depth. Generally, sodium increased with depth implying a natural source (bedrock) while the rest of the cations decreased with depth implying anthropogenic contamination from runoffs or discharges into the river. At site WO7, pH and electrical conductivity again remained virtually the same. The anions decreased with depth. This could be an indication that they may have had anthropogenic sources of origin. This was evidenced from nitrate which was found only at the top (0.7 mg L^{-1}) (Table 4) of the river at this site. Generally potassium and calcium did not show any trend with depth. Magnesium increased very slightly with depth while sodium decreased with depth. The properties were almost the same at both sites.

For Meme at site ME1, pH and electrical conductivity were about the same with depth with average of 7.2 and 76.0 µS/cm respectively (Table 4). Generally, chloride

Table 4. Variation of physicochemical properties of water from River Wouri with depth during the seasons.

Code	pH		E.C. (µS/cm)		Cl^- (mg L^{-1})		SO_4^{2-} (mg L^{-1})		NO_3^- (mg L^{-1})		Na^+ (mg L^{-1})		Mg^{2+} (mg L^{-1})		K^+ (mg L^{-1})		Ca^{2+} (mg L^{-1})		Ca^{2+}/Mg^{2+}	
	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
WO1	7.4	7.2	50.0	43.0	1.8	0.6	0.7	0.5	2.0	0.0	8.6	3.4	5.0	1.4	2.9	0.9	5.7	2.9	1.14	2.07
1WO1	7.8	7.2	50.0	41.7	1.8	0.4	1.8	0.2	n.d	0.0	9.5	3.4	3.6	1.4	3.0	0.9	5.9	3.5	1.64	2.50
2WO1	7.8	7.2	50.0	40.6	1.0	0.5	1.8	1.4	n.d.	0.0	9.2	4.4	2.6	1.3	2.9	0.5	5.6	3.3	2.15	2.54
3WO1	7.8	7.2	30.0	42.0	0.8	0.7	0.6	1.1	1.9	0.4	5.2	3.9	1.4	1.3	2.6	0.6	5.3	3.3	**3.79**	2.54
WO7	7.3	7.2	5890.0	46.5	1965.0	1.9	201.0	0.8	3.7	0.7	1022.0	3.6	43.0	1.7	137.0	1.0	53.0	3.5	1.23	2.06
1WO7	7.2	7.2	6700.0	48.7	2240.0	1.4	227.0	1.4	4.5	0.0	1175.0	5.4	48.0	1.8	156.0	0.4	59.0	3.1	1.23	1.72
2WO7	7.3	7.2	6800.0	49.9	2405.0	1.4	243.0	1.3	4.5	0.0	1179.0	5.2	48.0	1.8	155.0	0.5	59.0	3.6	1.23	2.00
3WO7	7.3	7.2	7230.0	48.6	2499.0	1.1	249.0	1.0	5.2	0.0	1274.0	3.7	51.0	1.9	167.0	0.8	62.0	3.4	1.22	1.79
ME1	9.5	7.2	190.0	78.8	6.2	2.1	3.0	1.9	0.4	0.9	15.8	5.2	3.5	n.d	10.5	5.4	13.0	5.4	**3.71**	**-**
1ME1	9.2	7.2	190.0	73.4	6.0	3.4	1.7	2.0	4.4	0.0	18.5	6.1	2.9	n.d	10.9	4.9	13.4	5.2	**4.62**	**-**
2ME1	8.6	7.2	190.0	79.8	6.2	2.9	3.6	3.2	n.d.	0.4	18.5	9.7	3.4	n.d	10.4	4.8	13.0	5.3	**3.82**	**-**
3ME1	n.d.	7.2	n.d.	73.1	n.d.	2.2	n.d.	2.3	n.d.	0.0	n.d.	7.3	n.d.	n.d	n.d.	4.8	n.d.	5.4	-	-
ME8	7.4	7.2	8710.0	141.4	3060.0	31.1	296.0	n.d	5.9	n.d	1584.0	21.6	65.0	n.d	212.0	5.2	76.0	2.0	1.17	-
1ME8	7.3	7.2	8540.0	138.7	2844.0	31.0	272.0	n.d	5.6	n.d	1530.0	21.2	59.0	n.d	207.0	4.7	74.0	1.9	1.25	-
2ME8	7.3	7.1	8660.0	129.0	3047.0	28.7	291.0	n.d	6.1	n.d	27.5	20.2	6.8	n.d	12.6	4.5	15.7	2.3	2.31	-
3ME8	7.4	7.2	8770.0	129.1	3095.0	29.2	297.0	n.d	6.8	n.d	n.d.	20.9	4.0	n.d	3.6	4.5	7.7	2.6	1.93	-

1, 2, 3 before codes represent depths of 1m, 3m and 5m respectively, n.d = not determined D = dry season W = wet season.

decreased while sulphate increased with depth implying anthropogenic and natural sources respectively. Sodium increased significantly, potassium decreased while there was a fluctuation in calcium with depth (Table 4). At site ME8, pH increased, while electrical conductivity decreased slightly with depth (Table 4). This is an indication of the influence of anthropogenic activities at this site. Chloride, sodium and potassium decreased slightly with depth thus confirming the influence of anthropogenic activities on the water quality of the river. Unlike at site ME1 where only ammonium and potassium were completely absent, at site ME8 sulphate, nitrate, ammonium and potassium were absent. The chloride, sodium and electrical conductivity of site ME8 were much higher than those of site ME1.

Physicochemical properties of streams during the seasons

The streams (Table 5) showed concentrations, which varied with locations during the dry season. This was very pronounced among the streams that feed Wouri. For example, the EC of site WOS1 was 410.0 while that of site WOS2 was <10.0 µS/cm. This could be an indication that Stream WOS1 suffered from anthropogenic incidence than stream WOS2. The streams that feed River Meme had same ECs of 60 µS/cm (Table 5). This may be an indication they had less anthropogenic disturbances than those that feed River Wouri, The streams feeding both rivers were weakly basic with average pH of 8.3 for those of Wouri and 9.0 for those around River Meme. The streams around River Meme had pH> 8.5 (Table 5). This was out of the allowable range of 6.5- 8.5 set by WHO (2008) and EPA (2018).

Streams WOS1 in Wouri and MES2 in Meme had Ca^{2+}/Mg^{2+} greater than the ideal value proposed by Rosborg (2015) during the dry season. These streams are located upstream. This could be an indication that the inhabitants of these localities who use the streams for various

Table 5. Physicochemical properties of water from streams that feed River Wouri and River Meme during the seasons.

Code	Name	pH		E.C. (µS/cm)		Cl^- (mg L^{-1})		SO_4^{2-}		NO_3^-		Na^+		Mg^{2+}		K^+		Ca^{2+}		Ca^{2+}/Mg^{2+}	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
WOS1	Akwa Nor	8.5	7.3	410.	179.3	22.0	7.4	4.0	3.6	13.0	3.9	70.4	12.6	12.4	-	2.0	4.3	20.5	20.5	1.65	-
WOS2	Bekoko	8.1	7.2	10.0	30.5	0.5	1.9	1.0	0.0	n.d.	0.0	4.1	4.9	0.6	-	0.5	0.4	2.9	2.3	4.83	-
MES1	Small	8.6	7.3	60.0	49.1	0.8	0.5	0.7	n.d	n.d.	n.d	7.5	2.9	4.5	-	5.5	1.8	7.9	2.2	1.76	-
MES2	E. Titi,M.B	9.4	7.3	60.0	66.3	1.7	1.9	1.0	n.d	0.9	n.d	6.8	n.d	1.6	-	4.1	2.1	5.4	2.6	3.38	-

n.d. = not determined.

Table 6. Physicochemical properties of water from the wells around River Wouri and River Meme during the seasons.

Code	Name	pH		E.C. (µS/cm)		Cl^- (mg L^{-1})		SO_4^{2-}		NO_3^-		Na^+		Mg^{2+}		K^+		Ca^{2+}		Ca^{2+}/Mg^{2+}	
		D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W	D	W
WOW1	Clinic Akwa N	**7.5**	7.2	660.0	701.0	21.0	8.4	117.0	213.0	49.0	10.0	32.1	32.3	24.3	n.d	8.0	26.3	82.5	104.0	**3.40**	**-**
WOW2	Opp.Council Bonaberi	6.9	7.2	60.0	530.0	43.0	38.2	44.0	21.9	32.0	7.2	37.9	39.3	16.5	n.d	3.1	13.8	32.9	60.5	2.00	-
MEW1	Ekondo Titi	6.3	7.2	30.0	91.4	1.8	5.0	0.8	21.1	5.0	21.1	4.7	8.5	1.8	n.d.	1.2	3.6	3.1	3.4	1.72	-
EW2	Bogongo	5.8	7.2	20.0	34.6	1.3	0.6	1.0	4.6	3.9	4.6	5.2	4.2	3.0	0.6	0.7	0.4	1.8	1.3	0.60	1.0
MEW3	Pa Balemba	7.6	7.3	340.0	73.8	0.7	1.9	4.9	17.3	3.7	17.3	14.1	3.7	5.8	n.d	23.5	2.4	32.8	2.4	**5.66**	**-**
MEW4	R.M Bridge	7.2	7.3	10.0	139.6	0.8	6.7	1.3	43.7	1.1	43.7	6.1	8.7	0.6	3.7	1.5	3.2	3.9	7.7	**6.50**	**1.76**

purposes could be exposed to the risks associated with excess calcium or magnesium deficiency.

During the wet season like in dry season, the streams showed concentrations which varied with locations (Table 5). This was very pronounced in stream WOS1 that feeds Wouri where the electrical conductivity of the site was 179.3 µS/cm while that of site WOS2 was 30.0 µS/cm. WOS1 was situated at Akwa Nord, at the heart of the city where there was much habitation. While WO2 was situated at Bikoko where there was no habitation at the moment. The streams that feed River Meme had different electrical conductivities of 49.1 and 66.3 µS/cm respectively (Table 5). The streams around River Wouri generally had higher physicochemical properties.

Physicochemical properties of wells during the seasons

Physicochemical properties of the wells of Wouri were generally higher than those of the streams during the dry season (Table 6). On the contrary, the physicochemical properties of the wells of Meme were generally lower than those of the streams (Tables 5 and 6). This could be an indication that ground water contamination is minimal and that anthropogenic activities were responsible for the higher levels in streams. The wells feeding both rivers were acidic with average pH of 6.7 for the wells in around Meme and 7.2 for wells around River Wouri. The wells MEW3 and MEW4 had very high Ca/Mg ratios during the dry season. This exposes the population who use these wells to the deleterious effects of excess Calcium or magnesium deficiency.

Physicochemical properties of the wells of Wouri were generally higher than those of the streams (Tables 5 and 6) in the wet season. This was same in the dry season. Just like Wouri, the

Table 7. Means of water properties from Rivers Wouri and Meme during the seasons.

River/Season	pH	Cond	Cl^-	SO_4^{2-}	NO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
		μS/cm	----------------------------------mg L^{-1}-------------------------------						
Wouri/dry	7.7	2943.0	1085.8	117.8	5.9	528.9	24.2	72.4	30.2
Wouri/wet	7.2	56.7	3.8	0.8	0.3	5.0	1.8	1.2	3.2
Mean	**7.5**	1499.9	1087.7	59.3	3.1	267.0	36.8	36.8	16.7
Meme/dry	8.0	5703.0	2005.2	201.2	6.3	1133.4	47.0	154.2	58.7
Meme/wet	7.2	109.3	15.8	1.4	0.7	13.4	n.d.	5.4	4.2
Mean/	**7.6**	2906.2	1010.5	101.3	3.5	573.4	n.d	78.9	31.5

n.d. = not determined.

Table 8. Correlation matrix of water properties for River Wouri during the wet season.

	pH	EC	Cl-	SO_4^{2-}	NO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
pH	1								
EC	-0.71*	1							
Cl^-	-0.68	**0.99****	1						
SO_4^{2-}	**-0.77***	**0.97****	**0.97****	1					
NO_3^-	-0.06	-0.23	-0.24	-0.13	1				
Na^+	-0.69	**0.99****	**0.99****	**0.96****	-0.26	1			
Mg^{2+}	**-0.73***	**0.98****	**0.98****	**0.98****	-0.11	**0.98****	1		
K^+	-0.56	**0.96****	**0.97****	**0.88****	-0.28	**0.97****	**0.91****	1	
Ca^{2+}	-0.50	0.48	0.45	0.52	0.56	0.44	0.61	0.32	1

** Correlation Significant at 0.01 level * Correlation Significant at 0.05 level.

physicochemical properties of the wells of Meme were generally higher than those of the streams (Tables 5 and 6). The wells feeding both rivers were acidic with same average pH of 7.2. The streams feeding both rivers were also acidic with similar pH, which ranged from 7.20 to 7.30. This was within the allowable range of 6.5 – 8.5 set by WHO (2008) and EPA (2018).

Comparison of the influence of seasonal changes on the physicochemical properties of the water sources

A comparison was done in order to find out if seasonal changes between the dry and wet seasons affected the concentration or magnitude of the properties as well as source of the properties.

Rivers

All the properties decreased drastically on moving from the dry season to the wet season (Table 7) in both rivers. Similar results of strong seasonal variation had been reported by Agbaire and Obi (2009), Ladipo et al. (2011) and Vaishali and Punita (2013). The variation in E.C. was significant ($p<0.05$) along the rivers. This was an indication that the dissolved salts were not evenly distributed.

There was a very significant correlation ($p<0.01$) between EC and the ions except nitrate and calcium ions in the wet season in Wouri (Table 8). However, during the dry season there was a similar significant correlation ($p<0.01$) between the ions and EC except nitrate ion (Table 9).

For River Meme, there was a very significant correlation ($p<0.01$) between EC and chloride, potassium and sodium ions during the wet season (Table 10). In the dry season, there was a very significant correlation between EC and all the ions (Table 11). This is an indication that in Meme chloride, potassium and sodium ions had natural origins while the rest of the ions had natural and anthropogenic sources. There was also a very significant correlation ($p < 0.01$) between nitrate and choride ions in both rivers during the dry season (Tables 9 and 11). Demlie et al. (2007) indicated that a positive correlation of NO_3^- and Cl^- was a diagnostic indicator of anthropogenic activity. This suggests an anthropogenic source of nitrate ions from the use of agrochemicals in the nearby plantations, other farms and inputs from domestic waste as was reported by Wotany et al. (2013). The nitrates leach into ground water sources and eventually into the river. The source of nitrate in River Wouri could be from the intense habitation and/or the industrialization.

Table 9. Correlation matrix of water properties for River Wouri during the dry season.

	pH	EC	Cl^-	SO_4^{2-}	NO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
pH	1								
EC	-0.40	1							
Cl^-	-0.38	**0.99****	1						
SO_4^{2-}	-0.37	**0.99****	0.99**	1	0.	0.			
NO_3^-	**0.96***	**0.96***	**0.98***	**0.98***	1				
Na^+	-0.38	**0.99****	0.99**	**0.99****	0.97**	1			
Mg^{2+}	-0.40	**0.99****	0.99**	**0.99****	0.97**	**0.99****	1		
K^+	-0.39	**0.99****	0.99**	**0.99****	0.97**	**0.99****	99**	1	
Ca^{2+}	-0.42	**0.99****	0.99**	**0.99****	0.96**	**0.99****	0.99**	0.99**	1

** Correlation Significant at 0.01 level. * Correlation Significant at 0.05 level.

Table 10. Correlation matrix of water properties for River Meme during the wet season.

	pH	EC	Cl^-	SO_4^{2-}	NO_3^-	Na^+	K^+	Ca^{2+}
pH	1							
EC	0.04	1						
Cl^-	0.02	**0.98****	1					
SO_4^{2-}	0.70*	-0.15	-0.59	1				
NO_3^-	-0.32	0.61	-0.14	-0.54	1			
Na^+	-0.01	**0.98****	**0.99****	-0.72*	-0.06	1		
K^+	0.13	0.90**	**0.83****	0.78**	0.06	0.80**	1	
Ca^{2+}	-0.05	-0.77**	-0.86**	0.78**	-0.08	-0.87**	-0.44	1

** Correlation Significant at 0.01 level *Correlation Significant at 0.05 level.

Table 11. Correlation matrix of water properties for River Meme during the dry season.

	pH	E.C	Cl-	SO_4^{2-}	NO_3^-	Na^+	Mg^{2+}	K^+	Ca^{2+}
pH	1								
E.C.	-0.73*	1							
Cl^-	-0.72*	**0.99****	1						
SO_4^{2-}	-0.71*	**0.99****	**0.99****	1					
NO_3^-	-0.79*	0.89**	**0.90****	**0.90****	1				
Na^+	-00.63*	**0.95****	**0.95****	**0.95****	0.85**	1		0.	
Mg^{2+}	-0.64*	0.95**	**0.95****	**0.94****	0.84**	0.99**	1		
K^+	-0.64*	**0.95****	**0.95****	**0.95****	0.85**	10.00**	99**	1	
Ca^{2+}	-0.63*	**0.95****	**0.95****	**0.94****	0.84**	0.99**	0.99**	0.99**	1

** Correlation Significant at 0.01 level *Correlation Significant at 0.05 level.

Streams around Rivers Wouri and Meme

Acidity, sulphate, nitrate, potassium and calcium concentrations were higher in the dry season than in the rainy season (Table 5). Stream WOS1 was located at Akwa Nord and Stream WOS2 was located at Bikoko junction. Stream MES1 was located at Small Nganjo while stream MES2 was located at Ekondo Titi where the main activity is agricultural. Akwa Nord is located at the heart of the city where there is human habitation. The activity around Bikoko junction is mostly industrial. The water properties of River Meme were generally higher than those of River Wouri.

Wells around Rivers Wouri and Meme

Electrical conductivity (E.C.), K, Na and Ca concentrations were generally lower in the dry season when compared to the wet season (Table 6). Nitrates were higher during the dry season than during the wet season among the Wouri wells. Among the Meme wells, they were higher during the wet season (Table 6). The higher concentrations during the wet season could be attributed to runoffs or increased dissolution from fertilizers, hence anthropogenic source of pollution.

Conclusion

During both seasons and in both rivers, there were variations in physico-chemical properties from upstream to downstream. The pH of the rivers and most other physico-chemical properties of the rivers were within the acceptable limits of WHO except in the upstream of River Meme where the pH > 9.00 was high. Some of the sources of pollution were anthropogenic. The properties during the dry season were generally higher for the rivers and streams and were lower for the wells. A stream at Meme had pH > 8.50 while the stream at Bikoko had a very high Ca/Mg ratio (4.83). The well in Akwa Nord had a comparatively high (49 mg/L) nitrate, Ca and Ca:Mg ratio (3.4). River Meme is more threatened. Proper and safer means of waste management such as reducing, re-using and recycling are recommended. The use of less acid forming fertilizers and more compost is also highly recommended.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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The roles of community-based water and sanitation management teams (WSMTs) for sustainable development: An example of the Bawku West District, Ghana

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Poor sanitation, water and hygiene are related to several and severe negative implications on health and the environment. In recent years, community-based management of water and sanitation facilities have been linked to improving access to these facilities. Ghana is also on its way to achieving the Strategic Development Goals (SDGs) for access to potable water. However, several studies have found gaps between increased access to water and sanitation in Ghana and have shown that more than a third of the water supply facilities breakdown within the first year of their inauguration. Despite these problems, Water and Sanitation Management Teams (WSMTs) have contributed immensely to the attainment of the SDGs. This study assessed the roles of fifteen communities in maintaining the momentum towards the SDGs. The study revealed that twelve communities (80%) out of fifteen have WSMTs in place. All the communities have water facilities but only four (27%) have access to toilet facilities and the WSMTs working effectively to provide good services to their community members. The existence and effectiveness of WSMTs aided in providing reliable water supply, periodic maintenance of Water Supply Systems (WSSs), less breakdown of WSSs, timely releasing of funds, effective monitoring and quick responses in repairing broken down facilities. However, these WSMTs faced challenges such as the inability to generate funds for the rehabilitation of WSSs, team members lacked skills in water and sanitation management, poor record-keeping and cooperation among the committee and community members in the delivery of their services. It is recommended that WSMTs should be given managerial and maintenance training on WASH projects before they are handed over to them, and community members should be encouraged to cooperate with the WSMTs.

Key words: Community-based, water, sanitation, management, teams, sustainable, development.

INTRODUCTION

The importance of Water, Sanitation, and Hygiene (WASH) to human development and wellbeing cannot be overstated and underestimated. In spite of the over half a century of investment in the water and sanitation sector, more than 10% and over a third of the world's population respectively lack access to potable drinking water and improved and adequate sanitation facilities according to the WHO/UNICEF (2017) Joint Monitoring Programme (JMP) report. Lane (2018) however indicates that in Ghana, access to drinkable water has improved since 2000. Notwithstanding the successes chalked in the WASH sector in some countries, the problems and challenges confronting the WASH sector are worse in rural communities in many developing countries (World Bank, 2019).

According to Baur and Woodhouse (2009), in Africa, the number of people in rural areas without improved water supply is six times higher than in the urban population. Thus, the United Nations adopted the SDGs to improve human life and provide a sustainable environment. The SDGs 6 seeks to ensure the sustainability of water and sanitation for all (United Nations, 2018). The Government of Ghana in collaboration with donors has provided WASH systems to communities in both urban and rural areas to make the lives of citizens more comfortable. Also, Non-Governmental Organizations (NGOs) and corporate societies have also contributed to the provision of such facilities. However, the continuity and scaling up of these WASH services pose a serious challenge to the Government. For instance, the Community Water and Sanitation Agency report (2014) stated that 16,959 new water points, 8,562 rehabilitated water points, and 71,505 sanitation facilities were constructed in 2013 across the country. However, studies have shown that between 30 and 40% of water supply systems become dysfunctional within the first year of usage as mentioned by the Rural Water Supply Network (RWSN) report (2010) and Lane (2018). The increasing population of human places more demand for water and places pressure on existing water supply facilities and a demand for new facilities. Sustainability is, therefore, one of the biggest challenges to satisfying this demand. Interestingly, Willetts and Wichen (2011) mentioned that it is one thing to construct systems that provide clean water and hygienic toilets, and it is another thing to ensure sustained behavioral change and local ownership of facilities for long term use.

According to the Dutch WASH Alliance report (2014), the scope of sustainability is divided into five thematic areas namely; financial, institutional, environmental, technical and social sustainability. This paper focuses on institutional sustainability. In ensuring the sustainability of WASH systems, community participation has also been espoused as one of the key strategies of the International Drinking Water and Sanitation Decade (IDWSD) (McCommon et al., 1990). It has been realized that community participation in WASH programs was limited to the mobilization of self-help labor or the organization of local groups to ratify decisions made by project planners outside the community (Laryea, 1994). Thus, the emphasis was shifted to community management.

Presently, drinking water and sanitation policies assume that facilities should be managed by local user communities (Braimah and Fielmua, 2011). To handle this, at the local level, Water and Sanitation Management Teams (WSMTs) are formed to ensure community-based provision and sustainability of WASH facilities. In principle, the WSMTs are responsible for the operation and maintenance (O&M) of community water facilities and are expected to collect fees/levies for maintenance. Therefore, this study assesses the role of institutional sustainability with regards to a case study of the role of Water and Sanitation Management Teams-WSMTs in ensuring the sustainability of WASH facilities in the Bawku West District in the Upper East Region of Ghana.

MATERIALS AND METHODS

Demographic characteristics

The total population of the Bawku West District is 94,034 consisting of 45,114 males and 48,920 females (Bawku West District Assembly (BWDA) 2015 report). The district has seven Area and Town Councils which include Zebilla, Binaba/Kusanaba, Zongoyiri, Gbantongo, Tanga/Timonde, Tilli/Widnaba, and Sapelliga Town/Area Councils. The Zebilla Area Council with a population of 73,968 comprising fifteen (15) communities was selected for this research.

Overview of the study area

The Bawku West District of the Upper East region of Ghana was carved out of the old Bawku District under the new local government system in 1988. It lies between latitudes 10° 30'N and 11° 10'N, and between longitudes 0° 20'E and 0° 35'E (Figure 1). The district shares boundaries with Burkina Faso to the North, Bawku Municipality, Binduri District and Garu-Tempane District to the East, Talensi, Nabdam and Bongo Districts to the West and the East Mamprusi District to the South. The District covers an area of approximately 1,070 km^2, which constitutes about 12% of the total land area of the Upper East Region. It has Zebilla as its administrative capital (BWDA, 2012).

Research methodology and sources of data

This study utilized qualitative data which comprised both primary and secondary information. The primary variables considered in this research comprised the concept of community ownership and management of WASH systems, access to WASH, frequency of breaking down and response to maintaining WASH facilities,

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Operation and Maintenance (O&M) of the facilities, the effectiveness of WSMTs, gender representations on the WSMTs, community perspectives on Community Ownership Management (COM), and the successes and challenges of WSMTs. Secondary data were sourced from the following: the Bawku West District Assembly, the Bawku West District Water, and Sanitation Team (DWST), community members and WSMT members within the study area. A descriptive, qualitative design was adopted. Key informant interviews were conducted and close-ended questionnaires were administered to the District Assembly, DWSTs, Project Areas Community Members (PACM), WSTMs and households to generate empirical data for the purpose of this study. Community meetings were conducted in the communities to validate the findings from the various groups. A checklist was also used to evaluate and record onsite observations.

Determination of sample size and sampling method

In determining the sampled households, three factors were considered; the desired level of confidence, the error tolerance level and the proportion of the population with access to potable water in the district. The sample size was determined following Kendie (2002) and Braimah and Fielmua (2011) as presented:

$$N = [z/e]^2\ [p]\ [1-p] \tag{1}$$

Where N = sample size, z = standard score at 92% Confidence Level (1.76), e = margin of error (0.07) and p = proportion of population with access to potable water in the district (89.9%) according to UNDP (2011).

$$N = [1.76/0.07]^2\ [0.899]\ [1-0.899]$$

$$N = 57.4 \sim 60$$

Therefore, sixty questionnaires that sought people's views on the roles, performance, successes, and challenges of WSMTs were also administered to household heads within the district. In this study, both probability and non-probability sampling techniques were adopted. The probability method was used to gather information from households. However, since the number of households of the individual communities was undetermined, a systematic approach where the sampled households were distributed evenly across the communities was used. This was presented as

$$[\frac{60\ (house\ holds\ heads)}{15\ (communities)} = 4\ household\ heads]$$

Therefore, four household heads were interviewed in each community. Also, the non-probability sampling technique (purposive) was adopted in deriving information from WSTMs and the various institutions involved in water-related issues within the district.

Functions of the institutions from which data was obtained

(i) Bawku West District Assembly: This is the local government authority that has the mandate of all planning and developmental programs at the local level.
(ii) Bawku West District Water and Sanitation Team (DWSTs): A unit within the Works Department of the District Assembly charged with the mandate of facilitating and providing technical assistance and services to WSMT in the various communities under the district.
(iii) Project Areas Community Members: The members of the project communities who have lived in the communities for at least the past twenty years or older than the oldest hand pump installed.
(iv) Project Areas of the WSMTs: These are the community level authorities responsible for the operations and management of the water facilities at the community level. These committees are charged with the responsibility of ensuring the continuity of water and sanitation facilities or the long term benefit of the beneficiaries.

Data analysis

The acquired data were analyzed using the Statistical Package for Social Sciences (2015 version) and Microsoft Excel (2016 version). Descriptive and statistical methods in the form of percentages, tables, and graphs were used to organize and interpret the acquired data.

RESULTS AND DISCUSSION

Access to safe water supply

Safe water is an important resource for mankind. However, a proportion of the world's population still lacks access to drinkable water. The findings of the study showed that the assessed communities relied on safe water sources. Thirteen communities had access to borehole water, whereas a community each depended on dugout wells and pipe source. The study identified seventy-seven improved water sources within the district (Table 1). Zebilla, the district capital which had the highest population had access to both borehole and pipe connection. It is inferred that the community which depended on dugout wells may be at risk to several health implications since the wells at the time of this study were not covered and/or lined.

Across the studied communities, based on the sources of water identified, water-borne diseases such as typhoid, cryptosporidiosis, giardiasis, and salmonellosis were not expected since according to Table 1, they had access to improved water sources. However, due to prolonged dryness, erratic and minimal rainfall, some of the boreholes and dugout wells dried up during the dry season. It is suspected that because the region has a high water table, the majority of the boreholes and wells were drilled to shallow depths. This was consistent with the findings by Anim-Gyampo et al. (2012) which indicated the drying up of underground water sources in some parts of the region. Due to this, people were compelled to resort to unsafe water sources such as streams and rivers for domestic and other purposes (UNDP, 2011) which could contribute to water-related diseases if pre-treatment of water is not properly done in these periods. In addition, the study identified the construction of new water supply systems as stated by (UNDP, 2011). Eighty-seven (87%) of the respondents attributed this progress to efforts by the WSMTs. Based on this, access to improved water is expected to rise

Figure 1. Locations of the communities.

Table 1. The types of water facilities within the communities.

Type of water facility	Total number	Number of communities
Boreholes	68	13
Dugout wells	2	1
Pipe connection	7	1

Table 2. Breakdown of water supply facilities in a year.

Frequency of breakdown	Number of facilities	Percentage
No breakdown	42	55
Once	15	20
Twice	5	6
Thrice	8	10
Four	4	5
Drought/dryness	3	4
TOTAL	77	100

considerably.

Frequency of breakdown of Water Facilities

Table 2 presents the frequency of dysfunctional WASH facilities in a year. According to the International Water and Sanitation Centre (IRC) (2018), one of the biggest challenges related to WASH is the sustainability of projects. The study showed the majority (42) of the facilities were functional after a year. The majority of these facilities were located in communities with effective WSMTs. Others were also located in less populated areas. However, Yelwoko, Alamboya, Kuboko, and

Zebilla have their facilities breaking down once in a year whereas facilities within Zebilla broke down two to three times in a year. The study further showed that WASH facilities at Gozeisi, Teogo, Saaka, and Kukore broke down twice in a year. These communities had mechanics in charge of maintenance and repairs. Meanwhile, Zabazoya had its facilities breaking down three times in a year whereas Timonde recording four. However, the Naringo community had just a dugout well which functioned during the rainy season. This made water accessibility a problem during the dry season, and surface water sources a perfect resort. Similar to the findings by Taylor (2009) and the RWSN report (2010), on average, 46 and 30% of rural boreholes were dysfunctional in Tanzania and Sub-Saharan Africa respectively. Further studies reflected in the findings by the RWSN (2012) and Fisher et al. (2015) also indicated that in Sub-Saharan Africa, at any given period, one-third of rural hand-pump boreholes are dysfunctional. The study identified that similar to the findings by IRC (2018), 45% of the water systems broke down within a year of construction. This result was further confirmed as 67% of the respondents observed the breakdown of these facilities within a year of construction.

The breakdown of WASH facilities could not be attributed to just the inexistence and ineffectiveness of WSMTs, but increased population, the rate of usage and the level of maintenance also contributed significantly. Larger and populated communities experienced frequent breakdown and deterioration of water supply facilities. Seventy-nine percent (79%) of the respondents stated that they had observed a correlation between population growths with the deterioration of water supply systems. However, the emergence and effectiveness of WSMTs created an avenue for funds to be generated for the construction of new WASH facilities to meet the growing population and to rehabilitate broken-down facilities. WSMTs also ensured a judicious use of these facilities to reduce intensified pressure. This was done by shutting down and locking the systems daily from evening to morning.

The availability of spare parts and attending to broken-down WASH facility

According to Braimah and Filmua (2011), the availability of spare parts for repairing water supply systems has become a major challenge in the country. It was observed that the unavailability of funds was not the only factor impeding repairs but the obsolete nature of the systems, unavailable skilled persons, poor road network, and unavailable spare parts also contributed significantly. The results of this study showed that spare parts for minor repairs (polyvinylchloride (PVC), primers) were available at Zebilla (the district capital) whereas major faults such as the breakdown of water pumps, riser main, pump cylinders, and tailpipes were purchased from towns/cities (Bolgatanga, Tamale, Kumasi, and Accra). However, these were costly. These results were consistent with the findings by Braimah and Filmua (2011). Seventy-three percent (73%) of the respondents affirmatively indicated to have seen WSMT members conveying purchased spare parts for repairs.

Figure 2 presents the institutions responsible for reporting the breakdown of WASH facilities for the consideration of appropriate and available measures. According to the WHO (2010) report, 64% of Overseas Development Aid (ODA) to WASH globally goes into the construction of new facilities whereas only 13% is allocated for the maintenance of projects. Thus, WSTMs either solicits or mobilizes funds from co-operating societies, NGOs, the Assembly or community members in order to maintain WASH facilities. They also monitor the functionality of the facilities to ensure their sustainability and longevity. From Figure 2, the majority of the communities had the WSMTs in charge of reporting the devastating conditions of WASH projects for corrective measures to be taken and to solicit funds to improve the quality and coverage of WASH in their respective communities. Observation made in this study coupled with the affirmative responses by 76% of the respondents indicated that the involvement of WSMTs in WASH networks was more formal, effective and recognized by donors, government and NGOs. The study evidentially showed that the WSMTs could easily represent the communities in seeking assistance related to WASH from NGOs, rich natives and outsiders, local and international donors, providers, trained mechanics, government agencies, political leaders and government appointees (Figure 3). On average, WSMTs have a wider scope of reaching support to solve community-based WASH problems.

Service downtime

The result revealed that all the communities with quicker responses (two days) in maintenance and repairs were under the management of the WSMTs as shown in Table 3. The study identified that none of the communities recorded a response to broken-down water facilities in less than a week. A significant number (4) of them had relatively quick responses through their respective WSMTs within a week. Irrespective of the existence of WSMTs, the response to repairing broken down WASH facilities was relatively slow. This was due to over-reliance on the District Assembly, area mechanics or the District Water Board which involved bureaucratic processes, political or ethnic influences, especially in the absence or ineffectiveness of WSMTs. The communities without WSMTs (Azoge, Kariga and Naringo) (Table 4) had responses to broken down facilities after two months. Poor road network, lack of funds, scarce spare parts, ineffective WSMTs also delayed maintenance and repairs. However, in cases where WSMTs worked effectively,

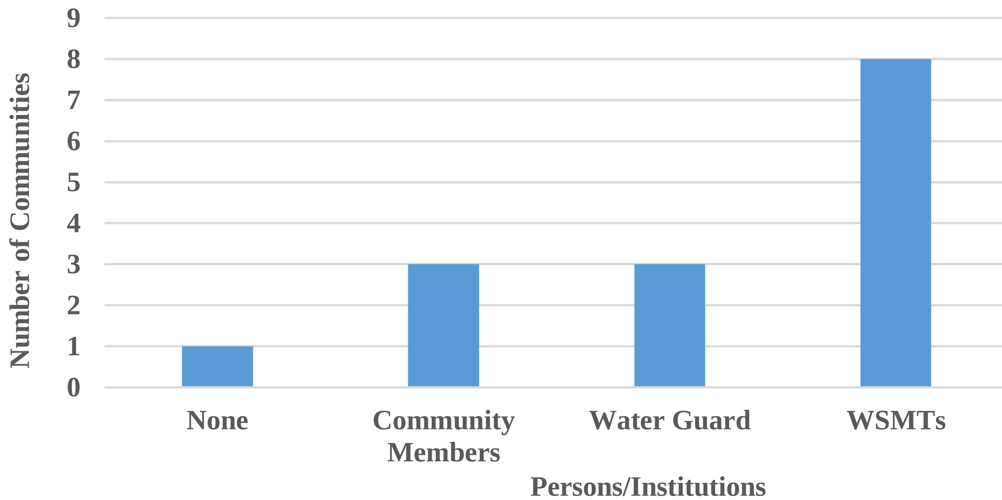

Figure 2. Persons responsible for reporting the breaking down of WASH facilities.

Figure 3. Chain in seeking for support.

these setbacks were handed by WSMTs to considerable levels. This fast-tracked the rehabilitation of existing facilities or construction of new WASH projects.

Responsibility for maintaining WASH facilities

The WSMTs were preferred by community members (87% of the respondents) to be in charge of the operation and maintenance of the water and sanitation facilities as compared to mechanics, the district assembly, Providers or the Water Board. The Respondents mentioned that they could easily communicate WASH related issues with the WSMTs and had quick responses in previous instances (Figure 4).

Fisher et al. (2015) indicated that the presence and effectiveness of skilled mechanics and WSTMs aided in the sustainability of water supply systems. Seven and four communities respectively depended on WSTMs and mechanics in responding to broken down projects. This reflects the importance of WSMTs and mechanics in conducting minor repairs instead of relying on external

Table 3. The duration of response to maintain WASH facilities.

Duration before responding to broken down wash facilities	Number of communities
No response	1
One week	4
Three weeks	2
One month	2
Two Months	6
TOTAL	15

Table 4. Female representation on the WSMTs.

Community	WSMTS availability	Male	Female	Leader	Total
Kubore	Yes	3	3	Male	6
Azonge			No WSMT		
Kamiga			No WSMT		
Yikurugu	Yes	7	5	Male	12
Saaka	Yes	8	7	Male	15
Alamboya	Yes	6	4	Male	10
Teogo	Yes	2	1	Male	3
Timonde	Yes	2	5	Male	7
Tanga	Yes	2	0	Male	2
Kuboko	Yes	2	2	Male	4
Zabazoya	Yes	2	2	Male	4
Naringo			No WSMT		
Zebilla	Yes	3	1	Male	4
Yelwoko	Yes	2	2	Male	4
Gozeisi	Yes	2	2	Male	4
	TOTAL	41	34		75

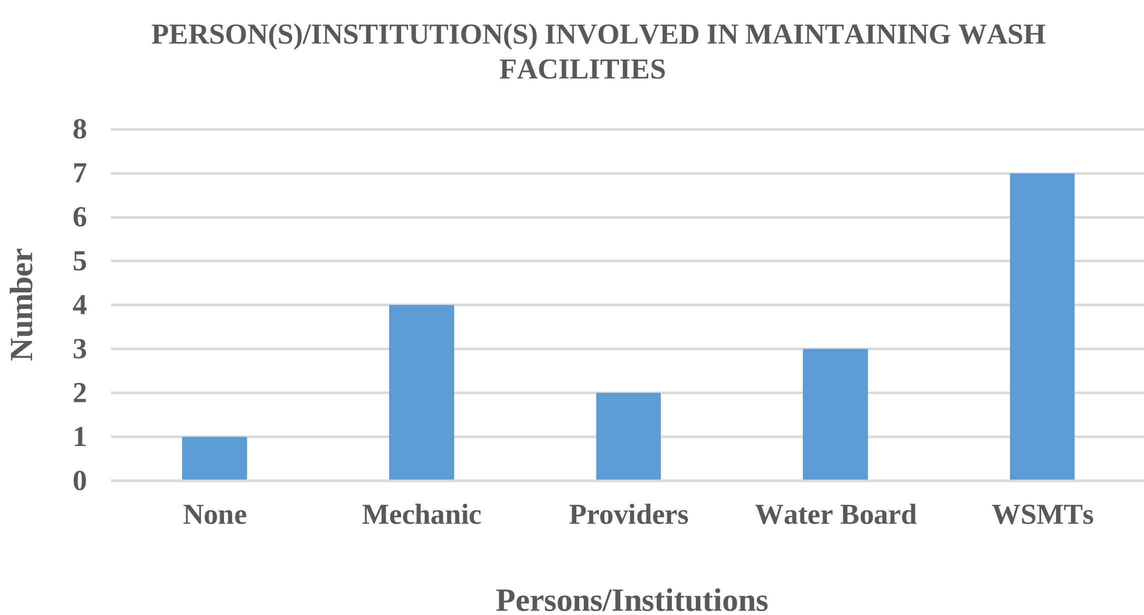

Figure 4. Persons responsible for the maintenance of the water facility.

technical and financial support as mentioned by Alexander et al. (2015) and Fisher et al. (2015), and Foster (2013) and Lane (2018) respectively. This significantly sustained WASH projects.

The availability of toilet facilities

Four communities (out of 15 communities) had toilet facilities. In totality, these four communities have about 12 toilet facilities which comprised of one Kumasi Ventilated Improved Pit (KVIP) at Alamboya, another at Timonde, seven at Zebilla and three pit latrines at Azonge. Apart from Azonge whose pit latrines were constructed by donors, sixty-eight percent (68%) of the respondents in the remaining three communities (Alamboya, Timonde and Zebilla) attributed this achievement to the WSMTs. Meanwhile, the KVIP at Timonde and three KVIPs at Zebilla had been dysfunctional for about two to three years. The WSMTs and assessed stakeholders attributed this to the lack of funds and external support, and increasing population. The remaining eleven communities (Kubore, Kamiga, Yikurugu, Saaka, Teogo, Tanga, Kuboko, Zabazoya, Naringo, Yelwoko, Gozeisi) had no toilet facilities. Out of the sixty households that were randomly assessed, twenty-nine had household pit latrines. Thus, they neither depended on public facilities nor practice open defecation. Interestingly, eighteen of these facilities were located in the communities which had public KVIPs and latrines. The absence of toilet facilities in most of the communities and households suggest that they resort to open defecation. However, apart from the stench, most of the community members (79%) did not know the environmental and health implication associated with open defecation. In addition, the payment of toilet user fee (averagely 20 peswas) at the time of the study, and queuing to use toilets made it inconvenient for some of the community members. Such people considered open defecation as a better option.

Female representation on the water and sanitation management teams

Studies have shown the marginalization of women in participating in rural WASH projects (Tigabu et al., 2013; Marks et al., 2014; Omorede, 2014; Mensah, 2015). Similarly, in this study (Table 5), five (5) communities (Kubore, Kuboko, Zabazoya, Yelwoko and Gozeisi) had gender-equal representations on the WSMTs whereas six teams (Yikurugu, Saaka, Alamboya, Teogo, Tanga and Zebilla) had the number of men outweighing women and one team (Timonde) had more women than men. In totality, there were forty-one men against thirty-four women on the WSMTs. Interestingly, in Tanga, there was no female representation on the team (Table 4). Unlike the findings by Mensah (2015) where the number of men in WSTMs outweighed women by one in each team, in this study, majority of the communities had men outweighing women by two.

One of the factors (Figure 5) influencing gender representation on the teams was culture values. The cultural certain of the studied communities undermined the contributions of women as they were relegated, and were not allowed to spare head affairs. This is highlighted in Table 5 where all the leaders of the teams were men. Also, the gender bias representation of men and women on the teams was prejudiced by the members' level of education. The men on the various teams were more educated, and thus, easily communicated the progress and plights of the communities in WASH issues for support. The women were less courageous and this undermined their influence as part of the WSMTs. Also, it was observed that women did not recognize the WASH facilities as theirs since they were unable to take part in the construction/implementation stage where physical labor is needed. They did not also place much focus and time on WASH-related issues due to domestic activities and were less motivated to take part. Finally, majority of the women could not contribute financially to the progress of the WASH facilities since they had no sustainable financial sources in serving majorly as housewives. Thus, they were not considered fit to manage WASH issues. However, it was identified that the women on the WSTMs were instrumental in encouraging and mobilizing their colleagues in ensuring the maintenance of WASH facilities by embarking on periodic clean-up exercises.

Educational and financial issues

According to Lane (2018), training WSTMs is an essential component that sustains the longevity of water supply systems. Marks et al. (2014) also indicated that training WSMTs occurred once and at the project inception stage. The study revealed that, though in some communities, team members were trained on how to fix minor mechanical problems on the WASH facilities; none of the WSMTs had been given formal education on the management of water and sanitation issues. However, they ensured maximum cleanliness at the various WASH facilities. Furthermore, unlike the findings by Foster (2013) and Lane (2018) where no relationship was established between the training of WSMTs and the sustainability of water facilities, this study showed a close relationship. Trained WSMTs knew how and where to purchase spare parts, handle finances, seek external support (financial, technical and managerial), and they knew the essence of cleanliness. Communities with trained WSMTs considerably manage WASH facilities better than those with untrained WSMTs. However, similar to the findings by Lane (2018), they had only received training once (before the facilities were

Table 5. Financial issues of the WSMTs.

Community	Training	WSMTs with bank accounts	Financial accountability
Kubore	No	No	No
Azonge		**No WSMT**	
Kamiga		**No WSMT**	
Yikurugu	No	No	No
Saaka	No	No	No
Alamboya	Yes	Yes	Yes
Teogo	No	No	Yes
Timonde	No	No	No
Tanga	Yes	Yes	Yes
Kuboko		No	No
Zabazoya	Yes	Yes	No
Naringo		**No WSMT**	
Zebilla	Yes	Yes	No
Yelwoko	No	No	No
Gozeisi	No	No	No

Figure 5. Factors affecting gender equality on WSMTs.

inaugurated). Therefore, it was difficult to replace absent, dead, ineffective or untrusted team members since the substitute would not have access to proper managerial or technical training to sustain the WASH projects.

From Table 5, out of the twelve communities with WSMTs, Alamboya, Tanga, Zabazoya and Zebilla had bank accounts of which only Alamboya and Tanga WSMTs ensured periodic accountability to their communities. Though Teogo Community had no bank account, its team ensured periodic accountability to its community members. Communities with vibrant and active WSMTs had both functioning and forecasted operational and maintenance plans in place. The inability of WSMTs to conduct periodic accountability to their members or open bank accounts discouraged the community members to be financially involved in WASH issues as fifty-seven (57%) of the respondents mentioned their disinterest in contributing financially to promote WASH due to the unaccountability of WSMTs and insecurity with the lack of bank accounts.

Successes of WSMTs

Communities with active WSMTs enjoyed the following benefits:

(i) Reliable supply of water; since the WSMTs are also community members who depend on the facilities, they ensured that the facilities were always in good condition to supply water regularly.
(ii) Fewer frequencies in the breakdown of facilities; facilities were managed and maintained regularly
(iii) Periodic maintenance practices; ensure that maintenance practices are carried out at the appropriate time to ensure the functionality and sustainability of the facilities.
(iv) Quicker response to the breakdown water facilities; tariffs were collected from the community members for the maintenance of the facilities so they do not seek funds from any other source which could delay their response to the repairs and maintenance of the facilities.
(v) Timely releasing of funds for maintenance, repairs or the construction of new facilities.
(vi) Effective monitoring of systems and facilities.
(vii) Encourages community involvement, ownership, and participation of WASH-related issues and facilities.

Challenges of the WSMTs

(i) Difficulty in levy collection; though some community members deliberately refrained from paying their respective levies, genuinely, others were financially handicapped to contribute.
(ii) Poor record keeping; some of the teams were not keeping records of expenditure. This hindered transparency and accountability.
(iii) Low motivation from the providers of the facilities; after the facilities have been handed over to them, the providers seem to leave everything in the care of the teams. However, the team members are not paid for the services they render.
(iv) Poor cooperation between the WSMTs and community members
(v) Inadequate training; the WSMTs only gain basic training to fix minor problems. Thus, they are unable to fix major problems. In some cases, they destroy these facilities instead of repairing them.
(vi) Obsolete systems; some of the facilities were old models. It was difficult getting their parts for maintenance and repairs.
(vii) The high cost of spare parts.

CONCLUSION AND RECOMMENDATIONS

The study showed that the formation of effective water and sanitation management teams aids in improving water, sanitation, and hygiene at the local level. They ensure that WASH facilities are properly managed and maintained to promote sustainability. However, they face certain challenges in the delivery of their services such as the influences of uncooperative community members, lack of water and sanitation education, inability to recover funds and poor records keeping. Based on the findings of this study, it is therefore recommended that;

(i) The district assembly should ensure proper coverage of WASH facilities across the district.
(ii) WSMTs should be properly trained on WASH and maintenance issues before projects are handed over.
(iii) The WSMTs should be motivated (financially) by the providers of the facilities to motivate them in the service rendered.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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A chemical speciation study of selected heavy metals in aquatic bottom sediment samples from *Mpenge* stream, *Musanze* District, Rwanda

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Mpenge stream is regarded as one of the most important domestic water resource in Musanze District; Rwanda. The chemical speciation study of selected heavy metals (Zn, Cu, Co, Cr, Ni, Pb, and Cd) in sediment samples collected from that stream was carried out by means of an analytical procedure involving sequential chemical extraction method and to determine the heavy metals content in different fractions of sediment. The heavy metals were found in five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual fraction. Their levels were determined by flame atomic absorption spectrophotometer and the total mean values were in the order Cr> Zn>Cu > Ni=Pb > Co > Cd. In fact the total metal content in mg/kg dry matter (mean values) were for Cr=169.17±8.77; Zn=136.67±2.88; Cu=44.17±1.44; Ni=33.33±5.22; Pb=33.33±14.33; Co=25.00±0.00; and Cd=5.00±0.00. As per United States Environmental Protection Agency's (US EPA) guidelines for sediments quality, sediments were moderately polluted for all analyzed elements apart from chromium that showed that the sediments were heavily polluted. Furthermore, the speciation results showed that high levels of these assessed metals (Zn, Cu, Co, Cr, Ni, Pb, and Cd) were associated with exchangeable and carbonate bound fractions for all heavy metals apart from copper, pointing out that they are in potentially available forms and may pose serious problems to water consumption.

Key words: Speciation, sequential chemical extraction, heavy metal, bottom sediment, stream.

INTRODUCTION

Water bodies are widely complex dynamic, chemical systems consisting of different components, namely various solutes, organic matter, and colloidal or particulate matter. Hence, a number of chemical processes between dissolved metal pollutants and components are expected to take place in these water systems and it is the distribution of the heavy metal pollutants between the different chemical species and forms which determines their geochemical and biological reactivity (Luoma, 2017; Saleem et al., 2015a). The chemical and physical

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changes associated with different forms of a chemical element in sediment are a key process in the cycling of heavy metals in natural water on wide range of time scales. In fact, it was found that heavy metals occurring in water bodies are predominantly carried by suspended particles and only a small fraction is transported in the soluble form (Ali et al., 2016; Jiang et al., 2014). The distribution of an element among different inorganic compounds and organic complexes impacts its transport and bioavailability. In order to understand the environmental chemistry of an element, it is necessary to obtain completely the concentrations and chemistry of its various species under the different conditions possible in natural environments. (Tessier et al., 1979) pioneered the area of chemical speciation as characterizing an element's forms for understanding the transformations between different forms and their availability to living organisms' bodies (Skorbiłowicz, 2014).

Sediments in water bodies are complex mixtures of various phases, namely residues of weathering and erosion of underground mate (Islam et al., 2015b). The geochemical fractions most commonly analyzed are the following: exchangeable (Fraction I), bound to carbonate (Fraction II), reducible (Fraction III), oxidizable (Fraction IV) and residual metals, such as rocks. Fractionation of water sediment by selective chemical extraction removes or dissociates a specific phase with the associated metal bound to it (Tessier and Campbell, 1987). Among the sequential extraction schemes proposed to investigate the distribution of heavy metals in soil and sediment, the five-step extraction scheme developed by Tessier et al. (1979), was the most widely used. Different researchers have used different methods for analysis of chemical speciation, such as voltametric, inductively coupled plasma-mass spectrometry (ICP-MS) and other methods (Islam et al., 2015a, b; Rahman et al., 2008, 2014). Use of total concentration as a criterion to access the potential effects of the sediment contamination implies that all forms (phases) of a given metal have an equal impact on the environment. Such an assumption is untenable (Huang et al., 2015; Yang et al., 2015). It is evident that just the speciation of metal pollutants with the various sediment phases determines their specific impact on the environment. Also the type of phase specific bounding of metals in contaminated natural sediments specifies suitable methods of their potential cleaning and utilization (Martín et al., 2015: 70). A common but time consuming analytical method if evaluating particular metal-sediment phase is the method of sequential extraction (SE) adapted from the methods of soil and sediment chemical analysis (Nazeer et al., 2014; Saleem et al., 2015b). The concept of the SE procedure is the portioning of a solid material into specific phases or fractions that are selectively extracted that is, liberated and released into solution (leached) along with the associated trace meals, by using appropriate reagents arranged in increasing strength. Speciation, using sequential extraction schemes, has been developed for assessing geochemical forms in soil and sediment (Saleem et al., 2015a).

Water bodies show important parts in the ecological system. These water bodies have been contaminated by different forms of heavy metals due to rapid industrialization growth, excessive mining activities, weathering and erosion (Huang et al., 2015; Wafula et al., 2018). This contamination poses severe ecotoxicological threats to aquatic wildlife and humans. The bio-geochemical behavior, nutritional bioavailability and toxicity of metals are widely dependent on the chemical speciation (Helliweli et al., 1983). In this study, bottom sediments collected from Mpenge stream, whose untreated water is largely used by local people as domestic water, were screened for selected heavy metals using five-step extraction method developed by Tessier and Campbell (1987). The work focused on selected heavy metals namely zinc (Zn), copper (Cu), cobalt (Co), chromium (Cr), nickel (Ni), lead (Pb), and cadmium (Cd) by partitioning them into specific phases and be analyzed using flame atomic absorption spectrometer Pelkin Elmer 2380, and the findings were to be compared with the guidelines values (Tessier et al., 1979).

MATERIALS AND METHODS

Mpenge stream is a natural source of water located in Musanze District, Northern Province of Rwanda. It is generally used by local people as drinking and cooking water and it is flowing trough volcanic rocks. Six sampling sites in Mpenge stream were selected for sediment samples collection. Three sediment samples were collected from each of the sampling selected sites. Sediment samples from each location were made into one composite representative sample and the latter was stored in a clean, sealable, washed with distilled water and rinsed with nitric acid. The bottom sediment samples were dried in an oven at 150°C, for five hours. The samples were then ground in an agate mortar and screened through a nylon sieve. A portion (1 g) of the sample with a size <0.2 mm was assigned for further studies. The partition into fractions of sediment samples was done according to a five–step chemical speciation method proposed by Tessier and Campbell (1987) followed by the analysis of heavy metal using flame atomic absorption spectrophotometer (FAAS).

Exchangeable heavy metals

One gram of dry sediment was dissolved in 10 ml of 1 M CH_3COONH_4 to pH 7 and shaken at room temperature for one hour followed by the centrifugation. The supernatant was acidified with one drop of concentrated nitric acid (65% w/w) and diluted into a 25 ml beaker to the mark with distilled de-ionized water. The final solution was used to determine the exchangeable heavy metals by FAAS.

Heavy metals bound to carbonates

The residue in (i) was treated with 20 ml of 1 M ammonium acetate acidified with acetic acid to pH 5. The shaking time was Five hours at room temperature. After centrifugation, the supernatant was acidified with one drop of concentrated nitric acid (65% w/w) and diluted into a 25 ml volumetric flask to the mark with distilled de-ionized water and used to determine the heavy metals bound to carbonates by FAAS.

Heavy metals bound to hydrated oxides of Fe and Mn

The residue in (ii) was dissolved in 20 ml of 0.04 M $NH_2OH.HC1$ (hydroxylamine hydrochloride acid) in acetic acid (25% v/v). The shaking time was two hours at 95°C. The supernatant, after centrifugation, was acidified with one drop of concentrated nitric acid (65%) and diluted into a 25 ml volumetric flask to the mark with distilled de-ionized water. Then the heavy metals bound to hydrated oxides of iron and manganese were determined by using FAAS.

Heavy metals bound to organic matter

The residue in (iii) was respectively treated with 5 ml 0.07M HNO_3, and 5 ml of 30% H_2O_2 to pH = 2 and the mixture was shaken for two hours). Then 5 ml of 30% H_2O_2 to pH = 2 was added to the resulting solution and was shaken for three hours. Finally 10mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added to that latter solution and the shaking time was 0.5 hour. The supernatant was acidified with one drop of concentrated nitric acid (65%) into a 25 ml volumetric flask and completed with distilled de-ionized water to the mark and used to determine the heavy metals bound to organic matter by FAAS.

Heavy metals in other forms

The heavy metal content in the last residue in (iv) was calculated by subtracting the sum of heavy metal content in Fractions I, II, III, IV, and from the total concentration of heavy metals determined by using a separate sample. To determine total heavy metals in, dried sediment sample (1 g) was transferred to a volumetric flask containing 50 ml H_2O and boiling chips. Then 50 ml HCl/HNO_3, 3:1 was added, mixed and heated respectively to 100°C for one hour, 125°C for 15 min, 150°C for 15 min, 175°C for 15 min, and to 200°C to near dryness. The residue was concentrated to about 5 ml in concentrated nitric acid. After cooling, 1 ml 30% H_2O_2 was added to the concentrated residue and the digestion was for 10 min. The digestion in 1 ml 30% H_2O_2 was repeated twice. After cooling again, 3 ml 30 % H_2O_2 was added and the digestion has been for 10 min. 50 ml water and 25 ml HCl were added, mixed, and heated till boiling. The whole solution was cooled, transferred to 250 ml volumetric flask, filled up to the mark, mixed, and left at least 15 h to settle. The clear solution was used to perform the measurements for total heavy metals by FAAS.

RESULTS AND DISCUSSION

In Mpenge sediment samples, the levels of heavy metals analyzed were shown in Table 1. It was generally observed that all elements in residual fraction were at the highest concentration. The concentration was ranged between 4.25 and 155.17 mg/kg dry matter. In that fraction heavy metals were not potentially bioavailable and might not be a threat to the environment, including living organisms. This is due to the association of heavy metals to the crystalline structure of the minerals implying that they are difficult to separate from the sediments. The mean values of the distribution of heavy metals in residual fraction were in the order Cr > Zn > Ni > Cu > Pb > Co > Ni >Cd. The high concentration of total Cr and low concentration of total Cd was reported by Skorbilowicz (2014) in bottom sediments of Bug River in Poland.

Zinc

The high concentration in Fraction I and II indicated that Zn would be released into the environment once the environmental conditions could become more acidic. The two fractions contain the most labile Zn which might be available under pH change and therefore the most dangerous. Zinc was also found bound to iron and manganese oxides in Fraction III and would be released if the sediments were subjected to more reductive conditions. Metals in reducible fraction may easily undergo removal from the sediments, be bioavailable and harmful to aquatic organisms including human beings. The presence of zinc in Fraction IV revealed that it occurred as stable organic complex and this could be due to the high organic content in sediment samples. Our findings are in agreement with earlier studies (Jiang et al., 2014). In Fraction I, zinc showed significant quantity (4.25 mg/L) compared to World Health Organization (WHO) drinking water guidelines (3 mg/L). The total content of Zn showed that the stream is moderately polluted.

Copper

The results obtained for this heavy metal indicated that the main partition is between the third (reducible) and the fourth (oxidisable) fractions. Copper content in those fractions were 5.17 and 5.25 mg/kg dry matter respectively and might be released and bioavailable if its matrix underwent reducing, oxidizing conditions and microbial activity (Zhang and Gao, 2015). Therefore it should constitute a real threat to the environment. The labile copper in Fraction I and II was in lower concentration (0.33-0.91 mg/kg) compared to its occurrence in other fractions and was below WHO's drinking water standards (1993).

Cobalt

Cobalt was mainly concentrated in the residual and organic matter fractions. Their concentrations were 3.33 and 19.17 mg/kg in Fractions IV and V respectively. Organic matter bound metals would be released in more oxidizing conditions and could be a threat to living organisms. Residual fraction bound metals are blocked in crystal lattice of mineral and cannot pose any harm to environment. Exchangeable and carbonate bound cobalt

Table 1. Distribution of Zn, Cu, Co, Cr, Ni, Pb, and Cd in different fractions in sediment samples, from Mpenge.

Element	Fraction I n =7	Fraction II n =7	Fraction III n =7	Fraction IV n =7	Fraction V n =7	Total content n =7
	mg/kg dry matter (Mean values)					
Zinc	4.25 ±1.98	35.67±17.89	23.91±12.20	18.25±3.36	54.67±27.39	136.67 ± 2.88
Copper	0.33±0.14	0.91±0.28	5.17±0.76	5.25±0.75	32.41±1.25	44.17±1.44
Cobalt	0.83±1.44	1.67±1.44	n.d	3.33±3.81	19.17±1.44	25.00±0.00
Chromium	0.25±0.25	0.50±0.25	5.91±0.38	7.33±2..26	155.17±11.02	169.17±8.77
Nickel	0.08±0.14	0.41±0.72	n.d	0.58.±0.62	32.60±5.96	33.33±5.20
Lead	5.00±2.50	4.17±5.20	0.83±0.14	1.67±2.88	21.67±7.21	33.33±14.43
Cadmium	0.08±0.14	0.33±0.14	n.d	0.17±0.14	4.25±0.43	5.00±0.00

n = Number of samples, n.d: not detected Fraction I: Exchangeable metals, Fraction II: Metals bound to carbonates, Fraction III: Metals bound to hydrated oxides of iron and manganese, Fraction IV: Metals bound to organic matter, Fraction V: metals in other forms (mainly metals built in crystal lattice of mineral) , Total content: I + II + III + IV + V.

was observed, and their levels were 0.83 and1.67 mg/kg respectively. Skorbilowicz (2014) reported the same results from the chemical speciation of Bug River (2014). Such levels in the acid-soluble fractions were significant compared to the limits set by WHO (1993) which meant that Cobalt was potentially bioavailable and might be a serious threat as it is transferred into the chain food from bottom sediment. Hydrated oxides of iron and manganese bound cobalt was not detected. Compared with other analyzed heavy metals, cobalt was the less concentrated in all fractions.

Chromium

Chromium was mainly found in the residual fraction (155.1 mg/kg) in sediment samples. Its decreasing order was as follows: residual fraction bound chromium, organic matter fraction bound chromium, iron and manganese oxides friction bound chromium, carbonate fraction bound chromium, and exchangeable metals fraction bound chromium. Metals in the above fractions are subject to the equilibrium shift with the conditions change such as pH, oxidizing, reducing factors and microbial activity (Haller et al., 2011). They could be readily bioavailable for biological uptake in the environment.

Nickel

In sediment samples, nickel was mainly detected in the residual fraction (32.67 mg/kg). This fraction is relatively stable and does not easily allow the metals to separate from the sediments. Therefore they are not bioavailable and cannot be toxic to aquatic organisms. The contribution of nickel to the fraction bound to organic matter, carbonate and exchangeable fraction decreased and was 0.58; 0.41 and 0.08 mg/kg respectively. Oxides of iron and manganese fraction bound nickel were not detected. The concentration of nickel was not in Fraction I and II and was above the acceptable limits proposed by WHO (Organization, 1973; Roth and Hornung, 1977; Saifuddin and Raziah, 2007) and could pose health problem to living organism.

Lead

Lead was mainly present in the residual fraction (21.67 mg/kg). Less lead was identified in exchangeable (5 mg/kg) and carbonate (4.17 mg/kg) fractions. Those fractions showed the amount of elements that would be released into the aquatic system (environment) if the environmental conditions became more and more acidic. They are the fractions with the most labile metals to the environment and therefore the most likely dangerous. The minor amounts of lead were found in the forms bound to organic matter (1.67 mg/kg) and hydrated oxides of iron and manganese (0.83 mg/kg). These results are in accordance with the work done by Zerbe et al. (1999) on speciation of heavy metals in bottom sediments of lakes in Poland. The mobility of the heavy metals bound to those fractions could increase under oxidizing and reducing factors leading to the bioavailability of the toxic heavy metals to the aqua system.

Cadmium

The relative main concentration of cadmium was in residual fraction (4.25 mg/kg) and in much smaller amount in the forms of carbonates 90.33 mg/kg); organic matter (0.17 mg/kg) and exchangeable (0.08 mg/kg). Cadmium in oxides of iron and manganese was not detected. In general Cd was relatively found in a very small amount and do not constitute a potential threat to the environment.

Conclusion

From the results, heavy metals levels were few and sporadically found in all fractions apart in residual fraction where heavy metals content was relatively high. Most heavy metals were relatively in organic bound fraction and may constitute a danger to the environment due to their release to water under aerobic and anaerobic conditions. Furthermore the findings showed that the heavy metals forms of Zn are bioavailable.

Taking into consideration the fact that the local surroundings of Mpenge stream did not show the presence of point sources of metal contamination and that legal protection of the area considerably limits anthropogenic pollution, it can be assumed that the heavy metals found in the stream sediment are to a predominant extent of natural origin and occur at concentrations typical of the geochemical background. Indeed in Musanze district (Rwanda), all sources of water used by people are groundwater and pass through volcanic rocks that may undergo the weathering processes, possibly releasing some toxic metals into those sources. The rock types are essentially volcanic. Work done by Barifaijo (2000) and Erasmus Barifaijo (2000) in the neighboring Bufumbira volcanic area (Uganda) indicates that the rocks contain some heavy metals in relatively high concentrations. Therefore, the metals content in the stream may be the result of weathering and leaching processes which take place in the studied stream. The findings of this chemical speciation analysis can be used as reference for investigating heavy metals content and chemical speciation in other local stream sediments and water. Moreover, the outcomes of this study provide a reference for monitoring the quality of local streams water and the effect of anthropopression on the natural water and for assessment of the actual hazard coming from heavy metals penetrating the environment as results of natural process and human activities.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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