



ORIGINAL RESEARCH PAPER

Residual organochlorine pesticide contaminants profile in fish and sediment from a dam

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ABSTRACT

BACKGROUND AND OBJECTIVES: The vulnerability of the Sankana dam to organochlorine pesticide contamination is a major cause for concern. Indigenes rely on the dam for drinking water and irrigation of their farmlands as well as for fish and other aquatic delicacies. Virtually there exists no study on the residual levels of organochlorine or other pesticide contaminants in the dam despite its susceptibility to pesticide contamination. In the present study, the levels of organochlorine residues in fish and sediments from the Sankana dam were assessed.**METHODS:** Pesticide residue extraction was achieved using acetonitrile containing 1% (v/v) acetic acid in the presence of sodium acetate, sodium citrate and magnesium sulphate followed by purification over activated florisil and sodium sulphate. Identification and quantification of residue extracts was done using a gas chromatograph conjugated with mass spectrometer.**FINDINGS:** In all, varying levels of 13 organochlorine residues were detected, 11 of which were found in fish and 12 in sediment. Average mean levels of organochlorine residues found in fish ranged from 0.001 - 0.277 mg/kg. Residual levels of beta-hexachlorocyclohexane, delta-hexachlorocyclohexane, gamma-hexachlorocyclohexane, endosulfan-A and dichlorodiphenyldichloroethane in fish were relatively higher than their respective levels in sediment. Organochlorine residues found in sediment also ranged from 0.001 - 0.091 mg/kg. Dichlorodiphenyldichloroethylene, aldrin, dieldrin, endrin, methoxychlor, heptachlor, gamma-chlordane and endosulfan-B residual levels in sediment were higher than the corresponding levels in fish.**CONCLUSION:** The study provides a baseline for continuous/regular monitoring of organochlorine contaminants in the Sankana dam and other waterbodies upstream and downstream. Where organochlorine residues exceeded their recommended permissible thresholds typically suggests possible recent/continuous use of such pesticides within the catchment area. There is therefore the need for appropriate measures and/or need to strengthen existing policies that bans the importation, sale and use of organochlorine pesticides via strict enforcement.DOI: [10.22034/gjesm.2021.02.09](https://doi.org/10.22034/gjesm.2021.02.09)

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INTRODUCTION

The world over, agriculture remains a major economic growth determinant contributing significantly to Gross Domestic Product (GDP) growth rate (Johnston, 1970; Enu, 2014). Citing Ghana as a case study, there exists a direct correlation between agricultural and GDP growth rates (Enu, 2014). According to the World Bank Group Economic Update, over 20% of Ghana's GDP is attributable to agriculture and is the major source of raw materials for Ghana's industry- supporting nearly 67% of non-oil manufacturing. Agriculture is a major employer of nearly half of Ghana's labour force and a principal livelihood source for the majority of individuals mostly found in the remote parts of Ghana (World Bank Group, 2018). Agriculture in Ghana and many low and middle-income countries extensively rely on the use of chemical or biological agents or their mixtures- collectively called pesticides to control insects and pests known to pose threat to crop yield and quality (Kaur et al., 2019). Thus, pesticide usage has become an integral part of present-day agriculture worldwide. The world has in the past few decades witnessed a surge in the use of various types of pesticides in huge quantities. As captured by Kaur et al. (2019), on the average, an estimated 5.2 billion pounds of pesticides are used annually across the globe. Aside the critical role pesticides play in agriculture, they constitute a major class of toxic environmental contaminants worthy of concern as they pose a threat to non-target organisms such as humans and other living organisms (Yadav and Devi, 2017; Jeyakumar et al., 2014). Quite a number of pesticides and their metabolites have been cited to adversely impact the environment and cause reproduction and birth defects in humans (Edwards, 1993), as well as immune system impairment, cancer and disruptions in the endocrine system (WWF, 1999). The estimated death toll worldwide due to pesticide toxicity is between 5000 - 20000 out of an estimated total of 500000 - 1000000 people who get exposed annually (Yadav et al., 2015; FAO/WHO, 2007). Close to 50% of those poisoned and 75% of those that die are agricultural sector workers (Yadav and Devi, 2017). One class of pesticides that have seen extensive usage on the global front are organochlorine pesticides (OCPs) (Darko et al., 2008). In Ghana, OCPs have been used for over 4 decades (Ntow, 2001) and perhaps counting. Despite being banned some 25 years ago (Darko et al., 2008),

OCPs till date remain the preferred choice of most Ghanaian farmers owing to their relatively low cost and effectiveness against a wide range of pests (Ntow et al., 2006; Racke et al., 1997; Sivakumar, 2015). Notwithstanding the fact that the use of OCPs is prohibited in Ghana, they nonetheless find their way onto most Ghanaian farms (Ntow et al., 2006; Akoto et al., 2016) particularly in the hinterlands suggestive of the illegal production, usage and trading in these chemicals (Darko and Acquah, 2007). The health threats posed by pesticide residues to humans and other life forms within the environment have ignited research interests into the subject matter the world over. In Ghana and Africa at large, several studies into the subject matter have confirmed several pesticide residue contaminants to be present in water bodies, sediments, fish and other aquatic organisms as well as food crops (Darko et al., 2008; Ntow et al., 2006; Akoto et al., 2016; Fosu-Mensah et al., 2016; Abagale et al., 2014; Essumang et al., 2009). For instance, the health risks posed by the consumption of fish from the Tono Reservoir in the Kassena-Nankana District of the Upper East Region of Ghana was evaluated by Akoto et al. (2016) having assessed the residual levels of organochlorine (OC) and organophosphorus (OP) pesticides in fish, sediment and water samples from the reservoir. Health risk assessment revealed aldrin to have the potential to cause toxicity to systems in persons consuming fish from the reservoir. Elsewhere in the Tolon District of Ghana, Abagale et al. (2014) also studied OCP levels in irrigation water from the Golinga Dam. Recorded OCP residue levels here were all above the WHO maximum residue limit (MRL) for drinking water except mirex posing a serious health hazard to humans, aquatic life as well as the irrigated crops. Fosu-Mensah et al. (2016) in a related study assessed OCP residue levels in soils and drinking water sources in selected cocoa growing areas in Ghana and detected residues of seven banned OCPs in the various matrices analysed, suggestive of the illegal use and trading in such pesticides. Prevalent in Ghana are crop farms that are often sited along the banks of waterbodies (streams, lakes, rivers, dams) for easy access to water for irrigation. The practice essentially has exposed most of such waterbodies to pesticide contamination through run-offs from these farms (Bocquene and Franco, 2005). Such is the case in Sankana, a small community within Nadowli-Kaleo District of the Upper West Region of Ghana

noted for producing the bulk of crops such as cereals and grains and vegetables in the District. Pivotal to the sustenance of crop farming here is the Sankana dam which is one of 84 dams within the Upper West Region (Kpieta *et al.*, 2013). The dam typically serves as a primary water source for irrigation and drinking particularly during the dry season (Kpieta *et al.*, 2013; Kpieta and Laari, 2014; Namara *et al.*, 2011). As may be the case elsewhere, the control of pest infestation by farmers here is largely by the use of pesticides, predominantly OCPs. Pesticide application within this catchment can be described as haphazard. Coupled with this is the unscrupulous disposal of pesticide wastes or their containers and washouts on farmlands. Thus, the Sankana dam as well as other water bodies upstream and downstream of these farmlands are prone to pesticide contamination from drifts during spraying, run-offs from farmlands when it rains and the disposal of pesticide wastes, their containers or washouts into these water bodies (Akoto *et al.*, 2016). The threat posed by OCPs to humans and other life forms is heightened by their persistent attributes and resistance to physical, chemical and biological degradation as well as their ability to bio-accumulate along the food chain owing to their lipophilicity and their tendency to be transported over long distances (Fosu-Mensah *et al.*, 2016; Chau, 2005; Pandit *et al.*, 2006; Guo *et al.*, 2008). The vulnerability of the Sankana dam to OCP contamination is a major cause for concern worth the necessary attention as indigenes aside relying on the dam for irrigation of their farmlands also rely on it for fish and other aquatic organisms and as a source of drinking water for both humans and livestock. Virtually, no study has been conducted to assess the levels of OCP or other pesticide residues in the Sankana dam despite the potential contamination of this dam with pesticide residues. The present study on this account was conducted to assess the levels of OCPs in fish and sediments obtained from the Sankana dam to establish a baseline for continuous monitoring of such contaminants in the Sankana dam and other waterbodies upstream and downstream. The study was conducted at Sankana in the Nadowli-Kaleo District of the Upper West Region of Ghana in 2020.

MATERIALS AND METHODS

Study location

Sankana is a village within Nadowli-Kaleo District of the Upper West Region of Ghana. Sankana is 26.3

km away from the administrative capital, WA. Located within this village is the Sankana dam built in 1972 (Kpieta *et al.*, 2013) which happens to be the largest of 4 dams in Sankana and the district at large (Peprah *et al.*, 2015). Sankana is located at 10° 12' 0" North, 2° 35' 0" West, surrounded by beautiful scenery of igneous rocks. Sankana is boarded by communities including Nadowli, Changu, Kaluri, Nyembale, Gyile, Papu, Perintabo and Gbanko, all within the Nadowli-Kaleo District of the Upper West Region of Ghana. Generally, the landscape has a smoothly rising and falling pattern, rising between 150 m to 300 m with spot heights of 600 m (Peprah *et al.*, 2015). Sankana falls within the Guinea Savanna Ecological Zone with one rainy season which lasts for six months beginning in May and ending in October with 1000 - 1150 mm of rainfall annually. The highest and lowest temperatures of 36°C and 27°C respectively occur in March and August with relative humidity during the rainy season being 70-90% and 20% during the dry season. The climate here is well suited for tussock grass and fire-resistant deciduous trees such as kapok, shea, baobab, mango, dawadawa, cashew, black berries, red berries, teak, acacia and neem (Peprah *et al.*, 2015; Dickson and Benneh, 1988). Fig. 1 depicts the relative location of the study area within the Upper West Region.

Glassware cleaning

Glasswares used were thoroughly washed with warm water and detergent and rinsed with distilled water. Glasswares were further rinsed with acetone and oven dried for 2 hours at 180°C (Darko *et al.*, 2008; Therdteppitak and Yammeng, 2003).

Sample collection

Sampling was done on a monthly basis over a period of 3 months beginning January to March, 2020. Random sampling was employed. Fish samples (FS) and sediment samples (SS) were obtained from each of three zones namely- upstream (U), midstream (M) and downstream (D) of the Sankana dam. A total of 45 FS and 90 SS comprising 15 FS and 30 SS per sampling zone were worked on. FS were purchased directly from fishermen at each sampling zone. Fish composite samples for each sampling zone comprised 5 different fish species. FS were wrapped in pre-cleaned aluminium foil (Ntow, 2001), placed in an ice thermo insulator box and transported to the

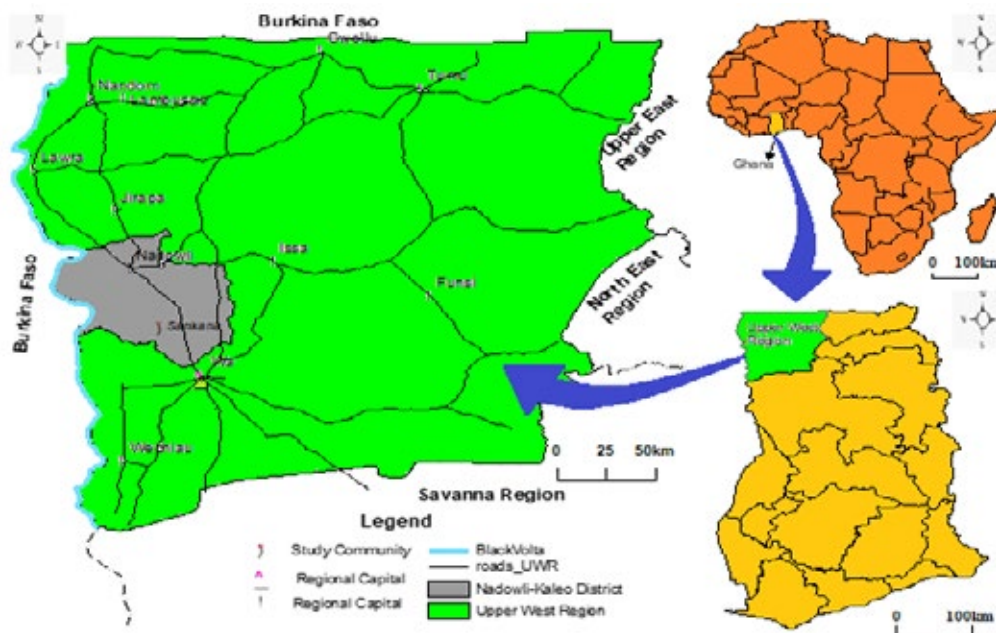


Fig. 1: Geographic location of Sankana in the Upper West Region of Ghana

laboratory (Darko *et al.*, 2008; Essumang *et al.*, 2009). SS were collected with the help of the fisherfolks at each of the sampling zones. At each sampling zone, SS were randomly collected from 10 different locations using a soil scoop and homogenized into a composite sample (Ntow, 2001; Fosu-Mensah *et al.*, 2016). Samples were transferred into 100 mL wide-mouthed glass bottles, capped, labelled and transported to the laboratory in an ice thermo insulator box (Darko *et al.*, 2008).

Sample preparation

In the laboratory the FS were rinsed severally with ion-free water. The intestines and scales of FS were removed and the muscle tissues cut into shreds and freeze dried for 72 hours. After freeze drying, the chopped muscle tissue samples were blended together using a waring blender (stainless) to form a homogenized powdered sample. The powdered fish sample was stored at 4°C in a fridge awaiting extraction (Darko *et al.*, 2008; Therdteppitak and Yammeng, 2003; Essumang *et al.*, 2009). Composite SS were poured out of their containers onto pre-cleaned aluminium foils and allowed to air dry for 72 hours followed by oven drying at 105°C for 24 hours. SS were then grinded with pestle and mortar, sieved

using 250 µm mesh size sieve (Ntow, 2001; Fosu-Mensah *et al.*, 2016).

Residue extraction

Pesticide residue extraction from powdered fish and grinded sediment followed the method used by Kolberg *et al.* (2010) with little modification. 100 mL of deionised distilled water was added to 200 g of powdered fish and grinded sediment in each instance and the mixture homogenized at high speed using an Ultraturrax blender to obtain a homogeneous slurry/paste. A 10 g portion of fish paste and sediment paste were weighed into individual 50 mL centrifuge tubes. 10 mL of acetonitrile (C₂H₃N), containing 1% (v/v) of acetic acid (CH₃COOH) was added to the content of each tube and each mixture hand shaken for 1 min. 3 g of magnesium sulphate (MgSO₄) was added to each mixture and immediately hand shaken for another minute. 1.7 g of sodium acetate (C₂H₃NaO₂) and 1 g of sodium citrate (Na₃C₆H₅O₇) were added sequentially to the content of each tube and the resulting mixture in each case vigorously hand shaken for another minute. The tubes with their content were finally centrifuged at 4000 rpm for 8 mins. The resulting supernatant in each instance was carefully transferred into a suitable container for subsequent clean up.

Purification of residue extracts

Prior to chemical analysis, the residue extracts were purified to rid them of interfering materials or compounds that may have been extracted along with the pesticide residues. Into a micro column plugged with glass wool was added 1.5 g of activated florisil (MgO_3Si) followed by the addition of 1.5 g sodium sulphate (Na_2SO_4). The clean-up was preceded with conditioning of the micro column with 10 mL ethyl acetate. The residue extract was transferred onto the column and allowed to elute. Using the Buchi RE-200 rotary vacuum evaporator, the eluted sample in each instance was evaporated to dryness. The resulting residue afterwards was dissolved in 2 mL of ethyl acetate. The dissolution step was repeated two more times and all samples pooled together. Using a glass pipette, a sample of the purified residue extract was transferred into a 1.5 mL vial for subsequent chemical analysis (Baah, 2016).

Analysis of residue extracts

Pesticide residue analysis was carried out at the Organic, Instrumental and Physical Research Laboratory of the Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ashanti Region, Ghana. Chemical analysis of residue extracts was done using a gas chromatography (GC) coupled with a mass spectrometer (MS).

Standardization

A certified pesticide standard mix (*Pesticide Mix 13, 10 µg/mL in Toluene*) containing 31 analytes was purchased from Ehrenstorfer, GmbH, Germany in a sealed vial for use. To 10 g of blank working samples were added 10 µL, 30 µL, 50 µL, 150 µL and 300 µL of the standard stock solution in each instance to obtain spiked calibration curves at 5 levels of 10, 30, 50, 150 and 300 ng/g. Standardization solutions for the calibration were prepared in triplicates. 10 µL of a stock solution of triphenylmethane (TPM) in acetonitrile at a concentration of 1 mg/mL was added to the spiked samples as internal standard. Spiked samples were subjected to same treatment as the working samples (Nasiri et al., 2016).

Residue analysis by GC-MS

The Agilent Technologies 6890 Network GC System with single quadrupole detector equipped with an Agilent 7683B autosampler was employed

for the analysis of residue extracts. Chromatographic separation was achieved using an HP-5 capillary column with dimensions-30 m × 0.25 mm internal diameter and 1 µm film thickness. Helium gas at 99.999% purity was applied as carrier gas at 1 mL/min steady flow rate. Oven temperature was 75°C initially, held for 3 mins and increased at 25°C/min ramp rate to 120°C and finally to 300°C at 5°C/min ramp rate. The final temperature of 300°C was held for 11 mins. The injector temperature was kept at 250°C. 1 mL aliquots of extracts were injected into the GC. The GC and MS were respectively operated in the splitless and electron ionization (70 eV) modes. The split valve was kept closed for 0.75 min. GC-MS interface, ion source and quadrupole temperatures were respectively 266, 230 and 150°C. The MS was operated in the time-scheduled selective ion monitoring (SIM) mode for the quantitative determination OCS (Nasiri et al., 2016; Jahanmard et al., 2016).

Identification and quantification

A sample of the pesticide standard mix of known concentration was run through the GC-MS setup under same conditions to ascertain the retention times and peak areas of the individual compounds/analytes in the standard matrix prior to analysis of the extracts. Identification and quantification of compounds/analytes in working samples (extracts) was achieved via comparison of the retention times and peak areas of compounds detected in the working sample (extracts) with that found in the standard. All analyses were conducted in triplicates (Baah, 2016).

Analysis of data

One-way analysis of variance (ANOVA) was performed to establish whether the differences in the means of experimental data for the various OC compounds/residues found across the different sampling zones were significant or otherwise. The degree of correlation between OC residual levels in fish and sediment for each sampling location was also evaluated. Statistical analyses were performed using Minitab statistical software (17) and Microsoft Excel (2016). Tests with $p < 0.05$ were deemed significant statistically.

RESULTS AND DISCUSSION

The quest to improve agriculture or crop yield and reduce losses caused by pests and insects has triggered a surge in the use of pesticides worldwide.

The present study sought to establish baseline levels of OC residues in the Sankana dam in the Nadowli-Kaleo District of the Upper West Region of Ghana. The present study revealed varying levels of 13 different OC compounds in fish and sediment (combined) obtained from the Sankana dam. Conveyed in Table 1 and Table 2 are the mean concentrations of OC compounds found in fish and sediment across the various sampling zones with Fig. 2 showing total OC residual levels across sampling zones. Table 3 compares the average mean levels of OC residues found in fish and sediment with their respective maximum residue limits (MRLs).

OC levels identified in fish and sediment across sampling zones

Varying levels of OC residues were detected in fish and sediment across the different sampling zones in the present study. Fish obtained upstream, midstream and downstream of the Sankana dam in all contained 11 OC residues including aldrin, endrin, endosulfan-A, heptachlor, methoxychlor, beta hexachlorocyclohexane (β -HCH), gamma-hexachlorocyclohexane (γ -HCH), delta hexachlorocyclohexane (δ -HCH), gamma (γ)-chlordane, dichlorodiphenyldichloroethylene (p,p' -DDE) and dichlorodiphenyldichloroethane (p,p' -

Table 1: Mean concentrations of OC residues in fish across sampling zones

OC Residues/ Compounds	Mean Concentration (mg/kg \pm SD)		
	Fish		
	FS _U	FS _M	FS _D
Aldrin	0.019 \pm 0.00	0.004 \pm 0.00	0.008 \pm 0.00
β -HCH	0.663 \pm 0.01	ND	0.167 \pm 0.01
γ -HCH	0.014 \pm 0.00	ND	0.080 \pm 0.01
δ -HCH	0.077 \pm 0.02	0.009 \pm 0.00	0.045 \pm 0.01
Dieldrin	ND	ND	ND
Endrin	ND	0.003 \pm 0.00	0.002 \pm 0.00
Endosulfan-A	0.043 \pm 0.00	0.011 \pm 0.00	0.045 \pm 0.00
Endosulfan-B	ND	ND	ND
Heptachlor	0.027 \pm 0.00	0.027 \pm 0.01	ND
p,p' -DDE	ND	ND	0.026 \pm 0.01
p,p' -DDD	ND	ND	0.003 \pm 0.00
Methoxychlor	0.049 \pm 0.01	ND	0.021 \pm 0.00
γ -Chlordane	0.016 \pm 0.00	0.006 \pm 0.00	ND

Table 2: Mean concentrations of OC residues in sediment across sampling zones

OC Residues/ Compounds	Mean Concentration (mg/kg \pm SD)		
	Sediment		
	SS _U	SS _M	SS _D
Aldrin	ND	ND	0.093 \pm 0.01
β -HCH	0.111 \pm 0.01	0.135 \pm 0.01	0.028 \pm 0.00
γ -HCH	0.029 \pm 0.00	ND	ND
δ -HCH	0.023 \pm 0.00	0.007 \pm 0.00	ND
Dieldrin	ND	ND	0.069 \pm 0.01
Endrin	0.004 \pm 0.00	0.003 \pm 0.00	0.002 \pm 0.00
Endosulfan-A	0.007 \pm 0.00	0.006 \pm 0.00	0.011 \pm 0.00
Endosulfan-B	ND	ND	0.003 \pm 0.00
Heptachlor	ND	ND	0.097 \pm 0.01
p,p' -DDE	ND	ND	0.156 \pm 0.01
p,p' -DDD	ND	ND	ND
Methoxychlor	ND	ND	0.103 \pm 0.01
γ -Chlordane	0.020 \pm 0.00	0.016 \pm 0.00	ND

*SD = Standard deviation

*ND = None detected

Table 3: Average mean OC residual levels in fish and sediment in relation to their MRLs

OC residues/ compounds	Average mean concentration (mg/kg)		MRLs (mg/kg)
	Fish	Sediment	
Aldrin	0.010	0.031	0.01
β -HCH	0.277	0.091	0.01
γ -HCH	0.031	0.010	0.01
δ -HCH	0.044	0.010	0.01
Dieldrin	ND	0.023	0.05
Endrin	0.002	0.003	0.01
Endosulfan-A	0.032	0.008	0.05
Endosulfan-B	ND	0.001	0.05
Heptachlor	0.009	0.032	0.01
<i>p,p'</i> -DDE	0.009	0.052	0.05
<i>p,p'</i> -DDD	0.001	ND	0.05
Methoxychlor	0.023	0.034	0.01
γ -Chlordane	0.007	0.012	0.01

DDD). Similarly, sediments obtained upstream, midstream and downstream in all also revealed the presence of 12 OC residues including the first 10 OC residues mentioned above in addition to dieldrin and endosulfan-B. Found absent in fish across the different sampling zones were dieldrin and endosulfan-B (Table 1) with *p,p'*-DDD being the only OC residue found absent in sediment across the different sampling zones (Table 2).

OC pesticide residue levels recorded in fish ranged from 0.002 ± 0.00 - 0.663 ± 0.01 mg/kg and from 0.002 ± 0.00 - 0.156 ± 0.01 mg/kg in the case of sediment. The upper limits in each instance exceeded the MRL of 0.05 mg/kg. The highest concentration of 0.663 ± 0.01 mg/kg was recorded for β -HCH in FS_U while the least concentration of 0.002 ± 0.00 mg/kg was recorded for endrin in FS_D (Table 1). *p,p'*-DDE emerged the OC residue in sediment that recorded the highest concentration of 0.156 ± 0.01 mg/kg with endrin recording the least concentration of 0.002 ± 0.00 mg/kg. The highest and least OC concentrations here were both recorded in SS_D (Table 2). Generally speaking, mean OC residual levels recorded in FS_U and FS_M were relatively higher than the levels found in their respective SS ($FS_U > SS_U$ and $FS_M > SS_M$). On the contrary, OC residual levels in SS_D were in general relatively higher than the corresponding levels in FS_D ($SS_D > FS_D$) (Table 1; Table 2). OC compounds characteristically accumulate more in aquatic organisms and settle considerably on sediments owing to their low solubility in water (Akan *et al.*, 2014). Per their lipophilic-hydrophobic nature, OC compounds have the propensity to bio-

accumulate in the fatty tissues of fish (Akoto *et al.*, 2016) and to be retained within the organic phase of sediments (Adeyemi *et al.*, 2008). In general, higher mean levels of OC residues recorded in fish in the several instances in the present study could be ascribed to the feeding habits of the different fish species across the sampling zones. According to Muralidharan *et al.* (2009), the degree/rate of OC accumulation in fishes is largely influenced by their feeding habits. In the case of sediment, studies have it that, smaller particles with large surface area as well as those with high organic content show highest adsorption/retention capacities (Elder and Weber, 1980). The level/degree of OC adsorption and retention here would thus be dependent on the surface area and organic matter content of sediments. That is to say, the relatively higher mean levels of OC residues recorded for sediment in the few instances in the present study were not far from expectation. The above observations were thus largely influenced by the different fish species and their feeding habits across the sampling zones and the possible variations in adsorptive capacities of upstream, midstream and downstream sediments. Prevalence of OC contaminants in relation to the number of OC residues identified at the various sampling zones followed the pattern $FS_D > FS_U > FS_M$ and $SS_D > SS_U > SS_M$ respectively for fish and sediment suggestive of a direct correlation between fish and sediment per sampling zone (Table 1; Table 2). Estimated total OC residual levels were highest in FS_U and least in FS_M . In respect of sediment, total OC residual levels contrarily were highest in SS_D and least in SS_M .

Residual organochlorine levels in fish and sediment

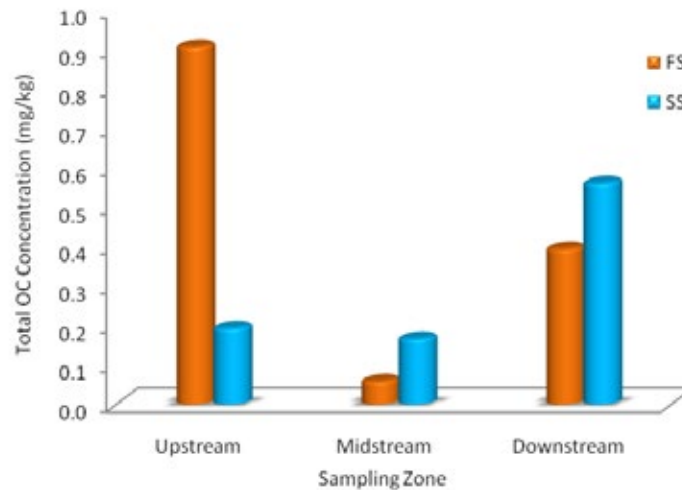


Fig. 2: Total OC residual levels in fish and sediment across sampling zones

(Fig. 2). These observations could be explained in relation to the prevalent farming activities upstream and downstream of the Sankana dam.

Total OC residual levels in fish across the different sampling zones were not statistically different ($p > 0.05$) per one-way ANOVA analysis conducted. Total OC residual levels in sediment across the different sampling zones were similarly not statistically different ($p > 0.05$). Tukey simultaneous tests for differences of means between the pairs FS_M-FS_U , $FSD-FS_U$, $FSD-FS_M$ in the case of fish and SS_M-SS_U , $SSD-SS_U$, $SSD-SS_M$ in the case of sediment were statistically insignificant ($p > 0.05$). One-way ANOVA analysis comparing mean OC levels in fish and

sediment from same sampling zone showed no statistical differences ($p > 0.05$) in each instance. Correlation analysis revealed a strong positive correlation ($r^2 = 0.904$) between OC residual levels in fish and sediment obtained upstream (Fig. 3) with OC residual levels in fish and sediment obtained midstream and downstream showing very weak positive correlations ($r^2 = 0.023$ and $r^2 = 0.026$ respectively) (Fig. 4 and Fig. 5). OC residual levels in essence were prevalent upstream relative to the levels midstream and downstream of the dam. Individuals are thus more prone to OC residue exposure from the consumption of fish particularly obtained upstream.

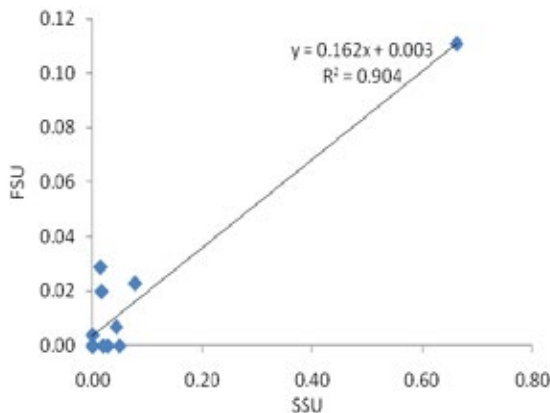


Fig. 3: Correlation between OC levels in FS_U and SS_U

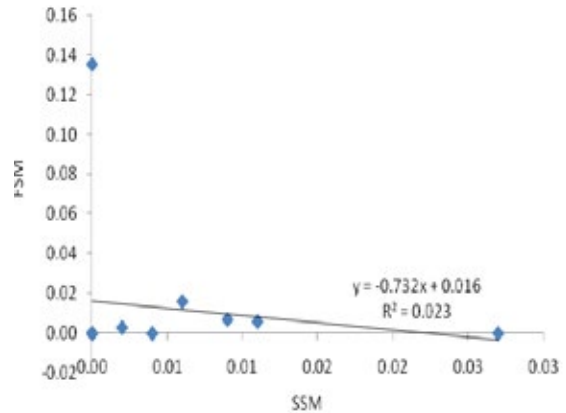


Fig. 4: Correlation between OC levels in FS_M and SS_M

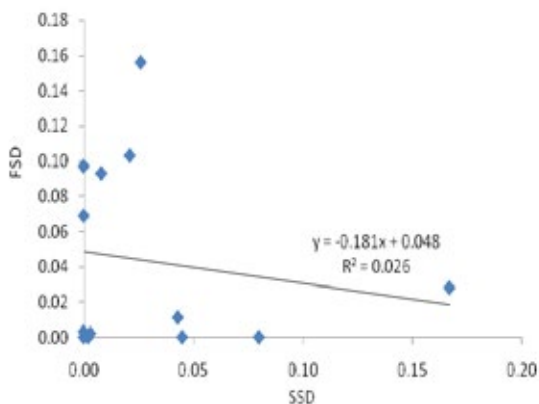


Fig. 5: Correlation between OC levels in FS_D and SS_D

β -HCH, γ -HCH and δ -HCH

β -HCH and δ -HCH were respectively absent in FS_M and SS_D with γ -HCH also being absent in FS_M as well as SS_M and SS_D. Thus β -HCH, γ -HCH and δ -HCH were in general prevalent in upstream and downstream fish as well as in upstream and midstream sediment (Tables 1; Table 2). The average mean levels of β -HCH, δ -HCH and γ -HCH in fish across the dam (in entirety) were respectively 0.277 mg/kg, 0.044 mg/kg and 0.031 mg/kg reflecting a prevalence pattern of β -HCH > δ -HCH > γ -HCH in fish. β -HCH and γ -HCH average mean levels in fish were about 3-times the average mean levels found in sediment (0.091 mg/kg, 0.01 mg/kg). In the case of δ -HCH, average mean level in fish was 4.4-times the average mean level in sediment (0.01 mg/kg) (Table 3). In contrast to the study by Akoto *et al.* (2016), that recorded no β -HCH, γ -HCH and δ -HCH residues, the present study found considerable levels of these compounds. β -HCH is well known to adsorb strongly to organic matter in soil and as such difficult to be lost through evaporation once adsorbed to soil compared to the other isomers. γ -HCH and other isomers of hexachlorocyclohexane (HCH) have been revealed in studies to be readily transformed within the environment into β -HCH (Unyimadu *et al.*, 2018). The relatively higher β -HCH levels than γ -HCH and δ -HCH recorded in both fish and sediment in the current study could thus be ascribed to the above reasons (Table 3) and may not necessarily be suggestive of continuous use of these pesticides within the study area for the control of pests and insects. Comparatively, the average mean levels of these compounds in fish exceeded their MRL

of 0.01 mg/kg. In the case of sediment, the average mean levels of these compounds were greater or equal to their MRL of 0.01 mg/kg.

Aldrin, dieldrin and endrin

Aldrin residues were present in all fish and sediment samples except SS_U and SS_M. Dieldrin however was only found in SS_D with endrin being absent in only FS_U (Table 1; Table 2). Average mean level of aldrin in fish and sediment were higher than the average mean levels of dieldrin and endrin in fish and sediment. The average mean levels of these OC compounds in sediment were higher than in fish. Average mean level of aldrin in sediment (0.031 mg/kg) was about 3-fold the aldrin level (0.01 mg/kg) in fish. For dieldrin, the average mean level in sediment was 0.023 mg/kg with the corresponding level in fish well below detection limit (< 0.001). Average mean level of endrin in sediment (0.003 mg/kg) was 0.001 mg/kg more than that found in fish. Average mean levels of these compounds followed the pattern: aldrin > dieldrin > endrin in sediment and aldrin > endrin > dieldrin in fish (Table 3). As studies have it, aldrin is readily broken down into dieldrin in plant and animal tissues or via photolysis to dieldrin in the environment (Akoto *et al.*, 2016; Akan *et al.*, 2014). In essence, the detection of dieldrin in the present study reflects the breakdown of aldrin by aquatic organisms or by photolysis and may signify past use of aldrin based pesticides within the Sankana locality. The high dieldrin levels may also be indicative of high rate of aldrin degradation in sediment. This observation agrees with that made by Kuranchie-Mensah *et al.* (2011) where low dieldrin levels were synonymous to low rate of aldrin degradation. Then and again, the detection of aldrin in fish was also suggestive of recent and possible continuous use of aldrin based pesticides within the study area despite its ban in Ghana. The average mean levels of aldrin and dieldrin recorded in fish and sediment in the present study were higher compared to mean aldrin and dieldrin levels reported by Darko *et al.* (2008) in their study on Lake Bosomtwi in the Ashanti region of Ghana. The present study also found the average mean levels of aldrin and dieldrin in fish to be lower than the levels found in sediment, agreeing with the findings of Darko *et al.* (2008). Similarly, average mean levels of aldrin and dieldrin attained for sediment in the present study were also relatively higher than mean

aldrin and dieldrin levels recorded in sediments by Kuranchie-Mensah *et al.* (2011). In the case of endrin however, average mean level recorded was below mean levels reported by Kuranchie-Mensah *et al.* (2011). Again, in the study by Kuranchie-Mensah *et al.* (2011), aldrin levels were comparatively higher than dieldrin which contrasts what was recorded in the present study. Unlike Akoto *et al.* (2016) that found no endrin residue in fish and sediment in their study, the present study detected endrin residues in fish and sediment. Average mean levels of aldrin and dieldrin detected in this study were above their respective established MRLs of 0.01 mg/kg, 0.05 mg/kg. Average mean level of endrin was however below its established MRL of 0.01 mg/kg.

p,p'-DDE and *p,p'*-DDD

Across the different sampling zones, *p,p'*-DDE was found present in only FS_D and SS_D while *p,p'*-DDD was present in only FS_D (Table 1; Table 2). Average mean level of *p,p'*-DDE in sediment comparatively was about 5.8-fold that in fish. *p,p'*-DDD on the contrary recorded an average mean concentration of 0.001 mg/kg in fish with sediment recording no *p,p'*-DDD (Table 3). *p,p'*-DDE and *p,p'*-DDD are both metabolites of *p,p'*-DDT and their detection in effect indicates photochemical or biological breakdown of the parent compound. *p,p'*-DDE and *p,p'*-DDD respectively result from the aerobic and anaerobic degradation of DDT. DDD to DDE ratios have been employed in many studies to indicate the pathway of DDT degradation. A DDD to DDE ratio less than 1 (< 1) is analogous to aerobic degradation whereas a DDD to DDE ratio higher than 1 (> 1) indicative of anaerobic degradation (Unyimadu *et al.*, 2018). On this premise it can be said that DDT degradation in fish and sediment both followed an aerobic pathway with a DDD to DDE ratio less than 1. As put forth by Akoto *et al.* (2016), the presence of these metabolites may typically suggest previous use of *p,p'*-DDT within the study area. No *p,p'*-DDD in sediment could typically be synonymous to complete degradation of the parent compound *p,p'*-DDT. Kuranchie-Mensah *et al.* (2011) found *p, p'*-DDE to be widespread in fish from the Volta Lake in Ghana. In the present study however, *p, p'*-DDE detection was limited to fish downstream of the studied dam. The present study corroborates the findings of Akoto *et al.* (2016), recording higher average mean levels of *p,p'*-DDE than *p,p'*-DDD in

both fish and sediment. Mean levels of both residues in fish emerged higher than their respective levels in sediment in the study by Akoto *et al.* (2016). The average mean *p, p'*-DDE level in fish on the contrary was lower than the level found in sediment in respect of the present study. Average mean levels of *p, p'*-DDE and *p, p'*-DDD in fish were below the established MRL of 0.05 mg/kg. Average mean level of *p, p'*-DDE in sediment was however above the established MRL.

Endosulfan-A and B

Endosulfan-A was the sole OC residue detected in all fish and sediment samples found upstream, midstream and downstream of the Sankana dam. Endosulfan-B on the other hand was only present in SS_D (Table 1; Table 2). Endosulfan-A levels detected in FS_U, FS_M and FS_D comparatively were higher than the respective levels detected in SS_U, SS_M and SS_D. Endosulfan-A levels in fish and sediment across the sampling zones followed the patterns FS_D > FS_U > FS_M and SS_D > SS_U > SS_M respectively. Mean levels of endosulfan-A in fish reflected an average mean that was 4-fold that in sediment. Average mean level of endosulfan-A in sediment was found to be 8-fold the level of endosulfan-B in sediment. Endosulfan is commercially available as a diastereomeric mixture of two biologically active isomers- alpha (A) and beta (B) in the ratio of 2:1 to 7:3 (Navarrete-Rodríguez *et al.*, 2016). The beta-isomer though more persistent than the alpha-isomer, has been demonstrated to be susceptible to conversion into the alpha-isomer while the reverse is impossible (Navarrete-Rodríguez *et al.*, 2016). The widespread detection and higher levels of endosulfan-A in fish and sediment as opposed to the lower levels of endosulfan-B in fish and sediment may not necessarily reflect recent use of the endosulfan pesticide. The higher mean levels of endosulfan-A in relation to B in both fish and sediment could result from the possible conversion of endosulfan-B to A. Darko *et al.* (2008) and Kafizadeh (2015) both recorded the highest (total) endosulfan concentrations in sediment contrary to this study which recorded the highest endosulfan level in fish. They also found endosulfan mean level in sediment to be respectively 14 and 16 times the level in fish. In contrast, the present study recorded an average mean level of endosulfan-A in fish that was 4-fold that in sediment. Average mean levels of endosulfan-A and B in fish and sediment were below the established MRL of 0.05 mg/kg.

Methoxychlor, heptachlor and γ -chlordane

Methoxychlor was detected in FS_U, FS_D and SS_D while heptachlor manifested in FS_U, FS_M and SS_D. γ -chlordane like heptachlor was detected in FS_U and FS_M as well as in SS_M (Table 1; Table 2). These OC residues were thus quite prevalent in FS_U. In entirety, (average) mean levels of these pesticide residues were relatively higher in sediment than in fish. Methoxychlor, heptachlor and γ -chlordane average mean levels in sediment were respectively 1.5, 3.6 and 1.7-fold the levels found in fish. Prevalence of these OC residues in terms of average mean levels measured in fish and sediment followed the order methoxychlor > heptachlor > γ -chlordane contrary to the pattern evident in the study by Kuranchie-Mensah *et al.* (2011) where mean concentrations of same OC compounds detected in sediments (from different stations) followed the order γ -chlordane > heptachlor > methoxychlor. Kafilzadeh (2015) recorded slightly higher mean levels of heptachlor than γ -chlordane in sediment samples from Lake Tashk, consistent with the relatively higher heptachlor than γ -chlordane mean levels attained in this study. In the study by Akoto *et al.* (2016), methoxychlor, heptachlor and γ -chlordane in the Tono reservoir were at undetectable levels contrary to levels recorded for the Sankana dam in the present study. Average mean levels of methoxychlor, heptachlor and γ -chlordane in sediments all exceeded established MRL of 0.01 mg/kg in the present study. In fish however, only methoxychlor had an average mean level above the established MRL of 0.01 mg/kg.

CONCLUSION

The study revealed varying levels of 13 OC residues in the Sankana dam. Eleven (11) of such OC residues were detected in fish and twelve (12) in sediment. Total OC residue levels were relatively predominant upstream and downstream and least midstream. Prevalence in terms of number of OC residues identified per sampling zone followed the sequence FS_D > FS_U > FS_M and SS_D > SS_U > SS_M respectively for fish and sediment suggestive of a direct correlation between fish and sediment in relation to the different sampling zones. Average mean levels of β -HCH, γ -HCH, δ -HCH, endosulfan-A and *p,p'*-DDD residues in fish were relatively higher than the respective levels in sediment. β -HCH, γ -HCH, δ -HCH, endosulfan-A and *p,p'*-DDD average mean levels in fish were respectively

3.1, 3.0, 4.4, 4.0 and 10-fold the levels in sediment. *p,p'*-DDE, aldrin, dieldrin, endrin, methoxychlor, heptachlor, γ -chlordane and endosulfan-B on the other hand recorded relatively higher residual levels in sediment than in fish. Average mean levels of these residues approximately were respectively 5.8, 3.1, 230, 1.5, 1.5, 3.6, 1.7 and 10-fold the levels in fish. Approximately 53.8% of OC residues found in fish upstream exceeded their established MRLs. For fish found midstream and downstream, respectively 92.3 and 76.9% of OC residues detected were at levels below their established MRLs. Sediments obtained upstream, midstream and downstream respectively had 69.2, 84.5 and 53.8% of identified OC residues below their established MRLs. OC residues in the Sankana dam most likely emanated from nonpoint sources such as run-offs, drifts during spraying of nearby farmlands and from the disposal of pesticide wastes or their containers and washouts. Taking into account the fact that the Sankana dam serves as sources of irrigation water, drinking water and fish for the locals within the catchment area, the very presence of these OC residues (in fish and sediment of the dam) raises health concerns. These health concerns are heightened by the very tendency of these compounds to bio-accumulate in the fatty tissues of fish or be retained within the organic phase of sediments owing to their lipophilic-hydrophobic nature. The study essentially provides a baseline for continuous monitoring of OC contaminants in the Sankana dam and other water bodies upstream and downstream. The presence of some of the above OC residues at levels above their recommended MRLs typically suggests the possible recent and continuous use of OCPs within the catchment area. There is thus the need for relevant stakeholders to put measures in place and/or strengthen already existing policies that bans the importation, sale and use of OCPs by way of strict implementation or enforcement. There is also the need to sensitize surrounding communities on the adverse health effects likely to arise from the consumption of fish and water from the Sankana dam.

AUTHOR CONTRIBUTIONS

N.J. Mensah was the principal investigator, conceived the study idea, gathered literature, conducted experiments and compiled experimental data for manuscript preparation. S. Antwi-Akomeah

performed literature review, designed and conducted experiments, analyzed and interpreted the data and prepared the manuscript text. G.E. Sebiawu assisted the literature review, manuscript preparation and conduct of experiments.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission and redundancy have been completely witnessed by the authors.

ABBREVIATIONS

<i>HCH</i>	Hexachlorocyclohexane
β - <i>HCH</i>	Beta-hexachlorocyclohexane
δ - <i>HCH</i>	Delta-hexachlorocyclohexane
γ - <i>HCH</i>	Gamma-hexachlorocyclohexane
<i>ANOVA</i>	Analysis of variance
C_2H_3N	Acetonitrile
$C_2H_3NaO_2$	Sodium acetate
CH_3COOH	Acetic acid
<i>D</i>	Downstream
<i>eV</i>	Electron volt
<i>FAO</i>	Food and agriculture organization
<i>Fig.</i>	Figure
<i>FS</i>	Fish samples
FS_D	Fish samples downstream
FS_M	Fish samples midstream
FS_U	Fish samples upstream
<i>g</i>	Gram
<i>GC</i>	Gas chromatography
<i>GDP</i>	Gross domestic product

<i>km</i>	Kilometer
<i>KNUST</i>	Kwame Nkrumah University of Science and Technology
<i>M</i>	Midstream
<i>m</i>	Meter
<i>mg/kg</i>	Milligram per kilogram
<i>mg/mL</i>	Milligram per milliliter
MgO_3Si	Magnesium silicate/florisil
$MgSO_4$	Anhydrous magnesium sulphate
<i>Min.</i>	Minutes
<i>mL</i>	Milliliter
<i>mL/min</i>	Milliliter per minute
<i>mm</i>	Millimeter
<i>MRL</i>	Maximum residue limit
<i>MS</i>	Mass spectrometer
$Na_3C_6H_5O_7$	Sodium citrate
Na_2SO_4	Sodium sulphate
<i>ND</i>	None detected
<i>ng/g</i>	Nanogram per gram
<i>OC</i>	Organochlorine
<i>OCP</i>	Organochlorine pesticide
<i>OP</i>	Organophosphorus
<i>p,p'-DDE</i>	Dichlorodiphenyldichloroethylene
<i>p,p'-DDD</i>	Dichlorodiphenyldichloroethane
<i>rpm</i>	Revolutions per minute
<i>SD</i>	Standard deviation
<i>SIM</i>	Selective ion monitoring
<i>SS</i>	Sediment samples
SS_D	Sediment samples downstream
SS_M	Sediment samples midstream
SS_U	Sediment samples upstream
<i>TPM</i>	Triphenylmethane
<i>U</i>	Upstream
<i>v/v</i>	Volume per volume
<i>WHO</i>	World health organization
<i>WWF</i>	World wildlife fund
$\mu g/mL$	Microgram per milliliter
μL	Microliter
μm	Micrometer

°C	Degrees Celsius
°C/min	Degrees celsius per minute
%	Percent
>	Greater than
<	Less than

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