



# Organochlorine Pesticides and Polychlorinated Biphenyls in Sediment Impacted by Cage Aquaculture in the Volta Basin of Ghana

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## Abstract

Seventeen organochlorine pesticides (OCPs) and seven indicator polychlorinated biphenyls (PCBs) residues in 80 sediment samples from four cage aquaculture farms on the Volta Basin were determined to find out the extent of their contamination as well as their risk to biota in the aquatic ecosystem. The extracted residues of the OCPs and PCBs were analysed on a gas chromatograph equipped with an electron capture detector and mass spectrometer, respectively. Eleven (11) OCPs: methoxy-chlor,  $\delta$ -HCH, *o,p'*-DDD,  $\alpha$ -endosulphan,  $\beta$ -HCH, *o,p*-DDE, *p,p*-DDE, *p,p'*-DDT,  $\beta$ -endosulphan, endrin, and heptachlor and seven (7) PCBs: PCB 18, PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180 were detected in the sediments from the farms. The OCPs level ranged < LOD – 33.0  $\mu\text{g/kg}$ .  $\delta$ -HCH ( $8.154 \pm 0.414 \mu\text{g/kg}$ ),  $\alpha$ -endosulphan ( $6.000 \pm 1.414 \mu\text{g/kg}$ ), *o,p'*-DDD ( $2.010 \pm 1.46 \mu\text{g/kg}$ ), endrin ( $13.867 \pm 8.716 \mu\text{g/kg}$ ), and  $\alpha$ -endosulphan ( $0.503 \pm 0.398 \mu\text{g/kg}$ ) were predominant with frequencies of detection 100%, 45%, 68%, 92%, and 25% in fish farms A, B, C, D and controls, respectively. PCBs concentrations ranged 0.042–5.320 ng/g wet weight. PCB 153 recorded the highest concentration of  $3.328 \pm 1.700 \text{ ng/g}$  in farm D. PCB 18 and PCB 180 dominated the profiles in the sediment from all the farms. The ecotoxicological risk of the OCPs and PCBs in the surface sediment using the SQGs indicated that  $\Sigma\text{HCH}$  in the sediment from all the farms except that the controls may pose a health risk to the benthic organisms. Therefore, a comprehensive remedial intervention is required to arrest the situation.

Some large groups of semi-volatile persistent organic pollutants (POPs) that are commonly found in the environment are organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). They are increasingly gaining concern globally because of their toxicity, persistence, long-range transmission, and bioaccumulation (Wong et al. 2005). Because POPs are generally hydrophobic, they easily attach to the particle portion in surface waters. They last a long time in the sediment processes because of their long half-lives and high stability (Darko et al. 2008; Sakan et al. 2017).

OCPs and PCBs input sources in riverine environments include public health, agriculture, forestry, household and industrial wastewater discharge, direct disposal of wastes into the river, as well as nonpoint source run-off after rainfall

(Montuori et al. 2014). Despite their prohibition or regulated usage, the PCBs and pesticides studied have been among the most common environmental contaminants, comprising abiotic (soil, sediment, air, water) and biotic (plankton to man) components. Surface sediments have been identified as one of the critical sources of PCB build-up in many studies (Kanzari et al. 2014; Albanese et al. 2010; Barhoumi et al. 2014; Zhao et al. 2010b). Because the sediment is the main base for chemical pollutants discharged into aquatic environments, it frequently receives large concentrations of these pollutants, posing a severe threat to benthic species and the whole aquatic food web (Botwe et al. 2012).

The Volta Basin in Ghana is known for producing many cage aquaculture fish, especially Nile tilapia (*Oreochromis niloticus*). There are many large farms including, irrigation facilities, dotted along the banks of the Basin, which produce large quantities of food and vegetables. Farmers have used pesticides extensively and unregulated throughout the Basin watershed to increase agricultural productivity and maximise profit. During run-off, after rainfall, residual pesticides in the soil are discharged into aquatic ecosystems, resulting

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in the contamination of all compartments of the ecosystem (water, sediment, flora, and fauna).

Additionally, about 80% of the small, medium, and large commercial cage aquaculture farms are located in the Volta Basin. Fish feed for the farms is sourced from the Rannan and Beacon Hills and others imported from other countries (Karikari 2017). These feeds are manufactured with grains, fishmeal, and fish oil from different sources and may contain persistent organic pollutants such as dioxin, PCBs, and organochlorine pesticides (Easton et al. 2002; Antunes and Gil 2004; Hites et al. 2004; Navas et al. 2005; Bordajandi et al. 2006; Maule et al. 2007; Kelly et al. 2007; McKee et al. 2008; Shaw et al. 2008; Botaro et al. 2011; Perugini et al. 2013). The recent expansion in the aquaculture industry by the Ghanaian Government initiative programme on planting for food and jobs will further exacerbate the residuals levels of these pollutants in the Basin. According to Yu et al. (2011), fish farms, boats, cages, and structures are prone to biofouling, and to reduce the effects of biofouling; antifoulants paints are applied to them. The antifoulants have DDT and some heavy metals as their active ingredients, which leaches gradually into the water column polluting the biota and threatening the entire aquatic ecosystem.

Whereas few studies on POPs (OCPs and PCBs) have been documented in freshwater and marine fishes in Ghana (Kuranchie-Mensah et al. 2012; Ntow 2005; Gbeddy et al. 2015; Adu-Kumi et al. 2010; Asante et al. 2013; Elegbede et al. 2015; Gbeddy et al. 2012; Karikari 2017), little or no studies have been carried out on these contaminants in sediment from the cage aquaculture farms on the Volta Basin. Therefore, it is imperative to examine the levels of these undesirable contaminants and their potential risk to aquatic organisms.

## Materials and Methods

### Study Area

The study area comprises the Asuogyaman District in the Eastern region and the Shai Osudoku of the Greater Accra region of Ghana. Figure 1 is a map showing the location of the fish farms, where samples were collected. The districts are situated roughly between latitudes 6° 34' N and 6° 10' N and longitudes 0° 1' W and 0° 14' E. The Basin has one of the largest hydroelectric dams that generate power to the country and other neighbour countries such as Togo. The Basin also has an inland port that facilitates goods from the southern part of Ghana to the northern territories and beyond. Rain-fed agriculture and irrigation are the major economic activities in terms of employment and rural income generation. To boost their crop yield, the farmers use agrochemicals extensively on their farms. As a result,

the potential usage of restricted or banned pesticides cannot be ruled out. The area is characterised by a double maximum rainfall pattern, with the major season being from September to November and the minor season occurring from May to July.

### Chemicals and Reagents

Pesticide grade ethyl acetate, distilled water (HPLC grade), acetone, and hexane (both analytical grade) were supplied by Fisher Scientific (Loughborough, UK); silica gel and sodium sulphate were purchased from E. Merck (Germany). Sigma-Aldrich Chemicals USA provided disposable solid-phase florisil cartridges (500 mg/6 mL). Dr. Erhenstorfer GmbH (Germany) provided the certified, high purity (> 99.0%), reference standards of  $\alpha$ -HCH,  $\gamma$ -HCH,  $\beta$ -HCH, delta-HCH, endrin, heptachlor, aldrin, dieldrin, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, *o,p'*-DDE,  $\alpha$ -endosulphan,  $\beta$ -endosulphan, and methoxychlor, and they were kept frozen to prevent them from degrading.

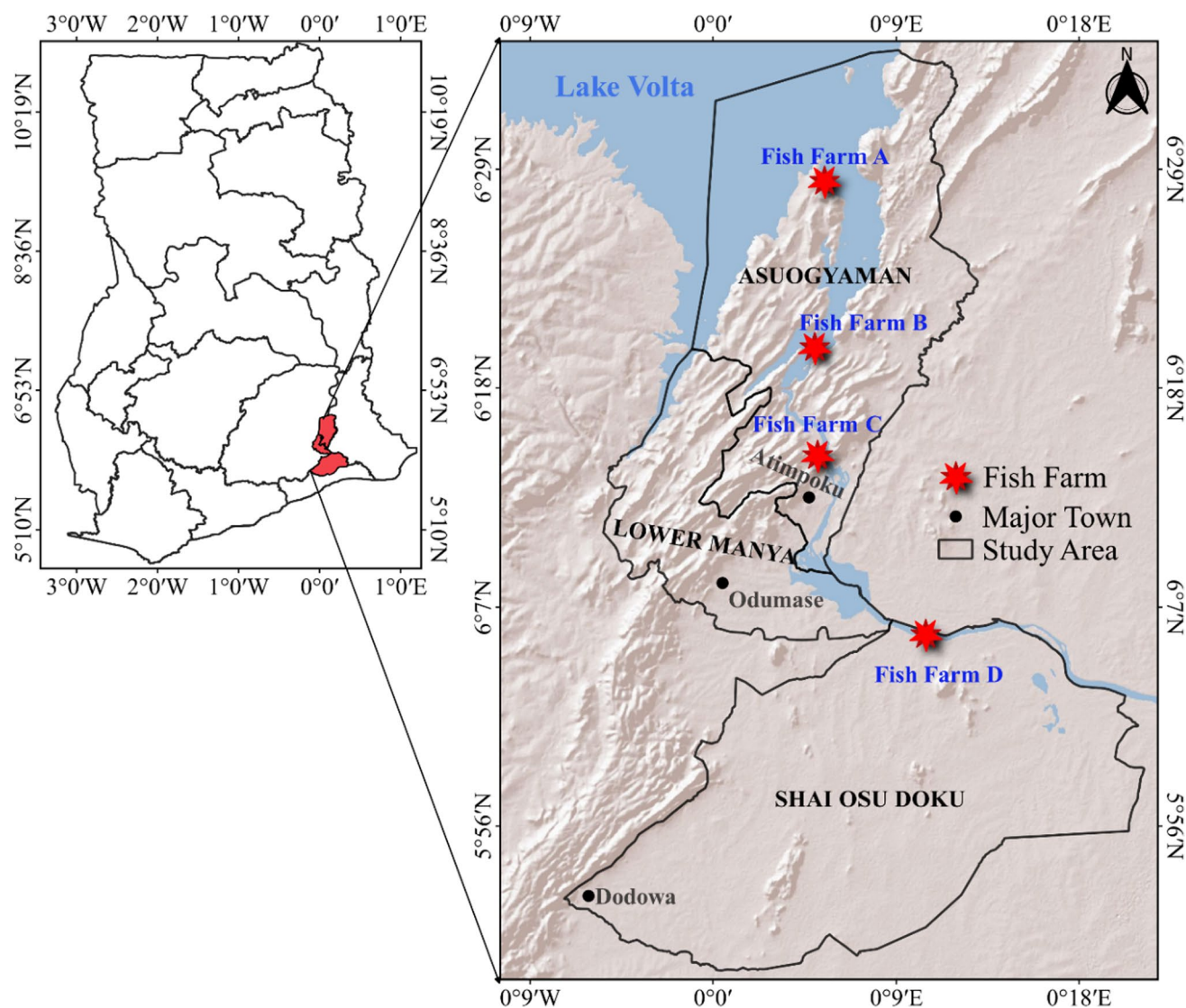
### Sample Collection and Preparation

A sampling of bottom sediment samples for POPs was obtained with an Ekman grab sampler. A total of 60 (Farm A = 15, farm B = 15, farm C = 15, and farm D = 15) sediment samples for the pesticide extraction were collected and stored in a cleaned zip lock bag, labelled with an indelible pen, and sealed to avoid cross-contamination. Two grabbed sediment samples were obtained at two separate locations in the cages in each of the fifteen randomly selected cages from each farm and combined to form composite samples. Samples were collected in March, May, and July 2019. All samples were obtained early in the morning between 6:00 am and 9:45 am to avoid the breakdown of specific contaminants.

Additionally, twenty (20) samples of sediment were collected as controls from the upstream in the Volta Basin above from where aquaculture is practised. For further investigation, all samples were transported to the Ghana Atomic Energy Research laboratory in an air-tight ice-chest at 4 °C for further investigation. The sediment samples were air-dried before being crushed with a pestle in a laboratory mortar (Fritsch mortar grinder P-2). The content was filtered with a 250  $\mu$ m mesh size sieve to remove stony particles and debris. The sieved fine samples were immediately used for the extraction.

### Extraction of Sediment for Organochlorine Pesticides and Polychlorinated Biphenyls

The US EPA 3550C method, as described by Solomon (2016) and Adeshina et al. (2019) with a slight modification,



**Fig. 1** Map of the study area of the Volta Basin, Ghana

was used to extract organochlorine pesticide residues from the sediment samples. A quantity of 10 g of sediment and 5 g of anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) was weighed into an extraction jar. A volume of 50 ml acetone/n-hexane (2:1 v/v) was thoroughly incorporated into the mixture. The organic extract was filtered through a Whatman filter paper into a volumetric flask after 30 min of sonication in a Bransonic 220 high-frequency ultrasonic bath at 60 °C. The extraction process was repeated twice. The combined extracts were concentrated to a volume of 25 ml at a temperature of 45 °C.

### Sample Clean-Up

In order to avoid interferences, the clean-up system is important for the pesticide residues analysis in a sample. Before the clean-up, silica gel was activated by heating it moderately to

about 150 °C in an air-tight oven. This process removes water content in the gel and increases its adsorptive capacity significantly. The glass separating column (20 cm) was packed with three layers. The agents were arranged with the activated charcoal (Kaipper et al. 2001) at the top, followed by 2 g of anhydrous granulated  $\text{Na}_2\text{SO}_4$  and the bottom packed with 4 g of activated silica gel (90% < 45 µm). The activated charcoal was purified using procedures reported by Kaipper et al. (2001). The activated charcoal removes colouration; the anhydrous  $\text{Na}_2\text{SO}_4$  serves as a demulsifier; and the silica gel removes co-extractants. Prior to cleaning, the column was moistened and rinsed with 10 ml n-hexane. The extract was then loaded into the column, and a 20 ml portion of acetone/hexane mixture was used to elute it. The eluates were collected into a round bottomed-flask and then concentrated to dryness using a rotary evaporator at a temperature

of 45 °C and picked in 2 ml ethyl acetate vial for gas chromatography analysis.

### Determination of the OCPs and PCBs Residues

A Varian CP-3800 gas chromatograph (Varian Association Inc. USA) with combiPAL auto-sampler and 63Ni electron capture detector was used to analyse the final extracts. VF-5 coated capillary column (30 m + 10 m EZ protection column, 0.25 mm inner diameter, 0.25 µm film thickness) was employed for the analysis. The temperature of the injector and detector was set at 270 °C and 300 °C, respectively. The furnace temperature was programmed as follows: 70 °C held for 2 min, ramp at 25 °C/min to 180 °C, held for 1 min, and finally ramp at 5 °C/min to 300 °C. In order to compensate for the relative retention times and the response behaviour, the GC conditions and the detector response were determined. N was used as carrier gas with a flow rate of 1.0–29 mL/min as detector additive gas. The injection volume of the GC was 1.0 µL. The total running time for one sample was 31.4 min.

GC–MS analysis was carried out with Agilent Technologies 6890 N (for GC) and 5975 (for MS) in EI mode. The ion source and interface temperatures were 300 °C and 280 °C, respectively. Chromatographic separation was conducted on a Phenomenex ZB-5MS capillary column (30 m × 0.25 mm × 0.25 µm). The gas flow of the carrier was 1.1 mL/min. The temperature of the injection was 265 °C. The amount of the samples infused was 1 µL. The temperatures were optimised as follows: The initial oven temperature was maintained for 1 min at 60 °C, increased to 170 °C with a 20° C/min ramp, kept for 0.30 min, and then increased by 10° C/min to 310 °C with a maintaining time of 1.20 min. A mixture of PCB 18, PCB 28, PCB 52, PCB 101, PCB 153, PCB 138, and PCB 180, at a concentration of 10 µg/mL in isooctane from Sigma-Aldrich, was injected into the GC 2 µL to determine each PCB holding time.

The residue of pesticide was identified based on comparison of the measured relative retention times to those of known standards. The levels were determined using an external standard approach that matched the peak heights of the samples with the corresponding peak heights of the reference standards for specified concentrations. The calculation was done within the detector's linear range. The peak heights which retention periods corresponded with the standards were then extrapolated to their individual calibration curves to determine the concentration.

### Quality Assurance and Quality Control

The analytical system integrated quality control and assurance. Measures were taken to guarantee the reliability of the results. All glass apparatus used for research

(extraction and cleaning) has been thoroughly rinsed with detergent and tap water. The glassware was cleaned with distilled water before being meticulously cleaned with analytical grade acetone and dried overnight in an oven set at 70 °C. They were taken out of the furnace and placed in dust-free cabinets after cooling. Routine analyses of procedural blanks, solvent blanks, spiking with internal standard (isodrin), sample replicates as well as samples of a Standard Reference Material for sediments (SRM) from the National Institute of Standards and Technology (NIST) were conducted to ensure the quality of the results of the organochlorine compounds (see Table 1). The target organic contaminants were not detected in both procedural and solvent blanks. Calibration curves were created by plotting mixed standards for seventeen organochlorine pesticides and seven PCBs with concentrations of 0.005, 0.01, 0.02, and 0.05 against the peak area.  $R^2 = 0.995$  was found in the curve's region. Each set of samples was subjected to recalibration guidelines to ensure that the correlation coefficient remained over 0.99. The analytical procedure was optimised by spiking samples with 0.05 mg/kg internal standard (isodrin). Spiked samples were taken through the same technique as the field samples, and the OCPs and PCBs were quantified with good recoveries of 78–95% for OCPs and 80–94% for PCBs, indicating that the approach used was reproducible.

**Table 1** Certified Reference materials results of sediment and LOD (µg/kg)

Compound	Sediment homogenate			
	SRM value	This study	SD	LOD
$\alpha$ -endosulphan	14.00	13.20	0.42	0.042
$\beta$ -endosulphan	5.10	4.80	0.14	0.015
$\beta$ -HCH	2.80	2.66	0.16	0.018
Endrin	7.10	5.54	0.15	0.041
Methoxychlor	NA	–	–	0.016
$\delta$ -HCH	NA	–	–	0.025
<i>o,p</i> -DDE	3.70	3.41	0.18	0.014
<i>p,p</i> -DDE	14.00	13.44	0.45	0.007
<i>o,p</i> -DDD	38.00	35.35	0.76	0.003
<i>p,p</i> -DDT	19.00	18.10	0.55	0.003
Heptachlor	2.00	1.88	0.13	0.028
PCB 18	51.00	47.94	2.10	0.024
PCB 28	80.80	74.34	1.70	0.016
PCB 52	79.40	78.10	4.30	0.023
PCB 101	73.40	66.10	2.50	0.034
PCB 138	62.10	49.68	4.70	0.048
PCB 153	74.00	69.56	2.90	0.072
PCB 180	44.30	40.75	1.20	0.087

SRM Standard reference material, LOD Limit of detection



## Statistical Analysis

The Kolmogorov–Smirnov (K–S) analysis was performed to assess the normality of the data, and at the  $p$  value less than 0.05, findings were considered to be statistically significant. Descriptive statistics such as the mean and standard deviation (SD) were used for the levels of OCPs, and PCBs. Ranges were computed for the contaminants. One-way ANOVA was used to test the differences in the contaminants from the fish farms and controls where samples were obtained, with a Tukey's post hoc test.

## Ecological Risk Assessments of the Pesticides in Sediment to Aquatic Species

Sediment quality values that provide a benchmark for evaluating the adverse effects in the aquatic ecosystem were used to calculate the sediment toxicity. Hong Kong Interim Sediment Quality Value (HK-ISQV), Canadian Sediment Quality Guidelines (CSQG), USEPA, and some published sediment quality guidelines (Eqani 2012) include Threshold Effect Concentrations (TECs) for freshwater, Probable Effect Concentrations (PECs), and Interim Sediment Quality Guidelines (ISQG). The Canadian Sediment Quality Guidelines (CSQG) uses the Threshold Effect Level (TEL) and Probable Effect Level (PEL), USEPA (1997) uses Effect Range Low (ERL) and Effect Range Median (ERM), while the Hong Kong Interim Sediment Quality Value (HK-ISQV) uses Lowest Effect Level (LEL) and the Severe Effect Level (SEL).

These benchmarks have been used as EPA Ghana does not have its own benchmarks. TEC (TEL, LEL, ERL, and CB-TEC) indicates concentrations at which pollution will start to be detected in sensitive aquatic life or concentrations at which adverse effects will not occur, while PECs (PEL, SEL, ERM, and CB-PEC) indicate concentrations above which adverse effects will occur in aquatic species. The range of OCPs and PCBs found in sediment samples from all four fish farms was compared to sediment quality parameters to determine the overall quality of sediments and the risk to aquatic species in the Volta Basin.

## Results and Discussion

### Levels of Organochlorine Pesticides in the Sediment

Table 2 presents the detected organochlorine pesticides in the sediments from the fish farms in the Volta Basin. In all, a total of eleven OCPs were found in the sediments, i.e. A

(9 OCPs), B (10 OCPs), C (10 OCPs), D (11 OCPs), and control (6 OCPs).

Generally, the OCP residues in the sediment ranged between <LOD and 33.00 µg/kg in all the studied fish farms, including the control. Endrin in fish farm D had the highest mean concentration of  $13.867 \pm 8.716$  µg/kg with 83% detection frequency. However, the same compound recorded the least level in fish farm B with a 20% detection frequency in the samples analysed. The OCPs,  $\delta$ -HCH (7.72–8.80 µg/kg),  $o,p'$ -DDD (0.52–2.12 µg/kg),  $\alpha$ -endosulphan (<LOD–2.00 µg/kg),  $o,p'$ -DDD (1.00–28.00 µg/kg), and heptachlor (0.234–0.472 µg/kg) were the predominant with frequency of detection 100%, 45%, 68%, 92%, and 25% in fish farms A, B, C, D, and control, respectively. All the eleven OCPs levels in the sediment from the farms were below the USEPA maximum residue levels.

In the present study,  $\sum$ DDTs (equivalent sum of  $o,p'$ -DDE,  $p,p'$ -DDE,  $o,p'$ -DDD,  $p,p'$ -DDT) in (µg/kg) in the fish farms were: 7.185 µg/kg, 3.483 µg/kg, 5.938 µg/kg, 12.263 µg/kg, and 0.163 µg/kg for fish farms A, B, C, D, and controls, respectively. The concentration of total DDT reached a maximum value at fish farm D (12.263 µg/kg wet mass) followed by farm A (7.185 µg/kg wet mass) and least in the controls (0.163 µg/kg wet mass).  $o,p$ -DDD (Fish farm A),  $o,p$ -DDD (fish farm B),  $o,p$ -DDE (fish farm C),  $o,p$ -DDD (fish farm D), and  $o,p$ -DDE (controls) were the predominant isomers detected, accounting for on average 45%, 45%, 67%, 93%, and 15% of detection frequency, respectively.  $p,p'$ -DDTs were detected in samples from fish farms C and D, but less frequently (8% of samples) in farm D. The higher amount of DDT in farm D in comparison with other farms is attributed to the fact that it is retained in most parts of the sediment and remains unchanged for a long period due to high stability, persistence, and resistance to degradation (Veljanoska-Sarafiloska et al. 2013). Additionally, the high  $\sum$ DDTs in fish farm D indicate predominant inputs of antifouling paints (with a high concentration of  $p,p$ -DDT as an active ingredient) from farm structures as well as maintenance of fishing boats (Li and Macdonald 2005; Guo et al. 2008; Yu et al. 2011), which leaches gradually into the water column. When the range of  $\sum$ DDTs (0.163–12.263 µg/kg) in the measured sediment was used to compare with studies within the world, it was found to be in the range of measured sediment in water bodies from Nigeria (Williams 2013), China (Sun et al. 2010; Zhao et al. 2010b), Pakistan (Eqani 2012), and Thailand (Sudaryanto et al. 2011).

The relative proportions of the parent DDT compound and its biological derivatives, DDD and DDE, can be utilised as benchmarks to evaluate potential contamination sources (Doong et al. 2002; Muhayimana et al. 2009). DDT can be metabolised into DDE and DDD in aerobic and anaerobic conditions, respectively. To measure the decomposition of the parent chemical and recent DDT input, different

**Table 2** Concentration ( $\mu\text{g/kg}$ ) of organochlorine pesticides in sediment from cage fish farms

OCPs	$\beta$ -HCH	$\delta$ -HCH	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDD	<i>p,p'</i> -DDT	Hept	Meth	Endrin	$\alpha$ -endos	$\beta$ -endos
<i>Fish farm A</i>											
Mean	2.336	8.154	2.120	–	5.065	ND	3.985	8.253	<LOD	2.753	1.037
SD	0.231	0.414	1.659	–	1.796	–	1.479	5.252	–	1.262	0.701
Frequency	71	100	29	–	45	–	57	57	–	43	43
	$\Sigma\text{HCH} = 10.490$		$\Sigma\text{DDE} = 3.779$		$\Sigma\text{DDD} = 5.065$	$\Sigma\text{DDT} = 7.185$	$\Sigma\text{Chlors} = 12.238$			$\Sigma\text{END} = 3.790$	
<i>Fish farm B</i>											
Mean	2.152	0.710	0.710	1.480	1.293	ND	2.585	1.860	0.275	6.000	0.970
SD	0.052	0.410	0.410	0.646	0.793	–	1.639	1.612	0.092	1.414	0.415
Frequency	20	20	20	30	45	–	40	20	20	20	20
	$\Sigma\text{HCH} = 2.862$		$\Sigma\text{DDE} = 2.190$		$\Sigma\text{DDD} = 1.293$	$\Sigma\text{DDT} = 3.483$	$\Sigma\text{Chlors} = 4.445$			$\Sigma\text{END} = 6.970$	
<i>Fish farm C</i>											
Mean	2.362	1.793	1.012	1.113	2.010	1.803	ND	ND	5.000	1.555	1.103
SD	0.091	1.053	0.125	0.196	1.406	0.981	–	–	3.606	0.492	0.179
Frequency	33	33	67	33	56	44	–	–	33	68	33
	$\Sigma\text{HCH} = 4.155$		$\Sigma\text{DDE} = 2.125$		$\Sigma\text{DDD} = 2.010$	$\Sigma\text{DDT} = 5.938$	$\Sigma\text{Chlors} = \text{ND}$			$\Sigma\text{END} = 2.658$	
<i>Fish farm D</i>											
Mean	1.613	1.325	1.163	1.510	4.590	5.000	1.080	0.908	13.867	1.103	1.615
SD	0.321	0.148	0.142	1.010	3.735	0.505	0.505	0.271	8.716	0.714	1.186
Frequency	25	17	25	42	93	8	25	42	83	33	92
	$\Sigma\text{HCH} = 2.938$		$\Sigma\text{DDE} = 2.673$		$\Sigma\text{DDD} = 4.590$	$\Sigma\text{DDT} = 12.263$	$\Sigma\text{Chlors} = 1.988$			$\Sigma\text{END} = 2.718$	
<i>Controls</i>											
Mean	0.486	0.242	0.163	ND	ND	ND	0.301	0.243	ND	0.503	ND
SD	0.196	0.223	0.024	–	–	–	0.300	0.022	–	0.398	–
Frequency	20	15	15	–	–	–	25	20	–	15	–
	$\Sigma\text{HCH} = 0.728$		$\Sigma\text{DDE} = 0.163$		$\Sigma\text{DDD} = 0.163$	$\Sigma\text{DDT} = 0.544$	$\Sigma\text{Chlors} = 0.544$			$\Sigma\text{END} = 0.503$	
USEPA MRL	30	40	40	40	40	50	30	50	40	50	40

*LOD* Limit of detection, *Hept.* heptachlor, *Meth.* methoxychlor, *endos.* endosulphan, USEPA ( $\mu\text{g/kg}$ )

suggestive ratios such as  $\text{DDE} + \text{DDD} / \sum \text{DDTs}$ ,  $\text{DDD} / \text{DDE}$ , and,  $p,p\text{-DDT} / \sum \text{DDTs}$  are extensively used (Sarkar et al. 2008). The ratio  $(\text{DDE} + \text{DDD}) / \sum \text{DDT} > 0.5$  is assumed to have undergone a long-term weathering process. If the  $\text{DDD} / \text{DDE}$  ratio is larger than 1, then the sediment is dominated by DDD, which is the result of anaerobic DDT degradation; if the ratio is less than 1, then the sediment was primarily influenced by DDE, which is the product of aerobic DDT breakdown (El Nemr and El-Sadaawy 2016). The ratios of  $(\text{DDE} + \text{DDD}) / \text{DDT}$  in the current study ranged from 0.59 to 1.23. This indicated that the farm sediments had undergone a long-term weathering process. Furthermore, several  $\text{DDD} / \text{DDE}$  ratios in fish farm A and D sediments were higher than 1, indicating a significant DDD in the environment and anaerobic conditions in that region. However, farms B and C showed an elevated proportion of DDE, suggesting aerobic conditions prevailing in sediments from those farms. In addition, the  $p,p\text{-DDT} / \sum \text{DDT}$  ratios were below 0.5 in sediment samples from farms C and D, indicating long-term degradation of  $p,p\text{-DDT}$  in the studied farms.

HCHs have been utilised as a broad-spectrum insecticide for agricultural purposes in the past. 55–80 per cent of  $\alpha\text{-HCH}$ , 5–14 per cent of  $\beta\text{-HCH}$ , 8–15 per cent of  $\gamma\text{-HCH}$ , and 2–16 per cent of  $\delta\text{-HCH}$  are found in HCHs (El Nemr et al. 2012).  $\beta\text{-HCH}$  and  $\delta\text{-HCH}$  were detected in all farms and accounted for 100% of  $\sum \text{HCH}$  concentrations. The  $\sum \text{HCH}$  ranges from 0.728  $\mu\text{g/kg}$  in the controls sediment to 10.263  $\mu\text{g/kg}$  in fish farm A. Apart from fish farm A, the levels of  $\beta\text{-HCH}$  were higher than that of  $\delta\text{-HCH}$  in all the farms. Two reasons could explain this phenomenon. Firstly, this can be attributed to the degradation of the  $\alpha$ - and  $\gamma$ -isomers to the more stable  $\beta\text{-HCH}$  (Buah-Kwofie and Humphries 2017; Muralidharan et al. 2009). That probably explains why  $\alpha$ - and  $\gamma$ -isomers were not detected in the farms. Secondly,  $\beta\text{-HCH}$  has low water solubility and vapour pressure and is relatively resistant to microbial degradation (Nguyen et al. 2020). The predominance of the  $\beta\text{-HCH}$  in the farms indicates no fresh input of the technical HCH. The reported levels of  $\beta\text{-HCH}$  in fish farms A, B, and C and delta-HCH for fish farm A for this study were similar to an earlier investigation by Koranteng (2015). The reported levels of  $\beta\text{-HCH}$  and  $\delta\text{-HCH}$  in fish farm D are in agreement with that of Gbeddy et al. (2015) on the same Volta Lake. The reported  $\beta\text{-HCH}$  level for fish farm D in this study was similar to the 1.81  $\mu\text{g/kg}$  and 1.54  $\mu\text{g/kg}$  found by Ezemonye et al. (2015) and Kamel et al. (2015) in sediment from Ogbesse River in Nigeria and Manzala Lake in Egypt, respectively. The  $\beta\text{-HCH}$  levels found in fish farms A, B, and C in this investigation were comparable to those found on the Egyptian Mediterranean coast by El Nemr et al. (2012).

The range of  $\sum \text{HCHs}$  in the measured sediment was used to compare with studies within the world. The range was found to be in the range of measured  $\sum \text{HCH}$  in

sediment from water bodies in Thailand (Sudaryanto et al. 2011) and Pakistan (Baqar et al. 2018). The range was, however, lower than measured sediment in water bodies from China (Sun et al. 2010; Zhao et al. 2010b).

Heptachlor concentration ranges from ND to 3.985  $\mu\text{g/kg}$ , with the pesticides being predominant in fish farms A and accounted for about 57% of the sediment sampled. Heptachlor concentrations were generally higher in farms A and B than the other farms' sediment. This is expected as heptachlor is rapidly metabolised in sediments to the more stable epoxide (Buah-Kwofie and Humphries 2017). Heptachlor was not detected in farm C indicating the complete degradation of this compound. The range in sediment from farm A was not different from one observed by Gbeddy et al. (2015) on the same Volta Basin and Malik et al. (2011) in River Chenab, Pakistan. Heptachlor is hydrophobic and poorly soluble in water (Taiwo et al. 2019). This observation probably reflects its higher level in sediment from farm A. The heptachlor concentration recorded for fish farm D for the study was 1.080  $\mu\text{g/kg}$ . This agrees with Ezemonye et al. (2015) and Kamel et al. (2015) in sediment from Ogbesse River in Nigeria and Manzala Lake in Egypt, respectively. Methoxychlor residues were highly detected in farm A ( $8.253 \pm 5.252 \mu\text{g/kg}$ ) followed by farm B ( $1.860 \pm 1.612 \mu\text{g/kg}$ ) with detection frequencies of 57% and 20%, respectively. The methoxychlor concentration found in fish farm A corresponds with that found by Musa et al. (2011) in the Yala/Nzoia River in Kenya's Lake Victoria Basin.  $\sum \text{chlor}$  concentrations from the study varied between.

ND and 12.238  $\mu\text{g/kg}$  were significantly lower than concentrations from Lake Sibaya (34.0 ng/g), Kosi Bay (31.6 ng/g), and Lake St Lucia (35.1 ng/g) reported by Buah-Kwofie and Humphries (2017) from iSimangaliso Wetland Park in South Africa.

Aldrin, dieldrin, and endrin are pesticides in the cyclodiene family that are used to kill rodents, termites in the soil as well as grasshoppers. Due to their powerful insecticidal properties, these chemicals are commonly used for crop defence in cotton-growing areas, from where these harmful chemicals make their way to the aquatic environment. In this study, the average concentration of endrin for the four farms ranged from < LOD to 13.867  $\mu\text{g/kg}$ . The range was within the measured sediment from Kala Shah in Pakistan (Syed and Malik 2011). Endrin was predominant in fish farms D and C and accounted for 83% and 33% of the sediment samples, respectively. The average level of endrin in this study for fish farm D complied with the level found by Musa et al. (2011) in Yala/Nzoia River within the Lake Victoria Basin, Kenya. In the environment, endrin breaks down to endrin ketone and endrin aldehyde through photodecomposition and microbial degradation (Bempah et al. 2011). This probably accounted for its low levels in fish farms A and B. The

low levels also suggest that the presence of this pesticide in the sediment was as a result of old inputs.

Concerning the endosulphans,  $\alpha$ -endosulphan was higher than  $\beta$ -endosulphan in all the farms, although the water solubility of  $\beta$ -endosulphan is higher (Eqani 2012). This is not surprising given that the Ghanaian Environmental Protection Agency (EPA) restricted endosulphan use in the agricultural sector in December 2008 (Afful et al. 2010). Additionally, the technical mixture of endosulphan has higher rates of the  $\alpha$ -endosulphan than its  $\beta$ -isomer, and that  $\beta$ -endosulphan is converted to  $\alpha$ -endosulphan in environmental matrices (Schmidt et al. 2001). The range of  $\alpha$ -endosulphan concentrations for the study was 1.555–6.000  $\mu\text{g/kg}$ , which was similar to the range; (0.01–14.21  $\mu\text{g/kg}$ ) obtained by Kuranchie-Mensah et al. (2012) in the Nsawam stretch of the Densu River.

### Levels of Polychlorinated Biphenyls in the Sediment

Six indicative PCB congeners (tri-18, 28, tetra-52, Penta-101, Hexa-153, and Hepta-180) were detected in the surface sediment from the fish farms, among which PCB 153 recorded the highest concentration of  $3.328 \pm 1.700$  ng/g in farm D (Table 3). CB 18 and CB 180 tend to dominate the profiles in the sediment from all the farms. There were more congeners determined in the studied farm D as compared to the other farms. According to Russell et al. (2011), if the input of PCBs into the sediment of fish farms is due to the input of fish feed, the profile will be dominated by higher chlorinated PCBs, depending on the chemical composition of the fish feed. It was therefore unlikely that the PCBs were originating from the uneaten fish feed in the bottom of the cages. There was, however, a more significant proportion of tri-18 and hep-180 PCBs in the profile of all fish-farm sediments, probably suggesting mixed contributions from the atmosphere and particulate matter. The detection of some of the higher chlorinated PCBs (Penta-CB 101, Hexa-CB 153, and Hepta-CB or PCB 180) in some fish farms is near the hydro dam and urban areas, where these contaminants are most likely entering the aquatic system by surface run-off

and direct effluent discharge. The higher chlorinated PCBs have a higher log  $K_{ow}$  than the less chlorinated congeners, which may explain why those congeners have a higher concentration in the sediment samples. Because of their high log  $K_{ow}$ , they have a higher affinity for adsorbing particulate matter, which leads to their build-up and deposition in farm sediment.

The sum of the six PCBs concentrations ( $\sum\text{PCBs}$ ) (ng/g) detected in sediment from the fish farms ranged from 0.172 ng/g to 6.202 ng/g, where the sum of the PCBs in fish farm D was significantly higher than the other farms. Meanwhile, the range of  $\sum\text{PCBs}$  (0.172–6.202 ng/g) in the measured sediment compared with other studies globally was within the range of  $\sum\text{PCBs}$  in Hong Kong coast (0.1–461 ng/g), Fenhe Reservoir and Watershed in China (ND–126.5 ng/g), and Haihe River in China (ND–253 ng/g) obtained by Wong et al. (2000), Li et al. (2012), and Zhao et al. (2010a), respectively. The range of the  $\sum\text{PCBs}$  for the study was, however, lower than the measured sediment of  $\sum\text{PCBs}$  in Pearl River in China (19.8–111 ng/g), Canada Basin (24–600 ng/g), and Donggang River in Taiwan (25.5–63.5 ng/g) established by Lai et al. (2015), Wang et al. (2011), and Hsieh et al. (2011), respectively.

### Ecological Concerns of OCPs in Sediment

The potential risk of organochlorine and PCB compounds in sediments from fish farms in the Volta Basin was assessed based on the sediment quality guidelines (SQG) developed for freshwater. The levels of OCPs and PCBs in the sediment samples found in all four fish farms and the controls were compared with the guidelines on sediment quality (Table 4) to evaluate the potential quality of sediments and the possible risk to aquatic life in the Volta Basin.

Sum concentrations of  $\sum\text{DDTs}$  ranged from 0.163 to 12.263  $\mu\text{g/kg}$  during the period of observations. Sum concentrations of DDT ( $\sum\text{DDTs}$ ) in fish farms A, C, and D exceeded the threshold effect concentrations (TECs) and the consensus-based threshold effect concentration (CB-TEC) except  $\sum\text{DDT}$  concentration in fish farm B and the

**Table 3** Mean concentrations (ng/g) of indicator PCBs in the sediments from the fish farm

PCBs	Fish farm A Mean $\pm$ SD	Fish farm B Mean $\pm$ SD	Fish farm C Mean $\pm$ SD	Fish farm D Mean $\pm$ SD	Controls Mean $\pm$ SD
PCB 18	0.296 $\pm$ 0.0008	0.248 $\pm$ 0.1006	0.141 $\pm$ 0.0516	0.296 $\pm$ 0.0002	0.059 $\pm$ 0.0120
PCB 28	ND	ND	ND	0.400 $\pm$ 0.0758	ND
PCB 52	ND	ND	ND	0.066 $\pm$ 0.0138	ND
PCB 101	ND	0.494 $\pm$ 0.2479	0.382 $\pm$ 0.1305	ND	ND
PCB 138	ND	ND	ND	ND	ND
PCB 153	ND	0.475 $\pm$ 0.0799	0.394 $\pm$ 0.0505	3.328 $\pm$ 1.700	ND
PCB 180	0.492 $\pm$ 0.1682	0.401 $\pm$ 0.0999	0.354 $\pm$ 0.0755	2.112 $\pm$ 0.7008	0.113 $\pm$ 0.1050
$\sum\text{PCBs}$	0.788 $\pm$ 0.1762	1.618 $\pm$ 0.6283	1.271 $\pm$ 0.3081	6.202 $\pm$ 2.4906	0.172 $\pm$ 0.187



**Table 4** Ecotoxicological risk assessment of OCPs and PCB in sediment using sediment guidelines

Pesticides	TECs				PECs				Pesticides concentration in sediment				
	TEL	LEL	ERL	CB-TE	PEL	SEL	ERM	CB-PEC	FF <sub>A</sub>	FF <sub>B</sub>	FF <sub>C</sub>	FF <sub>D</sub>	CC
<i>p,p'</i> -DDE	1.42	5	2.2	6.75	6.75	190	27	31.3	–	1.48	1.113	1.510	–
<i>p,p'</i> -DDT	–	–	1	4.16	–	710	7	62.9	–	–	1.803	5.000	–
$\Sigma$ DDT	3.89	7	1.58	5.28	51.7	120	46.1	572	7.185	3.483	5.938	12.263	0.163
$\Sigma$ HCH	0.32	–	–	–	0.99	–	–	–	10.490	2.862	4.155	2.938	0.728
$\Sigma$ PCBs	34.1	–	22.7	–	277	–	180	–	0.788	1.618	1.271	6.202	0.172

FF<sub>A</sub> Fish farm A, FF<sub>B</sub> fish farm B, FF<sub>C</sub> fish farm C, FF<sub>D</sub> fish farm D, CC controls

controls that were less than TEL. None of the sediment samples exceeded consensus-based probable effect concentrations (CB-PECs) of 572 for  $\Sigma$ DDTs from all four areas. In all sediment samples, the values for *p, p'*-DDE surpassed the threshold effect level (TEL) for fish farms B and D, while *p,p'*-DDT surpassed the low effect range (ERL) for fish farm C and D in all sediment samples. However, in sediment samples from fish farm D, *p,p'*-DDT concentrations ( $\mu\text{g/kg}$ ) surpassed the Census Based Threshold Effect Concentrations (CB-TECs) for this metabolite but were below the PECs. This comparison of the levels of DDTs with the appropriate sediment criteria for evaluating the contamination of DDTs and their metabolites shows that adverse biological effects are not likely to occur in the studied areas examined. Indoor residual spraying (IRS) of mosquitoes has been used in many parts of Ghana, especially in areas vulnerable to the epidemics of malaria. The situation tends to naturally present DDT and its metabolites in the aquatic environment, though it is no longer used in agricultural settings. As a result, routine steps must be implemented to minimise DDT pollution in aquaculture farms.

In the case of  $\Sigma$ HCH, all the mean concentrations of the sediment samples from the farms as well as the controls showed higher values than the threshold effect level (TEL) and the probable effect concentration (PEL), except the controls that recorded mean value less than the PEL. As shown, when the sums of HCHs were compared to the appropriate quality recommendations, the risk from HCHs was extremely high, except for HCHs from the controls. The levels of  $\Sigma$ HCHs should therefore be regularly monitored and primary sources established and abated.

PCBs can have harmful effects on aquatic creatures at an ERL value of 22.7 g/kg, according to Eqani (2012). The ERM value of 180 g/kg indicates that PCBs are highly likely to be hazardous to aquatic organisms. A PEL value of 277 g/kg can frequently have harmful effects on aquatic species, according to Canadian Sediment Quality Guidelines (CSQGs). At a TEL of 34.1 g/kg, on the other hand, the effects are minimal (CCME 1999). As a result,  $\Sigma$ PCB levels in sediments were lower than TEL, ERL, PEL, and ERM

levels in this investigation, and hence,  $\Sigma$ PCB concentrations are unlikely to pose harm to the aquatic ecosystem.

## Conclusions

Generally, eleven (11) OCPs were detected in the sediment, and the level ranged < LOD–33.0  $\mu\text{g/kg}$ . The OCPs; -HCH, *o,p'*-DDD,  $\alpha$ -endosulphan, *o,p'*-DDD, and heptachlor were predominant in fish farms A, B, C, D, and controls, respectively. The study revealed that the OCPs were from anthropogenic sources such as agricultural run-off, industrial and municipal waste. CB 18 and CB 180 were the predominant congeners in the entire sediment observed from the farms accounting for a detection frequency of 100% each. The levels of the OCPs and PCBs were below the MRL proposed by USEPA. Evaluating the ecological risk of the OCPs and PCBs in the surface sediment using the SQGs, it was evident that  $\Sigma$ HCH in the sediment from all the farms except the controls poses a health risk to the benthic organisms. Therefore, a comprehensive study followed by a remedial intervention is required to arrest the situation.

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**Data availability** The datasets generated during the current study are not publicly available due to the University policy on data restriction until the Ph.D. thesis is completely examined. However, data are available from the corresponding author on reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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