

# Assessment of organochlorine pesticides and polychlorinated biphenyls in water from cage aquaculture farms in the Volta Lake in Southern Ghana

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## Abstract

The Volta Lake system in southern Ghana has witnessed much agricultural activity in its catchment for over 50 years. There is documented evidence of an increased release of agrochemicals into the aquatic ecosystem. In recent years, cage aquaculture activities have also increased, raising the concern of further release of contaminants and issues of ecological risks in the lake environment. Therefore, this research documents the preliminary investigation into the possible release of contaminants by cage aquaculture activities into the aquatic medium. Sixty (60) water samples were taken from four (4) cage farms along the basin to examine the levels of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). Water samples in hexane solvent system were sonicated on an ultrasonic bath, electronically rocked, cleaned by liquid-phase extraction, and GC/ECD and GC/MS analyses for OCPs and PCBs, respectively. The water from the farms contained eleven (11) OCPs:  $\delta$ -HCH,  $\gamma$ -HCH, heptachlor,  $\alpha$ -endosulfan,  $\beta$ -endosulfan, endrin, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDT, and methoxychlor, as well as five (5) PCBs: PCB-18, PCB-52, PCB-101, PCB-138, and PCB-180. The OCPs concentration ranged  $0.026 \pm 0.018 \mu\text{g/l}$  (ww) for p,p'-DDE in fish farm B to  $1.541 \pm 0.031 \mu\text{g/l}$  (ww) for methoxychlor in fish farm A. Methoxychlor ( $1.541 \pm 0.031 \mu\text{g/l}$ ),  $\delta$ -HCH ( $0.520 \pm 0.001 \mu\text{g/l}$ ), endrin ( $1.173 \pm 0.161 \mu\text{g/l}$ ),  $\delta$ -HCH ( $0.280 \pm 0.057 \mu\text{g/l}$ ) and  $\delta$ -HCH ( $0.037 \pm 0.009 \mu\text{g/l}$ ) recorded the highest levels with detection frequencies of 90%, 10%, 30%, 20% and 30% in fish farms A, B, C, D and controls respectively. PCBs concentrations varied from  $0.070 \pm 0.011 \text{ ng/l}$  for PCB 138 in farm D to  $0.815 \pm 0.211 \text{ ng/l}$  for PCB 101 in the fish farm C. PCB-18 and PCB-180 were predominant and accounted for 100% PCB in the water samples. The levels of heptachlor in farms A, B, and D and endrin in farm C exceeded the WHO MRL for drinking water. The pesticides found in the water samples were largely due to polluted aquaculture activities and most probable from fish feeds used in the farms.

**Keywords:** Carcinogenic, Chromatography, Volta, Public health, water, aquaculture

## Introduction

Freshwater scarcity is a global issue, affecting over 1.8 billion people (UN, 2019). By 2025, three billion people in over forty (40) countries will be lacking access to clean drinking water, according to estimates (UN, 2019). Global water usage surged at a 1% annual rate during the 1980s, and this trend is predicted to continue until 2050. As a result, by 2050, global water consumption will have increased by 20-30% over current levels (Chen et al., 2021). The forecast for global water quality is not good, particularly in fast-growing emerging countries.

Organochlorine compounds (OCs), including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are frequent contaminants in aquatic ecosystems.

Their chronic toxicity, bioaccumulation, and persistence have become a cause of worry. Because of their high lipophilicity, OCPs and PCBs biomagnify swiftly in the aquatic food chain (Yu et al., 2020). Because of their refractory nature, OCP and PCBs are still identified in aquatic ecosystems despite the Stockholm Convention prohibiting their manufacture in 2004 (Li et al., 2018). PCBs are still being released into water habitats through industrial effluents, landfill leachate, port activities, and the incineration of chlorine-containing substances (Yu et al., 2021). When pesticides reach water bodies, they are quickly adsorbed and absorbed by bottom sediment and enter the food chain of aquatic invertebrates, algae, plankton, fish, and aquatic plants (Ogunfowokan et al., 2012). According to the

World Health Organization, ingestion of food and water, particularly fish, meat, and dairy products, account for approximately 90% of human pesticide exposure (Romani et al., 2018). OCPs such as DDTs, HCHs, PCBs, and PAHs can cause carcinogenicity, reproductive toxicity, immunotoxicity, endocrine disruption, and genotoxicity (Bhutto et al., 2021).

OCPs have been utilized for Ghana's agricultural and public health objectives for over 40 years, with residues found in humans, sediments, water, fish and vegetable crops (Gbeddy et al., 2015). Even though many countries, including Ghana, have severely restricted the manufacturing and use of several types of OCP compounds, they are illegally still used in substantial amounts in different parts of the country under various trade names due to insufficient regulation and supervision of their production, trade, and use (Adu-Kumi et al., 2010; Darko et al., 2008).

The Volta system, which accounts for over 80% of Ghana's inland fisheries gross yield, is home to most large-scale commercial cage culture farms (Amenyogbe et al., 2018). The most commonly grown fish species in the basin are *Clarias gariepinus*, *Heterotis niloticus*, and *Oreochromis niloticus*. These fish have a high commercial value in Ghana and are consumed fresh, smoked, or salted. The water in the basin is subject to improper fishing methods such as explosives and poisonous agrochemicals. Because of the proximity of farming areas to the watershed, agrochemicals used in farms and irrigation infrastructure are more likely to reach the lake via runoff. These chemicals could negatively impact the lake's water quality and aquatic life, including farmed fish.

There has also been spring up of pottery industries, poultry farms, textile industries and metal scrap activities closer to some fish farms (Tiimub et al., 2015). Preliminary investigations conducted in 2003 to determine the status of POPs in Ghana found that no PCBs were produced in the country. However, PCB oils imported from other countries are being used in some of these industries illegally or uncontrollably in Ghana. Even though

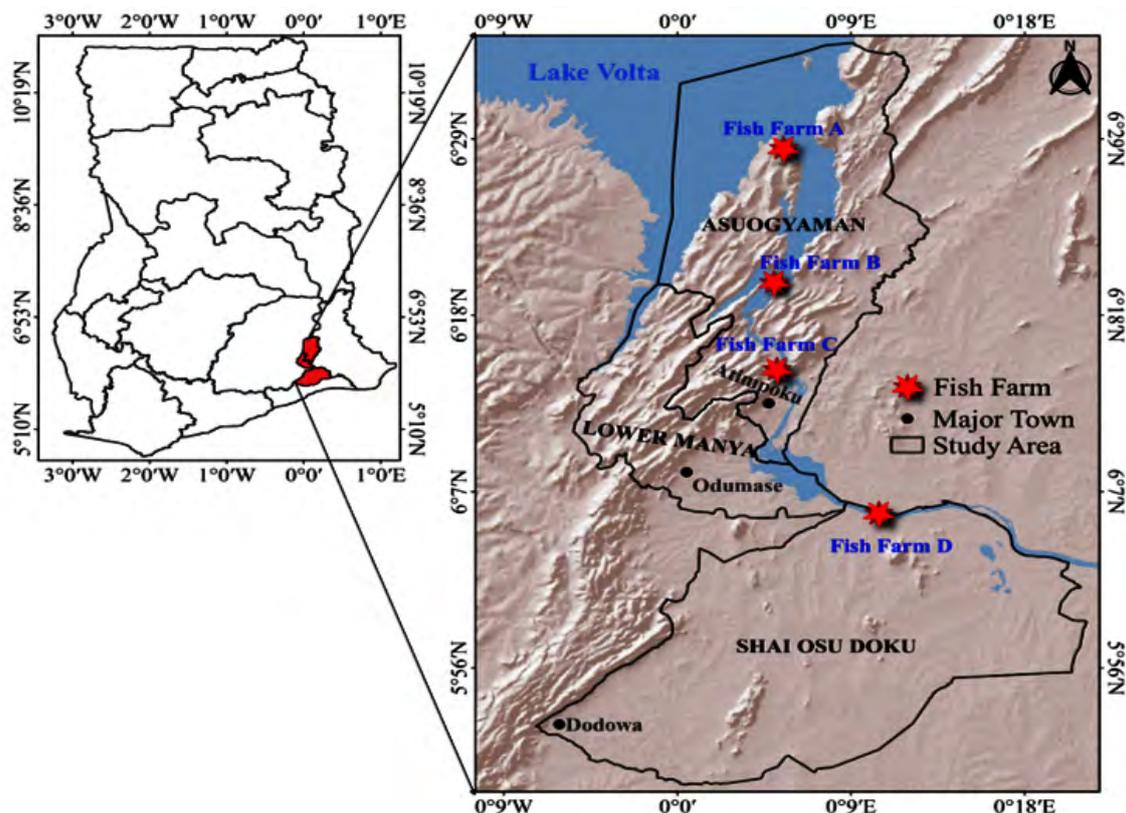
PCBs and other pesticides are no longer used in Ghana, the past use of these chemicals in plasticizers, electrical transformers, surface coatings, paints, hospitals, flame retardant, inks, adhesives, electricity companies as well as private or public buildings is still common (Asante et al., 2011). Wastewater effluents from these industrial activities are released into the open environment with or without any treatment. During runoff after rainfall, the effluents which contain some of these POPs are discharged into the lake column, polluting the entire aquatic ecosystem.

Additionally, depending on their composition and sources, fish feed used in the cage aquaculture farms may contain a substantial amount of these undesirable pollutants such as OCPs, PCBs and dioxin (Botaro et al. 2011; Perugini et al., 2013; Magna et al., 2021). The recent expansion of cage aquaculture systems will increase the lake's residual levels of these contaminants, contaminating the biota and endangering the overall aquatic ecosystem. Few studies have focused on the impact of cage culture on the lake's water quality (Asmah et al., 2014; Mensah et al., 2013; Ofori et al., 2010; Karikari et al., 2020). Other researchers have reported the levels of pesticides in sediments, wild fish and the opened waters of the Volta Lake (Adu-Kumi et al. 2010; Asante et al. 2013; Gbeddy et al. 2015; Gbeddy et al. 2012; Kuranchie-Mensah et al. 2012; Koranteng, 2016; Magna et al., 2021; Ntow, 2005). However, there is a paucity of data on the residual levels of organochlorine pesticides in cage aquaculture waters. Therefore, the present study aimed at examining the contribution of cage aquaculture to the release of PCBs and OCPs in the aquatic medium.

## Materials and methods

### *Study area*

The study area includes the Shai Osudoku District and the Asuogyaman District in the Greater Accra and Eastern regions, respectively. The locations of the fish farms



**Figure 1:** Districts map of the study area of the Volta system in Southern Ghana

from which samples were taken, are shown in Figure 1. The districts are located between latitudes  $6^{\circ} 34' N$  and  $6^{\circ} 10' N$  and longitudes  $0^{\circ} 1' W$  and  $0^{\circ} 14' E$ . Agriculture, both rain-fed and irrigated, is the most important economic activity in these Districts regarding employment and rural income generation. Farmers heavily rely on agrochemicals to boost crop productivity. Therefore, it is impossible to rule out the possibility of restricted pesticide use in the area. The area experiences two distinct seasons of rainfall, with the minor season lasting from May to July and the major season lasting from September to November.

#### *Sampling and sample preparation*

Sixty water samples were collected from four aquaculture farms (A, B, C and D) in southern Ghana's Volta Basin. The samples were obtained in July, May and March 2019. Water samples were collected using a Kemmerer water sampler at an average depth of approximately 3 - 5m within the cages and

placed in acid-washed 1L screw-cap glass bottles. Before collection, each glass bottle was rinsed three times with water from the cages. Fifteen cages were randomly selected from each farm. Two water samples were taken from two different locations within the cage and combined to create composite samples. All samples were taken between 5:30 am, and 9:00 am to avoid the degradation of specific OCP compounds. 5 ml of concentrated  $H_2SO_4$  was added to prevent biological activities (Ntow, 2005; Darko et al., 2008).

Twenty (20) samples were taken from areas upstream that do not have aquaculture as controls. All samples were stored in an airtight ice-chest at  $4^{\circ} C$  and transported to the Ghana Atomic Energy laboratory for further analysis.

In the laboratory, samples were filtered using a  $0.45 \mu m$  Whatman filter for the removal of particulates as well as other suspended solids. The samples were then placed in a freezer until they could be analyzed further.

### *Extraction and clean-up of water samples for OCPs and PCBs*

Organochlorine chemical residues were recovered from water samples using the US EPA 3510 method, slightly modified from Solomon (2016) and Williams (2013). To establish that the samples were neutral, the pH of the samples was determined. Fifty (50) ml hexane was added to 150 ml water sample in a jar, and the mixture was sonicated for 30 minutes in a Brasonic 220 high-frequency ultrasonic bath. After that, the organic layer was decanted into a 250 ml conical flask. The procedure was repeated and the organic phase combined. The organic fraction was then concentrated to a volume of 25 ml using a rotary vacuum evaporator set to 45 °C.

The extracts from the water samples were cleaned up using a column packed with 2 g of anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) at the top, followed by a bottom packed with 4g of silica gel (90% < 45  $\mu\text{m}$ ). The columns were pre-conditioned with 10 mL n-hexane before loading the extracts. The extracts were loaded into the columns with 10 ml hexane, and the flask was rinsed with extra 5 ml hexane and added. The column was then eluted with 20 ml of hexane. The eluate was then concentrated to near dryness with a rotary evaporator at 45°C and collected in a 2ml ethyl acetate vial for Gas Chromatography analysis.

### *Instrumental analysis*

The extracts were analysed using a Varian CP-3800 gas chromatograph (Varian Association Inc. USA) with 63Ni electron capture detector and combiPAL auto-sampler. A VF-5 coated capillary column (30 m + 10 m EZ protection column, 0.25 m film thickness, 0.25 mm inner diameter) was employed for the analysis. The detector and injector were both heated to 300°C and 270°C, respectively. The furnace was set to 70°C for 2 minutes, then a 25°C/min ramp to 180°C for 1 minute, followed by a 5°C/min ramp to 300°C. The G.C. parameters and detector response were determined to account for the different retention durations and reaction behaviour. The detector additive gas was 29 ml/min, while the carrier gas was

N, which had a flow rate of 1.0 ml/min. For one sample, the entire running time was 31.4 minutes. A 1.0 $\mu\text{l}$  was used as GC injection volume.

Agilent Technologies 6890N and 5975 for GC and MS, respectively in EI mode, were used for the GC-MS analysis. The contact and ion source were set to temperatures of 280 °C and 300 °C, respectively. A Phenomenex ZB-5MS capillary column (30 m x 0.25 mm x 0.25 m) was utilized for chromatographic separation. The carrier gas flow rate was peaked at 1.1 mL/min and 265 degrees Celsius, used as temperature for the injection. The injected samples totalled 1 litre. The following temperatures were considered to be the best: The oven temperature was held at 60°C for 1 minute, then increased to 170°C with a 20°C/min ramp, maintained for 0.30 minute, and then increased to 310°C with a 10°C/min ramp and a 1.20-minute maintenance period. A mixture of the seven indicators PCBs was injected into the GC 2 $\mu\text{L}$  at a 10 g/mL concentration in iso-octane from Sigma Aldrich to analyse each PCB retention duration.

The OCP and PCB residue levels were calculated by applying a conventional external approach that compared the sample peak heights to the respective peak heights of the reference standards.

### *Quality assurance and quality control*

Measures were taken to ensure the results' reliability. All glass equipment utilized in the study (for extraction and cleaning) was cleaned with detergent and tap water. The glassware was rigorously cleaned with analytical grade acetone and dried in a 70°C oven after being cleaned with distilled water. After cooling, they were removed from the oven and kept in a dust-free cabinet. To ensure the integrity of the OCPs and PCB residues, duplicate analyses of samples, solvent blanks, and procedural matrix blanks were performed. Simultaneous analysis of each batch of analytical extracts with procedural recoveries was performed. Each batch of samples was subjected to recalibration curves to ensure that the correlation coefficient remained greater than

$r^2=0.995$ . Samples were spiked with 0.05 mg/kg internal standard (isodrin) to optimize the analytical technique. Spiked samples were examined using the same procedure as field samples, and the pollutants were measured with high recoveries of 78–95 per cent for OCPs and 80–94 per cent for PCBs.

#### *Statistical analysis*

The normality of the data was determined using the Kolmogorov-Smirnov (K-S) technique. The concentrations of OCPs and PCBs were determined using descriptive statistics like standard deviation, means and range. A one-way ANOVA with Tukey's post hoc test was used to determine the differences in contaminants between the fish farms and controls from which samples were obtained. The Pearson correlation coefficient was used to assess the relationship between OCP in surface water and fish feed using two-tailed significance tests (with significance levels of 0.01 and 0.05).

## **Result and Discussions**

### *Levels of OCPs in water from fish farm cages*

The levels of various organochlorine pesticides in water from the four sampling aquaculture farms are summarised in Table 1. Residues of 11 OCPs p,p'-DDT,  $\alpha$ -endosulfan,  $\delta$ -HCH,  $\gamma$ -HCH, heptachlor, o,p'-DDD,  $\beta$ -endosulfan, endrin, o,p'-DDE, p,p'-DDE, and methoxychlor) were found in the four cage farms, including the control water samples. The mean OCPs concentration ranged 0.026±0.018  $\mu\text{g/l}$  (ww) p,p'-DDE in fish farm B to 1.541±0.031  $\mu\text{g/l}$  (ww) for methoxychlor in fish farm A with occurrence frequencies of 89% and 90%, respectively. The highest mean concentration of methoxychlor was 1.541  $\mu\text{g/l}$  (ww) in farm A, followed by endrin at 1.173  $\mu\text{g/l}$  in farm C. Endrin had the lowest level in controls, averaging 0.017 ± 0.014  $\mu\text{g/l}$ . Methoxychlor (90 %), o,p'-DDD (90 %),  $\alpha$ -endosulfan (60 %), and methoxychlor (40 %) were the most prevalent compounds detected in fish farms A, B, C, and D, respectively.

DDT was not detected in the study's water samples. However, four metabolites of p,p'-DDT, o,p'-DDD, o,p'-DDE, and p,p'-DDE were measured in water. The highest concentration of the o,p'-DDD metabolite was 0.146±0.041  $\mu\text{g/l}$ , which was detected in 40 % of water samples from farm C. DDT residues (p,p'-DDE, p,p'-DDT, o,p'-DDD, and o,p'-DDE) in the cage water varied between 0.049±0.031  $\mu\text{g/l}$  in farm A and 0.197±0.045  $\mu\text{g/l}$  in farm C. The  $\Sigma$ DDT reported <LOD -0.049  $\mu\text{g/l}$ , <LOD - 0.067  $\mu\text{g/l}$ , <LOD - 0.197  $\mu\text{g/l}$  and <LOD - 0.109  $\mu\text{g/l}$  in fish farms A, B, C and D respectively. DDT and its metabolites, DDD and DDE, are used extensively throughout the world to investigate potential sources of contamination. Technical DDT contains a greater proportion of DDT (approximately 85 per cent) than DDE and DDD components (ATSDR, 2002). As a result, high DDT/(DDE +DDD) ratios indicate recent technical DDT administration, whereas low values indicate long-term DDT decomposition (ATSDR, 2002). The current analysis revealed trace amounts of p,p'-DDT (LOD) in the water, indicating that DDT was once used on farms. Additionally, the predominance of DDD in the surface water samples from all farms than the DDE indicated that DDT degraded anaerobically. As a result, the primary source of DDTs in the freshwater environment of the Volta basin could be accrued DDTs in sediment that has been transmitted to the water after long-term deterioration, rather than current DDT usage. This is in accordance with Ghana's decision to ban the use of technical DDT in recent years. The  $\Sigma$ DDT concentrations in the cage farms on the Volta Basin were lower than that of 0.3  $\mu\text{g/l}$  obtained in the same Volta Lake by Gbeddy *et al.* (2015).

Although HCHs were once widely used, commercial use has been prohibited worldwide. HCH is primarily used as a mixture containing 10%–15%  $\gamma$ -HCH, 5%–12%  $\beta$ -HCH, and 60–80%  $\alpha$ -HCH, as well as other isomers. Additionally, lindane has over 99 per cent  $\gamma$ -HCH (ATSDR, 2002). Among the hexachlorocyclohexane (HCH) isomers,  $\delta$ -HCH was detected in all farm samples,

while  $\gamma$ -HCH was detected in only farm B. The low concentrations of  $\gamma$ -HCH in the controls ( $0.037 \pm 0.009 \mu\text{g/l}$ ) could be attributed to new lindane exposure from localized use and/or distant sources transported via volatilization. The highest concentration of  $\delta$ -HCH ( $0.799 \pm 0.058 \mu\text{g/l}$ ) was detected in fish farm A with an 89 per cent detection rate. Ntow (2005), on the other hand, observed gamma-HCH concentrations of  $0.008 \mu\text{g/l}$  in the open waters of Volta Lake. This was significantly lower than the level observed in farm B ( $0.041 \pm 0.001 \mu\text{g/l}$ ) for the current study. Comparatively, the  $\Sigma\text{HCHs}$  ( $0.037 - 0.799 \mu\text{g/l}$ ) were higher than  $\Sigma\text{DDTs}$  ( $<\text{LOD} - .197 \mu\text{g/l}$ ) for the study. This could be due to DDT isomers' lower water solubility and hydrophobicity as compared to HCHs. The logarithmic octanol-water partition coefficient values for DDT ( $6.02-6.91$ ) are greater than that of HCH values ( $3.70-4.14$ ) (Li et al.,

2021). The higher the logKow, the more hydrophobic the water column is, and the easier contaminants migrate from the water column to the sediment.

Endosulfan controls pests on fruits, vegetables, tea, and non-food crops, including tobacco and cotton worldwide. Endosulfan may spread beyond the places where it is used due to volatilization and air transmission. It enters the water column by deposition, spray drift, and soil runoff, where it bonds to bed sediments and becomes a source of dispersed endosulfan in adjacent waters (Shivaramaiah et al., 2005). Except in farm D,  $\beta$ -endosulfan levels were considerably greater than  $\alpha$ -endosulfan levels in this investigation. Farm C had the highest concentrations of alpha-endosulfan and beta-endosulfan, while farms A and D had the lowest mean levels of  $\alpha$ -endosulfan ( $0.034 \mu\text{g/l}$ ) and  $\beta$ -endosulfan ( $0.025 \mu\text{g/l}$ ), respectively. The level of alpha-endosulfan in

**TABLE 1**  
Concentration ( $\mu\text{g/L}$ ) of organochlorine pesticides in water from cage fish farms

FARM A	$\gamma$ -HCH	$\delta$ -HCH	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDD	<i>p,p'</i> -DDT	Hept.	Endrin	Meth.	$\alpha$ -endos.	$\beta$ -endos.	
Mean	ND	0.799	<LOD	ND	0.049	ND	0.062	ND	1.541	0.034	0.421	
SD	-	0.058	-	-	0.030	-	0.023	-	0.031	0.013	-	
Frequency	-	89	-	-	50	-	50	-	90	30	30	
		$\Sigma\text{HCH}=0.799$			$\Sigma\text{DDT}=0.049$					$\Sigma\text{Endo}=0.455$		
FARM B												
Mean	0.031	0.520	<LOD	0.026	0.041	<LOD	0.063	0.037	0.040	0.041	0.087	
SD	0.001	-	-	0.018	0.038	-	0.015	0.035	0.020	0.020	0.006	
Frequency	20	10	-	40	90	-	20	20	40	30	30	
		$\Sigma\text{HCH}=0.551$			$\Sigma\text{DDT}=0.067$					$\text{Endo}=0.128$		
FARM C												
Mean	ND	0.181	0.051	<LOD	0.146	<LOD	<LOD	1.173	0.641	0.184	0.834	
S.D.	-	0.078	0.004	-	0.041	-	-	0.161	0.084	0.077	0.058	
Frequency	-	20	30	-	40	-	-	30	30	60	40	
		$\Sigma\text{HCH}=0.232$			$\Sigma\text{DDT}=0.197$					$\text{Endo}=1.018$		
FARM D												
Mean	ND	0.280	<LOD	0.054	0.055	<LOD	0.068	0.054	0.238	0.068	0.025	
SD	-	0.057	-	0.024	0.005	-	0.012	0.010	0.131	0.005	0.007	
Frequency	-	20	-	30	30	-	30	30	40	30	20	
		$\Sigma\text{HCH}=0.280$			$\Sigma\text{DDT}=0.109$					$\text{Endo}=0.093$		
CONTROL												
Mean	ND	0.037	ND	<LOD	<LOD	ND	ND	0.017	0.025	ND	ND	
SD	-	0.009	-	-	-	-	-	0.014	0.008	-	-	
Frequency	-	30	-	-	-	-	-	25	25	-	-	
		$\Sigma\text{HCH}=0.037$										
Aust./ $\mu\text{g/L}$	0.05	0.05	0.06	0.06	0.06	0.06	0.05	-	0.20	0.05	0.05	
WHO/ $\mu\text{g/L}$	2.00	2.00	1.00	1.00	1.00	1.00	0.03	0.60	20.00	20.00	20.00	

LOD- Limit of Detection, Hept.- Heptachlor, Meth.- Methoxychlor, endos.-Endosulfan, Australian MRL, SD-standard deviation

fish farm A was comparable to that found in Lake Volta by Ntow (2005).

According to Varnosfaderany *et al.* (2020),  $\alpha$ -endosulfan is less persistent compared to  $\beta$ -endosulfan. Therefore, the  $\alpha$ -endosulfan/ $\beta$ -endosulfan ratio can be used to determine the age of the endosulfan pollutant and its sources of pollution. Surface water samples from fish farms A, B, and C had a ratio of less than one. However, the ratio was greater than one in surface water samples from fish farm D, indicating that the endosulfan technical mixture had been used recently in farm D.

Heptachlor was detected in all the farms with concentrations ranging between <LOD and 0.068  $\mu\text{g/l}$ . The highest concentration of heptachlor was observed for fish farm D. This farm is situated near cultivated fields of fruits and vegetables. Heptachlor was used in the past to kill termites, ants, and other soil insects. Heptachlor discharged into the environment is metabolized by abiotic activities, such as photolysis to produce hydroxyl radicals, which in the presence of water, is transformed to 1-hydroxychlorodene or heptachlor epoxide, known to be more toxic and persistent than the parent heptachlor (Necibi *et al.*, 2015).

Endrin and methoxychlor were among the other OCPs discovered in the water samples. Although these OCPs were outlawed in Ghana, their residual has persisted in much of the country's soil due to their chemical stability and inability to break down or migrate. As a result of soil erosion, pesticides in the soil can enter rivers and contaminate the entire

water column. Several degradation processes, including microbial activity and oxidation, photoionization, hydrolysis, electron transfer, photodegradation, and aerobic biodegradation, could explain their presence in surface water for the current study (Velagaleti *et al.*, 2002).

The correlation coefficients between residual OCPs in water and fish feed can provide useful information about pollution sources. Significant positive correlations were only observed between the OCPs in surface waters and some OCPs in fish feed (i.e., p,p'-DDT,  $\alpha$ -endosulfan, o,p'-DDE,  $\delta$ -HCH, heptachlor,  $\beta$ -endosulfan, o,p'-DDD, and p,p'-DDE). This indicates that the levels and distributions of OCPs in the surface waters of the fish farms are probably due to direct inputs of fish feeds. There was no significant correlation of  $\gamma$ -HCH, endrin, and methoxychlor in the study. It was, therefore, difficult to describe the sources of  $\gamma$ -HCH, endrin, and methoxychlor in the water, but it was most likely that they originated from variable sources such as; agricultural fields, illegal fishing practices and significant discharge due to shipping recreational activities (Gbeddy *et al.*, 2015; Dai *et al.*, 2011).

#### *Levels of PCBs in water from fish farm cages*

Table 2 lists the PCB congeners found in water samples from cage fish farms in the Volta Basin. At a 5% significance level, analysis of variance (ANOVA) indicated significant variations in PCBs among the farms tested ( $p = 0.001$ ). There were statistically significant

**TABLE 2**  
Levels (ng/l) of indicator PCBs in water from the cage fish farms

	<b>FARM A</b>	<b>FARM B</b>	<b>FARM C</b>	<b>FARM D</b>	<b>CONTROL</b>
<b>PCBs</b>	<b>Mean <math>\pm</math>SD</b>				
PCB 18	0.296 $\pm$ 0.005	0.304 $\pm$ 0.017	0.471 $\pm$ 0.076	0.297 $\pm$ 0.007	0.163 $\pm$ 0.013
PCB 28	ND	ND	ND	ND	ND
PCB 52	ND	0.528 $\pm$ 0.242	ND	0.594 $\pm$ 0.144	0.172
PCB 101	ND	ND	0.815 $\pm$ 0.211	ND	ND
PCB 138	ND	ND	ND	0.070 $\pm$ 0.011	0.072
PCB 153	ND	ND	ND	ND	ND
PCB 180	0.508 $\pm$ 0.176	0.391 $\pm$ 0.159	0.436 $\pm$ 0.237	0.396 $\pm$ 0.102	0.159 $\pm$ 0.014
<b><math>\Sigma</math>PCBs</b>	<b>0.804<math>\pm</math>0.177</b>	<b>1.223<math>\pm</math>0.418</b>	<b>1.722<math>\pm</math>0.525</b>	<b>1.357<math>\pm</math>0.258</b>	<b>0.566<math>\pm</math>0.027</b>

ND-Non detected

variations in PCB 18 concentration in the following farms: A and C ( $p=0.022$ ); B and C ( $p=0.014$ ); and C and D ( $p=0.001$ ), according to the Tukey HSD test at 5% ( $p < 0.05$ ). Farms A, B, C, and D differed significantly from the control ( $p < 0.001$ ).

In farms A, B, C, and D, PCB congener concentrations ranged from non-detect (ND) - 0.508 ng/l, ND - 0.528 ng/l, ND - 0.815 ng/l, ND - 0.594 ng/l and ND - 0.172 ng/l, respectively. CB-18 and CB-180 were the most common PCB indicator congeners compounds found in the water samples, accounting for 100 per cent of each. Farm C had the greatest concentration of PCBs 101 at 0.815 ng/l, whereas farm D had the lowest value at 0.070 ng/l.

$\Sigma$ PCBs levels in the water were  $0.804 \pm 0.177$  ng/l for farm A,  $1.223 \pm 0.418$  ng/l for farm B,  $1.722 \pm 0.525$  ng/l for farm C,  $1.357 \pm 0.258$  ng/l for farm D and  $0.566 \pm 0.027$  ng/l for the control. When compared to the other fish farms, the total concentration in farm C was substantially higher. Lower chlorinated congeners (CB-18, CB-52, and CB-101) made a significant contribution to the samples, consistent with research on freshwater in Spain (Bordajandi et al., 2003), which found that lower congeners accumulate in significant amounts in the air due to their high vapour pressure. Even though Ghana does not manufacture PCBs, there have been reports of unregulated handling and/or reuse of PCB-containing waste such as old capacitors and transformers (Asante et al., 2013). Furthermore, Asante et al. (2013) discovered in their study that significant PCB emissions from various sources, including shipyards in West Africa, are not taken into account in current global atmospheric emissions estimates. As seen in appendix 2, significant positive correlations between PCBs in surface waters and some PCBs in fish feed (i.e., PCB 18, PCB 101 and PCB 180) were observed in this investigation. This suggests that the levels of PCBs in the surface waters of the fish farms were much more likely attributable to continuous fish feed inputs. A significant proportion of the PCBs released by these sources ends up in the water, contaminating it. The PCB levels for the study

were lower than those in China's Minjiang River (203.9–2473.0 ng/l) (Zhou et al., 2000) and Baiyangdian Lake (Dai et al., 2011).

#### *Concentrations of organochlorine compounds in water in comparison to international standards*

Organochlorine pesticide residues could enter the human body through food, water, or the air. The amount of pesticide residue absorbed in water and food daily varies based on exposure and residue consumed. The Volta system in Southern Ghana is crucial because it provides water to a large portion of Accra's metro area and beyond. As a result, testing the safety of drinking water emanating from the basin is critical. In Ghana, there is no permissible pesticide limit for drinking water. As a result, the World Health Organization's (WHO) and Australian Drinking Water Guidelines were applied. Except for heptachlor in farms A, B, and D and endrin in farm C, all OCP levels in the water samples tested were below WHO guidelines (see table 1). Farm A had high levels of  $\delta$ -HCH, heptachlor, methoxychlor, and  $\beta$ -endosulfan; farm B had high levels of  $\delta$ -HCH, heptachlor, and  $\beta$ -endosulfan; farm C had high levels of  $\beta$ -HCH, o,p'-DDD, methoxychlor,  $\alpha$ -endosulfan, and  $\beta$ -endosulfan; and farm D had high levels of  $\alpha$ -HCH than the Australian Drinking water Guidelines.

#### **Conclusion**

Organochlorine pesticides were detected in varying concentrations in the caged aquaculture water. Methoxychlor recorded the highest mean concentration in farm A. Methoxychlor, o,p'-DDD,  $\alpha$ -endosulfan, and methoxychlor were the predominant compounds detected in fish farms A, B, C, and D, respectively. PCBs 101 reported the greatest concentration of 0.815 ng/l in fish farm C. PCB-18 and PCB-180 were the most encountered PCB congeners in all the farms. All OCP quantities in the water samples examined were significantly below WHO standards, except for heptachlor

in farms A, B, and D and endrin in Farm C. The OCPs in some of the samples were more significant than the Australian drinking water recommendations. Because OCPs are less soluble in water, their low concentrations in water were not surprising. Since the background concentrations of target pesticides were lower than levels found within cage aquaculture areas, the pesticides found in the fish farms water samples were attributed to polluted aquaculture activities, most probable from fish feeds used in the farms.

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## SUPPLEMENTARY DATA

## Appendix 1

Pearson's correlation for OCP concentrations fish feed against OCPs levels in water

Pesticide	$\delta$ -HCH	o,p-DDE	p,p-DDE	o,p-DDD	p,p-DDT	Hept.	Endrin	Meth.	$\alpha$ -endo	$\beta$ -endo	$\gamma$ -HCH
$\delta$ -HCH	.798**	.549**	.772**	.792**	.823**	.898**	.369	.110	.607**	.687**	.158
o,p-DDE	.549**	.847**	.764**	.598**	.486*	.417*	.082	.059	.677**	.695**	.076
p,p-DDE	.772**	.764**	.694**	.736**	.753**	.607**	.299	.060	.487*	.854**	.272
o,p-DDD	.792**	.598**	.736**	.861**	.515*	.588*	.343	.306	.694**	.515*	.162
p,p-DDT	.823**	.486*	.753**	.515*	.743**	.998**	.179	.176	.707**	.843**	.023
Hept.	.898**	.417*	.607**	.588*	.998**	.681**	.253	.106	.417*	.622**	.118
Endrin	.369	.082	.299	.343	.179	.253	.327	.106	.292	.183	.058
Meth.	.110	.059	.060	.306	.176	.106	.106	.318	.330	.120	.314
$\alpha$ -endos.	.607**	.677**	.487*	.694**	.707**	.417*	.292	.330	.832**	.695**	.215
$\beta$ -endos.	.687**	.695**	.854**	.515*	.843**	.622**	.183	.120	.695**	.886**	.084

\*\*. Correlation is significant at the 0.01 level (2-tailed).

\*. Correlation is significant at the 0.05 level (2-tailed).

## Appendix 2

Pearson's correlation for PCB concentrations feed against PCBs levels in water

PCBs	PCB 18	PCB 52	PCB 101	PCB 138	PCB 180
PCB 18	.998**	.110	.707**	.216	.754**
PCB 28	.252	.179	.411	.472	.311
PCB 101	.707**	.236	.656**	.044	.695**
PCB 180	.754**	.412	.931**	.267	.886**

\*\*Correlation is significant at P &lt; 0.01 level (two-tailed)