



Organochlorine pesticide residues in African catfish muscle, Nile tilapia Muscle and gills from the middle Volta basin, Kpando Torkor, Ghana and their potential health risks to humans

Gustav Gbeddy^{1,3}, Philip Yeboah³, Derick Carboo^{2,3}, Louis Doamekpor², Samuel Afful⁴, Vincent Nartey^{2,3}, Samuel Frimpong^{3,4}, Israel Doyi^{1,3}, Tetteh Glover^{1,3} and Courage Egbi^{3,4}

¹National Radioactive Waste Management Center, National Nuclear Research Institute (NNRI), Ghana Atomic Energy Commission (GAEC), Atomic, Ghana.

²Chemistry Department, University of Ghana, Legon, Ghana.

³Graduate School of Nuclear and Allied Sciences, University of Ghana, Atomic Campus, Ghana.

⁴Nuclear Chemistry and Environmental Research Center, NNRI, GAEC, Atomic, Ghana.

ARTICLE INFO

Article history:

Received: 5 June 2012;

Received in revised form:

22 July 2012;

Accepted: 30 July 2012;

Keywords

Pesticide,
Organochlorine,
Residue,
Gas chromatograph,
Electron capture detector,
Daily risk assessment and benchmark concentrations.

ABSTRACT

Forty two samples each of two fish species, *Tillapia zilli* and *Chrysichthys nigrodigitatus* were collected along the Kpando Torkor Lake in the Volta Region of Ghana. The samples were investigated for levels of organochlorine pesticide residues and their potential health risks to humans were also assessed. Composite sample of muscles and gills of each species were homogenized using a warring blender. The homogenized samples were Soxhlet extracted with hexane/dichloromethane mixture. The extracts were cleaned up on florisil adsorbent and analyzed for organochlorine pesticide residues using gas chromatography equipped with electron capture detector. In all, fifteen organochlorine pesticides (OCPs) were investigated of which thirteen organochlorines namely, β -HCH, δ -HCH, p,p'-DDT, p,p'-DDD, p,p'-DDE, heptachlor, aldrin, dieldrin, γ -chordane, α -endosulfan, β -endosulfan, endosulfan sulfate and methoxychlor were identified. Heptachlor, δ -HCH, p,p'-DDD, β -HCH, methoxychlor and endosulfan sulphate were the predominant OCP residues measured. The mean residue concentration in muscles and gills ranges from 0.10 to 17.35 ng/g wet weight and 0.56 to 37.75 ng/g wet weight respectively. A 100% incidence was recorded for β -HCH, δ -HCH, p,p'-DDD, heptachlor, endosulfan sulfate in the muscle. In the case of the gills a 100% incidence was also recorded for β -HCH, δ -HCH, p,p'-DDD, γ -chordane, endosulfan sulfate and methoxychlor. Risk assessment based on estimated daily intake (EDI) showed that values obtained for EDI for each organochlorine were far below the non-cancer and cancer benchmark concentrations. As a result the consumption of these fishes will have little or no significant adverse health effects on consumers. It is however, advisable to remove the gills from tilapia fish prior to preparation and consumption to reduce the cumulative and concomitant effect of OCPs in tilapia protein consumers in the long term.

© 2012 Elixir All rights reserved.

Introduction

Organochlorine pesticides (OCPs) are synthetic organic compounds containing extremely strong bonds between their chlorine and carbon components and are intended for preventing, destroying, repelling or mitigating pests. As persistent organic pollutants (POPs) many of them are resistant to environmental degradation through chemical, biological and photolytic processes. They therefore, persist in the environment for long periods, capable of long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, and have potentially significant impacts on human health and the environment (UNEP Stockholm Convention on POPs, 2009). The environmental behaviour of OCPs has been investigated for many years and as early as 1962, Rachel Carson's silent spring concluded that DDT and other pesticides, designated as OCPs today, had insidious effects, harmed birds and other animals and had contaminated the entire world food supply (Liu et al., 2010).

Organochlorine pesticides have been widely used in the past but due to the problem they pose to human health (Stoichev et

al., 2005) they have been phased out. Indeed the Stockholm Convention on POPs has banned the use of most organochlorine pesticides. Biological samples such as fish and other aquatic and terrestrial mammals as well as soils and sediments have higher concentrations of organochlorine pesticides than water or air. This makes them more suitable for routine monitoring for organochlorine residues and more relevant in the context of exposure of humans and wildlife (Muir et al. 2006). Food consumption represents a vital route for exposure to contaminants from a number of sources, including pesticide application (Dougherty et al. 2000). The average concentration of these organochlorine pesticides increases dramatically along a food chain. The bioaccumulation of organochlorines in fish and other animals is the reason why most of the human daily intake of such chemicals comes from our food supply rather than from water (Baird, 2005). It has been found that greater than 80% of the total intake of pesticide residues in human beings is through the food chain (Martinez et al. 1997; Trotter and Dickerson, 1993). There is therefore a vital need for the continuous

monitoring of pesticide residues in food since this will provide constant assurance of consumers about the safety and quality of our food commodities in term of pesticide residue contamination. In line with this, numerous legislations across the globe have established maximum residue limits (MRLs) for pesticides in foodstuffs. The maximum residue limit is the maximum amount of pesticide residue which if found in food substances will not cause any health hazard.

Volta Lake experiences bad fishing practices, including the use of explosives and chemicals and in particular organochlorine compounds. Indeed, lindane and endosulfan were used in the regions of the Volta Lake (Ntow, 2005). Moreover, the short distance between agricultural fields and waterways also has the propensity of elevating the probability of agrochemicals reaching the lake via run-off. The fish harvested from this lake is consumed within and outside of Ghana. In Ghana fish constitutes a vital source of animal protein (GFA, 2010) because of its availability and affordability. Adu-Kumi et al. (2010) reported relatively high ratio of p,p' -DDT to p,p' -DDE (p,p' -DDT/ p,p' -DDE) in tilapia and catfish with an extremely high value in catfish purchased from a local market at Madina in Ghana. Report indicated that the fish samples were originally obtained from the Volta Lake (Adu-Kumi et al., 2010) This finding suggests possible fresh contamination of the Volta Lake with DDT.

In the present study the profile of organochlorine pesticide residues in the fish samples from the Kpando Torkor Lake were investigated with the objective of establishing the extent at which the Lake has been polluted in terms of organochlorine pesticides residues. The potential risks pose to human upon consumption of the fish from the Lake was also evaluated. The two fish species *Tilapia zilli* and *Chrysichthys nigrodigitatus* were selected for the study based on their all year round availability and being major fish delicacies for Ghanaians.

Materials and Methods

Study Area

Map showing the study area is presented in figure 1. The Kpando Torkor Lake is located about 5km south west of Kpando, the capital of the Kpando district. The district lays within three physiographic regions namely the southern Voltarian plateau, the forest dissected plateau and the plains which stretch into the southern Voltarian Plateau. The Lake lies on longitude $0^{\circ}7'$ and latitude $6^{\circ}58'$. Kpando Torkor Lake constitutes a vital portion of the Volta Lake where intense agricultural activities such as irrigation and fishing occur. The Lake is an important resource which provides employment to many fishermen and fish mongers who have settled along the lake. The lake is a major source of water for the irrigation process for the production of vegetables all year round. Thus, the area apart from the fishing industry is also well known for the cultivation of vegetables and food crops. Therefore, the probable use of restricted or banned pesticides cannot be over ruled. There may also be deposition of residues of restricted or banned pesticide as a result of long range air transport associated with organochlorines and related compounds.

Sample collection

Forty two (42) samples each of *Tilapia zilli* and *Chrysichthys nigrodigitatus* were purchased from fishermen at the landing sites with scales and internal organs removed since this is the usual practice by most fish traders at the study area. This two species were selected on the basis of their regular availability throughout the year as well as their commercial

value. The fish samples were wrapped in a pre-cleaned aluminium foil and then packaged into zip lock plastic bags. They were stored in an ice chest and transported to the laboratory. On each sampling trip, twenty one (21) samples of each fish species were collected making a total of 42 samples per trip. Thus 84 samples in all were collected for analysis. Some important characteristics of fish species, including their feeding habits are presented in Table 1.

Figure 1: Map of Kpando Torkor Lake and Its Catchment Areas.



Preparation of fish samples

Fish samples were kept at -20°C until analysis within one week of sampling. The fish samples were taken from the deep freezer and thawed. The total length and body weight of the fishes were measured using a meter rule and weighing balance respectively. The muscle tissues were dissected between the dorsal and ventral portions of the fish and minced into smaller pieces using a warring blender (Kuranchie-Mensah, 2009). The operculum was also cut off leading to the subsequent removal of the gills in the case of tilapia. Three fish samples were pooled to form a composite sample of homogenized muscle tissue. The gill sample from the *Tilapia zilli* was also subjected to the same treatment. The gills of *Chrysichthys nigrodigitatus* was however, not analyzed.

Extraction and Analysis

Extraction of fish samples was carried out according to procedures described by Stoichev et al. (2005), Kuranchie-Mensah (2009) and Darko et al. (2008). About 10g portion of homogenized muscle tissue/gill was weighed into a mortar containing 30g of anhydrous sodium sulphate (35g in case of gills) and ground thoroughly using a pestle. The sample was then transferred into an extraction thimble that had been pre-cleaned with n-hexane and acetone and oven dried. The sample was Soxhlet extracted with 150ml of n-hexane/dichloromethane 1:3 v/v mixture for 10 hours. The Soxhlet procedure was monitored occasionally during the extraction to ensure that recycling is proceeding satisfactorily. After Soxhlet extraction the extract was evaporated into almost dryness using a rotary evaporator at 40°C and extract then dissolved in 10ml n-hexane and subjected to clean-up by passing it through 3g of activated florisil adsorbent column which had been packed with 1.5 g anhydrous sodium sulphate on top of the florisil adsorbent. The column was twice eluted with 10ml portions of hexane. The eluate was collected into a round bottom flask and evaporated to almost dryness. The extract was then dissolved with 2 ml ethyl acetate. About 1 ml of this was quantitatively transferred into 2 ml vial for GC analysis. A Varian CP-3800 Gas Chromatograph equipped electron capture detector was used for analysis. A volume of $1\mu\text{l}$ aliquots of extract was injected. The operation conditions were capillary column: VF – 5mS, $40\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$, temperature programme: 70°C (2min) to 180°C (1min)

25⁰C/min to 300⁰C at 5⁰C/min, injector temperature: 270⁰C, detector temperature: 300⁰C, carrier gas: nitrogen at 1.0ml/min, make up: nitrogen at 29ml/min. The pesticide residues were identified based on comparison of relative retention times to those of known standards and quantified by external standard method using peak area. The limit of quantification (LOD) was estimated as ten times the standard deviation of the blank.

Risk assessment

A basic approach used to assess the potential risk posed to ecosystems and human health by toxic effects of pollutants involves comparison of observed concentrations of pollutants in the environment with established maximum permissible levels (MPL). According to the Food and Agriculture Organization of the United Nation, Ghana's per capita consumption of fish is estimated at 25kg/year (GFA, 2010) which is equivalent to 68.5g/day. The acceptable daily intake (ADI) recommended by FAO and World Health Organization (WHO) is usually used to assess human exposure to target contaminants, without considering different eating habits and consumption rates. An individual's exposure to organochlorine pesticide residues from the fish species used for the study was achieved by calculating the estimated daily intake (EDI) in ng/kg body weight/day of organochlorine pesticides by the equation:

$$ED1 = (FDC \times CC) / BW$$

where FDC = fish daily consumption = 25kg/yr = 68.5g/day (FAO, 2010), CC = mean contaminant concentration of organochlorine pesticide, and BW = body weight; 60 kg is the typical value. To ascertain the potential public health risk of this estimated exposures, exposure values were compared to two benchmark concentrations for cancer and non cancer health effects. These benchmarks were founded on standard toxicological references. A benchmark concentration (BC) represents the daily concentration of a contaminant below which there is a high probability of no adverse health effect (Liu et al., 2010 and Dougherty et al., 2000).

Quality Assurance/Control

The quality of organochlorine pesticide residues determined was assured through the analysis of solvent blanks, procedure blanks and duplicate samples. Spiking with an internal standard (Isodrin) was also executed as well as the analysis of certified reference material. All reagents used during the analysis were exposed to same extraction procedures and subsequently run to check for interfering substances. Sample of each series was analyzed in duplicates. A mixed standard of fourteen organochlorine pesticides with concentrations of 0.005, 0.01, 0.02, and 0.05 were plotted against the peak area to obtain calibration curves. The calibration curves had $R^2 = 0.995 - 0.998$. Recalibration curves were run with each batch of samples to check that the correlation coefficient was kept above 0.99. The method for analysis was optimized and validated by spiking fish samples with 20 μ L of 0.02 ppm internal standard of Isodrin. Spiked samples were taken through same procedure as samples, and the Isodrin was measured with good recoveries between 85% and 105%. The certified reference fish material analyzed consisted of p,p'-DDE, p,p'-DDD and dieldrin and their respective recoveries were 75, 112 and 82%.

Results and Discussion

Some information on fish samples

Table 1 presents some characteristics features such as body weight, length and lipid content of the fish samples. The gills were analyzed for *Tilapia zilli* only since it constitutes a major delicacy in the head for most tilapia consumers in Ghana. This is

coupled with the fact that much higher levels of organochlorine pesticides were found in the gills in a study conducted by Yang et al. (2006) in fish from high mountain lakes and Lhasa River in the Tibetan Plateau of China. This could be explained by its larger surface areas per gram of tissue and also due to the fact that gills continuously transfer organic pollutants from both water and suspended particles onto its surface.

The length of the fish samples ranges from 20.0 to 24.4 cm and 24.5 to 43.0 cm for *Tilapia zilli* and *Chrysichthys nigrodigitatus* respectively. Their corresponding mean lengths were 21.5 cm and 29.4 cm. These mean lengths were small compared to those reported by Kuranchie-Mensah (2009). Kuranchie-Mensah (2009) reported of 26.6 cm and 42.5 cm for *Tilapia zilli* and *Chrysichthys nigrodigitatus* respectively. These reported figures by Kuranchie-Mensah were for samples collected from the Densu Basin in Ghana.

The average lipid content of muscle and gill of *Tilapia zilli* were 2.80% and 14.49% respectively whilst that for *Chrysichthys nigrodigitatus* muscle was 10.24%. The effects of pesticide residues on fish, as on other vertebrates, will depend in part on the condition of the fish, which is primarily determined by the lipid content of the tissues.

In times of physiological stress, such as starvation or spawning, these lipid reserves are metabolized, and the pesticide content of the remaining lipids will be increased, perhaps to a level at which the pesticide circulating in the vascular system may become toxic for some target organs or nerve centre (Holden, 1966). Although, the fat content of *Chrysichthys nigrodigitatus* muscle was higher than that of *tilapia zilli* muscle and gill tissues analyzed, the measured organochlorine pesticide residues was however, higher in the later. This observation, however, agrees with that reported by Kuranchie-Mensah (2009) on similar fish species from the Densu River Basin. This might however, be due their different feeding habits as well as the difference in their abilities to metabolize and excrete these contaminants.

General Organochlorine Pesticide Residues Contamination

Table 2 shows the individual organochlorines, their respective concentrations (mean and range) and percentage occurrence. Margin of errors are standard deviation based on replicates determination of each organochlorine. The Table also shows the total residue load in the muscles and gills of the fish species.

In all, fifteen organochlorine pesticide (OCP) residues were investigated, however, thirteen OCPs namely β -HCH, δ -HCH, p,p'-DDT, p,p'-DDD, p,p'-DDE, heptachlor, aldrin, dieldrin, γ -chlordane, α -endosulfan, β -endosulfan, endosulfan sulphate and methoxychlor were detected. Alpha HCH, γ -HCH and endrin were not detected. Afful et al. (2010) also detected fourteen organochlorines pesticides in fish samples from the Densu River in Ghana. The detection of these OCPs is not surprising because OCPs have been identified to be among the major pollutants introduced into the marine environment in Ghana and are discharged into the coastal environment from both industrial and agricultural activities (Nyarko et al. 2011). The mean concentrations of the thirteen detected OCPs ranged from 0.10 to 37.75ng/g wet weight whilst their percentage occurrence ranged from 17 to 100%. The highest mean concentration of 37.75 was recorded for heptachlor in the gill of *Tilapia zilli*. Thus the contamination of organochlorines in fish samples followed the order heptachlor (*Tilapia zilli* gill) > δ -HCH (*Tilapia zilli* muscle) > p,p'-DDD (*Tilapia zilli* muscle) > β -HCH (*Tilapia*

zilli muscle) > methoxychlor(*Tilapia zilli* gill) > α -endosulfan(*Tilapia zilli* muscle) > p,p'-DDE(*Tilapia zilli* gill) > dieldrin(*Tilapia zilli* muscle) > β -endosulfan(*Chrysichthys nigrodigitatus* muscle) > aldrin(*Tilapia zilli* muscle) > γ -chlordane(*Tilapia zilli* muscle) > p,p'-DDT(*Tilapia zilli* muscle gill). The frequency of occurrence was also of the order β -HCH = δ -HCH = p,p'-DDD = endosulfan sulphate = heptachlor > methoxychlor > γ -chlordane. Thus the most ubiquitous organochlorines detected in the study area were β -HCH, δ -HCH, p,p'-DDD, endosulfan sulphate and heptachlor. The highest total organochlorine pesticides residue load (i.e. the sum of the means of all detected organochlorine pesticides in a particular sample) of 66.70ng/g wet weight was recorded for *Tilapia zilli* muscle while the gills of *Tilapia zilli* recorded a total residual load of 63.44ng/g wet weight. In the case of *Chrysichthys nigrodigitatus* muscle, residual load of 33.23ng/g wet weight was obtained. These results show that the consumption of these fish species may have the tendency of elevating the overall levels of OCP residues in the individual since these residues have bio-accumulative effect.

Analysis of some Individual Organochlorine Pesticide DDT and metabolites

Figure 2 shows the distribution of p,p'-DDT and its metabolites, p,p'-DDE and p,p'-DDD in the fish samples investigated. In Ghana DDT had been used extensively in the past for agriculture activities. However, the use of DDT in Ghana has now been limited only to malaria programs to fight mosquitoes. Indeed its usage in agriculture had been banned by the Environmental Protection Agency (EPA) of Ghana. Mean concentrations of DDTs ranged from 0.15 to 10.06 ng/g. Results of the study showed higher concentration of p,p'-DDD than the other two pollutants in all the samples. The total concentration of p,p'-DDE and p,p'-DDD is higher than that of the parent p,p'-DDT. The ratio DDT / (DDE+DDD) was less than 1 in all samples. The low concentration of p,p'-DDT compare to total concentration of its metabolites is an indication that there might not be fresh input of the parent DDT in the study area. This therefore, suggests that DDT concentrations in the fish samples from Kpando Torkor Lake might mainly be due to historical use. It can also be a confirmation of the high rate of degradation of DDT under hot, dry climatic conditions as reported by Jiries et al. (2002) which is typical of tropical environment. It can therefore, be deduced that the effort of Ghana's EPA in reducing DDT in the environment is yielding the desired results. DDT concentrations have been reported in other fresh water fish species in Ghana (Afful et al. 2010; Ntow 2005). Afful et al. (2010) reported of mean concentration of 0.6, 0.8, 7.5 ng/g for p,p'-DDT respectively in *Clarius gariepinus*, *Chrysichthys nigrodigitatus* and *Heterotis niloticus* species sampled from the Densu basin in Ghana. These reported values compare favorably with values obtained from this study. DDT concentrations have also been reported in fish samples across the globe (Kannan et al. 1995; Sapozhnikova et al. 2004; Yim et al. 2005; Yang et al. 2006; Darnerud et al. 2006; Liu et al., 2010; Klump et al. 2002; Meng et al. 2007). The average DDT concentrations obtained in this current study were lower than those reported by Yang et al. (2006) at Dallian in China (212.16 ng/g), Klump et al. (2002) at Xiamen in China (220 ng/g), and Meng et al. (2007) in Indonesia (28ng/g), in Liaoning Province, China (18.54ng/g), Guangdong Province, China (6ng/g), Australia (22ng/g), India (15ng/g), Thailand (6.2ng/g), Solomon Islands (4.8ng/g), Korea (8.96ng/g), Sweden (7.02ng/g) and Salton Sea, USA (17.6ng/g).

The mean concentration in tilapia fish is however, higher than 0.43ng/g reported in Papua New Guinea.

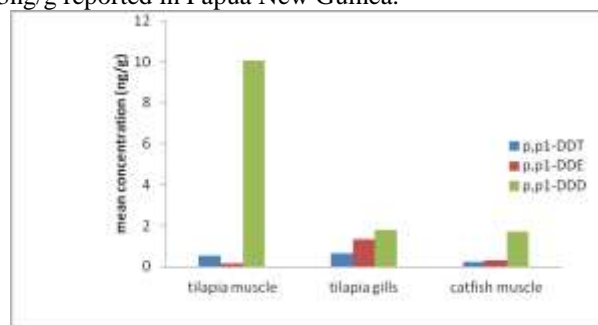


Fig 2: Distribution of p,p'-DDT, p,p'-DDE and p,p'-DDD in the fish samples

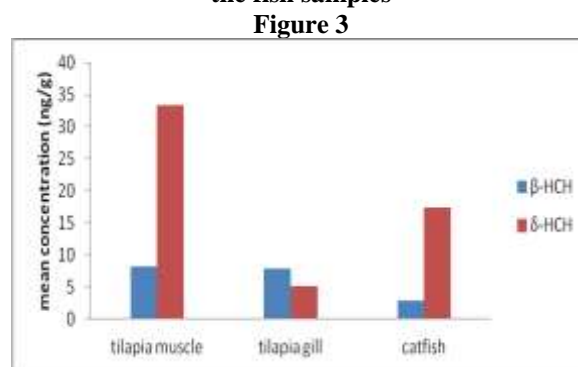


Figure 3

Hexachlorocyclohexane (HCH)

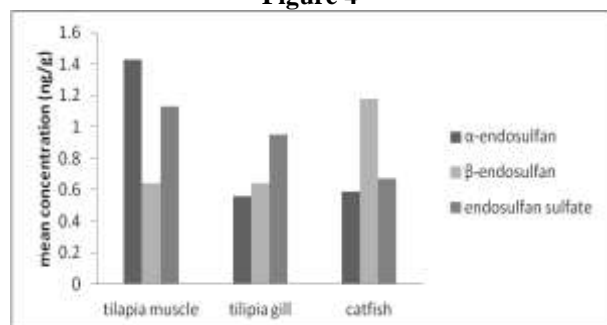
Hexachlorocyclohexane is a chemical that exist in eight isomeric forms. The most popular of forms are α , β , γ , δ - HCH. Research has shown that only one of the isomers, the gamma isomer, has insecticidal properties and was sold as insecticide under the trade name lindane (Baird 1997; Nollet 2000). In Ghana lindane was used widely in the cocoa industry to control the insects that spread the swollen shoot disease. It was also used by vegetable growers. Because of its persistency its usage in Ghana has been discontinued. Figure 3 shows the distribution of HCHs in the samples. In all the samples analyzed, γ and α isomers were not detected. Only two of the isomers, β and δ were detected, and they were identified in all the fish samples. The mean concentration for β -HCH and δ -HCH ranged from 2.78 to 33.40 ng/g wet weight. The highest mean concentration of 33.40 ng/g was obtained for δ -HCH in the tilapia muscle. In a study of organochlorines in fish samples from Lake Bosumtwi in Ghana, Darko et al. (2005) reported of mean concentration of 0.70 to 1.36 ng/g wet weight for γ -HCH. Adeyemi et al. (2008) also reported of levels of 559000 and 118200 ng/g in *Tilapia zilli* and *Chrysichthys nigrodigitatus* respectively from the Lagos lagoon. These values reported in the Lagos Lagoon were high compared to levels recorded in this study. The average of the mean concentrations of both β -HCH and δ -HCH in fish samples, 12.45ng/g ww in this study is more than 0.126ng/g lipid weight measured for Lindane in tilapia obtained from Lake Bosumtwi by Darko et al. (2008). It is also higher than HCH mean values in fish in Sweden (0.96ng/g) (Darnerud et al., 2006), Thailand (0.82ng/g), Australia (0.34ng/g), Indonesia (0.73ng/g), Papua New Guinea (0.57ng/g), the Solomon Islands (0.53ng/g) (Kannan et al., 1995), Korea (0.94ng/g) (Yim et al., 2005) and Vietnam (1.8ng/g) (Kannan et al., 1995) but lower than that in India (28ng/g) (Kannan et al., 1995).

Endosulfan and metabolite

Technical endosulfan consists of α - and β - isomers. In the environment, the cyclic sulphite group of endosulfan can be

oxidized to the corresponding sulphate, thus endosulfan sulphate. (Chandler et al. 1991; Guerin et al.1992; Kathpal et al. 1997). The metabolite, endosulfan sulfate is more persistent in the environment than its parents (Guerin, 2001). In Ghana endosulfan had extensively been used for agricultural activities. Its usage has now been restricted only to the cotton industry by EPA. Figure 4 shows how the endosulfans were distributed in the samples.

Figure 4

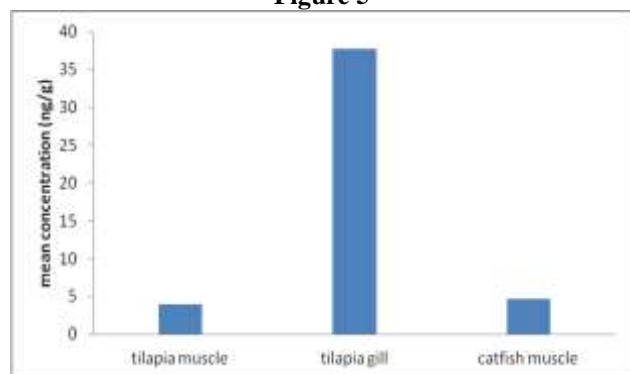


The mean concentration of the endosulfans ranged from 0.56 to 1.43 ng/g. The highest mean concentration of 1.43 was obtained for α -endosulfan in the tilapia muscle. The β isomer was the dominant endosulfan in the catfish while the metabolite endosulfan sulfate was dominant endosulfan in the tilapia gill. Darko et al. (2008) reported a mean concentration 0.713ng/g of endosulfan in fish samples from the Bosumtwi Lake in Ghana. Afful et al. (2010) also reported of mean concentrations of 8.5, 1.7 and 9.5 ng/g for endosulfan sulfate in *Channa obscura*, *Hepsetus odoe*, and *Tilapia zilli* respectively from the Densu River. These reported values compare positively with results of this study.

Heptachlor

In Ghana heptachlor is among the banned organochlorines pesticides in Ghana. It should however, be noted that it had been used in the past extensively as a termiticide and pesticide in homes and on food crops (Gerken et al. 2001). Figure 5 presents the distribution of the chemical in the fish samples.

Figure 5



The mean concentrations of the chemical in the samples ranged from 4.02 to 37.75 ng/g wet weight with the average concentration of heptachlor dominating in tilapia gill. The average concentration of the chemical obtained in muscles of tilapia and catfish were almost the same. Heptachlor has been investigated by other researchers in Ghana (Adu-Kumi et al. 2010; Afful et al. 2010). Adu-Kumi et al. (2010) reported lower concentrations of heptachlor residues in the Volta Lake compared to values obtained from this study. However, results obtained by Afful et al. (2010) in fish species from the Densu basin of Ghana were comparable to those obtained for this investigation.

Potential health risks upon consumption of fish from Kpando Torkor Lake.

Risks involved in consumption of the fish from the study area in terms of organochlorine pesticide residues was determined by estimating the average daily intake (EDI) of the pollutants and comparing EDI with benchmark concentrations for cancer and non-cancer. A benchmark concentration (BC) represents the daily concentration of a contaminant below which there is a high probability of no adverse health effect (Liu et al. 2010 and Dougherty et al. 2000). Table 3 shows the results of estimated daily intake (EDI), non-cancer BC and cancer BC.

These EDIs were compared to the two benchmarks by calculating hazard ratios (HR) for each contaminant. Hazard ratios were estimated by dividing the EDIs by the respective benchmark concentrations.

Hazard ratio greater than one (hazard ratio >1) indicates that the average exposure level exceeds the corresponding benchmark concentration and vice versa. All the calculated hazard ratios in this study were less than one (< 1). Hence the extent of non-carcinogenic and carcinogenic health risks in terms of OCPs contamination resulting from consumption of fish from the study area is highly insignificant. The total amount of OCP contaminants consumed through these fish samples might even be less based on previous studies, which reported that cooking and processing of fish decreases contaminants levels of chlordane, DDT, dieldrin, dioxins and PCBs with average losses ranging from 20 to 46% (Voiland et al.1991; Sherer and Price 1993, Zabik 1995; Zabik et al.1995). Consumption of fish from Kpando Torkor Lake will therefore, pose little or no health risks in terms of OCP residues in the short, medium and long terms. It must however, be emphasized that certain drawbacks in exposure estimation may give rise to some level of uncertainty in the risk analysis. Prominent among these limitations were same human body weight, inability to consider different ages and their fish consumption rates. The use of mean concentrations could lead to under-estimation

Conclusion

The investigation has shown that organochlorine pesticide residues are present in *Tilapia zilli* and *Chrysichthys nigrodigitatus* fish species from the Kpando Torkor Lake at concentrations that may not pose potential health risk to consumers. Indeed, the estimated hazard ratios (HRs) for all the OCPs were far lower than one (HR <<< 1).Thirteen OCPs in all were detected in the study area and the frequency occurrence ranges from 17 to 100 %. Heptachlor, β -HCH, δ -HCH, p,p¹-DDD and endosulfan sulfate were the most ubiquitous OCP in the study area.

The metabolites p,p¹-DDE, p,p¹-DDD of p,p¹ DDT and endosulfan sulfate of endosulfan were detected. The ratio of concentration of p,p¹ DDT to the sum of the concentrations of p,p¹-DDE and p,p¹-DDD was less than one (i.e p,p¹-DDT/ (p,p¹-DDE+ p,p¹-DDD) < 1) is an indication that there might not be fresh input of DDT in the study area. It is also advisable that fish protein patrons depend more on African catfish than Nile tilapia or possibly alternate these fish species in their diet rather depending solely on Nile tilapia as their delicacy. This will guarantee their long term safety from the chronic effects of OCPs.

There is the need for continuous monitoring of Kpando Torkor Lake and its vital fish resource for this and other pollutants so as to assure consumers of the fish product from this Lake of their sustainable and reliable protein source.

Acknowledgments

The authors graciously and thankfully appreciate the immeasurable contribution of Mr. Bob Essien, Mrs. Dorothy Akaho and Dr Raphael Clarke all of Chemistry Department, University of Ghana and Mrs. Afidemenyo Rhoda Gbeddy of Judicial Service (Exchange), Ghana.

References

- Adu-Kumi S, Kawano M, Shiki Y, Yeboah PO, Carboo D, Pwamang J, Morita M, Suzuki N, (2010). Organochlorine pesticides (OCPs), dioxin-like polychlorinated biphenyls biphenyls (dl-PCBs), polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in edible fish from Lake Volta, Lake Bosomtwi and Weija in Ghana. *Chemosphere* 81: 675 – 684
- Afful S, Anim AK, Serfor-Armah Y (2010). Spectrum of organochlorine pesticide residues in fish samples from the Densu basin. *Res. J. of Environ. & Earth Sci.* 2(3): 133 – 138
- Baird C (2005). *Environmental Chemistry*, 3rd edition: 307-333. W.H. Freeman and Company, New York, USA
- Chandler GT, Scott GI. (1991). Effects of sediment-bound endosulfan on survival, reproduction and larval settlement of meiobenthic polychaetes and copepods. *Environ. Toxicol. Chem* 10:375–383.
- Darko G, Akoto O, Opong C (2008). Persistent organochlorine pesticide in fish, sediments and water from Lake Bosomtwi, Ghana. *Chemosphere* 72: 21-24.
- Darnerud PO, Atuma S, Aune M, Bjerselius R, Glynn A, Grawe KP, Becher W (2006)
- Dietary intake estimations of organohalogen contaminants (dioxins, PCB, PBDE and chlorinated pesticides, e.g. DDT) based on Swedish market basket data. *Chem. Toxicol.* 44:1597–1606.
- Dougherty PC, Holtz SH, Reinert JC, Panyacosit L, Axelrad DA, Woodruff TJ (200) Dietary exposure to food contaminants across the United States. *Environmental Research Section A* 84: 170-185.
- Gerken A, Suglo JV, Braun M (2001). Crop protection policy in Ghana for Ministry of food and Agriculture. Integrated crop protection project. PPRST GTZ, Pokuase/Accra
- Global Fish Alliance (GFA), (2010). The Importance of Captured Fisheries in Food Security in Ghana. www.globalfishalliance.org/03_Ghana_G-FISH_Food_Security_8-09.pdf. Accessed November 2010.
- Guerin TF, Kennedy IR (1992). Distribution and dissipation of endosulfan and related cyclodienes in sterile aqueous systems: implications for studies on biodegradation. *J. Agr. Food Chem.* 40:2315–2323
- Guerin TF (2001). Biological loss of endosulfan and related chlorinated organic compounds in aqueous systems in the presence and absence of oxygen. *Environ. Pollut.* 115:219–230.
- Holden AV (1966). Organochlorine insecticide residues in salmon fish. *J. of Appl. Ecol.* 3; 45-53.
- Jiries AB, Al Nasir FM, Beese F (2002). Pesticide and heavy metals residue in waste water, soil and plants in waste water disposal site near Al-Lajoun Valley, Karak/Jordan. *Water, Air Soil Pollut.* 133: 97–107.
- Kannan, K., Tanabe, S. and Tatsukawa, R. (1995) Geographical distribution and accumulation features of organochlorine residues in fish in tropical Asia and Oceania. *Environ. Sci. Technol.* 29:2673–2683.
- Kathpal TS, Singh A, Dhankar JS, Singh G. (1997). Fate of endosulfan in cotton soil under sub-tropical conditions of northern India. *Pestic. Sci.* 50:21–27.
- Klump DW, Hong HS, Humphrey C, Wang XH, Codi S (2002) Toxic contaminants and their biological effects in coastal waters of Xiamen, China. I. Organic pollutants in mussel and fish tissues. *Mar Pollut Bull* 44:752–760.
- Kuranchie-Mensah H (2009). Studies of organochlorine pesticide residue in fish, water and sediment from the Densu River basin. MPhil Thesis in Environmental protection, University of Ghana.
- Liu Z, Zhang H, Tao M, Yang S, Wang L, Ma D, He Z (2010). OCPs in consumer fish and mollusks of Liaoning Province, China: distribution and human exposure implications. *Arch. Environ. Contam. Toxicol.* 59: 444-453.
- Martinez MP, Angulo R, Pozo R, Jodral M (1997). Organochlorine pesticides in Meng, pasteurized milk and associated health risks. *Food Chem. Toxicol.* 35: 621.
- Muir D, Sverko E (2006). Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: A critical appraisal. *Anal. Bioanal. Chem.* 386:769–789.
- Nyarko E, Botwe BO, Bampoe AA, Addo S, Armah AK, Ntow WJ. (2011). Organochlorine pesticide residues in *Sardinella aurita* from the coastal waters of Accra-Tema, Ghana and their potential health risks. *J. of Ghana Sci. Assoc.* 13(1): 39 – 46.
- Ntow JW (2005). Pesticide residues in Volta Lake, Ghana. *Lake and Reservoirs: Research and Management.* 10: 243–248.
- Roche R, Tidou A, Persic A (2007). Organochlorine pesticides and biomarker response in two fishes *Oreochromis niloticus* (Linnaeus, 1758) and *Chrysichthys nigrodigitatus* (Lacepede, 1803) and an invertebrate, *Macrobrachium vollenhovenni* (Herklot, 1857) from the Lake Taabo (Cote d'Ivoire). *J. Appl. Sci.* 7(24):3860-3869.
- Sapozhnikova Y, Bawardi O, Schlenk D (2004). Pesticides and PCBs in sediments and fish from Salton Sea, California, USA. *Chemosphere* 55:797–809.
- Sherer RA, Price PS (1993). The effect of cooking processes on PCB levels in edible fish tissue. *Qual. Assur.* 2: 396-407.
- Stoichev T, Rizov N, Kolarska, A., Ribarova, F. and Atanassova, M. (2005). Comparison of extraction procedures for determination of organochlorine pesticides in Fish. *40(3):* 251-254.
- Trotter WJ, Dickerson R (1993). Pesticide residues in composite milk collected through the US pasteurized milk network. *JAOAC Int.* 76, 1220.
- UNEP Stockholm Convention on POPs, (2009). The Nine New POPs ; An introduction to the nine chemicals added to the Stockholm Convention by the Conference of the Parties at its fourth meeting.
- USEPA (U.S. Environmental Protection Agency), (2006). Guidance for assessing chemical contaminant data for use in fish advisories. Vol. 2: Risk assessment and fish consumption limits.
- Voiland MP, Gall KL, Lisk DJ, MacNeill DB (1991). Effectiveness of recommended fat-trimming procedures on the reduction of PCB and mirex levels in brown trout from Lake Ontario. *J. Great Lakes Res.* 17:454-460
- Yang R, Tandong Y, Baiqing X, Guibin J, Xiaodong X (2006). Accumulation features of OCPs and heavy metals in fish from high mountain lakes and Lhasa river in the Tibetan plateau. *Environment International* 33: 151-156.

Yim UH, Hong SH, ShimWJ, Oh JR (2005). Levels of persistent organochlorine contaminants in fish from Korea and their potential health risk. Arch. Environ.Contam.Toxicol. 48:358–366.

Zabik ME, Zabik MJ (1995).Tetrachlorodibenzo-p-dioxin residue reduction by Zabik, M. E.,cooking/processing of 7sh 7llets harvested from the Great Lakes. Bull. Environ. Contam. Toxicol.55:264-269.

Zabik MJ, Booren AM, Daubenmire S, Pascall MA, Welch R, Humphrey H (1995). Pesticides and total polychlorinated

biphenyls residues in raw and cooked walleye and white bass harvested from the Great Lakes. Bull. Environ.Contam.Toxicol.54:396-402.

Zeng EY, Yu LP, Mai BX, Luo XJ, RanY (2007). Persistent halogenated hydrocarbons in consumer fish of China: regional and global implications for human exposure Environ. Sci. Technol. 41:1821–1827.

Table 1: Some important Information on Fish Species from Kpando Torkor Lake

Species (Scientific name)	Mean Fresh Body weight (g)± SD	Length(cm) ^a Mean± SD (Range)	Fat Content (%)		Feeding habit
			Muscle	Gill	
			Mean±SD (Range)	Mean±SD (Range)	
Nile Tilapia (<i>Tilapia zilli</i>)	164.86 ± 29.31	21.5 ± 1.1 (20.0 -24.4)	2.80 ± 1.83 (1.37 -5.60)	14.49 ± 4.28 (9.77 -19.41)	Herbivore; Plankton and Benthic algae
African catfish (<i>Chrysichthys nigrodigitatus</i>)	221.82 ± 131.21	29.4 ± 4.6 (24.5 - 43.0)	10.24 ± 4.70 (2.31 -15.91)	Omnivore; Seeds, insects bivalves and detritus

^a length measured from the anterior of the head to the end of the tail; SD= standard deviation

Table 2: Concentrations (mean ±SD, range in ng/g wet weight) and percentage occurrences of detected organochlorine pesticides in the fish species.

OCP Residue	<i>Tilapia zilli</i> , ng/g, ww. [n=15]							<i>Chrysichthys Nigrodigitatus</i> , ng/g, ww. [n=15]		
	Muscle			Gill			Average of Means	Muscle		
	Range	Mean± SD	% Occur.	Range	Mean± SD	% Occur.		Range	Mean ± SD	% Occur.
β-HCH	0.49-19.24	8.22± 8.15	100	2.80 -10.72	7.84± 3.06	100	8.03	0.39 -7.89	2.78± 2.95	100
δ-HCH	4.34-60.70	33.40± 24.95	100	0.60 -16.01	5.08± 5.54	100	19.24	2.67-37.86	17.35±13.78	100
p,p'-DDT	<LOQ-0.89	0.53± 0.35	50	<LOQ-0.89	0.67± 0.24	54	0.60	<LOQ-0.30	0.25± 0.07	33
p,p'-DDD	0.38 - 22.40	10.06± 9.21	100	0.72 - 2.92	1.79± 0.71	100	5.93	0.10 - 3.87	1.71±1.42	100
p,p'-DDE	<LOQ-0.20	0.15± 0.06	67	<LOQ-1.35	1.35± 0.36	17	0.75	<LOQ-0.49	0.30±0.28	33
Heptachlor	2.20 - 5.90	4.02± 1.30	100	1.33-85.35	37.75±32.31	100	20.89	0.10-13.28	4.73± 5.02	100
Aldrin	<LOQ-2.07	1.14± 0.83	83	0.57	<LOQ-0.89	0.89±0.53	17
Dieldrin	<LOQ-2.39	1.29± 1.21	67	<LOQ-0.59	0.59±0.14	17	0.94	<LOQ-0.10	0.10±0.06	17
γ-Chlordane	<LOQ-2.27	1.02± 1.01	83	0.10 - 2.51	0.84±0.85	100	0.93	<LOQ-0.79	0.49±0.30	50
α-Endosulfan	<LOQ-1.68	1.43± 0.49	33	<LOQ-0.56	0.56±0.21	17	0.95	<LOQ-0.59	0.59±0.40	17
β-Endosulfan	<LOQ-1.18	0.64± 0.76	33	<LOQ-0.90	0.64±0.31	50	0.63	<LOQ-1.18	1.18±0.92	17
Endosulfan sulphate	0.10 - 3.44	1.13± 1.24	100	0.10 - 3.48	0.95±1.27	100	1.04	0.39 - 1.39	0.67±0.36	100
Methoxychlor	<LOQ-7.39	3.76±3.30	83	3.26 - 8.21	5.40±1.74	100	4.58	0.49 - 5.82	2.19±1.88	100
		^a Load=66.70			^a Load=63.44				^a Load=33.23	

<LOQ= less than limit of quantification (ten times the standard deviation of the blank); SD= standard deviation; n= number of composite samples; % Occ. =percentage occurrence; ^aLoad=total of the means of all the organochlorine pesticide residues in a sample; ww= wet weight and Average of Means= average of the mean OCP concentrations for tilapia muscle and gill.

Table 3: Human Estimated Exposures to Organochlorine Pesticide (OCP) Residues and Benchmark Concentration (BC) for Organochlorine Pesticides in Fish.

OCPs	Sample	EDI (ng/kg body weight/day)	Non-cancer BC (ng/kg body weight/day) ^a	Non-cancer Hazard Ratio	Cancer BC (ng/kg body weight/day) ^b	Cancer Hazard Ratio
HCH	TF	7.38	300	0.025	1408	0.005
	CM	11.50	300	0.038	1408	0.008
DDT	TF	0.76	500	0.002	5383	0.0001
	CM	0.29	500	0.001	5383	0.00005
γ- Chlordane	TF	0.96	500	0.002	5230	0.0002
	CM	0.56	500	0.001	5230	0.0001
Endosulfan	TF	0.82	6000	0.0001
	CM	0.92	6000	0.0002
Heptachlor	TF	23.85	500	0.048
	CM	5.40	500	0.011
Methoxychlor	TF	5.23	500	0.010
	CM	2.50	500	0.005