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# Organochlorine pesticide levels in irrigation water of the golinga dam, Tolon District Ghana

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**ABSTRACT**

Golinga irrigation scheme is one of the few schemes in the Northern Region of Ghana. In this paper, types and levels of Organochlorine pesticide residues in the dam water have been investigated. Water samples were taken at two intervals (before and after crop planting) during the 2012 farming season. Water samples were processed using a liquid-liquid extraction method and gas chromatography equipped with electron capture detector (GC-ECD). Twenty- one (21) different organochlorine residues were identified namely: α-HCH (0.094 μg/g), β-HCH (0.21 μg/g), γ-HCH (0.109 μg/g), δ-HCH (0.23 μg/g), HCB (0.12 μg/g), Heptachlor (0.27 μg/g), Aldrin (0.25 μg/g), Cis-heptachlor epox (0.14 μg/g), Trans-heptachlor epox (0.080 μg/g), Trans-chlordane (0.123 μg/g), Cis-chlordane (0.076 μg/g), Trans-nonachlor (0.27 μg/g), Dieldrin (0.17 μg/g), Endrin (0.083 μg/g), O'P-DDE (0.15 μg/g), P'P-DDE (0.18 μg/g), O'P-DDD (0.36 μg/g), P'P-DDD (0.061 μg/g), O'P-DDT (0.126 μg/g). P'P-DDT recorded highest concentration of 0.52 μg/g whiles mirex recorded the least of - 0.057 μg/g. All residues except mirex were above the WHO Maximum Residue Limit (MRL) for drinking water. These compounds in the dam pose serious health hazards to humans, aquatic life and irrigated crops thus usage of chemicals which result in pollution of the dam should be controlled.



## Introduction

Pesticides are formulated for the purposes of killing pests and may refer to insecticides, herbicides, fungicides, or other pest control formulations inherently toxic and often associated with adverse health effects in non-target organisms (USEPA, 2009). Insecticides are mainly organochlorines, organophosphorus, carbametes and pyrethroids. Organochlorine compounds are synthetic organic insecticides that contain carbon, hydrogen, chlorine and sometimes oxygen. The essential structural feature about organochlorine insecticides is the presence of carbon-chlorine bond or bonds (Stimman *et al.*, 1985). They are characterized by high persistence, low polarity, low aqueous solubility and high lipid solubility and as a result they have a potential to bio-accumulate in the food chain posing a great threat to human health and the environment globally (Lars, 2000).

For several decades, pesticides have been employed in agriculture not only to control and eradicate crop pests but also in the public health sector for disease vector control in Ghana (Hodgson, 2003). Organochlorine pesticides have been used in Ghana for more than 40 years, for agriculture and public health purposes with their residues having been found in water, sediments and crops and in humans (Ntow, 2001).

Organochlorine have been implicated in a broad range of adverse human health effects including reproductive failures and birth defects, immune system malfunction, endocrine disruptions, and cancers (Garabrant *et al.,* 1992). The Golinga irrigation scheme is one of the few irrigation schemes in the northern region of Ghana which supplement agricultural production during the dry season. This scheme is mainly for the production of rice and vegetables and for domestic purposes by the inhabitants. Farmers in this scheme catchment area, as a result of their farming activities use pesticides in the environment. Increase accumulation of these chemicals in the food chain may pose serious health hazards in the general populace (Jayashree and Vasudevan, 2007). The study assessed the types and levels of Organochlorine pesticide in the dam water of the Golinga irrigation dam located in Tolon District of Ghana.

## Materials and Methods

### Study Area and Data Collection

The study area is the Golinga irrigation dam in the Tolon District of the Northern Region of Ghana. Golinga lies between latitudes 09º 15 and 10º 02 N and Longitudes 0º 53 and 1º 25 W. Farmers mainly produce rice and vegetables as well as fishing and potable water supply for domestic purpose.

Water samples were taken at two (2) intervals during the main cropping season that is, before planting and after planting. Six (6) water samples were taken at each sampling time. For each period of sampling, six (6) drops of hydrochloric acid was used to preserve the samples and samples were stored in an ice chest at 4 ºC and transported to the laboratory for analysis.

### Reagents and Laboratory Analysis

Reagents which were used for the extraction and analysis of the samples include hexane, ethyl acetate, sodium sulphate and hydrochloric acid.

### Liquid-Liquid Extraction

The separating or liquid-liquid method was used for the extraction of the organochlorine. 10 ml of the water sample which have been kept in a refrigerator and allowed to cool was measured and poured into a separating funnel, 30 ml of the ethyl acetate was added to the sample and shaken vigorously, the separating funnel was allowed to stand until the two liquids separated, with the organic on top and the aqueous layer beneath. Filter paper was folded and placed into a funnel and then allowed to stand in a conical flask. Sodium sulphate

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anhydrous was spread in the filter paper to help absorb any extra water that might accompany the extract. The tap of the separating funnel was opened gently to allow the liquid beneath which was waste to flow out, whilst taking notice of the separation, when all of the water got out leaving the organic layer, the tap was closed. The folded filter paper with sodium sulphate was placed under the separating funnel and then the organic layer was allowed to flow through it into the round bottom flask, the collected water phase was re-extracted twice with two separate aliquot of 30 ml ethyl acetate. The combined collected organic phase was evaporated to dryness by the rotary evaporator with water bath at 44 °C. The dried combined organic phase was dissolved in 20 ml of hexane. The same extraction procedure was followed for all other individual water samples.

**Gas Chromatographic Method**

The gas chromatograph was a Shimadzu 2010 (from Shimadzu Corporation, Analytical & Measuring Instruments Division, Kyoto, Japan) series equipped with Electron Capture Detector (ECD), split/split less injector (with volume of 1.0 µl), AOC-20s auto sampler and AOC-20i auto injector system. The column was Restek Rtx -1 capillary column with dimension 30 m x 0.25 mm x 0.25 µm. The carrier gas was nitrogen gas supplied from ANG 2381HC nitrogen - air generator with a column flow of 1.18 mL/min. The column temperature was programmed from 90 $^{o}$C (3 minutes) to 275.0 $^{o}$C (20 minutes) at the rate of 5 $^{o}$C /minute. The injector port (SPL 1) was set as follows: temperature at 250 $^{o}$C, injection mode as split less, flow control mode at pressure of 118.5 kPa, total flow rate of 63.5 ml/min, column flow rate of 0.70 ml/min, linear velocity at 17.9 cm/sec, and purge flow rate of 3.0 ml/min.

The detector was programmed as follows: temperature at 300 $^{o}$C, sampling flow rate of 40 ml/min, current of 1.00 nA, and makeup flow rate of 30.0 ml/min. The UNEP PCB Standard Mix reference material was used for the analysis. This is a mix standard for the determination of α-HCH, *ß*-HCH, ɣ-HCH, δ-HCH, O, P'-DDD dichlorodiphenyldichloroethane ; P, P'- DDE – dichlorodiphenyldichloroethylene ; O, P'-DDE, O, P'-DDT, P, P'-DDT, aldrin, dieldrin, heptachlor, trans-heptachlor epoxide, cis-heptachlor epoxide, trans-nanochlor, and trans-chlordane. The standard was serially diluted (with factors of 5, 10, 20, 50, 100, 200 respectively) and the retention times determined for each concentration. The calibration curves were then constructed for the analysis of the pesticide residues of the water samples.

**Results and Discussions**

**Organochlorine Pesticide Residues in Dam Water**

Twenty one (21) Organochlorine residues in the range of - 0.057 to 0.52 µg/g were detected under the categories of DDT, Hexachlorocyclohexane Chlordane and their respective Isomers, Heptachlor and Heptachlor Epoxide, Aldrin, Dieldrin and Endrin, Hexachlorobenzene and Mirex. p'p - DDT recorded the highest of 0.52 µg/g whilst mirex recorded the lowest concentration of - 0.057 µg/g. All the Organochlorine pesticide residues detected were found to be comparatively above the World Health Organization (WHO) Maximum Residue Limits (MRL) except for mirex which was below the limit.

**Organochlorine Residue Levels**

**DDT and Its Isomers**

Isomers of DDT identified in the samples of the study were o'p-DDE, p'p-DDE, o'p-DDD, p'p-DDD, o'p-DDT and p'p-DDT. With the results of the study, p'p-DDT recorded the highest concentration of 0.52 µg/g whilst p'p-DDD recorded 0.006 µg/g. According to WHO (1979), commercial DDT is a mixture of several closely related compounds with the major component of p'p isomer being 77% and the o'p isomer is 15%. The remaining components are dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD). Mean concentration of DDT and its metabolite such as DDE (< 0.368 µg/L) had been reported from the Lagos lagoon by Adeyemi *et al.,* (2011). The study results indicate concentrations of DDT and its metabolite such as DDE at extremely high levels compared to the results obtained by Adeyemi *et al.,* (2011). Figure 1 presents the concentrations of the isomers of DDT during the study

**Hexachlorocyclohexane (HCH) and Its Isomers**

The isomers of HCH identified in the analyzed water samples were α-HCH, β-HCH, γ-HCH (lindane) and δ-HCH and their concentrations are as shown in Figure 2. Amongst the isomers of HCH, δ-HCH recorded the highest concentration of 0.26 µg/g whilst α-HCH recorded the least concentration of 0.094 µg/g. Bempah *et al.* (2011) indicated that, γ-HCH (lindane) is a reasonably stable compound and only under alkaline condition decomposes to yield trichlorobenzene and it is considered as one of the less persistent organochlorine pesticide. The results of the current study indicated that γ-HCH realized low level of concentration of 0.109 µg/g. In a study by ATSDR (1994), γ-HCH does not remain in water longer than thirty days thus affirming the lower concentration in the study. The high concentrations of δ-HCH (0.23 µg/g) and β-HCH (0.21 µg/g) might be as a result of the ability of HCH isomers to break down quickly in water.

**Heptachlor and Heptachlor Epoxide**

A higher concentration of heptachlor (0.27 µg/g) was observed in the study whilst its epoxide isomers, that is, the cis- and trans- heptachlor epoxide recorded 0.14 and 0.08 µg/g as shown in Figure 3. ATSDR (2007) reported that, heptachlor sticks to soil very strongly and evaporates slowly into the air but does not dissolve easily in water. Heptachlor epoxide dissolves more easily in water than heptachlor does and evaporate slowly from water. The high concentration of heptachlor in this study can be attributed to its persistence in the soil as applied on farmlands and washed downstream by the effect of rain.

**Chlordane and Its Isomers**

Figure 7 that, among the isomers of chlordane identified, trans-nonachlor recorded the highest concentration with cis-chlordane being the least and according to US EPA (2004), the addition of one more chlorine atom to the chlordane structure (trans-nonachlor) increases the melting and boiling point for trans-nonachlor, decreases the water solubility and decreases the vapour pressure. The reverse occurred in this study. The high concentration of chlordane might be attributed to the excessive use of this pesticide by nearby farmers in the catchment area of the dam.

**Aldrin, Dieldrin and Endrin**

Aldrin is an alicyclic chlorinated hydrocarbon and is rapidly converted to the epoxide form; dieldrin (GESAMP, 1993). The presence of a high concentration of dieldrin as shown in Figure 9 declares that, there may be conversion of aldrin to dieldrin by an epoxidation in biological system (Rumsey and Bond, 1974).

According to ATSDR (2002), dieldrin in soil and water breaks down slowly. It sticks to soil and may stay there unchanged for many years thus, not easily washed away by water. Dieldrin does not dissolve in water very well and is therefore not found in water at high concentrations. This might be attributed to the low concentration of dieldrin. The low concentration of endrin might be attributed to its susceptibility to volatization, photodegradation and heat to form metabolites of endrin as stated by Fan and Alexeeff (1999).

**Hexachlorobenzene (HCB)**

Hexachlorobenzene showed a relatively high mean concentration of 0.12 µg/g as indicated Table 1. According to ATSDR (2002), if hexachlorobenzene is released to surface waters such as lakes, rivers and streams, the half-life is 2.7-5.7 years. This means that, half of the total amount will disappear after 2.7-5.7 years, half of the remaining amount will disappear in another 2.7-5.7 years and this process will continue each 2.7-5.7 years thereafter and hence, its persistent nature might be due to its high concentration.

**Mirex**

Mirex recorded the least grand mean concentration of -0.057 µg/g among the residues identified in the analyzed water samples. The low concentration of this residue might be due to its low solubility in water and probably the less usage of this pesticide in the area. Also, Mirex showed an increasing trend in concentration with respect to the sampling times as indicated by Figure 12 .The increasing trend of mirex might result from a build up traces in chemicals used at the study area.

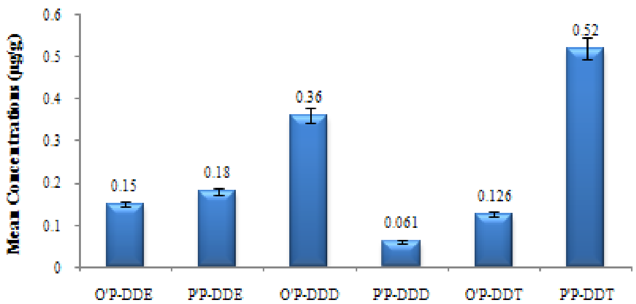


**Figure 1: Mean Concentrations of DDT and Its Isomers**

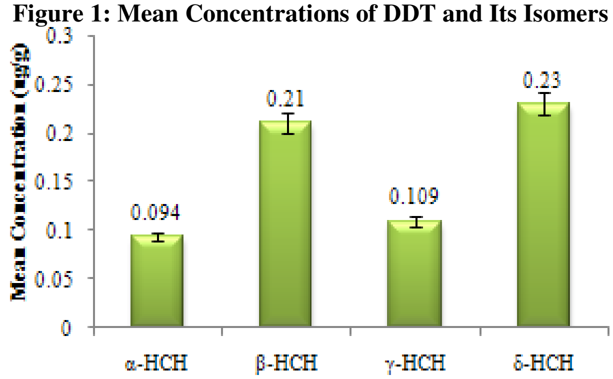


**Figure 2: Mean Concentrations of HCH and Its Isomers**

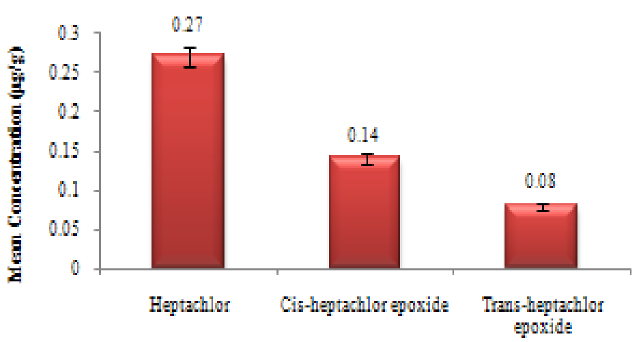


**Figure 3: Mean Concentrations of Heptachlor and Heptachlor Epoxide**

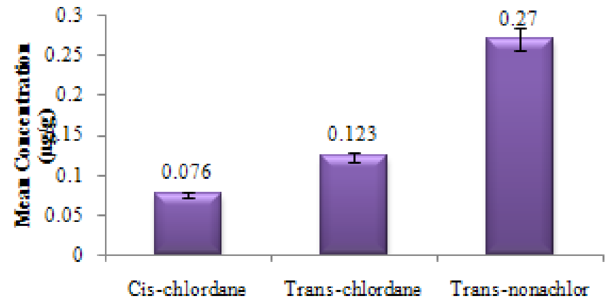


**Figure 4: Mean Concentrations of Chlordane and Its Isomers**

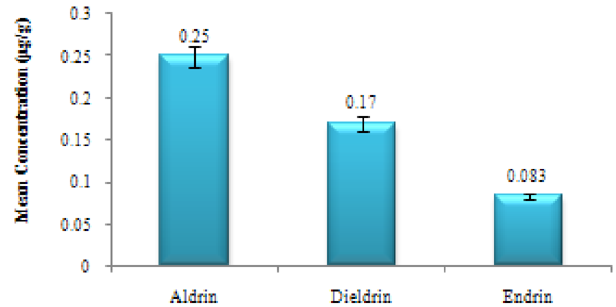


**Figure 9: Mean Concentrations of Aldrin, Dieldrin and Endrin**

**Time Variational analysis of Organochlorine Concentration**

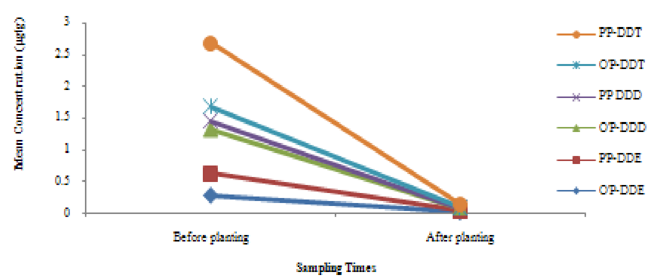


**Figure 2: Trend of DDT and Its Isomers With Respect to Sampling Times**

A decreasing trend of DDT isomers is observed from Figure 2. The concentrations of the residues at the time of preparation for the farming season, that is, before planting were higher than those observed after planting was done, that is, after sowing and emergence of seedlings. The decreasing trend might be as a result of rainfall intensification that might have caused the dilution of these redidues as the farming season progresses. Also, DDT can be degraded by solar radiation or metabolized by organisms.

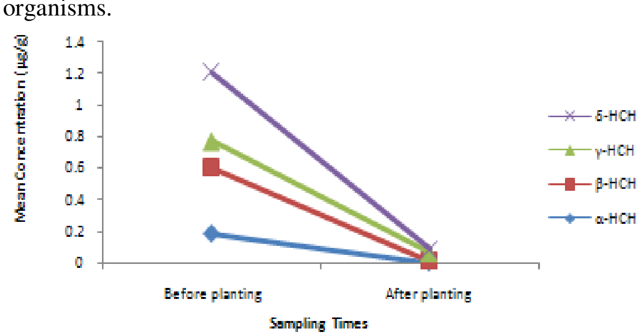


**Figure 4: Trend of HCH and Its Isomers With Respect to Sampling Times**

Figure 4 also shows a decreasing trend of the various residues of HCH isomers with respect to sampling times. The decrease in trend might be as a result of the heavy rainfall or rainfall intensification that might cause dilution of these residues from the dam as the season progresses.

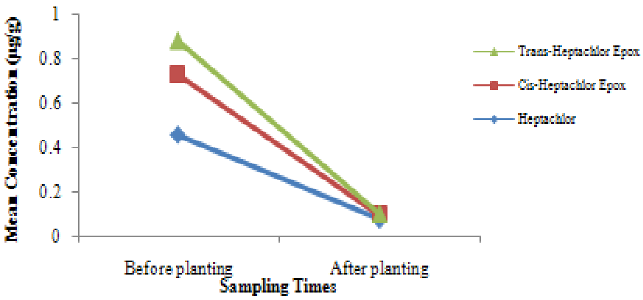


**Figure 6: Trend of Heptachlor and Heptachlor Epoxide With Respect to Sampling Times**

Observation from Figure 6 can also be as a result of rainfall intensification the season progresses. Heptachlor and its epoxide are slightly soluble in water, so as the intensity of rainfall increases, there is dilution of these residues and thus the reduction in concentration.

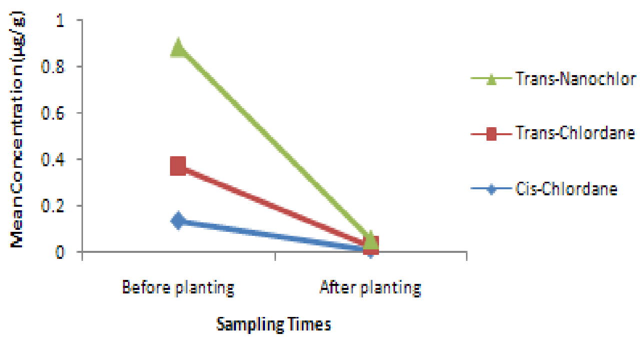


**Figure 8: Trend of Chlordane and Its Isomers With Respect to Sampling Times**

A decreasing trend of chlordane isomers with respect to their sampling times was observed from Figure 8. This might be attributed to the same observation made in Figure 6 and probably the photosensitive nature of these residues.

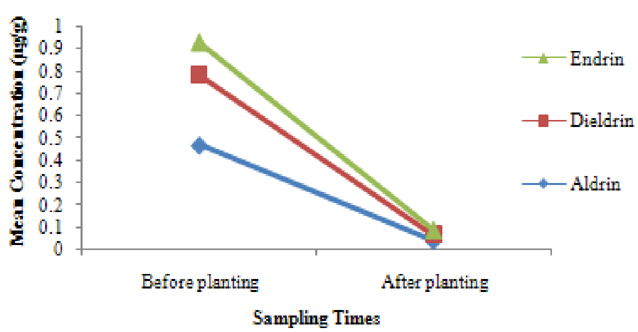


**Figure 10: Trend of Aldrin, Dieldrin and Endin With Respect to Sampling Times**

A decreasing trend of residues with respect to their sampling times can be observed from Figure 10. The decreasing trend might be attributed to rainfall intensification as the farming season progresses which might cause the dilution of these residues and probably the biodegradation of these residues by bacteria and fungi to form their metabolites.

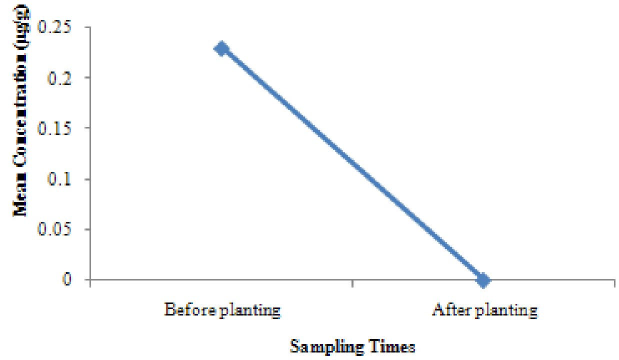


**Figure 11: Trend of Hexachlorobenzene With Respect to Sampling Times**

A declining concentration of hexachlorobenzene with respect to sampling times would be observed from Figure 11. The decreasing trend might be associated to rainfall intensification that might cause dilution as the season progresses.

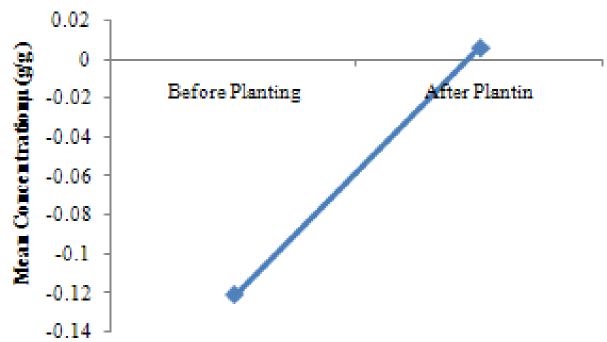


**Figure 12 Trend of Mirex With Respect to Sampling Times**

**Allowable Limits and ANOVA for Residues**

In accordance to WHO, (1996) for drinking water, the total pesticide level should not exceed 0.0005 µg/g and an individual pesticide not greater than 0.0001 µg/g. It is evidently clear from Table 1 that, all the pesticide residues except for mirex were above the World Health Organization (WHO) Maximum Residue Limits (MRL) indicating that, the water is unsafe for drinking. However, the dam serves as a main source of drinking water for the inhabitants of the area thereby posing a high risk of carcinogenic diseases and other disruptions such as low sperm count in males, birth defects, increased in testicular cancer and other reproductive and development effects to these people. According to Helfrich *et al.,* 1996, fish and other aquatic biota may be harmed by pesticide contaminated water also; insecticides are more toxic to aquatic life than herbicides and fungicides. Since all the residues identified are a type of insecticide and are also above the acceptable limits, there is a high occurrence of poisoning to the aquatic organisms in the dam water which might cause physiological and behavioural changes of this organisms leading to a reduction in population. Also, since these residues are lipophilic, they can potentially bio-concentrate into the fatty tissues of fishes and other aquatic organisms in the dam water, leading to biomagnifications in humans on the top of the food chain. Furthermore, the high level of residues in the dam together with the pesticides applied to the crops for pest control during the farming season can go a long way to affect the irrigated crops and increase the concentration of these residues in the soil and according to Rockets 2007, Nitrogen fixation, which is required for the growth of higher plants, is hindered by pesticides in soil. The insecticides DDT, methyl parathion, and especially pentachlorophenol have been shown to interfere with legume-rhizobium chemical signaling.

**Table 1: Results of the Analysis of Variance**

| Residues | Grand Mean | F-probability value | WHO/FAO MRLs |
|---|---|---|---|
| α-HCH | 0.094 | 0.358 | 0.002 |
| HCB | 0.12 | 0.346 | 0.001 |
| β-HCH | 0.21 | 0.334 | 0.002 |
| γ-HCH | 0.109 | 0.496 | 0.002 |
| δ-HCH | 0.23 | 0.364 | 0.002 |
| Heptachlor | 0.27 | 0.367 | 0.00003 |
| Aldrin | 0.25 | 0.368 | 0.00003 |
| Cis-Heptachlor Epox | 0.14 | 0.332 | 0.00003 |
| Trans-Heptachlor Epox | 0.080 | 0.254 | 0.00003 |
| Trans- chlordane | 0.123 | 0.318 | 0.0002 |
| O'P-DDE | 0.15 | 0.273 | 0.002 |
| Cis- chlordane | 0.076 | 0.277 | 0.0002 |
| Trans- nonachlor | 0.27 | 0.325 | 0.0002 |
| P'P-DDE | 0.18 | 0.304 | 0.002 |
| Dieldrin | 0.17 | 0.297 | 0.00003 |
| O'P-DDD | 0.36 | 0.324 | 0.002 |
| Endrin | 0.083 | 0.108 | 0.00003 |
| P'P-DDD | 0.061 | 0.214 | 0.002 |
| O'P-DDT | 0.126 | 0.292 | 0.002 |
| P'P-DDT | 0.52 | 0.35 | 0.002 |
| **Mirex** | **-0.057** | **0.201** | **0.000001** |

Reduction of these symbiotic chemical signaling results in reduced nitrogen fixation and thus reduced crop yields. Also, the high concentration of these residues in the soil can cause the extinction of certain micro organisms in the soil that facilitates microbial activities. In addition, since these residues are bio-accumulative, there is a high probability of their presence in irrigated crops which when consumed poses some amount of risk to consumers and the general populace.

Analysis of variance performed at 5 % level of significance indicated no significant difference among the mean concentration levels for all the organochlorine residues detected for the study as indicated by Table 1, and implies a virtually equal range of the residue levels in the dam water.

## Conclusions

The study revealed the presence of twenty-one (21) different organochlorine pesticide residues in the irrigation water of the Golinga dam. It was realized that, most of these residues identified decreases in concentration as the season progresses except for Mirex which showed an increasing trend. According to Afful *et al*. (2010), as at December 2008, the organochlorine pesticides; aldrin, chlordane, DDT, dieldrin, endrin, lindane (γ-HCH) and heptachlor were among the banned pesticides by Environmental Protection Agency of Ghana however, all these banned organochlorine pesticides by the Ghana EPA had their residues present in the dam at higher concentration with DDT having the highest concentration among the residues identified. Based on the World Health Organization (WHO) guidelines for drinking water (1996), the level of all the pesticide residues identified except for Mirex were extremely high for human consumption and possibly for irrigation purposes.

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