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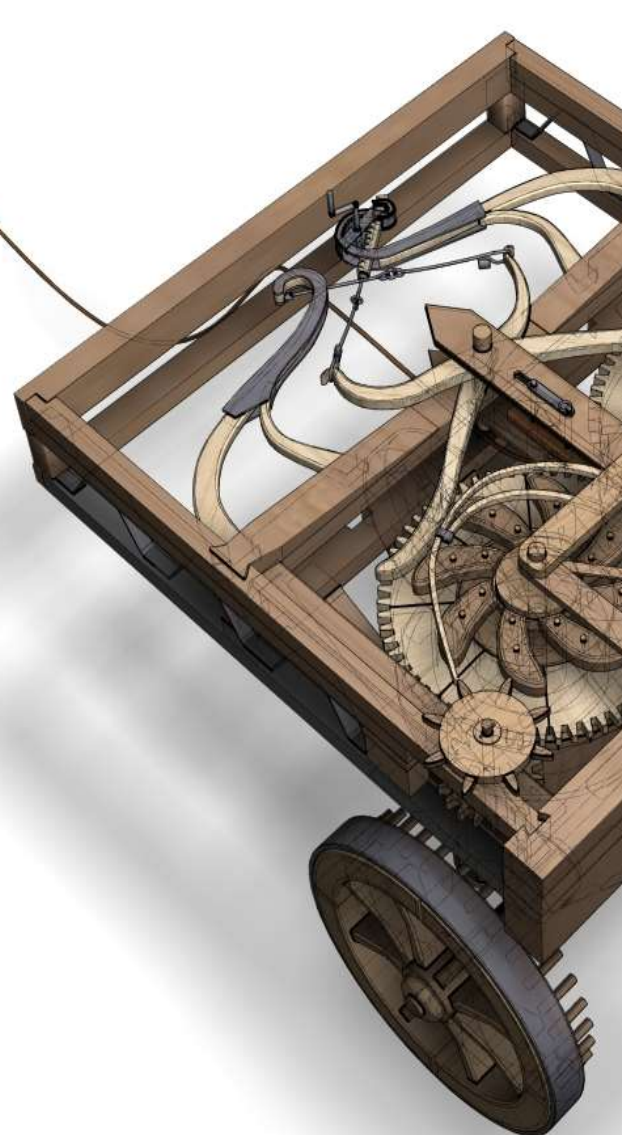
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Determination of Dissolved Pesticide Leachates in the West Africa's Largest Natural Lake

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Abstract

Lake Bosomtwe in the Ashanti Region of Ghana is one of the largest naturally occurring lake in West Africa. The lake is surrounded by about 36 farming and fishing communities that use synthetic pesticides and herbicide in the cultivation of crops. These chemicals are likely to leak into the tributaries, contaminate the lake, and threaten the life of the aquatic animals. For this reason, a study of the levels of the active components of the pesticides in the lake were measured to monitor the water quality. A Gas Chromatographic equipped with Electron Capture Detector (GC-ECD) was employed in the measurements and levels of organochlorine, organophosphorus and pyrethroids. The GC-ECD analysis revealed that, the mean concentrations of organochlorines in the water sample were, Beta – HCH (0.03µg/L), Gamma – HCH (0.015 µg/L), Delta – HCH (0.012 µg/L), Endrin (0.014 µg/L), Beta-endosulfan (0.01 µg/L), Endosulfan (0.028 µg/L), and p, p'- DDT (0.012 µg/L). Heptachlor, Alpha-endosulfan, p,p'- DDE and Lambda-cyhal had concentrations less than 0.01 µg/L. Chloropyrifos was the only organophosphate detected with a mean concentration of 0.013 µg/L. The mean concentrations

of the pyrethroids present were, permethrin 0.024 µg/L, cyfluthrin 0.016 µg/L and deltamethrin 0.017 µg/L. A comparison of the measured concentrations with the WHO pesticides limit in water displayed lower levels and compliance to the standards. Detection of these pesticides residues indicates that, regulating farming activities along the boundaries of the lake will reduce the leakages with corresponding positive effect on the aquatic life.

Keywords: Lake Bosomtwe; organochlorines; pesticide residues; synthetic pesticides; water quality.

JEL Classification: Q25; Q53; Q56; R11.

Introduction

Water is considered the most important compound found on Earth that has a direct impact on life and covering about 71 % of the Earth surface. It therefore can be concluded that life cannot exist on Earth without water (Dohare *et al.* 2014). However, the availability and supply of quality water is critical for human survival (Nketia *et al.* 2016). Poor water management practices over the years have negatively affected the quality of many water bodies especially rivers and lakes (Sanchez and Manuel 2007). The poor quality of most water bodies is mainly caused by domestic, industrial and agriculture related activities (Simeonov *et al.* 2003). Poor water quality has been reported to contribute about 80 % of all disease in human beings (Kavitha *et al.* 2010). Lake Bosomtwe found in Ghana, is the biggest natural lake in West Africa. The lake, which serves as a recreational and tourist site is surrounded by thirty-six (36) farming and fishing communities. The Lake is very rich in aquatic biodiversity thus, serving as a cheap source of fish protein to the communities around it. However, the use of pesticides and herbicides by farmers around the lake continues to threaten the quality of the lake. Pesticides are usually chemicals that are used to control and eliminate plants and pest with possible effect on the ecosystem. Pesticides end up in water bodies mainly through runoffs. Once in water bodies, they bioaccumulate in aquatic organisms. Organochlorine, Organophosphorus and synthetic pyrethroids are known to be highly toxic and can easily enter the food chain through bioaccumulation (Akoto *et al.* 2016; Essumang *et al.* 2009; Akoto *et al.* 2013).

Farmers continue to use it probably because of the low cost compared to other class of pesticides (Akoto *et al.* 2016, Saada *et al.* 2017). The frequency in the application of synthetic pesticide by smallholder farmers does not only results in pest resistance but also, increases the level of pesticide residues, which may end up in water bodies (Saada *et al.* 2017; Akoto *et al.* 2013). For example, it was estimated that about 80% of water entering Lake Bosomtwe in Ghana comes from annual rainfalls, which may transport residual pesticides into the lake (Nketia *et al.* 2016). Also, a previous study to measure the distribution of pesticides in Nyando River in Kenya indicated a mean concentration of 8.817 ± 0.020 mg/l for methoxychlor (Abongo *et al.* 2018). Subir *et al.* 2020 detected the presence of HCH, DDD, DDE, heptachlor, chlorpyrifos and dichlorvos in the Lake Chilika found in Indian. Another study identified 17 organochlorine pesticide residues in the Lake Naivashain found in Kenya (Abbasi *et al.* 2018). Additionally, aldrin, endrin, δ -BHC, 4,4-DDT, methoxychlor and endosulfan were the organochlorines found in the Sembrong Lake in Malaysia (Sharip 2017). Pesticides when transported through surface runoffs into lakes can bioaccumulate in aquatic organisms and threaten aquatic life (Koranteng *et al.* 2018). For instant, a study to assess organochlorine pesticides residue in Nile tilapia fish from the Lake Volta in Ghana, identified the presence of δ -HCH and heptachlor in the fish gill (Gbeddy *et al.* 2015). Also, β -HCH, pp-DDE, endrin, lambda-cyhalothrin, cyfluthrin, cypermethrin, fenvalerate, methamidophos, diazinon, chlorpyrifos, malathion fenitrothrin, parathion and profenofos were detected in an aquatic plant *Ceratophyllum demersum* found in the Lake Volta in Ghana (Koranteng *et al.* 2018). Furthermore, DDT, HCH, chlordane and heptachlors were found in organs of fish species in the Lake Ziway in Ethiopia and these compounds were mainly introduced into the lake from surface runoff from farming sites around the lake (Berhan *et al.* 2018).

In Ghana, application of most organochlorine and organophosphorus have been banned but there are no strict laws regulating the distribution and usage of pesticides (Akoto *et al.* 2016). With the numerous agriculture activities coupled with the application of pesticides around the Lake Bosomtwe, it is possible for these used pesticides to be transported into the Lake water through surface runoff according to literature (Nketia *et al.* 2016). In view of this, it is important for water quality of the lake to be monitored frequently. Hence, the work seeks to determine the presence and levels of pesticide residues from sampled water of Lake Bosomtwe as a follow up experiment of literature. Gas Chromatographic equipment was employed in the measurements of organochlorine, organophosphorus and pyrethroids levels in the Lake Bosomtwe.

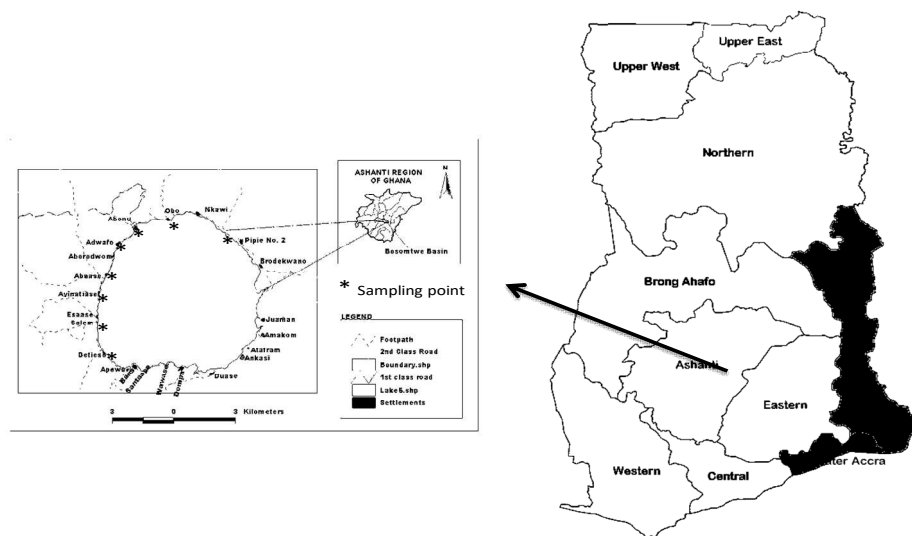
1. Methods

Sampling

Surface water from the lake was randomly sampled from eight (8) sampling points (Fig. 1) with the aid of a fishing boat into a 1000 ml sterilized glass bottles with caps. At sampling point, the sampling bottle with the lid

tightly fitted were lowered into the water and then opened while under the water to fill the bottle. Sampling bottles were sealed tightly with pre-cleaned aluminum foil.

Figure 1. A map of Lake Bosomtwi showing sampling point



Chemicals

Pesticides standards were of a 99% purity grade and obtained from the Ghana Standard Authority, Accra, Ghana.

Turbidity, conductivity and pH measurement

A pH meter (Mettler Toledo, FiveEasy) was used to measure the pH of the water sampled from the lake. The pH meter was first calibrated with a buffer solution of pH = 7.0, 4.0 and 10. The pH electrode previously washed with distilled water, was placed into the beaker containing the water sample. The pH meter was given time to stabilize at room temperature before recording the water sample pH. Furthermore, a conductivity meter (WTW, LF 538) with cell constant of 1.0 was used to record the turbidity and conductivity of the water samples. 50 ml of the sample was pipetted into a clean dried beaker and the electrode of the conductivity meter rinsed with distilled water and patted dry. It was then lowered into the beaker containing the sample.

Extraction of pesticide residue

About 300 ml of dichloromethane was poured into a separating funnel containing 1 litre of the filtered water sample followed by adding a brine solution. The resulting solution was then shaken for about 5 min followed by separating the organic layer from the aqueous phase. The organic phase was concentrated to about 2 ml using a rotatory evaporator at 40°C. Clean up of the extract began by preconditioning a cleanup cartridge containing 6 g silica and 4 g Magnesium Sulphate. Using dichloromethane, the extract was passed through the cartridge into a pear-shaped flask. 20 ml of dichloromethane was then used to wash the sample down into the pear-shaped flask. The sample was concentrated to dryness and 1 ml ethyl acetate added to the pear-shaped flask.

Analysis of organochlorine and synthetic pyrethroids by GC

Organochlorine and synthetic pyrethroids in the water samples were analyzed using a Gas Chromatographic (Varian CP-3800) equipment with Electron Capture Detector (ECD) and a VF-5ms column (30 m, 0.25 mm, 0.25µm). The oven temperature was maintained at 70°C for 2 min and programmed at 25°C/min to 180°C where it was held for 1 min, then at 5°C/ min to 300°C. Nitrogen served as the carrier gas with a flow rate of 1 ml/min.

Analysis of organophosphorus by GC

Organophosphorus present in the water sample was analysed using a GC (Varian CP-3800) equipped with Pulsed Flame Photometric Detector (PFPD) and VF-1701ms column (30 m, 0.25 mm, 0.25µm). The oven temperature was maintained at 70 °C for 2 min and programmed at 25°C/ min to 200°C where it was held for 1 min, then at 20°C/ min to 250°C. Nitrogen served as the carrier gas with a flow rate of 2 ml/min.

2. Results and Discussion

Physico-chemical parameters

Table 1. Average pH, conductivity and turbidity of the Lake water.

Parameters	Range	Mean	WHO limits
pH	9.44 - 9.53	9.505	6.5-8.5
Conductivity $\mu\text{S/cm}$	1156 - 1194	1179.4	1500
Turbidity NTU	5.13 - 5.88	5.56	5.00

The average pH of the lake was recorded at 9.50, which was above the recommended levels ranging from 6.5 to 8.5 (Table 1) (Dohare *et al.* 2014). This was attributed to the rocky nature of the lake's boundary surroundings which leaked hydroxide compounds into the lake through rain runoffs (Boahma *et al.* 2007). Furthermore, a measure of the conductivity, which is the capacity of the water to carry electric charges, and acts as an indicator of the amount of total dissolved solids (TDS) was determined. Our results show that the average value of conductivity, 1179.40 was within the acceptable level, (Table 1). We also recorded an average turbidity of 5.56 NTU in the lake slightly above the recommended level of 5.00 NTU, (Table 1) which was due to the soil runoffs from the boundaries. Hence, the increase in the water pH requires attention to secure the lives of the aquatic animals and plants who depend on the lake for survival (Kleinhappel *et al.* 2019).

Pyrethroid identified in the water sample

Table 2. Levels of pyrethroid present in the Lake Bosomtwe water in May 2019.

Pesticide	Range($\mu\text{g/L}$)	Mean $\pm$ SD($\mu\text{g/L}$)	WHO limits($\mu\text{g/L}$)
Permethrin	0.01 - 0.05	0.024 $\pm$ 0.02	20.00
Cyfluthrin	0.01 - 0.04	0.016 $\pm$ 0.011	-
Deltamethrin	0.01 - 0.03	0.017 $\pm$ 0.008	0.05

We identified permethrin, cyfluthrin and deltamethrin as the pyrethroids found in the lake (Table 2). Permethrin had the highest concentration (0.024 $\mu\text{g/L}$) among the detected pyrethroids even though it occurred in traces, which was below the WHO standard, (Table 2). Similarly, lower levels were recorded in a previous study for fenprothrin (3.50 ng/mL), in the Weija Lake, Accra, Ghana (Afful *et al.* 2013). However, slightly higher levels were reported for pyrethroids residues in water samples from cocoa farms in Ghana, and ranged from 0.01-0.05 $\mu\text{g/L}$ for allethrin, 0.01-0.04 $\mu\text{g/L}$ for fenvalerate, 0.01-0.04 $\mu\text{g/L}$ for cypermethrin and 0.01-0.05 $\mu\text{g/L}$ for deltamethrin, (Fosu-Mensah *et al.* 2012). Pyrethroids are lipophilic and so the gills of fishes easily absorb them even though they may be at trace levels. Nonetheless, they may cause damage to the fish cells with prolonged accumulations (Bhardwaj *et al.* 2020). For this reason, the toxicity of pyrethroids to the fishes cannot be overlook and hence, must be effectively controlled on neighboring farms to reduce leakages into the lake (Bhardwaj *et al.* 2020).

Twelve organochlorines were detected in the lake water samples, (Table 3). Beta-HCH had the highest mean concentration of 0.03 $\mu\text{g/L}$ while heptachlor, alpha-endosu, p,p'-DDE, dieldrin and lambda-cyhal were only present in trace amounts. Some organochlorines such as DDT and dieldrin known to have high lipophilicity (Saada *et al.* 2017) may have reduced solubility in water and accounted for the trace concentration recorded. This is similar to the previously reported work that identified lindane as organochlorine with a trace level of 0.071 ng/L in the Lake Bosomtwe (Darko *et al.* 2008). Additionally, a comparison of the Alpha-endosulfan in Lake Bosomtwe to that of Manzala Lake (71 to 2,815 pg/L) in Egypt shows a consistency in the low levels which indicates minimal tendency of the organochlorine to contaminate water or leak from farms into neighbouring Lake or river (Nobuyoshi *et al.* 2000).

Organochlorine levels

Table 3. Organochlorine pesticides residues present in Lake Bosomtwe water (trace represent concentration less than 0.01 $\mu\text{g/L}$)

No.	Pesticide	Range($\mu\text{g/L}$)	Mean $\pm$ SD($\mu\text{g/L}$)	WHO limits($\mu\text{g/L}$)
1.	Beta-HCH	0.01 – 0.05	0.03 $\pm$ 0.018	2.00
2.	Gamma-HCH	0.01 – 0.03	0.015 $\pm$ 0.009	2.00
3.	Delta-HCH	0.01 – 0.02	0.012 $\pm$ 0.005	2.00
4.	Heptachlor	trace	-	-
5.	Alpha-endosulfan	trace	-	-

6.	p,p'-DDE	trace	-	2.00
7.	Dieldrin	trace	-	-
8.	Endrin	0.01 – 0.025	0.014 ± 0.007	-
9.	Beta-endosulfan	0.01 – 0.015	0.01 ± 0.006	-
10.	Endosulfan	0.02 – 0.04	0.028 ± 0.008	-
11.	p,p'-DDT	0.01 – 0.02	0.012 ± 0.004	2.00
12.	Lambda-cyhal	trace	-	-

Similarly, Endosulfan was found in low levels (0.036 µg/L) in the Ghanaian Volta Lake (Ntow *et al.* 2005). Nonetheless, its derivate, the endosulfan sulfate in the Ghanaian Densu river was reported to have concentration of which 0.185 µg/L which was above the general trace levels of Endosulfan (Kuranchie-Mensah *et al.* 2012). This indicates that, the organochlorines and their derivatives leak into rivers and lakes at different rates, which is attributable to their chemical composition and hydrophilicity. Furthermore, the high tendency of these forms of pesticides to bioaccumulate provides a cause for concern. Since the bioaccumulation in fish will have corresponding effect on humans who consume the fish (Chang *et al.* 2018). It is therefore imperative that, a regulatory mechanism is put in place to reduce the use of organochlorines in applications that are closer to rivers and lakes, and a subsequent replacement with safer alternatives.

Organophosphate levels

Table 4. Organophosphorus pesticides residues present in the Lake Bosomtwe.

Pesticide	Range (µg/L)	Mean ± SD (µg/L)	WHO limits
Chloropyrifos	0.01 – 0.015	0.013 ± 0.004	-

Chloropyrifos was the only organophosphate that was determined in the experiments on the lake water, (Table 4). The continuous use of pesticides containing the organophosphate on surrounding farms demonstrates the consistent presence of the chloropyrifos in the water, which has the potential to bioaccumulate in fishes with consequential disruption of the endocrine systems of the consumers (Otieno *et al.* 2015). The pollution of the lake by the pesticide residue will affect the quality of water that serves as a habitat for a variety of aquatic organisms, as well as a recreational site for human visitors (Abdulai and Kuyini 2018). Hence, it is needful to protect the water body to ensure the safety of the aquatic lives and tourist. A high quality of the water will improve tourism to the lake and offer good drinking water to the residents of the community who depend on the lake water for their daily water needs. As a result, there is the need for the Municipal Assembly to put in place a monitoring team to oversee and control farming activities around the lake. This will advance the preservation of the water quality and conservation of rare aquatic organism species.

Conclusion

In all, permethrin, cyfluthrin and deltamethrin were the pyrethroids detected in the lake water. The organochlorines detected in the lake water included the Beta-HCH, Gamma-HCH, Delta-HCH, Heptachlor, Alpha-endosu, p,p'-DDE, Dieldrin, Endrin, Beta-endosulfan, Endosulfan, p,p'-DDT and Lambda-cyhal. Chloropyrifos was the only organophosphorus present in the lake. Although study shows that the levels of the organochlorines, organophosphate and pyrethroids were within the WHO accepted limits, there is an urgent need to put in place a management strategy that will prevent an upsurge of levels to and above the acceptable limits. The study has revealed that, the pH of the lake ranged from 9.44 - 9.53, which also required attention that will reduce it to acceptable limits for the survival of aquatic animal inhabitants of the lake.

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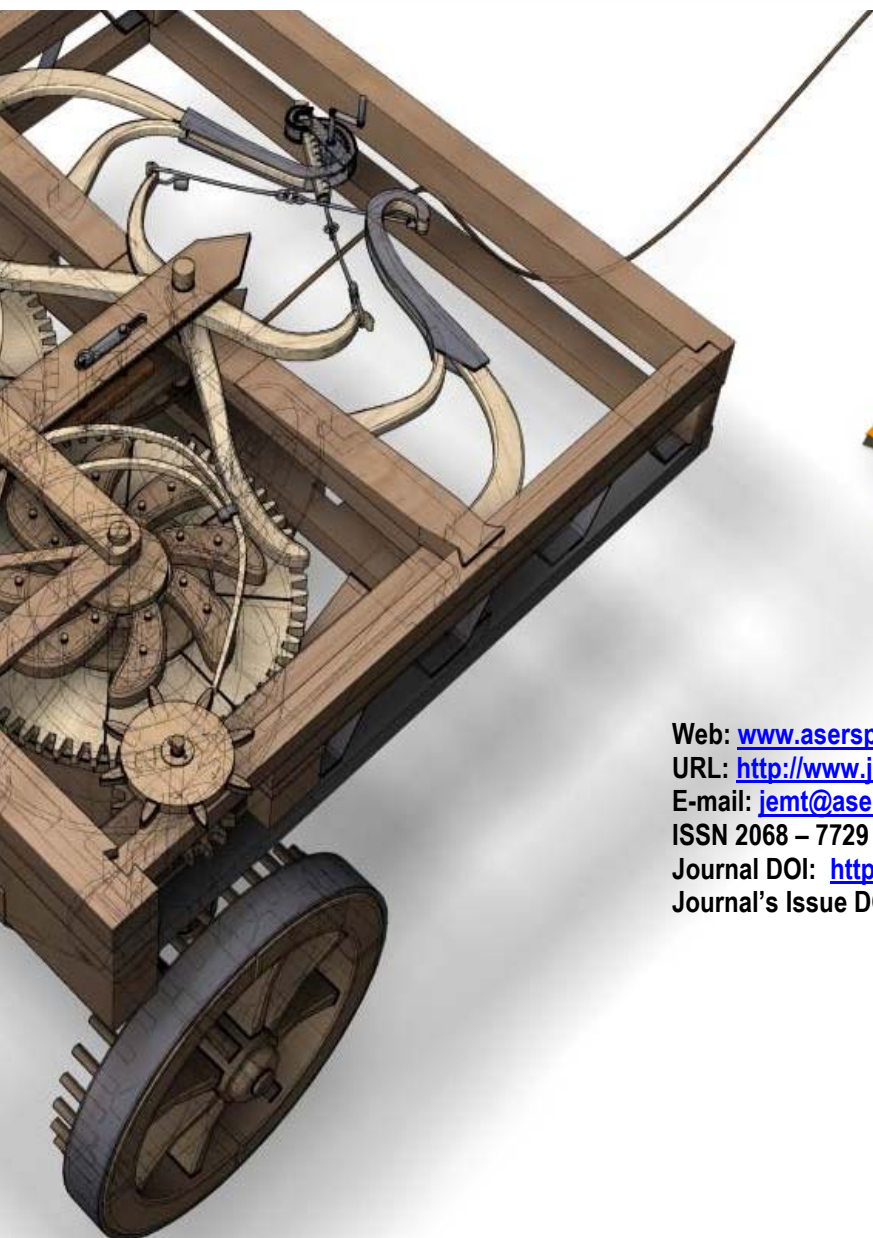
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