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Persistent organic pollutant in soil, plants and water in the Vicinity of Savannah Sugar Company, Numan LGA, Adamawa State, Nigeria

Mustapha A.B., Maitera O. N., Nkafamiya I. I. and Milam C.

Department of Chemistry, Modibbo Adama University Yola, Nigeria

ABSTRACT

This study investigated the persistent organic pollutant in soil, plants and water in the Vicinity of Savannah Sugar Company, Numan LGA, Adamawa State, Nigeria.The rapid growth of industrial activities, including sugar production, often leads to the emission of pollutants that can have detrimental effects on the environment and human health. Sampling is conducted in selected locations within the vicinity of the Savannah Sugar Company, with measurements taken using established scientific protocols and state-of-the-art equipment. All the samples revealed the presence of organic pollutants such as Delta Lindane, Alpha Lindane, Beta Lindane, Gamma Lindane, Heptachlor, Aldrin, Heptachlor epoxide, Endosulfan I., P,P' – DDE, Endrin, Endosulfan II, P,P' – DDD, P,P' – DDT and Methoxyclor. These results highlights the urgent need for pollution control measures, public health interventions, and environmental management strategies.

Keywords: Organic pollutant, soil, plants, water, vicinity and Savannah sugar.

INTRODUCTION

Environmental pollution is posing significant public health risks worldwide, becoming a major concern in developing countries because of rapid economic activities and poor waste management. It is challenging to establish an association between environmental pollution and health effects because of the nature of pathways to exposure, limited data availability and the absence of a monitoring system. Furthermore, associations between environmental pollution and health are difficult due to the occurrence of multiple exposures, and the latency period of effect [1]. Prolonged farming activities involving the use of fertilizers, herbicides and insecticides also contribute to soil pollution. Rapid industrialization has also brought about dangerous pollution of soil by heavy metals in many countries [2]. The pollution of soils with heavy metal is of global concern as a result of its potential impact on the environment and to human health. Vast portions of farmlands have been contaminated by metals as result of the activities of mining, smelting, fossil fuel burning, phosphate fertilizers and sewage sludge [3]. Based on high toxicity of heavy metals, their accumulation in farmland could lead to contamination of agricultural soil. Once soil is contaminated, it will not only affect the rapid growth of crops and quality yield of agricultural products but also pose a threat to human health via the food chain [4]. All over the world, especially in developing nations, there is a growing public concern over the potential accumulation of heavy metals in soil, water and plants owing to rapid industrial development [4]. Pollution of fresh water bodies, especially the rivers is no longer within safe limits for human consumption as well as aquatic fauna. Disposal of sewage wastes into a large volume of water could reduce the biological oxygen demand to such a great level that the entire oxygen may be removed. These may be derived from inputs of suspended solids to which toxic substances are absorbed; such as soil particles in surface water run-off from fields treated with pesticides [5]. On the other hand, these chemicals disrupt the ecological system balance due to pollution of water, air, soil and nutrients with the remains left behind in large areas, while the use of pesticides provides benefits for public health and hunger. In addition, some of them are toxic to the only specific living species because of their selective properties, while others are harmful to people, domestic animals and wild animals which are outside the target of the pesticides. In such cases they can cause acute and chronic poisoning [6].

Pesticides also play a very important role in the contamination of water resources. Since herbicides and nematicides are applied directly to the soil, they are considered to be the most important pesticides that pollute environmental waters. The ways for pesticides to interfere with the aquatic environment can be listed as; direct inputs

from the agricultural industry, industrial effects, waste water effects, spraying of cattle and sheep, dust and flooding, and atmospheric transmission (wind effect, evaporation from application areas, erosion of pesticide applied lands in various ways) [7].

Pesticides, which can be dissolved in water or can be sediment in the case of exceeding the solubility criterion, pass through aquatic organisms in various ways through the food chain and cause bioaccumulation. Pesticides, which are transmitted to waters in different ways, are a threat with the adverse consequences of reaching people through water ecosystems and food chains. The fact that a person is a living creature that feeds on both plant and animal nutrients, and that it forms the last ring of the food chain, causes such compounds to appear in large measure in humans. Compostable compounds such as pesticides or heavy metals can enter the human body first with fish consumption [8]. Chemical and physical analyses of these samples can reveal the presence and concentration of pollutants such as heavy metals, pesticides, and organic compounds [9]. Additionally, ambient air can be monitored to identify pollutants and estimate the associated health risks. Air quality monitoring stations can measure the concentration of various pollutants in the air, such as particulate matter, ozone, and nitrogen dioxide. Health risk index can be calculated based on the level of exposure to the pollutants and the potential health effects associated with that level of exposure [10]. Overall, investigating pollution accumulation and estimating health risk index is an important step in identifying potential environmental and health hazards, and can help guide policy and decision-making to minimize exposure to pollutants and protect public health. Pollution of soil, water, and plants is a significant environmental and public health concern that can result from a variety of human activities, including industrial processes, agricultural practices, transportation, and waste disposal. These pollutants can accumulate in the environment and have adverse effects on human health, such as respiratory diseases, cancers, and developmental disorders. Identifying potential sources of pollution and assessing health risks associated is crucial to protect public health and the environment [11]. One way to investigate pollution accumulation is through the collection and analysis of soil, water, and plant samples. However, there are several challenges associated with this approach. For example, pollutants may be distributed unevenly in the environment, making it difficult to obtain representative samples [12]. Additionally, the detection and analysis of pollutants can be complex and require specialized equipment and expertise. Moreover, it can be challenging to identify the specific sources of pollution, as pollutants can originate from a variety of activities and may be transported long distances by air and water currents. Ambient air can also be monitored to identify pollutants and estimate associated health risks [13]. However, air quality monitoring can be similarly challenging due to the spatial and temporal variability of pollutants [14]. Furthermore, the relationship between air quality and health effects can be complex and influenced by individual factors such as age, sex, and pre-existing health conditions [15]. Despite these challenges, investigating pollution accumulation in soil, water, and plants, as well as the analysis of ambient air and estimation of health risk index, is critical for identifying potential environmental and health hazards and guiding policy and decision-making to minimize exposure to pollutants and protect public health. Ongoing research is needed to improve our understanding of pollution sources and associated health risks, as well as to develop effective mitigation strategies to prevent or minimize pollution accumulation in the vicinity of Savanna Sugar Company, Numan, Adamawa State [16].

Aim of the Study

The aim of this research was to determine the persistent organic pollutant in soil, plants and water using Gas Chromatography Mass spectroscopy (Gc-Ms).

MATERIALS AND METHODS

Study Area Savannah Sugar

The study area, as shown in Figure 1, is an area located between latitudes 9^0 22' 00" N and 9^0 38' 00" N and longitudes 11^0 45' 00" E and 12^0 00' 00" E, covering the farm and factory of the Dangote Sugar Company (formerly Savannah Sugar Company). The Dangote Sugar Company being the main focus of the study is located north of the river Benue and about 20km North of Numan town in Adamawa state, Northeast Nigeria (Savannah Sugar Company Ltd., 2014). It lies at an elevation of 150 m above sea level. The company has a land mass of about 32,000 hectares spread, along Yola-Gombe highway. The out-grower farms of the Savannah Sugar Company are situated in five out-grower zones, respectively managed by estate mangers. Irrigation is done by the use of irrigation water from Kiri Dam (Figure 1), connected by a 30km distance canal to the sugar cane estate and commences two to three weeks after the rainfall cessation [17]. The climate of the area is semi-arid characterized by wide seasonal and diurnal temperature ranges. There are two main marked tropical seasons. The wet season, lasting from April-October and dry season lasts from November to March. The mean rainfall of about 905mm is recorded with peaks in August and September [18]. Between November and January, the Harmattan pushes the Inter-tropical Discontinuity (ITD) to its most southerly latitudinal position of 2-5°N. Throughout this period, most of Adamawa State is influenced comparatively by stable dry continental air mass from the northeast and hence rainfall is absent or very low. The average monthly temperature is 26.9^0C, with minimum temperature of 18^0C and a maximum of 40^0C.

Sampling Area

Samples of soil, water and plants in this research work were collected in and around savannah sugar company, Numan, Adamawa State.The areas include Gyawana, Lafia in Lamorde LGA, Ngwabalang, Imburu Numan LGA, Boshikiri, Kola in Guyuk LGA and Kiri, Kem Shelleng LGA Adamawa state. Soils samples were collected from

the north, south, east and west directions, 1 km, 2 km, 3 km and 5 km radius also from 5 cm, 10 cm, 15 cm and 20 cm depth at each distance respectively from the milling plant, Simple random method was used in the sample collection. The soil sample was placed in a clean polythene bag for transport to the laboratory. Water samples were collected from wells, boreholes and the river. The water samples were placed in a clean polypropylene bottle for transport to the laboratory. Plants samples were collected from surrounding farms.

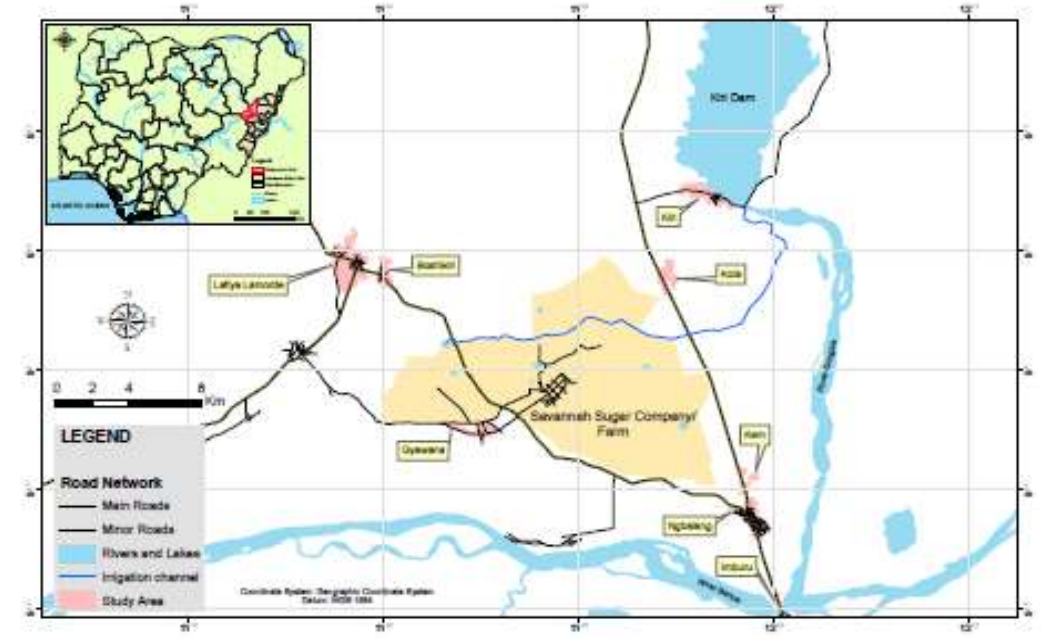

Figure A: Showing the map of study Savannah Sugar Company and other study areas.

Soil Samples Collection

Sampling was carried out using standard protocols [19]. A stainless-steel auger capable of retrieving a cylindrical plug of soil was used for soil collection. Soil samples analysed in this research work were collected from the vicinity of company. Samples were collected from twelve sampling sites where the surface is free of plant material and debris. Samples were taken from surface till the depth of 15 cm also from 15-30 cm. Samples were placed in plastic bags sealed and labelled for transport and storage. The samples were collected in the dry and wet season. The samples were air-dried in the laboratory, mechanically ground, and sieved to obtain <2-mm fraction. About 10 g subsample will be drawn from the bulk soil (<2-mm fraction) and reground to obtain <200-µm fraction using a mortar and pestle.

Plant Samples Collection

Some plants were selected as the indicator plant. The samples were collected from the vicinity of savannah sugar company. Samples were collected from twelve sampling sites in the dry and wet season. The branches about 30-40 cm and parts of roots were collected and were placed in a polythene bag.

Ground water samples Collection

Water samples to be analysed were collected from any source of water in the vicinity of the savannah sugar company. The samples were collected in a polypropylene bottle, which was pre-washed and rinsed with 10% HNO_3 (v/v).

Soil and Plant Samples Pre-treatment:

The soil samples collected were air dried in the laboratory and pulverized using porcelain pestle and mortar to pass through a 2 mm sieve. The plants samples collected was washed thoroughly with tap water then with distilled water to remove soil dirt. It was then be dried in the lab at room temperature. The dried plant samples were pulverized using porcelain pestle and mortar.

Analysis with GCMS

GCMS were used for the analysis of pesticides residues. The prepared samples were extracted with a suitable solvent and then analyzed using GCMS. The instrument has separated the different components in the sample based on their chemical properties, and then the mass spectrometer detected and quantified the individual components.

Statistical Analysis

The obtained results were analysed using Microsoft Excel 2007 for descriptive statistics and SPSS 24 was used for ANOVA test of significant, Person's correlation analysis and Hierarchical cluster analysis.

RESULTS AND DISCUSSION

Organochlorine Pesticides residue

Organochlorine pesticides are resistant to degradation, which allows them to persist in the environment for a long time and become widespread via atmospheric and water transport mechanisms [20]. In this study, organochlorine pesticides in soil, water and plant samples were determined and analyzed by GC-MS. The optimized conditions were found to be 1 ml/min for flow rate in the mobile phase, 1µl for injection volume, and 70 V for fragmentation potential. The optimized method was applied for the determination of organochlorine pesticide in soil, water and plant samples. The target pesticides were analyzed with good reproducibility and low detection limits using gas chromatography-mass spectrometry. After elution-cleaning with SPE cartridge for pesticides in vegetables we developed a simultaneous method for analysis by GC-MS. The main advantage of this method is that extraction and clean-up are performed in less time with a low volume of solvent [21]. Additionally, the proposed method is a sensitive, reproducible, and reliable alternative to the normally used methods; moreover, it is inexpensive, easy, and rapid (QuEChERS method) [22]. This study demonstrated that the method using QuEChERS and GC-MS is very effective in analyzing the organochlorine pesticides in the soil, water and plant samples from Boshikiri, Gyawana, Imbru, Kiri, Lafiya, Ngwabalang, and Kem.

Organochlorine pesticide in soil samples

Figures below shows the concentrations of organochlorine pesticides measured in the soil samples from Boshikiri, Gyawana, Imbru, Kiri, Lafiya, Ngwabalang, and Kem. Soil samples analysed showed the presence of the fourteen (14) organochlorine pesticides namely Delta Lindane, Alpha Lindane, Beta Lindane, Gamma Lindane, Heptachlor, Aldrin, Heptachlor epoxide, Endosulfan I., P,P' – DDE, Endrin, Endosulfan II, P,P' – DDD, P,P' – DDT and Methoxyclor. There were however no statistically significant sites difference ($p > 0.05$) in mean concentrations of the detected residues in the soil samples.

Lindane

The highest concentration of lindane (Delta, alpha, beta and gamma lindanes) was detected in all the samples. Delta lindane, alpha lindane, beta lindane and gamma lindane were detected in all the soil sample within the range of 0.04 to 0.54 ppm, 0.03 to 1.40 ppm, 0.10 to 3.38 ppm and 0.07 to 0.85 ppm respectively. The mean concentration of Delta lindane was highest at Lafiya but lowest at Imbru during dry and seasons respectively. Similarly, the mean concentration of alpha lindane was highest at Lafiya during dry season with a mean value of 1.40ppm but lowest at Kem and Ngwabalang with a mean value of 0.03ppm during dry and seasons respectively. However, the concentration of beta and gamma lindane were highest at Kiri during dry season with a mean value of 3.38ppm and 0.85ppm respectively, but lowest at Lafiya and Ngwabalang during wet season with a mean value of 0.10 and 0.07ppm respectively. The presence of lindane in the soil samples may suggest the historical use or illegal use of technical HCH mixtures in the study area [23]. The mean lindane value recorded in this study was higher than the mean values of 0.0001 mg/kg recorded in soil samples from Ilawe-Ekiti, Ekiti State, Nigeria [24]. On the contrary, the mean concentration reported in this study was lower than 8.60 mg/kg reported by [25] in soils from selected cocoa farms in the Central Region of Ghana.

Heptachlor and Heptachlor epoxide

Heptachlor was found in all the soil samples analysed, with concentrations ranging from 0.01 to 0.12 ppm whereas Heptachlor epoxide were not detected in Ngwabalang and Lafiya during dry and wet seasons respectively. The highest concentration of Heptachlor was found in soil sample from Kiri during dry season with a mean of 0.12ppm while the lowest concentration was found in Boshikiri, Gyawana and Imbru with a mean of 0.01 ppm. Similarly, the highest value of Heptachlor epoxide was found at Boshikiri during wet season with a mean concentration of 0.09 ppm while the lowest value was found at Kiri, Kem, Boshikiri, Imbru and Lafiya with the mean concentration of 0.01ppm. The measured concentrations of Heptachlor and Heptachlor epoxide in the studied soils confirmed the previous use or current use of lindane in the study area [26].

Aldrin

Aldrin was detected at all the sites during dry and wet seasons. Due to its persistent nature and hydophobicity, aldrin is known to accumulate and/or bioconcentrate mainly as its conversion product dieldrin. The mean concentration of Aldrin was found in all the soil samples with ranged from 0.33 to 4.29 ppm. The highest value was found at Lafiya during dry season with a mean concentration of 4.29 ppm while the lowest value was found at Imbru during wet season with the mean concentration of 0.33 ppm. The presence of aldrin could be attributed to the current or previous use of aldrin as insecticide.

p,p′-DDE, p,p′-DDD, and p,p′-DDT

p,p'-DDE and p,p'-DDD were detected in all the soil samples. The mean concentration of p,p'-DDE and p,p'-DDD ranged from from 0.00 to 0.10 ppm and 0.02 to 0.13 ppm respectively. The concentration of p,p-DDE was highest at Gyawana during dry season with a mean value of 0.10 ppm while it is lowest at Imbru during dry season with a mean value of 0.00 ppm. Similarly, The concentration of p,p-DDD was highest at Kiri during dry season with a mean concentration of 0.13 ppm and lowest at Ngwabalang, Imbru and Lafiya with a mean concentration of 0.02 ppm. However, p,p′-DDT occurred in all the soil samples analysed at a mean concentration that ranges from 0.01 to 0.17 ppm. Some values are lower while some are higher than the US MRL of 0.05 mg/kg for agricultural soils. The presence of p,p′-DDT in the soil samples might be as a result of its previous

use in the studied farms. The mean concentration of p,p′-DDT reported in this study was higher than the mean values of 0.007 mg/kg reported in soils from Ekiti State in Nigeria [27].

Endrin

Endrin was detected in site all the soil samples. The mean concentration of Endrin ranged from 0.03 to 0.81 ppm. The highest concentration for Endrin was detected in Lafiya during dry season with the mean values of 0.81 ppm while the lowest concentration was found in Imbru during wet season with a mean value of 0.03 ppm. Presence of endrin could be as a result of previous use or atmospheric deposition [28].

Endosulfan I and II.

Endosulfan I and II were detected in the soils from all the sampling sites. The means values for both Endosulfan I and Endosulfan II ranged from 0.09 to 17.96 ppm and 0.22 to 1.93 ppm respectively. The highest concentration for Endosulfan I was found in Kiri during wet season with the mean values of 17.96 ppm while the lowest concentration was found in Imbru during wet season with a mean value of 0.09 ppm. Similarly, the highest concentration for Endosulfan II was found in Kem during wet season with the mean values of 2.74 ppm while the lowest concentration was found in Boshikiri during wet season with a mean value of 0.22 ppm.

Methoxychlor

Methoxychlor is not banned or restricted but was commonly used. The pesticide residue levels detected in the samples were within the range of 0.00 to 0.08ppm. The highest concentration for methoxychlor was found in Gyawana during dry season with the mean values of 0.08ppm while the lowest concentration was found in Ngwabalang during dry season with a mean value of 0.00 ppm. The mean concentration levels detected were shown below. Pesticide leaching or drainage from cultivated land into the surface waters and underlying ground water are a source of pollution because of their environmental mobility and persistence [29]. According to [30], the amount of methoxychlor in the environment is seasonal due to its periodic utilization in farming. Sprayed methoxychlor settles in the ground and degrades more rapidly in the soil that has supply of oxygen and therefore does not lead to significant bioaccumulation [18]. The results reveal that pesticide residue levels leached much more in the wet season than in dry. As expected, leaching of pesticide residue is higher during the wet season than the dry. This is, obviously due to the higher flow of water during the wet season. However, ecosystem effects will depend on not only the leaching but also the concentrations in the water. Although leaching is higher during wet than dry seasons, the absolute concentrations in the recipient waters may be lower during wet season due to higher dilution [20].

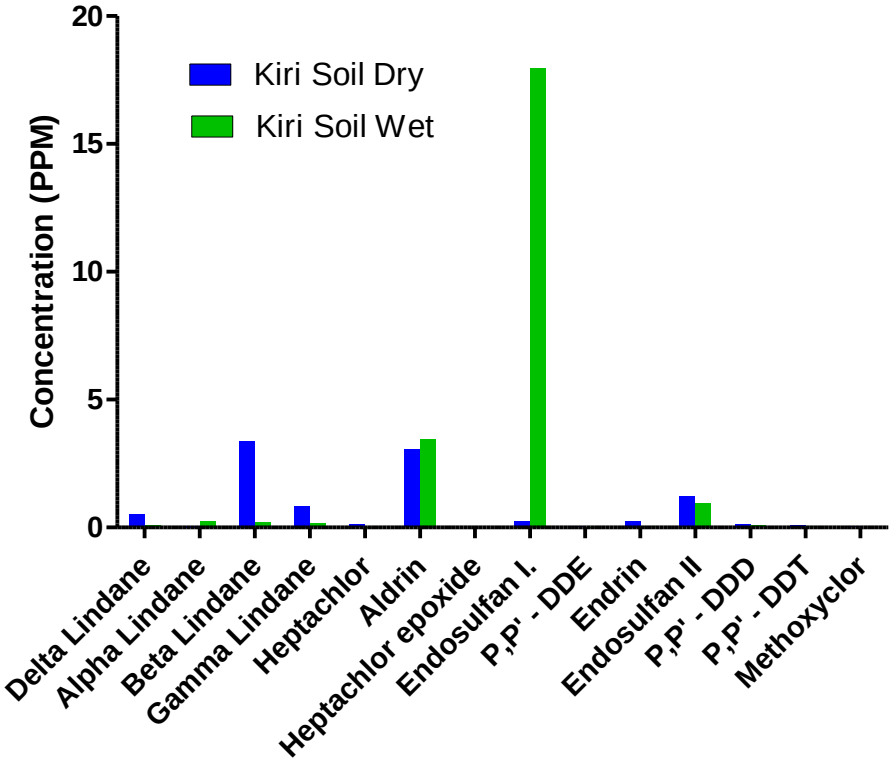

Figure 1: Mean concentration of organochlorine residues level in soil (dry and wet season) from Kiri

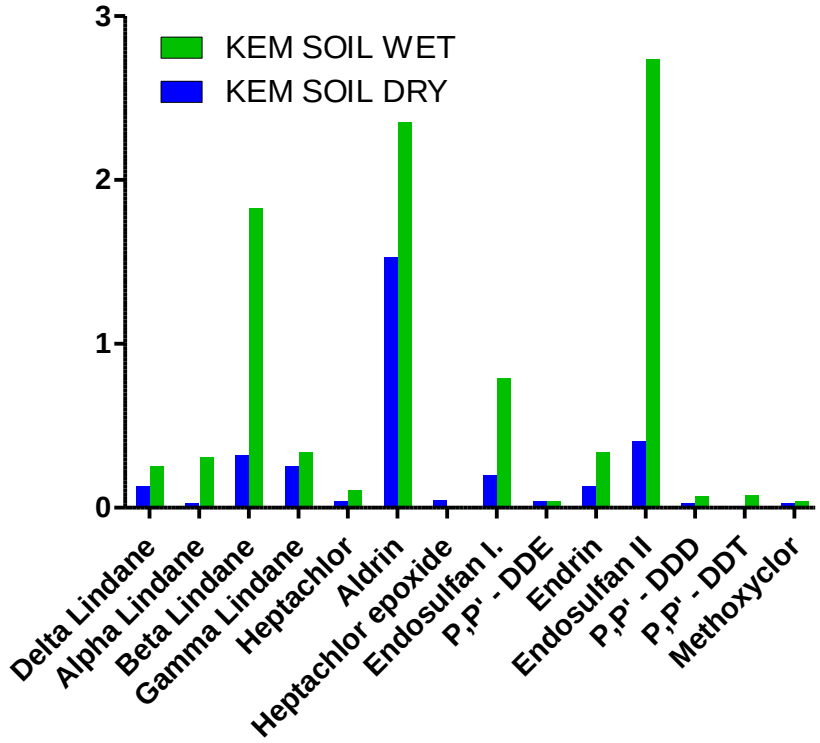

Figure 2: Mean concentration of organochlorine residues level in soil (dry and wet season) from Kem

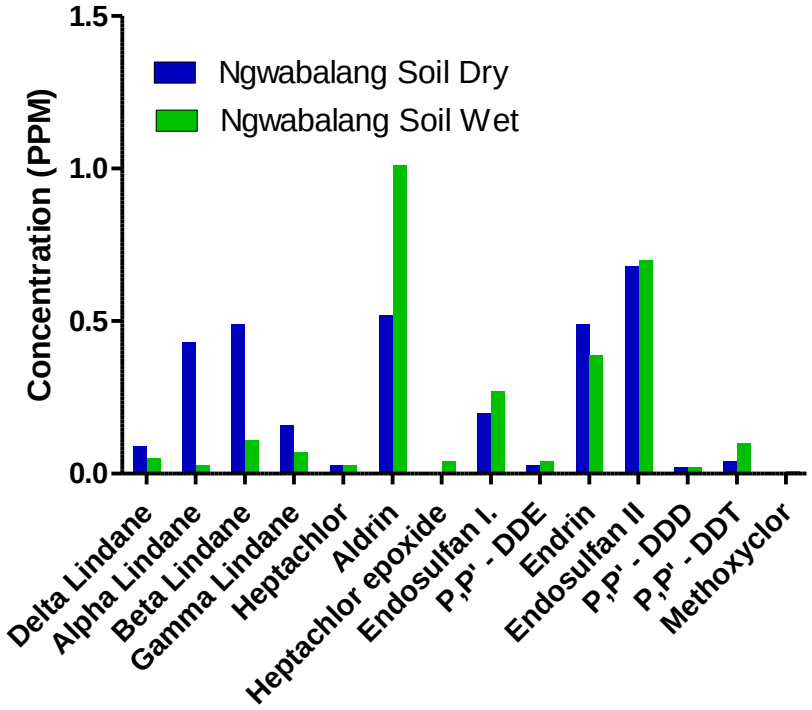

Figure 3: Mean concentration of organochlorine residues level in soil (dry and wet season) from Ngwalam

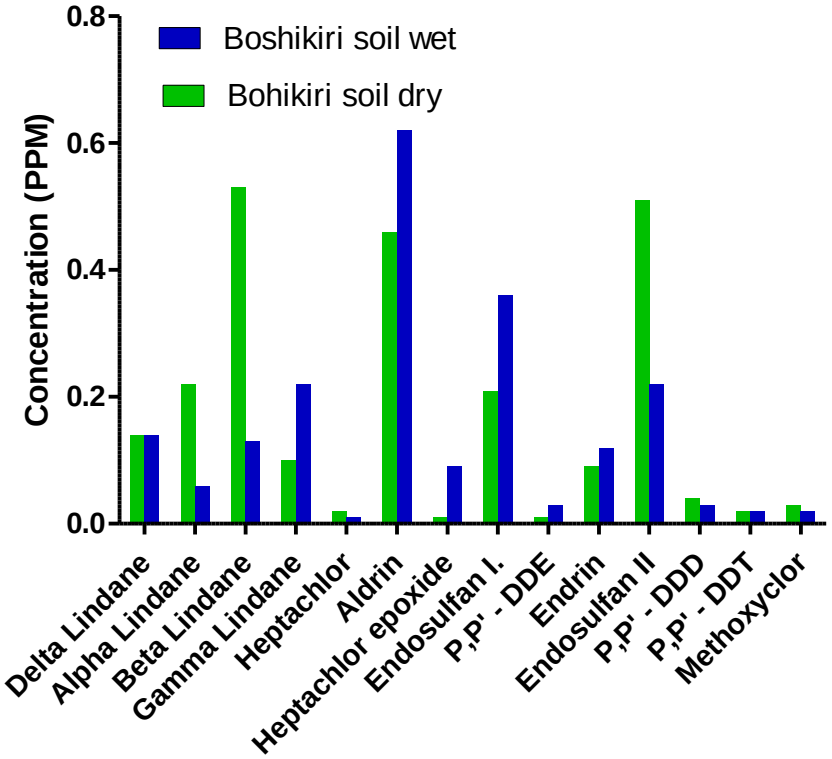

Figure 4: Mean concentration of organochlorine residues level in soil (dry and wet season) from Boshikiri

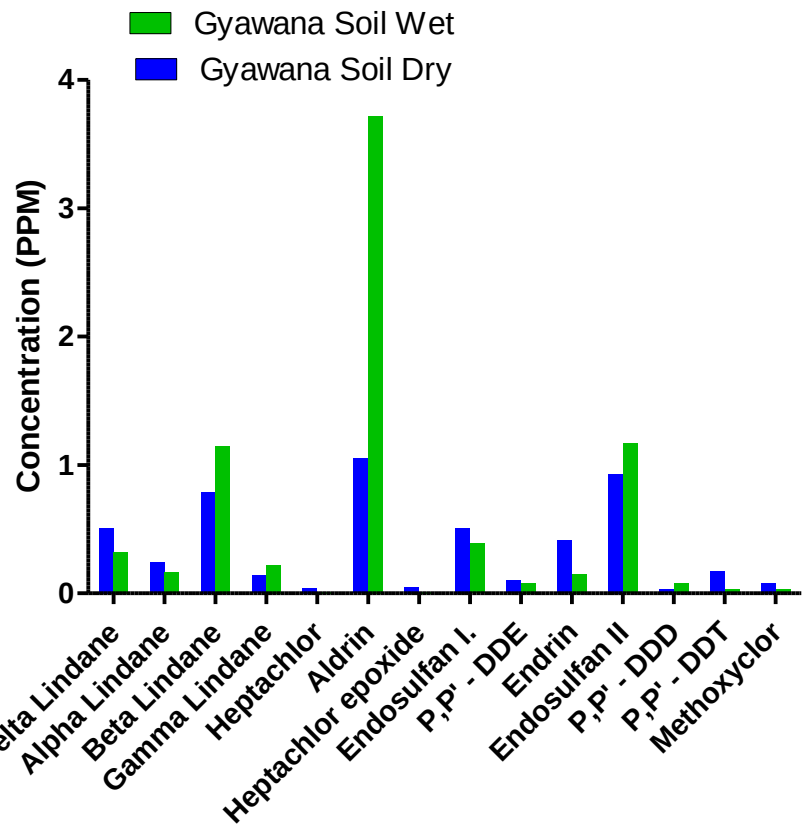

Figure 5: Mean concentration of organochlorine residues level in soil (dry and wet season) from Gyawana

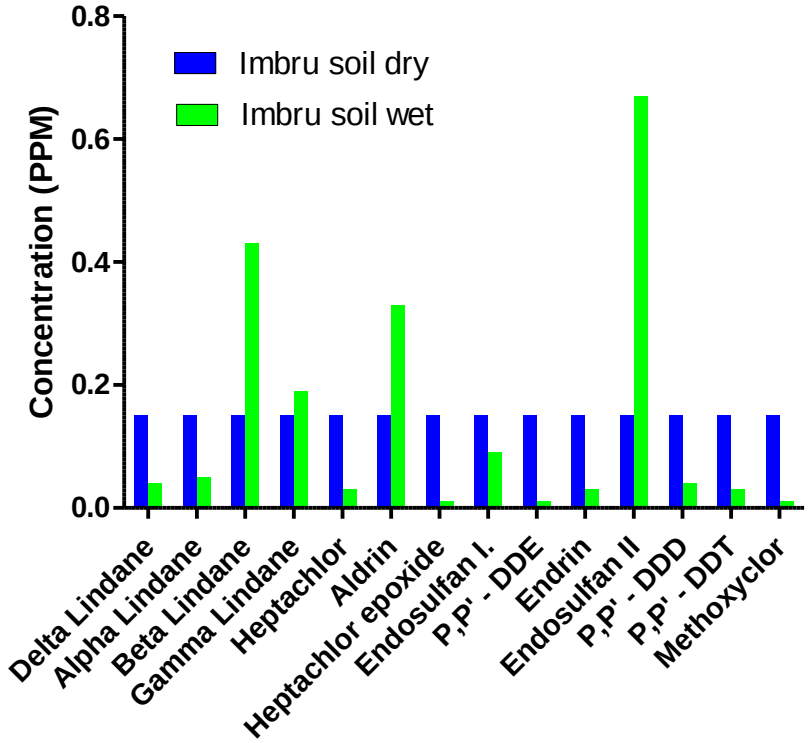

Figure 6: Mean concentration of organochlorine residues level in soil (dry and wet season) from Imbru.

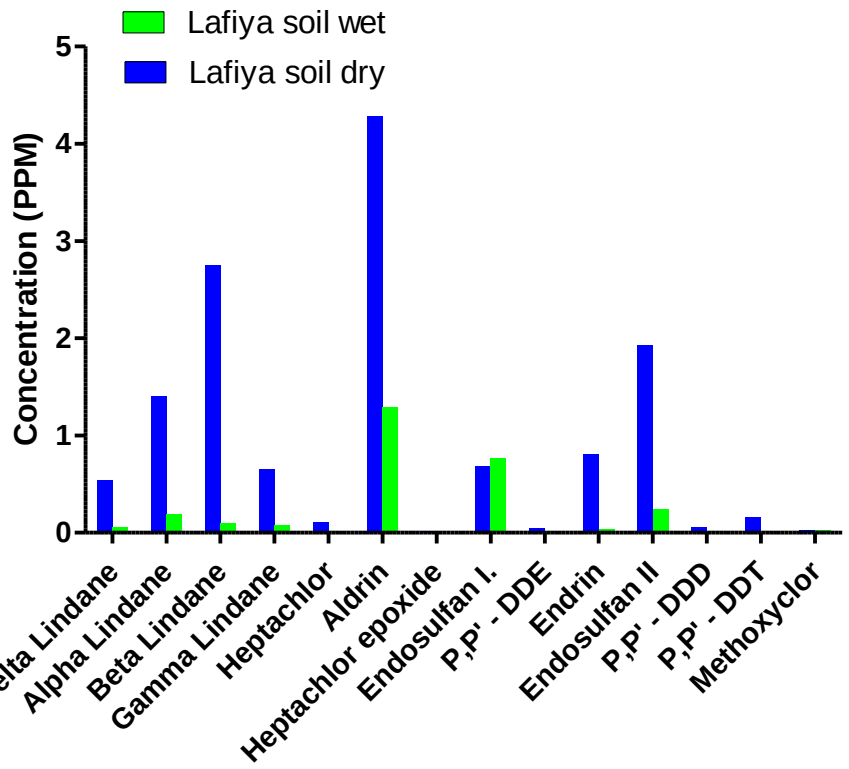

Figure 7: Mean concentration of organochlorine residues level in soil (dry and wet season) from Lafiya

Organochlorine pesticides in plant samples

The concentrations of organochlorine pesticides measured in the plant samples from Boshikiri, Gyawana, Imbru, Kiri, Lafiya, Ngwabalang, and Kem were presented in Table 4.8. Plant samples analysed showed the presence of the fourteen (14) organochlorine pesticides namely Delta Lindane, Alpha Lindane, Beta Lindane, Gamma Lindane, Heptachlor, Aldrin, Heptachlor epoxide, Endosulfan I., P,P' – DDE, Endrin, Endosulfan II, P,P' – DDD, P,P' – DDT and Methoxyclor. There were however no statistically significant sites difference ($p > 0.05$) in mean concentrations of the detected residues in the soil samples.

Lindane

The highest concentration of lindane (Delta, alpha, beta and gamma lindanes) was detected in all the plant samples. Delta lindane, alpha lindane, beta lindane and gamma lindane were detected in all the plant samples within the range of 0.02883 to 0.142757 ppm, 0.025213 to 0.087495 ppm, 0.053329 to 0.348687 ppm and 0.022819 to 0.199418 ppm respectively. The mean concentration of Delta lindane was highest at Kiri with a mean value of 0.142757 ppm but lowest at Kem with mean value 0.02883 ppm. Similarly, the mean concentration of alpha lindane was highest at Ngwabalang with a mean value of 0.087495 ppm but lowest at Kiri with a mean value of 0.025213 ppm. However, the concentration of beta and gamma lindane were highest at Boshikiri and Kem with a mean value of 0.348687 ppm and 0.199418 ppm respectively, but lowest at Imbru and

Boshikiri with a mean v alue of 0.053329 and 0.022819 ppm respectively. The mean concentrations of delta lindane, alpha lindane, beta lindane and gamma lindane recorded at the sampling sites were all below the WHO permissible limit. The presence of lindane in the plant samples confirmed the previous use or continuous illegal use of the pesticide in the study area, as it was also detected in the soil samples analysed. Lindane is in the WHO category II insecticide group and is capable of causing acute as well as chronic intoxication [9]. Although, the levels of lindane detected in the water samples did not exceed the WHO limit, exposure to large amount of lindane have been reported to have negative effects on the nervous system with symptoms from headaches and dizziness to convulsions and more rarely, death [21].

Heptachlor and Heptachlor epoxide

Heptachlor was detected in Boshikiri, Kiri and Imbru plant samples analysed, with respective mean concentration 0.005615ppm, 0.026971ppm and 0.014137ppm, while Heptachlor epoxide was only detected in Boshikiri with a mean a value of 0.00576ppm. The highest concentration of Heptachlor was detected in Kiri with a mean of 0.026971ppm while the lowest concentration was found in Boshikiri with a mean of 0.005615ppm. The mean concentrations of heptachlor recorded at the various sampling sites were below the WHO permissible limit. The high occurrence of heptachlor in the plant samples suggests the continual usage of the illegal pesticide by cocoa farmers in the study area. It may also be attributed to previous contamination as well as environmental persistence from past usage of the chemical. Heptachlor is known to have implications in a broad range of adverse human health effects including endocrine disrupting properties, reproductive failures and birth defects, immune system malfunction, Parkinson's disease and cancers, hence their presence is of serious concern [18].

Aldrin

Aldrin was detected in all the plant samples from all the sites. The mean concentration of Aldrin was detected in all the plant samples with ranged from 0.044797 to 0.726186 ppm. The highest value was detected at Boshikiri with a mean concentration of 0.726186 ppm while the lowest value was found at Imbru with the mean value of 0.044797ppm. The mean values were above the WHO MRL value. However, current or direct application and bioaccumulation of aldrin as an insecticide cannot be entirely ignored. The occurrence of aldrin in the plant samples from the various farms may be linked to its detection in the soils of the various farms from which water samples were taken.

p,p′-DDD, p,p′-DDE, and p,p′-DDT

p,p'-DDD and p,p'-DDE were detected in all the plant samples. The mean concentration of p,p'-DDD and p,p'-DDE ranged from from 0.008752 to 0.051752ppm and 0.004656 to 0.01753ppm respectively. The concentration of p,p-DDD was highest at Ngwalam with a mean value of 0.051752ppm while it is lowest at Kiri with a mean value of 0.008752ppm. Similarly, The concentration of p,p-DDE was highest at Imbru with a mean concentration of 0.01753ppm ppm and lowest at Kiri with a mean concentration of 0.004656ppm. However, p,p′-DDT were also detected in all the plant samples analysed at a mean concentration that ranges from 0.018782 to 0.075569ppm. The concentrations of p,p′-DDT recorded in this study were however below the WHO MRL of 2.00 µg/l for drinking water. The presence p,p′-DDT in the plant samples confirmed the assertions made early, that there is a likely current application of pesticides which might contain DDT by farmers in the study area (probably with different trade names). It might also be as a result of previous contamination, as they degrade slowly and persist in the environment for a long time. Long-term exposure to low doses of DDT has been shown to affect the endocrine, reproductive systems, immune system and cause cancers [8].

Endrin

Endrin was detected in site all the plant samples analyzed. The mean concentration of Endrin ranged from 0.022732 to 0.307102 ppm. The highest concentration for Endrin was detected in Lafiya with the mean values of 0.307102ppm while the lowest concentration was detected in Imbru with a mean value of 0.022732 ppm. Presence of endrin could be as a result of previous use or atmospheric deposition [9].

Endosulfan I and II.

Endosulfan I and II were detected in the plant samples analysed at an average of 0.02323 to 0.195553 ppm and 0.049694 to 1.12097ppm respectively, which was higher than the WHO MRL values. The mean residue concentration of Endosulfan I and Endosulfan II recorded in this study was higher at Boshikiri with a mean value of 0.195553ppm and 1.12097ppm but lower at Lafiya and Kem with a mean value of 0.02323 and 0.049694ppm respectively. The occurrence of endosulfan in the plant samples most likely reflects the current use of the pesticide. Long-term exposure to low doses of endosulfan has been shown to cause endocrine disruptions, reproductive and developmental damage in animals and humans [8]. It can therefore be concluded that rice polluted by endosulfan poses a threat to consumers in the study area.

Methoxychlor

The pesticide residue (methoxychlor) levels detected in the plant samples were within the range of 0.007647 to 0.056188ppm. The highest concentration for methoxychlor was detected in Kiri with the mean values of to 0.056188ppm while the lowest concentration was detected in Lafiya with a mean value of 0.007647ppm. The mean concentration levels detected were shown below.

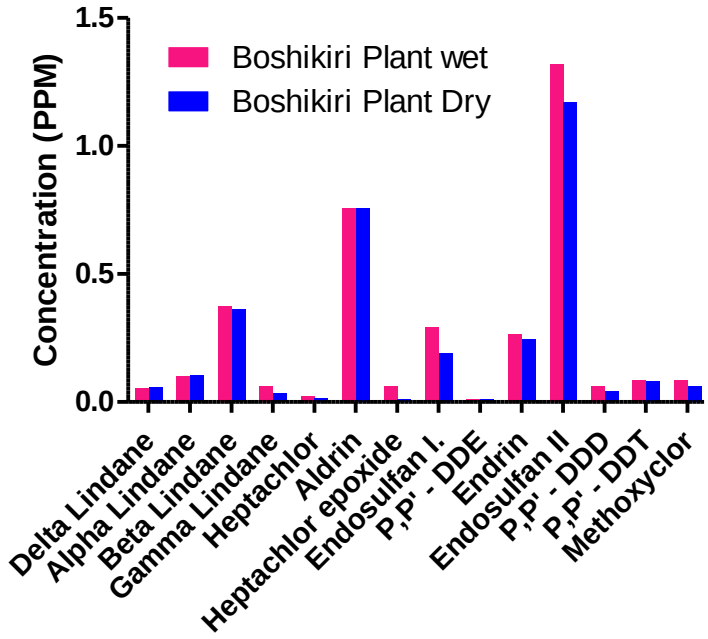

Figure 8: Mean concentration of organochlorine residues level in plant (dry and wet season) from Boshikiri

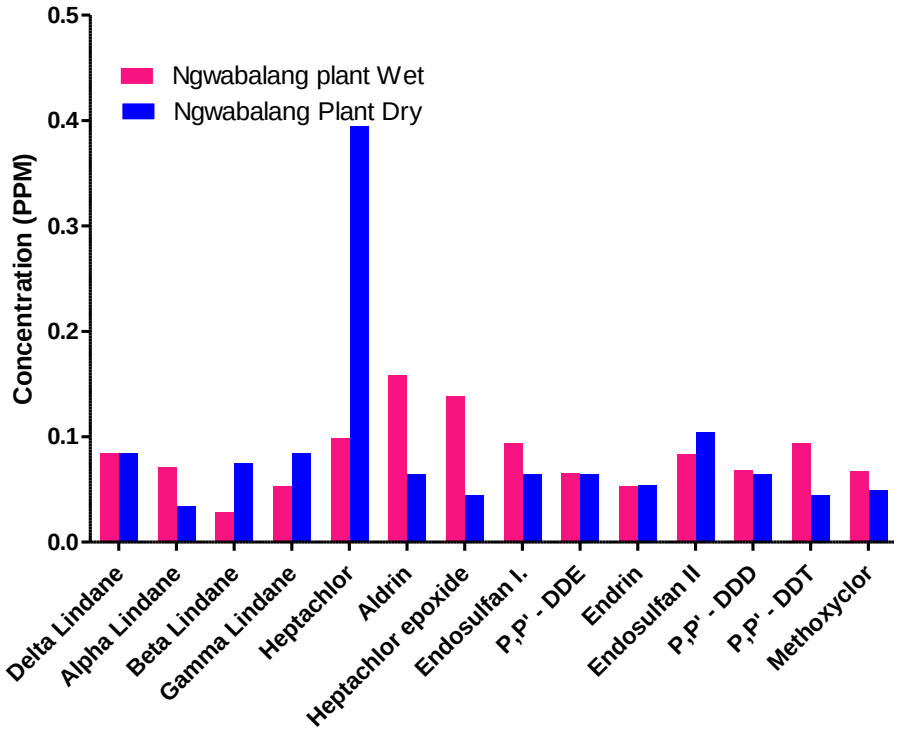

Figure 9: Mean concentration of organochlorine residues level in plant (dry and wet season) from Ngwabalang

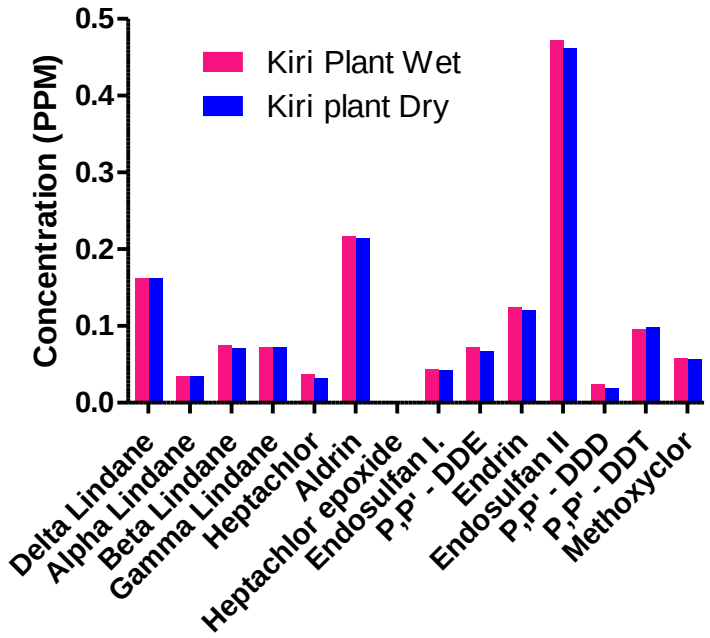

Figure 10: Mean concentration of organochlorine residues level in plant (dry and wet season) from Kiri

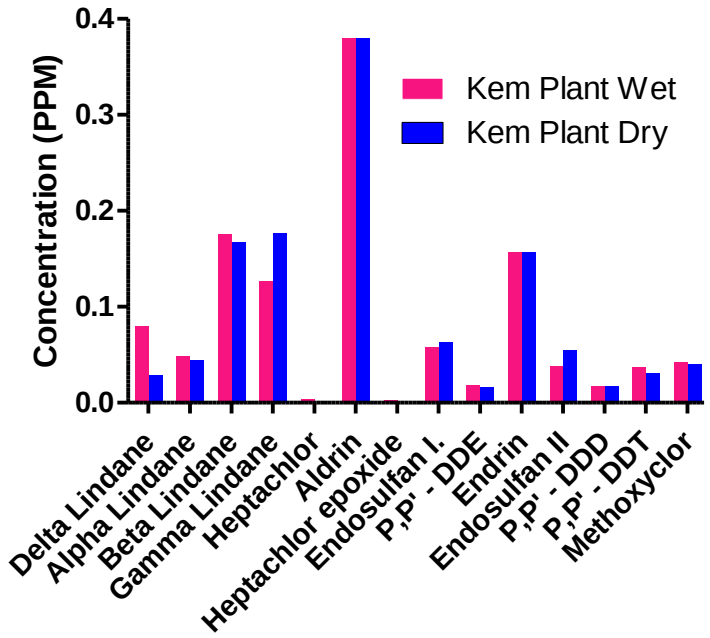

Figure 11: Mean concentration of organochlorine residues level in plant (dry and wet season) from Kem

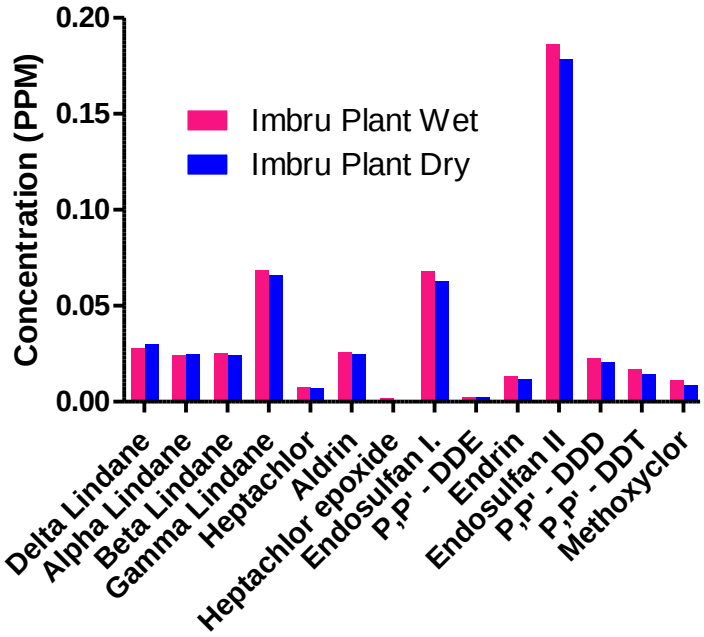

Figure 12: Mean concentration of organochlorine residues level in plant (dry and wet season) from Imbru

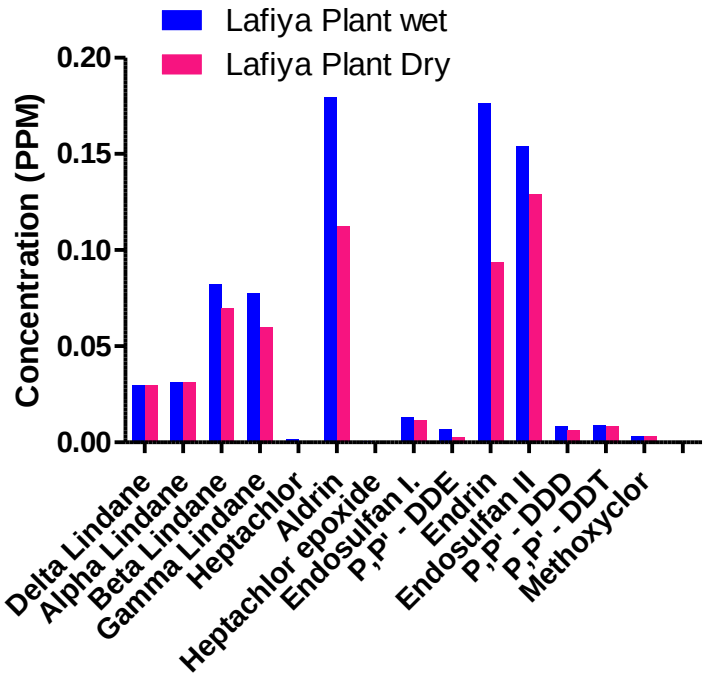

Figure 13: Mean concentration of organochlorine residues level in plant (dry and wet season) from Lafiya.

Organochlorine pesticides in water samples

Organochlorine pesticide residues in water samples The organochlorine pesticide residues detected in the water samples were Delta Lindane, Alpha Lindane, Beta Lindane, Gamma Lindane, Heptachlor, Aldrin, Heptachlor epoxide, Endosulfan I., P,P' – DDE, Endrin, Endosulfan II, P,P' – DDD, P,P' – DDT and Methoxyclor. Similarly, there were no statistically significant differences ($p > 0.05$) in mean values of the pesticide residues detected in relation to distance of water sources to the farms at Boshikiri, Gyawana, Imbru, Kiri, Lafiya, Ngwabalang, and Kem sampling sites.

Lindane

The highest concentration of lindane (Delta, alpha, beta and gamma lindanes) was detected in all the water samples. Delta lindane, alpha lindane, beta lindane and gamma lindane were detected in all the water samples within the range of 0.01 to 0.7ppm, 0.01 to 0.72ppm, 0.05 to 1.29ppm and 0.01 to 0.45ppm respectively. The mean concentration of Delta lindane was highest at Boshikiri with a mean value of 0.7ppm but lowest at Imbru and Ngwabalang with mean value 0.01ppm. Similarly, the mean concentration of alpha lindane was highest at Imbru with a mean value of 0.72ppm but lowest at Ngwabalang with a mean value of 0.01ppm. However, the concentration of beta and gamma lindane were highest at Kiri and Boshikiri with a mean value of 1.29ppm and 0.45ppm respectively, but lowest at Gyawana and Lafiya with a mean value of 0.05 and 0.01ppm respectively. The mean concentrations of delta lindane, alpha lindane, beta lindane and gamma lindane recorded at the sampling sites were all below the WHO permissible limit of 2.00 µg/l for drinking water. The presence of lindane in the water samples confirmed the previous use or continuous illegal use of the pesticide in the study area, as it was also detected in the soil samples analysed. Lindane is in the WHO category II insecticide group and is capable of causing acute as well as chronic intoxication [8].

Although, the levels of lindane detected in the water samples did not exceed the WHO limit, exposure to large amount of lindane have been reported to have negative effects on the nervous system with symptoms from headaches and dizziness to convulsions and more rarely, death [8]. The mean concentration of lindane recorded in this study was lower than the mean concentrations of 37.0µg/l reported [12] in river water samples from cocoa producing area in Ilawe-Ekiti, Ekiti State, Nigeria.

Heptachlor and Heptachlor epoxide

Heptachlor was detected in all water samples analysed but borehole water from Ngwabalang. The mean concentration ranged from 0.01 to 3.00 ppm. Similarly, heptachlor epoxide was also detected in all but borehole and well water within the range of 0.01 to 0.07ppm. The highest concentration of Heptachlor was detected in borehole wate from Imbru during wet season with a mean of 3.00ppm. The highest concentration of Heptachlor epoxide was detected in the well water from Lafiya during wet season with a mean of 0.07ppm. The mean concentrations of heptachlor recorded at the various sampling sites were comparable, below and above the WHO guideline limit of 0.03 µg/l for drinking water. The high occurrence of heptachlor in the water samples suggests the continual usage of the illegal pesticide by cocoa farmers in the study area. It may also be attributed to previous contamination as well as environmental persistence from past usage of the chemical. Heptachlor is known to have implications in a broad range of adverse human health effects including endocrine disrupting properties, reproductive failures and birth defects, immune system malfunction, Parkinson's disease and cancers, hence their presence is of serious concern [8].

Aldrin

Aldrin was detected in all the water samples from all the sites. The mean concentration of Aldrin was found in all the soil samples with ranged from 0.13 to 6.34ppm. The highest value was detected in well water from Imbru during dry season with a mean concentration of 6.34 ppm while the lowest value was detected in well water from Boshikiri during wet seasons with the mean value of 0.13ppm. The mean values were above the WHO MRL of 0.03 µg/l for drinking water. However, current or direct application and bioaccumulation of aldrin as an insecticide cannot be entirely ignored. The occurrence of aldrin in the water samples from the various farms may be linked to its detection in the soils of the various farms from which water samples were taken.

p,p′-DDD, p,p′-DDE, and p,p′-DDT

p,p'-DDD and p,p'-DDE were detected in all the water samples. The mean concentration of p,p'-DDD and p,p'-DDE ranged from from 0.0 to 0.28ppm and 0.0 to 0.07ppm respectively. The concentration of p,p-DDD was highest in borehole water from Boshikiri during wet season with a mean value of 0.28ppm while it is lowest at borehole water from Ngwabalang during dry season with a mean value of 0.00ppm. Similarly, The concentration of p,p-DDE was highest borehole water from Boshikiri during wet season with a mean concentration of 0.07ppm ppm and lowest Boshkiri, Imbru, Ngwabalang, Kem and Lafiya with a mean concentration of 0.00ppm. However, p,p′-DDT were also detected in all the water samples analysed at a mean concentration that ranges from 0.0 to 0.09ppm. The concentrations of p,p′-DDT recorded in this study were however below the WHO MRL of 2.00 µg/l for drinking water. The presence p,p′-DDT in the water samples confirmed the assertions made early, that there is a likely current application of pesticides which might contain DDT by farmers in the study area (probably with different trade names). It might also be as a result of previous contamination, as they degrade slowly and persist in the environment for a long time. Long-term exposure to low doses of DDT has been shown to affect the endocrine, reproductive systems, immune system and cause cancers [8]. The mean concentration of p,p′-DDT recorded in this study was higher than the mean values of 0.03 and 0.02 µg/l recorded in river water samples from cocoa producing areas in Ilawe Ekiti, Ekiti State, Nigeria [12] and in Ondo State, Nigeria [13], respectively.

Endrin

Endrin was detected in site all the water samples analyzed. The mean concentration of Endrin ranged from 0.02 to 12.62 ppm. The highest concentration for Endrin was detected in borehole water from Boshikir during wet season with the mean values of 12.62 ppm while the lowest concentration was detected in borehole water from Imbru during dry season with a mean value of 0.02 ppm. Presence of endrin could be as a result of previous use or atmospheric deposition (Abongo *et al*., 2015).

Endosulfan I and II.

Endosulfan I and II were detected in the water samples analysed at an average of 0.02 to 5.49 ppm and 0.20 to 74.65 ppm repectively, which was higher than the WHO MRL of 0.01 µg/l for drinking water. The mean residue concentration of Endosulfan I and Endosulfan II recorded in this study was higher in borehole water from Imbru and Boshikiri during wet season with a mean value of 5.49 ppm and 74.65 ppm but lower in borehole and well water from Ngwabalang and Lafiya during dry season with a mean value of 0.02 and 0.20ppm respectively. These values were lower than the mean value of 3200 µg/l recorded in river water samples from cocoa producing areas in Nigeria by [10]. The occurrence of endosulfan in the water samples most likely reflects the current use of the pesticide. Long-term exposure to low doses of endosulfan has been shown

to cause endocrine disruptions, reproductive and developmental damage in animals and humans [11]. It can therefore be concluded that water pollution due to endosulfan poses a threat to consumers in the study area.

Methoxychlor

The pesticide residue (methoxychlor) levels detected in the water samples were within the range of 0.00 to 0.05ppm. The highest concentration for methoxychlor was detected in borehole and well water from Gyawana during dry and wet season respectively, with the mean values of to 0.05ppm while the lowest concentration was detected in well water from Ngwabalang during dry season with a mean value of 0.00ppm. The mean concentration levels detected were shown below.

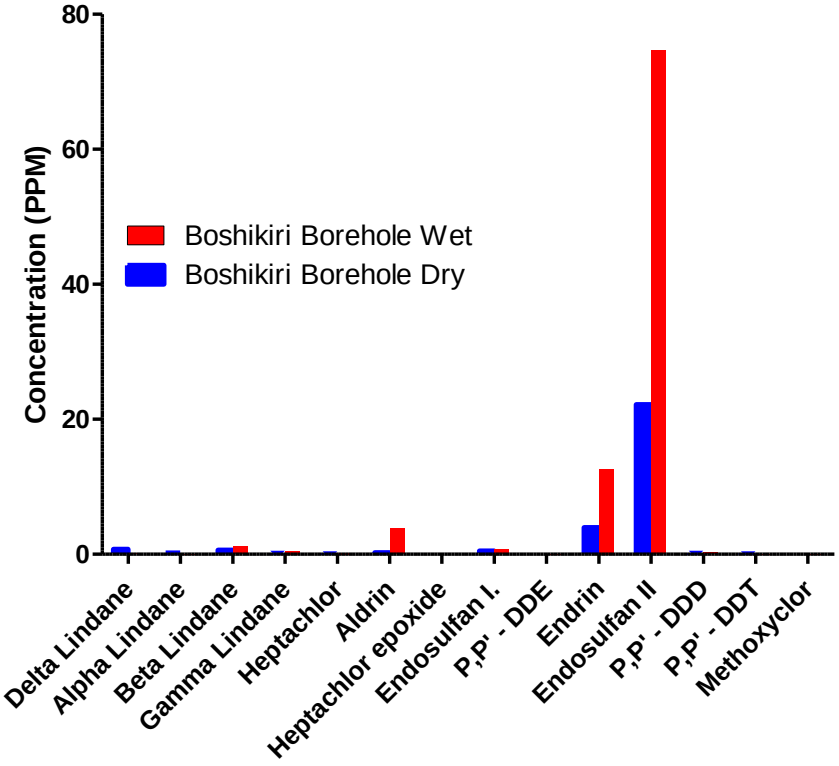

Figure 14: Mean concentration of organochlorine residues level in ground water from Boshikiri

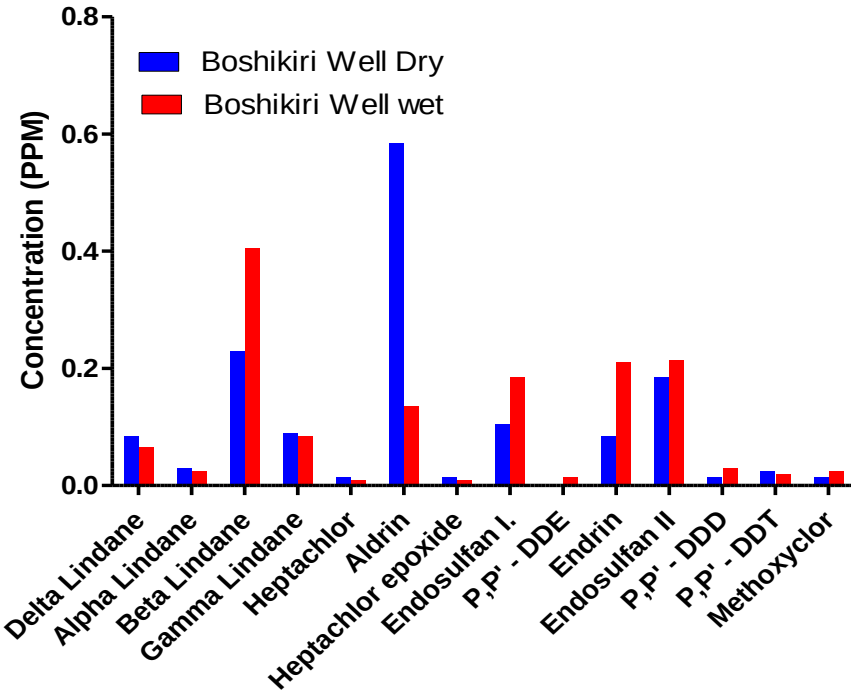

Figure 15. Mean concentration of organochlorine residues level in ground water from Boshikiri

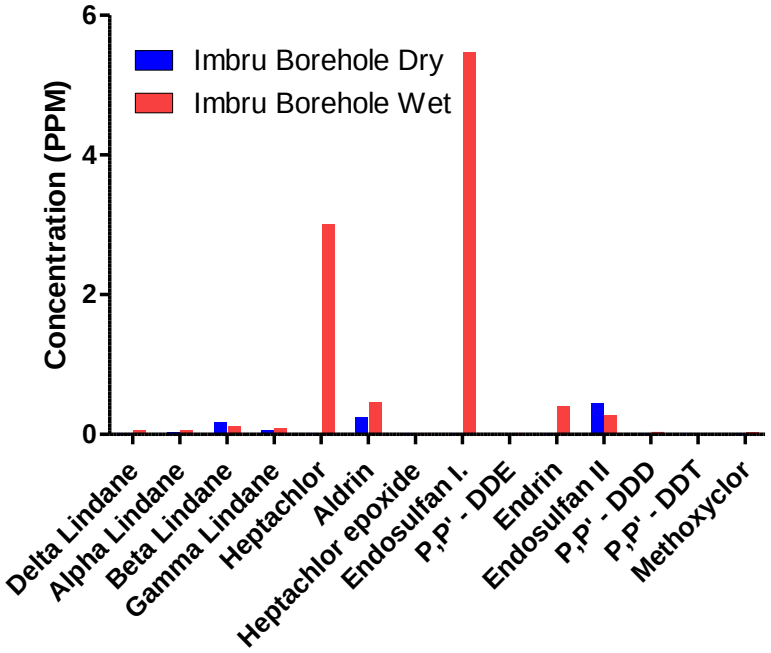

Figure 16: Mean concentration of organochlorine residues level in ground water from Imbru

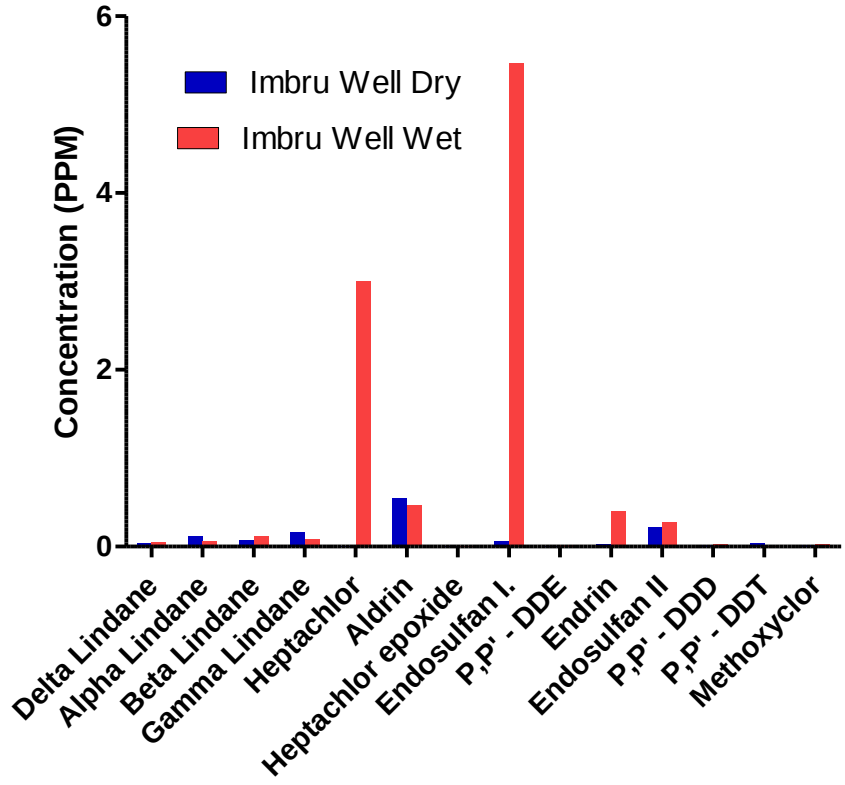

Figure 17: Mean concentration of organochlorine residues level in ground water from Imbru

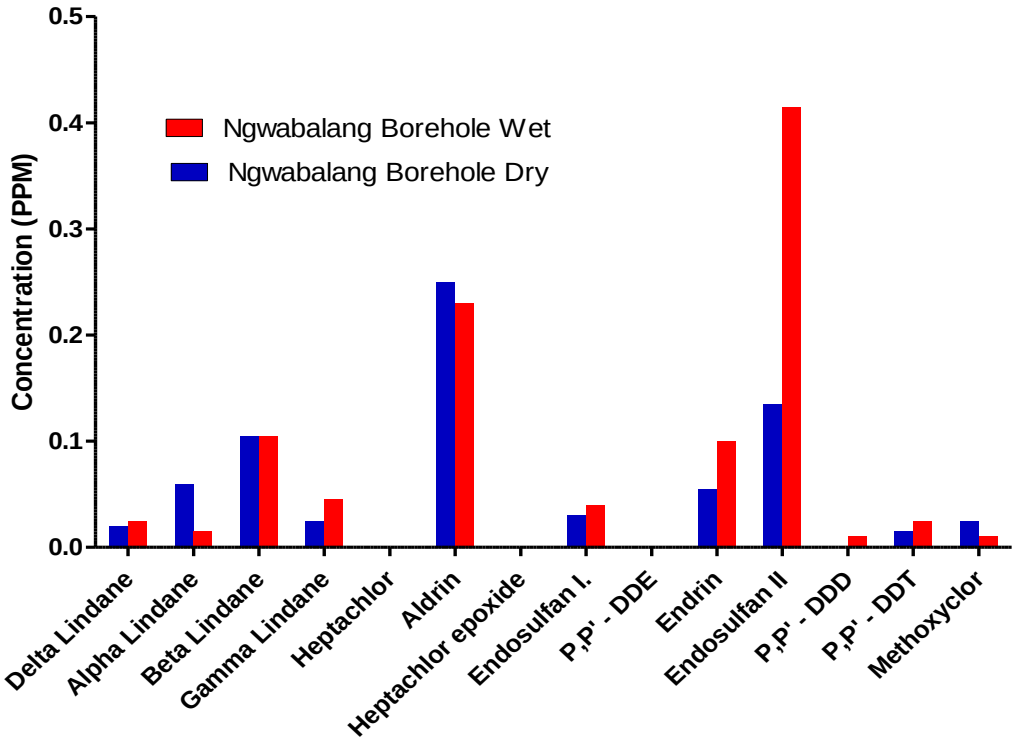

Figure 18: Mean concentration of organochlorine residues level in ground water from Ngwabalang

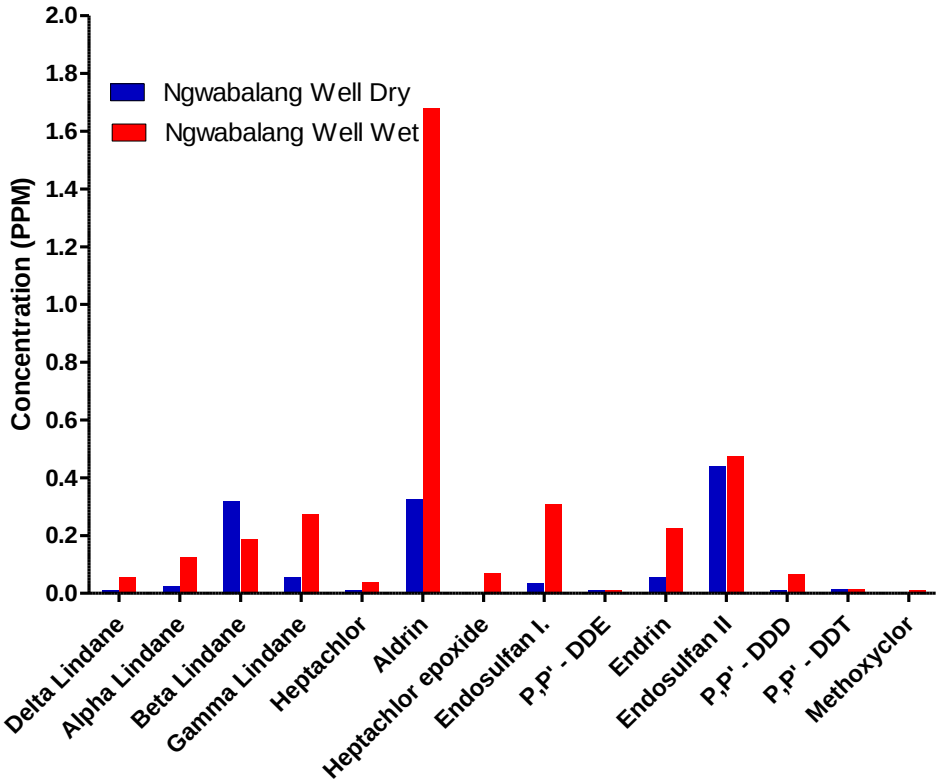

Figure 19: Mean concentration of organochlorine residues level in ground water from Ngwabalang

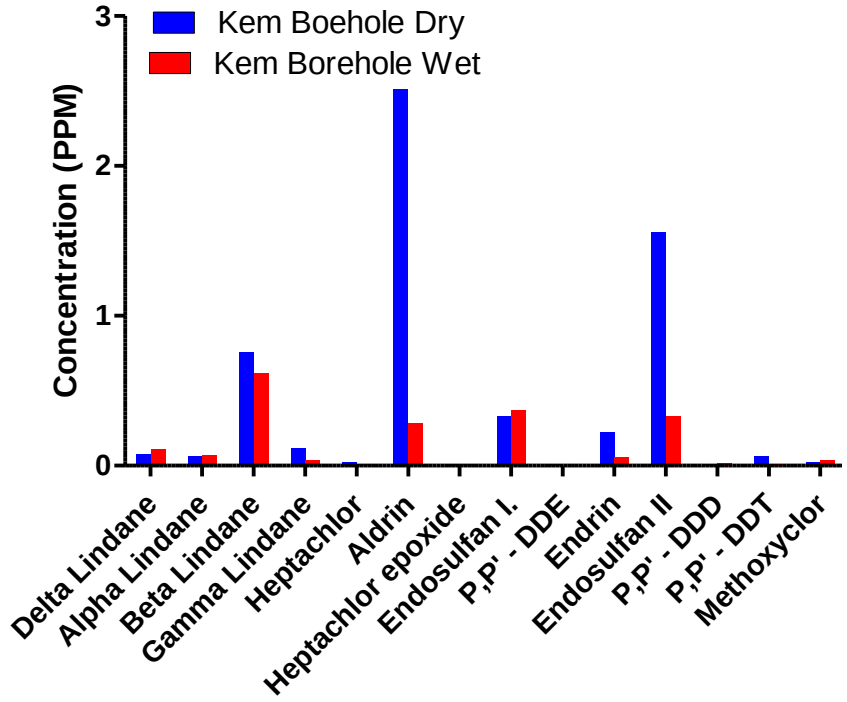

Figure 20: Mean concentration of organochlorine residues level in ground water from Kem

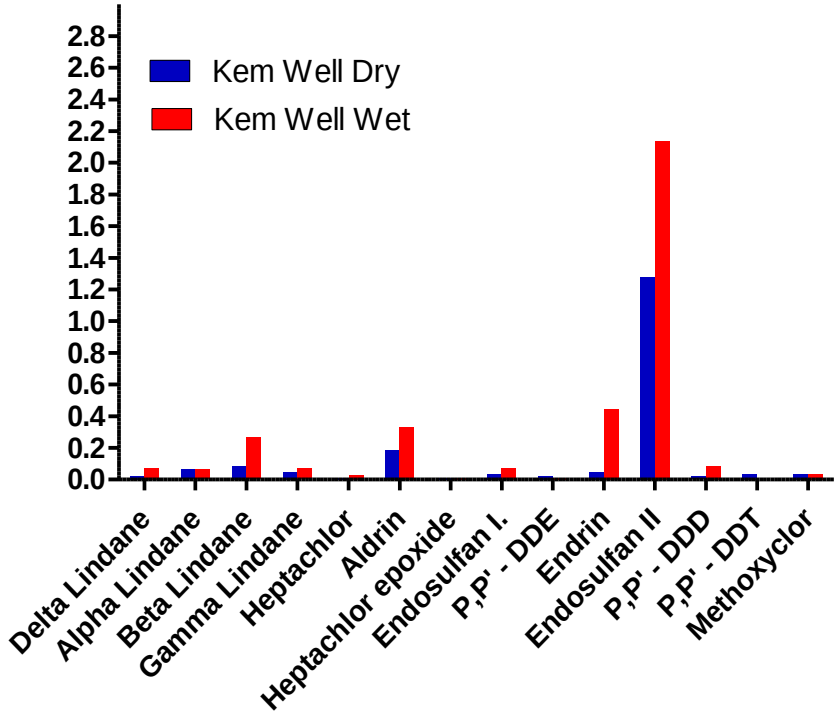

Figure 21. Mean concentration of organochlorine residues level in ground water from Kem

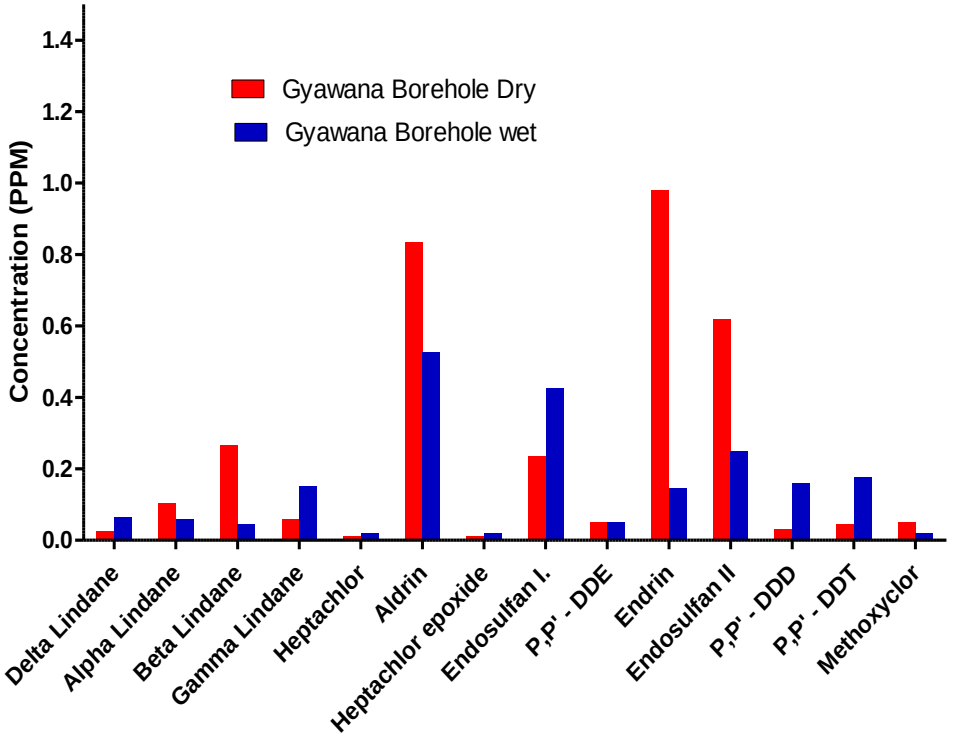

Figure 22: Mean concentration of organochlorine residues level in ground water from Gyawana

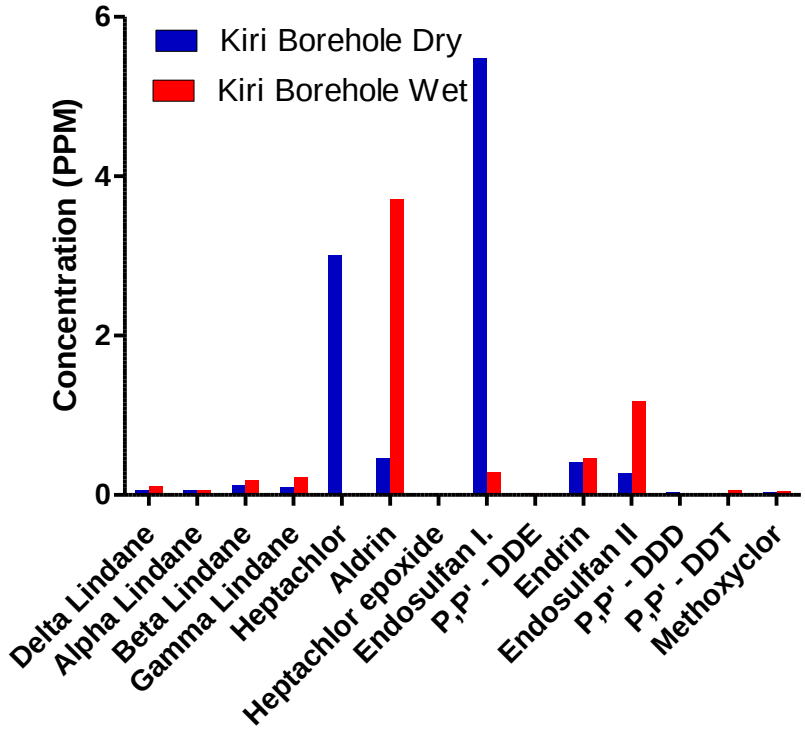

Figure 23: Mean concentration of organochlorine residues level in ground water from Kiri

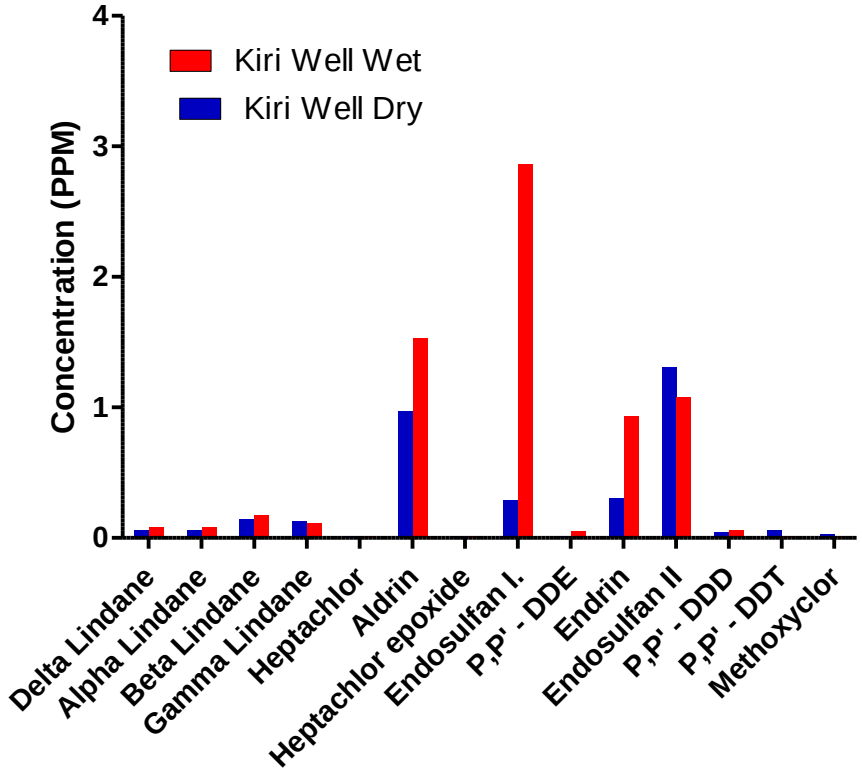

Figure 24: Mean concentration of organochlorine residues level in ground water from Kiri

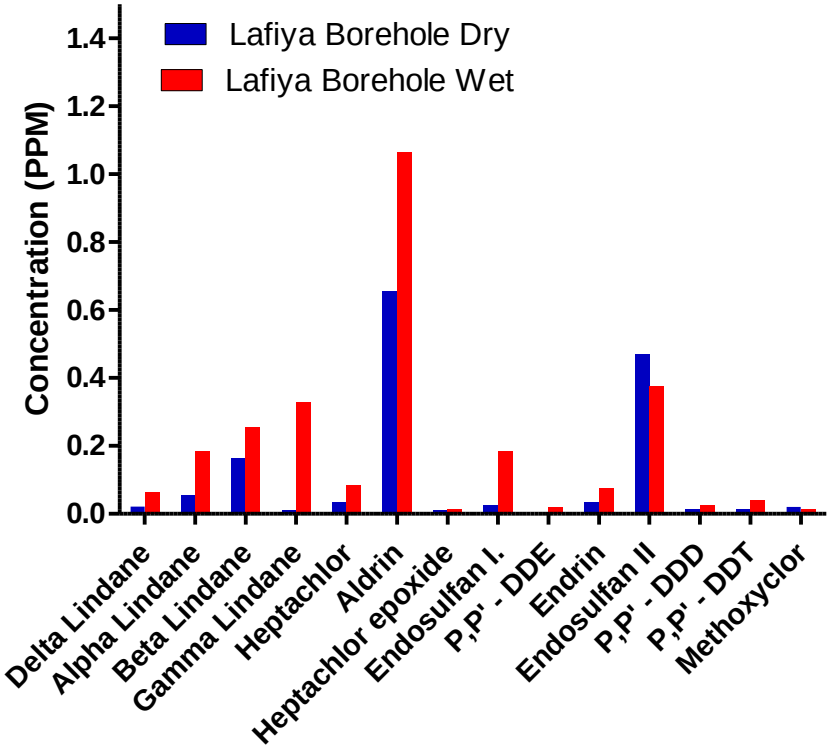

Figure 25: Mean concentration of organochlorine residues level in ground water from Lafiya

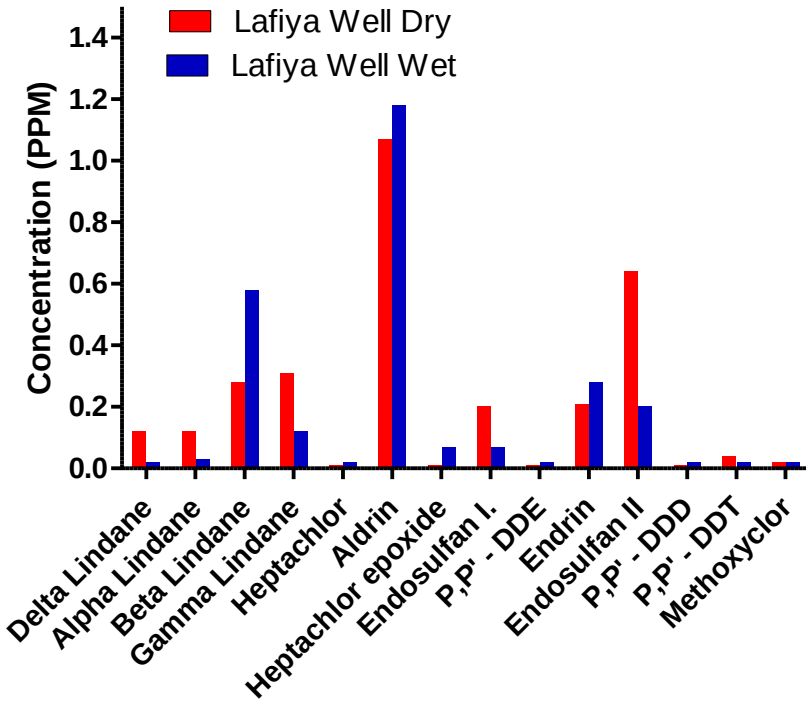

Figure 26: Mean concentration of organochlorine residues level in ground water from Lafiya

CONCLUSION AND RECOMMENDATIONS

Figures 1-26 presented the concentrations of organochlorine pesticides measured in the soil, water and plant samples from Boshikiri, Gyawana, Imbru, Kiri, Lafiya, Ngwabalang, and Kem. The samples analysed showed the presence of the fourteen (14) organochlorine pesticides namely Delta Lindane, Alpha Lindane, Beta Lindane, Gamma Lindane, Heptachlor, Aldrin, Heptachlor epoxide, Endosulfan I., P,P' – DDE, Endrin, Endosulfan II, P,P' – DDD, P,P' – DDT and Methoxyclor. There were however no statistically significant sites difference ($p > 0.05$) in mean concentrations of the detected residues in the soil samples. The pesticides detection frequency was high in wet seasons than in the dry.

CONCLUSION

The results of the investigation of pollution accumulation in soil, water, and plants revealed significant levels of pollutants in the study area. The analysis was performed using gas chromatography-mass spectrometry (GCMS).

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