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Quantitative Analysis of Organophosphate Pesticides Residues in Water and Sediment Samples of River Benue, Jimeta Adamawa State

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ABSTRACT

Environmental pollution by synthetic pesticides in water bodies have been a great concern globally and in developing countries such as Nigeria in particular as most of these pesticide compounds are persistent and bio-accumulative with high toxicity effects on ecosystems and humans. This work was aimed at quantifying synthetic pesticide residues of Organophosphate origin in the River Benue, Jimeta Adamawa State, Nigeria with specific objectives of investigating the presence of organophosphate synthetic pesticide residues; determine the respective concentrations of the residues. Water and sediment samples were collected from the River. A total of six samples each of water and sediment samples were collected from six points at an interval of 1 kilometer apart from the Downstream of the River Benue. One kg sample of sediment was also collected from the six points. The samples were taken to the laboratory and extracted using acetone, n-hexane and Dichloromethane. The extracts were analyzed using Gas Chromatography (GCMS, 7890, MSD, 5977A, Agilent Tech). The results revealed a total of 6 pesticides residues from the two media belonging to the class of pesticide Organophosphate on the basis of chemical composition. Organophosphate residues range from 0.01±0.01 to 0.97±0.10 (μ/l) in water and 0.01±0.0 to 1.23±0.11 (μ/kg) in sediment respectively. The results revealed higher concentration in sediment than water. The Organophosphate residues exceeded the normal value, hence, far beyond negligible limit as they may post adverse effects. This therefore necessitates a continuous monitoring of these residues.

Keywords: [Quantitative, Organophosphate, water, sediment, Jimeta]

INTRODUCTION

Water pollution is the contamination of water bodies such as rivers, streams, lakes, oceans and groundwater by human activities such as the application of pesticides. Water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging not only to the individual species and populations but also to the natural biological communities. Water pollution occurs when pollutants are discharged either directly or indirectly into water bodies without adequate control or treatment. It is a major cause of global concern as it leads to onset of numerous fatal diseases such as cancer which are responsible for the death of over 14000 people everyday globally (Erickson, 2013).

Synthetic pesticides are xenobiotic (man-made) substance use in the modern agriculture for the control of several groups of pests. The primary aim of pesticides is to control diseases, insects and weeds in agricultural crops. But these pesticides are harmful to man and the environment in general as non target organisms. The most commonly used pesticides include insecticides, herbicides, fungicides and rodenticides (Yadav, Devi, Syed, Cheng and Jones, 2015).

Modern agricultural pesticides rely on the usage of synthetic pesticides (mainly herbicides, insecticides and fungicides) in order to prevent losses by pests. The global pesticides production become higher after the Second World War which rose from approximately 500,000 t/h in the 1950s to over three (3) million t/h at the beginning of the 21st century (Eldridge, 2008). The application of pesticides may lead to contamination of aquatic environments through several ways such as spray drift, surface runoff and leaching. Besides habitat loss, overexploitation of species, introduced species, aquatic organisms are affected by the pollution of surface waters with pesticides from agriculture in particular (IUCN, 2009). If water contains pesticides at concentration which substantially reduce populations of aquatic plants, it is likely to be associated with low numbers of small animals relative to predators' populations and increased numbers of parasites hence, affecting the ecological balance of the water body (Beasly, 2010).

The circumstances for pesticide use present a high risk to communities of aquatic species from spray drift for insecticides and runoff from fields for herbicides. Surface waters are frequently contaminated with insecticides through normal use at levels above those known to affect fish and other aquatic invertebrates such as the Shrimps (Bagchi, Azad, Alomgir, Chowdhury, Uddin and Rahman, 2009).

Pesticides are also useful in public health for killing vectors of diseases, such as mosquitoes while, pests damaging agricultural crops are the key target of the pesticides. Essentially, pesticides are potentially toxic to other non-target organisms, including human beings and other animals. Hence, it is necessary to use them safely and dispose all related items properly. The role of pesticides in controlling unwanted insects and weed has been recognized since the mid-nineteenth century. From that time to present, their use has increased in the control of different pests where they are potentially hazardous to the people and wild plants and animals of the affected areas (Yadav et al., 2015).

Though there is no denial on the fact that pesticides are essential in modern agriculture, there is growing concern of possible environmental contamination and pollution from these chemicals ranging from agrochemical industries, household, rain water runoff from agricultural systems and disposal of outdated chemicals among other sources (Domagalski and Kuivila, 2009). These chemical compounds when discharged into aquatic system play an important role in contaminating such systems. Research has also revealed that atmospheric transport also represents an important source of pesticides residue accumulation in water bodies (Schmiit and Linder, 2010).

The persistent and bioaccumulation tendency of these substances, their metabolites and residues in the environment make them not only remain where they are applied but instead they go to major aquatic ecosystems in accordance with their physicochemical properties and hence transported to far distances from the application sites (Agarwal, 2009). Sediments which serve as a habitat for benthos/benthic organisms such as clams and some aquatic insects that are commonly consume by nektons such as fish also get contaminated by pesticides. Aquatic biotas on the other hand are important in the food web of terrestrial organisms, with some aquatic biota, such as fish, being consumed by man and some wild animals. Alternatively, the herbicide glyphosate for example, grew in popularity and has long been considered to be more environmentally benign than other pesticides. Nevertheless, in 2015 a report from the International Agency for Research on Cancer [IARC] concluded that glyphosate is probably carcinogenic to humans especially non-Hodgkin's lymphoma (Erickson, 2015a). A class of pesticides known as neonicotinoids has received the most attention from the public in recent years. The use of neonicotinoids pesticides rose higher as a result of restrictions implemented on the use of carbamates and organophosphates for the raised concerns over their effects on aquatic organisms and human health respectively (Erickson, 2015b).

Pesticides can enter rivers and other surface waters through different routes, among which are runoff driven by precipitation or irrigation which is the most important in terms of peak concentrations. Pesticides exposure can cause direct effects on all levels of biological organizations, while the toxicant mode of action largely determines which group of organisms from primary producers, microorganisms, invertebrates or fish is affected (Carriger and Rand, 2008). Due to the interconnectedness of the freshwater communities, direct effects of pesticides can entail several indirect effects. Runoff and erosion therefore account for highest routes of pesticides into aquatic medium (Sumon, 2018). In rural agricultural areas, pesticides reach water bodies such as rivers, streams, ponds and lakes through deliberate application to water bodies for the control of undesirable aquatic plants and insects, aerial application for terrestrial pests, wind blowing, drifts from aerial application where much of the spray remains for a time in the atmosphere, adherence to soil particle, thereby to the water bodies by runoff as well as accidental spills (Vanden-Brink, 2013).

Runoff which is the movement of water across the soil surface and occurs when water collects either as a result of rainfall or irrigation at a rate faster than it can infiltrate the soil. As rain falls, small soil particles are dislodged and are carried by water through a process called erosion (Naidoo and Buckley, 2003). Pesticides are mostly known to be applied directly to the soil; large amounts eventually end up there via runoff. As water runs off and soil erodes, dissolved and sorbed pesticides go along. Runoff and erosion have the potential to move more pesticides off site than leaching due to the fact that they are surface phenomenon (Halstead, McMahon, Johnson, Raffel, Romansic, Crumcrine, 2014). Hence, surface runoff and erosion move pesticides and other pollutants laterally from points of higher concentrations to collection points such as Rivers, Streams, ponds and lakes at lower elevations. Climatic factors such as rainfall timing, duration and intensity as well as surface features such as slope length and grade, soil permeability and soil cover all together greatly influence the degree to which pesticides are mobilized by runoff and erosion into water bodies (Halstead et al., 2014).

Non-point source pesticide pollution from agricultural activities conducted adjacent to water bodies such as rivers, streams, ponds and dams is widely regarded as one of the greatest causes of contamination of surface waters. It is believed that conditions in countries where the active ingredients were developed and tested and as a consequence, can lead to unexpected impacts (Ansara-Ross, Wepener, Vanden-Brink and Ross, 2012).

The infrastructure to monitor and control pesticide contamination especially in water resources is poorly developed in most developing countries. The duration of effects depends on the exposure dose, recovery potential of the affected organisms and the environment, which is determined by several key factors. Long term effects of pesticides have been shown to occur in the field. However, the extent of the effects is mostly uncertain, mainly because of a lack of large-scale data on pesticides peak concentrations (Mann, Hyne, Choung and Wilson, 2009).

The role of pesticides is to kill the target pest, but this property of pesticides makes them a poison to other organisms including aquatic organisms, birds, animals and humans. These pesticides are not target specific. The constant exposure of pesticides to non-target species may lead to induce toxicity once it crosses the threshold limit in the system. It is known that the major portion of the pesticide applied in an area reaches into healthy environmental components such as aquatic reserves (ponds, lakes, rivers and oceans), where they gradually get accumulated into other organisms (Azab, Darwish, Mahmoud and Sadeek, 2013).

MATERIALS & METHODS

3.1. Sampling sites

A preliminary hydrographical survey of the study area was conducted during which the sampling sites were selected. For the purpose of this study, six sampling sites were marked at and interval of 1km apart. The sites were simply assigned locations as A, B, C, D, E and F. These locations were selected on the basis of agricultural activities undergoing around the River bank. All data collection on commonly used pesticides as well as samples collection for the study was strictly restricted within the six selected sites.

3.2. Methods of Data Collection

The data samples of both water and the sediments samples were collected using the procedures described and adapted from (Akan et al., 2015).

3.2.1. Water samples collection

Water samples were collected at a depth of approximately one (1) foot below the surface and at ten meters (10m) from the river bank. The samples were collected using 1 litre plastic bottle and then transported to Chemistry Department laboratory of Yobe State University, Damaturu where the determination of pesticides residues and their concentrations in water was conducted. The sampling bottles were cleaned with water using a non-ionic detergent and then rinsed with tap water for several times before collecting the samples.

At each of the sampling sites/locations (A-F), water samples were collected at a distance of 1kilometer apart from each other. The samples were then labeled and transported to laboratory for the analysis. In order to avoid pesticides breakdown before the analysis, the samples were stored in a refrigerator at a lowest temperature of 5ºC.

3.2.2. Collection of Sediment samples

One kilogram of sediment samples were collected at each sampling point (A-F) using a plastic hand trowel and then wrapped in an aluminum foil, and stored tightened to prevent drying prior to the analysis of the samples. Thus, the samples were collected in kilograms from all the six sites. The tightened samples were then taken to the laboratory for the analysis of organophosphate pesticide residues. To avoid breakdown of the pesticides prior to analysis, the sediment sample were stored in a refrigerator at a low temperature of 5ºC.

3.2.3. Analytical Methods

All concentrations of pesticides in water were expressed in milligrams per liter (mg/l) and pesticide concentrations in sediment samples were expressed in micrograms per kilogram (µg/kg). Pesticides standard analysis were used for this analysis using a GC model of GC 7890B, MSD 5977A.

3.2.4. Extraction of organophosphate residues in water samples

The water samples were adjusted to $p^{H}4$ with 2 ml H_2SO_4, while 10g of Nacl was added to all water samples to increase extraction efficiencies. N-hexane (50ml) was introduced into a two litre separating funnel containing 1 litre of filtered water and was shaken vigorously for 5 minutes and allowed to settle. After complete separation, the organic phase was drained into a 200ml conical flask. The aqueous phase was re-extracted with 50ml of n-hexane. The samples were then centrifuged at 490g for 6 minutes to separate the extract from the pellet. Then, the extracts were combined, evaporated to normal under Nitrogen stream and dissolved again in hexane and then finally analyzed using gas chromatography as presented in the results.

3.2.5. Extraction of organophosphate residues in sediment samples

For sediment extraction, the samples were extracted using 1 kg of sediment sample which was transferred into an extraction thimble that had been previously washed with n-hexane and acetone. It was then dried with an oven. The sample was extracted using 150ml of n-hexane and acetone mixture of 4:1 v/v for good eight hours with a Soxhlet extractor. The extract was then evaporated using a rotary evaporator at 45°C. Each of the extracts was dissolved in a 10ml n-hexane and then subjected to the analysis.

3.2.6. Chemicals and reagents used

The chemicals and reagents used were Acetone, n-hexane and Dichloromethane. Others were pure Silica gel and ultrahigh purity water. All the solvents and reagents used were of pesticide grade standard.

3.2.7. Gas Chromatography analytical conditions

The career gas of the GC, was 2ml/m throughout the analysis. However, temperatures were 50ºC, -120ºC and -140ºC respectively. The injector temperature of GC machine and the Detector temperature was 300ºC while Detector temperature ranges from 280ºc-290ºC.

Statistical Analysis

All data obtained were analyzed using analysis of variance (ANOVA). A significant level of $p<0.05$ was adopted for the analysis of variance (ANOVA) which was done using statistical package for social sciences (SPSS) software version 23.

RESULT

Table 1: Organophosphates residues in water samples of the Downstream of the River Benue, Jimeta, Adamawa State (Concentrations in (mg/l).

Sample collection site	Diazinon	Malathion	Dichloros	Glyphosate	Fenthion	Fenitrothion
A	0.04±0.01^{b}	0.33±0.41^{b}	0.93±0.12^{a}	0.97±0.10^{a}	0.11±0.21^{b}	ND^{b}
B	0.72±0.23^{a}	0.70±0.21^{a}	0.51±0.11^{b}	0.69±0.19^{a}	0.07±0.11^{b}	ND^{b}
C	0.73±0.11^{a}	0.77±0.09^{a}	0.74±0.11^{a}	0.76±0.13^{a}	0.31±0.04^{b}	0.11±0.31^{b}
D	0.87±0.01^{a}	0.39±0.13^{b}	0.29±0.20^{b}	0.89±0.02^{a}	0.43±1.01^{b}	0.50±0.12^{b}
E	0.23±0.22^{b}	0.25±1.00^{b}	ND^{b}	0.01±0.01^{b}	0.77±0.41^{a}	0.79±0.39^{a}
F	0.25±0.12^{b}	0.97±0.00^{a}	0.01±0.34^{b}	0.04±0.12^{b}	0.39±0.31^{b}	0.97±0.04^{a}
Total	**2.84±0.70**	**3.41±1.84**	**2.48±0.88**	**3.36±0.51**	**2.08±2.09**	**2.37±0.86**

Values are expressed as ± standard error of mean. Values with different superscript in the same row indicate significant difference at 0.05 level ($p<0.05$) while values having same superscript on same row shows no significant different. While ND denote not detected.

Table 2: Organophosphate residues in sediment samples collected from the Downstream of River Benue, Jimeta, Adamawa State, Nigeria (Concentration in (µ/kg).

Sample collection site	Diazinon	Malathion	Dichloros	Glyphosate	Fenthion	Fenitrothion
A	0.43±0.23^{b}	0.01±0.11^{b}	0.82±0.18^{a}	0.83±0.21^{a}	0.85±0.23^{a}	0.07±0.01^{b}
B	0.76±0.02^{a}	ND^{b}	0.77±0.06^{a}	0.77±0.05^{a}	0.45±0.10^{a}	0.03±0.00^{b}
C	0.21±0.01^{b}	0.31±0.21^{b}	1.21±0.11^{a}	0.23±0.01^{b}	1.23±0.11^{a}	0.09±0.02^{b}
D	0.23±0.00^{b}	0.21±0.13^{b}	0.91±0.24^{a}	0.89±0.21^{a}	0.93±0.23^{a}	0.92±0.19^{a}
E	0.12±0.00^{b}	0.23±0.17^{b}	ND^{b}	0.78±0.11^{a}	0.76±0.12^{a}	0.77±0.15^{a}
F	0.31±0.90^{b}	0.12±0.12^{b}	ND^{b}	0.63±0.12^{a}	0.67±0.09^{a}	0.65±0.10^{a}
Total	**2.06±1.16**	**0.88±0.74**	**3.71±0.59**	**4.13±0.71**	**4.89±0.88**	**2.53±0.47**

Values are expressed as ± standard error of mean. Values with different superscript in the same row indicate significant difference at 0.05 level ($p<0.05$) while values having same superscript on same row shows no significant different. While ND denote Not detected.

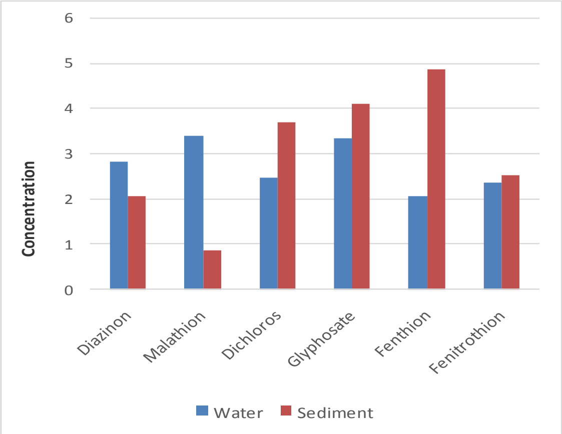

Fig. 1 Comparison of concentrations of organophosphate pesticides in water and sediment samples from the Downstream of River Benue, Jimeta Adamawa state Nigeria.

DISCUSSION

Occurrence and concentrations of Organophosphate Pesticide Residues in the Downstream of River Benue, Jimeta Adamawa State.

Six residues of organophosphate were detected from the analyzed samples of water and sediment with about Eighty Seven percent positivity. The six organophosphate pesticide residues detected were Diazon, Malathion, Dichloros, Glyphosate, Fenthion and Fenitrothion. Some of the organophosphate residues were below detectable limit from the analyzed samples in water. In the water samples, Fenitrothion was below detectable limit in samples A and B while Dichloros was below detectable limit in sample E respectively. The findings of this study however, contradicts with that of Ogah et al. (2017), who recorded higher values in a similar study conducted in the Niger Delta region of southern Nigeria. Malathion had the highest value in water while Fenthion had the highest in sediment samples analyzed. However, Malathion had the least mean value in sediment samples as shown by the study.

Table 1 presented the mean concentration of organophosphate pesticide residues in water. The results showed that Fenitrothion was below detectable limit in both samples A and B while Dichloros was below detectable limit in sample E and recorded 0.01±0.34 (mg/l) in F respectively. In table 2 however, Dichloros was below the detectable limit in both E and F samples unlike in the water sample where it was detected in sample F. Malathion had recorded the total highest concentration in water with 3.41±1.84 (mg/l) followed by Glyphosate with 3.36±0.51 (mg/l) while Fenthion recorded the total least with 2.08±2.09 (mg/l) as shown in table 1. In the sediment samples however, Dichloros was below detectable limit in both sample E and F. Fenthion had recorded the total highest concentration in sediment with a concentration of 4.89±0.88 (μ/kg) closely followed by Glyphosate with 4.13±0.71 (μ/kg) while Malathion recorded the total least concentration of 0.88±0.74 respectively.

Fig. 1 showed the comparison of organophosphate residues in water and sediment samples. Fenthion had it values in sediment doubled that of water. Malathion had the least value from the detected organophosphate residues in both the sediment and water samples. Diazon and Malathion were highest in water than in sediment while Dichloros, Glyphosate, Fenthion, Fenithrothion were all higher in sediment.

CONCLUSION

This research attempted to provide the pollution load by organophosphates synthetic pesticide residues in the River Benue, Jimeta of Adamawa State. The results of the laboratory analysis of this study provide threshold values of pesticide residues of organophosphates pesticides that were present in both water and sediment samples collected from the River Benue. The finding revealed 87% positivity in water and 91% positivity in the analyzed sediment. This study indicates that organophosphate residues showed concentrations values that may have potential risk to the ecological balance of the River Benue, Jimeta. One of the reasons of high concentration of these organophosphate pesticides residues could be their overdose or irrational use. As the threshold values of organophosphate residues exceeds the recommended dosage in the analyzed samples from the River Benue, a potential eco-toxicological effects to both target and non-target organisms of different trophic levels in food chain is anticipated.

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