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Level of Persistent Organic Pollutants (Pops) in River Yedzaram Mubi-Uba Area, Adamawa State, Nigeria

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Abstract

The levels of persistent organic pollutant (POPs) in water, soil and Sediment sampled from river Yedzaram were determined. The POPs in these samples were extracted by Soxhlet extraction process using n-hexane. The extracts were cleaned and analysed using Gas Chromatograph, Mass Spectrometer (GC-MS) equipped with Ni 63 electron capture detector. In all the three samples analysed namely; water, soil and sediment. The POPs determined include Dieldrin, DDT (Dichlorodiphenyltrichloroethane), HCH (Hexachlorocyclohexane), Aldrin and Heptachlor. The level of HCH, (0.50 µg/g) was the highest POP detected in sediment from Mayo-Bani while Aldrin level of (0.01 µg/g) was the lowest POP detected in soil from Mubi. The concentrations of these POPs were more in sediments from Mayo-Bani. The concentrations of POPs in water, soil and sediment from all the locations studied ranges from 0.0096 µg/g to 0.5002 µg/g are below the Australian maximum residue limit (MRL) of 0.05 µg/g to 10.00 µg/g for water, soil and sediment and the allowable limits by the Federal Environmental protection Agency (FEPA) now Federal Ministry of Environment and also below the FAO/WHO tolerance limits. Conclusion, the findings from all the parameters revealed that River Yedzaram is somewhat safe for now but proper attention must be given to controlled use of POPs.

Keywords: Persistent Organic Pollutants (POPs), Pesticide, River Yedzaram and Environment

Introduction

For the past thirty years, a serious concern has risen due to the presence of persistent organic pollutants (POPs) in the environment and their threat to the wild life and humankind. As is well known, DDT and PCBs were listed by the Stockholm Convention as 2 of 12 persistent organic pollutants (POPs) in 2004, and more recently, α-HCH, β-HCH, and γ-HCH (lindane) were added to the list in 2009 (Hu *et al.*, 2009). Hexachlorocyclohexane (HCH), Dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) are ubiquitous chemicals and are persistent, toxic and bio-accumulative in nature (Minh *et al.*, 2006). These are long-range transport pollutants and can be transported to regions far from their original sources, such as the Arctic (Halsall *et al*., 1998 and Becker *et al*., 2009). They have a wide range of acute and chronic health effects, including cancer, neurological damage, reproductive disorders, immune suppression, birth defects, and are also suspected endocrine disruptors (Van Den Berg *et al*. 2006; Wang *et al*., 2008 and Maitera *et al.*, 2011).

Effective risk management for chemicals depends on tracking the pathways, fate and exposure implications of chemicals, yet data on the pathways, emission, environmental fate and exposure for risk assessment are only available for a very few chemicals (UNEP, 2002).

Special attention has been given to the persistent toxic organic substances, which are widely found in the environment. These substances can travel through air, water and migrating species. They are released into the environment in one part of the world and through a repeated process of release and

deposit, emerge on region far away from their original source (UNEP, 2003). They can become increasingly concentrated in the tissues of animals at high levels of the food chain, which include human through bioaccumulation. Therefore, realizing the potential risk of long time adverse effect of these chemicals, Environmental toxicologists have extensively studied the exposure, fate and effect of their presence since early sixties (UNEP,2003) For practical reasons, human health and environmental risk assessment methodologies have develop independently. Classical risk assessments have evaluated health and ecological risks independently, typically assessed and report by researchers from different disciplines. However, with increasing recognition of the need to protect both human and the environment more effectively an integrated approach to risk assessment that addresses situations of multi-chemicals, multi-media, multi-route and multi-species exposures are needed. International programmes and chemical safety (IPCS), in collaboration with the U.S Environmental Protection Agency (USEPA), European Commission and other International and National Organizations, have developed a working partnership to foster the integration of assessment approaches to evaluate human health and ecological risk.

In 1997 the United Nation Environmental Program (UNEP) governing council decided that international action should be initiated to protect human and the environment through measures which reduce and eliminate the emission and discharges of an initial set of 12 “persistent organic pollutants” (POPs). Nine of which are organochlorine pesticides (UNEP, 2003).

In practice, threshold levels produce no effect concentrations or other approaches such as acceptable daily intake (ADIs) outline by national and international organizations which have been estimated for specific environments. However, it should be realized that such risk assessment cannot be applied across the regions of the world as several geographical and climatic factors affect the assessment significantly.

Furthermore, certain chemicals particularly those that were realized as mixtures of compounds such as polychlorinated biphenyls (PCBs), would impose greater challenge in setting up critical levels for risk assessment of persistent organic pollutant (POPs) which is relatively new in Adamawa State. Data on human exposure to POPs such as organochlorine pesticide (OCPs) and (PCBs) in Adamawa State are insufficient to establish their effects.

The use of chemical pesticides is still indispensable in Adamawa State due to the hot and humid tropical environmental condition that are conducive to the development of myriad of pest, weed and disease vectors. Generally, public health sector also heavily depends on pesticides to control vector borne diseases such as malaria, sleeping sickness, bilharzias and filariasis through pesticides spray programs aimed at controlling disease vectors such as mosquitoes, tsetse flies and water snails (Balogun, 2010).

Several chemical contaminants from the agricultural field comprising of pesticides and other agrochemicals have been reported in drainage system and are likely to jeopardize the quality of water bodies that support fishery industry that are used for domestic human consumption (Madadi *et al.,* 2002).

Studies on the status and levels of persistent organic pollutant in water bodies, soil and sediment in river Yedzaram Mubi-Uba area is yet to get recognition. There is need for the data on the persistent organic pollutant in drainage system of River Yedzaram for proper management of river water, quality and sustainability of the river ecosystem. Most villagers along the river earn their livelihood

through fishing and farming especially dry season farming.

This study aimed at providing baseline information on the current level of persistent organic pollutant (POPs) in water, soil and sediments from River Yedzaram Mubi-Uba area. Persistent organic pollutants threaten the health and wellbeing of human and wildlife in every region of the cosmos. This study is put forward to create awareness based on toxic nature of POPs and provide protection for the present and future generation from adverse effect such as cancer, birth defect and other tragedies caused by POPs and to provide a means to have a scientific plan for the reduction and/or possible elimination of POPs in River Yedzaram. It is recognized that POPs resist degradation under natural conditions and are associated with adverse effects on human health and the environment. POPs accumulate in the food chain, they can be transported over long distance in the atmosphere resulting in wide spread distribution across the earth, including regions where they have never been used.

Materials and Methods

Description of Study Area

The study was carried on River Yedzaram Mubi-Uba area all in Adamawa State North-Eastern part of Nigeria. The Yedzaram basin lies between latitude 11^{o} 15' and 13^{o} 45' north of the equator and longitude 11^{o} 00' and 7^{o} 15' east of the Greenwich meridian.

Sampling Procedures

The sampling areas were categorized into three sites namely:

Site A (entrance of the river from Mubi-Shuware)

Site B (Mayo-Bani part of the river, where irrigation activities takes place)

Site C (Uba-Adamawa part of the river, where farming activities takes place).

Three (3) samples were collected from each sampling spot in order to obtain a composite sample for each location. From each sampling site (i.e. three different samples of soil, sediment and water were collected from each spot), at an interval depth levels of 0-5cm (surface), 10cm and 20cm.The soil samples were collected in a well label polyethylene bags, while water and sediment were collected in three litre amber bottles each. The samples were safely transported to the laboratory for analysis and kept under controlled temperature. The sample mass collected was based on the method according to Zakir *et al.* (2008)

Methods for POPs Determination in Water

The method described by Hess *et al*.(1995) was adopted. Two litres of water were transferred into a separator funnel, pH was measured. A 50ml of sodium hydrogen phosphate buffer were added to the sample and the pH was adjusted to 7.0 by adding drop of 0.1 sodium hydroxide and hydrochloric acid solution. The neutralized samples were treated with 100g NaCl to salt out POPs from the aqueous phase. 60ml triple distilled by dichloromethane were added and shaken for 2 minutes while releasing pressure. The samples were allowed to settle for 30 minutes to enhance separation of the phase. The organic layer were collected in 250ml Erlenmeyer flask and stored at 40°C in refrigerator. Fractions were repeated twice using 60ml portion of dichloromethane. The clean extract were concentrated on rotor-evaporator to near dryness and reconstitute in GC-MS hexane to 5ml. Pure distilled water was used, incorporated as blank and these together with external standard were used to determine detection limit of each POPs investigated.

Methods for Soil and Sediment extraction

Extraction method described by Hess *et al.* (1995) was adopted. Soxhlet system was pre-cleaned with n-hexane for 24hours. About 3.0g of soil sample or sediment sample was weighed and mixed with 8-10g anhydrous sodium phosphate powder; and placed in the soxhlet extraction thimble and extracted with 150ml n-hexane for 5hours. After extraction, the soil

extract or sediment were evaporated on a vacuum rotary evaporator. After solvent exchange with dichloromethane was concentrated to 5ml, the extracts were then fractionated to remove humid substances and sulphur. The fractions were solvent-exchanged with n-hexane and then diluted with 100ml n-hexane through a silica gel column and $2cm^3$ anhydrous sodium sulphur. The column was pre-rinsed with 80ml n-hexane before loading the sample. After it concentrated, it was then evaporated before instrumental analysis using GC-MS.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

A Gas Chromatograph Mass Spectrometer (GC-MS) model GCMS-QP 2010 plus (Shimadzu, Japan) equipped with 63 **Ni** electron capture detector. A 30cm × 0.34mm, 0.25 *am* low polar Hp-5 column was used. Nitrogen was the carrier gas. The operating conditions were; column oven temperature (60.0^oC), Detector temperature (300^oC), Injection temperature (250.0^oC), flow rate of 1.61ml/min at a pressure of 100.2kpa and a linear velocity of 46.3cm/second as well as Injection mode split. Volumes of 1.0 α1 of the sample extracts were injected and 0.1ppm mined standard solutions were analysed in a similar manner. Peak identification was conducted by comparing the retention time of authentic standards and those obtained from the extracts. Concentration was calculated using a fives point calibration curve.

Results and Discussion

Analysis and Interpretation

The level of persistent organic pollutants in water, soils and sediments from Mubi-Uba catchment area were determined and presented on Tables 1, 2 and 3 respectively.

Table 1: Concentration (ppm) of POPs in Water

Samaple	Dieldrin	DDT	HCH	Aldrin	Heptachlor
Mubi	0.14	0.09	0.23	0.02	0.11
Uba	0.06	0.03	ND	0.07	0.15
Mayo-Bani	0.21	0.16	0.39	0.09	0.20
FAO/WHO Tolerance Limit	**10**	**50**	**10**	**10**	**10**

ND: Not Detected

Table 2: Concentration (ml/kg) of POPs in Soil

Samaple	Dieldrin	DDT	HCH	Aldrin	Heptachlor
Mubi	0.12	ND	0.29	0.01	0.15
Uba	0.03	0.07	0.35	0.07	0.06
Mayo-Bani	0.18	0.16	0.44	0.08	0.17
FAO/WHO Tolerance Limit	**10**	**50**	**10**	**10**	**10**

ND: Not Detected

Table 3: Concentration (ml/kg) of POPs in Sediment

Samaple	Dieldrin	DDT	HCH	Aldrin	Heptachlor
Mubi	0.08	0.16	0.48	ND	ND
Uba	0.10	0.18	0.29	0.11	ND
Mayo-Bani	0.20	0.29	0.50	0.17	0.11
FAO/WHO Tolerance Limit	**10**	**50**	**10**	**10**	**10**

In all the three samples analysed namely; water, soil and sediment, the POPs level determined (Dieldrin, DDT, HCH, Aldrin and Heptachlor) were present. The level of HCH, (0.50 µg/g) was the highest POP detected in Mayo- Bani Sediment while Aldrin level of (0.01 µg/g) was the lowest POP detected in Soil from Mubi-Shuware location. The POPs detected in Mayo-Bani and Mubi-Shuware were relatively higher than those detected in Uba in all samples and this may be attributed to the discharge of municipal wastes into the Yedzaram river as the major underground drainage system in the entire area empties into the river and also there is comparatively high level of extensive farming activities around the river compared to Uba sites where mostly, cattle rearers dominate the river sides. Another factor may be due to the human activities around most populated areas like Mubi, which tends to be responsible for the high concentrations of these organic pollutants. Looking at Mayo-Bani, the intensity of farming and agricultural activities in the area revealed the increase in concentrations of the organic pollutants. Low concentration detected from samples collected from Uba is due to other factors such as run-offs, leaching etc. The concentration of organic pollutants is more effective in fatty tissues than in water and other substances, because it is not easily excreted, metabolized or broken down. POPs evaporate more easily at warmer locations and they fall out more easily in colder locations (Weinberg, 2008). This is as a result of what is called "the grasshopper effect".

The concentration of POPs ranged from 0.0096 to 0.5002 – µg/g and is below FAO/WO tolerance limit for water, soil and sediment (as in table 1, table 2 and table 3) and the allowable limits by the Federal Environment protection Agency (FEPA) now Federal Ministry of Environmental Limits and can be harmful if the breed is not checked.

Conclusion

This study revealed that contamination of water, soil and sediment in River Yedzaram by persistent organic pollutants is very low and that the concentrations of POPs ranged from 0.0096 to 0.5002 µg/g which is in compliance with FAO/WHO standard for water, soil and sediment and the allowable limits by the Federal Environmental protection Agency (FEPA) now Federal Ministry of Environmental limits. Hence, River Yedzaram in the region studied is relatively safe for human use at the moment, as it cannot be considered to be polluted now but they stand the risk of getting polluted in the future if the use of these chemicals are not checked and regulated. This agreed with the findings of Maitera *et al. (*2011).

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