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## ANALYSIS OF DIAZINON, CHLORPYRIFOS, MEVINFOS IN RIVER BENUE USING GAS CHROMATOGRAPHY EQUIPPED WITH FLAME PHOTOMETRIC DETECTOR (GC-FPD)

### RESEARCH ARTICLE

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#### ABSTRACT

This study reports the concentration levels and distribution pattern of the pesticide residues in water of the Benue river at Agatu, Buruku, Benue Brewery, Katsina-Ala and NASME collected seasonally over a period of one year using gas chromatography-flame photometric detector. Among the pesticides analyzed, concentration of diazinon at some sample locations were below and higher than the USEPA MRL of 0.017 ppm while the concentrations recorded for chlorpyrifos were below the MRL OF 0.40 ppm. There was however no record of the MRL for mevinfos in drinking water. Also the study revealed that chlorpyrifos and mevinfos are more widely distributed than diazinon, which is in agreement with the pesticides audit conduct at the beginning of the research.

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Key Words: Diazinon, chlorpyrifos, GC-FPD, mevinfos, River Benue.

#### INTRODUCTION

The primary objective of using pesticides in the fields and the environment in general is to achieve a control of crop pests and disease vectors. This has been a deliberate human effort in a search for increasing agricultural yields and improving public health (Helweg, 2003). The pesticides, generated by the increase in agricultural activities are regarded as some of the most dangerous contaminants of the environment, despite their numerous merits (Reemtsma and Jekel, 2006).

The widespread use and disposal of pesticides by farmers, institutions and the general public provide many possible sources of pesticides in the environment. Pesticides once released into the environment may have many different fates. Pesticides that are sprayed can move through the air and may eventually end up in other parts of the environment, such as in soil or water. Pesticides that are applied directly to the soil may be washed off the soil into nearby bodies of surface water or may percolate through the soil to lower soil layers and groundwater (Harrison, 1990).

Organophosphorus pesticides are known to degrade rapidly depending on their formulation, method of application, climate and the growing stage of the plant. Pesticide residues reach the aquatic environment through direct runoff, leaching, and inappropriate disposal of empty containers, washing of equipment etc. (Milindis, 1994). Surface water contamination may have ecotoxicological effects for aquatic flora and fauna as well as for human health if used for public consumption (Leonard, 1988; Miyamoto *et.al*, 1990). Sediments are ecologically important components of the aquatic habitat, which play a significant role in maintaining the trophic status of any water body (Singh *et. al.*, 1997). Highly polluted sediments adversely affect the ecological functioning of rivers due to persistence in the environment and long range transport (Singh *et. al.*, 2002). Since the pesticides are lipid soluble in nature, cumulative accumulation of low concentration of these in the body fat of mammals might pose potential hazards in the long run (Metcaf, 1997).

#### Materials and Method

All glass wares used for this work were washed and rinsed thoroughly with distilled deionized water and oven dried at 40 °C for 2 hours and cooled before use. All chemicals and reagents used in this study were of high purity quality and were of residue grade. Hexane and dichloromethane of special grade for pesticide residue analysis were

purchased from Sigma Aldrich, Germany. Organic solvents particularly dichloromethane which is toxic, were handled with care observing safety precautions, using efficient fume hoods and wearing protective gloves. Silica gel (60-100 mesh ASTM) were purchased from Merck, Germany. Standard stock solutions of diazinon (94.2 % w/w), mevinfos (94.2 % w/w), purchased from Restek Corporation U.S.A., chlorpyrifos (99.0 % w/w), purchased from Chem Service (West Chester, PA, USA) were prepared in acetonitrile at a concentration of 1000 mg L<sup>-1</sup> and stored at 4 °C. From the dilution of stock, solutions were prepared containing the three pesticides at concentrations of 10 and 20 mg L<sup>-1</sup> in the same solvent. Anhydrous sodium sulphate with a purity superior to 99% was also purchased from Vetec.

### Sampling

Water samples were collected from river Benue at Agatu, Buruku, Katsina-Ala, Benue Brewery and NASME using clean plastic containers (1.5 litre capacity), and stored in the refrigerator at + 4 °C and extracted within 24 hours during the rainy and dry seasons, i.e between May, 2013 and March, 2014. The following sample codes were assigned to the sample stations: Agatu; 1, Buruku; 2, Katsina-Ala; 3, Benue Brewery; 4 and NASME; 5 while the monthly sample codes were assigned as: May 2013: A, June 2013: B, August 2013: C, September 2013: D, February 2014: E and March 2014: F.

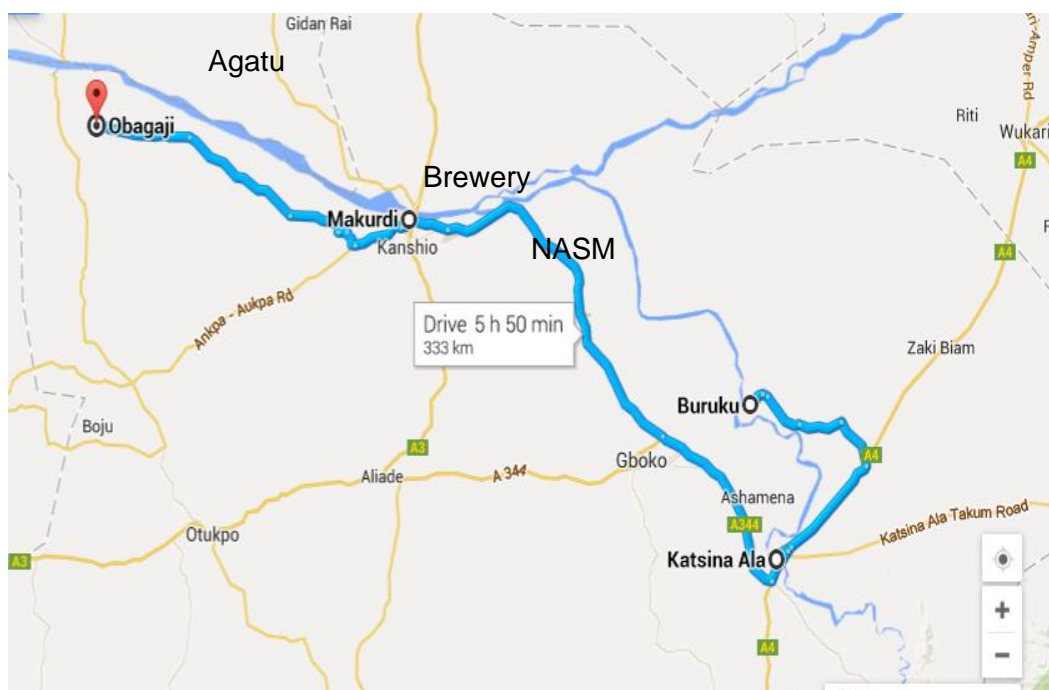


Figure 1: Map of Benue Showing the sampling stations along the River

### Sample Pre-treatment

One hundred mL of water sample was placed in a separating funnel and 100 mL of dichloromethane was added. The mixture was removed from the retort stand and shaken for 5-10 minutes. This was allowed to stand and settle. The bottom solvent (water) was drained into a conical flask and 10 g of sodium sulphate was added to trap residual water. The extraction procedure was repeated and the two extracts combined and evaporated to dryness using a rotary evaporator. 1:1 of hexane/acetone was used to reconstitute the extract and put in 2 mL vial for analysis of organophosphate.

### GC-FPD Analysis of OPPs

An Agilent 7890 Gas Chromatograph (GC) with Agilent 7693 Autosampler equipped with a flame photometric detector was used for quantification. OP compounds were completely separated using a HPS MS fused silica capillary column (30 m × 0.25 μm × 0.32 mm id). Prior to use, deactivation with 3.3% water in 500 mL glass jar, mix thoroughly and allowed to equilibrate in the sealed glass jar for 6 hours in a dessicator. 1.0 μl of analyte was injected into the GC on splitless mode with a 0.75 min vent delay. The injector temperature was maintained at 250°C and the initial oven temperature was set at 60°C for 1 min and then increased at a rate of 10°C/min until it reached 200°C, where it remained for 2 min. The temperature was then increased at a rate of 10°C/min until it reached 280°C, where it remained for 3 min using this temperature program. The retention times of diazinon, chlorpyrifos, and mevinfos were 11.469, 18.576, and 15.355 min, respectively.

## Results

The concentrations of OPPs in water ( $\mu\text{g/L}$ ) are shown in Table 1. The graphical representation of diazinon, chlorpyrifos and mevinfos are depicted by Figures 2, 3, and 4 respectively while sample chromatograms of the pesticides are shown in figure 5, 6, 7. There was no observable difference in concentrations of diazinon, chlorpyrifos and mevinfos during the wet and dry seasons ( $p \leq .05$ ).

Table 1: Concentration of organophosphate pesticides n water samples at various locations

Sample Codes	Diazinon	Chlorpyrifos	Mevinfos
1A	–	0.051	–
1B	1.759	14.972	0.048
1C	1.152	5.377	0.058
1D	–	0.257	–
1E	–	0.130	–
1F	0.501	13.397	0.030
2A	–	0.047	0.026
2B	–	0.082	0.311
2C	–	0.060	0.031
2D	–	0.090	–
2E	–	0.060	0.020
2F	–	0.089	0.026
3A	–	0.037	–
3B	2.084	7.540	0.020
3C	–	0.085	0.029
3D	–	0.102	0.032
3E	–	0.120	0.025
3F	–	0.032	–
4A	–	0.060	–
4B	–	0.052	–
4C	–	0.058	0.022
4D	–	0.068	–
4E	–	0.068	0.014
4F	–	–	0.025
5A	–	–	–
5B	0.048	2.360	0.019
5C	–	0.045	0.034
5D	–	0.015	–
5E	0.193	3.883	0.018
5F	–	0.091	0.025

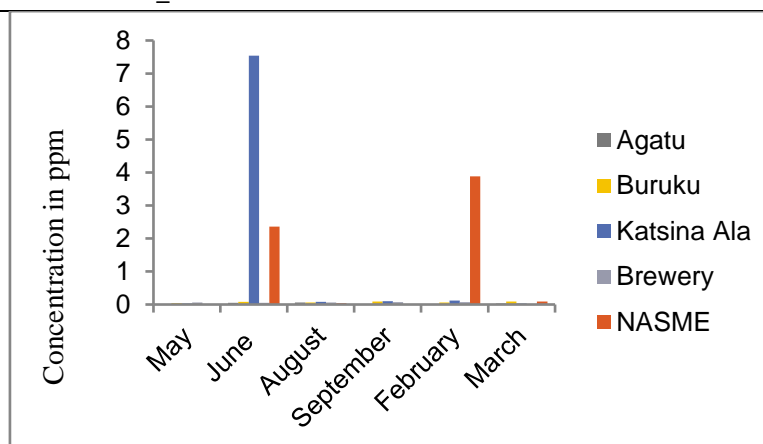


Figure 2: Concentration of chlorpyrifos (May –Sept, 2013 and Feb–March, 2014)

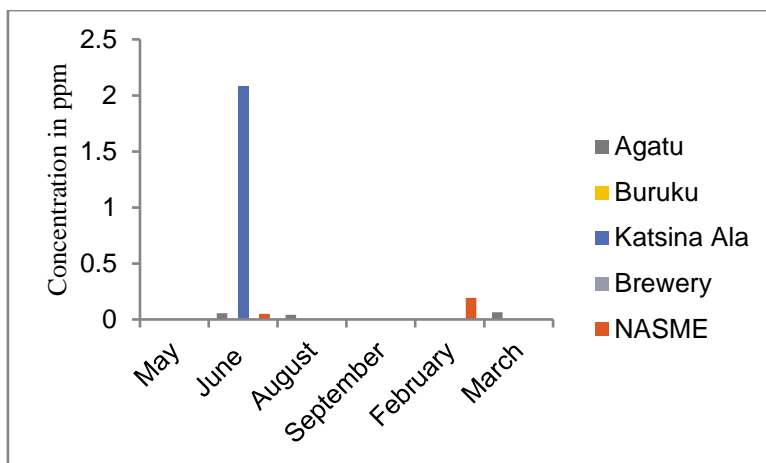


Figure 3: Concentration of diazinon (May-Sept, 2013 and Feb-March, 2014)

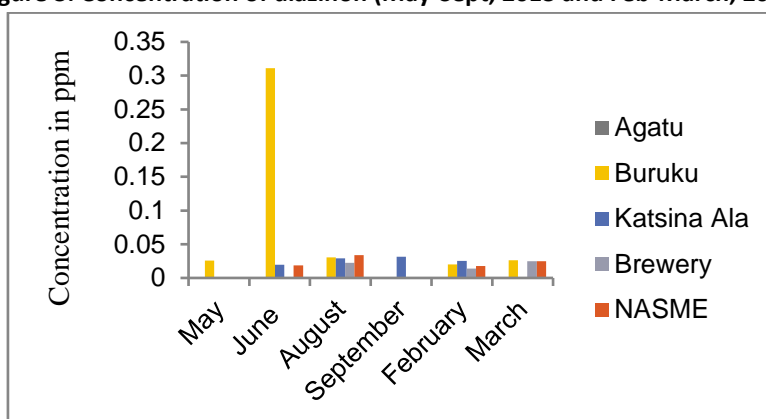


Figure 4: Concentration of mevinfos (May-Sept, 2013 and Feb-March, 2014)

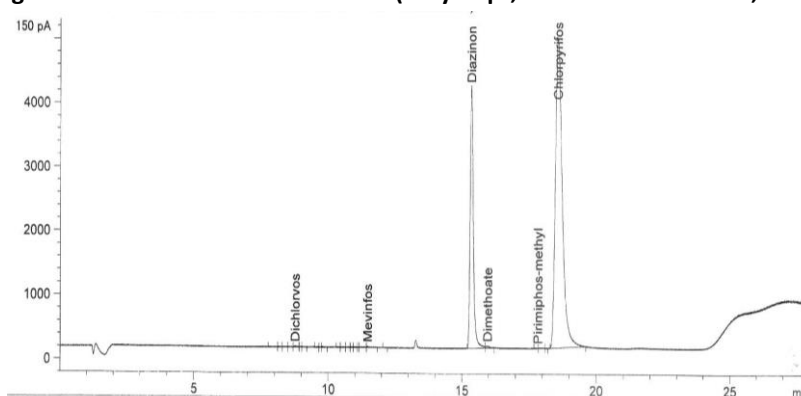


Figure 5: Chromatogram of organophosphate pesticides at Agatu in March, 2014

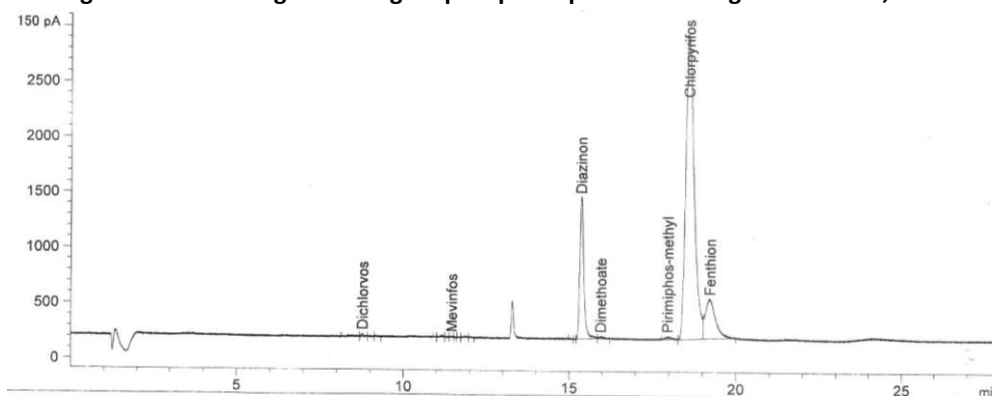
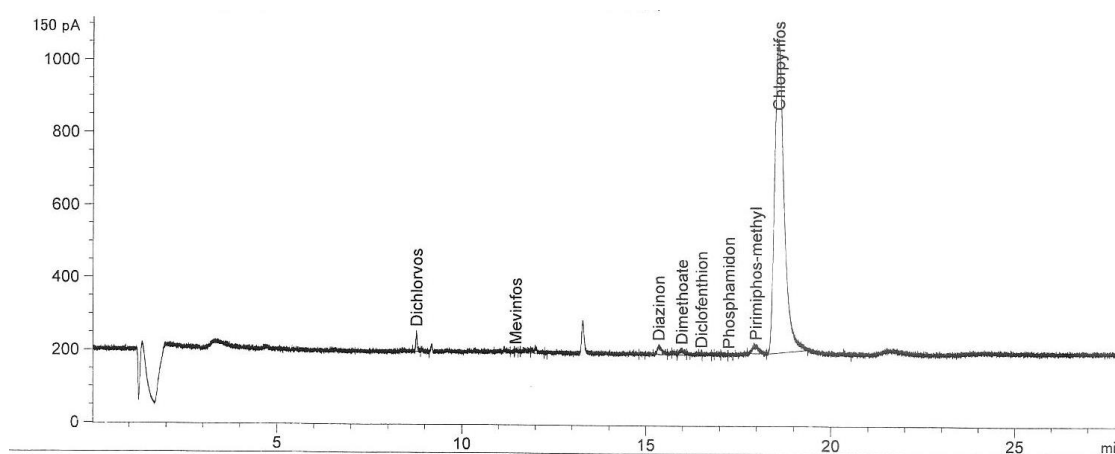


Figure 6: Chromatogram of organophosphates at Katsina-Ala in June, 2013



**Figure 7: Chromatogram of organophosphates at NASME in June, 2013**

## DISCUSSION

### Diazinon

The results of the analyses are depicted graphically by figure 3. The maximum concentration of 2.084 ppm at location code 3B while the minimum concentration of 0.049 ppm was reported at location code 5B. Diazinon is a non-priority pollutant. The MRL of diazinon (USEPA) in drinking water is 0.17 ppm which is above the MRL at most locations in this study.

### Chlorpyrifos

The maximum concentration of chlorpyrifos was detected at sample code 1B (14.972 ppm) while the minimum concentration of (0.015 ppm) was detected at location code 5D. The graphical distribution of chlorpyrifos concentrations were represented in figure 2. This is not unconnected with the widespread application of chlorpyrifos-based organophosphate pesticides by farmers at the study locations.

Chlorpyrifos is a broad-spectrum organophosphorus insecticide with potential for both acute toxicity and larger amounts and neurological effects in foetuses and in children even at very small amounts. For acute effects, the EPA classifies chlorpyrifos as class II, moderately toxic pesticide. It is used for the control of mosquitos, flies, various crop pests in soil and on foliage, household pests and aquatic larvae. It is used as a soil treatment (pre-plant and at planting), as a seed treatment and as a foliar spray, directed spray and dormant spray. Chlorpyrifos is strongly absorbed by soil and does not readily leach from it (HSDB, 1988). It persists in soil for 60–120 days and degrades there primarily through microbial action.

US EPA (1998) has reported detecting chlorpyrifos in surface waters, with the majority of results being below 0.10µg/litre and with a maximum reported concentration of 0.40 µg/litre. It was detected in groundwater in less than 1% of the wells tested, with the majority of measurements being below 0.01µg/litre. The primary degradation product is 3,5,6-trichloro-2-pyridinol, which is further broken down to organochlorine compounds and carbon dioxide (FAO/WHO, 2000). Owing to its non-polar nature, chlorpyrifos has a low solubility in water and great tendency to partition from aqueous into organic phases in the environment.

### Mevinfos

The concentration of mevinfos is represented in figure 4. It was found to have its maximum concentration of 0.311 ppm at location code, 2B while the minimum concentration of 0.011 ppm was detected at location code, 4E. Mevinfos does not readily adsorb to soil particles, and that which does become adsorbed comes unbound, or 'desorbed,' easily. It therefore has a high tendency to leach, or move with soil moisture. Mevinfos is very mobile in sandy loam, silt loam, loam, and clay loam soils (Meister, 1992). It is more active in moist soils than in dry soils (Wagenet *et al.* 1985).

It disappears from soil in approximately one day. A soil half-life of 3 days has been reported. No harmful effects to soil microorganisms have been observed from application of mevinfos formulations. One study indicated that this material lost its insecticidal capability in two to four weeks.

Mevinfos dissolves in water and is readily broken down by water (hydrolyzed), losing its insecticidal activity within 2 to 4 weeks (Wagenet *et al.* 1985). In aqueous solution, it is hydrolyzed with a half-life of 1.4 hr at pH 11, 3 days at pH 9, 35 days at pH 7, and 120 days at pH 6.

Thus we can say that a using pesticide effectively while maintaining water quality presents an important challenge and is need of the hour. As citizens, we must recognize the significant role of pesticides in maintaining a high quality of life. We must acknowledge that the effective production of food and fiber relies on pesticides to control weeds, insects and plant diseases that interfere with the growth, harvest and marketability of crops, and also acknowledge the importance of pesticides in controlling pests in our homes, restaurants, hospitals, parks, ornamental plantings, golf course etc. but at the same time we must be aware that pesticides application can affect water quality of both surface and ground water sources. Human and environmental health may be threatened when excessive concentration of pesticides enters surface or ground water (Singh *et. al.*, 2012).

### Conclusion

The present study is the first known study of organophosphate pesticides distribution in water along River Benue. The study has revealed that regular monitoring and strict enforcement of law is necessary to develop a strategy to manage the environmental hazards due to these elements and to improve environmental protection of this area.

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