World Journal of Water Resource and Environmental Science
Vol. 2, No. 1, November 2015, pp. 1-13, E-ISSN: 2375 - 1622
Available online at http://wjwres.com/

Research article

INVESTIGATION OF HERBICIDES PRESENCE IN SURFACE WATERS IN OBUBRA TOWN, CROSS RIVER STATE, NIGERIA

[1] Obia, C. I., [2]Ogwuche, J. A. and [3]Alao, J. S.

[1 and 3]Department of Social & Environmental Forestry, University of Agriculture, Makurdi, Nigeria.

[2]Department of Geography, Benue State University, Makurdi, Nigeria.

E-Mail: ogwuche.jonathan@yahoo.com

ABSTRACT

Of all activities that greatly pollute surface water, agricultural inputs such as insecticides, herbicides and fertilizers are most worrisome. Investigation of the presence and nature of herbicides in surface waters in Obubra Town, Cross River State, Nigeria was carried out from July, 2014 to February, 2015. Water samples were collected bimonthly from four perennial surface water bodies; one river and three streams. Nine parent herbicidal active ingredients; atrazine, dalapon, simazine, glyphosate, butachlor, mecoprop, 2,4-D, picloram, alachlor and one insecticide; methoxychlor were discovered in all the water samples investigated after extraction using gas chromatography mass spectrometry (GC-MS). Analysis of variance (ANOVA) revealed that all the herbicides and residues discovered in this study showed marked significant variations across the study period, season of sample collection and sites of sample collection at $p \leq 0.05$; except for methoxychlor insecticide. The analysis also showed that in the season of samples collection all the herbicides showed higher values in the wet than in the dry season. The study also revealed that the surface waters investigated in this study contained herbicide properties (except picloram) above the recommended limits of the WHO for drinking water and are therefore not fit for drinking. The study therefore recommends proper treatment before using the water, especially for drinking and household activities.

Key words: Surface Waters, Herbicides,

INTRODUCTION

The use of herbicides for agricultural practice has become an important activity which significantly enhances crop yield. Although this benefits the agricultural industry, the risk to the environment by polluting the soil, ground and

surface waters must be considered seriously. Due to rapid urbanization and expansion of agricultural activities near sensitive environments such as estuaries, wetlands, lagoons, streams and other catchment areas, large amounts of pesticides and herbicides are discharged especially during the wet season.

Herbicides are important and essential components of weed management in the world of agriculture. Kolo (2004) opines that the 23rd Food and Agricultural Organization of the United Nations Conference recognized that increased food production is a high priority in many parts of the world and this need cannot be met without the use of indispensable agricultural inputs such as herbicides. Although herbicides lead to increased food production; there is every reason to use them properly to safeguard the people and the environment.

Forestry activities have the potential to interact both positively and negatively with aquatic resources. Careful planning and management will mitigate against potential negative impacts while maximizing the positive aspects of forestry, such as aquatic biodiversity enhancement and the creation of appropriate riparian ecosystems, as each river or stream has a unique drainage basin or catchment area. Some catchments are more vulnerable than others to changes in water quality, due to their peculiar soils and underlying geology. The type of landuses and associated operations within the overall catchment area can have a major bearing on the volume and quality of water flowing into a particular river or lake.

A review of scientific literature shows that intensive forest management methods can significantly impact biodiversity by affecting a wide range of taxa (lichens) (Lesica, 1991), bryophytes (Fenton, 2001), vascular plants (Roberts, 2002), nematodes (Paresar *et al*., 2000), amphibians (Naughton *et al*., 2000), birds (Lambert and Hannon, 2000), and mammals (Lomolino and Perault, 2000). Natural ecosystems are characterized by negligible nutrient export levels (DeAngelis, 1992; Dobrovolsky, 1994). The use of herbicides will most likely lead to an increase in yield. However, increased productivity accelerates the exportation of biomass (i.e. nutrients) from harvest sites and will ultimately result in the depletion of soil nutrients. Furthermore, as a result of mineral depletion of the soil, acidification can occur which will lead to leaching and further nutrient loss (Flueck and Flueck, 2006; Lovett *et al*, 2002).

There is a global outcry to reduce herbicide use in forests (Little *et al*., 2006; McCarthy *et al*., 2011). Some governmental agencies like Nigerian Conservation Foundation (NCF), the Federal Environmental Protection Agency (FEPA), the National Resources Council (NARECO) in collaboration with the United Nations Environmental Programme (UNEP) and the World Wide Fund (WWF) and several other agencies have embarked on programmes to protect and preserve the nations' biodiversity (Iment and Adebobola 2001)

One of the primary concerns about herbicides and other pesticides usage is their effect on non-target organisms with emphasis on mammalian toxicity (Shaner, 2003). It is reported that only 1% of sprayed pesticides are effective, while 99% of the pesticides applied are often released to non-target soils, water bodies, and atmosphere and finally absorbed by almost every organism (Zhang *et al*., 2011).

Dem (2007) reports that plant uptake of herbicides and other pesticides pose health risk to domestic livestock that forage on crop stubble, and consumers of food from these animals; as majority of herbicides are reported to constitute between 40-60% of pesticides used for agricultural purpose (Zimdahl, 2002; Fishel, 2010), with only a few reaching their primary target.

Health effects such as immune systems malfunction, endocrine disruption, breast cancer, irritation, dizziness, tremor, toxic and chronic convulsion have been reported in human beings (Adeboyejo *et al.*, 2011; Adeyemi *et al.*, 2011). This study was therefore set to investigate the presence and nature of herbicides in surface waters in Obubra town, Cross River State, Nigeria.

Statement of the Problem

In spite of the efforts of Obubra Local Government Area of Cross River State, Nigeria, to ensure a healthy populace by providing health services, the incidence and prevalence of illnesses are on the increase. The source of the illnesses seems to be tied to common sources of water supply in the area. The sources of fresh water include the rivers, streams, springs, boreholes and hand dug wells of which the Cross River, Upper Source, Iwuwohk and Ogoh streams are some of the surface water sources most depended on, especially during the dry season. There is therefore the need to assess the relevant physico-chemical properties of the surface waters in Obubra town, in relation to the water quality requirements for domestic use, with a view to ascertaining their suitability.

MATERIALS AND METHODS

Study Area

Obubra is one of the eighteen (18) Local Government Areas of Cross River State, Nigeria, with administrative headquarters at Obubra town. It is located in the Central Senatorial District of the State and is made up of eleven (11) Council wards. Obubra Local Government Area has a land mass of 1,115km^2 (Wikipedia, 2014).

The Local Government Area lies between latitude 8°12′ and 8°32′North; and longitude 5°52′and 6°15′ East of the Equator. Height above sea level is 109 metres. It is bounded in the north by Ikom Local Government Area, Yakurr Local Government Area in the South, Yala Local Government Area in the West and Akamkpa Local Government Area in the East (Figure 1).

From the 2006 census, the Local Government Area has a total population of 172, 543 (NPC, 2006). The soil is mainly ultisols; dark red in colour and does not allow for plating. Obubra Local Government lies within the rich fringes of the tropical rainforest zone of South Earthen Nigeria with abundant natural resources including agricultural, forest and mineral resources. It is basically an agrarian society.

World Journal of Water Resource and Environmental Science
Vol. 2, No. 1, November 2015, pp. 1-13, E-ISSN: 2375 - 1622
Available online at http://wjwres.com/

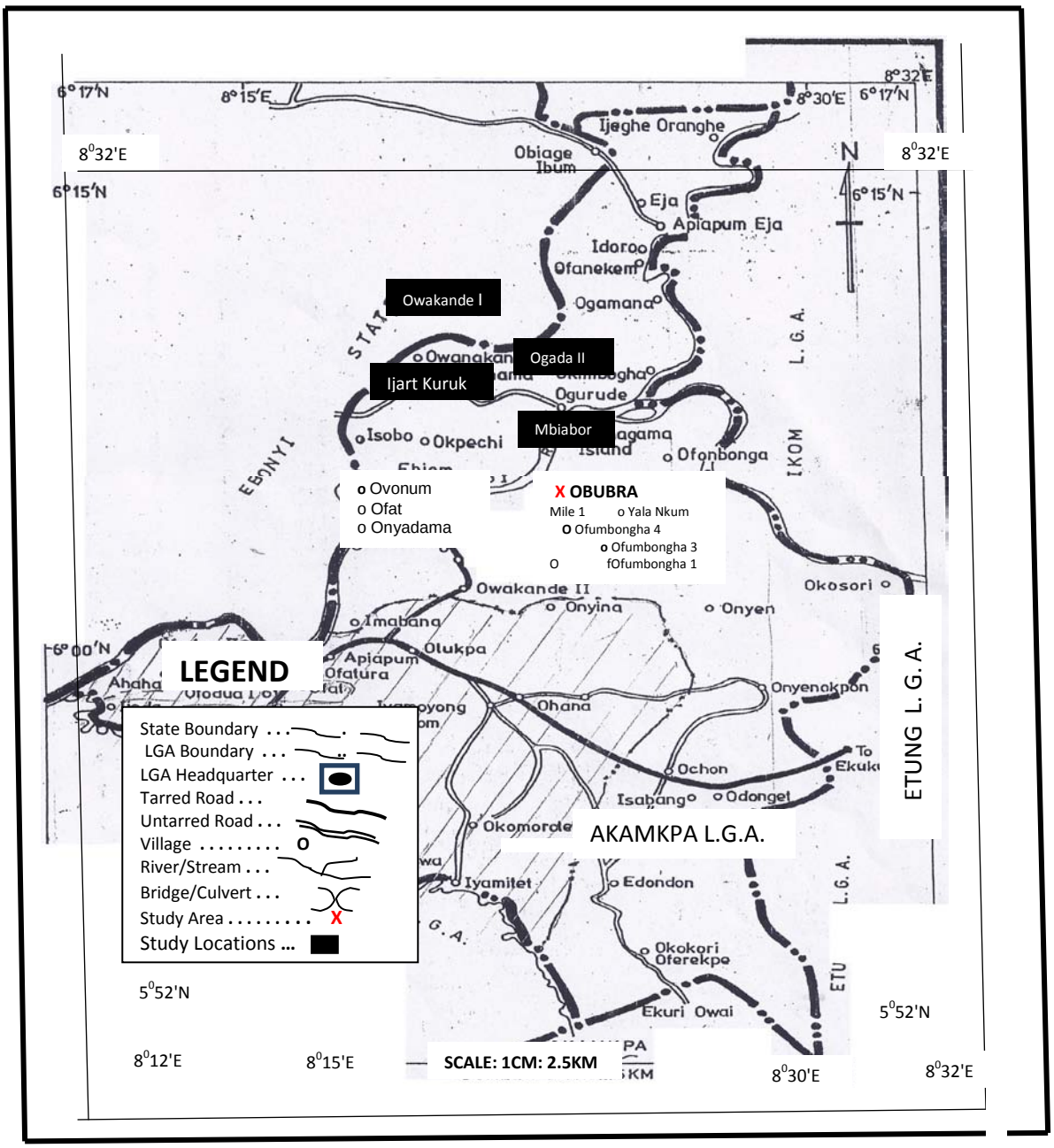

Figure 1: Map of Obubra Local Government Area showing study location and sites of samples collection

Data Collection

Water samples were collected from four stations; one river and three streams. Water samples were collected bi-monthly for eight months; July 2014 to February 2015. Grab water samples were collected using one litre amber glass bottles with caps lined with teflon. The containers were sterilized and labeled accordingly; S1 to S4 according to the 4 sampling stations. Canoe was used to collect river water samples at the depth of 30cm below the surface, at the middle of the river. Stream samples were collected at the point of use. Sample bottles were filled completely to eliminate any airspace. Water samples for herbicides analysis were preserved with 2ml of concentrated, pesticide-grade sulphuric acid, and packed with iced blocks and transported to the laboratory of the Cross river State Water Board Limited for analysis.

Procedure

Three surrogate compounds; 2,3-dichlorophenoxyacetic acid, deuterium (d14-trifluralin) and d10-malathion in acetone (100µl) were added to the water samples to assess the recovery of the pesticides before extraction. Nine herbicidal parent active ingredients; atrazine, dalapon, simazine, glyphosate, butachlor, mecoprop, 2,4-Dichlorophenoxyaceticacid (2,4-D), picloram and alachlor); and one insecticide (methoxychlor) were discovered in the water samples after extraction.

Water samples for herbicide extraction were reduced to 1 litre and dichloromethane added. The extracts was concentrated at 5ml using Kurderna-Danish evaporation and transferred to a test tube. The extract residue was then dissolved in 4mls of 5% weight volume in 200 µl acetone of Pentafluorobenzle bromide. The mixture was heated for 60°C for 3 hours to form the Pentafluorobenzyl esters. 2mls of *Iso*-octane was added and the reaction mixture evaporated to approximately 1.0ml using a gentle stream of nitrogen gas. The sample extracts were transferred to silica gel deactivated with 5% water cleanup columns topped with 0.5cm anhydrous sodium sulfate. The columns were eluted with 5% methanol in toluene and the eluate concentrated to 1ml volume before gas chromatography.

The insecticide extracts were transferred onto a silica gel deactivated with 10% volume of water cleanup columns. They were then eluted with 10% acetone in hexane.

Gas Chromatography-Mass Spectrometric Analysis

A gas chromatography model 6290 interfaced with a model 5773 mass selective detector (Agilent Technologies, Wilmington, DE, USA) was used for the analysis.

The sample solution was injected into the Gas chromatogram inlet. It was vaporized and swept into a chromatographic column and the compounds comprising the mixtures of interest were separated by interacting with the coating of the column (stationary phase) and the carrier gas (mobile phase).

The herbicides and insecticide samples were analyzed through the electron ionization mode. Helium (99.999%) was used as the carrier gas at a constant flow rate of 1 mL/min. The temperature Injector was kept at 250ºC in splitless

mode (5min), and oven temperature was programmed as follows: initial temperature 100°C (hold 2 min), 20°C/min to 180°C, and 10°C/min to 250°C (hold 2 min). The MS ionization was carried out in the electron ionization mode. The GC–MS interface and the ion source temperature were set at 250 and 200ºC, respectively. For each analyte, the most abundant and characteristic mass fragment ion was chosen for quantification and two others were used for confirmation. The quantification ions and relative abundances of confirmation ions were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio (*m/z*) ranging from 50 to 500 *m/z*. Pesticides were confirmed by their retention times, the identification of quantification and confirmation ions, and the determination of confirmation to quantification ratios.

Quality assurance/quality control measures taken included laboratory blank sample (type 1) water and two fortified laboratory blank samples with every surface water samples. No herbicide compounds were detected in the laboratory blank samples.

Statistical Analysis:

A two-way analysis of variance was used to analyze the data. Duncan multiple Range Test (DMRT) was used to separate mean values where there was significant difference in results. We selected $p \leq 0.05$ for statistical significance, and results are reported as mean ± S.E and actual p-values.

RESULTS

The analysis revealed nine parent herbicidal active ingredients; atrazine, dalapon, simazine, glyphosate, butachlor, mecoprop, 2,4-D, picloram, alachlor and one insecticide; methoxychlor were discovered in all the water samples investigated. All the 9 herbicides and residues discovered in this study showed marked significant variations across the study period, season of sample collection and sites of sample collection (tables 1, 2 and 3) at $p \leq 0.05$; except for methoxychlor insecticide that showed no significant difference across the sites of sample collection at $p > 0.05$. ANOVA also showed that all in the season samples collection all the herbicides showed higher values in the wet than in the dry season (table 3).

World Journal of Water Resource and Environmental Science
Vol. 2, No. 1, November 2015, pp. 1-13, E-ISSN: 2375 - 1622
Available online at http://wjwres.com/

Table 1: Mean levels of Herbicide Concentration (mg/L) across the Study Period; July, 2014 – February, 2015 in Obubra Town

Month	Atrazine	Dalapon	Simazine	Glyphosate	Butachlor	Mecoprop	2,4-D	Picloram	Alachlor	Methoxychlor
				Mean ± S.E.						
July	0.28^{b}	0.33^{b}	0.33^{b}	0.42^{b}	0.48^{b}	0.46^{b}	0.15^{bc}	0.27^{b}	0.26^{cd}	0.11^{b}
Aug	0.26^{b}	0.36^{b}	0.31^{b}	0.40^{b}	0.44^{b}	0.43^{b}	0.14^{b}	0.25^{b}	0.25^{c}	0.09^{b}
Sept.	0.31	0.41^{b}	0.38^{d}	0.46^{b}	0.52^{b}	0.49^{b}	0.19^{b}	0.32^{c}	0.29^{d}	0.14^{c}
Oct.	0.32^{b}	0.39^{b}	0.38^{b}	0.46^{b}	0.54^{b}	0.48^{b}	0.19^{b}	0.33^{c}	0.29^{d}	0.15^{c}
Nov.	0.02^{a}	0.03^{a}	0.03^{a}	0.03^{a}	0.04^{a}	0.03^{a}	0.03^{a}	0.02^{a}	0.02^{ab}	0.03^{a}
Dec	0.03^{a}	0.02^{a}	0.02^{a}	0.03^{a}	0.02^{a}	0.03^{a}	0.02^{a}	0.02^{a}	0.02^{a}	0.03^{a}
Jan.	0.03^{a}	0.02^{a}	0.03^{a}	0.01^{a}	0.03^{a}	0.02^{a}	0.03^{a}	0.05^{a}	0.05^{b}	0.03^{a}
Feb.	0.02^{a}	0.09^{a}	0.01^{a}	0.01^{a}	0.02^{a}	0.02^{a}	0.02^{a}	0.02^{a}	0.03^{ab}	0.02^{a}
S.E.	0.06	0.06	0.03	0.02	0.04	0.02	0.02	0.01	0.01	0.01
F	6.41	11.03	32.62	100.93	40.78	151.16	26.08	102.49	110.92	31.66
P.value	0.00***	0.00***	0.00***	0.00***	0.00***	0.00***	0.00***	0.00***	0.00***	0.00***

*** significant at $p \leq 0.01$; **Results given as Mean ± Standard Error (S.E.)**
Mean values in the same column with same alphabet in superscript are not statistically different from each other.

Table 2: Mean Levels of Herbicide concentration (mg/L) for the Time of Samples Collection – First and Second Weeks I Obubra Town

Time	Atrazine	Dalapon	Simazine	Glyphosate	Butachlor	Mecoprop	2,4-D	Picloram	Alachlor	Methoxychlor
				Mean ± S.E.						
First wk.	0.16	0.22	0.19	0.23	0.28	0.25	0.10	0.16	0.15	0.08
Second wk.	0.16	0.20	0.18	0.22	0.24	0.24	0.09	0.16	0.16	0.07
S.E.	0.03	0.03	0.02	0.01	0.02	0.01	0.01	0.15	0.01	0.01
F	0.02	0.34	0.02	0.40	2.01	0.14	1.56	0.08	0.64	0.36
P. Value	0.90	0.57	0.88	0.53	0.16	0.71	0.22	0.78	0.43	0.55

Results given as Mean ± Standard Error (S.E.)

World Journal of Water Resource and Environmental Science
Vol. 2, No. 1, November 2015, pp. 1-13, E-ISSN: 2375 - 1622
Available online at http://wjwres.com/

Table 3: Mean Levels of Herbicides Concentration (mg/L) across the Seasons of Sample collection in Obubra Town

Season	Atrazine	Dalapon	Simazine	Glyphosate	Butachlor	Mecoprop	2,4,-D	Picloram	Alachlor	Methoxychlor
	Mean ± S.E.									
Wet	0.29	0.39	0.35	0.44	0.49	0.46	0.17	0.29	0.28	0.12
Dry	0.02	0.04	0.02	0.02	0.03	0.02	0.03	0.03	0.03	0.03
S.E	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.01
F	1.02	462.02	1.98	5.01	1.40	5.45	502.2	795.19	1.15	212.66
P. Value	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**

*** significant at $p \leq 0.05$

Result given as Mean ± Standard Error (S.E.)

Table 4: Mean Levels of Herbicide Concentration (mg/L) across Sampling Sites in Obubra Town, detection limits (µg/l), retention time (min), mass –charge ratio, and WHO Limit

Site	Atrazine	Dalapon	Simazine	Glyphosate	Butachlor	Mecoprop	2,4-D	Picloram	Alachlor	Methoxychlor
	Mean ± S.E.									
Site 1	0.32^{c}	0.31^{c}	0.25^{d}	0.23^{b}	0.34^{c}	0.24b	0.13^{c}	0.19^{c}	0.18^{c}	0.09^{b}
Site 2	0.13^{b}	0.23^{b}	0.17^{b}	0.28^{c}	0.27^{b}	0.29^{c}	0.09^{b}	0.16^{a}	0.16^{b}	0.07^{ab}
Site 3	0.10^{a}	0.21^{b}	0.22^{c}	0.23^{b}	0.25^{b}	0.25^{b}	0.09^{b}	0.14^{a}	0.12^{a}	0.08^{ab}
Site 4	0.08^{a}	0.10^{a}	0.12^{a}	0.17^{a}	0.19^{a}	0.19^{a}	0.07^{a}	0.16^{a}	0.15^{b}	0.07^{b}
D. L	0.12	0.38	0.22	0.42	0.29	0.34	0.49	0.24	0.42	0.26
R.T	7.82	8.35	6.93	8.75	8.28	8.22	9.29	7.12	9.31	8.56
M/Z	200	210	201	214	213	184	226	195	215	187
WHO	0.03	0.2	0.004	0.7	N.A.	0.02	0.07	0.5	0.002	0.04
S.E	0.01	0.02	0.01	0.01	0.01	0.01	1.01	0.01	0.01	0.01
F	163.62	27.72	74.54	57.83	24.92	43.55	15.92	5.13	11.98	1.84
P.Value	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	0.00**	$0.15^{N.S.}$

*** Significant at $p \leq 0.01$; N.S. = Not Significant

Mean values in the same column with same alphabet in superscript are not statistically different from each other.

N.A = Not Available

D.L = Detection limit (µg/l), R.T = Herbicide Retention Time (minutes), m/z = herbicide mass to charge ratio

Analyses of the herbicides show the following:

Atrazine: The highest atrazine mean value was recorded in the month of October (0.32mg/l ± 0.06), while the lowest value was recorded in November and February; 0.02mg/l ± 0.06 (table 1). Sampling site 1 recorded the highest value of 0.32mg/l ± 0.01, while site four recorded the lowest mean value of 0.08mg/l ± 0.01(table 4).

Dalapon: ANOVA showed that dalapon was highest in the month of September (0.41 ± 0.06), while the lowest mean (0.03mg/l ± 0.02) was recorded in December and January each (table 1). Sampling site 1 recorded the highest mean value of 0.31mg/l ± 0.02, while site four recorded the lowest mean of 0.10mg/l ± 0.02 (table 4).

Simazine: The months of September and October each with mean simazine level of 0.38mg/l ± 0.03 was the highest across the study period, February was lowest with mean value of 0.01mg/ ± 0.03 (table 1). Among the sampling sites, site 1 recorded the highest mean of 0.25mg/l ± 0.01, while site 4 recorded the lowest mean value of 0.12mg/l ± 0.01 (table 4).

Glyphosate: Glyphosate was highest in the months of September and October with mean value of 0.46mg/l ± 0.02 each, while January and February recorded the lowest mean of 0.01mg/l ± 0.02 (table 1). Sampling site 2 recorded the highest value of 0.23mg/l ± 0.00, while site 4 recorded the lowest 0.17 ± 0.00 (table 4).

Butachlor: The month of October recorded the highest mean value of 0.54mg/l ± 0.04. The months of December and February each recorded the lowest mean value of 0.02mg/l ± 0.04 (table 1). Sampling site 1 recorded a mean value 0.34mg/l ± 0.01, while the lowest was recorded in site 4; 0.19mg/l ± 0.01 (table 4).

4.2.6 Mecoprop: Mecoprop was highest in September with mean value 0.49mg/l ± 0.02, January and February recorded the lowest mean; 0.02mg/l ± 0.02 each (table 1). Sampling site two recorded the highest mean value of 0.29mg/l ± 0.01, while site 4 was the lowest with mean of 0.19mg/l ± 0.01 (table 4).

2,4-D: The mean values of 2,4-D were highest in the months of September and October with means of 0.19mg/l ± 0.02 each, while December and February recorded the lowest mean; 0.02mg/l ± 0.02 each (table 1). Sampling site 1 recorded the highest mean value; 0.13mg/l ± 0.01, site 4 recorded the lowest mean value of 0.07mg/l ± 0.01 (table 4).

Picloram: Picloram was highest in October with mean value of 0.33mg/l ± 0.01, while the lowest mean; 0.02mg/l ± 0.01 was recorded in November, December and February each (table 1). Sampling site 1 recorded the highest mean value of 0.19mg/l ± 0.01, while site 3 recorded the lowest value; 0.14mg/l ± 0.01 (table 4).

Alachlor: The months of September and October recorded the highest mean value of 0.29mg/l ± 0.01 each, while November and December recorded the lowest value; 0.02mg/l ± 0.01 each (table 1). Among the sites of sample collection, site 1 recorded the highest mean of 0.18mg/l ± 0.01, while site 4 recorded the lowest mean value of 0.12mg/l ± 0.01(table 4).

4.2.10 Methoxychlor: ANOVA showed significant variation in the mean levels of methoxychlor obtained across the study period and season of sample collection ($p \leq 0.05$), while no significant variation was observed among the sites of sample collection ($p > 0.05$) (tables 1, 3 and 4). Methoxychlor was highest in October with mean value of 0.15mg/l ± 0.01, while the lowest mean of 0.03mg/l ± 0.01 was recorded in November, December and January (table 1). Sampling site 1 recorded the highest mean value of 0.09mg/l ± 0.01, while sites 2 and 4 recorded the lowest mean values of 0.07mg/l ± 0.01 each (table 4).

Discussion

All the surface waters investigated in this study contained all the nine herbicides - Atrazine, Dalapon, Simazine, Glyphosate, Butachlor, Mecoprop, 2,4,-D, Picloram and Alachlor, and one insecticide (Methoxychlor at different levels.

Cassee *et al*. (1998) provide a detailed discussion of toxicological interaction between chemicals in mixtures, and Chevre *et al*. (2006) present a method of defining a risk quotient for mixtures of herbicides with similar modes of action. Thus, when assessing environmental exposure involving mixtures of pesticides (athough single chemical evaluations of toxicity provide useful information), generally have little practical value.

The wet season recorded a very high concentration of all the herbicides than the dry season. The wet season is the period where weed growth is at its highest peak and people seek for alternative means of weed control such as spraying of herbicides other than manual means. In Obubra, the wet season begins in April and ends in October, with the peak being in September. This marked variation is attributed to urban runoff from lawns, farms and agricultural fields where herbicides have been sprayed and from non-point sources. The low concentration during the dry season is as a result of the break in use of herbicides because of the non-availability of weeds during the dry season.

Among the sampled sites, site 1 had the highest concentrations of almost all the herbicides except for mecoprop (0.24ug/l) and roundup (0.23ug/l). These levels exceed the allowable limits of 0.01µg/l for individual pesticides and 0.05µg/l for total pesticides present in water stipulated by WHO. The high concentration could be attributed to the large volume of water and runoff from fields and farms through drainage channels that empty themselves into the river. Also the proximity of farms to the river is a contributory factor to the pollution level in the river. In Obubra Local Government Area several communities are located along the river bank and make good use of the alluvial deposits for farming of yam, rice, sugarcane, cassava and sweet potato along the river bank. Herbicides applied to these farms to control weeds are washed into the river especially during wet season..

Sampled site 2 equally contained all the herbicides with glyphosate and mecoprop being the most concentrated in the water at levels 0.28mg/l and 0.29mg/l, respectively. This suggests that these two herbicides are the most used in the location. The abundant presence of herbicides in the water is attributed to the farming practices in the area. The

concentration of human habitat around the water is also a contributory factor to the high herbicide pollution in upper source stream. These levels of herbicides detected in this stream far exceed WHO limits of 0.01µg and 0.05µg/l for both individual and total pesticide concentration in water and is therefore not safe for drinking without treatment.

All the herbicides and pesticide were also detected in sampled site 3 with butachlor, mecoprp, glyphosate, simazine and dalapon being more concentrated at levels 0.25, 0.25, 0.23, 0.22 and 0.21mg/l each. These high levels are indications that these brands of herbicides are the most used in this location. However, the reduction in concentration in these herbicides in Iwuwohk stream compared to the River and Upper part of the stream could be attributed to the vegetation along the course of the stream, which help in absorbing some of the toxins. The concentration of herbicides in this water equally exceeds the WHO limit of 0.01µg/l for individual and 0.05µg/l for total pesticides and is therefore not safe for drinking.

In sampled site 4, butachlor, mecoprop, glyphosate, picloram and alachlor were the most concentrated at levels, 0.19, 0.19, 0.17, 0.16 and 0.15mg/l each. This can also mean that they were the most commonly used in the location. Although the values were lower compared to the concentrations of these herbicides in river, upper course and Iwuwohk streams, they still exceeded the WHO limit for individual and total pesticides presence in drinking water hence not safe for drinking without proper treatment.

All the surface waters investigated in this study contained herbicide properties, except picloram, that are above the recommended limits of WHO for drinking water and are therefore not fit for drinking without treatment.

Implications

In forestry this has great implications as both the micro and macro flora and fauna are affected. The microbial biomass plays an important role in the soil ecosystem where they fulfill a crucial role in nutrient cycling and decomposition (De-Lorenzo *et a*l., 2001). Herbicides, when applied could then accumulate to toxic levels in the soil and become harmful to microorganisms, plant, wild life and man. There is an increasing concern that herbicides not only affect the target organisms (weeds) but also the microbial communities present in soils, and these non-target effects may reduce the performance of important soil functions (De-Lorenzo *et al*., 2001).

Stumps of many brushwood species may rapidly sprout after cutting. Glyphosate, at concentration of 8-10% in water, applied to the stump surface after cutting have been found to eliminate or reduce sprouting of the most deciduous trees (Lund-Hoie, 1985). Also, after *Eucalyptus* timber, stump rapidly re-grows, however, glyphosate, at 50% in water, will prevent re-growth from Eucalyptus stumps (Kogan and Zinuga, 2001). This treatment is most effective applied immediately after the tree or brush is cut.

Health effects such as mild skin irritation, birth defects, tumors, genetic changes, blood and nerve disorders, endocrine disruption, coma or death, leukemia, reduction in male penis size and undescended testicles in animals,

killing of human embryonic, placental, and umbilical cells *in vitro,* genetic damage and urinary *schistosomiasis* in humans and animals have been linked with herbicides presence in drinking water.

Conclusion

It is important to establish if the toxicity of a mixture of pesticides is different from the sum of the toxicities of the single compounds, or if two or more pesticides simultaneously seen in drinking water have synergistic effects when viewed from the aspect of environmental and human toxicity. Results obtained showed high significant variations in the herbicide properties of water. This means that they are highly polluted with herbicides; yet these waters are used for drinking, cooking, washing, fishing and other domestic purposes. These herbicides with values above the recommended limits of WHO have negative effects on both flora and fauna, and are therefore not safe for drinking and other uses as they are responsible for the illnesses in the area. However, for the sustenance of good health of the populace in the area, the water, especially, for domestic uses should be adequately treated.

REFERENCES

[1] Adeboyejo, O. A., Clarke, E.O. and Olarinmoye, M.O. (2011): Organochlorine Pesticide Sediment and Fish from Warri River, Niger Delta, Nigeria. African Journal of Ecology, 48, No 1, pp. 248–254. doi/10.1111/j.1365-2028.2009.

[2] Adeyemi, D., Anyakora, C., Ukpo, G. and Adedayo, A.and Darko, G. (2011): Evaluation of the Levels of Organochlorine Pesticide Residues in Water Samples of Lagos Lagoon Using Solid Phase Extraction Method. Journal of Environmental Chemistry and Ecotoxicology, Vol. 3, No. 6, (June 2011), pp. 160-166. ISSN-2141-226X.

[3] Cassee, F. R., Groten, J. P., van Bladeren, P. J., Feron, V. J. (1998). Review Toxicological Evaluation and Risk Assessment of Chemical Mixtures. Critical Review of Toxicology 28(1):73-101.

[4] Chèvre, N., Loepfe, C., Singer, H., Stamm, C., Fenner, K., Escher, B. I. (2006). Including Mixtures in the Determination of Water Quality Criteria for Herbicides in Surface Water. Environmental Science Technology 15; 40(2):426-35.

[5] De Lorenzo M. E., Scott, G. I., Ross, P. E. (2001). Toxicity of Pesticides to Aquatic Microorganisms: A Review. Environmental Toxicology, 20: 84-98.

[6] DeAngelis, D. L. (1992). Dynamics of nutrient cycling and food webs. London, United Kingdom. Chapman and Hall.

[7] Dem, S. B. (2007). Pesticide Resdiues in Soil and Water from Four Cotton Growing Areas of Mali, West Africa.Agricultural, Food and Environmental Sciences.Vol.1.Issue 1. 1-12.

[8] Dobrovolsky, V. V. (1994). Biogeochemistry of the World's Land. CRC, Editor. Boca Raton, Florida, USA. Effects on Biota in Regenerating Northern Forests. Wildlife Society Bulletin 32:1061-0170.

[9] Fenton, N. (2001). Factors Influencing (Re)Assembly of Forest Floor Bryophyte Communities after Forest Harvest: Disturbance Severity and Potential Refugia. Saint John, N.B.: University of New Brunswick.

[10] Fishel, F. M. (2010). Pesticide Use Trends in the U.S.: Global Comparism, University of Florida, IFAS Extension.1-3.

[11] Flueck, W. T., Flueck, J. A., (2006). Herbicides and Forest Biodiversity: An Alternative Perspective. Wildlife Society Bulletin 34(5):1472-1478. Following removal of understory vegetation. Soil Sci. Soc. Am. J. 60:1614-1621.

[12] Iment .N and Adebobola .N. (2001) The Effects of Poverty in Conservation of Biodiversity: The Nigeria Experience. http://www.scienceinafrica.co.20

[13] Kogan, M., and M. Zuñiga (2001). Dew and Spray Volume Effect on Glyphosate Efficacy. Weed Technology 15:590-593.

[14] Kolo, M.G.M. (2004). Herbicide Utilization in Niger State, Nigeria. Nigerian Journal of Weed Science. 17:21-28.

[15] Lambert, J. D., Hannon, S. J. (2000). Short-term Effects of Timber Harvest on Abundance Territory Characteristics, and Pairing Success of Ovenbirds in Riparian Buffer Strips. The Auk 117:687-698.

[16] Lesica, P., McCune, B., Cooper, S., and Hong, W. S. (1991). Differences in Lichen and Bryophyte Communities Between Old-Growth and Managed Second-Growth Forests in the Swan Valley, Montana. Canadian Journal of Botany, 69:1745-1755.

[17] Lindenmayer, D. B., Swanson, F. J. (2011). The Forgotten Stage of Forest Succession: Early-Successional Ecosystems on Forest Sites. Frontiers in Ecology and the Environment 9, 117–125.

[18] Lomolino, M. V., Perault, D. R. (2000). Assembly and Disassembly of Mammal Communities in a Fragmented Temperate Rain Forest. Ecology, 81:1517-1532.

[19] Lovett GM, Weathers KC, Arthur MA. (2002). Control of Nitrogen Loss from Forested Watersheds by Soil Carbon: Nitrogen Ratio and Tree Species Composition. Ecosystems 5(7):0712-0718.

[20] Lund-Hoie, K. (1985). Efficacy of Glyphosate in Forest Plantations. p. 328-338. In Grossbard, E., and D. Atkinson (eds.) The Herbicide Glyphosate. Butterworth, London, UK.

[21] National Population Commission (2006). Population and Housing Census, NPC, Abuja.

[22] Naughton, G. P., Henderson, C. B., Foresman, K. R., McGraw, R. L. (2000). Long-toed Salamanders in Harvested and Intact Douglas fir Forests of Western Montana. Ecological Applications 10:1681-1689.

[23] Paresar, T. S., Marshall, V. G, Barclay, H. J. (2000). The Impact of Clear Cutting and Partial Harvesting Systems on Population Dynamics of Soil Nematodes in Coastal Douglas fir Forests. Pedobiologia 44:641-665.

[24] Zimdahl, R. I. (2002). My View. Weed Science. 50:687.