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The Persistence of Herbicide Residues in Fadama and Upland Soils in Plateau State, Nigeria

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Abstract

Fadama and upland soil in Plateau State, Nigeria were monitored for the residues of five herbicides widely used for farming within the areas under investigation from June 2010 to June 2012. The average concentration in mg/kg of the residues in the soils were; atrazine (0.123), 2,4-D (0.013), paraquat (0.020), oxadiazon (0.100) and pendimethalin (0.020) for *fadama* soils. While the concentration of the atrazine, 2,4-D, paraquat, oxadiazon and pendimethalin in upland soils were 0.180, 0.023, 0.030, 0.0130 and 0.010 mg/kg respectively, suggesting the herbicide residues persist at considerably high concentration. Physicochemical factors such as pH, Low Organic matter and textural characteristics of the soils were the factors identified to contribute to the persistence of the herbicides. Other factors like microbial activities were also suggested to play significant roles in the degradation or the persistence of the herbicide residues. The distributions of the residues were monitored seasonally over a period of time within the study area. This was sampled for laboratory analysis during the farming seasons covering planting to harvesting time where most of these herbicides and other chemical farm inputs are still believed to be active in the soils within the study area. The herbicides under investigation were observed to persist more in *fadama* soils which is characterized by high water holding capacity and low organic matter content.

Keywords: Persistence, herbicide residues, *fadama*, upland, soil.

1. Introduction

The option of using herbicides for the control of weed in vegetable and root crops widely grown in *fadama* and upland soil within the study is fast gaining acceptance amongst peasant farmers, having observed that there is increase in the yield of their farm produce when the these chemical farm inputs are used. The other side of the herbicides which have to do with their persistence and toxicity is not known by the most of the end users, this work hope to look at that aspect. The f*adama* and the upland soils are farmlands with different soil conditions. The former is a soil condition with characteristic water-lock and high water holding capacity, while the latter is a drain soil with very low water holding capacity, farming activities here is restricted to rainy season alone. The *fadama* soils is mostly located within the banks around rivers and other major water sources that stays throughout the year and are often used for irrigation activities covering but not limited to the irrigation of assorted vegetables and other root crops (Adeleye, 2005; Jauro *et al*., 2006; Mustafa and Nnalee, 2007).

Herbicides persistence in soil is expressed as half life or time required for degradation of 50% of the original molecule and it persistence with the nature of chemical, soil and climatic conditions (Janaki, 2006). The fate of herbicides and other pesticides in soil and water environments is influenced by the physicochemical properties of the pesticide, the properties of soil and water and these factors includes; presence of materials, organic matter, pH, eliminate, biological and other factors (Singh, 2001). For instance, the effect of clay content on herbicide residues is reported to be similar to organic matter as it tends to adsorb the herbicides as well as improve the water-holding capacity (Johnson, 2003). Similarly, herbicide adsorption of organic matter may reduce its bioavailability and the moisture holding capacity of high organic matter soils which makes it conducive for increased microbial activity (Eliason, *et al.* 2004).

Herbicides molecules are more or less toxic, they present both environmental and health risk (Manahan, 2000). Some of these chemical farm inputs are reported to reach targeted crops and weeds, while some of them are deposited in soils (Itoodo *et al,* 2010*).* Increase in herbicides and other pesticides use in the two soil types within the study area have resulted in the accumulation of the residues of the herbicides and other organic pollutants. This is believed to significantly contribute in increasing the magnitude of contamination of surface and ground water sources within the farming areas. The persistence of the herbicide commonly used in the soil and crops in the study area is not known. With the documented cases of phenoxy-sensitive crops damage from 2, 4-dichlorophenoxyacetic (2,4-D) contaminated irrigation water obtained from ponds and other environmental sources (Frank *et al.,* 1990), it become important to investigate the persistence of the herbicides used in these places. The aim of this work is to monitor the persistence of herbicides in *fadama* and upland soil with a view to observing the soil condition that favors the degradation or the persistence the herbicides widely used within the study area, and thereafter advice most appropriately.

2. Methodology

2.1 Sampling and Preparation

Samples were collected within the depth range of 0-15cm from the study areas using a 50cm Oakfield soil auger as described by Opeolu *et al* (2010). This was done for two (2) different seasons (rainy and dry) starting from June 2010 during which all sampling were carried out between 8:30-11:30am. A global positioning system (GPS) was used to record the coordinate position of places where all the samples are collected. On each site, sampling began 3m away from the borders into the farmland where samples were randomly collected every 50m until atleast 20 samples were obtained. To ensure a fair representation of soil sample, each soil sample collected was composite of atleast 20 samples collected at each site. In line with standard procedures as described by Dem et al (2007), the samples were air-dried and sieved through a No. 0.5mm brass sieve and refrigerated at 4^{o}C ready for further analysis.

2.2 Extraction and GCMS analysis of soil samples

The soils samples were extracted by the solvent partition techniques using the separating funnel. 50g of each of the samples were soaked in 30ml of hexane-washed water (HWW) for 30 minutes. 150ml acetone was then added to the mixture and before shaking it with a shaker for 1hour. The resulting solution was transferred into a separating funnel containing 200ml hexane and 650ml hexane-wash water before shaking it for another 10-20 min. The hexane extract was washed three times with HWW and dried by passing it through anhydrous sodium sulphate. It was then concentrated to a 5ml using the rotary evaporator.

The cleaning of the extract was done by setting a column packed with 6g of silica gel topped with 2cm of anhydrous sodium sulfate and eluting with hexane and dichloromethane, both collected as a single fraction. This is modification of the method used and suggested (Dem et al, 2007; Duan, 2000 and BCPC, 2003). The extract was finally allowed to evaporated and packed in sample bottles at -20^{o}C for GC-MS analysis. A GCMS Model QP 2010 PLUS was used to analyse the purified extracts. This was controlled by a version of National Institute of Standards and Technology (NIST) mass spectral library containing more than 130000 entries. The operating conditions are as follows, oven temperature-60^{o}C, injection temperature-250^{o}C, injection mode-split, total flow-133.5 mL/min and the carrier gas was helium.

3. Results & Discussion

Table 2 and Figure 1 shows the correlation of the herbicides distribution between the *fadama* and upland soils widely used for agricultural activities within the State, indicating that the herbicides are more in *fadama* soil owing to their high water retention capacity and the *fadama* soil is predominantly clay/loamy as indicated in Table 1. Giving that most of the leafy vegetable crops (mostly consumed raw or half-cooked) are cultivated more in the *fadama* soils, most of the consumers are at the risk of exposure from the herbicide residues contaminants if absorbed into the vegetable plants. Atrazine was observed to be higher in the upland soils and this could be as a result of other factors such as low microbial activities thereby making degradation of the herbicide much slower (Hagar and Nordby, 2004).

The major herbicides residues detected in the study are atrazine, 4,4-bypridine, chlorophenoxy acetics, oxadiazon representing the residues of atrazine, paraquat dichloride, 2,4-dichlorophenoxy acetic acids and oxadiazon respectively. Apart from atrazine being one of the most frequent occurring among the five herbicides, it is observed to be stable among all the herbicides under investigation in the soils. This is attributed to the persistent nature of atrazine and the long history of its usage in the study area. Other soil properties are factors that have been reported to be responsible for the persistence of herbicides and these are; organic matter content, soil texture and soil pH. They are reported to play important role in the carryover potential of residual herbicides (Johnson, 2003).

The area under study with a average temperature of 22^{o}C and pH values of 5.2 (Table 2) for *fadama* soils in which atrazine was dictated further suggest that these soil conditions favors the persistence of herbicides. For instance, soil with pH of 7.0 or higher is reported to persist for longer period because the rate of hydrolysis is slow at higher pH values (Hager, 2012). With the pH values of the soils samples averaging 5 in this study, it will be expected to facilitate the degradation of atrazine if other factors does not come into play. Soils with high clay and organic matter content adsorb more herbicides onto soil colloids than coarse texture soils. Herbicides tends to bound to the soil colloids making it unavailable for uptake by plants, as such it moves down through the soil profile and eventually the ground water, this is made possible by the water molecules displacing the bound molecules of residues into more stable water bodies, the choice of herbicides is therefore most critical to farmers on vulnerable soil and water resources (Paraiba *et al.* 2003 and Hager, 2012). The high clay composition of the *fadama* could be a main factor enhancing the persistence of herbicides.

The high profile of organic compounds such as benzene dicarboxylic acid ester, phthalate, dioxolane, chlorinated phenols and chlorpyrifos, oxadiazon etc (Table 2 and 3) are most likely the derivatives of some organic based farm chemical inputs and other pesticides commonly used in farming activities within the study area. Some of these toxic organic loads in soil can be reduced be encouraging the regular application of organic waste matters as this will help adsorp the toxic residues.

On the whole, the degradation of pattern of the herbicides and their derivatives indicates a high concentration in June for most of the herbicides and this attest to the fact that it is during that period that most of the herbicides are used by farmers about a month after commencement of the farming season. The less and lowest concentration of the herbicides in the environmental sector was observed in the month of March which further suggest that the active ingredient most have degraded into other forms (Figure 2). The GCMS spectra of a specimen of each of *fadama* and upland soil is indicated with some of the residues dictated shown in Figure 3.

4. Conclusion

Herbicides use is gaining wide acceptance within the study area resulting in increase of the pollution load of the agricultural soils and other environmental sectors. Although no wide distinct difference was observed for the persistence of the herbicides in the *fadama* and the upland soil, the *fadama* soil was observed to be slightly higher for of the herbicides residues under investigation. It is worthy to note that the concentration and of atrazine residues were high, as such related herbicides which degrades faster were recommended for used in place of the atrazine within the study area. The studies also recommended the use of organic fertilizer and organic compost materials to enrich the soils as it will facilitate the adsorption some of the life threatening residues.

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Table 1: Some physical parameters of soils samples from selected *fadama* and upland soils in Plateau State.

Sample Code	pH	Temp (°C)	OM	OC	CEC (mol/kg)	Texture	Particle Size Distribution (%)		
							Clay	Sand	Silt
BKK-F	5.58	22	1.56	0.91	8.23	Clay loam	39.32	36.32	24.36
BLD-F	4.63	21	2.15	1.16	33.77	Clay loam	30.00	36.08	33.02
JSS-F	5.37	22	0.32	0.23	7.41	Clay loam	13.81	05.00	81.19
MGU-F	4.71	23	1.90	1.10	12.10	Clay loam	16.88	24.00	67.12
BSU-U	5.72	24	2.86	1.68	14.57	Sandy Loam	12.80	24.00	63.12
SHD-U	5.82	27	3.79	2.19	33.77	Sandy Loam	16.00	24.00	69.20
JJN-U	6.40	24	1.46	0.85	15.33	Sandy Loam	16.00	24.00	69.20
LSS-U	5.30	28	2.61	1.68	31.03	Sandy Loam	16.88	24.00	67.12
CTRL-F	6.62	24	3.20	1.49	19.50	Clay Loam	10.88	20.00	69.20
CTRL-U	6.41	27	1.35	0.78	13.57	Sandy Loam	10.80	22.00	67.12

OM=Organic Matter, OC=Organic Carbon, CEC= Cation Exchange Capacity

Table 2: Herbicide/organic residues profile of selected soil samples

Sample Code	Source	Residues available	RT (min)	Percent area (%)	Conc mg/kg
SHD-F_s	Fadama	2,4-diclorophenoxy acetyl	17.26	2.49	0.05
		n-hexadecanoic acid	23.94	6.56	0.13
		Chlorpyrofos	22.82	16.21	0.32
		octadecanoic acid	28.27	19.64	0.39
		oxadiazon	27.77	7.92	0.15
		heptyl octyl ester, phthalic acid	33.81	11.25	0.22
		diis oocyl ester, 1,2-benzene DC acid			
BKK-F_s	Fadama	Atrazine	18.96	23.89	0.48
		oxadiazon	27.82	25.71	0.51
		benzenedicarboxylic acid ester	31.98	13.90	0.27
		oleic acid	28.01	3.59	0.07
		2,4-diclorophenoxy acetyl	22.02	5.11	0.10
JSS-F_s	Fadama	Atrazine	19.06	7.03	0.14
		2t-butyl-4-hydroxymethyl quinolin			
		Hexadecanoic methyl esters	23.55	5.78	0.12
		n-hexadecanoic acid	21.70	7.27	0.15
		benzenedicarboxylic acid ester	32.80	37.44	0.74
		oleic acid	27.56	5.96	0.12
		oxadiazon	27.72	7.72	0.15
BLD-F_s	Fadama	4,4-bypyridine	12.09	33.62	0.67
		Atrazine	18.90	3.83	0.07
		Oleic acid	27.73	0.83	0.01
		benzenedicarboxylic acid ester	33.76	53.57	1.07
		Octadecanoic acid	28.26	4.21	0.08
BSA-U_s	Upland	Atrazine	18.94	1.99	0.04
		2,t-butyl-4-hydroxymethyl quinolin			
		N-[(2,4-dichlorophenoxy) acetyl L-histidine	21.12	1.44	0.03
		2,4-dichloro phenol			
		Mono (2-ethhylhexyl) ester 1,2 benzene DCA	33.87	47.84	0.96
		Dioxolane	32.03	3.47	0.07
		7-methyl-7H-Purin-6-amine	33.94	36.18	0.36
		Pyridinecarboxaldehyde			
LSS-U_s	Upland	octadenoic acid	27.74	33.29	0.67
		Mono (2-ethylhexyl ester) 1,2-benzene DC acid	33.80	66.71	1.33
		di-n-octyl phthalate			
		diis ooctyl ester, 1,2-benzene DC acid			

DC = dicarboxylic acid

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Table 3: GCMS of herbicides/derivatives in *fadama* and upland soils from Plateau State

Sample	Herbicide/ derivative	Scan #	m/wt	m/z	% area	RT
SHD-F_s	Atrazine	2949	215	200(100 -BP), 58(35), 173 (27), 68 (23), 92 (20)	4.13	18.96
	N-[(2,4-dichloro phenoxy) acetyl] L-histidine	3291	220	162 (100-BP), 105 (52), 175 (28), 145 (26), 109 (27), 63 (28)	1.65	20.92
	Butyl nonyl ester phthalate	3420	279	149 (100-BP), 167 (28)	1.81	21.71
JNN-F_s	Atrazine	2967	215	200 (100-BP), 58 (40), 173 (31)	7.03	19.06
	Oxadiazon	4480	344	55(100-BP), 69(77); 83(62), 97(53), 258(19)	7.72	27.72
	mono (2-ethylhexyl) ester-1,2-benzyldicarboxylic acid	5545	279	149 (100-BP), 167 (29)	28.80	33.82
SHD-F_s	heptadecyl ester dichlorocetic acid	2652	252	57 (100-BP), 69 (65), 83 (78), 97 (58)	2.49	17.26
	Chlorphyrifos	3623	351	197 (100-BP), 314(75), 258 (47), , 97 (80),	32.15	28.82
	1,2-benzyldicarboxylic acid	5536	279	149 (100-BP), 167 (37)	53.57	33.76
	*oxadiazon	4488	344	175 (100-BP), 258 (50), 302 (33), 57 (32), 302 (25)	7.92	27.77
BLD-F_s	3, 3-Bis-tert-butylsulfanyl-2-fluo ro-acrylonitrile	1516	247	191 (100-BP), 57 (100)	1.00	15.63
BSA-U_s	Atrazine	2946	215	200 (100-BP), 173 (25), 58 (35)	1.99	18.94
	N-[(2,4-dichloro phenoxy) acetyl] L-histidine	3327	220	162 (100-BP), 55 (75), 69 (48), 83 (60), 97 (57), 111 (50), 144 (30),	21.12	1.44
	Bis (2-mthylpropyl esther), 1,2-benzyldicarboxylic acid	3428	223	149 (100-BP), 105 (80)	1.25	21.70
	1-cyano-1-[2-(-phenyl-1,3-dio xolan-2-yl)ethyl pentyl ester, ethaneperoxide acid	5233	256	149 (100), 105 (80), 77 (29)	3.47	32.03
LSS-U_s	diis ooctyl ester 1,2-benzyldicarboxylic acid	5543	279	167 (36), 149(100-BP)	66.76	33.80
QPN-U_s	3, 3-Bis-tert-butylsulfanyl-2-fluo ro-acrylonitrile	1516	247	191 (100-BP), 57 (96)	1.00	15.63
	*Bis (1,1-demethyl)-1,2-ditert-butyl -1,2-dichlorodiphosphane	1516	246	191 (100-BP), 57 (198)	0.36	15.63
SHD-U_s	3,3-bis-tert-butylsulfanyl-2-flu oro acrylontrile	1517	247	191 (100-BP), 57 (62), 41 (60)	0.58	15.63
	N,N'-ditert- butylcarbodiimide	1595	154	83 (100-BP), 57 (94)	0.67	16.28

F_s= Fadama Soil, U_s = Upland soil, m/wt = molecular weight, m/z = mass to charge ratio, RT = retention time BP-base peak

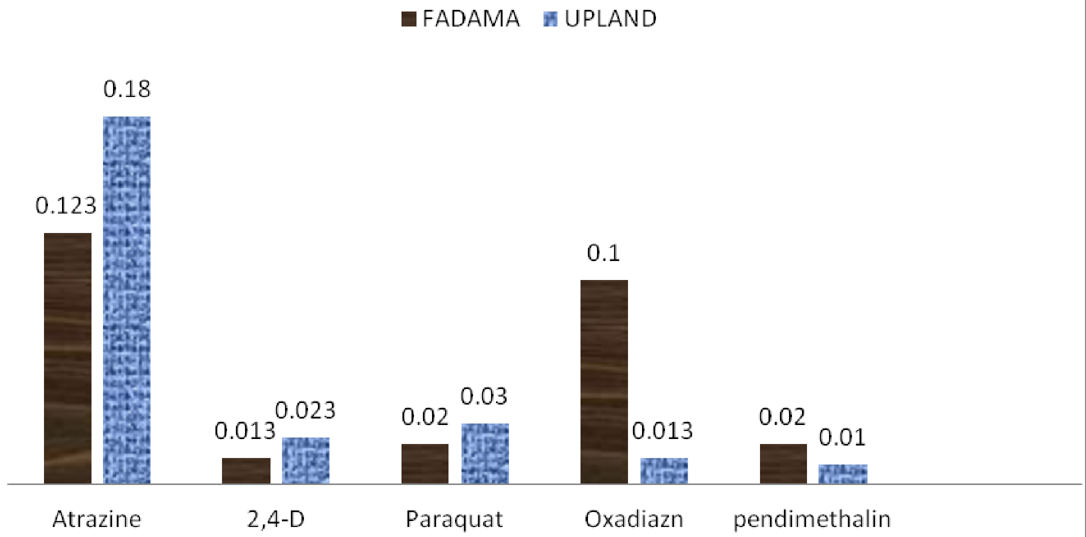

Fig 1: Average concentrantion (mg/kg) of five herbicide residues in *fadama* and upland soil in Plateau State, Nigeria.

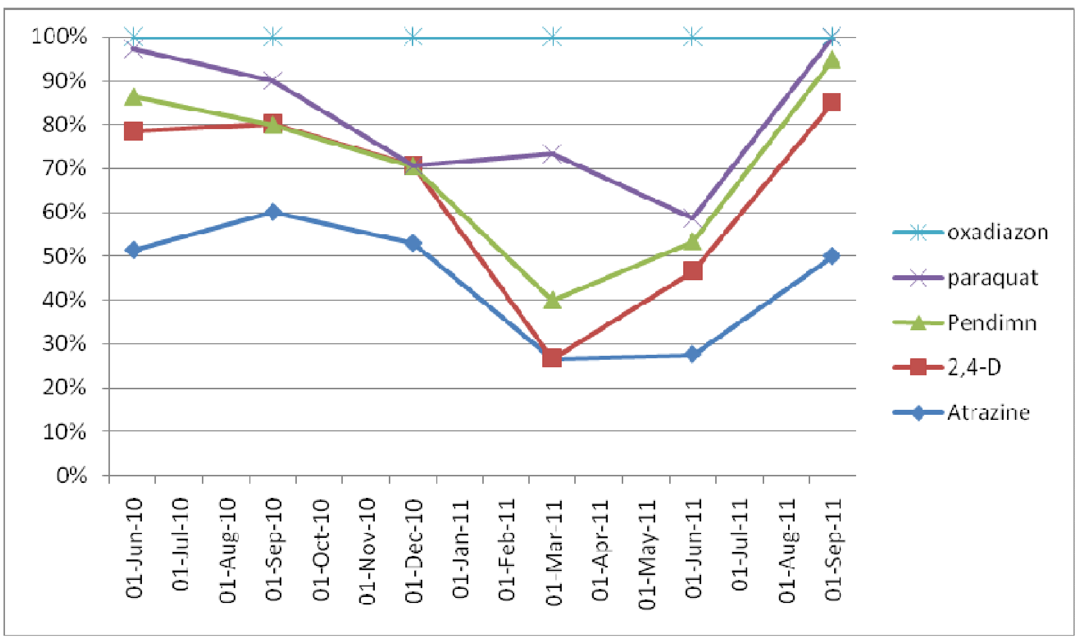

Figure 2. Seasonal variation of the level of herbicides in soil in Plateau State

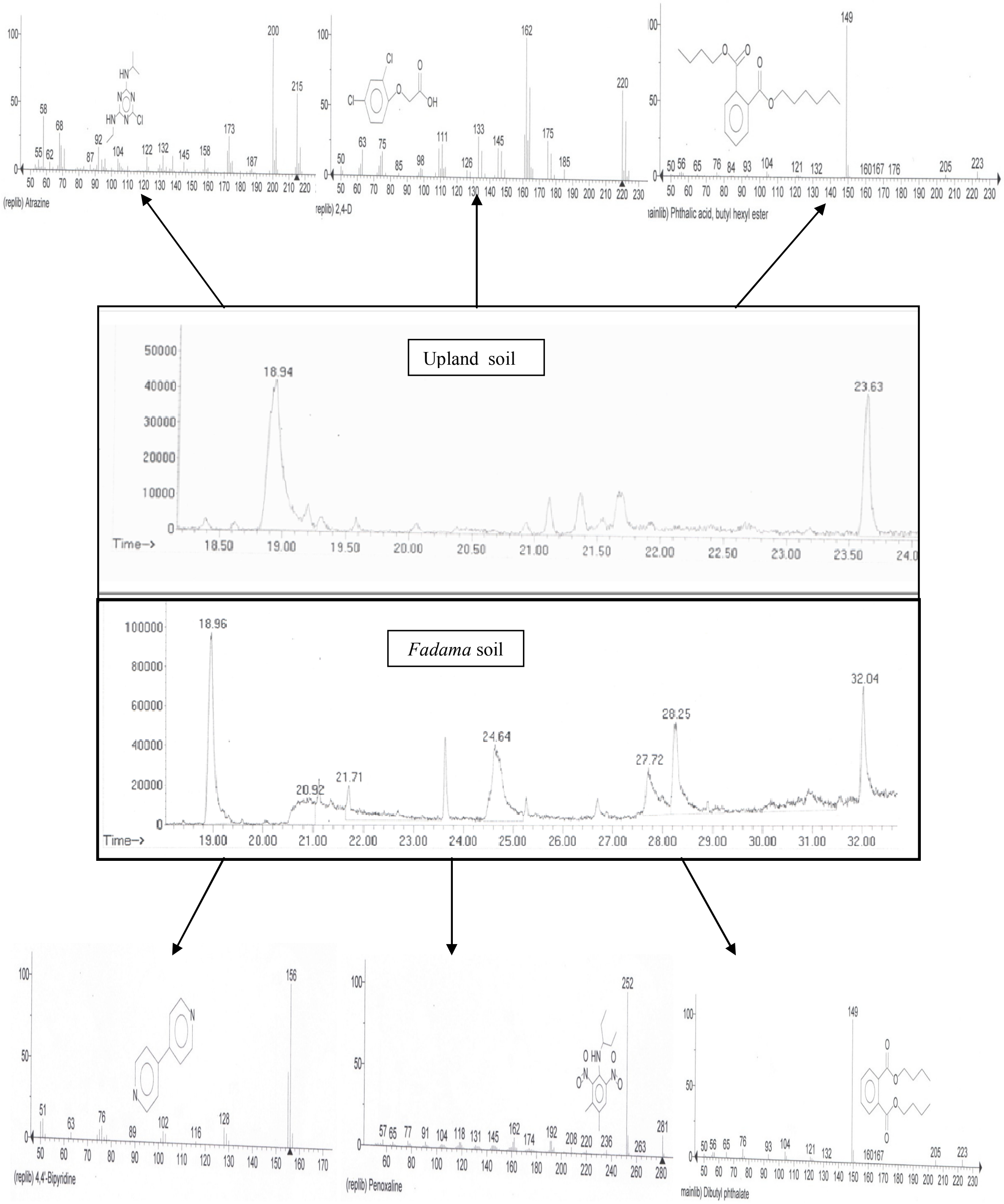

Figure 3: The GCMS Spectra of a *fadama* and an upland soil showing some of the residues.