World Journal of Analytical Chemistry, 2013, Vol. 1, No. 2, 23-28
Available online at http://pubs.sciepub.com/wjac/1/2/2
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DOI:10.12691/wjac-1-2-2

Analysis of Herbicide Residues and Organic Priority Pollutants in Selected Root and Leafy Vegetable Crops in Plateau State, Nigeria

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Received April 11, 2013; Revised May 08, 2013; Accepted May 09, 2013

Abstract Herbicide residues and organic priority pollutants in roots and leafy vegetable crop samples from Plateau State, Nigeria were determined using gas chromatography mass spectrometry (GCMS). The average concentration of the herbicide residues such as atrazine and 2,4-D which were discovered to be more in the root crops and nuts (cassava, yam, potato, groundnuts) are 0.04mg/kg and 0.02mg/kg respectively. The distribution of pendimethalin and paraquat in the root crops was scanty, except for paraquat concentration in potato which was abnormally high (0.67mg/kg). The distribution of herbicide residues in leafy vegetables under investigation was very scanty as it was not detected in most of the samples. The organic priory pollutants identified includes; organochlorines, benzene amine, polyaromatic hydrocarbons (PAHs) phthalate and phenols, they were found to occur in the samples in the rates of 6.98, 16.25, 4.67, 37.12 and 9.28% respectively. Other organic priority pollutants identified which was not any of the organic pollutants family identified above had an occurrence rate of 25.52%. The conclusion and the recommendation arrived at in this work was that when root crops are almost ripe, herbicides should not be applied in those farmland as it was observed that the farming practice in this area is characterized by mix cropping, as such herbicides and other pesticides are applied to control weed and other pests which tends to affects the root crops when the tubers are formed. This makes the residues of such pesticides to be absorbed by the tubers prior to harvest, and the consumption of such could constitute a health risk.

Keywords: *herbicides, organic priority pollutants, roots and leafy vegetable crops*

1. Introduction

The use of pesticide in farming activities has significantly provided more hope and assurance for sustainable food security in most countries of the world. However, the residues of the pesticides could be a threat to human beings and other non-target organisms after they have performed their primary roles. It is reported that only 1% of sprayed pesticides are effective, while the 99% of the pesticides applied are often released to non-target soils, water bodies, and atmosphere and finally absorbed by almost every organism [1]. One of the primary concerns about herbicides and other pesticides usage is their effect on non-target organisms with emphasis on mammalian toxicity [2]. Pesticide residues in food items have been a concern to the environment and consumers of the food and products contaminated with such categories of pesticides [3]. The intensive application of herbicides have resulted in the contamination of the atmosphere, ground/waste water and agricultural products which includes; wheat, corn, fruit, vegetables, etc. It also results in the direct pollution of food and food products as well as the biological system [4]. It was reported that plant uptake of herbicides and other pesticides post health risk to domestic livestock that forage on crop stubble and consumers of food from these animals [5]. When ingested, they can accumulate in human body fats and the environment thereby posing problems to human health [6]. Majority of herbicides are reported to constitute between 40-60% of pesticides used for agricultural purpose [7,8,9], and they ends up either in the environmental sectors or food substances with only a few reaching their primary target. For Instance, herbicide like atrazine in the triazine family, commonly used within the study area is much less expensive than other related herbicide is widely known to be persistent and toxic. It is referred to as priority pollutant since they are harmful to organisms even at micro (μg) levels [10]. Lack of precise ability to predict the persistent behavior of herbicides by the farming population in this part of the world enhances their risk of exposure. It is therefore important that farmers understand the factors that affects the persistence of residual herbicides to enable them make alternative plan [11]. It often finds its way into the water bodies used for drinking and other domestic purposes [12], that is aside the residues which accumulates in crops widely consumed within the area covered in this study. The study determines the residues of herbicides in selected root and leafy vegetable crops widely grown in the study area. The conditions responsible for the accumulation of the residues in the crops will be considered and thereafter recommendations and suggestions will be made to help reduce and if possible eliminate the herbicide residues in edible crops.

2. Materials and Methods

2.1. Samples Collection, Storage and Preparation

As soon as it was established that the samples were ripe for harvest, the samples which includes; ground nuts, potatoes, cassava, yam etc were taken from all over the plots, and to provide a fair representation of sample of the raw commodity, adhering soil were removed by brushing the roots and tuber samples before both were rinsed with distilled water. Other farm products such as fresh rice stems were collected after 30-40 days (3-6cm) with effect from when the rice was planted and period of the herbicides' application on the farms. According to FAO manual for sampling of crops and vegetables [13], an average of 12 fruits from 12 separate plants were collected, washed and stored in new sterile plastic bags. An average of 2kg each of the roots and tubers were produced from a blend of 12 roots and 12 tubers respectively from different plants within each farmland. For the storage, samples were analysed as quickly as they were collected and prepared to avoid chemical or physical changes occurring, where it is not possible they were stored at -20^{o}C, this help removes the residues from contact with enzymes which might degrade the pesticide [14].

2.2. Extraction of Crop Products

100g of each of the samples which include, potatoes, groundnuts, rice straw, vegetables where collected from the farmlands in which the herbicides were used for the control of weeds. They were chopped and blended, and 40g of each placed in a 150ml beaker. 1.0ml of the standard stock solution was spiked into the various products. This was then extracted by soaking it 50ml acetone for 30mins. It was then shaken in 100ml of dichloromethane and hexane (2:3) using a shaker for 45minutes. After the solution was clearly separated into 2 layers, the aqueous layer was discarded and the non aqueous layer was further dehydrated using anhydrous sodium sulphate, it was filtered and the filtrate evaporated using a rotary evaporator to 5ml. This was finally subjected to column cleansing using silica gel prior to GC-MS analysis.

Table 1. Residue profile of selected crop samples

Sample Code	Crop type	Residues available	RT (min)	**% area**	**Conc (mg/kg)**
SHD-g	G/Nut	(E, E) 2, 4-Decadienal 4,4-bypyridine atrazine n-hexadecanoic acid pendimethalin Oleic acid Mono (2-ethylhexyl ester) 1,2-benzene DCacid 2,6,10,14,18,22-tetracosahexaene 1-(methoxymethoxy) butylthiane	4.42 11.43 18.89 24.74 25.15 27.17 33.28 38.76 41.43	1.84 2.67 5.15 18.53 3.29 17.16 12.62 2.57 2.75	0.04 0.03 0.10 0.37 0.07 0.34 0.25 0.05 0.06
BKK-p	Potato	2,5-bis (1,1-dimethylethyl) phenol 1-heptadecene 2,4-diclorophenoxy acetyl (E)-5-Octadecene Buty-1,2-ethylhexyl ester 1,2-benzene DC acid Diis oocyl ester 1,2-benzene DC acid	12.28 15.80 19.20 21.12 23.63 33.80	3.49 2.77 0.94 3.17 2.18 87.46	0.07 0.06 0.02 0.06 0.04 1.75
JJN-c	Cucumber	Atrazine buty-1-octyl ester, 1,2-benzenedicarboxylic acid mono (2-ethylhexyl) ester, 1,2-BenzeneDC acid 1,3,3-trimethyl-2-(1-methylbut-1-en-3-on-1-yl)-1cyclohexene	19.06 23.63 33.84 41.18	7.03 0.68 37.60 60.31	0.14 0.01 0.75 1.20
BSA-r	Rice straw	4,4-bypyridine Atrazine Oleic acid benzenedicarboxylic acid ester Octadecanoic acid	12.09 18.90 27.73 33.76 28.26	33.62 3.83 0.83 53.57 4.21	0.67 0.07 0.02 1.07 0.08
SAD-y	Yam tuber	3,3-bis-tert butylsulfanyl-2-fluorocylonitrile 3,5-bis (1,1-dimethyl) phenol	15.63	1.82	0.36
QPN-c	Cassava tuber	Atrazine Butyl cyclohexyl ester-1,2-benzyldicarboxylic acid	18.91 33.58	4.12 23.00	0.08 0.40
BKK-a	Acha straw	1,2-benzyl dicarboxylic acid 4,4-bypridine	33.67 33.34	53.07 1.02	1.06 0.02

DC – dicarboxylic, Acha-Digitaria exilis
Sample Code- The 3 capital letters is the acronyms of the farm locations, while the small letter after hyphen is the first letter of the product sampled.
RT- Retention time of each of the components in the samples
% area- Percentage area the chromatogram of the components
Conc (mg/kg)-The concentration of residues obtained from the % area of the residues chromatogram and corresponding herbicides standards

Shimadzu Japan, GCMS-QP2010 PLUS was model of the gas chromatography equipped with a mass spectrophotometer detector was used to analyse the purified extracts. The column was held at 60°C in injection volume of 1µL programmed to 250°C. It was set at a mass to charge (m/z) ratio starting at 40 and ending at 420. The mass spectrometer detector was held at 250°C above the maximum column temperature. The sample size of 1µL was split in 100-1 onto the column so that the total charge on the column was 1. Helium was used as carrier gas at a linear velocity of 46Cmsec-1and pressure of 100.2kPa. The amplification and resolution for the test herbicides was achieved by adjusting the threshhold to 6000 in this analysis. This allows for the screening interference and solvent peaks leaving majorly the deflection of target compounds as revealed in the spectra [13]. This was controlled by a version of National Institute of Standards and Technology (NIST) Mass spectral library containing more than 130000 entries.

3. Results and Discussion

The GCMS analysis results of the herbicide residues and organic priority pollutants in selected crop samples are indicated in Table 1 and Table 2 respectively. A spectrum of one of the samples is shown in Figure 1. Table 1 presence the summary of the retention time, percentage areas of all the herbicide residues and their derivatives detected in the various samples analysed. This information provides the needed guide for the determination of the concentrations of the herbicides and their residues in the samples and other useful hints for their identification.

Table 2. Organic Priority Pollutants in Selected Crop Samples from Plateau State

Sample Code	Residues available	Occurrence rate (%)
Organo Chlorine	Atrazine 2,4-diclorophenoxy acetyl 2,6,10,14,18,22-tetracosahexaene	6.98
Benzene Amine	4,4-bypyridine penoxaline pendimethalin 1-(methoxymethoxy) butylthiane 9-methyl thiazolo [4,5-f] quinoline	16.25
Poly Aromatic Hydrocarbon [PAHs]	A-Neogrammacer-22 (29)-ene 3,20-Allopregnanediene	4.67
Phthalate	buty-1-octyl ester, 1,2-benzenedicarboxylic acid bis-2-methylpropyl ester1,2- benzene DC acid (2,4-di-t-butyl phenyl) mono ester pentanedioc acid buty-1,2-methylpropylester,1,2- benzeneDC acid mono (2-ethylhexyl) ester, 1,2-BenzeneDC acid 1,3,3-trimethyl-2-(1-methylbut-1-en-3-on-1-yl)- Buty-1,2-ethylhexyl ester 1,2-benzene DC acid Bis (2-ethylhexylphthalate 1cyclohexene Mono (2-ethylhexyl ester) 1,2-benzene DC acid Dis-n-ocyl phthalate Monocyclohexyl ester, phthalate acid benzenedicarboxylic acid ester	37.12
Phenol	2,5-bis (1,1-dimethylethyl) phenol 2,4-bis (1,1-dimethylethyl) phenol 3,3a,4,5-tetrahydro-3a-methyl, (3s-cis)2H-Benz [E] inden-3-ol Hexadeca-2,6,10,14-tetraen-1-ol	9.28
Others	n-hexadecanoic acid Octadecanoic acid 1-heptadecene 2, 6, 11, 15-tetramethyl-Hexadecane (E)-5-Octadecene (E)-9-Octadecene (E, E) 2, 4-Decadienal 3,7,11,16-tetramethyl, (E,E,E)-squalene S,S-dioxide 4H-pyran-2-carboxylic acid 6-[p-chlorophenyl]-4-oxo-ethyl ester	25.52

For the crop plants under investigation, it was clear that the root crops like potato, yam and cassava were observed to contain considerably high concentration of herbicide residues with their derivatives. For instance, samples BKK-p, SHD-g and QPN-c consist of at least one or two of the residues of herbicides which include 2,4-D-0.02mg/kg, atrazine-0.10mg/kg and atrazine-0.08mg/kg respectively, being residues with relatively high concentration. These are identified as the residues of the herbicides widely used in these farms. The trend showed benzene carboxylic acid and its derivatives detected in majority of crops categories under investigation, and are most likely the derivatives of organic based chemical farm inputs and other pesticides commonly used for farming activities within the study area [15]. Atrazine and 2,4-D derivatives observed in the samples was high with an average concentration of 0.09 and 0.59 mg/kg respectively. The average concentration of 2,4-D is below the Thai maximum residue limit (MRL) of 0.10mg/kg set for edible offals and is above the MRL of 0.10mg/kg for rice husked and polished rice. While the average concentration of atrazine was well below the Thai MRL of 0.10mg/kg set for atrazine in maize, pineapple, sugar cane and sweet corn [16].

Except for ground nut samples with pendimethalin concentration obtained being 0.10mg/kg which may be attributed to the regular use of this herbicide for the control of weed by groundnuts growers in the State. This is within accepted limited of the EPA detection limited of 0.1mg/kg reported [17]. The level of the herbicides concentration in root crops may not be unconnected with the farming practice which is mostly characterized with mixed cropping. In which case, the herbicides are used to control weeds when the tubers of these crops are already formed and almost matured for harvest, leading to absorption of the herbicides and their derivatives. Aside the residues accumulation in the crops already ripe for harvest, which tend to affect non-target organisms and potential public health threat to consumers of such crop products, inappropriate use of the herbicides could also result in the bushiness and stunting of the plants. This is observed in most crops exposed to higher concentration of herbicide application [18]. The differential effects of herbicide could be attributed to their differential penetration through the roots of the crops and absorption to the shoots and subsequently the accumulation in leaves which may be as a result of the degradation and detoxification within differently treated plants [19]. It is therefore very necessary to adhere to the precautions and guidelines required in handling and applying of herbicides in farmlands. This could be made possible through regular training of users as it will minimize injuries sustained by crop arising from inappropriate herbicide usage.

Table 2 provides the classification of the categories of the organic pollutants detected, from which the phthalate had the dominance (37.12%) in samples, the least occurring were organochlorine and polyaromatic hydrocarbons (PAH) with average percentage occurrence of 6.98% and 4.67% respectively. Related grouping of organic pollutants was reported [20], and it provides a useful hint and guide towards investigating other likely sources of these pollutants which will assist in proposing remediation techniques to control or removed them.

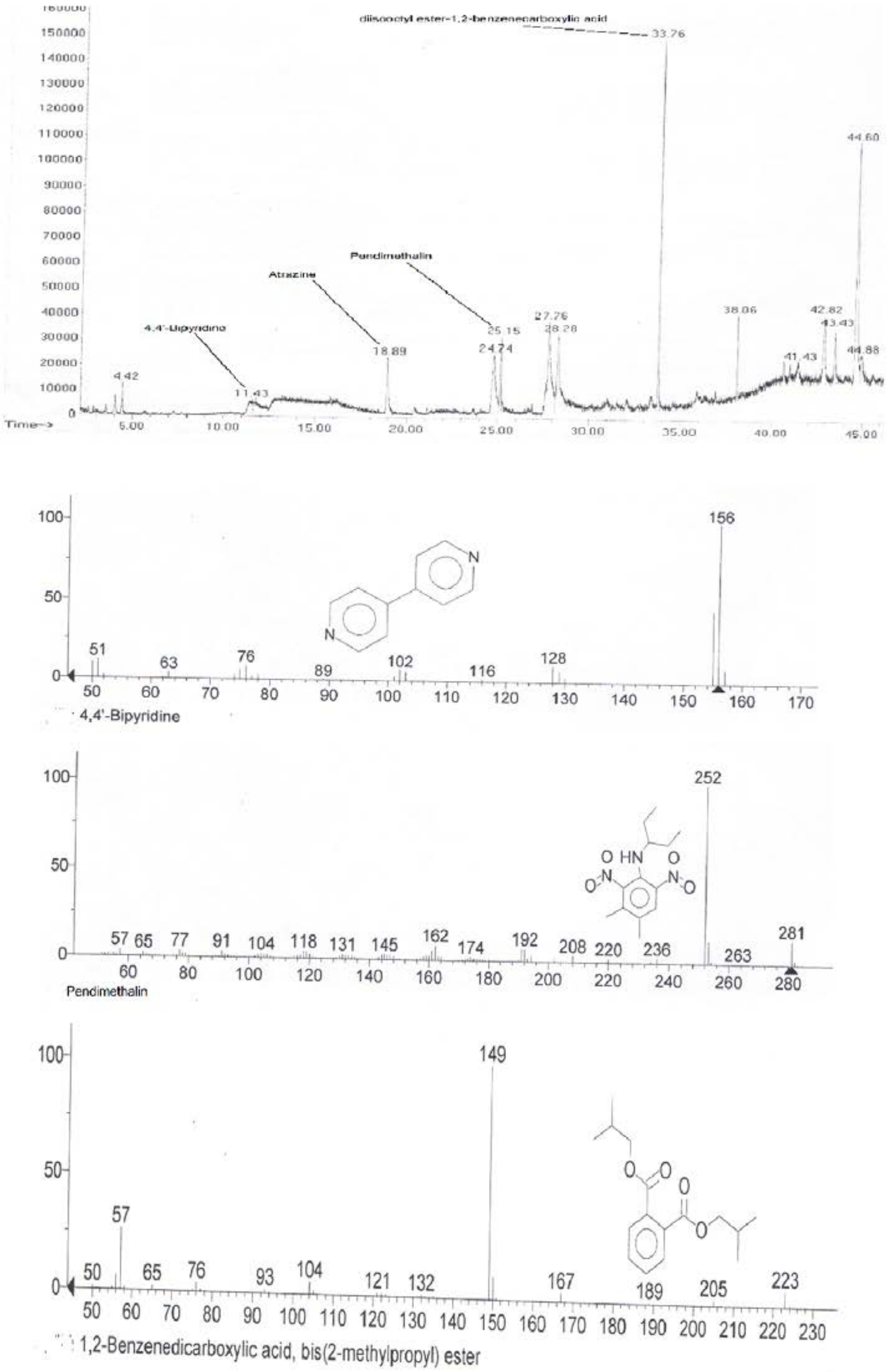

Figure 1. The GCMS of the extracts of samples of a crop product (SHD-g) within the study area

4. Conclusion

The root crops and leafy vegetable crop samples which were collected and analysed for the organic and the herbicides residues within the period covered in this research were found to contain relatively high concentration of atrazine and 2,4-dichlorophenoxy acetic acid. The distribution of herbicides like pendimethalin and paraquat dichloride residue like 4,4-bypridine in most of the sample. Organochlorines, benzene amine, polyaromatic hydrocarbons (PAHs), phthalates and phenols were the organic priority pollutants detected in the crop sample in traces. The relatively high concentration of some of the residues may not be unconnected with the farming practice within the study area in which farmers are limited in skills and basic regulations needed in effective utilization of these chemical farm inputs. To ensure the safety and sustainable health and well being of end users of these crops, it was recommended that the users of herbicides and other pesticides be adequately trained on best-practice required in utilizing pesticides. It was also suggested that there should be a legislation to regulate the use of herbicide within the area covered in this study.

Acknowledgement

We thank the management and staff of Chemistry Department-University of Jos and Chemistry Programme of Abubakar Tafawa Balewa University (ATBU) Bauchi. The Chemistry Department of the Usuman Danfodio University Sokoto are also acknowledge and appreciated for allowing us run the GCMS analysis in their Laboratories. Also acknowledged are the senior staffs of the Plateau State Agricultural Development Programme (PADP) for guiding use in samples collection.

References

[1] Zhang, W., Jiang, F. and Ou J. Global Pesticide consumption and Pollution: with China as a focus. Preceding of the International Academy of Ecology and Environmental Sciences. 1 (2): 125-144. Aug., 2011.

[2] Shaner, D.L., Herbicide safety relative to common targets in Plants and mammals. *Pest management science.* **60.** 17-24. Jul. 2003.

[3] Darko, O. and Acquaah, S. O., Level of organochlorines pesticide residues in meet. Int. J. Environ. Sci. Tech., 4 (4): 521-524. Sept 2007.

[4] Johnen, B.G., Herbicides and food quality a misfit? *In* Proceedings of Brighton Conference, *weeds.* Vol 3. British Crop Protection Council UK. 875-882. Aug. 1999.

[5] Dem, S.B., 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. Mar. 2007.

[6] Ejobi, F.; Kanja, L.W.; Kyule, M.N.; Muller, P.; Kruger, J.; Latigo, A.A.R., (1996). Organochlorine pesticide residues in mothers' milk in Uganda. Bull. Environ. Contam. Toxicol., **56**, 873-880.

[7] Sattin, M., Berti, A. and Zanin, G., Agronomic aspects of herbicide use. In. Vigh, M., Funari, E. (Eds.) Pesticide risk in groundwater. CRC press. Inc. Lewis Publishers, Boca Raton. Florida, 1995, 45-70.

[8] Zimdahl, R. I.. My View. *Weed Science.* 2002. 50:687.

[9] Fishel, F.M. Pesticide use Trends in the U.S.: Global Comparism, University of Florida, IFAS Extension.1-3. July 2010.

[10] Agdi, K. Bouaid, A., Martin, E., Fermandez, H. Azmani, A. and Camara, C. Removal of atrazine from environmental water by diatomaceous earth remediation method. *Journal of Environmental Monitor.* 2. 420-423. Jan. 2000.

[11] Johnson E., Herbicides soil residues. Agricultural and Agri-foods Canada, Scott, SK. 2003. 134-139.

[12] Solomon, K. R. D. B. Baker, R. P. Richards, K. R. Dixon, S.J. Kaline,T.W. LaPoint, Villas-Horns, C., Senior Hydrologist, Minnesota Department of Agriculture, St. Paul, MN. Personal conversation, December 1, 1999.

[13] Food and Agriculture (FAO) Manual, Plant Production and Protection Paper 197. Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed. 163-73. Rome, 2009.

[14] Itodo, A. U., Abdulrahman, F. W., Hassan, L.G., Maigandi, S.A. and Itodo, H. U. Application of GC/MS Quantification in the Adsorption of Herbicide by Sorbents from Two Abundant Nut Shells. *Researcher.* 2 (2). 64-73. 2010.

[15] Gushit, J.S., Ekanem, E.O., Adamu, H. M. and Abayeh, O. J. The Persistence of herbicide residues in *Fadama* and Upland soils in Plateau State, Nigeria. Journal of Environment and Earth Science. Vol. 2. No. 10. 148-156. Nov., 2012.

[16] Thai Agricultural Standard [TAS]. Pesticides residues: Maximum Residue Limits. National Bureau of Agricultural Commodity and Food Standards Ministry of Agriculture & Cooperatives. 2008. 16-17.

[17] United States Department of Agriculture (USDA). Pesticide Residue Testing of Organic Produce. 2010-2011 Pilot Study USDA National Organic Programme. 28-29. Nov., 2012.

[18] Sanjay, K. Kumar, A.S. and Ramasare, P. Herbicides (2,4-dichlorophenoxy acetic acid, Isoproturon) and its interaction with *Triticum aestivum L.* alone and in combination. *Research Journal of Biotechnology.* Vol. 7 (4). 232-249. Sep. 2012.

[19] Abdel Haleem, M.A.M. and Amin, R.S.H. Prometryn effects on growth, yield and chemical composition harvested seeds of soyabean plants. *Journal of Applied Science and Research.* **3**. 467-484. Jun. 2007.

[20] Wang, H., Wang, C., Wu, W., Mo, Z. and Wang Z. Persistent of organic pollutants inwater and surface sediments of Taihu Lake, China and risk assessment. *Chemosphere.* 50 (2003). 557-562. Aug., 2002.