



Risk Assessment of Pesticide Residues in Soil Samples along River Gongola, Adamawa State

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ABSTRACT

The use of some pesticides has been banned worldwide due to their toxicities. However, some farmers still use them illegally because of their acclaimed relevance. This practice may result to the prevalence of pesticide residues in the environment and agricultural produce which has been linked to several negative health effects. The aim of this study was to estimate the concentrations of pesticide residues in soil samples obtained along river Gongola, Adamawa state. A total of 10 soil samples of about 500g were collected and labeled as plot1 to plot10. They were grouped in to five places with plot 1 and 2 forming group1, and so on. To 10 g of soil sample was added 30ml 1:20 Acetonitrile. The resulting mixture was covered with clean aluminium foils and kept at room temperature for about 48 hours. The extracts were filtered (Whatman no. 42) and concentrated to about 5 mL by exposing to atmosphere to allow evaporation. To the concentrated filtrate, 1ml of n-hexane was added followed by separation of organic layer from the aqueous layer using separating funnel. This was then placed in sample bottles. The samples were then analyzed using Gas chromatography-Mass Spectrometer equipped with an auto injector (10µl syringe). The analytical result showed that aldrin, metalaxyl, trans-nonaclor, dicloran, 2,3,5,6-tetrachloroaniline, monolinuron, mecarbam, 2,3,4,5-tetrachloroanisole, ronnel, propham, cycluron, clamazone, 2,5-dichloroaniline, methyl-parathion, clorpyrifos, and nitrapyrin were detected in various concentrations. The residuals of the pesticides varied from 0.013±0.006mg/kg to 0.450±0.064mg/kg. The highest mean concentration of 0.450±0.064 mg/kg was recorded for aldrin which was detected in soils from all locations. Methyl-parathion recorded the least mean concentration of 0.013±0.006mg/kg which was detected in soil samples from group 1 to 3. The pesticide residue concentrations found in the studied soils were highly above maximum residue limits by Food and Agriculture Organization of the United Nations (FAO). The findings of this study provided information on residue levels of pesticides in soils along river Gongola, Adamawa state. Routine monitoring of pesticide residues in this study area is necessary for the prevention, control and reduction of environmental pollution, leading to minimize health risks.

Keywords: Pesticide residues, Soil, River Gongola, Pesticides

1. Introduction

As the world's population is growing rapidly, human societies benefit from or even rely on pesticides to ensure food safety and disease control. Pesticide use, either in field or postharvest, has largely contributed to improved crop yield, with its attendant economic benefits [1]. However, inappropriate use of pesticides may lead to the prevalence of pesticide residues in the environment and agricultural produce [2]. The global pesticide expenditures from the production perspective are estimated to be \$56 billion [3], and nearly 2.4 million tons and over 50,000 commercial formulations of pesticides are being used annually in agriculture [4, 5].

The soil serves as a reservoir for persistent organic pollutants and plays an important role in their global distribution [6]. Soil not only has a large retention capacity but also re-emits OCPs into the environment as a secondary source [7]. A significant proportion of hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), ranging from 20 to 70% of its degradation products, may remain in the soil after having been applied [8]. DDT and the rest of persistent OCPs have been found in soil samples and distributed throughout the environment [8]. The transfer of OCPs from the soil surface layers to lower depths may impact their volatilization rates from surface soil and thus impose potential risks for shallow groundwater [9, 10]. The application of these man-made chemicals to the environment has resulted in the need for development of methods to assess, monitor and mitigate their impact distributed throughout the environment [11]. Pesticide ingestion either by direct or indirect exposure may lead to generation of reactive oxygen species (ROS), which are detrimental to the health of humans and non-target organisms such as domestic fowls and pets (distributed throughout the environment [11]). It has been reported that bioaccumulation of pesticides in the food chain can lead to potentially adverse effect in humans and useful animals owing to their putative toxic action distributed throughout the environment [11, 12]. This toxicity as reported by distributed throughout the environment [11] may occur directly as a result of pesticides being converted to free radicals or via the formation of superoxide as by-product of their metabolism.

Pesticides are applied for both agricultural and residential purposes. They are transported and remain in the soil and sediment, depending on their physicochemical properties, sediment and soil types, particle sizes, and other environmental conditions such as moisture, micro-organisms, pH, and

groundwater levels [13]. Although many pesticides such as persistent organic pollutants have been banned for over decades owing to their severe toxicity [14], excessive historical usage and environmental persistence still make them frequently detectable in the environment in high levels and can threaten ecological and public health [2, 12, 14]. Exposure to pesticides through surface soil and sediment is one of the most common exposure routes, which include direct ingestion of soil, inhalation of soil dust, and dermal contact with pesticide-contaminated soil [14, 15, 16]. Because of the exposure frequency, behavior patterns, and physiological conditions, children are usually mainly exposed to pesticides via soil and are more vulnerable than adults [16].

Among the variables used in risk assessment models, pesticide soil level is one of the most important ones as it directly determines the potential degree of exposure dose and adverse health effect. Therefore, generating and exploring a robust and accurate model to describe the distribution of pesticide residues in soil is essential; this might help risk scientists and regulatory agencies to better quantify population health risks [16]. This study will provide relevant information on the potential risks associated with the inappropriate use of pesticides along river Gongola, Adamawa State, Nigeria.

2. Methodology

2.1. Soil sampling

Topsoil samples from the sampling site were collected at 0–30 cm depth using a spiral auger and composited. A total of 10 soil samples of about 500g were collected and labeled as plot1 to plot10. These were grouped in to five places with plot 1 and 2 forming group1, and so on. The samples were wrapped in clean plastic bags. They were then placed in clean zip lock bags. The soil samples, directly after collection, were kept in a refrigerator prior to laboratory analysis.

2.2 Reagents and solvents

Analytical grade reagents and solvents were used. They were n-hexane and acetonitrile.

2.3 Soil preparation and extraction

To 10 g of soil sample was added 30ml 1:20 Acetonitrile. The resulting mixture was covered with clean aluminium foils and kept at room temperature for about 48 hours. The extracts were filtered (Whatman no. 42) and concentrated to about 5 mL by exposing to atmosphere to allow evaporation. To the concentrated filtrate, 1ml of n-hexane was added followed by separation of organic layer from the aqueous layer using separating funnel. This was then placed in sample bottle.

2.4 Gas chromatography-mass spectrometer analysis

A gas chromatography from Agilent USA hyperated to a mass spectrophotometer (5975C) with triple axis detector equipped with an auto injector (10µl syringe) was used. Helium gas was used as a carrier gas. All chromatographic separation was performed on capillary column having specification: length; 30m, internal diameter; 0.2µm, thickness; 250 µm, treated with phenyl methyl silox. Other GC-MS conditions are ion source temperature (EI), 250°C, interface temperature; 300°C, pressure; 16.2psia, out time; 1.8mm, 1µl injector in split mode with split ratio 1:50 with injection temperature of 300°C, the column temperature started at 35°C for 5mins and changed to 150°C at the rate of 4°C/min. The temperature rose to 250°C at the rate of 20°C/min and held for 5mins. The total elution was 47.7minutes. MS solution software provided by supplier was used to control the system and to acquire the data; identification of the compounds was carried out by comparing the mass spectra obtained with those of the standard mass spectra from NIST library (NIST11).

3. Results

Of the ten soil samples analysed, 16 different pesticide residues were detected, which includes aldrin, metalaxyl, trans-nonaclor, dicloran, 2,3,5,6-tetrachloroaniline, monolinuron, mecarbam, 2,3,4,5-tetrachloroanisole, ronnel, propham, cycluron, clamazone, 2,5-dichloroaniline, methyl-parathion, chlorpyrifos, and nitrapyryn. The concentrations of pesticide residues detected in the soil at different plots along river Gongola are presented in table 3.1 below. The results show that the mean concentration of pesticide residues in the soils ranges from 0.013±0.006mg/kg to 0.450±0.064mg/kg. Plot3 has the least pesticide residue concentration while plot4 has the highest concentration.

Table 3.1 Pesticide residues detected in soil samples along river Gongola, and their concentrations (mg/kg).

	Plot1	Plot2	Plot3	Plot4	Plot5	Plot6	Plot7	Plot8	Plot9	Plot10
Pesticide residues										
Aldrin	0.258	0.324	0.404	0.489	0.188	0.369	0.404	0.495	0.350	0.330
2,3,4,5-tetrachloroanisole	0.094	0.039	0.130	0.117	-	0.088	0.079	0.095	0.069	-
Cycluron	0.052	0.039	-	0.057	0.026	0.044	0.043	0.046	-	-
Ronnel	0.025	-	0.021	-	0.076	-	-	-	-	-
Metalaxyl	0.207	-	-	-	-	-	-	-	-	-
Methyl-parathion	0.042	-	0.023	-	0.013	-	-	-	-	-
Trans-nonaclor	0.021	-	-	-	-	-	-	-	-	-
Dicloran	-	-	0.054	-	-	-	-	-	-	-
2,5-dichloroaniline	-	-	-	0.312	0.105	0.228	0.217	0.251	0.203	0.193
Propham	-	-	-	-	-	0.056	0.078	0.050	0.078	0.066

Clamazone	-	-	-	-	-	0.099	0.098	-	0.148	0.159
Monolinuron	-	-	-	-	-	0.021	-	-	-	-
Chlorpyrifos(-ethyl)	-	-	-	-	-	-	0.023	-	0.024	0.023
Nitrapyrin	-	-	-	-	-	-	-	0.063	-	-
2,3,5,6- tetrachloroaniline	-	-	-	-	-	-	-	-	0.029	-
Mecarbam	-	0.097	0.025	-	-	-	-	-	-	-

Table 3.1 presents the pesticide residues concentrations in plot1 to plot10.

Table 3.2 Mean of pesticide residues concentrations (mg/kg) in the soils along river Gongola

Pesticide residues	Group 1	Group2	Group3	Group4	Group5
Aldrin	0.291±0.047	0.446±0.060	0.278±0.128	0.450±0.064	0.340±0.014
2,3,4,5-tetrachloroanisole	0.067±0.039	0.124±0.009	0.088±0.028	0.087±0.011	0.069±0.028
Cycluron	0.046±0.009	0.057±0.010	0.035±0.013	0.045±0.002	-
Ronnel	0.025±0.013	0.021±0.012	0.076±0.013	-	-
Methyl-parathion	0.042±0.007	0.023±0.007	0.013±0.006	-	-
2,5-dichloroaniline	-	0.312±0.087	0.167±0.024	0.234±0.007	0.198±0.063
Propham	-	-	0.056±0.013	0.064±0.020	0.072±0.008
Clamazone	-	-	0.099±0.032	0.098±0.032	0.154±0.008
Chlorpyrifos(-ethyl)	-	-	-	0.023±0.001	0.0235±0.001
Mecarbam	0.049±0.024	0.025±0.013	-	-	-

Table 3.2 presents the mean±standard deviation (n=2) of pesticide residues concentrations in the soil samples. Aldrin shows the highest mean concentrations across the groups.

Table 3.3 Pesticide class, type, and their maximum residue Levels.

Pesticide residues	Type	Class	MLR (mg/kg)
Aldrin	Organochlorine	Insecticide	0.10
Clamazone	Organochlorine	Herbicide	0.01
Trans-nonaclor	Organochlorine	-	0.01
Dicloran	Organochlorine	Fungicide	0.01
Methyl-parathion	Organophosphate	Insecticide	0.01
Chlorpyrifos	Organophosphate	Insecticide	0.01
Mecarbam	Organophosphate	Insecticide	0.01
Ronnel	organophosphate	Insecticide	0.01
Propham	Carbamate	Herbicide	0.01
Monolinuron	-	Herbicide	0.01
Nitrapyrin	-	Bactericide	0.01
Metalaxyl	-	Fungicide	0.01
Tetrachloroaniline (-2,3,5,6)	-	Fungicide	0.01
Tetrachloroanisole (2,3,4,5)	-	-	-
Cycluron	-	Herbicide	0.01

Table 3.3 presents the types of pesticides, class and their maximum residue levels [17].

4. Discussion

Inappropriate use of pesticides may lead to the prevalence of pesticide residues in the environment and agricultural produce [2]. Soils are known to serve as sinks for pesticides. Soils do not only have large retention capacity but also re-emit OCPs into the environment as a secondary source [7]. In this study, the detected pesticide residues reflect the types of pesticides that have been used in the respective plots, particularly aldrin which was detected in almost all the samples. The differences in the concentrations of these residues in the soil samples may be due to the substantial inter-farm variation in intensive use of pesticide as well as the differences in their degradation rate [18].

The result from this study also showed the presence of four OCPs (aldrin, trans-nonacor, dicloran, and clamazone) from the soil samples obtained from the ten plots along river Gogola in Varian concentrations. The levels of aldrin ranged from $0.278 \pm 0.128 \text{ mg/kg}$ to $0.450 \pm 0.064 \text{ mg/kg}$. Aldrin was detected in soil samples from all locations. The highest concentrations of aldrin were found in soil from Group 4, while the least concentration was detected in group3. Contrary to this result, the lower residues have been reported by [19], where aldrin was found in agricultural soil from région des plateaux in togo, with concentrations of $0.04 \pm 0.01 \mu\text{g/kg}$ to $0.93 \pm 0.03 \mu\text{g/kg}$.

Organochlorines can be highly toxic to the ecosystem through bioaccumulation. Most were banned from use [2, 12]. Aldrin was detected above the FAO maximum residues limit; hence the result indicates that the soil samples within the studied area were contaminated by organochlorines. This observation is in tandem with the findings of [2]. Trans-nonaclor and dicloran were detected only in group1 and 2 respectively, and concentrations of $0.021 \pm 0.013 \text{ mg/kg}$ and $0.054 \pm 0.024 \text{ mg/kg}$ respectively. The highest concentration was recorded in group5 with clamazone whose concentration was 0.154 ± 0.008 . The least concentration of clamazone was detected in group4 (0.098 ± 0.032). The levels of organochlorine pesticides detected from all locations were far greater than the FAO maximum residue limits (MRL).

Four organophosphates (methyl-parathion, chlorpyrifos, mecarbam and ronnel) were also detected in soil samples analyzed. The level of methyl-parathion ranged from $0.013 \pm 0.015 \text{ mg/kg}$ to $0.042 \pm 0.015 \text{ mg/kg}$. Methyl-parathion was present in group1, 2 and 3 only, but not present in other groups. Group1 shows the highest mean concentration of methyl-parathion. Methyl parathion is highly toxic by inhalation and ingestion, and moderately toxic by dermal adsorption. As with all organophosphates, methyl parathion is readily absorbed through the skin. Skin which has come in contact with this material should be washed immediately with soap and water and all contaminated clothing should be removed. Accidental skin and inhalation exposure to methyl parathion have caused human fatalities [11]. Chlorpyrifos was present in group4 and 5, but absent in other groups. Group5 show the highest concentrations of chlorpyrifos. Mecarbam was detected in group1 and 2 only. Group1 have the highest mean concentrations of mecarbam, while ronnel was present in group1, 2, and 3 only with concentrations ranging from $0.021 \pm 0.012 \text{ mg/kg}$ to $0.076 \pm 0.013 \text{ mg/kg}$. The highest concentration of ronnel was found in group3. Again, the levels of these pesticide residues which were detected from the 10 locations were unusually higher than the FAO maximum residue limit.

One carmate (proham) was detected in the soil samples analyzed with concentrations ranging from $0.056 \pm 0.013 \text{ mg/kg}$ to $0.072 \pm 0.008 \text{ mg/kg}$. Propham was present in group3, 4, and 5, but was not present in other groups. Group5 and group3 shows the highest and the least mean concentration of propham respectively.

Nitrapyrin, monolinuron, 2, 5-dichloroaniline, 2, 3, 4, 5-tetrachloroanisole, metalaxyl and cycluron were also present in soil samples analysed from the sampling site. Tetrachloroanisole (-2, 3, 4, 5) was found in all the groups with concentrations ranging from $0.067 \pm 0.039 \text{ mg/kg}$ to 0.124 ± 0.009 . The highest concentrations of tetrachloroanisole (-2, 3, 4, 5) was found in group1 while the least concentration was found in group2. Cycluron was detected in group1-4 with concentrations ranging from $0.035 \pm 0.013 \text{ mg/kg}$ to $0.046 \pm 0.009 \text{ mg/kg}$. The highest and the lowest concentration of cycluron were recorded in Group1 and 3 respectively.

5. Conclusion

The levels of pesticides detected in all the soil samples analyzed from different locations in this study were found to be highly greater than the maximum permissible concentrations of the pesticide residues in contaminated soils in which vegetables and tubers are cultivated. This study indicated that the presence of high concentrations of these pesticide residues is a sign of recent use of these pesticides by farmers and continuous consumption or exposure of vegetables or any other crop cultivated on this contaminated soils may present health risk to individuals.

REFERENCES

- [1] Were, K., Gelaw, A. M., & Singh, B. R. (2016). "Smart strategies for enhanced agricultural resilience and food security under a changing climate in sub-Saharan Africa," in *Climate Change and Multi-Dimensional Sustainability in African Agriculture*, 431–453. <https://doi.org/10.1007/978-3-319-41238-223>
- [2] Abah, M. A., Otitaju, O., Okoli, E. C., Ozioma, P. E., Bando, D. C., & Zephaniah, H. S. (2021). Determination of selected pesticide residues in leafy vegetables (*Amaranthus spinosus*) consumed in Donga, Taraba state. *International Journal of Biochemistry, Bioinformatics and Biotechnology Studies*, 6(2), 9-16. <https://doi.org/10.37745/ijbbs.15>
- [3] Atwood, D., & Paisley-Jones, C. (2017). Pesticides industry sales and usage 2008–2012 market estimates. In: US Environmental Protection Agency. DC Google Scholar, Washington, 7-9.
- [4] Damalas, C. A., & Eleftherohorinos, I. G. (2011). Pesticide exposure, safety issues, and risk assessment indicators. *International Journal Environmental Resources Public Health*, 8(5), 1402-1419. <https://doi.org/10.3390/ijerph8051402>
- [5] Brasil, V. L. M., Ramos Pinto, M. B., Bonan, R. F., Kowalski, L. P., & Da Cruz Perez, D. E. (2018). Pesticides as risk factors for head and neck cancer: a review. *Journal of Oral Pathology*, 47(7), 641–651. <https://doi.org/10.1111/jop.12701>
- [6] Meijer, S., Ockenden, W., & Sweetman, A. (2003). "Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes," *Environmental Science & Technology*, 37(4), 667-672. <https://doi.org/10.1021/es0258091>
- [7] Barra, R., Popp, P., Quiro, R., Baue, C., & Cid, H. (2005). "Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja River Basin.
- [8] Miglioranza, K., Moreno, J., & Moreno, V. (2003). "Trends in soil science: organochlorine pesticides in Argentinean soils," *Journal of Soils and Sediments*, 265(3), 264-265. <https://doi.org/10.1007%2Fs11783-011-0354-y>

- [9] Zhang, G., Li, J., Cheng, H., Li, X., & Xu, W. (2007). "Distribution of organochlorine pesticides in the Northern South China Sea: implications for land outflow and air—sea exchange," *Environmental Science and Technology* 41(11), 3884–3890. <https://doi.org/10.1021/es070072r>
- [10] Weaver, T. B., Ghadiri, H., Hulugalle, N. R & Harden, S. (2012). "Organochlorine pesticides in soil under irrigated cotton farming systems in Vertisols of the Namoi Valley, northwestern New South Wales, Australia," *Chemosphere* 88(3), 336–343. <https://doi.org/10.1155/2018/3269065>
- [11] Otitoju, O., & Onwurah, I. N. E. (2007). Glutathione S-transferase (GST) activity as a biomarker in ecological risk assessment of pesticide contaminated environment, *African Journal of Biotechnology*, 6(12), 1455-1459.
- [12] Okoli, E. C., Otitoju, O., Abah, M. A., Ozioma, P. E., Bando, D. C., & Zephaniah, H.S. (2021). Ecological risk assessment of pesticide residues in fish samples from river donga in Donga, Taraba state, nigeria. *International Journal of Biochemistry, Bioinformatics and Biotechnology Studies*, 6(2), 1-8. <https://doi.org/10.37745/ijbbbs.15>
- [13] Yadav, I. C., & Watanabe, H. (2018). Soil erosion and transport of Imidacloprid and Clothianidin in the upland field under simulated rainfall condition. "Science of the Total" Elsevier, 640(1), 1-8. <https://doi.org/10.1016/j.scitotenv.2018.06.008>
- [14] Jennings, A. A., & Li, Z. (2014). Scope of the worldwide effort to regulate pesticide contamination in surface soils, *Journal Environmental Management*, 146, 420–443. <https://doi.org/10.1016/j.jenvman.2014.07.020>
- [15] Ghadiri, H., Rose, C. W., & Connell, D. W. (1995). Degradation of organochlorine pesticides in soils under controlled environment and outdoor conditions, *Journal of Environmental Management*, 43(2), 141–151. [https://doi.org/10.1016/S0301-4797\(95\)90123-X](https://doi.org/10.1016/S0301-4797(95)90123-X)
- [16] Li, Z. (2018a). The use of a disability-adjusted life-year (DALY) metric to measure human health damage resulting from pesticide maximum legal exposures, *Science Total Environment*, 639, 438–456. <https://doi.org/10.1016/j.scitotenv.2018.05.148>
- [17] FAO, WHO. (2020). Pesticide residues in food 2019 – Joint FAO/WHO Meeting on Pesticide Residues Evaluation Part I: Residues. Rome. <https://doi.org/10.4060/ca7953en>
- [18] Owusu-Boateng, G., & Amuzu, K. K. (2013). A survey of some critical issues in vegetable crops farming along River Oyansia in Opebea and Dzorwulu, Accra-Ghana. *Glo. Adv. Res. J. Phys. Appl. Sc.*, 2(2), 024031.
- [19] Kolani, L., Mawussi, G., & Sanda, K. (2017). *Assessment of organochlorine pesticide residues in vegetable samples from some agricultural areas in Togo*. *Am. J. Anal. Chem.*, 7, 332-341. <https://doi.org/10.4236/ajac.2016.74031>