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Heavy Metal Levels in Paddy Soils and Rice (*Oryza Sativa* (L)) Exposed to Agrochemicals at Ikwo, South-East Nigeria

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Abstract- **The heavy metal levels of rice grains produced on soils and water contaminated with agrochemicals was studied, in 2013, at Ebonyi State Rice Project, Ikwo south-eastern Nigeria. The heavy metals studied were Mercury (Hg), Copper (Cu), Arsenic (As), Lead (Pb), Chromium (Cr), Fe (Iron) Cadmium (Cd), Zinc (Zn), Manganese (Mn), and Nickel (Ni). Soil and water samples and Rice grains of different varieties were collected from paddy fields of the various locations of the project and analyzed for their levels of heavy metals contamination. The results indicated that the levels of the heavy metals in the soils and water were all above the permissible levels for agricultural soils and water. The results further showed that the levels of Cadmium, Chromium, Copper Lead, Zinc, Arsenic, Nickel, Manganese and Iron in polished rice were generally within the acceptable levels for human food. However, the concentration of Hg found in the polished grains of Landrace, FARO44, FARO52 and Fadama rice varieties, were higher than the World Health Organization maximum permissible concentration of mercury in polished rice for human consumption, suggesting the significance of establishing regulation measures for application of agrochemicals in the wetlands of Ikwo.**

Keywords – **Agrochemicals, Heavy Metals, Paddy Soils, Water, Rice Grains.**

I. Introduction

In environmental term, heavy metals are attributed to metals which are toxic substances to living organisms [1, 2]. They are trace metals which occur naturally in rocks and soils, but increasingly are being released into the environment by anthropogenic activities. Some of these heavy metals are released into the soil from various sources, including agrochemicals such as fertilisers, pesticides, fungicides and so on. The heavy metals frequently reported in literature with regards to potential hazards and occurrences in contaminated soils are Cd, Cr, Pb, Zn, Fe and Cu [3, 4].

These heavy metals are reported to be the major components of agrochemicals [5]. These components of Pesticides, herbicides and chemical fertilizers usually enter into soil through our agricultural activities.

Concerns have been expressed with regard to heavy metal transmission through natural ecosystems [6, 7]. This is because excess concentrations of these heavy metals in soils have been reported to cause the disruption of natural terrestrial ecosystems [8, 9]. Also, the activities of microorganisms that promote plant growth have been shown to be altered by high concentrations of the metals [10, 11]. Sharma *et al* [5], on their part have shown that heavy metals are potentially toxic to crops, animals and humans when contaminated soils were used for crop production, because heavy metals are easily accumulated in vital organs to threaten crop growth and human health.

The Ebonyi State/World bank Rice Project started rice cultivation simultaneously throughout the Ikwo locations in 1982. The project has since its inception made use of the Green Revolution programme which involves intensive use of various forms of agrochemicals. The agrochemicals applied in the paddy fields include but not limited to herbicides (organo-phosphates, propanil based), insecticides (dimethoate, carbofuran), fungicides (lindane, dithane) and fertilizers (superphosphates, urea and compound fertilizers). There is therefore, the urgent need to evaluate the risk of heavy metal uptake by crops and to minimize the risk by decreasing soil heavy metal contamination to improve food safety and safeguard human health. In addition to the determination of heavy metal concentrations in soils, the establishment of appropriate land-use systems and soil remediation technologies to deal with soil pollution is also important. Because the risk of human exposure to heavy metals arising mainly from consuming crops grown in polluted soil and from drinking contaminated water exists in the study area, regulations for controlling heavy metal pollution are essential, and these are what this study set out to pave the way for the achievement.

II. Materials and Methods

2.1 Location:

The study was carried out in the 2013 rainy season and covered the wetland occupied by the Ebonyi State/World Bank Rice Project. The project area is located within latitudes 800 151 E and longitude 6 01 N in the derived savanna zone of Southeast Nigeria. The project has locations at Item, Obegu, Ndiagu, Enyibichiri and Ekpanwudele communities. The soils of the area are described as wetland soils, and the parent materials made of shale, with impervious layer at shallow depth, and usually water-logged owing to poor water-drainage.

2.2 Field study:

The study was conducted in fifty plots in the rice fields at Item, Obegu, Ndiagu, Enyibichiri and Ekpanwudele locations of the project. Ten composite soil samples were taken at 0-40 cm depth from each of ten sampling zones having varied topographic features in each of the locations. The values for the 100 samples from each location were drawn as representative of the location. The grains of six newly introduced, improved rice varieties cropped in the area, bearing names as used by the breeders, (Faro-52, IRRI-1416, Faro-44, IRRI-1650, Long ridge-MASS, and FADAMA), and one Landrace check (IRRI-5) were collected from the fields of each location at the dry mature stage. They were separately parboiled, dried, dehusked, polished and assessed for heavy metal contamination. Water samples were also collected with the aid of sterile 250ml beakers from the paddy field in each location and transferred into new and clean 1 litre plastic containers with cover, previously rinsed with the runoff water of the particular location and taken to the laboratory for analysis of heavy metal contamination.

2.3 Laboratory study

The soil, water and plant samples were analysed for heavy metals including Mercury (Hg), Copper (Cu), Arsenic (As), Lead (Pb), Chromium (Cr), Fe (Iron) Cadmium (Cd), Zinc (Zn), Manganese (Mn), and Nickel (Ni)] content. For the rice grains, the heavy metals were determined after wet digestion with a mixture of HCL and HNO_3. The metals were measured by Sp 1900 pyre Unican recording flame atomic absorption spectrophotometer.

III. Results

3.1 Heavy metals in the soils

Table 1 shows the effect of soil exposure to agrochemicals. The levels of the various heavy metals detected in the soils of all the locations were generally above the world health organization's permissible levels for agricultural soils. Romić and Romić [12], also showed that long-term and extensive use of land for agriculture with frequent application of agrichemicals is one of the major causes of trace metal, such as copper, nickel, zinc and cadmium, accumulation in soil. The levels of the elements however varied among the locations. The soil at Enyibichiri, Obegu and Ndiagu locations indicated higher Hg contamination compared to the soils at Item and Ekpanwudele locations, whereas higher levels of Pb contaminations were detected in the soils at Enyibichiri and Ekpanwudele than at Item, Obegu and Ndiagu locations. The soil at Obegu had higher AS contamination compared to the soils at Item, Ndiagu, Ekpanwudele and Enyibichiri locations, while the soils at Enyibichiri and Ekpanwudele locations also showed higher AS contamination than that of Item location. The soil of Obegu location also exhibited higher levels of Fe contamination than the other locations. The level of Cd contamination observed in the soils at Obegu and Item locations on one hand were higher than that of Ndiagu, Enyibichiri and Ekpanwudele locations, whereas the soils of Enyibichiri and Ekpanwudele locations on the other were more contaminated with Cd compared to the soil of Ndiagu location. It was also observed that the soil of Enyibichiri and Obegu locations were more contaminated with Zn than all other locations, while the soil of Ndiagu also had higher Zn contamination than the soils of Item and Ekpanwudele locations. The soils of Obegu and Enyibichiri were more contamination with Ni than all the other locations, while that of Item also exhibited higher Ni contamination compared to Ndiagu and Ekpanwudele locations. The level of Cu concentration in the soil at Obegu and Ndiagu locations were higher than the other locations, whereas the soil of Item location exhibited higher Cu content than that of Ekpanwudele and Enyibichiri locations. The level of Cr was equally higher in Ekpanwudele, Ndiagu and Obegu soils than in the soil at Item and Enyibichiri locations.

3.2 Heavy metals in run-off water

Table 2 shows the effect of agrochemicals on the run-off water at the locations. The heavy metals contaminations of the run-off water seem to exhibit the same pattern as in the soil. Generally, the levels of the heavy metals detected in the run-off water in the whole locations were above the permissible levels recommendations of the world health organization. The level of Hg contamination detected in the run-off water from the paddy fields in Obegu and Ndiagu were statistically higher than the other locations, whereas the level of Pb contamination of the run-off water from the paddy field at Ekpanwudele and Enyibichiri were higher than the other locations. The run-off water from the paddy fields at Obegu and Enyibichiri on one hand had higher AS contamination than the other locations, whereas the run-off from the fields of Ndiagu and Enyibichiri on the other were more contaminated with AS than the run-off of the Item fields. Total Fe contamination was higher in the run-off of Enyibichiri, Ndiagu and Ekpanwudele locations than that of Item and Obeagu locations, whereas higher Cd contaminations were detected in the run-off of Obegu and Ndiagu than the other locations. Cd contamination was also higher in the run-off of Ekpanwudele than in that of Item and Enyibichiri locations. The Zn contamination in the run-off water from the paddies of Enyibichiri was statistically higher than the other locations, while higher contamination of Zn was also detected in the run-off water from the fields of the Item location than Obegu and Ndiagu locations. The level of contamination of Ni in the run-off of Ekpanwudele, Enyibichiri and Obeagu locations were higher than in the run-off water of Item and Ndiagu locations. The concentration of Cu was higher in the run-off from the paddies of Obegu and Ekpanwudele than the other locations, whereas the contamination of Cr was higher in the run-off from the fields at Ekpanwudele and Ndiagu than the other locations, and also higher in Ekpanwudele and Obegu than that of Item location.

3.3 Heavy metals in the rice grains

The effect of application of agrochemicals on the rice grains are presented in table 3. Elevated concentrations of Mercury were detected in the grains of the Landrace, FARO44, FARO52 and FADAMA varieties; these were beyond the World Health Organization, set standards for the maximum permissible concentration of heavy mercury in polished rice [13, 14]. The other heavy metals including As and Ni had no traces at all, in all the varieties tested, whereas some of the varieties including IRRI1416, IRRI1650, and MASS-Longridge had traces of certain metals, although these were within World Health Organization permissible levels for polished rice.

IV. Discussion

The heavy metals contaminations of the soils seem to be location-specific, and various factors may have contributed to the variations in the levels of soil contamination, including factors related to the pollutants such as the source, the transport and degradation pathways, and the chemical form of the heavy metals and factors related to soils such as adsorption capacity, buffering capacity, and clay mineral content. It is believed that the heavy metals got into the soil via adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals into the inner matrix. In such states the metals accumulated in time in the soils through the profiles, contaminated the water, and were taken up by some of the rice varieties. Pollution problem arose when it was observed that the heavy metals mobilized into the soil solution and were taken up by plants or transported to the surface water run-off. Ogbodo [11] had shown that in these heavy-metal-polluted soils, plant growth were inhibited by metal absorption since such contamination would have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange and nutrient absorption) determining the reductions in plant growth, dry matter accumulation. Heavy metals had been widely reported to be potentially toxic for plants; phytotoxicity results in chlorosis, weak plant growth, yield depression, and may even be accompanied by reduced nutrient uptake, [15 - 17]. Studies have also demonstrated that high concentration of heavy metals for example; Cd, Pb and Hg reduce soil fertility and agricultural output [18]. Therefore generally the Soil contamination with heavy metals observed in this study will lead to losses in agricultural yield and hazardous health effects as they enter into the food chain. Although in the present study, only mercury has been implicated to have affected grain quality of the rice; while the effects of the other heavy metals on rice grain quality were minor. This situation however should be noted with caution and monitored from time to time. This is because it was believed that the rice parboiling and polishing processes might have in part reduced the heavy metals contamination of the rice grains to tolerable levels. [19 - 21] had earlier established that heavy metal uptake by crops growing in contaminated soil is a potential hazard to human health because of transmission in the food chain.

V. Counter Measures

There are two promising soil chemistry–based remediation methods that could be employed for minimizing the risk of heavy metal contamination in the soils: (1) water management practices to reduce the bioavailability of soil heavy metals to rice plants. Large volume of irrigation water should be applied periodically to the fields to dilute the concentration of the heavy metals in the soil. This practice holds the promise of flushing the soil, hence channelling away the excess heavy metals through the drainage system and additionally leaching the salts below the root zone. (2) Remediation of the heavy metal contaminated soil by soil washing with solutions of chemicals such as iron salts. Addition of organic matter to the soils can also enhance sorption and reduce risk to soil and water pollution.

VI. Conclusion

The soils of the locations exhibited elevated concentrations of heavy metals, although at varying degrees. There was also no clearly established consistency in the level of concentration of the elements among the locations. The high levels of heavy metals generally detected in the soils were suspected to have occurred as a result of sorption interaction most probably between the soil and agrochemicals and resulting in limited degradation as well as transport in soil. Once in the soil, some of these metals became persistent because of their fairly immobile nature. Because a few metals however were more mobile therefore the potential of transfer either through soil profile, runoff water and plant - root uptake (bio available) occurred leading to bioaccumulation in the grains of some of the rice varieties.

The soils of the Ndiagu location seem to be worst hit by the number and levels of heavy metal contamination.

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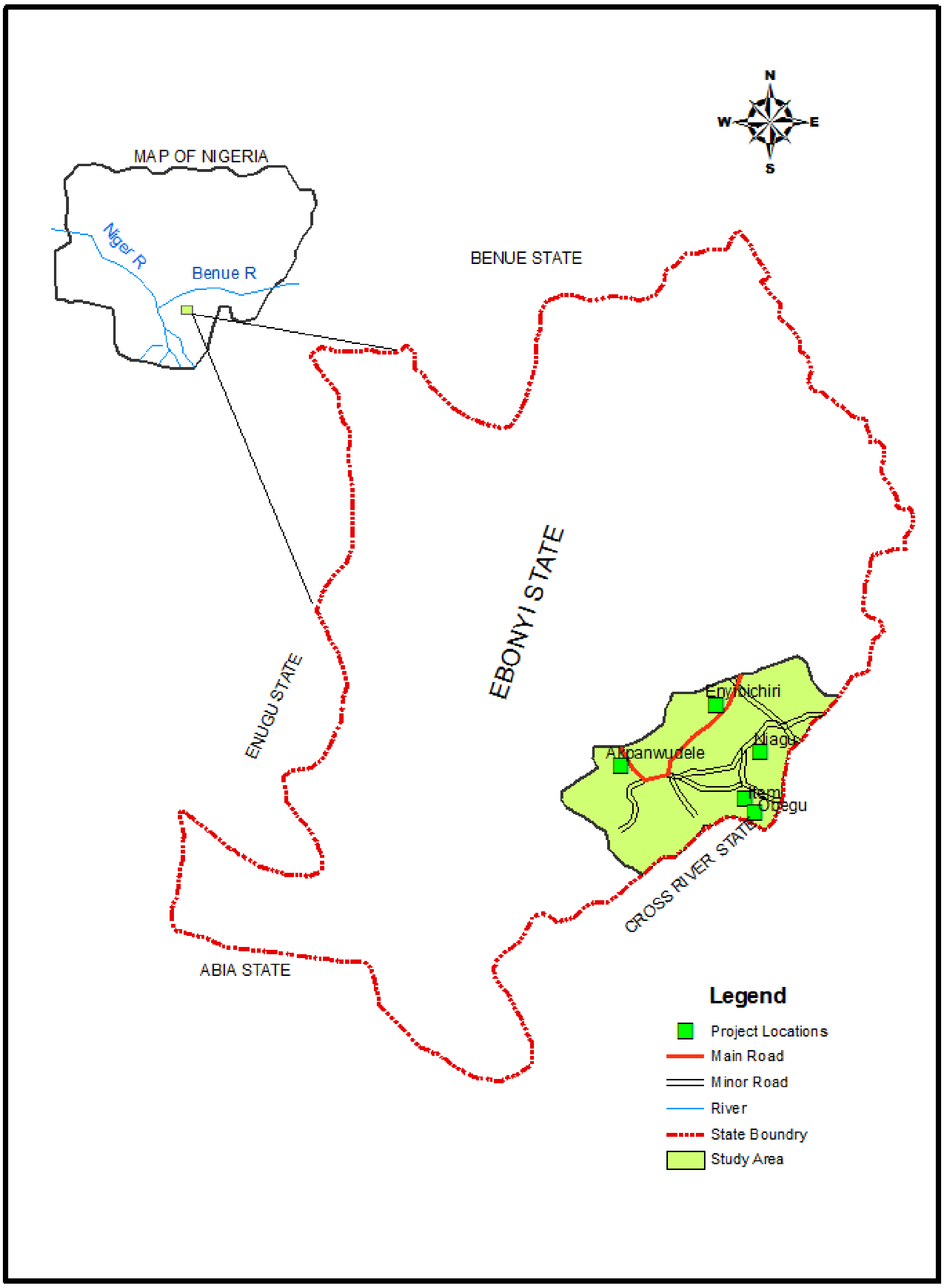

Fig.:1 Enlarged Map of Ebony State Showing the study area/ project locations

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Table 1: Levels of heavy metal in soil

Sampling zone	Hg (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	As (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Cd (mg/kg)	Zn (mg/kg)	Ni (mg/kg)
Item	162.50	625.00	750.00	2125.00	662.50	200.00	175.00	462.50	40.00
Obeagu	180.00	842.00	1000.00	1250.00	1450.00	375.00	137.50	587.50	50.00
Ndiagu	176.62	1126.00	625.00	2750.00	1121.00	225.00	162.00	500.00	25.00
Ekpanwudele	132.52	727.00	1625.00	2100.00	827.00	251.00	160.00	397.00	25.00
Enyibichiri	198.00	253.00	1250.00	1984.00	721.00	212.00	157.50	541.00	55.00
Mean	169.93	714.60	1050.00	2041.80	956.30	252.60	158.40	497.60	39.00
Std. Dev.	24.44	318.90	401.17	534.36	327.59	71.00	13.50	73.01	13.87
Permissible Level	0.01	2.00	0.01	366	0.01	100	100	85	75

Table 2: Levels of heavy metal in run-off water

Sampling zone	Hg (ml/l)	Cu (ml/l)	Pb (ml/l)	As (ml/[)	Cr (ml/l)	Fe (ml/l)	Cd (ml/l)	Zn (ml/l)	Ni (ml/l)
Item	0.002	0.40	0.10	0.10	0.53	0.20	0.12	0.59	1.05
Obeagu	0.008	0.30	0.40	1.60	0.45	0.10	0.20	0.24	0.98
Ndiagu	0.004	0.72	0.50	0.80	0.60	0.80	0.18	0.31	1.11
Ekpanwudele	0.002	0.80	1.60	1.20	0.66	1.00	0.15	0.22	1.15
Enyibichiri	0.003	0.50	2.80	0.70	0.58	1.10	0.13	0.32	1.19
Mean	.004	0.40	0.90	0.88	0.56	0.64	0.16	0.34	1.10
Std. Dev.	0.0025	0.24	1.26	0.56	0.08	0.46	0.033	0.15	0.08
Permissible Level	0.001	0.05	0.01	0.05	0.05	0.03	0.005	0.03	0.05

Table 3: Levels of heavy metal in rice grain

Sampling zone	Hg (mg/g)	Cu (mg/g)	Pb (mg/g)	As (mg/g)	Cr (mg/g)	Fe (mg/g)	Cd (mg/g)	Zn (mg/g)	Ni (mg/g)
IRRI1650	-	0.16	-	-	0.06	2.85	0.15	-	-
IRRI1416	0.01	0.21	0.18	-	0.03	2.21	0.39	0.74	-
MASS	-	0.14	-	-	0.10	0.56	0.11	-	-
FADAMA	0.02	0.19	0.09	-	0.09	1.81	0.32	-	-
FARO52	0.03	0.13	0.03	-	0.08	2.28	0.09	0.78	-
FARO44	0.05	1.16	0.05	-	0.04	1.76	0.15	-	-
Landrace	0.03	0.17	0.03	-	0.07	1.78	0.26	-	-
Mean	0.020	0.31	0.099	0.00	0.067	1.89	0.21	0.22	0.020
Std. Dev.	0.018	0.142	0.018	0.000	0.025	0.74	0.114	0.371	0.000
Permissible level	0.01	2.9	0.19	0.16	1.4	0.70	0.4	19	0.19