RESEARCH ARTICLE

HEAVY METAL SPECIATION AND POTENTIAL IMPACT OF RICE MILLING OPERATION ON METALS CONCENTRATION ON SOILS AROUND KILEMA RICE MILLING INDUSTRY LAFIA, NASARAWA STATE, NIGERIA

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ARTICLE INFO	ABSTRACT
	This study assesses the impact of some heavy metals on soils around the rice milling factory using indices such as geo-accumulation index and contamination factor while metal mobility was assessed using mobility factor. The results reveal that the dominant metal concentration were in the order: Fe > Pb > Co > Ni while Cd and Cr were below detection limit. The potential mobility of the metals within the soil was in the order: Co > Ni > Fe > Pb. The Geo-accumulation index of all the heavy metals determined showed that the test and control soils were strongly contaminated with Pb and its relative potential mobility was 36% and 51% respectively. The mobility of metals was less pronounced in the test soil due to high organic matter content of 5.38% in soil around the milling industry usually generated as waste during rice processing compared to the 0.54% organic matter content in the control soil.

INTRODUCTION

Rice is a vital food material for more than half of the world's population, the importance of which as a food crop has been increasing with increase in population. According to Vanguard News of 12th February 2012; in Nigeria only, five million metric tons of rice, amounting to about 100 million 50kg bags of rice, is consumed yearly in the country and the consumption is projected to reach 35 million tonnes by 2050, from 5 million tonnes, rising at the rate of seven per cent yearly. To make rice ready for consumption after harvest would normally involves several processing steps such as: removal of the husks, milling the shelled rice to remove the bran layer and an additional whitening step to enhance marketability from the sight point of view. This process is said to generate several streams of material which include the husks, the bran and the milled rice kernel (Schramm, 2006). The milling process that helps in removing the hulls and brans from paddy grains to produce polished rice typically comprises of the dehusking, Polishing/Whitening and Blending, Grading and Packaging stages where in between the processes, the use of water to

parboil at an elevated temperature may influence the chemical reactions that occur in the containing vessels as well as its physical state. The material humidification and saturation is said to favor dissolution and diffusion of substances. Material drying determines the migration of water from deep pores toward the material surface and precipitation of dissolved species. Continuous variation in temperature, humidity and carbon dioxide, functional stresses imposed on vessel over time can cause mechanical and chemical changes such as material swelling, cracking corrosion and degradation leaving behind deposit of products that can be hazardous to the environment (Tiruta-Barna and Barna, 2013). The aim of this study is to assess the impact and mobility of some heavy metals on soils around the rice milling factory.

Study Area: Kilema rice milling industry with the geographical coordinates $8^o36'19.2258''$N (latitude) and $8^o42'14.67''$E (longitude), is situated along Doma road in Lafia the capital of Nasarawa State located in the North-Central geopolitical zone of Nigeria. The industry has been on operation for about forty years with about forty machines currently on operation.

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Sample Collection: The stratified sampling technique was applied for soil sample collection (Xie, 2001). Under this sampling technique, the sampling site was broken into four (4) stratums (small areas) north, south, east and west with respect to Kilema rice milling industry, Lafia. Each strata were further subdivided into four quadrants of equal size before five (5) samples were taken randomly by grab method within the depth of 0–15 cm in the individual quadrant (smaller area) making a total of twenty (20) samples per strata (small area) and a total of eighty (80) samples from the four stratums situated at the north, south, east and west of the industry were pooled together to form the composite sample labeled S1 to enable detailed representation of variability within the study area. The control soil sample for the industry was collected in a farmland within 1.2 km radius from the industry from site remote to possible sources of contamination associated with the industry.

Sample preparation: The composite and the control sample were each sorted, pebbles and coarse materials removed and then air-dried at room temperature over three days with occasional breaking of aggregated materials with wooden roller; followed by sieving through a nonmetallic sieve with mesh hole of 2 mm diameter to remove stones, plant and animals debris. The air dried and sieved soil was employed as soil sample for extraction and analysis.

Determination of Soil Physiochemical Parameters: The pH was determine by homogenizing 1g of the sample in 10 cm^3 distilled water and stirred gently to enhance H$^+$ (Hydrogen ions) release from soil, the mixtures was then be allowed to stand for 30 min. pH meter (JENWAY 2000) was used to read the pH value after calibration with buffer solutions of pH values 5.5, 7.0 and 8.0 respectively (Motsara, 2008). Soil organic carbon was determined by means of wet dichromate oxidation by the addition of 50 mL potassium dichromate (0.5 M K$_2$Cr$_2$O$_7$) and 2.5 mL concentrated sulphuric acid in 5 % FeSO$_4$. Considering that the average content of carbon in soil organic matter is equal to 58 % the conversion factor 1.724 was used to calculate the percentage of organic matter from the content of organic carbon (Walkley, 1934; Souza et al., 2016). Nitrogen in the soil was estimated using distillation and titrimetric method describe by Kjeldahl while the phosphorus content usingmolybdate reagent on the spectrophotometer at a wavelength of 660 nm (Motsara, 2008; Bray, 1945). Cation exchange capacity was determine by weighing 5.0 g of the dried soil was extracted with 25mL of 1M NH4OAc solution four consecutive times. The leachate was used for atomic absorption spectrophotometric determination of Ca and Mg while flame photometer was used for the determination of K and Na (Brown, 1988; Ross 2009). While the textural property of the soil was determined using the Hydrometer method (Motsara, 2008).

Sequential Extraction Procedure: The five step sequential extraction procedure described by Tessier, where the chemical partitioning of heavy metals allows distinguishing five fractions representing the following chemical phases: exchangeable metals, bound to carbonates, bound to Fe–Mn oxides, bound to sulphides and organic matter and residual fraction (Tessier, 1979). The procedure was carried out with an initial weight of 1 g of the sieved dry soil sample. Deionized water was used in preparing blank solutions for each step of the leaching procedure.

Fraction 1—Exchangeable fraction (F1): Samples (1 g) of soil were extracted at room temperature for 1 hour with 16 mL of magnesium chloride solution (1 M MgCl$_2$) at pH 7. Soil and extraction solution were thoroughly agitated throughout the extraction. Metals extracted in the exchangeable fraction include weakly adsorbed metals and can be released by ion-exchange process. The extracted metals were then decanted from the residual soil.

Fraction 2—Bound to carbonates (F2): The residue of Fraction 1 was extracted with 16 mL of 1 M sodium acetate/acetic acid buffer at pH 5 for 5 hours at room temperature. The extracted metal solution was decanted from the residual soil. The residual soil was used for the next extraction.

Fraction 3—Bound to oxides (F3): The residue from fraction 2 was extracted under mild reducing conditions. Hydroxyl amine hydrochloride (NH$_2$OH·HCl) (13.9 g) was dissolved in 500 mL of distilled water to prepare 0.4 M NH$_2$OH·HCl. The residue was extracted with 20 mL of 0.4 M NH$_2$OH·HCl in 25% (v/v) acetic acid with agitation at 96°C in a water bath for 6 hours. To release metals bound to Fe (III) and Mn (IV). The extracted metal solution was decanted from the residual soil which was used for the next extraction.

Fraction 4—Bound to organics (F4): To release metals bound to organic matter, the residue from fraction 3 was oxidized as with 3 mL of 0.02 M HNO$_3$ and 5 mL of 30% (v/v) hydrogen peroxide, which has been adjusted to pH 2. The mixture was heated to 85°C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3 mL of 30% hydrogen peroxide, adjusted to pH 2 with HNO$_3$, was then added. The mixture was heated again at 85°C for 3 h with occasional agitation and allowed to cool down. Then 5 mL of 3.2 M ammonium acetate in 20% (v/v) nitric acid was added, followed by dilution to a final volume of 20 mL with de-ionized water. The extracted metal solution was decanted from the residual soil which was used for the next extraction.

Fraction 5—Residual or inert fraction (F5): To extract metals firmly bonded within crystal structure of the minerals comprising the soil, the residue from Fraction 4 was oven dried at 105°C. Digestion was carried out with a mixture of 5 mL conc. HNO$_3$ (HNO$_3$, 70% w/w) and 10 mL of perchloric acid (HClO$_4$, 60% w/w) in a beaker.

Determination of Heavy Metals: The concentration of the heavy metal in the various fractions was determined using Atomic Absorption Spectrophotometer equipped with Zeeman's background correction. Prior to sample analysis, the flame condition was optimized for maximum absorbency and linear response while aspirating known standards.

Impact assessment

The index of geoaccumulation(Igeo): Actually enables the assessment of contamination by comparing the current status and pre-industrial concentrations originally bottom sediments (Muller, 1969; Itodo, 2018); it has also been applied in the assessment of soil contamination. The method assesses the degree of metal pollution in terms of seven enrichment classes (Table 1) based on the increasing numerical values of the index. The index of geoaccumulation was calculated using the Equation (1)

$$Igeo = \log_2(Cn/1.5Bn) \tag{1}$$

where Cn is the measured concentration of the element in soil or sediment and Bn is the geochemical background value.

The constant value, 1.5, is back-ground matrix correction factor due to the lithological variations. Table 1: presents a descriptive classification for theIgeo values (Shaari et al., 2015).

Contamination Factor: The assessment of soil contamination was also carried out using the contamination factor (C_f) The C_f is the single element index while the sum of contamination factors for all elements examined represents the C_d of the environment; the contamination factor was calculated using Equation (2)

$$C_f \equiv \frac{(M)}{(M)_b} \tag{2}$$

Where (M) = Concentration of heavy metal in the studied area; $(M)_b$ = Background concentration levels of metals in soil. Background value of the metal is equal to the world surface rock average given by (Barbalace) (2007). The C_f values between 0.5 and 1.5 indicates that the metals are entirely from the coastal materials whereas C_f values greater than 1.5 indicates that the sources are most likely to be anthropogenic activities (15).The different levels of degree of contamination include: low contamination for C_f value < 1; moderate contamination for $C_f \geq 1$ to < 3; considerable contamination for C_f value ≥ 3 to < 6 and very high contamination for C_f value ≥ 6 as describe by (Rahman et al., 2012).

Mobility Factor (MF): The mobility of metals in soil samples may be evaluated on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a 'mobility factor' (MF) (Salbu *et al.,* 1998; Yusuf, 2007). The MF was calculated using equation; where F1 to F5 are the various geochemical fractions.

RESULTS AND DISCUSSION

As presented in Table 2: the pH, organic carbon and organic matter content of the test and control soils were (7.50 and 8.50), (9.88 and 0.93%) and (5.38 and 0.54%) respectively. The pH values were moderately alkaline and are within the status of agronomical soil. The organic carbon and organic matter content of the test soil were about ten times the content of the control soil which may be due to the continuous disposal of rice husks and other. There was a strong positive correlation between organic matter and organic carbon content of the soil. Soil organic matter is the organic matter component of soil, consisting of plant and animal residues at various stages of decomposition, cells and tissues of soil organisms as well as substances synthesized by soil organisms. It also help in improving the soil structure, enhanced cation exchange capacity and minimize erosion (Itodo et al., 2018). The available phosphorus content, nitrogen and effective cation exchange capacity of the test and control soil samples were (1.411 and 0.077 %), (5.38 and 4.00 mg/kg) and (44.92 and 13.78 Meq/100g) respectively as shown in Table 2: where the nitrogen content of the test soil is about 18 fold the content in the control soil suggesting that rice milling may have enrich the soil. the available phosphorus were generally within the limits of normal agronomical soil stipulated by USDA, the effective cation exchange capacity of the of the test soil is

more three times the capacity of the control soil which is traceable to the high organic matter content and loam nature of soils around the rice milling industry compare to the sandy loam nature of the soil around the control site (Ramos et al., 2018).

Determination of iron concentration: The mean concentrations of iron in the test and control soil were 2547.69±0.41 and3676.44±0.57 mg/kg respectively as presented in Table 3: The values are generally far below the average crustal value (background concentration) 41000 mg/kgof Iron reported by Barbalace, (2007). Likewise the I_{geo} and C_f pollution indices indicate non contamination on soils around both the industry and the control site as describe in Table 1. The mean concentration of iron in the various geochemical fractions F1 to F5 were in the order: F5> F3> F4> F2> F1 for the test soil and F5> F3> F2> F4> F1 for the control soil implying bulk of the iron content are from lithogenic source while the respective motility factors were 38% and 16% as shown in Figure 1 and Table 4 respectively. This implies that the mobility factor of iron in the respective soil is quite low, nevertheless the mobility factor of iron in soil around the industry is twice the mobility in the control soil. The relatively higher concentration of iron in bound to iron organics (F4) in the test soil compare to the control is traceable to metal -organic matter interaction in the organic matter rich soil.

Determination of nickel concentration: The mean concentrations of Ni in the test and control soil were 22.96±0.06 and27.50±0.11 mg/kg respectively as presented in Table 3: These concentrations are generally lower than the 80 mg/kg concentration of Ni in the background as reported by Barbalace, (2007) and as well as the 75 mg/kg maximum limit set by the European union (20, 21). Likewise the I_{geo} and C_f pollution indices indicate un-contamination with respect to Ni on soils around both the industry and the control site as describe in Table 1. The mean concentration of Ni in the various geochemical fractions F1 to F5 were in the order: F5> F3> F4> F1> F2 for the test soil and F5> F3> F2> F1> F4 for the control soil implying the bulk content of Ni content are not due to anthropogenic source while the respective motilityfactor of Ni were 38% and 43% as shown in Figure 2 and Table 4 respectively. This implies that Ni is mobilewithin the respective soil, and there is no statistical difference between the mobility at 95% confidence limit. Also, the relatively higher concentration of Ni in bound to organics fraction (F4) in the test soil compare to the control is traceable to its relatively high organic matter content (Quenea et al., 2009).

Determination of cobalt concentration: The mean concentrations of cobalt in the test and control soil were 50.98±0.02 and51.94±0.084 mg/kg respectively as presented in Table 3: These concentrations are generally higher than the 20 mg/kg concentration of Co in the background as reported by (Barbalace, 2007) as well as the 50 mg/kg maximum limit of Australian standard for soils (Maleki, 2014). Likewise the I_{geo} and C_f pollution indices of (0.77 and 0.79) and (2.549 and 2.597) respectively indicates low contamination though tending towards moderate contamination in soils around both the rice milling industry and the control site respectively as describe in Table 1. The mean concentration of iron in the various geochemical fractions F1 to F5 were in the order: F5> F2> F1> F3> F4 for the test soil and F5> F3> F4> F2> F1 for the control soil while the respective mobility factors were 53% and 54% as shown in Table 3 and Figure 2.

Table 1. Classification of geo-accumulation index

I_{geo}	I_{geo} class	Description of soil quality
0	0	Uncontaminated
0-1	1	Uncontaminated to moderately contaminated
1-2	2	Moderately contaminated
2-3	3	Moderately to strongly contaminated
3-4	4	Strongly contaminated
4-5	5	Strongly to extremely strongly contaminated
5-6	6	Extremely contaminated

Table 2. Physicochemical parameters of soil samples around Kilema rice milling industry

S/no	Parameter	Test soil	Control soil	USDA standard
1	pH	7.50	8.50	6.1-8.5
2	Organic carbon (%)	9.88	0.93	-
3	Organic matter (%)	5.38	0.54	0.4-1.5
4	Nitrogen (%)	1.411	0.077	0.1-0.2
5	Avail P(mg/kg)	5.38	4.00	1.0-10
6	K (Meq/100g)	0.338	0.20	0.2-1.0
7	Na (Meq/100g)	1.04	2.26	0.1-2
8	Ca (Meq/100g)	34.00	8.40	2.0-20
9	Mg (Meq/100g)	6.50	2.92	0.3-8.0
10	AE $(H^+ + Al^{3+})$ (Meq/100g)	0.05	0.05	0.05-2.5
11	ECEC (Meq/100g)	44.92	13.78	-
12	Sand (%)	41	54	-
13	Silt (%)	49	40	-
14	Clay (%)	10	6	-
15	Textural class base on USDA standard	Loam	Sandy Loam	-

**Table 3. Mean concentration (mg/kg) average shale (mg/kg), geo-accumulation index (Igeo)
values and enrichment factor of heavy metals in soils**

	Parameter	Fe	Ni	Co	Pb	Cd	Cr
Test Soil	Mean (mg/kg)	2547.69±0.41	22.96±0.06	50.98±0.02	145.15±0.034	-	-
	average shale (mg/kg)	41000	80	20	14	0.11	90
	Igeo value	0	0	0.77	2.8	<0	<0
	Igeo class	Uncont.	Uncont.	Uncont.	Moderately cont.	Uncont.	Uncont.
	C_f	0.062	0.287	2.549	10.367	<0	<0
	C_f remark	Uncont.	Uncont.	Cont.	Cont.	Uncont.	Uncont.
Control Soil	Mean (mg/kg)	3676.44±0.57	27.50±0.11	51.94±0.084	174.67±0.044	-	-
	average shale (mg/kg)	41000	80	20	14	0.11	90
	Igeo value	0	0	0.79	3.1	<0	<0
	Igeo class	Uncont.	Uncont.	Uncont.	Strongly cont.	Uncont.	Uncont.
	C_f	0.089	0.343	2.597	12.476	<0	<0
	C_f remark	Uncont.	Uncont.	Cont.	Cont.	Uncont.	Uncont.

**Figure 1. Mean Concentration (mg kg^{-1}) of Iron in each
Fraction of the Soil Samples**

**Figure 2. Mean Concentration (mg kg^{-1}) of Nickel in each
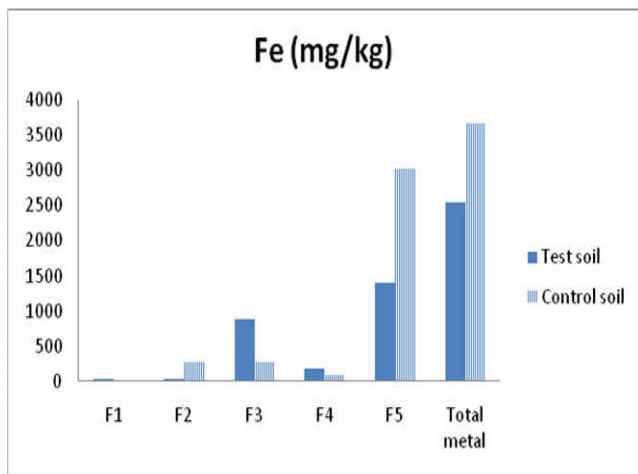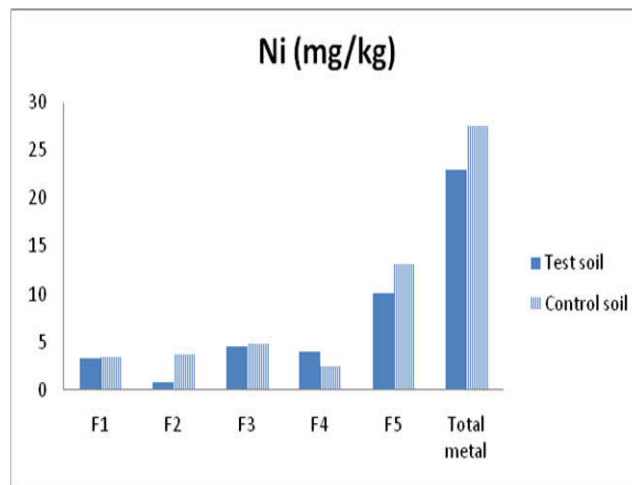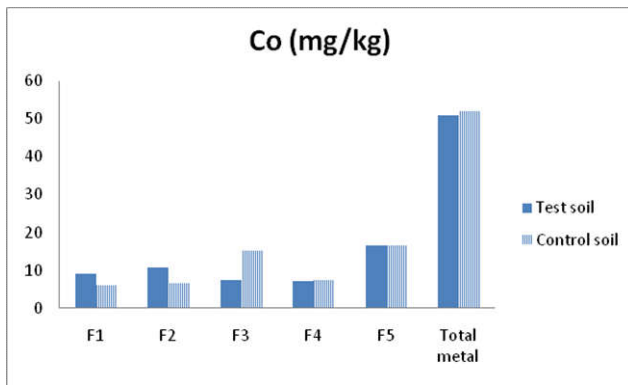Fraction of the Soil Samples**

Figure 3. Mean Concentration (mg kg⁻¹) of Cobalt in each Fraction of the Soil Samples
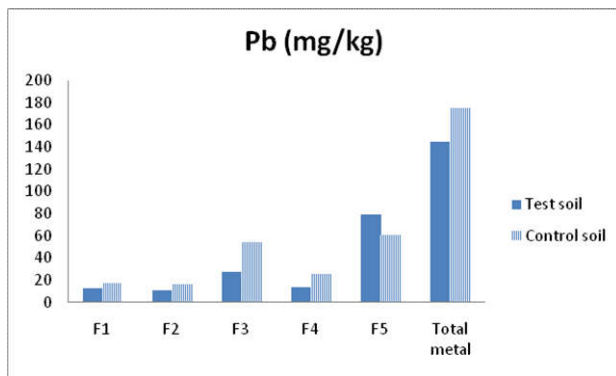

Figure 4. Mean Concentration (mg kg⁻¹) of Lead in each Fraction of the Soil Samples

Table 4. Potential mobility (%) of heavy metals in soils around Kilema rice mill

S/no	Metal	Test soil (%)	Control soil (%)
1	Fe	38	16
2	Ni	38	43
3	Co	53	54
4	Pb	36	51
5	Cd	-	-
6	Cr	-	-

This implies that the mobility factor of Co is generally high in the respective soil, and there is no statistical difference between the mobility at 95% confidence limit. Also, the relatively high concentration of cobalt in the exchangeable fraction (F1) and bound to carbonate fraction (F2) in the test soil compare to the control implies enrichment due to the anthropogenic activities around the industry.

Determination of lead concentration: The mean concentrations of lead in the test and control soil were 145.15±0.034 and174.67±0.044 mg/kg respectively as presented in Table 3: These concentrations are generally much higher than the 14 mg/kg concentration of Pb in the background as reported by (14), (2007) and are also above the 100 mg/kg maximum limit of Australian standard (Maleki et al., 2014) but well below the value 210 mg/kg intervention values by the Department of Petroleum Resources (EGASPIN, 20002; Agbaji, 2015). Likewise the I_{geo} and C_f pollution indices of (2.8 and 3.1) and (10.367 and 12.476) respectively indicates moderately to strongly contamination in soils around both the rice milling industry and the control site respectively as describe in Table 1. The mean concentration of iron in the various geochemical fractions F1 to F5 were in the order: F5> F3> F4> F1> F2 for the test soil and F5> F3> F4> F1> F2 for

the control soil while the respective mobility factor of Pb was 36% and 51% as shown in Figure 2 and Table respectively. The mobility factor of Pb in the test soil is relatively low in respect to the control soil which may likely due to its high organic matter content which is usually associated with retention, decreased mobility and reduced bioavailability of trace metals (Quenea et al., 2009; Sauvé et al., 2009).

Statistical analysis: Statistical analysis reveals that there is significant difference in organic carbon, organic matter, nitrogen and the cation exchange capacity but not in pH and available phosphorus. Likewise the concentration of metals in soils around the rice milling industry are significantly different with the concentration in the control soil ($P<0.05$). Correlation of heavy metals in the test soil reveals a strong positive relationship of 0.866 between Ni and Pb as well as a relationship of 0.756 between Co and Pb ($P<0.05$) implying that they may have emanated from the same source while in the control soil sample, a strong positive relationship of 0.866 was observed between Fe and Pb and Co and Pb ($P<0.05$).

Conclusion

The results evaluating soils around Kilema Rice Milling Industry, Lafia reveals that the dominant metal concentration were in the order: Fe > Pb > Co > Ni while Cd and Cr were below detection limit, the potential mobility of the metals within the soil were in the order: Co > Ni = Fe > Pb. The Geoaccumulation index of all the heavy metals determined showed that the test control soils were strongly contaminated with Pb only with relatively high mobility factor. The mobility of metals was less pronounced in the test soil due to high organic matter content around the milling industry usually generated as waste during rice processing.

Competing Interests: Authors have declared that no competing interests exist.

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