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Edaphology Sorptivity and Bioaccessibility of Chromium in a Tropical Rangeland Soil

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Abstract: The study investigated influence of some soil properties on sorption and bioaccessibility of cationic chromium [Cr (III)] of rangeland soils proximal to military settlement at Obinze, Southeastern Nigeria in 2006. Field sampling was guided by a transect drawn from an open dump site away towards River Otamiri, Owerri, Southeastern Nigeria. Three land units, namely A, B and C from which soil samples were collected and analyzed using routine and special techniques. Soil and plant data were subjected to analysis of variance (ANOVA) of the Mix-model of SAS computer software and multiple regression analysis for purpose of modelling. Results showed that Cr sorption and biaccessibility varied among land units with the entire site having high potentials of bioavailability and biotoxicity. It was also found that clay-content, cation exchange capacity, soil pH and total inorganic carbon are good predictors of Cr (III) bioaccessibility in studied soil.

Key words: Adsorption, biotoxicity, plant uptake, spatio-temporal variability, tropical soils

INTRODUCTION

Soil chromium is a biotoxic heavy metal. It is widespread and accumulates in soils mainly from industrial processes and agricultural activities. Tanning and metallurgical industries use chromium (Cr) on daily basis, suggesting that soils around these industries could be heavily polluted with Cr. Chromium exists into two thermodynamically stable oxidative states, namely Cr (III) and Cr (IV). While Cr (III) is more environmentally stable, Cr (Vi) is very mobile (Patterson *et al.*, 1997). Abundance and mobility of Cr (III) could be decreased by strong adsorption on negatively charged soil surfaces, complexation by organic fractions and formation of oxides and hydroxides (Losi *et al.*, 1994; Dragun, 1998). In kinetic studies of Cr oxidation and reduction in soil by Kozuh *et al.* (2000), net Cr (Vi) production was much greater in high Mn and low organic matter soils. Manganese oxides oxidize Cr (III) to Cr (Vi) (Kim *et al.*, 2002) while iron (Fe) reduced oxidized Cr (Fendorf and Li, 1996). There is substantial evidence that manganese (Mn) abundance and oxidation state correspond to Cr oxidizing capacity in soils (Negra *et al.*, 2005), especially hydroquinone- extractable Mn. The presence of clay in soil particle sizes is of great influence to sorptivity of cationic chromium since clay has negatively charged surfaces (Klein and Hurburt, 1993). Several kinds of crystalline clay minerals such as zeolites, kaolinites and montmorrilonite are used to remove heavy metal cations likechromium (Babel and Opiso, 2007).

Exposure to the pathway of Cr (III) and Cr (VI) is worrisome since Cr is mutagenic and carcinogenic (Shechan *et al.*, 1991; Skowronski *et al.*, 2001). Although Cr (VI) is considered the most

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harmful of the two oxidation states, Cr (III) can also be dangerous since it has the potential of being oxidized to Cr (VI) (Fendorf *et al.*, 1992). Bioaccessibility of soil-bound heavy metals, such as Cr has received less attention (Ruby *et al.*, 1996). Bioaccessibility in soils which is the amount of contaminant that is soluble due to stimulated *in vitro* gastric functions especially the potential to cross the intestinal wall (Hamel *et al.*, 1998) is relatively well studied (Linz and Nakles, 1997) but not in southeastern Nigeria agroecology. Because trivalent cationic chromium can be sequestered by the soil system, we strongly felt that it will in turn influence bioaccessibility of this form of chromium. The aim of this study was to determine sorptivity and bioaccessibility of Cr (III) characteristics of rangeland soils in relation to soil physicogeochemical properties. Specifically, the study identified soil properties related to sorptivity bioaccessibility and used them for modelling purposes.

MATERIALS AND METHODS

Study Area

Obinze is a military settlement and satellite town to Owerri Municipality lying between latitudes $5°10^1 55^{11}$. 510 and $5°25^1 10^{11}.120$ N and longitudes $6°45^1 20^{11}.110$ and $7°00^1 5.^{11}210$ E. but Obinze is a home of nomads who settle proximal to the barracks where they graze their herds in readiness for sale to the southern Nigerian users. As a result of this settlement, surrounding rangelands have lost their original rainforest vegetation, making the current vegetal form more of a derived savanna. A major lithological material from which soils are derived is the Coastal Plain Sands of Oligocene-Miocene geological era. The study area has a lowland geomorphologic setting. Soils of the area were earlier classified as Isohyperthermic Arenic Kandiudult (Onweremadu *et al.*, 2006). It has an average annual rainfall range of about 2400 mm with distinct 3 months of dryness. Temperatures are high and change only slightly during the year (27-29°C). Land is used for military activities, arable crop production, free range grazing, commercial and residential activities. These activities resulted to a ranch, which is 200 m away from the military range.

Field Sampling

Soil and plant sampling were done in 2006. A transect was established from the middle of the open waste dump site, 100 m away from the Obinze Military Cantonement towards the Otamiri River in Owerri West Imo State, Southeastern Nigeria. Military equipment wastes, agroprocessing industrial wastes including waste water, wastes from slaughter houses and domestic wastes from the military cantonement are deposited on this open space. Presence of open dump refuse disposal system is not hygienic as it exudes pungent and irritating odour and with heightened volatilization, air pollutants load increases. In a similar environment proximal to the study site, Okoli *et al.* (2006) reported high concentrations of methane, SO_2, CO and H_2S. The open dump site is about 30 km away from Owerri, Imo State, Southeastern Nigeria and along Port Harcourt expressway. Beginning from the dump site to the last sampled location was a distance of 200 m. A total of 3 sampled points (units), namely A, B and C were used for the study and are described in Table 1.

Target sampling was done perpendicular to the transect and in each of the 3 sampled units, 10 surface (0-20 cm) and 10 subsurface (20-40 cm). Soil samples were collected at a 10 m equidistance, giving a total of 60 soil samples for the scientific investigation. These soil samples were air dried, gently crushed and sieved using 2 mm sieve before laboratory analysis.

Leaves of *Panicum maximum, Calopogonium mucunoides, Axonopus compresses* and *Imperata cylindricl* were used for plant analysis. The leaves were harvested at early rains of 2006 when they were very succulent. Leaves of five stands of each forage type were oven-dried at 80°C for 24 h after washing, crushed and later ground using a mortar. Coning and quartering were used to obtain sub-samples of oven-dried plant materials for analysis. Ground sample were placed in clean glass bottles and oven dried again at a temperature of 65°C for 24 h preparatory to Cr analysis.

Table 1: Description of study site

Location	Distance from barracks (M)	Human influence	Vegetation
A	100	Open dump site	Dominated by grasses (*Panicum maximum*) and legumes (*Calopogonium mucunoides*)
B	150	Bid of dump site	Grasses (*Panicum maximum, Sida acuta, Imperata cylindinca*)
C	200	Ranch	Scanty grass populations (*Panicum maximum, Axonopus compressus, Imperata cylindrica*)

Laboratory Techniques

Particle size distribution was determined by hydrometer method (Gee and Dr, 2002) Soil pH was estimated potentiometrically in 1:2.5 soil/solution (distilled water) and a clear supernatant was measured with a microprocessor ionalyzer /901 (Orion Research, Beverly, M.A) using a combination of glass and Calomel electrode (Beckman, Fullerton, CA). Total Organic Carbon (TOC) and total inorganic carbon were estimated by combustion on a Perkin-Elmer 2400 Series II CHNS/O analyzer. Soil TOC was determined on pretreated samples to remove TIC, involving near-boiling and use of 3 M HCl, extractant method on agitated samples. Soil TIC was got as a difference between total soil carbon (without pre-treatment) and TOC Cation exchange capacity was determined by using the procedure of Darmody *et al.* (2000). Extractable ion (Fe) and Manganese (Mn) were measured using atomic absorption spectrometer (Varian AAS -400, Varian Techtron, Victoria, Australia) according to Mehra and Jackson (1960) and Blume and Schwertmann (1969). For the plant material I g was weighed into 50 mL beakers followed by the addition of 10 mL of 6 M HCl (analytical grade). The beakers containing the samples for different sampled points were covered and heated for 15 min, followed by the additions of 1 M HNO_3. The digestion was performed at 95°C unit about 4 mL was left in the beaker. Then a further 1 mL of 6 M HCl was added, swirled and 10 mL of water added. The beakers with the contents were heated again on the steam bath to complete dissolution. On cooling, the solution was filtered through a Whatman no 541 filter paper into a 50 mL volumetric flask and made to mark with water (Alegria *et al.*, 1991). Mineralization blanks were carried out using the same procedure but without plant materials. Thereafter, concentrations of Cr (III) in the extracts were analyzed using atomic absorption spectrometer (Varian AAS-400, Varian Techtron, Victoria Australia).

Total chromium was obtained using a modification of EPA method 3052. Soil digestion was done with a CEM microwave model MDS-81D in hydrofluoric and HNO_3. In order to facilitate the removal of fluoroboric acid from the solution through the formation of fluorobric acid, boric acid was added before sample analysis. Samples were stored and analyzed for total Cr using inductively coupled plasma.

Addition of Cr contaminant to the soil was also done. Ten-grams soil was placed in a 200 mL glass centrifuge vessel along with 100 mL of 500 mg kg^{-1} Cr (III) as $CrCl_3$ at pH of 4. The resulting slurry was agitated on a reciprocal shaker for 48 h and centrifuged. The supernatant was later decanted for analysis. This was repeated thrice and after the fourth addition of Cr, soils were washed thrice with distilled water to achieve 30% moisture content. Soils were shaded from direct impact of light and maintained at 30% saturated moisture status. These soils were incubated for 100 days.

Determination of Bioaccessibility

A Physiologically Based Extraction Test (PBET) adapted from Ruby *et al.* (1996) was used to determine in vitro bioaccessibility of Cr (III) from contaminated soils in human beings. The PBET method agrees with in vivo studies in lead-contaminated soil (Ruby *et al.*, 1996), arsenic-contaminated soils (Rodriguez *et al.*, 1999) and Cr-bioavailability in contaminated soils has been successfully evaluated using in vivo methods (Gargas *et al.*, 1994). In this study, 0.39 g moist samples measured in triplicates, were placed in 50 mL polyethylene tubes to which 30 mL 0.4 m glycine at pH 1.5 and 37°C was added. The slurries were quickly put in a rotating water bath of 37°C and agitated at 30±2 revolutions per minute for 1 h. Supernatant was separated from the solid via centrifugation. The pH

of the supernatant was estimated to ensure that the final pH was within + 0.5 pH units of the initial pH. This was reported in all cases. Later, bioaccessibility was computed as:

$$Bioaccessibility = \frac{Cr \ in \ PBET \ Supernatant \ (\mu gmL^{-1} \times 30.0 \, mL/0.3 \, g \, soil}{Cr, \ on \ soil \ surface \, (mg \, kg^{-1})} \times \frac{100}{1} \qquad (1)$$

To analyse Cr, in the PBET supernatant, soil spiking solution and equilibrium solution were measured for Cr (VI) and total Cr (Cr -). Chromium (VI) was measured using UV-VIS Spectrophotometer at a wavelength of 540 mm (Hp model 8453, Palo Alto, C.A), according to the modified s-biphenyl carbohydrazide colorimetric method (Bartlett and James, 1979). To avoid possible reduction of Cr (VI) to Cr (III) by glycine, analysis of Cr (VI) was performed immediately on rapidly cooled PBET solution (Jardine *et al.*, 1999). Total Cr_t was got by measurement on a Perkin Elmer AAnalyst 800 atomic absorption spectrophotometer (Wellseley, PA). Standards were made using an atomic absorption Cr standard (EM Industries, Hawthorne, NY). Chromium (III) was computed as a difference between CR_T and CR (VI).

Data Analyses

Soil and plant data were subjected to analysis of variance using PROC Mix-model of SAS (Little *et al.*, 1996). A multiple regression relating Cr (III) sorption and bioaccessibility to common soil properties was performed using PC SAS Version 8.2 (SAS Institute, 2001). Backward-stepwise regression analysis was run to identify crucial soil properties for calculating sorption or bioaccessibility. Multiple linear regression was employed to determine linear equations to use when computing the Cr (III) bioaccessibility.

RESULTS AND DISCUSSION

Soil Properties

Soils were sandy, acidic and of low cation exchange capacity (Table 2). Total Organic Carbon (TOC) values were higher than total inorganic carbon (TIC) and decreased away from the dump site (Table 2). While Fe content increased away from the dump site, Mn showed a contrasting trend (Table 2). Soil properties especially soil texture reflected the nature of parent material (Coastal Plain Sands) while other soil properties were influenced by a combination of parent material, climate and land use. Results were consistent with the findings of Akamigbo (1999) in the same agroecology.

Bioaccessibility of Cr (III) on soil was significantly (p<0.001) influenced by clay content and TIC and as follows:

$$Cr \ (III) \ bioaccessible = 11.6 + (0.517 \times clay) + (12.24 \times TIC) \qquad (2)$$

Where:
TIC = Total Inorganic Carbon

The R^2 value in the above equation was 0.699, implying that 69.9% of the variability in Cr bioaccessibility was explained by this multiple regression model (Table 4). Table 4 also indicated the Variance Inflation Factor (VIF) was approximately 1.00, suggesting that there was no redundant information in other soil properties, thus collinearity does not pose a problem among independent variables.

Table 2: Selected soil properties (mean values) (N = 60)

Location	Depth (cm)	Sand	Silt	Clay	TOC	TIC	Fe	Mn	CEC (cmol kg⁻¹)	pH water
					----- (g kg⁻¹) -----					
A	0-20	820	40	140	1.68	0.91	19.2	0.21	9.6	5.0
	20-40	830	30	140	1.32	0.86	20.6	0.28	9.4	4.9
B	0-20	860	60	80	1.22	0.46	21.3	0.19	9.1	4.8
	20-40	840	50	110	0.10	0.38	25.9	0.26	8.0	4.9
C	0.20	860	80	60	1.14	0.41	28.4	0.14	7.6	5.2
	20-40	850	70	80	0.86	0.39	30.7	0.19	77.0	5.0

TOC = Total Organic Carbon, TIC = Total Inorganic Carbon, Fe = Iron, Mn = Manganese CEC = Cation Exchange Capacity

Table 3: Temporal distribution of Cr (III) in the studied soil (means values) (N = 60)

Location	Depth (cm)	Total Cr (mg kg⁻¹)	1 day Cr (111) bioaccessibility (mg kg⁻¹)	100 days bioaccessibility (mg kg⁻¹)
A	0-20	36.0	5.9	2.9
	20-40	27.9	4.7	2.7
B	0-20	29.0	5.7	2.3
	20-40	22.5	4.5	2.2
C	0-20	18.0	3.6	1.5
	2-40	16.9	2.1	1.4
SED (p = 0.05)		3.8	0.7	0.2
Pr > t		<0.0001	<0.0001	<0.0001

SED = Standard Error of the difference in means

Table 4: Parameter estimates, Standard Errors (SE) and other statistics got from a multiple regression analysis that related total inorganic carbon and clay content to Cr (III) bioaccessibility (N = 60)

Parameters	Value	SE	p	VIF
TIC	17.010	0.98	<0.001	-
Clay	-6.890	1.12	<0.001	1.008
R^2	0.699	-	<0.001	-

TIC = Total Inorganic Carbon, VIF = Variance Inflation Factor

Stepwise multiple regression analysis also showed that TOC and clay content significantly influenced Cr (III) bioaccessibility (Table 5) ($R^2 = 0.711$; p = 0.001)

The equation is given as follows:

$$\text{Cr (III) bioaccessible} = 16.6 + (0.502 \times \text{Clay}) - (4.11 \times \text{TOC}) \qquad (3)$$

Where:
TOC = Total Organic Carbon

Bioaccessibility of Cr and Soil Properties

Table 3 shows the bioaccessibility of Cr for a period of 100 days. Results showed that values of bioaccessibility varied among land units, A, B and C with time. Higher values of bioaccessibility were recorded in I day-aging when compared with 100 day-aging as well as in surface soil layers relative to subsurface soil layers. These results indicate greater sorptivity at 1 day and in surface layers in all land units when compared to 100 day time and in subsurface layers, respectively. However temporal variability in Cr (III) bioaccessibility shows that it is more stable at 100 day period when bioaccessibility levelled off which is attributable to show precipitation reactions of Cr with time (Karthein *et al.*, 1991), suggesting the use of 100 day bioaccessibility for modelling. Variability in bioaccessibility could be due to aggregate binding caused by higher organic fractions at epipedons than in sub-surface layers (Gerke and Hermann, 1992) or competition for the same surface sites (Celi *et al.*, 2003). Results of monitoring process in the oxidation of Cr (III) to Cr (VI) showed that the proportion of bioaccessible Cr that was Cr (VI) was less than 0.8% throughout the investigation, possibly due to

Table 5: Parameter estimates, standard error (SE) and other Statistics obtained from a multiple linear regression analysis that related total organic carbon and clay content to Cr (III) bioaccessibility (N = 60)

Parameters	Value	SE	p	VIF
TOC	- 3.640	0.69	<0.001	1.11
R^2	0.711	-	<0.001	-
Intercept	14.820	1.92	<0.001	-
Clay	0.410	0.08	<0.001	1.11

Table 6: Parameter estimates, standard errors (SE) and other statistics obtained from a multiple regression analysis that related edaphic properties to sorptivity of Cr (III) (N = 60)

Parameter	Value	SE	p	VIF
Intercept	498.2	89.8	<0.001	-
Clay content	96.4	22.6	<0.001	1.121
pH in water	142.3	36.5	<0.001	1.110
CEC	128.1	35.6	0.023	1.618
TIC	321.5	77.8	0.050	1.321
R^2	0.817	-	<0.001	-

CEC = Cation Exchange Capacity, TIC = Total Inorganic Carbon, VIF = Variance Inflation Factor

the fact that Cr (VI) oxidation products were tightly held by the soil exchange sites. It was found that decrease in clay content and increased TOC reduced Cr (III) bioaccessibility. Results were consistent with the findings of Dodor and Oya (2000). Organic fractions of soils create negatively charged sites in the soil which attract and adsorb cations such as Cr (III). This reduced mobility of Cr (III) out of the soil system, but this depends on the presence or absence of other negatively charged surfaces like phosphates. Phosphate out-competes some organic compounds, such as Dissolved Organic Carbon (DOC) which it displaces in sorption sites of mineral soils (Arbestain *et al.*, 2002). By implication, Cr (III) sorbs in phosphates sites where it also precipitates, thereby reducing its lability. But, Cr (III) is Lewis hard and forms stable complexes with carboxyl group of organic matter (Sparks, 1995) which are popularly referred to a ternary complexes (Giesler *et al.*, 2005).

Relationships Between Chromium Sorption and Selected Soil Properties

Adsorption and surface precipitation of Cr differed among land units, with clay content, cation exchange, soil pH and TIC as shown in the multiple linear regression equation below:

$$\text{Cr (III) bioaccessible} = 489.6 + (78.6 \times \text{clay}) + (62.7 \times \text{pH}) + (173.4 \times \text{CEC}) + (677.3 \times \text{TIC}) \quad (4)$$

Where:
Cr (III) = Trivalent cationic chromium
CEC = Cation Exchange Capacity
TIC = Total Inorganic Carbon

There was a strong positive correlation (R^2 = 0.817) between Cr (III) sorption and soil properties (clay content pH, CEC and TIC). About 78% of the variability in Cr (III) sorption was achieved without TIC but it was included in the model since it improved it. Oxides of Fe and Mn as well as TOC, sand and silt did not improve the model hence discarded. Variance inflation factor values are slightly greater that 1.0 (Table 6), suggesting that the independent variables (Clay, pH, CEC and TIC) are reliable predictors and that they do not show multi collinearity. Collinearity becomes a factor when if exceeds 4.0. In addition to the above, the model is normally distributed based on the normality test and the dependent variable Cr (III) was constant after Constant Variance Test. High correlation between Cr (III) sorption and pH was in contrast to the findings of Dodor and Oya (2000) that there was an non-significant relationship between P- sorption and soil pH. The influence of soil pH is easily seen in the solubility characteristics of Cr (III). Cationic Cr is adsorbed on soil negative charges at

Table 7: Distribution of total Cr in selected forage leaves (Mean values) in mg kg^{-1} (N = 15)

Location	Panicum maximum	Calopogonium mucunoides	Axonopus compressus	Imperata cylindrica
A	0.50	0.80	0.40	0.40
B	0.20	0.30	0.50	0.40
C	0.10	0.20	0.40	0.10
SED (p = 0.05)	0.03	0.04	0.030	0.020
Pr > t	<0.0001	<0.0001	<0.0001	<0.0001

SED = Standard error of the difference in means

acidic pH ranges but precipitation of Cr at alkaline ranges. In the same manner, CEC and clay content influenced Cr (III) sorptivity. Because clays are negatively charged (Klein and Hurburk, 1993), they attract Cr^{3+} to form electrostatic bonds and this implies a higher CEC (Okada *et al.*, 2005). The use of crystalline forms of clay to sorb heavy metals in soils such as Cr is of great importance in the remediation of highly polluted soils. It implies that crops growing on clayey soils are less vulnerable to biotoxicity of Cr due to its strong adsorption onto negatively charged soil surfaces (Babel and Opiso, 2007).

Forage Uptake

Uptake of Cr by selected forages is shown in Table 7. In all, there were significant (p<0.0001) differences in the distribution of Cr in forages in the study site. Total Cr in studied soils (Table 3) were above critical limits of 16 mg kg^{-1} (Chen, 2000), suggesting, the soils of the study site have great potentials of bioavailability and biotoxicity. But bioaccessibility values were low (1 day) and very low (100 day) as in Table 3. However, plant content of Cr (Table 7) indicated that they were above permissible limit of 0.16 mg kg^{-1} as recommended by Lin (1991) for vegetable crops. The fear is that livestock may browse on these forage plants and this gets to humans through the food chain. Nonetheless, bioavailability and uptake of Cr depend on crop type and crop age (Wang and Liao, 1999).To ensure biosafety, the use of vermicompost(Carrasqueros *et al.*, 2006), coconut shell and seed hull of palm tree (Gueu *et al.*, 2006) could be viable options for such vulnerable soils as photocatalytic process is expensive (Desrosiers *et al.*, 2006) for the study site,s ituated in a developing country. It becomes necessary to study vulnerable crops and the phenological stages when biotoxicity of Cr is lethal.

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