Research Journal of Environmental Sciences

ISSN 1819-3412

Academic
Journals Inc.

www.academicjournals.com

Research Journal of Environmental Sciences 1 (3): 116-121, 2007
ISSN 1819-3412

Boron Distribution and Relationship with Selected Soil Properties in an Oil-Polluted Arenic Paleudult

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Abstract: This study investigated the distribution of soil boron and its relationship with some soil properties in a sandy Paleudult polluted by crude oil in southeastern Nigeria. Three pedons representing 3 land units influenced by crude oil spillage were dug, sampled and soil samples were used for various laboratory analyses. Results showed high values of organic carbon and cation exchange capacity in spilled sites. Iron and aluminium oxides were higher in non-spilled sites and generally increased with depth. Highest values of B (0.09-146 mmol kg^{-1}) were found in spilled land unit while soil B ranged from 0.01-0.03 mmol kg^{-1} in non-spilled land unit. Soil B varied widely in spilled land units but little variation was observed in non-spilled site. Higher values of correlation coefficients were recorded in non-spilled land unit than spilled site. Best predictions was found when soil pH, surface area of clay, clay content and organic carbon predictors were combined linearly.

Key words: Biotoxicity, degradation, oil exploration, prediction, ultisol

INTRODUCTION

Boron (B) is both an essential micronutrient required for optimum crop performance and a toxicant at elevated concentration. It is an element of great concern because for many plants the ratio of toxic to adequate B concentrations is smallest among the essential micronutrients (Su and Suarez, 2004). The range between B deficiency and toxicity is narrow, typically 0.028 to 0.093 mmol L^{-1} for sensitive crops and 0.37 to 1.39 mmol L^{-1} for tolerant crops (Keren and Bingham, 1985). The narrow range between deficiency and toxicity necessitates monitoring and accurate quantification of soil B concentrations, which are controlled by B adsorption-adsorption reactions on soil minerals. This is because soil mineral and organic surfaces constitute sinks that adsorb B and the source that release B to the soil solution for plant uptake (Goldberg *et al*., 2004). Apart from mineral and organic surfaces, increased membrane permeability in zinc-deficient plants might lead to enhanced B uptake by such plants (Marschner, 1995).

Crude oil spillage and consequent entry into the soil system alter the physico-chemical properties of soils. Osuji and Onojake (2004) reported that soil soaked with crude oil instantly loses fertility and initiates environmental degradation. Changes in soil pH influence the solubility of and relative abundance of micronutrients (Brady and Weil, 1999).

Although, some studies on the impact of crude oil spillage on soils and soil-related natural resources within the Niger Delta area have been conducted and reported (Odu, 1996; Osuji and Onojake, 2004; Aiyesanmi, 2005; Onweremadu *et al*., 2005), little work has been done on its influence on individual micronutrients, such as boron. Our objectives in this study were to: (i) investigate the distribution of boron in crude oil polluted site of Oguta in southeastern Nigeria (ii) relate boron distribution to some soil properties in the area.

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MATERIALS AND METHODS

Study Area

The study was conducted in a rainforest agroecology at the environs of Addax Petroleum Oil Company Ltd., Oguta, southeastern Nigeria. It is located on latitude 5°53^{1}16^{11}. North and 7°20^{1} 32^{11}. 400 East with an elevation of 50 m above sea level (Handheld Global Positioning System Receiver). It has a total annual rainfall of about 2500 mm and 26-29°C annual temperature range. Soils belong to Amakama-Orji-Oguta Soil Association (Federal Department of Agricultural Land Resources, 1985) and area derived from lacustrine alluvium (Lekwa and Whiteside, 1986). Soils were classified as Arenic Paleudult (Onweremadu, 2006). Crude oil spilled in study sites 7 months before this study in an area where farming is a major socio-economic activity.

Field Sampling

Three soil morphological units, namely severely spilled (origin of spillage), moderately spilled and non-spilled site. A transect was drawn to link the three identified morphological land units. Three pedons representing the 3 land units were dug along the transect at an inter-pedon distance of 100 m. The area of spillage is almost flat (0-1% slope). Soil sampling was done starting from the bottommost horizon upwards and 3 soil samples were collected per horizon, giving a total of 45 soil samples for the study. The soil samples were air-dried, crushed and sieved using 2 mm sieve.

Laboratory Analysis

Particle size distribution was determined by hydrometer method (Gee and Or, 2002). Cation exchange capacity was obtained using the procedure described by Rhoades (1982). Surface area of soil clay was measured using ethylene glycol monoethyl ether (EGME) adsorption described by Cihacek and Bremner (1979).

Free Fe and Al oxides were extracted using the method of Coffin (1963): Soil samples were reacted in a water bath at 50° with a 0.15 m sodium citrate 0.05 m citric acid buffer and 0.5 g of sodium hydrosulphite for 30 min. Aluminium and iron concentrations in the extracts were determined by Inductively Coupled Plasma (ICP) emission spectrometry. Organic carbon (OC) and inorganic carbon (IOC) contents were determined using a UIC full Carbon System 150 with a C coulometer (UIC, Inc, Joliet IL). Organic C was obtained directly by furnace combustion at 375°C while IOC was estimated using acidification module and heating.

Boron adsorption experiments were performed in batch systems to determine amount of B adsorbed as a function of equilibrium solution B concentration. Five grams of soil samples were mixed with 25 mL of equilibrating solutions for 20 h on a reciprocating shaker (160 strokes per min). Reaction temperature was 24.4±0.1°C. The equilibrating solutions contained 0, 0.0925, 0.185, 0.463, 0.925, 1.39, 2.31, 4.63, 9.25, 13.9, 18.5 and 23.1 mmol B L^{-1} from H_3BO_3 and a background electrocyte of 0.1 M NaCl. On completion of mixing time, the samples were centrifuged for 20 min at a relative centrifugal force of 7800 x g at 25°C. The liquid decanted was analyzed for pH, filtered through 0.45 μm membrane filters and analyzed for B concentrations using ICP emission spectrometry.

Statistical Analysis

Variability among horizons in the distribution of boron was calculated using coefficient of variation (Gomez and Gomez, 1984) and ranked according to the procedure of Aweto (1982). Data were also subjected to correlation and regression analyses. Highly correlated variables were used to establish pedotransfer functions.

RESULTS AND DISCUSSION

Soil Properties

Mean values of soil properties in the study site are shown in Table 1. Generally, surface area (M^2 g^{-1}) increased with depth in all the land units and this trend was followed by the vertical distribution of clay. Soil pH values were higher in non-spilled land unit but formed a bulge intra-pedally in all land units. Higher values of CEC and organic carbon were observed in severely spilled land units and this decreased geospatially towards non-spilled unit of the study site. Similar findings were reported by Akamigbo and Jidere (2002) in their investigation of soil polluted wetland soils of Anambra, southeastern Nigeria. However, these high values were more surficial in all the land units and could be attributed to crude oil spillage especially in severely and moderately spilled land units.

Iron and aluminium oxides increased with depth in all the pedons, indicating pronounced eluviation-illuviation processes. Generally, eluviation depleted Fe and Al concentrations in the topmost horizons. However, the concentration of Fe in deeper horizons (Bt-horizons) implied migration of silica out such pedogenic horizons. The dispersion of Fe and its possible progressive oxidation could be responsible for the reddish brown (rubifaction) and red (ferrugination) colours of deeper horizons. Earlier, Esu (2005) reported the predominance of hematite mineralogy and identified eluviations, illuviation, leaching, plinthization and humification of clay and Fe-oxyhydroxides in soils of the study area. Highest values of Fe and Al were recorded in non-spilled land units, suggesting that crude oil spillage may have influenced the pedogenesis of these trivalent cations.

Distribution of Boron

Table 2 shows B distribution and variability in the study site. Boron distribution decreased vertically in soils and varied spatially among land units, decreasing towards non-spilled land units. Computed coefficient of variation values showed moderate variation in crude oil-spilled land units and variability decreased with depth. On the non-spilled land units, little variation in B-distribution occurred. Highest values of B were observed among surficial horizons in all pedons. This could be the result of higher accumulation of organic carbon in the affected horizons. This is consistent with the findings of Foth (1984) that B occurs as borate iron and accumulates in soil organic matter from where it is released for subsequent uptake by plants.

Table 1: Soil properties in the study site (mean values)

Horizon	Depth (cm)	SA (m^2 g^{-1})	Total sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})	pH	CEC (mmol kg^{-1})	OC (g kg^{-1})	IOC (g kg^{-1})	Fe (g kg^{-1})	Al (g kg^{-1})
Severely spilled unit											
Ap	0-12	22	865	40	95	4.2	166	36	2.600	12.2	1.2
AB	12-28	20	900	15	85	4.1	96	18	0.002	13.9	4.6
Bt$_1$	28-75	65	840	20	140	4.3	92	12	0.002	29.6	4.1
Bt$_2$	75-145	62	820	20	160	4.4	96	9	0.001	26.6	2.0
Bt$_3$	145-190	66	900	14	186	4.1	78	6	0.001	20.6	1.6
Moderately spilled unit											
Ap	0-9	28	890	28	82	4.1	120	30	2.300	15.1	0.9
AB	9-32	20	900	30	70	3.9	88	14	0.002	18.6	5.6
Bt$_1$	32-80	68	830	40	130	4.3	96	12	0.001	20.2	2.3
Bt$_2$	80-148	68	815	40	145	4.5	98	10	0.001	26.2	1.6
BC	148-200	78	900	22	78	4.0	76	4	0.001	24.2	1.9
Non spilled unit											
Ap	0-10	26	900	10	90	4.5	142	22	1.900	19.1	1.2
E	10-23	20	910	20	70	4.4	90	18	0.003	13.6	5.3
Bt$_1$	23-90	68	830	30	140	4.9	110	12	0.002	30.6	5.6
Bt$_2$	90-140	98	800	30	170	5.2	170	9	0.001	38.2	2.8
BC	140-195	62	894	10	76	4.6	90	6	0.001	30.3	1.6

SA = Surface Area; IOC = Inorganic Carbon; OC = Organic Carbon; CEC = Cation Exchange Capacity

Boron-toxicity is very likely for both B-sensitive and B-tolerant crops in the crude oil-spilled units while B-deficiency is imminent in non-spilled unit. A study conducted by Isirimah *et al.* (2003) showed low B-content of highly weathered soils of the site. They reported that B released to soil solution during weathering interacts primarily with Fe and Al hydroxides, with adsorption maxima at pH 7 to 9. But these soils are below pH 7, suggesting possible B-deficiency in non-spilled sites in the region.

Relation Between Soil Boron and Soil Properties

There existed relative variabilities in the relationship between soil B and selected soil properties (Table 3) in the three land units. Higher correlation coefficients at 1 and 5% levels of significance were obtained as effect of crude oil spillage decreased. Soil pH was negatively but significantly correlated

Table 2: Distribution and variability of boron in the study area (n = 45)

Land unit	Origin	Horizon	Depth (cm)	B (mmol kg^{-1})	CV (%)	Ranking
Severely spilled	Pedon	A	0-12	1.46	38.0	MV
		AB	12-28	0.96	25.0	MV
		Bt_1	28-75	0.26	22.0	MV
		Bt_2	75-145	0.22	18.0	LV
		Bt_3	145-190	0.12	19.0	LV
Moderately spilled	Pedon	Ap	0-9	1.34	34.0	MV
		AB	9-32	0.66	36.0	MV
		Bt_1	32-80	0.18	26.0	MV
		Bt_2	80-148	0.13	23.0	MV
		BC	148-200	0.09	16.0	LV
Non spilled	Pedon	Ap	0-10	0.03	11.0	LV
		E	10-23	0.01	6.0	LV
		Bt_1	23-90	0.02	5.0	LV
		Bt_2	90-140	0.01	6.0	LV
		BC	140-195	0.01	4.0	LV

CV = Coefficient of Variation; MV = Moderate Variation; LV = Little Variation; *Classification is based on Aweto (1982)

Table 3: Correlation coefficients (r) for linear relationships between soil boron and some properties (n = 15)

Soil property	R	Level of significance
Severely spilled land unit		
Soil pH	-0.8	*
Organic carbon (g kg^{-1})	0.6	*
CEC (cmol kg^{-1})	0.4	NS
Fe (g kg^{-1})	0.2	NS
Al (g kg^{-1})	0.5	*
Clay (g kg^{-1})	0.7	*
SA (m^2 g^{-1})	0.8	*
Moderately spilled land unit		
Soil pH	-0.6	*
Organic carbon (g kg^{-1})	0.7	*
CEC (cmol kg^{-1})	0.5	*
Fe (g kg^{-1})	0.4	*
Al (g kg^{-1})	0.7	*
Clay (g kg^{-1})	0.8	**
SA (m^{2}g^{-1})	0.9	**
Non-spilled land unit		
Soil pH	-0.5	*
Organic carbon (g kg^{-1})	0.8	**
CEC (cmol kg^{-1})	0.6	*
Fe (g kg^{-1})	0.6	**
Al (g kg^{-1})	0.9	**
Clay (g kg^{-1})	0.8	**
SA (m^{2}g^{-1})	0.9	**

CEC = Cation Exchange Capacity; Fe = Iron; Al = Aluminium; SA = Aurface Area; **Significant at ≤0.01; *Significant at p≤0.05; NS = Not Significant

Table 4: Pedotransfer functions relating boron distribution with selected soil properties (n = 15)

Predictors	Regression equation	R^2
Severely spilled land unit		
Soil pH, SA, Clay, OC	B = 85.3-2.5 pH+1.81 SA+3.3 clay+2.8. OC	0.6
Soil pH, SA, CEC, Al	B = 28.2-1.8 pH+2.3 SA+0.8 CEC+5.4 Al	0.4
SA, Fe, Al	B = 43.8+2.6 SA+0.2 Fe+5.5 Al	0
Moderate spilled land unit		
Soil pH, SA, Clay, OC	B = 72.0-1.9 pH+0.92 SA+2.5 clay+1.1 OC	0.7
Soil pH, SA, CEC, Al	B = 35.0-2.5 pH+1.9 SA+0.9 CEC+2.2 Al	0.6
SA, Fe, Al	B = 25.0+1.3 SA+0.9 Fe+1.5 Al	0.7
Non-spilled land unit		
Soil pH, SA, Clay, OC	B = 92.4-0.5 pH+1.3 SA+0.8clay+0.4OC	0.9
Soil pH, SA, CEC, Al	B = 21.3-0.2 pH+0.9 SA+1.1CEC+0.3Al	0.6
SA, Fe, Al	B = 35.2+0.4 SA+1.2 Fe+0.7Al	0.8

SA = Surface Area, OC = Organic Carbon

with soil B ($p = 0.05$). As in pH was increasing in the non-spilled land unit, soil B content decreased, suggesting high soil B availability at lower pH values. High significant positive correlation coefficients between soil B and some soil properties such as clay content, surface area, Fe and Al implied that soil B increased as their values increased. These findings are consistent with the findings of Su and Suarez (2004).

The most highly correlated soil properties were used as independent variables (predictors) and regressed with soil B content and results are presented in Table 4. A pedotransfer analysis was conducted on the predictability of soil boron distribution and content using some predictors that correlated significantly at 1 and 5% levels of significance and results are shown in Table 4. It was observed that predictors were more efficient in non-spilled land units when compared with results from severely and moderately spilled and units, suggesting crude oil spillage on soils influence the predictability of soil B given the studied soil properties.

A combination of soil pH, surface area of soil clay content and organic carbon gave the highest prediction of soil boron distribution ($R^2 = 0.9$) while surface area of soil clay Fe and Al oxides associated highly with soil B ($R^2 = 0.8$). However, more detailed and intensive sampling, may be necessary for improved prediction certainty and results could be tested using Root Mean Square Error and bias statistics.

CONCLUSIONS

Crude oil spillage influenced the distribution of soil properties which varied with depth and this influenced the distribution of soil boron in the study site. Soil boron distribution varied widely in the crude oil spilled land units unlike it did in the non-spilled land units. Higher values of correlation coefficients were recorded in non-spilled land unit using the available data. Soil pH, surface area of clay, amount of soil clay and organic carbon gave the highest prediction of soil B-distribution on studied soils.

ACKNOWLEDGMENTS

We are grateful to laboratory and technical staff of the Department of Soil Science, University of Nigeria, Nsukka.

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