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Distribution of Mercury in a Polluted Toposequence

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Abstract: The effects of automobile and municipal solid wastes on soil mercury (Hg) distribution were studied in soils of a toposequence at Nekede, Southeastern Nigeria in 2005. Three pedons representing 3 physiographic units of the site namely Upper Slope (US), Lower Slope (LS) and Foot Slope (FS) were aligned and dug along a transect. Results show that heaviest concentrations of Hg were reported in epipedal and subsurface horizons in LS land unit. Highest values of Hg concentration was found in the surface layers in all land units. Minimal Hg concentrations were recorded in the FS soil classified as Fluvaquentic Eutropept (Eutric Fluvisol). Soil organic carbon, CEC, pH and texture had significant correlations with Hg using the available data hence reliable predictors of Hg distribution and availability. There is need to evaluate uptake of Hg by common crops of the study area since epipedal contents were above critical limits.

Key words: Heavy metals, soil pollution, mercury, physiography, tropical soils

INTRODUCTION

Heavy metal inputs to the soil include those from commercial fertilizers, liming materials, sewage sludges, atmospheric depositions (Sensesi *et al.*, 1999) and repeated applications of organic manures, fungicides and pesticides (Li *et al.*, 1997; Moore *et al.*, 1998; Hans *et al.*, 2000). Nonetheless, these heavy metals are naturally occurring (Ojanuga *et al.*, 1996) and possibly from weathering of rocks but their concentrations in the pedosphere increase due to anthropogenic inputs (He *et al.*, 2004).

One great source of these heavy metals in Southestern Nigeria is motor vehicle servicing centres popularly called mechanic villages. In urban and peri-urban towns of this sub-region, automobile wastes are disposed unhygienically, leading to excess accumulation of heavy metals, such as cadmium chromium, nickel, lead and mercury (Onweremadu *et al.*, 2007). A major activity of these automobile service stations is deforestation and encroachment into nearby farms, rivers and other natural resources which often lead to soil erosion and alteration of mercury (Hg) levels (Fostier *et al.*, 2000). Again, in these automobile stations vegetal debris resulting from deforestation are burnt as a diffuse source (Roulet *et al.*, 1999). All these influence the accumulation and distribution of Hg especially in the study site with a steep to undulating river slope. Soil Hg, accumulation may be short-term or long (Brabo *et al.*, 2003) but essentially enhances the transport and leaching of neurotoxic heavy metals, such as mercury (Farella *et al.*, 2001) to soil and water resources.

At the foot slope of the toposequence, dry season vegetable farming takes, involving fluted pumpkin (*Telfairia occidentalis*), Amaranth (*Amaranthus cruentus* L.) and several species belonging to the Solanaceae. At the upper and middle slopes of the toposequence, rainfed arable farming is practiced. It is feared that Hg may be absorbed by these crops which are readily consumed by the teeming urban population. Again, fish farming is common in the study area and there is high tendency of Hg accumulation. In similar riparian communities, mercury contamination of fish has been reported (Sampaio da Silva *et al.*, 2005) and such Hg exposure is dangerous to human life (Brabo *et al.*, 2000) when concentrations exceed maximum soild dump sites and deforestation permissible limits. Based on

the above, this study investigates the distribution of Hg in soils receiving automobile wastes at toposequence in Owerri Southeastern Nigeria. It is hypothesized that these automobile depositions, solid wastes and deforestation increase soil Hg content and distribution in the ecosystem.

MATERIALS AND METHODS

Study Site

Nekede is a town within Otamiri watershed in southeastern Nigeria and lies between latitudes 5°10¹ 55.510¹¹¹ and 5° 25¹10120¹¹N and longitudes 6°45¹25.110¹¹¹ and 7° 05¹ 06.210¹¹ E. The northeastern part of the town juts into Owerri municipality, Southeastern Nigeria. Proximity to Owerri Urban has led to the urbanization. This part of Nekede despite its fragile and rugged physiographing. A large expanse of the site is occupied by automobile servicing enterprises, who discharge wastes on adjoining farms and wetlands. The major geological material in the study area is coastal plain sands (Benin formation) of the Oligocene-miocene era. It is a humid tropical environment, with an average annual rainfall of about 2500 mm and temperatures are high, changing only slightly during the year (27-29°C). The vegetation is highly altered by anthropogenic activities, such as farming, fishing sand mining, deforestation for fuel wood and establishment of automobile service stations. Varying forms of agriculture are practiced in response to sloping terrain that finally juts into the Otamiri River. Generally slash and burn system of clearing farms is practiced and soil fertility regeneration is still by bush fallowing. Rainfed agriculture is common but during dry seasons (3 months), farmers move towards the foot slope proximal to the river to for dry season vegetable production.

Field Sampling

A transect was established from soils nearest to the automobile service station 50 m away from the centre towards the Otamiri River in Imo State, Southeastern Nigeria. From the origin of the transect to the foot slope of the topography is about 1500 m. Three profile pits were dug along the transect, representing 3 identified physiographic units, namely Upper Slope (US) Lower Slope (LS) and Foot Slope (FS). Soil profile pits were described according to FAO (1998) procedure. Soil samples were collected based on morphologically identifiable pedogenic horizons. In each profile pit, 5 soil samples were obtained, giving a total of 15 soil samples for the investigation. These soil samples were air-dried and sieved using 2 mm sieve preparatory to laboratory determinations. Three core samples were collected in each horizon, giving a total of 45 core samples for bulk density analysis (Table 1).

Laboratory Analyses

Bulk density was measured by core method of Grossman and Reinsch (2002) while particle size distribution was determined by hydrometer method (Gee and Or, 2002). After equilibrating for 30 min, soil pH was estimated in water, with a soil-liquid ratio of 1:2.5, using a Beckman Zeromatic pH meter (Hendershot *et al.*, 1993). Soil Organic Carbon (SOC) was determined by combustion at 840°C (Wang and Anderson, 1998). Total Nitrogen (TN) was estimated by microkjeldahl method (Bremner, 1996). Cation Exchange Capacity (CEC) was determined by ammonium acetate leaching at pH 7.0 (Blakemore *et al.*, 1987).

Table	1:	Site	characteristics

Sampling point	Physiography	Description
50 m away from automobile	Upper Slope (US)	Nearest to automobile service station,
Service station	(10% slope)	Automobile wastes, highly deforested. Few shrubs are found growing.
500 m away from the automobile	Lower Slope (LS)	Open dump site for disposal of municipal solid
Service station.	(4-6% slope)	wastes, few grasses are growing.
1000 m away from the automobile	Foot Slope (FS)	Extension of the dump site. Tall luxuriant grassy
Service station	(1-2% slope)	weeds mainly hydropphytes.

Total mercury (Hg) levels were measured with the Cold Vapour Atomic Fluorescence (CVAF) technique as described by Pichet *et al.* (1999). In this method, 250 mg of sieved soil was digested in a 10:1 nitric and hydrochloric acid mixture and heated before injection into spectrophotometer.

Classification

Soils were classified using USDA Soil Taxonomy (Soil Survey Staff, 2003) and FAO/UNESCO legend (FAO, 1998).

Data Analyses

Analytical data were subjected to correlation and regression analysis using SAS computer programme (SAS Institute, 2001).

RESULTS

Soil Properties

Soils are deep and sandy, with US and LS being sandier (Table 2). Values of bulk density in LS were higher than the rest of other physiographic units (Table 2). Argillation is most prominent in US and least developed in FS soils. Soils are strongly (LS soil) to moderately acidic (US and FS Soil). Soil organic fractions (SOC and TN) decreased with depth in all pedons except in FS where this consistency was broken with Bg₂ having 16.0 and 1.3 g kg⁻¹ of SOC and TN, respectively when compared with 10.0 and 1.0 g kg⁻¹ values of SOC and TN, respectively in Bg₁. Higher values of SOC were obtained downslope. Cation exchange capacity values were generally low (CEC < 6.9 cmol kg⁻¹) and this agrees with the findings of Igwe (2001) in his study of a Nigerian floodplain in Southeastern Nigeria. Heavy concentrations of Hg were recorded the surficial horizons in all pedons of the study site (Table 3). Heaviest concentrations were found in LS soil (0.26-1.88 mg kg⁻¹).

Soil Mercury and Soil Properties

Highly significant negative correlations (p = 0.01, n = 15) were established when Hg was related with SOC and sand while clay content had a significant positive relationship with soil Hg (r = 0.758; p = 0.05, n = 15) (Table 4). There was strong correlation between Hg and CEC in soils of the study site (r = -0.834; p = 0.05 n = 15) as well as between Hg and pH (r = 0.826; p = 0.01' n = 15). However, there was no significant relationship between Hg and BD.

	Depth	Sand	Silt	Clay	Bulk density
Physiography	(cm)	(g kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)	$(mg m^{-3})$
Upper Slope (US)					
A	0-12	800	80	120	1.48
AB	12-25	740	60	200	1.51
Bt_1	25-90	640	60	300	1.52
Bt_2	90-140	620	60	320	1.56
Bt_3	140-190	760	40	200	1.58
Lower Slope (LS)					
A	0-15	820	40	140	1.51
Bg_1	15-95	760	60	180	1.56
Bg_2	26-95	780	40	180	1.57
Bg_3	95-130	800	40	160	1.57
Bg_4	13-180	920	20	60	1.57
Foot Slope (FS)					
A	0-20	620	200	180	1.50
Bg_1	20-48	600	160	240	1.50
Bg_2	48-90	600	160	240	1.48
Bg_3	90-142	660	140	200	1.51
Bg_4	142-195	660	100	240	1.55

Table 3: Chemical properties of studied soils

Horizon	Depth (cm)	pH (H ₂ O)	CEC (cmol kg ⁻¹)	SOC (g kg ⁻¹)	TN (g kg ⁻¹)	Hg (mg kg ⁻¹)
Upper slope	e					
A	0-12	5.2	3.0	18	1.6	1.88
AB	12-25	5.0	3.5	9	0.7	1.11
Bt_1	25-90	4.7	6.5	7	0.6	0.69
Bt_2	90-140	5.1	6.9	4	0.4	0.63
Bt_3	140-190	5.0	3.9	2	0.2	0.22
Lower slop	e					
A	0-15	4.3	2.9	25	2.3	1.88
Bg1	15-26	4.5	3.0	20	1.2	1.32
Bg2	26-95	4.8	3.1	10	0.9	0.92
Bg3	95-130	4.8	3.8	5	0.2	0.82
Bg4	130-180	4.8	3.6	3	0.2	0.26
Footslope						
A	0-20	5.6	3.1	20	1.8	1.36
Bg_1	20-48	5.4	3.8	10	1.0	1.34
Bg_2	48-90	5.6	4.1	16	1.3	0.38
Bg_3	90-142	5.8	3.9	5	0.2	0.62
Bg_4	142-195	6.0	4.2	3	0.1	0.03

CEC = Cation Exchange Capacity, SOC = Soil Organic Carbon, TN = Total Nitrogen, Hg = Mercury

Table 4: Relationship between soil Hg and selected soil properties (n = 15)

Soil property	R	\mathbb{R}^2	Level of significance
SOC	-0.926	0.857	aje aje
CEC	-0.834	0.695	*
Clay	0.758	0.574	ope sole
Sand	-0.633	0.400	**
BD	0.181	0.033	NS
pH	0.826	0.682	ote ate

SOC = Soil Organic Carbon, CEC = Cation Exchange Capacity, BD = Bulk Density, **: Significant at p = 0.01, *: Significant at p = 0.05, NS = Not Significant

Table 5: Classification of soils

Physiography	USDA soil taxonomy	FAO/UNESO legend
Upper Slope	Typic Hapludult	Dystric Nitisol
Lower Slope	Fluventic Dystrudept	Dystric Fluvisol
Foot Slope	Fluvaquentic Eutropept	Eutric Fluvisol

Soil Classifications

Available soil data (Table 2 and 3) plus field information show that soils exhibit properties of Typic hapludult (Dystric Nitisol), Fluventic Dystrudept (Dystric Fluvisol) and Fluvaquentic Eutropept (Eutric Fluvisol) for US, LS and FS physiographic land units, respectively (Table 5).

DISCUSSION

Soils are generally sandy although US and LS physiographic units were sandier. The implication of this in terms of soil Hg distribution is that translocation of Hg from epipedal to sub-surface horizons is rapid since sandy textures are associated with poor retentively (Bouma, 1991). This could by the reason for very high concentrations of Hg in LS soil profile pit (Table 3) despite the high Bulk Density (BD) values. But in FS soils with higher clay contents, high Hg values were limited to epipedal horizons. Bulk density values were highest in LS and FS soils. This could be attributed to the weight of the automobile and municipal solid wastes impacting on soils in LS soils. Seasonal flooding of the Otamiri River could be the reason for high BD in FS soil. High BD implies lower porosities, suggesting poor translocation of soil Hg across horizons with high values. However, movement through pores could be affected by pore size distribution, pore continuity and tortuosity (Eynard *et al.*, 2004) and chemical nature of the metal (He *et al.*, 2004). Slow movement of mercury across these subsurface

horizons may serve as watershed to protect groundwater form contamination by agrochemicals and/or other pollutants (Ezeaku and Anikwe, 2006). Least pH values were found in LS soils and this could be responsible for high Hg values in the profile pit since most heavy metals and trace elements become more available and biotoxic at low to very low pH values.

Soil CEC was generally low, suggesting minimial availability of exchange sites for the adsorption of soil Hg. This means that more soil Hg will be available for translocation within the pedosphere for onward movement to surface and groundwater bodies. This could exceed the maximum permissible limits in Nigerian waters (FEPA, 1988). The same reason is true for low SOC values especially in US soils since high SOC content implies more exchange sites for adsorption of Hg on the soil micelle. High epidedal concentration especially in LS is attributed to heightened dumping of automobile wastes as well as municipal solid wastes on the physiographic land unit by the State Environmental Projection Agency. There is high possibility of increased transportability of Hg from LS to FS soils due to slope effect and these will eventually move downstream where the metal causes entrophication and poisoning of aquatic life (Giesler *et al.*, 2005), Similar findings were reported by Mainville *et al.* (2006) in the Andean Amazon, Napo River Valley in Ecuador. With the exception of US, soils of the study site are Inceptisols, implying that these soils are still young and further weathering and pedogenesis can filter the pedons of the current Hg contamination.

CONCLUSIONS

The study has revealed poor retentivity of Hg due to sandiness of soil textures and very high possibility of surface and ground water Hg pollution. Soil Hg had the highest concentrations on surficial horizons, portending great danger to most arable crops and human health. There is need for modelling using the soil parameters that significantly correlated with Hg. Again, popular crops in the study site should be assessed to ascertain the levels of bioavailability.

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