



Speciation of Cr, Fe, Cu, Pb in the surface and under water sediment of Trans-Ekulu river, Enugu State, Nigeria

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ABSTRACT

This study investigated the distribution and speciation of Cr, Fe, Cu and Pb between the surface and bottom sediments of Trans-Ekulu river Enugu, Nigeria, using flame atomic absorption spectrometric technique. The results showed that the concentrations of Fe vary significantly in the two sediment samples. Iron was observed at elevated concentrations in exchangeable, carbonate bound and Fe-Mn oxide bound fractions (76.04 to 81.03 $\mu\text{g/g}$). Very low concentration in comparison was recorded at the organic matter bound fraction (5.01 $\mu\text{g/g}$). This observation was in contrast to bottom sediment where Fe recorded an elevated concentration at the organic matter bound fraction (73.01 $\mu\text{g/g}$) and reduced concentrations at the exchangeable and carbonate bound fractions (2.01 $\mu\text{g/g}$ and 4.02 $\mu\text{g/g}$) respectively. The result also indicated an increase in Cr concentrations at Fe-Mn oxide fraction of the bottom sediment (14.04 $\mu\text{g/g}$) compared to the surface sediment where Cr was not detected at the Fe-Mn oxide phase. Copper and Pb were generally not detected in the fractions studied. However, Cu was observed at Fe-Mn oxide phase for the bottom sediment (25.01 $\mu\text{g/g}$) and reduced phase for the surface sediment (7.01 $\mu\text{g/g}$). These results indicate an objectionable values in the concentration of the parameters analysed.

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INTRODUCTION

Heavy metals occur naturally in soils and rocks, but high quantities are also being released onto sediments due to anthropogenic activities. In the environment, these metals are very reactive resulting in their mobility and bioavailability to living organism. Irrespective of the origin of soil metals either from a natural source or from anthropogenic activity, trace elements appear in groups and not a single element as a source of contamination. The distribution, mobility, bioavailability and toxicity of metals are dependent not only on metal concentration but also on the form in which metal exit. Metal speciation is one of the most important properties that determine

the behavior and toxicity of metals in the environment. The environmental damage might be small comparatively if these metals are fixed in sediments and pore-water concentrations (Zoumis et al., 2001). It is important to determine and quantify the forms in which heavy metals are present in sediments to obtain an understanding of the potential and actual impacts of elevated concentrations, and to evaluate processes of downstream transport, deposition and release under changing environmental conditions (Li et al., 2000). The dominant geochemical processes responsible for the exchange of metals at the water-sediment interface are

adsorption and precipitation (Salomons and Forstner, 1984; Wang et al., 1997).

Fe and Mn oxides and organic matter either as bulk phase or as coatings of mineral particles are the main binders in sediments (Tessier et al., 1980). Binding of heavy metals in the sediments can be divided into five groups: exchangeable, carbonates, hydroxides, organic and residuals. At each step of the analytical scheme, samples are exposed to the action of an extractant, which solubilizes a specific component and its associated metals.

Speciation is the process of identification and determination of different chemical and physical forms of elements present in a sample (Wang et al., 2006). Metals that occur in cationic forms have a higher ability of binding to negatively charged soil colloids, and are thus less bioavailable, but more easily accumulate in soil, unlike the anionic forms that are mainly present in soil solution and are more bioavailable, but are more readily leached from the soil.

In this study, associated risks of heavy metals in the sediments of Trans-Ekulu have been evaluated with reference to nearby industries generating huge amounts of metallic wastes. The assessment is made based on the sequential extraction procedure to understand the binding fractions and mobility of metals to the surrounding environment.

MATERIALS AND METHODS

Study area

Enugu is the capital of Enugu State in south-east Nigeria (Figure 1). It is situated at a latitude of 6° 26' N and a longitude of 7° 29' E. It is a thickly populated metropolitan city with a population of about 1.2 million inhabitants. The city contains the largest deposit of coal ore and other minerals such as galena. Due to the presence of many industries such as automobile, plastics, mining and small scale groups, anthropogenic activities is on the increase and increasing waste disposal is now a problem to the city. Some of these wastes are discharged to nearby Trans-Ekulu river which ultimately affect the eco-system negatively. Others are recycled for reuse.

Sampling

Sediment samples were collected from estuarine region using square PVC tubing during June and July 2011. The samples were stored in plastic containers in the laboratory. For each analysis the samples were oven-dried at 60 °C until no further weight loss was observed. The samples are labeled A (Sediment from bottom of river) and B (Sediment from river bank).

Materials

The materials used in this study are Buck Scientific AAS Model AVG 210 (England), IECCentra-CL Centrifuge, Brannan Nitrogen filled thermometer, Memmert 854 Oven Schwabach Germany, Mettler Toledo PR 2002 analytical top balance, Hanna pH211 Microprocessor pH meter, Water bath (B & T Searle company Greenfield Oldham). All reagents and chemicals used are analytical grade. The chemicals used are 8 ml, 1M MgCl₂, 8 ml 1M sodium acetate, 20 ml, 1M hydroxylaminehydrochloride, 3 ml of 0.02 M HNO₃, 5 ml of 30% V/V H₂O₂, 5 ml, 3.2 M Ammonium acetate, 20% V/V HNO₃, distilled water and 60% w/w perchloric acid.

Sequential extraction

This was carried out by the method of Tessier et al. (1979). The fractions studied and procedures used are:

Exchangeable fraction: One gram of each of samples A and B was extracted separately at room temperature for 1hr with 8 ml of MgCl₂ solution at pH7. The sediment and extract were thoroughly agitated throughout the extraction.

Bound to carbonate: The residue from exchangeable fraction was extracted with 8 ml of 1M sodium acetate at pH 5 for 5 hrs at room temperature. This was followed with agitation.

Fe – Mn oxides bound fraction – The residue from carbonate bound fraction was extracted under mild reducing conditions. The residue was extracted with 20 ml of 0.4 M hydroxylamine hydrochloride in 25% (V/V) acetic acid with agitation at 96 °C 6 hrs.



Figure 1: Map of Enugu, Nigeria.

Bound to organic matter and sulphide – The residue from Fe-Mn oxides was oxidized as follows: 3 ml of 0.02M HNO₃ and 5 ml of 30% (V/V) H₂O₂ was added to the residue. The mixture was heated to 85 °C in a water bath for 2 hrs with occasional agitation and allowed to cool down. Another 3 ml of 30% H₂O₂, adjusted to pH 2 with HNO₃ was then added. Dilution to a final volume of 20 ml with deionized water was made.

Residual fraction:- The residue from organic bound fraction was oven dried at 105 °C for 15 mins. Digestion was carried out with a mixture of 5 ml conc. HNO₃ (70% w/w). After centrifugation for 10 mins at 400 r/min, the supernatant of each step was separated for triplicate analysis using Buck scientific AAS.

RESULTS

The result of the speciation of Cr, Fe, Cu and Pb from the surface and underwater

sediments of Trans-Ekulu River Enugu State Nigeria are shown in Tables 1 and 2. The metals Fe and Cr exhibited high concentrations in the surface sediments. Iron is mostly bounded with carbonates and Fe – Mn oxide with respective concentrations of 76.04±0.03 µg/g and 81.03±0.04 µg/g. However, the exchangeable Fe was observed to be 76.26±0.74 µg/g which is also high and of serious concern. The Cr at the exchangeable fraction had a concentration of 3.00±0.03 µg/g, while the carbonate bound and organic bound fractions are 1.07±0.24 µg/g and 5.01±0.03 µg/g respectively.

The results obtained in surface sediment can be compared to the result from the bottom sediments. Exchangeable Cr was slightly lower in the bottom sediment (2.01±0.01 µg/g). This low variation may be attributed to oxidation of more of the Cr as

Table 1: Surface sediment (Site A).

Element	Parameters in µg/g														
	Exchangeable			Bound to carbonate			Bound to Fe-Mn oxide			Bound to organic matter			Residual fraction		
	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD
Cr	3.00			1.00			ND			5.00			7.00		
	3.03	3.00	0.03	0.87	1.07	0.24	ND	ND		5.03	5.01	0.03	7.00	7.01	0.01
	2.97			1.34			ND			4.99			7.02		
Fe	77.09			76.07			81.00			7.01			436.00		
	76.01	76.26	0.74	76.02	76.04	0.03	81.07	81.03	0.04	7.07	7.03	0.03	436.40	436.20	0.20
	75.68			76.05			81.04			7.02			436.20		
Cu	ND			ND			ND			ND			7.00		
	ND			ND			ND			ND			7.02	7.01	0.01
	ND			ND			ND			ND			7.01		
Pb	ND			ND			ND			ND			ND		
	ND			ND			ND			ND			ND		
	ND			ND			ND			ND			ND		

ND = Not detected

Table 2: Bottom sediment (Site B).

Element	Parameters in µg/g														
	Exchangeable			Bound to carbonate			Bound to Fe-Mn oxide			Bound to organic matter			Residual fraction		
	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD	Analysis	Mean	SD
Cr	2.00			4.00			14.04			6.00			109.10		
	2.01	2.01	0.01	4.21	4.08	0.11	14.06	14.04	0.02	6.00	6.00	0.01	109.30	109.13	0.02
	2.03			4.03			14.03			6.01			109.00		
Fe	2.00			4.01			74.00			73.02			756.00		
	2.00	2.01	0.01	4.03	4.02	0.01	74.00	74.00	0.01	73.01	73.01	0.01	756.24	756.11	0.12
	2.03			4.03			74.00			73.00			756.09		
Cu	ND			ND			25.00			ND			ND		
	ND	ND		ND	ND		25.00	25.01	0.02	ND	ND		ND	ND	
	ND			ND			25.03			ND			ND		
Pb	ND			ND			ND			ND			ND		
	ND	ND		ND	ND		ND	ND		ND	ND		ND	ND	
	ND			ND			ND			ND			ND		

ND = Not detected

observed in the Fe–Mn oxide fraction ($14.04 \pm 0.02 \mu\text{g/g}$).

The organic matter bound fraction at the bottom sediment recorded elevated concentrations for Fe ($73.01 \pm 0.01 \mu\text{g/g}$) and Cr ($6.00 \pm 0.01 \mu\text{g/g}$) compared to surface sediments. The relationships among acid-volatile sulphides, total organic carbon and Fe indicate interactions among trace metal-binding phases.

DISCUSSION

The high concentration of Fe in the Fe–Mn oxide fraction agrees with previous study that suggests that sediments at the top layer are mostly bounded with oxidizable matter (Krupadam et al., 2003). This observation can also be attributed to the direct input of pollutants along with oxidizable matter from the major tributaries leading to enhancing the sedimentation rates in the estuary (Haake et al., 1993). Apart from residue Cu with a concentration of $7.01 \pm 0.01 \mu\text{g/g}$, Cu and Pb were not detected in all the fractions plausibly suggesting that the mobilization potential of trace metals like Cu and Pb may get increased in dredged (oxidized) sediments compared to submerged (reduced) sediments (Tack et al., 1998; Vandecasteele et al., 2007).

The exchangeable metal in sediments is labile, highly toxic and the most bioavailable fraction. The Fe in the exchangeable fraction also reduced drastically ($2.01 \pm 0.01 \mu\text{g/g}$) compared to that of surface sediment ($76.26 \pm 0.74 \mu\text{g/g}$). This is an indication of a reduction activity occurring at the bottom sediment.

The result of the Cr and Fe bound to carbonate occurred at $4.08 \pm 0.11 \mu\text{g/g}$ and $4.02 \pm 0.01 \mu\text{g/g}$ respectively. The observed concentration for Cr in this fraction is higher

than that observed at the surface sediments ($1.07 \pm 0.24 \mu\text{g/g}$). In contrast to this result, Fe exhibited elevated concentrations in the carbonate bound fraction of the surface sediments ($76.04 \pm 0.03 \mu\text{g/g}$) compared to $4.02 \pm 0.01 \mu\text{g/g}$ in the bottom sediment. Such lower concentrations are possibly due to an accumulation of sulphide as FeS_2 rather than as acid-volatile sulphides and a sulphide re-oxidation at surface layers due to bioturbation, presence of roots, and tidal mixing (Holmer et al., 1994).

Since organic matter oxidation employing sulphate as an electron acceptor results in acid-volatile sulphide production, the organic carbon input, reactivity, and oxidation will affect the accumulation of acid-volatile sulphides and hence that of sulphide-forming metals within sediments (Gobeil et al., 1997; Teasdale et al., 2003). Organic matter and sulphides are important factors controlling the mobility and bioavailability of heavy metals. There are conflicting reports on the toxicity of heavy metals influenced by organic matters. Hoss et al. (2001) proposed that Cd complexation by organic matter, serving as food, might elevate the toxicity of Cd to nematode in sediment, while Besser et al. (2003) in contrast thought that amendments of humus shifting the partitioning of Cd and Cu towards greater concentrations in sediments and lesser concentrations in pore waters reduced the toxicity of Cd and Cu.

In comparison to surface sediments, Pb was not detected at the bottom sediment. Copper was detected at the Fe-Mn oxide fraction ($25.01 \pm 0.02 \mu\text{g/g}$) only. The reason for this may be that Cu and Pb may get increased in dredged (oxidized) sediments compared to submerged (reduced) sediments

(Tack et al., 1998; Vandecasteele et al., 2007).

Conclusion

From our study, the following deductions can be made:

1. Iron had the highest concentration in all the fractions analysed for surface sediments followed by Cr and Cu. Lead was not detected. This was attributed to increase in anthropogenic activities along the river banks.
2. Chromium in exchangeable fraction was more in the surface sediment than in the bottom sediment.
3. Iron bound to organic matter indicated elevated concentrations at the bottom sediments than at the surface sediments.
4. Copper was only detected at the residual fraction in the surface sediment and Fe-Mn oxide bound fraction in the bottom sediment.

The above deductions showed that the risk level from Pb and Cu to the ecosystem could be non existing while Cr and Fe through bioaccumulation could enter the food chain and pose a lot of threat to the ecosystem.

REFERENCES

- Besser JM, Brumbaugh WG, May TW, Ingersoll CG. 2003. Effects of organic amendments on the toxicity and bioavailability of cadmium and copper in spiked formulated sediments. *Environ. Toxicol. Chem.*, **22**: 805-815.
- Gobeil C, MacDonald RW, Sundby B. 1997. Diagenetic separation of cadmium and manganese in suboxic continental margin sediments. *Geochimica et Cosmochimica Acta*, **61**: 4647-4654.
- Hake B, Bartsch M, Rixen R, Ramaswamy V, Nasir RR, Cury WB. 1993. Seasonality and international variability of particle fluxes to the Arabian Sea. *Deep-Sea Res.*, **40**: 1323-1343.
- Holmer M, Kristensen E, Banta G, Hansen K, Jensen MH, Bussawarit N. 1994. Biogeochemical cycling of sulphur and iron in sediments of a Southeast Asian mangrove Phuket Island, Thailand. *Biogeochemistry*, **26**: 1653-1668.
- Hoss S, Henschel T, Haitzer M, Traunspurger W, Steinberg EEW. 2001. Toxicity of cadmium to *Caenorhabditis elegans* (Nematoda) in whole sediment and pore water – the ambiguous role of organic matter. *Environ. Toxicol. Chem.*, **20**: 2794-2801.
- Krupadan RJ, Sarin R, Anjaneyulu Y. 2003. Distribution of trace metals and organic matter in the sediments of Godavari estuary of Kakinada bay, East coast of India. *Water, Air and Soil Pollut.*, **150**: 299-318.
- Li XD, Wai OWH, Li YS, Coles BJ, Ramsey MH, Thornton I. 2000. Heavy metal distribution in sediment profiles of the Pearle River estuary, South China. *Appl. Geochem.*, **15**: 567-581.
- Salomons W, Forstner U. 1984. *Metals in the Hydrocycle*. Springer-Verlag. Berlin, Heidelberg, New York, Tokyo.
- Tack FMG, Singh SP, Verloo MG. 1998. Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environ. Pollut.*, **103**(1): 109-115.
- Teasdale PR, Apte SC, Ford PW, Batley GE, Koehnken L. 2003. Geochemical cycling and speciation of copper in waters and sediments of Macquarie Harbour, Western Tasmania. *Estuarine, Coastal and Shelf Science*, **57**: 475-487.

- Tessier A, Campbell PGC, Bisson M. 1979. Sequential extraction procedure for the speciation of trace metals. *Anal. Chem.*, **51**: 244-251.
- Tessier A, Campbell PGC, Bisson M. 1980. Trace metal speciation in the Yamask and St. Francois rivers (Quebec). *Can. J. Earth Sci.*, **17**(1): 90-105.
- Vandecasteele B, Quataert P, Tack FMG. 2007. Uptake of Cd, Zn and Mn by willow increases during terrestrialisation of initially ponded polluted sediments. *Sci. Total Environ.*, **380**: 133-143.
- Wang G, Su M, Chen Y, Lin F, Luo D, Gan S. 2006. Transfer characteristics of cadmium and lead from soil to the dibble parts of six vegetable species in Southeastern China. *Environ. Pollution*, **144**: 127-135.
- Wang P, Qu E, Li Z, Shuman LM. 1997. Fraction and availability of nickel in soil amended with sewage or sewage sludge. *J. Environ. Qual.*, **26**: 795-801.
- Zoumis T, Schmidt A, Grigorova L, Calmano W. 2001. Contaminants in sediments: remobilization and demobilization. *Sci. Total Environ.*, **266**: 195-120.