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Monitoring the distribution of cadmium in sediment samples from Obajana stream in North central Nigeria

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ABSTRACT

The distribution of cadmium species in sediments of different depths from Obajana stream was investigated by sequential extraction procedure and flame atomic absorption spectrometric detection. Index of geoaccumulation was used to assess the level of sediment pollution and it was found not to be polluted. However, the speciation results were found to contain Cd in the order exchangeable > organic matter/sulphide > residual > carbonate bound > Fe-Mn oxide at top soil and 5 cm depths. For 10 cm, 15 cm and 25 cm depths the observed trend in Cd concentration is Fe-Mn oxide bound > exchangeable > organic matter/sulphide > residual > carbonate bound. The order of decreasing concentration of Cd at 20 cm and 30 cm is Fe-Mn oxide > exchangeable > residual > organic matter/sulphide > carbonate bound. The Cd species in the exchangeable fraction occurs mostly at the topsoil followed by 5 cm and decreases progressively as the depth is increased. Thus plants and animals that may be exposed to this environment may, as a result of bioaccumulation, have concentrations of Cd in their systems beyond the acceptable limits prescribed by world health organisation.

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INTRODUCTION

Cadmium and its compounds are part of the most hazardous pollutants in the environment. Previous and established research has indicated that sediments and dusts transported and stored in the urban environment have the potential to provide often considerable quantities of heavy metals to receiving water bodies with changing environmental conditions. Sediments that accumulate along pavements in urban environments originate mainly from atmospheric deposition and anthropogenic activities such as quarrying and construction

(Ferguson and Kim, 1991; De Miquel et al., 1997; McAllister et al., 2000, 2005).

The fate and character of heavy metals is dependent on some physico-chemical parameters which govern their availability and mobility in soil and sediment systems (tack and Verloo, 1995). These sediments depending on their binding forms are more or less available for mobilization and subsequent uptake by plants and living organisms (Förstner, 1989; Lund, 1990; Ramos et al., 1994). The cement factory in the study area in the course of its quarrying activities release fine Particles into the atmosphere which

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eventually settles and dissolves in nearby stream, thereby increasing the loadings of metals present in it. Works by various authors have shown that Cd compounds have found their way into modern society (IARC, 1993; WHO, 1992; Morrow, 1998; OECD, 1994; ASTDR, 1999). In humans, uptake of Cd may occur via the inhalation of contaminated air or the ingestion of food and drinking water. Workers may be exposed to the metal or its compounds present as fumes or dust in the air at the workplace.

The quality of the environment is a matter of serious concern, especially today that the consequences of human intervention are already evident. Although environment is extremely valuable for people and other organisms living in it, it is also endangered due to human activities that are continuously ruining it (Davis et al., 2006). Once absorbed, Cd is widely distributed and retained in the body where it accumulates throughout life.

The aim of this work was to monitor the distribution of Cd species at different depths in the sediments from the Obajana stream.

MATERIALS AND METHODS

Geoaccumulation Index, I_{geo}

To ascertain the degree of contamination due to human activities and to compare Cd concentration that appear in different depths in the sediments, an approach known as the geoaccumulation index (I_{geo}) was used (Müller and Suess, 1979; Förstner et al., 1993) (Table 1). A quantitative equation called the index of geoaccumulation was proposed by the authors as

$$I_{geo} = \ln(C_n/1.5B_n)$$

Where C_n = measured concentration, $\mu\text{g/g}$ and B_n = geoaccumulation background value, $\mu\text{g/g}$. The factor 1.5 is introduced as the lithologic variations of trace metals. This index (I_{geo}) compares the measured concentration of the element in the fine-grained sediment fraction C_n with the geochemical background value B_n . The

average value of Cd in Okene stream (which is taken as the reference) is considered as B_n value. The index of geoaccumulation consists of seven classes whereby the highest grade (6) reflects a 100-fold enrichment above background values.

Study area

The Obajana town is located in Western part of Kogi State, Nigeria, at a latitude of $7^{\circ} 54'N$ and longitude $6^{\circ} 25'E$ (Figures 1 and 2). The inhabitants are predominantly farmers whose type are basically subsistent. The area is very rich in solid minerals and has a large deposit of gypsum. It is against the backdrop of this large mineral deposit that the Obajana cement factory was established. The factory in the course of its quarrying and milling discharge some fine particles into the surrounding. These are transported by air to the surrounding river and some are deposited on land. There is a high tendency that these fine particles may find their way into the benthic biota and health consequences as a result of its deposition may arise.

Sediment sampling

Sediment samples were collected using an Eckman sampling device from the top to 30 cm depth. The samples were immediately air-dried and stored in plastic containers. Other materials such as stones and plant fragments were removed by passing the dried sample through a 2-mm sieve. The sieved samples were ground to powdered form using a mortar and pestle. These powdered samples were then passed through a $75 \mu\text{m}$ sieve to filter the silt/clay fraction. The silt/clay fraction are most recommended for sediment speciation studies because they generally contain the highest concentrations of pollutants, and are most readily transported in suspension in natural waters.

Materials

All reagents used are analytical grade. These include distilled water, KNO_3 ,

CH₃COONa, CH₃COOH, NH₂OH.HCl, HNO₃, H₂O₂, CH₃COONH₄. The instrument used are, pH meter (Hanna pH 211 Microprocessor), analytical balance (Mettler Toledo PR2002), centrifuge (IECCentra-CL), FAAS (Buck Scientific Model AVG 210 UK), mortar and pestle, Eckman sampler.

Sample digestion

The sequential extraction procedure used was the one proposed by Tessier et al. (1979). Table 2 shows the procedure used in this work. The mixtures were separated from the supernatant by 30 mins centrifugation at 10,000rpm. All fractions were subjected to analysis for Cd using Buck Scientific FAAS Model AVG 210 UK.

Table 1: Geoaccumulation index classification.

Geoaccumulation index, I_{geo}	I_{geo} class	Contamination intensity
>5	6	Very strong
>4 - 5	5	Strong to very strong
>3 - 4	4	strong
>2 - 3	3	Moderate to strong
>1 - 2	2	Moderate
>0 - 1	1	Uncontaminated to moderate
<0	0	Practically uncontaminated

(Förstner et al., 1993)

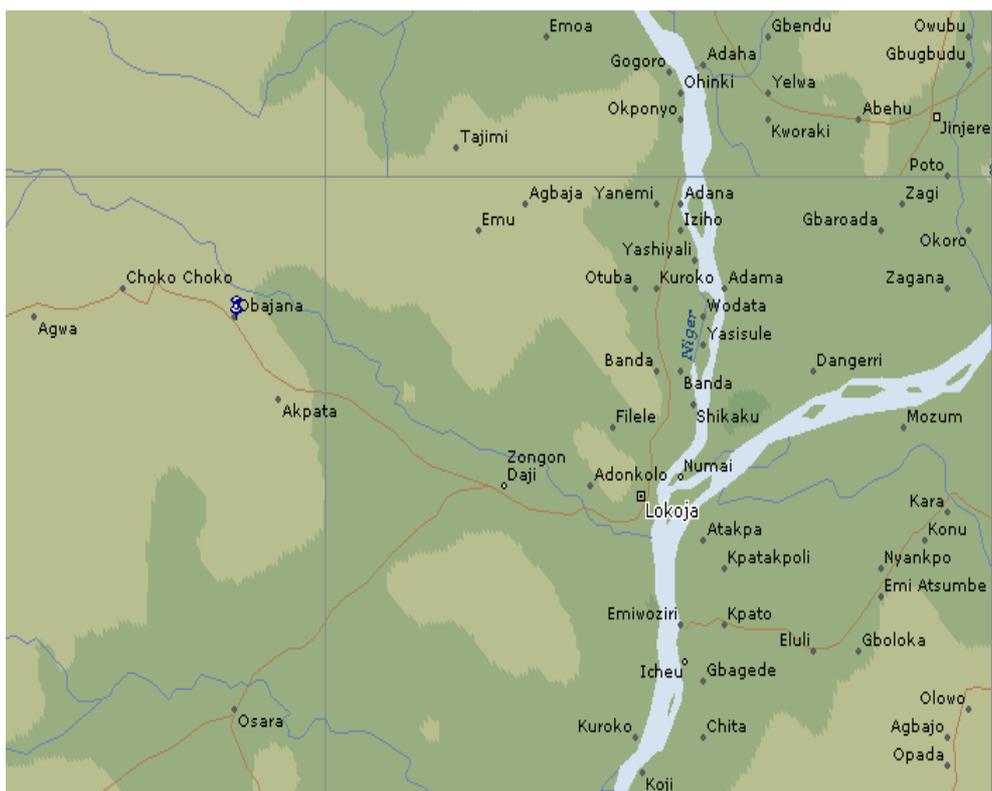


Figure 1: Map showing Obajana in Kogi State, Nigeria.

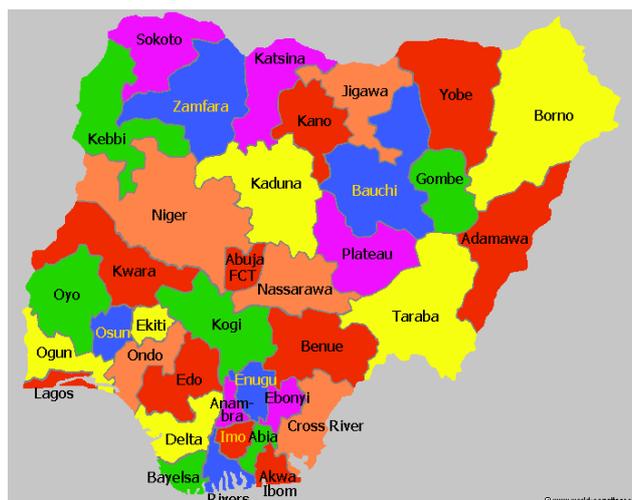


Figure 2: Map of Nigeria showing 36 states and the Federal Capital Territory.

RESULTS

The results of the monitoring of Cd distribution in the Obajana stream are shown in Table 3. From the results of the distribution of Cd in sediment samples from Obajana stream, it was observed that the exchangeable fraction which is the most lethal fraction occurred more at the topsoil (0.097 $\mu\text{g/g}$) followed by 5 cm depth (0.092 $\mu\text{g/g}$) and 10 cm depth (0.072 $\mu\text{g/g}$). At 15 cm depth, a concentration of 0.040 $\mu\text{g/g}$ was recorded, however there was an increase at 20 cm depth (0.047 $\mu\text{g/g}$) followed by a decrease and an increase at 25 cm and 30 cm depths respectively. The observed Cd concentration was constant from topsoil to 10 cm depth (0.020 $\mu\text{g/g}$), and afterwards increased at 15 cm depth (0.024 $\mu\text{g/g}$) before reducing at 20 cm depth (0.010 $\mu\text{g/g}$). At 25 cm and 30 cm depths, Cd was not detected at this fraction.

Cadmium was not detected at the topsoil in this fraction. This trend changed from 5 cm depth (0.015 $\mu\text{g/g}$) to 30 cm depth (0.090 $\mu\text{g/g}$). The sequence decreased from 0.109 $\mu\text{g/g}$ in 10 cm to 0.086 $\mu\text{g/g}$ (25 cm). The concentrations of Cd at the organic matter/sulphide bound fraction are considerably lower than that of Fe-Mn oxide

bound. The range is 0.030 – 0.037 $\mu\text{g/g}$. The residual fraction for all the sampled depths ranged from 0.181 – 0.262 $\mu\text{g/g}$.

DISCUSSION

Exchangeable fraction

It can therefore be said that the exchangeable fractions decrease with increasing depth up to 15 cm depth. The decrease and subsequent increase at 25 cm and 30 cm is consistent for all the fractions studied. It can therefore be established that fractions at 20 cm depth could be referred to as the zone of transition. These elevated concentrations of Cd at exchangeable fraction indicate that Cd has posed a threat to benthic biota in the river and local residents.

Fraction bound to carbonate

Previous research on the geochemical behaviour of some heavy metal ions such as Cd^{2+} indicated that this metallic ion can be adsorbed onto the surfaces of carbonate minerals followed by incorporation into the crystal lattice to form $\text{Cd}_x\text{Ca}_{1-x}\text{CO}_3$ solid solution (Billon et al., 2002). This surface phenomenon may have accounted for the observation of Cd from topsoil to 20 cm depths.

Table 2: Extraction procedure as proposed by Tessier et al. (1979).

Fractions	Procedure
Fraction1 - exchangeable	8 mL of 1M KNO ₃ for 1h, 25 °C with continuous agitation.
Fraction2 – carbonate bound	Residue from fraction 1, add 8 mL of 1M CH ₃ COONa; pH 5.0 adjusted with CH ₃ COOH and continuous agitation for 4 hrs.
Fraction3 – Fe-Mn oxide bound	Residue from fraction 2, add 20 mL of 0.04M NH ₂ OH.HCl in 25 % (v/v) CH ₃ COOH and heated to 96 ± 3 °C with occasional agitation for 6 hrs.
Fraction4 – organic matter/sulphide bound	Residue from fraction 3, add 3 mL of 0.02M HNO ₃ and 5 mL of 30 % H ₂ O ₂ (adjusted to pH2 with HNO ₃). Heated to 85 ± 2 °C, 2 hrs with occasional agitation. A second 3 mL of aliquot of 30 % H ₂ O ₂ (pH2 with HNO ₃) is added and the mixture is heated again to 85 °C for 3 hrs with intermittent agitation. After cooling, 5 mL of 3.2M CH ₃ COONH ₄ in 20 % (v/v) HNO ₃ is added and mixture diluted to 20 mL and agitated continuously for 30 mins.
Fraction5 - residual	Residue from fraction 4, add 5 mL HNO ₃ + HClO ₄ (4:1) for 2 hrs at 96 ± 3 °C with intermittent agitation.

Table 3: Results of speciation of Cd at various depths.

Depths (cm)	Fractions concentration, µg/g					Total Cd in sediment	I _{geo}	Contamination intensity
	Exchangeable	Carbonate bound	Fe-Mn oxide bound	Organic matter/sulphide bound	Residual			
0	0.097	0.021	ND	0.037	0.026	0.181	0.19	Not polluted
5	0.092	0.021	0.015	0.037	0.025	0.190	0.24	Not polluted
10	0.072	0.021	0.109	0.032	0.028	0.262	0.56	Not polluted
15	0.040	0.024	0.094	0.031	0.028	0.217	0.37	Not polluted
20	0.047	0.010	0.092	0.032	0.034	0.215	0.36	Not polluted
25	0.036	ND	0.086	0.030	0.028	0.180	0.18	Not polluted
30	0.042	ND	0.090	0.031	0.032	0.195	0.26	Not polluted

ND = not detected

Fraction bound to Fe-Mn oxide

Due to their chemical characteristics, Fe and Mn extracted by hydroxylamine hydrochloride solution are regarded as amorphous hydrous Fe-Mn oxides in sediments or soils (Ariza et al., 2000). Much of the observed Cd was detected at this fraction and this plausibly suggests that hydrous Fe-Mn oxides may play a major role in controlling the fate and transport of Cd in the sediments of Obajana stream.

Fraction bound to organic matters and sulphides

Previous studies has proved that Cd²⁺ has a strong affinity for chloride ion but a weak affinity for organic matter compared to many trace metals in sea water (Tipping et al., 1998). Thus, Cd may exist in chlorocomplexes forms rather than free Cd²⁺ in various sediment and water samples. Therefore, the adsorption on Fe-Mn oxides and coordination with organic matter are appreciably hindered due to the decreased availability of free Cd²⁺ ions despite that these materials have a strong affinity for Cd²⁺ (Turner et al., 2008). These low values of Cd at this fraction may also be explained in terms of the fact that Cd bound to acid volatile sulphides can be liberated rapidly as a result of aeration of sediments and elevated oxygen level can significantly increase the bioavailability of Cd in sediments (Zhuang et al., 1994; Schaanning et al., 1996).

Residual

This fraction is less toxic for organisms in aquatic environment. For this study, the bulk of Cd are in the residual phase. From the geoaccumulation index, Cd in Obajana stream falls within the not polluted to moderately polluted class. The stream can therefore be considered fit for benthic biota. However, bioaccumulation may set in with the continual discharge of Cd into the water body.

Conclusion

The distribution of Cd in sediment samples from Obajana stream revealed that the Cd species occur in the fractions in the following order in the topsoil and 5cm depth: exchangeable > organic matter/sulphide

bound > residual > carbonate bound > Fe-Mn oxide bound. The observed order for 10 cm, 15 cm and 25 cm depths is: Fe-Mn oxide bound > exchangeable > organic matter/sulphide bound > residual > carbonate bound. The order of decreasing Cd concentrations in 20 cm and 30 cm depths is Fe-Mn oxide bound > exchangeable > residual > organic matter/sulphide > carbonate bound. The Cd specie in all the fractions is not polluting the Obajana stream from the geoaccumulation index.

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