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I.A. Ololade ^{a b}, L. Lajide ^c, O.O. Ololade ^d & O. Adeyemi ^e

^a Department of Chemistry and Industrial Chemistry, Adekunle Ajasin University, P.M.B. 001, Akungba-Akoko, Ondo State, Nigeria

^b State Key Laboratory for Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^c Department of Chemistry, Federal University of Technology, P.M.B. 734, Akure, Nigeria

^d Department of Geography, Environmental Management and Energy Studies, Faculty of Science, University of Johannesburg, Auckland Park Campus, Johannesburg, South Africa

^e Department of Environmental Sciences, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria

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Metal partitioning in sediment pore water from the Ondo coastal region, Nigeria

I.A. Ololade^{ab*}, L. Lajide^c, O.O. Ololade^d and O. Adeyemi^e

^aDepartment of Chemistry and Industrial Chemistry, Adekunle Ajasin University, P.M.B. 001, Akungba-Akoko, Ondo State, Nigeria; ^bState Key Laboratory for Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; ^cDepartment of Chemistry, Federal University of Technology, P.M.B. 734, Akure, Nigeria; ^dDepartment of Geography, Environmental Management and Energy Studies, Faculty of Science, University of Johannesburg, Auckland Park Campus, Johannesburg, South Africa; ^eDepartment of Environmental Sciences, Federal University of Petroleum Resources, Effurun, Delta State, Nigeria

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Distribution and equilibrium partitioning of metals (Cd, Cu, Cr, Fe, Ni, Pb, Mn, and Zn) between pore water and surface sediments at the Ilaje coast of Ondo State, Nigeria, were studied. The Ilaje River can be one of the interesting research locations because of its economic nature and history of oil pollution. Seasonal variations were observed to investigate possible variations in the availability of metals for organisms throughout the year. The concentrations in both sediments and pore water during the dry and wet seasons were as follows: Cu > Fe $\gg$ Mn > Pb > Ni > Cr > Cd > Zn. The pore water–sediment partition coefficient (K_p) showed that Zn and Cd were highly mobile while Fe and Cu have restricted mobility. Dissolved organic carbon (DOC) in pore water had a strong influence on mobility and bioavailability of all the metals ($p < 0.05$) except Cr whose concentration was pH and DOC-dependent. Based on the normalized organic carbon partitioning coefficient (K_{oc}), increased levels of Fe and Cu were linked to lithological origin. Concentrations of Pb and Ni were associated with petroleum-related sources. The significance of the field-based techniques for ecotoxicological purposes is discussed.

Keywords: sediments; pore water; heavy metals; equilibrium partitioning; bioavailability

Introduction

Metals are a class of important anthropogenic inorganic pollutants and due to their various health-related problems and widespread environmental occurrences, they have garnered much attention around the world (Paulson et al. 2006; Yalcin, Narin, and Soylak 2007; Lalah, Ochieng, and Wandiga 2008; Liu et al. 2009; Hiller, Jurkovic, and Utriepka 2010; Uluturhan 2010). Certain trace elements, Cr, Cu, Ni, and Zn, are essential micronutrients required for the normal growth and function of organisms. Other trace elements like Cd, Hg, and Pb are considered toxic with respect to human health and aquatic life (Uluturhan 2010). In aquatic ecosystems, sediments are the main sink for these

*Corresponding author. Email: olisa200@yahoo.com

metals but when environmental conditions change (pH, redox potential, particle size, etc.), sediments can act as a source of metals (Di Toro et al. 1990; van Den Berg et al. 1999; Wilson and Chang 2000; Freret-Meurer et al. 2010).

Assessment of the risk associated with contaminated sediments is a function of bioavailable fraction, defined as the freely dissolved concentration (FDC) of contaminants. The guidelines established by US Environmental Protection Agency (EPA) for protecting benthic organisms in heavy metal-contaminated sediments are based on FDC in sediment interstitial water or pore water (US EPA 2005). The FDC can be assumed as the effective bioavailable concentration, critical for understanding the mobility, bioavailability, and ecotoxicological consequences of heavy metals in aquatic ecosystems. Thus, the FDC is a relevant parameter for risk assessment associated with heavy metals and other pollutants within the aquatic ecosystem.

Sediment–pore water partition is an important process that controls the transport, fate, and ecotoxicological risk of the microlevels of contaminants in aquatic environments. A relatively simple approach for calculating the distribution of heavy metals in sediment is the so-called equilibrium partitioning (EP) concept (van der Kooij et al. 1991). The EP concept assumes that chemical concentrations among environmental compartments are at equilibrium and that the partitioning of metals among environmental compartments can be predicted based on partition coefficients. This partition coefficient, K_p , which expresses equilibrium distribution of chemical substances between the sediment (C_s) and the aqueous phase (C_{aq}) can also be expressed as a function of organic carbon normalized partition coefficient, K_{oc} . These chemical parameters are related to the fraction of organic carbon, f_{oc} , according to Equations (1) and (2) (Chen et al. 2007).

$$K_p = \frac{C_s}{C_{aq}} \quad (1)$$

$$K_{oc} = K_p/f_{oc} \approx C_s/(C_{aq}f_{oc}) \quad (2)$$

This study has been focused on the sediment–pore water partition behavior of eight heavy metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in Ilaje Rivers, Ondo State, Nigeria. The study area is a very important water resource for fishing and agriculture in Nigeria. Major source of contamination into the area results from oil spill through the activities of Chevron Nigeria Ltd. Heavy metals and total hydrocarbons, including polycyclic aromatic hydrocarbons' (PAHs) concentration in surface sediments of this area and possible sources have been reported in previous studies (Ololade, Lajide, and Amoo 2007; Ololade and Lajide 2009; Ololade 2010). Therefore, current studies mainly investigate the concentration of heavy metals in pore waters and *in situ* sediment–pore water partition coefficients of eight heavy metals in the river. The results will be helpful in predicting partitioning behaviors of metals, their bioavailability, and fate in sediment–pore water system.

Materials and methods

Study area and sample collection

The study area covers the oil-producing zone of Ondo State in South-West Nigeria (Figure 1). The river flows from Ayetoro (S-1) downstream to Awoye (S-13). A global positioning system (GPS) was used for site identification to enhance future monitoring. The sampling sites were all located, on an average, at a distance of 2 km from each other. Water at S-9 has the greatest oceanic influence due to closeness to Atlantic Ocean and the

Figure 1. Map of sampling locations (inset: area map of Nigeria and Africa showing geographical locations).

oceanic influence is expected to decrease downstream to S-13. Oils, in the form of spills, usually flow through the Atlantic to the areas. Fourteen representative sediment samples including one control were collected, each during the dry season (December 2005) and the wet season (June 2006) along this reach. The surface sediment (0–10 cm) samples were collected from the river bed (close to the bank) using a stainless steel Van-Veen grab sampler and placed in labeled polythene bags. Samples were transported to the laboratory within few hours after sampling for pore water separation.

Separation and extraction of pore water samples

The sediment samples were centrifuged in 250 mL glass centrifuge tubes at 6000 rpm for 15 min to separate the pore water from the sediment (Janssen et al. 1997). In order to provide an adequate volume of solution for analysis, the multiple extractions were pooled after filtering through 0.45 μm Millipore filters. A portion of the sample for the analysis of DOC were stored in the dark at 4°C until analyzed using a Shimadzu total organic carbon analyzer 5050 A (Shimadzu, Tokyo, Japan), while another portion was acidified with high-purity concentrated nitric acid and refrigerated until analysis; the remainder of the sediment samples were frozen at -20°C before analysis.

Analytical procedure

In the laboratory, sediment samples were defrosted at room temperature, air-dried, and then ground and sieved through a 0.125 mm sieve. Salient physicochemical characteristics of the sediment were measured. The values of pH and conductivity were obtained with pre-calibrated pH meter (portable Orion 290A digital pH meter; error ± 0.1 pH unit) and conductivity meter (Model MC-1, Mark V, by Electronic Switchgear, London), respectively. Particle size distribution of sediments was determined using the pipette method. Organic carbon content (f_{oc}) of sediments was determined by the method of potassium dichromate–sulfuric acid oxidation (van Reeuwijk 2002). For the determination of total metal concentrations, sediment samples were digested with HCl/HNO₃/HF acid mixture (1:3:1 v/v) (Loring and Rantala 1992). Reference sediment and blanks included in all runs (PACS-2 heavily contaminated marine sediment from the National Research Council, Canada) were certified. Digests were filtered through 0.45 m Millipore filters and diluted appropriately for analysis.

Concentrations of metals in the surface sediment and pore water extracts (Cd, Cu, Cr, Fe, Pb, Ni, Mn, and Zn) were determined with atomic absorption spectrometry (Alpha 4AAS, Chemical Tech. Analytical, UK) with air–acetylene or nitrogen–acetylene oxide flame. Three analytical replicates were measured for each sample. The certified reference material (PACS-2) gave 92%, 94%, 94%, 102%, 89%, 96%, 86%, and 94% recovery percentages ($n=3$) of Cd, Cu, Cr, Fe, Pb, Ni, Mn, and Zn, respectively, with precision varying from 3.2% to 10.7% relative to mean values. Procedural blanks, consisting of 100 mL of double distilled water, was extracted in the same manner as the sediment/pore water and analyzed concurrently with the samples. The concentrations of heavy metals in the blanks were not detected or found much lower than the detection limits of the method, which were 0.011–0.021 $\mu\text{g L}^{-1}$.

Descriptive statistical analysis was carried out wherein the mean, minimum and maximum values, and standard deviation (SD) were evaluated. Correlations and simple regression analyses between the concentrations of bulk sediment, pore water, pH, and DOC were performed using SPSS version 13 for Windows.

Results and discussion

Selected sediment properties of the study areas during the dry and wet seasons are summarized in Table 1. The pH was 5.9 ± 0.5 and 6.6 ± 0.7 for the dry and wet seasons, respectively. The mean specific conductivity showed significant seasonal variations with an average of $10.1 \pm 4.7 \text{ mS cm}^{-1}$ during the dry season and $8.7 \pm 3.7 \text{ mS cm}^{-1}$ during the wet season. Generally, the sediment had high clay content. The mean clay contents were $18.6 \pm 3.6\%$ and $18.0 \pm 9.4\%$, and that for silt, it was $3.4 \pm 0.6\%$ and $3.4 \pm 0.5\%$ during the dry and wet seasons, respectively. The coastal areas are also characterized by high organic matter. Contents of organic carbon in the dry and wet seasons were $10.0 \pm 2.8\%$ and $8.5 \pm 1.9\%$, respectively. The relatively high concentrations of organic carbon may be due to the fact that only surface sediments (<10 cm depth) were collected. In soils, for instance, these accumulations of organic matter may result in the enrichment of heavy metals (Suavé 2006).

The total content of metals in mg kg^{-1} during the two seasons follows similar order: $\text{Cu} > \text{Fe} \gg \text{Mn} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Zn}$ in mg kg^{-1} (Table 2). However, significant mean differences were noticeable in some of the metals. This may be due to the fact that

Table 1. Physical and chemical characteristics of surface sediments collected from Ilaje Rivers, Ondo State, Nigeria.

Stations code	Location	Season	pH(H ₂ O)	EC (μS cm ⁻¹)	Clay (%)	Silt (%)	OC (%)
S-1	Ayetoro	D	6.5 ± 0.3	8.4 ± 0.4	16.2 ± 0.5	3.6 ± 0.2	10.3 ± 0.6
		W	7.5 ± 0.6	8.1 ± 0.2	15.7 ± 0.8	3.3 ± 0.5	9.7 ± 0.3
S-2	Oroto	D	4.7 ± 0.4	7.3 ± 0.2	13.8 ± 0.7	2.4 ± 0.1	5.3 ± 0.1
		W	5.8 ± 0.6	6.9 ± 0.5	12.5 ± 0.5	2.4 ± 0.1	5.2 ± 0.2
S-3	Asumaga	D	5.1 ± 0.4	11.4 ± 0.6	13.2 ± 0.3	2.6 ± 0.3	5.2 ± 0.1
		W	6.1 ± 0.2	7.2 ± 0.2	12.9 ± 0.5	2.4 ± 0.1	5.1 ± 0.1
S-4	Ilepete	D	6.1 ± 0.4	19.2 ± 0.4	15.7 ± 0.3	2.9 ± 0.3	10.4 ± 0.2
		W	6.5 ± 0.5	13.9 ± 0.6	15.2 ± 0.8	2.6 ± 0.5	9.5 ± 0.3
S-5	Obe Nla	D	5.8 ± 0.5	8.2 ± 0.1	16.9 ± 0.7	3.3 ± 0.3	8.8 ± 0.9
		W	6.7 ± 0.3	10.1 ± 0.3	16.0 ± 0.9	3.6 ± 0.4	6.9 ± 0.5
S-6	Ikorigbo	D	5.6 ± 0.2	9.1 ± 0.2	18.6 ± 0.3	3.7 ± 0.4	9.5 ± 0.1
		W	6.4 ± 0.3	10.3 ± 0.4	19.2 ± 0.7	3.4 ± 0.6	9.2 ± 0.3
S-7	Obereweje	D	5.5 ± 0.5	5.8 ± 0.1	18.8 ± 0.1	3.9 ± 0.5	7.2 ± 0.1
		W	6.2 ± 0.2	5.9 ± 0.3	19.1 ± 0.5	3.7 ± 0.2	7.1 ± 0.2
S-8	Ojumole	D	6.1 ± 0.3	9.9 ± 0.2	20.8 ± 0.3	4.2 ± 0.1	10.2 ± 0.9
		W	7.8 ± 0.6	8.3 ± 0.6	22.1 ± 0.8	3.6 ± 0.2	8.2 ± 0.6
S-9	Atlantic Ocean	D	6.7 ± 0.4	21.1 ± 0.3	24.1 ± 0.9	3.9 ± 0.4	10.5 ± 0.8
		W	6.9 ± 0.2	18.3 ± 0.5	22.6 ± 0.6	3.7 ± 0.3	8.4 ± 0.4
S-10	Otumara	D	5.9 ± 0.4	7.8 ± 0.4	23.1 ± 0.7	3.7 ± 0.1	10.3 ± 0.5
		W	6.1 ± 0.1	7.3 ± 0.2	21.3 ± 0.4	3.2 ± 0.1	9.1 ± 0.3
S-11	Jinrinwo	D	6.5 ± 0.2	9.6 ± 0.3	22.7 ± 0.4	3.7 ± 0.3	12.2 ± 1.3
		W	6.7 ± 0.3	7.4 ± 0.4	21.2 ± 0.8	3.3 ± 0.2	9.2 ± 1.1
S-12	Odofado	D	5.9 ± 0.4	9.6 ± 0.5	22.1 ± 0.3	3.4 ± 0.4	12.1 ± 1.2
		W	6.7 ± 0.3	7.3 ± 0.2	19.2 ± 0.9	3.3 ± 0.2	9.3 ± 0.9
S-13	Awoye	D	5.8 ± 0.2	10.1 ± 0.5	19.4 ± 0.6	3.2 ± 0.1	13.2 ± 1.2
		W	6.4 ± 0.5	7.8 ± 0.3	17.8 ± 0.9	3.7 ± 0.3	9.8 ± 0.9
SCT	Igbokoda ^a	D	5.8 ± 0.3	3.7 ± 0.4	15.1 ± 0.8	2.6 ± 0.1	15.2 ± 1.2
		W	5.2 ± 0.1	2.5 ± 0.2	16.9 ± 0.4	3.2 ± 0.3	12.2 ± 0.8

Notes: Data are presented as means ± SD for both dry and wet seasons ($N=3$ for each season).
^aReference location. SCT, control; D, dry season; and W, wet season.

several factors control the level of metals with changing environmental conditions, e.g., pH, salinity, and temperature.

The cadmium concentrations for dry and wet seasons were $1.7 \pm 0.6 \text{ mg kg}^{-1}$ ($n=26$) and $2.0 \pm 0.6 \text{ mg kg}^{-1}$ ($n=26$), respectively, with significant mean difference ($F=6.946$, $p=0.036$). In general, adsorption of cadmium onto sediments is strongly pH-dependent, increasing as conditions becomes more alkaline. When the pH is below 6–7, as the case in this study, cadmium is desorbed from these materials (Federal Remediation Technology Roundtable, FRTR 2010). The higher concentration during the wet season can be associated with the resuspension of “disturbed” sediment during flooding.

Average chromium concentration was $3.0 \pm 0.6 \text{ mg kg}^{-1}$ ($n=26$) in dry season but with a slightly higher and significantly different value of $3.1 \pm 0.8 \text{ mg kg}^{-1}$ ($n=26$) in wet season ($F=37.398$, $p=0.001$). Two forms of the hexavalent Cr (Cr^{6+}) can be inferred in the study based on pH, dichromate ion (Cr_2O_7)⁻² (at pH > 6) and chromate ion (CrO_4)⁻² (at pH < 6) (FRTR 2010). These typified the forms of Cr metal during the wet and dry seasons, respectively (Table 1). The mean Cr concentration in the study is far below the Great Lake background concentration 31 mg kg^{-1} (Fletcher, Welsh, and Fletcher 2008).

Table 2. Trace metal concentrations and sediment organic carbon–water partition coefficients (K_{oc}) in sediments and pore waters from Ilaje Rivers, Ondo State, Nigeria.

Metal	Season	Sediment (total, mg kg ⁻¹)		Pore water (mg L ⁻¹)		K_{oc} (L kg ⁻¹)
		Samples	Control	Samples	Control	
Cd	D	1.7 ± 0.6	0.45 ± 0.03	0.8 ± 0.4	0.67 ± 0.02	26 ± 12
	W	2.0 ± 0.6	0.7 ± 0.1	1.1 ± 0.3	0.13 ± 0.01	23 ± 6.6
Cu	D	2396.5 ± 385.6	1842.3 ± 13.0	209.6 ± 41.7	184.6 ± 0.6	138.0 ± 54.6
	W	2458.3 ± 353.3	1983.6 ± 17.2	169.7 ± 37.0	102.1 ± 0.9	186.9 ± 41.6
Cr	D	3.2 ± 0.6	0.76 ± 0.03	0.8 ± 0.3	0.41 ± 0.01	44.0 ± 17.9
	W	2.8 ± 0.5	0.6 ± 0.1	1.1 ± 0.3	0.67 ± 0.01	35.5 ± 12.6
Fe	D	1738.3 ± 801.2	11904.3 ± 12.1	124.5 ± 39.1	104.7 ± 4.6	151.4 ± 44.4
	W	1905.7 ± 705.3	1201.4 ± 2.7	119.1 ± 40.6	96.2 ± 3.0	210.1 ± 67.0
Ni	D	6.0 ± 1.4	2.31 ± 0.03	1.3 ± 0.6	0.50 ± 0.01	59.1 ± 32.0
	W	7.7 ± 1.9	4.70 ± 0.02	1.8 ± 0.5	0.90 ± 0.02	55.1 ± 17.3
Pb	D	13.7 ± 5.9	4.3 ± 0.1	2.5 ± 1.3	0.70 ± 0.02	71.3 ± 44.8
	W	16.1 ± 7.3	6.20 ± 0.04	3.3 ± 1.6	1.21 ± 0.01	61.9 ± 14.9
Mn	D	28.7 ± 6.9	25.7 ± 0.3	11.1 ± 1.6	9.4 ± 0.3	29.2 ± 11.6
	W	37.2 ± 15.6	27.2 ± 0.4	14.2 ± 3.7	11.8 ± 0.3	32.4 ± 9.7
Zn	D	0.22 ± 0.04	0.18 ± 0.01	0.14 ± 0.03	0.11 ± 0.01	17.1 ± 6.2
	W	0.18 ± 0.04	0.13 ± 0.01	0.10 ± 0.02	0.08 ± 0.01	22.4 ± 5.9

Notes: Tabulated results are means ± SD ($N = 13$, re-calculated from means of triplicate determinations from each location). Data excluded reference location. D, dry season; W, wet season.

This may be due to differences in pH and Cr^{6+} anionic nature which makes it associates only with sediment surfaces at positively charged exchange sites. This association decreases with increasing sediment pH coupled with further adsorption by Fe and Al oxide at an acidic or neutral pH (Fletcher, Welsh, and Fletcher 2008).

Concentrations of Cu, Fe, and Mn are found to be very high. The average concentrations during the dry (wet) seasons are 2400 ± 385 (2460 ± 350) mg kg⁻¹ for Cu, 1740 ± 800 (1905 ± 705) mg kg⁻¹ for Fe, and 28.7 ± 6.9 (37.2 ± 15.6) mg kg⁻¹ for Mn. Increased level of these metals has been linked to their ability to enter water systems through surface run-off and leaching (Lee et al. 1998). Significant mean difference exists only with Mn ($F = 59.417$, $p = 0.001$). In soils, it has been reported that Cu adsorbs to the dissolved organic carbon (DOC) more strongly than any other toxic metal, except Pb (Peijnenburg and Jager 2003). The formation of these organic complexes enhances sedimentation and co-precipitation with iron and manganese oxides through exchange and specific adsorption (Jaagumagi 1990).

Lead and Ni, like Cd, are nonessential metals for humans. In this study, average concentrations were 13.68 ± 5.90 mg Pb kg⁻¹ and 16.08 ± 7.26 mg Pb kg⁻¹; for Ni it was 6.00 ± 1.36 mg Ni kg⁻¹ and 6.68 ± 1.91 mg Ni kg⁻¹ during the dry and wet seasons, respectively. Only Ni showed significant mean difference ($F = 39.731$, $p = 0.001$). Lead tends to remain tightly bound to sediments under oxidizing conditions as the case in this study. This is reflected in the concentration of Pb in the pore water (Table 2). This is the characteristic of Pb in the form of insoluble sulfide (Jaagumagi 1990). Except at S-9 for Pb, the concentrations of Pb (though threatening) and that of Ni fall below the background (Pb of 23 mg kg⁻¹ and Ni of 0.031 mg kg⁻¹) values based on Great Lakes pre-colonial sediment horizon analysis (Fletcher, Welsh, and Fletcher 2008).

In comparison with all the metals, least metal concentration in sediment was recorded in the case of Zn. The mean pseudo total concentration was 0.22 ± 0.04 and $0.18 \pm 0.04 \text{ mg Zn kg}^{-1}$ during the dry and wet seasons, respectively, and without any significant mean differences ($F=2.572$, $p=0.1857$, $n=26$). The relatively low concentration observed may be due to the scavenging nature of iron and manganese oxides/hydroxides due to their close association with zinc. In addition, Zn compounds are highly soluble (Jaagumagi 1990).

Total concentrations of Pb, Ni, and Cd in sediments are generally high in the samples collected within the Atlantic Ocean (S-9) and decreases sharply downstream to S-11. These metals are petroleum-related, thus, indicating contributions from oil pollution as reported earlier (Ololade, Lajide, and Amoo 2007; Ololade and Lajide 2009).

The trend in metal concentrations in pore waters slightly differ from those observed for whole sediment metal concentrations during the two seasons (Table 2). During the dry season, the highest 210 mg L^{-1} and least 0.1 mg L^{-1} metal concentrations were found in Cu and Zn, respectively. Similarly, highest 170 mg L^{-1} and least 0.1 mg L^{-1} concentrations were found in Cu and Zn, respectively, during the wet season. In Cu, concentrations were relatively higher in dry season while in Cr, Fe, and Zn,; levels of pore water concentrations were very close between the two seasons. However, for the other metals, pore water concentrations in wet season were higher. The perturbations in wet season lead to the oxidation of metal sulfides which release metals and increase their concentrations in the pore water.

Zinc, Cd, and Cr showed considerable mobility as evident from the higher pore water concentrations relative to the levels in whole sediment (Table 2). Mobility is also significant in Ni and Mn. Though highest metal concentrations in pore water were recorded in Cu and Fe, the percent mobility along with those of Pb are relatively low compared to the percent mobility in other metals. In Pb, restricted mobility has been reported (Jaagumagi 1990). In addition, the lack of mobility may be associated with high OM in the sediment. However, the extensive remobilization of Zn, Cd, and Cr into the dissolved state is indicative of metals associated with mineral surfaces (e.g., clay) or organic materials associated metal. Also, the acidic condition of the sediment may have contributed to the solubility and mobility of these metals as widely reported for soils (Knight et al. 1998; Meers et al. 2006, 2007).

High concentrations of Zn, Cd, Cr, and Ni in pore water signaled potential risk to benthic species. This is further supported by the fact that concentrations of all the US EPA priority metals (Cd, Cr in form of Cr^{6+} , Cu, Pb, Ni, and Zn) in pore waters exceeded the US EPA chronic water quality criteria of 0.0088, 0.050, 0.0031, 0.0081, 0.0082, and 0.081 mg L^{-1} , respectively (US EPA 2009). However, the heterogeneous nature of sediments which account for significant variation in remobilization of the accumulated metals may result in variability of probable side effects from heavy metals across various locations.

In general, the results indicated that sediment pore water of Ondo coastal rivers is rich in virtually all the metals though at different levels. The increased mobility/solubility of these metals in the sediment showed that they are loosely bound and are therefore readily released into pore water solutions. In addition, the sediment characteristic must have favored the solubility and the eventual release into pore water. Anthropogenic enrichment has been associated with this kind of behavior (Förstner 1983; Cheevaporn, Jacinto, and San Diego-McGlone 1995; Blasco, Saenz, and Gomez-Parra 2000). Considering the relative proportion of pore waters resulting from each metal, it can be hypothesized that Zn, Cd, Mn, and Ni are incorporated into the sediment predominantly as adsorbed

species, while others form more insoluble precipitates. This is in agreement with another study (von der Heyden and New 2004).

Attempts were made to establish possible relationship between pore water concentrations and DOC concentration. Highest significant correlation ($p < 0.05$, $n = 28$) were recorded for Zn ($r = 0.9172$) and Cd ($r = 0.9318$). This may likely be responsible for the relatively high solubility of these metals as observed in this study. Highly significant but lower correlation values were recorded in Cu ($r = 0.9013$), Fe ($r = 0.8919$), Pb ($r = 0.8062$), Mn ($r = 0.7827$), and Ni ($r = 0.7505$) with log DOC. This correlation data explored the significance of DOC as a factor in remobilization of these metals in the sediment. Concentration of Cr in pore water was not only insignificant but also negative with log DOC ($r = -0.3069$). Thus, it can be inferred that its remobilization in the study is probably dependent on other sediment characteristics.

In general, Cr, Pb, Ni, and Mn concentrations appeared to be higher in pore water from the study area compared to control samples (SCT). However, pore water concentrations of other metals were similar to those of control sediments.

The sediment–pore water partitioning (K_p) coefficient was evaluated using Equation (1) (Figure 2). The conditional distribution coefficient provides information on the relative mobility of trace metal in the pore water phase with respect to the sediment phase. The lower the value of log K_p , the greater the trace metal remobilization. In this study, the decreasing order of log K_p is as follows: Fe $\approx$ Cu $>$ Pb $>$ Ni $>$ Cr $>$ Mn $>$ Cd $\approx$ Zn. Thus, Zn and Cd dissolved more from the sediment solid phase to the bioavailable pore water phase while Fe and Cu dissolved less. In addition, the observed log K_p indicated greater remobilization of Cd, Cu, Cr, and Pb during the wet season and Fe and Zn during the dry season. The remobilization pattern is undefined for Ni and Mn between the two seasons.

The coefficient K_p of all the metals showed significant correlations with log DOC except in Cr (Figure 3(a) and (b)). Correlation coefficients were high for Zn ($r = 0.939$), Mn ($r = 0.938$), and Cu ($r = 0.9181$). Also for other metals, Cd ($r = 0.875$), Ni ($r = 0.803$), and Pb ($r = 0.7378$). Similar sorptive pattern has been reported for Cu, Zn, Cd, and Pb (Elliot, Liberati, and Huang 1986). Again, K_p for Cr displayed a weak and negative correlation ($r = -0.579$) with log DOC. This further suggests the independence of its partitioning/solubility on the concentration of DOC unlike other metals. However, Cr along with two other metals showed significant positive correlation in sediment pH and log K_p : Cr ($r = 0.8694$), Pb ($r = 0.874$), and Mn ($r = 0.920$). Also, significant negative correlations were recorded in Cu ($r = -0.704$) and Cd ($r = -0.863$). The correlation in Cr is most significant and suggests the dependence of its remobilization on the pH of the sediment.

In order to explore possible relationship between total metal and pore water concentrations, correlation plots between the log of the total metal concentrations (log TM) and log of pore water concentrations (log PW) were generated (Figure 4). Only Pb showed significant positive correlation ($r = 0.897$, $p < 0.05$, $n = 28$). Correlation with Zn was negative ($r = 0.756$, $p < 0.05$, $n = 28$). Correlations with other metals are weak or absent. These observations demonstrate that total metal content in sediment is a poor indicator of partitioning and bioavailability. Therefore, with less available information on correlation trend, the concentration of DOC appears to be a significant factor controlling the bioavailability of significant percentage of the metals.

The trend in K_{oc} is as follows: Fe $>$ Cu $\gg$ Pb $\approx$ Ni $>$ Cr $\approx$ Mn $>$ Zn $\approx$ Cd (Table 2). The values of K_{oc} for Zn and Cd are particularly, relatively low compared to other metals but not close to zero, indicating that the metals interact with sediment.

Figure 2. Field-based partition coefficient ($L\ kg^{-1}$) of (a) Cd, Cu, Fe, and Ni and (b) Cr, Mn, Pb, and Zn during dry (D) and wet (W) seasons across sampling locations.

The low values imply that the metal moves freely within water and biologically available for aquatic biota. However, when K_{oc} is very large as in the case of Fe, Cu and to some extent Ni and Pb, the fractional transport of the metal compared with the water solvent approaches zero, signifying that the compound may be immobilized (Gary and Stephen 2001). In the hydrosphere, humic materials typically make up about 50% of the dissolved organic matter (Aiken 1985). The humic material when bound to mineral phases usually forms coatings which prevent the release of metals into aqueous solution. Consequently, the presence of Cu and Fe could probably be due to lithological source. This is because humic material is a naturally occurring organic matter of plants and microbial origin (Gary and Stephen 2001).

Figure 3. Variation of partition coefficient (L kg⁻¹) of sediment with log DOC of (a) Cd, Cr, Mn, and Zn and (b) Cu, Fe, Pb, and Ni ($n = 28$; $p < 0.05$).

Conclusions

In this study, it was clear that trace metals in sediments can actively partition solid phase and pore water but the modes and the degree of partitioning will vary spatially and temporally according to the predominant biogeochemical processes and conditions characterizing the sediments. Based on our study of the sediment–pore water partition coefficient from Ondo coastal rivers, we hypothesized that significant fraction of the measured Zn, Cd, Cr, Mn, and Ni in the sediment were available to partition rapidly into sediment pore waters. The extraction of interstitial sediment pore water is potentially an important step in the ecotoxicological assessment of polluted sediment as it isolates the aqueous phase to which aquatic organisms are exposed. Cadmium and Ni are metals without any known biological function in the body. Therefore, the considerable mobility in the study gives cause for concern.

All metals, except Cr, showed significant positive correlation with DOC. However, the linear regression analyses of pH and DOC with partition coefficient indicate the dependence of Cr partitioning on pH and those of other metals mainly on DOC. The study also revealed that the total metal content in sediment is a poor indicator of partitioning and bioavailability. These observations are subject to further field-based studies to provide

Figure 4. Correlation plots of log total metals (log TM) in sediment against log pore water (log PW) concentration.

a clear insight into these phenomena. Further studies are also required for evaluating the partitioning behavior with sediment particle sizes, especially the colloidal particles that are mobile and, therefore, easily bioavailable to aquatic organisms.

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