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Exchangeable Metals in the Warri Coastal Sediments, Nigeria

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Abstract: An investigation of the pollution by heavy metals of the surface sediments of Warri River was carried out at three selected industrial locations. The levels of eight exchangeable metals iron, copper, barium, lead, cadmium, chromium, nickel and cobalt in mg/kg were determined by flame atomic absorption spectrophotometry at upstream, effluent zone and downstream of the river in each industrial location. The higher concentrations of some of the metals observed at the discharge points implicated an adjacent industry as one of the contributors of heavy metals in the aquatic system. The concentration ranges of the exchangeable metals decrease in the order Fe» Cu> Cd> Cr> Ba>Ni> Pb> Co in the vicinity of a refinery and Fe» Cu> Cr> Ni> Pb> Cd> Co in steel works, while those in crude oil drilling area decrease in the order Fe» Cu>Ba>Pb> Cd> Ni> Co> Cr. In descending order of predominance, the overall mean ranges of the exchangeable metal concentrations in the sediments are Fe (0.32-5.82), Cu (0.02-3.00), Ba (0-2.01), Pb (0-1.67), Ni (0.03-1.27), Cd (0-0.81) and Cr (0.02-1.27) Co (0-0.34). This order reflects the magnitude of the metals likely to be released into the liquid phase and/or that will be readily available for uptake by aquatic flora and fauna. Correlation analysis of elemental concentrations suggest that some of them are strongly associated, indicating a common source or chemical similarity for the metal pairs.

Key words: Heavy metals, sediments, pollution, flame atomic absorption spectrophotometry

INTRODUCTION

Environmental pollution by heavy metals attracts public interests because they exhibit behaviour consistent with those of persistent toxic chemicals. Unlike many organic contaminants that lose toxicity with biodegradation, metals cannot be degraded further and their toxic effects can be long-lasting[1]. And whilst their concentrations in biota can increase through bioaccumulation, heavy metals are also known to have toxic effects at very low concentrations[2]. Metals are naturally distributed in all phases of the environment, but as a result of technological processes, they often occur at much higher concentrations or in different chemical forms, other than those naturally present. Heavy metals at elevated levels in natural aquatic systems are toxic to organisms[3].

Sediments play a useful role in the assessment of heavy metal pollution[4]. This is because in unperturbed environments, heavy metals are preferentially transferred from the dissolved to the particulate phase and as a result metal concentrations in sediments are generally much higher than in the overlaying water and therefore more easily detected[5]. The benefit of using sediments over water is the elimination of analytical problems associated with the detection of low but significant amounts of metals in water. Hence, preconcentration of metals in sediments need not be addressed. Also, continuous monitoring of water is not essential as sediments concentrations reflect contamination loads over long periods of time[4]. More importantly, when metals enter into the aquatic environment, most of them are scavenged by the bottom sediments, which serve as abode for many sedentary organisms such as Mollusks and Shell fishes. This study attempts to reveal the metals held in exchangeable sites on the surfaces of sediments that are very sensitive to solution chemistry. This implies metals that are readily bioavailable as they are weakly bound and may equilibrate rapidly with the aqueous phase[6]. In Nigeria, there are very few reports of this kind of study and none on Warri River.

Warri River stretches within latitudes 5°21`- 6°00 N and longitudes 5°24`-6°21 E. The outlet of the river to the Atlantic Ocean through the Forcados Estuary made trade between the riverine inhabitants and the Portuguese possible in the 19th century and qualified Warri as the second largest port in Nigeria before 1975.

Warri River supports major commercial activities such as shipping of crude oil, fishery and recreational fishing and prawing. The river has been implicated in heavy metal contaminations in the past[7,8]. However, no attempt was made in any of the previous works to establish

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specifically the sources and levels of readily available metals in the river. This report identifies the sources and the magnitudes of exchangeable metals in the sediments of Warri River.

MATERIALS AND METHODS

Samples of sediments from Warri River were collected into polythene containers at three industrial areas. Location 1 is a Refinery; Location 2 a Steel Company while location 3 is an Oil Drilling Company. Samples were collected at these locations in October 1997. Samplings were made downstream and upstream of the river from effluent zone at a distance of 2.5 km either way. The samples were air-dried, sieved and then stored inside a refrigerator pending analysis.

Five gram air dried, sieved sample was weighed into a 150 mL polythene beaker and 25 mL 1 M ammonium acetate was added. The content was shaken vigorously and left overnight for the supernatant liquid to separate out. The supernatant liquid was filtered into a polythene beaker. This extraction and filtration was repeated five times on the same five gram sediment to allow for complete extraction of the exchangeable metals. The filtrates were pulled together and evaporated to dryness on a silica-evaporating basin on a water bath. 2.5 mL each of HNO_3 and H_2O_2 was added to the residue and the mixture covered with a clock glass. There was effervescence and when it stopped, the clock glass was washed with a few ml of distilled water. The content was evaporated to dryness and the procedure repeated with addition of 2.5 mL each of HNO_3 and H_2O_2. Then, 10 mL of 0.6 M HCl was added to the dry residue and the basin was warmed for 20 min. The content was transferred to a 100 mL volumetric flask and made to the mark with distilled water. The blank was taken on the reagents through the complete procedure except the sample which was omitted[9]. Triplicate determinations were made on the samples.

The concentrations (mg/kg) of eight exchangeable metals iron, copper, barium, lead, cadmium, chromium, nickel and cobalt were determined in the sediments and the blanks with a Computerized Buck Scientific Model 200a/210 Flame atomic absorption spectrophotometer[10]. The instrument working condition and parameters for the determinations are shown in Table 1. Standard solutions of the respective metals were used for calibrations. All chemicals were analytical reagents grade obtained from British Drug Houses.

RESULTS AND DISCUSSION

The result of the analysis of the blank solution indicates no contamination from the reagent used as all the metals were below their detection limits. The mean concentrations of the eight exchangeable metals: iron, copper, barium, lead, cadmium, chromium, nickel and cobalt at upstream, effluent discharged point and downstream of various industrial locations in Warri River are presented in Table 2. Nearly, all the metals were detected in the sediments.

The concentration ranges (mg/kg) of the exchangeable metals decrease in the order Fe» Cu> Cd> Cr> Ba>Ni> Pb> Co in Location 1 and Fe» Cu> Cr> Ni> Pb> Cd> Co in location 2, while those in location 3 decrease in a order Fe» Cu>Ba>Pb> Cd> Ni> Co> Cr. In descending order of predominance, the overall mean ranges of the exchangeable metals in the sediments are Fe (0.32-5.82), Cu (0.02-3.00) and Ba (0-2.01), Pb (0-1.67 Ni (0-0.81), Cd (0-0.81), Cr (0.02-1.27) and Co (0-0.34).

This order reflects the magnitude of the metals likely to be released into the liquid phase and/or that will be readily available for uptake by aquatic flora and fauna. The higher values of the metals at the effluent zones lead naturally to the implication that industries adjacent to the river are responsible for elevated levels of metals in Warri river sediments (Table 2).

The mean values of the metals reveal Fe and Cu to be the most readily bioavailable metals in all the three locations (Table 2).

However, the sediment from location 2 has the highest value of Fe, being a major pollutant from iron and steel company despite the irregular operation of the steel company (Table 2).

The high levels of Ba and Pb in both locations1 and 3 are due to the composition of Ba in drilling mud and the use of Pb as antiknock in petrol[11]. The overall mean ranges of the metals show Fe, Cu and Ba as the most weakly bound metals in the sediments.

Generally, in descending order of predominance, the mean levels of the metals in the sediments may correlate with the concentrations or bioaccumulation of the metals in benthic organisms. However, the bioavailability of metals may not depend on its concentration, but also on those of the sediment components (i.e. oxides of Fe or organics) to which it is sorbed[6]. In particular, exchangeable metals are always considered the fractions that are more readily available to aquatic biota. This indicates that a coating of iron and manganese oxides or organic colloids, which might have inhibited metal exchange, does not protect the exchangeable sites of Warri river sediments.

The correlation matrix with the significant values highlighted is presented in Table 3. The linear regression data was obtained by calculating the Pearson's correlation coefficient, r, with a computer programme

Table 1: Working conditions of Buck Scientific Spectrometer for the determination of metals

Metals	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Characteristic concentration (mg L^{-1})	Detection limit (mg L^{-1})
Fe	248	2	6.5	0.060	0.020
Cu	247	7	5.0	0.035	0.005
Ba	554	7	6.5	0.008	0.170
Pb	283	7	7.5	0.100	0.080
Cd	228	7	5.5	0.010	0.010
Cr	357	7	6.5	0.050	0.005
Ni	232	2	6.5	0.059	0.020
Co	240	2	6.5	0.048	0.005

Table 2: Mean total concentrations of heavy metals in sediments of Warri River at different locations

		Metals (ppm)							
Locations zone		Fe	Cu	Ba	Pb	Cd	Cr	Ni	Co
1	Upstream	3.50±0.02	0.48±0.02	ND	0.27±0.02	0.76±0.03	0.40±0.01	0.29±0.01	0.23±0.02
	Effluent point	4.14±0.03	1.46±0.17	0.62±0.02	0.48±0.03	0.90±0.03	0.7±00.02	0.5±40.01	0.34±0.01
	Downstream	3.50±0.03	1.00±0.02	0.47±0.03	0.39±0.12	0.79±0.19	0.64±0.02	0.38±0.10	0.32±0.04
	Range	3.50-4.14	0.48-1.46	0.00-0.62	0.29-0.48	0.76-0.90	0.40-0.70	0.29-0.54	0.23-0.34
2	Upstream	0.32±0.02	0.02±0.01	ND	ND	0.04±0.02	0.03±0.01	0.03±0.01	ND
	Effluent point	5.82±0.89	3.13±0.03	ND	0.18±0.07	0.10±0.01	1.27±0.03	0.21±0.06	0.08±0.02
	Downstream	3.68±0.28	2.04±0.04	ND	0.15±0.02	ND	0.79±0.16	0.11±0.02	ND
	Range	0.32-5.82	0.02=2.04	0	0.00-0.18	0.00-0.10	0.03-1.27	0.03-0.21	0-0.08
3	Upstream	1.36±0.02	0.02±0.01	ND	ND	0.09±0.02	0.02±0.01	0.06±0.01	ND
	Effluent point	3.96±0.23	3.00±0.08	2.01±0.02	1.67±0.02	0.81±0.32	0.11±0.02	0.81±0.29	0.11±0.02
	Downstream	2.63±0.03	2.68±0.01	1.01±0.01	1.00±0.02	0.36±0.11	01.0±0.01	0.10±0.03	0.11±0.02
	Range	1.36-3.96	0.02-3.00	0.00-2.01	0.00-1.67	0.09-0.81	0.02-0.11	0.06-0.81	0.11
	Overall range	0.32-5.82	0.02-3.00	0.00-2.01	0.00-1.67	0.00-0.81	0.02-1.27	0.03-0.81	0.00-0.34

Values are means of triplicate analysis, ND- Not Detected, (1) Petroleum refinery (2) Steel works (3) Crude oil drilling station

Table 3: Pearson's correlation matrix of the analyzed parameters

	Fe	Cu	Ba	Pb	Cd	Cr	Ni	Co
Fe	1.000	0.692	0.182	0.252	0.370	0.825	0.475	0.463
Cu		1.000	0.556	0.629	0.069	0.424	0.369	-0.007
Ba			1.000	0.981	0.553	-0.333	0.758	0.212
Pb				1.000	0.542	-0.286	0.721	0.198
Cd					1.000	-0.032	0.805	0.872
Cr						1.000	0.005	0.268
Ni							1.000	0.549
Co								1.000

n=9, ά=0.05 if r≥ is 0.360, then the value is significant.

Table 4: Number of significant relationship between parameters obtained by linear regression analysis, R

Couples	Significant correlation values
Fe–Cu	0.692
Fe–Cd	0.370
Fe–Cr	0.825
Fe–Ni	0.475
Fe–Co	0.463
Cu–Ba	0.556
Cu–Pb	0.629
Cu–Cr	0.424
Cu–Ni	0.369
Ba–Pb	0.981
Ba–Cd	0.553
Ba–Ni	0.758
Pb–Cd	0.542
Pb–Ni	0.721
Cd–Ni	0.805
Cd–Co	0.872
Ni–Co	0.549

n=9, ά=0.05 if r≥ is 0.360.

PROCC CORR SAS[12]. Nearly, all the exchangeable metal pairs have positive coefficients. The critical multiple correlation coefficient, R, was obtained from the Table 3 of significant value in order to indicate which of these are significant in statistical sense. The critical value of R with n=9, ά=0.05 is 0.360.

By extracting the values r≥R from Table 3, the number of significant relationships between the parameters, became clear as shown in Table 4. Apparently, there is strong association between most of the couples, suggesting a common source or chemical similarity for them.

CONCLUSIONS

The higher values of the exchangeable metals obtained at the effluent zones implicate the industry adjacent to the river as one of the sources of heavy metals in the sediments of Warri River. The results also reveal the intensity of metals released to the liquid phase and/or metals that are readily available for uptake by aquatic flora and fauna

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