

Seasonal Bioavailability of Heavy Metal Contaminants From the University of Lagos Lagoon, Nigeria

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Abstract

Heavy metals have been implicated as Lagoon pollutants from sources such as agriculture, mining and manufacturing industries and waste water treatment works. A study was carried out in the University of Lagos lagoon to investigate the seasonal bioavailability of the heavy metal contaminants Cd, Cr, Cu, Pb and Zn. The physical parameters pH, redox potential, temperature, TDS and conductivity were measured on site. Dried sediment samples were extracted using the Community Bureau of Reference (BCR) sequential procedure and analysed by ICP-OES. A certified reference material (CRM), BCR 701 (lake sediment) was used for quality assurance with recoveries ranging between 80-120%. Statistical analysis (ANOVA) showed that there was a significant difference between metal distribution in the dry and wet seasons. Cr and Cd were partitioned in the residual fraction (unavailable for uptake). Cu, Pb and Zn were in the available fractions (carbonate, Fe/Mn oxide and organic). Cu was highest in the Fe/Mn oxide and organic fractions. This indicated that an increase in reducing agents and organic matter will avail the Cu. Zn was distributed in all fractions while Pb was found in the Fe/Mn oxide fraction (3.93- 21.3 %). Results showed that the bioavailability of Cu, Pb and Zn was high. Metal bioavailability by BCR indicates a potential risk of pollution in lagoon sediments as the available metals exceeded the permissible Sediment Quality Assessment Guidelines (SQAG's) from Environmental Protection Agency (EPA).

Background

Heavy metals (Cd, Cr, Cu, Pb, Hg) are toxic at elevated concentrations and may cause health problems to users of water from lagoon, reservoirs, dams and wells which has been exposed to metal input (Musyoka *et al.*, 2013). Sources of metal pollutants include weathering of soil, waste water discharge, solid waste deposited into the lagoon by surface runoff transporting pollutants (Grabowski *et al.*, 2001; Jain, 2004; Singh *et al.*, 2005). Metals settle in sediments and bind through processes of adsorption, ion exchange and precipitation (Filgueiras *et al.*, 2002). They are released depending on a number of factors, that include pH, conductivity, salinity, total dissolved solids, temperature and turbidity (Ramirez *et al.*, 2005) (Calmano *et al.*, 1993). For example a slightly acidic environment may increase the availability of metals, as most metals are soluble in acid more than alkaline, however Cr is reported to have high mobility in alkaline environments (Babale *et al.*, 2011).

It is well established that total metal concentration is not an indicator of mobility or toxicity to living organisms. Bioavailability studies are used to measure metal mobility and bioavailability in the environment (Adriano, 2001). This involves fractionation of the total metal contaminant using chemical extraction procedures (Jain, 2004). To assess how metals are partitioned and their availability for uptake, single or selective extractants are used (Adriano, 2001). The extractants are chosen based on selectivity, precipitation and adsorption. Chemical sequential extractions are most commonly used to evaluate metal partitioning and mobility in sediment (Davidson *et al.*, 1998; Margui *et al.*, 2004).

The most common and widely used sequential extraction was first developed by Tessier *et al.* (1979) (Baffi *et al.*, 1998; Tessier *et al.*, 1979). This method involves exposing the sample to the selected extractants in order to leach out the metals depending on their partitioning. The Tessier sequential procedure releases metals from five fractions. The fractions are metals bound to the exchangeable, carbonates, Fe/Mn oxides, organic matter and residual. A standardised sequential extraction procedure, the BCR sequential extraction is used for extraction of metals in soils and sediments (Ho *et al.*, 1997). The BCR sequential extraction assists in identifying and quantifying different defined species, forms or phases in which an element occurs in the material (Van Herreweghe *et al.*, 2003).

Metals bound to carbonates are in the exchangeable phase where mobility is high. There may be the release of the metals due to ion exchange as these weakly adsorbed metals are held by weak electrostatic force. Low pH accelerates the mobility as it breaks the carbonate structure and increases the solubility of metals making them bioavailable to the living organisms (Atwell *et al.*, 1999; Kazi *et al.*, 2005). Metals bound to other fractions typically require a change in environmental conditions to become available.

Constant deposition of the metal onto the surface of most minerals causes co-precipitation. The metals can be mobilised by an influx of reducing conditions in the environment (Kazi *et al.*, 2005). Metals bound to the organic phase are more difficult to mobilise as a result of metals forming strong complexes with organic compounds in an oxidising environment (Atwell *et al.*, 1999). The residual phase is the unreactive or the non-available phase, which is mostly bound to the silicate and can be made available from weathering (Filgueiras *et al.*, 2002) (Farkas *et al.*, 2007; Ianni *et al.*, 2000; Ianni *et al.*, 2001).

Numerous studies have been carried out using the BCR sequential extraction procedure for measuring the mobility of Pb, Cd, Cr, Cu and Zn (Coetzee, 1993; Filgueiras *et al.*, 2004; Singh *et al.*, 2005). In Nigeria sediment quality studies have been carried out in some rivers, dams and estuaries. These were done by analysis of the physical parameters, particle size distribution and metal pollutants. The amount of metal contaminant that is bioavailable was measured by the amount accumulated in an organism (especially fish) and this was used as a measure of toxicity (Wepener *et al.*, 2011). There is limited data on the bioavailability of metals in Nigeria lagoon sediments. Analysis must be undertaken to understand the chemical behaviour of metals and their impact on the environment. Therefore, it will require study into its pollution status and potential impact using bioavailable metal information (Howard *et al.*, 1995). This study investigates the seasonal bioavailability of Cd, Cr, Cu, Pb and Zn. To the best of our knowledge, no data is available in literature on the bioavailability of these metals in the University Lagoon.

Materials And Methods

2.1 Study Area

The University of Lagos also called UNILAG, situated within Lagos Mainland LGA of Lagos state lies between latitude 03.2343°E - 03.34554°E and longitude 06.2135°N - 06.4323°N. It is bounded on the north by Bariga, at the south by Onike and Iwaya, the east by Lagos Lagoon and at the west by Yaba.

The University of Lagos is an institution of higher learning founded in 1962. It presently has three campuses in Yaba and Surulere. The main campus which is of interest in this research is located at Akoka North eastern part of Yaba in Lagos Mainland LGA. It is largely surrounded by the scenic view of the Lagos Lagoon and with an area of 802 acres of land.

2.2. Experimental

2.2.1. Chemicals

The extracting chemicals used were purchased from Merck; Glacial Acetic acid, hydroxylammonium chloride, nitric acid $\geq 69\%$, hydrogen peroxide, ammonium acetate and hydrochloric acid $\geq 37\%$. The certified reference material, BCR 701 was purchased from European Commission, Canada.

2.2.2. Sampling

Eight locations were sampled in two seasons; Dry and Wet season. On site measurements were pH, redox potential (Eh) and temperature using a combined Hanna™ digital pH meter. An electrical conductivity (EC), total dissolved solids (TDS) and salinity were measured using a WTWTM, Oxi 320 oximeter was used for the dissolved oxygen. Lagoon water and surface sediment samples were collected.

2.2.3. Procedure

Sediment samples were air-dried, ground and sieved to 90 μm . A mass of approximately 0.5 g of the samples and the certified reference material (BCR 701) was dried prior to analysis and sequentially extracted using the adapted BCR procedure (Rauret, 2001). The sediment samples and extraction blank were extracted as shown below.

1. Exchangeable	20mL of 0.11 molL ⁻¹ HOAc, was added to the samples and shaken overnight for 16h at 25°C. The samples were centrifuged at SPEED and supernatant was refrigerated for analysis.
2. Fe/Mn oxide	The residue from step 1 was treated with 20mL of 0.5 molL ⁻¹ NH ₂ OH.HCL and shaken overnight for 16h at 25°C. Centrifuging was done as in step 1.
3. Organic	5mL of H ₂ O ₂ at 85°C was added to the residue from step 2: then first hour manual shaking with uncovered vessel and last hour with a covered vessel, 25mL of 1.0 molL ⁻¹ NH ₄ OAc was later added and the samples were shaken for 16h at 25°C. Centrifuging was done
4. Residual	Samples were digested with aqua regia 3:1 (HCl: HNO ₃)

The extracts from each step were analysed using ICP-OES (Perkin Elmer 5300 DV). Analysis of variance (ANOVA) was done for seasonal variations, $p < 0.05$.

Results And Discussion

Statistical analysis (one way-ANOVA) for the total metals showed that there was no significant difference between spring and summer and between winter and autumn. However, there is a significant difference between the dry season and wet season. Therefore we present data from 1 season from each grouping. The data presented shows winter and summer extractions to represent the dry and wet season respectively.

3.1. Quality Assurance

The method was validated (Table 1) with the CRM. The percentage RSD was typically $< 3\%$.

Table 1: Experimental and certified (bold) values for the certified reference material BCR 701

Metal	Step 1	Step 2	Step 3
Cd	8.1 ± 0.1	3.65 ± 0.01	0.24 ± 0.03
	7.3 ± 0.4	3.77 ± 0.28	0.27 ± 0.06
Cr	2.29 ± 0.02	38.2 ± 0.2	114 ± 1
	2.26 ± 0.16	45.7 ± 2	143 ± 7
Cu	59.0 ± 1.3	108 ± 0.4	49 ± 2
	49.3 ± 1.7	124 ± 3	55 ± 4
Pb	3.50 ± 0.09	107 ± 2	7.6 ± 0.1
	3.18 ± 0.21	126 ± 3	9.3 ± 2
Zn	233 ± 2	96 ± 0.1	53 ± 0.6
	205 ± 6	114 ± 5	46 ± 4

Values in mg kg⁻¹

3.2. Physico-chemical parameters

The results (Table 2) show the physico- chemical parameters. The pH ranges from 6 to 8 which is typical for lagoon water (Babale *et al.*, 2011).

Table 2: Physico- chemical parameters

Site code	Seasons	pH		Temperature/ °C		Eh/ mV		TDS/ mg L-1		DO/ mg L-1		EC/ µS cm-1		Salinity/ mg L-1	
A	Wet	6.02		14.8		80		440		11.2		860		0.2	
dry		6.04	24.2			35		18	6			31.2		0	
B	Wet	6.79		15.3		49		395		10.5		772		0.1	
Dry		6.84	26			74		26	6.6			45.4		0	
C	Wet	6.47		16.4		73		396		9.6		774		0.1	
Dry		6.6	25.6			130		26	6.75			45.4		0	
D	Wet	6.38		16.3		79		400		10.7		702		0.1	
Dry		6.77	25.7			115		26	6.9			48.6		0	
E	Wet	6.38		15		158		48		2		1000		0	
Dry		6.59	25.3			97		28	5.8			47		0	
F	Wet	7.1		16.1		55		562		2.9		1269		0.3	
Dry		7.38	26.2			60		44	6.1			75.8		0	
G	Wet	7.25		17.3		59		1594		3.7		5690		1.5	
Dry		7.47	26.3			58		88	6.6			151.7		0	
H	Wet	6.6		15.4		44		820		1.2		1440		0.6	
Dry		7.24	24.4			8		69	6.6			118.5		0	

3.3. Extractable metals

The BCR extraction showed Cd and Cr mostly in the residual fraction. The behaviour has been shown to be typical for these two metals (Babale *et al.*, 2011; Kartal *et al.*, 2006). Seasonally winter had the highest number of metals in the potentially available fractions and when exposed to changes in the environment these metals will become available.

High temperatures in the wet season increase the rate of chemical weathering which in turn release metals and through runoff are deposited in solubilised form into the lagoon (Dekov, Komy, Araújo, *et al.*, 1997). Some data presented will be explained using the physical parameters as studies have shown that they influence the bioavailability of metals (Sauve *et al.*, 2000).

3.3.1. Cadmium

The distribution of Cd was in the following order; residual> organic> exchangeable~ Fe/Mn oxide. This was observed in the wet season where Cd was in high concentration whereas in the dry season most of the measurements were below the detection limit. Though the Cd concentration was high in the wet season, it was mostly in the residual fraction (not available). The Cd concentration that was in the available fractions (carbonate, Fe/Mn oxide and organic) were consistent throughout ranging from 2.0 to 3.0 mg kg⁻¹. All sites showed Cd input from residential to industrial areas as Cd ions immediately discharged from point sources are absorbed into the sediment as they are not mobile over long distances. When the ions are detected in high concentrations in the carbonate phase, it generally implies that a nearby source had some influence (Tsai *et al.*, 2007).

Cd in the exchangeable fraction meant that it was held by weak electrostatic forces and can be removed by ion exchange (Babale *et al.*, 2011). The EPA Sediment Quality Assessment Guideline (SQAG) value for Cd in lagoon sediment is 0.676 mg kg⁻¹ (FDEP, 1994). This indicates that Cd in the exchangeable fraction has a possibility of negatively impacting the biological processes of the ecosystem as it is exceeding the limit value (Klavinš *et al.*, 2000). It has also been shown in other

bioavailability studies that even though Cd exists in low concentrations, it is found mostly in the exchangeable phase and is bound to carbonates (Gunther *et al.*, 2005; Tsai *et al.*, 2002). Metals bound to carbonates (acid soluble fraction) are susceptible to pH changes but in this case Cd bioavailability will not be highly influenced by pH because it is in the optimum level (6- 8).

3.3.2. Chromium

Cr was found mostly in the residual fraction meaning that it is retained in the crystalline structure and not bioavailable (Kazi *et al.*, 2005). It has relatively low amounts in the Fe/Mn oxide fraction, followed by organic and finally exchangeable fractions for all seasons (Table 2). The available fractions do not exceed the EPA SQAG permissible value of 52.3 mg kg⁻¹ therefore there is low toxicity. As shown in Table 2, Cr in winter from the industrial zone was predominantly in the organic fraction whereas in summer it was in the Fe/Mn oxide fraction.

Cr is used in industries and if deposited as hazardous waste into the lagoon, the metal oxides that is CrO₂ will flow with the water and some particulates settle in the sediments (Metze *et al.*, 2005). There is a possibility of Cr input entering from the waste sludge which flushes down the catchment until it reaches the ocean.

Cr exists as Cr (III) and Cr (VI) states and its bioavailability is dependent on the chemical state. The highly soluble, more toxic and bioavailable form of Cr is Cr (VI) (Dirilgen *et al.*, 2002). Both of them are predominant and highly available in humic environments, but Cr (VI) in acidic solution has a high redox potential which shows that it is strongly oxidising and unstable in the presence of electron donors for example organic matter (Metze *et al.*, 2005). The pH in dry season is approximately 6.0 which is weakly acidic and high redox potential up to 130 mV, therefore these can avail Cr (VI) that is bound to the Fe/Mn oxide phase.

3.3.3. Copper

Sediments typically have high concentrations of Cu in the wet season (Dekov, Komy, Araújo, *et al.*, 1997). Cu was predominantly in the organic and residual phase in the dry season (Table 2) making its potential mobility to be limited. In addition these partitioned stable complexes are highly mobile and toxic (Artiola, 2005). Cu bound to the organic fraction in the dry season has the highest percentage (32% of the total concentration). The stable Cu organic complex can be described by anion exchange from binding with hydroxyl and carbonyl functional groups (Iwegbue, 2011) (Coetzee, 1993).

Cu in the dry season has a possibility of being bioavailable under oxidising conditions and can be toxic to the ecosystem. The metals bound to organic matter will be released into the environment by oxidising agents (decomposition processes) (Artiola, 2005). Cu²⁺ is usually adsorbed onto clays especially Fe/Mn oxide while the stable Cu is mostly in organic soils. In the wet season Cu was consistently associated with the Fe/Mn oxide fraction. The EPA SQAG permissible limit for Cu in lagoon sediments is 18.7 mg kg⁻¹ (FDEP, 1994). For highly mobile soluble Cu the levels are below the permissible EPA SQAG limit which indicates less toxicity.

3.3.4. Lead

Pb is predominantly in the Fe/Mn oxide phase (Table 2) in the wet season and mostly unavailable in dry season. This shows that in winter Pb²⁺ is able to replace Fe²⁺ in the Fe/Mn oxide because of the adsorbing capacity and surface area (Iwegbue, 2011). High concentrations of Pb will be bioavailable depending on the reducing conditions and changes in redox conditions. Our data follows the reported trend that Fe/Mn oxide fraction has a high affinity of Pb in the dry season (Fonseca *et al.*, 2013). The available Pb partitioned to carbonates in the dry season is below the EPA SQAG permissible limit (30.2 mg kg⁻¹) hence there is low toxicity threat.

In the wet season Pb was in the residual fraction indicating that it is not bioavailable. However if the Pb-Fe-Mn-oxide phase become available; the concentration of Pb would be above the permissible levels and would pose a threat to the environment. These results are in agreement with another study on seasonal bioavailability of Pb in sediments which showed that Pb was mostly in the Fe/Mn oxide phase in the dry season as compared to the wet season (Iwegbue, 2011).

3.3.5. Zinc

Zn is distributed in all the fractions (Table 2). Soluble Zn attaches to Fe/Mn oxides or organic matter and the mobility and availability is dependable on pH (Balintova *et al.*, 2012). When the pH is basic the metal is likely to be mobile and bioavailable. Concentrations of Zn range from; 3.48- 302 (exchangeable), Fe/Mn oxide (1.08- 95.51), organic (1.09- 23.62) and residual phases (1.05- 259.35) mg kg⁻¹, the year through. In the dry season Zn was consistently unavailable until sites G and H where Zn was primarily bound to the carbonate fraction. The percentage of Zn in the carbonate fraction was 64.4% and 44.2% of the total metal concentration for sites G and H respectively. This indicated that a high amount of Zn in the lower catchment was bioavailable. The same trend was observed in the wet season except that from A to F Zn had an association with the Fe/Mn oxide and organic fractions. The abundance of Zn in the carbonate (easily mobilised) fraction in site G and H shows that there may be influence from the waste sludge management and on-going construction. This flushed down in summer yielding a decrease in total concentration but not percentage contribution. It can be concluded that Zn is a pollutant and primarily from anthropogenic sources. The concentrations are exceeding the EPA SQAG value of 124 mg kg⁻¹ (FDEP, 1994) which shows that the Zn will be toxic to the ecosystem. Zn will be highly bioavailable as the pH and redox in the sediment changes (Iwegbue, 2011).

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Figures



Figure 1

Existing digital map of UNILAG (Source: Department of Geography, university of Lagos.)