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Interaction Profile for As, Cd, Cr and Pb in Surface Water, Superficial Sediments and Background Sediments of Lake Alau, Maiduguri, Nigeria

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ABSTRACT

The interaction profiles for the quaternary heavy metals (As, Cd, Cr and Pb) was investigated in the aquatic media, surface water (SW), superficial sediments (SS, 0-1cm), and background sediments (BS, 20-30 cm) of Lake Alau, Nigeria. SW samples were digested with HNO_3 and sediment samples extracted with 1 M solution of ammonium acetate (NH_4OAc) in a 1:10 weight ratio and analysed by standard calibration methods of flame atomic absorption spectrophotometry. The results show that Cr was found in the highest concentration in all media and the order of concentration in SW was Cr > Cd > As > Pb and Cr > Pb > As > Cd in SS and BS. The inter-metal correlation coefficient (r) values revealed the highest negative correlation values (r= -0.95; -0.92) between Cd and Cr in BS for both wet and dry seasons. Seasonal variations imparted dilution effects which was not statistically significant. However, the metal concentrations are within limits suitable for irrigation and drinking water though with possible long term health implications.

Keywords: correlations, FAAS, heavy metals, quaternary, seasonal variation

INTRODUCTION

Lake Alau is located on latitude 11° 41′ N and longitude 13° 16′ E on the South Eastern (SE) part of Maiduguri, capital of Borno State, Nigeria (Idakwo and Abu 2004; Google Earth 2008). The lake supplies the municipal water treatment plant, the major source of drinking water supply to the capital, apart from sporadic water obtained from boreholes. It also supports a significant number of agricultural activities for an estimated population of 521,492 in Maiduguri, and immediate surroundings, Jere (211,204) and Konduga (156,564) (FRN 2007). They are 16 species of fish in Lake Alau (Bankole and Mbagwu 2000) and farming of several fresh vegetables (Uwah *et al*. 2007) takes place all year around, thus making Lake Alau a very significant water body to Maiduguri and Nigeria.

Lake water quality assessment is an important pollution monitoring tool and has been carried out in similar significant lakes around the world such as Lake Dianchi, South West China (Gray *et al*. 1999), Lake Sapanca, Turkey (Yalcin and Vahdettin 2001), Lake Balaton, Hungary (Nguyen *et al*. 2005), Lake Seneca, NY (Kinnevey and Halfman 2006), Lake Bellandur, India (Lokeshwari and Chandrappa 2006) and, in Nigeria, Lake Chad (UNEP 2004) and Oguta Lake (ILEC 2008), amongst several others. In most studies, pollution associated with heavy metals release into lake waters is being treated as a major cause for concern due to their toxicity, but very little or no attention is given specifically to the quaternary interaction profile for some of the pertinent heavy metals (HMs) such as the quaternary HMs (arsenic, cadmium, chromium, lead; As, Cd, Cr and Pb) as indicated by ATSDR (2004), though the results of such assessment studies may indicate the levels of some or all of this quaternary HMs. According to ATSDR (2004), these metals are found to be frequently occurring as quaternary mixtures especially in hazardous waste sites and have been implicated in joint toxicity actions that are a result of synergy or additivity. However, the individual toxicological profiles for these quaternary metals have been well documented in ATSDR (1999a) for Cd, ATSDR (1999b) for Pb, ATSDR (2000a) for As, and ATSDR (2000b) for Cr. Their joint toxicity and interaction is profiled in ATSDR (2004) in which these metals have been reported to be implicated in a number of human health diseases and environmental degradations such as damage to the vascular system in humans, including Blackfoot disease (a progressive loss of circulation in the fingers and toes that may lead to gangrene), Raynaud's disease, and cyanosis of fingers and toes. It has also caused leucopenia; anemia in humans exposed by the oral route, irritation of the gastrointestinal mucosa and increased hemolysis (ATSDR 2000a). Cd is considered to be a cumulative toxicant with renal diseases as its major cause for concern (ATSDR 1999a). Cr (VI) has been associated with respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects in humans (ATSDR 2000b). Pb has been shown to affect virtually every organ and system in the body in both humans and animals. The most sensitive effects of Pb appear to be neurological (particularly in children), hematological, and cardiovascular (ATSDR 1999b). Since these HMs are commonly associated with hazardous wastes and are known to accumulate in the environment; air, water and soil through anthropogenic activities (ATSDR 2004), the quality of the environment is undermined and human exposures are enhanced thereby from direct contact such breathing contaminated air and from food chain accumulation in plants and animals (ATSDR 1999a).

In view of the immense role of Lake Alau to Borno State and Nigeria, this work seeks to present the concentration levels of these quaternary metals in terms of pollution particularly because they are very likely to be polluted with domestic and agricultural wastes (Wong 1979; Diamant

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1980; Nikoladge *et al*. 1994), which are observed to be the major sources of pollutants in Lake Alau. Also, particular attention is here given to the interaction profile for these HMs particularly for Lake Alau, not reported hitherto, which may provide supportive information on existing literatures i.e. ATSDR (2004) on the profile for these quaternary HMs from a lake system that has relatively low influence from human activities.

MATERIALS AND METHODS

Samples and sampling

Samples of surface water (SW), superficial sediments (SS, 0-1 cm), and background sediments (BS, 20-30 cm) from Lake Alau were collected at six sampling stations for a period of 8 months. These sampling stations were located on the satellite map (**Fig. 1**) using Geko 101 (2003) with position accuracy of 15 m Reset Max Speed (RMS). The duration was categorized into two: dry season (February-May) and wet season (July-October) for 2007. Sampling stations were located on the basis of outlets to water treatment plants and irrigation, S1, S2 and S5 and points of water collection for domestic use by residents around the lake area S3, S4 and S6. Sampling was carried out as described by Radojevic and Bashkin (2006). Samples were collected using precleaned polythene containers on a 2-week basis in each month of the respective season. Homogenized composite triplicates at each sampling station, within about a 50 m radius, and were collected.

Sample preparation

Total metal was analysed in surface water samples according to methods described by Radojevic and Bashkin (2006). This consisted of digesting 50 ml water sample with about 10 ml HNO_3 and heating until a clear solution was obtained, and was made to the mark of a 100 ml volumetric flask with distilled water. Sediment samples were prepared according to the methods described by Dauvalter (2001) which involves the extraction of HMs with 1 M solution of ammonium acetate (NH_4OAc) in 1:10 weight ratio for about 15 h, agitated for 2 h, then centrifuged at 3000 rpm using a Labofuge 300 (Thermo, Germany), and the quaternary metals determined in the solution.

Determination of HMs

Flame atomic absorption spectrophotometry (FAAS) was used to determine the concentrations of four HMs (As, Cd, Cr, Pb) in the prepared samples. A Shimadzu AA-6800 equipped with an ASC-6100 auto sampler and air-acetylene atomization gas mixture system was used for the analyses. The standard calibration method was employed according procedures described by SC (2000) and Vogel (2000).

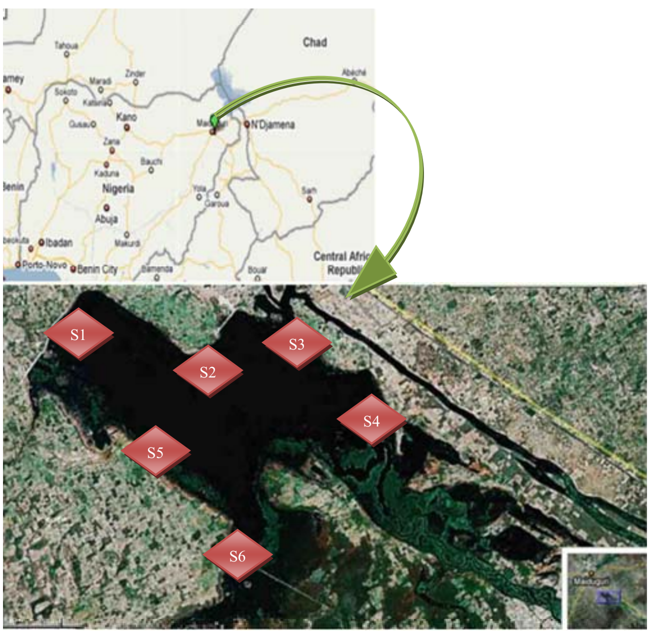

Fig. 1 Map of Lake Alau, Maiduguri-Nigeria showing sampling stations.

Data analysis

Results obtained were expressed as the mean and statistically analysed following ANOVA. The Student's *t*-test was used to assess variations between seasons using a coupled Microsoft Excel+Analyse-it v. 2.10 (Analyse-it® 2007). Variations were considered significant at $p<0.05$.

RESULTS

A summary result of the quaternary heavy metal concentrations in the different aquatic media and seasons at Lake Alau, Maiduguri (**Table 1**) shows a general increase in the concentrations of the four metals in each of the media during the dry season than the wet season with negligible exceptions for Cr which shows an almost steady concentration level. The result also depicts higher concentrations of all quaternary metals in the SS than in SW, and much higher concentrations in BS. Generally, with the exception of Pb in SW, the general increases imparted by seasonal variations in each medium are not statistically significant (**Table 1**).

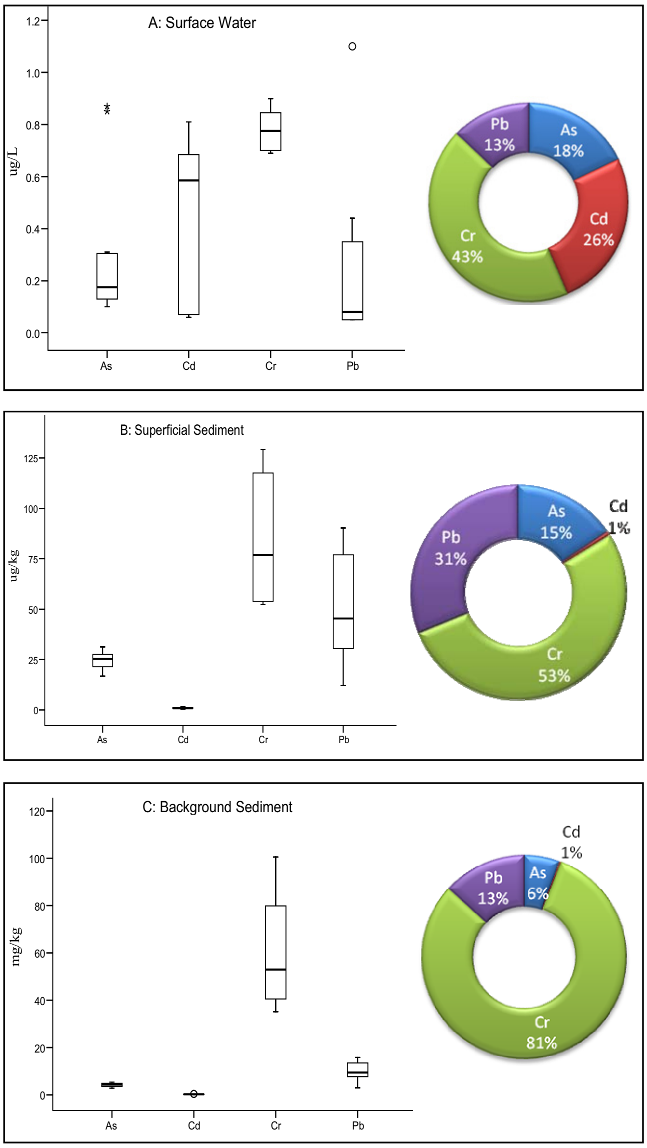

Fig. 2 Box-plots of concentration ranges and interaction profile in percentages of the quaternary heavy metals in the aquatic media of Lake Alau, Maiduguri.

Table 1 Summary (mean ± SEM) result of quaternary heavy metal concentrations in the different aquatic medium and season at Lake Alau, Maiduguri, Nigeria.

		Heavy metals			
Medium	**Season**	**As**	**Cd**	**Cr**	**Pb**
SW (μg/L)	Wet	0.28 ± 0.08	0.43 ± 0.01	0.78 ± 0.11	0.15 ± 0.01
	Dry	0.32 ± 0.06	0.49 ± 0.07	0.78 ± 0.09	0.31 ± 0.04*
	Mean	0.32 ± 0.07	0.46 ± 0.04	0.78 ± 0.10	0.23 ± 0.03
SS (μg/kg)	Wet	24.14 ± 4.12	0.77 ± 0.02	83.62 ± 10.22	48.18 ± 8.44
	Dry	25.27 ± 3.78	1.03 ± 0.11	83.94 ± 9.87	51.05 ± 7.32
	Mean	24.71 ± 3.95	0.90 ± 0.07	83.78 ± 10.05	49.62 ± 7.88
BS (mg/kg)	Wet	4.17 ± 1.02	0.18 ± 0.04	59.45 ± 8.32	9.12 ± 1.69
	Dry	4.18 ± 1.22	0.20 ± 0.01	61.23 ± 9.02	10.57 ± 1.21
	Mean	4.18 ± 1.12	0.19 ± 0.03	60.34 ± 8.67	9.85 ± 1.45

SW = Surface water, SS = Superficial Sediment (0 -1 cm), BS = Background Sediment (20 – 30 cm)
* Significant, $p<0.05$ (Student's t-test) between seasons for each metal

Table 2 Correlation coefficient (r) between concentration values of the quaternary heavy metals in the aquatic media of Lake Alau in wet and dry seasons

		As			Cd			Cr			Pb				
		SW	SS	BS	SW	SS	BS	SW	SS	BS	SW	SS	BS		
Wet season	As				-0.69	0.04	0.84	0.59	-0.46	-0.84	-0.30	0.22	0.88	As	**Dry season**
	Cd	-0.75	0.48	0.89				-0.28	0.62	-0.92	0.24	0.88	0.72	Cd	
	Cr	0.80	-0.35	-0.83	-0.57	0.11	-0.95				0.12	-0.20	-0.54	Cr	
	Pb	-0.18	0.58	0.85	-0.38	0.62	0.70	-0.04	-0.30	-0.51				Pb	

SW = Surface water, SS = Superficial Sediment (0 -1 cm), BS = Background Sediment (20 – 30 cm)

The concentration ranges and percentages of the interaction profile for the quaternary HMs in the aquatic media of Lake Alau, Maiduguri is graphically presented in **Fig. 2A-C**. In SW (**Fig. 2A**), Cd shows the widest range in concentration variation while Cr has the highest concentration (0.78 ± 0.10 μg/L) and thereby constitutes about 43% (v/v). Thus in SW, the order of concentration is Cr > Cd > As > Pb. In SS (**Fig. 2B**), Pb shows the widest concentration range, the least being Cd, but Cr maintained the highest mean concentration (83.78 ± 10.05 μg/kg; 53% w/v). The order of concentrations of the heavy metals in SS is Cr > Pb > As > Cd. This order is similarly maintained in BS, though with a much higher Cr concentration (60.34 ± 8.67 mg/kg; 81% w/v). The percentages per volume (SW) and weight (SS; BS) are only in relation to the quaternary HMs in each media. Thus, Cr increased significantly in the sediments, while the inverse was observed for As and Cd.

The foregoing results are further enumerated by the inter-metal correlation coefficient (r) values shown in **Table 2** in which the highest negative correlation values (r = -0.95; -0.92) were observed between Cd and Cr in BS for both wet and dry seasons. High positive correlations (r = 0.89; 0.85) were observed between As and Cd and As and Pb, respectively in BS.

DISCUSSION

The quality analysis of surface water from Lake Alau for its suitability in irrigation and some related agronomic implications was indicated by Odo and Ijere (1997) about a decade ago, in which the lake water was considered to be in the no-problem limits in respects of some ions (Cl^-, SO_4^{-2}; NO_3^-), metals (Ca, K, Mg, Na; Fe) and other physical parameters (TDS, temperature hardness) which had been measured. Similarly, from the results of this work the concentrations of the quaternary metals are within the limits set by FEPA (1991) and Metcalf and Eddy Inc. (2004) for use in irrigation. Also from the WHO (2006) drinking water quality guideline, the water may be regarded as safe for drinking in terms of these quaternary metals but with long-term health implications, since the water serves as potable water for an appreciable population of resident farmers and fishermen around Lake Alau. However, with an annual rainfall ranging from 500 to 1000 mm (Idakwo and Abu 2004), it was observed that the HM concentrations were reduced (**Table 1**), which is likely to be due to dilution effects during the wet season (Manahan 2005). The results of this work also show that superficial sediments contained higher concentrations of the quaternary HMs than in the surface water. This phenomenon is in agreement with the general observations in the HM concentrations reported in similar study by Dauvalter (2001). In that work Ni, Mg, Fe and Cu showed an average increase of 23% in the SS than in the SW, associated with the mining activities for which the study was conducted. Though in this work, the quaternary HMs indicated by ATSDR (2004) were the metals of concern due solely to their joint toxicity reports. However, in all instances, the general implications of increases in HMs in SS are the increased ecological risks for aquatic biota (Dauvalter 2001; Lokeshwari and Chandrappa 2006). Superficial sediments result from a number of physical, chemical and biological processes, they are important reservoirs of trace amounts of metals, and they are assessed on the basis of bioavailability of toxic metals that pose a danger to aquatic organisms. Their deposition is dependent on the pH and redox potentials of the surface water. Therefore, increasing total concentrations in superficial polluted sediment are very likely to amplify the part of the mobile forms (Dauvalter 2001; Manahan 2005).

The influence of nitrates on As was a very likely cause of the variations observed between SW and SS. This is due to the fact that nitrate accumulates in water systems through agricultural fertilizer and from animal waste runoff, and is known to act as a powerful oxidant and thus has the potential to oxidize arsenite released from lake and stream sediments to the more toxic arsenate, and depending on the concentration of iron in the water, arsenate may accumulate in the water (Senn and Hemond 2002).

The high concentrations of Cr observed in the aquatic media of this work may be connected with natural minerals of the water system, the prevalence of dust deposition during the Harmattan and to the tanning activities, a common vocation in northern Nigeria (ATSDR 2000b; Hati *et al.* 2005). This is very likely to pose long term health implication for the residents who apply the Lake water for domestic purposes.

The complex interactions between metals in the aquatic environment as depicted in the results of the HM interaction profile (**Fig. 2**) and from correlation analysis (**Table 2**) are usually imparted by the cation exchange capacity (CEC) and the exchangeable cation status (ECS) of the metals and the sediment materials. This is also due to the anoxic, reducing conditions and continuous leaching of metals in aquatic bottom sediments, and the likely reason for the variations in the order of concentrations of the quaternary HMs in SW against SS and BS (Bartram and Ballaco 1996; Manahan 2005).

CONCLUSION

The concentration levels and interaction profile for the quaternary heavy metals (As, Cd, Cr and Pb) was investigated in the aquatic media, surface water, superficial sediments (0-1 cm) and background sediments (20-30 cm) of Lake Alau, Maiduguri, Nigeria. The result shows that the HM concentrations are within limits suitable for irrigation and drinking water though with long-term health implications, as it has been observed that some residents around the Lake use its water for domestic purposes. Seasonal variations imparted dilution effects which were only statistically significant on Pb. The interaction profiles for the HMs show varied concentrations and order in each of the aquatic media, with Cr consistently maintaining the highest concentration and order while the other metals varied.

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