

Distribution and chemical fractionation of arsenic in surficial sediments of the Lami coastal environment in Fiji

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Abstract

A case of arsenic contamination has recently been detected in the Lami coastal environment during the course of a heavy metal monitoring in Fiji's coastal environment. Twenty two surficial sediment samples were sampled during the 2008-2009 period, extracted for arsenic and analysed using graphite furnace atomic absorption spectrometry. Two sites within the Lami estuary recorded the highest As levels of 334 and 282 mg kg⁻¹ as dry weight in sediments samples, which has greatly exceeded the local and global average background concentrations. Chemical fractionation studies using a standard sequential protocol showed that As is mostly associated with residual (strong acid extractable) phase of the sediments, however significant amounts of As were also detected in bioavailable (exchangeable, water and acid soluble), reducible and oxidisable fractions. Comparison with standard sediment quality guidelines (SQGs) indicate that As levels are likely to be highly toxic to biota, hence further ecotoxicological studies are warranted to evaluate possible environmental effects on the aquatic environment.

Keywords: Arsenic contamination, estuary, coastal, sediments, trace metal monitoring, Fiji

1. Introduction

The metalloid, arsenic (As), is an environmentally significant element which has been now recognised as one of the world's greatest environmental hazards (Ravenscroft *et al.*, 2009). The average concentration of As in the continental crust is 1–2 mg kg⁻¹ (Taylor, 1972). However, highly elevated levels of arsenic have been documented worldwide in aquatic environments due to natural and anthropogenic causes. Arsenic emission from human activities such as mining, the burning of fossil fuels, wood preservation and pesticide application, account for widespread contamination of soil and aquatic environment (Sharma and Sohn, 2009). The Suva-Lami coastal environment in Fiji is highly exposed industrial areas and has been shown to be polluted with heavy metals like copper, lead and zinc (Gangaiya *et al.*, 2001; Maata and Singh, 2008). Continuous monitoring of toxic metalloids/metals in the Fiji's aquatic environment is thus considered very important to evaluate ecological risks arising from anthropogenic contamination. Therefore, as part of an ongoing environmental monitoring project, this study for the first time reports the incidence of As contamination in the Lami estuary.

2. Experimental

Twenty-two sites (located from 18°6'15"S to 18°7'24"S, 178°23'50"E to 178°25'42"E) throughout the Lami estuary and its surrounding coastal areas as shown in Figure 1, were selected as the sampling sites from October 2008 to September 2009 in three monthly intervals. The sediment samples were collected using a plastic scoop into acid-washed plastic bags, placed in ice and transported to the laboratory where they were homogenised and frozen. The frozen sediments were then oven-dried at 60°C to constant weight and fractions of < 2 mm were obtained using nylon sieves. The < 2 mm fraction of the above samples were then ground with mortar and pestle to obtain < 0.1 mm size for analysis. In order to study As fractionation and potential mobility of As in sediments, the harmonised three stage Community Bureau of Reference

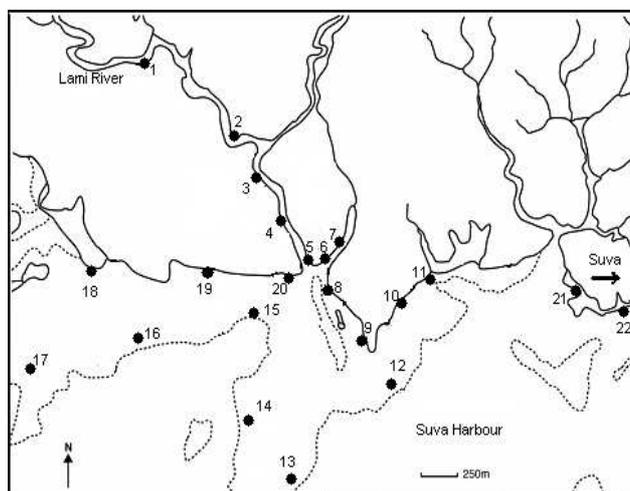


Figure 1. Map of sediment sampling sites in the Lami coastal area, Fiji (Modified from Gangaiya *et al.*, 2001).

(BCR, now called as Standards, Measurements and Testing Programme SM&T) sequential extraction protocol (SEP) was followed strictly (Ure *et al.*, 1993). The residual (fourth) phase of the As fraction was obtained after subtracting the sum of three SEP fractions from the pseudo-total As content of sediment samples, which was extracted using 1.0 g of the sample in a mixture of 10 mL of 1:4 HCl (v/v) and 4 mL of 1:1 HNO₃ (v/v) under reflux for 30 minutes at 95°C, as per the procedure of USEPA Method 200.9 (USEPA, 2001). Arsenic in sediment extracts was analysed using a Perkin Elmer AAnalyst 400 atomic absorption spectrometer with deuterium background correction, equipped with As Lumina hollow cathode lamp, HGA900 graphite furnace and autosampler.

3. Results and Discussion

The levels of As determined in the estuarine and the coastal sediments from the present study are given in Table 1, which were compared with local background levels and global average values for crustal abundance and shale value for As. Generally As levels were low in most

Table 1. Description of geographical coordinates of the location of sampling sites and corresponding As concentrations in sediments (mg kg^{-1} dry weight).

Site	Longitude	Latitude	[As]	C.O.V., %
1	178°24'13.5"E	18° 6'14.7"S	1	4
2	178°24'27.9"E	18° 6'29.2"S	1	6
3	178°24'30.7"E	18° 6'33.9"S	5	4
4	178°24'35.8"E	18° 6'42.6"S	5	15
5	178°24'40.9"E	18° 6'48.5"S	334	150
6	178°24'44.5"E	18° 6'48.5"S	282	110
7	178°24'47.5"E	18° 6'44.9"S	8	12
8	178°24'44.3"E	18° 6'53.4"S	15	25
9	178°24'50.3"E	18° 7'3.0"S	6	15
10	178°24'57.5"E	18° 6'55.9"S	2	8
11	178°25'5.8"E	18° 6'50.6"S	2	10
12	178°24'54.8"E	18° 7'10.1"S	1	4
13	178°24'39.4"E	18° 7'23.9"S	1	5
14	178°24'29.8"E	18° 7'15.6"S	2	13
15	178°24'30.8"E	18° 6'57.2"S	3	8
16	178°24'8.5"E	18° 6'59.9"S	2	3
17	178°23'49.5"E	18° 7'6.1"S	1	14
18	178°24'0.8"E	18° 6'50.3"S	8	11
19	178°24'24.8"E	18° 6'52.7"S	9	13
20	178°24'38.8"E	18° 6'52.2"S	13	27
21	178°25'24.8"E	18° 6'52.7"S	1	15
22	178°25'42.4"E	18° 6'56.2"S	19	5
Local Background ^a			0.27-12.4	
Crustal Abundance ^b			1.8	
Shale value ^c			13	
Effect Range Low (ERL) ^d			8.2	
Effect Range Median (ERM) ^d			70	
Threshold Effect Level (TEL) ^d			7.2	
Probable Effect Level (PEL) ^d			41.6	

C.O.V. – coefficient of variation; ^aMorrison *et al.*, 1997; ^bTaylor, 1972; ^cKrauskopf and Bird, 1995; ^dLong and MacDonald, 1998.

samples and close to background range, except for two sites in Lami estuary. It can be seen that these two adjacent sites, 5 and 6, recorded As levels of as much as 334 and 282 mg kg^{-1} as dry weight in surficial sediments. These were classified as contaminated sites, since the As levels greatly exceeded the background levels. Two sets of SQGs developed for marine and estuarine ecosystems (Long and MacDonald, 1998) were applied in this study to assess the biological significance of As contamination in sediments. Accordingly, the effect range low (ERL), effect range median (ERM), threshold effect level (TEL) and probable effect level (PEL) values and the results from the present studies given in Table 1 clearly show that the sediments from sites 5 and 6 represent As concentrations above which adverse effects are predicted to occur to sediment-dwelling organisms. Thus sites 5 and 6 within the Lami estuary are potentially toxic due to high exceedance of the TEL, PEL, ERL, as well as ERM values. Nevertheless, in the absence of local SQGs, site-specific toxicity tests would better evaluate the toxicity of As to biota, since site conditions may modify the toxicity of As.

It is well known that As contaminated sediment serves as a long-term source of arsenic because its mobility and transport in the environment are strongly influenced to associated solid phase. Arsenic may be distributed among many sediment components in different ways such as: adsorbed on clay surfaces or iron and manganese oxyhydroxides; present in lattice of secondary minerals like carbonates, sulphates or oxides; occluded in amorphous materials such as iron and manganese oxyhydroxides; complexed with organic matter or lattice of primary minerals such as silicates (Sharma and Sohn, 2009). Therefore, the BCR SEP procedure was utilised to study As associations in different sediment chemical phases. The results shown in Figure 2 clearly show that most of the As (68-70%) in the contaminated sites 5 and 6 were associated with the residual fraction, where As is strongly bound to minerals and is least mobile. However, the reducible (bound to Fe-Mn oxyhydroxides) and oxidisable (bound to organic matter and sulfides) fractions of the sediments also had high As content, 15-16% and 9-11%, respectively, which can potentially be mobilised and

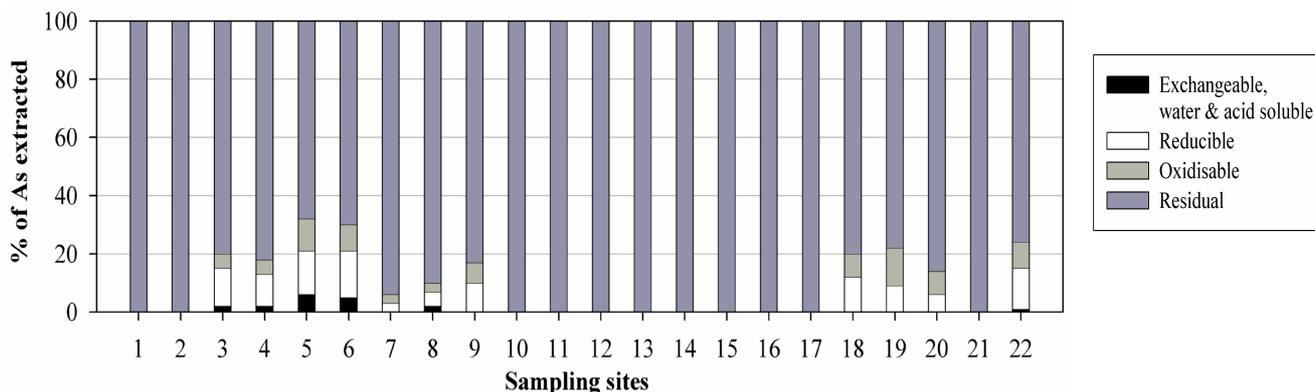


Figure 2. The percentage of As extracted from sediments in each step of the sequential extraction procedure.

Table 2. Comparison of the average As concentrations range (mg kg^{-1}) from locally studied sites and some estuarine and coastal sediments of different regions of the world.

Reference	Location	[As]	Classified
Local (Fiji)			
Present study	Lami estuary and coastal area	1.0-334	contaminated
Gangaiya <i>et al.</i> (1986)	Vitogo River	1.4-14	uncontaminated
	Teidamu estuary	1.3-13	
Htay and Flint (1991)	Navua River mouth	2.83	uncontaminated
Naidu and Morrison (1994)	Lami Rubbish Dump	0.7-45	contaminated
Naidu and Morrison (1994)	Local background	0.1-3.5	uncontaminated
Morrison <i>et al.</i> (1997)	Great Astrolabe Lagoon	0.27-12.4	uncontaminated
Nand (2002)	Laucala Bay	15.8	uncontaminated
	Suva Harbour	9.5-18.0	
Hasan (2004)	Wainibuku River	4.2-9.6	uncontaminated
	Samabula River	<0.5-14.4	
Garimella <i>et al.</i> (2009)	Kadavu Passage	10.6-19	uncontaminated
Other regions of the world			
Acevedo-Figueroa <i>et al.</i> (2006)	Puerto Rico	4.5-24	contaminated
Gonzalez-Perez <i>et al.</i> (2008)	Spain	20-1156	contaminated
De Vallejuelo <i>et al.</i> (2010)	Basque Country	0.6-220	contaminated
Hatje <i>et al.</i> (2010)	Brazil	1-22	contaminated
Luo <i>et al.</i> (2010)	China	5.6-13	contaminated

become bioavailable under changing physicochemical conditions (Sharma and Sohn, 2009). Significant amounts of As (5-6%) were also found in the bioavailable (exchangeable and carbonate) fractions, which has the potential to cause adverse biological effects in the estuary. The significant proportions of As in non-residual fractions, probably indicative of anthropogenic inputs to the Lami estuary.

Present results were compared to similar studies done locally and elsewhere in the world and presented in Table 2. Table 2 shows that the maximum level of As found in the present study was determined to be the highest so far in the Fiji's coastal environment, especially when compared to background As concentrations for Fiji. Naidu and Morrison (1994) had found elevated As near Lami Rubbish Dump, a site physically separated for Lami estuary, however the levels were comparatively low (Table 2). Emergence of this localised incidence of arsenic contamination suggests a separate and recent anthropogenic source from industrial activity in the

vicinity of the sites 5 and 6. The current ongoing research is in progress to identify probable sources of As and the trace metals pollution to Fiji's environment.

3. Conclusions

Arsenic, with a maximum level of 334 mg kg^{-1} (dry weight), was found in surficial sediment samples taken from locations close to the Lami industrial area in the present study. The As levels are well above international standards for sediments and pose ecological risks, however ecotoxicological studies are needed to further evaluate the risk of As to the environment. Such environmental contamination has highlighted the importance of environmental monitoring work in the South Pacific region, in order to create awareness and prevent further degradation of aquatic environments due to anthropogenic activities.

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