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Trace element concentrations in sediments from Kadavu passage, Fiji

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Abstract

Grab sediments, collected from 11 locations from the Pacific Ocean floor in the region between Suva Peninsula and Kadavu Island, Fiji, were investigated for concentrations of 20 elements using neutron activation and high-resolution gamma ray spectroscopy techniques. The sediments were collected at distances between 5-35 km from the mainland and at ocean depths ranging from 500 to 2000 m. A comparison of the elemental abundances of these sediments with those of the Suva lagoon and other nearby locations indicates that the ocean sediments are likely to be derived from sediments washed out to sea from the mainland. The sediments also show no evidence of any metal contamination from the industrial activity in the Suva metropolitan area.

Keywords: *Marine sediments, Suva-Kadavu passage, trace elements, neutron activation, HPGe spectrometer*

1. Introduction

Most of the Fiji islands belong to a class of islands, known as high-standing oceanic islands (HSIs). In HSIs, rivers emanate from relatively high mountains (1000 m or more), flow through steep gradients and traverse short distances before merging with the ocean. The intensity of rainfall in HSIs is generally high and their rivers contribute large quantities of sediment to the ocean (Milliman and Syvitski, 1992; Asquith *et al*., 1994; Carey *et al*., 2002). For Pacific Island countries like Fiji, apart from small areas of the coastal zone, only a very limited amount of data is available about the marine sedimentary resources. There are few opportunities to collect samples from the deep water zones and carry out analysis of them. This project took advantage of a cruise by the Japanese research vessel Koyo Maru to Fiji in December 1998 to collect marine sediments in the Kadavu Passage between Viti Levu, the main island of the Fiji group, and the island of Kadavu (Figure 1). The region surveyed also lies offshore from Suva, the main industrial centre in the Pacific Islands. This study facilitated an assessment of any movement of the metal contaminants found in the near shore area around Suva (Naidu and Morrison, 1994; Morrison *et al*., 2001; Morrison *et al*., 2006) into deeper offshore waters.

2. Materials and Methods

2.1 Sample Collection

Samples were collected from 11 sites as shown in Figure 1. Specifications for the sites are given in Table 1. Station 1 was too close to the coral reef for the cruise vessel to approach and sediment was not collected. The sites were determined by a combination of attempts to cover a good cross section of the Kadavu Passage and the requirements to comply with other research components (water properties as a function of depth, plant/animal life at ocean bottom, fisheries, etc.) of the cruise. Between stations 2 and 9 (*i.e.*, ST2 and ST9) the ocean floor has a relatively uniform slope of 107 m per kilometre from the reference point A, but the depth thereafter remains almost constant around 1900 m. Grab samples were collected using a very large (110 kg) Van Veen sampler. On return to the surface, samples were checked for winnowing (loss of fines), but this was visually determined to be minimal. Subsamples (1 kg) were immediately removed from the top of the grab. Previous work (Pickering and Suda, 2003) had indicated that sediments in the area were predominantly mud (< 63 μ g fraction is $\geq$ 90 %), so no specific particle analysis was completed.

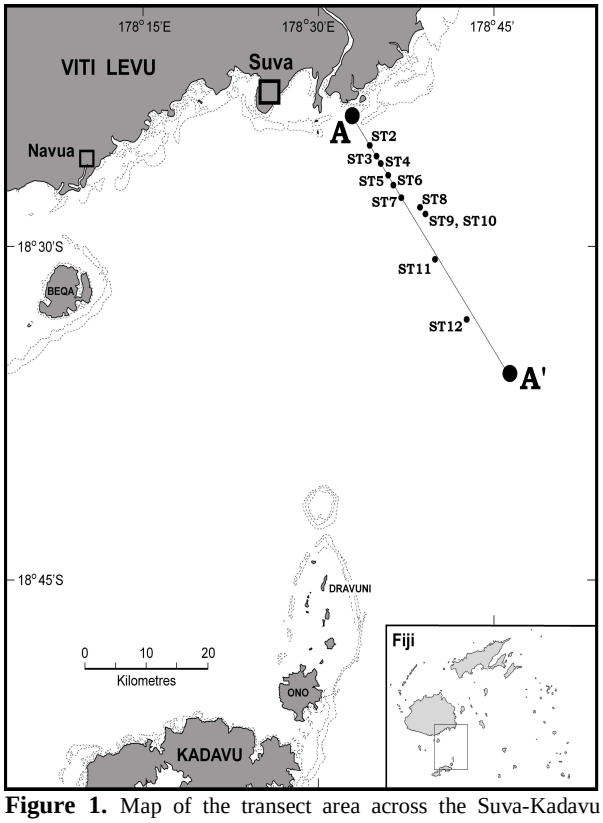

Figure 1. Map of the transect area across the Suva-Kadavu passage showing the sampling stations.

Table 1. Site specifications for the sampling along the Suva-Kadavu transect.

Site	Distance from point A	Start Retrieval		End Retrieval		Depth
	(km)	Longitude	Latitude	Longitude	Latitude	(m)
ST2	4.9	178º 35.5' E	18º 12.4' S	178º 35.5' E	18º 12.4' S	112
ST3	6.3	178º 36.1' E	18º 13.2' S	178º 36.1' E	18º 13.0' S	308
ST4	7.7	178º 36.4' E	18º 13.8' S	178º 36.3' E	18º 13.7' S	547
ST5	9.8	178º 37.4' E	18º 14.5' S	178º 37.5' E	18º 14.5' S	947
ST6	11.2	178º 38.0' E	18º 15.2' S	178º 38.1' E	18º 15.2' S	1232
ST7	13.3	178º 38.5' E	18º 16.3' S	178º 39.1' E	18º 16.2' S	1329
ST8	16.1	178º 40.3' E	18º 17.0' S	178º 39.1' E	18º 17.0' S	1400
ST9	17.5	178º 40.9' E	18º 17.5' S	178º 40.6' E	18º 17.7' S	1870
ST10	17.5	178º 40.9' E	18º 17.5' S	178º 40.6' E	18º 18.1' S	1864
ST11	23.8	178º 41.6' E	18º 21.0' S	178º 41.6' E	18º 20.5' S	1759
ST12	33.6	178º 44.4' E	18º 25.6' S	178º 44.5' E	18º 25.7' S	1915

2.2 Sample Handling and Analysis

In the laboratory, the samples were dried (40°C) and ground to a fine (< 63 μ m) powder. Single aliquots of each sample (about 100 mg) were accurately weighed into a clean polythene bag (12 mm X 12 mm) and heat sealed. Each sample bag was sealed within a second polythene bag as a precaution to contain any leakage of radioactivity after irradiation with neutrons. Duplicate USGS (United States Geological Survey) and IAEA (International Atomic Energy Agency) standard samples of similar size were prepared and stacked together with sediment samples and loaded into an aluminium irradiation can. The USGS standards are finely ground rock powders, while the IAEA standards were of an environmental nature (lake sediment and vegetation). It is well known that the matrix of standards or samples under investigation is not critical in the neutron activation technique using gamma spectroscopy, since self-absorption effects are minimal and can be ignored. The aluminium can was sent to the Australian Nuclear Science and Technology Organisation (ANSTO) for thermal neutron irradiation (4 h at a flux of 2.75 X 10^{12} cm^{-2} s^{-1}). The standards were intended to serve three purposes: a) to correct for the non-uniformity of neutron flux received by the samples during irradiation in the reactor (this correction in the present work was found to be about 18%), b) to measure the elemental concentrations in sediments by using the comparator method, and c) to cross-check the accuracy and reliability of results by treating some of the standards as unknowns.

The irradiated samples were allowed to cool for 5 d and then returned to Suva for analysis using a hyperpure germanium (HPGe) gamma-ray spectrometer (efficiency 24.5 % and resolution 1.84 keV). Neutron activation analysis (NAA) determinations of 20 elements were completed on each sample and the reference materials. Activation products were identified by their characteristic gamma energies and were confirmed later by half-life measurements. Each sample was counted several times to minimise counting errors and improve precision. Measurements were carried out in two phases – immediately upon receipt in Suva for the short-lived radionuclides ($T_{1/2}$ < 7 d) from which concentrations of elements As, Br, La, Na, Sb, Sm were determined. A second set of measurements was carried out after cooling for 3-4 weeks (when all the short lived radionuclides had virtually disappeared) to assess the concentrations of the elements Ce, Co, Cr, Cs, Eu, Fe, Hf, Nd, Sc, Sr, Tb, Th, Yb, and Zn.

Table 2. Elemental concentrations in a standard reference material.

Element	RGM-1	
(mg/kg)	This work	Certified Value*
As	3.1 ± 0.7	3
Br	#	1.34
Ce	52.8 ± 0.6	47
Co	2.14 ± 0.05	2
Cr	6.1 ± 0.5	3.7
Cs	12.4 ± 0.8	9.6
Eu	0.67 ± 0.03	0.66
Fe (%)	1.39 ± 0.04	1.31
Hf	6.6 ± 0.1	6.2
La	24 ± 0.2	24
Na(%)	3.06+0.06	3.02
Nd	18 ± 2	19
Rb	168 ± 10	149
Sb	1.64 ± 0.07	1.26
Sc	4.99 ± 0.02	4.4
Se	0.060 ± 0.009	0.006
Sm	4.31± 0.03	4.3
Sr	134 ± 21	108
Ta	1.2 ± 0.1	0.95
Tb	0.57 ± 0.08	0.66
Th	16.6 ± 0.2	15.1
Yb	3.0 ± 0.3	2.6
Zn	28 ± 1	32
Zr	225 ± 33	219

Used as Standard for calculating bromine. *Govindraju (1994)

3 Results and Discussion

3.1 Reference Material Data

Measured concentrations for the various elements in the reference material RGM-1 and the certified values

(Govindaraju, 1994) are given in Table 2. There was generally good agreement between the experimental and certified values.

3.2 Kadavu Passage Data

Measured concentrations for the various elements of the Kadavu Passage samples are summarised in Table 3. Examination of the data shows that there is some variability in the results, but there are no major patterns with depth or distance from the Viti Levu shore. It is interesting to note that the sediment data in the present work for elements Co, Cr and Zn is close to the HSI data of Carey *et al*. (2002), which would tend to support the possibility that the sediments came from river discharges. As the present work did not, however, measure the other elements (Cu, Mn, Ni and Pb) investigated by Carey *et al*. (2002), this agreement is marginal.

Pearson correlation coefficients for the Kadavu Passage samples were calculated and are presented in Table 4. Correlation analysis shows that there are patterns for some elements, but not for others: Few or very poor correlations were found for As, Br, Cs, Na, Nd, Sb, Tb, Th and Yb. Many of these are not surprising as they do not often give significant correlations in sediments. Strong correlations ($r > 0.9$) were found between Fe and Sc and between Fe and the lanthanides Ce, Eu, La, and Sm as might be expected with the strong geochemical linkage of these elements (Munksgaard *et al*., 2003). Weaker correlations ($0.7 < r < 0.8$) were found between Fe and Co, Cr and Zn; these elements are often closely linked in marine sediments (Chester, 1990). Negative correlations were found between Sr and Fe, Ce, Co, Cr, Eu, Hf, Sc, Sm and Zn as might be expected if the Sr was derived mainly from reef carbonate materials entering the sediment, with the other elements being derived from terrestrial/fluvial sedimentary materials.

There are few data from the South Pacific region with which to compare the results found in this study. A previous study in the Kadavu Passage along a transect slightly further to the west of the present investigation (Pickering and Suda, 2003) found that Zn concentrations (measured by atomic absorption spectrophotometry) averaged 67 mg/kg (range 5.7-103 mg/kg), slightly lower than in this study. Comparison with other sediment metal concentration data is given in Table 5. It should be noted that sites used for comparison do vary in their sedimentary environments and thus conclusions should be treated with caution. Data from the pristine Astrolabe lagoon (Morrison *et al*., 1997) show similar ranges or only slightly lower concentrations (for a limited number of elements where comparable data is available) to the sediments in Kadavu Passage. Comparison with data from Laucala Bay, lying adjacent to the Suva metropolitan area (Nand, 2002) shows similar ranges to the Kadavu Passage samples indicating that there is no significant change in moving offshore and no evidence of movement from the metal pollution hotspots in Suva to the surrounding sediments. Another river, apart from the Rewa river, which discharges considerable amounts of sediment into the ocean is the Navua river (see Figure 1). However, comparison with sediment data from Navua river mouth (Htay and Flint, 1991) shows that the site (Navua) is too far to the west to be of significant interest especially with the predominantly westward movement of sediment along the South coast of Viti Levu.

Table 3. Trace metal concentrations (from neutron activation analysis) of the Kadavu Passage deep sea sediments. All concentrations are in mg/kg, except for Fe and Na (in %).

Element	ST2	ST3	ST4	ST5	ST6	ST7	ST8	ST9	ST10	ST11	ST12
s	14.2	12	19	13	13	16	14.8	14	15.1	10.6	13.6
Br	76.3	49	65	65	74	67	48.6	80.1	49.1	63.3	63
Ce	16.9	19	20	18	17	15	15.6	13.9	15.3	14.8	15.4
Co	23.5	25	23	22	20	19	23.9	18.1	19.8	19.2	20
Cr	85.7	87	94	89	82	73	95.2	70.7	75.9	71.9	73.3
Cs	<0.1	1	0.7	1.2	0.6	1	<0.1	<0.1	0.44	<0.1	1.34
Eu	1.22	1.3	1.3	1.1	0.8	1	1.01	0.76	0.85	0.79	0.84
Fe (%)	6.35	6.5	6.5	6.2	5.7	5.5	5.88	5.49	5.46	5.48	5.66
Hf	2.71	2.9	2.3	2.6	2.6	2.3	2.53	2.18	2.15	1.92	1.86
La	8.99	9.1	8.7	8	7.6	6.8	7.93	6.98	7.44	6.73	7.69
Na (%)	2.72	2.3	0.3	2.6	2.5	2.2	2.24	2.6	2.12	2.37	2.44
Nd	11	12	6	6	8	6	8	11	8	4	8
Sb	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.27	0.61	0.47	0.27
Sc	12.8	13	13	12	11	10	11	10.4	10.1	10.2	10.9
Sm	4.2	4.3	4.3	3.8	3.4	3.1	3.47	2.97	3.1	2.91	3.26
Sr	320	352	550	534	578	691	682	903	1150	869	863
Tb	0.7	0.9	0.6	0.6	0.5	0.5	0.6	<0.1	0.5	0.7	0.5
Th	0.94	1.2	1.1	1.1	0.9	0.8	1.14	0.97	1.04	1.03	0.95
Yb	2.85	3.2	2.9	2.8	2.5	2.5	2.92	2.22	2.58	2.67	3.8
Zn	107	139	178	152	142	73	84	81	79	99	92

Table 4. Correlation coefficients for Kadavu Passage sediment metal concentrations.

	As	Br	Ce	Co	Cr	Cs	Eu	Fe	Hf	La	Na	Nd	Sb	Sc	Sm	Sr	Tb	Th	Yb	Zn
As	1																			
Br	0	1																		
Ce	0.28	-0.18	1																	
Co	0.14	-0.44	0.75	1																
Cr	0.33	-0.32	0.76	0.88	1															
Cs	0.02	-0.18	0.38	0.07	0.01	1														
Eu	0.36	-0.22	0.85	0.88	0.76	0.19	1													
Fe	0.23	-0.09	0.91	0.87	0.81	0.21	0.95	1												
Hf	-0.05	-0.09	0.6	0.75	0.69	0.01	0.67	0.71	1											
La	0.2	-0.2	0.83	0.9	0.75	0.16	0.89	0.94	0.71	1										
Na	-0.73	0.2	-0.58	-0.25	-0.42	-0.09	-0.45	-0.39	0.11	-0.28	1									
Nd	-0.02	0.06	0.06	0.29	0.08	-0.11	0.23	0.26	0.5	0.47	0.3	1								
Sb	-0.28	-0.46	-0.33	-0.28	-0.28	-0.22	-0.22	-0.46	-0.26	-0.34	0.16	-0.2	1							
Sc	0.14	-0.01	0.84	0.83	0.71	0.23	0.93	0.98	0.71	0.92	-0.26	0.31	-0.47	1						
Sm	0.25	-0.12	0.9	0.88	0.77	0.21	0.96	0.99	0.73	0.97	-0.38	0.34	-0.42	0.97	1					
Sr	0.03	-0.16	-0.72	-0.74	-0.64	-0.15	-0.77	-0.84	-0.81	-0.75	0.04	-0.27	0.58	-0.86	-0.84	1				
Tb	-0.27	-0.49	0.62	0.72	0.5	0.21	0.62	0.6	0.48	0.61	-0.08	-0.12	0.15	0.59	0.62	-0.58	1			
Th	-0.05	-0.71	0.49	0.67	0.61	-0.05	0.5	0.51	0.36	0.53	-0.34	0.15	0.12	0.42	0.48	-0.18	0.47	1		
Yb	-0.03	-0.4	0.32	0.44	0.21	0.51	0.34	0.36	-0.07	0.47	-0.12	0.08	-0.25	0.37	0.38	-0.2	0.46	0.31	1	
Zn	0.11	0.06	0.9	0.5	0.64	0.33	0.6	0.77	0.45	0.61	-0.51	-0.12	-0.35	0.7	0.71	-0.6	0.44	0.39	0.15	1

Table 5. Average elemental concentrations in the sediments from the Suva-Kadavu passage compared with other marine environments and continental crust materials. Units are in mg/kg, except for Na and Fe (in %).

Element	Suva-Kadavu Passage, Fiji	Laucala Bay, Fiji	Navua River Mouth, Fiji	Continental Crust	Deep Sea Clay
	This work	Nand (2002)	(Htay and Flint, 1991)	(Chester, 1990)	(Chester, 1990)
As	13.9 ± 2.2	15.8 ± 2.5	2.83	7.9	13
Br	64 ± 11	107 ± 25	4.04	4	100
Ce	16 ± 2	23.2 ± 1.2	11.7	86	100
Co	21 ± 2	20.1 ± 1.1	8.82	13	55
Cr	82 ± 9	80 ± 5	17.3	71	100
Cs	0.6 ± 0.5	NA	< 1	3.6	5
Eu	1.0 ± 0.2	1.1 ± 0.1	< 0.5	1.2	1.5
Fe (%)	5.9 ± 0.4	6.3 ± 0.2	1.78	3.5	6.5
Hf	2.4 ± 0.3	2.3 ± 0.2	1.71	5	4.5
La	7.8 ± 0.8	8.9 ± 0.8	4.15	41	45
Na (%)	2.2 ± 0.7	2.4 ± 0.4	NA	1.42	4
Nd	8 ± 2	12 ± 3	NA	37	40
Sb	0.3 ± 0.1	0.2 ± 0.1	< 0.2	0.9	0.8
Sc	11 ± 1	24.8 ± 0.9	9.09	10	20
Sm	3.5 ± 0.5	2.5 ± 1.7	2.37	7.1	7
Sr	681 ± 250	792 ± 87	NA	278	250
Tb	0.6 ± 0.2	0.4 ± 0.1	NA	1.05	1
Th	1.0 ± 0.1	1.1 ± 0.1	0.79	9.3	10
Yb	2.8 ± 0.4	2.9 ± 0.5	1.27	3.5	3
Zn	111 ± 35	127 ± 7	< 100	127	120

NA – Not analysed

Comparison with data from deep sea sediments in general (Table 5, Chester, 1990) shows that there are no unusual concentrations for the elements measured in this study.

4. Conclusions

Deep sea sediments from the Kadavu Passage, south the Viti Levu, the main island of the Fiji group show no evidence of metal contamination from the industrial activity in the near by Suva city. The metal concentrations are in line with data from other deep sea zones and can be explained by considering the sediments as being derived from terrestrial materials with some coralline inputs.

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