Concentrations of heavy metals and trace elements in the marine sediments of the Suva Lagoon, Fiji

Sitaram Garimella

Alastair McArthur

Marie Ferland

Oswin Snehaleela

Introduction

The Suva Lagoon (which includes the Suva Harbour and the Laucala Bay) is located in the south-east of Viti Levu, the largest of the Fiji islands. The lagoon is sheltered from the Pacific Ocean by a series of barrier reefs (Figure 1) which are submerged at high tide. Seawater enters the lagoon twice a day mainly through the harbour entrance and the Nukulau and the Nukubuco passages. Freshwater enters the lagoon predominantly through the Rewa river and to a lesser extent through the Tamavuva, Lami, Vatuwaqa and the Nasinu rivers. The Rewa river continuously brings a large volume of sediment into the Laucala Bay with the load increasing significantly during periods of heavy rain (Kyaw, 1982). The annual rainfall in the region is about 3000 mm and for most of the year the south-east trade winds prevail. The turbidity levels in the bay are high throughout the year.

There is considerable industrial and commercial activity in the Suva region (consisting the Lami town, Suva City and Nasinu town)

which has a population of about 170,000. The Suva Harbour is surrounded by two major industrial zones which contain shipyards, manufacturing plants, oil storage depots, food processing industries, and the Lami rubbish dump is located on the edge of the waterline. Two sewage treatment plants are located close to the Laucala Bay. A major plant at Kinoya discharges effluents directly into the bay via an outfall pipe 800 m offshore. A minor plant at Raiwaqa discharges into the Vatuwaqa river. Another rubbish dump is located along the Rewa river at Nausori town (not shown in the figure). Two minor industrial zones (at Vatuwaqa and Laucala Beach Estate) are also active around the Laucala Bay. These activities inevitably lead to the discharge of pollutants into the lagoon. According to Naidu and Morrison (1994), much of Suva is located on marl which does not allow septic tank effluents to seep into the ground. Most seepages move into the numerous creeks that discharge into the Suva Lagoon. Further, many storm water drains transport litter from the streets into the lagoon during periods of heavy rain.

A few studies have been done on contamination of the Suva Lagoon. Naidu *et al.* (1991) measured major sewage related contaminants, while Stewart and de Mora (1992) and Maata (1997) found high levels of TBT in the sediment of the Suva harbour. Using chemical methods, Narayan (1993) measured heavy metals in the sediment and shellfish of the Laucala Bay, while Naidu and Morrison (1994) measured the same in parts of the Suva Harbour (close to the Lami dump and the battery factory). Tabudravu (1995) measured Zn, Pb and Cu in sediments collected from the coastal waters of Lami.

The present study aimed to measure the concentration of heavy metals, as well as other trace elements, in sediments from the entire Suva Lagoon. Sediment samples were collected from a wide range of sites (Figure 2) such that the entire lagoon was well represented in terms of environment (shipping channel,reef and the harbour), water depth (range 1-66 m), likely sources of pollution input (industrial areas, shipyards, seafront hotels, Lami dump, sewage treatment plants outfalls) and rivers entrances (the Rewa, Nasinu, Samabula, Vatuwaqa, Tamavuva and Lami rivers). This is also the first major environmental study (in the Suva region) in which the nuclear technique of instrumental neutron activation analysis (INAA) has been used to determine elemental concentrations.

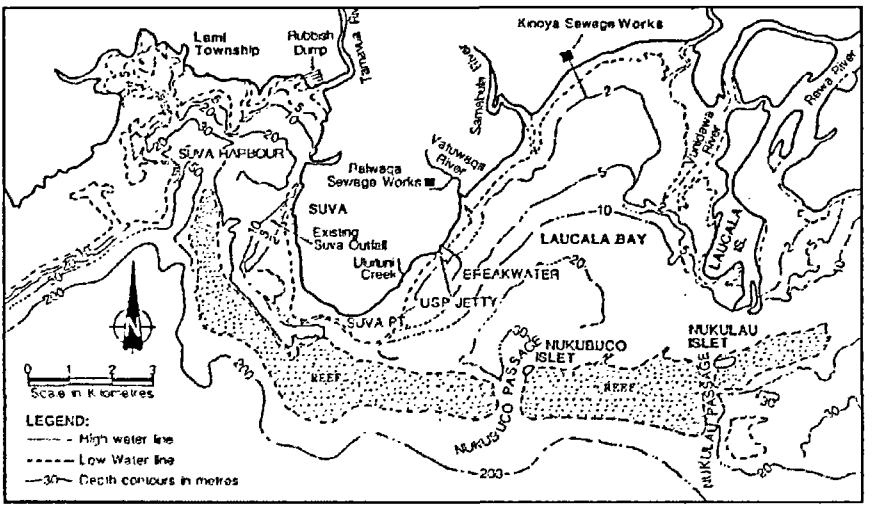

Figure 1
Map of the Suva Lagoon (Naidu *et al.*, 1991).

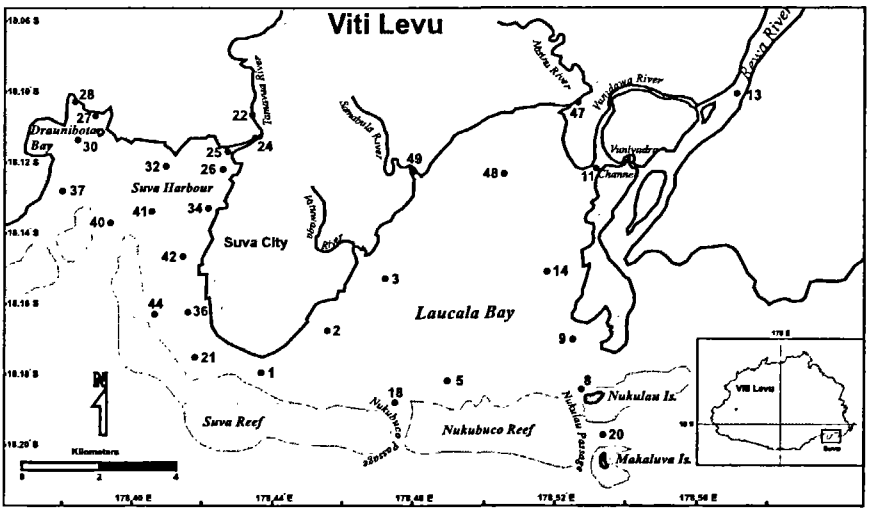

Figure 2
Suva Lagoon with the sampling sites (latitudes and longitudes in decimal notation).

Materials and methods

Method of INAA

In INAA, the irradiation of a multi-element sample with thermal neutrons produces radionuclides with long half-lives. The sample can then be transferred to a counting room for analysis of the induced radioactivity. The radionuclides are identified by their characteristic gamma-ray energies. The elemental abundances can be calculated from the measured activities, nuclear data and the irradiation conditions. Details of the method are described fully by Landsberger (1994), De Soete *et al.* (1972) and Adams and Dams (1970).

To eliminate possible errors in some of the nuclear data (gamma-ray transition probabilities and thermal neutron cross-sections) and irradiation conditions (constancy of irradiation flux over long irradiation periods), elemental abundances were determined by the comparator method. In this method, a 'standard' sample (of known elemental concentrations) and an unknown sample are stacked together and irradiated. Later, the two samples were analysed in the counting room, one after the other, under identical conditions by the same detector. The ratio of the number of gamma-rays counted in each sample for any given radioisotope (normalised to the same sample mass and after correction for the decay of the radionuclide due to delay time) is equal to the ratio of their respective elemental abundances. The accuracy of this method depends mainly on the counting statistics when a *good* standard is chosen, i.e. when its elemental abundances are known accurately.

Sample preparation and irradiation

Sediments were collected from 49 sites (Figure 2) by means of a grab sampler from a boat. Thirty of these sites were then selected for sediment analysis. All samples were dried and ground to a fine homogeneous powder. One aliquot of each was accurately weighed (about 100 mg) into clean polythene bags (12 x 12 mm) and heat sealed.

Each sample bag was then sealed into another polythene bag as a precaution. Three *United States Geological Survey* standards AGV-1 (andesite, four aliquots), RGM-1 (rheolite, two) and STM-1 (syenite, one) and two *Community Bureau of Reference* standards CRM-38 (flyash, one) and BCR-176 (citywaste, one) were similarly prepared. The standards and the sediments were put together into two stacks, with one aliquot of AGV-1 at the ends of each stack (to permit correction for the neutron flux gradient during irradiation). The stacks were then loaded into separate aluminium irradiation cans. Since Fiji does not have its own nuclear reactor, the samples were irradiated in a reactor of the *Australian Nuclear Science and Technology Organisation*, for 4.0 h at a thermal neutron flux of 4×10^{12} $cm^{-2}.s^{-1}$. The irradiated samples were allowed to cool for 5 d, and were flown back to Suva for analysis using a hyperpure germanium (HPGe) gamma-ray spectrometer (efficiency 24.5% and resolution 1.84 keV).

Measurements

The concentrations of 25 elements were measured in each of the 30 sediment samples using the nuclear data provided by Landsberger (1994). The activation products were identified by their characteristic gamma energies and were also confirmed later by their half-lives. The measurements on each sample were repeated one or more number of times, to ensure reproducibility of the data as well as to decrease the counting errors.

The first set of measurements was carried out immediately after the irradiated samples arrived in Suva. A gamma-ray spectrum for each sample was taken over a period of 4000 s. From this set, the short-lived radionuclides ($T_{1/2} < 7$ days) were analysed and the concentrations of As, Br, La, Lu, Mo, Na, Sb, Sm and U in the samples were determined.

A second set of measurements was carried out after about a cooling period of 3-4 weeks. A gamma-ray spectrum for each sample was taken over a period of 6000 s. In this set, the activities of the short-lived nuclides are practically absent and, therefore, the long-lived nuclides could be more accurately measured. From these measurements, the concentrations of Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, Nd, Rb, Sc, Sr, Ta, Tb, Th, Yb, Zn and Zr were determined.

Results

Table 1 presents the calculated concentrations of 25 elements present in the sediments from 4 sites in the Suva Lagoon. Two of these 4 sites (26 and 48) are likely to be fairly polluted. In order to check the accu-

Element	AGV-1*	RGM-1		Yacht Moorings SH26	Harbour Centre SH41	Off VatuwaqaRiver LB3	Kinoya Sewage Outfall LB48
		Measured	Ref.†				
As	0.88	2.3 ± 0.2	3.0	21	12	18	16
Br				22	32	14	32
Ce	67	44 ± 7	47	11.7	10.6	18.4	21.7
Co	15.3	2.0 ± 0.1	2.0	21	10	21	23
Cr	10.1	6.4 ± 1.5	3.7	48	33	88	64
Cs	1.3	11 ± 2	9.6	NP	NP	NP	NP
Eu	1.64	0.62 ± 0.02	0.66	1.30	0.60	1.30	1.20
Fe (%)	4.74	1.2 ± 0.3	1.3	7.1	3.6	5.8	6.8
Hf	5.1	5.6 ± 0.8	6.2	2.0	1.5	2.9	2.7
Hg	**	NP	0.02	0.7	0.6	NP	0.4
La	38	23.4 ± 0.6	24	5.6	4.4	9.9	8.8
Mo	2.7	7.3 ± 6.2	2.3	NP	0.7 ± 0.5	NP	NP
Na (%)	3.2	3.1 ± 0.1	3.05	1.7	1.9	2.1	3.0
Nd	33	17 ± 8	19	ND	ND	ND	ND
Rb	67.3	136 ± 38	149	NP	NP	NP	NP
Sb	4.3	1.3 ± 0.2	1.3	NP	NP	NP	NP
Sc	12.2	4.6 ± 0.6	4.4	31	16	24	28
Sm	5.9	4.1 ± 0.1	4.3	3.4	2.0	3.1	3.6
Sr	662	112 ± 21	108	NP	3155	369	NP
Ta	0.90	0.9 ± 0.3	0.95	ND	ND	ND	ND
Tb	0.70	0.7 ± 0.5	0.66	0.6	ND	0.5	0.6
Th	6.5	14 ± 2	15.1	0.4	0.4	1.1	1.0
Yb	1.72	2.5 ± 0.3	2.6	2.7	1.4	2.4	2.5
Zn	88	28 ± 15	32	219	111	122	149
Zr	227	257 ± 44	219	NP	NP	NP	NP

* used as standard. ND - not determined. NP - No peak observed.

** BCR-176 used as standard. † Govindaraju (1994)

Table 1
Concentrations of trace elements (ppm) measured in USGS standard RGM-1 and in four sediments of the Suva Lagoon.

racy and reliability of our analyses, the concentrations of these elements were also calculated for standards RGM-1, STM-1, CRM-38 and BCR-176, treating them as unknowns. As an illustration, the results thus obtained, together with counting errors (one standard deviation only), for RGM-1 are shown in Table 1 and compared with reference values (Govindaraju, 1994). The agreement (measured versus reference value) is generally good.

Table 2 shows calculated concentrations of some environmentally important elements (As, Cr, Fe, Hg, Zn and Sb) in all 30 sediments samples.

Discussion

The elemental concentrations reported in Table 2, were compared with the Environmental Protection Agency (EPA) Guidelines for Pollution Classification, and with the USGS Sediment Alert Levels (Batley, 1992). The EPA pollution guidelines prescribe margin concentration values, above which the element is said to be a pollutant in the environment. The USGS Alert Levels are concentrations above which the element could pose a threat to the ecosystem and its components. The status of heavy metal pollution in the lagoon will now be considered.

Arsenic

At most sites in the Suva Lagoon, the level of As is 3-7 times the EPA level. The highest level of As reported here, about 20 ppm, was observed near the Lami dump, near some seafront hotels in the Lami town, and at the two sewage treatment outflows. In comparison, Naidu and Morrison (1994) measured As levels of 27-45 ppm at sites close to the Lami dump, and 3-6 ppm at sites within 100 m of the dump (most of these sites have water depths less than 5 m). The fairly high levels of As reported in the present work at locations farther away from the dump indicate a general increase in As levels since 1994.

Site	As	Cr	Fe (%)	Hg	Zn	Sb
LB1	ND	41	2.5	NP	59	NP
LB2	14	160	4.9	NP	95	NP
LB3	18	88	5.8	NP	122	NP
LB5	21	38	4	0.3	84	NP
LB8	16	60	6.4	NP	136	NP
LB9	ND	75	11	NP	138	NP
LB11	ND	73	6.3	NP	135	NP
LB13	ND	198	6.7	NP	95	NP
LB14	ND	79	6.6	NP	138	NP
LB18	ND	20	1.5	NP	33	NP
LB20	16	69	5.8	0.3	128	NP
LB21	ND	26	1.3	NP	32	NP
LB47	19	89	7.3	0.55	172	NP
LB48	16	64	6.8	0.36	149	NP
LB49	18	78	6	0.7	188	0.49
SH22	ND	44	8.1	0.79	258	NP
SH24	ND	53	7.7	0.42	279	NP
SH25	ND	20	6.3	0.84	202	0.53
SH26	21	48	7.1	0.7	219	0.49
SH27	22	22	5.9	0.8	198	NP
SH28	16	88	3.2	0.48	88	NP
SH30	10	38	6.6	0.2	149	NP
SH32	ND	35	7.3	NP	301	NP
SH34	18	34	5.3	0.8	208	NP
SH36	15	71	4.1	NP	94	NP
SH37	18	30	2.2	0.5	64	0.22
SH40	ND	65	4	0.4	150	NP
SH41	12	33	3.6	0.64	111	NP
SH42	ND	79	4.6	0.5	155	NP
SH44	ND	48	2.8	0.9	76	NP
Range	10-22	20-198	1.3-11.0	0.2-0.9	32-301	?
Average	17	62	5.4	0.56	142	?
EPA Pollution Level*	3	25	1.7	1	90	No data
USGS Alert Level *	200	200	No data	20	5000	No data

Key: LB - Laucala Bay, SH - Suva Harbour, ND - Not determined, NP - No peak seen
EPA - Environmental Protection Agency, USGS - United States Geological Survey
* taken from Batley (1992)

Table 2
Concentrations (ppm) of some environmentally important elements in the sediments of the Suva Lagoon.

Chromium

The major sources of chromium are industries and workshops that use paints. The observed concentrations of Cr are more than three times the EPA levels at a third of the sites in the lagoon. Naidu and

Morrison (1994) reported chromium concentrations in the range 16-160 ppm in sediments. At sites close to the Lami dump, their values are in the range of 20-40 ppm. For comparison, our Cr values are 53, 20 and 48 ppm at sites 24, 25 and 26 respectively. Thus, there appears to have been a small increase in Cr levels in sediments since 1994. The highest concentration of 198 ppm for Cr, at site 13 (near mouth of the Rewa river) and down stream of the Nausori rubbish dump, is close to the USGS Alert Level.

Iron

The concentrations of Fe in the present work are in the range of 1.3-11.0%. Tabudravu (1995) reported Fe values in the range 0.13-0.24% in the sediment samples from the coastal waters of Lami. In the present study, the sediment sample from site 32 at the mouth of the Lami river had a much higher concentration of 7.3%. However, the Fe concentrations in our work are much below the EPA pollution levels.

Mercury

Mercury contamination in the lagoon may be due to the use of antifouling paints in the shipyards and other workshops. The concentrations measured in this work are in the range 0.2-0.9 ppm, consistent with those reported (0.3-1.34 ppm) by Naidu and Morrison (1994). Thus, mercury concentrations in sediments of the lagoon remain below the EPA levels.

Zinc

The principal uses of zinc in this region are in the manufacture of galvanised iron, white paint and wood preservatives (which contain $ZnCl_2$). The concentrations of zinc reported here are in the range 32-301 ppm, with 22 out of 30 sites showing levels higher than the EPA limit (90 ppm). Naidu and Morrison (1994) reported zinc concentrations in the range 200-487 ppm in sediments close to the Lami dump. Their figures are similar in magnitude to our Zn

values of 279, 202 and 209 ppm at sites 24, 25 and 26 (which are close to the dump), respectively. Tabudravu (1995) reported Zn values in the range 52-514 ppm in the sediment samples from the coastal waters of Lami. In the present study, the highest Zn concentration was 301 ppm in sediment from site 32 at the mouth of the Lami river.

Antimony

Naidu and Morrison (1994) reported Sb concentrations in the range 15-5625 ppm in sediments close to the seawall near a battery factory (Suva Harbour area). They concluded that the area could be declared a hazardous waste site. The concentrations of Sb observed in our study are much lower, in the range 0.2-0.5 ppm. No EPA and USGS values are available for comparison.

In addition to the above, we measured many trace elements (including the rare earth elements Ce, Eu, La, Nd, Sm, Tb and Yb), in the sediments of the Suva Lagoon (see Table 1). The significance of these elements to environmental studies is not known, but their concentrations are reported here for completeness.

Due to logistic problems (transportation of irradiated samples from abroad), the concentrations of several elements which involve radioisotopes with low half-lives (eg. As, Au, Mo, and Sb) could not be measured satisfactorily. The elements Cs, Se, Sr and Zr are detectable in sediments using NAA, but the technique is not sensitive enough to measure the existing concentrations. Lead (Pb), which is one of the most environmentally important elements, cannot be measured using NAA due to its closed-shell nuclear structure.

Conclusion

The present work, which was undertaken in the entire region of the Suva Lagoon, has shown considerable heavy element contamination in the sediments of the Suva Lagoon. The pollution levels at many

sites are higher than the EPA limits, but remain much below the USGS alert levels. Comparison with previous works suggests that contamination of the Suva Lagoon is increasing with time.

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