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ARSENIC LEVELS IN WATER, SEDIMENTS AND MARINE ORGANISMS
AFTER A SPILLAGE OF ARSENIC (V) OXIDE IN
VILA HARBOUR, VANUATU

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1. INTRODUCTION

Increasing environmental awareness has resulted in considerable importance being placed on contaminants such as toxic metalloids and their deteriorating effects on the quality of the environment. Arsenic, an element used widely in industry and agriculture, is such a contaminant and several studies have been carried out to determine the different forms in which it can be present in the environment (Penrose et al, 1975;Fondekar and Gupta, 1976; Edmonds et al, 1977; Andreae, 1977; 1978; Cannon et al, 1979; Edmonds and Francesconi, 1981; Maher, 1983) and their associated toxicities (Bencko, 1977; Lunde, 1977; Cannon et al, 1983). It appears the inorganic forms are more toxic. An ingestion of 100 mg of inorganic arsenic (As^{3+}) by human beings will result in severe poisoning and as little as 130 mg has proved to be fatal (Browning, 1961). The realisation of the dangers of this substance should result in extreme care being exercised during handling.

Thus when 15 kg of arsenic pentoxide (As_2O_5) , a water soluble powder, was accidentally spilt into Vila Harbour in Vanuatu the authorities responsible were justifiably extremely concerned over the implications of the contamination. The Insititute of Natural Resources was commissioned to investigate the effects of the spill on the water, sediments and biota in the vicinity of the affected area. This report describes the findings of the investigation.

2. METHOD OF INVESTIGATION

2.1 The Spill

On the afternoon of Friday June 29 1984 twelve 15 kg tins of arsenic pentoxide were transported to the BP wharf in the centre of Port Vila on the Island of Efate in Vanuatu (Figure 1). The arsenic pentoxide, 2 tins per cardboard box, each filled with a soluble powder of As_2O_5 in plastic bags was consigned for

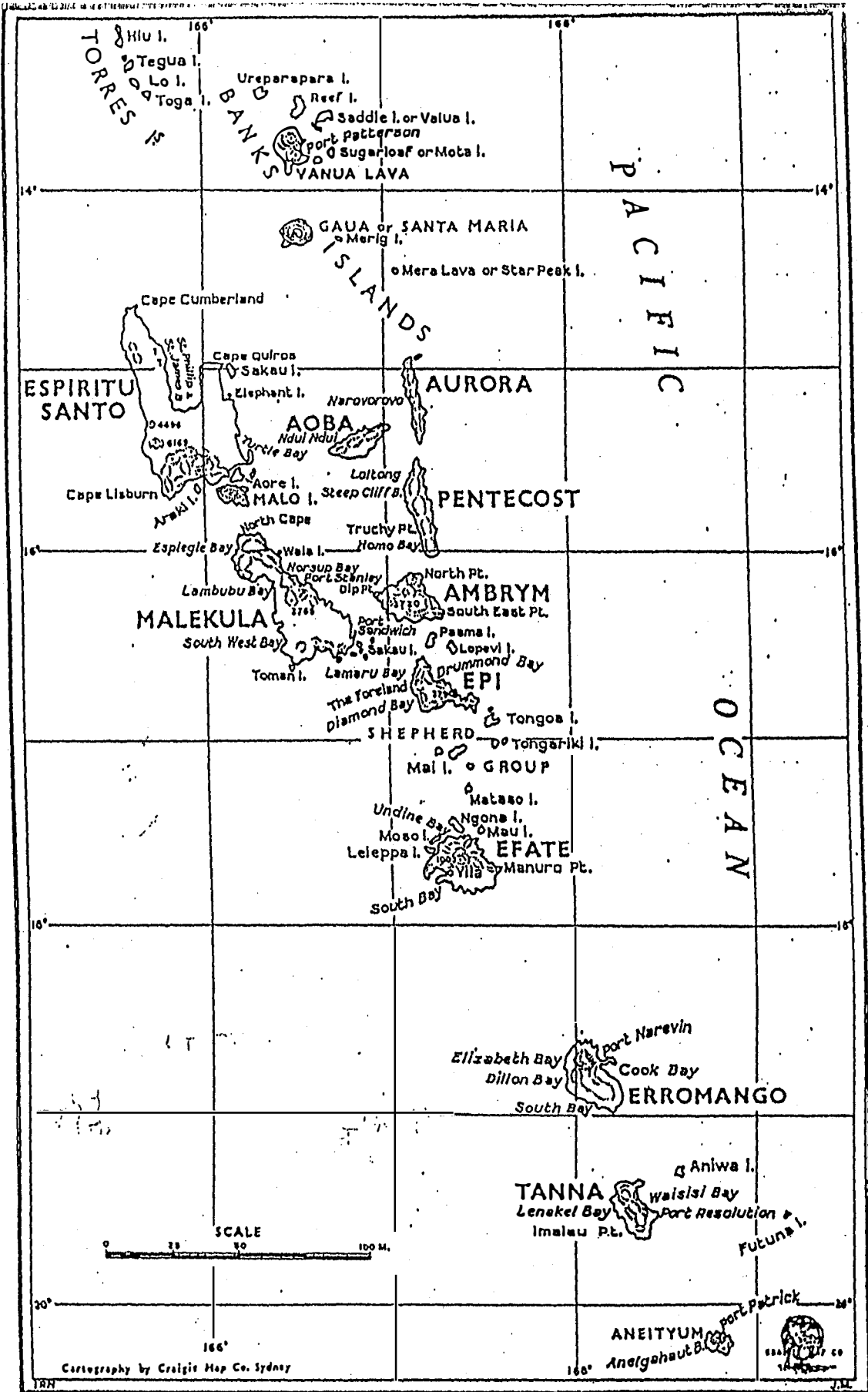


FIGURE 1 VANUATU

shipment to the northern islands of Vanuatu. The next day one case containing two tins was accidentally knocked into the sea between the wharf and a nearby cargo vessel. The tins were retrieved on 3rd July 1984 and it was noticed that they had become ruptured by the movement of the cargo vessel up and down with the tide. About 15 kg of the arsenic pentoxide had dissolved into the sea water. Figure 2 shows the location of the spill in the harbour area.

2.2 Sampling

Taking into account the bathymetry of the spill area, tide movements and shellfish collection areas water, sediment, invertebrates and some fish were collected from four locations around the spill area in early August for arsenic analysis. Figure 3 shows the location of the sampling sites in an enlarged section of the spill area.

Water was only sampled at the two depressions (Sites 1 and 3) where the arsenic combined with sea water may have collected. Site 1 which is the depression south of the spillage point seemed most vulnerable because it is relatively confined and since the tins containing the arsenic pentoxide were ruptured by the movement of the boat at low tide, it seemed likely that the greatest movement of the dissolved arsenic pentoxide would have been in a southerly direction on the first rising tide after the rupture.

Sediment was collected from the two depressions and also at the spill site where the arsenic solution may have penetrated the sea bed.

Shellfish were generally absent in the two depressions but some were found in the adjacent shallower waters and at the spill site and were collected although there was virtually no shellfish collection in the area of the spill because of ship movements and

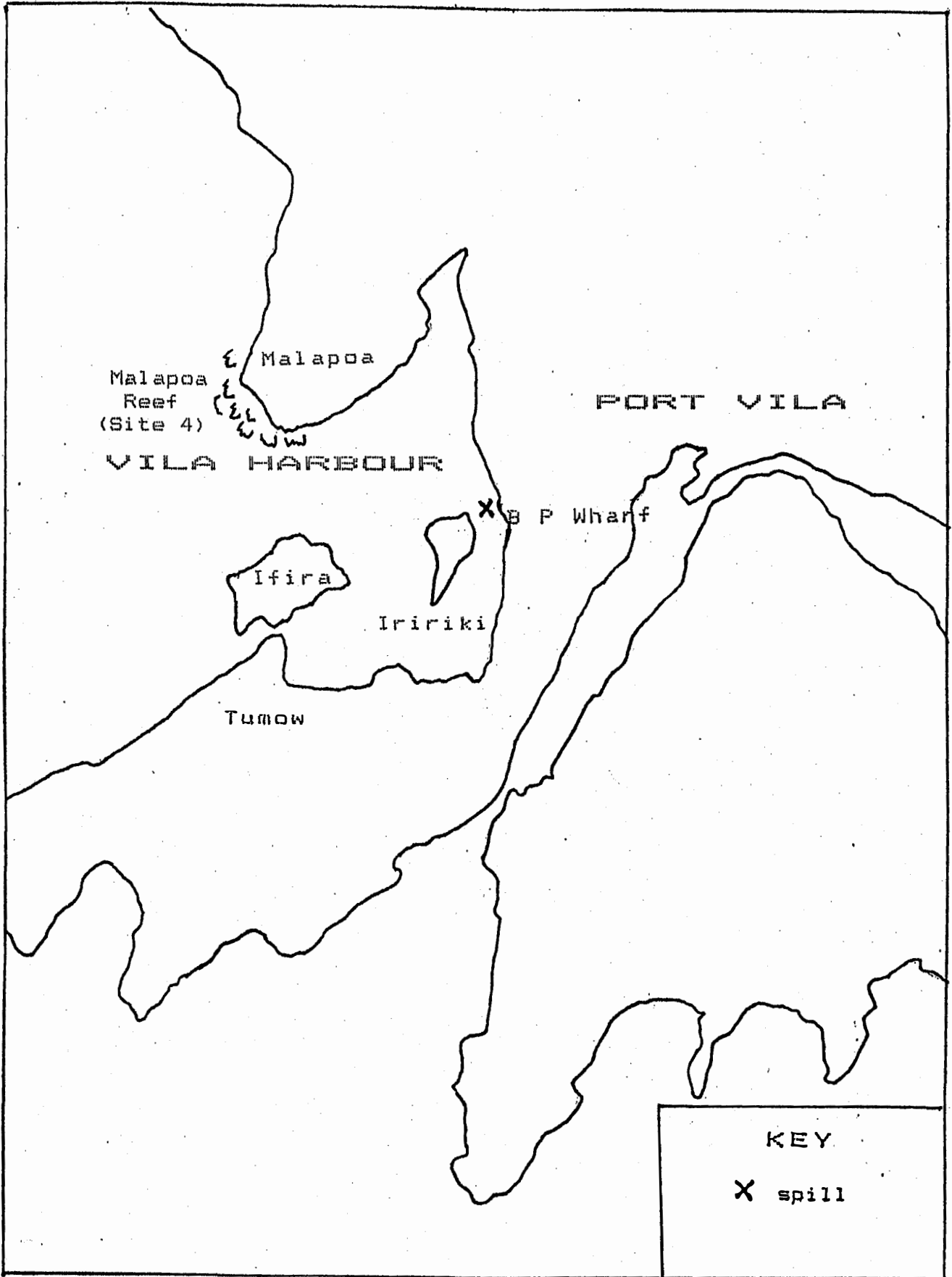


FIGURE 2 Location of spill in Vila Harbour

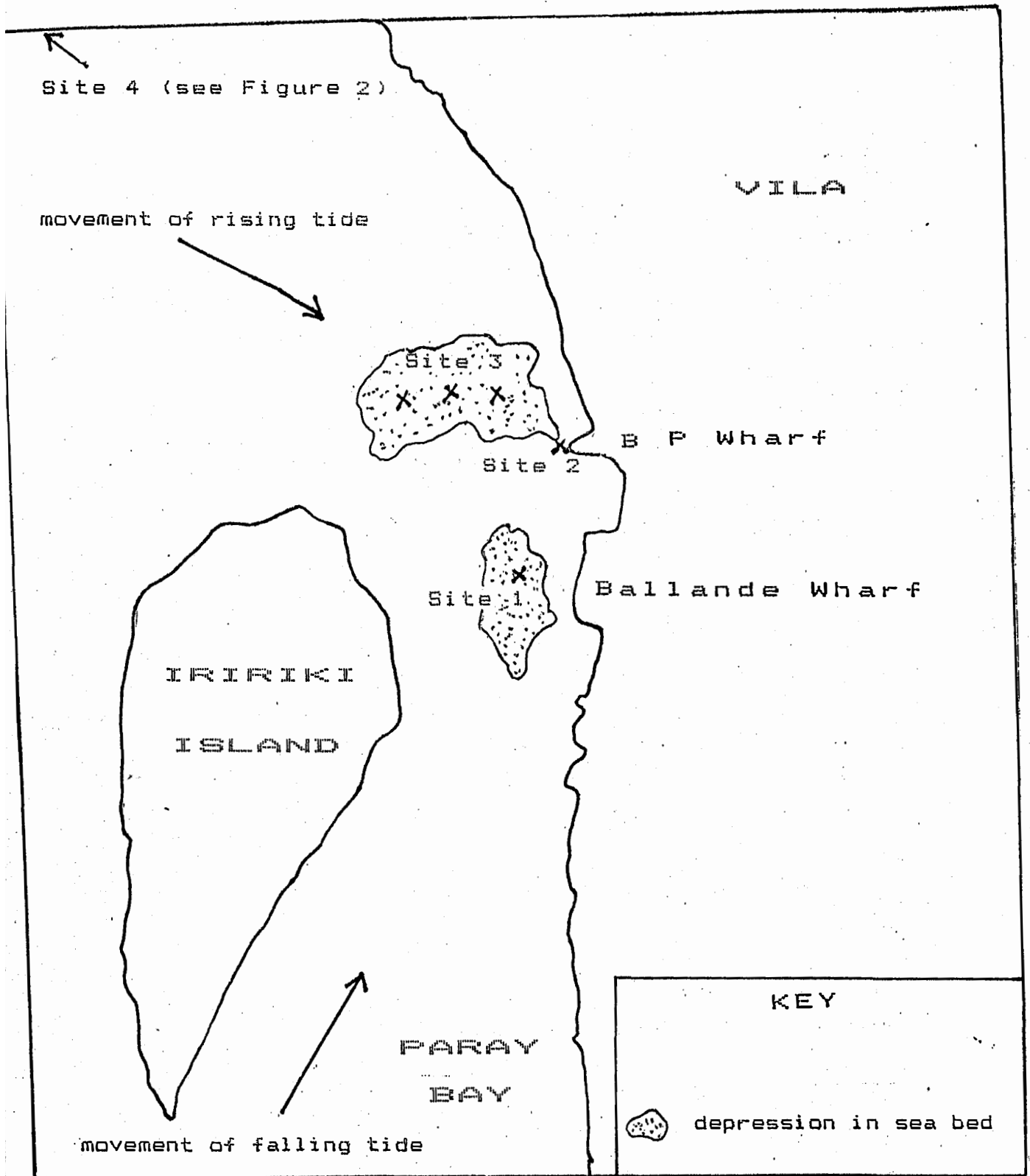


FIGURE 3 Location of sampling sites

limited growth. Malapoa Reef (Site 4) which is just to the north of the map in Figure 3 (see Figure 2) is the closest area to the spill where shellfish is collected. A range of invertebrates was collected from this site. Table 1 lists the types of samples collected from each site.

TABLE 1 Details of Sampling

Site no	Site description	Sample no	Sample type	Species
1	Depression south of spill, Ballande Wharf	1a	Sediment	
		1b	Water	
2	Spill site B P Wharf	2a	Sediment	
		2b	Bivalve	<u>Pinna</u> sp.
		2c	Bivalves	<u>Spondylus butleri</u> and <u>Chama</u> sp.
		2d	Fish	<u>Arothron hispidus</u> and <u>Melichthys buniva</u>
3	Depression north of spill	3a	Sediment	
		3b	Water	
		3c	Bivalve	<u>Chama</u> sp.
4	Malapoa Reef	4a	Reef grazers	<u>Nassarius albescens</u> , <u>Nerita polita</u> , <u>Euchlus atratus</u> , <u>Trochus maculatus</u> , <u>Cypraea tigris</u> , <u>Cypraea annulus</u>
		4b	Filter feeders	<u>Crassostrea echinata</u> , <u>Malleus</u> sp., <u>Chama</u> sp., <u>Spodilyus</u> sp., <u>Arca</u> sp., <u>Atactodea cf. striata</u>

2.3 Sample Preparation and Analysis

Water samples (750 cm³ in plastic bottles) were acidified with 3 cm³ of nitric acid immediately after collection. The water and frozen samples of sediments and biota were airfreighted from Vanuatu to Fiji. They were prepared for analysis as follows :

Water

To 50 cm³ sample in a 150 cm³ beaker, 10 cm³ of conc HNO₃ and 12 cm³ of 1+1 H₂SO₄ were added and evaporated to SO₃ fumes (a final volume of about 20 cm³). This was cooled slightly and 25 cm³ of water and 1 cm³ of HClO₄ added and again evaporated to SO₃ fumes. 40 cm³ of conc HCl was then added and the solution brought to a volume of 100 cm³ with water (APHA-AWWA-WPCF, 1980). This procedure measures the total arsenic content of the sample.

Sediment

The sample was well mixed and a subsample (approximately 1g) placed in a digestion bomb with 3 cm³ of conc HNO₃ and mineralised at 120-150°C. The digested sample was transferred to a beaker and 0.2 cm³ of HClO₄ and 0.5 cm³ of H₂SO₄ added and heated to at least 310°C until SO₃ vapours appeared. After cooling the solution was brought up to a volume of 25 cm³ with distilled water.

Biota

Similar species were combined to form composite samples which were then put through a high speed blender to give homogeneous samples. The samples were mineralised as for sediments.

The arsenic in the digested samples was determined by the arsine generation method described in APHA-AWWA-WPCF(1980). The method is essentially an atomic absorption spectrophotometric technique using a nitrogen-hydrogen flame for atomisation of the arsine (AsH₃) which is generated by reacting the arsenic(III) in the digested samples with sodium borohydride under acidic conditions. Prior to the addition of the borohydride, potassium iodide is added to reduce all forms of inorganic arsenic to arsenic(III) so that the results obtained by this procedure indicate the total arsenic content of the test samples. Optimising the experiment

parameters under these conditions gave a detection limit of 5 ug/l in the test sample.

3. RESULTS AND DISCUSSION

The total arsenic content of the samples analysed are given in Table 2. Before discussing the results of the analyses it is important to point out the extreme difficulty in critically evaluating the effects of the spill on the environment because :

- a. there is no local baseline data available for the samples studied with which the test results can be compared.
- b. sampling was carried out more than a month after the spill and this could have allowed the extinction of any short term effects that may have occurred.

With the above constraints in mind an attempt is made to interpret the results obtained.

Water

The level of arsenic in the two water samples could not be detected by the analytical technique used. Hence the results are expressed as less than the detection limit (ie <5ug/l). The average concentration of arsenic in ocean water is 2.3 ug/l (Riley and Chester, 1971). Geyer (1981) reports that the coastal waters of the Mediterranean contain 2-3.5 ug/l arsenic with the minimal risk concentration being 10.0 ug/l. Although the arsenic concentration in the two water samples is definitely less than the risk concentration reported, the detection limit obtainable with the experimental technique is such that the exact concentration cannot be determined. However given the massive dilution of the arsenic in the sea water and the length of time before sampling was carried out it is probable that the arsenic

concentration in the sea water had dropped to levels reported as average in the literature.

TABLE 2 Results of the Arsenic Analysis

Site no	Sample no	Description	Total As Content
1	1a	Sediment	< 400 ug/kg
	1b	Water	< 5 ug/l
2	2a	Sediment	900 ug/kg
	2b	Bivalve	2.4 mg/kg
	2c	Bivalves	6.5 mg/kg
	2d	Fish	370 ug/kg
3	3a	Water	< 5 ug/l
	3b	Sediment	< 400 ug/kg
	3c	Bivalve	5.9 mg/kg
4	4a	Composite reef grazers - gastropods	6.2 mg/kg
	4b	Composite filter feed- ers-bivalves	5.6 mg/kg

Sediments

The results show that there is an accumulation of arsenic at Site 2. It is possible that this accumulation is the result of the spill since similar sediment samples at adjacent sites contain markedly lower concentrations of arsenic.

The arsenic content at Site 2 is considerably lower than the levels (1.4 to 14 mg/kg) found occurring naturally in some coastal sediments of north west Viti Levu, Fiji (Gangaiya et al, 1986). However it cannot be concluded from this that the Vanuatu sediments contain natural background levels of arsenic. It is actually the bioavailable fraction rather than the total quantity that is of environmental importance. Perhaps a

measurement of the bioavailable fraction of arsenic at Site 2 would have showed interesting results.

Biota

The results of the analysis show that the fish contained the lowest level of arsenic (0.37 mg/kg). A range of 2 to 7 mg/kg was obtained for the various bivalves and the average content in gastropods was found to be 6.2 mg/kg. The comparatively higher levels of arsenic in these organisms in itself is not an indication of arsenic contamination. Marine organisms have been found to have a distinct ability to accumulate arsenic in their bodies by several orders of magnitude over the concentration in the surrounding waters. An examination of the literature for the arsenic content of marine organisms indicates the wide ranges reported. For example, clam species off the west coast of Canada are reported to contain from <0.5 mg/kg to 15.6 mg/kg of arsenic (LeBlanc and Jackson, 1973). Benson and Summons(1981) have worked on arsenic accumulation in Great Barrier Reef invertebrates and have shown considerable accumulation of the order of 1000 mg/kg in giant clam and other symbiotic inveterbrates. Work on some bivalves commonly found in the coastal waters of Fiji has shown their arsenic content to be 2 to 3 mg/kg (Institute of Natural Resouces, unpublished data). The point being made is that given the wide range of values reported and without any baseline values for the species studied it is virtually impossible to determine whether the arsenic contents in these organisms are natural or the result of contamination.

However, regardless of the origin of the arsenic in these organisms it is most probable that that the arsenic has been concentrated in a form that is non-toxic. It was not possible with the resources available

to determine the different forms of arsenic but other studies have shown that most of the arsenic in marine organisms is present as methylated compounds such as trimethylarsine and arsenobetaine which have been found to be non-toxic to human beings (Cannon et al, 1983). These compounds are excreted in the urine. A study carried out to determine whether any toxic inorganic forms were also present has indicated this fraction to be insignificant (Maher, 1983). Thus the ability of these marine organisms to methylate arsenic and accumulate it is considered a natural detoxifying mechanism in the environment.

4. CONCLUSION

This investigation showed that the arsenic content of the water, sediments and biota in the Vila Harbour area are comparable to or less than levels found naturally in such samples. However, as already pointed out, it cannot be concluded from this observation that the arsenic spill did not have any effect on the marine environment. Changes in the arsenic content of the various samples could be manifested in only slight increases whilst still remaining in the ranges reported as average. Therefore without any appropriate baseline data it is difficult to assess fully the effect of the spill. In spite of these shortcomings it may be concluded that the spill did not exert any gross effects on the environment in Vila Harbour.

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