TRACE ELEMENTS IN FISH OVERLYING SUBAQUEOUS TAILINGS IN THE TROPICAL WEST PACIFIC

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Abstract. From 1972–1989, Bougainville Copper Limited (BCL) discharged mine tailings into Empress Augusta Bay on the west coast of Bougainville Island, Papua New Guinea. For a decade (1977–1987), trace elements (Cu, Pb, Zn, Cd, Hg and As) were measured in muscle tissue and organs of 8 species of tropical marine fish common to both the east and west coasts of the Island. Metal concentrations were not elevated in muscle tissue of west fish compared with those from the east coast. Concentrations of Cu, Pb, Zn and Cd in fish muscle from both coasts ranged from 10–15% of recommended maximum residue limits (MRLs), whereas concentrations of Hg in muscle were slightly higher, ranging up to $\leq$ 80% of the MRL (0.5 mg kg^{-1} Hg wet wt.). Maximum total As concentrations (3.6 mg kg^{-1} wet wt.) were recorded in the shark (*Rhizoprionodon acutus*), while highest Hg values (0.76 mg kg^{-1} wet wt.) were found in hammerhead sharks (*Sphyrna lewini*) from both coasts. Despite significant temporal variations in Hg and As concentrations in muscle tissue of some west coast fish populations ($p < 0.05$), there was no evidence for bioaccumulation or biomagnification of any of these metals during the 10 yr period, even in the soft organs (liver and kidney) of fish. Several site specific factors contributing to absence of metals uptake from tailings are discussed.

Keywords: Bougainville Island, coastal marine fish, environmental monitoring, heavy metals, marine tailings disposal, Papua New Guinea

1. Introduction

Industrial development in the 20th Century has brought with it increases in metals and metalloids in virtually all compartments of the Earth's ecosystems (Stoeppler, 1992). Coastal marine environments are potentially among the most significantly effected by trace elements because the compartment is convenient for waste disposal and is also being recommended for dumping if accompanied by adequate geochemical engineering (Forstner, 1995). Evidence for release of trace elements from sediments dumped in the marine environment has been presented for dredge spoil (Holmes *et al*., 1974; Prause *et al*., 1985) and mine waste (Ellis, 1988; Salomons and Eagle, 1990) while increased concentrations of trace elements in coastal fish resulting from waste disposal has been documented for sewage, including industrial and stormwater (Chan, 1995; Gibbs and Miskiewicz, 1995) and mine waste (Ellis, 1988).

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Mining history has created an acute social perception that sub-aqueous waste disposal, has high potential for deleterious alteration of aquatic environments. There are certainly adequate reasons for this view with well documented cases of surface water contamination from both abandoned (Allan, 1995) and operating mines (Sengupta, 1993) leading to formulation of complex strategies for detection and control of acid rock drainage (Hutchinson and Ellison, 1992).

Like other areas of the world, standards for new mining ventures in Papua New Guinea (PNG) have become progressively tightened in order to balance conservation with development demands. In the early 1970's however, when Conzinc Rio Tinto Australia (CRA), now Rio Tinto started its Bougainville Copper Mine in PNG, the Australian Administration sanctioned direct disposal of tailings into the Jaba River system which flows into Empress Augusta Bay on the west coast of Bougainville Island. Tailings input exceeded 120 000 tonnes per day by 1989 when civil unrest forced mine closure. Over 60% of this input was conveyed to Empress Augusta Bay (Jeffery *et al*., 1988), a shallow (< 60 m deep) coastal environment with a uniform soft bottom (Figure 1).

The geochemical behaviour of trace elements in tailings, waste dump leachate and river water has been described for the terrestrial portion of Bougainville Copper's tailings disposal system by Jeffery *et al*. (1988), while natural background trace element concentrations in fish from the east coast of Bougainville Island up to 1981 have been documented by Powell *et al*. (1981). However, tailings disposal effects on the marine environment of the west coast have not been previously described despite a more generally stated need for research of disposal sites by Allen (1995).

The purpose of this paper therefore, is to examine the extent of bioaccumulation of trace elements in the west coast aquatic foodchain, by comparing trace element concentrations in east and west coast tropical fish populations during a decade of monitoring from 1977–1987. The west coast fish stocks were associated with uncontrolled tailings dispersal into Empress Augusta Bay starting in 1972.

2. Methods and Materials

Fish were collected from three east coast sites and four west coast sites (Figure 1) using 10 cm stretched mesh surface gillnets. Four days were spent at each site as described by Powell *et al*. (1981) and on each day, nets were set at 1200 hr and fished at 1800, 2400 and 0600 hr on the following day. Captured fish were placed immediately on ice, transported to the laboratory each morning and the standard length (mm) and weight (g) of individual fish recorded. A sample of edible muscle tissue was taken from the dorso-lateral musculature (Powell *et al*., 1981; Brooks and Rumsey, 1974) skinned, washed in distilled water, wrapped in aluminium foil and frozen prior to analysis. Liver and kidney tissue was also removed and similarly preserved for analysis.

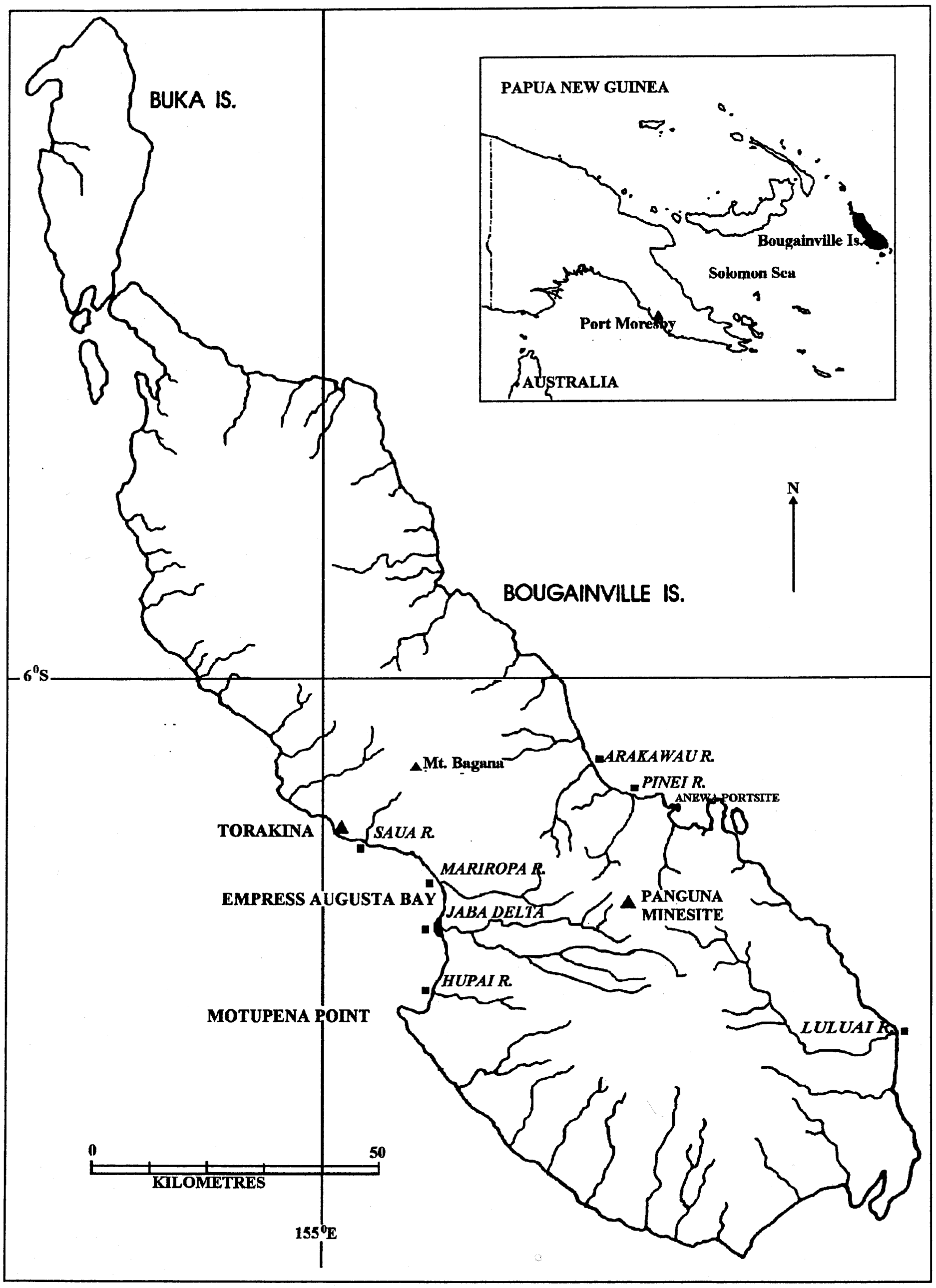

Figure 1. Map of sampling locations, Bougainville Island.

The elements chosen for study are listed as priority pollutants by the USEPA (1986) and analytical methods were industry standard procedures for the time. Sample preparation for determination of Cu, Pb, Zn and Cd involved digestion of a known weight of thawed sample in a 250 mL conical flask with a mixture of analytical grade nitric and perchloric acids. Each flask was fitted with an air condenser to provide refluxing conditions. Sample weights, acid volumes and final volumes are listed in Powell *et al*. (1981).

Aqueous digests were analysed directly using a Perkin-Elmer 603 flame atomic absorption spectrophotometer (AAS) with background correction. Small samples of kidney were analysed whole, while larger ones were homogenized and a representative sample taken for analysis.

For determination of total Hg, samples were dissolved in nitric acid at room temperature to prevent loss of methyl Hg. When the digestion was complete, organic matter together with organic Hg compounds were decomposed by addition of potassium permanganate solution. Excess permanganate and manganese oxide were reduced by the addition of hydroxylamine hydrochloride. The Hg^{2+} ion was reduced to metallic Hg with stannous chloride prior to determination of total Hg by flameless atomic absorption spectrophotometry.

Arsenic concentrations were determined by digesting samples in a mixture of nitric, perchloric and sulfuric acids. Nitric and perchloric acids were then removed by fuming and, after dilution, As was reduced to the trivalent state by addition of potassium iodide and stannous chloride solution. Zinc was added to the solution liberating arsine and hydrogen. These gases were passed through a hydrogen sulphide scrubber and then bubbled through a solution of silver diethyl-dithiocarbamate dissolved in pyridine. Here the As formed a soluble red complex having an absorption maximum of 540 nm. The plot of absorbance versus (μg) As is linear in the range 0–25 μg As. Determinations were conducted on a Bausch and Lomb Spectronic 70 spectrophotometer.

Detection limits for the various elements using this methodology are listed below

Element	Detection limit (mg kg^{-1} wet wt.)	Standard deviation (mg kg^{-1} wet wt.)
As	0.10	0.4 at 2 mg kg^{-1}
Hg	0.02	0.04 at 3 mg kg^{-1}
Zn	0.20	0.2 at 5 mg kg^{-1}
Cu	0.01	0.06 at 0.3 mg kg^{-1}
Pb	0.10	0.06 at 0.07 mg kg^{-1}
Cd	0.01	0.01 at 0.02 mg kg^{-1}

The accuracy of the methods was verified by analyzing the National Bureau of Standards (NBS) bovine liver sample, No 1577 for Cu, Pd, Zn and Cd. Four replicate determinations were conducted for each element. Two reagent blanks were included with each determination.

Results are shown below (mg kg^{-1} wet wt.)

	Cu	Pb	Zn	Cd
NBS listed value	193 ± 10	0.34 ± 0.08	130 ± 10	0.27 ± 0.04
Bougainville Copper Ltd Analytical Laboratory	183	0.4	127	0.24

To examine areal differences in trace element concentrations, the 8 species of fish most common to both coasts were compared with respect to each of the elements using analysis of covariance (ANCOVA, Statistica 1994). Powell *et al*. (1981) reported significant correlations (both positive and negative) between size of fish and trace metal content, with the relationship between size of fish and Hg content being always positive. To correct for potential size effects on metal content, both concentration and weight (the covariate) were $\log_{10}$ transformed. Temporal variations in As and Hg within selected west coast species were examined using time-series analysis.

3. Results and Discussion

3.1. Trace elements in muscle tissue

Of the 8 species of fish common to both the east and west coasts of the Island, 3 are sharks (Elasmobranchi) and 5 are bony fishes (Teleostomi). All species are carnivorous and occupy positions high up the trophic pyramid.

Concentrations of trace elements in muscle tissue of 8 fish species from the three east coast sites described by Powell *et al*. (1981), were up-dated and recalculated to include data for the period 1981–1987, thereby equalizing the overall observation period for both coasts (1977–1987). In this study, the milk trevally (*Lactarius lactarius*) was substituted for *Chorinemus toolooparah* listed in Powell *et al*. (1981) because of higher numbers in common from both coasts. Results for the east and west coasts are summarized in Tables I and II respectively. For each element, geometric mean concentration was calculated for each species within sites; all data combined for the entire observation period. Geometric mean was considered as the most reliable measure of central tendency, following re-examination of data presented by Powell *et al*. (1981), and previous use of geometric mean by Brooks and Rumsey (1974). Results listed in Tables I and II are illustrated in Figure (2) together with the maximum residue limits (MRLs) recommended by the Australian National Health and Medical Research Council (NHMRC 1988).

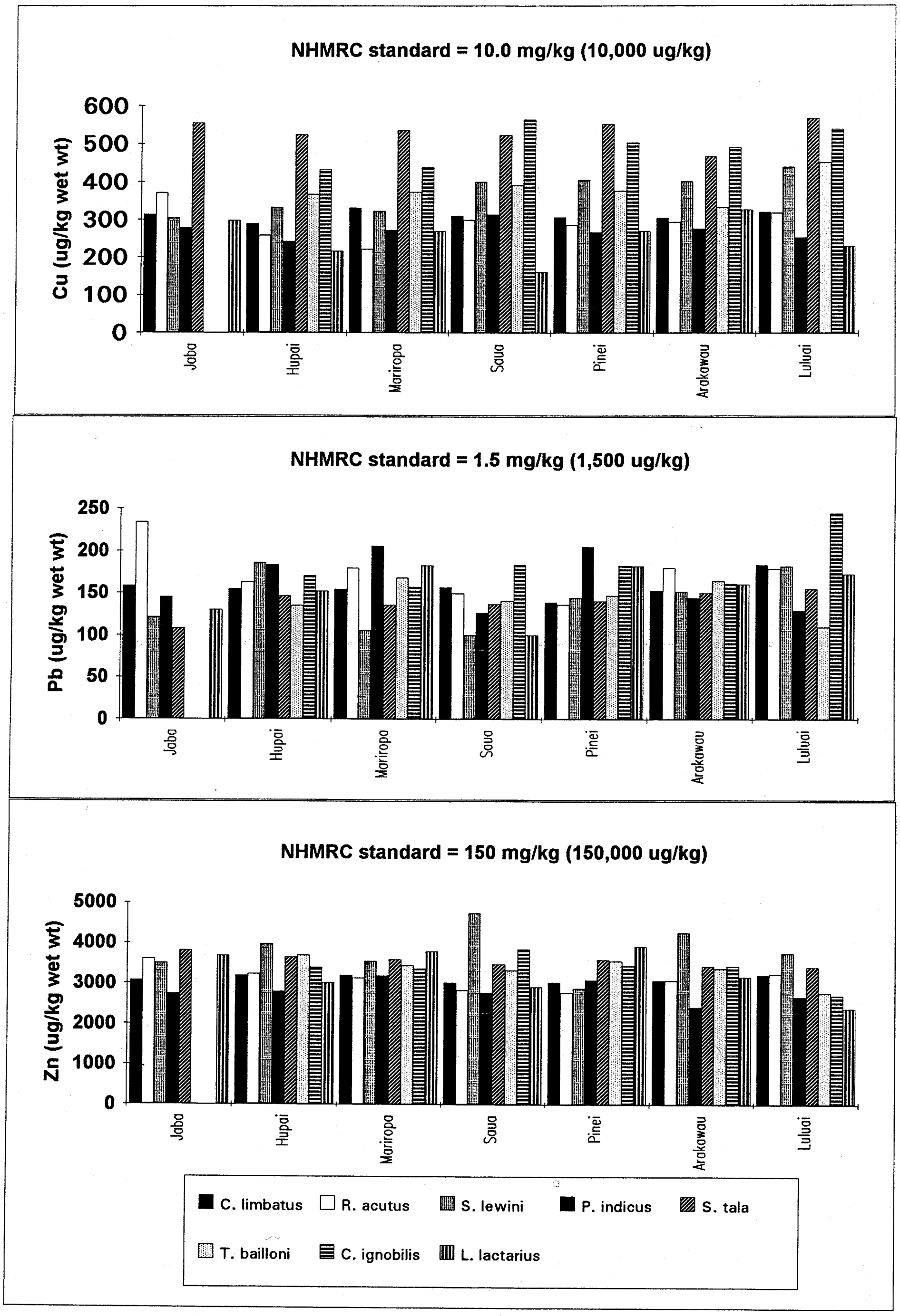

Figure 2a. Concentrations of trece elements (geometric mean) in 8 species of marine fish from 4 sites on the west coast and 3 sites on the east coast of Bougainville Island.

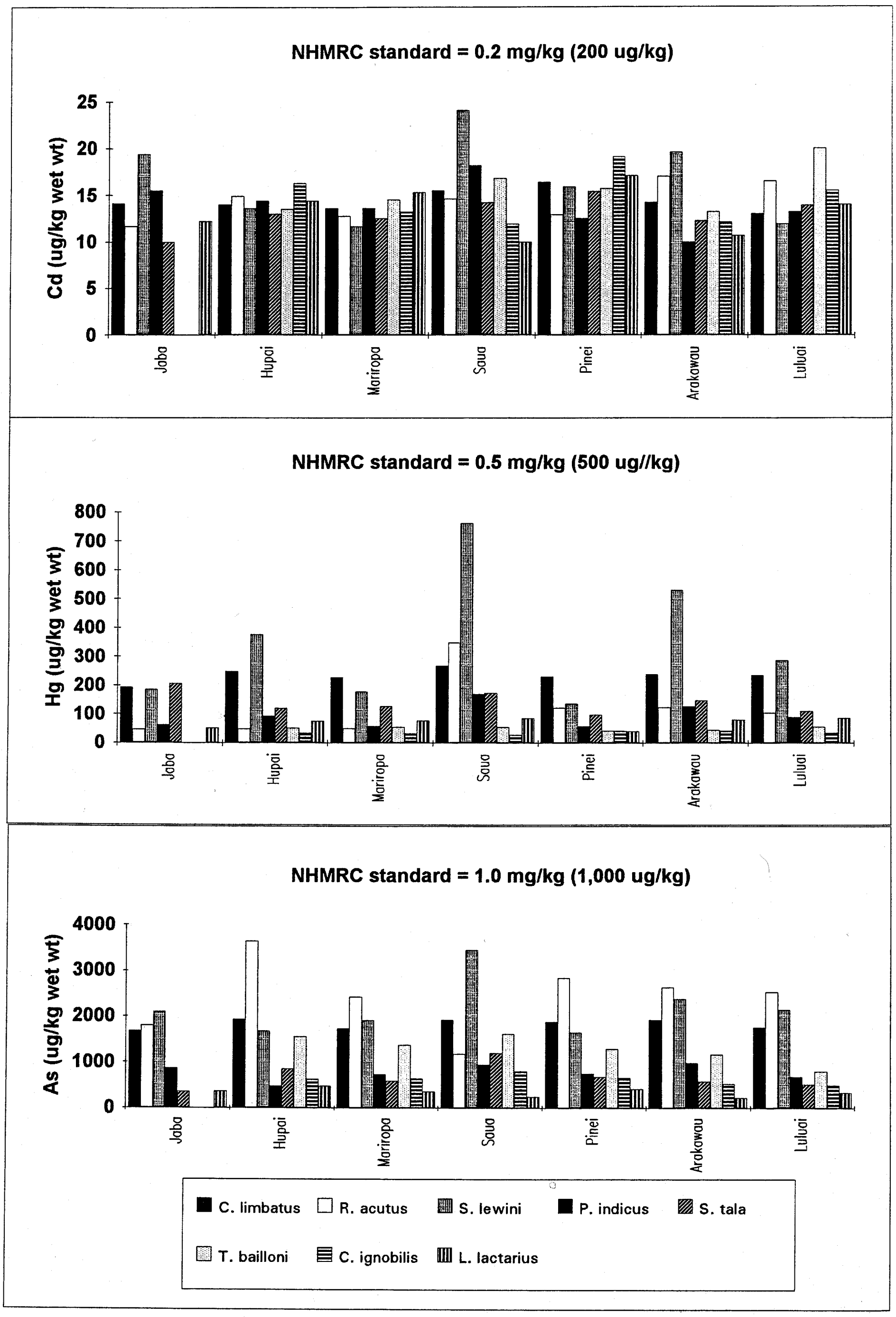

Figure 2b. Concentrations of trace elements (geometric mean) in 8 species of marine fish from 4 sites on the west coast and 3 sites on the east coast of Bougainville Island.

TABLE I

Concentrations (geometric mean μg kg^{-1} wet weight) of trace elements in muscle tissue of 8 species of marine fish from the east coast of Bougainville Island from 1977–1987

Species	Site	Cu			Pb		
Elasmobranchii (sharks and rays)		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N
Carcharhinus limbatus	P	305.8	100–1,120	140	138.7	100–700	140
	A	305.1	60–1,500	220	152.9	100–800	220
	L	321.6	90–1,200	145	183.3	100–600	145
Rhizoprionodon acutus	P	285.5	140–1,340	18	135.6	100–500	18
	A	293.4	100–1,100	81	179.5	100–600	81
	L	318.9	100–2,500	96	179.3	100–1,500	96
Sphyrna lewini	P	404.9	310–630	3	144.2	100–300	3
	A	401.0	180–1,410	36	151.9	100–600	36
	L	439.6	240–1,200	14	181.8	100–500	14
Teleostomi (bony fish)							
Polydactylus indicus	P	267.4	200–450	5	204.8	100–600	5
	A	276.4	160–600	3	144.2	100–300	3
	L	253.0	40–2,070	126	129.2	100–1,00	126
Scomberoides tala	P	552.5	100–1,430	87	140.0	100–600	87
	A	466.8	140–2,600	70	150.2	100–600	70
	L	566.6	270–960	25	154.8	100–800	25
Trachinotus bailloni	P	375.8	100–1,280	74	146.8	100–800	74
	A	333.0	60–1,730	95	164.4	100–1,600	97
	L	451.1	260–780	12	109.6	100–300	12
Caranx ignobis	P	503.4	130–3,400	64	182.1	100–2,400	64
	A	490.5	190–1,770	33	161.2	100–700	33
	L	539.0	330–950	6	244.9	100–600	6
Lactarius lactarius	P	270.5	200–430	3	181.7	100–600	3
	A	327.6	170–1,140	9	160.3	100–700	10
	L	230.0	80–810	18	172.3	100–500	18

P = Pinei River Site, A = Arakawau River Mouth, L = Luluai River Mouth.

Concentrations of Cu, Pb, Zn and Cd in edible tissues of fish from all sites were low, and generally within 10–15% of recommended MRLs (NHMRC 1988).

Concentrations of Hg in edible tissues tended to be higher for most species (10% to $\leq$ 80% of NHMRC guidelines) with highest concentrations in the sharks *S. lewini* and *C. limbatus*. Concentrations of Hg in *S. lewini* from the Saua estuary on the west coast, frequently exceeded the MRL (Figure 2b) and it is worth noting

TABLE I
(continued)

Species	Site	Zn			Cd		
Elasmobranchii (sharks and rays)		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N
Carcharhinus limbatus	P	3,029.7	1,900–6,200	140	16.4	10–80	140
	A	3,072.6	1,100–6,000	220	14.2	10–760	220
	L	3,211.4	2,200–6,100	145	13.0	10–70	145
Rhizoprionodon acutus	P	2,773.3	1,500–3,900	18	12.9	10–50	18
	A	3,075.4	2,400–5,100	81	17.0	10–140	81
	L	3,227.8	2,400–7,000	96	16.5	10–330	96
Sphyrna lewini	P	2,874.7	2,500–3,800	3	15.9	10–20	3
	A	4,225.0	3,100–10,000	36	19.6	10–370	36
	L	3,754.0	2,900–5,100	14	11.9	10–30	14
Teleostomi (bony fish)							
Polydactylus indicus	P	3,086	2,500–4,800	5	12.5	10–30	5
	A	2,416.7	2,100–2,800	3	10.0	10–10	3
	L	2,670.5	1,200–84,000	126	13.2	10–130	126
Scomberoides tala	P	3,590.9	2,000–5,800	87	15.4	10–230	87
	A	3,429.3	2,400–5,100	70	12.3	10–70	70
	L	3,405.6	2,400–5,400	25	13.9	10–50	25
Trachinotus bailloni	P	3,553.0	1,500–8,000	74	15.7	10–120	74
	A	3,373.6	1,700–6,000	97	13.2	10–150	97
	L	2,776.5	1,400–4,100	12	20.0	10–160	12
Caranx ignobis	P	3,443.5	1,900–8,000	63	19.1	10–320	64
	A	3,431.6	2,100–6,600	33	12.1	10–40	33
	L	2,708.3	2,300–3,300	6	15.5	10–70	6
Lactarius lactarius	P	3,917.4	2,700–5,300	3	17.1	10–50	3
	A	3,159.4	2,300–4,300	10	10.7	10–20	10
	L	2,376.8	1,200–4,200	18	14.0	10–50	18

P = Pinei River Site, A = Arakawau River Mouth, L = Luluai River Mouth.

that Mt. Bagana, an active fumerole and itself a possible source of trace elements (Salomons and Forstner, 1984; Nriagu, 1979), is a dominant feature of the Saua river catchment. Concentrations of Cu, Zn and Cd were also elevated in *S. lewini* from the Saua estuary but not to levels considered a threat to public health.

No direct comparison can be made with the recommended MRL for As in either fish (*T. bailloni*) or sharks (*R. acutus, S. lewini and C. limbatus*). The arsenic concentrations reported in this study are total As, including inert organically

TABLE I
(*continued*)

Species	Site	As			Hg			Size (mm)
Elasmobranchii (sharks and rays)		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N	
Carcharhinus limbatus	P	1,882.8	100–5,700	117	230.8	10–1,610	137	240–1,500
	A	1,922.6	200–5,600	207	237.7	20–3,270	209	250–1,260
	L	1,757.5	300–6,900	139	235.9	20–2,040	141	110–1,260
Rhizoprionodon acutus	P	2,828.8	1,400–6,800	18	122.2	20–6900	17	320–590
	A	2,629.7	300–7,900	75	123.0	20–1,700	62	220–3,700
	L	2,527.0	300–7,500	85	103.9	10–2,050	76	260–640
Sphyrna lewini	P	1,643.2	1,000–2,700	2	135.6	20–390	3	340–560
	A	2,381.2	900–5,900	34	528.6	60–3,130	34	320–1,650
	L	2,148.3	700–5,400	12	286.7	30–1,400	13	340–3,000
Teleostomi (bony fish)								
Polydactylus indicus	P	763.5	500–1,800	5	57.2	10–240	5	370–570
	A	983.1	600–1,800	3	126.3	60–210	3	260–480
	L	680.5	100–2,400	123	88.8	20–1,500	121	300–770
Scomberoides tala	P	681.7	200–3,200	51	98.2	20–470	60	220–520
	A	576.6	100–2,800	57	147.0	20–490	62	240–470
	L	516.8	100–1,900	16	109.8	20–470	21	280–420
Trachinotus bailloni	P	1,285.9	200–5,190	47	40.7	10–500	51	180–290
	A	1,168.2	100–4,300	82	45.0	20–580	77	200–340
	L	798.9	100–2,700	9	55.4	30–160	6	210–330
Caranx ignobis	P	661	10–2,700	38	40.9	10–920	44	210–490
	A	526.9	100–2,100	29	42.0	10–150	26	220–800
	L	499.8	100–1,300	4	34.6	30–40	2	230–500
Lactarius lactarius	P	416.0	200–1,200	3	40.0	20–80	2	230–296
	A	224.5	100–400	6	79.4	30–240	7	150–330
	L	332.6	100–2,000	15	85.7	20–160	11	230–330

P = Pinei River Site, A = Arakawau River Mouth, L = Luluai River Mouth.

bound As, whereas the recommended MRL refers to inorganic As only. However, similar (total arsenic) results were reported by Gibbs and Miskiewicz (1995) who also presented evidence to show that exceedence of the MRL was highly unlikely when the proportion of inorganic to organic As is taken into account for marine Elasmobranchs.

Figure (2) shows that although species varied considerably with respect to metal content, no species dominated as a general bioindicator for all metals. Furthermore,

TABLE II

Concentrations of trace elements (geometric mean μg kg^{-1} wet weight) in muscle tissue of 8 species of marine fish from the west coast of Bougainville Island from 1977–1987

Species	Site	Cu			Pb		
		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N
C. limbatus	JD	313.6	120–3,500	197	158.3	30–700	197
	HU	288.5	100–1,300	187	154.5	10–800	187
	MA	330.6	60–1,740	264	153.8	100–1,100	265
	SA	309.7	20–1,200	271	156.1	100–900	271
R.acutus	JD	369.8	130–1,100	29	133.9	20–1,900	30
	HU	258.6	90–750	12	162.7	20–500	12
	MA	221.1	40–1,200	67	179.3	100–700	67
	SA	298.7	160–480	10	149.0	100–600	10
S. lewini	JD	303.7	200–630	12	121.1	100–500	12
	HU	331.4	240–630	14	185.3	100–400	14
	MA	322.3	160–510	14	105.1	100–200	14
	SA	399.2	230–670	5	100	100–100	5
S. tala	JD	555.0	330–1,000	9	107.7	70–300	10
	HU	524.2	180–1,300	58	146.3	10–700	58
	MA	534.6	10–1,770	97	135.4	30–900	97
	SA	522.6	130–2,140	48	136.2	100–500	48
P. indicus	JD	278.0	100–770	122	145.2	100–800	123
	HU	241.9	120–520	15	183.0	100–600	15
	MA	272.0	130–770	13	205.5	100–900	13
	SA	313.0	330–580	3	126.0	100–200	3
T. bailloni	JD		NS			NS	
	HU	366.7	170–650	20	134.6	100–400	20
	MA	372.7	60–2,000	119	167.8	50–8,400	119
	SA	391.2	140–950	31	140.0	100–800	31
C. ignobilis	JD		NS			NS	
	HU	431.9	100–1,500	39	169.7	10–1,200	39
	MA	437.3	170–1,240	107	156.6	30–700	109
	SA	564.8	200–1,200	35	183.1	100–700	35
L.lactarius	JD	297.3	100–2,900	141	129.8	10–600	141
	HU	216.3	100–1,800	26	151.6	100–700	26
	MA	269.0	90–1,100	82	182.1	100–600	81
	SA	161.3	130–200	2	100	100–100	2

JD = Jaba River outfall, HU = Hupai River, MA = Maríropa River, Sa = Saua River, N = Number of observations, NS = Not sampled.

TABLE II
(continued)

Species	Site	Zn			Cd		
		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N
C. limbatus	JD	3,075.4	600–5,900	197	14.1	10–2,500	197
	HU	3,191.5	2,000–7,700	187	14.0	10–100	187
	MA	3,194.5	1,500–39,00	265	13.6	10–70	265
	SA	3,020.6	1,100–5,700	271	15.5	10–500	271
R.acutus	JD	3,608.3	2,500–5,300	30	11.7	10–50	30
	HU	3,235.2	2,700–3,800	12	14.9	10–60	12
	MA	3,126.1	1,600–4,900	67	12.8	10–80	67
	SA	2,832.0	2,200–3,400	10	14.6	10–50	10
S. lewini	JD	3,501.9	2,700–5,600	12	19.4	10–120	12
	HU	3,969.2	3,400–5,100	14	13.6	10–60	14
	MA	3,546.5	2,500–4,400	14	11.7	10–30	14
	SA	4,745.7	3,200–8,000	5	24.1	10–30	5
S. tala	JD	3,814.2	2,600–6,200	10	10.0	10–10	10
	HU	3,644.2	2,300–5,300	58	13.0	10–50	58
	MA	3,587.6	1,900–8,200	97	12.5	10–70	97
	SA	3,481.0	1,500–5,901	47	14.2	10–70	48
P. indicus	JD	2,740.3	1,700–6,200	123	15.5	10–110	123
	HU	2,797.7	2,200–4,100	15	14.4	10–30	15
	MA	3,184.9	2,200–4,700	13	13.6	10–70	13
	SA	2,770.1	2,200–4,200	3	18.2	10–30	3
T. bailloni	JD		NS			NS	
	HU	3,696.6	1,900–5,800	20	13.5	10–40	20
	MA	3,437.2	1,800–6,200	119	14.5	10–90	119
	SA	3,328.1	2,000–5,900	31	16.8	10–60	31
C. ignobilis	JD		NS			NS	
	HU	3,392.3	2,400–5,500	39	16.3	10–180	39
	MA	3,362.0	2,000–7,200	109	13.2	10–500	180
	SA	3,848.6	2,200–5,800	35	11.9	10–50	35
L.lactarius	JD	3,683.8	1,800–8,900	141	12.2	10–70	141
	HU	3,023.3	2,300–5,500	26	14.4	10–50	26
	MA	3,787.0	2,100–9,000	82	15.3	10–100	82
	SA	2,915.4	2,500–3,400	2	10	10–10	2

JD = Jaba River outfall, HU = Hupai River, MA = Maritropa River, Sa = Saua River, N = Number of observations, NS = Not sampled.

TABLE II
(continued)

Species	Site	As			Hg			Size (mm)
		Geometric Mean	Absolute Range	N	Geometric Mean	Absolute Range	N Range	
C. limbatus	JD	1,671.9	80–11,300	176	192.7	20–720	181	230–11,700
	HU	1,931.5	130–8,000	172	247.1	30–1,510	183	300–2,150
	MA	1,727.0	100–9,900	214	226.6	10–2,150	249	400–1,500
	SA	1,914.7	100–16,600	261	267.5	10–1,930	263	300–2,900
R.acutus	JD	1,794.3	300–4,300	19	46.4	10–900	28	260–620
	HU	3,634.1	2,000–5,700	9	48.6	20–110	11	240–630
	MA	2,413.2	100–7,200	54	49.9	20–1,200	64	220–670
	SA	1,175.2	100–5,600	10	347.5	40–1,590	9	270–630
S. lewini	JD	2,088.3	500–6,400	10	186.0	20–790	12	310–7,400
	HU	1,677.6	1,000–3,100	12	376.1	120–1,340	14	360–1,500
	MA	1,908.1	300–5,100	8	178.1	30–630	14	220–2,290
	SA	3,447.5	1,400–9,300	4	761.7	280–2,900	5	360–2,900
S. tala	JD	356.8	100–900	4	205.6	70–780	7	260–470
	HU	854.5	300–2,300	45	119.4	30–470	52	200–480
	MA	586.0	100–2,200	61	126.6	20–430	83	255–640
	SA	1,199.2	100–8,700	39	173.1	20–830	35	240–430
P. indicus	JD	859.6	200–4,400	118	62.0	10–650	118	200–700
	HU	476.5	100–1,800	15	92.8	20–460	14	310–620
	MA	729.8	100–3,300	12	58.2	20–280	13	290–590
	SA	943.6	600–2,000	3	168.8	150–190	2	280–420
T. bailloni	JD		NS			NS		
	HU	1,553.5	800–2,500	10	50.4	20–100	17	200–270
	MA	1,372.1	200–630	83	54.9	20–500	99	200–340
	SA	1,610.6	1,000–3,000	18	54.9	20–420	14	190–260
C. ignobilis	JD		NS			NS		
	HU	625.2	100–3,200	33	33.9	10–240	33	79–430
	MA	641.7	100–2,800	82	31.7	10–540	99	150–640
	SA	795.6	100–1,800	29	27.2	10–2,100	32	230–310
L.lactarius	JD	366.4	100–3,600	74	51.2	20–270	133	80–320
	HU	475.7	100–2,700	18	75.7	30–360	21	200–310
	MA	356.3	100–3,400	61	76.4	20–590	68	213–340
	SA	245.0	200–300	2	84.9	80–90	2	260

JD = Jaba River outfall, HU = Hupai River, MA = Maríropa River, Sa = Saua River, N = Number of observations, NS = Not sampled.

TABLE III

ANCOVA results comparing trace element content of 8 species of fish among 7 sampling sites in Bougainville Island, PNG

Species	Element					
	Cu	Pb	Zn	Cd	As	Hg
C. limbatus	d	a	b	a	d	a
R. acutus	c	d	c	a	a	c
S. lewini	d	b	d	d	a	a
P. indicus	d	a	d	d	a	c
S. tala	d	d	d	a	c	c
T. bailloni	d	d	a	d	a	d
C. ignobilis	d	d	b	b	d	d
L. lactarius	a	d	c	a	d	a

[a] = P < 0.05.
[b] = P < 0.01.
[c] = P < 0.001.
[d] = NS.

interspecific metal differences often exceeded differences among sites. Queenfish (S. *tala*) from most sites for example, contained the highest Cu concentrations in tissues (almost twice the values in milk trevally *L. lactarius*) but for both species, there was little variation in concentrations among sites. Interspecific differences such as these are consistent with other studies (Gibbs and Miskiewicz, 1995) including Hg in fish skeletal muscle (Mathieson and McLusky, 1995). Apart from *S. lewini* at the Saua estuary, there were no additional indications that fish from the Jaba river mouth, or from the west coast generally, contained elevated values of trace elements in muscle tissues compared to natural background concentrations in fish from the east coast.

Twenty-six of 48 possible ANCOVA analyses (54%) revealed significant differences among sites with respect to metal content of species ($p < 0.05$, Table III). However, there was no consistent pattern for higher concentrations of any element in fish from west coast sites, even Hg (Table IV). West and east coast sites were linked in homogeneous sub-sets of sites that were not significantly different. High Hg concentrations in *S. lewini* from the Saua river for example, were not significantly different from those in *S. lewini* from other west and east coast sites (particularly the Arakawau estuary on the east coast) when the significant effects of size differences ($p < 0.05$) were taken into account. Comparison of means therefore, provided no evidence for uptake of metals in west coast fish living in the water column overlying large volumes of sub-aqueous tailings.

There is a need however, in trace element biomonitoring investigations of this sort, to examine differences in both space and time (Mance, 1987; Ellis, 1988).

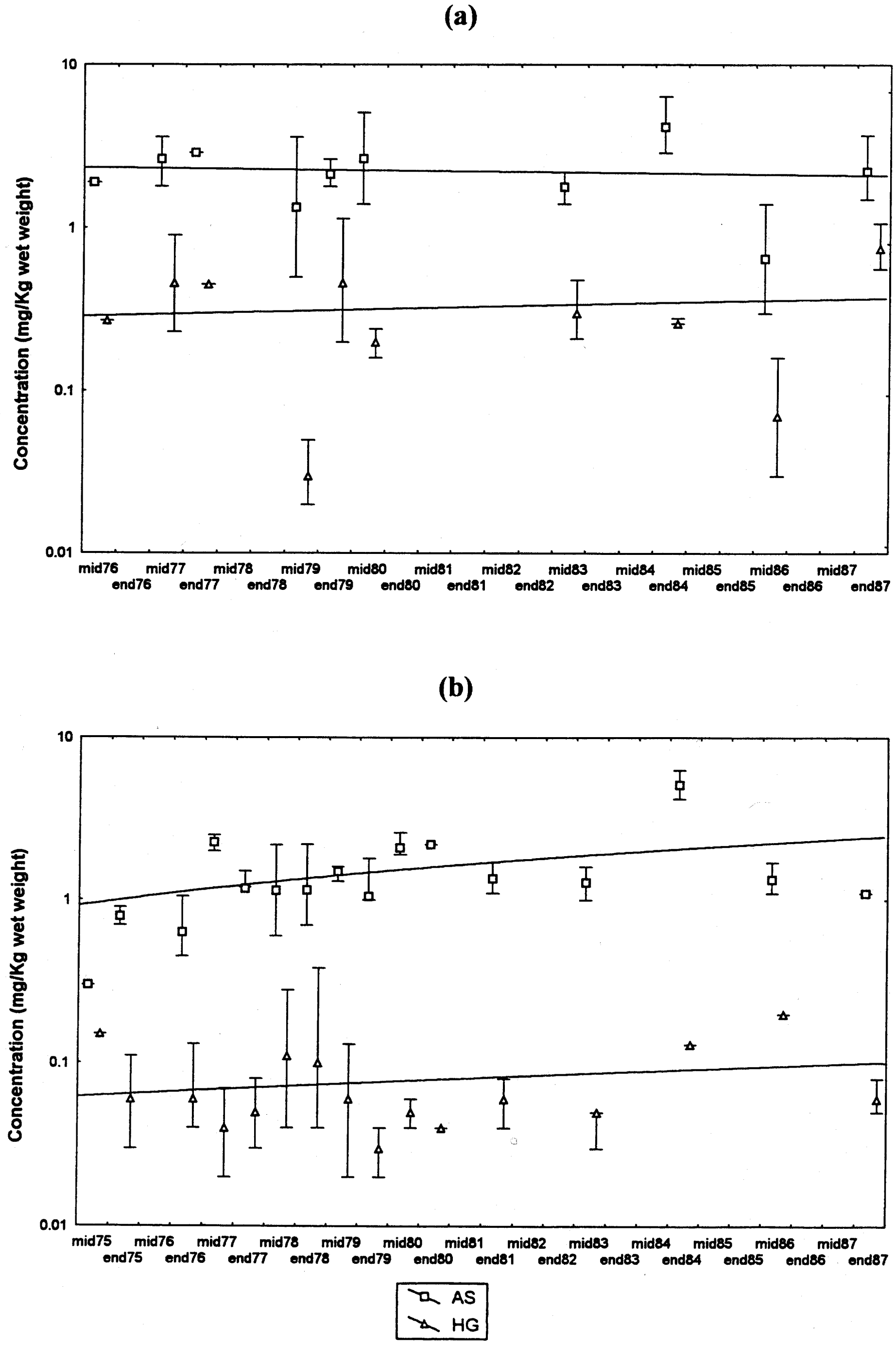

Figure 3. Temporal variation in concentrations of As and Hg (geometric mean; 25/75% quartiles) in muscle tissue of *S. lewini* (a) and *T. bailloni* (b) from the west coast of Bougainville Island.

TABLE IV

Homogeneous sub-sets of sites (underlined) which are not significantly different with respect to metal content

Metal	Species	Site						
CU	R. acutus	A	H	J	L	M	P	S
	L. lactarius	A	H	J	L	M	P	S
Pb	C. limbatus	A	H	J	L	M	P	S
	S. lewini	A	H	J	L	M	P	S
	P. indicus	A	H	J	L	M	P	S
Zn	C. limbatus	A	H	J	L	M	P	S
	R. acutus	A	H	J	L	M	P	S
	T. bailloni	A	H	J	L	M	P	S
	C. ignobilis	A	H	J	L	M	P	S
	L. lactarius	A	H	J	L	M	P	S
Cd	C. limbatus	A	H	J	L	M	P	S
	R. acutus	A	H	J	L	M	P	S
	S. tala	A	H	J	L	M	P	S
	C. ignobilis	A	H	J	L	M	P	S
	L. lactarius	A	H	J	L	M	P	S
As	R. acutus	A	H	J	L	M	P	S
	L. lewini	A	H	J	L	M	P	S
	P. indicus	A	H	J	L	M	P	S
	S. tala	A	H	J	L	M	P	S
	T. bailloni	A	H	J	L	M	P	S
Hg	C. limbatus	A	H	J	L	M	P	S
	R. acutus	A	H	J	L	M	P	S
	S. lewini	A	H	J	L	M	P	S
	P. indicus	A	H	J	L	M	P	S
	S. tala	A	H	J	L	M	P	S
	L. lactarius	A	H	J	L	M	P	S

A = Arakawau, H = Hupai, J = Jaba river mouth, L = Luluai, M = Mariropa, P = Pinei, S = Saua.

Mercury and As were chosen for examination of temporal variations because they are more likely to be bioaccumulated from water and progressively biomagnified during trophic transfer. The shark (*S. lewini*) and trevally (*T. bailloni*) were selected as 'typical' examples of the coastal assemblage and concentrations (of Hg and As) in muscle tissue of these two species plotted to examine trends (Figure 3).

Temporal variations in As content of *T. bailloni* were significant (ANCOVA, $p <$ 0.001) with concentrations at end – 1984 (114 months after the start of observation) being higher than in all other surveys. Concentrations in 1983 and 1986 were not significantly different from those during 1975–1981 ($p > 0.05$). Similar results were obtained from examination of Hg in *S. lewini* (Figure 3)(a)). Fitted trend lines for the whole period did not deviate significantly from zero (horizontal) in either species, confirming absence of bioaccumulation (*S. lewini* As p = 0.81 and Hg p = 0.71; *T. bailloni* As p = 0.13 and Hg p = 0.38; Figure 3).

3.2. METALS IN SOFT ORGANS

Although fish can absorb metals from both water and food, Langston and Spence (1995) leave no doubt that dietary intake is the major pathway for uptake of metals by fish. Metals of dietary origin are absorbed in the gut and distributed to other tissues, particularly those high in metal binding ligands such as metallothionein (MT). As a result, metals tend to be preferentially accumulated in the soft organs (liver and kidneys) of fish (Saward *et al*., 1975; Fisher and Reinfelder, 1995; Roesijadi, 1992). This pattern was demonstrated for fish from Bougainville's east coast by Powell *et al*. (1981).

Concentrations of Cu, Pb, Zn, Cd and Hg (geometric means, all data combined for the entire monitoring period), in liver and kidney of the species of bony fish are shown in Figures (4) and (5) respectively. *Scomberoides tala* is the main species for which there are instances of elevated concentrations of trace elements in west coast fish; and this refers to concentrations of Cu, Zn and Cd in liver, and Cu and Cd in kidney, which were significantly higher in west coast fish compared with concentrations in fish from the east coast ($p \leq 0.05$). The reverse was true for concentrations of Cd in the liver of *T. bailloni* (Figure 4) and Cu and Cd in kidney of *T. Bailloni* (Figure 5) which were significantly higher in east coast fish ($p < 0.05$). Concentrations of Hg in liver were not significantly different between coasts for any of the 3 species examined ($p > 0.05$, Figure 4). This is of interest in the case of *T. bailloni* from the west coast which had higher – though not significantly higher – concentrations of Hg in liver, but this was not accompanied by bioaccumation of Hg in edible tissue (Figure 3). Thus the soft organ and muscle tissue results were consistent and confirmed absence of uptake of Hg. Taken overall therefore, there was little evidence to indicate consistent uptake and sequestering of metals even in the soft organs.

3.3. FACTORS MODIFYING UPTAKE

These results are specific for a suite of conditions at Bougainville including the chemical characteristics of BCL's waste, the water quality and catchment characteristics of the Jaba river and the hydrodynamics of Empress Augusta Bay. Results should not be extrapolated to other estuaries and sub-aqueous tailings deposits

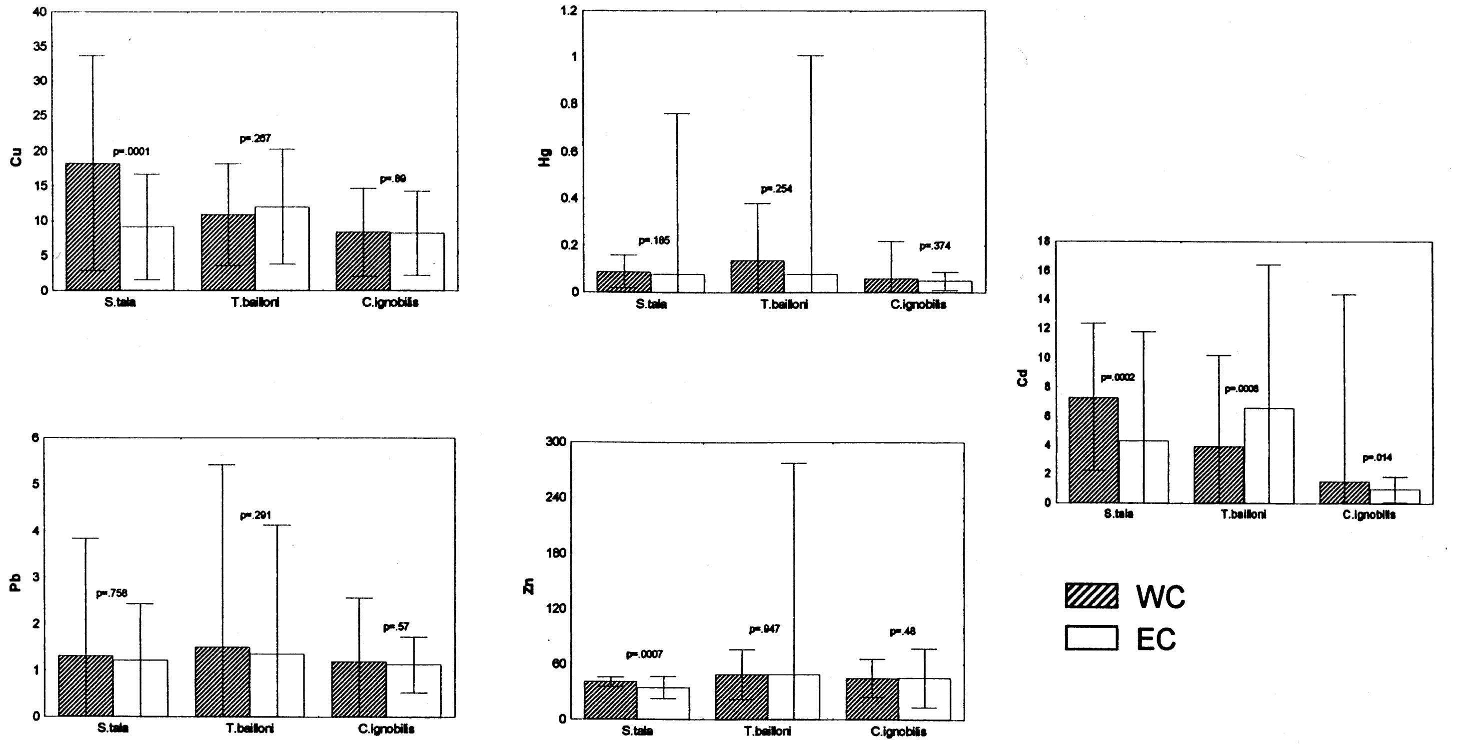

Figure 4. Concentrations of trace elements (geometric mean, mg kg^{-1} wet weight) in livers of 3 bony fish species from the east (EC) and west (WC) coasts of Bougainville Island.

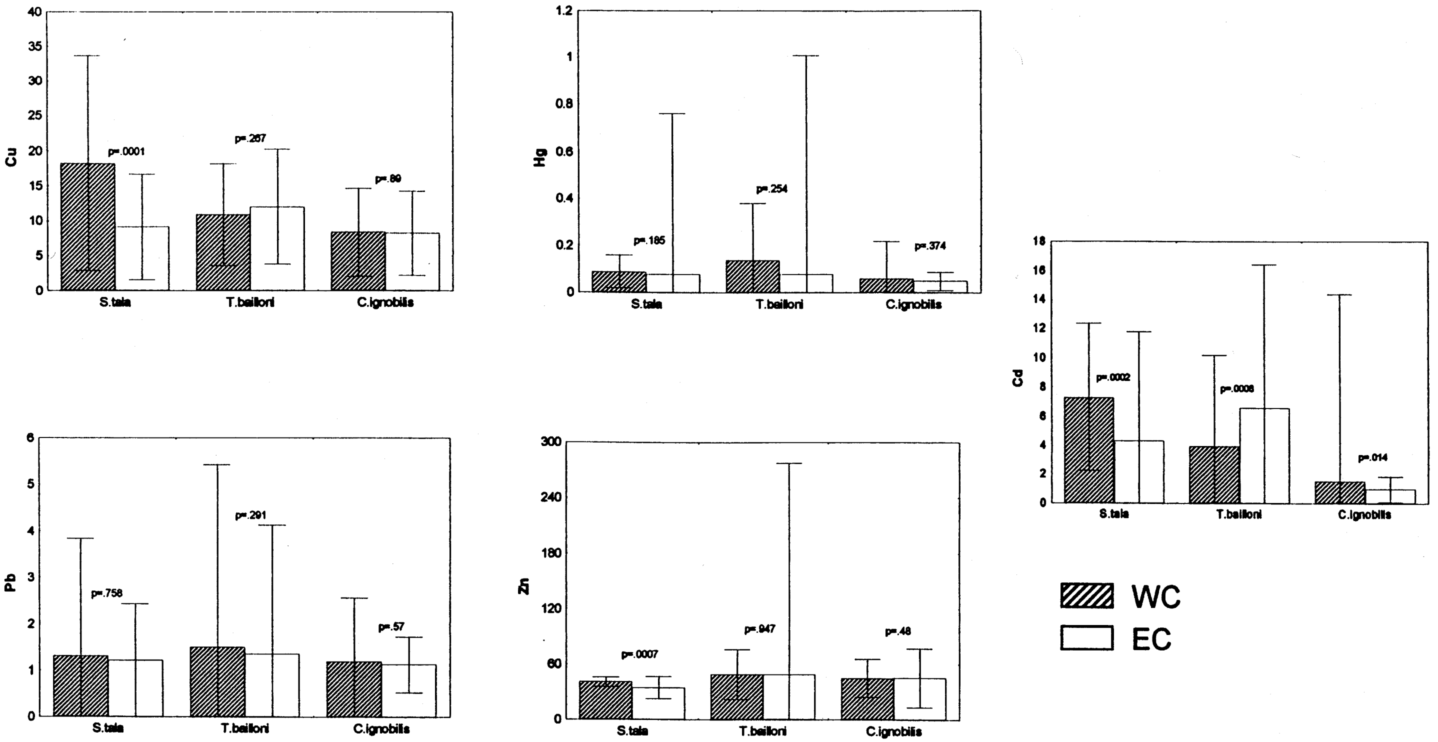

Figure 5. Concentrations of trace elements (geometric mean, mg kg^{-1} wet weight) in kidneys of 3 bony fish species from the east (EC) and west (WC) coasts of Bougainville Island.

without appropriate studies of specific chemical, hydrodynamic and biological processes involved. Each site has unique features.

Fortunately for the Bougainville situation, concentrations of priority (non-essential) metals (Pb, Cd and Hg) were low in both ore and waste, the tailings/river water mixture remained quite alkaline (pH > 8.0) during transit to the coast, tributaries were also alkaline effectively neutralizing acid mine drainage (AMD) generated from waste dumps and the volume of AMD was small relative to river discharge. This resulted in very low concentrations of dissolved metals at the Jaba river mouth (Hg < 0.04 μg L $^{-1}$, Cd and Pb < 1 μg L^{-1}), due to precipitation and/or absorbtion of trace elements onto particulates during transport to the coast (Jeffery *et al*., 1988).

The Jaba river discharged to sea via a salt wedge estuary (Salomons and Forstner, 1984) with the mixing zone offshore. Mean annual river discharge was small (40–45 m^3 s^{-1}) but, because of high sediment load, a large delta, 700 ha in emerged area, formed at the Jaba river mouth (Archer *et al*., 1988). Tailings sediments settled in the coastal zone, covering an area of 10 000 ha of the Empress Augusta Bay seabed by 1982 (Powell, 1986). Trapping of sediment in the coastal zone is not unusual for tropical systems of this sort (Wolanski, 1992). Wolanski (1992) also described the phenomenon of separation of river plumes of this kind into patches on contact with seawater with the possibility of forming a coastal boundary layer creating potentially adverse local effects. This was not formally studied.

There may have been limited release of copper (and other metals) from suspended tailings as soluble chlorides (Bourg, 1988; Salomons and Forstner, 1984). However, following discharge, river water mixed with oxygen rich seawater containing low natural background concentrations of trace elements. Mixing was rapid as evidenced by a very restricted zone of low salinity (30–35‰) close to the river mouth. Dilution was enormous, favouring rapid reduction in trace element concentrations to natural background values.

Empress Augusta Bay is an open system with unrestricted connection to the Solomon Sea, maintaining pH > 8.0 even close to the Jaba outfall. Equilibria under these discharge conditions favour re-adsorbtion of trace elements onto sediment particles (Salomons and Forstner, 1984) and, in addition, absorbtion and removal of trace elements from seawater by phytoplankton (Eaton, 1979; Fisher and Reinfelder, 1995).

Absorbtion of trace elements by phytoplankton is possible in near in-shore waters of Empress Augusta Bay although removal via this pathway could be expected to be limited by low phytoplankton densities resulting from general nutrient impoverishment of the marine equatorial tropics (Raymont, 1963). Low phytoplankton densities were confirmed by measurement of chlorophyll ‘a’ concentrations at 6 m depth ($\leq$ 0.28 mg m^{-3}), which are considered typical of the equatorial tropics (Raymont, 1963). However, concentrations of essential nutrients in Empress Augusta Bay (PO_4–P and NO_3–N) were typically 5–14 and $\leq$ 50 μg L^{-1} respectively, which are much higher than expected. Nutrient contributions certainly resulted from other rivers draining coastal wetlands fringing the Bay but, in addition, the tailings themselves were rich in phosphorus, some of which may have been apatite and unavailable for plant growth (Archer *et al*., 1988). Nutrients at these concentrations would have been sufficient to support a much higher phytoplankton density, leading to a conclusion that zooplankton grazing could have been playing a part in lowering phytoplankton standing crop. Unfortunately, the plankton study was terminated prematurely and zooplankton counts not be obtained but, because of the nutrient concentrations, phytoplankton production (as distinct from standing crop) may well have been significant in removal of dissolved trace elements from the water column. Fisher and Reinfelder (1995) also considered that zooplankton (as a marine herbivore) functioned as a break in the trophic transfer of non-essential metals to carnivores further up the foodchain by packaging (and removal) of non-essential particle reactive metals in waste products.

Release of trace elements from pore water of subaqueous tailings deposits to overlying seawater is also a possible pathway which may have been limited by a number of important factors. Empress Augusta Bay lies in the Indo-Pacific doldrums, the largest of three persistent oceanic zones of light and variable winds (Trewartha 1954), with a $< 5\%$ probability of wave height exceeding 0.5 m and current speed (15 min interval) exceeding 0.1 m sec^{-1} (Lawson and Treloar, 1986). The capacity of such waves to create bottom stirring was limited to depths < 10 m close to the coast. However, perturbation of the submarine deposits could have resulted from occasional seismic events. During 12 yr of disposal (1972–1984), there were two major earthquakes (Ms 7.6); one in 1975 accompanied by a tsunami, and the other in 1983. Both seismic events, resulted in subsidence of the deposit which may have released trace elements to the overlying water column. However, EAB was open to the Solomon Sea with enormous available dilution.

Thompson (1975) reported negligible release of Cu to overlying seawater from submarine tailings deposits in Rupert and Holberg Inlets, Vancouver Island, probably because, as Allen (1995) pointed out, acid mine drainage (AMD) generation in submarine tailings deposits was effectively blocked by low oxygen and the toxicity of seawater to the mediating bacterium (*Thiobaccillus oxidans*). Perturbation of tailings by marine benthic organisms was also limited in Empress Augusta Bay because of the adverse effects of tailings deposition and smothering on benthos. This will be described separately.

There was no opportunity to examine the extent of benthic recolonization of submarine tailings deposits at cessation of mining, but an increase in marine benthic consumer activity in the absence of tailings smothering could mediate release of trace elements to overlying seawater (Fisher and Reinfelder, 1995). There may also have been conflicting processes involved with Hg. On the one hand, microbial methylation and mobilization is possible (Wood and Wang, 1983), while Craig and Moreton (1984) showed that marine sulphidic conditions inhibit formation of monomethyl mercury, some forms of which are more toxic, volatile and capable of biomagnification in the aquatic foodchain.

The fish species of this study, as suggested by Harris (1995), integrated these complex processes during a decade of field observation; a monitoring period substantial enough to establish steady state (Langston and Spence, 1995) and help counteract some of the variations and influences suggested by Phillips (1977, 1980). These include tide, salinity, wind, river discharge, physical condition, seasonality, age, growth, reproduction, longevity and most importantly, mobility. Even if the west coast fish assemblage was taken as indicative of the Island assemblage as a whole (assuming total mobility and mixing of the east and west coast populations), there were no trends for increasing trace elements in tissues through time. Marine fish have the capacity to wholly or partially regulate at least the essential elements Cu and Zn in muscle tissue over a range of ambient concentrations (Bryan, 1976; Phillips 1980; Langston and Spence, 1995), while the non-essential elements (Pb, Cd and Hg), would have increased in concentration in the soft organs if those elements had been bio-available.

Taken in isolation, there is doubt about analysis of fish muscle tissue having the requisite bio-indicator capacity (Phillips, 1980) to demonstrate whether or not the submarine tailings deposits were benign. However, taking the results of chemical analysis soft organs into account, it seems that fish, within the Island's coastal food-web, provided confirmation of the acceptability of the marine segment of the BCL tailings disposal system with respect to metal mobility. Carnivorous fish high up the chain were targetted for study since they were the biological endpoint most likely to demonstrate uptake (of the least, Pb, Cd, As and Hg in organs) either from water (bioaccumulation) or via the food chain (biomagnification) to use the definitions of Manse (1987). Neither contamination of muscle tissue nor sequestering of metals in soft organs was apparent. Absence of bioaccumulation is not completely unexpected. Fish contamination does occur (uptake exceeds depuration/excretion) and must be checked by direct measurement, but Mance (1987) considered that there are very few studies that conclusively demonstrate trace element biomagnification – except for mercury.

The coastal fish of Bougainville Island remained safe for human consumption throughout the period with very little likelihood of contamination developing while the mine operated. In the event of an attempted re-start to marine tailings disposal, this study provides the basis for comparison of trace element concentrations in coastal marine fish following 9 yr or more of premature mine closure. Follow – up results would provide a valuable indication of the longer – term role of benthos in the biogeochemical cycling of trace elements in the coastal environment. The results of this study are also of value to mine management and Government regulators, in that under certain circumstances – particularly in areas of high seismicity – shallow sub-aqueous (marine) disposal of mine tailings can be an effective and environmentally preferable method of waste handling compared with impoundments on land.

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References

Allen, R. J.: 1995, in W. Salomons, U. Forstner and P. Mander (eds), *Heavy Metals Problems and Solutions*, Springer-Verlag, NY, p. 119.

Archer, I. M., Marshman, N. A. and Salomons, W.: 1988, in W. Salomons and U. Forstner (eds), *Environmental Management of Solid Waste Dredged Material and Mine Tailings*, Springer-Verlag, NY, p. 166.

Bourg, A. C. M.: 1988, in W. Salomons and U. Forstner (eds), *Chemistry and Biology of Solid Waste Dredged Material and Mine Tailings*, Springer-Verlag, NY, p. 3.

brooks, R. R. and Rumsey, D.: 1974, *N. Z. J. Mar. Freshw. Res.* **8**, 155.

Bryan, G. W.: 1976, in R. Hohnson (ed.), *Marine Pollution*, Academic Press, London, p. 185.

Chan, K. M.: 1995, *Mar. Pollut. Bull.* **31**, 277.

Craig, P. J. and Moreton, P. A.: 1984, *Mar. Pollut. Bull.* **15**, 406.

Eaton,: 1979, *Environ, Sci. Technol.* **13**, 425.

Ellis, D. V.: 1988, in W. Salomons and U, Forstner (eds), *Chemistry and Biology of Solid Waste, Dredged Material and Mine Tailings*, Springer-Verlag, New York, p. 73.

Fischer, N. S. and Reinfelder, J. R.: 1995, in A. Tessier and D. R. Turner (eds), *Metal Speciation and Bioavailability in Aquatic Systems*, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 3., John Wiley and Sons, Chichester, p. 363.

Forstner, U.: 1995, in W. Salomons, U. Forstner and P. Mader (eds), *Heavy Metals Problems and Solutions*. Springer-Verlag, Germany, p. 237.

Gibbs, P. J. and Miskiewicz, A. G.: 1995, *Mar. Pollut. Bull.* **30**, 667.

Harris, J. H.: 1995, *Aust. J. Ecol.* **20**, 65.

Holmes, C. W. Sladem E. A. McLerran, C. J.: 1974, *Environ. Sci. Technol.* **8**, 255.

Hutchison, I. P. G. and Ellison, R. D.: 1992, *Mine Waste Management A Resource for Mining Industry Professionals, Regulators and Consulting Engineers*, Sponsored by the California Mining Associatiom, Lewis Publ., Chemsea, Michigan, U.S.A.

Jeffery, J. Marshman, N. and Salomons, W.: 1988, in W. Salomons and U. Forstner (eds), *Chemistry and Biology of Solid Waste Dredged Material and Mine Tailings*, Springer-Verlag, New York, p. 259.

Langston, W. J. and Spence, S. K.: 1995, in A. Tessier and D. R. Turner (eds), *Metal Speciation and Bioavailability in Aquatic Systems*, IUPAC, John Wiley and Sons Ltd., New York, p. 407.

Lawson, N. V. and Treloar, P. D.: 1986, *Analysis of Wave and Current Data Empress Augusta Bay*, Technical Report No. 1110 prepared for Bougainville Copper Limited, January 1986, Lawson and Treloar Pty, Ltd., Nord Sydney, Australia.

Mance, G.: 1987, in *Pollution Threat of Heavy Metals in Aquatic Environments*, Pollution Monitoring Series, Elsevier Applied Science, London, p. 287.

Mathieson, S. and McLusky, D. S.: 1995, *Mar. Pollut.* **30**, 283.

NHMRC: 1988, *MRL Standard: Standard for Maximum Residue Limits of Pesticides, Agricultural Chemicals, Feed Additives, Veterinary Medicines and Noxious Substances in Food*, National Health and Medical Research Council, Australian Government Publishing Service, Canberra.

Nriagu, J. O.: 1979, *Nature* **279**, 409.
Phillips, D. J. H.: 1977, *Environ. Pollut.* **13**, 281.
Phillips, D. J. H.: 1980, *Quantitative Biological Indicators. Their Use to Monitor Trace Metal and Organochlorine Pollution*, Applied Science Publ. Ltd., Barking, Essex, England.
Powell, J. H.: 19986, *The Effect of Mine Tailings on Shallow Coastal Benthos and tropical Demersal Fish Assemblages*, Ph. D. Dissertation, Zoology Department, University of Queensland, University of Queensland Press.
Powell, J. H. Powell, R. E. and Fielder, D. R.: 1981, *Water, Air, and Soil Pollut.* **16**, 143.
Prause, B., Rehm, E. and Schulz-Baldes, M.: 1985, *Environ. Technol. Letts.* **6**, 261.
Raymont, J. E. G.: 1963, *Plankton and Productivity in the Oceans*, Pergamon Press, Oxford, UK.
Roesijadi, G.: 1992, *Aquat. Toxicol.* **22**, 81.
Salomons, W. and Forstner, U.: 1984, *Metals in the Hydrocycle*, Springer-Verlag, New York.
Saward, D., Stirling, A. and Topping, G.: 1975, *Mar. Biol.* **29**, 351.
Sengupta, M. : 1993, *Environmental Impacts of Mining: Monitoring, Restoration and Control*, Lewis Publ., Boca Raton U.S.A.
Stoeppler, M.: 1992, *Techniques and Instrumentation in Analytical Chemistry*, Volume 12. Hazardous Metals in the Environment, Elsevier, London.
Statistica.: 1994, Statistica^{TM} for Windows^{TM} Statsoft^{TM}, Tulsa, US.
Thompson, J. A. J.: 1975, in *International Conference on Heavy Metals in the Environment*, Vol. 2, Part 1, Toronto, Ontario, Canada, October 27–31, p. 273.
Trewartha, G. T.: 1984, *An Introduction to Climate*, MCGraw-Hill Book Company, Inc., New York, U.S.A.
USEPA: 1986, *Quality Criteria for Water 1986*, United States Environmental Protection Agency. Office of Water Regulations and Standards, Washington, DC, 20460.
Wood, J. M. and Wang, H. K.: 1983, *Environ. Sci. Technol.* **17**, 582.
Wolanski, E.: 1992, in D. W. Connell and D. W. Hawker (eds), *Pollution in Tropical Aquatic Systems*, Crc Press Inc, Boca Raton, Florida, US. p. 4.