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Preliminary Studies on the Effects of Past Mining on the Aquatic Environment, Coromandel Peninsula

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Edited by

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Preliminary Studies on the Effects of Past Mining on the Aquatic Environment, Coromandel Peninsula

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This report describes the history and some of the effects of past mining on water quality (in particular heavy metals) and on the ecology of streams in the Coromandel Peninsula. It also examines metal concentrations in edible marine and freshwater species in the region and presents a management approach to setting heavy metal limits and monitoring the effects of future mine discharges

Elevated metal levels were found both in streams subjected to past mining and those unmined but passing through zones of high mineralisation. The impoverishment of aquatic fauna was clearly associated with mine waste release into streams. The extent of impoverishment, however, could not be directly correlated with the concentrations of specific heavy metals in the water, since the relative concentration of metals in the sediment and the extent of sedimentation also contributed to impoverishment.

The mean levels of heavy metals in seafood and other edible species were generally below the recommended maximum for safe human consumption.

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COVER: Gabion dam, Tui Stream, Coromandel Peninsula. The reddish-brown precipitate of iron oxides and hydroxides is a result of the oxidation of leachate draining from the Tui Mine tailings dam.
Photo: D. A. Carter, Hauraki Catchment Board.

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Foreword

This report presents the results of biological and chemical studies carried out on Coromandel streams to examine the effects of past mining on heavy metal levels and stream biota. The report also includes a survey of the levels of heavy metals accumulated in seafood and freshwater species. The objectives were to gain understanding of the extent to which heavy metals in streams affect stream life and to furnish a basis for development of appropriate safeguards for future mining activities in the region.

The impetus for the studies arose from public concern over the effects mining activity could have on the environment, and realisation that past impacts of mining in the region had not been adequately monitored. A few determinations of heavy metal concentrations had been made (Hauraki Catchment Board 1981) but little was known of the effects of heavy metals on stream life or levels in edible fish or shellfish. Knowledge of this is fundamental to the development of adequate environmental safeguards for any future mining operations.

The findings reported here warn of the effects mine-waste release could have on instream biological communities by showing that impoverishment of the fauna was associated with mine-waste release, even though the specific causes were not identified. The results of the survey of heavy metals in fish and shellfish show that levels are mostly below the maximum levels regarded as safe for human consumption and provide no evidence to link elevated levels with past mining activities.

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M. E. Livingston

Contents

CHAPTER 1: General Background to Coromandel Aquatic Studies

D. Carter, S. Rabone and M. E. Livingston

1.1 Introduction

In 1981 the Minister of Science requested the Chemistry Division, Department of Scientific and Industrial Research, (DSIR) to carry out a heavy metal survey of streams in the Coromandel region. At that time a research contract on the effects of past mining on stream biology was being let by the National Water and Soil Conservation Authority (NWASCA), and a study on bioaccumulation in fish and shellfish was being initiated by Fisheries Research Division, Ministry of Agriculture and Fisheries (MAF). The National Authority, therefore encouraged the regional water manager (the Hauraki Regional Water Board) to establish a committee to co-ordinate and assist these studies.

1.2 General Aims of Studies

The aims of each study were:

Heavy Metal Survey (Chapter 2): To attempt to establish baseline water quality in Coromandel streams, with particular reference to their heavy metal concentrations (lead, zinc, copper, cadmium, arsenic) and acidity.

Stream Biology Survey (Chapter 3): To attempt to assess the effects of contamination (metals, acidity) from naturally occurring mineralisation and past mining activities on biological communities in selected Coromandel streams. In conjunction with the results from the heavy metal survey, this biological survey was expected to permit assessment of the applicability of overseas water quality criteria (e.g., those of the United States Environmental Protection Agency) for the protection of aquatic life in the Coromandel region.

Fish and Shellfish Survey (Chapter 4): To attempt to establish the degree, if any, to which fish and shellfish have accumulated heavy metals in their tissues while living in streams and coastal waters of the Coromandel region.

The implications of the results to water resource management in Coromandel and future research requirements are discussed in Chapter 5.

1.3 Physiography of the Coromandel Region

The Coromandel Peninsula, which lies approximately 80 km east of the city of Auckland in the North Island of New Zealand, forms a large promontory, separating the sheltered waters of the Hauraki Gulf and Firth of Thames to the west, from the Pacific Ocean to the east (Figure 1.1). Southward, the axis of the peninsula continues into the Kaimai Ranges, and thence into the Mamaku Plateau north of the Central Volcanic Region.

The Coromandel-Kaimai region is characterised by a generally steep, rugged topography with elevations commonly exceeding 600 m; high rainfall (from 1275 to 2400 mm y^{-1}) and generally dense vegetation cover (minor primary native forest; extensive secondary native bush, scrub and exotic forest; limited pasture areas). High rainfall and steep topography render large areas vulnerable to erosion.

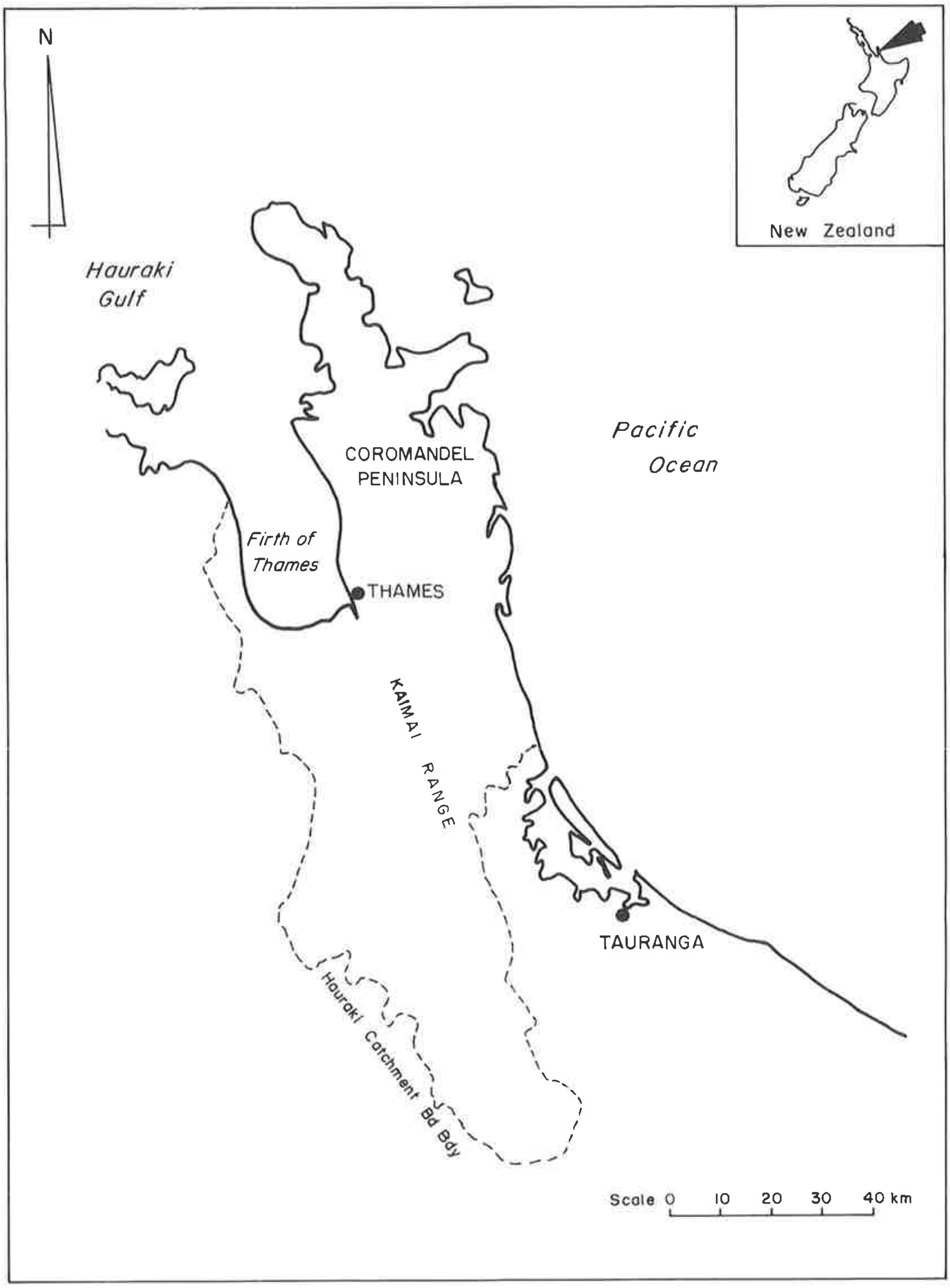


Figure 1.1: Coromandel Peninsula.

The shoreline mostly comprises short beaches and bays with intervening rock-bordered coast and a steep hinterland. Estuaries and harbours with mangroves and mudflats occur in some inlets.

1.4 Regional Geology

1.4.1 General geological outline

The rocks of the Coromandel-Kaimai region (Hauraki Volcanic Region) consist of a basement of Mesozoic age ($\simeq$ 140 million years old) greywacke sandstones, overlain by andesitic volcanic rocks of Miocene age ($\simeq$ 15 million years old). These in turn are overlain by younger (Pliocene, i.e., 3–5 million years) rhyolitic volcanic rocks. The entire region has a tilt to the south-east, so that progressively older rocks are exposed westwards and northwards. Hence the basement greywackes are exposed in the north and west of the Coromandel Peninsula. Locally, the basement rocks and overlying andesites are intruded by plutonic igneous rocks (diorite and diorite porphyry), notably north of Thames.

1.4.2 Tectonic setting

The igneous rocks of the Hauraki region have been produced by intrusive and volcanic activity occurring in a north-northwest trending continental margin arc active from the Miocene (20 million years ago) to the Pleistocene ($<$ 2.5 million years) periods. The main phase of andesitic volcanism was probably about 10–15 million years ago, and high level porphyry intrusives were emplaced at this time. Subsequent rhyolitic volcanism occurred mainly between 5 and 2.5 million years ago.

1.4.3 Alteration

Small discrete areas of hydrothermal alteration are scattered throughout the Coromandel Peninsula. This type of alteration is caused by hot meteoric (ground) waters, and possibly also some water derived from the igneous intrusives themselves, which are heated by the intrusive and volcanic activity to temperatures of 200–400°C. In circulating through the overlying volcanic rocks, along fault zones and other permeable structures, these hydrothermal solutions alter the host rocks by leaching some elements and converting the metastable silicate minerals of igneous rocks (e.g., pyroxenes) to other minerals stable at lower temperatures (e.g., clays, quartz). As they contain a significant amount of dissolved sulphur, extensive pyritisation of host rocks can occur through combination with contained iron.

The main types of alteration (in increasing order of intensity) are:

Propylitisation—weak alteration, with development of such secondary minerals as chlorite, calcite and pyrite. Rock strength is reduced but not to a great degree.

Argillisation—strong alteration, with extensive development of clay minerals and pyrite, and a severe decline in rock strength. This type of alteration commonly results from acid hydrothermal solutions, whereas propylitisation may be caused by relatively neutral solutions.

Silicification—strong alteration, with extensive replacement of earlier minerals by silica (quartz) and sometimes other minerals. Rock strength is high.

The transition from one alteration type to another is usually gradual, but sometimes abrupt. Areas of altered rock are scattered throughout the Hauraki volcanic region. On a local scale, alteration is usually comparatively limited in extent but, even within an area of strongly altered rocks, variations in alteration from unaltered to intensely altered occur.

1.4.4 Mineralisation

Two types of mineralisation are recognised in the Hauraki region—disseminated "porphyry" type, containing base metal sulphides and gold; and "epithermal" vein mineralisation, containing gold-silver, sometimes accompanied by base metals (Figure 1.2). Both have been formed from the hydrothermal solutions associated with the igneous activity, but porphyry-type mineralisation represents the deeper, higher temperature ($> 350°C$) part of the hydrothermal system, associated with the intrusive body. Porphyry-type mineralisation therefore tends to be dispersed and not confined within discrete structures, whereas the epithermal mineralisation has been formed by deposition of quartz, and sometimes calcite, as veins in comparatively near-surface fissures and fault zones. These veins (which have formed at temperatures of up to $\simeq 330°C$) contain mainly gold and silver in a ratio of approximately 1:5; gold concentration is typically in the range 3 to 30 g m^{-3}. While pyrite is relatively common (at about 2–4 percent by volume) in the adjacent country rock, actual pyrite content of the veins themselves is usually low ($< 1\%$). Base metal mineralisation, if present, usually occurs in the deeper, higher temperature parts of some veins, and while quite common at low concentrations ($< 1\%$ combined base metal sulphides) it occurs in higher concentrations (i.e., $\geqslant 3\%$ combined base metals) in only a limited number of deposits (Coromandel, Waiomu, Thames, Waitekauri (Jubilee), Karangahake and Tui-Waiorongomai).

In addition to gold, silver, copper, lead and zinc, both porphyry and epithermal mineralisation in the region may contain minor amounts of one or more of the following: selenium, tellurium, cadmium, mercury, arsenic, antimony, bismuth, molybdenum, tin or tungsten.

Porphyry mineralisation and alteration is associated with intrusive rocks at Paritu, Whangapoua, Manaia and Tararu. The epithermal vein deposits and their associated alteration are similarly localised in several distinct areas—Coromandel, Whangapoua, Kuaotunu, Tapu-Waiomu-Thames, Hikuai, Karangahake-Komata-Waitekauri, Waihi and Te Aroha—in response to overall controlling factors, particularly deep-seated crustal structures. Hence, it is common for a series of individual deposits to be associated within a structural belt—for example, Karangahake, Komata, Maoriland-Jubilee, Golden Cross (Waitekauri) and Maratoto, which all lie within, and are probably controlled by, a north-northeasterly fault belt.

The distribution of porphyry mineralisation, epithermal gold-silver vein deposits, and areas within which the volcanic or the greywacke basement rocks are at least moderately altered, are shown in Figure 1.2. Areas of significant past mining and a subdivision of the vein deposits into three categories dependent on their base metal sulphide content are also shown.

Where there is a coincidence of high base metal content (more than several percent), strong clay-pyrite alteration and significant mining activity, environmental contamination could be expected close to the source of the heavy metals. Mining activities may have increased the likelihood of contamination by excavation (and therefore greater exposure) and by waste remains, such as mullock tips, old ore dumps and tailings.

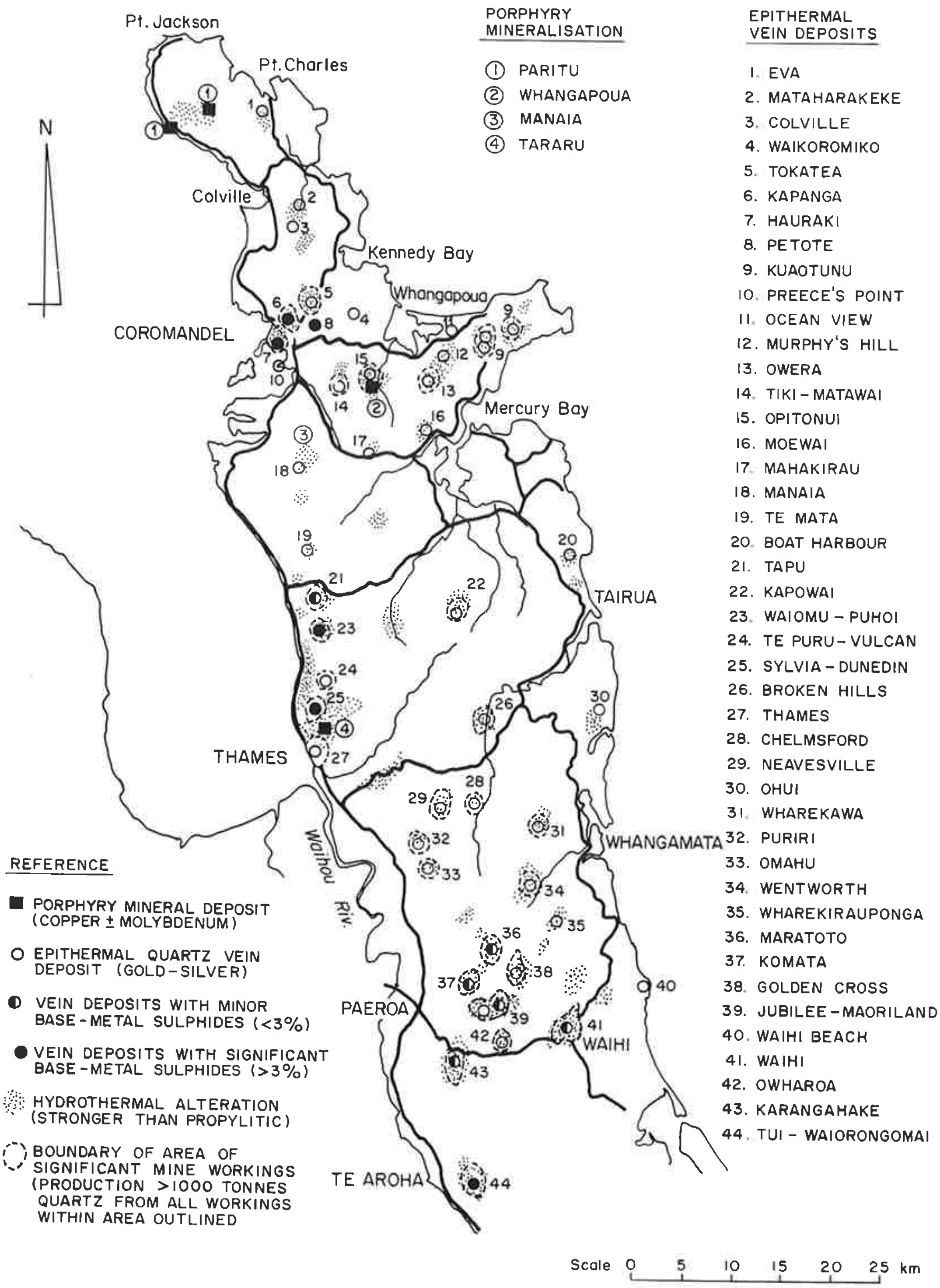


Figure 1.2 Hauraki Region: Location of mineral deposits and areas with significant mine workings (partly after Brathwaite 1981).

While any naturally occurring mineralised rock potentially poses an environmental contamination hazard, the risk may be high or low depending on local conditions and the degree of human interference. Hence, it is evident that any new mining in the Hauraki region may increase the risk of heavy metal or acid contamination of the environment.

1.5 Mining History of the Coromandel Region

Coromandel was the site of the first discovery of gold in New Zealand when, in 1852, Charles Ring, under the incentive of a reward of £100 for the discovery of a goldfield offered by the colonial administrators, found specimen gold at Driving Creek, north of Coromandel Township. However, his find did not live up to its early promise, and Gabriel's Gully (Otago) became the first recognised goldfield, in 1861. It was not until the early 1870s that the Coromandel region became a major focus for gold exploration.

Gold prospecting and mining followed kauri logging, and in the early days of gold mining, numerous small near-surface deposits yielded rich and easily won gold. Many of these had been formed by secondary enrichment of the gold by weathering and re-deposition during prolonged erosion of gold-bearing quartz lodes.

By 1880, most of these deposits were exhausted, and attention was increasingly focussed on the less widespread but larger lower-grade quartz-vein bodies. There was a consequent decrease in the number of companies involved in mining and a trend towards larger operations. The lower-grade ores frequently presented serious recovery problems using traditional mercury amalgamation techniques, and it was not until the advent of the cyanide process in 1894, first used commercially in New Zealand at Karangahake, that these larger veins could be worked profitably. From the late 1890s to 1910, many larger vein deposits were actively worked, including those at Waihi, Karangahake, Owharoa, Waitekauri, Broken Hills, Thames, Kuaotunu, and Coromandel. By the end of this period, all but the largest deposits had been exhausted of their comparatively readily won and higher grade (i.e., profitably workable) ore, and were closed down. Of those remaining, the Waihi Mine continued in production until 1952, while others were worked until the early 1940s (e.g., Owharoa).

The closure of the Martha mine at Waihi heralded a long hiatus in mining activity in the Hauraki region, and it was not until the late 1960s that any further mining took place. At this time the Tui Mine at Te Aroha was redeveloped as a base metal mine (attempts had been made to work it as early as the 1880s), and it was worked until 1973, producing 25 000 tonnes of zinc and lead-copper concentrates. Also of note at this time was a mining operation at Maratoto, where approximately 15 000 tonnes of quartz ore were extracted for silver concentrates.

Since mining began in the late 1870s, there can be little doubt that environmental impacts have in some cases been quite severe. While some operations, notably the Tui Mine, left a lasting legacy of environmental contamination and hazard both to waterways and the land, others had comparatively little lasting environmental effect. Past mining has no doubt contributed to sedimentation of riverbeds and estuaries, but whether it has done so more or less than other land uses is unknown.

1.6 Current Mineral Exploration

Resurgence of exploration in the Hauraki region from 1970–1973 was mainly stimulated by vigorous exploration activity in Australia, which had commenced slightly earlier, and by a strengthening in the price of precious metals (particularly silver). At this time most of the region ($\simeq$ 85%) was covered by mining privileges. A period of decline from 1974 to 1977 was followed by renewed interest, initially in porphyry-type mineralisation for copper and molybdenum. A weakening of the world price of these commodities in the late 1970s-early 1980s coincided with an upsurge in the price of precious metals, particularly gold, and resulted in a switch to emphasis on exploration of the precious metal epithermal vein deposits. It had been recognised since the 1930s, that many of the larger deposits of this type, e.g., Waihi, contained significant quantities of lower-grade ores, which could potentially be worked profitably with modern larger scale and mechanised methods. This surmise has been borne out at Waihi, where on Martha Hill recent drilling has indicated a resource of 10 million tonnes of low-grade gold-silver ore (3.2 g m^{-3} gold and 32 g m^{-3} silver). Plans to establish a new mine on this deposit are proceeding.

In addition to such comparatively large-scale situations, some of the smaller deposits in the Coromandel region may also have potential for profitable small-scale working. Currently a development is proposed at Monowai (Paroquet Stream, Waiomu Stream), and others may arise from time to time in the future.

1.7 Study Site Selection

During 1981, preliminary chemical and biological surveys of freshwater streams were carried out. From this, more detailed surveys of the chemistry and macroinvertebrates of selected streams were designed, and the fisheries survey was extended to coastal waters. Study sites were selected from accessible locations to represent a range of conditions, including those that were visibly contaminated by mine water discharges, those expected to be contaminated by mineralised rocks and/or past mining activities, and those expected to be uncontaminated.

On the basis of the August 1981 preliminary chemical survey, 15 streams were selected for detailed chemical studies and these included the six streams selected for biological studies (Appendix 1.1). As a result of the November 1981 pilot survey of biological communities in 18 streams in the Coromandel region, three catchments (Waitaia, Buffalo, Waiomu) were selected for detailed work, incorporating six of the 18 streams surveyed originally (Appendix 1.1). Freshwater and coastal sample sites from the fish and shellfish survey are listed in Appendices 1.1 and 1.2.

1.8 Geology of Study Streams

The geology relevant to the heavy metal and stream biology surveys is tabulated in Table 1.1. In each case only the upstream part of the catchment, relative to where the water sample(s) were collected, is considered. With the exception of the Waipupu Stream, all the water samples came from catchments containing a combination of altered rocks, veins (with or without base metals) and mines, and as a result of this might be expected to have elevated heavy metal concentrations or acidity.

Table 1.1: Alteration, mineralisation and old mine workings in surveyed Coromandel streams

Stream	Country Rock Alteration	Mineralisation	Mine Working	Mullock Tips, Tailings
Waitawheta	Mainly unaltered or weakly propylitised	Some veins with minor base materials (Mangakino tributary)	None known	None known
Waipupu	Mainly unaltered or weakly propylitised	None known	None known	None known
Waitekauri	Mainly strongly clay-altered and silicified	Several large veins, with trace base metals	Extensive mine workings (Golden Cross)	Present
Komata	Both propylitised and silicified rocks	Several large veins, minor base metals locally	Extensive mine workings (Komata, Te-ao-marama)	Extensive, contain minor base metals
Mangakara	Mainly strongly clay-altered or silicified	Numerous small, commonly pyritic veins	Extensive mine workings (Scotia, Maoriland)	Present
Buffalo	Mainly propylitised or clay-altered	Minor veins with minor base metals	Present	Present
Mangatoetoe	Mainly unaltered; local strong clay alteration	None known	Extensive on Martha Hill	Present
Waiorongoamai	Mainly propylitised, minor silicification	Several large base-metal bearing veins	Extensive mine workings	Present, probably contain minor base metals
Jubilee	Mainly clay-altered, minor propylitisation	Large, locally base-metal bearing vein	Extensive mine workings	Extensive, contain significant base metals
Comstock	Propylitised	Several veins with minor base metal sulphides	Some minor workings	Not known
Waiomu (U/S Paroquet)	Propylitised, some clay alteration	Several veins with minor base metals	Some mine workings (Comstock)	Present
Paroquet	Mainly clay-altered	Base-metal bearing vein	Extensive workings (Monowai)	Present, contain base metals
Waitaia	Propylitised, clay-altered and silicified	Many small veins, several larger veins	Extensive mine workings (Waitaia)	Present
Tui	Propylitised, clay-altered, minor silicification	Several large veins with significant base metals	Extensive mine workings	Extensive, contain significant base metals

1.9 General Water Quality of Study Streams

The general water quality characteristics of each study site were measured by Hauraki Regional Water Board. Results for temperature, conductivity, pH, nitrate, phosphate, sulphate, dissolved oxygen, suspended solids, (Table 1.2) showed no features that would make water quality unsuitable for biological communities. Relatively low alkalinity, relatively elevated sulphate and hardness values in Waitaia Mine Stream (W9, W10), Paroquet Stream (P2), Waiorongomai, Comstock and Tui Streams (Table 1.2) suggest influence from oxidised sulphide minerals. The lower alkalinities also indicate that the buffering capacity of these streams is lower than other streams.

Table 1.2: Summary of water quality data at freshwater sample sites in Coromandel

	Determinand									
Stream Sites	t°C	pH	DO $g\ m^{-3}$	NO_3-N $mg\ m^{-3}$	PO_4-P $mg\ m^{-3}$	SO_4 $g\ m^{-3}$	SS $g\ m^{-3}$	Cond. $mS\ m^{-1}$	Alk. $g\ m^{-3}$ $CaCO_3$	Hard. $g\ m^{-3}$ $CaCO_3$
Waitaia Control Stream W3	11–16	6.1–7.3	8–10	10–36	4	14	nd	21.2	28.7	38
Waitaia Control Stream W4	105.	7.74	10.8	46	18	nd	nd	21.2	nd	nd
Waitaia Stream W5	11–16	6.2–7.4	9–10	26–144	5–12	47	2–8	13–25	6–19	29–32
Waitaia Stream W6	11.1	7.1–7.4	9.4	10	10	49	nd	25	17	56
Waitaia Mine Stream W7	11.1	6.9–7.4	10.6	28	5	nd	nd	27	nd	nd
Waitaia Mine Stream W8	nd	6.0–6.8	9.5	nd	nd	nd	nd	nd	nd	nd
Waitaia Mine Stream W9	15	6.1–7.0	9–9.3	17	6	77	7.9	28.5	9.2	72
Waitaia Mine Stream W10	14–17	6.0–7.1	nd	26	1–8	73	2	30.5	2–8	70–73
Waiomu Stream WC	9–16	6.6–7.6	9–12	28–68	3–8	16.1	10.9	11–13	15.8	28
Waiomu Stream WP2	9–17	6.6–7.5	9–11	14–61	1–17	25.5	10.6	7–23	10.15	21–35
Paroquet Stream P2	9–20	6.3–7.8	9–11	11–50	7	60.5	3–41	16–23	10.7	59
Buffalo Stream B4	10–17	6.8–7.5	9–11	7–17	4–13	15.0	0–2	7–21	11–18	17–26
Everetts Stream E	nd	5.8–6.4	nd	nd	nd	nd	nd	nd	nd	nd
Waipupu	8–23	7.0–7.3	9–12	84–212	2–8	6–8	<1	6–10	17–19	22–23
Waitekauri	7–16	7.1–7.6	10–12	132–285	2–6	7.3	2.6	6–7	11	15
Mangakara	9–19	6.4–7.3	9–12	144–203	1–7	7.2	<1	7–9	9	13
Waitawheta	7–10	7.1–7.8	11	114–290	2–4	4.1	<1	5–9	12–16	15
Komata	9–19	7.0–7.8	9–12	38–198	2–4	9	1.3–2.2	7–11	15–16	21
Waiorongomai	8–16	6.8–7.3	10–12	54–96	1–5	33.5	1.1	8–14	8–9	34–42
Jubilee	14–15	6.7–6.9	10–11	124	2–6	nd	1–7.1	9–10	nd	nd
Comstock	9–15	6.0–7.3	10–11	88–233	1–6	54.9	19–16*	15–20	4–9	53–67
Tui	9–14	5.9–6.4	10–11	143–221	3–4	90.2	11–16*	15–23	1–2	70

*Includes ferric iron compounds precipitated during storage.

nd = not determined
t°c = temperature
DO = dissolved oxygen
SS = suspended solids
Cond = conductivity
Alk = alkalinity
Hard = hardness
NO_3-N = nitrate nitrogen
PO_4-P = phosphate phosphorus
SO_4 = sulphate

1.10 Reference

Brathwaite, R. L. 1981 : Size patterns of gold-silver deposits in the Hauraki Gold Field, Coromandel Peninsula. Australian Institute of Mining and Metallurgy. New Zealand Branch. 1981 Annual Conference Proceedings.

Appendices

Appendix 1.1: Freshwater Site Locations

Detailed biological and heavy metal survey sites surveyed 1982-83 are asterisked. Site number is in brackets.

River or stream	Distance from nearest town	Fisheries study sites (1981)	Chemical study sites (1982)	Biological study sites (1983)
Waihou River	11 km SE Te Aroha	N57 264663	-	-
Waipupu Stream	9 km SE Te Aroha	N57 282701	N57 285698	N57 285698
Wairongomai Stream	5 km SE Te Aroha	N57 248748	N57 247746	N57 247746
Tui Stream	1 km N Te Aroha	N57 197794	N57 197794 217794 483052	N57 217794
Comstock Stream	6 km SE Paeroa	N53/54 212912	N53/54 212912	N53/54 212912
Waitawheta Stream	9 km SE Paeroa	N53/54 237894	N53/54 237894	-
Komata River	5 km NE Paeroa	N53/54 209998	N53/54 199004	N53/54 199004
Waitekauri Stream	6 km NWW Waihi	N53/54 265973	N53/54 265973	N53/54 265973
Mangakara Stream	5 km W Waihi	-	N53/54 273944	N53/54 273944
Jubilee Stream	6 km NWW Waihi	-	N53/54 266972	N53/54 266972
Grace Darling Stream	7 km NWW Waihi	-	-	N53/54 266979
Mangatoetoe Stream	At Waihi	N53/54 325955	N53/54 325955	N53/54 325955
Maratoto Stream	9 km E Hikutaia	N53/54 247058 253050	-	-
Apakura Stream,	13 km SE Thames	N49 158159	-	-
Ohaumuri Stream	13 km SE Thames	N49 152162	-	-
Tararu Stream	4 km N Thames	N49 042303	-	-
Ohio Stream	4 km N Thames	N49 042306	-	-
Waiomu Stream	2 km E Waiomu	N49 032394	N49 040394*(WC) 037395*(WP1) 032394*(WP2)	N49 045393*(WF) 040394*(WC) 039395*(WP1) 032394*(WP2)
Paroquet Stream	2 km E Waiomu	-	N44 049407*(P1) N49 039395*(P2)	N44 049407*(P1) N49 039395*(P2)
Puhoi Stream	0.5 km N Waiomu	N49 014397	-	-
Otuturu Stream	1 km E Ruamahanga	N44 018410	-	-
Tapu River	1 km E Tapu	N44 010447 051436	-	-

Appendix 1.1: Freshwater Site Locations—*continued*

River or stream	Distance from nearest town	Fisheries study sites (1981)	Chemical study sites (1982)	Biological study sites (1983)
Whareroa Stream	12 km N Coromandel	N40 047855	-	N40 847855
Heretaunga Stream	9 km NE Coromandel	N40 028780	-	N40 027777
Buffalo Stream	1.5 km N Coromandel	N40 006736	N40 008739(B4)	N40 018744*(B1) 017744*(B2) 016744*(B3) 008739*(B4)
Everett's Stream	1.5 km N Coromandel	-	N40 017744(E)	N40 017744(E)
Waitaia Stream	2 km S Kuaotunu	N40 231739	N40 W1 228732* W3 228737* W4 228739* W5 228742* W6 228740* W7 228740* W8 234737* W9 238737* W10, 11 240737* W12 235736*	N40 228732*(W1) 228737*(W3) 228739*(W4) 228742*(W5) 228740*(W6) 228740*(W7) 234737*(W8) 238737*(W8G) 235731*(W9) 235736*(W10)
Mapauriki Stream	10 km SW Whitianga	N44 126540	-	-
Ounuora Tributary	8 km SW Whitianga	N44 149562	-	-
Rangihau Stream	6 km S Coroglen	N44 184451	-	N44 183451
Wentworth River	6 km SW Whangamata	N49 313128	-	-
Otahu River	7 km SW Whangamata	N49 325105	-	N49 325105
Third Branch Stream	6 km SW Hikuai	N49 229286	-	-

Appendix 1.2: Coastal sites

Status column shows no history of mining (—) or known history of mining (#) in the hinterland.

Location	Map No.	Offshore fish site	Offshore shellfish site	Onshore shellfish site	Status
Port Jackson	N36	845060	845060	845060	-
Port Charles	N36	963010	963010	963010	-
Goat Bay	N36	-	-	829020	-
Fletcher Bay	N36	-	892067	892067	-
Fantail Bay	N36	-	-	830002	-
Darkie Stream	N39	835978	-	-	-
Colville Bay	N39	922890	-	970885	#
Colville Channel	N39	946887	-	-	#
Amodeo Bay	N39	930825	-	-	-
Long Bay	N39	965735	-	-	#
Coromandel Harbour	N39	975705	-	-	-
Waiaro Bay	N39	-	-	919924	-
Kikowhakorere Bay	N39	-	-	979748	-

Appendix 1.2: Coastal sites—*continued*

Location	Map No.	Offshore fish site	Offshore shellfish site	Onshore shellfish site	Status
Koputauaki Bay	N39	–	–	904984	–
Wyuna Bay	N39	–	–	963715	–
Hope Stream Mouth	N39	–	–	889942	–
MacGregor Bay	N39	–	–	970722	#
Waitoitoi Stream Mouth	N39	–	–	845974	–
Te Puru Bay	N49	000375	–	–	#
Te Puru Stream Mouth	N49	–	–	017373	#
Whakatete Bay	N49	–	–	015320	–
Waiomu Stream Mouth	N49	–	–	015395	–
Tararu Stream Mouth	N49	–	–	017292	#
Haupapa Point	N40	062917	–	–	–
Kennedy Bay	N40	077820	077820	–	–
Whangapoua Harbour	N40	122740	–	–	#
Quarry Point	N40	208768	208768	–	#
Otama Beach	N40	250790	–	–	#
Opito Bay	N40	290789	290789	293775	–
Matapaua Bay	N40	–	302738	–	–
Esk Reef	N43	–	–	940658	–
Wilson's Bay	N43	–	–	928559	–
Te Mata River	N43	–	–	995462	#
Mercury Bay	N44	222645	–	–	#
Buffalo Bay	N44	202647	–	–	#
Cooks Bay	N44	238630	–	248627	#
Pauanui Beach	N44	365405	365405	403421	#
Tairua Tidal Flats	N44	–	–	408429	#
Tairua Beach	N44	–	–	400418	#
Tapu River Mouth	N44	–	–	000442	#
Whitianga Harbour	N44	–	–	201620	#
" "	N44	–	–	202625	#

CHAPTER 2: Heavy Metal Survey of Coromandel Streams

Helen M. Beaumont, J. Clair Tunnicliff and Craig D. Stevenson

2.0 Abstract

This study of heavy metals in selected Coromandel streams reveals relatively low (background) levels of arsenic, cadmium, copper, lead and zinc in some streams, including some where mining has occurred in the past, and relatively high levels of these metals in other streams. The highest heavy metal levels occurred in streams that receive discharges from old mine workings or tailings.

The concentrations of "non-residual" metals (see Section 2.1.7) in the sediments, and parameters which indicate the amount of acid addition to a stream (sulphate concentration and total hardness minus alkalinity) were useful to corroborate the presence of heavy metals in the water.

The results of this study show that the background heavy metal concentrations in Coromandel streams are considerably lower than most overseas water quality criteria. On this basis, at least, it would be appropriate to use these criteria in the management of water quality in these streams.

2.1 Introduction

2.1.1 Objectives

The main objective of the chemical study was to determine typical heavy metal levels in Coromandel Peninsula streams. Streams were selected to cover a range of conditions from background to grossly contaminated. The purpose of obtaining such information was to assist in providing a basis for future water right considerations for control of heavy metals, by:

(1) providing an indication of existing heavy metal levels;

(2) comparing the metal levels with overseas water quality criteria for the protection of aquatic life, as a preliminary assessment of the appropriateness of these criteria for local stream conditions;

(3) providing a basis for the site selection and subsequent interpretation of concurrent biological studies (Chapter 3) that examine the biological communities in streams receiving contaminated mine wastes.

2.1.2 Water quality criteria for the protection of aquatic life

Heavy metals are generally present at very low levels in natural waters and many are essential to life at trace concentrations. However, at higher concentrations even the essential metals become toxic to aquatic organisms. Humans can tolerate much higher levels of metals in waters than aquatic organisms and water quality criteria for metal concentrations in potable water supply are up to two orders of magnitude greater than those generally proposed for the protection of aquatic life (Table 2.1). The aquatic life criteria are largely based on laboratory experiments and involve safety factors (application factors) to protect all life stages of the test organism and other organisms. This introduces some uncertainty about the applicability of the criteria to specific streams where conditions may be quite different from the experimental conditions under which the criteria were derived.

The United States Environmental Protection Agency (US EPA) criteria are two-fold to protect against chronic and acute toxicity (Table 2.1). They also take into account the hardness of the water body, because laboratory experiments (mainly acute toxicity testing) have shown that metals are more toxic in soft waters (such as found in New Zealand) than in hard waters. This ameliorating effect on the toxicity of some heavy metals may be due to one or more of a number of interrelated ions, such as hydroxide, carbonate and bicarbonate (constituents of alkalinity), calcium and magnesium (constituents of hardness), (US EPA 1985). The carbonate and bicarbonate ions form a range of heavy metal complexes which may diminish the effective metal toxicity. Hardness is used by US EPA (1985) as a "surrogate" for those ions which affect heavy metal toxicity but this approach may be invalid where total hardness and alkalinity are not equivalent (Section 2.1.6).

There has been concern in the past over the apparent similarity in concentration between the laboratory-determined criteria and the reported metal concentrations in uncontaminated streams. More recent information indicates that the typical concentration ranges for natural waters are much lower than previously thought (e.g., Mart 1982). This relates to increasing awareness among researchers of the contamination problems associated with trace metal analysis, and the improvements in sampling and analysis methods to minimise these problems (see Section 2.1.3).

During the period of this work, the US EPA water quality criteria underwent revision. New criteria (US EPA 1985) for selected heavy metals, which supersede the previous (1980) US EPA aquatic life criteria, are now available (see Table 2.1). Of particular note is the new four-day average criterion for cadmium, which is considerably higher than the 24-hour average criterion given in 1980.

Thus, the difficulty for water managers in trying to apply water quality criteria that were as low if not lower than 'natural' concentrations, has now diminished. Nevertheless, uncertainties involved in the development of water quality criteria remain, and there is some doubt surrounding their applicability to New Zealand (see Chapter 3, Section 3.3).

Previous studies of streams in the Coromandel Peninsula area have not provided measurements of background heavy metal levels, either because they focussed on contaminated streams, such as the Tui Stream (e.g., Tay 1980), or because the intention was to determine suitability of the water for human consumption and therefore measurement of metal levels below drinking-water standards was not attempted (e.g., Petricevic and Stanton 1983).

2.1.3 Difficulty of low-level heavy metal measurements

The occurrence of extremely low levels of heavy metals in uncontaminated natural waters poses special problems for water sampling and analysis. Over the last few years it has become clear that many earlier studies of heavy metal levels in natural waters were seriously in error because of metal contamination introduced during the sampling and analysis procedures. This is illustrated by studies of trace metals in the open ocean, where recent data give levels that are several orders of magnitude lower than those previously reported (parts per 10^{12} compared with parts per 10^{9}) (Bruland 1980, Hunter 1982, Mart 1979, Settle and Patterson 1980). Accurate analysis of low metal concentrations has been made possible through the development of rigorous

Table 2.1: Some water quality criteria and standards (mg m^{-3})

	Criteria for the protection of freshwater aquatic life								Drinking-water standards	
	US EPA (1980) (also Smith 1982)		US EPA (1985)		Canada IWD (1979)	EIFAC (Alabaster and Lloyd 1980)		Australia (Hart 1982)	New Zealand Board of Health (1984)	
	24 Hour Average	Maximum	4 Day Average	1 Hour Average	Objective	50 percentile	95 percentile	Maximum	Highest Desirable	Excessive
Arsenic	-	440[a]	190[a]	360[a]	50[c]	-	-	50[c]	-	50[i]
Cadmium	0.012[b]	1.5[b]	0.66[b]	1.8[b]	0.2	0.4[b]	0.9[b]	0.2[g]	-	5[i]
Copper	5.6	12[b]	6.5[b]	9.2[b]	2.0	6.0[b]	22.0[b]	5[h]	50[j]	1,000[j]
Lead	0.75[b]	74[b]	1.3[b]	34[b]	5.0[d]	-	-	5[h]	-	50[i]
Mercury	Under revision		0.012[k]	2.4	0.2[e]	-	-	0.1	-	1[i]
Zinc	47	180[b]	-	-	50[f]	50[b]	200[b]	50[h]	5,000[j]	5,000[j]
Form of metal determined	Total recoverable		Acid-soluble		Total	Soluble		Total (As, Cd, Hg) Filterable (Cu, Pb, Zn)	Total	

[a]Trivalent arsenic. Insufficient data for pentavalent arsenic.
[b]Water hardness of 50 g m^{-3} $CaCO_3$.
[c]Total arsenic.
[d]Hardness less than 95 g m^{-3} $CaCO_3$.
[e]0.1 to protect consumers of fish.
[f]Hardness less that 120 g m^{-3} $CaCO_3$.
[g]May need to be reduced in some very soft waters.
[h]May be increased in waters with high hardness or complexing capacity.
[i]Health significance.
[j]Aesthetic quality.
[k]Based on methyl mercury.

procedures for the collection and handling of natural water samples to ensure low levels of contamination at every stage (Batley and Gardner 1977, Mart 1979, Mart 1982). For analysis at trace levels, particularly when the analysis procedure requires extensive sample manipulations, specialised clean laboratories are required. Full class 100 facilities (see Glossary) are ideal but less expensive approaches, such as class 10,000 rooms, laminar flow hoods, or even installation of air conditioning to give a slight positive pressure of filtered air in a small, easily washed room can give major improvements over regular laboratory space.

Analysis of metals in waters in this study was carried out by differential pulse anodic stripping voltammetry. This technique is sufficiently sensitive that procedures to pre-concentrate the metal ions in solution (for example, by evaporation or using an ion exchange resin) are rendered unnecessary. The possibility of contamination is thus reduced (Wang 1982, Nurnberg 1984).

2.1.4 Sources of metals in water

Metals are released to the aquatic environment by the dissolution of rock. The dissolved metal levels present in unpolluted natural water bodies are largely dependent on the geology of the catchment.

Hydrothermal ore deposits such as those occurring in the study area (Section 1.8) contain sulphide minerals, such as pyrite (FeS_2), galena (PbS), sphalerite (ZnS), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), arsenopyrite ($FeAsS$). When water containing oxygen comes in contact with these minerals, acid is produced and metals are released into solution. For example, the oxidation of pyrite:

$$\begin{array}{ccccccccccc} 2FeS_2 & + & 2H_2O & + & 7O_2 & \rightarrow & 2Fe^{2+} & + & 4SO_4^{2-} & + & 4H^+ \\ \text{pyrite} & + & \text{water} & + & \text{oxygen} & \rightarrow & \text{metal} & + & \text{sulphate} & + & \text{acid} \\ & & & & & & \text{(ferrous ion)} & & & & \end{array} \quad (1)$$

This occurs as a result of weathering processes at the surface and where oxygenated groundwater comes into contact with the rock underground. The solubility of most metals increases as pH decreases, so the production of acid tends to increase the rate of dissolution of metals. The metals remain in solution until a change in the chemical environment occurs, such as emergence of the water at the surface, where conditions are more oxidising and may be less acidic (due to dilution). The metal ions may then precipitate or be adsorbed or complexed by organic and inorganic ligands which may then coagulate and precipitate. The ferrous (Fe^{2+}) ion is readily oxidised to the ferric (Fe^{3+}) ion, which forms a highly insoluble hydroxide precipitate, with the production of further acid:

$$\begin{array}{ccccccccc} 2Fe^{2+} & + & 2H^+ & + & \tfrac{1}{2}O_2 & \rightarrow & 2Fe^{3+} & + & H_2O \\ \text{ferrous ion} & & \text{acid} & & \text{oxygen} & & \text{ferric ion} & & \text{water} \end{array} \quad (2)$$

$$\begin{array}{ccccccc} 2Fe^{3+} & + & 6H_2O & \rightarrow & 2Fe(OH)_{3(s)} & + & 6H^+ \\ \text{ferric ion} & & \text{water} & & \text{ferric hydroxide} & & \text{acid} \end{array} \quad (3)$$

The iron hydroxide may incorporate other elements by co-precipitation. The sediments formed from these precipitates have the tendency to adsorb metals from the water column.

2.1.5 Effects of mining on metal levels

Mining activity in areas of hydrothermal mineralisation can cause increased levels of metals in stream water and sediments by accelerating the rate and extent of the processes described in Section 2.1.4. Mining exposes rock surfaces to contact with infiltrating water, and mineralised groundwater may be intercepted and brought to the surface. Contaminated water may flow out of the mine, commonly characterised by the deposition of ferric hydroxide as a bright orange floc.

Other sources of heavy metals are debris and tailings from mine workings, which may contain sulphide minerals. Their oxidation may produce acid leachates, high in dissolved metals. The rate of oxidation increases with surface area exposed and the finely ground tailings associated with modern mining techniques (e.g., at Tui Mine) present the greatest problems.

Heavy metal contamination of streams is not an inevitable result of mining activity, nor is mining the only cause of such contamination. Elevated heavy metal levels may occur naturally in stream waters as a result of natural weathering of mineralised strata (see Chapter 1).

2.1.6 Acid generation

As well as releasing heavy metals to solution, the oxidation of sulphide minerals produces acid (H^+) (see reactions (1)–(3), Section 2.1.4). It can be a useful indicator of the likely extent of heavy metal contamination in a stream, and it has both direct and indirect adverse effects on aquatic life.

Acid generation as an indicator of heavy metal contamination

The amount of acid generated by sulphide oxidation is related to the amount of heavy metals released, because both are produced by the same mechanism. Acid addition to a water body causes a decrease in pH that is dependent on the level of alkalinity present in the water. Addition of acid to water with low alkalinity will cause a larger decrease in pH than addition of the same amount of acid to water with higher alkalinity, so the decrease in pH does not provide a direct measure of the amount of acid added. Estimates of the amount of acid produced can be gained from the total hardness minus alkalinity, and sulphate concentration, as discussed below.

(1) *Total hardness minus alkalinity*

In most natural waters total hardness and alkalinity are usually approximately equal (if expressed as equivalent concentrations of, for example, calcium carbonate). This is because calcium and magnesium ions (the constituents of hardness) mainly enter water as a result of the dissolution of rocks, particularly limestones (calcium carbonate) and equivalent concentrations of carbonate and bicarbonate ions (the main constituents of alkalinity) are also dissolved.

However, in waters affected by the acid-generating oxidation of sulphide minerals, the total hardness and alkalinity are unequal because the acid has been partially neutralised by reaction with carbonate and bicarbonate:

$$\underset{\text{acid}}{H^+} + \underset{\text{carbonate}}{CO_3^{2-}} \rightarrow \underset{\text{bicarbonate}}{HCO_3^-} \qquad (4)$$

$$\underset{\text{acid}}{H^+} + \underset{\text{bicarbonate}}{HCO_3^-} \rightarrow \underset{\text{carbonic acid}}{H_2CO_3} \rightarrow \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide gas}}{CO_2} \qquad (5)$$

The acid dissolves associated minerals in the rock matrix so that the resulting drainage may have very high hardness levels, but the alkalinity is reduced relative to total hardness by an amount equivalent to the quantity of acid neutralised.

On mixing with stream water, further acid neutralisation may occur, reducing the stream alkalinity. Downstream of the discharge the difference between total hardness and alkalinity is a measure of the acid generated.

(2) *Sulphate concentration*

Sulphate (see Equation 1) can be used to indicate the amount of acid generated. The increase in sulphate concentration over that naturally found in the stream is taken to be an indication of acid production associated with sulphide oxidation.

Toxic effects of acid generation

When the alkalinity of stream water is reduced by acid addition (thereby lowering the buffering capacity), any future acid additions are less able to be neutralised, resulting in progressively larger decreases in pH. The effects of reduced pH on aquatic fauna are discussed in Chapter 3. The addition of acid may also cause adverse biological effects by dissolving heavy metals from the sediments, and increasing the toxicity of heavy metals by lowering the alkalinity. The US EPA (1985) recognise that some heavy metals are more toxic at lower alkalinity and/or hardness levels and use total hardness to adjust water quality criteria concentrations (Section 2.1.2). This approach may be invalid where total hardness and alkalinity are not equivalent and it is probably more appropriate for water quality criteria for streams affected by acid addition to be calculated on the basis of stream alkalinity rather than total hardness.

The hardness-related EPA criteria are calculated from the formula $e^{[x\ln(\text{hardness})-y]}$ where hardness is expressed in units of g m^{-3} $CaCO_3$, and x and y

Table 2.2: US EPA water quality criteria calculated for different levels of hardness (or alkalinity)

Metal	Criterion formula[a]		Hardness or alkalinity	US EPA (1985) criteria for aquatic life protection (mg m^{-3})	
	4 day average	1 hour average	(g m^{-3} $CaCO_3$)	4 day average	1 hour average
Cadmium	x = 0.7852 y = 3.490	x = 1.128 y = 3.828	10 25 50 100	0.19 0.38 0.66 1.1	0.29 0.82 1.8 3.9
Copper	x = 0.8545 y = 1.465	x = 0.9422 y = 1.464	10 25 50 100	1.7 3.6 6.5 12	2.0 4.8 9.2 18
Lead	x = 1.273 y = 4.705	x = 1.273 y = 1.460	10 25 50 100	0.17 0.54 1.3 3.2	4.5 14 34 82
Zinc[b]	not related to hardness	x = 0.83 y = −1.95	10 25 50 100	47	48 102 180 320

[a]Formulae are of the form: criterion concentration (mg m^{-3})$=e^{[x\ln(\text{hardness})-y]}$ where hardness is expressed in g m^{-3} as $CaCO_3$, x and y are constants

[b]1980 criteria are given for zinc (24 hour average and maximum concentrations).

2.2 for the metals cadmium, copper, lead and zinc (the arsenic criteria are not related to hardness). The same formulae can be used to calculate alkalinity-related criteria instead of hardness-related criteria, simply by substituting alkalinity for hardness, i.e., $e^{[x\ln(\text{alkalinity})-y]}$. Alkalinity must be expressed in the same units as hardness (g m^{-3} $CaCO_3$). Table 2.2 lists the criteria calculated for values of hardness or alkalinity of 10, 25, 50 and 100 g m^{-3} as $CaCO_3$.

Thus if hardness and alkalinity are equivalent in a stream, the water quality criteria will be the same regardless of whether hardness or alkalinity is used as the calculation base. If, however, alkalinity is significantly less than hardness (as in streams affected by acid addition), the criteria based on alkalinity will be lower (more stringent) than those based on hardness.

2.1.7 Forms and toxicity of metals

In an aquatic system, heavy metals occur in different phases (Canada Inland Waters Directorate 1979, Huang *et al.* 1977).

(1) *In the water column*

- — In solution ('dissolved', conventionally defined as that fraction which passes through a 0.45 µm filter)—as free ions, or complexed with organic and inorganic ligands.
- — In suspended solids ('particulate', defined as that fraction which is retained by the filter)—as inorganic precipitates, organic or inorganic complexes, and adsorbed onto other particles.

(2) *In bottom sediments*

- — As inorganic precipitates, organic or inorganic complexes and adsorbed onto other particles—"non-residual metals".
- — Occluded within the mineral matrix of the sediment particles—"residual metals".

(3) *In biota*

- — Adsorbed or incorporated into the biomass of living organisms.

The chemical form (or speciation) of a heavy metal influences its availability and toxicity to biota, its transport and mobilisation, and its behaviour in sediment-water interactions (Hart 1982). In the past, most water quality criteria have expressed metal concentrations as "total recoverable", determined after mineral acid digestion of unfiltered water samples. The "total recoverable" value includes free and complexed metal ions in solution and metal ions adsorbed, complexed or precipitated with suspended sediments, and represents a maximum value for metals which might be biologically available in natural waters. It has been suggested, however, that most solid forms of the metal can be considered non-toxic and that complexation and adsorption can both regulate availability and reduce toxicity (Chau and Wong 1976, Canada Inland Waters Directorate 1979, Florence 1977, Batley and Florence 1976, Florence 1982). The free ionic form is now thought to be the most toxic form of many heavy metals. Consequently, the US EPA (1985) now consider that "acid-soluble" rather than "total recoverable" metal concentrations are more appropriate for measurements of biologically active forms. Acid-soluble metal is defined as the metal that passes through a 0.45 µm membrane filter after the sample is acidified to pH = 1.5 to 2.0 with nitric acid. Acid-soluble concentrations in ambient water samples should include all forms of the metal that are toxic to aquatic life or can be readily converted to toxic forms under natural conditions (US EPA 1985). As well as having toxicological advantages, the acid-soluble measurement has the practical advantage over the total recoverable determination that no digestion step is required so there is less potential for sample contamination.

The metal concentrations measured in water samples in this study (defined for the purpose of this report as "acid-extractable") would fall somewhere between the "total recoverable" and "acid-soluble" concentrations as outlined above. The acid-extractable concentrations were measured by differential pulse anodic stripping voltammetry (DPASV), after acidification of the samples to about pH 1.8 with nitric acid. The acidification releases some of the adsorbed and complexed metal ions and analysis by DPASV determines all but the strongly complexed metal ions in solution. It is unlikely that metals not released from particulate material by acidification would be measured by DPASV. The metal levels measured in this study should therefore be close to acid-soluble concentrations and not much lower than the levels that would have been determined by total recoverable techniques because of the low suspended solids, hardness, alkalinity and organic content of the study streams.

2.1.8 Metal levels in stream sediments as indicators of water quality

Metal levels in stream water fluctuate daily and seasonally, depending on flow and other variables. Intensive monitoring is necessary to accurately establish the concentration range.

An alternative approach is to use metal levels in the stream sediments as an indicator of the general quality of the associated waters (Ellaway *et al.* 1982). Sediments act as a net sink for heavy metals over time (Hart 1982), and thus provide a time-integrated representation of metal levels in the water. The advantage of measuring metals accumulated in the sediments is that the concentrations are usually higher and more stable than in the associated water, so less rigorous sampling and analysis procedures are required. The relationship between metal concentrations in the water and sediment is complex. Non-residual metal levels in the sediments depend on a number of factors (Vuceta and Morgan 1978, Huang *et al.* 1977, Warren 1981), in particular:

(1) metal levels typically present in the water;

(2) co-precipitation or adsorption by hydrous iron and manganese oxides—this mechanism is likely to be important in the case of mine drainage, where very large amounts of iron can be precipitated as ferric hydroxide;

(3) pH conditions—most metals tend to become more soluble in acidic conditions. The adsorption of metals on hydrous oxides and soils decreases abruptly over the pH range 7 to 5 (Huang *et al.* 1977). An exception is arsenic which is present in anionic form and is precipitated even under very acidic conditions;

(4) sediment particle size—the amount of adsorption increases as the particle size decreases because of the overall increased surface area within the sediment;

(5) amount of organic matter—this increases the adsorption of metals.

If metal levels in sediments from different sites are to be used to infer and compare metal concentrations in the waters, it is important to eliminate or account for variations in the remaining controlling factors (2)–(5). Sediments containing a significant amount of organic matter should be avoided, and the samples should be of comparable particle size. It is normal to sieve the samples and analyse a constant size fraction.

Provided inter-site variation has been accounted for and the sediments have been in contact with the overlying waters for sufficient time, the following relationships between the metal levels in the sediments and the waters are expected:

(1) Sediment metal levels will tend to correlate with average water metal concentration, with low levels in the waters being reflected by low metal levels in the sediments.

(2) When co-precipitation and/or adsorption with iron is the major controlling factor, the absolute levels of metals in the sediments may not correlate with the levels in the waters, but the metal/iron ratios in the sediments will follow the metal levels in the waters.

(3) Under acidic conditions, with the exception of arsenic, the absolute levels of metals and the metal/iron ratios in the sediments will be lower, as the metals have a greater tendency to remain in solution.

2.1.9 Sediment digestion methods

Heavy metals associated with different phases can be removed from the sediment by selective extraction schemes. Only loosely bound metals are removed by leaching with cold, dilute acid, while at the other extreme digestion with hot, concentrated acids will liberate all forms of metals, including those bound in the sediment rock matrix.

In this study, interest focussed on the levels of metals in the sediments that resulted from interactions between the sediments and the stream waters. For this reason metals were extracted with cold dilute acid. This dissolves non-residual metals, including oxides and hydroxides of manganese and iron (Agemian and Chau 1976).

The metal levels measured in this study would not be comparable to those measured using total digestion procedures.

2.2 Methods

2.2.1 General

This report presents the heavy metal levels measured in samples of unfiltered acidified stream water, and in stream sediment samples.

The heavy metals measured in this study were arsenic, cadmium, copper, lead and zinc (in both water and sediment samples), plus iron in sediment samples and mercury in some sediment samples. The metals chosen are representative of those potentially released from sulphide minerals, including those which are more toxic to aquatic life. Iron concentrations in sediments were measured because of the likely co-precipitation/adsorption of heavy metals with iron hydroxide precipitates (see Section 2.1.8).

Mercury was not measured in water samples because the collection of samples and determination of mercury in natural waters is extremely difficult, requiring different procedures from other heavy metals for container preparation, sample preservation and analysis. Mercury concentrations were however measured in the sediments of some study streams (M. H. Timperley, *pers comm*, December 1982).

Other water quality determinands are discussed in Section 1.9.

The study intended to obtain an indication of the typical heavy metal levels in the waters of the streams surveyed. Concurrent sediment heavy metal analyses and estimates of acid input to the streams were used to confirm that the limited number of water analyses obtained at each site were reasonably representative of typical water quality conditions.

No attempt was made to measure heavy metal levels in either waters or suspended sediments during flood flows and the results are not suitable for estimating the total load of metals carried by the study streams.

The aim was to measure metal levels in streams with varying geology and mining history, but not to draw quantitative relationships between the metal content of ores, the extent of mining, and metal concentrations in streams.

2.2.2 Sampling programme

Water samples for heavy metal analysis were collected in a preliminary survey of Coromandel Peninsula streams, conducted by the Hauraki Regional Water Board and Fisheries Research Division, MAF, during August 1981. Evidence of contamination problems in some samples led to the rejection of these data and the adoption of special sampling and analysis procedures to provide more reliable results. Particular effort was made to minimise contamination at every stage and this, combined with refinement of analysis methods, enabled the satisfactory measurement of low heavy metal levels.

In March 1982, sediments and water samples were collected from streams expected to give a range of heavy metal levels from background to those obviously contaminated by past mining activities (Figure 2.1). Results from this survey were then used to assist in the selection of sites for the biological studies. The biological study catchments (Figure 2.2) were sampled more intensively with additional water samples collected in July, August and November 1982, and January 1983; and sediment samples collected in July and August 1982. Water sampling of the streams surveyed in March 1982 was repeated in August 1982.

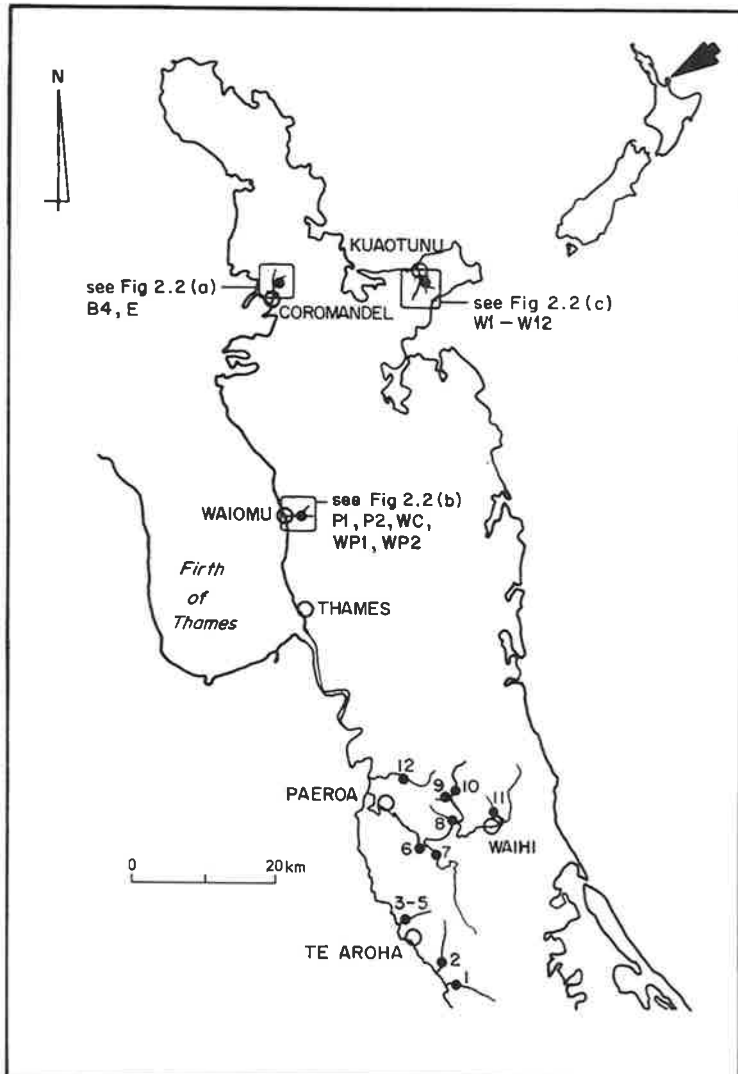
2.2.3 Preparation of sample containers

The sample containers (1 L unfilled polyethylene bottles for water samples and 400 mL polyethylene jars for sediments) were cleaned by soaking in 6M nitric acid (AR grade) for one week, rinsing and soaking in distilled water for 24 hours, and rinsing once again.

Nitric acid has been shown to be effective as a leaching agent for the removal of trace element contamination from polyethylene, with a recommended minimum leaching time of three days (Karin *et al.* 1975). Acid-leaching is essential to remove surface contamination from container material, but can also activate adsorption sites capable of removing trace metals from solution. For this reason, the containers must be well-rinsed and soaked with distilled water after acid treatment (Batley and Gardner 1977).

2.2.4 Collection of samples

Water samples were collected from as near to the middle of the stream as possible, with the sample bottle immersed well below the surface and the opening facing upstream. The bottle was thoroughly rinsed once with the stream water and then refilled. Special care was taken to avoid any potential source of contamination, especially by touching the inside of the bottle or cap with the fingers.



KEY TO SAMPLING LOCATIONS (•)

		N.Z.M.S. 1	MAP REF.
1.	WAIPUPU STREAM	N57	285698
2.	WAIORONGOMAI STREAM	"	247746
3.	TUI STREAM (Tui Rd.)	"	217794
4.	TUI STREAM (Highway 26)	"	196792
5.	TUI STREAM (Waihou R.)	"	186788
6.	COMSTOCK STREAM	N53/54	212912
7.	WAITAWHETA STREAM	"	237894
8.	MANGAKARA STREAM	"	273944
9.	JUBILEE STREAM	"	266972
10.	WAITEKAURI RIVER	"	265973
11.	MANGATOETOE STREAM	"	325955
12.	KOMATA RIVER	"	199004
WC	WAIOMU CONTROL	N49	040394
WP1	WAIOMU STREAM	"	037395
WP2	WAIOMU STREAM	"	032394
P1	UPPER PAROQUET STREAM	N44	049407
P2	LOWER PAROQUET STREAM	N49	039395
B4	BUFFALO STREAM	N40	008739
E	EVERETT'S MINE	"	017744
W1	WAITAIA CONTROL STREAM (Upstream of seepage zone)	"	228732
W2	WAITAIA CONTROL STREAM (Downstream of seepage zone)	"	228732
W3	WAITAIA CONTROL STREAM	"	228737
W4	LOWER WAITAIA CONTROL STREAM	"	228739
W5	WAITAIA STREAM	"	228742
W6	WAITAIA STREAM	"	228740
W7	WAITAIA MINE STREAM	"	228740
W8	" " "	"	234737
W9	" " "	"	238737
W10	" " "	"	240737
W11	" " "	"	240737
W12	MULLOCK STREAM	"	235736

Figure 2.1 Sampling locations, heavy metals survey.

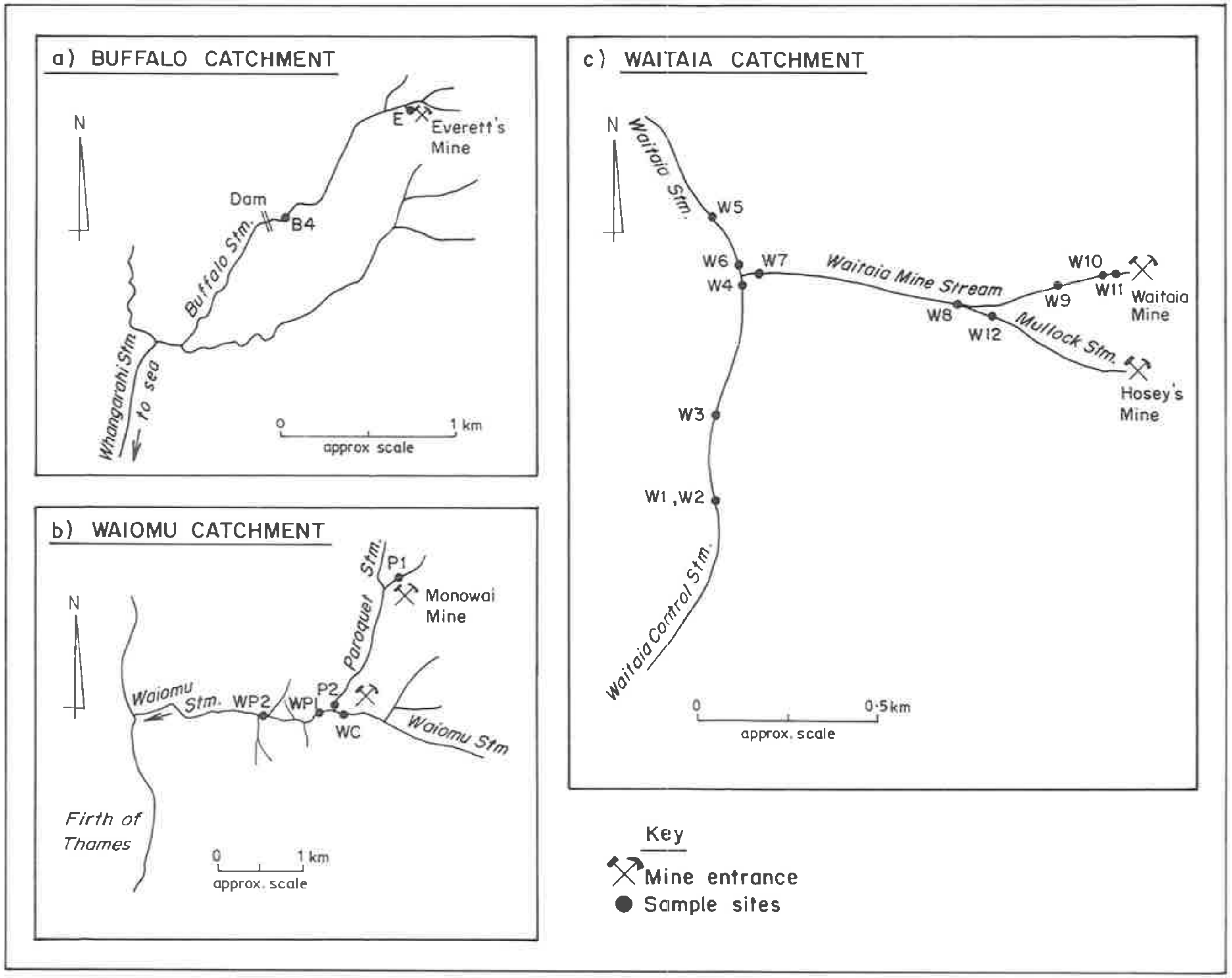


Figure 2.2 Water chemistry sampling locations in biological study catchments.

Sampling locations were chosen to avoid contamination from extraneous sources of metals (e.g., roads, bridges, vehicles), and cigarette smoking was prohibited throughout the sampling procedure.

Sediment samples were collected by hand from as near to the middle of the stream as possible (depending on depth of water), taking care to avoid organic matter. Two or three separate sediment samples were generally collected from each site on each occasion.

2.2.5 Preservation of water samples

To minimise trace metal losses by adsorption to the container walls, samples were preserved by the addition of acid immediately after collection. The preservative acid was AR grade nitric acid which had been further purified before use by non-boiling distillation in an all-teflon apparatus. A small vial containing 1 mL of the distilled nitric acid and 3 mL deionised distilled water was attached to each sample bottle, ready for acid addition to the sample in the field.

2.2.6 Analysis of water samples

The concentrations of cadmium, copper, lead and zinc were measured by differential pulse anodic stripping voltammetry using a thin mercury film electrode. The metals were concentrated by reduction onto the electrode, followed by anodically re-oxidising (stripping) to produce a peak-shaped plot of current as a function of potential.

The analyses were performed using a Princeton Applied Research 174A polarographic analyser in the differential pulse mode. The mercury film was produced *in situ* on a polished glassy carbon electrode by adding mercuric nitrate to the sample solution and depositing at a potential where both mercury ions and the metal ions to be determined are reduced (Florence 1970, Valenta *et al.* 1977). The glassy carbon working electrode was rotated at 1500 rpm during deposition and the surface was refurbished between each analysis by polishing with finely ground alumina paste. It was operated in conjunction with a platinum wire counter electrode and a silver/silver chloride reference electrode, which was isolated from the sample by a potassium nitrate salt bridge. Oxygen-free nitrogen was bubbled through the sample for five minutes to purge oxygen and then an atmosphere of nitrogen was maintained over the sample solution to prevent oxidation during analysis (Landy 1980). Potassium nitrate electrolyte was added to each sample and a sodium acetate buffer used when determining zinc and cadmium, to obtain a flatter voltammetric baseline.

Arsenic was determined using the hydride generation technique and atomic absorption spectroscopy.

2.2.7 Analysis of sediment samples

The sediments were air-dried and passed through a 0.4 mm nylon sieve, analyses being performed on the $<$ 0.4 mm fraction. The size fraction chosen allows a wider range of particle size than desirable but the choice was dictated by the varying nature of different stream sediments included in the survey. If a smaller size fraction had been used, insufficient sample for analysis would have been obtained from some sites.

Metals (arsenic, cadmium, copper, iron, lead, zinc) were extracted with dilute acid, by shaking 0.5 g sediment samples with 10 mL 0.5M hydrochloric acid (purified by non-boiling distillation) for 17 hours at room temperature. The solutions were then filtered and metal levels (with the exception of mercury) in the filtrates measured by either flame atomic absorption spectroscopy or inductively coupled plasma spectroscopy.

Mercury analyses were carried out on the < 0.4 mm fractions, after digestion for 60 minutes using boiling concentrated nitric and sulphuric acids (Vigor-Brown and Timperley 1981).

2.2.8 Data analysis

The range and geometric mean (see Glossary) of heavy metal concentrations measured for each stream have been used to summarise the results for presentation in this report. A few data were excluded from calculation of the mean, on the basis of obvious contamination. Geochemical data usually have a log normal distribution so geometric means, which give more weight to low values, tend to represent the average of sample concentrations better than arithmetic means. However, in terms of water quality management for the protection of aquatic life, it may be more appropriate to give greater weight to high concentrations, i.e., arithmetic means may be more relevant to aquatic life water quality criteria (Stephan *et al.* 1985).

2.3 Results

2.3.1 Introduction

The results are summarised in Tables 2.3–2.5, which give the geometric mean and range of heavy metal concentrations measured in water and sediment samples from each site, and of metal/iron ratios calculated for sediment samples.

In the tables of results, streams are divided into four groups as follows:

(1) *Streams not included in biological study (Chapter 3)*

- (a) Background metal levels—Waipupu, Waitekauri, Mangakara, Waitawheta, Komata, Mangatoetoe Streams.
- (b) Elevated metal levels—Waiorongomai, Jubilee, Comstock, Tui Streams.

(2) *Biological study streams*

- (a) Waitaia catchment—Waitaia Control, Waitaia Mine, Waitaia, Mullock Streams.
- (b) Waiomu and Buffalo catchments—Waiomu, Buffalo (Whakanekeneke Stream or Courthouse Creek), Paroquet Streams, Everett's Mine.

The streams in group (1)(a) have been defined as 'background' on the basis of low metal levels in the waters and sediments, low sulphate concentrations (less than 10 g m^{-3} SO_4), and total hardness approximately equal to alkalinity (hence no evidence of acid addition) (Section 2.3.4).

2.3.2 Metal levels in waters

The heavy metal levels measured in water samples from different sites cover a wide range of concentrations, from levels below the detection limit (some background streams) to levels that are two to five orders of magnitude above the detection limit (Tui Stream) (Table 2.3). The heavy metal levels in the background streams are very low compared to various overseas criteria for the protection of aquatic life (see Tables 2.1 and 2.2) and within the range of metal concentrations reported for other unpolluted natural waters (see Section 2.3.5). The lead levels found are below but quite close to the US EPA criteria in a number of the background streams. This may reflect the relatively wide environmental distribution of lead from various anthropogenic sources (Settle and Patterson 1980). With the exception of arsenic levels in the Waitaia Control Stream (W1-W4), the heavy metal levels in the control streams of the biological study catchments are generally within the range of concentrations in background streams. The waters of the test streams within these catchments have heavy metal concentrations which are significantly elevated above those from background streams for one or more of the metals determined.

2.3.3 Metal levels in sediments

Within-site variation

Within-site variation in metal concentations is small for a number of sites (Table 2.4) (e.g., Waitawheta, Waipupu, Waitekauri, Komata, Mangakara, Waiorongomai, Jubilee, Tui Streams).

Where the samples contain widely differing amounts of iron, as found in Waitaia Mine Stream sites (particularly sites W8 and W10) within-site variation is greater. However, the within-site variation of the metal/iron ratios is generally much less than absolute metal levels (Table 2.5) indicating that metal levels are largely controlled by co-precipitation and/or adsorption with iron.

Within-site variations in the concentrations of metals measured in samples from the Waiomu and Paroquet Streams are not obviously related to variations in iron concentrations. The iron concentrations in the sediments are not as high as in the Waitaia Mine Stream, and co-precipitation and adsorption onto iron hydroxide may not be the dominant factor controlling metal levels in the sediments. Paroquet Stream had slipping evident along the stream bank and the sediments may be too recent to indicate the long-term water quality conditions in the stream.

Relationship to water quality

The factors governing the relationship between metal levels in stream sediments and waters have been described in Section 2.1.8.

A direct relationship between metal levels in the water and sediment samples is observed for the Waitawheta, Waipupu, Waitekauri, Komata, Mangakara, Mangatoetoe, Jubilee, Waitaia Control, and Waiomu Control Streams. (Tables 2.3 and 2.4.)

In the Waitaia Mine Stream the metal levels in the sediments are influenced by high and variable iron levels so they do not relate directly to metal levels in the waters. Arsenic/iron ratios in the sediments correlate with arsenic levels in the waters at all sites. Metal/iron ratios for the other metals are lower than expected at the sites approaching the mine entrance (W8–W10), probably due to periods of lowered pH conditions as suggested by low alkalinity.

The effect of lowered pH is more marked in the Tui Stream which receives a substantial input of acidic drainage. The levels of cadmium, copper, lead and zinc in the waters are high, but the sediment metal levels and metal/iron ratios are lower than expected. The metal/iron ratios increase with distance from the source of the contamination. Arsenic/iron ratios, on the other hand, are unaffected by low pH conditions, and correlate well with arsenic levels in the water.

Table 2.3: Geometric mean concentration (and concentration range) in unfiltered water (mg m^{-3})

Sampling location	Number of samples (n)	Arsenic	Cadmium	Copper	Lead	Zinc
1 (a) Background metal levels						
Waipupu Stream	2	<1(<1)	0.010(0.006–0.015)	0.09(0.07–0.11)	<0.10(0.06–<0.18)	0.28(0.19–0.40)
Waitekauri River	2	<1(<1)	<0.008(<0.005–0.013)	0.32(0.12–0.87)	<0.14(0.11–<0.18)	<0.77(<0.20–2.96)
Mangakara Stream	2	<3(<1–7)	0.009(0.007–0.012)	0.33(0.12–0.88)	<0.12(0.08–<0.18)	<0.30(<0.20–0.44)
Waitawheta Stream	1	<1	0.010	<0.05	0.05	0.43
Komata River	2	<1*	0.010(0.006–0.016)	0.27(0.23–0.31	0.16(0.12–0.21)	<0.33(<0.20–0.53)
Mangatoetoe Stream	2	<1(<1–1)	0.019(0.016–0.023)	0.11(0.10–0.13)	0.13(0.07–0.26)	<0.39(<0.20–0.78)
1 (b) Elevated metal levels						
Waiorongomai Stream	2	<1(<1–1)	0.024(0.020–0.028)	0.29(0.23–0.36)	0.32(0.22–0.47)	<0.6(<0.20–1.8)
Jubilee Stream	1	<1	0.065	0.99	0.49	7.4
Comstock Stream	2	175(118–260)	0.020*	<0.11(<0.05–0.24)	0.49(0.23–1.05)	21*
Tui Stream (Tui Road)	2	1.2(1–1.5)	9.3 (4.3–20)	90 (35–230)	36 (23–57)	5950(2080–17000)
Tui Stream (Highway 26)	1	2	14	91	32	9800
2 (a) Waitaia catchment						
W1 Control	1	8	0.019	0.20	<0.05	0.73
W2 Control	1	9	0.007	0.15	<0.05	0.55
W3 Control	3	17(12–22)	0.024(0.011–0.067)	<0.20(<0.10–0.30)	0.23(0.06–0.63)	<0.31(<0.20–0.46)
W4 Control	4	25(18–48)	0.013(0.007–0.016)	<0.21(<0.10–0.67)	0.10(0.05–0.26)	<0.20(0.16–0.23)
W5 Test	3	10(7–14)	0.013(0.009–0.022)	<0.28(<0.10–0.96)	0.14(0.07–0.23)	5.6 (2.8–16.3)
W6 Test	4	12(9–15)	0.019(0.013–0.030)	<0.34(<0.10–0.84)	<0.09(<0.05–0.12)	4.2 (2.2–8.2)
W7 Test	4	3.5(2–5)	0.016(0.013–0.021)	<0.14(<0.10–0.20)	<0.08(<0.05–0.12)	4.3 (1.1–9.7)
W8 Test	5	3.7(3–5)	0.029(0.020–0.037)	0.24(0.16–0.37)	<0.09(<0.05–0.18)	8.0 (5.1–12.2)
W9 Test	2	4(4)	0.034(0.027–0.044)	<0.11(<0.05–0.24)	0.11(0.10–0.11)	14 (10–20)
W10 Test	3	7.3(6–11)	0.096*(0.061–0.15)	<0.09(<0.05–0.14)	<0.10(<0.05–0.18)	27 (14–52)
W12 Test	2	3.5(3–4)	0.019(0.015–0.023)	0.24(0.21–0.28)	<0.05(<0.05)	8.6 (8.1–9.2)
2 (b) Waiomu and Buffalo catchments						
WC Control	5	<1(<1–<2)	0.013(0.009–0.032)	<0.35(<0.10–0.80)	0.23(0.08–0.39)	<0.66(<0.20–2.4)
WP1 Test	2	<1(<1)	0.043(0.036–0.052)	0.62(0.3–1.3)	0.14(0.07–0.29)	14.5(8.8–24)
WP2 Test	3	<1(<1)	0.062(0.058–0.070)	0.72(0.12–2.3)	0.86(0.33–2.31)	10.4(8.0–12.6)
P1 Control	1	<1	0.015	0.74	0.31	1.6
P2 Test	5	<1*(<1)	0.36(0.24–0.58)	2.0 (1.2–5.0)	3.1 (0.89–7.0)	58 (31–120)
B4 Test	5	<1*(<1)	0.023(0.013–0.034)	<0.28(<0.10–0.61)	0.24(0.15–0.33)	3.7 (1.8–6.1)
E Test	3	<1.3(1–<2)	4.5 (2.4–11.4)	33 (16–77)	61 (48–71)	1341(1060–2070)

*Mean of (n−1) samples

Table 2.4: Geometric mean concentration (and concentration range) in dry sediment (<0.4 mm, cold extraction) (mg kg^{-1})

Sampling location	Number of samples (n)	Arsenic	Cadmium	Copper	Lead	Zinc	Iron
1 (a) Background metal levels							
Waipupu Stream	3	0.48(0.31–0.68)	<0.4(<0.4–0.5)	2.5(2.1–2.9)	<2(<2–2.1)	8.5(7.6–9.8)	2922(2530–3140)
Waitekauri River	2	0.75(0.64–0.88)	<0.5(<0.4–0.6)	3.7(3.5–4.0)	3.7(3.6–3.8)	15(12–20)	3684(3590–3780)
Mangakara Stream	3	3.8(3.0–5.2)	<0.4(<0.4)	2.5(1.7–3.7)	5.2(4.4–5.7)	14(12–18)	2684(1970–3880)
Waitawheta Stream	2	0.30(0.29–0.31)	<0.4(<0.4)	<0.3(<0.3)	<2(<2)	9.6(8.4–11)	1912(1700–2150)
Komata River	3	0.37(0.28–0.44)	<0.4(<0.4)	5.1(4.7–5.6)	6.4(5.3–7.9)	14(12–16)	3113(2520–3640)
Mangatoetoe Stream	2	0.21(0.16–0.28)	0.4(0.4–0.5)	2.5(1.4–4.4)	8.5(2.9–25)	16(8.2–30)	2005(1310–3070)
1 (b) Elevated metal levels							
Waiorongomai Stream	3	0.66(0.63–0.72)	0.5(0.4–0.7)	5.5(5.1–6.1)	14(12–18)	40(37–44)	2984(2540–3290)
Jubilee Stream	3	0.77(0.60–1.05)	0.7(0.6–0.8)	12(10–13)	16(13–18)	48(44–53)	5211(4500–5770)
Comstock Stream	1	1440	1.1	7.0	11.1	100	31700
Tui Stream (Tui Road)	2	3.4(2.7–4.3)	5.1(4.8–5.4)	164(137–197)	171(155–189)	575(560–590)	36138(35200–37100)
Tui Stm (Highway 26)	2	1.9(1.6–2.2)	2.1(1.6–2.8)	56(45–70)	65(60–70)	364(335–396)	8868(7350–10700)
Tui Stm (Confl Waihou)	1	2.8	4.9	48	58	600	6460
2 (a) Waitaia catchment							
W3	6	33(22–56)	<0.4(<0.4)	<1.4(<0.3–4.5)	<3.5(<2–6.9)	20(15–25)	5718(4240–7760)
W4	3	189(95–267)	<0.4(<0.4)	<2.9(1.8–4.4)	<2(<2)	19(17–21)	14066(10100–16700)
W5	6	33(25–51)	<0.4(<0.4)	<1.6(<0.3–3.2)	<3.3(<2–5.7)	41(38–43)	4699(3700–5760)
W6	3	24(18–27)	<0.4(<0.4)	<0.5(<0.3–<0.8)	<2(<2)	44(28–63)	4874(3710–5890)
W7	3	37(28–44)	0.5(0.5–0.6)	1.7(1.6–1.9)	<2(<2)	107(96–125)	10441(7670–14000)
W8	5	81(25–258)	1.4(0.5–4.4)	12(5.7–29)	<6(<2–23)	190(106–300)	29217(9160–106000)
W9	2	57(26–127)	2.5(1.6–3.8)	<6.8(<1.8–26)	<11(<10–13)	511(500–522)	61853(47000–81400)
W10	4	68(47–93)	1.6(1.0–2.6)	<2.6(<1.8–6.8)	<10(<10)	435(140–840)	55725(23600–112000)
W11	1	215	4.6	26	12.4	470	162000
W12	1	102	1.1	–	<8	244	27200
2 (b) Waiomu and Buffalo catchments							
WC	5	0.41(0.28–0.97)	<0.4(<0.4–0.4)	<3.9(<2–5.6)	<4.1*(<2–9.1)	29(25–33)	4253(3550–7080)
WP2	4	<0.08(<0.04–0.16)	<0.6(<0.4–0.9)	7.7(6.0–9.3)	<8.5(6.5–<13)	31(6.9–122)	1568(841–2750)
P2	5	<0.06(<0.04–0.10)	1.6(1.0–2.8)	17(12–22)	20(6.9–41)	244(195–329)	2360(1880–3010)
B4	4	1.9(1.0–3.2)	1.4(1.0–1.6)	9.6(7.8–10.9)	46(41–53)	150(120–247)	4245(3550–6630)

*Mean of (n−1) samples

Table 2.5: Geometric mean metal/iron ratio (and ratio range) in dry sediment (x 10^3)

Sampling location	Number of samples (n)	Arsenic/Iron	Cadmium/Iron	Copper/Iron	Lead/Iron	Zinc/Iron
1 (a) Streams with background metal levels						
Waipupu Stream	3	0.16(0.12–0.22)	<0.14(0.13–0.16)	0.86(0.83–0.92)	<0.68(<0.64–<0.79)	2.9(2.6–3.1)
Waitekauri River	2	0.20(0.18–0.23)	<0.14(<0.11–0.16)	1.0(0.93–1.1)	1.0(0.95–1.1)	4.1(3.2–5.6)
Mangakara Stream	3	1.4(1.3–1.5)	<0.15(<0.10–<0.20)	0.93(0.86–1.0)	1.9(1.5–2.2)	5.2(4.6–6.1)
Waitawheta Stream	2	0.16(0.14–0.17)	<0.21(<0.19–<0.24)	<0.16(<0.14–<0.18)	<1.0(<0.9–<1.2)	5.0(4.9–5.1)
Komata River	3	0.12(0.11–0.13)	<0.13(<0.11–<0.16)	1.6(1.4–2.0)	2.1(1.8–2.4)	4.5(4.4–4.8)
Mangatoetoe Stream	2	0.11(0.09–0.16)	0.22(0.16–0.31)	1.2(1.1–1.4)	4.2(2.2–8.1)	7.8(6.2–9.6)
1 (b) Streams with elevated metal levels						
Waiorongomai Stream	3	0.22(0.20–0.25)	0.17(0.13–0.21)	1.8(1.7–2.0)	4.7(4.0–5.3)	13(12–15)
Jubilee Stream	3	0.15(0.11–0.23)	0.13(0.10–0.18)	2.3(2.2–2.4)	3.1(2.2–3.9)	9.2(8.8–9.8)
Comstock Stm (gold camp)	1	45	0.03	0.22	0.35	3.2
Tui Stream (Tui Road)	2	0.09(0.08–0.11)	0.14(0.14–0.15)	4.5(3.9–5.3)	4.7(4.4–5.1)	16(16)
Tui Stream (Highway 26)	2	0.21(0.21–0.22)	0.24(0.22–0.26)	6.3(6.1–6.5)	7.3(6.5–8.2)	41(37–46)
Tui Stm (confl Waihou)	1	0.43	0.76	7.4	9.0	93
2 (a) Waitaia catchment						
W3	6	5.8(4.3–7.2)	<0.07(<0.05–<0.09)	<0.24(<0.04–0.80)	<0.61(<0.26–1.2)	3.5(2.8–4.4)
W4	3	13(9.4–16)	<0.03(<0.02–<0.04)	<0.21(0.11–<0.30)	<0.14(<0.12–<0.20)	1.4(1.1–1.7)
W5	6	7.0(5.7–11)	<0.09(<0.07–<0.11)	<0.34(0.06–0.75)	<0.70(<0.35–1.5)	8.7(7.3–10.8)
W6	3	4.9(4.6–5.1)	<0.08(<0.07–<0.11)	<0.10(<0.06–<0.14)	<0.41(<0.34–<0.54)	9.0(7.5–10.7)
W7	3	3.5(3.1–4.0)	0.05(0.04–0.08)	0.16(0.12–0.21)	<0.19(<0.14–<0.26)	10.2(8.9–13.4)
W8	5	2.8(2.4–3.1)	0.05(0.04–0.05)	0.41(0.28–0.62)	<0.21(<0.10–<0.44)	6.5(2.8–11.7)
W9	2	0.92(0.55–1.6)	0.04(0.03–0.05)	<0.11(<0.04–0.31)	<0.18(0.16–<0.21)	8.3(6.1–11.1)
W10	4	1.2(0.8–2.0)	0.03(0.02–0.04)	<0.05(<0.02–0.29)	<0.19(<0.09–0.39)	7.8(5.9–9.5)
W11	1	1.3	0.03	0.16	0.08	2.9
W12	1	3.8	0.04	-	<0.29	9.0
2 (b) Waiomu and Buffalo catchments						
WC (Waiomu)	5	0.10(0.07–0.14)	<0.09(<0.06–0.11)	<0.92(<0.3–1.4)	0.96*(<0.5–2.3)	6.8(4.7–8.5)
WP2 (Waiomu)	4	<0.05(<0.04–0.06)	<0.38(0.30–<0.48)	4.9(2.2–9.4)	<5.4(2.4–8.9)	20(8.2–44)
P2 (Waiomu)	5	<0.03(<0.01–0.04)	0.68(0.52–0.93)	7.2(6.5–9.0)	8.5(3.7–13)	103(90–134)
B4 (Buffalo)	4	0.45(0.27–0.77)	0.33(0.15–0.43)	2.3(1.6–2.8)	10.8(6.2–14)	35(18–67)

*Mean of (n − 1) samples

In Waiomu catchment, both sediment metal levels and metal/iron ratios generally correlate with metal levels in the water, indicating an absence of iron and pH effects, although some sediment metal levels cover a wider concentration range than expected (see above). In Buffalo Stream (B4) sediments, the absolute metal levels and metal/iron ratios for arsenic, lead and possibly cadmium, are higher than expected from the metal levels in the water samples. This may be explained by the large proportion of very fine material in the sediment-size fraction analysed from this stream (59% of the < 0.5 mm fraction was < 0.125 mm, compared to typical proportions of 10–25%, (see Table 3.6).

To summarise, metal levels measured in the waters tend to correlate with those in the sediment when factors such as co-precipitation/adsorption with iron, particle size and pH conditions are eliminated.

Mercury levels in sediments

The mercury levels measured in sediment samples collected in March 1982 are listed in Table 2.6. Only one sample from each site was analysed.

Mercury concentrations in the background and control stream sediments range from 0.09 to 0.52 mg kg^{-1}, including Waiomu (WP2), Paroquet (P2), Waitaia (W5, W9), Waiorongomai, Comstock and Tui Streams. Higher concentrations were measured in the sediments from the Jubilee Stream, Buffalo Stream and Waitaia Mine Stream (W8, W10). The higher concentration in the Buffalo Stream sediment is believed to be caused by the presence of a large proportion of very fine material in the < 0.4 mm fraction analysed, relative to other sites (see above). The results suggest the possibility of increased mercury levels in the Waitaia Mine Stream.

Table 2.6: Concentration of mercury in single samples of dry sediment (< 0.4 mm, hot extraction) (sampled March 1982)[a]

Stream	Mercury (mg kg^{-1})
1 (a) Background streams	
Waipupu Stream	0.19
Waitekauri River	0.52
Mangakara Stream	0.16
Komata River	0.40
Mangatoetoe Stream	0.18
(b) Streams with elevated metal levels	
Waiorongomai Stream	0.15
Jubilee Stream	0.70
Comstock Stream	0.25
Tui Stream (Tui Road)	0.42
Tui Stream (confluence Waihou)	0.34
2 (a) Waitaia catchment	
W3 Waitaia Control Stream	0.09
W5 Waitaia Stream	0.17
W8 Waitaia Mine Stream	1.27
W9 Waitaia Mine Stream	0.40
W10 Waitaia Mine Stream	0.62
(b) Waiomu and Buffalo catchments	
WC Waiomu Control	0.10
WP2 Waiomu Stream	0.07
P2 Lower Paroquet Stream	0.22
B4 Buffalo Stream	1.16

[a]Analyses carried out by M. H. Timperley, Division of Marine and Freshwater Science, DSIR, Taupo.

A low concentration of mercury in water is usually recommended to protect aquatic life against mercury toxicity (Tables 2.1 and 2.2), and even lower concentrations are recommended to protect against the accumulation of mercury in fish for human consumption (e.g., Canada Inland Water Directorate 1979). Measurement of such low levels is difficult. Background mercury concentrations in natural waters are usually below detection limits. For example, Weissberg (1975) found that mercury concentrations in most water samples from the Waikato River were below his limit of detection (0.02 mg m^{-3}). Nevertheless the mercury concentrations in some trout from the Waikato River exceeded the maximum concentration commonly considered acceptable for human consumption (0.5 mg mercury kg^{-1} fish) (New Zealand Statutory Regulations 1984/262). Mercury concentrations in the tissues of fish from Coromandel streams are discussed in Chapter 4.

The sediment analyses carried out in this study suggest that the future collection of a limited number of water samples for mercury analysis is desirable for selected sites (e.g., Jubilee Stream, Buffalo Stream, Waitaia Mine Stream).

2.3.4 Estimates of acid generation

The sulphate concentration and/or total hardness minus alkalinity of a water body may indicate the likely degree to which the water body is contaminated with heavy metals (Section 2.1.6).

Total hardness, alkalinity and sulphate concentrations were measured in a number of study streams (Hauraki Regional Water Board) (Table 2.7). Total hardness minus alkalinity and sulphate concentration in samples collected on the same day are highly correlated (Figure 2.3).

In the background streams there is little difference between total hardness and alkalinity (less than 6 g m^{-3} as calcium carbonate ($CaCO_3$)), and the sulphate concentrations are low (less than 10 g m^{-3} SO_4) indicating no significant acid addition. Metal levels measured in these streams are all low. In contrast, those streams with high sulphate concentrations and large differences between total hardness and alkalinity, indicating a considerable amount of acid addition (e.g., Tui Stream, Waitaia Mine Stream, Paroquet Stream, Comstock Stream) have high concentrations of one or more metals.

In catchments such as the Waitaia and the Waiomu/Paroquet, progressively higher sulphate concentrations and larger differences between total hardness and alkalinity are found towards the source of the acid discharges. Within each catchment, increasing metal levels were found in the water also (Table 2.8), although the correlation between estimates of acid addition and metal levels is different for each catchment. For example, the levels of sulphate and total hardness minus alkalinity are significantly higher in the Waitaia Stream (W9, W10) than in the Paroquet Stream (P2), but the levels of cadmium, copper, lead and zinc are all lower. Similarly, the metal levels in the Waiorongomai Stream are only slightly elevated above background, while the estimate of acid addition is relatively high.

Most acid is generated from pyrite oxidation, since this is the most abundant sulphide mineral. Heavy metals are released from the associated oxidation of other sulphide minerals, which may or may not be present in the rock. Thus estimates of acid addition give an indication of the possible extent of heavy metal contamination, but the actual level of a specific metal depends on the local occurrence of that metal sulphide.

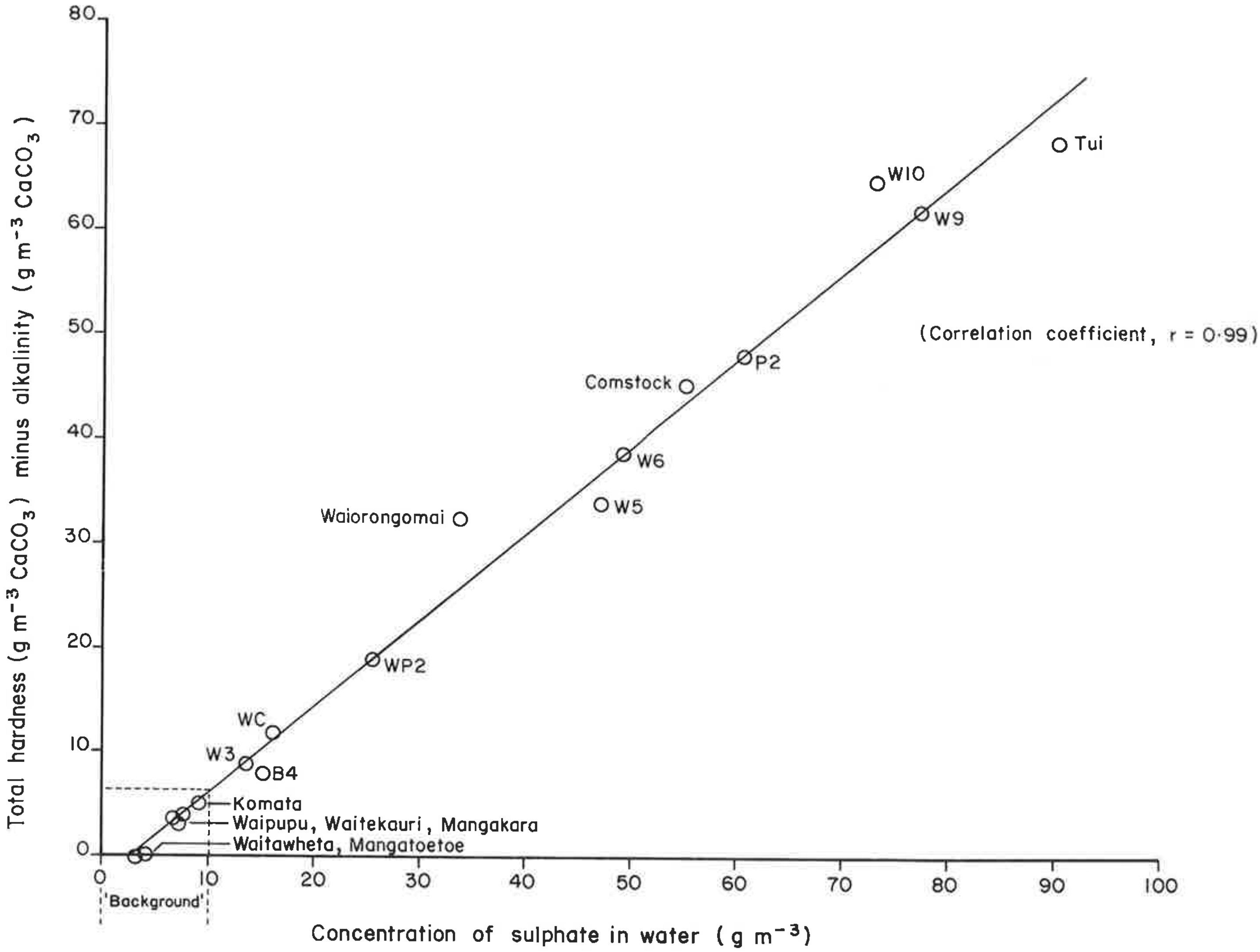


Figure 2.3 Estimates of acid addition to streams as total hardness minus alkalinity, and sulphate concentration.

Table 2.7: Total hardness, alkalinity and sulphate concentrations in Coromandel streams[a]

	Total hardness ($g\ m^{-3}\ CaCO_3$)	Alkalinity ($g\ m^{-3}\ CaCO_3$)	Sulphate ($g\ m^{-3}\ SO_4$)
1 (a) Background Streams			
Waipupu Stream	23.3	19.4	6.8
Waitekauri River	14.8	11.2	7.3
Mangakara Stream	12.7	8.7	7.2
Waitawheta Stream	14.9	15.8	4.1
Komata River	20.2	15.8	9.0
Mangatoetoe Stream	15.4	16.8	4.0
1 (b) Streams with elevated metal levels			
Waiorongomai Stream	41.5	8.9	33.5
Comstock Stream	53.6	8.4	54.9
Tui Stream (Tui Road)	69.8	1.1	90.2
2 (a) Waitaia catchment			
W3 Waitaia Control Stream	37.8	28.7	13.6
W5 Waitaia Stream	51.6	17.2	47.0
W6 Waitaia Mine Stream	55.6	16.8	49.0
W9 Waitaia Mine Stream	71.6	9.2	77.3
W10 Waitaia Mine Stream	72.9	8.1	73.0
2 (b) Waiomu and Buffalo catchments			
WC Waiomu Control	27.6	15.8	16.1
WP2 Waiomu Stream	34.9	15.6	25.5
P2 Lower Paroquet Stream	58.9	10.7	60.5
B4 Buffalo Stream	26.1	18.0	15.0

[a]Measurements provided by D. Carter, Hauraki Catchment Board (single samples collected August 1982).

Table 2.8: Metal levels and estimates of acid generation in Waiomu and Waitaia catchments

	Estimates of acid generation		Mean concentration of metal in water ($mg\ m^{-3}$)			
Sampling location	Sulphate ($g\ m^{-3}\ SO_4$)	Total hardness minus alkalinity ($g\ m^{-3}\ CaCO_3$)	Cadmium	Copper	Lead	Zinc
Waiomu catchment						
WC	16.1	11.8	0.013	$<$0.35	0.23	$<$0.66
WP2	25.5	19.3	0.062	0.72	0.86	10.4
P2	60.5	48.2	0.36	2.0	3.1	58
Waitaia catchment						
W3	13.6	9.1	0.024	$<$0.20	0.23	$<$0.31
W5	47.0	34.4	0.013	$<$0.28	0.14	5.6
W6	49.0	38.8	0.019	$<$0.34	$<$0.09	4.2
W9	77.3	62.4	0.034	$<$0.11	0.11	14
W10	73.0	64.8	0.096	$<$0.09	$<$0.10	27

2.3.5 Comparison of results with other studies

There are few data available for direct comparison with background metal levels measured in this study. Most of the overseas literature on metal levels in freshwaters and their toxic effects is for polluted rivers and streams and few studies attempt to measure "natural" metal levels. Recent advances in measuring low concentrations of metals have shown that much of the existing data are unreliable (see Section 2.1.3).

Coromandel Peninsula

Tay (1980) reported concentrations of metals in filtered water samples from Tunakohoia Stream and Tui Stream, and other streams in areas of sulphide mineralisation where mining has occurred. The analysis methods were too insensitive to detect the very low metal levels found in a number of streams, but were able to measure the higher metal concentrations present in the Tui Stream and Everett mine drainage. With the exception of copper in the Tui, Buffalo and Waiomu (WP2) Streams, and zinc in the Waiomu (WC), the metal levels reported by Tay are consistent with those measured in this study (Table 2.9). Our study used much more sensitive methods, and where the metals were not detected by Tay (reported as less than (<) the analytical detection limit), the concentrations measured in our study are below Tay's detection limit.

Tay also reported metal levels in Tui Stream sediments, but used finer size fractions and a more vigorous extraction method than were used in this study, giving higher metal concentrations.

Other areas

Ahlers and Hunter (1984) measured total dissolved metal levels in the Upper Manuherikia River, Central Otago. Particular attention was paid to minimising contamination during sampling and analysis. The concentrations, listed in Table 2.10, are similar to the range of background concentrations measured in streams in this study. The results of both these studies are in close agreement with probable concentration ranges for cadmium, copper and lead

Table 2.9: Comparison of metal levels reported by Tay (1980) with the present study

Sampling location	Reported by:*	Metal levels in water (mg m^{-3})				
		Arsenic	Cadmium	Copper	Lead	Zinc
Tui Stream (Tui Road)	Tay (1980)	-	20	<30	<30	5320
	This study	1-1.5	4.3-20	35-230	23-57	2080-17000
Buffalo Stream (B4)	Tay (1980)	<4	<10	35	<60	<10
	This study	<1	0.013-0.034	<0.10-0.61	0.15-0.33	1.8-6.1
Everett Mine (E)	Tay (1980)	<4	<10	50	60	968
	This study	1-<2	2.4-11.4	16-77	48-71	1060-2070
Waiomu Stream (WC)	Tay 1980	<4	<10	<30	<60	37
	This study	<1-<2	0.009-0.032	<0.10-0.80	0.08-0.39	<0.20-2.4
Waiomu Stream (WP2)	Tay (1980)	<4	<10	30	<60	<10
	This study	<1	0.058-0.070	0.12-2.3	0.33-2.31	8.0-12.6

*NB: Metal levels reported by Tay (1980) are for filtered water samples, while the levels reported by this study are for unfiltered samples.

Table 2.10: Comparison of metal concentrations from the present study with data from other areas

Sampling location	Reported by:	Metal levels in water (mg m^{-3})			
		Cadmium	Copper	Lead	Zinc
Background Coromandel Streams —'acid-extractable' (range of means)	This study	<0.005–0.019	<0.05–0.33	<0.05–0.16	<0.2–0.8
Upper Manuherikia River —total dissolved	Ahlers and Hunter (1984)	0.005–0.020	0.12–0.42	0.050–0.30	0.07–0.50
Waikato River (Lake Taupo to Arapuni)[a] —'acid-extractable'	Beaumont (1982)	0.003–0.024	0.13–1.1	0.84–2.3	0.76–2.9
Probable natural background range (river waters)[b]	Mart *et al.* (1985)				
—dissolved		0.005–0.02	0.05–0.2	0.01–0.05	-
—total		0.01–0.05	0.1–1.0	0.02–1.0	-

[a]One sampling only, at six locations.
[b]Estimated probable range of natural background levels in river waters without geological anomalies.

proposed by Mart *et al.* (1985) as realistic for river waters unaffected by anthropogenic discharges and without geological anomalies of the river bed (see Table 2.10). These workers have considerable experience in the measurement of heavy metals in natural waters (mainly coastal and estuarine), with special emphasis on minimising contamination during sampling, handling and analysis.

Beaumont (1982) recently measured heavy metals in Waikato River water using the same methods as those described in this report. The concentrations (Table 2.10) are considerably lower than previously measured in the Waikato River by Timperley (1979), prior to recognition of the full significance of contamination problems in measuring trace metal levels in natural waters. Beaumont's measurements are at the upper end of the range of background concentrations found in streams in this study, with slightly higher levels of some metals (particularly lead). The Waikato River has a higher level of agricultural and industrial development than Coromandel, and also has natural geothermal discharges.

2.4 Discussion and Conclusions

2.4.1 Background metal levels compared with water quality criteria

The ranges of geometric mean concentrations measured during base flow conditions in the background streams are compared with US EPA (1985) and Canada Inland Waters Directorate (1979) water quality criteria for the protection of aquatic life in Table 2.11 (other water quality criteria are listed in Tables 2.1 and 2.2). Background streams are defined as those with low sulphate concentrations (less than 10 g m^{-3} SO_4), low total hardness minus alkalinity (less than 6 g m^{-3} $CaCO_3$), and low metal levels in both the waters and sediments. Some of the streams classified as background drain catchments with a history of significant mining activity (Waitekauri, Mangakara, Komata, Mangatoetoe). While concentrations vary from the means in the background streams as a result of natural fluctuations in flow and catchment conditions, when these concentrations are exceeded by an order of magnitude or more, contamination by heavy metals is indicated.

The background concentrations measured in this study are considerably lower than the overseas water quality criteria with the possible exception of lead (see Section 2.3.2). An assessment of the appropriateness of these criteria for the protection of aquatic life is provided in Chapter 3.

2.4.2 Biological study catchments

Waitaia catchment

The left tributary of the Waitaia Stream (sites W3, W4) used as a control for the biological studies in this catchment has elevated levels of arsenic compared with the background streams and even with Waitaia Mine Stream. The levels of copper, cadmium, lead and zinc at control sites W3, W4, are low and within the range of the background streams. There is no history of mining activity in this valley and the arsenic is presumed to be released by natural weathering of mineralised outcrops or the collection of mineralised groundwaters. Small seepages into the stream, characterised by a narrow zone of orange/brown iron floc immediately downstream of the seepage, were observed at a number of locations along the stream bank. The stream has

Table 2.11: Background metal levels comapred with water quality criteria for aquatic life protection

	Total hardness ($g\ m^{-3}\ CaCO_3$)	Concentration of metal in water ($mg\ m^{-3}$)				
		Arsenic	Cadmium	Copper	Lead	Zinc
Background streams						
This study (range of geometric mean concentrations, base flow)	12-23	<1-<3	<0.005-0.019	<0.05-0.33	<0.05-0.16	<0.2-0.8
Water quality criteria						
US EPA (1985 = 4 day average	10	190 (trivalent)	0.19	1.6	0.17	47[a]
	25		0.38	3.6	0.54	
	50		0.66	6.5	1.3	
1 hour average	10	360 (trivalent)	0.29	2.0	4.5	48[a]
	25		0.82	4.8	14	102[a]
	50		1.8	9.2	34	180[a]
Canada Inland Waters Directorate (1979)	<95	50 (total)	0.2	2.0	5.0	50

[a]1980 criteria (not revised in 1985).

some acid addition (based on slightly elevated sulphate concentration and a small but significant difference between total hardness and alkalinity).

Waitaia Mine Stream (sites W7–W11) flows directly from an old mine adit and carries a heavy load of the characteristic red/brown iron floc commonly associated with drainage from mines or tailings heaps. There is indication of significant acid addition to the stream water, below the mine entrance (W9, W10). At the biological test sites on this stream (W7, W8), zinc is the only metal measured at a concentration significantly above background and above concentrations in the Control Stream, and the levels of all metals measured (including zinc) are much lower than aquatic life criteria. However, in the upper reaches of the stream, near the mine entrance (W9, W10), the levels of cadmium and zinc approach the US EPA (1985) recommended four-day average concentrations (Table 2.11). The alkalinity is low at sites W9, W10 (less than 10 g m^{-3} $CaCO_3$) and the cadmium and zinc criteria may be exceeded at times if calculated on the basis of alkalinity, rather than hardness (Table 2.2; Section 2.1.6).

The main tributary to Waitaia Mine Stream, Mullock Stream, flows through a mullock dump to Waitaia Mine Stream between sites W8 and W9. Mullock Stream (W12) contains elevated levels of zinc, similar to those measured at site W8.

Below the confluence of the Waitaia Mine Stream and the Waitaia Control Stream, the Waitaia Stream (sites W5, W6) still shows the effect of acid and heavy metal inputs. The levels of zinc and arsenic are elevated above background, but are well below aquatic life criteria.

Waiomu catchment

The Waiomu Control Stream (WC) has generally low metal levels compared with other study sites in this catchment. There are only slight indications of acid addition. The single water sample collected from the upper Paroquet Stream (P1, above existing mine drainage) also contained low levels of metals (within the concentration ranges measured in the Waiomu Control Stream).

The lower Paroquet Stream (P2) receives discharges from the old Monowai Mine and has indication of large acid additions. The levels of cadmium, copper, lead and zinc are all high compared to background streams and are at or slightly above the US EPA (1985) four day average and one hour average criteria values, particularly if the criteria are calculated for the low stream alkalinity (about 10 g m^{-3} $CaCO_3$) (Table 2.11).

Waiomu Stream below the Paroquet confluence (WP1, WP2) has indication of significant acid addition, and metal levels elevated above those measured upstream of the Paroquet confluence (WC), reflecting the influence of heavy metal inputs from the Paroquet Stream.

Buffalo catchment

The Buffalo Stream receives a very small input of drainage from the disused Everett mine (E). This drainage contains high levels of cadmium, copper, lead and zinc (Table 2.3). The Buffalo Stream (B4) water has consistently low levels of arsenic, copper and lead, with cadmium and zinc slightly elevated above background concentrations. There are indications of small acid additions.

2.4.3 The impact of mining on heavy metal levels

This study shows that streams with a past mining history do not always have elevated levels of all metals in their waters. Some streams have background levels (at the study sites) of all the metals studied (e.g., Waitekauri, Mangakara, Komata, Mangatoetoe), while others have elevated or high levels of some metals (e.g., Paroquet, Waitaia Mine, Tui, Comstock). The concentration of each metal in water depends on the type and extent of mineralisation in the area, as well as such factors as the extent of disturbance, scale of mining operations, flow rates, and grain size of tailings. For example, the Tui and Paroquet Streams have low arsenic levels but high levels of cadmium, copper, lead and zinc; whereas the Comstock Stream has high arsenic and elevated zinc levels with low cadmium, copper and lead. The Waitaia Mine Stream has low copper and lead levels with elevated zinc and cadmium.

The highest metal levels were measured in streams that are known to receive discharges from old mine workings (Tui, Paroquet, Comstock Streams). While it is sometimes impossible to distinguish between the impact of the mining operations and the effects of weathering processes on naturally exposed strata or inputs of mineralised groundwaters, where major discharges from mine workings can be identified the direct impact of the mining operation can be quantified. For the Tui, Comstock, Waitaia and Paroquet Streams substantial discharges from mine adits and tailings dumps have been identified. Tay (1980) has shown that the high levels of metals in the Tui Stream are due to discharges from the tailings dam, which contains substantial quantities of base metal sulphides. Similarly, drainage from the old Monowai Mine appears to be the main contributor, at least during low flow conditions, to increased heavy metal levels in the lower Paroquet Stream (Crusader Minerals NZ Ltd 1984).

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2.7 Glossary

Acid-soluble metal: Operationally defined as the concentration of metal that passes through a 0.45μm membrane filter after the sample is acidified to pH = 1.5 to 2.0 with nitric acid (US EPA 1985).

Alkalinity: A measure of the capacity of a solution to neutralise hydrogen ions (H^+). In natural waters alkalinity is caused mainly by the presence of carbonates, bicarbonates and hydroxides, and is often expressed in terms of an equivalent amount of calcium carbonate ($CaCO_3$).

Arithmetic mean: The arithmetic mean of N numbers $X_1, X_2, X_3, \ldots X_N$, where X is a variable, is defined as:
arithmetic mean $= {}^1/_N\,(X_1 + X_2 + X_3 + \ldots + X_N)$

Class 100: Air containing no more than 100 particles per cubic foot (3.5 particles per litre) of a size 0.5 micron and larger (US Federal Standard No. 209B, 24 April 1973, amended 30 May 1976).

Class 10,000: Air containing no more than 10,000 particles per cubic foot (350 particles per litre) of a size 0.5 micron and larger or 65 particles per cubic foot (2.3 particles per litre) of a size 5.0 micron and larger.

Dissolved metal: The metal fraction which passes through a 0.45 μm filter.

50 percentile: Concentration which, for 50 percent of the time, should not be exceeded.

Four-day average concentration: The concentration, averaged over 4 days, that should not be exceeded more than once every 3 years on the average, to protect against chronic effects (i.e., Criterion Continuous Concentration) (US EPA 1985).

Geometric mean: The geometric mean of N numbers $X_1, X_2, X_3, \ldots X_N$, where X is a variable, is defined as:
geometric mean $= (X_1X_2X_3 \ldots X_N)^{1/N}$

Ligand: An atom, ion or molecule that forms a co-ordination complex with a metal atom or ion.

95 percentile: Concentration which, for 95 percent of the time, should not be exceeded.

Non-residual metals: Metals in the form of inorganic precipitates, organic or inorganic complexes, and adsorbed onto other particles.

One-hour average concentration: The concentration, averaged over 1 hour, that should not be exceeded more than once every 3 years on the average, to protect against acute effects (i.e., Criterion Maximum Concentration) (US EPA 1985).

Particulate metal: The metal fraction which is retained by a 0.45 μm filter.

Residual metals: Metals bound within the mineral matrix of sediment particles.

Soluble metal: see Dissolved metal.

Speciation: Chemical form.

(Total) hardness: The sum of the calcium and magnesium concentrations in a solution. (Water hardness was originally understood to be a measure of the capacity of water to precipitate soap, which is mainly a function of the calcium and magnesium ion concentrations.)

Total metal: The concentration of metal in an unfiltered sample (i.e., Dissolved plus Particulate fractions).

24 hour average concentration: The average concentration that should not be exceeded during a 24 hour period, to protect against chronic effects (US EPA 1980).

Water quality criteria: The scientific information relating exposure to a pollutant and the risk or magnitude of the effects caused by such an exposure (Hart 1982). There are several possible forms of criteria, including numerical (the most common), narrative and operational forms.

CHAPTER 3: Stream Biology Survey of Three Coromandel Catchments Containing Past Mines

S. F. Penny

3.0 Abstract

The effects of mining of sulphide minerals on water quality and stream communities are reviewed. Methods for detecting biological perturbations are discussed. A study on the macroinvertebrates found at control sites (selected as having healthy aquatic communities and no apparent influence from past mining) and at test sites (located downstream of obvious mine waste discharges) in three Coromandel catchments is described.

The macroinvertebrate communities were found to be stressed or impoverished at some test sites. This correlated with concentrations of some heavy metals, particularly zinc, in stream waters and sediments, but possible toxic effects could not be isolated from possible effects from deposition of iron floc or other sediments. Downstream drift of invertebrates apparently tended to mitigate stress effects.

Heavy metal concentrations in the waters at biologically stressed or impoverished sites were largely below recommended water quality criteria as calculated on the basis of hardness.

3.1 Introduction

3.1.1 Background

The resurgence of interest in mining in the Coromandel Peninsula has raised the possibility of excess acid mine drainage and heavy metals entering inland and coastal waters (Chapter 1).

Overseas studies have demonstrated the need for the implementation of effective land and water management if stream and coastal life is to be protected from mining activities. They have also demonstrated the usefulness of studying changes in stream community structure as a method of impact assessment and bio-monitoring (e.g., Letterman and Mitsch 1978, Moon and Lucostic 1979).

The stream community comprises a large variety of organisms controlled in type and abundance by many interrelated factors. Winterbourn (1981) summarises these as: large-scale factors (geography, altitude, geology, water chemistry, catchment type), medium-scale factors (stream size, gradient, bed stability, hydrological regime, canopy, type of food available, and sources of nutrient enrichment and/or sources of contamination), and small-scale factors (substrate particle size, food substances, current velocity, and physico-chemical factors such as temperature, oxygen concentration).

Some of these factors vary naturally with time, and the stream community is able to adjust to the normal range of conditions experienced. A change or "perturbation" outside this range may not be tolerated by all the stream's inhabitants and there may be disruption of "biological integrity" (Weber 1981) with organisms declining, migrating, or out-competing others. The result is a change in the types and abundances of organisms making up the stream community.

In the words of Weber (1981):

> "The concept of biological integrity as embodied in the American Clean Water Act 1977 refers to "ecosystem diversity, productivity and stability, and species and community structure" and is interpreted to include all communities of aquatic organisms such as phytoplankton, zooplankton, periphyton, macrophytes, macroinvertebrates and fish. It is defined in terms of the basic properties of communities of aquatic organisms:
>
> (1) Standing crop or abundance (numbers of organisms, weight, size or biomass).
>
> (2) Community structure (kinds of organisms present and relative abundance of each kind).
>
> (3) Community metabolism and condition (pathways for energy transfer, food chains, rates of physiological processes such as nitrogen fixation, photosynthesis, accumulation of toxic substances, disease, histopathological conditions, parastism and flesh tainting)."

Ongoing discharges from past mining operations in the Coromandel provide an opportunity to investigate the effects of sedimentation, pH and heavy metal contamination on New Zealand stream fauna. A preliminary biological survey was made in November 1981 of a number of streams draining the Coromandel and Kaimai Ranges. Following this survey a more detailed investigation of the effects of mine discharges on stream invertebrates was made in 1982–83 by surveying and comparing streams draining watersheds in the Waiomu, Waitaia and Buffalo catchments. Concurrent heavy metal and water quality surveys were carried out between August 1981 and August 1982 by Chemistry Division, DSIR and Hauraki Regional Water Board (see Chapter 2).

3.1.2 Objectives

This study set out to review the effects of sulphide ore-body mining practises on biota, to review methods for evaluating biological perturbations to the bottom fauna of streams, and to study the bottom fauna in a range of Coromandel region streams, some of which receive waters draining mined or mineralised areas. The ecological study objectives were:

— To compare the bottom fauna in uncontaminated streams (control sites) and contaminated streams (test sites) from selected catchments of the Coromandel region.

— To identify probable causes of differences in biological communities found between control sites and test sites.

— To provide information on the effects of mine wastes on instream biota that will assist in the management of streams receiving mine-waste discharges.

3.2 Review of the Effects of Sulphide Ore-body Mining Practices on Streams

3.2.1 Introduction

The potential of poorly managed mining to harm water, soil, and plant and animal life is discussed in the New Zealand Water and Soil Guidelines for

Mining (Lawrence and Smith, 1983). More detailed reviews are given by Andrews (1977), Forstner and Whittmann (1979) and Ripley *et al.* (1978).

Freshwater systems can be affected by mining activities at all stages in the development of a mine and effects may persist after the mine ceases operation. The severity depends on the scale of operation, the climate, geography and geology of the area, the particle size of tailings, the method of tailings disposal selected and its subsequent management.

3.2.2 Water quality

The effects of mining operations on water quality have been discussed in Chapter 2. Those which present the greatest hazard to instream organisms are acid mine drainage, heavy metal contamination and sedimentation.

Numerous studies have reported heavy metal contamination of waters and excess sedimentation downstream from some mining operations. For example, in riverbeds (Brown 1977, Eyres and Pugh-Thomas 1978, Fuller *et al.* 1978, Gale *et al.* 1976, Johnston *et al.* 1975, Lesaca 1977, Norris *et al.*1981, Savage and Rabe 1973, Thorne *et al.* 1980, Tyler and Buckney 1973, Ward *et al.* 1976), in lakes (Austin and Munteanu 1984, Jennett and Foil 1979, Moore *et al.* 1979, Murdoch 1980) in estuaries (Bryan and Hummerstone 1978, Eustace 1974, Foster *et al.* 1978, Thornton 1977, Yim 1976) and in groundwater (Bell 1977, Kempe 1983, Mink *et al.* 1972, Schrader and Furbish 1978, Spry 1976, Weatherly and Dawson 1973). It is generally recognised that heavy metal contamination and sedimentation can adversely affect aquatic life and there are many overseas examples of serious water pollution problems reported in the literature. Some examples are in Western Pennsylvania where 3,700 km of stream have been adversely affected by acid-mine drainage (Letterman and Mitsch 1978), and in Bougainville, Papua New Guinea where fish no longer live in sediment-choked rivers draining mining areas or in associated tributary streams where migratory fish passage has been prevented (Brown 1974). In Tasmania, the discharge of supernatants from slime dams has caused severe water pollution (Tyler and Buckney 1973).

The effects of the low pH, heavy metal contamination and high sediment loadings are not confined to inland streams but can continue out to coastal waters (see Chapter 4) and affect the marine ecosystem. For example, Nielsen and Nathan (1975) found that levels of copper in rock oysters (*Saccostrea glomerata*) taken from the vicinity of a closed copper mine on Kawau Island, Hauraki Gulf were higher than in rock oysters from other sites around the New Zealand coast.

Marine disposal of tailings from copper mining has caused faunal impoverishment off the coast of Chile (Castilla and Nealler 1978), and similar damage has been reported from Rupert Inlet, Canada (Vermeer 1978).

Heavy metal contamination tends to be the most severe in areas of historic mining activity where neither environmental safeguards nor rehabilitative practices have applied. Modern mining practices are designed to minimise environmental damage, however, even where these practices have been applied, excess releases can sometimes occur (e.g., Jennet *et al.* 1973).

3.2.3 Stream habitat and ecology

Erosion and increased sedimentation

In an undisturbed, well vegetated catchment, the rate of introduction of new material to streams is slow and larger substrate elements in the stream are usually well weathered. Distinct eroding and depositional zones correspond to changes in the stream gradient. Eroding zones are characterised by boulders and stones with or without interstitial gravel, and a typical riffle community is found. In contrast, depositional zones have finer sediments and sometimes substantial amounts of decaying vegetation. Here, a soft substrate detrital community develops. Where catchment disturbance leads to an increased rate of erosion there are usually influxes of unsorted material (e.g., rocks and clay) into the stream, particularly during heavy rain.

Fine sediments (silt and clay) affect the stream community by increasing turbidity, and causing partial or complete blanketing of the stream bed (Call 1980). Increased turbidity can also reduce photosynthesis and can have a direct effect on fish (Alabaster and Lloyd 1980).

Blanketing of a stony bottomed stream by fine inorganic material may eliminate the stream community and under stable conditions a new soft substrate community may grow up in its place. Increased turbidity and a partial blanketing of a stony bottomed stream leads to partial or complete obliteration of the green algae and diatoms which grow on stones in open streams, and inhibition of the fine organic layer which develops on stony substrates in shaded forest streams (Rounick 1982).

Infilling of spaces between stones with sediment reduces the availability of hard substrate for hard surface dwellers and reduces shelter for those organisms which need to avoid direct exposure to the current. Infilling also prevents the retention of large detritus such as leaf and twig fragments which are the food supply of some insect larvae (Anderson and Cummins 1979, Winterbourn 1981). Addition of fine organic material will lead to colonisation between stones by burrowing organisms normally found in soft substrates (Marshall and Winterbourn 1979). These organisms are less favoured by fish as food than species associated with coarse sediments (Briggs 1948). Another effect of increased fine sediments can be the development of macrophyte beds.

In the case of coarser sediment (sand and gravel) input, suspended particle feeders are likely to increase, but an overall reduction in diversity and total animal numbers usually occurs following deposition of sand or gravel over a stony substrate (Duda and Penrose 1980, Nuttall 1972).

During floods, a stream which has been subjected to deposition of coarse particles such as sand and gravel, may become less habitable because of the abrasive action of sand in suspension or the molar action of stones and boulders. This removes surface layers of algae and organic material, and may induce migration of animals downstream. Rosenberg (1978) noted 2–3 times more drifting invertebrates following increases in suspended sediments.

The effects of sediments on New Zealand fisheries are reviewed by Church *et al.* (1979). Silt deposition causes a reduction in spawning sites, and prevents successful development of eggs and larvae. Suspended solid concentrations as low as 100 g m^{-3} can reduce growth rate of fish and increase their susceptibility to disease and adverse environmental factors (Alabaster and Lloyd 1980, Herbert and Merkens 1961). Concentrations of several thousand g m^{-3} may be required before fish kills occur, but only poor quality fisheries can be sustained when suspended solids persistently exceed 80 g m^{-3} (European Inland Fisheries Advisory Commission 1965). The latter is partly due to the reduction or elimination of the food supply.

Iron floc

Streambeds covered by metal precipitates such as iron floc tend to have an impoverished and quite different community compared with streams that have elevated metal levels but no precipitate (McKnight and Feder, 1984). This may be partly due to lack of interstitial spaces, and partly due to the tendency of iron-rich sediments to consolidate (US EPA, 1976). It is also possible that the form of the metals in such precipitates is more available and therefore more toxic to benthic organisms than in metal-rich sediments with no precipitate (McKnight and Feder, 1984).

Iron floc deposits cause a significant reduction (up to 80–90%) in faunal abundance at neutral pH (Letterman and Mitsch 1978, Moon and Lucostic 1979, Scullion and Edwards 1980). Mayflies seem especially susceptible (Gale *et al.* 1976). The Hydropsychidae and Chironomidae did not appear to be as severely affected and the Chironomidae apparently benefited from the lack of competition and predation by other organisms. Iron floc reduces or eliminates the standing crop of periphyton, firstly by preventing its attachment to a stable substrate and secondly by the inhibition of photosynthesis, thereby limiting growth. Animals are thus affected by smothering and by loss of their algal food source (Gale *et al.* 1976).

Colloidal ferric hydroxide has a strong affinity for heavy metal ions, which may be adsorbed or co-precipitated (Forstner and Wittmann 1979), a process that is pH dependent. Therefore, iron floc may also act on stream biota as a result of its heavy metal content.

Acid drainage

A large number of studies on the effects of acid mine drainage on stream communities have been carried out in the UK and USA (e.g., Armitage 1980, Cairns *et al.* 1971, Canton and Ward 1981, Dills and Rogers 1974, Greenfield and Ireland 1978, Hereda and Keller 1978, Hoehn and Sizemore 1977, Koryak *et al.* 1972, Letterman and Mitsch 1978, Moon and Lucostic 1979, Parsons 1965, Wood and Rutschky 1972). Adverse effects of acid mine drainage may also extend to the estuarine environment (e.g., Foster *et al.* 1978).

The main effects of acid mine drainage are lowering of pH, reduced buffer capacity, reduced complexation capacity, ferric hydroxide deposition, and increases in heavy metal availability in water and from sediment.

A reduction in pH may act by directly affecting the physiology of the organisms, by increasing toxic heavy metal concentration in the water, and by altering the availability of food resources and predator-prey relations (Haines 1981, Townsend *et al.* 1983). The first two mechanisms appear to be the most important at pH 4 or less (Hall *et al.* 1980), while the third is more likely to be the main effect in less acid streams at pH 4–6.5.

Very little is known about the physiological effects of acid pH on stream invertebrates but the ecological effects are more pronounced in waters that have low concentrations of dissolved ions. Low concentrations of Na, K, Ca and Cl in particular may limit some aquatic animals even where pH is above pH 5.7, by inducing osmoregulatory failure (Sutcliffe 1983).

Long-term acute stresses from acid mine drainage produce a reduction in both density and diversity of stream invertebrates (Ripley *et al.* 1978).

Sutcliffe (1983) concluded, from work in the UK and an extensive literature review on the affects of acid rain, that the pH regime of stream waters has a profound effect on the distribution of many benthic invertebrates. In Cumbria, for example, many benthic invertebrates common in hill streams where pH was above 5.7, did not occur in more acid streams. Reductions in species diversity associated with the lowering of pH caused by acid mine drainage have been noted by Dills and Rogers (1974) and Tomkiewicz and Dunson (1977).

Different functional feeding groups (Figure 3.1) may also be affected by pH. Friberg *et al.* (1980) (cited in Haines 1981) found that scraper species were three times as abundant at pH 6.5–7.3 than at pH 4.3–5.9, whereas shredder species were twice as abundant in the low pH streams. In an extensive study of streams in the Ashdown Forest, England, only collectors, shredders and predators occurred at the more acid sites whereas grazer/scrapers and filter feeders were also present at the less acid sites (Townsend *et al.* 1983).

Increased acidity can lead to a reduction in periphyton (Zeimann 1975, Muller 1980, Haines 1981) and this in turn may lead to reductions in invertebrate herbivores (scrapers) (Sutcliffe and Carrick 1973). The rate of cellulose (plant fibre) decomposition in streams declines with pH below about 5.8 (Townsend *et al.* 1983) and inhibition of organic layer formation can occur. Hall *et al.* (1980) noted a reduction in the density of *Hypomycete* fungi (typically part of the organic layer) at pH 4. Napier and Hummon (1976) noted the disappearance of a pH-tolerant predator species following the disappearance of its food source—a species that was sensitive to pH change.

Molluscs are highly sensitive to acidification because of their $CaCO_3$requirement for shell formation (Haines 1981), but other invertebrates groups vary in their responses to low pH (Haines 1981, Sutcliffe 1983). Stonefly populations often decline as pH declines, but in some acid situations they have been found to dominate the invertebrate fauna (Minshall 1969). Two European species of *Gammarus* (fresh water crustaceans) were reported to avoid water with pH less than 6 (Haines 1981) whereas Lackey (1938) found *Gammarus* species in two streams with pH values 2.2 and 3.2 respectively.

Alabaster and Lloyd (1980), Fromm (1980), Haines (1981) and McWilliams (1982) have reviewed the ecological and physiological effects of acid water on freshwater fisheries. Some effects of different pH levels are tabulated in *Church et al.* (1979). There is no definite pH range within which a fishery is unharmed and outside which it is damaged, but rather there is a gradual deterioration as pH extends outside the natural range (Alabaster and Lloyd 1980). At pH values of < 5 or > 9, the toxicity of other constituents may be enhanced. In general, fish mortality is expected at a pH of less than 5 though some species have acclimated to levels as low as 3.7 (*Ripley et al.* 1978).

Heavy metals

The effects of heavy metals in the aquatic environment are reviewed by Alabaster and Lloyd (1980), Bryan (1971), Hart (1982b), Forstner and Wittmann (1979), and US EPA (1976). Hart (1982a, 1982b) discusses sources and physico-chemical forms of heavy metals in natural waters, sediments and particulate matter, biogeochemical cycling, and bioavailability.

The toxicity of heavy metals varies with the type of metal, its chemical form and the organism affected. The free ionic forms of some metals are more acutely toxic to algae, benthic invertebrates and fish, than complexed, adsorbed, particulate or organic forms. However, all forms may need to be considered with respect to chronic toxicity (Hart 1982b).

Higher proportions of free metal ions occur in acidic waters containing low concentrations of dissolved organic carbon and suspended solids, low alkalinity and low hardness. It follows that heavy metals will be most toxic under these conditions. These are conditions which can occur in forest streams receiving acid mine drainage.

Hart (1982b) notes that biota can receive heavy metals from the water column, from particulate matter or sediment particles (important to filter feeders), or by transfer through the food chain. Most attention has been devoted to quantifying the toxic effects of individual species of metals in water on individual animal species. Early laboratory investigations concentrated on determining acute lethal concentrations for individual species (LC 50 over 96 hours) (Chubb *et al.* 1975, Rehwoldt *et al.* 1973, Thorp and Lake 1974). After longer exposures (e.g., 28 days) it was found that stream insects were susceptible to the effects of much lower concentrations of metals than in short-term experiments (Spehar *et al.* 1978, Warnick and Bell 1969). Other studies have shown that lethal concentrations vary with season (Thorp and Lake 1974, Wood 1980), stage of the organism in its life cycle (Rehwoldt *et al.* 1973, Wier and Walter 1976), and the ability of species to acclimate (Stockner and Antia 1976, Wood 1980). Other environmental factors such as oxygen concentration, pH and temperature also influence both the organisms' susceptibility and the toxicity of the metal.

Alabaster and Lloyd (1980) concluded from their review that trout populations are likely to suffer toxic effects at a lower concentration of the heavy metals copper, zinc and cadmium than invertebrates.

Less information is available on the toxic effects of contaminated sediments and it is difficult to distinguish between effects caused by sediment-bound metal and those caused by metal in the water column or interstitial water. Toxic effects arising from direct uptake of contaminated sediments have not been quantified (Hart 1982b). In spite of these difficulties however, Eyres and Pugh Thomas (1978) concluded that the absence of fish and general paucity of the macroinvertebrate benthos in the River Irwell, UK, was due to heavy metal contamination of the sediments rather than toxic levels in the water. Wentsel *et al.* (1977) demonstrated that midge larvae (*Chironomus tentans*) actively avoid contaminated sediment.

Although sediments adsorb heavy metals (Hart 1982a, 1982b) they can be released again to the water column or interstitial water under anaerobic conditions, reduced pH, or increased salinity. Reece *et al.* (1978) demonstrated experimentally that heavy metals in the sediments of the Coeur d'Alene river-lake system are a source of contamination in the water. Metals may also be returned to solution through the feeding activity of biota (Renfro 1973) and by bacterial activity (Smith *et al.* 1981).

Some evidence suggests that bacteria provided a vehicle for the transfer of chromium and perhaps other metals to higher trophic levels. Periphytic bacteria on algae, plants and animals have been shown to concentrate chromium. Sediment bacteria can solubilise chromium, concentrate it in extracellular polysaccharides and facilitate its entry to food chains. (Loutit *et al.* in press). Fungi, because of their ability to concentrate metals, may play a similar role (Gadd and Griffiths 1978).

The interactions of bacteria and heavy metals are particularly critical where heavy metals are discharged along with organic materials likely to stimulate bacterial growth. Bacterial uptake of metals leads to a concentration of the metal at the effluent entry point and prevents its dispersal or dilution. (Loutit 1979).

Sterritt and Lester (1980) consider that bacteria are generally the first organisms to be affected by heavy metal contamination. Low concentrations of heavy metals may have imperceptible effects on total viable counts of natural bacterial populations but the balance of species and thus the metabolic characteristics of the population may be drastically altered. This may have repercussions throughout the aquatic foodweb. Detrital processing is at the base of major foodchains in forest stream habitats and processing takes place through the activity of microbes (bacteria, fungi, protozoa, etc.).

Strojan (1978) demonstrated that decomposition of terrestrial detritus is inhibited by heavy metal contamination. Weatherly *et al.* (1979) suggested that high metal concentrations and low pH conditions may inhibit this process in the aquatic environment. Microbial activity in the stream bed may be inhibited also by heavy metals adsorbed onto sediments or iron precipitate, and this may in turn lead to a reduction or cessation of detrital processing and organic layer formation at the sediment/water interface. Rounick (1982) noted that organic layer formation did not occur in sterile channels.

Uptake of Heavy Metals by Stream Organisms

Numerous studies have included measurement of heavy metals levels in the tissues of stream organisms, e.g. Brown (1977), Spehar *et al.* (1978) and Zanella (1982). Burrows and Whitton (1983) found that elevated concentrations of zinc, cadmium, and lead in water and sediments in the River Derwent, England, were in general, paralleled by higher concentrations in macroinvertebrates, the relationships differing according to the taxon and metal examined. Enk and Mathis (1977) studied the distribution of cadmium and lead in a stream ecosystem receiving diffuse inputs from non-mining sources. In general, concentrations of metals increase successively from water to fish and from sediments to aquatic invertebrates. Aquatic insects exhibited cadmium concentrations over five times greater than those found in fish or sediments. Snails contained the highest level of lead of any other component including aquatic insects (Enk and Mathis 1977).

This work indicates a capacity of some freshwater invertebrates to concentrate heavy metals, a capacity shared with some marine invertebrates, in which factors of hundreds or thousands are commonly found (Bryan 1971). The duration of exposure to heavy metals at sublethal levels may be as important as the maximum concentration in determining sublethal effects.

3.2.4 Recovery of streams from mining impacts

Downstream recovery of the biota from the effects of mine drainage pollution does not necessarily occur when there is a return to baseline concentrations of metals in the water. If elimination of the fauna upstream is extensive, it will affect populations well below the point of chemical recovery, especially if the zone of contamination forms an impassable barrier to animals moving down from an uncontaminated zone above the input of mine drainage. For example, the King River, Australia, shows little biological recovery up to 15 km downstream from the source of mine drainage, although there is a marked reduction in all heavy metal levels (unfiltered water samples) and a rise in pH towards neutral (Swain *et al.* 1981). In the South Esk River, Tasmania, 80 km from the pollution source, numbers of both individuals and taxa were still low compared with upstream sites although again there had been a marked decline in heavy metal concentrations (Norris *et al.* 1982).

The displacement of organisms downstream in freshwater systems is compensated for to some extent by egg deposition and hatching and by upstream migration of invertebrates. However, much of the invertebrate population at any given point is recruited from animals that have drifted downstream (Williams and Hynes 1976).

Major improvements are usually noted below the confluence of a contaminated stream with an uncontaminated tributary (e.g., Burrows and Whitton 1983). This occurs partly as a result of dilution and partly as a result of drift.

3.3 Derivation of Water Quality Criteria to Protect Stream Organisms

3.3.1 Overseas

In order to preserve water quality and at the same time allow inland waters to be used for waste disposal, many countries have adopted water quality criteria which suggest concentrations of water constituents to maintain water quality for designated uses (Chapter 2, Tables 2.1 and 2.2).

The aim in establishing criteria for the protection of aquatic life is to ensure a reasonable degree of safety for the more sensitive species that are important to the functioning of the aquatic ecosystem. The criteria are not intended to offer the same degree of safety for survival and propagation at all times to all organisms within a given ecosystem. Neither are they intended to become effluent or receiving water standards although they can provide a basis for the derivation of these (US EPA 1976).

The approach to derivation of water quality criteria for heavy metals adopted by most American, European and Australian water quality protection agencies (e.g., US EPA, Canadian Inland Waters Directorate, Great Lakes Water Board, EEC, EIFAC) is based usually on 96 hour LC 50 determinations on selected test organisms and the use of application factors. Criteria so derived are periodically reviewed and updated as new information from field observations, chronic toxicity studies and simulated stream studies come to hand.

Earlier criteria (e.g., US EPA 1973, Hart 1974) provided one concentration for each metal and each use (e.g., drinking water, irrigation water etc.). The shortcomings of this approach are acknowledged by the US EPA (1976) in a preface which states:

> "National criteria can never be developed to meet individual needs of the nation's waterways—the natural variability within the aquatic ecosystem can never be identified with a single numerical value."

Recognising that the toxicity of heavy metals in a receiving water will vary with a number of other water quality variables such as pH, alkalinity, organic content and water hardness, the US EPA (1976) specified criteria for a number of metals including cadmium, zinc and copper in the broad terms of an application factor.

US EPA (1980) recommended use-related criteria for water of different hardness as expressed in mg l^{-1} $CaCO_3$. Mean values, not to be exceeded over a 24 hour period, and permissible maxima, were provided. A similar approach had been adopted by the Canadian Inland Waters Directorate (1979) and European Inland Fisheries Advisory Commission (EIFAC 1978). The most rigorous criteria are those derived for the protection of salmonid fisheries, the general assumption being that trout are more sensitive to heavy metal toxicity than most other aquatic organisms (Alabaster and Lloyd 1980, EIFAC 1978).

The most recent criteria for Australian waters (Hart 1982b) placed considerable emphasis on heavy metal speciation and instead of recommending criteria, lists concentrations at which "investigations should begin".

There has been considerable criticism of the use of criteria derived from conventional toxicity studies. Wentsel *et al.* (1977) asserted that the toxic properties of the *sediment* should be considered when the effect or impact of a substance on an aquatic system is being considered. Too often levels of heavy metals and other toxic substances in the *water* are not indicative of the real toxic threat present for organisms in aquatic ecosystems (e.g., Wong *et al.* 1978).

EIFAC (1978) questioned the relevance and reliability of water quality criteria for fish derived solely from chemical and toxicological data because water quality is only one aspect of the stream environment. EIFAC (1978) recommended a closer integration between this approach and biological monitoring and fisheries management, with a view to improving the capacity for predicting the consequences of human activity on the aquatic biota.

Abel (1980) showed that animals in a population may continue to die for up to three weeks after a brief exposure to a poison, and that conventional toxicity tests underestimate the mortality that can occur with certain combinations of toxicants and exposure time. Norris *et al.* (1982) found little correlation between the concentrations found to be lethal in laboratory studies and those found to produce harmful effects in the South Esk River.

The general conclusion reached from this review is that the response of an organism to heavy metals under experimental conditions often bears only a partial relationship to its response in the wild. The effect of a given dose rate of a heavy metal on an aquatic organism will be determined by the way the metal is partitioned among water, particulates, and biota, and this in turn will depend on other environmental factors. Laboratory testing procedures are rarely able to account for all the combinations of variables found in nature.

Although many individual species may be able to tolerate exposure to quite high levels of heavy metals over a short period of time, a disruption of "biological integrity" (Weber 1981) is likely to occur following exposure to lower heavy metal levels over prolonged periods. Biological monitoring is seen as an essential check on the efficacy of laboratory derived chemical water quality standards and effluent conditions for protecting aquatic life (e.g., Jones 1980, Weber 1981). A further consideration is the effects of two or more heavy metals in combination. Together they may have synergistic or antagonistic effects (Bryan 1971).

3.3.2 New Zealand

With regard to heavy metal concentrations, there are no accepted criteria which would protect aquatic life in receiving waters in New Zealand. There have been very few attempts to test the sensitivity of New Zealand aquatic life to heavy metal toxicity. The National Water and Soil Conservation Authority (NWASCA) has published a compilation of US EPA toxic chemical criteria (Smith 1982) to assist water managers faced with the problem of setting water right conditions for selected toxic materials. Other information, again based largely on overseas information, is provided in the NWASCA Water and Soil

Guideline for Mining (Lawrence and Smith 1983). More information is required on the effects of heavy metals on New Zealand aquatic ecosystems.

3.4 Review of Methods for Evaluating Biological Perturbations

3.4.1 Introduction

Perturbations can be evaluated by measuring the stream community structure in relation to other environmental factors. This usually involves comparing the stream community at "control" and "test" sites, or measuring "test" sites before and after an event. Response may be measured by changes in total numbers, biomass, types and relative abundance of species, and community metabolism and condition, and these provide a basis for evaluating stream health. Sampling programmes should take into account seasonal changes in temperature and flow.

3.4.2 Choice of organisms for study

Some investigations have involved quantitive sampling of all components of the aquatic community (fish, macroinvertebrates, algae etc) e.g., Kaesler and Cairns 1972. However, Kaesler and Crossman (1974) showed that there was a large amount of redundant data generated by such extensive surveys and that the effect of perturbations could be detected by analysing just one section of the community e.g., macroinvertebrates.

Many workers have found the macroinvertebrate riffle community to be an easy and informative section of the stream community to study for impact assessment and biomonitoring (e.g., Hawkes 1964, Hynes 1965, Gaufin 1973, Penny 1976, Welch 1980). Macroinvertebrates are relatively easy to collect and many groups can be identified at low magnification, at least to genus level. Many species have a life cycle of a year or more and therefore changes in community structure brought about by a perturbation persist for a considerable time.

Riffles offer the most diverse habitat within streams and rivers and are often inhabited by a greater variety of macroinvertebrate species than runs or pools. Riffles, as defined by Hawkes (1964), are shallow aerated reaches less than 30 cm deep with a flow greater than 0.3 m per second, and a broken water surface. The characteristic flora consists of attached filamentous algae, encrusted micro-algae and mosses.

Each macroinvertebrate species occupies a "niche" (unique set of habitat characteristics) and responds slightly differently to any one environmental change. Many show great sensitivity to changes in water quality or physical factors such as sedimentation. The life cycle of aquatic macroinvertebrates has to be taken into account in design of a sampling programme and in the interpretation of stream population measurements (Lemkuhl 1979).

3.4.3 Functional feeding groups

Perturbations to the stream usually disrupt the energy pathways (food webs and chains) in the ecosystem and alter the relative abundance of different feeding groups of animals. Animals can be assigned to a particular functional feeding group on the basis of their food preference and mode of food collection. Alterations in the relative abundance of various functional feeding groups has been used as a tool for assessing water quality (Cummins 1980). This type of analysis enables comparison of results geographically since similar feeding groups occur worldwide even though taxonomic groupings differ.

In streams and rivers the two primary food sources are aquatic plants and plant material of terrestrial origin. Macrophytes and their epiphytes (attached algae) are often found in soft sediments in slow reaches, especially at stream margins. In general, macrophytes are not found in shaded, stony streams. In open streams, the periphyton community is the major primary food source. Periphyton forms on the surface of stones and consists mainly of sessile green algae and diatoms, but it also includes bacteria, protozoa and fungi. In heavily shaded forest streams, dead and decomposing plant material and its associated microflora provide the major food source. Here it is thought that the "organic layer" may play a key role in the food web (Winterbourn *et al.* 1981, Rounick and Winterbourn 1983).

The interrelation of the major functional feeding groups in New Zealand streams are shown schematically in Figure 3.1 (arrows show the direction of energy flow). From studies so far it appears that most animals found in New Zealand streams are fine particle feeders and/or algal grazers (Winterbourn 1982). Some collect organic material from the water column (*seston collectors*) and others from the substrate (*collector-browsers*). This latter category includes some grazers which can scrape attached material from the substrate surface as well as gathering free particles. A few species are able to utilise large items of detritus (*shredders*). Another group includes *predators* which feed primarily on other macroinvertebrates.

Seston Collectors

Seston collectors have anatomical structures for filtering food particles from the water (e.g., sandflies—Simulidae, and the spiny gilled mayfly—*Coloburiscus humeralis*) while others spin nets (e.g., caddisflies—Hydropsychidae). Some net-spinners catch small animals as well as plant material. The number of seston collectors, particularly net-spinners, increase as suspended organic matter increases.

Collector-Browsers (sometimes called "grazers" or "scrapers")

Collector-browsers are adapted to scrape or browse on food particles and the range of food selected depends on their body size and mouth part morphology (Winterbourn 1982). Some specialised feeders such as leptophliebiid mayflies, small stoneflies and cased caddisflies appear to feed on the fine organic layer or stone surfaces in forest streams (Rounick 1982). In open streams, these species feed on the periphyton. Some groups tolerate a wide range of temperatures—*Deleatidium* (mayfly), *Pycnocentrodes, Beraeoptera roria, Olinga* (cased caddis) and *Potamopygrus antipodarum* (snail)—and are abundant in forested, partially open, and open streams. Most Plecoptera (stoneflies) on the other hand are restricted to the colder headwaters of forest catchments, since they cannot withstand the higher temperatures of open streams (McLellan 1975).

Shredders

Shredders break down leaves, small sticks and bark fragments into smaller particles which can be eaten by fine particle detritivores (Cummins 1974, 1980). In New Zealand where most forest streams are steep and turbulent, detrital material is not retained in one place long enough to permit processing by shredders, so relatively few shredder species are found. Shredder species such as *Triplectides obsoleta* are often absent or present only in small numbers. Some of the more common shredder species which occur in New

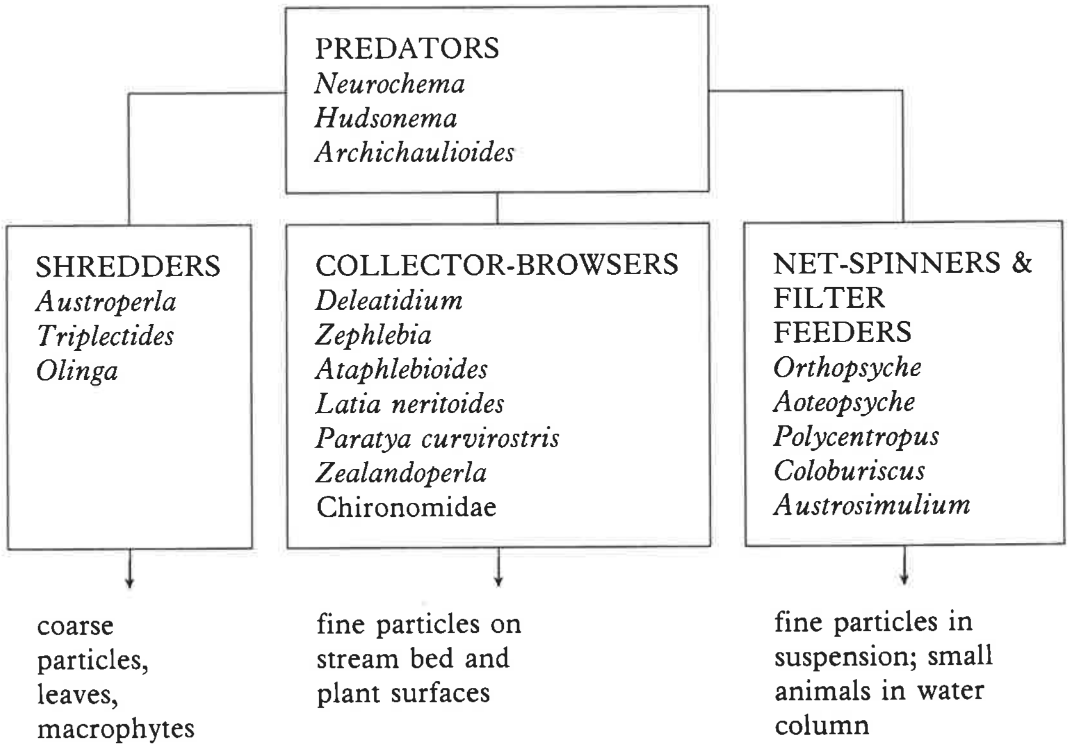


Figure 3.1 Diagram of simplified functional feeding groups of New Zealand stream macroinvertebrates.

Zealand such as the stonefly *Austroperla cyrene* and the caddis *Olinga*, ingest either coarse or fine detrital particles depending on the food available.

Predators

Predators feed on macroinvertebrates. A species is considered to be a predator if it feeds on macroinvertebrates during its late instar development, irrespective of diet during early instar phases e.g., *Hudsonema amabilis*.

In New Zealand stony streams, collector-browsers are the dominant functional feeding group both numerically and with respect to species diversity. Species are usually from the mayfly, stonefly, caddis, midge, beetle, snail and/or limpet groups. Seston collectors, represented by a few species of filter feeders and net spinners, are usually sub-dominant except in situations where high levels of suspended organic material occur. Several predatory species are usually present. Shredders may be present in stable streams in forest catchments and in macrophyte beds.

As streams flow from forest to pastoral country there is an increase in stream bed illumination and water temperature, and the benthic algae increases relative to detritus as a food source. There is an accompanying change in species composition and relative abundance within the invertebrate community. For example, the number of stonefly and predatory caddis species declines. However, in both forest and farmland, an undisturbed stream with a stable substrate and no excessive inputs of nitrogen, phosphorus, or silt, will have a well balanced invertebrate community consisting of mayflies, caddis and midges, at least one species of seston-collector and several predator species.

3.4.4 Algae as a food source

Since algae are a major source of food for benthic macroinvertebrates in streams, it is important to evaluate the algal community in assessments of the causes of perturbations.

The algal community can range in structure from a thin film or slime on rocks to extensive green and brown mats covering the entire river bottom. The form it takes depends on three primary factors—stability of flow (frequency of fresh events), water velocity (optimum 0.2–0.5 m sec^{-1}), river bed sediment type and stability. Unstable substrates and sandy sediments provide unsuitable habitat. The type of algae, rate of growth, and eventual standing crop are also determined by water quality (nutrient concentration, suspended solids, presence of toxins) and by light intensity (a function of shading, water depth, and turbidity) (Biggs 1984).

A considerable amount of work on the toxicity of heavy metals to algae has been carried out. In a study such as this a record of the algal species and the presence of proliferations is desirable to determine whether or not algal growth correlates with the expected growth conditions at different sites.

3.4.5 Study design

In this section the guiding principles for the design of environmental impact assessment studies are discussed and then applied to the Coromandel macroinvertebrate study in Section 3.5.

Environmental impact assessment studies, like experimental work, should address a central hypothesis/hypotheses even if they are not expected to conclusively demonstrate cause and effect relationships (Beanlands and Duinker 1983). The use of statistically based designs is recommended, even if the data set must be restricted by resources to a simple statistical test of the null hypothesis "nothing is going on" (Green 1979).

Initial tasks in designing environmental studies are to:

(1) balance the level of statistical precision and generality required (Hall *et al.* 1978);

(2) efficiently allocate effort, time and funds (Ellis 1976, Hall *et al.* 1978).

The generality of a study increases with the number of localities and sites sampled. The precision of population estimates at each site, and thus the reliability of statistical tests, increases with the number of samples collected from each site at one time. At one extreme there is the extensive study designed to show broad trends and involving the collection of a few samples from each of many localities (Hall *et al.* 1978). At the other is the intensive study of a control and an impacted site, preferably before and after impact, for example, "optional impact studies" (Green 1979). Many samples are collected in order to provide the precise population estimates required for validation of cause and effect.

Finance and time invariably constrain the total number of samples which can be collected and processed. Management techniques such as preparation of a cost/benefit trade-off curve can be of assistance in making decisions, but value judgements are almost always required at some stage in developing a sampling design. Savings can be made by restricting the number of species to be counted or by making qualitative or semi-quantitative assessments instead of fully quantitative assessments. Reducing field trips may increase the number of samples that can be processed, but this may reduce the opportunity for observation of the water body and its biotic community under varying seasonal and climatic conditions. As a consequence, objectives may have to be redefined. Optimisation of cost/benefit can be achieved by intensive field sampling trials and statistical analysis of results at the beginning of the programme (Green 1979, Greeson *et al.* 1977, Resh 1979) and a literature search for life history information about common species collected during these early trials. The ultimate goal should be sufficient samples from sufficient sites and/or seasons to provide a statistically sound (usually at a probability level of 1 in 20) test of the hypotheses.

3.4.6 Population estimation and number of samples

Aquatic organisms are not usually randomly distributed on the stream bed (Allen 1959). The dispersion of an individual species is a function of its response to environmental factors such as velocity (Jaag and Ambuhl 1964) and substrate (Cummins and Lauff 1969) to life history factors (Resh 1979) and to the tendency of individuals within a species to aggregate or separate within the micro-habitat (Allen 1959). The number of samples required to provide a true population estimate varies with the physical nature of the stream bed, the degree of uniformity of the habitat being sampled, the type of sampler employed and its size relative to irregularities in the substrate (Allen 1959, Resh 1979).

Many previous water quality studies have involved the collection of three Surber samples from riffles. Statistical studies have shown that although most of the more common invertebrates will be collected in three samples many more are required (30–50) to calculate reliable population estimates, that is, to within ± 25% at the 95% confidence level (Needham and Usinger 1956, Chutter and Noble 1966, Greeson *et al.* 1977). Taking such large numbers of samples is not normally considered realistic because of budget and time constraints. Using as fine a net as practicable can reduce the number of samples required to get a reliable population estimate. This is particularly relevant where streams have low population numbers because fewer samples cause less disturbance to the stream bed.

Macroinvertebrates have been defined as those organisms retained by a 595 μm mesh net (Standard No 30) (Mason *et al.* 1975). However, many invertebrates in this category have small, early instars, which will not be retained by this mesh size. In toxicity studies, where the presence or absence of a species needs to be established, ideally all life stages should be collected. Mason *et al.* (1975) showed that a coarse mesh (595 μm) could result in significant underestimation of the number of benthic invertebrates and the number of taxa. Greeson *et al.* (1977) recommended that a medium fine mesh (250 μm) be used in studies requiring more accurate population estimates. However, this is not always practical in streams with abundant algal growth since the net is easily clogged thus enabling the larger motile animals to escape (Macan 1958).

3.5 Methods Used in Present Study

3.5.1 Introduction

The steps recommended by Green (1979) were followed in this study.

The purpose of the study was to ascertain whether contamination from sulphide mineralisation (be it from mining or erosion of naturally occurring formations) has an impact on stream macroinvertebrate communities in the Coromandel. The study examined these questions:

(1) Are the macroinvertebrate communities of unperturbed forested streams in Coromandel typical of those found in unperturbed forested streams elsewhere in New Zealand?

(2) Are the macroinvertebrate communities in contaminated streams in Coromandel significantly different from similar streams in Coromandel which are not contaminated?

(3) Can any such differences be correlated with the principal effects of contamination such as elevated heavy metal concentrations, superficial sediment deposition, low pH?

(4) At what level do such effects cause perturbations of the macroinvertebrate communities?

3.5.2 Pilot survey

A pilot survey of 18 streams was carried out in 1981 (Penny, 1983). Three samples per stream were collected in eight different catchments known to have a range of point source and diffuse sources of contamination (Figure 3.2); a species list and their relative abundance is given in Appendix 3.1.

A plot of mean abundance of organisms per sample against total number of taxa (Figure 3.3) shows that diversity and abundance tended to be greatest in streams with lowest metal concentrations (Waipupu, Buffalo, Mangakara, Waitaia Bridge, Waitekauri, Komata). Where metal concentrations were slightly higher (Paroquet, Waiorongomai, Jubilee, Waiomu Ford) diversity and abundance were lower and in Tui Stream where metal levels were much higher, very few organisms were found. The pilot survey suggested that there might be a link between heavy metal contamination and biological impoverishment in the streams. Three catchments were selected for a more detailed survey to examine this link.

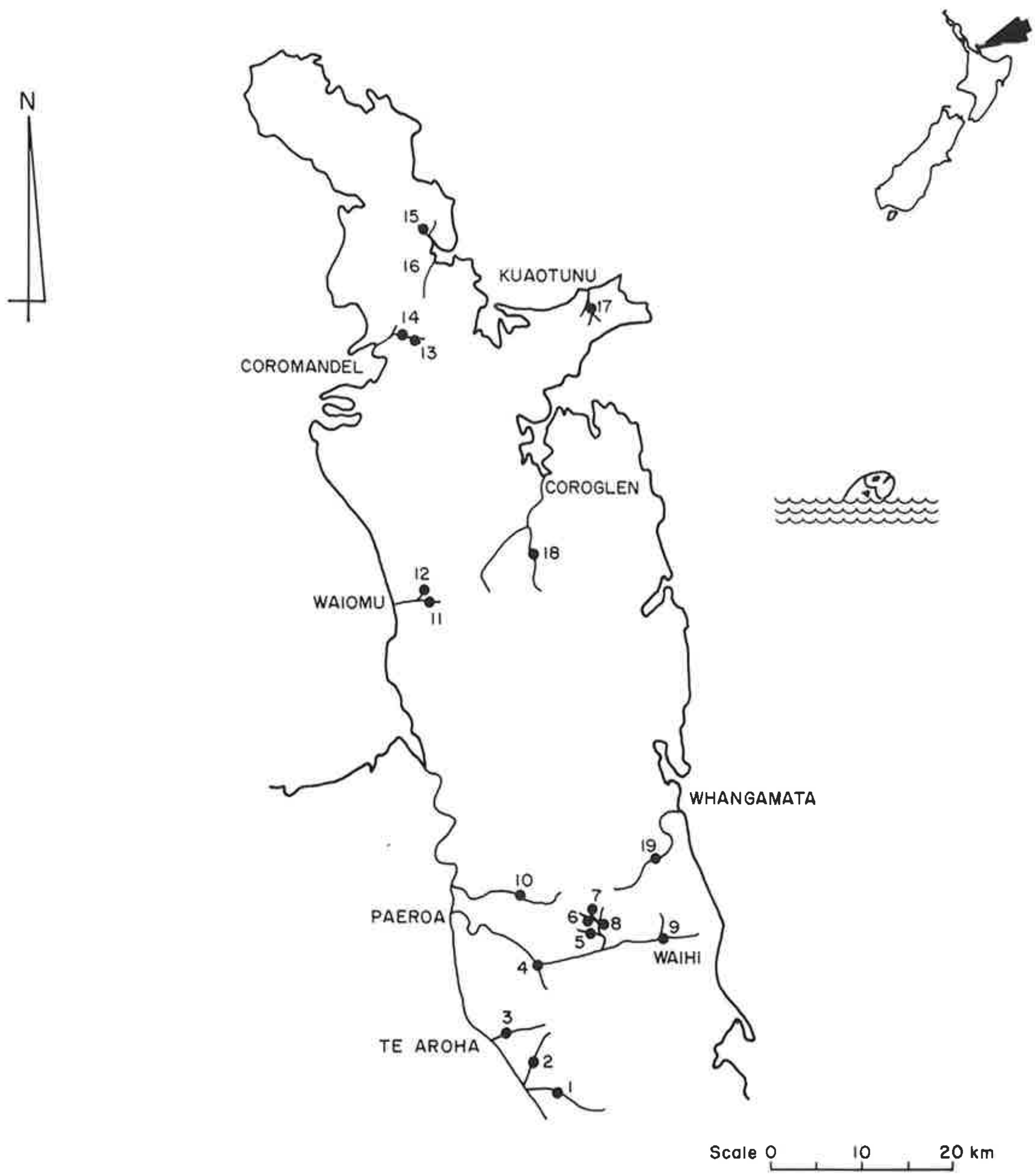
3.5.3 Catchment and sample site selection

Waiomu, Buffalo and Waitaia catchments were selected for further study. Each is relatively accessible and exposed to a range of mining effects.

In March 1982, each stream was followed as far as possible into the headwaters and detailed notes made about catchment stability, vegetation, location of old mine shafts, stream gradient and morphology. The macroinvertebrate fauna were sampled at a number of sites using the "kick" method (Biggs 1983).

Sampling sites were selected to be representative of the stream with respect to channel morphology, size, shading and vegetation. Control sites were selected to be, as far as possible, free of the influence of mining or mineralisation. Test sites were selected for the presence of possible impacts from heavy metals, sedimentation and low pH. Control sites and test sites for statistical comparison were paired up as closely as possible taking into account other factors such as shading, size, substrate type, gradient and flow, and general water quality. Each site had to be amenable to the same sampling technique and preferably included riffle habitat.

Test sites below mine drainage inputs in the Waiomu, Buffalo and Waitaia Streams were selected so as to give a range of severity of environmental impact, and where possible through a range of stream types.



1. WAIPUPU
2. WAIORONGOMAI
3. TUI
4. COMSTOCK
5. MANGAKARA
6. JUBILEE
7. GRACE DARLING
8. WAITEKAURI
9. MANGATOETOE
10. KOMATA
11. WAIOMU
12. PAROQUET
13. EVERETTS
14. BUFFALO
15. WHAREROA
16. HARATAUNGA
17. WAITAIA
18. RANGIHAU
19. OTAHU

Figure 3.2 Pilot survey sample sites, Coromandel 1981 (see Table 1.3 for grid references).

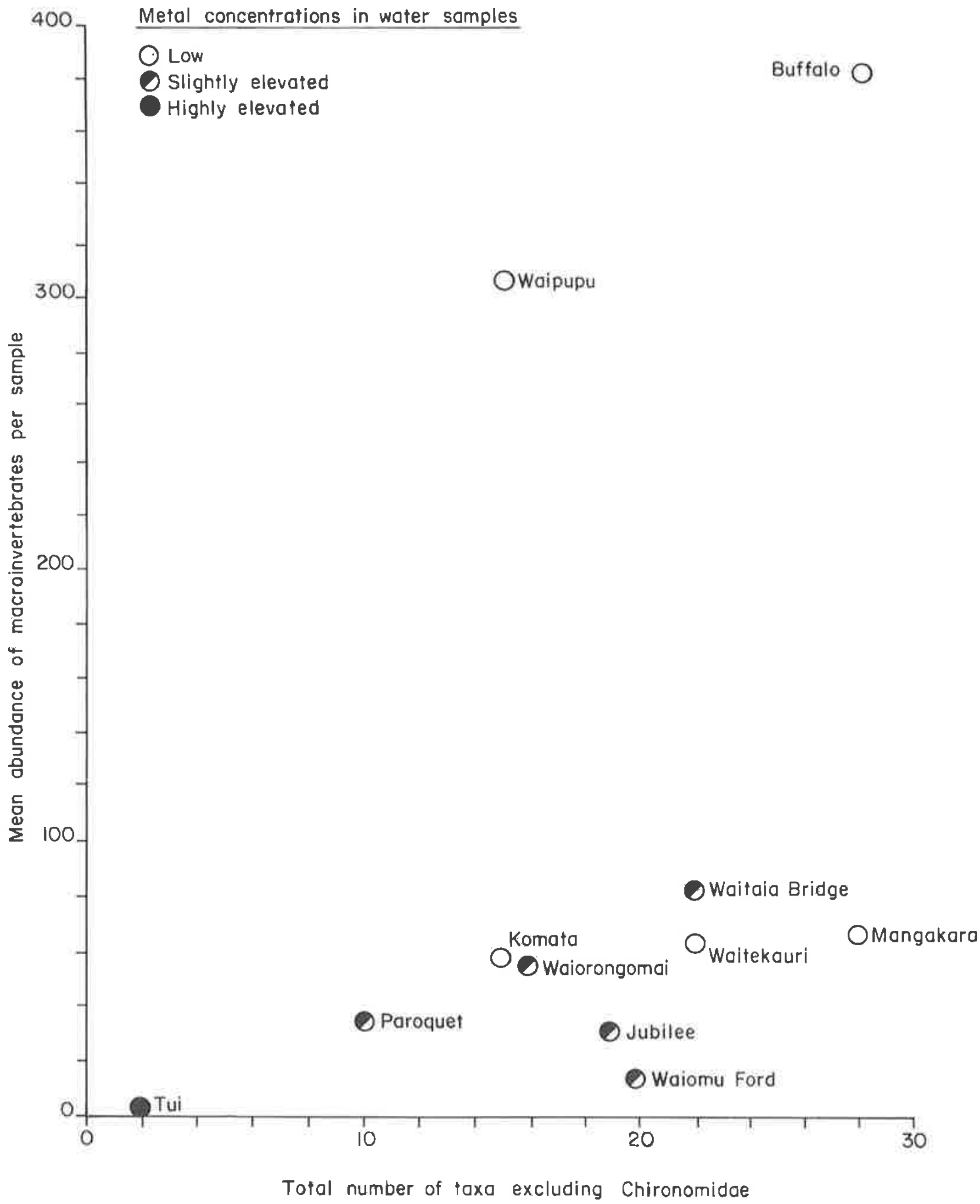


Figure 3.3 Mean abundance and total diversity of taxa at pilot survey sites where heavy metal measurements were also made, Coromandel (refer Chapter 2, Table 2.2 for explanation of metal concentrations).

Stream stability at control and test sites was assessed using the Pfankuch Survey procedure (Pfankuch 1975), a systematic method in which a series of physical factors are examined and scored numerically. The procedure summarises the capacity of the stream channel to resist detachment of bed and bank materials, and of the stream to adjust and recover from a potential change in flow and/or increase in sediment production (Pfankuch 1975). Rounick and Winterbourn (1982) used such a procedure in 43 streams in New Zealand forest catchments to evaluate catchment stability and found that experienced users obtained scores within 5% of each other. The stability evaluation form from Rounick and Winterbourn (1982) was used in this study.

Samples for analysis of grain size composition of the fine sediments (< 9.5 mm grain width) were collected from control and test sites in April and September 1982. Sediments were sieved into the size fractions recommended by Hynes (1970) after Cummins (1962), dried to 105° and weighed. Silts and clays were not separated. Fine sediments from some contaminated streams contained unattached iron precipitate, and all samples contained varying amounts of organic material including diatoms.

A description of the individual catchments and sample site locations, is given in Section 3.6.

Water quality measurements were made during the study by Hauraki Regional Water Board staff (Section 1.9, Table 1.2). Heavy metal concentrations in water and sediment samples at each site are described in Chapter 2 (Tables 2.3–2.6).

3.5.4 Population estimation and number of samples

Sampling trials were carried out to determine which mesh size was most suitable for use in this study and how many samples per site would give acceptable population estimates. Eleven samples were collected in early March 1982 with a Surber sampler fitted with nets of mesh size 525 μm, 320 μm and 250 μm, one inside the other. Contents of each net were stored and processed separately. In this trial the 250 and 320 μm nets together contributed 21% to 71% of the total counts and the 250 μm net contributed 0.7%–27% of total counts. Use of the fine net resulted in a significant increase in the numbers of Leptophlebiidae and Chironomidae that were retained but did not significantly alter the numbers of *Coloburiscus humeralis, Potamopyrgus antipodarum*, cased caddis, Elmidae, or free living caddis that were collected. Problems with clogging and eddying were not experienced. As a result of this trial, 250 μm mesh netting was selected for use throughout the survey.

Trials were carried out to determine the number of samples required to give a reasonable estimate of population. These showed that six samples per site would provide a population estimate with a 25–40% error on the 95% confidence limit, as recommended by Greeson *et al.* (1977).

Retrospective analysis of total numbers obtained at each site from each sampling occasion during the main survey showed that the error in the population estimates for total animals varied between 13% and 87% for six samples (mean 40%) and between 14% and 88% for three samples per site (mean 48%). Thirty percent of means were inside the 25% confidence limits. It was calculated that for 15 samples per site 50% of means would have been inside the 25% confidence limits and for 30 samples per site 90% of means would have been inside the 25% confidence limits. These results are consistent with those of other workers and emphasise the difficulty of acquiring reliable population estimates within a limited sampling budget.

Between 15 and 30 samples per site were included in the main survey.

3.5.5 Qualitative sampling method

A dip net fitted with a 250 µm detachable bag (using "Velcro") was used to collect organisms disturbed by the "kick" method from an area of approximately 0.5 m^2. A qualitative description of the benthic algae present at each site was made.

3.5.6 Quantitative sampling method

The quantitative sampler most commonly used in stony streams is the Surber sampler (Biggs 1983) but it proved difficult to use in the steep bouldery streams of Coromandel. For the main study, a round, solid-sided Waters and Knapp type sampler (Waters and Knapp 1961) with a mesh window and collecting net was found to be more suitable. This was constructed from a polypropylene bucket, 300 mm deep with a diameter of 260 mm and fitted with a detachable 250 µm mesh net (Figure 3.4).

Choice of a selected habitat for sampling reduces the number of samples required for between stream comparisons (Chutter and Noble 1966). Boulders less than 260 mm across (the diameter of the sampler) and their underlying gravels were the micro-habitat within riffles selected in this study. Six such boulders were sampled randomly at each site on each occasion. As far as possible samples were collected at depths of 150–200 mm, where water velocity was 0.2–0.3 m sec^{-1}.

To collect each sample, the sampler was placed in position over the selected boulder which was then removed as quickly and carefully as possible into a separate container and taken to the bank. The remaining gravel was stirred up immediately so that animals were dislodged and carried into the net by the current. The boulder which had been removed to the bank was then examined to determine the distribution of organisms over the rock surface. Hand picking of the boulder ensured that organisms living firmly attached to the stone were collected in the sample. Samples were preserved in 70% ethanol.

In the laboratory, samples were washed through sieves to remove preservative and assist sorting. The animals contained in the fine fraction were counted and identified without being removed from the residue. Animals were picked out of the coarse fraction prior to counting. Detritus was separated from gravel, drained and wet-weighed.

Identifications were made to genus, and species level where possible, using keys by Winterbourn and Gregson (1981) and references cited therein.

3.5.7 Sampling strategy

Sampling was carried out to cover all seasons between March 1982 and January 1983. Qualitative samples were collected March 1–5 1982, March 24–26 1982, August 20–23 1982. Quantitative samples were collected April 15–17 1982, July 1–3 1982, September 29—2 October 1982, November 24–28 1982 and January 20–23 1983. The number of samples collected is given in Table 3.1.

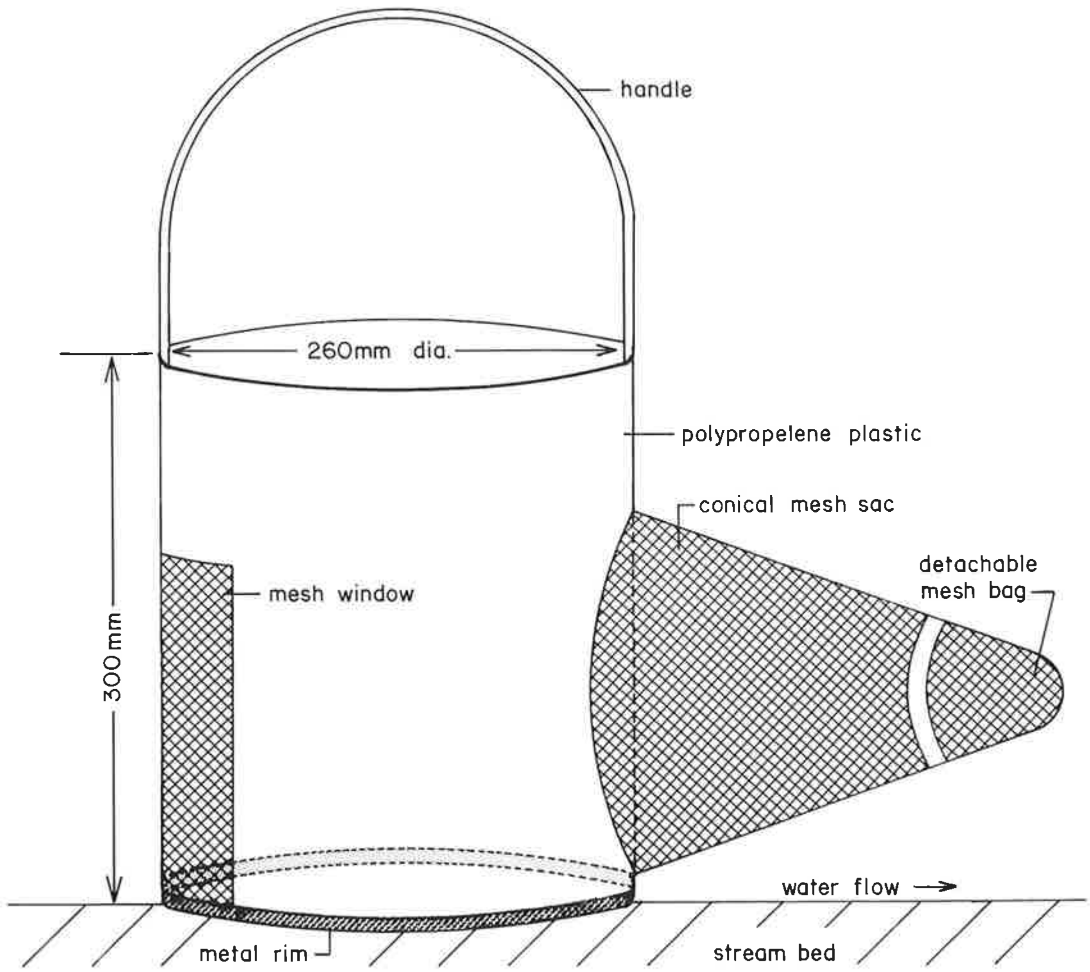


Figure 3.4 Stream bottom macroinvertebrate sampler (after Waters and Knapp 1961).

The extent of sampling differed between sites—at some sites sampling was repeated four or five times (yielding 15 or more samples) and at others sampling was only carried out once or twice (yielding 3–6 samples). Statistical comparisons are limited to sample sites with 15 or more samples and these were paired as follows:

	Test Site	Paired Control Site
Waitaia catchment	W8	W3
	W7	W4
	W6	W4
Waiomu catchment	WP1 + WP2	WC
	P2	B4*

In the absence of a suitable paired control for test site P2, site B4 (Buffalo Stream) was used from the Buffalo catchment as it had the most similar stream bed characteristics to P2 and a healthy fauna similar to the control sites. Site characteristics and location are given in Section 3.6.

Table 3.1: Sampling programme, biological survey Coromandel 1983

Catchment and stream sampled		Site No.	Status* (see below)	Dates sampled	Total number quantatitive samples
WAITAIA (Kuaotunu Peninsula)	Waitaia Control Stream	W1	Control	Mar 1982 Aug 1982 (qualitative only)	–
		W2	Control	Mar 1982 Aug 1982 (qualitative only)	–
		W3	Control	Mar 1982– Jan 1983	33
		W4	Control	Jun 1982– Jan 1983	18
	Waitaia Stream	W5	Test	Mar 1982	3
		W6	Test	Jun 1982– Jan 1983	21
	Waitaia Mine Stream	W7	Test	Mar 1982– Jan 1983	18
		W8	Test	Mar 1982– Jan 1983	30
		W8G	Test	Mar 1982– Jan 1983	6
		W9	Test	Mar 1982 (qualitative only)	–
		W10	Test	Mar 1982 (qualitative only)	–
	Mullock Stream	W12	Test	Nov 1983	3

See Chapter 1, Table 1.1 for map references.

Table 3.1: Sampling programme, biological survey Coromandel 1983—*continued*

Catchment and stream sampled		Site No.	Status* (see below)	Dates sampled	Total number quantatitive samples
WAIOMU (above Waiomu town)	Waiomu Stream	WF	Control	Mar 1982 (qualitative only)	-
		WC	Control	Mar 1982–Jan 1983	30
		WP1	Test	Mar 1982–Jan 1983	18
		WP2	Test	Mar 1982 Jan 1983	15
	Paroquet Stream	P1	Test	Nov 1982	6
		P2	Test	Mar 1982 Jan 1983	30
BUFFALO (above Coromandel town)	Buffalo Stream	B1	Control	Mar 1982	6
		B2	Control	Mar 1982 Jan 1983 (qualitative only)	-
		B3	Test	Nov 1982 Jan 1983 (qualitative only)	-
		B4	Test	Mar 1982–Jan 1983	30
	Everetts Stream	E	Test	Nov 1982 Jan 1983 (qualitative only)	-
		EC	Control	Nov 1982 Jan 1983 (qualitative only	-

Status: Control sites were those with no obvious source of contamination either from mine discharges, mullock heaps or large seepages from altered rock.

3.5.8 Data analysis

Uncontaminated forest streams in Coromandel were compared qualitatively with other New Zealand forest streams by comparison of species lists and community structure. Quantitative comparisons between control and test sites were made by four methods:

Abundance

Mean counts for all data at individual sites were compared between pairs of sites using Student's t test. To normalise the data for statistical analysis, mean counts were transformed to log x + 1 (Green 1979). Paired site comparisons were made, testing the null hypothesis "there is no significant difference in the number of organisms between control and test sites within each pair of sites". A probability $\leqslant$ 0.05 was selected as the level of significance below which the null hypothesis was rejected.

Diversity of taxa

Mean number of taxa at each site and numbers of taxa within each major order at each site were compared among sites.

Ordination

Ordination (Hocutt 1975) provides a systematic procedure for comparison of species diversity and abundance. Numbers of organisms were plotted (y axis) against number of taxa (x axis) (Figure 3.5). In each ordination plot the means of species and organism counts for the control site were plotted as vectors. The areas defined by the vectors were then designated quadrants I-IV. The distribution of these data within the quadrants can show perturbations in the communities and may assist interpretation of the cause (Hocutt 1975).

Optimal conditions (i.e., maximum species diversity and abundance) are represented in quadrant II (Figure 3.5). A community affected by organic pollution would have an overall reduction in numbers of species, but an increase in numbers of organisms of tolerant forms (quadrant I). The effect of flooding or scouring on a healthy community would be a reduction in abundance, but not necessarily a reduction in species (quadrant III). Communities stressed by a sublethal or toxic substance would react by a reduction in abundance and species (quadrant IV), and show adaptation and recovery by a few highly productive species (quadrant I). Improved water quality would lead to an increase in interspecific competition and niche partitioning and therefore an increase in the number of taxa (quadrant III and then II, (Hocutt 1975).

Species composition, functional feeding groups and algae

Relative abundances and species composition within functional feeding groups were compared between sites. Two groups of organisms, leptophlebiid mayflies and cased caddis, were compared between quantitative control and test sites using Student's t test to make paired site comparisons on data transformed to log x + 1. A qualitative comparison of the algal community at each site was also made.

Inter-relationships between water and sediment chemistry, stream morphology and macroinvertebrate data were examined using scatter plots to determine any correlations.

3.6 Physical and Chemical Character of Sample Sites

3.6.1 General description of catchments, contamination sources, and sample site locations Waitaia catchment

The Waitaia Stream arises in two parallel quartz-bearing ridges, Bald Spur and Waitaia Ridge, and flows into the Kuaotunu River (Table 3.2).

The Waitaia Stream has two main branches, the right hand branch, "Waitaia Mine Stream", which flows out of a Waitaia Mine drive and is joined by "Waitaia Mullock Stream" draining Hosies Mine drive, and the left hand branch, which has no direct discharge from mine streams and only small traces of iron floc seepages. The left hand branch of the Waitaia was chosen as a control stream to compare with Waitaia Mine test stream (Figure 3.6).

Both branches of the Waitaia had "steep forest", "flat forest" and "flat swamp" zones. The steep forest zones were characterised by large kauri and tanikaha with a lush understorey of ferns. Here the streams were well shaded, with dense moss, algae and ferns growing on rocky outcrops, the stream

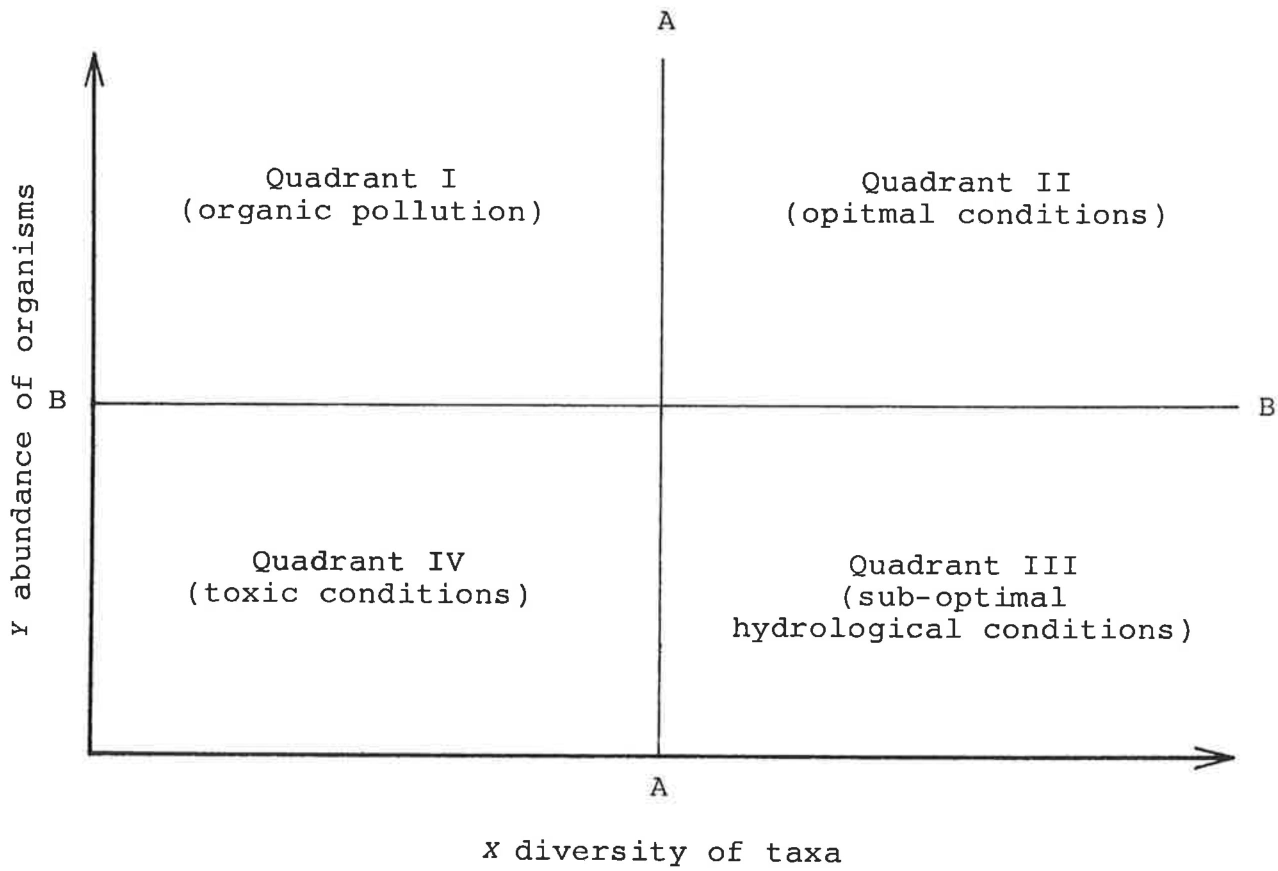


Figure 3.5 Method of ordination (Hocutt 1975). Reference vectors A and B are means calculated from the control data. The data to be compared are then plotted to determine their distribution among the four quadrants.

banks and large boulders. In the Waitaia Control stream there was little loose sediment, but there was a considerable amount of organic debris, and the substrate was blackened with manganese compounds. In Waitaia Mine and Mullock test streams, the stream bed was largely devoid of vegetation and it was deeply stained with an iron hydroxide deposit. This was most apparent at the exit of the mine and diminished downstream over about 1 km.

The flat forest zones were characterised by a lower gradient with the forest giving way to a swamp flora of ponga, nikau and kanuka. In Waitaia Control stream the stream banks had been trampled by cattle. The canopy, however, was dense and the stream was shaded. The stream had undercut the bank in several places and resulting in the release of fine sediment into the stream. More rubble was present on the stream bed than in the upper reaches, and after dry weather, small seepages of metal-bearing groundwater as evidenced by small patches of iron hydroxide precipitate were observed along 200 m of the true left bank. The flat forest zone in Waitaia Mine stream was much shorter than in the Control stream (Figure 3.6). 100 m below the confluence of the Mullock and Mine Streams the bush canopy opened out and there had been an invasion of blackberry and cutty grass. The stream substrate consisted of small weathered boulders lightly coated with a fine brown deposit of iron, firmly embedded in fine sediments.

In the flat swamp zones, the adjacent land was largely pasture. The stream flowed through a riparian strip of ponga, nikau, kanuka, blackberry and cutty grass.

Twelve sites in the Waitaia catchment were selected for study (Figure 3.6). All twelve sites were surveyed for a qualitative assessment of the stream communities. Sites W3, W4 (control) and W6, W7, W8 (test) were sampled quantitatively. The sites nearest to the mine exit (W9 and W10) were only surveyed once since no algae or macroinvertebrates were found.

Waiomu catchment

The Waiomu River flows into the Firth of Thames 13 km north of Thames township (Table 3.2). The upper part of the catchment supports luxuriant podocarp-hardwood-kauri forest. One tributary, Paroquet Stream, has evidence of several mine discharges into its waters in the middle reaches from Monowai Mine. Leaching occurs from mullock heaps, and old drives are evident along the east bank; above the confluence with the Waiomu Stream a stamper battery used to operate. Paroquet Stream flows down a steep valley with many slips along the east bank as a result of a road that once serviced the Monowai Mine.

Six sites were sampled in this catchment. Two sites were selected in Paroquet Stream (test site P2, control site P1) and two sites in Waiomu Stream were selected as controls (sites WC, WF, Figure 3.7). Two further sites downstream from the confluence of the Waiomu and Paroquet Streams were also sampled (sites WP1, WP2, Figure 3.7). Sites P2, WC, WP1 and WP2 were used for quantitative analysis. Site characteristics are tabled in Appendix 3.2.

Buffalo catchment

Buffalo Stream (also known as Courthouse Creek) is a small steep tributary of the Whangarahi River (Table 3.2).

In the upper reaches of Buffalo Stream, the gradient was gentle and the substrate composed of small boulders in a bed of soft sediments and detritus. Approaching Everett's Drive, the gradient increased and below, Buffalo Stream fell steeply through a series of boulders and small pools. The stream

Table 3.2: Catchment characteristics of streams for biological survey

	Waitaia catchment	**Buffalo catchment**	**Waiomu catchment**
Map Nos	N40 (NZMSI)	N40 (NZMSI)	N49, N44 (NZMSI)
Streams studied	Two branches in the headwaters of Waitaia Stream, left branch (N40 228375) and right branch (N40 235738).	Buffalo Stream (N40 008739), Everetts Stream (N40 017743).	Waiomu Stream (N49 037395), Paroquet Stream (N49 042398).
Access	Waitaia Road off State Highway 25 (N40 223750) 1.5 km south of Kuaotunu Town.	No-exit road 1 km north of Coromandel before Kennedy Bay Road turnoff (N40 003736).	Waiomu Road off State Highway 25 at Waiomu (N49 015394).
Topography	Headwaters arise at 150 m asl in steep bush clad hills of the Kuaotunu Peninsula, East Coromandel. Both branches drop through 1.5 km to 3 m asl at their confluence. After a further 1 km, the Waitaia Stream joins the Kuaotunu River at 20 m asl.	Headwaters arise at 400 m asl in steep bush clad mountains of the central Coromandel Range. The Buffalo ascends rapidly through 0.5 km to 240 m asl, and over a further 2 km to 30 m asl, before its confluence with the Whangarahi Stream.	Headwaters of Waiomu arise at 540 m asl in steep coastal mountains, west Coromandel, and descend through 1.5 km to 100 m asl. It joins the Paroquet Stream at 30 m asl and flows across coastal delta for 2 km to the sea. Paroquet arises at 420 m asl and descends through 2.5 km to the Waiomu at 30 m asl.
Geology	Waitaia Stream originates in Miocene andesites passing rapidly into feldspathic greywacke of the Moehau Formation. Large mineral bearing quartz reefs cross the source of the right branch (Mine and Mullock Streams).	Buffalo Stream traverses Beeson Islands volcanics from its source downstream for 1 km. It then crosses the Moehau formation into more volcanics before draining into alluvial coastal plains. A large mineral bearing quartz reef crosses the stream at Everetts Drive.	Waiomu and Paroquet Streams are confined to andesitic Beeson Island volcanics of the Southland and Pareora series. Quartz veins and outcrops extend down eastern ridge of Paroquet Valley.
Land classification	NZ Land Resource Inventory Worksheet N40. Land units VIIel and VOe8. Slight sheet and soil slip erosion. Potential for severe erosion on headwaters.	NZ Land Resource Inventory Worksheet N40. Land units VIIe4, VIIe2, VIe10. Negligible erosion at present, potential for severe soil slip, sheet and debris avalanche erosion in the headwaters.	NZ Land Resource Inventory Worksheet N49. Land unit VIIe8. Potential for very severe debris avalanche erosion. Present erosion: severe debris avalanche and scree. 1–10% affected by soil slip erosion.
Land use	Source to 0.5 km downstream, dense native forest. 0.5–1 km downstream, native forest with pasture. 1 km—Kuaotunu River, pasture.	Source to impoundment (N40 008739), native bush.	Both streams: native bush, primary and secondary growth.
Past mining	Waitaia and Hosier Mines at source of Mine and Mullock Streams (right branch of Waitaia Stream). Other mines in area include Try Fluke and Great Mercury. Mullock heaps are found along both Mine and Mullock Streams.	Everetts Drive at source of Everetts Stream. Other drives also drain into the Buffalo. Other mines in the area include Royal Oak, Tokatea and Success.	Numerous drives from Monowai Mine Drain into Paroquet Stream on the east bank. Mullock heaps along Paroquet. Other drives are found in Golden Cross Stream Valley.

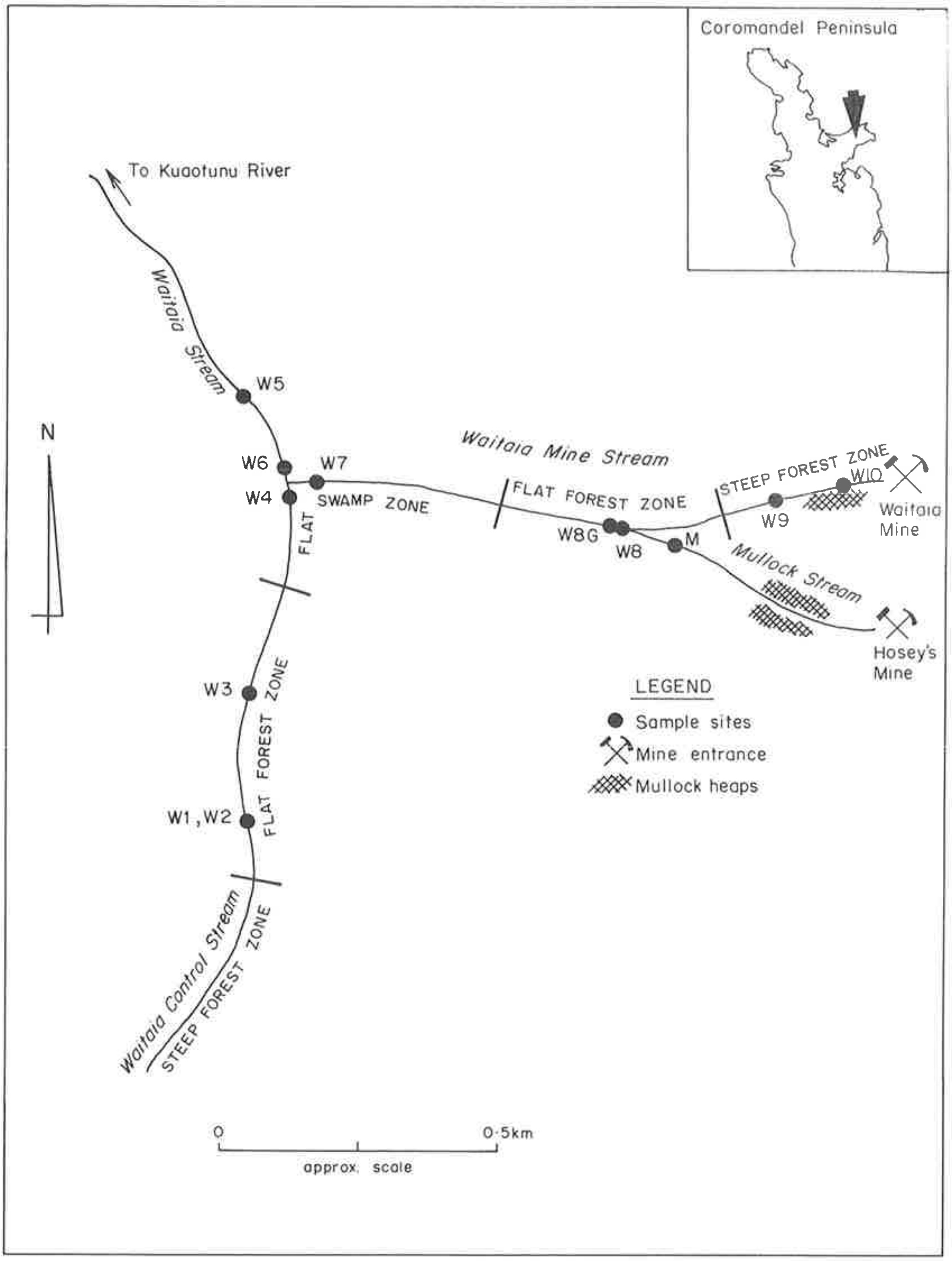


Figure 3.6 Biological sampling sites, Waitaia Catchment, Coromandel 1982-83. Site details are listed in Appendix 3.2b.

was heavily shaded; the banks were strewn with debris and the stones and boulders in the stream were stained with manganese and thickly coated with moss. The adjacent banks were steep and well vegetated, and showed little evidence of erosion. There was some deposition of gravel and sand in pools.

Further downstream, immediately above the impoundment, the stream descended in 400–600 mm steps through a bed flanked and strewn with boulders, most of which were covered with mosses (*Fissidens rigidulus, Phthuidium* sp., *Brachythecium hypopterygium* and *Plagiochyla rotulatum*). The stream bed was completely shaded by ponga, coprosma, mahoe, kanuka and kamahi. The banks were stabilised by a dense understorey of ferns, native shrubs and exotic weeds, and the substrate was composed of large stones overlying a bed of coarse gravels with little fine sediment.

Four sample sites were chosen in the Buffalo Stream, two above Everett's Drive and two below (Figure 3.8); however, only one site immediately upstream of the impoundment (B4) was sampled regularly for quantitative analysis (Table 3.1).

A small stream (200–300 mm width) flowing directly from Everett's Mine Drive to Buffalo stream, and a similar size stream flowing into Everett's Drive stream were mossy, and choked with organic debris. There was no iron floc in the pool at the mine exit. Organic debris was coated with a blue-green algal scum. Following heavy rainfall, the stream flow was turbid and had smelled of hydrogen sulphide. These two streams were only sampled once and have not been included in the quantitative analysis. This was because both streams were too small to obtain adequate samples of macroinvertebrates, and irrespective of perturbations, few organisms would be expected in either stream.

3.6.2 Stream size, substrate composition, Pfankuch stability ratings

Waitaia Mine Stream and Waitaia Control Stream were the smallest streams studied and had the shallowest gradient (Appendix 3.2). Paroquet and Buffalo Streams were slightly larger than the Waitaia Streams and had the steepest gradients. The largest stream studied, Waiomu Stream, had an intermediate gradient (Appendix 3.2).

The stream bed at test and control sites can be described as a gravel sand matrix with a variety of boulder sizes (Table 3.3).

Within the gravel matrix (0.5–9.2 mm) less than 7% was in the finer ($<$ 0.5 mm) fraction in all sites sampled (Table 3.4). In Paroquet Stream, an extremely fine covering of clay was observed on the streambed but was difficult to measure since disturbance immediately released it downstream. There was some superficial covering by iron hydroxide precipitate at Waitaia Mine site (W8). Further upstream at sites W9, W10, iron floc deposits were thicker.

Overall, the study sites had bouldery gravel beds with few fines. There were some differences in the proportion of medium and coarse sand. The Pfankuch Index suggested stability for Paroquet Stream at site P2 was poor compared with all other streams examined in this study. This was caused by large slips along the left bank contributing large amounts of coarse and medium sediment to the stream bed. The effects of this sedimentation and the observed deposition of an extremely fine layer of clay (visible but undetected by particle size analysis) over the stream bed during low flows, may have affected the biological community.

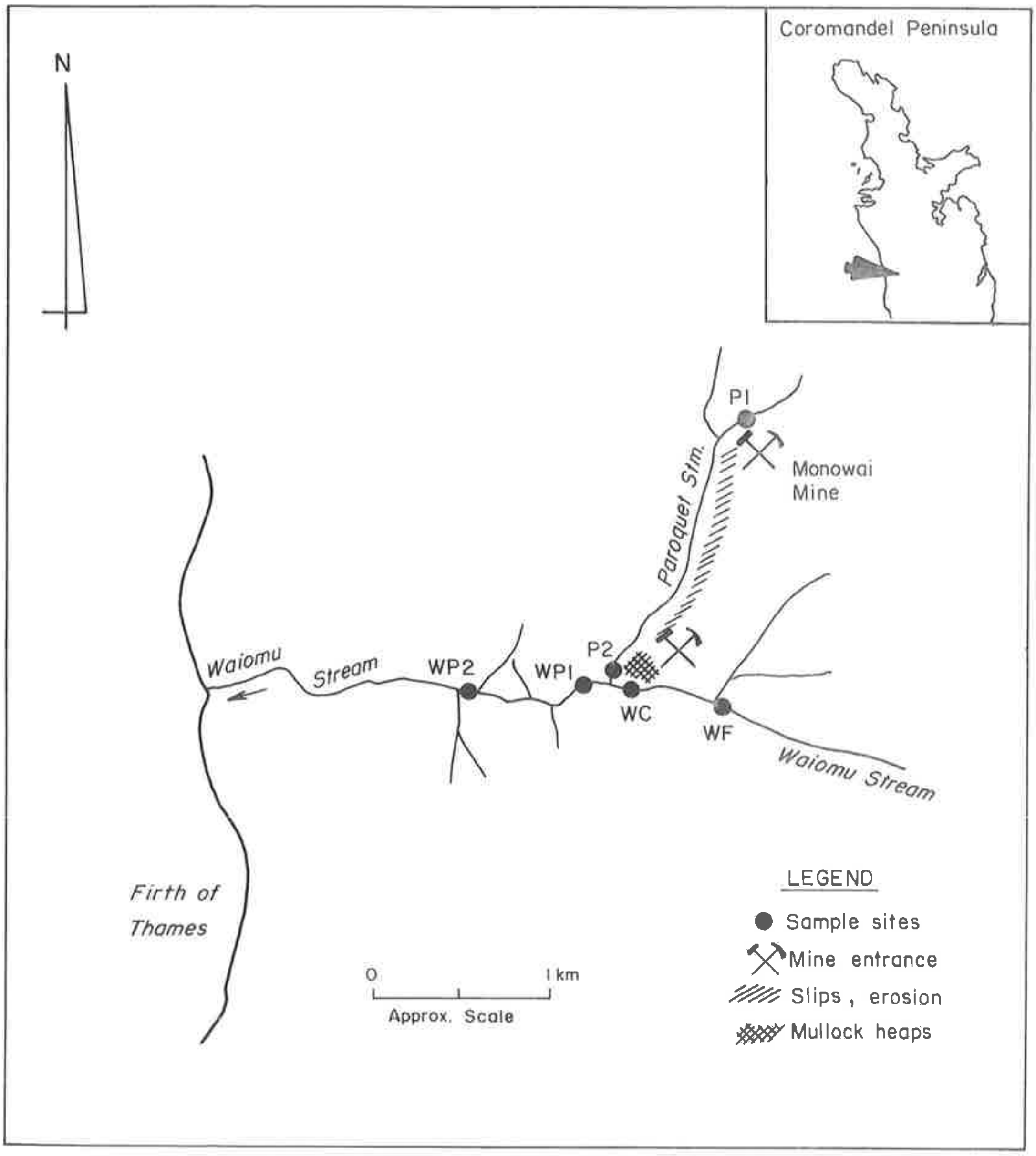


Figure 3.7: Biological sampling sites, Waiomu Catchment, Coromandel 1982-83. Site details are listed in Appendix 3.2b.

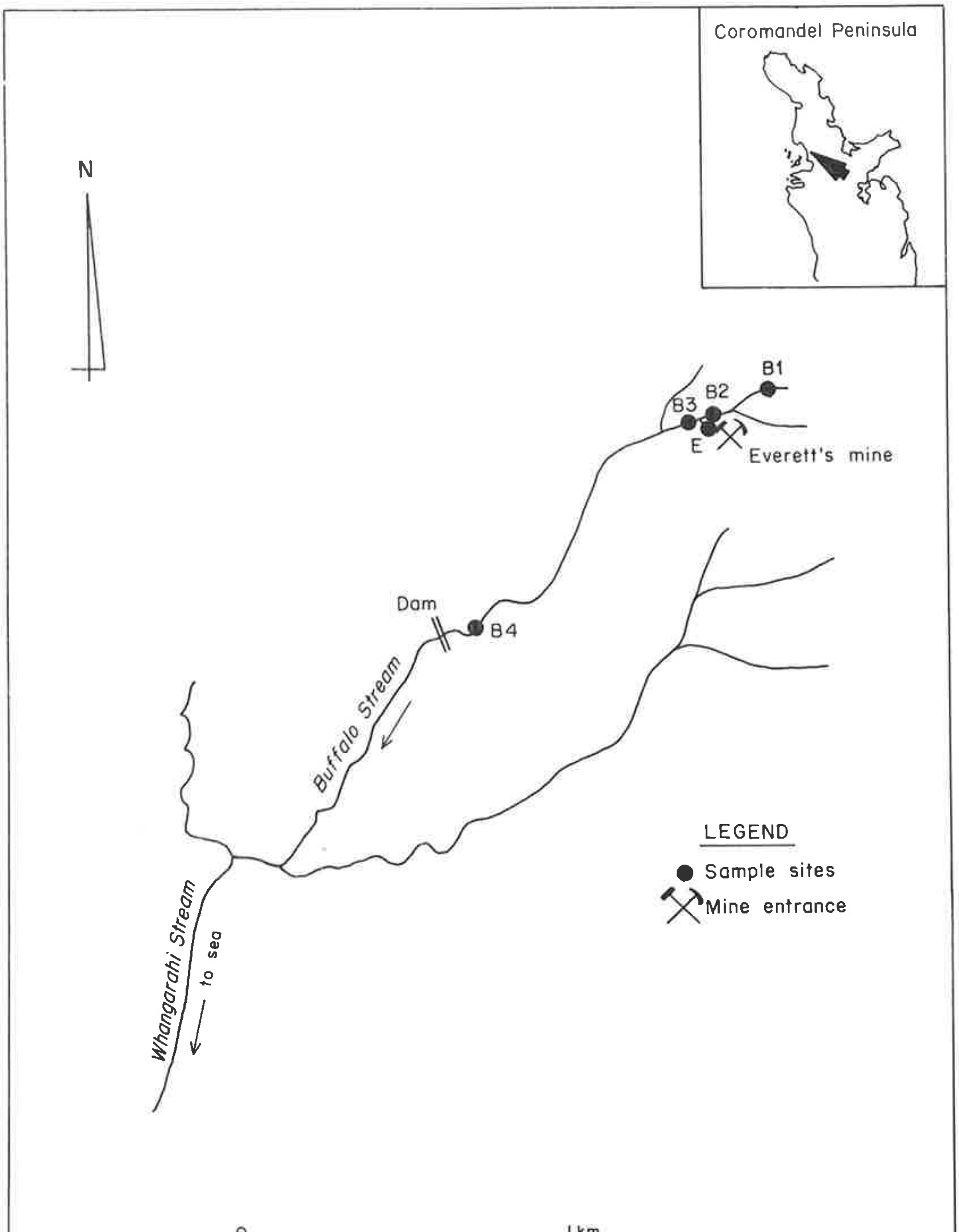


Figure 3.8: Biological sampling sites, Buffalo Catchment, Coromandel 1982–83. Site details are listed in Appendix 3.2b.

Table 3.3: Percent composition (estimate by eye) of substrate at quantitative sample sites, biological survey—Coromandel 1982-83

Stream name	Stream site	Maximum width (mm) of substrate particle	% Area of substrate with particle size > 9.5 mm	% Area of substrate with particle size < 9.5 mm
Waitaia Control Stream	W3	250	80-85	15-20
Waitaia Mine Stream	W8	350	80	20
Waitaia Control Stream	W4	180	70-80	20-30
Waitaia Mine Stream	W7	130	90	10
Waitaia Stream	W6	170	60	30-40
Paroquet	P2	1500	40-50	40-50
Buffalo	B4	2500	60-70	30-40
Waiomu	WC	800	80-90	10-20
Waiomu	WP1	500	80-90	10-20
Waiomu	WP2	1500	60-70	30-40

3.6.3 Water quality (including pH)

Temperature, dissolved oxygen, nitrate, phosphate and suspended solid measurements did not differ significantly between test sites and control sites (Table 1.2), and were well within acceptable ranges to sustain a healthy instream community.

Both control and test sites except Everett's Drive (E) were weakly acid to weakly alkaline (pH 6.0-7.5), a range not expected to have a deleterious effect on instream organisms. Relatively high sulphate concentrations, and large differences between hardness and alkalinity at test sites indicate, however, that acid addition occurs above these sites. Under conditions of further acid addition, sites with low alkalinity would be more susceptible to fall in pH because buffering capacity is low (Chapter 2). Sub-optimal pH conditions may arise from time to time in the Upper Waitaia Mine Stream.

3.6.4 Heavy metal concentrations

Concentrations of arsenic, cadmium, copper, lead, and zinc were measured at test and control sites in both the water column and on the surfaces of sediment particles (< 0.4 mm diameter) (Tables 2.3-2.6 pp. 32-35). Concentrations of most metals at test sites tended to be higher than at control sites. Metal concentrations at test sites were of a similar level to those of the slightly elevated group identified in Chapter 2, Section 2.3.2. Metal concentrations at control sites were of a similar level to the background group. The only site with high metal concentrations equivalent to Tui Stream was Everett's Drive. In most streams arsenic concentrations were low, irrespective of other metal concentrations, and were only significantly elevated in Waitaia Control Stream (W3, W4).

3.6.5 Summary of sample site information

The study streams drain forested catchments that have undergone significant mine workings in the past (Nos 8, 9, 23, Figure 1.2). Waitaia Mine Stream and Waitaia Control Stream were the smallest and had the shallowest gradient. Paroquet and Buffalo Streams were slightly larger with a greater depth of water and steepest gradients. Waiomu Stream was the largest stream

Table 3.4: Percent composition by weight of substrate particles (less than 9.5 mm) at principal sample sites, biological survey—Coromandel 1982-83

Stream name	Stream site	% Gravel (2.0-9.5 mm)	% Very coarse sand (0.5-2.0 mm)	Analysed for metal content: % Medium, fine sand (0.125-0.5 mm)	Analysed for metal content: % Very fine sand, silt (<0.125 mm)
Waitaia Control	W3	70.9	24.2	4.4 (81%)	1.0 (19%)
Waitaia Mine	W8	59.5	33.6	5.6 (85%)	1.0 (15%)
Waitaia Control	W4	87.9	8.7	2.7 (90%)	0.3 (10%)
Waitaia Mine	W7	87.4	10.9	1.4 (88%)	0.2 (12%)
Waitaia	W6	95.2	3.4	1.1 (85%)	0.2 (15%)
Paroquet	P2	86.9	9.9	2.7 (87%)	0.4 (13%)
Buffalo	B4	96.9	3.2	0.07 (41%)	0.1 (59%)
Waiomu Control	WC	83.7	14.5	1.6 (84%)	0.3 (16%)
Waiomu	WP1	77.0	21.7	1.7 (89%)	0.2 (11%)
Waiomu	WP2	92.6	6.1	1.2 (75%)	0.4 (25%)

(Size fraction groups, other than for gravel (after Hynes, 1970)).

studied and had a substantially greater discharge than the other streams (Appendix 3.2).

All the streams were essentially gravel-boulder streams, although superimposed on this were a range of additional deposits, including fine sand and clay from bank erosion (Paroquet Stream), iron floc (Waitaia Mine Stream), mine-waste sediments (Waitaia Mine Stream, Buffalo Stream) and a small amount of deposition from bank collapse (Lower Waitaia Control Stream).

Pfankuch stability ratings were 'fair' except for Paroquet Stream which rated as 'poor', and Buffalo Stream which rated as 'good'. Background water quality (dissolved oxygen, conductivity, nutrient concentrations, suspended solids) was suitable for biota but elevated sulphate levels and total hardness minus alkalinity below mine-waste discharges were indicative of acid addition.

Heavy metal concentrations (except arsenic) were not elevated in control streams, being of a similar level to the background group described in Chapter 2. Arsenic levels were slightly elevated in Waitaia Control Stream. Below mine-waste discharges, metal concentrations (except arsenic) in the water and sediments were generally higher than in control streams, although the amount differed between streams. Arsenic levels were only elevated in the sediments at Waitaia Mine exit. The degree of metal elevation in the water at test sites was similar to that of the Jubilee and Comstock group described in Chapter 2 except that metal levels at the test site in the Paroquet Stream were significantly higher. Only Everett's Drive Stream matched the highly elevated levels of metal enrichment found in Tui Stream.

An important factor to be noted in summarising the physical and chemical character of the sample sites is whether macroinvertebrate drift occurs (and hence recolonisation from upstream). All control sites and test sites in Paroquet, Waiomu and Buffalo Streams had macroinvertebrate drift from healthy upstream sites, whereas test sites in Waitaia Mine Stream did not, since the entire stream flowed from the mine.

3.7 Biology of Streams Surveyed

The macroinvertebrate taxa collected from each catchment and the original data of species and counts from individual samples are available as an unpublished report held at Water and Soil Directorate, MWD, P O Box 12-041, Wellington (Penny 1983).

3.7.1 Control sites

In this section the macroinvertebrate communities of the control streams are described and compared with those of forested streams elsewhere in New Zealand.

Surveys of the control streams found a total 88 macroinvertebrate taxa from 43 different families (Appendix 3.3). This number of taxa is greater than numbers collected by workers in other forested streams in New Zealand (e.g., Penny 1976, Winterbourn 1978, Rounick and Winterbourn 1982) and is partly a function of the large number of samples collected in the present study. The characteristic macroinvertebrates of the three control streams are summarised in Table 3.5. The main feeding groups are well represented in all three streams and the greatest variety of taxa were in the collector-browser feeding group.

The Waiomu Stream control sites (WC, WF) had a diverse and abundant macroinvertebrate fauna characteristic of a reasonably stable and varied substrate (Table 3.5). The dominant taxa were small browsing mayflies, cased caddis, and filter feeding mayflies (*Coloburiscus humeralis*). In addition, stoneflies, midge larvae, net spinning caddis and dobsonfly larvae were common to abundant. Algal growths were found where the canopy was open and this led to increased numbers of cased caddis, which feed on the algae.

Buffalo Stream control sites (B1, B2) and also test site B4 had diverse macroinvertebrate fauna dominated by browsing mayflies and caddis (Table 3.5). Stoneflies, filter-feeding mayflies and net spinners were common but there were few predators. Where the stream was steep and bouldery (site B2) the dominant taxa were browsers adapted to cling to surfaces. The two "limpet" species *Latia neritoides* and *Ferrissa dohrnianus* were abundant. There were no visible growths of algae.

In Waitaia Control Stream relative abundance of taxa varied amongst the stream zones (Figure 3.6), but overall, the macroinvertebrate fauna was dominated by browsers, in particular the mayfly *Deleatidium*. Seston collectors were moderately abundant with filter feeding taxa more abundant than net spinners. The flat swamp zone had the highest numbers of the sandfly *Austrosimulium*. The flat forest zone had the highest total numbers of macroinvertebrates with *Pycnocentrodes* and other cased caddis making a significant contribution to the high numbers. Predatory species were commonest in this zone.

The macroinvertebrate fauna was similar in all three control streams and was also similar to that found in other bush streams in the Coromandel region (Appendix 3.1). The fauna was dominated by browsing leptophlebeiid mayflies, cased caddis, elmid beetles and snails. The relative abundances of families, genera and species varied from one stream to another as might be expected because of differing flows and substrate types. The genera *Deleatidium, Zephlebia, Olinga, Helicopsyche, Pycnocentrodes* and *Potamophrgus* were represented in all streams.

Table 3.5: The relative abundance of the main taxa of five functional feeding groups collected from control sites, biological survey—Coromandel 1982–83

Taxa and feeding group	**Stream site** Waitaia W3 + W4	Waiomu WF + WC	Buffalo B1 + B2
Fine particle collector-browsers			
Deleatidium sp	****	****	****
Zephlebia sp	**	*	***
Zelandoperla sp		*	
Acroperla trivacuata	*	*	*
Helicopsyche zelandica	**	****	*
Pycnocentrodes	****	****	***
Pycnocentria funerea	**		
Bereoptera roria		****	
Hydora spp	****	*	*
Chironomidae	****	****	*
Paratya curvirostris	*		
Potamopyrgus antipodarum	***	***	***
Ferrissia dohrnianus		*	
Latia neritoides	*		
Filter feeders			
Coloburiscus humeralis	**	**	***
Austrosimulium australense	***		
Net spinners			
Orthopsyche spp	*		***
Aoteapsyche colonica	*	**	*
Shredders			
Austroperla cyrene	*		*
Olinga sp	*	**	**
Triplectides obsoleta	*		
Predators			
Archichauliodes diversus	*	*	*
Psilochorema spp	*		*
Hydrobiosis spp	**	*	
Neurochorema sp		*	
Hudsonema amabilis	*		

Numbers per sample (0.053 m²)
* = 1–5
** = 6–10
*** = 11–20
**** = 21–100
***** = greater than 100.

Table 3.6: Comparison of control stream faunas with a core list of genera for New Zealand forest streams

Core list (Rounick and Winterbourn, 1982)	**Waitaia** W3 + W4	**Buffalo** B1 + B2	**Waiomu** WF + WC
Deleatidium	+	+	+
Nesameletus	−	+	+
Coloburiscus	+	+	+
Stenoperla	+	−	+
Zelandoperla	−	−	+
Zelandobius	−	+	+
Olinga	+	+	+
Hydrobiosis	+	−	+

+ = present
− = absent

Seston collectors were a smaller but important group with the filter feeding mayfly *Coloburiscus humeralis* and net-spinning caddis (Family Hydropsychidae) present in all control streams. The predatory dobsonfly *Archichauliodes diversus*, and several hydrobiosid caddis species also occurred in all streams.

Rounick and Winterbourn (1982) derived a list of eight invertebrate genera which they considered formed a core element in the New Zealand forest stream fauna. A comparison between this list and the faunas of the Coromandel control streams (Table 3.6) shows that all of the core genera were present in the control streams as a whole, although some core genera were absent at certain sites.

The control stream populations were thus not dissimilar to typical New Zealand forest stream macroinvertebrate populations. All control streams had diverse and abundant faunas represented by all functional feeding groups and were regarded as healthy ecosystems.

3.7.2 Test sites and a comparison with control sites

In this section the macroinvertebrate faunas of stream sites identified as potentially contaminated (i.e., test sites) are described and compared with those of control sites. In addition, a discussion of the differences in functional feeding groups and the algal species present is given.

Abundance, diversity and ordination

Abundance of macroinvertebrates was significantly lower at test sites than at control sites (Table 3.7). The greatest difference (95%) was between test site W8 and control site W3 (Waitaia catchment). Recovery was observed at downstream sites below W8 and below test site P2 (Paroquet Stream) at test site WP1/WP2 (Waiomu Stream) in the Waiomu Catchment.

Species diversity (number of taxa) was lower at test sites than at control sites (Table 3.8). The only exception occurred at test site P2 where despite their low abundance, macroinvertebrates were reasonably diverse.

Mean number of species and mean number of invertebrates for control and test sites were ranked by ordinations. Chironomid data were omitted from the analysis because most chironomids were not identified beyond family level, and the number of taxa could not be easily determined. Because those chironomid species that are resistant to pollution are difficult to distinguish from sensitive species, the chironomid group can confuse trends in the numerical abundance. The ordinations provide an effective means of presenting the observed differences in macroinvertebrate abundance and diversity between control and test sites. Both sets of ordinations show that the abundance and diversity of macroinvertebrates at test sites was markedly lower than at the control sites (Figures 3.9, 3.10).

Data points for both Waiomu test sites (WP1 & WP2) and Paroquet test site (P2) were grouped in quadrant IV (Figure 3.9) showing that the macroinvertebrate communities at these sites were highly stressed in comparison to those at the control sites (Waiomu control WC and Buffalo B4). The Paroquet communities in particular shows signs of severe stress with the elimination of many taxa and sparse numbers of individuals.

The data points for test sites in the Waitaia catchment (W7, W8) group principally in quadrant IV (Figure 3.10) show that the macroinvertebrate communities of these sites were highly stressed in comparison to those at their paired control sites (Waitaia controls W3, W4). The W8 site community

Table 3.7: Differences in abundance of instream macroinvertebrates between paired test and control sites, biological survey—Coromandel 1982–1983

Site pairs	Stream name	Mean No macroinvertebrates per sample	Percent difference from control	Confidence limits	Number of samples* (n)	t-Test probability
W8 (test)	Waitaia Mine Stream	11	95% less	±30%	24	P<0.01
W3 (control)	Waitaia Control Stream	226	-	±19%	27	-
W7 (test)	Waitaia Mine Stream	112	64% less	±48%	15	P<0.01
W4 (control)	Waitaia Control Stream	311	-	±26%	15	-
W6 (test)	Waitaia Mine Stream	122	61% less	±48%	18	P<0.01
W4 (control)	Waitaia Control Stream	311	-	±26%	15	-
WP1/WP2 (test)	Waiomu Stream	251	42% less	±25%	27	P<0.01
WC (control)	Waiomu Stream	434	-	±21%	27	-
P2 (test)	Paroquet Stream	47	81% less	±26%	27	P<0.01
B4 (control)	Buffalo Stream	245	-	±21%	27	-

Statistical test used = 't' test.
Null hypothesis = the difference in the mean number of macroinvertebrates between paired sites is not statistically significant.
Null hypothesis rejected if $P < 0.05$.
*excludes August 1982 samples since counts from these samples were not completed.

was most severely stressed with most taxa absent and very sparse numbers of individuals.

Species composition, functional feeding groups, algae

This section considers which species contributed to the differences described in the previous section.

Caddis and mayflies were the principal groups dominating all control sites, while at test sites, midges (Chironomidae) tended to dominate (Table 3.9). T-test results on the differences in abundance of both cased caddis larvae and leptophlebiid mayfly larvae between test and control sites confirmed that the differences were statistically significant, with the exception of cased caddis at sites W6/W4 (Tables 3.10 and 3.11).

The dominant functional feeding group at all test and control sites consisted of the collector-browser group (Table 3.12). The relative proportions of each functional feeding group were similar at control and test sites (Table 3.12). This shows that despite a marked drop in abundance at test sites, the main feeding groups remain represented in the population. Within the collector-browser group chironomid abundance was similar at control and test sites but the abundance of the other collector-browser feeders were markedly reduced at test sites. It is concluded that chironomids were considerably more tolerant to the conditions at the test sites than the other collector-browsers.

The details of macroinvertebrate species composition and the algal community are discussed below by catchment.

Table 3.8: Differences in diversity of macroinvertebrates between paired control and test sites, biological survey—Coromandel 1982-1983

Site pairs	Stream name	Mean No. taxa per sample	Percent difference from control	Number of samples* (n)	Total No. taxa	Percent difference from control
W8 (test)	Waitaia Mine	3	85% less	24	24	51% less
W3 (control)	Waitaia Control	20		27	49	
W7 (test)	Waitaia Mine	12	40% less	15	34	19% less
W4 (control)	Waitaia Control	20		15	42	
W6 (test)	Waitaia Mine	15	25% less	18	42	no difference
W4 (control)	Waitaia Control	20		18	42	
WP1/WP2 (test)	Waiomu	12	40% less	27	30	32% less
WC (control)	Waiomu	20		27	44	
P2 (test)	Paroquet	9	55% less	27	40	17% less
B4 (control)	Buffalo	20		27	48	

*Number of samples excludes August 1982 since these samples were not fully analysed.

Waiomu catchment

In Waiomu Stream above the confluence with Paroquet Stream (control site WC) the community was dominated by cased caddis larvae (in particular *Pycnocentrodes* sp, *Beraeoptera rorea, Helicopsyche zelandica*) and mayfly larvae (*Deleatidium* sp and *Coloburiscus humeralis*). Below the confluence (sites WP1 and WP2) these species were either absent or only present in low numbers (Table 3.5). Chironomidae, however, were present in substantially larger numbers at the downstream sites, than at control site WC.

Within Paroquet Stream, the upstream site P1 (sampled once) was dominated by mayflies. Stoneflies, beetles and chironomids were also present but cased caddis and snails were rare or absent. Downstream (test site P2) the community was dominated by the mayfly (*Deleatidium*) and chironomid midges. Other species of mayfly, caddis and other macroinvertebrates were absent or present in extremely low numbers.

In Waiomu Stream, algal growth above and below the confluence with Paroquet Stream consisted mainly of diatom species (see Appendix 3.4). Growth was reasonably obvious and included 10 species. In Paroquet Stream (including test site P2), however, few species of algae were collected and algal growth was not evident to the naked eye. During January 1983 after an extended dry spell, algae grew extensively at control site WC but at test sites WP1/WP2 and P2, this did not occur. While test sites WP1/WP2 and P2 had lower substrate suitability than site WC it was considered that this alone did not account for the absence of algal growths during the extended low flow period.

Waitaia catchment

In Waitaia Mine stream, macroinvertebrates and algae were absent near the mine, but apparently recovered to normal abundance and diversity 1 km downstream.

At site W10 (0.2 km from the stream source at the mine exit) no macroinvertebrates or algae were found. At site W9 there were very few

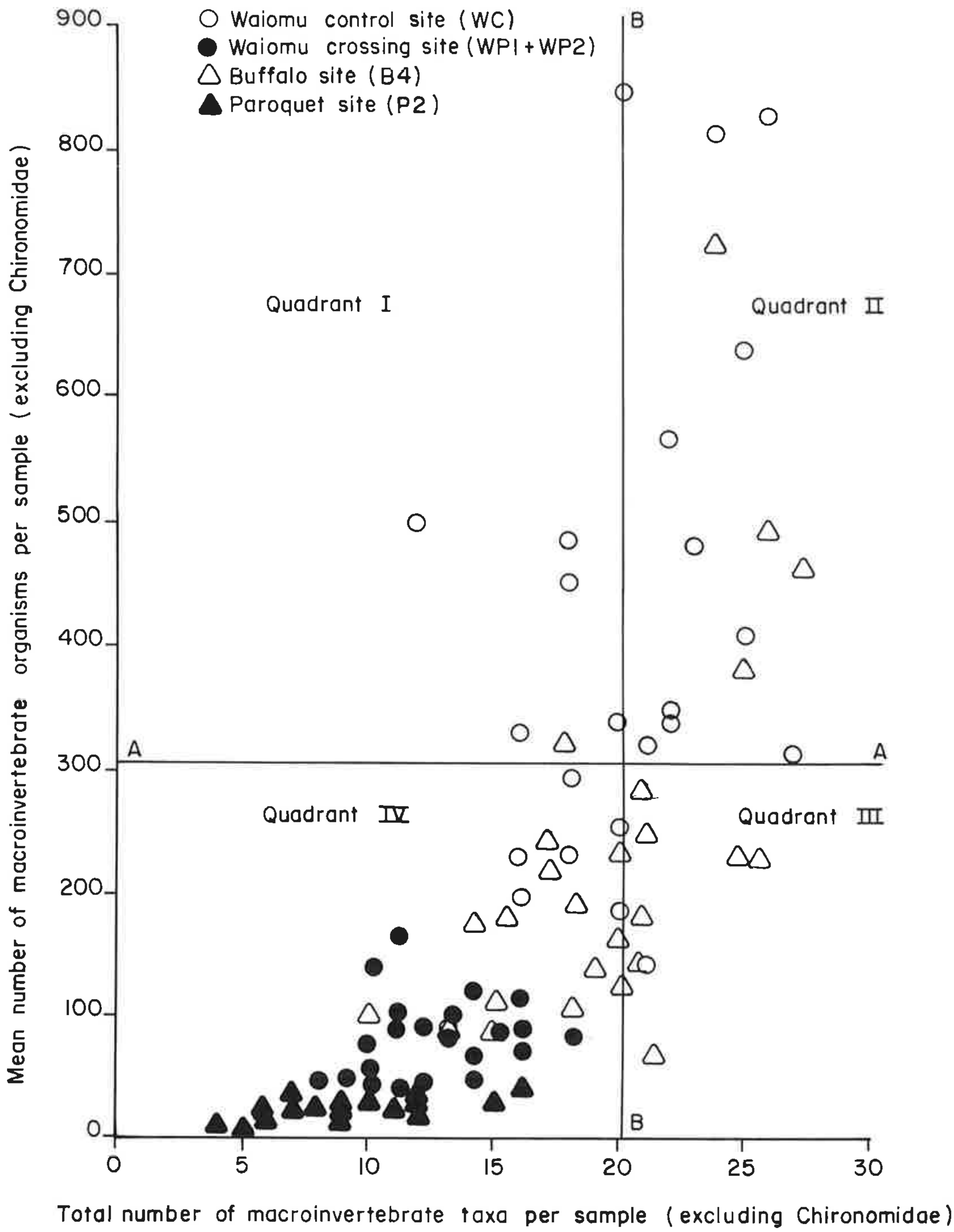


Figure 3.9: Ordination of data from paired test and control sites in Waiomu and Buffalo Catchments, Coromandel. Reference vectors A and B represent mean values for data from control site WC. Numbers are counts per 0.053 m².

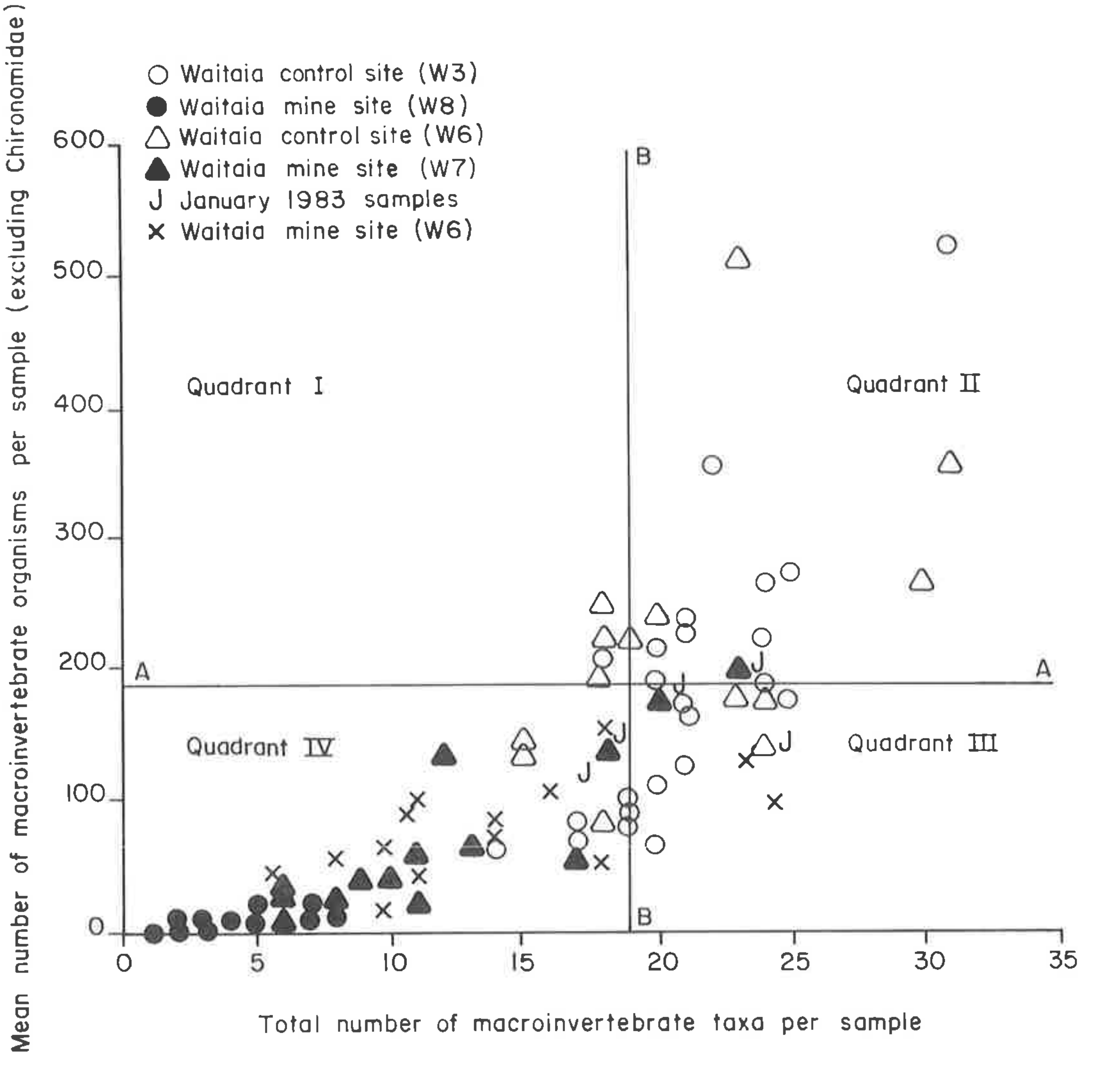


Figure 3.10: Ordination of data from paired test and control sites in Waitaia Catchment, Coromandel. Reference vectors A and B represent mean values for combined data from control sites W3 and W4. Numbers are counts per 0.053 m^2.

Table 3.9: Mean numbers of the more widely occurring macroinvertebrate taxa collected at paired control and test sites, biological survey—Coromandel 1982–1983

Feeding group taxa		Mean number macroinvertebrates occurring at paired sites (control: test)									
		Cont	Test	Cont	Test	Cont	Test	Cont	Test	Cont	Test
		B4	P2	WC	WP1 & WP2	W3	W8	W4	W7	W4	W6
Collector-browsers											
Deleatidium sp	mayfly	29	10	60	7	27	0	53	8	53	14.5
Ataphlebioides sp	mayfly	<1	0	0	0	6	0	2	<1	2	5
Zephlebia sp	mayfly	15	1	12	<1	15	<1	1	<1	1	1
Zelandoperla spp	stonefly	1	2	3	1	0	<1	0	0	0	0
Acroperla trivacuata	stonefly	1	1	1	3	2	<1	3	4	3	2
Helicopsyche zelandica	caddis	32	0	28	<1	12	0	2	<1	1	<1
Pycnocentrodes sp	caddis	4	1	120	4	27	<1	32	4	32	18
Pycnocentria funerea	caddis	0	0	0	0	9	<1	1	1	1	<1
Beraeoptera roria	caddis	<1	<1	32	6	0	0	0	0	0	0
Hydora spp	beetle	2	<1	2	<1	9	<1	56	3	56	15
Paratya curvirostris	shrimp	0	0	0	0	1	<1	1	4	1	2
Aphrophila neozelandica	fly	<1	<1	7	0	2	<1	1	<1	1	<1
Paranephrops planifrons	crayfish	0	0	0	0	<1	<1	<1	0	<1	5
Potamopyrgus antipodarum	snail	11	0	16	2	11	<1	14	14	14	0
Ferrissia dohrnianus	limpet	10	0	1	3	0	0	0	0	0	0
Latia neritoides	limpet	35	0	<1	0	4	0	1	0	1	<1
Oxyethira albiceps	caddis	<1	<1	<1	7	<1	0	0	0	0	0
Chironomidae	midge	12	16	38	120	59	5	83	40	83	33
Filter feeders											
Coloburiscus humeralis	mayfly	2	1	13	2	6	0	<1	<1	<1	<1
Austrosimulium austrolense	sandfly	0	<1	0	<1	10	0	25	1	25	9
Net spinners											
Orthopsyche spp	caddis	2	<1	<1	0	2	2	<1	<1	<1	<1
Aoteapsyche colonica	caddis	<1	0	10	2	<1	<1	<1	0	<1	<1
Shredders											
Austroperla cyrene	stonefly	1	1	<1	0	<1	0	2	1	2	2
Olinga sp	caddis	13	0	6	<1	4	<1	<1	<1	<1	<1
Triplectides obsoleta	caddis	0	0	<1	<1	<1	0	2	<1	2	2

Table 3.9: Mean numbers of the more widely occurring macroinvertebrate taxa collected at paired control and test sites, biological survey—Coromandel 1982–1983—*continued*

Feeding group taxa		Mean number macroinvertebrates occuring at paired sites (control: test)									
		Cont	Test	Cont	Test	Cont	Test	Cont	Test	Cont	Test
		B4	P2	WC	WP1 & WP2	W3	W8	W4	W7	W4	W6
Predators											
Archichauliodes diversus	dobsonfly	3	1	3	1	1	<1	3	<1	3	<1
Psilochorema spp	caddis	1	0	0	0	1	<1	2	<1	2	<1
Hydrobiosis spp	caddis	0	1	1	1	1	<1	4	4	4	3
Neurochorema sp	caddis	0	<1	1	<1	<1	0	0	0	0	<1
Hudsonema amabilis	caddis	<1	<1	<1	0	2	0	2	1	2	1
Number of Samples		27	27	27		27	24	15	15	15	15

0 = absent Numbers are counts per 0.053 m².

Table 3.10: Differences in mean numbers of mayfly larvae (Leptophlebiidae) at paired control and test sites, biological survey—Coromandel 1982–83

Site pair	Site status	Mean No. mayflies	Confidence limits (%)	Number of samples (N)	t-Test probability
WC	control	87	±30	27	P <0.1
WP1/WP2	test	11	±51	33	
B4	control	93	±28	27	P < 0.01
P2	test	10	±31	32	
W3	control	60	±42	27	P < 0.001
W8	test	0.2	±17	24	
W4	control	56	±44	17	P < 0.01
W7	test	8	±45	18	

Numbers are counts per 0.053 m^2.
Null hypothesis = "these is no significant difference between mean numbers of mayfly larvae at control and impacted sites at each pair of samples sites" (degrees of freedom = N—2).

species apart from the occasional freshwater crayfish (*Paranephrops planifrons*), predatory insect larvae (Rhyacophilidae sp, *Archichauliodes diversus*) a few midge larvae and sparse algae (Appendix 3.4). At W8, about 0.9 km from the mine exit, there were still very few organisms and even midge larvae were few in number. A few more animals were collected at site W8G (100 m downstream from W8 but receiving more sunlight), in particular net spinning caddis (Orthopsyche), midges, and shrimps (*Paratya curvirostris*).

Further downstream at W7, more species were found, in particular the snail (*Potamopyrgus antipodarum*) and mayfly (*Deleatidium* sp) and algae were almost as abundant as in the Control stream. From July to November 1982, a coating of blue-green algae developed at site W7 in the Waitaia Mine Stream but by January 1983 had disappeared. This did not occur at either control site.

Below the confluence with Waitaia Control stream, the species composition at sites W5 and W6 closely resembled that of control sites W3 and W4, consisting principally of mayflies (*Deleatidium* sp), cased caddis (*Pycnocentrodes* sp), beetles (*Hydora* sp) and chironomid species. Other species of sandfly, caddis, snails and mayflies dominated in certain months (Penny 1983).

Buffalo catchment

The only sites within the Buffalo catchment that appeared to be impoverished were in two small streams (Everett's Drive Stream site E, and Everett's Control Stream site EC) near to Everett's Mine Drive but this could have resulted from their small size. Buffalo Stream fauna showed no obvious signs of impoverishment immediately above or below the point where Everett's Drive Stream drained into it although these sites were only sampled qualitatively (Appendix 3.3).

Species compositions at upstream control sites B1, B2 in Buffalo Stream (Appendix 3.3) were dominated by mayflies (*Deleatidium* sp., *Zephlebeia* sp.), cased caddis (*Pycnocentrodes* sp., *Pycnocentria funerea*) and snails (*Potamopyrgus antipodarum*). Downstream at site B4 (Table 3.9) there were increased numbers of caddis (*Helicopsyche zelandica*), limpets (*Ferrissia dohrnianus, Latia neritoides*) and chironomids.

Table 3.11: Differences in mean numbers of cased caddis larvae (Conoesucidae and Helicopsychidae at paired control and test sites, biological survey—Coromandel 1982-83

Site pair	Site status	Mean No. cased caddis	Confidence limits (%)	Number of samples (N)	t-Test probability
Wc	control	208	±34	30	$P < 0.001$
WP1/WP2	test	11	±34	33	
B4	control	58	±32	30	$P < 0.001$
P2	test	1	±22	30	
W3	control	50	±33	33	$P < 0.001$
W8	test	1	±14	24	
W4	control	30	±44	18	$P < 0.01$
W7	test	4	±56	18	

Numbers are counts per 0.053 m^2.
Null hypothesis = "there is no significant difference between mean numbers of mayfly larvae at control and impacted sites at each pair of sample sites" (degrees of freedom = N—2).

The algal community was abundant and diverse at site B4. Other sites were not examined for algal growth.

Relative stream biological status

By pooling the results, it is possible to examine the relative stress observed in biological communities at each stream site. In Figure 3.11 the means of abundance and diversity from data used for ordination of every test and control site have been plotted. The curve shows that at control sites, mean abundance ranged from mean values of 176 to 386 organisms per sample, and mean species diversity levelled off at about 20 taxa per sample (i.e., per 0.053 m^2). Mean abundance and mean species diversity were lower at all test sites (Figure 3.10). The number of taxa at test sites W7, W6, WP1 and WP2 were 20-50% lower than control sites while at sites P2, W8, W9 and W10, species diversity was 50-95% lower than at control sites. The mean abundance of organisms also steadily decreased with decreasing diversity such that at sites with a 20-50% reduction in diversity, the mean number of organisms per sample ranged from 40-100, and at sites with even lower diversity, the mean number of organisms was less than 40 per sample.

For the purposes of this report, mean number of taxa and the associated mean number of organisms have been used to define three types of community—Healthy, Stressed and Impoverished (Figure 3.11).

As abundance and diversity decreased, a shift in species composition was apparent. In healthy communities, Chironomidae formed less than 33%, while other collector-browsers formed 59-82% (Table 3.11). At stressed sites, the balance shifted towards 36-72% Chironomidae, with a reduction in other collector-browsers to 22-55%. At impoverished sites W8 and P2 the relative proportions of these two groups were similar to stressed sites.

3.7.3 Summary of stream biology

Most of the test sites have a significantly reduced abundance and diversity of stream macroinvertebrates compared with their paired control sites. Ordination analysis suggests that the cause of ecological impact is toxic stress since the data points of tests sites cluster in quadrant IV (Figures 3.9, 3.10). Leptophlebiid mayflies and cased caddis showed greatest reductions in diversity (Tables 3.10, 3.11). Chironomid midges showed the least reduction and were the only group to increase in numbers at some test sites. This showed

Table 3.12: Functional feeding group abundance and diversity at control and test sites, biological survey—Coromandel 1982-83

Abundance (% in brackets) Numbers are mean counts per 0.053 m^2

Sample Site	n	Chironomids	Other collector browsers	Filter feeders	Net spinners	Shredders	Predators	Totals
Control site								
W3	27	59(26)	139(62)	14(6)	3(1)	3(1)	8(4)	226
W4	15	99(32)	184(59)	10(3)	1(0)	3(1)	15(5)	311
WC	27	48(11)	325(75)	15(3)	25(6)	7(2)	14(3)	434
B4	27	15(6)	201(82)	2(1)	3(1)	15(6)	11(4)	245
Means (control) sites		55(14)	212(70)	10(3)	1	7(2.5)	12(8)	-
Test site								
W6	18	44(36)	55(45)	10(8)	1	41(3)	8(7)	122
W7	15	43(38)	62(55)	1(1)	1	1	6(5)	112
W8	14	5(45)	4(36)	1	2(18)	1	1	11
P2	27	21(45)	18(38)	1(2)	1(2)	1	4(9)	47
WP1/WP2	27	183(72)	56(22)	2(1)	1	1	8(3)	251
Means (test) sites		59(47)	59(39)	3(2)	1(4)	1	5(6)	-

Diversity (total number of taxa per site)

Sample Site	n	Chironomids	Other collector browsers	Filter feeders	Net spinners	Shredders	Predators	Totals
Controls								
W3	27	-	30	2	3	3	11	49
W4	15	-	25	2	3	3	9	42
WC	27	-	26	2	3	3	10	44
B4	27	-	30	2	3	4	9	48
Tests								
W6	18	-	25	1	2	3	11	42
W7	15	-	22	2	2	3	5	34
W8	24	-	14	0	2	1	7	24
P2	27	-	24	2	2	1	11	40
WP1/WP2	27	-	17	2	2	2	7	30

up as a decrease in the proportion of non-chironomid collector-browsers at the test sites (Table 3.12).

Algal abundance and diversity appeared to be reduced at test sites. The relative status of the study sites are described as Healthy, Stressed and Impoverished (Figure 3.11), on the basis of relative abundance and species diversity.

3.8 Linking Stream Biology to the Physical and Chemical Characteristics of the Streams

Potential causes of biological stress in streams receiving mine wastes were identified in the review section as toxic metal concentrations, acid pH conditions (and associated factors), and the deposition of excess fine sediments (including iron floc). In this section, differences in stream biology between site pairs is compared with pH conditions, metal concentrations and sedimentation (iron floc and associated fines) to identify possible links between mine-waste contamination and stress or impoverishment. Complicating and mitigating factors that may have influenced the degree of stress or impoverishment are considered. Test and control site pairs were selected to have minimal differences in other factors such as shade, stream size, gradient,

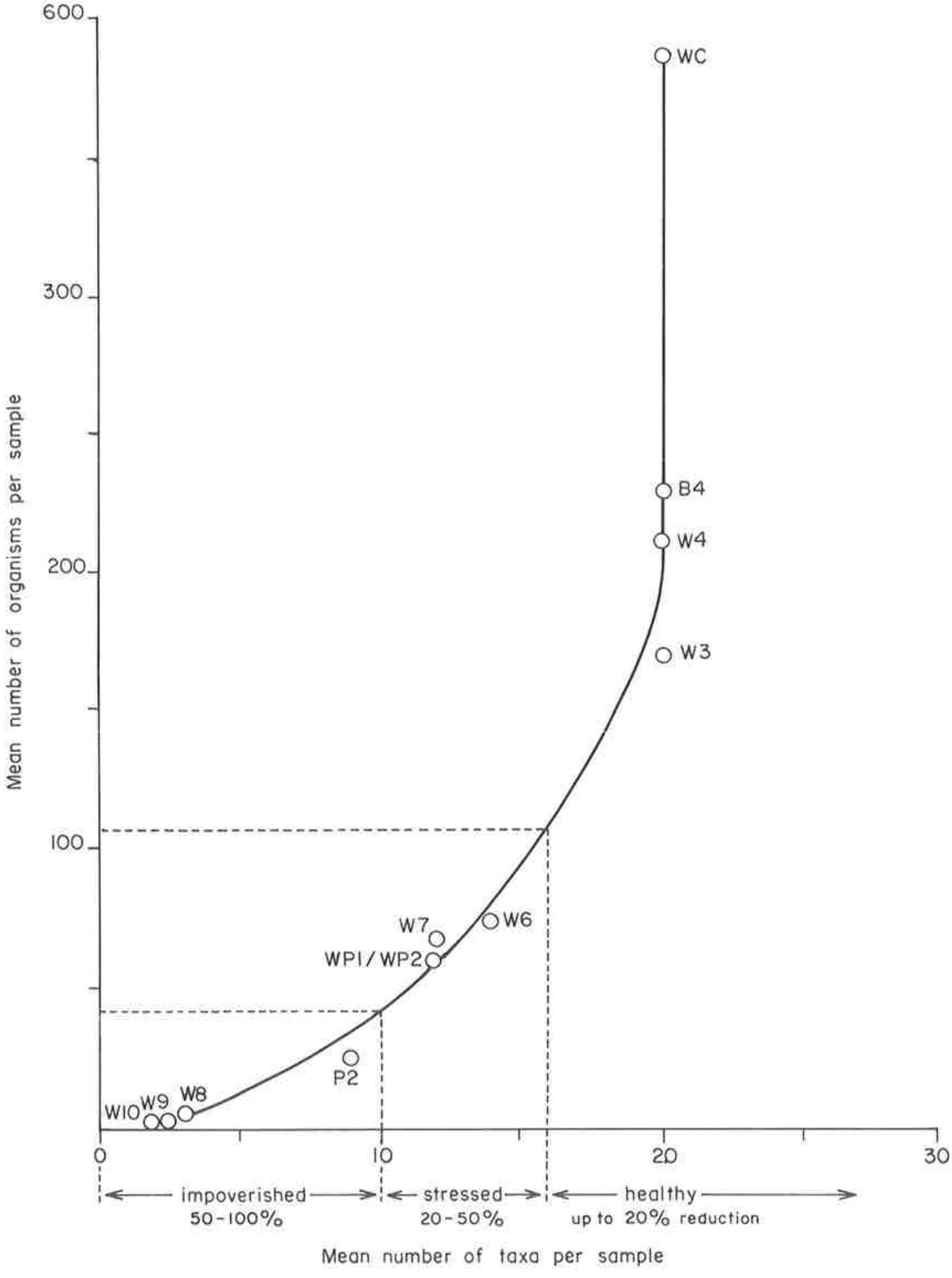


Figure 3.11 Relative biological status in study streams, Coromandel points on the graph are means of data from the quantitative sampling of control and test sites that is presented in Figures 3.9 and 3.10. Sample area is $0.053m^2$.

substrate composition, stability, and background water quality. In the case of site comparisons B4/P2, however, the stability ratings were 'good' and 'poor' respectively. The stream bed at P2 provided a sub-optimal habitat for macroinvertebrates compared with control site B4, irrespective of the effects of mine-waste discharges.

3.8.1 pH and related measurements

The level of stress or impoverishment in the macroinvertebrate population did not correlate with pH, but did correlate well with sulphate concentrations and hardness minus alkalinity values (Figure 3.12). This correlation is regarded as non-causal, since sulphate and alkalinity in themselves do not, at this range, influence the physiology of instream organisms. Sulphate and alkalinity are, however, indicators of buffering capacity (and thus susceptibility to pH change) and increased metal availability.

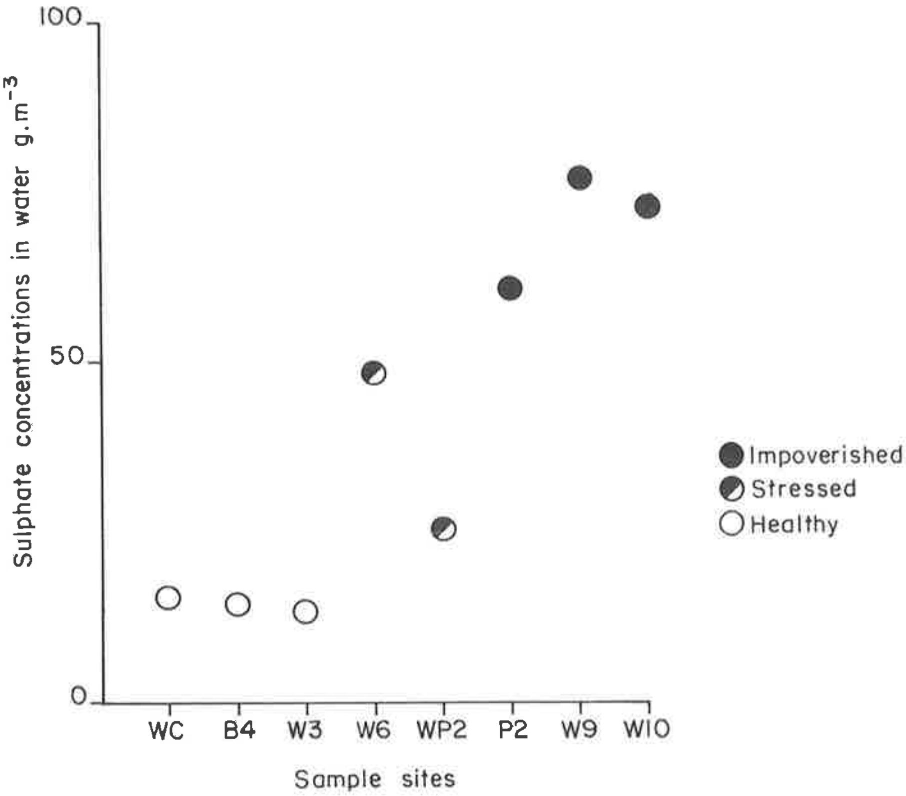
3.8.2 Surficial sedimentation, iron floc

Field observation has shown that all impoverished sites either supported a coating of iron floc (W8, W9, W10) or were subject to excess blanketing by fine sediments (i.e., clay) as a result of erosion (P2). Iron floc was not evident at biologically stressed sites, but fine sediments were present at downstream sites WP1, WP2. Iron floc is potentially unsuitable for colonisation by macroinvertebrates because of its physical character (few interstitial spaces) and its chemical character (accumulates heavy metals). McKnight and Feder (1984) found that destabilisation of the rock surface in a stream by hydrous metal-oxide precipitation can have a more adverse affect on stream communities than low pH and high concentrations of free metal ions. It is difficult to separate the deleterious physical effects of iron floc from chemical effects. A community tolerant of soft sediment conditions might be expected to occur if chemical effects were insignificant. Since this was not the case, it is considered that the physical effects of iron floc at sites W8, W9, W10 were not the principal cause of impoverishment. Poor bed stability and the fine deposit of clay particles in Paroquet Stream (P2) may have been sufficient to contribute to impoverishment at site P2.

3.8.3 Heavy metals

The question of whether heavy metal criteria should be calculated on the basis of hardness or alkality has been discussed earlier (Section 2.1.6). The basis chosen for Coromandel streams, where hardness is often greater than alkalinity, influences how the potential toxicity of the heavy metal concentrations found in the waters is interpreted.

Metal concentrations in the water at test sites were generally higher than at control sites (Table 2.3) but all were below the USEPA 1-hour exposure maximum water quality criteria calculated on hardness (Table 2.1). However, at P_2 (Paroquet Stream) the cadmium and zinc levels were slightly higher than the 1-hour exposure criteria calculated on alkalinity (Table 2.2). At P_2, the concentrations of cadmium, copper, lead and zinc all exceeded the USEPA 4-day average exposure calculated on alkalinity, as did lead at WP2 (Waiomu Stream below Confluence). Most metal concentrations were below the US EPA 4-day average exposure calculated on hardness with the exception of lead at P2 (Paroquet Stream) and WP2 (Waiomu Stream below confluence), and zinc at P2 (Paroquet Stream). Metal concentrations in the



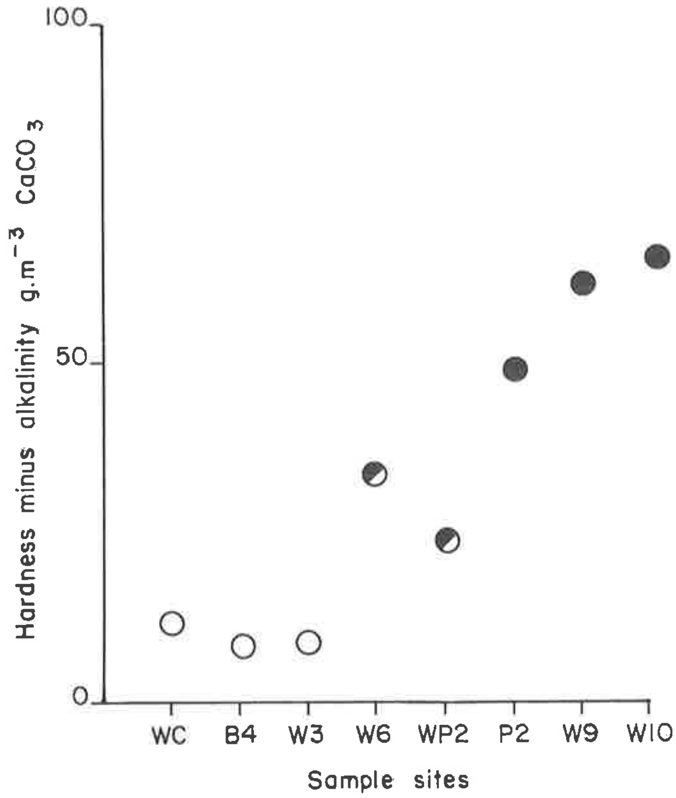


Figure 3.12 Biological status versus sulphate concentration (upper graph) and hardness minus alkalinity (lower graph), Coromandel.

sediments at test sites were higher than at control sites (Table 2.3) but no criteria are available for sediments.

Waitaia catchment

The stream emerging from Waitaia Mine (above site W10) had relatively high concentrations of cadmium and zinc in both the water and sediments. These progressively decreased in concentration downstream (Figure 3.13). At W8, copper concentrations increased as a result of input from Mullock Stream (site M, Figure 3.13). Lead concentrations in the water column were near background levels throughout the catchment, but in the sediments were highest nearest to the mine exit in Waitaia Mine stream (sites W8, W9, W10). Arsenic and copper concentrations were slightly higher at control sites W3, W4 than at test sites. The virtual absence of browsing and most other macroinvertebrates from sites W8, W9, W10 in Waitaia Mine stream is strongly suggestive of a toxic effect. Zinc was the metal most strongly correlated with biological impoverishment in this catchment (Figure 3.13).

Waiomu catchment

Water and sediment concentrations of cadmium, copper, lead and zinc at site P2 (Paroquet Stream) were higher than at sites WC (Waiomu Stream) and WP2 (downstream from the Waiomu/Paroquet confluence), and correlated well with biological impoverishment (Figure 3.14).

The degree of biological impoverishment in Paroquet (P2) was less than in Waitaia Mine Stream (W8, W9, W10) (Section 3.8.3.1), yet metal concentrations are higher in Paroquet Stream.

Buffalo catchment

Metal concentrations in the small stream draining Everett's Drive were extremely high and far exceeded that of Waitaia Mine stream or Paroquet Stream (Table 3.8). In Buffalo Stream at site B4, concentrations of all metals in the water were low, but in the sediment, cadmium, copper, lead and zinc concentrations were as high, if not higher than Paroquet or Waitaia Mine streams. This has been explained in Chapter 2 as being caused by the relatively high proportion (59%) of particles < 0.125 mm diameter in the size fraction used for sediment analysis in Buffalo Stream compared with other sites. Although the biological community in Everett's Stream was highly impoverished, no sites in Buffalo Stream showed any signs of impoverishment or stress.

3.8.4 Discussion and summary

The study found correlations between biological impoverishment and the presence of mine-wastes but did not identify the cause of impoverishment. This is partly because pH, the presence of iron floc, and metal contamination of stream waters and/or sediments are chemically interdependent, and partly because it is difficult to separate toxic effects from smothering effects on instream biota. The ordination analysis (Figures 3.9, 3.10) suggests fauna were impoverished as a result of a toxic effect. The correlation between some metal concentrations, particularly zinc, and biological stress or impoverishment again indicates a toxic effect. Zinc and cadmium concentrations correlate with biological stress or impoverishment in Waitaia catchment, and zinc, cadmium, lead and copper correlate with biological stress or impoverishment in Waiomu catchment. Elevation of metals in the sediments correlates with impoverishment in Waitaia catchment and in Waiomu catchment. These correlations do not confirm heavy metal toxicity causes biological stress or

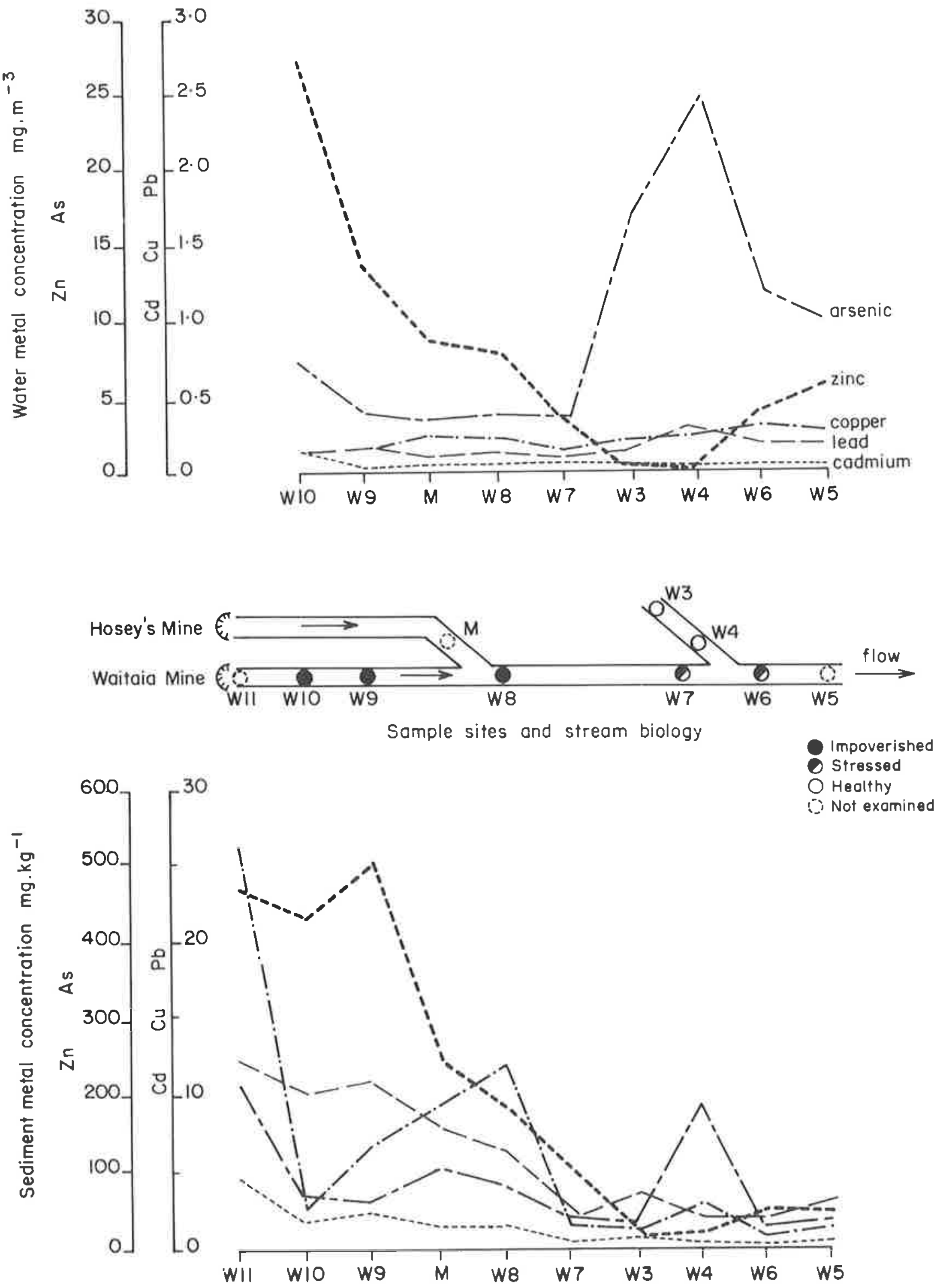


Figure 3.13 Metal concentrations in water column (upper graph), sediments (lower graph), and biological status (centre) in Waitaia Catchment, Coromandel, 1983.

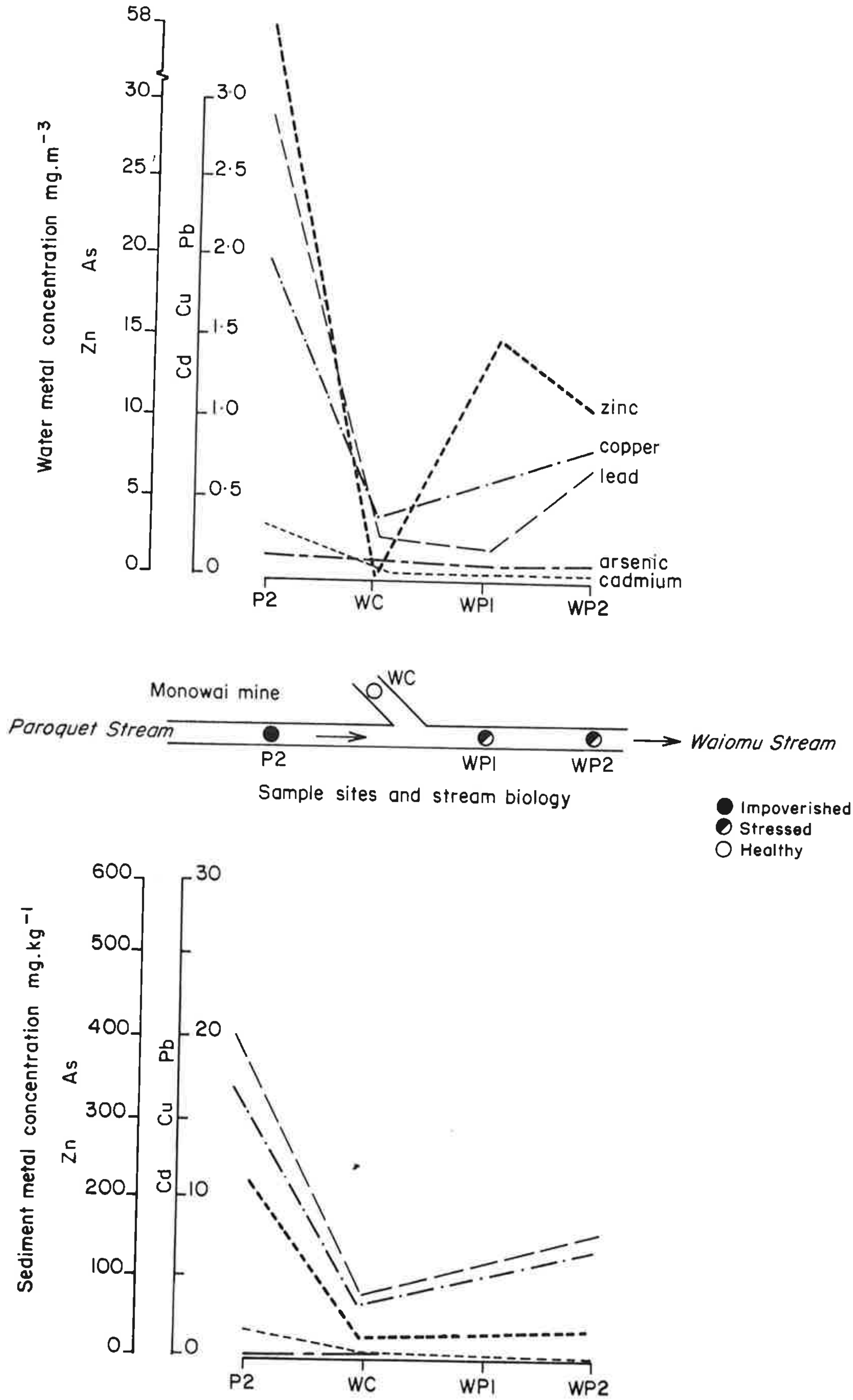


Figure 3.14 Metal concentrations in water column (upper graph), sediments (lower graph), and biological status (centre) in Waiomu Catchment, Coromandel, 1983.

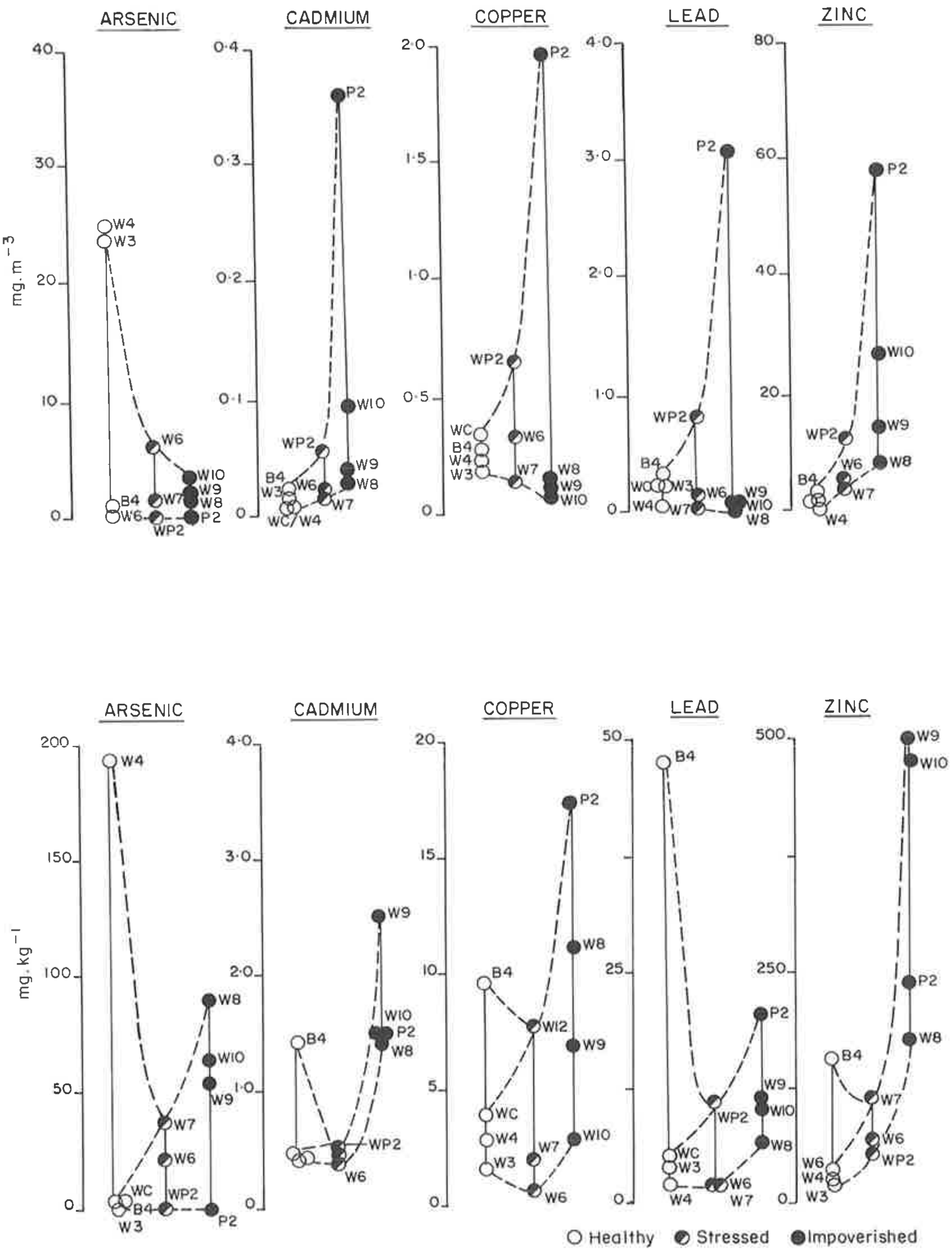


Figure 3.15 : Metal concentrations in water column (upper graphs) and sediments (lower graphs) at Healthy, Stressed and Impoverished sites, Coromandel.

Figure 3.15 Metal concentrations in water column (upper graphs), and sediments (lower graphs) at biologically healthy, stressed, and impoverished sites, Coromandel.

impoverishment at any test sites. Confirmation could only come if it were possible to experimentally manipulate the concentration of particular heavy metals in the test streams and monitor biological response.

The metal concentrations in the water were largely below recommended water quality criteria calculated on the basis of hardness. However, the concentrations in Paroquet Stream were at or above the criteria as calculated on the basis of alkalinity (refer Table 2.2). Similarly, in the Waitaia Mine Stream above the biological test sites some metal levels at times approached or exceeded alkalinity-based criteria levels. Unfortunately, there are no heavy metal criteria against which to judge the potential toxicity of the sediments.

The correlations found suggest that heavy metal levels in waters and sediments may have contributed to the biological stress or impoverishment found in the test streams. The degree of sedimentation also appears to contribute. Drift of invertebrates downstream was believed to be a factor mitigating the effects of stress in the Paroquet Stream.

Unfavourable conditions such as small stream size, lack of drift of organisms from upstream sites, lack of dilution of mine-wastes, elevated metal concentrations and the presence of iron floc characterise Waitaia Mine Stream where the highest degree of impoverishment was observed. Unfavourable conditions in Paroquet Stream include silt deposition, elevated metal levels and bed instability, but this is counterbalanced by dilution from upstream sites and a continual source of drift from upstream sites. In Buffalo Stream, the stable stream bed, almost complete absence of silt deposition, recolonisation by drift from upstream sites, and low water metal levels are all favourable. It is considered that the differences in the above circumstances combine to give the different biological statuses observed.

3.9 Resume of Study Findings and of Conclusions from the Stream Biology Survey

The control sites in Upper Buffalo Stream (B1, B2, B3), Upper Waiomu Stream (WC, WF), Upper Paroquet Stream (P1), and Waitaia Control Stream (W2, W3, W4) had diverse and abundant macroinvertebrate fauna comprising species compositions and functional feeding groups typical of small gravel/boulder streams in bush catchments of New Zealand.

Everett's Control Stream (site EC) had fewer species and numbers of organisms than other control sites, but this was expected because of the small size of the stream (width 10 cm).

The test sites in Lower Waiomu Stream (WP1, WP2), Lower Paroquet Stream (P2), Waitaia Mine Stream (W10, W9, W8, W7), below the confluence of Waitaia Mine Stream and Waitaia Control Stream (W5, W6), Mullock Stream (W12), and Everetts Drive Stream (E) had impoverished or stressed macroinvertebrate fauna in comparison with control sites. Statistical comparison of control and test sites that had been paired for similarity of stream characteristics lead to the conclusion that the differences in fauna were a result of some effect other than habitat differences.

Test site B4 (Buffalo Stream) had a diverse and abundant macroinvertebrate fauna equivalent to control sites.

Biological impoverishment at sites P2, W8, W9, W10 correlated with proximity to mine waste discharges. It was considered that elevated metal concentrations in the water column and/or sediments, were a possible cause of biological impoverishment but the stability of the stream bed, the presence of iron floc or fine sediments and whether or not there was invertebrate drift from upstream, greatly influenced the level of stress observed.

Management to ensure that accepted heavy metal criteria were met in the test streams would not alone have been sufficient to protect instream macroinvertebrates in this environment. Research into the role of sedimentation, iron floc and the toxicity of heavy metals in sediments is required. Water quality criteria for the protection of aquatic life from heavy metal toxicity need to be applied with caution.

3.10 Acknowledgements

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Lastly I thank my husband for his support and assistance throughout the study.

3.11 References

Abbreviations are based on ANSIZ39.5 Standard, used by BIOSIS.

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Appendix 3.1: Relative abundance of main taxa collected at stream sites in pilot survey—Coromandel 1981

Macroinvertebrate group / **Stream sampled and NZMS1 original reference**	**Otahu** (N49 325105)	**Rangihau** (Nrr 183451)	**Mangatoetoe** (N53/54 325955)	**Grace Darling below confluence** (N53/54 266975)	**Grace Darling** (N53/54 266979)	**Jubilee** (N53/54 266972)	**Mangakara** (N53/54 273944)	**Waitakauri** (N53/54 265973)	**Comstock** (N53/54 212912)	**Komata** (N53/54 199004)
Seston collectors										
Oligoneuridae (mayfly)	x		xx		•		/	x	x	/
Hydropsychidae (caddis)	x	xx	xx	xxxxxx	•		/	x	x	/
Simulidae (sandfly)						x	/			/
Benthic browsers										
Leptophlebiidae (mayfly)	xxx	xxxxx	x	xx	xxxxxx	xxx	/	x	xxxxxx	/
Siphlonuridae (mayfly)	•	•		x	x		/	•		/
Grypopterygidae (stonefly)		•		xx	x		/			/
Conoesucidae (caddis)	xxx	xxx	x		xx	x	/	xxxxxx	x	/
Helicopsychidae (caddis)	xxxx		x		xx		/			/
Elmidae (beetle)	x	xxxx	x		x	xx	/	xxxx	xxx	/
Chironomidae (midge)	xx	x		xx	xx	xxxxx	/		x	/
Hydrobiidae (snail)	x	xx	xx		x	xx	/	xx		/
Predators										
Corydalidae (dobsonfly)	x	x		x	x		/	•	xx	/
Eusthenidae (stonfly)					x		/	•		/
Rhyacophilidae (caddis)	x	x	x	xx	•	x	/	•	x	/

Legend blank = not present
• = less than 1%
/ = relative abundance not calculated
x = 1–5%; xx =5–10%; xxx = 10–20%; xxxx = 20–30%; xxxxx = 30–40%; xxxxxx = 40–50%

Appendix 3.1: Relative abundance of main taxa collected at stream sites in pilot survey—Coromandel 1981—*continued*

Macroinvertebrate group / Stream sampled and NZMS1 original reference	**Tui** (N57 217794)	**Waiorongomai** (N57 247746)	**Waipupu** (N57 285698)	**Waitaia Mine** (N40 210737)	**Waitaia Road Bridge** (N40 228743)	**Buffalo** (N40 018744)	**Paroquet** (N49 039394)	**Waiomu** (N49 049393)	**Whareroa** (N40 8478855)	**Haratаunga** (N40 027777)
Seston collectors										
Oligoneuridae (mayfly)	x	/	x	x	xx	xx	xx		xx	•
Hydropsychidae (caddis)	xxxxx	/	xx	x	xx	xx	x		x	•
Simulidae (sandfly)		/		x	xx				x	
Benthic browsers										
Leptophlebiidae (mayfly)	xx	/		x	xxx	x	xxxx	x	xxxxx	xx
Siphlonuridae (mayfly)		/	•	x	x					
Grypopterygidae (stonefly)		/	x	x	xx	xx			x	x
Conoesucidae (caddis)		/	xx	xxxx	x	xxx	xx		xxxxx	xxxxx
Helicopsychidae (caddis)		/				x	x		•	x
Elmidae (beetle)	xx	/	xx	xxxxxx	xxx	xxx	xxx	xxxxx	x	xx
Chironomidae (midge)	xxxx	/	xxxx	xx	xxxxx				x	xx
Hydrobiidae (snail)	x	/		x	x			xxxx		x
Predators										
Corydalidae (dobsonfly)	•	/	x	xx					•	x
Eusthenidae (stonefly)	•	/			x				x	
Rhyacophilidae (caddis)	xx	/	x	x	xx	x	x	x	x	•

Legend blank = not present
• = less than 1%
/ = relative abundance not calculated
x = 1–5%; xx = 5–10%; xxx = 10–20%; xxxx = 20–30%; xxxxx = 30–40%; xxxxxx = 40–50%

Appendix 3.2a: Site characteristics for the sites from which limited numbers of biological samples were collected

SITE NUMBER	W1	W2	W5	W6	W8G	W9	W12	P1	B1	B2	B3	E	EC
STREAM NAME	Waitaia Control	Waitaia Control	Waitaia	Waitaia	Waitaia Mine	Waitaia Mine	Mullock	Paroquet	Buffalo	Buffalo	Buffalo	Everett's	Everett's Control
SITE STATUS	control	control	impacted	impacted	impacted	impacted	impacted	impacted?	control	control	impacted	impacted	control
TOTAL NUMBER OF SAMPLES	qual only	qual only	3	18	6	qual only	3	6	6	qual only	qual only	qual only	qual only
STREAM WIDTH (m)	2	2	2	2	1–2	1.5	1.5	1	2	1.5	1.5	0.2	0.1
DEPTH (mm)	80–120	80–120	50–100	50–100	70–100	150	8–165	100–200	150	250	250	50	50
VELOCITY (m sec-1)	-	-	-	0.15–0.4	0.25–0.45	0.14–0.4	-	-	-	-	-	-	-
DISCHARGE (1 sec-1	7	7	16	16	9	-	-	-	-	-	-	-	-
GRADIENT	7	7	6	6	11	11	-	-	-	-	-	-	-
CHANNEL TYPE	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread
SUBSTRATE TYPE	stones 250 mm in matrix of fine silt	stones 250 mm in matrix of fine silt	stones 200 mm in matrix of silt, gravel	angular + rounded stones 120 mm in loose matrix of silt, gravel	angular rubble 200 mm in loose matrix of silt, gravel	bedrock and stones 400 mm	angular rubble 200 mm	stones 200 mm in matrix of silt	stones 250 mm in matrix of silt, detritus	boulders gravel and sand in pools	bounders gravel and sand in pools	silt moss and organic debris	silt, moss and organic debris
PFANKUCH PFANKUCH STABILITY RATING	fair	fair	fair	fair	fair	fair	fair	fair	good	good	good	good	good
SHADE	total	total	partial	partial	partial	total	total	total	total	total	total	total	total
ADJACENT LANDUSE	bush	bush	pasture	pasture	bush	bush	bush	bush	bush	bush	bush	bush	bush
RIPARIAN VEGETATION	nikau ponga	nikau ponga	kanuka blackberry	kanuka ponga	blackberry kanuka	podocarp hardwood	kanuka	podocarp hardwood	podocarp hardwood	podocarp hardwood	podocarp hardwood	podocarp hardwood	podocarp hardwood
KNOWN SOURCE OF CONTAMINATION	none	none	drainage from Waitaia Mine shaft and Mullock Stream	drainage from Waitaia Mine shaft and Mullock Stream	drainage from Waitaia Mine shaft and Mullock Stream	drainage from Waitaia Mine shaft and Mullock Stream	drainage from Hosie Mine shaft Mullock leachate	drainage from Monowai Mine?	none	none	drainage from Everett's Stream	drainage from Everett's Mine drive	none
DISTANCE km DOWNSTREAM FROM CONTAMINATION	-	-	2.0	1.6	1.0	0.4	0.7	-	-	-	0.5	0.5	-
ACIDITY	neutral	neutral	neutral	neutral	weakly acid	weakly acid	weakly acid	-	neutral	neutral	neutral	weakly acid	-
RELATIVE METAL CONCENTRATION	background	background	slightly elevated	slightly elevated	slightly elevated	slightly elevated	slightly elevated	slightly elevated	background	background	background	highly elevated	-
IRON FLOC DEPOSIT	local seepage	local seepage	none	none	light	heavy	moderate	none	none	none	none	none	-

Blank (—) = Not measured.

Appendix 3.2b: Site characteristics for the control and test sites used in the main biological study

SITE PAIRS	W3	W8	W4	W7	WC	WP1 WP2	B4*	P2
STREAM NAME	Waitaia Control	Waitaia Mine	Waitaia Control	Waitaia Mine	Waiomu	Waiomu	Buffalo	Paroquet
SITE STATUS	control	test	control	test	control	test	control	test
TOTAL NUMBER OF SAMPLES	30	30	15	15	30	33	30	30
STREAM WIDTH (m)	2	1-2	1-2	1	6	6-8	3	3
DEPTH (mm)	80-120	80-150	50-100	50-100	150-330	140-260	100-330	100-180
VELOCITY (m/sec-1)	0.1-0.55	0.1-0.5	0.2-0.4	0.15-0.4	0.16-0.45	0.16-0.73	0.1-0.6	0.15-0.5
DISCHARGE (1 sec-1)	7	9	7	9	122-896	140-1036	11-14	18-140
GRADIENT	7	11	6	6	7-8	9-10	13	14
CHANNEL TYPE	single thread	single thread	single thread	single thread	single thread	single thread	single thread	single thread
SUSTRATE TYPE	stones 250 mm in matrix of fine silt, gravel	rounded stones 350 mm in matrix silt and gravel	rounded stones 200 mm in matrix of fine silt, gravel	angular stones 130 mm in matrix of gravel	boulders; stones 800 mm in matrix of coarse gravel and sand	boulders; stones 800 mm in matrix of unsorted gravel, sand, silt	boulders; stones 300 mm in matrix of coarse gravel	boulders; stones 800 mm in matrix of unsorted gravel, sand, silt
PFANKUCH STABILITY RATING	fair	fair	fair	fair	fair	fair	good	poor
SHADE	partial	total	partial	partial	partial	total	total	partial
ADJACENT LAND USE	bush	bush	pasture	pasture	bush	bush	bush	bush
RIPARIAN VEGETATION	nikau ponga	kanuka ponga	kanuka ponga	kanuka ponga	podocarp hardwood	podocarp hardwood	podocarp hardwood	podocarp hardwood
KNOWN SOURCE OF CONTAMINATION	none	drainage from Waitaia and Hosie's Mines; mullock leachate	none	drainage from Waitaia and Hosie's Mines; mullock leachate	none	Paroquet triburary (see P2)	drainage from Everett's Drive	drainage from Monowai Mine; high erosion, mullock leachate
DISTANCE (km) DOWNSTREAM FROM CONTAMINATION	-	0.8	-	1.6	-	0.2-0.4	1.0*	0.5
ACIDITY	neutral	weakly acid	neutral	neutral	neutral	neutral	neutral	weakly acid
RELATIVE METAL CONCENTRATION**	background except arsenic	slightly elevated	background except arsenic	slightly elevated	background		background	elevated
IRON FLOC DEPOSIT	local seepage	light	none	none	none	none	none	none

* Control site B4: Although downstream from a mine, this site had a healthy ecosystem. This site was therefore used as a control for site P2 in the paired comparisons as it had the most similar stream characteristics.

** See Chapter 2, Section 2.3.1.

Appendix 3.3: Occurrence of invertebrates in the control streams between April 1982 and January 1983

	Waitaia Control Stream (W3, W4)	Upper Waiomu Control Stream (WC)	Upper Buffalo Control Stream (B1, B2, B3)	Buffalo Stream (B4)	Upper Paroquet Control Stream (P1)
Megaloptera (Dobson fly)					
CORYDALIDAE					
Archicaulioides diversus	X	X	X	X	X
Ephemeroptera (May fly)					
EPHEMERIDAE					
Ichthybotis hudsoni	X	X	X	X	X
OLIGONEURIDAE					
Coloburiscus humeralis	X	X	X	X	X
LEPTOPHLEBIIDAE					
Deleatidium	X	X	X	X	X
Ataphlebioides	X			X	
Zephlebia cruentata		X		X	
Zephlebia nodularis	X				
Zephlebia Indet.	X	X	X	X	X
SIPHLONURIDAE					
Nesameletus		X	X	X	X
Ameletopsis		X	X	X	X
Onigaster wakefieldii		X			
Plecoptera (Stone fly)					
EUSTENIIDAE					
Stenoperla prasina	X	X		X	X
AUSTROPERLIDAE					
Austroperla cyrene	X	X	X	X	X
GRYPOPTERYGIDAE			X		
Megaleptaperla grandis	X		X	X	
Zelandoperla decorata		X		X	
Zelandoperla agnetis		X	X	X	X
Zelandobius furcillatus		X	X	X	
Zelandobius unicolor					X
Zelandobius confusus			X		X
Acroperla trivacuata	X	X		X	X
NOTONEMOURIDAE					
Notonemoura	X				
Spaniocerca zelandica	X				X
Trichoptera (Caddis fly)					
HYDROPSYCHIDAE					
Orthopsyche fimbriata	X			X	
Orthopsyche thomasi	X	X	X	X	
Orthopsyche Indet.	X		X	X	X
Aoteapsyche colonica	X	X		X	
Aoteapsyche raruraru		X			
HYDROPTILIDAE					
Oxyethira albiceps	X	X			
RHYACOPHILIDAE					
Costachorema			X		X
Psilochorema	X		X	X	
Psilochorema tautori	X				
Psilochorema macroharpax			X		
Psilochorema nemorale type	X	X			X
Hydrobiosis	X	X		X	X
Hydrobiosis parumbripennis		X			
Hydrobiosis silvicola	X				
Hydrobiosis spatulata	X				
Hydrochorema crassicaudatum	X	X			X
Neurochorema	X	X			
POLYCENTROPIDAE					
Polyplectropus pueriles	X	X	X		X
PHILOPOTAMIDAE					
Hydrobiosella mixta	X		X		
LEPTOCERIDAE					
Hudsonema amabilis	X	X		X	
Triplectides obsoleta	X	X		X	
Oecetis			X		
CALOCIDAE					
Pycnocentrella eruensis			X		
HEICOPHIDAE					
Alleocentrella magnicornis			X		
CONOESUCIDAE					
Conuxi gunni			X		
Pycnocentrodes	X	X		X	
Beraeoptera roria	X	X		X	
Olinga	X	X	X	X	
Pycnocentria funeria	X				
Pycnocentria evecta		X			

Appendix 3.3: Occurrence of invertebrates in the control streams between April 1982 and January 1983—*continued*

	Waitaia Control Stream (W3, W4)	**Upper Waiomu Control Stream** (WC)	**Upper Buffalo Control Stream** (B1, B2, B3)	**Buffalo Stream** (B4)	**Upper Paroquet Control Stream** (P1)
Pycnocentria sylvestris			X		
HELICOPSYCHIDAE					
Helicopsyche zealandica	X	X	X	X	X
Coleoptera (Beetle)					
HELODIDAE					
Species	X		X		
PTILODACTYLIDAE					
Species	X	X	X	X	X
ELMIDAE					
Hydora	X	X	X	X	
HYDRAENIDAE					
Species	X	X	X	X	X
Diptera (Two winged fly)					
TIPULIDAE			X		
Aphrophila neozelandica	X	X		X	
Paralimnophila skusei	X	X	X		
Eriopterini	X	X	X		X
Hexatomini			X		
SIMULIDAE					
Austrosimulium austrolense	X		X		
CHIRONOMIDAE	X	X	X	X	X
Tanypodinae	X	X	X		X
Lobodiamesini					
Tanytarsus		X			
Polypedilum		X			
Calospectra	X		X		X
Paucispinigera			X		X
Orthocladinae "O"	X	X			X
Orthocladinae "L"	X				
TANYDERIDAE	X				
CERATOPOGONAE	X	X			X
EMPIDIDAE	X	X			
TABANIDAE	X	X			
PSYCHODIDAE	X				
DIXIDAE					
Nothodixa	X				X
PLANORBIDAE	X				
Gastropoda (Snail, limpet)					
HYDROBIIDAE					
Potamopyrgus antipodarum	X	X	X	X	X
ANCYLIDAE					
Ferrissia dohrnianus		X		X	
LATIDAE					
Latia neritoides	X	X	X	X	
Decapoda					
Paratya curvirostris	X				
Paranephrops planifrons	X				

Appendix 3.4: Diatoms, green and blue-green algae genera from periphyton samples collected during biological survey, Coromandel (1982–83)

Site number	WC		WP1		WP2		P2		B4		W3		W8		W4		W6		W7	
Date of sample collection	J	A	J	A	J	A	J	A	J	A	J	A	J	A	J	A	J	A	J	A
DIATOMS																				
Melosira distans				x																
Frangilaria	*	*		1		x			*	x	x									
Eunotia																			x	
Achnanthes	x														x		x		x	
Cocconeis	x	x		2		x			*	*	x	x						x		
Rhoicosphenia	x	x									x	x		x	x		x	x		
Navicula	*	x		1		*			x		*	x			*		x	x	x	3
Gyrosigma											x									2
Gomphonema	x			x		x				x	*	*			x		x	x		x
Cymbella	x			x		x				x										
Epithemia									x											
Surirella	*	x	x				*			x								x	x	
Amphora	x																			
BLUE-GREEN ALGAE																				
Cladophora											*	x		*	x		x	x	x	1
Spirogyra						x														
Lyngbya							x												*	
Oscillatoria	x	*		2							x									x
Oedogonium	*	x								x										
Netrium	*			2												*	x			
Mougeotia							x			*										
Cosmarium						x														
Scenedesmus						x														
Coccoidgreen						x														

Legend * Dominant 1 Predominant 2 Secondary 3 Tertiary x Present
J July A August

CHAPTER 4: Survey of Heavy Metal Levels in Coromandel Shellfish and Finfish

D. Tracey and W. L. F. van den Broek

4.0 Abstract

Concentrations of the heavy metals mercury, cadmium, copper, lead, zinc, and arsenic in the tissues of shellfish and finfish species from Coromandel Peninsula were analysed. The samples comprised a total of 9 shellfish species and 19 marine and freshwater fish species from 86 sampling sites around the coast and inland.

Wide variations in heavy metal concentrations found in shellfish tissue could not be related to any particular causative factor. Mean concentration of mercury, cadmium, copper, zinc and lead in marine finfish were all below safe limits for human consumption (New Zealand Statutory Regulations 1984/262). Maximum mercury concentrations in finfish at some sites exceeded the safe limits but mercury levels were considered comparable to other areas of New Zealand. Mean concentrations of mercury, copper, lead, and arsenic in shellfish were below safe limits for human consumption, with a few isolated exceptions in the cases of copper and arsenic.

Maximum mercury concentrations in freshwater eels frequently exceeded safe limits and mercury concentrations in eels were regarded as naturally high in the Coromandel region.

4.1 Introduction

The perceived implications of large-scale mining in the Coromandel Peninsula prompted several enquiries from local fishing people about the possible effects of mining on the marine and freshwater biota. The potential impacts of mining, either directly through toxic effects on fish, or indirectly through bioaccumulation in lower orders of the food chain, were of concern to those involved in an economic fishery. In addition, metal bioaccumulation in edible seafood species is potentially hazardous to human health.

In June 1981, Fisheries Research Division (MAF) staff proposed that a qualitative sampling programme be carried out in the Coromandel Peninsula that would provide background information on the range of heavy metal concentrations currently in the aquatic animals.

Previous studies have investigated heavy metal levels in New Zealand molluscs and have included the Coromandel Peninsula as a sampling area (Nielsen and Nathan 1975; Winchester and Keating 1980).

The present study provides a more extensive evaluation of heavy metal bioaccumulation in shellfish and finfish in Coromandel, and attempts to examine the distribution of shellfish contamination in relation to the geology and mining history of the Coromandel. The study also compares metal concentrations in fish and shellfish tissues with permitted levels for safe human consumption (New Zealand Statutory Regulations 1984/262). It should be noted that the Regulations specifically omit shellfish concentrations of zinc and cadmium from their listings. The figures given in the tables for these two metals are the limited specified for all foods other than shellfish.

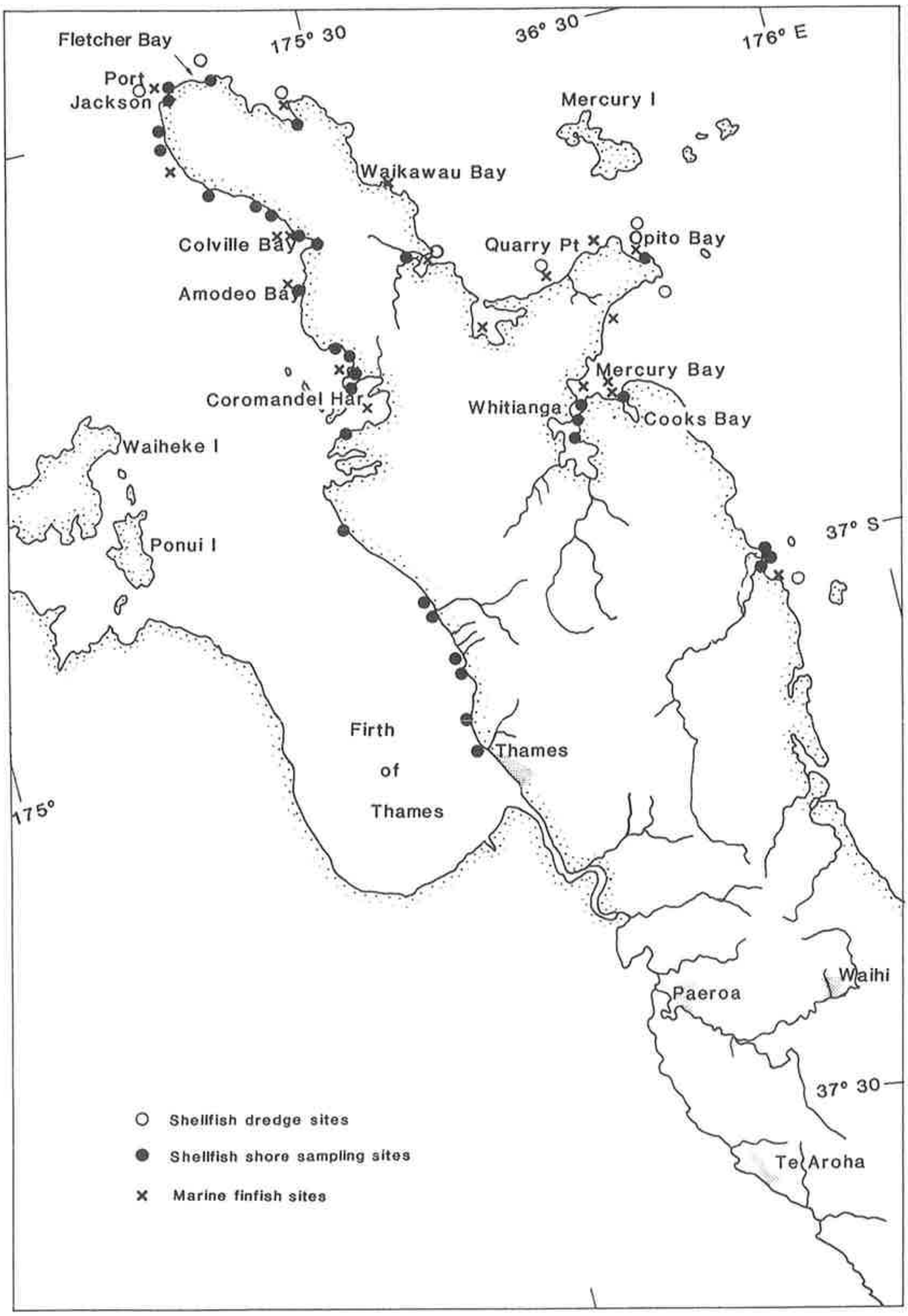

Figure 4.1: Marine sites, fish and shellfish survey, Coromandel. See Table 1.2 for location details.

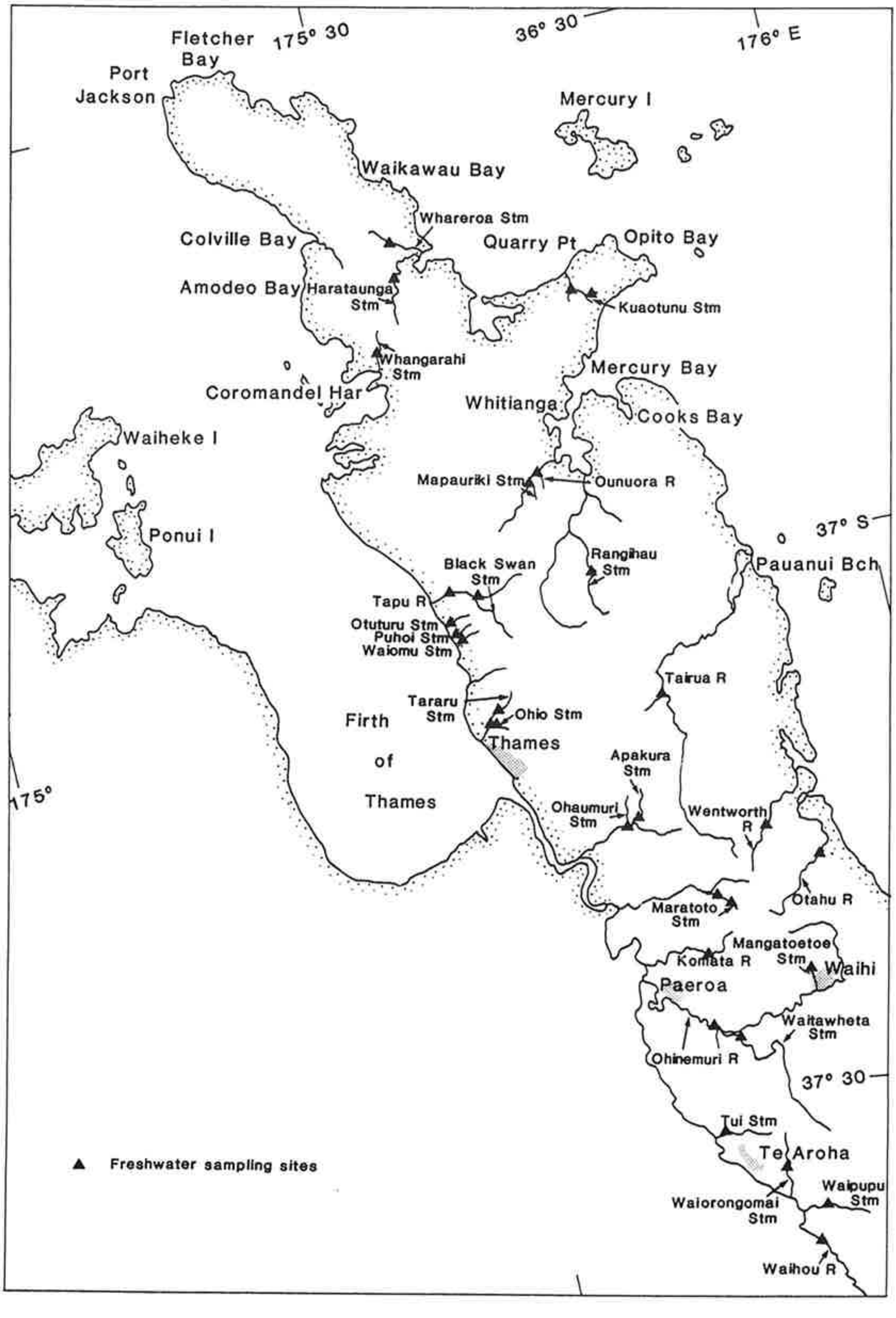

Figure 4.2: Freshwater sites, fish and shellfish survey, Coromandel. See Table 1.1 for location details.

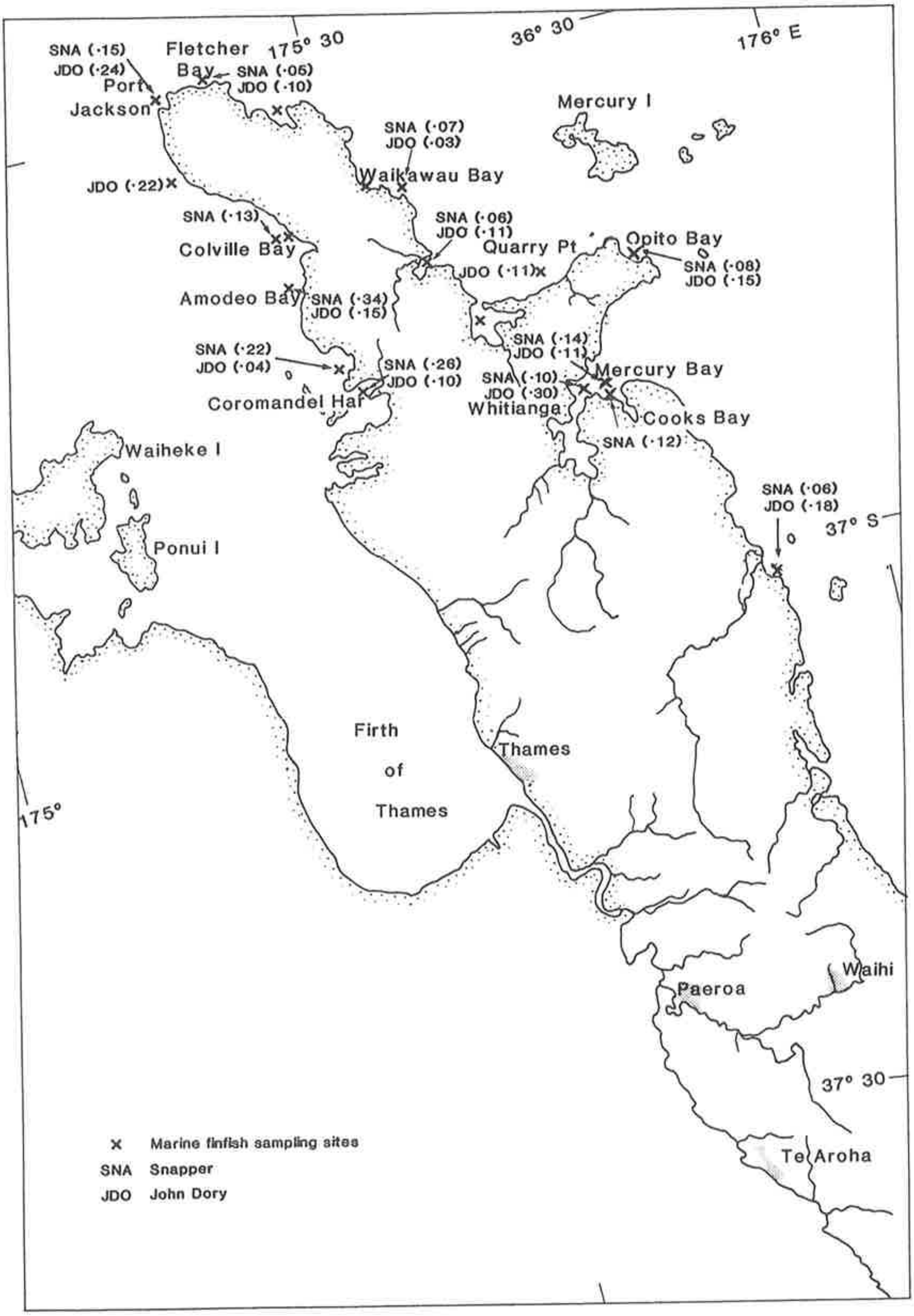

Figure 4.3: Mean mercury levels in snapper (*Chrysophrys auratus*) and John Dory (*Zeus japonicus*), fish and shellfish survey, Coromandel (see Table 4.3).

4.2 Methods

4.2.1 Shellfish and marine finfish sampling

A number of key commercial fish and invertebrate species were selected for the investigation of bioaccumulation of heavy metals (Appendices 4.1, 4.2, 4.3). Samples of these species were collected in July and August 1981 from 55 coastal sites (Figure 4.1) and 31 inland stream sites (Figure 4.2). Some sites were chosen for their proximity to areas where mining activity had been carried out in the past or where prospecting was likely to occur, and others were taken in areas with no history of mining.

Live marine fish and shellfish were collected from coastal sites by dredging, trawling, diving, and shore wading. Fisheries Research Division vessel 'Ikatere' was used for trawling and dredging operations. Fish were measured, sexed, and in the case of snapper (*Chrysophrys auratus*), aged from their otoliths. Approximately 10 g of muscle tissue were cut from each fish and frozen for heavy metal analysis. Dredged shellfish samples were frozen whole.

Other shellfish samples were collected from the shoreline by wading at low tide, except for scallops (*Pecten novaezelandiae*) which were sampled using SCUBA. A sample of at least 20 individuals per shellfish species was collected at each site. The time between collection of the samples and freezing was no longer than six hours.

Colville Bay was sampled more intensively than other areas to establish whether there was any variability in naturally occurring levels of the heavy metals in shellfish within the bay.

4.2.2 Freshwater fish sampling

Freshwater fish were collected by electric fishing from streams, 4–10 August, 1981 (Figure 4.2) and all fish caught or seen were recorded. General habitat (stream width, water clarity, substrate type, presence/absence invertebrates) and water quality (pH, temperature, dissolved oxygen) were also recorded. Eels (*Anguilla australis* and *A. dieffenbachii*) were present at most sampling sites and approximately 10 g of muscle tissue was taken from specimens longer than 16 cm Total Length. Muscle samples from trout (*Salmo trutta* and *S. gairdnerii*) over 14 cm Fork Length were also taken for heavy metal analysis.

4.2.3 Analytical techniques

Frozen homogenates of shellfish tissues from each sample site, and fish muscle tissue samples were forwarded for heavy metal analysis to the Meat Monitoring Division, Wallaceville Research Centre. The analytical techniques used to determine heavy metals in animal tissue are described by Gorsuch (1959) and Brooks and Rumsey (1973). A mean concentration of each heavy metal (Hg, Cd, Cu, Zn, Pb, As) was calculated from the homogenate at each site. Because of time limitations only the Colville Bay shellfish samples included arsenic analyses. Detection limits were as follows: Cd 0.01 mg kg^{-1}; Cu 0.5 mg kg^{-1}; Hg 0.01 mg kg^{-1}; Zn 1.0 mg kg^{-1}; Pb 0.2 mg kg^{-1}.

Table 4.1: Mean heavy metal levels in shellfish dredge samples

		Heavy metals (mg kg^{-1} wet weight)					
		Hg	Cd*	Cu	Zn*	Pb	As
New Zealand Statutory Regulations (1984/262)		0.5	1	30	40	2	2
Sample location	*Species*						
Port Jackson	Whelk	0.12	1.90	26.0	51.6	0.16	- †
	Cockle	Tr	3.68	1.64	17.5	0.52	-
	Scallop	Tr	-	-	-	-	-
	Limpet	0.01	0.32	10.3	24.0	1.3	-
	White Rock shell	0.06	8.42	39.4	394.1	0.16	-
Fletcher Bay	Scallop	Tr	48.7	1.55	39.7	0.33	-
	Cockle	Tr	6.61	2.06	20.6	0.71	-
	Whelk	0.03	12.7	30.7	74.3	0.12	-
	Whelk	Tr	1.56	19.5	53.7	0.10	-
Kennedy Bay	Ostrich foot	Tr	0.06	4.26	13.6	0.10	-
	Ostrich foot	Tr	0.08	0.74	11.2	0.35	-
	Whelk	0.02	0.80	6.96	34.1	0.15	-
Pauanui Beach	Whelk	0.06	0.33	4.46	17.4	0.08	-
	Cockle	0	0.64	1.18	14.5	0.27	-
	Ostrich foot	0	0.08	1.63	11.3	0.07	-
	Olive shell	0.03	-	-	-	-	-
Matapaua Bay	Cockle	0.01	-	-	-	-	-
	Whelk	0.03	0.90	14.3	39.0	0.01	-
Quarry Point‡	Scallop	0.01	9.30	1.03	32.7	0.15	-
	Whelk	0.03	0.97	5.23	22.4	0.07	-
	Ostrich foot	0.01	0.07	3.9	17.7	0.17	-
Opito Bay	Whelk	-	-	-	-	-	-
	Cockle	Tr	0.53	1.6	16	0.2	-
	Cockle	0.01	0.66	1.44	16.7	0.1	-
Port Charles	Whelk	0.01	0.58	11.0	25.7	0.11	-
	Ostrich foot	0.01	0.70	8.06	53.0	0.13	-
	Ostrich foot	Nil	0.13	1.93	16.1	0.40	-

Tr = Trace (<0.01) † = sample not tested for this particular metal.
‡ = areas with historical mining activities in their hinterland.
* The cadmium and zinc standards do not apply to shellfish.

4.3 Results

4.3.1 Metal concentrations in shellfish

Mean heavy metal concentrations (mg kg^{-1}) in shellfish from each sample site are summarised in Tables 4.1 and 4.2.

In shellfish, mean mercury, copper, lead, and arsenic content were mostly well below safe limits permitted by the New Zealand Statutory Regulations (1984/262). Zinc and cadmium in rock oysters from Cape Colville, and cadmium levels in scallops from Opito Bay, Quarry Point and Fletcher Bay were higher than levels permitted in foods other than shellfish (New Zealand Statutory Regulations 1984/262).

Variability in mean heavy metal concentrations of Colville Bay samples was low, as illustrated in Table 4.2 by the pipi (*Paphies australis*) analyses. Throughout the Coromandel Peninsula as a whole, however, variability in mean heavy metal concentrations is high between sites. For example, rock oysters in Colville Bay had a mean zinc level of 44 mg kg^{-1} whereas at Port Jackson, they had a mean zinc level of 384 mg kg^{-1} (Table 4.2).

4.3.2 Metal concentrations in marine finfish

Mean, minimum, and maximum mercury levels in marine finfish species are given in Table 4.3 with their mean lengths, size ranges and age. Mean mercury levels did not exceed the safe limit (0.5 mg kg^{-1}) at any of the sample sites. Maximum mercury levels of some species did, however, exceed the safe level at some sites, e.g., john dory (*Zeus japonicus*) at Port Jackson (this was the highest mercury level recorded); snapper at Port Jackson, Amodeo Bay, Colville Bay, Coromandel Harbour, Mercury Bay; gummy

Table 4.2: Results of analyses of mean heavy metal levels in shellfish shore samples

		Heavy metals (mg kg^{-1} wet weight)					
		Hg	Cd*	Cu	Zn*	Pb	As
New Zealand Statutory Regulations (1984/262)		0.5	1	30	40	2	2
Sample location	*Species*						
Tapu River mouth‡	Pipis	0.06	-†	-	-	-	-
	Cockles	0.08	-	-	-	-	-
	Mussels	0.05	-	-	-	-	-
Whakatete Bay	Mussels	0.05	-	-	-	-	-
	Rock oysters	0.05	-	-	-	-	-
Waiomu Stream mouth‡	Mussels	0.06	-	-	-	-	-
Tararu Stream mouth‡	Pipis	0.03	-	-	-	-	-
Te Puru Stream mouth‡	Rock oysters	0.07	-	-	-	-	-
Cooks Bay‡	Mussels	Tr*	0.07	0.76	16	0.09	-
Whitianga Harbour‡	Cockles	0.01	0.04	0.68	7.4	0.15	-
" "	Mussels	0.02	0.06	0.58	11.0	0.14	-
" "	Pipis	0.02	0.06	1.14	11.4	0.04	-
Whitianga Wharf‡	Mussels	0.01	0.08	0.66	15.2	0.04	-
Tokoroa Beach‡	Rock oysters	0.02	2.2	14.7	226.2	0.04	-
Tairua Tidal flats‡	Cockles	Tr*	0.05	0.7	9.3	0.07	-
Tairua Beach (harbour entrance)‡	Mussels	0.01	0.26	0.76	17.0	0.12	-
	Rock oysters	0.04	3.22	19.6	484.3	0.25	-
Opito Bay	Scallops	0.05	8.03	1.36	16.9	0.20	-
Koputauaki Bay	Cockles	0.07	0.06	1.36	7.5	0.18	-
	Pipis	0.03	0.05	1.31	11.6	0.17	-
	Rock oysters	0.04	0.81	22.2	362.0	0.14	-
Kikowhakorere Bay	Cockles	0.06	0.07	1.23	7.9	0.19	-
	Pipis	0.01	0.04	0.96	10.7	0.14	-
	Rock oysters	0.02	0.54	13.1	165.0	0.18	-
Port Charles	Cockles	0.02	0.05	1.23	8.7	0.37	-
	Rock oysters	0.02	0.32	37.5	109.4	0.35	-
Waiaro Bay	Pipis	0.01	0.02	0.96	11.2	0.22	-
	Cockles	0.02	0.12	1.27	12.1	0.62	-
	Rock oysters	0.02	1.76	20.3	297.2	0.12	-
Esk Reef	Rock oysters	0.03	0.78	9.72	187.5	0.21	-
Wilsons Bay	Rock oysters	0.02	0.75	11.3	240.8	0.18	-
	Pipis	0.02	0.05	0.61	10.2	0.23	-
	Mussels	0.03	0.05	1.00	17.3	0.42	-
MacGregor Bay‡	Rock oysters	0.05	0.21	20.8	139.2	0.24	-
	Cockles	0.08	0.04	1.33	13.7	0.59	-
Port Jackson	Rock oysters	0.04	2.60	31.9	384.0	0.22	-
Goat Bay	Rock oysters	0.02	2.71	21.6	233.9	0.32	-
Hope Stream mouth	Rock oysters	0.02	1.65	28.3	361.6	0.14	-
Waitoitoi Stream mouth	Rock oysters	0.03	2.29	30.0	520.0	0.21	-
Wyuna Bay	Pipis	0.04	0.04	1.30	11.9	0.23	-
	Cockles	0.08	-	-	-	-	-
Te Mata River‡	Pipis	0.03	0.04	1.27	10.8	0.24	-
Fletcher Bay	Rock oysters	0.02	2.72	20.0	19.6	0.27	-
Fantail Bay	Rock oysters	0.03	3.60	31.8	428.0	0.43	-
Colville Bay‡	Rock oysters	0.03	0.78	12.58	43.96	0.08	0.53
	Cockles	0.08	0.04	0.50	13.98	0.07	1.70
	"	0.03	0.04	0.50	10.94	0.03	3.20
	"	0.03	0.04	0.60	14.11	0.05	3.10
	"	0.03	0.05	0.55	13.38	0.06	3.20
	Pipis	0.02	0.04	0.71	15.25	0.03	0.28
	"	0.01	0.03	1.12	26.00	0.03	0.25
	"	0.02	0.03	0.73	17.86	0.02	0.19
	"	0.02	0.04	0.78	15.04	0.04	0.43
	"	0.01	0.03	0.69	16.35	0.05	0.50
	"	0.01	0.04	0.67	17.42	0.06	0.80
	"	0.01	0.04	0.78	12.87	0.08	0.60
	"	0.02	0.02	0.52	14.05	0.06	0.85
	"	0.03	0.02	0.35	14.99	0.07	0.77
	"	0.02	0.02	0.51	13.67	0.05	0.60
	"	0.05	0.03	0.59	13.92	0.08	0.65
	"	0.15	0.03	0.79	16.48	0.12	0.76

* = Trace (<0.01) † = sample not tested for this particular metal.
‡ = areas with historical mining activities in their hinterland.

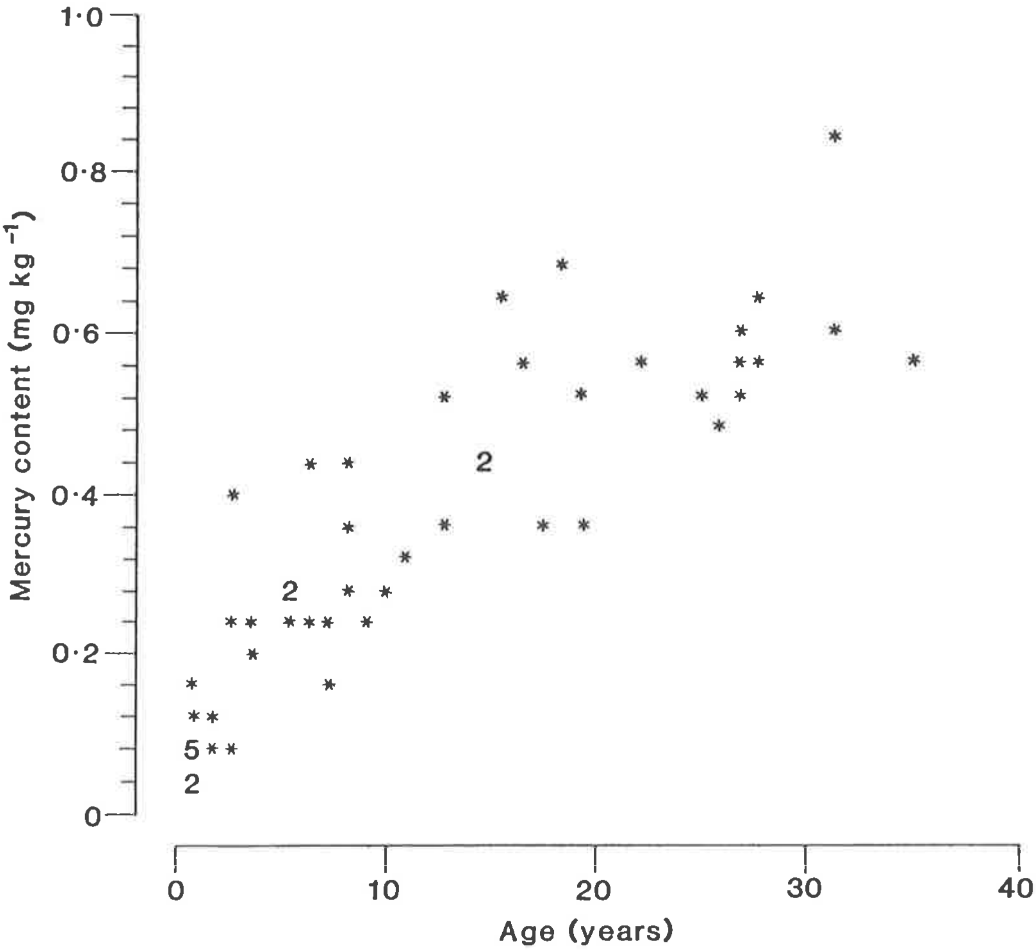

Figure 4.4: Relationship between mercury content and age of snapper (*Chrysophrys auratus*) trawled in Amodea Bay, Coromandel.

shark (*Mustelus lenticulatus*) in Colville Channel and Amodeo Bay; jack mackerel (*Trachurus declivis*) in Te Puru Bay and in Buffalo Bay.

Mean mercury levels in snapper and john dory varied little between areas (Figure 4.3). Figure 4.4 shows that there is a positive correlation between age and mercury concentration in the flesh of snapper.

Results of heavy metal levels other than mercury are listed in Table 4.4. Mean levels of cadmium, copper, zinc, and lead in fish flesh were always below the safe limits.

4.3.3 Metal concentrations in freshwater fish

The range of mean mercury levels in eels around the Coromandel Peninsula is given in Figure 4.5. Table 4.5 indicates relative abundance of all freshwater fishes counted in the surveyed streams. Trout were encountered at only 4 sites. Many streams in this region had suffered heavy damage during the floods of April 1981, and it is possible that as a result, fish populations were somewhat lower than normal.

Table 4.6 summarises the results of mercury analyses from shortfinned eel (*Anguilla australis*), longfinned eel (*Anguilla dieffenbachii*), brown trout (*Salmo trutta*), and rainbow trout (*Salmo gairdnerii*). The sample size of trout was generally small, but was larger for eels in several locations. Eels varied in

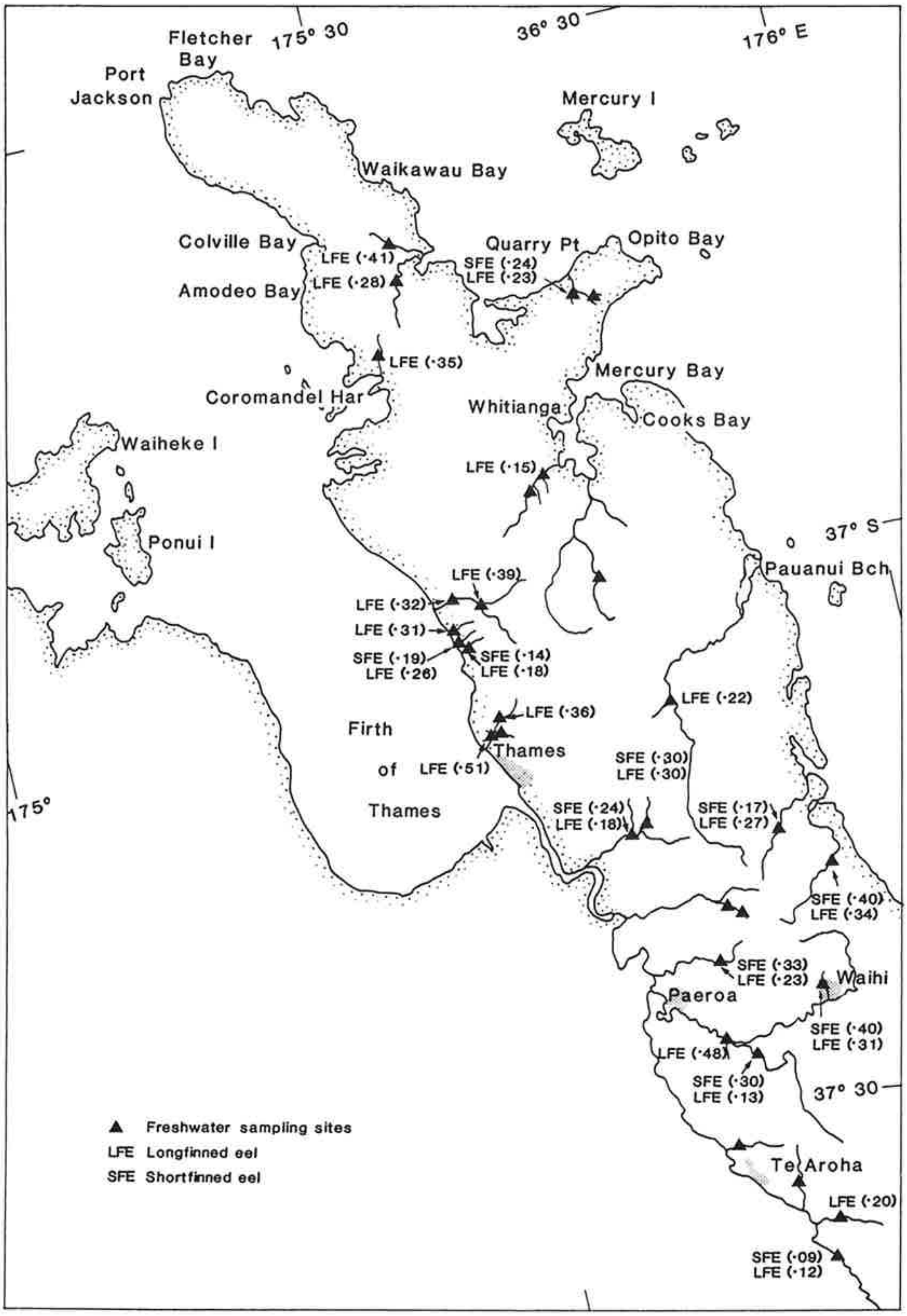

Figure 4.5: Mean mercury levels in eels (*Anguilla spp*), Coromandel.

length from 16 to 104 cm. Maximum mercury levels in eels regularly exceeded the safe limit; mean mercury level only once exceeded the safe limit (Tararu Stream).

Table 4.3: Mercury concentrations in muscle tissue of marine fish

Area	Species	Mean mercury level (mg kg^{-1} wet weight)	Minimum mercury level (mg kg^{-1} wet weight)	Maximum mercury level (mg kg^{-1} wet weight)	Number of fish	Mean fish length (cm)	Length range (cm)	Mean age (years)
Port Jackson	John Dory	0.24	0.03	1.15	6	35	25–47	-
	Leatherjacket	0.04	0.01	0.09	20	24	20–28	-
	Snapper	0.15	0.03	0.68	51	24	15–44	4.1
	Trevally	0.01	0.01	0.01	10	16	11–24	-
Darkie Stream	Sand flounder	0.05	0.03	0.08	6	20	17–24	-
	Gummy shark	0.13	0.12	0.14	3	75	63–83	-
	Red gurnard	0.09	0.05	0.17	13	29	25–39	-
	Jack mackerel	0.05	0.02	0.11	22	19	17–23	-
	John Dory	0.21	0.10	0.33	2	40	38–43	-
	Snapper	0.07	0.03	0.29	20	16	9–28	1.1
Colville Bay‡	Sand flounder	0.02	0.02	0.03	2	25	25–26	-
	Yellowbelly flounder	0.04	0.02	0.09	7	32	26–37	-
	Red gurnard	0.03	0.02	0.03	2	24	21–27	-
	Koheru	0.06	0.01	0.15	20	19	14–24	-
	Snapper	0.13	0.03	0.69	23	19	14–46	2.8
Colville Channel‡ (i.e., in Colville Bay)	Gummy shark	0.42	0.13	0.70	2	87	76–98	-
	Red gurnard	0.07	0.02	0.16	13	30	23–42	-
	John Dory	0.18	0.03	0.48	8	36	26–46	-
	Leatherjacket	0.05	0.02	0.09	7	23	22–25	-
	Red mullet	0.05	0.03	0.06	2	14	13–15	-
	Skate	0.07	0.06	0.08	3	63	59–71	-
	Snapper	0.04	0.01	0.08	22	13	10–19	0.6
	NZ sole	Trace	-	-	1	24	-	-
Amodeo Bay	Gummy shark	0.18	0.05	0.62	18	69	54–84	-
	Red gurnard	0.15	0.03	0.04	4	34	23–44	-
	John Dory	0.15	0.03	0.64	10	40	34–50	-
	Snapper	0.34	0.04	0.82	50	34	15–58	11.6
Long Bay‡	Sand flounder	0.03	0.02	0.04	2	31	26–37	-
	Yellowbelly flounder	0.04	0.03	0.04	2	31	32–34	-
	Red gurnard	0.32	-	-	1	37	-	-
	Jack mackerel	0.09	0.01	0.25	22	19	12–27	-
	John Dory	0.04	0.03	0.05	5	35	34–37	-
	Kahawai	0.06	0.03	0.11	21	22	20–25	-
	Snapper	0.22	0.04	0.40	24	32	22–48	6.5
Coromandel Harbour‡	Red gurnard	0.08	-	-	1	37	-	-
	John Dory	0.10	0.05	0.15	11	37	33–46	-
	Snapper	0.26	0.05	0.65	51	33	13–51	9.4
Te Puru Bay‡	Sand flounder	0.02	-	-	1	19	-	-
	Jack mackerel	0.25	0.10	0.67	22	32	20–40	-
	Yellowbelly flounder	0.03	0.01	0.06	7	33	28–42	-
Port Charles	Red gurnard	0.09	0.02	0.20	14	33	24–39	-
	John Dory	0.09	0.02	0.40	14	32	17–44	-
	Leatherjacket	0.05	0.01	0.18	21	25	14–29	-
	Snapper	0.05	0.01	0.13	19	12	7–20	0.6
	Trevally	0.02	0.01	0.03	11	12	11–16	-
Haupaupa Point	Gummy shark	0.09	-	-	1	73	-	-
	Red gurnard	0.06	0.03	0.12	6	29	22–39	-
	John Dory	0.02	-	-	1	34	-	-
	Leatherjacket	0.05	0.01	0.09	10	23	21–26	-
	Snapper	0.07	0.02	0.13	29	16	15–27	1.2
Kennedy Bay	Red gurnard	0.10	0.04	0.23	5	35	30–43	-
	John Dory	0.11	0.02	0.34	15	37	29–49	-
	Leatherjacket	0.05	0.02	0.13	22	23	20–27	-
	Snapper	0.06	0.03	0.15	20	18	14–23	1.5
Whagapoua Harbour‡	Gummy Shark	0.14	0.04	0.28	13	76	57–87	-
	Red gurnard	0.11	-	-	1	44	-	-
	John Dory	0.09	0.01	0.48	9	35	29–48	-
Quarry Point‡	John Dory	0.11	0.04	0.16	3	39	36–42	-
	Leatherjacket	0.04	0.01	0.10	20	25	22–27	-
	Skate	0.17	0.10	0.24	2	67	62–71	-

Table 4.3: Mercury concentrations in muscle tissue of marine fish—*continued*

Area	Species	Mean mercury level (mg kg^{-1} wet weight)	Minimum mercury level (mg kg^{-1} wet weight)	Maximum mercury level (mg kg^{-1} wet weight)	Number of fish	Mean fish length (cm)	Length range (cm)	Mean age (years)
Otama Beach‡	Red gurnard	0.15	0.04	0.24	5	38	32–44	–
	Leatherjacket	0.06	0.01	0.17	19	24	19–30	–
Opito Bay	Gummy shark	0.12	–	–	1	80	–	–
	Red gurnard	0.18	0.04	0.31	5	41	38–45	–
	John Dory	0.15	0.03	0.27	4	39	33–44	–
	Leatherjacket	0.05	0.01	0.11	19	26	21–29	–
	Snapper	0.08	0.03	0.20	19	19	15–25	1.8
Mercury Bay‡	Red gurnard	0.16	0.12	0.19	2	34	33–35	–
	John Dory	0.11	0.01	0.41	20	36	30–45	–
	Leatherjacket	0.09	0.02	0.20	20	25	21–29	–
	Snapper	0.14	0.04	0.76	50	26	16–59	4.9
Buffalo Bay‡	Sand flounder	0.07	0.06	0.08	2	27	25–30	–
	Yellowbelly founder	0.10	0.14	0.06	2	37	36–37	–
	Red gurnard	0.11	0.05	0.22	12	30	20–38	–
	Jack mackerel	0.22	0.6	0.88	20	30	21–39	–
	John Dory	0.29	0.11	0.61	4	39	37–45	–
	Snapper	0.10	0.08	0.11	2	19	18–20	1.5
	NZ sole	0.09	0.05	0.12	2	30	33–28	–
Cooks Beach‡	Sand flounder	0.08	–	–	1	28	–	–
	Red gurnard	0.13	0.02	0.28	10	35	23–42	–
	Jack mackerel	0.07	0.02	0.11	19	22	16–28	–
	Yelloweyed mullet	0.06	0.03	0.13	21	22	19–25	–
	Snapper	0.11	0.07	0.17	4	27	17–47	4
Pauanui Beach	Red gurnard	0.22	0.09	0.45	6	39	–	–
	Jack mackerel	0.08	–	–	1	21	–	–
	John Dory	0.18	0.04	0.32	2	35	35–35	–
	Kahawai	0.04	0.03	0.06	6	22	20–24	–
	Leatherjacket	0.10	0.04	0.20	17	27	24–29	–
	Snapper	0.06	0.04	0.08	3	20	19–22	2

‡ Areas with historical mining in their hinterland.

Table 4.4: Mean levels of heavy metals (mg kg^{-1} wet weight) in marine fishes

Area	Species	Cd	Cu	Zn	Pb
New Zealand Statutory Regulations (1984/262)		1	30	40	2
Colville Bay‡	Koheru	0.02	0.32	5.12	<0.10
Amodeo Bay	Gummy shark	0.03	0.45	2.83	0.08
	John Dory	0.01	0.09	4.8	0.10
Long Bay‡	Sand flounder	Tr*	0.29	4.0	0.06
	Yellowbelly flounder	0.01	0.32	5.2	0.18
	Red gurnard	Tr	0.29	3.4	0.10
	Jack mackerel	0.01	0.47	4.14	0.05
Coromandel Harbour‡	John Dory	0.01	0.12	3.75	0.06
	Snapper	0.01	0.16	4.1	0.06
Otama Beach‡	Leatherjacket	0.01	0.32	3.8	0.04
Mercury Bay‡	John Dory	0.03	0.32	4.33	0.13
	Leatherjacket	Tr	0.27	3.93	0.03
Cooks Beach‡	Yelloweyed mullet	0.01	0.75	0.8	0.04
Pauanui Beach	John Dory	Tr	0.15	2.88	0.10

* = Trace ‡ = areas with historical mining activities in their hinterland.

4.4 Discussion and Conclusions

The presence of elevated heavy metals in water can be attributed to a variety of sources: leaching of natural minerals from stream beds, mining activities, and run-off from agricultural chemicals applied to the land. For example, superphosphate, which is used in aerial topdressing, contains relatively large amounts of cadmium (Winchester and Keating 1980).

Shellfish, particularly filter feeders such as oysters, pipis and scallops, are especially prone to the accumulation of heavy metals. Nielsen and Nathan 1975, found an average zinc concentration of 337 mg kg^{-1} in the *Saccostrea* *glomerata* sampled nationwide, and a comparatively high level of cadmium as well.

The scallop stomach has a unique ability to accumulate cadmium (Brooks and Rumsey 1965), however, cadmium does not appear to accumulate significantly in the adductor muscle or gonad, which are the parts normally eaten (Nielsen and Nathan 1975).

Of the shellfish samples collected in the present survey, mean levels of mercury, lead, and arsenic were mostly well below the safe levels (New Zealand Statutory Regulations 1984/262). Zinc, copper, and cadmium were high in the rock oysters, and a high level of cadmium also occurred in the scallops. These high levels showed no relationship to areas of past mining activity.

In the Colville Bay area, high levels of zinc were recorded in oysters. These are of a similar order of magnitude to zinc concentrations recorded by Winchester and Keating (1980) in their Coromandel oyster samples.

Although there was little variation in heavy metal concentrations among individuals of a particular species within a localised area, (e.g., Colville Bay), there is wide variation in mean heavy metal levels of shellfish throughout the Coromandel region.

In general, finfish do not accumulate metals to the same degree as molluscs and in New Zealand it has already been demonstrated that for several commercial fish species, heavy metals in edible muscle tissue are usually below the statutory safe levels (Brooks and Rumsey 1973, van den Broek *et al.* 1981). Many fish species do however accumulate mercury in their flesh, and, because of the potential hazard to people, are monitored more closely.

Mercury levels in fish from Coromandel coastal waters showed no obvious connection with former mining sites. High maximum mercury levels were measured both at control sites and at sites within close proximity to former mining sites (see Port Jackson and Coromandel Harbour maximum mercury levels, Table 4.3). It is considered that high mercury levels are more likely to be due to a combination of ambient levels, the fish's position in the food chain and its age than to past mining activities (van den Broek *et al.* 1981).

In other parts of the New Zealand coastline, mercury levels in marine fish have reached maxima similar to those reported here for the Coromandel (Brooks and Rumsey 1973; Robertson *et al.* 1975; van den Broek *et al.* 1981; van den Broek and Tracey 1983).

In examining the freshwater fish results it was noted that although only one sample of *Anguilla* spp. had a mean mercury level exceeding 0.5 mg kg^{-1}, maximum mercury levels exceeded the permissible level at 9 out of the 37 sites. Again, as with the marine fish, variation can be attributed to the size, age, and diet of the eels and since relatively high mean mercury levels occurred in eels throughout the Coromandel area (Figure 4.4), it is considered unlikely that the high levels result from contamination by mine wastes. However, comparison with mercury levels in both species of eels from Lakes Otamangakau and Ellesmere (Table 4.7), suggests that mercury levels in Coromandel eels are naturally high.

Two streams that were known to be heavily contaminated by heavy metals and acid input had few or no freshwater fish (Tui and Ohio—Table 4.6), which may indicate the toxic effects. Other streams known to be contaminated e.g., Waiomu had a diversity of fish species. This survey provides no clear evidence that mining has caused the accumulation of mercury in freshwater fish.

Table 4.5: Relative abundance of freshwater fish

Station	Sampling site	*Anguilla dieffenbachii* (longfinned eel)	*Anguilla australis* (shortfinned eel)	*Salmo trutta* (brown trout)	*Salmo gairdneri* (rainbow trout)	*Galaxias maculatus* (inanga)	*Galaxias faciatus* (banded kokopu)	*Galaxias brevipinnis* (koaro)	*Galaxias argenteus* (giant kokopu)	*Gobiomorphus huttoni* (redfinned bully)	*Gobiomorphus basilis* (Cran's bully)	*Gobiomorphus cotidianus* (common bully)	*Cheimarrichthys fosteri* (torrent fish)	*Retropinna retropinna* (smelt)	*Geotria australis* (lamprey)	*Paranephrops planifrons* (koura)	
481	Waihou River	5	19	-	-	-	-	-	-	-	-	-	-	-	-	-	
482	Waipupu River	12 +	10	-	3	-	-	-	-	-	8 +	-	19 +	-	-	-	
483	Waiorongomai Stream	-	-	-	9	-	-	-	-	-	2	-	1	-	-	-	†
484	Tui Stream	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	†
485	Ohinemuri River tributary	5	1	-	-	-	-	-	-	-	-	-	-	-	-	1	†
581	Waitwheta Stream	2	6	2	-	-	-	-	-	-	9	-	-	-	-	1	
582	Komata River	10	21	-	-	-	-	-	-	-	3	-	-	-	-	1	†
583	Maratoto Stream	12	-	-	6	-	-	-	-	-	2	-	4	-	-	-	†
584	Apakura Stream	20	4	-	-	-	-	-	-	-	10	-	8	1	-	-	
681	Maratoto Stream	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
682	Ohaumuri Stream	25 +	7 +	-	-	-	-	-	-	-	-	-	14	-	-	-	
683	Tararu Stream	4	-	-	-	-	-	1	-	-	-	-	-	-	-	-	
684	Ohio Stream	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	†(W)
685	Tararu Stream	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	†
781	Waiomu Stream	3	2	-	-	3	5	-	-	3	-	4	13	-	-	-	
782	Tapu River	2	-	-	-	20 +	-	-	-	-	-	1	-	-	-	-	
783	Tapu River	11	3	-	-	-	-	-	-	7	-	-	-	-	-	-	
784	Otuturu Stream	2	-	-	-	-	16	-	-	1	-	-	-	-	-	1	
785	Puhoi Stream	10	9	-	-	1	3	-	-	-	-	26	3	5	-	P	
881	Whareroa Stream	15	5	-	-	2	1	-	1	36 +	-	-	-	-	-	1	
882	Harataunga Stream	23 +	2 +	-	-	-	1	-	-	72	-	-	16	-	-	-	
883	Whangarahi Stream	5	1	-	-	-	17	1	-	13	-	-	-	-	-	-	†
981	Kuaotunu Stream tributary	6	10	-	-	-	7	-	-	31 +	-	-	-	-	-	-	
982	Mapauriki Stream	-	2	-	-	-	-	-	-	6	-	-	-	-	-	-	
983	Ounuora River tributary	3	-	-	-	P	-	-	-	2	-	-	-	-	-	-	
984	Rangihau Stream	-	-	-	-	-	-	-	-	16	-	-	-	-	-	-	
985	Kuaotunu Stream tributary	-	-	-	-	-	25 +	-	-	-	-	-	-	-	-	3	†
1081	Tairua River tributary	8	3	-	-	-	-	-	-	P	-	-	-	-	-	-	†
1082	Wentworth River	15	11	-	-	-	-	-	-	P	-	-	2	-	-	-	
1083	Otahu River	6	15	-	-	-	-	-	-	P	-	P	-	-	2	-	†
1084	Mangatoetoe Stream	1	12	-	-	-	-	-	-	-	3	-	-	-	-	3	

Table 4.6: Summary of mercury levels in the muscle tissue of freshwater species

Area	Species	Mean mercury level (mg kg^{-1} wet weight)	Min mercury level (mg kg^{-1} wet weight)	Max mercury level (mg kg^{-1} wet weight)	Number of fish	Mean fish length (cm)	Length range (cm)
Waihou River	Shortfinned eel	0.09	0.05	0.14	14	49	47–52
Waipupu River		0.33	–	–	1	34	–
Waitawheta Stream		0.30	0.12	0.46	5	26	19–37
Komata River		0.33	0.17	0.56	8	27	25–31
Apakura Stream		0.30	0.15	0.38	3	27	25–30
Ohaumuri Stream		0.24	0.21	0.28	2	32	30–39
Waiomu Stream		0.14	0.09	0.18	2	34	29–40
Puhoi Stream		0.19	0.18	0.23	5	25	21–40
Buffalo Stream		0.26	–	–	1	19	–
Kuaotunu Stream tributary		0.24	0.11	0.32	4	25	17–36
Wentworth River		0.17	–	–	1	18	–
Otahu River		0.40	0.15	0.70	5	27	20–38
Mangatoetoe Steam		0.39	0.25	0.49	12	41	24–85
Waihou River	Longfinned eel	0.12	0.07	0.17	5	46	41–49
Waipupu River		0.24	0.10	0.43	8	48	19–104
Ohinemuri River tributary		0.48	0.28	0.72	5	54	41–75
Waitawheta Stream		0.13	–	–	1	39	–
Komata River		0.23	0.15	0.30	9	42	23–56
Maratoto Stream		0.33	0.19	0.71	8	38	23–48
Apakura Stream		0.30	0.14	0.82	16	41	22–85
Ohaumuri Stream		0.18	0.13	0.32	19	40	27–58
Tararu Stream		0.36	0.36	0.36	2	19	16–22
Tararu Stream		0.51	0.28	0.52	3	37	32–44
Waiomu Stream		0.18	–	–	1	37	–
Tapu River		0.32	–	–	1	44	–
Tapu River		0.39	0.17	0.67	9	38	19–61
Otuturu Stream		0.31	0.26	0.36	2	33	16–49
Puhoi Stream		0.26	0.15	0.34	7	39	29–58
Whareroa Stream		0.41	0.25	0.74	8	34	19–61
Harataunga Stream		0.28	0.15	0.49	22	32	17–55
Whangarahi Stream		0.35	0.23	0.47	3	48	39–64
Kuaotunu Stream tributary		0.23	0.15	0.34	5	35	21–69
Ounuora River tributary		0.15	0.11	0.17	3	46	30–57
Tairua River		0.22	0.09	0.43	6	40	19–67
Wentworth River		0.27	0.14	0.71	11	31	19–49
Otahu River		0.34	0.13	0.44	6	45	34–59
Mangatoetoe Stream		0.31	–	–	1	36	–
Waitawheta Stream	Brown trout	0.07	–	–	1	22	–
Waipupu River	Rainbow trout	0.11	0.05	0.17	5	30	14–48

Table 4.7: Summary of mercury levels (mg kg^{-1} wet weight) found in shortfinned and longfinned eel samples from Lake Otamangakau and Lake Ellesmere

Area	Eel Species	Number of fish in sample	Mean mercury level (mg kg^{-1})	Minimum mercury level (mg kg^{-1})	Maximum mercury level (mg kg^{-1})
Lake Otamangakau	Longfinned	24	0.07	0.03	0.25
Lake Ellesmere	Shortfinned	30	0.10	0.03	0.25

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4.7 Appendices

Appendix 4.7.1: Shellfish species list

Common name	Scientific name
Mussel	*Perna canaliculus*
Pipi	*Paphies australis*
Rock oyster	*Saccostrea glomerata*
Scallop	*Pecten novaezelandiae*
Whelks	*Penion sulcata*
	Cominella adspersa
Cockles	*Venericardia purpurea*
	Tawera spissa
	Chione stutchburyi
	Bassinia yatei
Ostrich foot	*Struthiolaria papulosa*
	Struthiolaria vermis
White rock shell	*Thais orbita*
Slipper limpet	*Maoricrypta costata*
Olive shell	*Baryspira australis*

Appendix 4.7.2: Marine fish species list

Common name	Scientific name	Commercial size range (cm)
Sand flounder	*Rhombosolea plebeia*	25–45
Yellowbelly flounder	*Rhombosolea leporina*	25–50
Gummy Shark	*Mustelus lenticulatus*	60–100
Red gurnard	*Chelidonichthys kumu*	25–40
Jack mackerel	*Trachurus declivis*	35–50
John Dory	*Zeus japonicus*	30–40
Kahawai	*Arripis trutta*	40–60
Koheru	*Decapterus koheru*	25–40
Leatherjacket	*Parika scaber*	25–35
Yelloweyed mullet	*Aldrichetta forsteri*	20–40
Red mullet	*Upeneichthys lineatus*	15–30
Skate (rough)	*Raja nasuta*	50–60
Snapper	*Chrysophrys auratus*	30–80
NZ sole	*Peltorhamphus novaezelandiae*	25–45
Trevally	*Caranx georgianus*	30–60

Appendix 4.7.3: Freshwater species

Common name	Scientific name
Longfinned eel	*Anguilla dieffenbachii*
Shortfinned eel	*Anguilla australis*
Brown trout	*Salmo trutta*
Rainbow trout	*Salmo gairdnerii*
Inanga	*Galaxias maculatus*
Banded kokopu	*Galaxias fasciatus*
Koaro	*Galaxias brevipinnis*
Giant kokopu	*Galaxias argenteus*
Redfinned bully	*Gobiomorphus huttoni*
Cran's bully	*Gobiomorphus basalis*
Common bully	*Gobiomorphus cotidianus*
Torrentfish	*Cheimarrichthys fosteri*
Smelt	*Retropinna retropinna*
Lamprey	*Geotria australis*
Koura	*Paranephrops planifrons*

CHAPTER 5: Application of Study Findings to Aquatic Resource Management

M. E. Livingston

5.1 Introduction

This chapter examines the application of the findings reported in the previous chapters to the management of streams affected by mine-waste discharges. For effective water quality management the levels at which factors such as sedimentation, heavy metals and acidity start to cause a decline in the health of New Zealand stream communities need to be known. Once determined, they can in theory be used in the determination of water right conditions for mining discharges. Ideally, the conditions should be tailored to the particular stream type and the sensitivity of the particular ecosystem as well as the flows, but usually the only information available is a range of overseas water quality criteria derived in the main from extensive toxicity tests under laboratory conditions on selected organisms (see Chapter 3, Section 3.3).

Such criteria deal simply with materials dissolved in the water column and may bear little relation to the complexity that occurs in the field. Aquatic organisms may be affected by toxic metals received from the water column, from sediments, or through the food chain. Other factors are bioamplification of toxic substances up the food chain, or starvation through death of the primary food source. Organisms which ingest or contact contaminated sediment might suffer metal toxicity even though metal concentrations in the water column were below the toxic level. Human health problems may arise when organisms such as fish and shellfish are consumed.

In the studies reported here it was found that the effects on water quality of drainage from past mining sites varied considerably. This shows that new mining developments should be treated on a case by case basis taking special note of the existing baseline conditions in the catchment. The background levels of heavy metals in uncontaminated Coromandel streams were significantly lower than overseas water quality criteria for the protection of aquatic life so it is considered realistic to use these criteria in managing Coromandel waters. An important aspect of this is recognising that background levels can only be measured satisfactorily in laboratories designed and equipped for the detection of trace concentrations of heavy metals.

Analysis of sediments for biologically available heavy metals may be useful in providing a record of previous heavy metal contamination in the stream. It is also important in interpreting the causes of any stress or impoverishment observed in the aquatic community.

The method used to measure species composition and abundance of macroinvertebrates in the study streams provided a reliable and sensitive means of detecting community stress and impoverishment. Those study streams receiving discharges from past mining sites tended to have stressed or impoverished macroinvertebrate communities even though metal concentrations in the stream waters were mostly lower than recommended water quality criteria. Stress or impoverishment appeared to be attributable to some combination of heavy metal toxicity derived from the sediments and water column but modified in degree by stress from siltation and by amelioration from downstream invertebrate drift. The results warn against assuming that water quality criteria derived mainly in the laboratory will guarantee to protect aquatic life when applied in the field but they are inadequate to support alternative criteria or to identify metals of special concern.

5.2 Management Strategy for the Protection of Water and Soil Values and Human Health in the Coromandel Peninsula

In order to meet legislative requirements to protect water and soil values, and fishery values, it is necessary to ensure that the release of mine-wastes to the aquatic environment is adequately controlled (Lawrence and Smith, 1983). Control procedures will involve the selection of suitable criteria for protection of aquatic life and human health, decisions on the degree of change in aquatic communities that are publicly acceptable, and the setting and monitoring of discharge conditions for any given water.

5.2.1 Selection of criteria

In their discussion of water quality standards to protect aquatic life from toxic substances, Lawrence and Smith (1983) recommend consultation of US EPA water quality criteria (US EPA, 1980). Some of these have since been updated and reviewed (US EPA, 1985). The present studies have shown, however, that impoverishment of fauna can occur when metal concentrations in the water are below the US EPA water quality criteria based on hardness. Even if metal concentrations were controlled at levels around such criteria in the receiving waters, stress and impoverishment of the fauna might still result from metal accumulation in the sediments for example. Low stream alkalinity needs to be taken into account when deriving water quality criteria and there is some justification for calculating criteria on the basis of alkalinity rather than hardness for the Coromandel streams. Criteria for no-effect levels of toxic metals in sediments do not currently exist. However, to specify more stringent water quality criteria without addressing the causal mechanisms is indefensible and is not going to guarantee better protection of aquatic life.

The present studies have suggested that impoverishment may have been in part due to the physical effects of metal floc and fine particles on the stream bed. Lawrence and Smith (1983) recognise the damaging effects of excess sediment loads. They provide guidance in terms of minimising sediment release to streams and recommended limits for suspended solid concentrations. However, the relationships between suspended solids, sediment deposition on the stream bottom, and any resultant impoverishment of aquatic fauna have yet to be determined.

5.2.2 Acceptability of change to aquatic community

Another important consideration in setting water rights is the degree to which stress or impoverishment of aquatic fauna is publicly acceptable. Where human health is concerned, the position is clear-cut; human health should not be in any way compromised. Where ecosystem health is concerned, however, there are no well defined criteria of acceptability. The requirement set out in the Water and Soil Conservation Act 1967 schedules that "there shall be no destruction of natural aquatic life by reason of a concentration of toxic substances" may be unenforceable since it does not adequately identify the processes by which ecosystems respond to natural or man-made change. Biological responses can include selective mortality, reduced abundance, altered competitive selection of species, excessive growth of certain species assemblages, inferior condition leading to reduced breeding capacity or disease, and genetic change. The problem is what constitutes 'destruction' and how it can be detected and measured in a way that quantitative links can be made with the level of toxicant. At present, no accepted methods exist for New Zealand use. The use of biological parameters which can be measured such as abundance, species diversity and community structure provide a useful approach to measurement, but it is still necessary to define the degree of change in such parameters which constitutes 'destruction'.

In the stream biology study (Chapter 3) the following definitions of stress and impoverishment were used:

Stressed: Where abundance of organisms was 100 or less individuals per 0.053 m^2 sample, and the average number of taxa per sample was 20–50% lower than expected.

Impoverished: Where abundance of organisms was 50 or less per 0.053 m^2 sample, and the average number of taxa per sample was 50–100% lower than expected.

These definitions are specific to the sampling method and the Coromandel streams studied, but similar or better ones could be generated for other systems provided that their biology was adequately understood.

The community interest groups, water managers and dischargers will need to consider the degree and type of change in an ecosystem that a discharge should be allowed to cause, bearing in mind that the levels agreed upon should be reasonably detectable against natural variation. This would form the basis for any biological monitoring programme and help in its design.

5.2.3 Setting and monitoring water right conditions

The matching of acceptable levels of stress in the aquatic community with the allowable load of heavy metals on the aquatic system presents the most difficult challenge. With the current state of knowledge it is not possible to do this. Water right conditions cannot be set with the certainty of how well, if at all, the desired results will be achieved.

It is proposed that the most satisfactory approach to setting water right conditions for toxic materials at present is to continue to use or take account of substantiated water quality criteria to set the discharge conditions, and alongside this to establish the degree of ecosystem stress that is acceptable. The receiving waters and stream ecology would then be monitored to determine how well the system is responding. The discharge parameters would be revised if necessary. By this process, appropriate discharge levels could be arrived at iteratively over a period of time.

A typical management strategy would be as follows:

1. Determine the relevant measurable characteristics of the receiving water body, including expected species presence, their abundance, and if appropriate, the concentrations of potential toxicants in their tissues.

2. Ensure that concentrations of toxicants in discharges are set initially so as to take account of accepted water quality criteria for receiving waters.

3. Examine other favourable/unfavourable factors that may minimise or emphasise the impacts of mine wastes in the stream and modify the allowable levels of toxicants if necessary.

4. Establish the level of change in the aquatic community that is acceptable in terms of the biological and other properties defined in (1) above and design a monitoring programme accordingly.

5. Monitor these properties after discharges begin and assess the effectiveness of the applied control in protecting the desired instream values.

6. Redefine water right conditions (or acceptability parameters) as necessary.

5.3 Research Needs and Directions

These studies indicate that stream organisms can be impoverished where water concentrations of toxic metals are lower than accepted criteria (ie, US EPA). One possibility is that metals are having a toxic effect through the sediments. The sources of toxicity to impoverished stream communities therefore require further investigation. Also required is experimental work to isolate the relative effects of sediment deposition, iron floc and metal contamination on stream ecology. Better information is required on the stream faunas expected to occur under a range of stream environments so as to provide a baseline against which streams suspected of impoverishment can be compared.

Drift and its contribution to the observed ecology of a stream, and the sensitivity of different age classes and life stages to toxic materials needs to be understood. Methods for routine monitoring of possible biological changes downstream of discharges containing heavy metals need to be developed. Methods for monitoring the sources of metals in the flesh of fish and shellfish, and bioaccumulation by key food chain organisms, also need to be developed.

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