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Heavy Metals in the New Zealand Aquatic Environment: A Review

National Water and Soil
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Heavy Metals in the New Zealand Aquatic Environment: A Review

by

D. G. Smith

Technical Editor

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Private Bag, Hamilton

WELLINGTON 1986

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This review attempts to put into perspective the effects of past and present discharge of heavy metals into the New Zealand aquatic environment.

The sources of heavy metals are briefly described and concentrations of metals that have been found for geothermal, precipitation, weathering and erosion, agricultural and urban land use, sewage, refuse tip, and industrial inputs are summarised.

A national perspective of natural background levels of metals in water, sediments and biota is attempted, drawing on overseas data where New Zealand information is lacking. Concentrations of metals found in the New Zealand aquatic environment are summarised on a regional basis.

Overseas metal criteria and standards for the protection of human health, aquatic life, stock and irrigation are described and compared.

To aid in the understanding of the information presented in this review, there are chapters on the biology and chemistry of heavy metals in the aquatic environment, and sampling and analytical methods.

Recommendations are made to improve management of heavy metal discharges. Areas for further study are also suggested.

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PREFACE

The aim of this document is:

To review all information relevant to heavy metals in the New Zealand aquatic environment and to identify appropriate future studies.

The objectives are:

(i) To review all available published and unpublished data on heavy metals in the New Zealand aquatic environment with special reference to the relationships between levels in the physical environment and levels in biota.
(ii) To identify gaps in the data pool and recommend appropriate studies to fill them.
(iii) To gauge the implications of the review for water management and to recommend appropriate action.

In August 1983, the (then) Water Resources Council approved the production of the following reviews by staff of Water and Soil Division of the Ministry of Works and Development (MWD):

A The existing baseline information on heavy metals in rivers, streams, and coastal waters.
B The discharges containing significant quantities of heavy metals.
C Biological surveys of waters receiving discharges of heavy metals.

This review contains the information required in A, B, and C, above. To assist in the review, Council approved (December 1983) the involvement of Cawthron Institute, Dr M. F. Larcombe (Bioresearches Ltd), and Mr P. C. Kennedy (University of Auckland), by way of consultancies. Many others were requested to submit information for inclusion and ‘open’ letters requesting information were placed in *Soil and Water* and *Chemistry in New Zealand*. The use of such letters was singularly unsuccessful. Much of the information received was by way of personal contact and the majority in ‘raw’ form. Very little interpretation of data was received and this made production of the review very much more difficult.

Prior to the approval of the above reviews a two day workshop on heavy metals in the aquatic environment was held in Wellington in March 1983, by Water and Soil Directorate. Attendance was by invitation and based on an individual’s known expertise and work experience in the field of heavy metals pollution. Twenty-three people were present of whom one was a private consultant; the remainder represented Water and Soil, and Civil Directorates of MWD; Chemistry, and Marine and Freshwater Science Divisions of the Department of Scientific and Industrial Research; Fisheries Management Division, Ministry of Agriculture and Fisheries; Department of Health; Hauraki Catchment Board; Waikato Valley Authority; Taranaki Catchment Commission; Otago and Waikato Universities. Most of the participants presented a discussion paper indicating the current and likely future positions of their organisations (and themselves) with respect to heavy metals.

The objectives of the workshop were to ascertain:

(a) the scope of the perceived problems in the New Zealand aquatic environment;
(b) the work being undertaken;
(c) the research and surveys which ought to be carried out.

Numerous ideas for research and surveys were discussed and after the workshop they were summarised and forwarded in a questionnaire to participants for priority ranking. Also asked were questions concerning the nature and extent of the current and possible future problems.

The conclusions of the workshop are summarised below.

1. Most replies suggested minor existing and potential problems. Public perception of problems was raised and allaying unnecessary fears of problems were seen as real issues.
2. The possibility of long-term effects was frequently raised but there was little hard evidence presented to demonstrate whether or not metals were actually causing such problems.
3. Eight metals were identified as being of potential importance viz., As, Cd, Cr, Cu, Hg, Ni, Pb, Zn.

4. With respect to work priorities, there was a wide variety of responses for each study area reflecting individual preferences. However, certain topics tended to be favoured and those ranked with averaged priorities ‘essential and urgent’ to ‘necessary but longer term’ are:
    (i) baseline (background) heavy metal concentrations in selected rivers, streams, and coastal waters;
    (ii) review of discharges containing ‘significant’ quantities of heavy metals;
    (iii) investigation of the adequacy of overseas standards and criteria;
    (iv) methodology to derive water rights conditions;
    (v) biological surveys of waters receiving discharges of heavy metals.

CONTENTS

Note: All sections in this publication were written by D. G. Smith unless otherwise stated in the section concerned.

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Special thanks go to Dr R. B. Williamson who, besides contributing several sections, provided much valuable comment in technical editing of this publication.

The document was reviewed and edited by Dr R. H. S. McColl and Mr M. E. Yates (MWD, Head Office) and by Dr J. B. Macaskill (MWD, Water Quality Centre). Their role in providing many valuable suggestions for improvement is acknowledged with thanks.

The sterling efforts of Mrs M. L. Stokes on the word processor are acknowledged with much gratitude.

D. G. Smith

Chapter 1

INTRODUCTION

(D. G. Smith and R. B. Williamson)

Heavy metals are sometimes defined as metals having a density greater than 5 g/cm^3. This classification includes transition elements and the higher atomic weight elements of groups III to V. Arsenic is also included although it is probably best classified as a metalloid. A workshop held in Wellington in 1983 (see Preface) concluded that arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) were of prime concern in New Zealand. This review focuses on these metals.

It is convenient to divide heavy metals into two classes: essential and non-essential to life. Essential elements follow the general trend that an undersupply to an organism leads to deficiency (and hence a failure to grow or complete its life cycle), sufficient supply results in optimum conditions, and an oversupply results in toxic effects and possibly death (Figure 1.1a). Non-essential elements can never be in deficiency but at low concentrations they are tolerated by organisms. At higher concentrations they become toxic (Figure 1.1b). All heavy metals are potentially toxic.

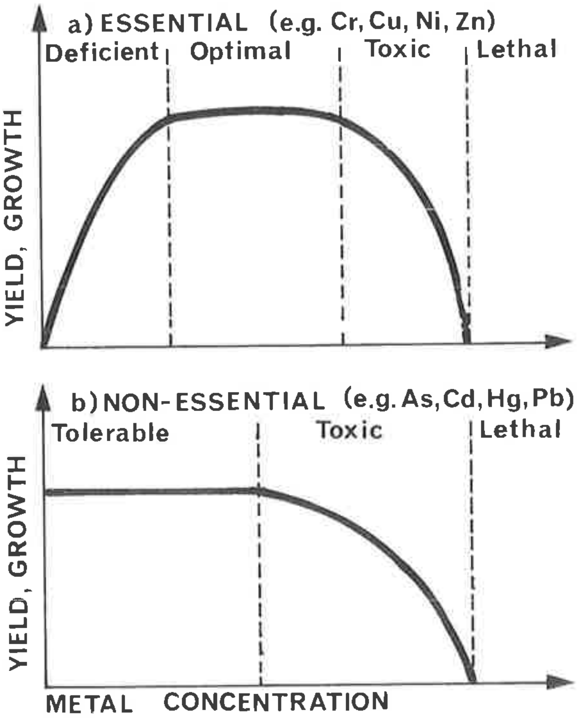


Figure 1.1: Deficiency and oversupply of essential and non-essential trace elements (from Forstner and Wittmann, 1983)

Concentrations of heavy metals in water which are protective of aquatic life are usually much lower than those required to protect human consumers of the water. The latter are derived from considerations of safe body burdens, and safe concentrations for drinking water are based on the proportion of metals ingested via water. On the other hand, aquatic animals are continually immersed in the water, and some are filtering it.

Heavy metals enter water bodies by a variety of routes, of both natural and anthropogenic origin (e.g., discharges from industry, dumps, stormwater). They have received considerable public attention lately, partly because of concern that they will cause long-term damage to the aquatic environment. Such long-term damage can be due to high concentration pollution, produced over a short time, remaining in one place, or due to low concentration, insidious pollution requiring considerable time to produce an effect. Insidious effects are difficult to measure and establish with certainty and public concern often surrounds activities which are thought to have the potential to cause such effects.

These concerns have presumably arisen out of overseas incidents such as the Minamata Bay disaster in the early 1950s (due to a Hg discharge), 'itai-itai' disease (due to a discharge of Cd), and Pb poisoning due to, for instance, Pb plumbing. In New Zealand, contamination of sediments in, for instance, Otago Harbour and the Hutt River estuary by uncontrolled industrial discharges, and the polluting of some streams in Coromandel by inadequately managed mining activities have exacerbated such concerns. These examples are fairly obvious, but it is the less obvious low concentration pollution which also gives rise to public concern. To show an absence of such possibly very long-term effects is probably impossible. Mackay (1982) summarised problems due to possible long-term insidious effects with the following comment: 'The primary problem with assessment of toxic effects as illustrated in (Figure 1.2) is that the exposure levels are often orders of magnitude below those which cause obvious adverse effects such as death. There is often need for extrapolation of the response data into regions which are experimentally impossible for statistical reasons (i.e., natural variation exceeds the effect), and in which the knowledge about the extent or existence of the toxic event may be simply inaccessible.' This review attempts to put the 'problem' into some sort of perspective.

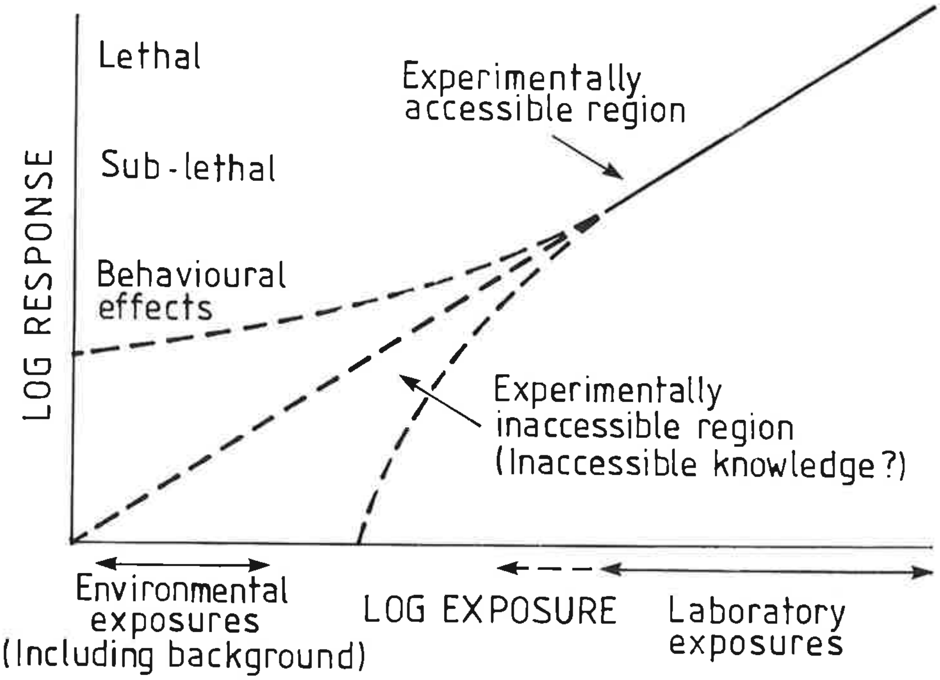


Figure 1.2: Schematic plot of log response as a function of log exposure (after Mackay, 1982).

To fulfil the aim and objectives outlined in the Preface, this review presents separate chapters on:

Sources of heavy metals in New Zealand (Chapter 4).
Overseas criteria and standards and their application in New Zealand (Chapter 5).
New Zealand data on heavy metal concentrations in water, sediments, and biota (Chapter 6).

To aid readers unfamiliar with the environmental implications of heavy metals, there are chapters briefly reviewing:

The chemistry and biology of heavy metals (Chapter 2).
Sampling and analytical methods (Chapter 3).

Neither of these is essential reading before approaching the other chapters.

The review concludes with a summary of:

Known past and present pollution in New Zealand, and recommendations for further scientific research and survey (Chapter 7).

Chapter 2

BIOLOGY AND CHEMISTRY OF HEAVY METALS IN NATURAL WATERS AND SEDIMENTS

Although the presence of heavy metals in the aquatic environment may be of concern for reasons of human and animal health, the main focus in this chapter is on the effects on aquatic biota. The following sections briefly summarise aspects of biology and chemistry relevant to this issue. The biology section introduces the processes which take place within the biological domain. Following this, the chemistry of heavy metals in soils, waters and sediments is summarised with an emphasis on the chemical species most likely to affect toxicity to aquatic biota.

2.1 **Biology** (M. F. Larcombe)

All aquatic organisms concentrate heavy metals from their surrounding waters, sediments, or food and it is important to recognise that this is a universal and often essential process. Metal levels in aquatic organisms (based on overseas data) have been summarised by Bryan (1976) and Forstner and Wittman (1983). A selection from Bryan (1976) is presented in Table 2.1. New Zealand derived information is presented in Chapter 6, and comparisons are made there with the data in Table 2.1. Table 2.1 should be used with some caution bearing in mind that the data are geometric means and that very wide (order of magnitude) natural variations in concentration are often found (see for instance Nielsen and Nathan, 1975; Nielsen, 1974; Bryan, 1973).

Eleven heavy metals are known to be essential for aquatic life viz., Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se, Ni, Sn (Bryan, 1976). These metals are seldom limiting in natural aquatic systems, and most organisms concentrate greater quantities of metals than they actually require. Other metals, such as Ag, Cd, Hg and Pb are not regarded as essential to life (Bryan, 1976) but these too are bioconcentrated.

Different forms of trace metals are concentrated to differing extents by aquatic organisms. In many cases it has been demonstrated that the free ionic form is more readily concentrated and hence more toxic, than particulate or complexed forms (e.g., Luoma, 1983).

Some metals e.g., As and Hg are methylated by bacteria (EPA, 1979a) and these organic compounds are taken up quickly from solution by biota because they are more lipid-soluble than inorganic compounds. Methylated metals are also readily available to higher consumers when present in the diet. Biomethylation has also been shown to occur with Sb, Se, and Sn but the implications for biota have not been established.

The geochemical partitioning of a number of important trace metals in particulates will be described in Section 2.2. The uptake of metals from sedimentary particulates will depend upon the digestive conditions of the animal (e.g., pH, presence of other competing elements, complexing agents) as well as the form of the metal, with those metals present in ion-exchangeable and easily reducible forms expected to be more available.

2.1.1 Bioconcentration (Bioaccumulation)

Bioconcentration (bioaccumulation) is a process whereby organisms concentrate metals from their surrounding medium or food. The concentration of a metal in an organism is the product of an equilibrium between the concentration of the metal in an organisms environment and its rates of ingestion and excretion. Many organisms are able to regulate the concentrations of metals in their tissues (and hence toxic effects) by controlling absorption, excretion, and depuration rates, or by detoxification either by changing the metal to a less toxic form or by storage at sites in the body where the metal does not have an adverse effect. The ability of marine invertebrates to detoxify

Table 2.1: Geometric mean concentrations of metals (mg/kg dry weight) in different organisms (excluding mollusc shells) (Bryan, 1976). Samples taken from areas not known to be contaminated by metals

	Plants		Filter-feeding groups				50-50 carnivorous and herbivorous or particulate feeders		Basically carnivorous groups			
Metal	Seaweeds (all types)	Phytoplankton	Zooplankton (copepods)	Tunicates (mainly ascidians)	Bivalve molluscs	Oysters	Gastropod molluscs	Echinoderms	Decapod crustaceans	Coelen-terates	Cephalopod molluscs	Fish
Ag	0.2	0.2	<0.1	–	0.3	6	1	1	0.4	0.03	1	0.1
As	20	–	–	5	15	10	20	5	30	20	40	10
Cd	0.5	2	4	1	2	10	6	2	1	1	5	0.2
Co	0.7	<1	<1	2	1	0.3	1	0.4	0.2	0.5	0.1	0.1
Cr	0.9	1.5	<1	*	1.5	1.5	1	0.4	0.3	0.4	0.1	0.5
Cu	15	7	10	30	10	100	60	10	70	10	130	3
Hg	0.15	0.17	0.1	0.1	0.4	0.4	0.2	0.3	0.4	0.1	0.3	0.4
Ni	3	3.2	2	8	3	1	2	2	1	3	0.1	1
Pb	4	4	3	2	5	3	5	2	1	10	3	3
Sb	0.1	–	–	0.1	0.05	0.01	0.05	0.02	0.02	0.03	0.02	0.02
Se	0.1	–	–	–	3	2	–	–	4	–	3	1
Sn	1	3	–	4	0.5	7	0.3	0.2	2	2	0.4	–
V	3	<3	<3	70	2	2	0.1	1	2	3	0.4	1
Zn	90	38	113	200	100	1700	200	100	80	50	250	80
% dry wt	~20	–	~11	~5	~20	~20	~20	22-54	~30	3-19	~25	~25

* Two values of 0.8 and 108

some metals, or sequester them in a manner in which they do not poison the animal itself, can lead to considerable build up of metals in some marine foods.

Rates of metal uptake are dependent on the form of the metal and its concentration. Some organisms have mechanisms to prevent the uptake of certain forms of metals, or to restrict uptake when a certain tissue concentration is reached. The length of time metals stay within living organisms is highly variable.

It is common for metal concentrations in an organism to increase with increasing age, notwithstanding the ability of the organism to regulate metals concentrations (Bioresearches, 1982). Regional and even local variations are to be expected as a result of variation in geology, input of metals, hydrology, and anthropogenic effects.

2.1.2 Biomagnification (Bioamplification)

Increases in the concentration of elements at higher trophic levels is termed biomagnification (bioamplification). It is not commonly found for heavy metals in the aquatic environment (Bryan, 1976; Forstner and Wittman, 1983) but it has been shown to occur in some instances between two successive trophic levels (Patrick and Loutit, 1978; Loutit *et al.*, 1973; Patrick and Loutit, 1976; Johnson *et al.*, 1981). However, it does not normally occur over several successive trophic levels and therefore does not result in large concentrations or body burdens of metals in predators.

The slight biomagnification of Hg by fish (van den Broek and Tracey, 1981; van den Broek *et al.*, 1981) is probably the most important example of biomagnification of metals in New Zealand. Many of the larger fish-eating fishes accumulate Hg to a flesh concentration which is close to, or exceeds, the New Zealand Food Regulations limit of 0.5 mg/kg wet weight (see Table 5.4). For North Atlantic hake, this elevation has been shown to be a result of natural processes, not twentieth century industrial pollution (Barber *et al.*, 1984).

2.1.3 Biotransformation and Other Biological Effects on Availability of Metals

The ability of bacteria to transform metals into different chemical forms was mentioned earlier. The most common type of biotransformation of heavy metals is methylation (EPA, 1979a). Methylation of mercury sulphide in sediments mobilises Hg making it available to aquatic organisms. Methyl mercury is the most readily accumulated and retained form of Hg in aquatic organisms (EPA, 1979a; Forstner and Wittman, 1983) and is the most common form present in fish tissue, being accumulated from both water and food.

The burrowing activity and pumping of water through sediments by a range of invertebrates can increase the rate of metals recycling from sediments.

The breakdown of organisms results in the formation of dissolved and particulate organic material which can then form complexes with metals. Metals present as organo-metallic complexes are often soluble, mobile, and available to aquatic organisms.

2.1.4 Toxicity

A very large body of scientific literature is devoted to the toxic effects of metals on aquatic organisms. Most toxicity data are derived from laboratory experiments with single metals under conditions which are usually not representative of the natural aquatic environment. A good review of the toxicity of metals to marine organisms was prepared by the Taranaki Catchment Commission (TCC, 1981). Various water quality criteria documents (see Chapter 5) contain reviews of metal toxicity effects.

The toxicity of a metal is usually defined in terms of the concentration required to cause either an acute response (usually mortality), or a sublethal response, by 50% of a test population for exposure of a specified duration. Toxicity testing is usually undertaken under controlled laboratory conditions in which organisms are continuously exposed to constant toxicant concentrations for standardised experimental periods. There are very little toxicity data available for organisms exposed to toxicants in natural environments. Some acute toxicity data for New Zealand organisms were derived by the Taranaki Catchment Commission (TCC, 1981).

Common sublethal responses of aquatic organisms to increased heavy metals concentrations are inhibition of growth, inhibition of settlement by marine invertebrate larvae, and interference with reproduction, metabolism, and behaviour.

Factors that can influence the toxicity of a metal include its chemical form and concentration. These will depend on a wide range of environmental variables such as temperature, dissolved oxygen concentration, pH, hardness, salinity, suspended solids concentration, and presence of other toxicants, organic material etc. (EPA, 1979a). The toxicity to an organism also varies with the stage of life cycle, nutritional condition, physiological condition, and environmental level of the toxicant to which the organism is acclimatised. Toxicity is also a function of exposure time.

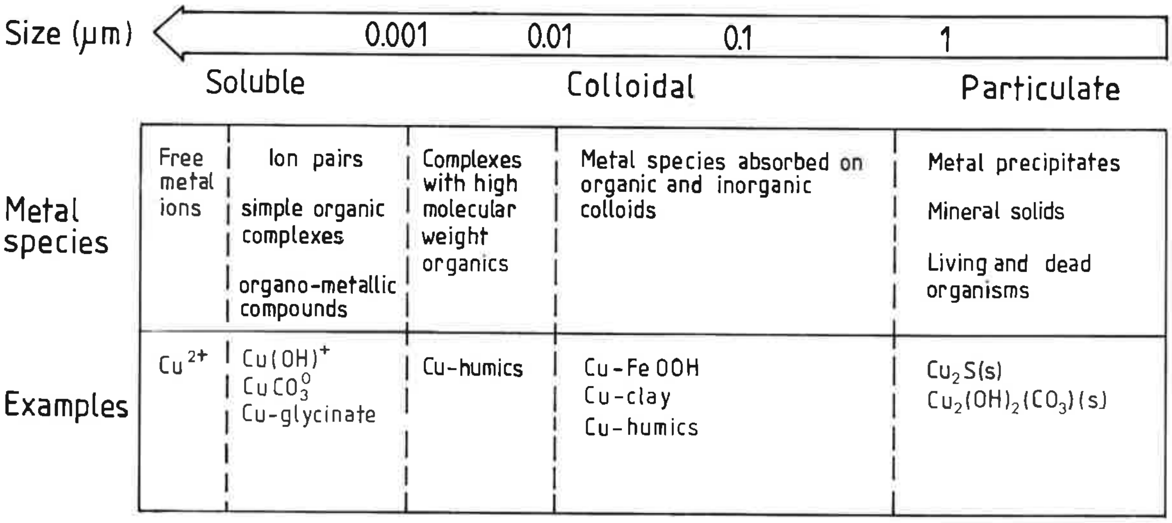
A metal may have different types of biological effect at different concentrations. For example, at high concentrations a metal may kill by disrupting respiratory surfaces, whereas at lower concentrations it may be lethal only when sufficient time has elapsed for it to be accumulated to a lethal level in internal organs.

The metals Ag, Cu, Cd, Hg and Pb are particularly toxic, and usually inhibit enzymes by forming mercaptides with the sulphydryl groups which are responsible for catalytic activity (EPA, 1979a).

Synergism is not common for mixtures of two or more metals and the toxicity of metals in mixtures is normally approximately additive (EIFAC, 1980). It seems as though metals, if they are present at concentrations lower than their individual no-effect levels, do not contribute to the toxicity of a mixture, i.e., they have no effect either singly or in mixtures (EIFAC, 1980).

2.2 **Chemistry** (D. G. Smith and P. C. Kennedy)

In natural waters, dissolved metals can form a wide variety of complexes. For instance, taking Cu as an example, complexes can form with water itself (e.g., $Cu(H_2O)_6^{2+}$ often simplified to Cu^{2+}) inorganic ligands (e.g., $CuCO_3^0$, $CuCl_3^-$, $Cu(OH)^+$, $Cu(OH)_2^0$), and organic ligands (e.g., Cu-humic acid complexes). If the concentration of metal is sufficiently high, precipitates can form (e.g., $Cu(OH)_2$, $Cu_2(OH)_2CO_3$). In heterogeneous systems, the chemistry of metals is further complicated by adsorption onto sediments (suspended or bottom), colloidal and plant materials, and also by formation of co-polymers. The most important adsorbing components are organic matter and iron and manganese hydrous oxides. Although the chemistry of metals in simple aqueous systems is fairly well characterised, in complex natural systems the interaction with naturally occurring organic compounds and particulate material is much less understood. An indication of some of the possible physico-chemical forms of metals in water classed according to their size, is given in Figure 2.1 using Cu as example. When analysing waters, the convention is to distinguish between 'dissolved' and 'particulate' metal by passing the water through filters (often with 0.45μm pore size). This distinction is arbitrary, as indicated by Figure 2.1, and the species are not really defined by this process. This method remains in general use, nonetheless, because it is simple and there is no analytical way to rigorously define the different metal species. Most existing techniques can only group together broad classes of species (Laxen, 1983), they are complicated, and require specialised apparatus (see Section 3.1).



Metal species	Free metal ions	Ion pairs simple organic complexes organo-metallic compounds	Complexes with high molecular weight organics	Metal species absorbed on organic and inorganic colloids	Metal precipitates Mineral solids Living and dead organisms
Examples	Cu^{2+}	$Cu(OH)^+$ $CuCO_3^0$ Cu-glycinate	Cu-humics	Cu-Fe OOH Cu-clay Cu-humics	$Cu_2S(s)$ $Cu_2(OH)_2(CO_3)(s)$

Figure 2.1: Examples of metal forms in water classified according to size (after Laxen, 1983).

The availability of metals to biota (i.e., the proportion of metal which can be taken up by an organism, with possible toxic effects) depends on the form the metal is in. Because it is probable that the most toxic form of many metals is the free ion, it is desirable to have an understanding of the implications of metal speciation in natural waters. While acknowledging that the chemistry of metals in natural waters is very complex, it is possible to derive some broad generalisations. For instance, metal speciation within a water body will be influenced by the water's pH, Eh, concentration and types of organic and inorganic ligands and particulate surfaces. These will vary considerably between different receiving waters. A proportion of, say, a dissolved metal discharged to a natural water will remain in dissolved form (see Figure 2.1), some may be precipitated and a proportion may be adsorbed onto particulate material. In most natural waters, only a very small proportion of most metals will be in the free metal ion form (e.g., Cu^{2+}). High pH and alkalinity, and high concentrations of organic and inorganic particulate material will all lower the free metal ion concentration.

Because of the interaction of many competing effects and the lack of the necessary data, it is rarely possible in practice to precisely predict speciation in natural waters. However, in general, adsorption can be expected to occur rapidly and to reduce by a large proportion the concentration of dissolved trace metal (WRC, 1976). The majority of metal transported by rivers will be in the particulate phase.

Metal adsorbed on the sediments can be regarded as isolated from the water column, with two important exceptions. Biological methylation has been demonstrated for some metals (e.g., As and Hg) and these elements can therefore be liberated from the sediment in a very toxic form. Secondly, suspended particles encountering saline water in an estuary would tend to release some adsorbed metals, particularly those forming stable chloride complexes (e.g., Hg and Cd). However, even in the more saline conditions of the open sea the equilibrium between adsorbed and dissolved metal favours adsorption (WRC, 1976).

Several reviews of heavy metal chemistry in the aquatic environment are available, e.g., Hart (1982), EPA (1979a), Florence and Batley (1980), Moore and Ramamoorthy (1984), and Forstner and Wittmann (1983), from which further details may be obtained. The remainder of this section contains some detailed information on the chemistry of As, Cd, Cu, Cr, Hg, Pb, Ni and Zn.

2.2.1 Arsenic

Arsenic can exist in the metallic (As(0)), trivalent (As(3+)) and pentavalent (As(5+)) states in a variety of minerals. As(0) occurs in arsenide minerals in sulphidic ores, and As(3+, 5+) in a number of arsenite and arsenate minerals (Boyle and Jonasson, 1973; NAS, 1977). During weathering, As is released primarily as soluble arsenates and generally (under neutral or alkaline conditions) As is then immobilised by co-precipitation with hydrous iron oxides (NRC, 1978).

Arsenic can occur in soil as an impurity in minerals, complexed with organic matter or adsorbed onto clays, and in organic material. The chemistry of As in soil is very similar to that of phosphorus especially under aerobic conditions with the arsenate ion resembling orthophosphate (Walsh *et al.*, 1977). Sorption phenomena appear to immobilise As compounds in soil.

As(0) will not normally be found in natural waters. The As cycle in natural waters has been reviewed by Fergusson and Gavis (1972), and the analysis, occurrence, and significance of As has been reviewed by Penrose (1974). In New Zealand, Aggett and O'Brien (1985) have recently studied the chemistry of As in lacustrine sediments and overlying waters.

Arsenate, As(5+), is thermodynamically favoured over arsenite, As(3+), in well oxygenated fresh waters and occurs mainly as $H_2AsO_4^-$ and $HAsO_4^{2-}$. Studies in New Zealand (Aggett and Aspell, 1980) have confirmed that the common oxidation state in freshwater is As(5+) but on occasions considerable amounts of As(3+) were detected, presumably as a consequence of biological activity.

Under mildly reducing conditions, arsenious acid species (H_3AsO_3 and the arsenites $H_2AsO_3^-$ and $HAsO_3^{2-}$) are formed. Sulphides of As and arsine (AsH_3) are the thermodynamically favoured forms at low pH and under strongly reducing conditions. In fresh water the oxidation of arsenite to arsenate occurs slowly at neutral pH, while methylation of arsenic to methyl and dimethylarsine by methanogenic bacteria is known to occur (EPA, 1980a).

The concentration of arsenates and arsenites in natural waters will be controlled by co-precipitation or adsorption on to particles, especially ferric oxide (Crecelius *et al.*, 1975). Arsenite can also be scavenged by co-precipitation or adsorption and is readily adsorbed on to metal sulphides. About 20% of the total As in fresh water from the Waikato River was found to be retained on a 0.8-1.0 μm filter (Reay, 1973).

Aggett and O'Brien (1985) have shown that the As cycle is dominated by inorganic processes in the organic rich sediments of Lake Ohakuri. Provided that surficial sediments remain oxic, any As(3+) released to interstitial waters is then immobilised by adsorption onto hydrous iron oxides near the sediment surface.

A diagram showing the As cycle in a stratified lake is given in Figure 2.2.

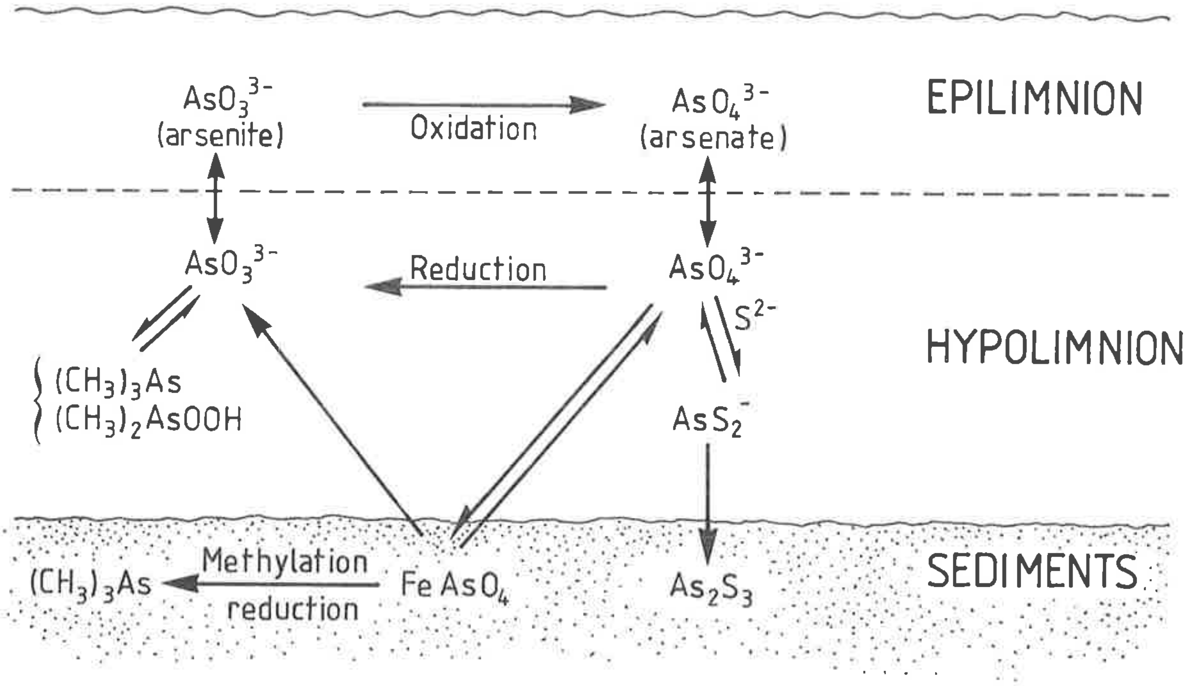


Figure 2.2: A simplified arsenic cycle in a stratified lake (after Ferguson and Gavis, 1972; and Hart, 1982).

Arsenic in sea water is present as As(5+) and (3+), the ratio of As(5+) to As (3+) ranging from 15:1 in aerobic water to 1:12 in anaerobic water (Peterson and Carpenter, 1983). Thermodynamically, As(5+) should completely predominate over As(3+) in seawater and the disequilibrium of As species is thought to be due to bacteria reducing arsenate to arsenite (and dimethylarsenic) under normal aerobic conditions (Reay, 1973; Johnson, 1972; Waslenchuck, 1978).

2.2.2 Cadmium

The most general soil mineral containing Cd (as an impurity) is biotite. Cd is often associated with Zn and is abundant in zinc sulphides (e.g., sphalerite ZnS) (Peterson and Alloway, 1979). In well aerated soils, adsorption by hydrous manganese and iron oxides could be important. In badly drained reduced soils, the precipitation of CdS in the presence of sulphide is likely to occur. Organic complexes of Cd may be important in some soils (Peterson and Alloway, 1979).

Compared with other trace metals, Cd is relatively mobile in the aquatic environment and is less readily removed by adsorption and complexation. In fresh water, Cd is present predominantly as the free ion (Cd^{2+}) with the remainder as bicarbonate and humic species (Mantoura *et al.*, 1978).

The marine chemistry of Cd has been reviewed by Eaton (1976). Cd is calculated to be strongly associated with Cl^- in a variety of chloro complexes in the marine environment (Hart, 1982) in addition to a small component possibly associated with iron oxide particulate phases in bulk sea water (Mantoura *et al.*, 1978).

Cd can be co-precipitated with calcium carbonate and has been found in large proportions in the carbonate phase of sediments (Forstner *et al.*, 1978; Rapin, 1983). Cd is also found in sediments associated with organic or sulphide phases, and with iron and manganese oxides and hydroxides (Gupta and Chen, 1975). Increasing anthropogenic Cd loadings appear to become incorporated into the Fe-Mn oxide phase of sediments (Viel *et al.*, 1981). Except in sediments rich in organic matter, Cd in sediment pore waters is generally present as labile complexes (Abdullah and Reusch-Berg, 1981).

2.2.3 Chromium

Cr is never found in nature as a pure metal. The most common Cr containing soil minerals are the spinels of which chromite (a mixed oxide of Cr(3 +) and Fe(2 +)) is the most common. These Cr bearing minerals are virtually inert.

Cr(3 +) is the dominant form of Cr in most soils and tends to be strongly adsorbed to inorganic and organic particles, but can be mobilised if complexed with organic molecules. Cr(6 +) is not strongly adsorbed by soil components, and in soils with poor drainage and abundant organic matter it is rapidly reduced to Cr(3 +) (as the poorly soluble $Cr(OH)_3$) (de Haan and Zwerman 1979). Under alkaline soil conditions Cr(6 +) will be more mobile and will be reduced to Cr(3 +) more slowly (Cary *et al.*, 1977).

In the aquatic environment, Cr is known to exist only as Cr(3 +) and Cr(6 +). In aerobic waters Cr(6 +) is thermodynamically more stable than Cr(3 +) and will nearly always be in the form of the anions CrO_4^{2-} and $Cr_2O_7^{2-}$ (NRC, 1976). Cr(6 +) does not readily form complexes with anionic particulate material and is therefore more mobile than Cr(3 +). However, there is a tendency for Cr(6 +) compounds to react with oxidisable substances to form Cr(3 +). Cr(3 +) attains its minimum solubility in the pH range covered by natural fresh waters. Thus, accumulation would probably occur in sediments where chemical equilibria favour the formation of Cr(3 +), while Cr(6 +), if favoured, would presumably dissipate in soluble forms (EPA, 1980c).

The presence of MnO_2 in both fresh water and sea water helps to oxidise Cr(3 +) via adsorption, surface oxidation and desorption. This process is much slower in sea water than in fresh water (van der Weijden and Reith, 1982).

Studies in Otago Harbour (Smillie *et al.*, 1981), have confirmed the role of sulphate-reducing bacteria in the reduction of Cr(6 +) to Cr(3 +) in sea water. Cr was found to then accumulate in the sediments and not to dissipate as the more soluble Cr(6 +).

The dissolved Cr(6 +) content of the ocean surface water is maintained low because of its interaction with organic particles (adsorption), the formation of insoluble hydroxides or interaction with living organisms. The Cr(6 +) is replenished by inputs from fresh water. Organic Cr(3 +) complexes are very stable. The ratio of inorganic Cr(6 +) to Cr(3 +) averaged 2.7 in the Pacific Ocean (Nakayama *et al.*, 1981).

About one half of the Cr in sediments was found to be associated with the hydroxide (reducible) phase, with a small amount associated with either sulphide (or organic matter) or exchangeable, and the remainder with the residual matter (at least 50%) (Gupta and Chen, 1975; Forstner *et al.*, 1978; Gibbs, 1977; Rapin, 1983). There is no Cr-carbonate phase in aquatic systems.

A model of Cr speciation in sea water is presented in Figure 2.3.

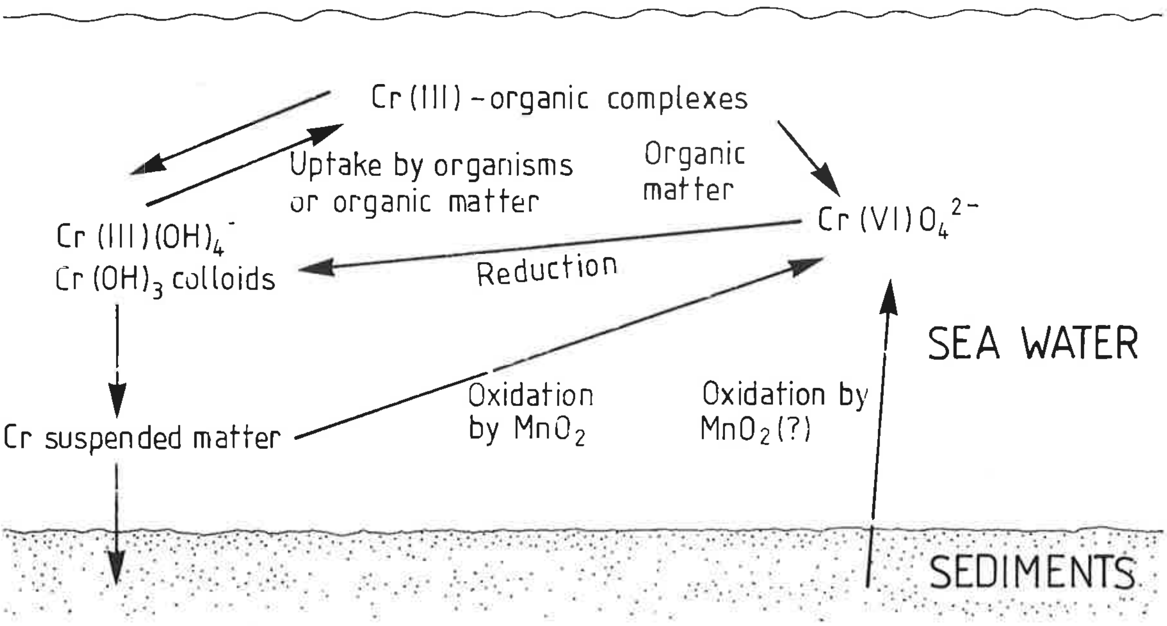


Figure 2.3: A model of the chromium cycle in the ocean (based on Hart, 1982).

2.2.4 Copper

Cu is found in the chalcophile or sulphidic phase of igneous rocks. Large proportions of the Cu in some soils and sediments can be present in relatively inert minerals such as titanomagnetites.

Under reducing conditions, formation of Cu(1 +) producing insoluble Cu_2O (cuprite) is favoured, whereas under oxidising conditions the formation of soluble Cu^{2+} is favoured. The chemistry of Cu in soils is reviewed in detail by McBride (1981).

In aerobic fresh waters Cu(2 +) is thermodynamically favoured. The hexa-aquo (or free) Cu^{2+} ion dominates at pH <5, but as the pH increases the contributions of $CuCO_3$, $Cu(CO_3)_2^{2-}$ and $Cu(OH)^+$ increase depending upon the total carbonate content of the water. However, recent work indicates that a large amount of Cu in fresh water can be found associated with humic or other organic materials (Mantoura *et al.*, 1978; Batley and Gardner, 1978). In the estuarine mixing zone, the level of dissolved Cu is expected to increase as a result of the desorption of Cu from particulates (Spear and Pierce, 1979; EPA, 1980d).

Lion and Leckie (1981) calculated that Cu is primarily present in sea water as complexes with hydroxides and organic ligands. At pH 8.1, Zirino and Yamamoto (1972) calculated that only 1% of Cu would be present as Cu^{2+} (in the absence of organic ligands). Increases in cuprous oxide concentrations as a result of antifouling paints in waters of Port Hacking, Australia were noted by Batley and Gardner (1978).

Cu in sediments is generally dominated by the residual fraction, with the remainder associated with the hydroxide (reducible), organic or sulphide phases (Gibbs, 1977; Gupta and Chen, 1975; Forstner *et al.*, 1978). The association of Cu with the reducible phase is probably a result of the co-precipitation of the Cu with hydrous Fe and Mn oxides (Groth, 1971). Boulegue and Church (1981) identified the importance of organic material in complexing Cu even in highly reduced environments.

2.2.5 Lead

Pb is found in the environment in two oxidation states, Pb(2 +) and Pb(4 +). Inorganic compounds would usually exist in the Pb(2 +) state while organic compounds are more stable in the Pb(4 +) state (EPA, 1980e). The most abundant form of Pb mineral is galena (PbS) but Pb can also occur as an impurity in feldspars, mica and apatites. Soils tend to accumulate Pb in their clay fraction as a result of ionic adsorption. Humic substances can also be important.

Pb released from the combustion of leaded petrol as halides such as Pb-chlorobromide are converted to relatively insoluble compounds such as $PbCO_3$, $Pb_3(PO_4)_2$ and $PbSO_4$ in soils.

Pb speciation in oxygenated natural waters is dominated by the free ion Pb^{2+}, inorganic complexes and associations with organic and inorganic colloids and particulates (Florence and Batley, 1980). In most natural environments, sorption (e.g., to Fe and Mn oxides) may be a more effective removal process than precipitation (EPA, 1979a). At the low concentration in which Pb is normally found in the aquatic environment, almost all of the Pb in the dissolved phase may be complexed by organic ligands (EPA, 1979a).

In bulk ocean water in the absence of solids, the Pb chloro ($PbCl^+$) or carbonate ($PbCO_3$) species will dominate. Zirino and Yamamoto (1972) have calculated that the free ion (Pb^{2+}) will exist at less than 2% of the total Pb. The presence of small amounts of alkyl lead compounds is possible in water and sediments adjacent to leaded petrol sources. Biomethylation of lead is not likely (Reisinger *et al.*, 1981).

In offshore ocean sediments, Gupta and Chen (1975) found that 35-48% of the Pb was associated with organic matter, sulphides and amorphous FeO and micro-nodules. Only a small fraction was water soluble and exchangeable.

2.2.6 Mercury

The three stable states of Hg are elemental Hg (Hg^0), the mercurous ion (Hg_2^{2+}) and the mercuric ion (Hg^{2+}). Elemental Hg is rare in nature. Metallic Hg can be oxidised to the halides and sulphates as a result of weathering. Cinnabar (HgS) is a common Hg mineral and in New Zealand is found in a number of Hg deposits in Northland. Cationic Hg is easily adsorbed onto soil constituents and immobilised in the form of low solubility Hg compounds such as Hg phosphate, carbonate and sulphide (NRC, 1979).

In the absence of organic species, computer modelling predicts that the hydroxy mercury species ($Hg(OH)^+$ and $Hg(OH)_2$) should predominate in fresh waters. In the presence of organic material a significant proportion of the Hg may become associated or complexed with it. Under mildly reducing conditions Hg will be precipitated as the extremely insoluble sulphide. Compounds in which the Hg is bound through sulphydryl groups to carbon atoms play important roles in the aquatic chemistry of Hg. In aerated sea water the anionic complex $HgCl_3^-$ is the most stable compound whereas in brackish water, at high pH, $Hg(OH)_2$ dominates (Baeyers *et al.*, 1979).

In sediments, Hg occurs as HgS and is also associated with dissolved organic carbon. However, little work appears to have been carried out on speciation of Hg in sediments.

The finding that certain microorganisms have the ability to convert inorganic and organic forms of mercury to the highly toxic methyl or dimethyl mercury has shown that any form of mercury is highly hazardous to the environment. In water, under naturally occurring conditions of pH and temperature, inorganic mercury can be converted readily to methyl mercury (EPA, 1980f).

Figure 2.4 shows a simplified mercury cycle in natural water.

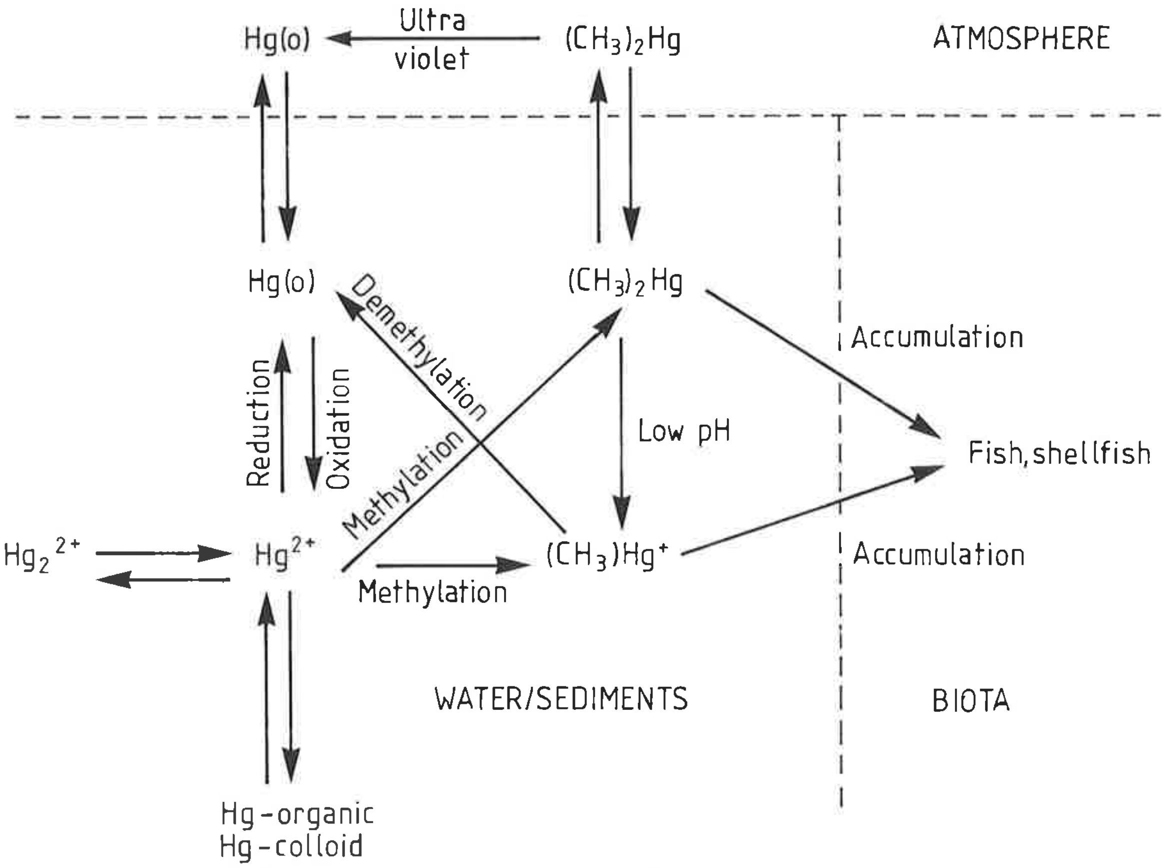


Figure 2.4: A simplified mercury cycle in natural water (based on Hart, 1982).

2.2.7 Nickel

Most Ni is present in soils and rocks as Ni(2 +) ionic compounds in addition to sulphides, arsenides and Fe-Ni alloys (NRC, 1981).

The Ni^{2+} ion is the most important species in fresh water followed by carbonate complexes (in the absence of low concentrations of suspended solids and organic matter) (Hem, 1970; Mantoura *et al.*, 1978; and EPA, 1980g). In reducing environments, precipitation of the sulphide will control the dissolved Ni concentration.

The Ni^{2+} ion is probably strongly sorbed by Fe and Mn oxides (Hem, 1970; EPA, 1979a). Equilibria with natural substances such as clays, humic acids and microorganisms are poorly understood (EPA, 1980g). There are few experimental studies of Ni speciation in natural waters. However, those that have been carried out appear to indicate considerable association of Ni with suspended solids, organic matter or co-precipitation with hydrous Fe and Mn oxides. In sea water, equilibrium calculations show that Ni species are dominated by the free ion and carbonate complexes (Mantoura *et al.*, 1978).

Ni speciation in sediments is probably dominated by residual or crystalline phases with the remainder principally associated with Fe-Mn oxides and minor organic, exchangeable and carbonate forms (e.g., Rapin, 1983).

2.2.8 Zinc

Zn is found in soils as the Zn^{2+} ion adsorbed onto clays and organic matter.

In a low alkalinity aquatic environment, and in the absence of complexing agents, the aquo complex ($Zn(H_2O)_6^{2+}$) is thought to dominate, with hydroxy and carbonate complexes becoming significant above pH 7. In sea water, $ZnCl_2$ is important but in lower salinity waters, $ZnSO_4$ and $ZnCl^+$ will be formed (Mantoura *et al.*, 1978). Zn complexes with organic and inorganic ligands are sufficiently soluble to prevent them becoming a limiting factor for the solubility of the low concentrations of Zn found in most aquatic environments. Adsorption on to clay minerals, hydrous metal oxides and organic matter probably limits Zn concentrations in water. Precipitation of the sulphide is an important control on the mobility of Zn in reducing environments.

In freshwater sediments, Zn can be associated with the carbonate phase because of the high stability of zinc carbonate (Hem, 1970; Forstner *et al.*, 1978). Forstner *et al.*(1981) examined the distribution of Zn in a variety of unpolluted and contaminated sediments from Germany. In these instances, the easily reducible (Mn-oxide) phase was dominant. Zn in sediment pore waters appears to be present as labile species (Abdullah and Reusch-Berg, 1981).

Chapter 3
SAMPLING AND ANALYTICAL METHODS

The purpose of this chapter is to give the reader an appreciation of the techniques employed in modern trace metal analysis, sampling, sample preparation, and analytical quality control. Critical to the reliable determination of ultra-low metal concentrations, such as are found in uncontaminated natural waters, is the adoption of an appropriate overall quality assurance programme. Stress on the adoption of such programmes is made.

3.1 WATER (P. C. Kennedy, D. G. Smith, K. A. Hunter)

With the range of suitably sensitive instrumental methods now available, a competent analyst should be able to make reliable determinations of heavy metals in aqueous samples. However, despite this favourable situation with instruments, it can be categorically stated that few published data accurately describe the actual metal concentration of the natural water **before** it was sampled. Until recently, most results were in positive error by orders of magnitude (Stevenson, 1985). For instance, estimates of Cu concentrations in surface sea water have fallen by three orders of magnitude over the past few decades with much of the reduction taking place in the late 1970s. All of the important problems in this work arise during the sampling and sample handling operations prior to actual analysis.

This state of affairs has come about because of an almost universal failure to realise that the real concentrations of most heavy metals in natural waters are minute by comparison with those in airborne dust, paint and skin flakes, grease, cosmetics, fumes and rust that envelope the sampler, analyst and equipment.

3.1.1 Sampling and Processing

Natural waters: Sampling and analytical procedures for heavy metal study are available that are free from the above problems, but they bear little resemblance to classical water quality analysis methods. For the analysis of natural waters, a dust-free, clean laboratory in which rigid controls on airborne and surface-borne contamination are exercised through meticulous use of specialised apparatus, clothing and sample handling protocol, is a minimum starting point for secure results (Patterson and Settle, 1976; Moody, 1982). The entire sampling and analytical scheme must be thoroughly evaluated, stage by stage, under such controlled conditions so as to understand the certainty and amount of contamination during each step in the procedures and minimise the entry of contaminants. At any stage, a speck of dust or a careless fingerprint can negate the most careful work. It is especially important that the sampling operation (and indeed all sample handling procedures) be conducted **only** by workers skilled in the protocols of clean laboratory work. Collection bottles (polyethylene for all metals with the possible exception of Hg) must be scrupulously cleaned before use.

Sampling and processing strategies for examining lead in natural waters have been described by Patterson and Settle (1976). More detailed description of the extreme care needed in handling snow samples for lead analysis (1.7 $\mu g\ Pb/m^3$) is presented by Boutron and Patterson (1983) and, for sea water containing 5-15$\mu g\ Pb/m^3$, by Schaule and Patterson (1981). Descriptions of recent sampling procedures used for sampling fresh and sea waters in New Zealand is given by Hunter (1981a), Dickson and Hunter (1981), Ahlers and Hunter (1986) and Hunter and Ho (1986). Other useful reviews are contained in Florence (1982), Nurnberg (1984) and Cescon *et al.* (1984).

A recent conclusion (Florence, 1982; Cescon *et al.*, 1984) is that natural fresh and sea waters do not appear to require preservation (even if stored for several months) other than chilling to 4°C, provided the pre-cleaned bottles are conditioned by rinsing with sample water prior to final filling.

Waste waters: Stringent precautions in sampling and processing **waste waters** may be less important if the samples contain very much higher metal concentrations than natural waters. However, problems may arise in obtaining representative samples. A thorough knowledge of the industrial processes and treatment methods used is essential before the sampling strategy is designed. Detailed recommendations are beyond the scope of this publication.

3.1.2 Analytical Methods and Speciation

Trace metals in natural water are present in a wide variety of forms (species) (see Section 2.2) and the amount of detail required depends on the problem being addressed. There are three ways of obtaining information on speciation.

Firstly, by direct measurement using a combination of extraction, ion exchange or other separation techniques. Complex schemes for dissolved metals have been drawn up by, for example, Florence and Batley (1980) and Hart and Davies (1981a and b). To date, these techniques have been confined to research purposes. They are also expensive and not readily available in New Zealand.

Secondly, metal speciation can be inferred in a qualitative manner with a knowledge of concentrations of substances present in the water which are known to affect metal complexation or adsorption (pH, carbonate, chloride, sulphate, suspended solids, organic carbon).

Thirdly, the above two methods can be combined and, together with thermodynamic data, used to obtain models for a water's metal speciation. These models cannot, as yet, be used for predictive purposes in other waters.

For most water management purposes, water quality standards and/or criteria are used (see Chapter 5). In such cases, knowledge of detailed speciation is not required because the standards/criteria used define the extent to which analysis has to be carried out. For instance, if the US EPA criteria are used to manage a water body, then total-recoverable (or acid soluble) metal will be required. A general appreciation of the way water chemistry may affect metal speciation is also helpful in understanding how metal speciation, and hence toxicity, may change in a water body. Water hardness should be determined in instances where metal standards/criteria are hardness related. In such instances hardness is used as a surrogate for the ions which mitigate toxicity.

Trace metal analysis for waters are generally carried out by flameless Atomic Absorption Spectrometry (AAS) following a concentrating technique, or by various forms of Anodic Stripping Voltametry (ASV) (Gawne and Mitchell 1984; Adeloju *et al.*, 1986). An example of a concentrating technique involving ammonium pyrrolidine dithiocarbamate with cobalt carrier was used for Cu and Ni by Dickson and Hunter (1981) with a detection limit of around 13 $\mu g/m^3$ for Cu and 53 $\mu g/m^3$ for Ni. A similar method was used by Bruland (1980) for the analysis of Cd, Zn, Ni and Cu in North Pacific waters. See Section 3.2.4 for further discussion on analytical methods.

3.1.3 Quality Control

Examination of interlaboratory comparisons for trace metals reveals that many laboratories have a great deal of trouble in analysing aqueous samples at the sub mg/m^3 level. The type of problems are described in a 1973 interlaboratory study of lead analysis (Anon, 1974). Although this study was carried out 13 years ago, many of the problems occurring then are still faced by many laboratories. For instance, in a recent interlaboratory study carried out in New Zealand, two independent laboratories obtained results differing by up to three orders of magnitude for Cd and Pb. The levels obtained by the 'low' laboratory were between 0.002-0.008 mg/m^3 for Cd and between 0.04-0.16 mg/m^3 for Pb (J. B. Macaskill, Water Quality Centre, MWD, pers. comm.).

Problems are also found at much higher concentrations. In 1978, Chemistry Division, DSIR, conducted a collaborative interlaboratory trace metals investigation of water analysis (Timperley, 1978). The concentrations of metals used in the investigation were between 50 and 4000 mg/m^3, i.e., comparable with effluents or polluted waters. They would not be representative of most natural waters. The results showed that Cd and Ni could be accurately determined, but poorer accuracy was found for Co, Cu, Pb, and Zn. Results for Cr at both concentrations tested (i.e., 76 and 830 mg/m^3) showed wide variations due to problems with analytical procedures.

The precautions required to ameliorate the problems described above, add considerably to the time and cost involved in heavy metal analysis of water, and therefore significantly reduce the scope of surveys and the number of heavy metals that may be studied at one time. However, the natural desire of the water scientist to mount a study programme of reasonable scope must not become an excuse for lowering standards, otherwise meaningless information is the inevitable result.

3.2 BIOTA (P. C. Kennedy and M. F. Larcombe)

3.2.1 Sampling

The sampling rationale should define the following before sampling is started:

(a) Species to be studied
(b) Number of sampling stations
(c) Number of replicate samples per station
(d) Whether pooled samples of several individuals or single individuals to be analysed
(e) Size, age, sex of samples to be analysed
(f) Other biological data required (e.g., condition factor)
(g) Timing of sampling
(h) Method of taking samples
(i) Sample handling, cleaning, storage
(j) Method of preparation for analysis.

Ideally, sampling should be undertaken on a random basis at each station. Usually, however, to obtain the advantages of sampling a 'standard' organism, a combination of random determination of sample site and selections of the nearest 'standard' organism (or group of organisms) is appropriate.

Sampling a standard organism is usually undertaken once the influence of age, size and season (or reproductive state) on metal concentration is determined. Sample replication is greatly dependent upon the population available and the size of the organism; however, sampling should aim toward enabling the results to express the site variability.

In view of the high cost of analytical preparation and the analysis itself, it is advisable to consider the merits of grouping individuals from the sample population for analysis. It is possible to estimate the number of individuals necessary in a sample pool to reach a desired level of precision, so that the grouped sample will represent the population. This can be done by analysing random individuals and then statistically examining the data. This is ideal for organisms if there is no correlation between size and metal concentration.

It is important that the analyst has a detailed knowledge of the sampling and storage procedures used from the start of any programme to avoid uncertainty regarding the integrity of the sample. This may occur through contamination or changes in composition during transport (Sansoni and Iyengar, 1980). The total error introduced during the entire sampling procedure should be less than, or of the same order of magnitude as, the error of the subsequent analytical procedure.

Contamination may result from the sampling procedures, the environment or the personnel. Sampling should be made by hand or using non-metallic sampling tools (non-coloured plastics, polyethylene, teflon) and titanium or stainless steel should be used for cutting.

The person taking samples should also be alert to possible influences that could result in a high variability of metals concentrations in the biota. Such influences could include the presence of dumped metals (tin cans, pipes, iron, electric cables, etc.), paint flakes from stormwater systems or ship and pleasure boat maintenance areas, treated timber, galvanised steel or pipework, and metal-based paints. Where metals concentrations in biota are expected, or found, to be highly variable, a greater number of subsamples may be required to adequately define the situation.

When collecting biota for trace metal analysis, appropriate additional information should be obtained. This could include river flow, tidal state, weather conditions, water temperature, state of the local environment, redox condition and texture of sediment (if sediment dweller) and, depending upon the species collected, age, health and condition, reproductive state, size, weight, etc. Most organisms can be transported live to the laboratory in cool conditions.

Samples should be sorted and washed as soon as practical and specimens should be transported in sealed non-metallic containers. When analysis of whole organisms is required, only undamaged organisms should be included in samples because loss of blood or haemolymph, or some organs could result in considerable bias in the results. Procedures following the sampling will depend on the type of organism being examined. For example, macro-algae, after being cut, may need to be first cleaned, then sealed in clean plastic bags and refrigerated. For molluscs, a period of depuration (e.g., >24 hours) is necessary in 'filtered' water to allow the gut contents to be voided (not necessary in public health studies if the whole organism is consumed by humans). For organisms where only a part is consumed, a procedure must be established for obtaining a representative sample of those parts actually eaten.

3.2.2 Sample Preparation

It is important that during the preparation of material for trace element analysis that all stages of sample handling, possible loss of elements and possible sample contamination be assessed. Minimal handling is always advisable. Sample processing tools should always be made of materials that contain insignificant levels of the element(s) of interest. Disposable and acid washed plastic gloves and teflon tweezers are often necessary pieces of equipment.

During the sub-sampling of bulk organisms such as fish, precautions must be taken to avoid contamination of their skin surface (in the mucus etc.) by touching the sample. Samples should not be cut when frozen because up to 10 times more Cr contamination occurs using steel scalpels as when thawed (Iyengar and Sansoni, 1980).

Elements such as Cu, Fe and Zn are usually present in the mg/kg concentration range in biota and can usually be analysed in most routinely clean laboratories, but for elements present at the μg/kg level, clean laboratories and clean workstations are important during the preparation for analysis because sophisticated analytical instrumentation is no palliative for contamination (Hamilton, 1980).

After initial preparation, long term storage is usually carried out at $-15\,^{\circ}$C, but irreversible damage is done to the sample by the formation of ice in cells. Some loss of element can occur with haemolymph loss during thawing, and samples can dehydrate during storage. Preservation can be carried out by freeze drying or rarely by radiation sterilisation or the use of preservatives such as ethanol-formalin mixtures. Preservatives are not advised because of possible contamination or leaching effects. Oven drying at 90-105 °C is the most common method of drying, although Hg is not retained in many tissues at that temperature and freeze drying is preferred. Microwave drying can also be used for rapid drying.

Many laboratories prepare wet homogenates of the study organism by blending. Subsampling is often extremely difficult because of differential settling of material. Digestion of fresh whole organisms is often the best solution to the subsampling problem if the organism size permits. Dry grinding is not always necessary, but many techniques (e.g., X-Ray Fluorescence Spectrometry (XRFS)) require material in powder form. Sub-sample size for analytical work is dependent on homogeneity and particle size. Grinding equipment should be made of inert materials such as titanium, tungsten, teflon or quartz.

3.2.3 Ashing and Digestion

Common ashing methods include wet ashing using acids, dry ashing in a muffle furnace, and low temperature (150 °C) ashing utilising microwave excitation in a low pressure oxygen atmosphere. Dry ashing at 500 °C volatilises elements such as Ag, As, Co, Cr, Hg, Pb, and Sn. Mercury and Sb show tissue specific differences in volatility at 120 °C (Iyengar and Sansoni, 1980). High temperature ashing up to 750 °C can be carried out using ashing aids such as sulphuric acid. Wet ashing methods are varied and dependent on the element to be determined, but $HNO_3/HClO_4$, H_2SO_4/H_2O_2, HNO_3/H_2SO_4 and HNO_3 digestions are those most frequently used. Digestion can be carried out in glass or quartz containers cold, or at low temperature in teflon pressure vessels, and with acid vapour under pressure (Kiltenick *et al.*, 1983).

The use of ultrapure acids is necessary for many determinations at trace levels (e.g., high Cr concentration occurs in Analar laboratory HNO_3). These acids can be bought or commercial grade can be purified by distillation using the two bottle sub-boiling teflon still, which is especially useful for producing clean nitric acid (Mattinson, 1972; Mass and Dressing 1983), and commercial quartz sub-boiling distillation units. Redistilled acids are often hundreds of times lower in metal content than commercial analytical grade acids.

3.2.4 Analytical Methods

A wide variety of methods is available to the analyst depending upon the element and the concentration of the element. For elemental analysis, atomic absorption spectrophotometry (AAS) is the most commonly used technique in New Zealand and world wide. Colorimetric and Fluorimetric methods are used for some elements, e.g., Se (Watkinson 1960, 1966). Other less commonly used techniques available in New Zealand include electrochemical techniques such as ASV, Spark Source Mass Spectrometry and Emission Spectrometry (Wells and Smidt, 1978) and Atomic Emission Spectrometry. Wavelength dispersive XRFS has become more routinely used in this country for the analysis of some heavy metals above 1 mg/kg dry weight.

The multi-element technique, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) (Lee, 1983a,b; Pritchard and Lee, 1984), has comparable detection limits to Neutron Activation Analysis and is often the better technique for the important trace elements Cd, Cr, Fe, Ni, Pb and Zn. Other X-ray techniques such as Energy Dispersive XRFS (Winchester, 1978), Particle Induced X-Ray Emission and various microprobe based XRFS analytical techniques are also available but not usually used for routine analytical work.

Metals are often preconcentrated before analysis using a chelate complex such as sodium diethyl dithiocarbamate or ammonium pyrrolidine dithiocarbamate with an organic solvent such as ethyl acetate or methyl isobutyl ketone. As well as concentrating the element, this step may also remove certain interferences. Generation of the volatile hydride of As by adding a reducing agent such as borohydride is commonly used with or without flame (cold vapour) and a similar technique is used for Hg, since elemental Hg is produced when Hg in solution is treated with a reducing solution such as $SnCl_2$.

Electrothermal atomisation, where small liquid samples (generally $< 20\ \mu l$) are transferred to an electrically heated graphite tube or cup and dried, ashed and atomised, provides optimum production of a cloud of metal atoms in the light path of the spectrometer. Matrix effects are severe, background correction is needed and multi-element analysis is not possible.

3.2.5 Speciation Techniques

The identification of *in vivo* speciation of elements in biota is not an easy task hence very few elements are determined as anything other than totals. Mercury is one of the elements routinely subdivided into inorganic and organic mercury during analysis because of its extreme toxicity (especially of the latter) to human consumers.

3.2.6 Quality Control

Irrespective of the analytical methods used in a laboratory, there is always a need to assure adequate quality control by using certified reference materials and participating in interlaboratory comparisons (Hamilton, 1980). From the result of many interlaboratory studies, it is often evident that many laboratories are often overconfident in their ability to analyse many trace elements in biological tissues. The level of agreement is often not good enough to enable future comparisons of the individual laboratory's field results. Laboratories which use standard addition methods, cross-checking with neighbouring laboratories (preferably using different techniques) should still routinely examine local or international reference materials. Currently available reference materials of high quality are available world wide. Examples include oyster tissue, pine needles, orchard leaves, bovine liver, wheat and rice flour, and spinach leaves etc, from the National Bureau of Standards, USA, and milk powder, animal blood, bone and muscle, copepod, fish flesh, rye flour and cotton cellulose from the International Atomic Energy Agency (IAEA) in Austria. Other standards are available and there are usually numerous worldwide laboratory and methodology intercomparisons being carried out in any year (e.g., those run by the IAEA and the International Council for the Exploration of the Sea).

Results should always be expressed on a dry weight basis because of difficulties of standardising wet weight for most aquatic organisms. Where public health considerations are of interest it is usually necessary to express results on a wet weight basis, to enable comparison of results with Food Regulations limits (see Section 5.2). Wet to dry weight factors can be obtained when freeze drying or oven drying. Separate determinations may have to be made when determining volatile elements.

3.3 SEDIMENTS (P. C. Kennedy)

3.3.1 Sampling

Many researchers pay insufficient attention to basic sampling principles. Problems arising from bad sampling may impose limitations on the conclusions reached in any study. It is very important to report sampling procedures. Sampling methods used will depend upon the study aims. If the sediments are thick and continuous, techniques using mechanical grabs, scoops and spades etc., may be used but where they are thin and irregular other techniques are needed. During surface sediment sampling, the presence of bank erosion in tidal areas, slumping in subtidal areas, localised contamination (especially rust) and variable sediment oxidation/reduction conditions should be noted. A knowledge of the local deposition rates may influence the depth of sediment sampled.

If sedimentary records are being examined, cores may be taken by hand (surface or diver) using perspex tubes, using piston cores from a barge or using gravity corers. It is important to be able to identify and record the amount of sediment loss from the top of piston cores and any degree of sediment movement in any core taken. Contamination during core cutting requires careful removal of outer core layers during subsampling. The use of box cores or large diameter gravity cores are best for obtaining undisturbed sediment cores which can be used for detailed analysis of sedimentary records.

3.3.2 Processing

Processing of soils and sediments presents fewer problems than water or biota. Air drying does not usually have any effects on the total trace element content but if phase distribution is of interest, the sample should be examined fresh. Air drying may result in contamination (through air deposition), especially when there is little extractable metal in the sample. Drying usually results in the alteration of pH, cation exchange capacity, and phase distribution. Although freezing is often recommended for storage, changes in organic complexes may possibly occur. Oven drying at 90-100°C is permissible and is a rapid method for total metals. However, some of the volatile metals in organic form, especially Hg, are lost and it is advisable to analyse the fresh sample or freeze a subsample and correct for water content determined from a separate sample. Prolonged heating of sediments at 100°C will result in the loss of organic carbon.

3.3.3 Determination of Phase Distribution (P. C. Kennedy and R. B. Williamson)

An examination of the phase distribution of trace metals in sediments may be carried out for a number of reasons. These include the determination of the geochemical phase distribution of the element, and examination of the availability of sediment trace elements to the biota.

The determination of the phase distribution of a metal in a sample of sediment is a complex problem because there are a wide variety of phases present (e.g., weakly and strongly absorbed ions, metal carbonates, sulphates, oxides, hydroxides, phosphates, organo-metallic compounds and silicates). Many phases are not crystalline, i.e., they are amorphous, and some are present as coatings on other phases. Because of this, a wide range of techniques and extracting solutions have been employed to help in phase identification. Extraction methods have been examined by several authors (e.g., van Valin and Morse, 1982).

One of the most commonly used management tools in evaluating the impact of heavy metal inputs, is to compare sediment metal concentrations in space and/or time. Meaningful comparisons using statistical tests involve the knowledge of the variability in the site metal concentrations (sample variance). This variance can be extremely high, because the concentration may not only depend on the magnitude, exposure time and proximity of the source, but also on the sediment characteristics. The most important characteristics are sediment surface area (particle size) and composition (phase distribution). By measuring some or all of these characteristics, and including them in the statistical tests (e.g. analysis of variance, multiple regression), there can be a considerable reduction (explanation) of sample variance, and hence more powerful comparisons.

3.3.4 Determination of Total Element Content

X-ray fluorescence spectroscopy is probably the most routine geochemical survey technique used in New Zealand. The method has been employed by Glasby *et al.* (1979) and Kennedy *et al.* (1983). Spark source mass spectrometry and emission spectrometry are also used. Total metal levels can also be obtained using HF digestion; strong oxidising acids (see Section 3.2.3) will probably not solubilise metals intimately bound in the mineral matrix.

Analysis of metal-containing solutions may be carried out by a wide range of techniques as described for biota and waters. The technique of choice will depend upon the element and its concentration. Atomic absorption spectrometry is generally the routine technique for most solubilised and extracted elements. Arsenic and Hg are determined by similar techniques as used for biota.

3.3.5 Quality Control

The need for use of standard reference materials during routine analysis has been stressed several times in this chapter. There is a wide range of geochemical reference materials available today, which have certified and non-certified data for a range of elements virtually covering the periodic table. The most comprehensive summary of data available for standard samples is that of Abbey (1980).

Chapter 4

SOURCES OF HEAVY METALS

Sources of metals can be divided into two main classes, natural and anthropogenic, the latter referring to those caused directly or indirectly by man. It is sometimes difficult to separate them. Most natural sources of metals are diffuse, that is, the metals from them will not always enter a water body at a fixed point but rather, sources will be spread over a wide area (e.g., erosion). Natural sources produce the normally very low background level of metals in waters. By contrast, many anthropogenic sources are point sources, that is, they enter a water body by say a pipe, outfall, drainage ditch or some other means whereby the location of the discharge can be pin-pointed. These sources are controllable via the water rights procedure and regional water boards can, and do, impose stringent limits on metals discharged to the aquatic environment.

Figure 4.1 summarises the main sources, and their inter-relationships, and is briefly amplified by the following points:

1. Geologic weathering includes natural erosion with subsequent loss from the land of material either directly to water or indirectly via the atmosphere as dust, and dissolution of metals from rocks.
2. Geothermal activity will normally result in fluid passing directly into a watercourse with only a small contribution venting to the atmosphere (of, for instance, Hg). Man's development of geothermal energy amplifies both processes.
3. Volcanic activity will result in dust and ash containing metals being ejected from the volcano to the atmosphere.
4. Transport contributes metals, e.g., Pb and vehicle corrosion products, to the roadside environment and atmosphere which can end up in stormwater runoff to a water body.
5. Industry can discharge directly to a water or may vent metals to the atmosphere, e.g., as fly-ash from the burning of coal.
6. Mining can be a source of pollution by exposing and processing metal-containing rocks.
7. Municipal wastes are made up from sewage (i.e., household liquid waste) and possibly industrial liquid waste discharges.
8. Agricultural inputs would include animal dietary additivies, pesticide residues and fertiliser runoff.
9. Dump leachates can be as a point source if the dump is well managed, and a diffuse source if not well managed.
10. Sea spray can result in fresh water receiving sea salts via the atmosphere.
11. The atmosphere is a major source of metal to the aquatic environment, but one which is frequently overlooked. Man-made additions to the atmosphere are most noticeable since natural inputs are usually small.

Man's use of many metals has contributed to the total annual world metal mobilisation for thousands of years and it has been estimated that it now exceeds natural mobilisation for many metals (Table 4.1).

Not all of man's use of metals results in aquatic pollution and most of the problems in the aquatic environment are likely to be very localised but potentially with considerable consequences.

Further information on sources of metal pollution is contained in Forstner and Wittmann (1983), Nriagu (1978, 1979a and b, 1980a, b and c), Hart (1982), EPA (1980a-h) and EPA (1979a).

The following sections describe known sources of metal pollution in New Zealand. Where a particular source is regarded as potentially important in New Zealand but local data are lacking, overseas information is presented as a guide. Normally only total metal concentrations are available, and it is very difficult to speculate on likely environmental consequences, except where they are obvious or relate directly to the nature of the source. Wastes which present immediate hazards to the aquatic environment are those which contribute significant amounts of metals in the more toxic forms (frequently the free metal ion). A high concentration of total metal in a source is not

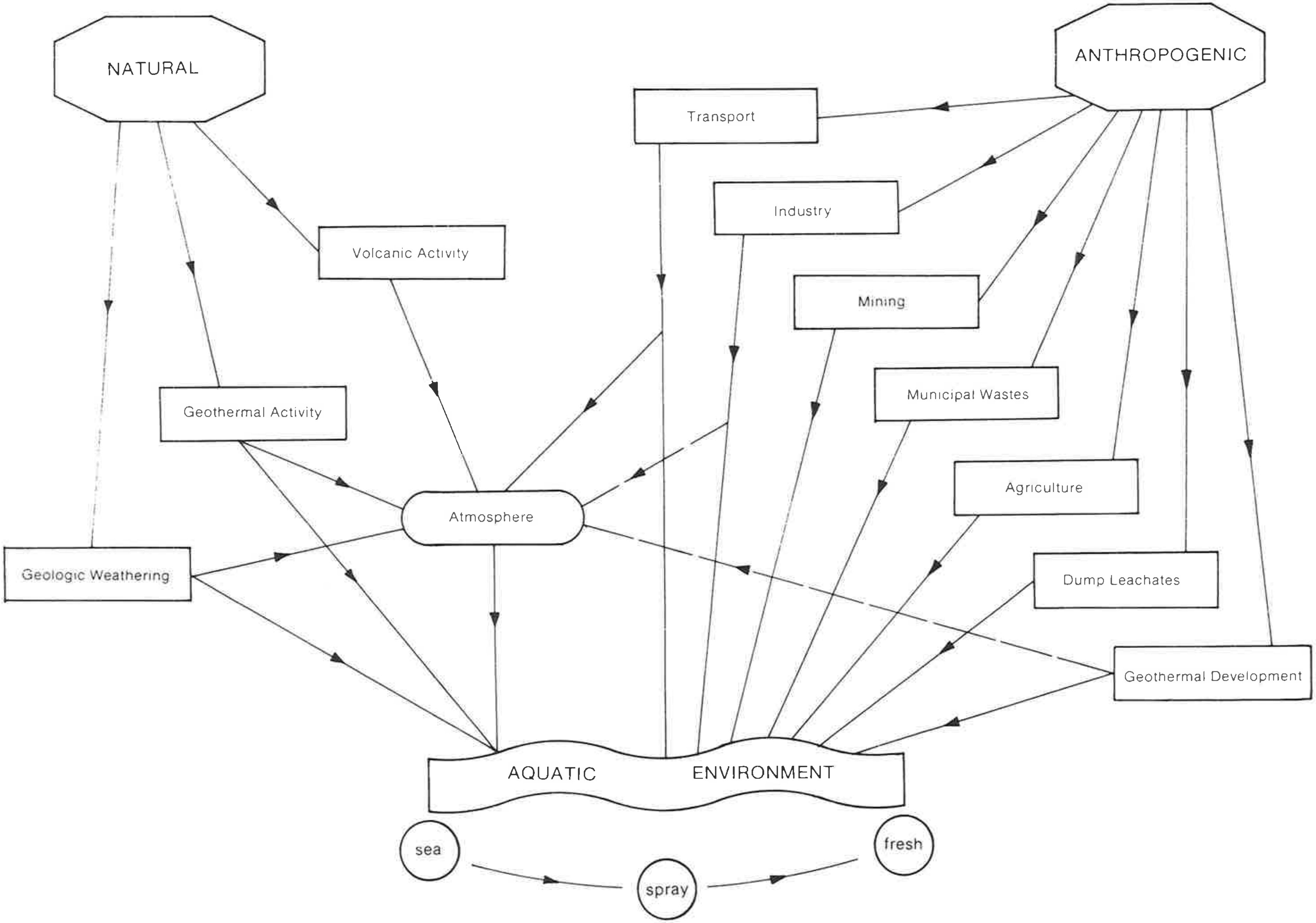


Figure 4.1: Sources of metal input to the aquatic environment (Smith, 1985).

Table 4.1: Global natural and anthropogenic mobilisation of heavy metals ($\times 10^3$ tonne/annum) (Ketchum, 1972). Values in brackets are estimates for atmospheric emissions (Nriagu 1978, 1979a and b, 1980a, b and c).

Metal	Natural	Anthropogenic
Ag	5	7
Cd	– (0.8)	– (7)
Cu	375 (19)	4460 (56)
Hg	3	7
Mo	13	57
Ni	300 (26)	358 (57)
Pb	180 (19)	2330 (438)
Sb	1.3	40
Zn	370 (43)	3930 (314)

always a good indication of potential hazard because there may be high dilution in receiving waters and the metal species concerned may pose little biological threat. Metal speciation is considered in Chapter 2.

4.1 GEOTHERMAL

The chemical composition of geothermal fluids is variable. The concentration of heavy divalent elements in the water increases with the square of the water salinity as a consequence of the chemical equilibria in deep geothermal systems. Because of this, surface contamination by heavy metals from geothermal fluid of high salinity is very much greater than would be expected from comparing the dissolved solids content with that of less saline waters (Ellis, 1978). Heavy metal contamination of receiving waters should be anticipated in very saline (salinity $>10\ 000$ g/m^3) or low pH geothermal fluids (Ellis, 1978). It also appears that the higher the temperature of connecting fluid, the higher the concentration of metals (L. Constable, Ministry of Works and Development, pers. comm.).

Fortunately in New Zealand, low pH high salinity geothermal fluids are in the minority. The main geothermal areas used for power production now or in the near future, i.e., Wairakei, Broadlands, Ngawha, have near neutral, low salinity waters. The main New Zealand geothermal regions are shown in Figure 4.2. Hot springs are largely confined to three main regions (areas 1, 2 and 3). Scattered cooler springs of mainly non-volcanic origin are found in region 4 (Nathan, 1974).

Levels of heavy metals found in natural springs, pools and drains, and from man-made bores are given in Table 4.2. Only As and Hg are normally at elevated levels. With few exceptions, levels of other metals are very low. The concentrations of Cu and Zn are exceptionally high in waters from Noisy Nellie Crater on White Island; here the pH of the waters is generally less than 1 (Koga, 1967).

Much of the Hg from bores may be found in the steam fraction (see Table 4.2) and a large fraction of this can be dissipated into the atmosphere. Various estimates (0.2 mg Hg/m^3 in the vapour plume at Broadlands (Ellis, 1978) and 17.5 kg Hg/year discharged into the atmosphere at Ngawha (Browne *et al.*, 1981)) have been made but the significance of these discharges to the aquatic environment is very difficult to assess. Giggenbach (1982) has estimated that As and Hg emitted from cooling towers at Ngawha will lead to insignificant increases in surface water concentrations.

4.2 PRECIPITATION

The main natural sources of metals in the atmosphere are volcanic emissions, dust, forest fires and sea spray. Examples of anthropogenic sources are fuel combustion (vehicles, factories, household fires) and wind erosion of stockpiled fertilisers. In New Zealand, geothermal areas may also be important.

Atmospheric material is deposited at the earth's surface by both 'wet' and 'dry' processes. Gravitational deposition is the primary dry process. Wet processes include the accumulation of aerosols in clouds and washout of particles during rainfall. Wet precipitation probably dominates in humid climates (Dethier, 1979).

New Zealand studies which yield information on atmospheric contributions to water bodies are sparse and no work appears to have been published with this as the prime reason for the study.

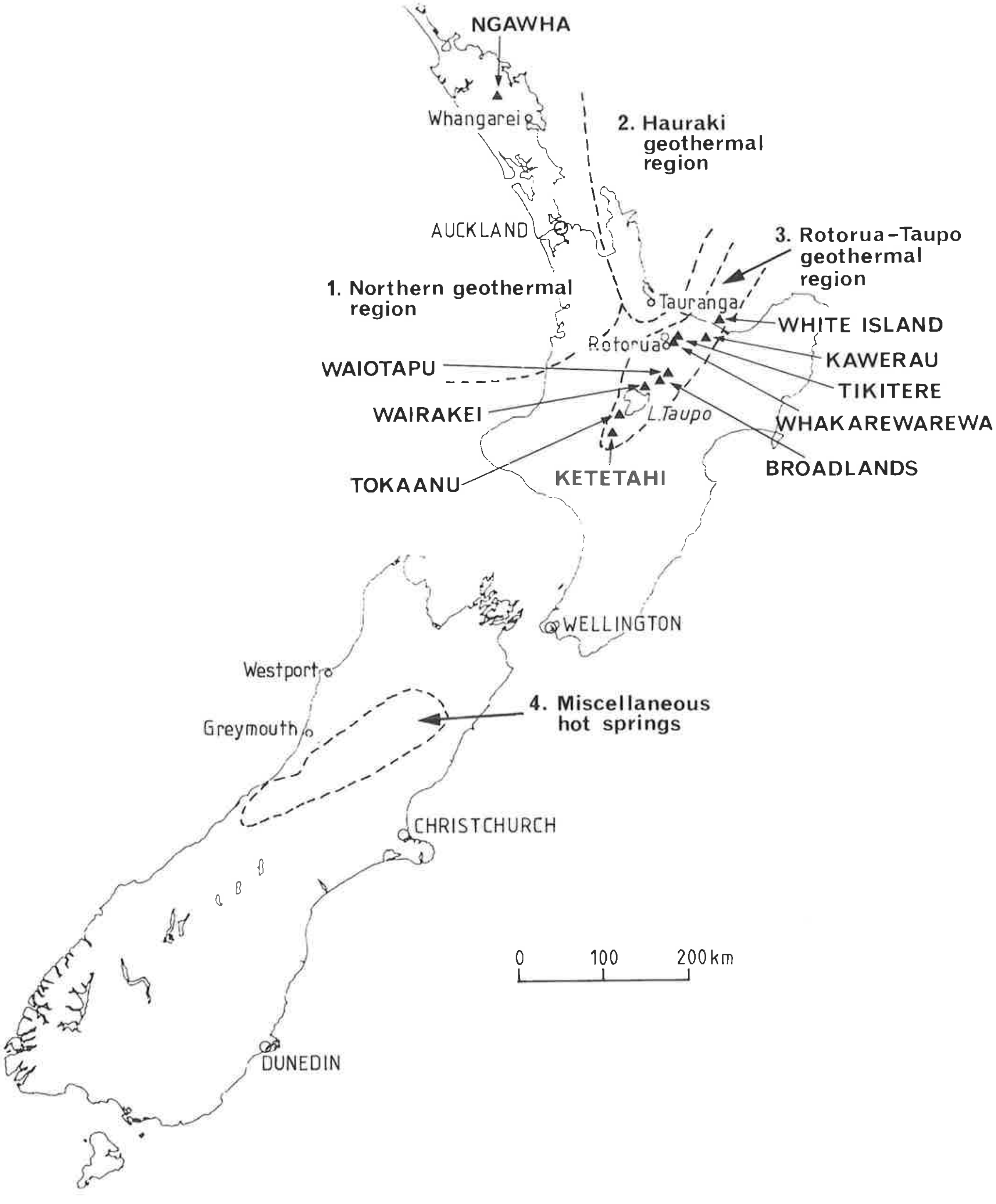


Figure 4.2: Locations of the main geothermal regions of New Zealand including areas referred to in the text (based on Nathan, 1974).

Table 4.2: Levels of heavy metals found in New Zealand geothermal waters (mg/m^3). (The sources are natural springs and pools, and values given are for total metal, except where indicated.)

Location	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn	Source	Ref.
Broadlands	3300		2-3	2-3	0.05	2-3			Discharge Water	(1)
	5700	0.02	1		0.05-0.1 2-5	4		1	Discharge Water Steam condensate	(2)
		≤0.07	<0.1-1.7			0.1-10	<0.1-0.5	0.2-2.2	Well water	(3)
		0.01	0.6			0.8	0.1	0.6	Well water	(4)
					0.04				Well water	(5)
					4.4-23				Steam condensate	(6)
Wairakei	4700	0.5	2		0.1 1.4	4		2	Discharge Water Steam condensate	(2)
					0.08-0.16				Discharge Water	(5)
			1.3			1	0.7	1.5	Well water	(4)
	2000-5000	<1	<1			5-8		<1	Discharge water	(8)
Ngawha	900				2.1 48 26-28.5				Well water Discharge water Pool water	(9)
Ketetahi Spring		<1	<1			<5		<1		(8)
Tokaanu-Taupo	<20-6000									(10)
Whakarewarewa	60-520									(10)
Rotorua	10-340									(10)
Tikitere (Hell's Gate)	≤14				≤16 ≤0.8(d)					(11)
		<0.5	370		<1	<5	23	<0.5		(12)
Waiotapu (Champagne Pool)	4690-5770		<27			<225		<26		(7)
	<1000-6000	<1	<1			<5		<1		(8)
Kawerau					0.05 9.7-61				Well water Steam condensate	(6)
White Island (Noisy Nellie Crater)			25200					25000		(13)

Note: (d) dissolved Hg

References:

(1) Broadlands EIR (1977)
(2) Ellis (1978)
(3) Ritchie (1973)
(4) Ellis and Mahon (1977)
(5) Weissberg (1975)
(6) Weissberg and Rohde (1978)
(7) Liddle (1982)
(8) J. W. Hedenquist and A. Mann DSIR, pers. comm.
(9) Giggenbach and Sheppard (1980)
(10) Ritchie (1961)
(11) Williamson and Cooke (1982)
(12) Coulter (1977)
(13) Koga (1967)

There is only one recent, published study carried out in New Zealand on atmospheric contributions of heavy metals (Stevenson, 1980). Snow from the Southern Alps and rain from the Christchurch urban environment were analysed for Pb. The two snow values obtained were 1.6 and 3.1 mg/m^3; the eight rain values ranged from 5.0 to 30.6 mg/m^3, with a mean of 16.8 mg/m^3. R. B. Williamson (Water Quality Centre, MWD, pers. comm.) examined Pb and Zn in rainwater collected in a residential area of Hamilton. The mean Pb concentration from 3 storms was 5.6mg/m^3 (range $<$0.8-34 mg/m^3 for samples collected every 0.5 mm of rain). Zn was found to be usually $<$10 mg/m^3. In a study on total Pb deposition in Auckland between August 1978 and March 1979, the mean dissolved Pb content of combined wet and dry deposition for Mt Albert (residential area) and Penrose (industrial area) was found to be 20 mg/m^3 (range 4-40 mg/m^3) and 21 mg/m^3 (range 12-42 mg/m^3) respectively (B. Graham, Department of Health, pers. comm.).

The mean level of Pb (2.4 mg/m^3) in Southern Alps snow found by Stevenson (1980) is considerably higher than levels obtained for Antarctica (median 0.033 mg/m^3) and Greenland (median 0.2mg/m^3) (Galloway *et al.*, 1982). This may indicate sample contamination. The urban rain Pb concentrations found in New Zealand are comparable with, but generally lower than, values obtained in other cities (see Table 4.3).

Table 4.3: Concentrations* (mg/m^3) of some heavy metals in rainwater collected from urban, rural and remote areas (from Galloway *et al.*, 1982).

Metal	Urban	Rural	Remote
Ag	3.2	0.54	0.007
As	5.8	0.29	0.019
Cd	0.7	0.5	0.008
Co	1.8	0.75	–
Cr	3.2	0.88	–
Cu	41	5.4	0.060
Hg	0.75	0.09	0.079
Ni	12	2.4	–
Pb	44	12	0.09
Sb	–	–	0.034
V	42	9	0.16
Zn	34	36	0.22

* values are median concentrations

Overseas data on deposition rates, for various locations, have been tabulated by Dethier (1979) and a selection is presented in Table 4.4. The Greenland rates would presumably be the least affected by the sources identified earlier in the section. The only New Zealand data on deposition rates (i.e., wet plus dry) are for Pb in two areas of Auckland. These were found to be 44 mg/m^2.yr for Mt Albert and 95 mg/m^2.yr for Penrose (B. Graham, Department of Health, pers. comm.).

Table 4.4: Deposition rates (mg/m^2.yr) of some heavy metals in precipitation at several worldwide locations (from Dethier, 1979 and Kuntz, 1980)

	As	Cu	Pb	Zn
Greenland	0.01	0.06	0.02	0.15
Washington, North Cascade Range	2	12	16	17
Seattle, Washington	6	16	21	6?
South Lake Michigan	2.5	32	70	35
Rural Tennessee	–	25	25	51
Knoxville, Tennessee	9	–	108	–
Rural England	2	33	56	122
Gottingen, Germany	–	10	23	47
Great Lakes*	–	5	11	53

* Average, for bulk precipitation (i.e., wet and dry), of total metal for four lakes (Kuntz, 1980).

For large water bodies, the deposition of metals by the atmosphere may constitute a high proportion of the total input (Larsen, 1983). For instance, of the total inputs of Pb and Zn to New York Bight, the atmospheric inputs have been estimated at 16% and 25% respectively (see Forstner and Wittman, 1983).

4.3 WEATHERING AND EROSION

Weathering of rocks is one of the main sources of background metal levels in the aquatic environment, and, in areas containing metalliferous ore bodies, water and sediment metal levels may be elevated. These aspects will be discussed further in Chapter 6.

Erosion of soils is the major source of suspended solid material in waters. These solids will contain lithologically bound metals and hence will be largely unavailable to fauna and flora. During flood events, the suspended solids concentration in flood waters can be several thousand g/m^3. The metal concentration in the water can be estimated from the metal levels in the eroding material.

The top soils of New Zealand have been mapped by DSIR Soil Bureau for a variety of single factors. However, to date the only heavy metals mapped are Zn, Cu and Cr. The maps show that total Zn can vary throughout the country from <30 mg/kg to >100 mg/kg, the highest values being around the Waikato, total Cu can vary from <5 mg/kg to >40 mg/kg, and total Cr from <10 mg/kg to >100 mg/kg with high values immediately south of Lake Taupo, in Northland and in Southland. Some further details can be found in NZ Soil Bureau (1968). Average metal levels in New Zealand subsoils are given in Table 4.5.

Table 4.5: Metal (total) levels in average New Zealand subsoils (mg/kg on a dry weight basis). (Wells, N. and Whitton, J. S., Soil Bureau, DSIR, pers. comm.).

Metal	Level	Metal	Level
Ba	700	Ni	7
Cd	0.2	Pb	10
Cu	18	Sn	3
Co	3	V	90
Cr	40	Zn	54
Mo	2	Zr	250

4.4 URBAN RUNOFF (P. C. Kennedy and R. B. Williamson)

In New Zealand, urban stormwater is separated from domestic and industrial sewer systems and the untreated storm runoff is usually discharged directly into the closest water be it fresh, estuarine, harbour or coastal.

From consideration of total metal levels alone, stormwater runoff is often regarded as a more serious pollution problem than municipal waste overseas (Ellis, 1976; Weibel *et al.*, 1964). Field and Lager (1975) and Helsel *et al.* (1979) have shown that the annual pollution load of stormwater can equal the load exerted by treated domestic sewage from the same area.

From an examination of street gutter dusts in the Wellington area (P. C. Kennedy, unpublished data) and Christchurch (Fergusson and Ryan, 1984), it is known that many metals occur in higher concentrations than local soils. For instance Cu, Pb and Zn consistently show the greatest difference from soils, the geometric mean concentrations of Cu, Pb, and Zn in whole dusts sampled in the Wellington region being 186, 1983, and 672 mg/kg respectively. These concentrations are 11, 165 and 10 times higher than those found in soils in the Wellington region. Cd is also enriched but the enrichment is more variable. Twenty six samples of dust ($<36\mu$m fraction) sampled in the Wellington area contained 0.18 to 8.9 mg Cd/kg, compared with a normal range expected of 0.1 to 0.2 mg/kg.

Input of Cd, Cu, Zn and Pb to the urban environment is usually attributed to vehicles (Shaheen, 1975; Hopke *et al.*, 1980). Probable sources are exhaust emission (Pb, Cd, Cu), tyre wear (Zn, Cd) and brake wear (Cu). The concentration of metals and their accumulation will be greatly dependent on the traffic density, season and climate and the nature of human activity on and around the street, as well as removal of dust by wind, traffic turbulence, street cleaning and stormwater runoff.

Concentrations of Cd, Cr, Cu, Ni, Pb and Zn have been measured in urban runoff in Hamilton and Auckland, New Zealand (Williamson, 1985a and b). Two of the three catchments studied were predominantly residential (in Auckland and Hamilton), while another Auckland catchment had significant areas of light industrial and developing land use. The results are shown in Table 4.6. As with overseas findings, most metals were principally (i.e. >90%) associated with particulate material, and highest concentrations were usually observed during the first flush of runoff. Cd, Cu, Pb and Zn levels in the suspended solids appeared to be significantly enriched, compared with background soils. Table 4.6 also summarises the results of a comparison of the concentration distributions in the three catchments. Cd, Pb and Zn concentrations were similar, while higher Cu concentrations were found in the catchment with industrial and developing land use, but no direct source could be identified from a sediment survey. Higher Cr and Ni concentrations in the Auckland catchments were probably due to higher levels in local soils. Table 4.7 lists the specific yields of metals from these catchments. Both yields and concentrations lie within the range reported in overseas studies.

Table 4.6: Median concentrations (mg/m^3) of metals in urban runoff. Ranges are given in brackets (Williamson, 1985a and b).

Catchment	Cd	Cr	Cu	Ni	Pb	Zn
Hillcrest, Hamilton (H) 1.1 km^2 residential	 (<0.5-3)	 (<3-40)	23 (4-250)	 <2	95 (<1-2600)	190 (10-1820)
Wairau Ck at Chartwell, Takapuna (C) 1.5 km^2 residential	1.0 (0.2-11)	37 (11-82)	22 (6-158)	33 (6-136)	157 (16-1294)	260 (144-900)
Wairau Ck at Motorway, Takapuna (M) 11 km^2 residential, industrial, developing	1.8 (0.1-7)	34 (9-150)	50 (14-436)	34 (7-101)	144 (13-820)	378 (118-1320)
Catchment differences	nsd[a]	M,C>H	M>C,H	M,C>H	nsd	nsd

[a] = only Auckland catchments compared

Table 4.7: Specific loads (kg/ha.yr) of metals from urban catchments. Catchment details are given in Table 4.6.

Catchment	Cd	Cr	Cu	Ni	Pb	Zn
Hillcrest			0.05	<0.005	0.6	0.5
Wairau Ck at Chartwell	0.02	0.07	0.13	0.13	0.7	1.5
Wairau Ck at Motorway	0.005	0.08	0.17	0.11	0.5	1.2

4.5 MUNICIPAL WASTES

Most community sewage effluent in New Zealand is discharged into saline waters with 33% going to estuaries and harbours and 25% to the ocean. Only 20% is discharged to inland waters with 18% to streams and rivers and 2% to lakes. Of the sewage discharged to the ocean, 50% receives some treatment; the percentages for estuaries and harbours, streams and rivers, and lakes are 98%, 80% and 95% respectively (Gunn, 1980). The contribution from domestic effluent is approximately 250 l/person per day.

Some New Zealand municipal waste waters have been characterised for metal content (Table 4.8). Differences in the metal content of untreated municipal waste waters will depend, to a large extent, on the industrial contributions. Industrial inputs may vary throughout the day, week and season making sewage characterisation difficult. In some large cities, there may be trade waste by-laws which will be designed to protect the sewage treatment plant from malfunction caused by toxic loads. The use of a municipal sewer to dispose of industrial wastes has the obvious advantage of affording an immediate large dilution. The level of treatment employed by the municipality will have a bearing on the quality of the final effluent (Petrasek and Kugelman, 1983).

Table 4.8: Metal levels in raw and treated sewage (mg/m^3).

		As	Cd	Co	Cr	Cu	Hg	Pb	Ni	Zn	References
Wainuiomata :	Raw	<10	<1	<7	<7	15	<1	30-80	<6	180	(1)
	Treated^a	<10	<1	<7	<7	10	<1	<7	<6	90	
Templeton :	Raw		0.4	0.4	10	50		20	2	180	(2)
	Treated^b		<0.1	<1	<1	1		1	<1	15	
Palmerston :	Raw				10	1010		180		4360	(3)
	Treated^c				10	240		10		100	
Palmerston North :	Raw	<10	<10		20	90	1	<50	<50	250	(1)
	Treated^d	<10	<10		<20	60	<1	<50	<50	160	
Wellington (Moa Point) :	Raw^f	10	2		200	300	0.4	80	80	900	(4)
Auckland (Manukau Works) :	Raw				150	110		120	40	548	(5)
									170	810	(6)
		<10	<10		270	190	<1	110	150	450	(1)
	Treated^e	20	<10		<20	60	<1	<50	50	40	(1)
Mosgiel :	Raw				1930	560		20		490	(7)
	Treated^a				600	530		8		170	
Sawyers Bay :	Raw				9	380		130		200	(7)
	Treated^a				6	250		120		180	

References:

(1) D. G. Smith (unpublished data)
(2) Quin and Syers (1978)
(3) Smillie and Loutit (1982)
(4) Beca Carter-Caldwell Connell (1980)
(5) ARA (1981)
(6) ARA (1983)
(7) Smillie (1980)

Notes:

a Clarifier plus bio-filter
b Imhoff tank plus oxidation pond
c Two stage pond system
d Aeration plus sedimentation
e Aeration, sedimentation, bio-filtration, sedimentation, oxidation ponds
f Design value for treatment plant based on several years analysis of sewage

The sewage from Wainuiomata, Templeton, Sawyers Bay and Palmerston has a very low level of industrial input, and this is reflected in the concentration of most metals. The Mosgiel plant accepts a high industrial input compared with its population. This is reflected in its exceptionally high Cr content.

Klein *et al.* (1974) surveyed the heavy metal contributions from a variety of industrial sources to New York city wastewater treatment plants. Their data are presented in Tables 4.9 and 4.10. Table 4.9 shows some considerable surprises: viz. laundry, soft drinks and ice cream industrial effluents contained high levels of copper, bakery wastes are high in Ni. The relative contributions of metals from industries (Table 4.10) also contains some surprises to the casual observer. For instance, industry with the exception of the electroplaters contributes less than 9% of the metals; the residential contribution for Cd, Cu and Zn is larger than any other source.

A limited amount of work was recently carried out in Auckland (ARA, 1981, 1983) on inputs to the Manukau sewage purification works. It was shown that the proportion of industrially derived Ni and Zn from industries not involved with metal finishing is not large, and that metal finishers produced the highest concentration and mass of Ni and Zn. It was also shown that the subcatchment which had the highest Ni and Zn concentrations (i.e., that which contained the Onehunga industrial area) contributed around 60% of the total Ni mass, but only about 27% of the Zn mass, to the sewage purification works. A large proportion of these masses would be industrially derived. However, Zn concentrations were not very much higher in this industrialised subcatchment than in more residential subcatchments. ARA (1983) noted that its Trade Wastes By-Laws limiting metal levels were frequently violated. Table 4.11 shows that industrial volume inputs are small compared with

Table 4.9: Metals in industrial wastewaters (Klein *et al.*, 1974).

Industry	Average concentrations (mg/m^3)				
	Cu	Cr	Ni	Zn	Cd
Meat processing	150	150	70	460	11
Fat rendering	220	210	280	3890	6
Fish processing	240	230	140	1590	14
Bakery	150	330	430	280	2
Miscellaneous foods	350	150	110	1100	6
Brewery	410	60	40	470	5
Soft drinks and flavourings	2040	180	220	2990	3
Ice cream	2700	50	110	780	31
Textile dyeing	37	820	250	500	30
Fur dressing and dyeing	7040	20140	740	1730	115
Miscellaneous chemicals	160	280	100	800	27
Laundry	1700	1220	100	1750	134
Car wash	180	140	190	920	18

Table 4.10: Relative contributions of metals to New York City wastewater plants (Klein *et al.*, 1974).

Source	Percentage of total weights received				
	Cd	Cu	Cr	Ni	Zn
Water supply	0	20	0	0	7
Electroplaters	33	12	43	62	13
Other industrial	6	7	9	3	7
Runoff	12	14	9	10	31
Residential	49	47	28	25	42
Unknown	0	0	11	0	0
Total (kg/day)	(73)	(1160)	(674)	(509)	(1780)

domestic input, and that the industries whose discharges are likely to be highly contaminated with metals (e.g., tanners, electroplaters, metal industry, battery manufacturers, wood industry) produce only about 3% of the total flow to the treatment plant. A detailed metals survey has been carried out for Christchurch sewage but data were not available.

In 1983/84 Steven, Fitzmaurice and Partners characterised individual effluent streams in the Waitara region, for proposed collective disposal to the Waitara outfall, by carrying out spring, summer and autumn surveys (SFP, 1984). The wastestreams examined were the domestic, meat works, woolscour, the newly-commissioned methanol plant, a dairy factory, and a car assembly plant. The heavy metals analysed were Cd, Cr, Cu, Hg, Ni, Pb and Zn. An indication of metal levels in the woolscour, methanol plant, and car plant effluents is presented later (Sections 4.8.5, 4.8.8, and 4.8.3 respectively). One disposal option is to combine the industrial wastes with the current coastal discharge of domestic and meatworks sewage. In terms of heavy metal concentrations, it seems as though these added wastes would have a negligible effect.

Thus, for cities and towns, industry may not always be the major contributor of heavy metals in sewage. The same may not be true for some small towns whose sewage works accept a considerable industrial load, e.g., Mosgiel.

Much of the metal removed during sewage treatment will be contained in the sludge (Table 4.12). Of the large towns and cities listed in the table, only Auckland and Christchurch raw sewage contain a large industrial input. Sludges from these cities contain higher concentrations of Cr, Cu, Pb, Ni than those from non-industrialised areas. However, except for Cr in Christchurch sludge, these metal levels are not high when compared with those from the other parts of the world (Whitton and Wells, 1978; Livingstone, 1980). Sludges still have to be disposed of safely. Disposal to pasture (Livingstone, 1980), home gardens, and tips are the more common New Zealand practices, and guidelines are available which ensure that metal levels in soils are not increased to dangerous levels (Harding, 1984).

Table 4.11: Industrial wastewaters treated at the ARA Manukau treatment plant 1980-1981 (after Shanks, 1982).

Industry	Average flow m^3/day	% of total
Meat industry	12000	5.0
Casing processors	100	<0.1
Milk products	1900	0.8
Bacon and small goods	600	0.3
Brewers	2800	1.2
Canners	200	<0.1
Ice cream manufacturers	500	0.2
Tanners	600	0.2
Wheat processors	700	0.3
Laundries	3900	1.6
Wood industry	2500	1.0
Woolscourers	1500	0.6
Margarine manufacturers	1000	0.4
Glue manufacturers	100	<0.1
Tallow refiners	100	<0.1
Electroplaters	3700	1.6
Metal industry	900	0.4
Aerated water manufacturers	600	0.2
Fish processors	400	0.2
Biscuit manufacturers	200	<0.1
Confectionary manufacturers	700	0.3
Fruit preservers	200	<0.1
Battery manufacturers	300	0.1
Stockyards	100	<0.1
General	2000	0.8
Approx. total industrial	37500	15.5
Total domestic	204500	84.5
Total	242000	100.0

Table 4.12: Metal levels in sewage sludge (mg/kg on dry weight basis).

	Cd	Cr	Cu	Pb	Sn	Ni	V	Zn	Reference
Auckland (Manukau works)	4.5	850	720	610	80	350	80	700	(1)
Levin		100	310	180	90	32	14	1200	(2)
Templeton (a)	0.6	46	65	35		5.5		250	(3)
(b)	2.5	66	340	95		12		1100	
Christchurch	2-4	4780	595	359		142		2080	(4)
Average NZ sludge	8.5	270	750	290	100	110	48	1400	(5)

References: (1) Whitton and Wells (1978)
(2) Wells and Whitton (1976)
(3) Quin and Syers (1978)
(4) Livingstone (1980)
(5) Wells and Whitton, DSIR, pers. comm.

Notes: (a) Pond sludge
(b) Imhoff tank sludge

4.6 REFUSE TIPS

The Department of Health has published data on 567 tips sited throughout New Zealand; 79 are classified as sites which accept and properly manage 'hazardous wastes' (Board of Health, 1983). The sites which accept metal-containing wastes were not specifically identified in the report. Of the sites which accept hazardous waste, all but 16 are run by local authorities.

Tip leachates will contain heavy metals, but their concentration will depend on what is dumped, the degree of treatment, and the management of the site. In large cities, tip leachate may be intercepted by a trade waste sewer (and possibly subject to trade waste by-laws); in other instances leachate may cause pollution by percolating to groundwater (East Cape Catchment Board, 1984) or discharging directly to a surface watercourse. In a well-managed tip, good perimeter drainage and covering filled areas with impermeable materials will minimise throughflow and hence the leachate discharge. Generally, only around 25% of the annual precipitation over a tip will emerge as leachate (Thom, 1984).

Levels of heavy metals found in the few New Zealand studies on tip leachates are given in Table 4.13, and would indicate that Zn levels can be very high. High levels of Cu (up to 3100 mg/m^3) and Ni (up to 880 mg/m^3) in land-fill leachate, and one instance of high Cr (100 000 mg/m^3) from a tannery dump leachate have also been recorded (A. Cooke, Cawthron Institute, pers. comm.). Leachate from the Silverstream and Horokiwi tips was approximately neutral; Auckland tip 'F' pH was around 6, so metal mobilisation by low pH is not likely to be a problem.

Table 4.13: Tip leachate heavy metal levels (mg/m^3) (G. MacFarlane, Department of Health, pers. comm.).

		Cd	Co	Cr	Cu	Ni	Pb	Zn
Hutt City	(1981)	5	10	30-100	10-50	20-140	80-300	510-3190
(Silverstream)	(1973)	1		20	10		10	200
Wellington	(1975)							
(Happy Valley)								470-2400
(Horokiwi)								10-20
Auckland Tip "F"	(1978- 1982)	10-50		60-190	130-500	80	320-710	7800-41800

A recent New Zealand survey (O'Grady, 1983) identified the types and volumes of 'hazardous waste' generated in five of the 18 New Zealand health districts, and commented on their disposal to land. It was found that many of the wastes are quite dilute and include large volumes of water, and 85% of the wastes were liquid or sludges. O'Grady (1983) found that timber treatment, metal finishing and tanning wastes posed the greatest potential hazard if not satisfactorily disposed of. However, none of the hazardous wastes seem to pose a significant problem in the areas surveyed, but there is still a need to manage them properly.

A recent assessment by the Ministry of Works and Development of hazardous waste disposal practices (Wareham, 1983) concluded that although there is a lack of specific information on waste quantities and types, quantities are small. The report recommended the production of regional and national waste inventories and the use of co-disposal sites with appropriate management techniques. The use of co-disposal practices, as well as good tip siting and management, are also being recommended by Thom (1984). The Ministry of Works and Development is currently preparing guidelines for the selection and appraisal of sites for the disposal of domestic and industrial solid wastes, and the co-disposal of hazardous wastes.

It would seem that practices leading to the satisfactory disposal of hazardous wastes (i.e., those which cannot be disposed of to a sewer or natural water) are becoming established in New Zealand. However, it may still be necessary to monitor leachates and runoff from disposal sites.

4.7 AGRICULTURE

The New Zealand Agricultural Chemicals Board (now called The Pesticides Board) has published a list of chemicals which have been registered in New Zealand for agricultural use (Agricultural Chemicals Board, 1980). A later publication (Agricultural Chemicals Board, 1981) listed the trade names, common names, preferred chemical names and use of registered chemicals. Most agricultural chemicals are wholly organic, but several compounds are registered which contain heavy metals, e.g., Cu and Zn. The metals occur in a variety of chemical forms and are used mainly as fungicides. A survey of chemicals in the Upper Waitemata Harbour catchment (van Roon, 1982) revealed that they were in use in vineyards, orchards and market gardens. In apple orchards, the annual loading of Cu-containing 'Bordeaux' is 120 kg/ha (R. J. Wilcock, Water Quality Centre, MWD, pers. comm.), i.e., about 30 kg Cu/ha. Assuming a value of 20 mg Cu/kg of soil (see Section 4.3) and a soil density of 2 t/m^3, there are approximately 40 kg Cu/ha in the top 10 cm of soil. Thus, the annual loading of Cu is equivalent to the Cu content of the top 10 cm soil. The potential threat to the aquatic environment due to agricultural chemicals is unknown and work is in progress to assess the situation (R. J. Wilcock, Water Quality Centre, MWD, pers. comm.).

The pig production industry produces wastewater which can contain high levels of heavy metals (Overcash *et al.*, 1978). Raw wastes would not normally be discharged direct to natural water, but are treated via lagoons or by application to land. The industry uses high levels of copper and moderate levels of other metals as growth stimulants and diet supplements respectively (Overcash *et al.*, 1978). Overseas effluent data are presented in Table 4.14, together with data obtained from analysis of single samples of 'typical' effluent from two North Island piggeries (D. G. Smith, unpublished results). After treatment, the Cu levels are similar to a raw municipal sewage with some industrial input (Table 4.8). Zn levels seem variable, while other metal levels are low. On a single grab sample of raw effluent from an unnamed North Island piggery, Whitton and Wells (1974) obtained a Zn level of 800 mg/m^3. In all probability, much of the metal discharged would be bound to organic material or inorganic particulates, and this would affect bioavailability. Flows from piggeries would be approximately 20 l/day per pig (Davis, 1973).

Table 4.14: Piggery effluent metal levels (mg/m^3) for a 2 pond lagoon system. (Values in brackets are for dissolved metal.)

Metal	Raw effluent	Primary pond effluent	Secondary pond effluent	Reference
Cd			0.8	(2)
			1.1	(2)
Cr			<10	(2)
			<10	(2)
Cu	14000	410-530	180-220	(1)
			334 (87)	(2)
			65 (15)	(2)
Ni			<7	(2)
			<7	(2)
Pb			<3	(2)
			<3	(2)
Zn	8000	360-440	140-190	(1)
			1575 (425)	(2)
			65 (75)	(2)

References: (1) Overcash *et al.*, (1978)
(2) D. G. Smith, unpublished results

Rock phosphate and the product superphosphate can contain considerable quantities of heavy metals. Production of superphosphate fertiliser in New Zealand is about 1.7 × 10^6 t/annum. Approximately half of the sown grassland receives fertiliser annually of which half is aerially distributed (New Zealand Official Yearbook, 1984). Nauru Island phosphate rock contains 86 mg/kg Cd and 770 mg/kg Zn (Bioresearches, 1983a), and Williams and David (1973) have reported around 30 mg/kg Cd in a New South Wales superphosphate sample. The effects of the use of agricultural chemicals, and in particular fertilisers, are unknown. A few years ago it was estimated that fertilisers were the most significant source of the build-up of Cd in agricultural land (5 g/ha per annum in Europe) (Hutton, 1982). The data presented in Hutton (1982) would seem to imply a potential for high Cd input to waters by use of phosphate fertilisers. Studies in New Zealand (see McColl and Hughes, 1981) have shown that several percent of phosphate from the superphosphate applied to a catchment may be lost to streams, most directly during application. The potential for water contamination by Cd would seem high especially during application.

4.8 INDUSTRIAL

Many industries have the potential to discharge heavy metals to the environment (see Table 4.15) but not all discharge directly to natural water. Many industries treat their wastewater thereby producing sludge. Solid wastes and sludge would not normally be disposed of to the aquatic environment but may still present a threat if not disposed of in an appropriate manner.

Industries in New Zealand dispose of their wastewater in four main ways:

1. discharge to a municipal sewer;
2. discharge to a surface water;
3. discharge onto land;
4. transportation of small volumes to commercial treatment plants.

Discharge to a municipal sewer is generally the most common method of disposal and the trend in New Zealand is for such disposal wherever this is possible.

Table 4.15: Potential industrial sources of heavy metal pollution (OECD, 1982).

Industrial source	As	Cd	Cr	Co	Cu	Pb	Hg	Ni	Sn	V	Zn	No of plants in NZ
Agriculture												
(pesticides/fungicides)	X				X	X						8
(animal excreta)					X						X	
Electronics					X							
Engineering (soldering)					X						X	
Leather			X									19
Metal finishing												
(decreasing)					X						X	
(pickling)			X		X				X		X	
(electroplating)		X	X		X	X		X	X		X	
(bright dipping)		X	X		X						X	
(chemical colouring)	X		X		X	X		X				
(anodising and dyeing)			X	X				X				
(wet polishing)			X									
(brightening)			X									
(rust proofing)			X									
(painting) (P)												
Metal Mining (Pb/Zn)					X	X					X	0
Non-ferrous metals (smelting)		X			X	X	X				X	
Paints/pigments	X	X	X	X	X	X					X	31
Petroleum (refining)								X		X		9
Printing (P)			X		X							83
Rubber (foam)											X	
Storage batteries												
Ni-Cd		X						X				
Pb						X						
Textiles (dyeing)			X		X							15
Timber	X		X		X						X	44

P = pigments
The number of plants in New Zealand obtained from the New Zealand Yearbook (1984)

A survey of regional water boards (Smith, 1982b) showed that most boards had a good idea of the **number** of liquid discharges of toxic substances to the aquatic environment but few were able to provide a detailed account of the **nature** of these wastes, e.g., the concentration of heavy metals. In many cases it is likely that the data sought were simply not available. The Water Rights archive at the Vogel Computer Centre, MWD, gives no details of the conditions attached to water rights. It is impossible to make a simple rapid assessment of the concentrations and mass loads of heavy metals entering the aquatic environment from industry on present information.

In a survey of industrial wastewater treatment in New Zealand Shanks (1982) examines the characteristics of industrial wastewaters, their treatment and disposal. Unfortunately, and presumably because of a lack of available data, there is again little information on heavy metal levels.

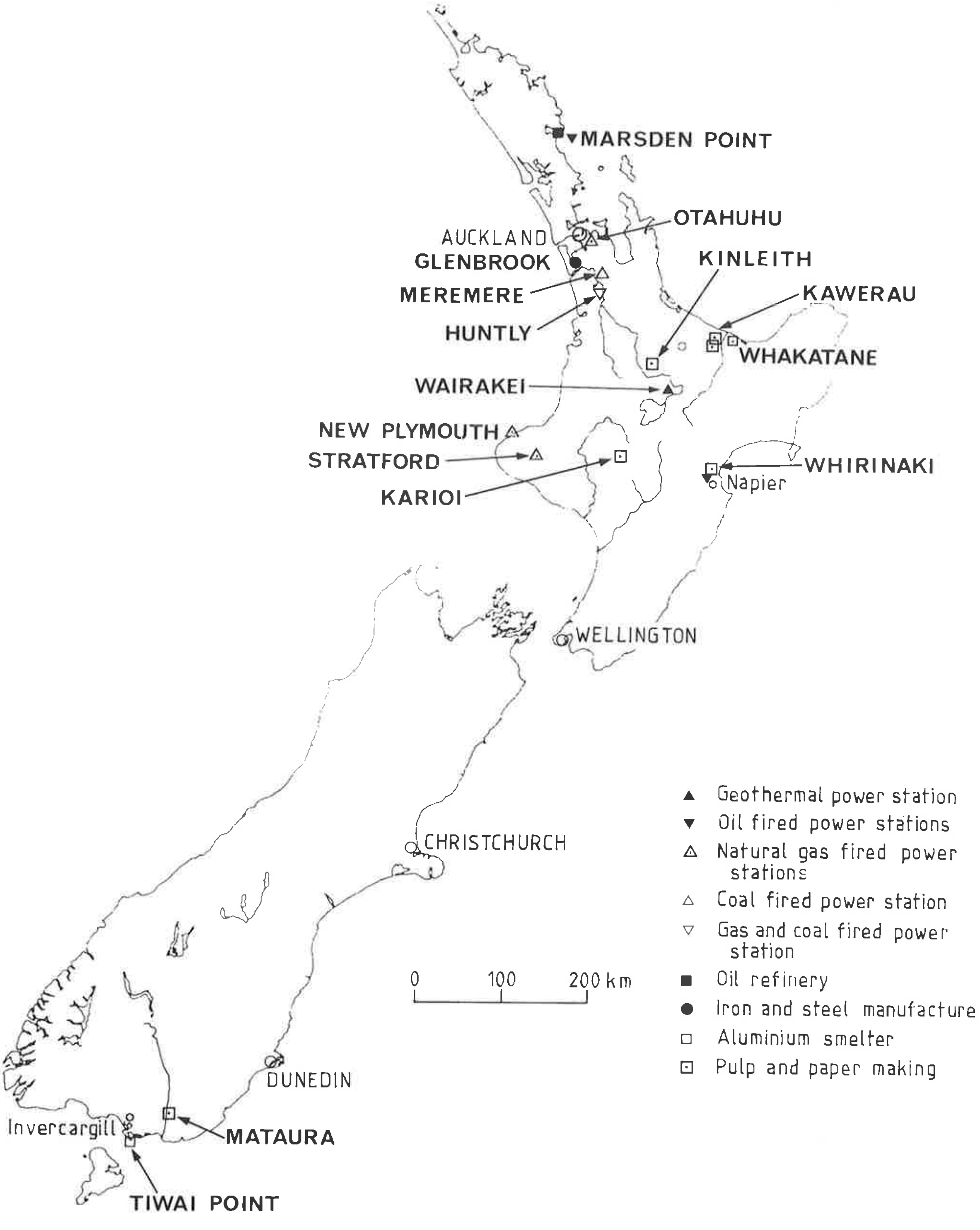


Figure 4.3: Locations of some of the major industries (based on New Zealand Official Yearbook, 1984).

The rest of this section is devoted to the wastes from classes of industry in New Zealand. Where no local data are available, information has been drawn from overseas sources to enable a picture of potential problems to be developed. The locations of the major industries are shown in Figure 4.3.

4.8.1 Mining

Mining, especially base metal mining, has the potential to discharge heavy metals unless wastes are treated (Lawrence and Smith, 1983). Currently, there are no base metal mines in New Zealand and it appears that few are likely. However, there are likely to be many gold and silver mines and there are likely to be several large scale coal mines for the foreseeable future, some of which may discharge heavy metals. Figures 4.4 and 4.5 indicate the main locations of New Zealand's coal fields and metal mining/prospecting areas respectively.

Potential sources of metals are exposed cuts, dumps (including ore concentrate piles and tailings), processing wastes (e.g., from cyanidation), the mine itself and possibly rehabilitated land. Management practices for mines in New Zealand have recently been published (Lawrence and Smith, 1983).

The concentration of heavy metals in waters from mining operations may be increased by the frequent presence of sulphide minerals. On exposure to atmospheric oxygen and water these materials oxidise and produce a water of low pH (even below 3, see for example, Stander *et al.*, 1970). Base metal, coal and some gold and silver mines can contain sulphides.

Historically, mining does not have a good reputation in New Zealand. The operation of the now closed Tui Mine near Te Aroha (which extracted Pb, Zn and Cu) left about 10^6 m^3 of tailings in an unstable tailings pond constructed on the slopes of Mt Te Aroha. Table 4.16 indicates the levels of metals emanating from the lowest mine drive and the combined discharge from the tailings pond (Hendy, 1981). The discharge waters resulted in severe contamination of a nearby stream (see Section 6.2.4).

Table 4.16: Average levels (mg/m^3) of metals emanating from the Tui Mine (Hendy, 1981).

	Cd	Cu	Zn
Waters from lowest mine drive ($pH \approx 7.7$)	103	<30-300	10900
Combined tailings discharge ($pH \approx 3.8$)	90	700	37800

New Zealand coals have been analysed for metal content (Sim and Lewin, 1975; Sim, 1977; Lynskey *et al.*, 1984). Following the recommendation of Aggett (1983) the wet ash analyses of Sim and Lewin (1975) for volatile metals have been used here and coal metal levels recalculated. The data are presented in Table 4.17. Where insufficient data are available to calculate a mean, a range is given.

Table 4.17: Metal content (mg/kg) of New Zealand coals.

	Sim and Lewin (1975)	Lynskey *et al.* (1984)
As	<1.5-12[1]	1.0-3.0
Cd[2]	<0.3-1.8[1]	<0.02-0.05; <0.8
Co	2.8	1.8-7.1
Cr	4.1	2.7-12
Cu		0.8-4.7
Ni	6	4.1-23
Pb	4.1[1]	0.2-1.1
Sn	1.9[1]	0.5-3.0
V	6.4	<3-19
Zn	7.0[1]	3.2-17

[1] Recalculated. For As and Cd the majority of results were below detection limit.

[2] Note the variable detection limits for Cd. The values given by Lynskey *et al.* are 'preferred values'.

The coals analysed have low metal concentrations compared with New Zealand subsoils (Table 4.5). New Zealand coals are also usually low in sulphur content with a weighted mean of mined coal being in the vicinity of 0.8% (calculated from data supplied by the Coal Research Association

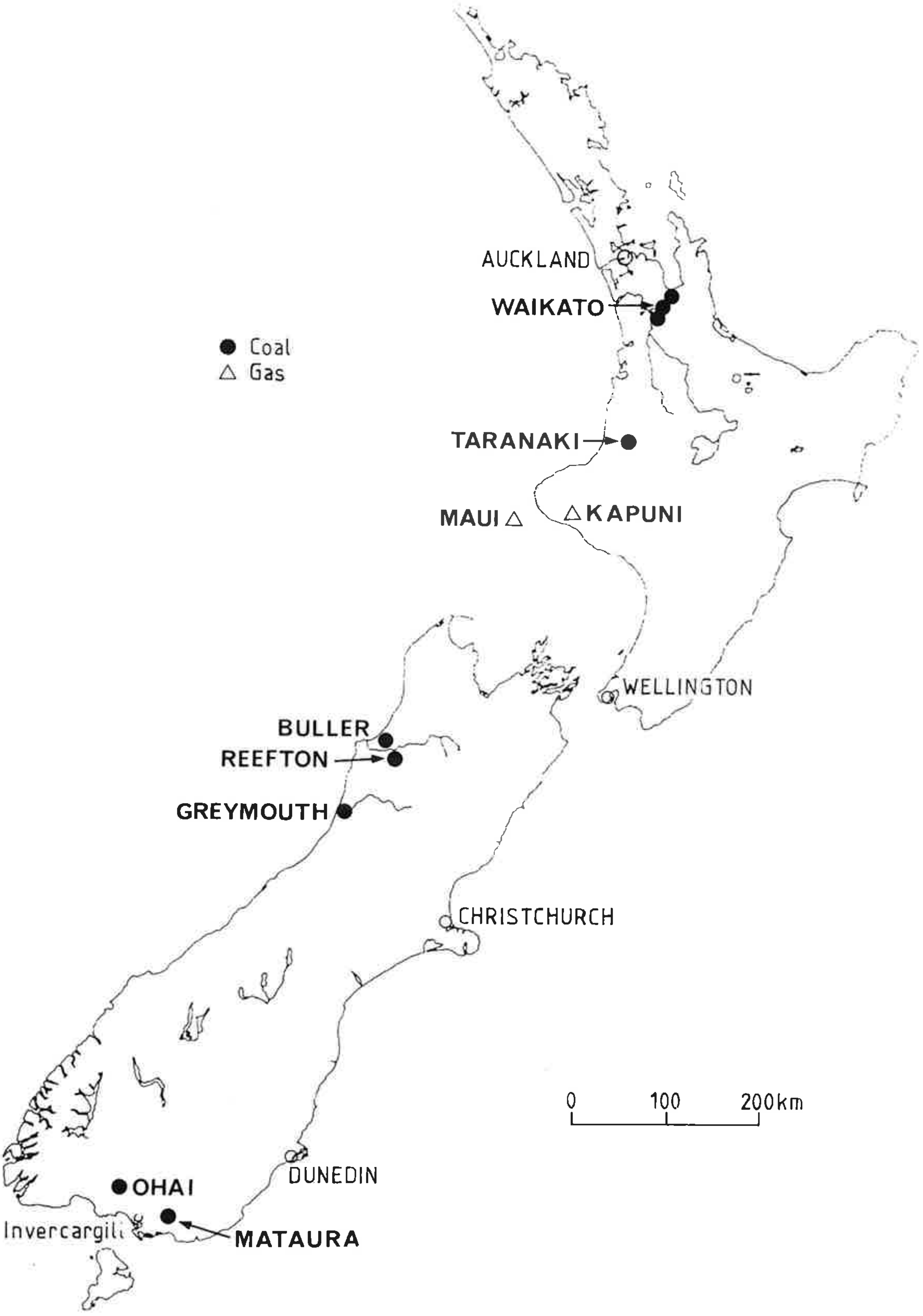


Figure 4.4: Locations of the main coal and gas fields of New Zealand (New Zealand Official Yearbook, 1982: for further detail see New Zealand Official Yearbook, 1984).

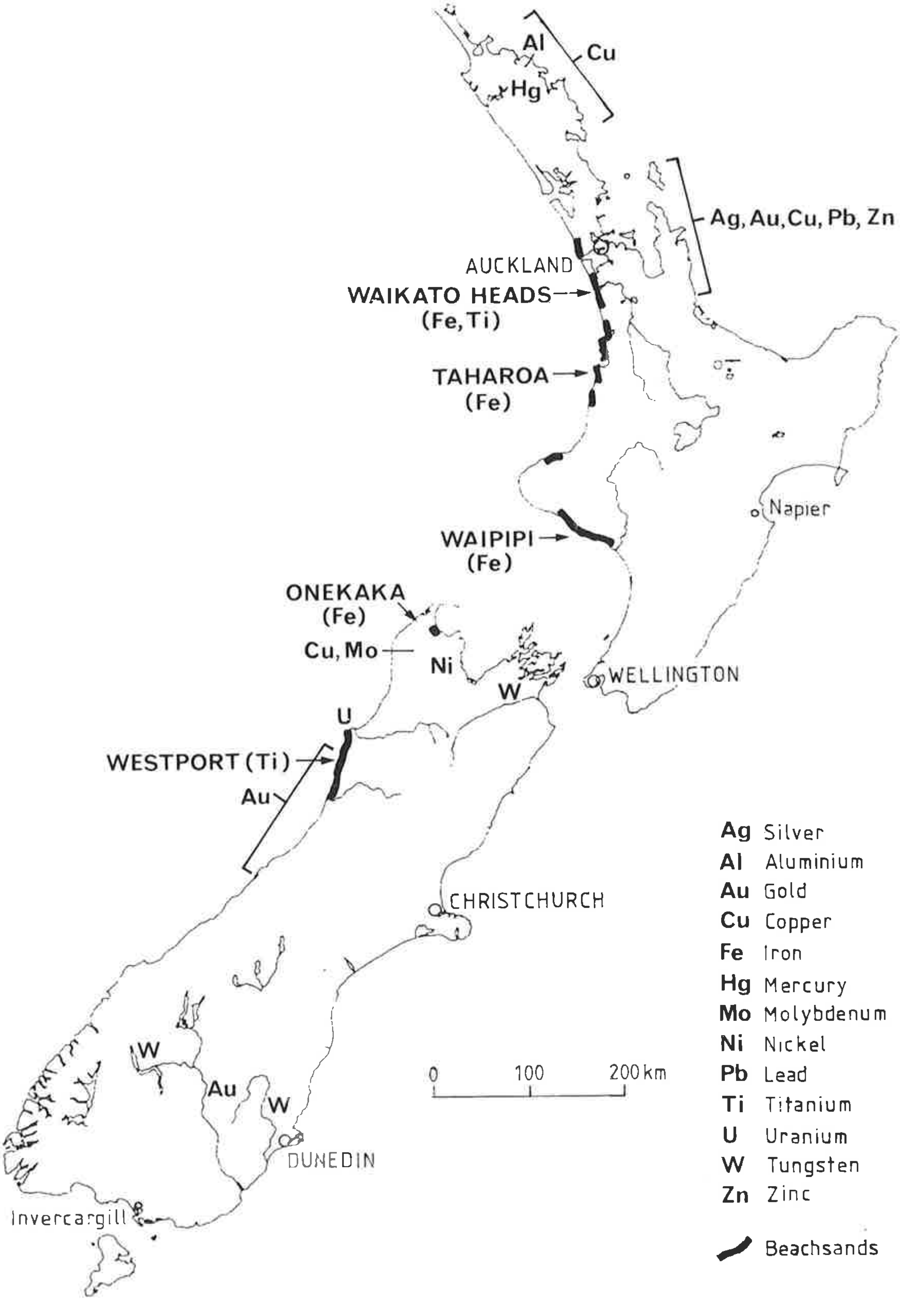


Figure 4.5: Main locations of metal mining and prospecting (New Zealand Official Yearbook, 1982).

of NZ Inc.). The highest sulphur content coals occur in the Buller and Otago regions. Acid wastewaters are not likely to occur in low sulphur coal thus the potential for metal discharge is reduced. Discharges from mines in the Huntly coalfield are generally free of significant concentrations of heavy metals (R. J. Matthews and B. J. Zuur, Waikato Valley Authority, pers. comm.); the pH values are usually in the 7-8 region. This is partially substantiated by analysis of a single effluent sample (pH 7.8) taken from the Weaver's Mine; levels determined for total metal were Cd $<0.2 mg/m^3$, Cr 24 mg/m^3, Cu $<11 mg/m^3$, Ni 21 mg/m^3, Pb $<3 mg/m^3$, Zn 55 mg/m^3 (D. G. Smith, unpublished data).

4.8.2 Timber

This section has been divided into two sections, the first considers the pulp and paper industry, the second the timber preservation industry.

Pulp and paper: There are seven mills in New Zealand which discharge a wastewater volume approximately equal to half the total New Zealand domestic wastewater (Shanks, 1982). In the past, Hg was used in the electrolytic generation of chlorine for bleaching, and zinc hydrosulphite used as a pulp leaching agent. Little heavy metals data for wastes appear to be available in the literature, but Campin (1981) reported the daily losses (in kg) from the Kinleith plant and they have been used here to estimate concentrations assuming a mean discharge of 2 m^3/s. These concentrations are presented in Table 4.18, together with results from analysis of a single sample of 'typical' effluent in 1984 (D. G. Smith, unpublished results) and a Zn concentration determined on a sample of effluent a decade ago (Whitton and Wells, 1974). The wastes from the Kinleith plant include a contribution from a timber treatment plant and may not be typical of mill effluent.

Table 4.18: Metal levels (mg/m^3) in effluent from the Kinleith pulp and paper plant.

	From Campin (1981)	Whitton and Wells (1974)	Smith, D. G. (Unpub. results)*
As	19		
Cd			1.6
Cu	7		22(<11)
Cr	16		28(30)
Hg	1.1		
Ni			14(<7)
Pb			5(<3)
Zn		132	<50(<50)

*Values in brackets are for dissolved metal.

Timber preservation: Exotic timbers produced in New Zealand are frequently treated with preservatives to prevent fungal attack and sapstain. The most common processes use copper-chrome-arsenate (CCA), boron salts, sodium pentachlorophenate or a mixture of fluoride and arsenite (Corson, 1973). Contamination to waterways can result from spillages, and the non-containment of preservative solution dripping from freshly treated timber. Many plants have concrete aprons with totally enclosed drainage systems so that the preservative solution can be recycled and not wasted. However, stormwater may be contaminated with preservative.

Discharges from timber preservation plants can be very variable in composition and site specific. In the past ten years the Cawthron Institute has analysed many liquid discharges, supplied to them by regional water boards. The results (Table 4.19) show wide concentration ranges (A. Cooke,

Table 4.19: Ranges and median values (mg/m^3) for timber preservation plant wastewaters (A. Cooke, Cawthron Institute, pers. comm.).

	Range	Median	n
As	<10-165000	2500	20
Cu	<50-102000	110	19
Cr	<20-114000	220	20

Cawthron Institute, pers. comm.). The most serious problem emanating from the use of treatment chemicals would seem to be the result of spillages (see Section 6.2.9 and Smith, 1982b).

4.8.3 Metal Working/Finishing

In this category are electroplating, galvanising, anodising, paint stripping and other metal working plants. The Auckland Regional Authority has recently carried out a small survey on discharges of Ni and Zn from the metal industry in the Onehunga area of Auckland (ARA, 1983) and some of their results are presented in Table 4.20.

Table 4.20: Average Ni and Zn levels (mg/m^3) in metal industry wastewaters (ARA, 1983).

Industry	Ni	Zn
Galvanising	140	200000
Metal plating	12000	33000
Anodising	3400	130
Other	200	1600

The ARA found that there was a high incidence of low pH discharges (i.e., less than the Trade Waste By-Law limit of pH 6). The galvanising and metal plating industries waste concentrations generally exceeded the Zn Trade Waste By-Law limit (5000 mg/m^3) while only the metal plating industry exceeded the Ni limit (5000 mg/m^3). On a mass basis, the high waste volume anodising industry produced the majority of the Ni (bronze anodising) and the hot-dip galvanisers the majority of the Zn. The metal plating industry produced smaller quantities of Ni and Zn, because the majority of firms in this category had lower volume discharges.

Metal industry wastewaters, analysed for regional water boards, show a wide range in metal concentrations (Table 4.21), although discharges are probably low and infrequent. For instance, wastewaters from a vehicle assembly plant in Taranaki, whilst containing some high metal concentrations (e.g., Cr 1970 mg/m^3, Zn 1250 mg/m^3), were of low volume (2 m^3) during the day of sampling (SFP, 1984).

Table 4.21: Ranges and medians of metal levels (mg/m^3) for metal working* wastewater (A. Cooke, Cawthron Institute, pers. comm.).

Metal	Range	Median	n
Cd	$<$10-3900	230	18
Cu	$<$20-1700	80	18
Cr	$<$50-17000	380	20
Nr	$<$50-16000	$<$50	17
Zn	$<$20-18000	180	17

*Includes metal repair/reconditioning, electroplating, corrosion inhibition, paint stripping.

4.8.4 Fossil fuel combustion (D. G. Smith and P. C. Kennedy)

Fossil fuel combustion is one of the most important sources of trace element emission to the atmosphere (Hart, 1982; Forstner and Wittman, 1983).

Coal: Coal production in New Zealand was 2.1×10^6 t per annum in 1982 (New Zealand Yearbook, 1984), 7×10^5 t of which were used at the Meremere Power Station. The newly-commissioned Huntly Power Station is expected to consume 2×10^6 t per annum. A third station by the Waikato river is being planned. Coal production and use are therefore expected to rise considerably.

Coal-fired power stations and other plants burning coal and coke can contribute heavy metals not only directly to water from stockpiles, cooling, blowdown and other process waste discharge and via disposal of ash, but also to the atmosphere in flue gases and fly ash. The effects of atmospheric discharge of metals is not known, but in the case of Huntly Power Station, fly ash metal concentrations appear to be similar to those of soils (C. D. Stevenson, Chemistry Division, DSIR, pers. comm.).

There is a wide variation in metal content in the ashes of coals from different regions of New Zealand (Table 4.22). The pH of ash pond waters is likely to be high enough (pH 8-10) to precipitate considerable quantities of metals. Analysis of a single sample of 'typical' pond effluent from the Huntly Power Station (D. G. Smith, unpublished) gave Cd 0.5 mg/m^3, $Cr < 10 mg/m^3$, $Cu < 11 mg/m^3$, $Ni < 7 mg/m^3$, $Pb < 3 mg/m^3$, $Zn < 50 mg/m^3$. Ash pond waters may be disposed of via the plant cooling waters in which case much dilution will have been achieved prior to discharge to the receiving water (as at the Huntly Power Station).

Table 4.22: Range of levels of some heavy metals in NZ coal ashes (mg/kg).

Metal	Sim (1977)	Soong and Berrow (1979)
As	<50-550	
Cd	<10-30	
Co	<5-250	2-100
Cr	35-250	6-380
Ni	40-500	30-240
Pb	5-500	20-200
Sn	2-150	15-150
V	25-500	25-150
Zn	25-500	52-270
Ash %	3.1-20.2	2.3-19.4

Oil: Oil use in power stations is small compared with coal consumption. In 1983, less than 2% of the total New Zealand thermal electricity generation was fueled by oil, whereas 21% of the energy consumed by industry and commerce was from oil (New Zealand Yearbook, 1984). Oil burning, without stack gas cleaning, is generally comparable with coal-fired units with 99% stack control efficiency. The burning of fuel oil does not seem likely to be having any effect on waterways.

Wood: Wood is used in home heating and in Europe it may be an important source of Cu and Zn emissions in some areas (Pacyna, 1983). The combustion of treated timber will be a source of As, Cr, and Cu to the atmosphere although this will probably be relatively minor. The contribution of metals to the atmosphere due to the burning of painted wood is also likely to be small.

Petroleum products in internal combustion engines: Petrol combustion in motor vehicle engines is a major source of Pb and in New Zealand, of the total amount of Pb emitted to the atmosphere, more than 99% comes from this source (Day, 1977). Other metals such as Cd, Cu, Ni and Zn are also emitted but the amounts are small compared with other sources. Day (1977) has calculated that, in 1976, around 1330 t of Pb were emitted from New Zealand motor vehicles in exhaust gases. This accounts for 75% of the Pb used as a petrol additive. Much of the exhausted lead will be deposited close to the road system and much of this will enter water bodies via stormwater run-off (see Section 4.4).

4.8.5 Tanneries/Dyers/Woolscourers

Tanneries: There are only two tanneries in New Zealand currently discharging effluent (secondary treated) to natural water (I. Mason, Leather and Shoe Research Association, pers. comm.). The remainder of the nation's tanners (17) discharge to sewage systems. Mason (1984) has compiled data on the aerated lagoon effluent characteristics of the Southland Tannery at Mataura and has indicated that the predominant heavy metal in the discharge is Cr which is employed for tannage and supplied in trivalent form as basic chromium sulphate. Other heavy metals would arise only as chemical reagent impurities or from the stripping of metals from the plant itself, e.g., from piping (I. Mason, LASRA, pers. comm.). Chromium levels found in discharges from tanneries are given in Table 4.23.

The Cr concentrations (mainly as insoluble Cr^{3+} species) in tannery effluents can be very high and variable. In one instance, a grab sample of discharged clean-up waters had a total Cr level of 7900 g/m^3 and a pH of 3.8 (G. W. Hooper, Hawkes Bay RWB, pers. comm.). Volumes discharged are fairly small e.g., the Southland Tannery discharge at Mataura averages around $150m^3/day$.

Table 4.23: Chromium levels (mg/m^3) in tannery effluents.

Mean	Range	Location	Reference
15000	1500-46000	Southland tannery	(1)
300^d	10-3600^d	Sawyers Bay, Otago Harbour	(2)
15730	<20-41250	Sawyers Bay, Otago Harbour	(3)
310^d	<20-2550^d	Sawyers Bay, Otago Harbour	(3)

References: (1) Mason (1984)
(2) Smillie *et al.* (1981)
(3) Smillie (1980)

Note: d = dissolved metal

Dyers: Into this category can be placed the dyeing of carpets, wools and other textiles. In 1981/82 there were 15 enterprises involved in the dyeing, printing, and finishing of yarns and textiles and 22 in manufacturing carpets and rugs (New Zealand Yearbook, 1984).

Carpet mills in New Zealand may use dyes containing Cu, Co, Cr and Ni complexed with organic molecules. Normally 95-99% adsorption onto the wool is achieved (D. Holey, Bayer NZ Ltd, pers. comm.). Polyester/cotton materials are not dyed with metal complexes (D. Holey, Bayer NZ Ltd, pers. comm.).

The United States EPA (EPA, 1980i) has found that the following metals are most likely to be found in treated effluents from textile mills: Ag, As, Cd, Cr, Cu, Hg, Pb, Ni, Zn. The levels of metals found in untreated dye bath wastes are very variable and depend to a large extent on the type of dyeing process and the material to be dyed (Table 4.24). Sludge from the dyeing baths can be high in metal levels.

Table 4.24: Range of mean values (mg/m^3) found for untreated textile bath wastes (from EPA, 1980i).

Metal	Range
Cd	10-7500
Cr	30-2710
Cu	50-12050
Pb	100-1950
Hg	310-2200
Zn	460-3430

The only New Zealand published data for dye effluent were obtained by Patrick and Loutit (1972) from a textile mill discharging into the Tokomairiro River (Table 4.25). Unfortunately no indication is given as to how the effluent was sampled. The potential for metal discharge exists, but levels do not seem likely to be high.

Table 4.25: Metal levels (mg/m^3) in textile mill effluent (Patrick and Loutit, 1972).

Metal	Level
Cr	200
Cu	600
Pb	<100
Zn	80

Woolscourers: In the main, the pollutants from woolscourers (of which there were 30 in New Zealand in 1981 (Jamieson, 1981) will be oxygen demanding substances and suspended material, e.g., grease, suint, dirt, detergent, wool fibres and vegetable matter (Shanks, 1982). Because heavy metals are not used in processing, levels would not be expected to be high. Three analyses of woolscour effluent are given in Table 4.26. The metal concentrations found are unlikely to pose a problem.

Table 4.26: Metal levels (mg/m^3) in woolscour effluent.

Metal	Patrick and Loutit (1972)	SFP (1984)[b]	Smith, D. G. (Unpublished results)[a]	
			Total	Dissolved
Cd		2	0.4	
Cr	200	115	38	14
Cu	900	53	32	<11
Hg		0.1		
Ni		122	14	13
Pb	300	33	11	<3
Zn	400	580	145	75

Notes:
a Sample taken (in 1984) from discharge point following treatment by an apparently inefficient pond system; flow ≈ 10 1/s.
b Mean of two sampling runs; discharge ≈ 14 1/s.

4.8.6 Abattoirs and Dairy Factories

Abattoirs: In 1978/9 there were 44 meat export works and 29 other abattoirs and rural slaughterhouses in New Zealand (New Zealand Yearbook, 1982). By 1983 the number of export works had dropped to 39 (Cooper, 1983). The volumes discharged by large abattoirs are comparable to the discharges from small city sewage works (Wells and Whitton, 1970).

Wells and Whitton (1970), in their study of the influence of meatworks effluents on soil and plant composition, examined the metal levels in several abattoir effluents (Table 4.27). The raw effluent metal concentrations are similar to those found in raw domestic sewage from non-industrialised communities (see Table 4.8). The treated effluent metal concentrations (Makarewa) are generally much lower than those of treated domestic sewage because a considerable proportion of most metals is removed by settling. Presumably much of the metal mass in raw effluent is derived from dust and dirt and not from processing. There do not seem to be any other publications on metal levels in New Zealand meatworks wastes.

Table 4.27: Metal levels (mg/m^3) in abattoir effluent* (after Wells and Whitton, 1970).

	Cu	Cr	Co	Mo	Ni	Pb	V	Zn
Islington, Christchurch Raw effluent	111	9	5.0	2.1	11.1	34	15	145
Fairfield, Ashburton Raw effluent	32	6	3.1	1.7	5.4	30	12	124
Makarewa effluent (after settling/oxidation)	14	0.2	<0.1	0.6	<0.1	<1	6	<5

* For Islington, mean of 2 samples; for Fairfield, mean of 3 samples; for Makarewa, 1 sample only. All collected at killing season peak.

Dairy Factories: The number of dairy plants in New Zealand disposing their effluent directly to natural waterways has decreased considerably since 1972, with a corresponding increase in the number of plants using spray irrigation (Parkin and Marshall, 1981). In 1980, there were 81 dairy plants (Parkin and Marshall, 1981). By 1984 there were 50 remaining, half of which were discharging waste to natural waters (J. W. Barnett, NZ Dairy Research Institute, pers. comm.). Wastewater flows fluctuate daily and seasonally, and depend upon the products manufactured.

Untreated dairy factory wastes were analysed for heavy metals nearly 20 years ago by Wells and Whitton (1966), but they expressed their results as concentration based on ashed material. Their results have been used here to estimate metal concentrations in wastewater (Table 4.28) assuming a mean ash concentration for dairy wastes of 1.8 g/l (Shanks, 1982). Also reported in Table 4.28 are unpublished results of both the NZ Dairy Research Institute (D. B. Galpin, D.R.I., pers. comm.) and D. G. Smith, and metal levels for raw milk (Casey, 1976). Some of the metal levels obtained by Wells and Whitton (1966) seem surprisingly high. However, the Zn values are supported by their more recent work (Whitton and Wells, 1974), where values for Zn of 150mg/m^3 and 470 mg/m^3 were obtained for casein factory and cheese factory effluents, respectively. Of all the metals, only the Zn levels in effluents are high, undoubtedly due to high levels in raw milk.

Table 4.28: Dairy factory effluent metal levels (mg/m^3).

Source Ref.	8 Factories (1) Mean (range)	Raw cheese whey (2) Daily composite	Untreated process waters (2) 6 day mean	Treated mixed effluent (a) (3) Single grab	Raw cheese whey (b) (3) Single grab	Raw casein whey (b) (3) Single grab	Untreated process waters (b) (3) Single grab	Raw milk (7 samples) (4) Mean (SD)
As		<7	9					
Cd		1	<5	0.1	1.1	<0.1	0.1	3 (0)
Co		2	<5					
Cu	1350 (7-6120)	50	15	13	46	890	63	60 (10)
Cr	56 (<2-380)		3	3.2	8.4	8.2	12.2	20 (10)
Hg		<1	1-4					
Ni	56 (<2-250)	8	4	1.8	12.5	17.8	17.7	11 (5)
Pb		30	15	1.7	27.4	6.7	6.2	50 (20)
Sn		20	4					
Zn	320 (45-700)	160	660	<30	160	2240	280	3980 (170)

References:
(1) Based on Wells and Whitton (1966)
(2) D. B. Galpin (NZDRI, pers. comm.)
(3) D. G. Smith (unpublished results)
(4) Casey (1976)

Notes:
(a) Factory 1; effluent skimmed, aerated, settled.
(b) Factory 2; untreated process waters are typical rinsings, washings, and excess factory wastes.

Wells and Whitton (1966) have suggested that metal levels in effluents can be, in part, related to the soils of the areas; e.g. high levels of Cr, Cu and Ni were found only in effluents from factories whose milk supply came from farms sited on yellow-brown loams derived from volcanic ash. It is likely that some of the factories sampled by Wells and Whitton (1966) are now defunct.

4.8.7 Metal Refining (M. F. Larcombe, P. C. Kennedy and D. G. Smith)

Iron and steel making: There is only one major iron and steel works in New Zealand, the Glenbrook Works of NZ Steel Ltd, which started production in 1968. Expansion presently underway will increase steel production from 150 000 t to 775 000 t per annum (Shanks, 1982). Hot and cold rolling mills will also be installed to process about 550 000 t of steel slab into a variety of finished flat products.

The future waste water discharges from the expanded iron and steelmaking plant and the existing finishing plants will be 90 l/s. The rolling mills will discharge about 24 l/s via a separate outfall. The water right granted for the expanded works has limits for metals discharge (Table 4.29).

Table 4.29: NZ Steel wastewater discharge limits* (mg/m^3) for metals (iron and steel making plant and existing finishing plants).

Metal	Maximum not to be exceeded	Monthly average
Ag	20	–
As	5000	600
Cd	600	2.5
Cr (III)	200	5
Cr (VI)	100	5
Cu	200	30
Hg	2.5	1.25
Pb	200	60
Ni	500	30
Zn	1500	200

* For the iron and steel making plant and existing finishing plant. Limits for the hot and cold rolling mills are as above but with a monthly average Zn concentration of 50 mg/m^3

All sections of the expanded works will not be fully commissioned and fully operational until 1990 and representative effluent quality data are not available. The levels of metals not to be exceeded in the effluent will be achieved by two stage pH adjustment, flocculation and sand filtration. Large effluent and stormwater retention ponds have also been provided. The effects of current wastewater discharges from the plant are commented on in Section 6.2.2.2.

Discharges of waste gases to the atmosphere are licensed and monitored by the Department of Health under the Clean Air Act 1972. Emissions of toxic metals are unlikely to be significant.

Primary aluminium smelting: At present there is only one Al smelter operating in New Zealand (Tiwai Point, Bluff). The smelter started production in 1971 and has recently been expanded to increase its production from 150 000 t to 244 000 t per annum (New Zealand Yearbook, 1984). The only wastewater production at the smelter is sewage, stormwater and rainwater leachate. Cooling waters are recycled, and leachate from the large stockpile of spent cathodes is treated (Shanks, 1982). No metals data are available on the effluent discharge. Of the atmospheric emission, fluorine is the only element of likely concern at Tiwai Point and a comprehensive monitoring programme evaluates emissions. Overseas, metals identified as being of environmental concern for the primary aluminium industry (EPA, 1979b) are As, Cr, Hg, Pb and Zn. Wastewater derived from cryolite recovery contributes these metals in larger amounts than other process wastewater streams.

Secondary metal smelting: There is a large number of small scrap-recycling firms in New Zealand (approximately 30 in Auckland) producing ingot metal from scrap. There are also three major secondary Pb smelters (Auckland, Lower Hutt and Christchurch) reprocessing battery scrap for reuse. Calculations for the Christchurch plant showed a negligible atmospheric Pb emission (400 kg/annum) compared with petrol Pb emission (90 000 kg/annum) for the Christchurch area (Day, 1977). B. Graham (Department of Health, pers. comm.) has indicated that the emissions from the Auckland and Lower Hutt plants will be similar. Localised contamination of the aquatic environment could occur via factory yard stormwater, roadside runoff, and careless dumping of wastes. Wastewaters are discharged to trade waste sewers.

4.8.8 Petrochemicals (P. C. Kennedy, M. F. Larcombe and D. G. Smith)

The petrochemical industry has a large number of subsidiary industries, products, processes, and recycling of used materials. With the rapid expansion of the petrochemical industry in New Zealand, centred at present in Taranaki, there is considerable interest being generated in the impact that the industry will have. In New Zealand, the offshore and onshore indigenous petroleum feedstock (see Figure 4.4) supplies a methanol plant, an ammonia-urea plant, and a synthetic petrol plant. Crude oil from overseas and condensate from local fields are refined at the Marsden Point Oil Refinery.

During exploration, metals can be introduced into the aquatic environment by accidental spillage of petroleum crude and products, drilling fluids, cuttings, lubricating oils, brines, and corrosion of metals on drilling platforms. Barytes (barium sulphate) is sometimes used as a weighting agent in oil and gas drilling mixtures (up to 20% Ba). Ba, as barytes, poses little threat to the aquatic environment. Cr as ferrochrome or chromium lignosulphonate has also been used overseas to keep formation cuttings and drilling mud solids in suspension. The use, spillage, and final disposal of the ferrochrome lignosulphonate drilling fluids at Maui were not expected to have any adverse effects on fish life (Shell, BP and Todd, 1974). In close proximity to offshore drilling platforms there may be increased levels of Zn if sacrificial Zn anodes are used on the rig. The tendency, however, is to use Al rather than Zn anodes.

Although heavy metals are present in crude oils and added to some petroleum products, they seem to present little threat to the aquatic environment because they are present at very low levels. On the other hand, tetraalkyl Pb added to produce leaded petrol, provides a potential risk. Extensive safety precautions have been instituted at the Marsden Point refinery to prevent accidental environmental contamination. Heavy metals occur in oil refinery wastewater in low concentrations but, provided good secondary treatment of process wastewater is undertaken, any metals present will be reduced in quantity to environmentally acceptable levels (EPA, 1982).

For the refinery at Marsden Point, the Northland Regional Water Board has imposed a condition to limit the Zn concentration of the final effluent if a zinc polyphosphate corrosion inhibitor is used. The average process wastewater flow, post-expansion, will be 4000 m^3/day. The maximum permitted Zn concentration in any one day is 1000 mg/m^3, and the maximum permitted 30-day average zinc concentration is 600 mg/m^3.

The wastewater from the Petralgas methanol plant in Taranaki was analysed soon after plant commissioning. Levels of heavy metals found (daily average) were Cd 6 mg/m^3, Cr 16 mg/m^3, Cu 50 mg/m^3, Hg$<$0.5 mg/m^3, Ni 13 mg/m^3, Pb$<$10 mg/m^3, Zn 120 mg/m^3; the average daily discharge was 1750 m^3 (SFP, 1984). These levels may not be representative of the effluent in the long term.

4.8.9 Fertiliser

There are five fertiliser companies in New Zealand with five works in the South Island and seven in the North (Shanks, 1982). Approximately 1.7×10^6 t of superphosphate fertiliser were manufactured in the year to June 1983 (New Zealand Yearbook, 1984).

Shanks (1982) has claimed that in the New Zealand fertiliser industry, process wastewaters are generally recycled in the chemical process so no process wastewater for discharge is generated. The main sources of water pollution would therefore be stormwater runoff, wastewater from gas scrubbers (which may contain fluorides and phosphates) and spillages (Shanks, 1982).

A preliminary study by the Hauraki Regional Water Board (Goldstone, 1983) has shown that the potential for Cd contamination of the receiving water from one fertiliser works process wastewater in their region may be high (Table 4.30). Analysis of effluents from the Ravensdown Fertiliser Works outfall (into Otago Harbour) have also been carried out (Table 4.30); the high Cu value obtained in 1982 was the result of copper sulphate manufacture (now ceased). The effects of these wastewaters are commented on in Sections 6.2.4.1 and 6.2.14 respectively. Localised metal (especially Cd) contamination of the marine environment as a result of spillage during the off-loading of phosphate rock at the wharf is a possibility (see Section 6.2.14).

Table 4.30: Metal concentrations (mg/m^3) in fertiliser factory wastewater.

Location		As	Cd	Cu	Hg	Pb	Zn	Reference
Kiwi Works, Morrinsville		12-35	20-30					(1)
Ravensdown Works, Otago Harbour	Feb 81	140	5	109	17	490	80	(2)
	Apr 82	10	130	6000	<1	40	50	(2)

References: (1) Goldstone (1983)
(2) K. J. Currie (Otago Regional Water Board, pers. comm.)

Arsenic and Cr may be present in wastewaters from ammonia-urea plants (Shanks, 1982) but no data are available for the New Zealand ammonia-urea plant at Kapuni. This plant discharges its liquid waste via a land disposal system hence contamination, by metals, of water courses is minimised.

4.8.10 Paint (P. C. Kennedy and R. B. Williamson)

The paint industry is probably one of the more complex of the metal-using industries because of the wide variety of metals (e.g., Cr, Cu, Hg, Pb, Zn) involved in paint formulations (several thousand products) and paints are used in a vast range of secondary industries. In the manufacturing census year 1978/9 there were 38 paint, varnish and lacquer plants in New Zealand (New Zealand Yearbook, 1982). Most, if not all, of these would be located in large cities and would discharge liquid wastes to trade waste sewers.

One of the most significant changes in the paint industry which has had a direct environmental effect has been the decreased use of white lead for house paints (2800 t/annum in the 1950s to 200 t/annum in the 1960s). However, most concern was for human disease because of ingestion of paint or soils (pica) near houses. Little ended up in the aquatic environment. Today Pb is used primarily as a metal primer (red lead, basic lead chromate, white lead, calcium plumbate). Hg is used in paints as a preservative (NRC, 1979). Trace metals in paint may reach the aquatic environment through a number of routes including directly from the factory (via waste discharges) and indirectly by runoff from roofs and other surfaces (Pb and Zn), and erosion of lead chromate road marking paints.

Antifouling paints on boat hulls function by the dissolution of metal toxicants from the paint. The commonest toxicants are Cu_2O and tri-butyl tin (TBT) compounds. In New Zealand, most of the paint applied to boats will end up in the marine environment, either by leaching or by spent paint from hull cleaning being washed or blown into the sea. Primer paints containing Pb and Zn can also be removed during hull cleaning. It is estimated that 1.3 t of Cu is applied annually to boats moored in Westhaven, Auckland, New Zealand's largest marina, most of which is expected to end up in the marina waters and sediments. TBT has been implicated in problems with oyster growth and spatfall in commercial oyster fisheries in the UK and France. These problems have been found in fisheries near marinas or boat moorings and have led to the French government banning the use of TBT based paints on craft < 20 m in length. The problem is being continually researched in the UK and is currently being assessed here in New Zealand (Williamson, 1985c).

Chapter 5

CRITERIA AND STANDARDS EMPLOYED FOR VARIOUS WATER USES

There is some confusion in the use of the terms criteria and standards. Here a **criterion** is a scientifically derived concentration of a pollutant which is estimated to provide a defined degree of protection (normally to aquatic life). A **standard** is a legally defined maximum pollutant concentration which is permitted in a water.

This chapter briefly presents some of the criteria and standards for heavy metals derived by various agencies throughout the world and recommended for the protection of water for aquatic life, human potable water supply, stock watering and irrigation. Data are presented here for As, Cd, Cr, Cu, Pb, Hg, Ni and Zn but note that the United States Environmental Protection Agency (Smith, 1982a) also gives aquatic life and human health criteria for Ag, Sb, Se and Tl, the American Fisheries Society (AFS, 1979) also gives aquatic life criteria for Ag, Ba, Fe and Se, and the Inland Waters Directorate, Canada (IWD, 1979) also gives aquatic life, human health, stock watering and irrigation criteria for Ag, Fe and Se. The EPA (1973) 'Blue Book' gives fairly comprehensive metals data for stockwatering and irrigation. The EPA (1976) 'Red Book' has been, in part, superseded by the Agency's 1980 metal criteria (EPA, 1980 a-h; summarised by Smith, 1982a) for aquatic life and human health, but information (not superseded) is given in the 'Red Book' for irrigation water (As only). Hart (1974) produced a general water quality criteria text which has been superseded (for metals) by Hart (1982). The Victorian Environmental Protection Authority (EPAV, 1983) has published metals criteria for numerous water uses, but most of its criteria for receiving waters are derived from the publications noted above. The most recent set of criteria are those of the United States EPA (EPA, 1985 a-f); these supersede earlier EPA criteria.

In the UK, water quality standards for the highly toxic List I substances, e.g., Cd and Hg, are defined by European Community Directives whereas others (i.e. List II substances which include the other metals considered in this review) are to be derived by the Community's member states. The UK Department of the Environment contracted the UK Water Research Centre to derive standards for this latter group of metals. All the UK water quality standards are published in one document (WRC, 1984a) although separate documents have been produced for each of the List II metals showing how the standards were derived (WRC, 1984 b-g). Standards have been produced for human drinking, stock and irrigation water, protection of salmonids, coarse freshwater fish and other freshwater life, and for protection of bathers, fish and other life in marine waters.

Waste discharges into New Zealand waters, or on to land, are controlled by water rights which may stipulate the levels of metals (and other pollutants) which may legitimately be discharged. Regional water boards grant and administer such rights and the National Water and Soil Conservation Authority exercises a general oversight of boards' activities to ensure that rights granted are within the law. When setting conditions on water rights it is frequently necessary to seek guidance from overseas criteria and standards although it has to be acknowledged that such criteria and standards may not be entirely relevant in New Zealand. This section reviews a range of criteria and standards from overseas. New Zealand has no legally set standards for heavy metals or other toxicants. The National Water and Soil Conservation Authority has published (Smith, 1982a) a compilation of information on US EPA criteria to assist regional water boards in deciding on appropriate water right conditions for heavy metal discharges but has not officially endorsed their use, preferring to allow boards to manage heavy metal discharges on a case by case basis. The information presented here should not be used without consulting the original documents to ascertain the relevance of each criterion or standard for the situation in which it is to be used.

5.1 Aquatic life protection

The criteria and standards for heavy metals derived by a selection of agencies are presented in Tables 5.1a-c. It is inappropriate in this publication to comment in detail on the methods of criteria derivation. Generally speaking they are based largely on the results from laboratory tests.

The United States EPA (1980 a-h) adopted an approach which takes into account both chronic and acute toxicological effects to aquatic organisms by deriving a 24 hour average criterion which, if not exceeded, would protect against chronic effects and maximum criterion which, if not exceeded, would protect against acute effects. The EPA criteria were developed to protect most aquatic species in healthy, balanced ecosystems but they were not intended to provide 100% protection to all species and all uses of aquatic life all the time.

The United States EPA (EPA, 1985 a-f) is now recommending a four day average concentration to protect against unacceptable chronic effects, and a one hour average concentration, to protect against unacceptable acute effects. Both averages should not be exceeded more than once every three years to enable an otherwise unstressed system to recover from a pollution event. The 1985 criteria are presented in Table 5.1b.

Alabaster and Lloyd (1980) have pointed out that the concentrations of water quality determinands follow statistical distributions. They did not derive maximum criteria but instead suggest 50 and 90 percentiles.

The UK water standards (Table 5.1c) are expressed, in the main, as annual averages but occasionally 95 percentiles are used.

Note that the criteria given in Table 5.1a-c are for single metals only. Combinations have not been addressed by the agencies. A comment on effects of mixtures of metals is given in Section 2.1.4.

Table 5.1a: Criteria for aquatic life protection (mg/m^3).

		EPA (1980^{a-h})				Alabaster and Lloyd (1980)				IWD
	Hart	Fresh		Marine				ASF (1979)		Canada
	(1982)	Av.	Max.	Av.	Max.	50%ile	90%ile	Fresh	Marine	(1979)
As	50	$-^{i}$	440^{d}	$-^{i}$	$-^{i}$	$-^{j}$	$-^{j}$	$-^{i}$	$-^{i}$	50
Cd	0.2^{a}	0.012^{e}	1.5^{e}	4.5	59	$15:0.4^{e,k}$	$30:0.9^{e,k}$	$2.0:1.0^{e,m}$	3.0	0.2
Cr	10	0.29^{f}	21^{f}	18^{f}	1260^{f}	$-^{j}$	$-^{j}$	$<100^{n}$	25^{f}	20
		$-^{g,i}$	$2200^{e,g}$	$-^{g,i}$	$-^{g,i}$				50^{g}	
Cu	5^{b}	5.6	12^{e}	4.0	23	$6.0^{e,l}$	$22.0^{e,l}$	5 – 15	5 – 15(?)	2
Pb	5^{b}	0.75^{e}	74^{e}	$-^{i}$	$-^{i}$	$-^{j}$	$-^{j}$	25^{e}	4^{p}	5^{e}
Hg	0.1^{c}	0.00057^{h}	0.0017^{h}	0.025	3.7	$-^{j}$	$-^{j}$	0.05^{q}	0.05^{q}(?)	0.2
Ni	25^{b}	56^{e}	1100^{e}	7.1	140	$-^{j}$	$-^{j}$	$-^{j}$	$-^{j}$	25
Zn	50^{b}	47	180^{e}	58	170	$175:50^{e,k}$	$700:200^{e,k}$	50^{e}	50	50^{e}

Notes:

(a) 2 mg/m^3 for marine waters.
(b) In soft waters of low complexing capacity. May be increased in hard waters with a high complexing capacity.
(c) May need to be lowered if more than 10% present as methyl mercury.
(d) For As (III). (But note that there may not be a difference in toxicity between As (III) and As (V).)
(e) Toxicity relationship with hardness (as $CaCO_3$) has been derived. The values given are for hardness of 50 g/m^3.
(f) For Cr (VI).
(g) For Cr (III).
(h) Incorrectly calculated by EPA. Recalculation (R. B. Williamson, Water Quality Centre, MWD, pers. comm.) gives 0.043 and 3.7 mg/m^3 respectively.
(i) Criterion not calculable because of lack of data.
(j) Not determined.
(k) The first criterion is for coarse fish, the second for salmonids. Criteria are described as annual maxima.
(l) For rainbow trout.
(m) For "less sensitive" and "sensitive" species respectively.
(n) 100 mg/m^3 estimated to be too high but no fixed criterion developed.
(p) Preliminary until further data available.
(q) With no more than 0.004 mg/m^3 as methyl mercury.

Table 5.1b: EPA 1985 ambient water quality criteria (mg/m^3) for the protection of aquatic life (EPA, 1985 a-f).

	Fresh Water		Marine Water	
Metal	4 day average (a)	1 hour average (a)	4 day average (a)	1 hour average (a)
As(III)	190	360	36	69
Cd	0.66(b,c)	1.8(b,c)	9.3	43
Cr(VI)	11	16	50	1100
Cr(III)	120(b)	980(b)		
Cu	6.5(b)	9.2(b)		2.9
Hg	0.012(d)	2.4(e)	0.025(d)	2.1(e)
Pb	1.3(b)	34(b)	5.6	140

Notes:
(a) 'Acid-soluble' concentrations, not to be exceeded more than once every 3 years.
(b) Criterion related to water hardness. The value given is for 50 g/m^3 $CaCO_3$.
(c) May not protect brook trout and brown trout.
(d) Based on methyl mercury bioconcentration and likely to be overprotective if a substantial proportion of Hg(II) present.
(e) Based on Hg(II) being the species most likely to be discharged and hence produce acute effects.

Table 5.1c: UK water quality standards (mg/m^3) for the protection of aquatic life (WRC, 1984 a-g).

	Fresh water$^{(a,b)}$	Marine water$^{(a,b)}$
As	50:50:150	25:25
Cd	$5^{(c)}:5^{(c)}:5^{(c)}$	$2.5^{(k)}:2.5^{(k)}$ $5^{(l)}:5^{(l)}$
Cr$^{(d)}$	$150^{(e)}:5^{(e)}:5^{(e)}$	15:15
Cu	$6^{(e,f)}:6^{(e,f)}:6^{(e,f)}$ $22^{(e,g)}:22^{(e,g)}$	$5^{(h)}:5^{(h)}$
Pb	$50^{(e)}:4^{(e)}:5^{(e)}$	25:25
Hg	$1^{(c)}:1^{(c)}:1^{(c)}$	$0.3^{(m)}:0.3^{(m)}$ $0.5^{(n)}:0.5^{(n)}$
Ni	$50^{(e)}:50^{(e)}:8^{(e,p)}$	30:30
Zn	$175^{(e,i)}:50^{(e,i)}:100$ $700^{(e,j)}:200^{(e,j)}$	40:40

Notes:
(a) Defined as annual averages of dissolved metal (i.e., that metal passing through a 0.45μm membrane filter) unless otherwise stated.
(b) Values given for freshwater are for the protection of coarse fish, salmonids, and other freshwater life respectively; for marine waters the values given are for the protection of fish and other life respectively.
(c) Total metal.
(d) Defined as CrIII + CrVI.
(e) Standards vary with hardness. Values given are for <50 g/m^3 $CaCO_3$ for Cr, Ni and Pb, and for 50 g/m^3 $CaCO_3$ for Cu and Zn.
(f) For waters not specifically designated as fisheries waters. A higher value may be acceptable where acclimation is expected or Cu is present in organic complexes.
(g) For waters specifically designated as fisheries waters. This is a guide value and is a 95%-ile.
(h) A higher value may be acceptable where acclimation is expected or Cu is present in organic complexes.
(i) For waters not specifically designated as fisheries waters.
(j) For waters specifically designated as fisheries waters. This is a mandatory value referring to total zinc and is a 95%-ile.
(k) For non-estuarial waters.
(l) For estuarial waters.
(m) For non-estuarial waters affected by discharges from the chlor-alkali electrolysis industry.
(n) For estuarial waters affected by a discharge from the chlor-alkali electrolysis industry.
(p) Based on limited data for *Daphnia magna*.

It is generally acknowledged that the most toxic form of most metals is the free ion, and that a considerable proportion of a metal in the aquatic environment is likely to be bound up in forms which would render it non-available to biota. Consequently, when setting discharge conditions for aquatic life protection, consideration ought to be given to those species of a metal which are in free ionic form and those which can be readily converted to this form in the aquatic environment. This assessment however, remains one of the major problems (see Section 2.2). Water quality criteria and standards are often derived using laboratory bioassay studies on 'clean' waters, i.e., without organic material, or suspended and settled sediments (see Section 2.2 for an indication of their significance). Therefore, the forms of the metals in the tests probably do not correspond to the forms of the metals in the environment. Criteria and standards may not adequately take account of bioavailability and it is sometimes difficult to decide what sort of analytical processes should be carried out. For example, levels may be stipulated without any indication as to whether a simple process such as filtration (0.45μm) for 'dissolved' metal (as opposed to no filtration for 'total' metal) should be applied to a water sample. The 'total' metal method for stipulating criteria and standards is the most conservative approach, and thus has merits from the environmental viewpoint. The EPA (1980 a-h) criteria documents use the term 'total recoverable' metal. The statement made for metals where fixed criteria have been derived is similar to the following extract from the Hg criteria document (EPA, 1980 f):

> 'Of the analytical measurements currently available, water quality criteria for mercury are probably best stated in terms of total recoverable mercury, because of the variety of forms of mercury that can exist in bodies of water and the various chemical and toxicological properties of these forms. The forms of mercury that are commonly found in bodies of water and are not measured by the total recoverable procedure, such as the mercury that is part of minerals, clays and sand, probably are forms that are less toxic to aquatic life and probably will not be readily converted to the more toxic forms under natural conditions. On the other hand, forms of mercury that are commonly found in bodies of water and are measured by the total recoverable procedure, such as the free ion, the hydroxide, carbonate, and sulfate salts, and the organic compounds, probably are forms that are more toxic to aquatic life or can be converted to the more toxic forms under natural conditions. Because the criteria for mercury are derived on the basis of tests conducted on soluble inorganic salts of divalent inorganic mercury and monomethylmercuric chloride, the total recoverable concentrations in the test should be about the same. Except as noted, all concentrations reported herein are expected to be essentially equivalent to total recoverable mercury. All concentrations are expressed as mercury, not as the compound.'

'Total recoverable' is not defined in the documents but a method description is given in EPA (1979c); it involves a less rigorous acid digestion than for 'total' metals. However, both methods would determine much of the suspended solids bound metal. A high value for potentially toxic metal may thus be obtained, especially if water from a river in flood were analysed.

The most recent EPA criteria documents (EPA, 1985 a-f) are recommending that metal concentrations be based on an 'acid-soluble' approach. 'Acid-soluble' metal is defined as the metal that passes through a 0.45μm membrane filter after the sample is acidified to pH 1.5-2.0 with HNO_3. This is estimated to measure all forms of metal which are toxic to aquatic life or can be readily converted to toxic forms under natural conditions. This was concluded to provide a 'more scientifically correct basis upon which to establish criteria for metals'. However, there is no EPA approved method for 'acid-soluble' and, until one is available, EPA are recommending use of 'total recoverable' metal. The criteria may therefore be overly protective if a 'total recoverable' analysis is carried out.

The 'acid-soluble' approach seems a more logical (although still probably conservative) way to determine potentially toxic metal levels. It could, however, provide an under-estimate of bioavailability to some sediment dwellers and filter feeders because of removal of some of the bound metal by the filtration step.

Alabaster and Lloyd (1980) clearly state 'soluble' (i.e., 'dissolved') metal in their Cd, Cu and Zn criteria and stipulate that a 0.45μm filter be used. For Cu it is recognised that this process may lead to errors because it could also include non-toxic cupro-organic complexes of low toxicity. On the other hand low estimates of biological availability may be obtained because of the filtration step.

Hart (1982) recommended 'total' levels for As, Cd, Cr, and Hg, but filterable levels for Cu, Pb, Ni and Zn.

The situation is even more complex in the case of the EPA 1976 criteria (EPA, 1976) and the American Fisheries Society (AFS, 1979) review of them. For example the 1976 EPA Cd, Cr, and Hg criteria merely state a maximum level. In the text's introductory section entitled 'The Philosophy of Quality Criteria' it is written:

> 'Unless otherwise stated, criteria are based on the total concentration of the substance because an ecosystem can produce chemical, physical and biological changes that may be detrimental to organisms living in or using the water.'

Thus it would seem as though the Cd, Cr and Hg criteria are indeed 'totals'. The AFS (1979) recommended that the 1976 EPA criteria should be for 'soluble' and 'dissolved' metal for Cd and Hg respectively. In both cases the water should be filtered (0.45μm filter). For Cu and Zn the criteria are recommended to be determined by a bioassay procedure but no guidance is given as to how to do this. For Pb the criterion is to be derived using a bioassay procedure, but here 'soluble' Pb measurements (0.45μm filter) are to be made. For Pb and Zn, the AFS (1979) recommended that the criterion be a 'total'!

The UK standards are for 'dissolved' metal except for the more toxic List I metals Cd and Hg which are defined as 'total' metal.

To add to the confusion, the problems get even more difficult when various types of digestions and analytical methods (e.g., AAS or ASV) which will give different analytical results, are contemplated.

It is evident that further work is required to tighten up which analytical procedures are to be employed, and the way criteria and standards are written. It would seem appropriate that for purposes of water rights conditions derivation, not only should a level (whether expressed as a maximum or as a percentile) be stipulated, but the analytical method to be employed in determining the level should also be stipulated.

5.2 Human Health Protection

Limits for heavy metals which either affect the toxicity or acceptability of water for domestic use are derived by the World Health Organisation (WHO). On the basis of the WHO Guidelines for Drinking Water Quality 1984, the New Zealand Board of Health has published a report containing New Zealand standards (*sic*) for drinking water quality. The relevant portions from this are given in Table 5.2.

Table 5.2: Standards (*sic*) for potable water (mg/m^3) (Board of Health, 1984).

Metal	Guideline Value	Comment
As	50	
Cd	5	
Cr	50	As total chromium
Cu	50$^{(a)}$	Can cause astringent taste, discolouration and corrosion of pipes, fittings and utensils
Pb	50	
Hg	1	
Ni	No guideline value set	Current available toxicological data indicate guideline value not required
Zn	5000$^{(b)}$	Can cause adverse taste, discolouration, deposits

(a) This guideline value is the 'highest desirable' value. The 'excessive' value for Cu is 1000 mg/m^3 above which potability would be markedly impaired.

(b) The guideline value for Zn is 5000 mg/m^3 for both the highest 'desirable' value and the 'excessive' value above which potability would be markedly impaired.

Note that the standards take the form of guideline values. A guideline value represents a maximum concentration which ensures an aesthetically pleasing water and does not result in any significant risk to the health of the consumer. Further details on the meaning of the term 'guideline value' should be obtained from the Board of Health (1984) report but note that:

1. 'short-term exposures to higher levels of chemical constituents may be tolerated', and
2. 'guidelines should . . . not be regarded as implying that the quality of drinking water may be degraded to the recommended level. Indeed a continuous effort should be made to maintain drinking-water quality of the highest level attainable'.

Water quality criteria have been derived by the United States EPA to protect human consumers of fish and shellfish. The EPA criteria (EPA 1980 a-h) seek to protect the water body from which the fish or shellfish are taken. By this means the criteria are calculated to afford adequate protection to human consumers of these animals. The EPA has adopted the approach that if a pollutant is, or is suspected of being a carcinogen, then there is no scientific basis for estimating safe levels ('non-threshold assumption') and hence the ambient water level should be zero. The EPA also accepts that this is probably unrealistic and developed the 'incremental increase of cancer risk over the lifetime', i.e., an incremental cancer risk of, say, 1 in 10^6 means that one additional cancer case could be expected in a population of one million people. For non-carcinogens, safe ambient concentrations in water have been derived. The EPA ambient water criteria, are given in Table 5.3; they are derived assuming a daily ingestion of 6.5 g of fish and shellfish (see Smith, 1982a). These types of EPA criteria are not used in New Zealand.

Table 5.3: Criteria for ambient water containing shellfish and fish for human consumption (EPA, 1980 a-h).

Metal	Criterion
As	$17.5\ \mu g/m^{3(a)}$
Cd	$10\ mg/m^3$
Cr	$3300\ g/m^{3(b)}$ $50\ mg/m^{3(c)}$
Cu	(d)
Pb	$50\ mg/m^3$
Hg	$146 \mu g/m^3$
Ni	$100\ mg/m^3$
Zn	(d)

(a) For an incremental cancer risk of 1 in 10^6.
(b) For Cr (III).
(c) For Cr (VI).
(d) Criterion not derived due to lack of data.

Table 5.4: Maximum permitted levels of heavy metals in New Zealand fish and shellfish (mg/kg as wet weight) Food Regulations, 1984).

Metal	Level
As	2
Cd[a]	1
Cu	30
Cr[b]	–
Hg[c]	0.5
Pb	2
Ni[b]	–
Sn	40
Zn[a]	40

(a) No limit set for shellfish.
(b) No limit set.
(c) For fish and fish products.

In New Zealand the Department of Health controls the sale of food containing heavy metals through the Food Regulations 1984. Limits for heavy metals may apply to foods generally (including fish and shellfish) or in some instances specific standards may be prescribed. Levels included in the regulations are those which, if exceeded, may present a hazard to the consumer or which are commercially achievable, whichever is the lower. Statutory levels were derived following the calculation of overseas literature such as that published by the World Health Organisaton or the regulations of other countries. Toxicological data are evaluated by the Department and the Food Standards Committee before being incorporated in legislation. Surveys are also conducted to assess the levels of particular metals in foods before establishing levels for them and as a means of monitoring compliance with the regulations once they are promulgated (G. R. Galbraith, Department of Health, pers. comm.). Table 5.4 gives the maximum permitted levels for heavy metals in fish and shellfish sold in New Zealand. For Cd, Hg, and Zn no limit has been set for shellfish. In the Food and Drug Regulations, 1973 (Amendment No. 7), it was stated that 'shellfish may contain these elements in the concentration occurring naturally'. Presumably this still applies. It appears then, that the Department of Health recognises that shellfish can bioaccumulate these metals to concentrations higher than the maximum permitted levels for fish. However, natural levels are very difficult to establish for shellfish (see Chapters 2 and 6) so the exact meaning of this statement is not clear.

5.3 Stock Watering and Irrigation

Several authorities have derived similar criteria for stock watering and irrigation waters (e.g., EPA, 1973; Hart, 1974; IWD, 1979; Anglian Water Authority, 1978). Those derived by the EPA are presented in Table 5.5.

Table 5.5: Criteria for stock watering and irrigation waters (mg/m^3) (based on information from EPA, 1973).

Metal	Livestock Watering	Irrigation[a] For waters used continuously on all soil	For use up to 20 yrs on fine textured soils of pH 6.0-8.5
As	200	100	2000
Cd	500	10	50
Cr	1000	100	1000
Cu	500	200	5000
Hg	10	b	b
Pb	100	5000	10000
Ni	b	200	2000
Zn	25000	2000	10000

(a) These levels will normally not adversely affect plants or soils. A water application rate of 0.91 m (3 feet) was used in the calculations.
(b) Criterion not derived.

5.4 New Zealand Situation (with the assistance of A. M. Becker, Ministry of Works and Development)

Conditions (for heavy metals) attached to water rights for the discharge of wastewaters are frequently derived to protect aquatic life in the receiving waters. Such protection will normally afford protection to water uses such as potable supply and irrigation. The Schedules to the Water and Soil Conservation Act 1967 provide standards for the levels of metals in receiving waters which will be protective to aquatic life. What is stated (Second to Ninth Schedules inclusive) is: 'There shall be no destruction of natural aquatic life by reason of a concentration of toxic substances.' Because of this, water managers rely on criteria and standards derived overseas; for examples see Tables 5.1 a-c. The United States EPA criteria are frequently used as a guide on the assumption that the overall susceptibility of New Zealand ecosystems is not substantially different from those of the United States. Clearly, there is a need to substantiate this assumption. Guidance could be achieved by monitoring waters subject to significant inputs of heavy metals (e.g., from past mining activities, urban drains, geothermal areas). Studies in the Coromandel may be of value in this assessment (Livingston, *in press*) (see Section 6.2.4.2).

For waters which are to be protected for human drinking water, the situation is clearer. In such cases the quality of the receiving water would not be permitted to fall below the values indicated in Table 5.2 and water rights conditions would be derived accordingly.

For stock watering, the Water and Soil Conservation Act 1967 states, (Second to Fourth Schedules): 'The waters shall not . . . contain toxic substances to the extent that they are unsafe for consumption by . . . farm animals . . .' There is no statement on irrigation waters. Because receiving waters are normally protected for aquatic life or human potable supply the majority should be suitable for stock watering or irrigation. Information derived by agencies such as the United States EPA (Table 5.5) could be used if necessary.

The rest of this section consists of examples of how water rights conditions have been derived for either crown water rights or consents approved by the National Water and Soil Conservation Authority based on recommendations from regional water boards. The examples are the only ones in the above categories which have heavy metals conditions attached.

All metal levels stipulated would, presumably, be for 'total' metal, i.e., a digestion on the unfiltered sample would be required. However, this is not stated clearly, and is thus subject to misinterpretation.

(a) Floorwool Products Limited

A recommendation for a Cr limit of 10 000 mg/m^3 on the wastewater discharge (105 m^3/day) to the Aparima River, Southland was put forward to the National Water and Soil Conservation Authority for approval in 1981. The minimum expected dilution was 500:1. This would give an increase in Cr concentration in the river of 20 mg/m^3. Downstream of the discharge, Riverton Borough has a potable supply intake so the WHO drinking water standard of 50 mg/m^3 was considered appropriate by the regional water board. After treatment of the waste to reduce biochemical oxygen demand and suspended solids to acceptable limits, it was found that a 20 mg/m^3 level for Cr could reasonably be expected to be achieved in the receiving water. Therefore a condition was set on the water right to achieve this value. Coincidentally, this level would probably also afford a high protection to aquatic life, although this water use was not specifically protected.

(b) Kawerau Geothermal

Crown Water Right 1230 was granted by the National Water and Soil Conservation Authority in 1981 for a discharge to the Tarawera River. In the agenda item to the Authority, US EPA 1976 criteria were quoted (for As, 50 mg/m^3 for domestic water supplies and aquatic life; for Hg, 0.05 mg/m^3 for aquatic life and human consumers of fish) but no limits were put in the water right. At low flows these criteria would be exceeded.

(c) Ngawha Geothermal

Crown Water Right 1252 was granted by the National Water and Soil Conservation Authority in 1983 but refers back to an earlier water right, *viz* 1028 granted in 1979. The discharge is into the Ngawha Stream. The limitations for As and Hg are based on the WHO standards for drinking water because of a downstream abstraction for potable supply.

The conditions are written in the form:

The concentration of metal in the effluent (m_e) shall not exceed the value given by the expression:

$$m_e \not> \frac{\text{flow in river}}{\text{flow in effluent}} \times (m - m_r) \qquad \ldots (1)$$

where m = is a stipulated metal concentration and m_r is the metal concentration in the river. In this case, for As $m = 50$ mg/m^3, and for Hg $m = 1$ mg/m^3.

(d) Marsden Point Oil Refinery

This water right was granted by the Northland Regional Water Board in 1983 for discharge into Whangarei Harbour. The only metal limit is for Zn (2000 mg/m^3). A minimum initial dilution of 70:1 was expected, giving a Zn concentration after initial dilution of 29 mg/m^3. This value is lower than any of the seawater criteria given in Tables 5.1a, b and c and would provide for an additional level of safety in what was seen as an ecologically sensitive area.

(e) Mokai Geothermal

Crown Water Right 1226 was granted by the National Water and Soil Conservation Authority in 1981 for discharges to the Waikato River and Waipapa Stream. The United States EPA 1976 criteria were recommended by the board (Waikato Valley Authority) but the following values for m (equation 1) were approved:

As: $m = 100$ mg/m^3
Cr: $m = 200$ mg/m^3
Hg: $m = 1$ mg/m^3

The acceptable concentration for Cr is therefore 200 mg/m^3; this was based on the Anglian Water Authority 'General Amenity and Conservation Standard' and not the EPA 1976 criterion of 100 mg/m^3 for aquatic life protection.

The acceptable concentration for As of 100 mg/m^3 is twice the EPA 1976 criterion. This increase was considered appropriate in view of the low fishery values perceived for the receiving waters.

The acceptable concentration for Hg of 1 mg/m^3 is higher than the EPA 1976 criterion (0.05

mg/m^3) for aquatic life protection. This increase on the recommended concentration was seen as appropriate because of the levels of Hg found downstream in the receiving waters.

Thus the derivation of water rights conditions for metals in New Zealand appears to be an *ad hoc* process with many decisions being made on an arbitrary basis. Overseas criteria and conditions are often employed as a guide, but the final conditions are often a compromise. Greater scientific guidance to aid the process of water rights conditions derivation is required in New Zealand.

For aquatic life protection, the literature is confusing and criteria are frequently changing. Because of this, it is difficult to choose any one set of criteria or standards for current use in New Zealand. The US EPA criteria, which seek to provide ecosystem protection, appear to be the most extensively researched, so, at present, it seems appropriate to use them as the basis for aquatic life protection in New Zealand. However, because much useful information is available elsewhere it is recommended that, prior to the derivation of water rights conditions, an awareness of current literature be established and original documents be consulted to ascertain the relevance of criteria to the situation under consideration.

Chapter 6
ENVIRONMENTAL LEVELS OF HEAVY METALS

The purpose of this chapter is to review published and unpublished New Zealand material in order to gain a perspective on past and present heavy metal pollution and to highlight areas of concern. In the first part, mainly published data from multi-regional studies are briefly reviewed and, where possible, national average concentrations of metals in water, sediments, and biota are derived. Published data are subject to refereeing and hence can be used with a greater degree of confidence. Overseas data have occasionally been used but only where local information is lacking. In the second part, published and unpublished data are summarised on a regional basis. Most of the data are from studies which have been carried out for specific purposes (normally pollution studies), e.g., the effects of the steel mill discharge into the Waiuku estuary, the effects of the tannery discharge into Sawyer's Bay, Otago Harbour. Recourse to unpublished data has had to be made because insufficient data would otherwise be available. The reliability of such non-refereed material may be questionable. Although some of the material presented below is not always critically reviewed, the picture presented in this chapter is, however, believed to be a fair representation of studies carried out in New Zealand over the past decade or so.

Due to the complexity of possible combinations of metals, subject of analysis (i.e., water, sediment, biota), biota (e.g., fish, shellfish), pollution vs non-pollution (plus natural and natural elevations), area, and type of water body, presentations envisaged involved either considerable repetition or a certain amount of 'jumping-around' and cross-referencing. Readers are therefore advised to 'search' a little for the information sought.

Many of the areas and sampling sites noted in the text are depicted in Figures 6.1 (North Island) and 6.2 (South Island).

6.1 Natural levels of heavy metals: national perspective

6.1.1 Water (D. G. Smith and P. C. Kennedy)

It is extremely difficult to determine natural background concentrations for heavy metals in water (see Section 3.1). Most studies carried out prior to the 1980s are likely to be overestimates due to contamination. It is only recently that this has been recognised, and techniques developed to overcome the problems. Thus, only data published within the last few years can be considered reliable (provided contamination problems have been given due consideration). Most 'historical' data should be discarded or used with caution (Borg, 1984; Nurnberg, 1984).

Many New Zealand natural waters have been analysed for heavy metals. However, analytical methods have frequently been used with detection limits which are more appropriate for drinking water criteria (see Table 5.2). Most results are therefore reported as 'less than detection limits'. However, there are still a substantial number of concentrations reported as being at or slightly above such detection limits even when, in reality, concentrations are likely to be very much lower. Apart from contamination problems, such values may be incorrect for the following reasons:

1. Detection limits are usually much higher than many analysts realise. Also, it is possible that the manufacturer's instrument sensitivities may be quoted as detection limits, a situation rarely achieved in a laboratory.
2. Instrumental response near detection limits is low compared with background noise.
3. Improper use of instrument (e.g., high Pb values have been reported for saline waters, the cause of which is inadequate background correction).

6.1.1.1 Fresh water

No studies have been carried out in New Zealand specifically to derive national fresh water average concentrations of heavy metals and the data available are inadequate for such purposes. Therefore,

Figure 6.1: North Island regional water board areas and main study sites referred to in text.

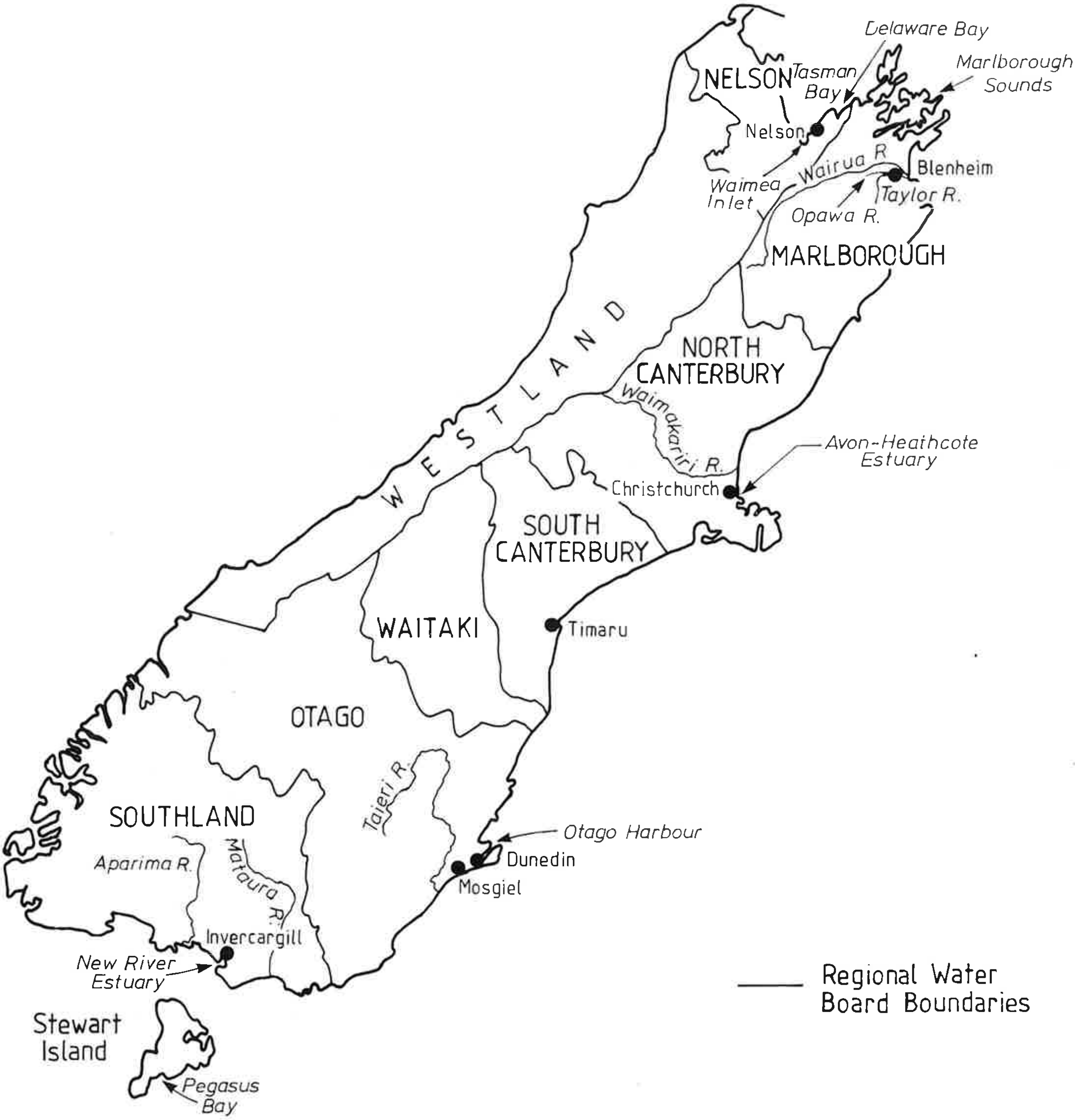


Figure 6.2: South Island regional water board areas and main study sites referred to in text.

to form some sort of basis with which to assess local concentrations, globally derived values are presented (Table 6.1). It is possible that concentrations may be different in New Zealand, because of its relatively young geologic age. Some reliable New Zealand derived concentrations are to be found in Sections 6.2.3.2, 6.2.4.2 and 6.2.14.2.

It is also difficult to derive global mean background values for individual heavy metal concentrations in fresh water because of variation in rock types and flow regimes (Forstner and Wittman, 1983). Therefore, the values in Table 6.1 should be used as guidelines only. Values for other metals are given in Forstner and Wittman (1983).

Table 6.1: Estimated global background concentrations (mg/m^3) for dissolved metals in fresh water.

	Borg (1984)	Forstner and Wittman 1983
As	0.1-0.5	2
Cd	0.005-0.05	0.07
Cr	0.1-0.5	0.5
Cu	0.2-2	1.8
Hg		0.01
Ni	0.01-1	0.3
Pb	0.05-0.5	0.2
Sn		0.03
V	<0.1-0.5	0.9
Zn	0.5-5	0.5

GEMS studies: Between early 1979 and mid 1980, the Water Quality Centre, MWD coordinated the collection and analysis of waters from 4 sites for the Global Environmental Monitoring System's (GEMS) worldwide water monitoring programme. The sites chosen were the Waimakariri River at a site unaffected by man's activities (Halkett Groyne), Bexley Pumping Station at Christchurch (a groundwater emanating in part from the Waimakariri River and possibly affected) and the Waikato River at Taupo (unaffected) and downstream at Mercer (unaffected). The metals analysed for (by the Cawthron Institute) were As (total and soluble), Cd and Pb (both totals), and Hg (total and soluble). Six samples from each site were collected up until December 1980 when, from a heavy metals viewpoint, the first three sites were closed. Subsequently the Auckland Regional Authority has collected samples and analysed for the same metals plus Cu and Cr at the Mercer site. Apart from As, the detection limits of the methods used approximately coincide with drinking water standards. Therefore, nor surprisingly, Cd, Hg, and Pb were not reliably detected apart from one value for the Waimakariri River, of 83 mg/m^3 for Pb at a time when it was in flood (5200 g/m^3 suspended solids concentration). Arsenic concentrations at Taupo averaged 6 mg/m^3 and at Mercer 19 mg/m^3. From 1980 to 1983 monthly samples taken at Mercer contained 8-40 mg/m^3 As.

Drinking water studies: Chemistry Division, DSIR, has recently published three reports (Bathurst and Scholes, 1981; Bathurst *et al.*, 1982; Petricevic and Stanton, 1983) on the analysis of drinking water supplies in the Timaru, Nelson, Northland, Auckland, and Bay of Plenty areas. The purpose of the analyses is to ascertain the potability of such supplies and so the detection limits are fairly high viz, As 5-20 mg/m^3, Cd 10-20 mg/m^3, Cr 20-50 mg/m^3, Cu 20 mg/m^3, Pb 50-100 mg/m^3 and Zn 20 mg/m^3. Not surprisingly the metal levels in the raw waters analysed are, in the vast majority of cases, below detection limits. Occasionally raw waters have Zn and infrequently Cu levels above detection limits. These are normally bore waters contaminated by the well liner or reticulation. The presence of As in the Waikato River is commented on in some detail in a later section (Section 6.2.3.2).

6.1.1.2 Sea water (P. C. Kennedy and D. G. Smith)

Most studies of the concentrations of trace metals in ocean waters published in the world literature prior to a few years ago are characterised by a great deal of scatter in the data and many inconsistencies in relation to other oceanographic determinands to which they are closely allied (e.g., silica and

Table 6.2: Concentrations (mg/m^3) of dissolved metals recently found in New Zealand and Pacific seawaters. (Values in brackets are geometric means.)

Site	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Ref.
200-1000m off the N. Taranaki coast NZ[a]		0.010-0.330 (0.035)		0.18-0.34 (0.22)			0.150-0.51 (0.40)	0.43-0.91 (0.69)	1
Taranaki Harbour, NZ[a]		0.002-0.030 (0.006)		0.18-0.88 (0.380)			0.18-0.65 (0.32)	0.86-9.25 (2.74)	1
Taranaki Bight/Cook Strait, NZ				0.15		0.15			2
Otago Harbour mouth NZ		<0.1		0.10-0.20		0.33			3
Taieri estuary, NZ[b]				0.06-0.16		0.12			4
N. Pacific) sfce		0.00016		0.03		0.12	0.005-0.015	0.0046	5,6(Pb)
) deep		0.124		0.32		0.65	0.0018	0.588	
NE Pacific	1.12-1.87								7
E. Pacific			0.00016						8
Central Pacific		0.009(u) <0.001(n)		0.57(u) 0.032-0.089(n)	0.005	0.176(u) 0.058-0.117(n)			9,10(Hg)
S. Pacific				0.06-0.21		0.24-0.46			11(Cu) 12(Ni)

References:
1 C. D. Stevenson (Chemistry Division, pers. comm.)
2 Hunter (1981b)
3 Dickson and Hunter (1981)
4 Hunter (1983)
5 Bruland (1980)
6 Schaule and Patterson (1981)
7 Andreae (1979)
8 Bruland (1983)
9 Boyle *et al.* (1983)
10 Fitzgerald *et al.* (1983)
11 Boyle and Edmond (1975)
12 Sclater *et al.* (1976)

Notes:
(a) Not filtered; sample treated to pH2 and analysed by ASV.
(b) Estimated for 35°/oo salinity.
(u) and (n) Refer to upwelling and non-upwelling waters respectively.

phosphate). More recently published data display less disagreement (Hunter, 1981a). Concentrations published since about 1975 are generally very much lower than older data mainly as a result of greater attention to preventing contamination. Table 6.2 summarises some of the more recent and reliable metals data for sea water and includes the work carried out in New Zealand. Concentrations for other metals obtained world-wide are given in Forstner and Wittman (1983).

It is important to recognise here that, for many metals, concentrations of dissolved species in open (especially surface) ocean waters are much lower than in natural fresh, estuarine and coastal waters and also, in the open ocean, the vast majority of metal is in dissolved forms.

A contribution to the high values obtained for Pb and Zn for surface waters off the North Taranaki coast, may have come from contamination during sampling rather than being the natural levels or resulting from environmental contamination. For Taranaki Harbour, the higher Zn levels are likely to be due to anthropogenic contamination of the harbour waters. However, because samples were not filtered prior to acidification an unknown contribution of metal would also be obtained by desorption from particulate material.

The Pb levels obtained by Schaule and Patterson (1981) appear to be the first reliable Pb data for oceanic water. These workers point out that the levels in the North Pacific are ten times higher than the expected mid-eighteenth century levels, and that concentrations in the South Pacific are not expected to be severely affected by anthropogenic contamination.

There do not appear to be many adequate analyses of Hg in sea water, due to its very low concentration and analytical difficulties arising therefrom.

6.1.2 Sediments

The most recent multi-regional study on metal levels in New Zealand aquatic sediments is that of Stoffers *et al.* (1983). One reason for the study was to provide a baseline for future surveys. One hundred and thirty one sediment samples, representing four different environments (lakes, sounds, harbours, and fiords), were analysed (XRFS) for chemical composition and mineralogy. The averaged heavy metals data are presented in Table 6.3. Other relevant studies, not reported on in detail here, are those of Glasby (1975) on South Island lakes and Glasby (1978) on South Island fiords. In general, the levels of metals found (AAS following $HNO_3/HClO_4/HF$ digestion) by Glasby (1975 and 1978) are similar to those presented in Table 6.3. Glasby (1978) noted that there was no marked variation in trace metal contents with depth in the sediment column in the fiords studied.

Table 6.3: Mean heavy metal concentrations and standard deviations (in brackets) (mg/kg) for sediments from 4 different New Zealand environments (Stoffers *et al.*, 1983). (n = no. of samples.)

Location	Metal							
	Ba	Cu	Co	Cr	Ni	Pb	V	Zn
North Island lakes (3)	555	20	5	32	7	32	32	62
n = 12	(192)	(20)		(11)	(6)	(6)	(11)	(20)
South Island lakes (17)	922	50	24	105	45	52	105	114
n = 61	(202)	(22)	(5)	(58)	(22)	(10)	(58)	(17)
North Island harbours and estuaries (6)	451	21	10	59	12	43	59	143
n = 24	(135)	(31)	(9)	(17)	(6)	(19)	(17)	(104)
South Island fiords and sounds (4)	518	21	15	64	28	35	64	84
n = 34	(128)	(20)	(5)	(23)	(14)	(10)	(23)	(57)

Stoffers *et al.* (1983) noted that New Zealand lakes are, in general, unpolluted by industrial compounds and are therefore useful in baseline studies of lake systems. They also pointed out that their trophic status (*sic*) has been influenced by the effects of agricultural developments and fertiliser use but it would seem as though lake metal sediment levels have not been affected. They noted that Wellington and Ohiwa Harbours, and the Thames estuary appear to have been affected by an anthropogenic influence, i.e., the levels of Cu, Pb or Zn are higher than might otherwise be expected. In the case of Ohiwa Harbour only one sample of sediment was analysed. It is possible that the odd sample of sediment taken from Ohiwa Harbour **could** be anthropogenically influenced but Akroyd and Kilner (1980) have noted that this remains relatively close to its natural state. However, small-scale illegal dumping (e.g., of old car bodies) has taken place. Anthropogenic modifications of metal levels in the Thames estuary are possibly due to past mining activities on the Coromandel Peninsula but this cannot be confirmed at this stage. Mean concentrations, calculated by Stoffers *et al.* (1983), for North Island harbours and estuaries are therefore likely to be on the high side.

Of note in the work of Stoffers *et al.* (1983) is the sometimes considerable spatial variability of metal content of many areas. It is important to note here that apparently high metal levels may be found in a particular area and that they may well be completely natural. Considerable caution must therefore be exercised in assigning a 'man-made pollution cause' to such apparently high levels found. A thorough knowledge of the mineralogy and geochemistry of an area should be gained before 'pollution' studies are embarked upon.

Comparison of the sediment metal concentrations (Table 6.3) with subsoil metal concentrations (Table 4.5) shows that many metals are present in both at similar concentrations; the metals Pb and Zn may be present in sediments at slightly higher concentrations.

Some data on As and Hg levels in central North Island lake sediments are given in Section 6.2.3.

6.1.3 Shellfish

Brooks and Rumsby (1965) conducted the first study on metals in New Zealand shellfish. Three species (the oyster, *Ostrea sinuata*; scallop, *Pecten novae-zelandiae*; blue mussel, *Mytilus edulis*) were dredged from Tasman Bay, 18 km north of Nelson at a depth of 22 m. Analysis was performed spectrographically on dried samples of whole shellfish and their organs. Some of their data for whole shellfish (and sediments) are presented in Table 6.4. Because of the relative remoteness of the sampling site from known anthropogenic inputs of metals, the levels found by Brooks and Rumsby must be considered to be background levels for the area. Thus, the apparently high (cf. Table 2.2) concentrations of Cd in scallops is probably natural. A comment made by Brooks and Rumsby was the possibility that the biosphere (in this instance, the shellfish studied) is a major pathway by which Cd and Zn are removed from sea water. Sediment metal concentrations reported by Brooks and Rumsby for Cu, Cr and Ni in Tasman Bay are all much higher than those found by Stoffers *et al.* (1983) for other areas of the country, whereas their Pb level is somewhat lower.

Table 6.4: Mean heavy metal concentrations (mg/kg dry weight*) in oysters, scallops, mussels and sediments taken from Tasman Bay sediments (Brooks and Rumsby, 1965) (n = 6 for all species; range given in brackets.)

Metal	Oysters		Scallops		Mussels		Sediments
Ag	5.6	(4.5-7.3)	0.7	(0.2-2.3)	0.1	(<0.2-0.3)	<0.1
Cd	35	(<20-43)	249	(210-299)	<10	(all <10)	<20
Cu	41	(21-53)	9	(2-12)	9	(5-11)	102
Cr	4	(<4-6)	10	(3-23)	16	(9-24)	307
Mo	0.3	(0.1-0.4)	0.9	(0.1-2.3)	0.6	(<0.2-1.0)	1.5
Ni	2	(<2-3)	6	(2-17)	7	(<2-17)	219
Pb	10	(6-14)	16	(10-23)	12	(<6-25)	<5
V	3	(2-4)	9	(5-14)	5	(2-8)	84
Zn	1103	(850-1500)	283	(195-368)	91	(<100-180)	<100

* To convert dry weight shellfish values to approximate wet weight values, divide by 5.

Hoggins and Brooks (1973) examined Hg concentrations in shellfish (cockle, *Chione stutchburyi* (now known as *Austrovenus stutchburyi*); rock oyster, *Crassostrea glomerata* (now known as *Saccostrea glomerata*); pipi, *Paphies australis*; green-lipped mussels, *Perna canaliculus*) in the Kaipara Harbour, which is situated over 100 km down the Wairua River (Northland) from the Puhipuhi Hg deposits (once mined). Mean Hg levels found (mg/kg wet weight; n usually = 10-11) were 0.03, 0.07, 0.02 and 0.02 respectively. These values are similar to those found by subsequent workers for unpolluted waters (see below). The only apparently anomalous values were obtained for *C. glomerata* (at up to 0.14 mg/kg) but these levels do not seem to be excessive (again, see below). Hg levels for all molluscs were well below Food Regulations limits. Hoggins and Brooks found that although Hg could be detected in the sediments at least 35 km from the deposits, it could only be found in water up to about 8 km away.

Nielsen and Nathan (1975) conducted a major survey on 13 species of edible molluscs from 199 sites around New Zealand to establish 'average or normal' metal concentrations. A summary of their very comprehensive data (obtained by AAS) is presented in Table 6.5.

Table 6.5: National average heavy metal concentrations (mg/kg wet weight) in New Zealand shellfish (Nielsen and Nathan, 1975). ($n \nless 14$; range given in brackets.)

Species	Cd	Cu	Hg	Pb(a)	Zn
Saddle oyster (*Anomia walteri*)	2.00	14.0		0.40	19.0
Rock oyster (*Crassostrea glomerata* now known *Saccostrea glomerata*)	1.30 (0.12-5.0)	40.0 (4.4-380)	0.18	0.90 (0.2-21.0)	337.0 (97-900)
Dredge oyster (*Ostrea lutaria*)	3.9 (0.12-7.9)	11.0 (1.0-41)	0.19	0.69 (0.1-2.2)	66.0 (19-246)
Green lipped mussel (*Perna canaliculus*)	0.30 (0.10-1.0)	1.8 (0.2-28)	0.09	1.80 (0.1-7.8)	21.0 (0.5-28)
Blue mussel (*Mytilus edulis*)	0.63 (0.26-1.6)	8.3 (1.7-18)	0.23	0.67 (0.1-2.0)	14.0 (3.8-26)
Ridged mussel (*Aulocomya maoriana*)	0.94 (0.16-2.4)	9.0 (3.3-19.0)		0.52 (0.2-0.8)	8.1 (3.2-11)
Black mussel (*Modiolus neozelanicus*)	0.04				
Scallop (*Pecten novae-zelandiae*)(b)	0.18 (0.14-0.28)	1.46 (0.9-2.5)	0.05	1.14 (0.4-3.5)	20.8 (18-31)
Paua (*Haliotis iris*)	0.17 (0.09-0.24)		0.10	0.50 (0.40-0.65)	13.5 (12.9-15.3)
Toheroa (*Paphies ventricosa*)	0.11 (0.07-0.17)	1.7 (1.1-2.9)		0.76 (0.5-1.0)	9.8 (6.9-15)
Pipi (*Paphies australis*)	0.13 (0.12-0.14)	1.0 (0.7-1.3)		0.40	13.0
Tuatua (*Paphies substriangulata*)	0.29 (0.29-0.34)	5.1 (1.4-8.7)		0.65 (0.4-0.9)	7.0
Cockle (*Chione stutchburyi*; now known as *Austrovenus stutchburyi*)	0.19			1.8	10.0

Notes: (a) The reliability of Pb values <0.5 mg/kg is questionable.
(b) Normally, only the stomach was analysed.

Nielsen and Nathan (1975) made the following comments:

1. There are few examples of suspected man-made heavy metal pollution in New Zealand. The green-lipped mussel, which seems to have a predilection for accumulating Pb, generally has higher Pb levels in the vicinity of large cities, e.g., 7.8 mg/kg near the Kaiwharawhara Stream mouth in Wellington Harbour, compared with 1-2 mg/kg in areas of the harbour relatively unaffected by man. (The authors ascribe these higher levels to the leaching of Pb from lead-based roofing paints via stormwater, and Pb from automobile exhaust emissions. Industrial pollution was not suspected because there were (and still are) no significant Pb discharges in the area).
2. There are some relatively high Cd levels in oysters and scallops, particularly in the Tasman Bay area (supporting Brooks and Rumsby's earlier work). (The possibility of a Cd contribution from superphosphate fertiliser and the Nelson city sewage outfall was suggested by Nielsen and Nathan. Natural causes cannot be ruled out.)
3. The variations in metal levels from one location to another may be so great that it is often difficult to determine what a 'normal' level is. (They sensibly suggested that future studies should examine individual sample locations in conjunction with geological data and knowledge of possible industrial and agricultural pollution.)
4. *Crassostrea glomerata* appears to have a definite tendency to accumulate Cu compared with other

species. Specimens taken close to a defunct Cu mine of Kawau Island had average Cu concentrations of 380 mg/kg; 40 m away the level had dropped to 160 mg/kg. Some of the oysters had a slightly green tissue. (Obviously spat-fall took place despite likely locally elevated environmental concentrations.)

5. New Zealand is basically an agricultural country, and there is relatively little heavy metal pollution from industrial sources. However, it is a geologically young country of volcanic origin and relatively rich in minerals, many of which may leach out and ultimately arrive in the sea via runoff from streams and rivers. This leads to large local variation in heavy metal levels.

More recently, Stephenson (1978) examined concentrations of Cd, Cu, Pb and Zn in four molluscs (*Chione stutchburyi*, *Amphibola crenata*, *Turbo smaragdus*, and *Cominella adspersa*) in Waikawa Bay, Marlborough Sounds, at the request of the Marlborough Harbour Board. Stephenson found large individual variations in metal concentrations and so no spatial or species trends are obvious. For *Chione stutchburyi*, Stephenson's results for Cu, Pb and Zn are very similar to those of Nielsen and Nathan (1975), but the former's values for Cd are very much lower (all concentrations <0.015 mg/kg dry weight). Stephenson postulated that all levels are natural.

Winchester and Keating (1980) reported results from a preliminary survey between April 1978 and May 1979 on trace metal (and organochlorine pesticide) residues in New Zealand farmed oysters. The areas covered in this survey were Northland, Auckland and the Coromandel Peninsula. Reasons for their use of oysters were that as well as indicating possible sources of water pollution (because they are good metal accumulators) they could also be used to provide data for export certification (if required). Some of the data of Winchester and Keating are presented in Table 6.6.

The main findings of Winchester and Keating (1980) are:

1. Though site-to-site variations are found, concentrations of most elements are within the ranges that would be expected for shellfish grown in relatively unpolluted waters. (Their results are also in keeping with those reported previously.)
2. Occasional high results occurred for Cd, and in excess of the Food Regulations limit of 1 mg/kg for foods other than shellfish (no limit for shellfish). (The authors suggested that a seasonal factor may be operating as most of the high values occurred in the summer months. No satisfactory explanation was offered, however.)
3. Arsenic levels occasionally exceed the Food Regulations limit of 2 mg/kg. (A possible contribution from wood preservative was suggested; preserved wood is used in timber supports in oyster farms.)

The problem of variability in metal levels in shellfish has been noted above several times. The difficulty in determining what a 'normal' level (Nielsen and Nathan, 1975) is, or showing real differences between sites or trend detection within sites, has received some attention around the world. For instance, Bryan (1973) showed that under natural conditions there is appreciable individual and seasonal variation in metal levels in scallops (*Pecten maximus* and *Chlamys opercularis*). There can also be variation

Table 6.6: Mean metal concentrations (mg/kg wet weight) in New Zealand farmed and wild oysters* (Winchester and Keating, 1980). (Range given in brackets.)

Metal	Farmed (17 samples)	Wild (5 samples)
As	1.95(1.1-3.6)	1.45(1.2-1.6)
Cd	[a,b]0.63(0.15-2.8)	[b]14(0.6-46)
Cr	0.23(0.07-0.50)	0.45(0.2-1.0)
Cu	20(5-42)	31(19-41)
Hg	0.04(<0.01-0.07)	0.02(<0.01-0.03)
Pb	0.61(0.20-1.0)	0.70(0.40-0.90)
Zn	202(74-352)	290(248-335)

* The farmed oysters are a mixture of Pacific (*Crassostrea gigas*) and rock oysters (*Saccostrea glomerata*); the wild oysters are all rock oysters. For each sample, n = 12.

(a) Excluding one high result of 20 mg/kg.

(b) See comment 2 in text.

in metal levels in shellfish due to location resulting from local upwelling (Goldberg *et al.*, 1983) as well as geologic, agricultural and anthropogenic variability noted by Nielsen and Nathan (1975). Variations are also possible due to shellfish size (Boyden, 1977) and depth (Nielsen, 1974). Therefore, the problem of detecting 'polluted' shellfish may not be easy except in a few instances. However, in New Zealand, it would seem as though it is rare that shellfish have been polluted (by metals) by man's activities to the extent that they are not fit for human consumption. This is further discussed later (see, for instance Section 6.2.10.2).

6.1.4 Fish

6.1.4.1 Freshwater species

Weissberg and Zobel (1973) examined Hg levels in the axial muscle tissue of trout taken from the Taupo, Waikato and Rotorua areas. Much higher levels of Hg were found in trout living in waters receiving considerable geothermal discharges (upper Waikato River, and Lakes Rotorua and Rotomahana) than in trout living in similar waters receiving little or no geothermal discharges (Lakes Taupo and Okareka)—see Table 6.7. They also found that average Hg concentrations in trout from the lower Waikato River were higher than those from the upper Waikato River and ascribed the differences to Hg-bearing industrial effluents (pulp and paper mill) into Lake Maraetai; this discharge has now ceased. Hg concentrations were found to increase with increasing fish weight, but no differences were found between rainbow and brown trout, nor between sexes. However, in several instances trout sample size was small (e.g., n = 4 for Lake Rotorua). Many of the fish had Hg levels well in excess of the Food Regulation limit of 0.5 mg/kg for fish and fish products.

Table 6.7: Mean concentrations and standard deviations (in brackets) of Hg in trout (mg/kg wet weight) and sediments (mg/kg) from several North Island locations (Weissberg and Zobel, 1973).

	Hg concentration	
Locality	Trout	Sediments
Lake Taupo	0.2 (0.08)	<0.05
Upper Waikato River	0.53 (0.31)	0.62 (0.38)
Lake Maraetai	0.70 (0.37)	0.89 (0.26)
Lower Waikato River	1.12 (0.89)	1.13 (0.49)
Lake Rotorua	1.68 (0.68)	1.18 (0.57)
Lake Rotomahana	2.10 (0.58)	0.54 (0.18)
Lake Okareka	0.35 (0.02)	0.17 (0.02)

A later study (Brooks *et al.*, 1976) showed very similar Hg concentrations (0.19 mg/kg wet weight) in 21 trout taken from Lake Taupo. Levels of other heavy metals were Cd 0.06 mg/kg, Cu 1.0 mg/kg, Zn 7.9 mg/kg. Other fish from several lakes in the central North Island were shown to have similar, low, Cd, Cu and Zn concentrations. Brooks *et al.* concluded that with the exception of Hg, the levels of elements contained in trout are unlikely to cause problems in public health. They further pointed out that although Hg levels in trout taken from Lake Taupo are relatively low compared with lakes near to geothermal discharges, the values found are nevertheless high (by a factor of about 5) compared with data from overseas areas far removed from geothermal or human sources of Hg. Brooks *et al.* speculated that for Lake Maraetai fish, it will be some considerable time before the elimination of Hg discharge from the pulp and paper mill results in a reduction of fish flesh Hg levels; this was because of the relatively long residence time of Hg in living tissue and the gradual release of Hg (as methylmercury) from lake sediments. Hg levels in fish taken from the Kaituna River (which intercepts geothermal discharges from the Rotorua region) are also elevated (Timperley and Vigor-Brown, 1982; see Section 6.2.5.2). M.H.Timperley (DSIR, pers. comm.) is currently examining Hg levels in central North Island trout and, in particular, Hg concentration via the food chain.

6.1.4.2 Marine species (P. C. Kennedy and D. G. Smith)

A number of studies (e.g., Hardisty *et al.*, 1974) have concluded that environmental contamination can lead to increased concentration of some trace metals in fish populations. Interpretation of variations in metal content is, however, likely to be complicated by the effects of age, size, weight, salinity, temperature, feeding habits, species, sex and season. For this reason, many authors have advised against using fish as indicators of trace metal pollution (see Phillips, 1977).

Table 6.8 summarises some of the work carried out by several New Zealand authors. Brooks and Rumsey (1974) analysed metals in edible muscle tissue and body organs of a number of commercial marine fish species. In edible muscle, metal concentrations decreased in the order Zn > Fe > Cu > Mn > Ni > Cr > Cd. The concentrations of most metals in muscle tissue were very low and well below Food Regulations limits (see Table 5.4) except for some high Zn values in kahawai (*Arripis trutta*) and kingfish (*Seriola grandis*). The geometric mean of Zn in kahawai was high compared with other species, but analysis of kahawai from Wellington harbours by P. C. Kennedy (unpublished data) produced results similar to other species. Brooks and Rumsey (1974) suggested that the higher level of Cd (and Mn) found in gurnard (*Trigla kumu*) was due to ingestion of sediment during feeding. These authors also suggested that gurnard was the most likely of the eight species they studied to show elevated concentrations of heavy metals should it be taken from heavily polluted areas.

Table 6.8: Mean* metal levels (mg/kg wet weight) in some New Zealand marine fish.

Fish	Sample location	Ref	n	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Gurnard	ECNI	1	70		0.015	0.01	0.34		0.16	0.02	5.5
	WH	2	4	2.0			0.44	0.3	<0.1		2.3
Hapuku	ECNI	1	70		0.005	0.02	0.35		0.87	0.02	5.2
	ECSI	3	35					0.31			
	Various	2	4					0.14			
Kahawai	ECNI	1	70		0.002	0.02	0.59		0.18	0.02	21.0
	WH	2	3	0.53			0.95	0.082	<0.1		4.3
Kingfish	ECNI	1	70		0.006	0.02	0.58		0.40	0.03	9.5
Moki	ECNI	1	70		0.005	0.01	0.46		0.23	0.07	8.5
Snapper	ECNI	1	70		0.016	0.03	0.11		0.22	0.04	3.7
	Various	5	65					0.25			
	WH	2	1	1.3			0.53	0.14	<0.1		3.7
Tarakihi	ECNI	1	68		0.006	0.02	0.28		0.18	0.03	2.8
	ECSI	3	11					0.18			
	WH	2	2	2.5			0.41	0.028	<0.1		2.2
Trevally	ECNI	1	70		0.01	0.01	0.28		0.20	0.02	11.2
Silver Warehou	WH	2	2	2.6			0.41	0.20	<0.1		2.2
	Various	1	92					0.04			
Flounder	WH	2	6	4.1			0.69	0.039	<0.1		3.1
Red Cod	WH	2	9	4.3			0.49	0.033	<0.1		2.4
	Various	3	39					0.07			
Barracouta	WH	2	3	0.8			0.65	0.042	0.39		2.4
	ECNI	3	24					0.12			
Sea Perch	WH	2	5	1.0			0.45	0.16	0.33		2.7
	E&WCSI	3	20					0.18			
Skate	WCSI	3	7					1.25			
Striped Marlin	BI	3	34					0.99			
Orange Roughy	CI	3	11					0.32			
	CI	4	31					0.35			

* Mean values given by Brooks and Rumsey (1974) are geometric means.

References:
1 Brooks and Rumsey (1974)
2 Kennedy, P. C. (unpublished data)
3 van den Broek *et al.* (1981)
4 van den Broek and Tracey (1981)
5 Robertson *et al.* (1975)

Locations:

WH	Wellington Harbour
ECNI	East Coast North Island
ECSI	East Coast South Island
CI	Chatham Islands
BI	Bay of Islands
WCSI	West Coast South Island

The concentrations of a range of metals in a number of fish species caught in Wellington Harbour are similar to those caught offshore, suggesting that past and present metal inputs to the harbour are not increasing fish flesh metal concentrations (P. C. Kennedy, unpublished data).

Brooks and Rumsey (1974) showed that metal levels in the liver were typically higher than in other organs and edible tissue. This was especially so for Cu and Cd. Hughes *et al.* (1980) analysed commercial fish for Cu, Fe, Mn and Zn and showed higher levels in the skin than in the fillets.

The work of Settle and Patterson (1980) and Patterson and Settle (1977) has demonstrated without doubt that most laboratories in the past were incapable of analysing the Pb content of fish muscle accurately. Even now, very few laboratories are able to prevent contamination during handling of the sample from reception to analysis and certainly only those with specialised clean room facilities can do so. Some doubt must therefore be cast on the Pb results in Table 6.8.

Robertson *et al.* (1975) analysed (by AAS) snapper (*Chrysophrys auratus*) from a number of coastal locations around New Zealand and noted higher Hg concentrations in fish from the Bay of Plenty (which receives water from some of the central North Island geothermal areas). van den Broek *et al.* (1981) found (by AAS) Hg mean concentrations greater than 0.5 mg/kg (the Food Regulations limit) in ling (*Genypterus blacodes*) from the west coast of the South Island, Auckland Islands and off Southland, in ghost shark (*Hydrolagus* sp.) from the Campbell plateau, in ribaldo (*Mora pacifica*), in skate (*Raja* sp.), in bluenose (*Hyperaglyphe antarctica*) from the west coast of the South Island, and in striped marlin (*Tetrapturus audax*) from the Bay of Islands. Several species displayed geographic differences in concentration. Water temperature may at times play an important role in influencing Hg concentration through uptake and diet. van den Broek *et al.* (1981) noted that Hg levels in hoki (*Macruronus novaezelandiae*) and gemfish (*Rexea solandri*) were higher in the warmer waters of Australia compared with New Zealand.

Barber *et al.* (1984) have examined deep sea blue hake (*Antimora rostrata*) caught (western North Atlantic) in 1880 and in 1972-4. Their results support the contention that the relatively high concentration of Hg found in marine fish that inhabit the surface and deep waters of the open ocean results from natural processes, not 20th century industrial pollution.

It is concluded from the above data that there is no elevation of metal concentrations in New Zealand marine fish due to human activity. However, many species of fish caught in New Zealand waters have Hg concentrations close to or in excess of the Food Regulations limit of 0.5 mg/kg; such levels are considered to be natural.

6.2 Area Specific Studies

Regional water boards and other agencies have generated a considerable amount of data on metal levels in waters, (the boards mainly via the analytical services of the Cawthron Institute). However, all too often, detection limits have been set far too high to determine actual metal levels (in many instances, e.g., potable supply analysis, this may not have been required, of course). Lack of precautions during sampling and subsequent handling in most instances would probably have compromised the obtaining of such levels anyway. The majority of metals data reported here for waters, has been obtained by direct aspiration flame (flameless for Hg) AAS on unfiltered samples. Detection limits will then be **approximately** as follows: As (hydride generation) 20 mg/m^3, Cd 20 mg/m^3, Cr 50 mg/m^3, Cu 20 mg/m^3, Hg (element reduction) 1 mg/m^3, Ni 50 mg/m^3, Pb 100 mg/m^3, Zn 20 mg/m^3. These methods, and approximate detection limits, should be assumed unless otherwise stated.

In many shellfish studies, sampling and analysis have been orientated towards public health standards (see Table 5.4) and little or no attempt made to identify or quantify causes of variation in metal levels, e.g., sediment character and particle size distribution, shellfish population, age and sex, local hydraulics, seasonal variations. Frequently, studies have not been systematic, and insufficient data have been generated to allow adequate interpretation. Analysis is normally by AAS following acid digestion. On many occasions, it was difficult to link occasional anomalously high metal levels in waters, shellfish, and sediments with discharges.

In much of the sediment work reported here, analysis has been performed on single, or very few, grab samples. Therefore statistical comparisons are not possible. Unless otherwise stated, the analysis (normally AAS) has followed simple acid (e.g., $HNO_3/HClO_4$) digestion and will thus not necessarily yield 'total' metal. However, in most instances, especially if sediments are contaminated, it is likely to be very close to 'total'.

Despite the above limitations the majority of the available data has been included here (often in raw form) if only to provide a record of work done.

6.2.1 Northland

6.2.1.1 Water Board Studies (with the assistance of L. L. Parker and G. C.Venus)

Very little sampling of waters for heavy metal analysis has taken place outside Whangarei Harbour. In 1982, four samples of Puhipuhi Stream water were taken from approximately 250 m downstream of Puhipuhi Springs and analysed for As, Cu, Hg, Pb and Zn. The samples were taken prior to exploration drilling. Metal levels from 12 streams in the Ngawha catchment were analysed in 1978 for As, Cd, Ni, Pb and Zn. Metal levels in all samples were below detection limits.

In March 1983, two samples of Ngawha Stream water were taken just downstream from the geothermal test discharge site at a time which was estimated to be typical of an expected normal working power station discharge. Arsenic levels were 80 mg/m^3 and Hg 3.5 mg/m^3. However, mixing was incomplete and it is estimated that these values would decrease downstream on complete mixing.

Metal levels in Whangarei Harbour sediments and shellfish are being investigated by the water board as part of the Whangarei Harbour Water Quality Management Programme.

6.2.1.2 Other Studies

Whangarei Harbour

As part of the Whangarei Harbour study, a single investigation was undertaken in September 1983 into metal levels in the waters (unfiltered) and sediments of the upper harbour (Venus, 1985). The results of the sediments analysis are summarised in Table 6.9. Cd, Cu, Pb and Zn levels appear elevated in the upper harbour, particularly so in the area of the town basin compared with levels found in the lower Hatea River. However, even these 'high' levels seem to be within a 'normal' range for unpolluted sediments except possibly the highest concentrations obtained for Pb and Zn (see Table 6.3).

Table 6.9: Metal levels (mg/kg dry weight) in upper Whangarei Harbour and lower Hatea River sediments (Venus, 1985).

Metal	Upper Harbour Mean (Range) n = 25	Hatea River Mean (Range) n = 5
Cd	0.2 (<0.05-0.78)	all values <0.05
Cr	11 (9-14)	15 (13-18)
Cu	27 (8-45)	14 (11-22)
Pb	31 (3-73)	11 (9-16)
Ni	11 (8-13)	12 (9-16)
Zn	111 (40-172)	61 (51-70)

A summary of harbour water metal concentrations is given in Table 6.10. The levels are all higher than expected for unpolluted water, but without information on the suspended sediment levels, the values are difficult to interpret. The Cd values however, are extremely high and cannot be accounted for by assuming a contribution due to suspended sediments. No explanation is available until harbour waters are re-examined but sample contamination cannot be ruled out.

Table 6.10: Total metal levels (mg/m^3) in upper Whangarei Harbour waters (Venus, 1985) (9 sites)

Metal	Mean	Range
Cd	2.0	0.4-3.0
Cr	all values < 2	
Cu	≈ 2	< 1-4
Pb	≈ 4	< 2-6
Ni	all values < 2	
Zn	7.6	3.2-16.3

In April 1984, Bioresearches Ltd were commissioned by the Whangarei City Corporation (WCC) to assess the implications of the discharge from the Pohe Island drainage system on the receiving water quality and the natural environment of Whangarei Harbour (Pohe Island contains a refuse tip). From an evaluation of information held by the WCC, Bioresearches (1984a) noted that the Hg concentration (highest value 4.5 mg/m^3) of drainage water was cause for concern, particularly in view of the potential of Hg to accumulate in biota and sediments (mean sediment concentrations of Hg close to the discharge area were found to be 0.31 mg/kg). The source of Hg could not be established. The metal concentrations in drainage waters from Pohe Island and nearby sediments are being investigated by the water board as part of the extensive Whangarei Harbour Water Quality Management Programme.

Marsden Point

The wet weight concentrations of Cd (≈ 0.2 mg/kg), Cr (<0.1 mg/kg), Pb (<0.1 mg/kg) and Zn (≈ 10 mg/kg) in the pipi (*Paphies australis*) were determined in a study around Marsden Point (site of oil refinery) for the Northland Harbour Board (Kingett, 1983). The levels found are around the New Zealand 'national averages' (see Table 6.5), and are within Food Regulation limits. No attempt was made to identify or quantify causes of variation in metal levels.

M. F. Larcombe (Bioresearches, 1983b), examined the effects of the Marsden Point oil refinery on shellfish and sediments in the Marsden Point area. Shellfish samples were taken from eight sites in the area during two surveys (April 1982 and September 1982). In his evidence to the Planning Tribunal, Larcombe (Bioresearches, 1983b) stated that there was no obvious increase in the metals concentrations of shellfish from near the refinery compared with those from the control sites, and in general the concentrations of metals in the shellfish were similar to or lower than concentrations that have been recorded elsewhere in New Zealand (see Table 6.5). Larcombe's conclusions were supported by his analysis of surface sediments taken in the vicinity of the refinery outfall (Table 6.11). Slightly higher metal levels were found in sediments very close to the outfall but it was pointed out that 'the magnitude and extent of metals enrichment of sediments in the immediate outfall area is not of major concern' (Bioresearches, 1983b). Thus, the current refinery does not appear to present any threat to the shellfish community by way of heavy metals. This situation will probably prevail after the extension has been built in view of the likely low metal levels in the discharge.

Table 6.11: Range of metal concentrations (mg/kg dry weight) in surface sediments from the Marsden Point area (Bioresearches, 1983b).

Metal	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	V	Zn
Range	<0.3-0.6	<0.4-3.8	2-3	<1.0-6.8	0.03-0.08	<1-3	<2	<2-9	<10	7-11

Nielsen and Nathan (1975) determined Cd, Cu and Hg concentrations in rock oyster (*Crassostrea glomerata*; now known as *Saccostrea glomerata*) in the Whangarei Harbour/Heads area and found levels very similar to the New Zealand mean (Table 6.5). Winchester and Keating (1980) found some anomalously high concentrations of Cd in oysters from Whangarei Heads but all other metal values were close to the New Zealand mean value (Table 6.6); they suggested that the high Cd values might, in part, be due to industrial pollution (presumably referring to the refinery) but also stated that their 'results must . . . be accepted with caution'.

Ngawha/Puhipuhi

Analysis of waters at Ngawha Springs (an area previously used as a Hg mine) from the Jubilee Bath, Cinnabar Bath and Sulphur Way Bath gave concentrations of 26.0, 27.5 and 28.5 mg/m^3 (Davey and Van Moort, 1974). Hoggins and Brooks (1973) found a rapid decrease in water Hg concentrations in the Wairoa River, Northland, downstream from the disused Puhipuhi mercury mine. Hg concentrations in the water were as high as around 0.5 mg/m^3 near the mine and rapidly decreased to a detection limit of 0.1 mg/m^3.

6.2.2 Auckland

6.2.2.1 Water Board Studies (with the assistance of D. Ogilvie, C. Hatton and D. A. Challis)
The Auckland Regional Authority (ARA) has carried out extensive heavy metal surveys on waters in their region. Analysis by their own laboratory was by direct flame AAS and routine detection limits are As 2 mg/m^3, Cd 5-20 mg/m^3, Co 20 mg/m^3, Cr 20 mg/m^3, Cu 10-20 mg/m^3, Hg 1 mg/m^3, Ni 10-50 mg/m^3, Pb 50 mg/m^3, Zn 5-10 mg/m^3. For many elements these limits are too high to detect small pollution effects, which might detrimentally affect aquatic biota, but are adequate in most instances (not Cd) for potable water management.

Streams sampled at various times from 1975-1985 were the Aroaro, Orere, Rautawhiti, and Wairoa in the Hunua catchment, the Ararimu, Rangitopuni, Hoteo, Orewa, Waiwera, Tamahunga, Kumeu, Waimauku, Paremoremo and Tihokupu in the northern catchments. Fifteen streams draining into the upper Waitemata Harbour (van Roon, 1980) and the harbour waters themselves (A. Cooke, Cawthron Institute, pers. comm.) were analysed for Pb in 1980. Lake Pupuke has been surveyed annually during autumn since 1975. Spot surveys of hydrothermal bore waters in the Parakai and Waiwera areas, and freshwater bores in the Omaha, Kaipara, Waimauku and Bombay-Franklin-Pukekohe areas have been carried out since 1974. Apart from occasionally high Cu and Zn concentrations in bore waters (probably from the well casing or reticulation) levels were normally below detection limits. Where concentrations are recorded at or slightly above these limits it seems likely that samples were contaminated.

Analyses have been carried out on the surficial sediments of the upper Waitemata Harbour, streams draining to it, and the adjacent Wairau Creek (which drains the Wairau industrial area). Of the streams, only Wairau Creek sediments showed possibly elevated levels of Pb (110 mg/kg) and Zn (195 mg/kg) (A. Cooke, Cawthron Institute, pers. comm.). In the upper harbour sediments, generally concentrations of heavy metals are not high, e.g., Cu $\approx$ 35 mg/kg (with one exception); Cr $\approx$ 65 mg/kg; Hg $\approx$ 0.15 μg/kg; Ni $\approx$ 15 mg/kg; Pb $\approx$ 25 mg/kg; Zn $\approx$ 100 mg/kg (Fry and Hume, 1980). They have been classed as relatively 'clean' despite the urbanisation of some contributing catchments (UWHCS, 1983). The authors were not able to distinguish whether the variation in metal concentrations is due to differing land uses, or whether it is indicative of differences in sediment sources (UWHCS, 1983).

6.2.2.2 Other Studies

Waiuku Estuary, Manukau Harbour

The marine area of the Waiuku River is generally shallow, with a large proportion of the total area being intertidal. New Zealand Steel Limited discharges wastewater (see Section 4.8.7) into the estuary at the right (east) bank at a point approximately one third of the distance between Waiuku township and the Manukau Harbour. In 1983, the process wastewater discharge (25 l/s) was via the northernmost of two outfalls. This discharge had been in operation since 1978. Prior to that time there were separate discharges into the centre of the bay adjacent to the mill and into the Ruakohua Stream (Bioresearches, 1984b). The limits on metal concentrations for the discharge (August 1984) were Zn 1500 mg/m^3, Cr^{3+} 200 mg/m^3, Cr^{6+} 10 mg/m^3, Ni 1000 mg/m^3, Pb 200 mg/m^3, Cu 1000 mg/m^3, Hg 1 mg/m^3, Cd 1 mg/m^3, and As 50 mg/m^3. Data on the discharge metal concentrations are difficult to interpret (see Section 4.8.7) but in 1982 2 kg/day and 18 g/day of Zn and Cr^{6+} respectively have been calculated to have been discharged (ARWB, 1983). Bioresearches Limited have conducted several water, sediment and biota surveys in the vicinity of the mill discharges, e.g., Bioresearches (1981a). From a metals viewpoint their findings, and those of the Auckland Regional Authority, have been summarised by Bioresearches (1984b). It seems as though the past discharges of New Zealand Steel wastewater have had no major adverse biological effects in the immediate outfall area and there are no dominant organisms present in habitats near the outfall which would not be expected (if the area were unaffected by the discharge). Of the dominant organisms present (cockles (*Chione stutchburyi*), pupu (*Amphibola crenata*), Pacific oysters (*Crassostrea gigas*), barnacles (*Elminius modestus*), burrowing crabs (*Helice crassa*)) recruitment of juveniles has occurred and they subsequently successfully survived to grow into apparently normal adults. There is a marked increase in Zn levels in oyster and pupu within 200 m of the outfall but the oyster Zn concentration is not significantly different from that in oysters from the rest of the Manukau Harbour. (A brief selection of data obtained by Bioresearches (1981a) is presented in Table 6.12.) There has been some enrichment of Zn, Cu, Cr, Mn, Fe and Hg in sediments adjacent to the outfall, but levels appear to drop to background values within a few hundred metres. Except for Zn, the highest concentration of metals recorded in the vicinity of the outfall are within the range of results for sediments from other areas of the Manukau Harbour. (A selection of data is presented in Table 6.13.) The metal sediment concentrations seem to be related to sediment grain size, with the finer sediments containing higher concentrations.

Table 6.12: Metal concentrations (mg/kg dry weight) in Waiuku River biota (Bioresearches, 1981a).

	At Outfall				4 km Downstream of Outfall
	Cockle	Pacific oyster	Pupu	Crab	Cockle
Cd	0.05	0.12	0.03	0.4	0.05
Co	0.64	0.67	0.75	3.1	0.73
Cr	0.45	1.67	0.62	9	0.45
Cu	0.55	11	13.2	23	0.64
Hg	<0.001	<0.001	0.12	<0.01	<0.001
Ni	1.1	<0.02	<0.12	4.2	1.6
Pb	0.02	0.67	0.12	6	0.3
Zn	8.5	670	13.6	22	7.0

Table 6.13: Metal concentrations (mg/kg dry weight) in surface sediments from the Waiuku River (Bioresearches, 1981a).

Location	Cd	Co	Cr	Cu	Hg	Ni	Pb	Zn
Upstream of outfall*	0.7	11	22	5.6	0.42	11	9	62
At outfall	0.6	15	46	12.0	1.15	20	22	387
Downstream (2 km) of outfall	1.2	10	24	6.9	0.21	12	20	65

*Mean of 2 sites (2 and 3 km upstream)

It appears, from temporal studies on an area now not receiving discharge from an outfall (due to the latter's relocation), that wastewater derived elevations of metal concentrations in the sediments quickly revert to background concentrations when discharge ceases.

6.2.3 Waikato

6.2.3.1 Water Board Studies (with the assistance of R. J. Matthews and B. J. Zuur)

In 1981, the Waikato Valley Authority (WVA) briefly examined the effects of coal mining activities on water quality in the area of the Huntly West coalfield. The majority of mine wastes discharge to the Lake Waahi catchment and the results from analysis of Lake Waahi waters (for dissolved As, Cd, Cu, Fe, Hg, Pb, Mn and Zn) 'indicate that there are no excessive levels of toxic heavy metals in the combined discharges of mining activities in the Lake Waahi catchment' (R. J. Matthews, WVA, pers. comm.) although on one occasion Zn analysis of a Lake Waahi water sample was reported as 90 mg/m^3. The Awaroa Stream, which takes discharges from three mines and a carbonisation works, appeared to show slightly elevated As concentrations (i.e., up to 16 mg/m^3). Sediments and biota were not examined in the survey. Generally speaking, however, waste waters from mining activities in the area have a near-neutral pH and are low in dissolved metal concentrations (see Section 4.8.1).

Occasionally, streams have been shown to have become contaminated by discharges of storm water or waste water from timber treatment plants. For example, on one occasion in November 1983, the Tauhei Stream upstream of a plant storm water discharge had levels of As, Cr and Cu below detection limits (10 mg/m^3, 20 mg/m^3 and 20 mg/m^3, respectively) whereas downstream levels were 130 mg/m^3, 70 mg/m^3 and 110 mg/m^3 respectively. The effect of such discharges of timber preservative on biota has not been assessed.

Several watercourses, which receive geothermal inputs, have also been investigated. In February

1983, the Tokaanu Stream, south of Lake Taupo, had an As concentration of 250 mg/m^3 downstream of a thermal pool discharge. In July 1978 the Waiotapu Stream, to the north of Taupo, contained 1-7 mg/m^3 Hg and 50-160 mg/m^3 As; sediment samples taken at the same time were found to contain 0.4-1.2 mg/kg Hg and 320-1000 mg/kg As. The discharges causing these high levels are natural but the effects on stream biota are not known. The Waikato River has been analysed monthly during the period April 1983-March 1984 for As and Hg at 6 sites from Lake Taupo (gates) to the Narrows bridge in Hamilton. The river receives several discharges of geothermal water close to Lake Taupo (Strachan, 1979). From an average As value of <10 mg/m^3 at Taupo gates there is an increase to 40-50 mg/m^3 between Mihi bridge and Hamilton. En route to Hamilton some of the As is adsorbed onto the sediments and diluted by tributaries. The potable water limit for As is 50 mg/m^3. However, most potable water supplies receive alum flocculation treatment which will considerably reduce the As concentration in the water supplies of consumers. Average Hg levels are at or about the claimed detection limit of 0.05 mg/m^3. The contributions of various natural and anthropogenic geothermal metal inputs to the Waikato River is currently being assessed after an intensive survey carried out in early 1985.

6.2.3.2 Other Studies

The Waikato River

A water resources study of the Waikato River (Strachan, 1979) reviews metal level studies (for water and sediments) carried out prior to 1978. The heavy metals reported were As, Cd, Cr, Cu, Hg, Ni, Pb, Zn. Apart from As and Hg which will be dealt with separately, the other metals were rarely detected and even then contamination cannot be ruled out; the data in the report should probably be treated with caution. A sediment survey, examining As, Cd, Cu, Hg, Pb and Zn concentrations in the Waikato lakes, was conducted in 1976. Cu and Zn concentrations up to 13.5 mg/kg and 66 mg/kg respectively were reported (for Lake Maraetai), and the highest Pb concentration (6.7 mg/kg) was reported for Lake Ohakuri. These Cu and Pb concentrations are lower than, and the Zn concentration equal to, the mean values obtained by Stoffers *et al.* (1983) for three North Island lakes.

Timperley (1979) studied heavy metals in waters flowing from the eight hydroelectric reservoirs on the Waikato River. Samples were collected monthly (by untrained staff) for one year and analysed by AAS following solvent extraction. His results are presented in Table 6.14 together with those of H. Beaumont (Chemistry Division, DSIR, pers. comm.) for a single sampling (in November 1982) at six locations. The lowest values found by Timperley for Cd, Cu, Ni and Pb are around the highest estimated global background concentrations (Table 6.1); the median values for Cd and Pb are an order of magnitude higher than the highest estimated global background concentrations.

Table 6.14: Total metal concentrations (mg/m^3) in the Waikato River system.

	Timperley	H. Beaumont	Rawlence and Whitton (1977)		
	(1979)	(Chem. Div., pers. comm.)	Lake Rotoaira	Lake Taupo (2 sites)*	Lake Aratiatia*
Metal	Range (median)	Range			
Cd	0.1-1.2 (0.5)	0.003-0.024			
Co	0.2-3.5 (1.5)		0.23	0.18; 0.06	
Cu	1-30 (6)	0.13-1.1	73	11; 1.0	0.28
Ni	1-20 (4)		7.3	5.8; 0.76	
Pb	1-50 (6)	0.8-4.5	3.0	1.4;	
Zn	$<$0.2-80 (4)	0.8-3.0	3.7	5.6; 1.1	1.1

*The first figure is for Waihi Bay (in the south); the second figure is for Two Mile Bay (in the north-east).

Because there appear to be no significant inputs of heavy metals from geothermal and industrial sources in the part of the river studied, Timperley (1979) attributed the levels he found to natural (and accelerated) weathering in the catchments. Although Timperley ruled out sample contamination, it seems as though the results should be viewed with some caution in the light of Beaumont's study.

Beaumont's concentrations (1982) for Cd and Cu are very much lower while Pb and Zn concentrations are similar only at the lower end of the range obtained by Timperley. Beaumont's results (obtained by Differential Pulse ASV) also agree well with those obtained by R. B. Williamson (Water Quality Centre, MWD, pers. comm.) (by Graphite Furnace AAS following Chelex extraction) from samples taken at the same time. Coulter (1977) has also examined metal levels in the Waikato River system. His results are similar to those of Timperley (1979).

The Cu concentrations obtained by Rawlence and Whitton (1977) for Lake Rotoaira (73 mg/m^3) and the southern site in Lake Taupo (11 mg/m^3) are higher than accepted average concentrations for the protection of freshwater aquatic life (around 5 mg/m^3 – see Tables 5.1a, b and c). These authors collected 10 l of sample which was then evaporated to dryness prior to analysis by XRFS (for Zn) or emission spectroscopy (for other heavy metals). The evaporation step is subject to considerable contamination problems, and the latter analytical technique has poor detection limits for some metals. Rawlence and Whitton (1977) noted that the element levels at each sampling site follow closely the dominant geochemical influences within each catchment area.

Rawlence and Whitton (1977) have reported metal concentrations for sediments, plankton and macrophytes taken from Lakes Rotoaira, Taupo and Aratiatia. They found that the element concentrations of the sediments generally reflect the prevailing geology of the various catchments. Concentrations of Cu, Pb, and Zn in plankton taken from Lake Rotoaira are high (47 mg/kg, 60 mg/kg and 122 mg/kg respectively) compared with samples taken elsewhere (e.g., Lake Aratiatia; 7 mg/kg, 23 mg/kg and 31 mg/kg respectively). The levels of Cu, Pb, and Zn in plankton decrease downstream in the Waikato River. In macrophytes, metal concentration was shown to vary substantially with season, growth stage, sampling site and location within a stand. Again element concentration reflected differences in catchment geology. In comparison with metal levels found in oceanic plankton, Rawlence and Whitton (1977) concluded that human influences on the region appeared to be restricted to 'high' Pb concentrations in plankton.

Pb levels in *Lagarosiphon major* taken from Lake Taupo boat harbour were shown by Liddle (1982) to be elevated (200-300 mg/kg) compared with samples taken elsewhere in the region (< 20 mg/kg, the approximate detection limit). This is likely to be due to the use of motorboats (fuelled by leaded petrol) in the area.

Arsenic

Reay (1973) estimated that the Wairakei Power Station provides nearly 75% of the total As input to the river system. A more recent estimate by Liddle (1982) has put the contribution of the geothermal field at 62% and the **incremental** effect of the development of the Wairakei Power Station is suggested to account for 55% of the total As input. Reay's estimates of As inputs to the Waikato River are reproduced in Table 6.15. Future geothermal developments (e.g., at Broadlands) will probably reinject waste waters rather than discharge them to the river (see, e.g., Willis, 1980).

Table 6.15: Estimates of the As inputs to the Waikato River from geothermal areas (Reay, 1973).

Natural	t/yr
Lake Taupo	30
Wairakei	22
Ohaki pool	0.5
Orakei-Korako	8-13
Waiotapu-Reporoa valley	1-2
	61-67
Geothermal development	
Wairakei	190

Total As in river water has been examined by Reay (1973) (random sampling during 1971-72) and Aggett and Aspell (1978) (monthly sampling during 1976). The results are presented in Table 6.16.

Aggett and Aspell (1978) found that the As was present largely as As(5 +) although on several occasions As(3 +) predominated. They could not explain this phenomenon but suggested that biological activity could reduce As(5 +) to As(3 +) (see Section 2.2). For the Waiotapu Stream,

Table 6.16: Total As (mg/m^3) in the Waikato River.

	Reay (1973)	Aggett and Aspell (1978)
Taupo	8	5-15
Aratiatia	28	36-95
Broadlands		31-60
Ohakuri	42	31-43
Arapuni	29	24-36
Hamilton		19-32

a major tributary of the Waikato River, Aspell (1979) found the total As concentration in the Waiotapu Stream to be 229 mg/m^3 (unfiltered) and 138 mg/m^3 (filtered) of which As(3+) comprised 69% and 75% respectively.

Several studies on the As content of sediments in Lake Ohakuri have been reported (Reay, 1973; Coulter, 1977; Aggett and Aspell, 1978). The most extensive survey (Aggett and Aspell, 1978) showed that the mean As sediment concentration was 335 mg/kg (dry weight) and that the mean accumulation rate was 8 t/yr. They estimated that 125 t of As had accumulated in the sediments since lake formation in 1961 (electricity production at Wairakei started in 1958) and noted that As accumulation is probably not restricted to Lake Ohakuri. Aggett and Aspell (1980) estimated that sedimentation of As in the Waikato River system accounts for 7-8% of the As input. Aggett *et al.* (1982) and Aggett and O'Brien (1985) have pointed out that Ohakuri stratifies in summer and during this time As is released from the sediments thereby increasing concentrations in the hypolimnion. In 1981, As concentrations reached 250 mg/m^3 in the hypolimnion compared with around 40 mg/m^3 in the epilimnion (Aggett and O'Brien, 1985).

Aggett and Aspell (1980) examined As assimilation by lake weeds in three lakes (Karapiro, Ohakuri, Aratiatia) in the latter half of 1976. Their results are summarised in Table 6.17 along with data from Liddle (1982).

Table 6.17: Mean As concentrations (mg/kg dry weight) in Waikato lake weeds.

Lake	Species	Aggett and Aspell (1980)	Liddle (1982)
Karapiro	*Egeria densa*	445	
	Ceratophyllum demersum	178	
Ohakuri	*C. demersum*	579	336
	Lagarosiphon major	510	
	E. densa		407
Aratiatia	*L. major*	546	393
Taupo	*L. major*		43
Manawatu River*	*C. demersum*		7.0
Mangaone River*	*E. densa*		23.3

*Non-geothermal areas for comparison.

In general, the levels found are in line with data reported by others (e.g., Lancaster *et al.*, 1971; Reay, 1973). There seems to be a tendency for higher levels to be found in plants taken from locations nearer the Wairakei Power Station discharge (but downstream from it). All three species investigated by Aggett and Aspell (1980) showed a marked seasonal variation of As concentration, falling as summer approached. Most of the As was in the As(3+) state.

Arsenic levels in 5 trout from Taupo and Broadlands were similar to the As concentrations in the water from which the fish were taken (Aggett and Aspell, 1980). If this sample is representative, the consumption of trout from areas affected by geothermal inputs was concluded to pose no health risk from As.

Mercury

Hg has been examined in waters of the central North Island by Weissberg (1975). In water samples from Lake Taupo, the Waikato River, and the Rotorua lakes, the Hg concentrations were mostly below 0.020 mg/m^3 (the limit of detection). The few samples which contained detectable concentrations were associated with either geothermal or industrial discharges. For example, the following levels were found: Champagne Pool, Waiotapu, 2.6 mg/m^3; the Wairakei geothermal field drain channel, 0.08-0.16 mg/m^3; the mouth of the Waiotapu River, 0.13 mg/m^3; Maraetai No. 1 tailrace (which draws its water from the bottom of Lake Maraetai, and which had received Hg in pulp and paper plant wastewaters), 0.04 mg/m^3.

Coulter (1977), reporting results obtained by NZ Electricity Department in 1975 from sediments between Lake Taupo and Ohakuri Dam, noted that the fine sediments at the mouths of the Parariki and Waiotapu Streams (0.78 mg/kg), and Lake Ohakuri (0.61 mg/kg) contain the highest Hg levels in the sediments examined.

6.2.4 Hauraki

6.2.4.1 Water Board Studies (with the assistance of A. J. Goldstone)

The water board has conducted a limited amount of work on the streams draining the area of Tui Mine (a disused Cu, Pb, Zn mine—see Section 4.8.1). A single sample of the Tui Stream, which intercepts leachate from an old tailings heap, was shown (June 1981) to contain the following metal levels: Cd 100 mg/m^3, Cu 690 mg/m^3, Hg 4 mg/m^3, Pb 160 mg/m^3, and Zn 28 000 mg/m^3. At the same time, the north branch of the Tunakahoia Stream, which drains the old mine workings region, had the following metal levels: Cd 60 mg/m^3, Cu 100 mg/m^3, Hg <1 mg/m^3, Pb 100 mg/m^3, Zn 9100 mg/m^3.

The sediments of the Topehahae Stream in the vicinity of a fertiliser works discharge have received some scrutiny from the board. Samples taken 2 km downstream of the discharge have been shown to be enriched by several metals compared with samples taken upstream of the discharge. As examples of the results, paired comparisons (in mg/kg) for 15 m upstream and 100 m downstream of the discharge are as follows: As 0.92, 2.0; Cd$<$0.05, 9.1; Cu 13, 76; Fe 25 000, 21 000; Hg 0.10, 14; Pb 23, 32; Zn 64, 270 (Goldstone, 1983). Goldstone (1983) recommended that the metals Cd and Hg are worthy of further investigation.

6.2.4.2 Other Studies

Ward *et al.* (1976) analysed the soils, stream sediments, waters and vegetation around the defunct Tui base metal mine outfall for Cd, Cu, Pb and Zn. Both the waters and sediments of the right branch of the Tunakohoia Stream (which intercepts drainage from two outlets (adits) of the mine) were shown to have very high levels of metals downstream of the mine drainage area (see Tables 6.18 and 6.19). A more recent study by Tay (1980) has confirmed these findings, except that the Zn contamination was quite exceptional (Tables 6.18 and 6.19). However, Tay also showed that the waters of the left branch of the Tunakohoia Stream, apparently not influenced by mining, were contaminated by Zn. There is also possible Cd contamination, but the level reported (10 mg/m^3) is at the detection limit.

Table 6.18: Metal concentrations (mg/m^3) in streams around the Tui Mine.

	Metal					
Location	Cd	Cu	Pb	Zn	pH	Reference
Tui Stream						
Above confluence with tailings discharge	<20	<30		20-500	7.5	(1)
	<10	<30	<30	20	7.1	(2)
Below confluence with tailings discharge	20-25	40-270		5100-11000	4.6	(1)
	37	270	80	10300	4.5	(2)
Tunakohoia Stream						
Vicinity of base metal deposits (a,c)		100-300	100-300	100-300		(3)
Away from mine influence (b)	10	10		300	7.2	(2)
Below mine adits (a)	100	30		12900	7.6	(2)

References:
(1) Hendy (1981)
(2) Tay (1980)
(3) Ward *et al.* (1976)

Notes:
(a) Right branch (affected by mining).
(b) Left branch (unaffected by mining).
(c) Stream not specifically named in paper.

Table 6.19: Metal concentrations (mg/kg) in sediments taken from streams around the Tui Mine.

Location	Cd	Cu	Hg	Pb	Zn	Reference
Tui Stream						
Above confluence with tailings discharge	6.4(d)	76(d)		49(d)	1360(d)	(2)
Below confluence with tailings discharge	14(a) 5.3(d)	660(a) 837(d)	1.8(a)	1700(a) 315(d)	2000(a) 557(d)	(1) (2)
Tunakohoia Stream						
Vicinity of base metal deposits (b,c)	50-300	300-2000		800-4000	2000-7000	(3)
Below mine adits (b)	359	10600	14	9560	147000	(2)

References:
(1) Hendy (1981)
(2) Tay (1980)
(3) Ward *et al.* (1976)

Notes:
(a) "Typical" analysis; $<125\mu m$.
(b) Right branch (affected by mining).
(c) Stream not specifically named in paper.
(d) Average values.

Tay (1980) and Hendy (1981) have shown elevated metal concentrations in the Tui Stream waters and sediments downstream of the confluence with the discharge from the mine tailings pond. This elevation is a direct consequence of inadequately managed tailings disposal and complete lack of treatment. Some contamination by Cu and Zn was also noted above the mining influences (Tables 6.18 and 6.19).

Tay (1980) also analysed for heavy metals in waters from other creeks and streams draining Coromandel mines but, although contamination of these waters due to mine drainage was evident, nothing was found on a scale comparable to the Tui Stream. The other most contaminated water seems to be obtained from an encrustation across the Monowai track (As 43 mg/m^3, Cd 31 mg/m^3, Cu 45 mg/m^3, Pb 140 mg/m^3, Hg 27.5 mg/m^3, Zn 9630 mg/m^3). Tay (1980) concludes that 'it appears as though the bonanza **gold** mining in the Coromandel Peninsula (has) not resulted in a serious present-day impact on the regional aquatic environment . . .' (emphasis added).

In 1981, the Minister of Science requested Chemistry Division, DSIR, to carry out heavy metal studies in the Coromandel region largely because of public concern about potential contamination by heavy metals of streams and coastal waters due to renewed precious metal prospecting and mining activites. At approximately the same time, two other studies on the effect of mining on stream ecology (NWASCA) and heavy metal concentrations in fish and shellfish (Fisheries Research Division (FRD), Ministry of Agriculture and Fisheries) were also started. The three studies were coordinated by the Hauraki Catchment Board.

The main objective of the Chemistry Division study was to establish the concentration range of trace metals in streams and sediments covering a range of conditions, including streams contaminated by past mining activities. Concentrations of Cd, Cu, Pb and Zn in waters were determined using differential pulse ASV and of As by using AAS following hydride generation. Detection limits were Cd 0.005 mg/m^3, Cu 0.05 mg/m^3, Pb 0.05mg/m^3, Zn 0.2 mg/m^3, and As 1 mg/m^3. Precautions were taken during collection, processing and analysis to ensure that samples were not contaminated. Some of the results are presented in Table 6.20. Very low levels of metals were found not only

Table 6.20: Total "baseline" metal concentrations (mg/m^3) in Coromandel streams* (Tunnicliff and Beaumont, 1986).

Metal	Concentration
As	<1-1
Cd	<0.005-0.03
Cu	<0.05-0.5
Pb	<0.05-0.5
Zn	<0.2-1.0

* Waipupu (nm), Waitawheta (nm), Komata (m), Waitekauri (m), Mangakara (m); (nm) no known mining history, (m) known mining history.

in streams draining catchments with no known history of mining activities, but also in some with extensive mining history. Concentrations were generally much lower than EPA criteria for aquatic life protection (see Tables 5.1a, b and c) and similar to estimated global background concentrations for fresh water (Table 6.1).

Streams draining catchments affected by past mining, or by natural weathering of mineralised strata, did not necessarily have high levels of all metals, and it was not always possible to distinguish between the effects of past mining operations and the effects of weathering processes (Tunnicliff and Beaumont, 1986). However, in streams receiving direct discharges from mine workings or tailings dumps, metal levels can be several orders of magnitude higher than the baseline concentration (Table 6.21).

Table 6.21: Total metal concentrations (mg/m^3) in Coromandel streams affected by past mining operations (Tunnicliff and Beaumont, 1986).

	Streams		
Metal	Comstock	Paroquet	Tui
As	118-260	<1	1-1.5
Cd	0.020	0.24-0.58	4.3-20
Cu	<0.05-0.24	1.4-5.0	35-230
Pb	0.23-1.1	0.5-7.0	23-57
Zn	21	31-120	2080-17000

Tunnicliff and Beaumont (1986) also studied sediment metal concentrations and found that consistently low metal levels in the waters are reflected by low metal levels in the sediments. Other things being equal, as water metal levels increase, so do sediment metal levels increase. When co-precipitation and/or adsorption with iron floc is thought to be a major factor controlling the levels of metals in the sediments, concentrations may not correlate with those in the waters, but the metal/iron ratios in the sediments will follow the metal levels in the waters. Under acidic conditions the levels of metals and the metal/iron ratios in the sediments will be decreased because the metal cations have a greater tendency to remain in solution. Arsenic is an exception probably because it is present in anionic form, even at low pH.

Several of the streams analysed by Chemistry Division were selected for biological studies (Penny, *in press*). Macroinvertebrate communities were found to be stressed or impoverished at sampling sites below some mine waste discharges and this tended to correlate with the concentrations of some heavy metals, particularly Zn, in the stream waters and sediments. However, the study was not able to demonstrate these relationships were causal. The dissolved heavy metal concentrations at the biologically stressed or impoverished sites were largely below EPA (1985) criteria calculated, where appropriate, on the basis of hardness. The study indicates that a range of factors (e.g., metal concentration in waters and sediments, iron floc deposition, and the degree of downstream macroinvertebrate drift) need to be taken into account in managing mine discharges.

The FRD fish and shellfish studies (Tracey and van der Broek (*in press*) provide data on the concentrations of As, Cd, Cu, Hg, Pb and Zn in the tissues of fish and shellfish from coastal and inland waters around Coromandel. The variation in tissue concentrations found could not be attributed to any particular causal factor. Tissue concentrations were largely below the limits for human consumption (see Table 5.4). However, maximum mercury concentrations for freshwater eels frequently exceeded the limit and mercury levels in eels were regarded as naturally high in the Coromandel region.

6.2.5 Bay of Plenty

6.2.5.1 Water Board Studies (with the assistance of J. J. McIntosh)

Little work on heavy metals has been carried out by the board. In June 1983, thirteen sediment samples (top 5 cm) from Tauranga Harbour were collected and analysed for Cd, Cr, Cu, Hg, Ni, Pb and Zn. Levels were found to be a very low and average values in mg/kg are approximately as follows: Cd<0.5, Cr<1, Cu 2, Hg 0.05, Ni 2, Pb<4, Zn 28.

A brief survey, also conducted in June 1983, on sediment samples taken from the Whakatane River at sites above and below the Whakatane Board Mills outfall, showed no differences in sediment metal levels. Likewise no metal level elevations could be detected in sediments from the Katikati River after spillage of preservative solution from a timber treatment plant.

6.2.5.2 Other Studies

Williamson and Cooke (1982) examined the waters of the Waiohewa Stream, Rotorua; this stream drains the Tikitere geothermal area. Hg was found at up to 0.8mg/m^3 in filtered samples taken from below Hell's Gate and 16 mg/m^3 in unfiltered samples. The unfiltered samples contained a milky-grey suspension of silica and sulphur. Near where the stream enters Lake Rotorua, filtered Hg concentrations dropped to 0.1 mg/m^3, the detection limit. Arsenic was also examined; inorganic As concentrations were normally at or below detection limits (5mg/m^3) except for samples taken from the Tikitere area (up to 14 mg/m^3).

Coulter (1977) has also examined Hell's Gate waters, but for most metals, concentrations (totals?) were below detection limits (i.e., Ag$<$1 mg/m^3, Cd$<$0.5 mg/m^3, Hg$<$1 mg/m^3, Pb$<$5 mg/m^3, Zn$<$0.5 mg/m^3). Cu and Ni were detected at 370 mg/m^3 and 23 mg/m^3 respectively.

Weissberg (1975) analysed waters from the Rotorua lakes area for Hg. The Puarenga Stream, which flows into Lake Rotorua, had a total Hg concentration of 0.10 mg/m^3, most of which was in particulate form. This stream probably derives its Hg from geothermal discharge at Whakarewarewa. One sample of Lake Rotorua water was reported as containing 0.02 mg/m^3 Hg (the detection limit).

Timperley and Vigor-Brown (1982) have assessed the Hg contamination in the Kaituna River system, the purpose being to estimate the consequences of diverting Rotorua City sewage effluent and Tikitere geothermal waters to the river. It was shown that Kaituna River waters contain elevated Hg levels (up to 0.57 mg/m^3) near the river mouth but usually contained $\leqslant$0.05 Hg/m^3 at the outlet from Lake Rotoiti. Sediments in the Maketu Estuary (adjacent to the river outlet to the Bay of Plenty) contained Hg concentrations in excess of 0.2 mg/kg at one station only. Shellfish (cockles, pipis, and oysters) had Hg levels well below the Food Regulation limit for fish and fish products (0.5 mg/kg). The highest level found (0.062 mg/kg) was for cockles at one site in the Maketu Estuary. However, in a brief survey, Bioresearches (1981b) found very high Hg levels in freshwater mussels (0.19-1.58 mg/kg), eels (0.19-0.71 mg/kg), and trout ($<$0.01-3.15 mg/kg).

McColl (1972) reported mean Cu and Zn concentrations in seven Rotorua area lakes of around 10 and 9 mg/m^3 respectively. The water samples were filtered (0.45μm) but because the filters were not acid washed, contamination cannot be ruled out.

6.2.6 East Cape

6.2.6.1 Water Board Studies (with the assistance of R. Dods)

Four surveys have been carried out since 1979 of metal levels in drains and bores around the Gisborne City Council tip at Paokahu. Many of the surveys are incomplete, but it seems as though tip leachate is contaminating the groundwater of the area. Two samples of water taken (May 1984) from the bore adjacent to and downstream of the tip, had the following averaged metal levels (mg/m^3): Cr 925, Cu 960, Hg 2, Pb 80, Ni 750 and Zn 1600. These levels are far higher than expected for a natural water in a sand aquifer. Despite these high concentrations, Armstrong (1984) considered that they are not cause for concern, but advocated continued monitoring.

6.2.7 Taranaki

6.2.7.1 Water Board Studies (with the assistance of J. R. Williams)

During late 1980 and early 1981 the board sampled the Waitara River on four occasions and the Manganui River once for subsequent metal analysis. During baseflow, total metal concentrations (for Cd, Co, Cr, Cu, Hg, Ni, Pb, Zn) were below detection limits. On the one occasion (December 1, 1980) when the Waitara River was in flood (Qmax = 610 m^3/s), the total (and soluble in brackets) concentrations (mg/m^3) were: Cr 70 ($<$50), Cu 50 ($<$20), Fe 63 000 (250), Ni 60 ($<$50) and Zn 150 (40). At the time of sampling for metal analysis, the river had a suspended solids concentration of 3300 g/m^3. Using a particulate Zn concentration during the flood of 110 mg/m^3 this gives a Zn concentration in the solids of 33 mg/kg. This is a little lower than that expected from a perusal of the DSIR Soil Bureau Single Factor Maps and may be accounted for by the use of different analytical methods.

In 1981, the board carried out a survey on trace metals in sea foods in North Taranaki (TCC, 1985). A summary of data is presented in Table 6.22. The levels found are as expected for an unpolluted region (see Section 6.1.3).

Table 6.22: Ranges of metal concentrations (mg/kg wet weight) in North Taranaki shellfish (a) (TCC, 1985).

Metal	Mussels (green lipped) (b)	Paua (c)
Cd	0.18-0.23	0.07-0.14
Cr	<0.02-0.6	0.05-0.33
Cu		<0.8-2.9
Hg	0.01-0.05	
Pb	0.04-0.27	<0.1-0.27
Zn	8.4-19.3(d)	9.2-12.1

Notes:
(a) After 24 hours depuration.
(b) Sample numbers ranged from 35 individuals at Waiwakaiho to 146 at Waiongana.
(c) Foot only: 36 individuals from Buchanan's Bay.
(d) Excluding one 'high' result of 26.3 mg/kg.

Further brief surveys were carried out on mussels in the winter of 1983 (at Waiwakaiho and Epiha) and the summer of 1984 (at Waiwakaiho). Results were very similar to those presented in Table 6.22. Additional data provided by these surveys were for Cu (around 2 mg/kg at both sites), Ni (0.8 and 3.1 mg/kg at Epiha and Waiwakaiho respectively, the latter containing one high result of 9.7 mg/kg) and Sn (<1 mg/kg, for Epiha only).

The board has also produced a very limited amount of data for limpet, sea anemone, crab and sea lettuce.

6.2.7.2 Other Studies

North Taranaki Coast: Waitara Estuary and Coastal Embayment

Matthews (1982) examined the physical and chemical characteristics of the Waitara estuary and coastal embayment with particular reference to effluent disposal from the Waitara outfall. He found no evidence of anthropogenic metal pollution other than a small increase in Pb concentration near the river mouth which was attributed to stormwater run-off. Concentrations of some of the metals studied are given in Table 6.23.

Table 6.23: Metal concentrations (mg/kg) in Waitara estuary sediments (Matthews, 1982).

	Mean	S.D.
As	4.9	3.5
Cr	56.5	17.6
Cu	34.0	12.4
Ni	28.3	14.1
Pb	15.1	4.6
V	279	249
Zn	99.5	56.2

New Plymouth

A very small survey (9 mussel samples) carried out in 1981 by the New Plymouth City Council on a reef adjacent to the New Plymouth West municipal outfall showed no metal elevations above those obtained from reefs several kilometres away. Levels obtained adjacent to the outfall were Cr 0.52 mg/kg, Cu 3.2 mg/kg, Hg <0.05 mg/kg, Ni 1.4 mg/kg, Pb 0.9 mg/kg, Sn 9 mg/kg, and Zn 12.2 mg/kg (wet weight?) (A. Cooke, Cawthron Institute, pers. comm.). Due to the survey design, not a great deal can be deduced from these data.

6.2.8 Hawke's Bay

6.2.8.1 Water Board Studies (with the assistance of G. W. Hooper)

In the Hastings, Havelock North, and Napier areas, urban drains were examined in the summers of 1983 and 1984. The metals Cr, Cu, Pb and Zn were analysed for and, in general, levels at or below detection limits were found. The highest metal concentrations were obtained for the Havelock North stormwater outlet, i.e., Cr 40 mg/m^3, Cu <20 mg/m^3, Pb 260 mg/m^3, and Zn 630 mg/m^3. The values for Pb and Zn are higher than the average stormwater concentrations found for several New Zealand cities (see Table 4.6). The effects of the Napier drains on the Ahuriri Estuary have also been examined (HBRWB, 1983). Metal levels below detection limits were obtained. Sediment and biota have not yet been examined.

A single sample of water taken from the Plantation drain downstream of a timber treatment plant after rain shows elevated metal levels (As 150 mg/m^3, Cr 170 mg/m^3, Cu 80 mg/m^3, Pb 70 mg/m^3) due to plant run-off. This elevation is likely to be very short term and the company concerned has now taken action to ensure that further discharges of waste to the drain do not occur.

Groundwater downstream of the Hastings City Council refuse dump was analysed in 1981 and 1982 for heavy metal content. Levels found (after pumping) were below detection limits.

6.2.9 Wairarapa

6.2.9.1 Water Board Studies (with the assistance of W. F. O'Donnell)

In August 1981, a spillage of about 500 l of Tanalith preservative (a mixture of As, Cr, and Cu compounds) occurred at a timber treatment plant in Masterton. The bund consisting of concrete blocks with mortar filling, provided to contain such spillages, proved ineffective. The preservative solution leaked through the mortar and seeped into the underlying highly permeable Tauherenikau stony loam. The chemical diffused away from the adjacent Waingawa River and contaminated a shallow unconfined aquifer. It seems as though the Cr (presumably as the mobile Cr^{6+}) component separated and moved through with the groundwater fairly rapidly but As appeared to become bound to particulate material in the soils below the treatment plant and then desorbed slowly into the groundwater. The water board established a network of wells and bores which could be used to determine the spread and effects of the chemicals on the local groundwater. Water analysis was conducted by Chemistry Division, DSIR, at the request of the Department of Health; the main objective was to assess contamination from a potable water viewpoint (i.e., As and Cr limits of 50 mg/m^3). The highest As and Cr levels (9300 mg/m^3 and 37 000 mg/m^3 respectively) were measured in groundwater taken from the timber plant's bore about two weeks after the spillage. High As concentrations were found a few weeks later (270 mg/m^3) in one other bore 200 m immediately downstream of the spillage. At both sites the As concentration decreased slowly but at the spill site it was still higher that the potable limit two years later. On the other hand, Cr tended to show a much more rapid decrease in concentration in the immediate vicinity of the spill and travelled much further in the groundwater. A 'slug' of Cr seemed to move through the aquifer becoming diluted as it travelled. Not all downstream bores were affected, presumably because they were not in direct line-of-travel. At a site 1000 m from the spillage the maximum Cr concentration found was around 100 mg/m^3 3-4 months later. A further 2-3 months were required before the concentration fell below the potable limit of 50 mg/m^3. Cu concentrations were not traced partly because of likely Cu contamination of samples by Cu piping at the sampling sites, and because it is also far less toxic than As and Cr. It would also be expected to be firmly adsorbed to soil particulate materials and hence have little effect on the groundwater.

6.2.10 Wellington

6.2.10.1 Water Board Studies (with the assistance of C. J. Wilson and K. R. Davis)

The water board, in conjunction with the New Zealand Oceanographic Institute, has recently (1983/4) conducted an extensive survey of the sediments of Wellington Harbour and the Waiwhetu Stream. The purpose of the study is to ascertain the present heavy metal pollution situation and to provide a comparison with results obtained in the late 1970s (see below). At the time of writing this review, analysis is complete and the data are being interpreted prior to publication.*

6.2.10.2 Other Studies

Wellington Harbour and environs

This section is largely based on an unpublished paper by C. J. Wilson (Wellington Regional Water Board) which was presented at a seminar on heavy metals held by the Royal Society of New Zealand/National Committee on Scientific Problems of the Environment, in Wellington, August 1984. It is, in turn, based on an unfinished report 'Heavy metals in Wellington Harbour' prepared for the Wellington Regional Council by P. C. Kennedy in 1981. Most of the conclusions stated here are based on the paper of C. J. Wilson and are referenced as C. J. Wilson, WRWB, pers. comm. It is anticipated that the data will be published shortly (K. R. Davis, WRWB, pers. comm.).

Since the turn of the century there have been numerous discharges of industrial waste and sewage into the Wellington Harbour. These have now largely ceased (apart from around 100 emergency sewage discharge points around the harbour) and the major metals input is now believed to be from urban stormwater. Hutt Valley sewage and industrial waste have been discharged into Cook Strait at Pencarrow since 1962; the main Wellington City discharge is into Cook Strait at Moa Point. Both are untreated shoreline discharges. An indication of the metals content of Wellington sewage is given in Table 4.8. Hutt Valley sewage has a slightly higher industrial component and this is reflected in the higher Pb and Zn concentrations (440 mg/m^3 and 1300 mg/m^3 respectively cf. 60 mg/m^3 and 630 mg/m^3 respectively for Wellington) (C. J. Wilson, WRWB, pers. comm.).

An analysis of sediments in the Moa Point area (Lavender Bay) in 1979/80 showed that most metal concentrations were higher there than in an area some distance away (Sinclair Head)—see Table 6.24—and that the highest levels were found closest to the outfall. However, no other sediment details are given and the analyses are, surprisingly, presented on a wet weight basis. No sediment data seem to be available for the Pencarrow outfall.

Table 6.24: Mean metal concentrations of sediments (mg/kg wet weight) in the vicinity of, and remote from, the Moa Point sewage outfall (C. J. Wilson, WRWB, pers. comm.).

Metal	Vicinity of outfall (Lavendar Bay)	Remote from outfall (Sinclair Head)
Cd	0.007	0.045
Cr	4.83	2.56
Cu	3.27	0.84
Ni	2.6	1.3
Pb	5.4	2.2
Zn	20	9

Studies on in-harbour sediments show that there are Pb and Zn elevations throughout the harbour, but in particular there are two areas of major contamination (Table 6.25) viz: the Lambton harbour basin sediments and wharf areas (Cd, Cu, Hg and Zn), and Evans bay sediments (Hg, Pb and possibly Zn). Such elevations are attributed to urban runoff, periodic emergency sewage overflows, wharf activities and a boating marina.

The sediments from the mouths of some streams on the western and north-western side of the harbour are also reported to have some metal elevations which seem to be related to discharge of leachate from an industrial tip (Horokiwi Stream), and industrial wastes (Ngauranga and Kaiwharawhara). The tip is no longer operational, and the industrial wastes are now discharged elsewhere (Moa Point).

The Waiwhetu Stream, which discharges into the Hutt River close to its estuary, has received relatively uncontrolled industrial and domestic wastes for 30 years and this has led to severe

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* Whilst this review was in press, the results of the survey were published; see Stoffers, P.; Glasby, G. P.; Wilson, C. J.; Davis, K. R. 1986: Heavy metal pollution in Wellington Harbour. *New Zealand Journal of Marine and Freshwater Research 20:* 495-512.

Table 6.25: Mean (and ranges in brackets) metal concentrations (mg/kg) in surface Wellington Harbour sediments (C. J. Wilson, WRWB, pers. comm.).

		Location		
Metal	Central harbour	Lambton Harbour and wharves	Evans Bay	Harbour cores (below 100 cm)
Cd	0.06	0.56	0.05	–
	(0.01-0.12)	(0.1-1.73)	(0.02-0.08)	
Cr	54	65	51	
	(45-61)	(43-100)	(38-58)	(39-64)
Cu	22	381	25	
	(19-30)	(34-2650)	(15-30)	(11-21)
Hg	0.24	1.3	0.8	
	(0.11-0.45)	(0.5-2.3)	(0.6-1.4)	(0.03-0.15)
Ni	20	20	18	
	(16-29)	(16-29)	(9-22)	(10-26)
Pb	57	450	128	
	(41-73)	(69-1066)	(81-137)	(19-28)
Zn	118	343	146	
	(100-135)	(126-889)	(103-172)	(55-84)

contamination of sediments in the stream (Table 6.26), and to a lesser extent the Hutt River estuary and adjacent harbour. Inputs were from a battery factory, a car assembly plant, a paint factory, and electroplating industries. These discharges are now intercepted by a sewer and discharged at Pencarrow. The Waiwhetu Stream appears to have the most heavily contaminated estuarine sediments in the country. Sediment in the stream contained paint fragments, oils, grease, plastics, glass, metal fragments and organic refuse. Since the above data were obtained, the stream has been extensively dredged for flood control and aesthetic purposes, resulting in removal of a considerable proportion of the affected sediments. Subsequently the stream has been re-examined (1983) by the Wellington Regional Council in conjunction with NZ Oceanographic Institute but data are not yet available*.

Table 6.26: Ranges of metal concentrations (mg/kg) in Waiwhetu Stream surface sediments (C. J. Wilson, WRWB, pers. comm.).

Metal	Waiwhetu Stream	Typical area background
Ba	494-13800	400
Cd	0.4-38	<2
Co	4-96	4
Cu	36-460	20
Cr	54-2900	45
Hg	0.05-38	0.1
Ni	16-110	20
Pb	117-146000	22
Sn	10-200	4
Zn	203-24000	80

Edible shellfish species (including paua (*Haliotis iris*), kina (*Evichinus chloroticus*), and mussels) are widely distributed in Wellington waters. From the limited shellfish data available from a study, in 1979/80, as part of the Moa Point Wastewater Treatment Plant and Outfall Study (Beca Carter-Caldwell Connell, 1980), there appears to be no significant accumulation of Co, V and Zn in Moa Point biota (paua, kina, duck's bill limpet (*Scutus breviculus*), Cook's turban (*Cookia sulcata*)) when compared with biota collected at a control site at Sinclair Head. However, concentrations of Cr and Ni were consistently higher in organisms living near the outfall (e.g., for paua, Cr 1.2 mg/kg compared with 0.22 mg/kg wet weight) but all metals were within Food Regulations limits. Cook's turban specimens had Zn concentrations of 54 mg/kg at Moa Point and 36 mg/kg at Sinclair Head.

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* Whilst this review was in press, the results of the survey were published; see Stoffers, P.; Glasby, G. P.; Wilson, C. J.; Davis, K. R. 1986: Heavy metal pollution in Wellington Harbour. *New Zealand Journal of Marine and Freshwater Research 20:* 495-512.

Paua taken from Sinclair Head may be (naturally?) Cd enriched (I. L. Vidal, Wellington City Council, pers. comm.); levels found were around 1 mg/kg wet weight.

Heavy metal accumulations in shellfish at Pencarrow are highly variable (C. J. Wilson, WRWB, pers. comm.).

Blue mussels (*Mytilus edulis*) collected from within Wellington Harbour (analysed by Wellington City Council) contained higher Zn and Pb levels than other New Zealand sites. For instance, mean Pb concentration in Wellington Harbour blue mussels was found to be 3.45 mg/kg wet weight (Food Regulations limit is 2 mg/kg). The New Zealand 'mean' is 0.67 (Nielsen and Nathan, 1975, see Table 6.5). Values for Zn are 45.8 mg/kg (Wellington) and 14.0 mg/kg (New Zealand 'mean'). Even higher Pb levels were found in green mussels, *Perna canaliculus*, (e.g., 7.8 mg/kg) taken close to stormwater outlets. Both mussel species seem to contain lower levels of Cd in Wellington Harbour than elsewhere in the country.

In the Waiwhetu Stream, Pb levels as high as 2600 mg/kg (cf. Table 6.31) have been found in the mud snail (*Amphibola crenata*), one of the few species found there (C. J. Wilson, WRWB, pers. comm.).

Kennedy (1981) reported that samples of the seaweed Neptune's necklace (*Hormosira banksii*) taken from inside the harbour and around the Moa Point outfall contained considerably more Zn (up to 9 mg/kg and 5-6 mg/kg wet weight respectively) than samples taken outside the harbour (around 2 mg/kg wet weight). Samples of kelp (*Durvillea antarctica*) from Pencarrow and flapjack (*Carpophyllum maschalocarpum*) from Moa Point and Pencarrow contained no unusual metal levels.

Pauatahanui Inlet

Baseline studies on the Pauatahanui Inlet, for which urban development has been proposed, were reported several years ago (Healy, 1980). In general, the inlet was found to be relatively unpolluted. In fish, As, Cd, Cu, and Hg concentrations were found to be similar to those expected from such an environment (Table 6.27) although Zn concentrations were slightly above Food Regulations limits (40 mg/kg).

Table 6.27: Heavy metal concentrations (mg/kg wet weight) in fish from Pauatahanui Inlet (Healy, 1980).

	As	Cd	Cu	Hg	Zn
Kahawai	0.4	0.004	1.1	0.10	48
Trevally	0.7	–	1.3	0.06	43

The sediments are also relatively uncontaminated by heavy metals (Table 6.28); sediments taken from Porirua Inlet, which is more industrialised and urbanised, have higher levels. In Table 6.28 data for sediments from the Waiwhetu Stream in the Hutt River estuary, a heavily industrialised area, are included for comparison; these sediments are very contaminated (see earlier in this section).

Table 6.28: Mean heavy metal concentrations (mg/kg) in intertidal sediments from 3 areas in the Wellington region (Healy, 1980).

Location	Cr	Cu	Ni	Pb	Zn
Pauatahanui Inlet (3 sites)	36	10	13	15	63
Porirua Inlet (4 sites)	61	18	16	31	94
Waiwhetu Stream (3 sites)	234	145	42	4300	2700

Sediments and spoil adjacent to the road around the Pauatahanui Inlet show increases of levels of Pb (480 mg/kg) and Cu (63 mg/kg). These levels decrease with distance from the road and the contamination is probably due to motor vehicle exhaust gases and oil (Healy, 1980).

Heavy metals levels in the sea rush (*Funcus maritimus*), a typical salt marsh species, are low, with Cu and Zn concentrations for live leaves 15 and 18 mg/kg (dry matter) respectively (cf. Waiwhetu 19 and 59 mg/kg respectively).

6.2.11 Nelson

6.2.11.1 Water Board Studies (with the assistance of H. Crutchley)

A recent survey (June 1983) has been carried out on the sediments and shellfish (*Chione stutchburyi*) in the area of Nelson Haven, Waimea Inlet and Moutere Inlet with a 'control' site in Delaware Bay. Delaware Bay and Moutere Inlet are relatively undisturbed but there is intense agriculture (grazing) in their immediate surroundings; there is also horticultural development near Moutere. Nelson Haven has been affected by infilling over a period of many years, e.g., harbour development, Nelson tip site, sewage oxidation ponds, highway development. Waimea Inlet has received discharge of industrial effluents. Concentrations of Cd, Cr, Cu, Hg, Pb, Ni and Zn were determined. No elevation of metal levels in the sediments were encountered, with the possible exception of Ni (at 117 mg/kg) in the sediments off Best's Island in the Waimea Inlet. Shellfish metal levels were all low and well within Food Regulations limits. These areas are likely to be resurveyed to confirm the earlier findings.

The Maitai River has been sampled (October 1982 and February 1983) at several sites in its upper reaches and analysed for Cd, Cu, Cr, Pb, Ni and Zn. The Motueka River was investigated once (for As, Cu, Pb) in August 1979. The metals Cd, Cr, Cu and Zn were analysed for in samples of Waimea plains well water (May 1978). Heavy metals were not detected.

Nelson City tip leachate was examined in 1977; the only metal detected was Zn and its highest level was 250 mg/m^3.

6.2.11.2 Other Studies

Tasman Bay

The sediments of three areas in Tasman Bay (viz Delaware Bay, Nelson Haven and Waimea Inlet) have been analysed for several heavy metals (P. A. Gillespie, Cawthron Institute, pers. comm.). A summary of the results is given in Table 6.29.

Table 6.29: Mean metal concentrations (mg/kg) in Tasman Bay inlets (P. A. Gillespie, pers. comm.). (Standard deviations in brackets.)

Location	Sediment Type	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Delaware	Sand (4 sites)	<0.2	24 (9)	12 (4)	<0.2	17 (3)	<0.2	64 (7)
Delaware	Mud (5 sites)	<0.2	25 (15)	30 (11)	0.8 (0.09)	28 (9)	4.7 (3.3)	88 (17)
Nelson Haven	Sand (6 sites)	<0.2	34 (13)	9 (2)	0.40 (0.35)	34 (8)	0.5 (1.2)	38 (4)
Waimea	Mud (a)	<0.2	63 (37)	23 (11)	0.06 (0.11)	65 (5)	5.0 (0.4)	88 (4)
	Mud (b)	<0.2	33 (6)	30 (6)	0.04 (0.06)	77 (2)	2.0 (3.5)	129 (8)
	Mud (c)	<0.2	130 (56)	22 (6)	0.04 (0.01)	107 (9)	1.8 (3.1)	90 (7)

(a) Adjacent to apple cannery effluent pipe.
(b) Adjacent to freezing works effluent pipe.
(c) Adjacent to mechanical wood chip mill.

Sampling was conducted twice over the 1980-1 summer, with an additional sampling of the Waimea sites in winter 1981. A full analysis of the data has not yet been carried out but slight sediment enrichment by metals in a few instances is suggested (e.g., Ni and Zn in the muds adjacent to the freezing works effluent, Cr and Ni near the chip mill effluent, Cr and Ni adjacent to the apple cannery) although none of the heavy metal concentrations are probably high enough to be of environmental concern. Although anthropogenic reasons are possible for the variations in concentrations it is also possible that differences in the geochemical natures of sediments from the individual catchments could be a major factor (P. A. Gillespie, Cawthron Institute, pers. comm.). The latter reason would appear to be the more likely because of the input of the ultramafic sediments (P. C. Kennedy, pers. comm.).

Chittenden *et al.* (1976) examined the sediments of Lakes Rotoroa and Rotoiti. Zn levels were similar to the South Island lakes mean values presented in Table 6.3.

6.2.12 Marlborough

6.2.12.1 Water Board Studies (with the assistance of J. J. Shearer)

In June 1982 the board conducted a wide single sample survey of 28 river and groundwater sites in its region (Shearer, 1985). Metals investigated (by graphite furnace AAS) were Cd, Cr, Cu, Ni, Pb and Zn. Detection limits are claimed to be 0.2, 0.5, 0.5, 1, 0.5 and 5 mg/m^3 respectively. Six inflows to Pelorus Sound (Kenepuru, Rai, Tinline, Pelorus, Wakamarina and Kaituna Rivers) showed metal levels less than detection limit except for the Tinline and Pelorus Rivers which had 1.0 mg/m^3 and 0.8 mg/m^3 Cr respectively. This is probably due to chromite deposits within the Dun Mountain ultramafics. Heavy metals could not be detected in the Wairau River and associated groundwater, apart from traces of Zn in two wells. Contamination from the reticulation and/or pump is suspected in these instances. A single sample of groundwater from the Tuamarina Valley had metal levels below detection limit. One of two water samples (analysed by flame AAS) taken from urban drains in the Riverlands industrial estate had Zn levels of 30 mg/m^3. No evidence of an elevation of metal levels in the Taylor/Opawa river system was apparent. In June 1983, The Taylor/Opawa system was again briefly examined and no evidence of metal contamination (at graphite furance AAS detection limits) was apparent in the waters (Shearer, 1985).

6.2.13 North Canterbury

6.2.13.1 Water Board Studies (with the assistance of R. Ayrey)

Between 1982 and 1984, the board has conducted occasional spot checks of groundwater downstream of several timber treatment plants. As, Cr and Cu were not detected.

6.2.13.2 Other Studies

Avon and Heathcote Rivers, and Estuary

The Avon-Heathcote Estuary is situated 8 km east of Christchurch City and forms a triangular shaped lagoon-type estuary behind a sand spit approximately 5 km in length along its eastern margin. It has two major freshwater inputs, the Avon and Heathcote Rivers. The Christchurch Drainage Board (CDB) has used the estuary as a receiving water for its treated sewage wastes continuously for almost 100 years; the sewage discharge (on the ebb tide) represents around 30% of the 454 Ml/day freshwater inflow to the estuary under non-flood conditions (Robb, 1977).

Robb (1977) briefly reviewed the pollution situation in the estuary. He noted that 'since the early 1870's the Heathcote River was indiscriminately utilised as a general dumping ground for many untreated and partially treated industrial wastes from the Woolston district particularly from gelatine and glue, malt, coal gas, tannery, woolscouring, battery manufacturing and textile industries.' Substantial quantities of As, Cu, Cr and Pb were contributed to the river from these sources, and a 'thick black glutinous highly sulphuretted mud particularly rich in Pb and Cr has been produced.' Most discharges to the river ceased around 1970 and its quality has improved since then (Robb, 1977). Robb (1977) suggested that it would take many decades before the biotic diversity within the lower reaches reverts to anything like its likely original composition. However, more recent observations indicate that improvement has been much more rapid than originally suggested (J. A. Robb, CDB, pers. comm.). Robb (1977) notes that the estuary supports, in addition to algae, a diverse and unique assemblage of plants and animals and serves as a nursery for young flounder.

Millhouse (1975) examined the trace metal content of five organisms (sea lettuce (*Ulva lactuca*), a gastropod (*Melagraphia aethiops*), cockle (*Chione stutchburyi*), a crustacean (*Palaemon affinis*) and the half crab (*Hemigrapsus crenulatus*)) from McCormack's Bay, an area separate from the main body of the estuary by virtue of a causeway carrying a main road. Estuarine water enters the bay on every flood tide via a culvert. A summary of Millhouse's data is presented in Table 6.30.

The concentrations of metals in water seem high, especially when compared with levels found in other New Zealand coastal waters (see Table 6.2). It seems likely that the samples were contaminated. Sediment concentrations seem low compared with those presented in Table 6.3. Levels for the edible species *Chione stutchburyi* are within Food Regulations limits except for Pb.

In 1976, Millhouse conducted a more extensive investigation on the occurrence of trace metals throughout the estuary (Millhouse, 1977). On this occasion *Chione stutchburyi*, *Melagraphia aethiops*,

Table 6.30: Mean metal concentrations (mg/kg dry weight; mg/m^3 for water) found for biota, sediment and water of McCormacks Bay, Avon-Heathcote Estuary (Millhouse, 1975).

	Cd	Cu	Ni	Pb	Zn
Ulva lactuca	18	113	227	46	114
Melagraphia aethiops	16	177	232	47	125
Palaemon affinis	2.0	183	56	90	139
Chione stutchburyi	1.4	16	70	52	91
Hemigrapsus crenulatus	1.4	83	53	58	63
Sediment	1.2	12	24	0.81	21
Water	1.1	2.7	24	16	13

Amphibola crenata, *Hemigrapsus crenulatus* and *Galaxias* sp. were examined. Millhouse (1977) found that mean animal Zn concentrations seem higher for estuary stations than for McCormack's Bay, but he suggested that Zn concentrations in animals at present do not cause concern (presumably with regard to human health). He also found some high Cu concentrations (up to 950 mg/kg dry weight) in *Amphibola crenata* taken from mid-estuary, and the range of values was large. Cd concentrations do not seem to be high compared with those presented in Table 6.5.

For the edible *Chione stutchburyi* and *Galaxias* sp., metal levels were well within Food Regulation limits, irrespective of where they were taken from.

Bennington (1979) studied shell morphology and sculpture, population size structure, sediment grain size preference, the reproductive cycle and tissue heavy metal levels for the common estuarine mud gastropod, *Amphibola crenata*, occurring both near and distant from the possible effects of the sewage outfalls in the estuary. The two areas investigated had similar salinity and exposure. The 'distant' site was almost due east across the Avon-Heathcote Estuary. Some of Bennington's data are presented in Table 6.31.

Table 6.31: Mean metal concentrations (mg/kg dry weight) in *Amphibola crenata* and surface sediments taken from the Avon-Heathcote Estuary (Bennington, 1979).

	Outfall Sites		Control Sites (Distant from Sewage Outfalls)		Lower Avon River Sediments
	A. crenata	Sediments	*A. crenata*	Sediments	
Cd	0.87	0.20	1.22	0.1	0.20
Co	9.0	1.8	11.9	2.1	2.8
Cu	74.7	1.3	65.3	0.7	6.0
Pb	6.5	9.9	8.1	5.4	59.1(a)
Ni	19.6	4.5	13.0	2.7	4.8
Zn	57.1	38.0	75.6	22.8	56.4

Note: (a) a mean value of 17.4 is obtained if one very high value is removed.

Bennington (1979) found that tissue levels of metals from the control and outfall sites differed little. Although sediments metal concentrations from both sites are not high (see Table 6.3), concentrations in *A. crenata* are much higher than those taken from the Waiuku River estuary (see Table 6.12).

Bennington's results for *A. crenata* are similar to those of Millhouse (1977) although the latter author found some higher values for Zn and Cu (in mid estuary) and Cd (in mid estuary and close to the mouth of the Heathcote River). Isolated areas of elevated metal concentrations were found by Bennington (1979) in the Avon River sediments.

The Christchurch Drainage Board (CDB) has recently carried out extensive, and intensive, studies on surface sediment (i.e., top 10 mm) metal concentrations in the Avon and Heathcote River catchments, and the Avon-Heathcote and Saltwater Creek Estuaries. Shellfish (i.e., cockle (*Chione stutchburyi*) and mud snail (*Amphibola crenata*)) from both estuaries were also examined. The Saltwater Creek Estuary lies about 26 km north of Christchurch and is probably the least modified large estuary in Canterbury. Sampling was conducted between 1980 and 1983. Extremely high metal concentrations were found in drain sediments taken from the Avon and Heathcote River catchments, e.g., in the

Avon catchment, up to 5300 mg/kg Pb and 1500 mg/kg Zn, and in the Heathcote catchment up to 8 mg/kg Cd and 885 mg/kg Zn (J. A. Robb, CDB, pers. comm.). Concentrations of metals in sediments of the lower river reaches and estuaries, and biota, are presented in Tables 6.32 and 6.33 respectively. Metal contamination is evident in both rivers, especially the Heathcote where some extremely high concentrations of Cr, Pb and Zn are evident. Levels of Pb and Zn are elevated in some of the Avon sediments. The Avon-Heathcote Estuary sediments do not seem to show a great degree of metal contamination when compared with both the Saltwater Creek Estuary sediments and the data presented in Table 6.3. There is little evidence for contamination of cockles in the Avon-Heathcote Estuary, but there seem to be some high values for Cr, Ni and Pb in mud snail. However, mean levels for mud snail are below Food Regulations limits and, moreover, it is not an important food source. The mean levels, given in Table 6.33, for both species from the Avon-Heathcote Estuary are very similar to those found by Bennington (1979) (Table 6.31). The findings from the CDB studies (a small selection of which is presented here) will be published in due course.

Table 6.32: Concentrations of heavy metals (mg/kg) in surface sediments of the lower Avon and Heathcote Rivers, and the Avon-Heathcote and Saltwater Creek Estuaries (J. A. Robb, Christchurch Drainage Board, pers. comm.).

	Lower Avon (a)		Lower Heathcote (b)		Avon-Heathcote Estuary (c)		Saltwater Creek Estuary (d)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cd	0.3	0.05-1.4	0.5	0.1-0.9				
Cu	23	8-103	41	9-115	6.4	1.4-37	6.5	2.0-12
Cr	17	8-23	80	9-420	12	6.2-43	7.9	3.8-12
Ni	9.4	4.7-16	12	5.4-21	7.4	4.4-14	8.6	4.0-14
Pb	79	15-246	208	14-1250	14	3.2-86	8.5	2.6-16
Zn	206	65-680	260	76-536	55	21-195	37	14-65

Notes:
(a) Lower 23 km; n = 29 except for Cd where n = 22.
(b) Lower 8 km; n = 27 except for Cd where n = 20.
(c) n = 330.
(d) n = 298.

Table 6.33: Concentrations of heavy metals (mg/kg dry weight) in shellfish taken from the Avon-Heathcote and Saltwater Creek Estuaries) (J. A. Robb, Christchurch Drainage Board, pers. comm.).

	Chione stutchburyi				*Amphibola crenata*			
	Avon-Heathcote		Saltwater		Avon-Heathcote		Saltwater	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Cd	1.0	0.3-3.6	2.1	0.4-15	1.2	0.3-8.2	0.4	0.3-0.9
Cr	13.6	4.8-25	13.6	5.5-34	26	5.6-202	4.7	1.2-22
Cu	10.5	6.5-25	8.0	6.3-9.2	115	66-181	153	102-195
Ni	23	10-45	20	10.5-3.6	21	6.2-134	4.6	1.7-12.4
Pb	<0.5 (a)	<0.5-3.4	<0.5 (a)	<0.5-3.6	8.0	3.8-18.2	1.9	1.1-3.7
Zn	83	63-117	74	61-85	63	46-96	54	42-68
No. of sites (n)		52		31		99		43 (b)

Notes:
(a) Median value.
(b) For Pb, n = 31.

6.2.14 Otago

6.2.14.1 Water Board Studies (with the assistance of K. J. Currie)

The Ravensdown Fertiliser Works outfalls and their immediate environs in Otago Harbour have been the subject of occasional investigation by the water board for several years. In February 1981, sediment samples collected near the outfalls (see Section 4.8.9 for an analysis of effluent) contained 1.8 mg/kg Cd, 253mg/kg Pb and 146 mg/kg Zn. At the same time the harbour waters were determined to have a Cu level of 32 mg/m^3, probably due to discharge of wastes from copper sulphate production. In June 1982, sediment samples taken close by the Ravensdown wharf, where rock phosphate is unloaded for processing at the plant, contained 2.2 mg/kg Cd and 126 mg/kg Zn. It is difficult to separate the effects of the discharges and spillages at the wharf, because of their close proximity. This area is further discussed below (Section 6.2.14.2).

The Mosgiel Borough Council sewage discharge into the Taieri River, with an emergency discharge to the Silverstream tributary, has come under some scrutiny from the water board between 1979 and 1984. Concentrations of some metals can be very high (Section 4.5) because of the proportionally high industrial inputs. On five occasions, the water board has sampled the river at several sites above and below the sewage discharge. On two occasions metals were detected. In March 1979, Cr, Cu and Zn were detected below the outfall (500 mg/m^3, 120 mg/m^3 and 180 mg/m^3 respectively) and in March 1981, Cr and Cu were detected (1230 mg/m^3 and 180 mg/m^3 respectively). These are high concentrations, but the effluent may not have been fully mixed with the river water. Sediments have also been examined, but no evidence for heavy metal accumulation has been obtained. Frequent flooding which occurs in the Taieri River would, in any case, disperse and dilute any affected sediments. It is not clear at this stage if a problem exists in the Taieri River.

Up to 1982, Sawyer's Bay in Otago Harbour received untreated effluent from a tannery (see Section 4.8.5) via a small stream. The water board took grab samples of the stream and central bay sediments in February 1981 and March 1982. The stream contained 710 mg/m^3 and 7100 mg/m^3 total Cr and the sediments 207 mg/kg and <1 mg/kg Cr for the two dates respectively. On both occasions heavy metal levels in bay waters were all below detection limits. The effects of the tannery discharge on Sawyer's Bay is further discussed below (Section 6.2.14.2).

Areas of Otago Harbour, other than those referred to above, e.g., Pulling Point, Vauxhall, Lower Portobello Bay, mouth of the Waters of Leith, Otafelo Point, have occasionally been investigated. A selection of data for sediments is presented in Table 6.34.

Table 6.34: Metal concentrations (mg/kg) in surface sediments of Otago Harbour.

Location	Date	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Pulling Point (a) (lower harbour)	1981	1.6	<0.5	4.9	2.5	0.02	<1	4	18.5
Lower Portobello Bay (a) (lower Harbour)	1982	9.8	0.5	10	15	0.22	18	26	80
Mouth of Water of Leith (upper harbour)	1982	10.3	<0.5	15	66	0.21	34	93	176

Note: (a) These areas are probably contamination-free.

Levels found at Pulling Point and Lower Portobello Bay do not seem high (compared, say, with data in Table 6.3). The sediments of the Water of Leith appear contaminated by Cu, Pb, and Zn, and urban stormwater runoff could account for this. Heavy metals in harbour waters were below detection limits.

Other work carried out by the water board has been on waters from Lakes Waihola and Waipori, and the Waipori, Tokomairiro, and Kaikorai Rivers in 1981 and 1982. No heavy metals were detected.

In May 1984, several samples of sediment were taken from the Tokomairiro River (above and below the Alliance Textiles discharge) and the Kaikorai Stream. No metal elevations were detected in the Tokomairiro River sediments. Without a thorough survey it is difficult to state with any degree of certainty whether sediment metal levels in the Kaikorai Stream are significantly above background but certainly some of the levels seem high, e.g., Pb up to 132 mg/kg and Zn up to 297 mg/m^3. Urban runoff would seem a likely cause.

The water board investigated an interesting suspected As contamination of a water supply in August 1983. The Ministry of Agriculture and Fisheries had confirmed that the death, at a Middlemarch property, of 22 cattle was the result of ingestion of As, either via water or soil. A subsequent survey showed water samples taken from the property's borewater, the Taieri River (over 2 miles away) and the stream draining a nearby mine shaft area had As concentrations in the range <0.9-5 mg/m^3, while a neighbouring stream had 20-57 mg/m^3 As. These levels are below the safe limits for the protection of livestock (see Table 5.5). Stream sediments (analysed by XRF) had an As range 19-81 mg/kg with one exception, viz, 411 mg/m^3 in stream sediments taken near a neighbouring mine shaft. These high concentrations are thought to be due to local deposits of arsenopyrite (Currie, 1983).

6.2.14.2 Other Studies

Sawyers Bay, Otago Harbour

Smillie (1980) examined metal levels in the sediments of Sawyers Bay, Otago Harbour. For many years, this bay had received untreated effluent from a nearby tannery (see Table 4.24). This discharge has now been discontinued. Smillie (1980) found extremely high Cr concentrations in sediments close to the tannery outfall, and they were also enriched with organic matter, Cu, Pb and Zn (Table 6.35). The sediment metal levels were found to correlate with organic matter content, and there was a relationship between Cr levels in bay sediments and in the crab, *Helice crassa*. Later work by Johnson *et al.* (1981) confirmed Smillie's findings.

Table 6.35: Metal concentrations (mg/kg) in Sawyer's Bay sediments (Smillie, 1980).

Sediment Location	Cr	Cu	Pb	Zn
Stream receiving tannery effluent	85000	490		1020
Sawyer's Bay below stream discharge	2250(a)	375(a)		795(a)
Sawyer's Bay approx. 150 m NE of stream discharge	3550(a)	245(a)	560	148(a)
Adjacent bay	18	140		120

Note: (a) Mean of 2 samples.

Smillie (1980) also found high concentrations of Cu (up to 6600 mg/kg) in upper Otago Harbour sediments. The levels found were two orders of magnitude higher than those found by the water board (Table 6.34) for two areas close by, and could indicate highly localised contamination (e.g., from a Cu containing metal object). Dickson and Hunter (1981) suspected that the high concentrations of Cu found by them in upper harbour waters (up to 3.2 mg/m^3) were due to release of Cu from sediments of the harbour basin and stated that further work in the area would concentrate on this aspect.

Ravensdown Fertiliser Discharge, Otago Habour

In 1983, Bioresearches Limited conducted a survey to ascertain the effects of discharges, to the upper Otago Harbour at Ravensbourne, from the seven outfalls from the Ravensdown Fertiliser Works (Bioresearches, 1983a). Metal levels were examined in surface sediments, biota and, occasionally water. The distribution of Cd, in the sediments in the area of the works indicates that spillage of phosphate rock from the conveyor transfer point on the wharf is a probable source of part, if not most, of the sediment Cd. At this point a Cd level of 28 mg/kg was found. This is at least an order of magnitude greater than the expected background concentration. The levels of Cd found in the sediments are similar to those found in phosphate rock. High Zn concentrations were also expected but Bioresearches (1983a) found no enrichment of Zn in the sediments near the works. One high concentration (584 mg/kg) could not be accounted for but it is possible that sacrificial Zn anodes attached to boats moored in the area or galvanised fittings dumped or lost could provide an explanation. Reasonably high Cu levels (50-240 mg/kg) were thought to be due to the now defunct $CuSO_4$ manufacturing plant.

Bioresearches (1983a) also concluded that there had been no major metal contamination of edible shellfish species (mussels and cockles) in the vicinity of the works such as would render them unfit for human consumption. However, Cd, Cu and Hg concentrations in shellfish taken from the works area are higher than those taken elsewhere in the harbour. Even so, these higher levels are still approximately the same as the New Zealand average and very much lower than Food Regulations limits.

Manuherikia River

Ahlers and Hunter (1986) have analysed the waters of the Upper Manuherikia River in Central Otago prior to possible lignite mining. Their more recent results, obtained after the development of extremely stringent sampling techniques, are presented in Table 6.36. The results are of the same order of magnitude as those obtained from other relatively unpolluted environments elsewhere and are considered to be highly reliable.

Table 6.36: Metal concentration (mg/m^3) in the Upper Manuherikia River (Central Otago). (Ahlers and Hunter, 1986).

Metal	Concentration
Cu	0.12-0.42
Ni	0.07-0.50
Pb	0.005-0.020
Zn	0.050-0.30

6.2.15 Southland

6.2.15.1 Water Board Studies (with the assistance of L. McKenzie)

Sampling of natural water has largely been confined to the Aparima River upstream and downstream of the Floorwool Products Ltd discharge (see Section 5.4). Effluent and river water samples were taken at irregular intervals between mid-1980 and mid-1982. Cr effluent levels were always high (averaging around 12 000 mg/m^3) but Cr was never detected in the river water downstream of the discharge. River sediments were examined once (April 1982) but no metal elevation was evident (i.e., Cr 8.5 mg/kg 40 m upstream, and 8.2 mg/kg 10 m downstream) but samples of filamentous algae taken in February 1982 did show elevations (i.e., Cr 6 mg/kg upstream, and 467 mg/kg downstream, dry weight basis).

The Mataura River was sampled once (September 1980) (for Cr analysis) downstream of the Mataura tannery discharge. No Cr elevation was observed at 50 mg/m^3 detection limits.

Sediments taken (May 1983) from within the Waihopai arm of the New River estuary (adjacent to Invercargill) and analysed by the Southland Phosphate Co. by XRF, show variable levels of Cr (45-187 mg/kg) and Zn (26-168 mg/kg). The estuary receives tip leachate, primary treated sewage and urban runoff. The lowest Cr and Zn levels (45 and 26 mg/kg respectively) occurred at Omaui beach just outside and down current of the the estuary. The highest Cr level (187 mg/kg) occurred several km upstream in the New (Oreti) River; the highest Zn level (168 mg/kg) occurred across the estuary from the tip outlet and near some dumped car bodies.

6.2.15.2 Other Studies

Brooks and Quin (1971) studied heavy metal levels in stream sediments of the Port Pegasus area (Tin Range) Stewart Island. The levels found are low and natural, and were related to the three rock types in the catchments.

Chapter 7
SUMMARY, RECOMMENDATIONS AND CONCLUSIONS

(D. G. Smith and R. B. Williamson)

7.1 Summary of past and present heavy metal pollution

An assessment of pollution by heavy metals in New Zealand has to be limited to the evaluation of their concentrations in water, sediments and biota. There are very few studies that have examined biological effects (e.g., toxicity) and long-term, insidious effects are probably impossible to assess.

Metal discharges or inputs are defined here to have an **impact**, if there is a reliably determined increase of heavy metal concentration in water, sediment or biota.

To assess the relative importance of impacts, each has been assigned a severity rating (Table 7.1), which was derived in the following manner. Water and biotic metal concentrations were compared with:

(i) New Zealand Food Regulation limits and Drinking Water Standards (i.e., for human consumption of food and water).
(ii) Criteria for the protection of aquatic biota and farm stock.

Table 7.1: Severity rating used to assess reported heavy metal impacts. (a)

Severity	Effect
1	Concentrations are well below the limits, standards and criteria. Ill-effects in humans or biota have not been reported.
2	Concentrations are below the limits, standards and criteria and there is no field information on, or any field evidence for, ill-effects in humans or biota.
3	Concentrations are above the limits, standards and criteria but so far available field evidence does not show that human/biota health has been impaired or at risk.
4	Concentrations are well above the limits, standards and criteria and human/biota health has been shown to have been impaired or at risk.

Note (a). Penny (in press) has made the observation that ill effects to biota may take place in Coromandel streams where concentrations are below criteria (See Section 6.2.4.2).

A high severity rating was assigned where these limits, standards and criteria had been clearly exceeded. There are no corresponding criteria for sediments, therefore a subjective assessment has been made of the implications of sediment metal impacts. In the absence of metal concentrations in water and biota, high sediment concentrations were assigned a high severity rating if the authors thought they reflected past or present situations where:

(i) (i) or (ii) above were exceeded
(ii) Biota were exposed to unacceptably high metal concentrations.

A summary of heavy metal impacts is given in Table 7.2. Information is grouped according to known or assumed major metal sources. The severity rating used in Table 7.2 has been designed to be used solely for comparing information contained in this table. There is a good deal of subjectivity in its derivation.

The number of reported incidences of heavy metal impacts (severity 3 or 4) is not large and they are discussed below. In only four or five instances has there been well established evidence of human/biota damage.

Table 7.2: Summary of reported heavy metal impacts.

Major or most obvious source	Location	Text ref.	Impact (a)	Severity (b)	Remedial action taken (c)
Geothermal (natural and power development)	1 Wairoa/Wairua R	6.2.1.2	Water (Hg)	2	
	2 Tokaanu Str	6.2.3.1	Water (As)	2-3 (B)	
	3 Waiotapu Str (and others)	6.2.3.1	Water/sediments (As and Hg)	2-3 (B,H?)	
	4 Waikato R	6.2.3.1/2	Water/sediments/plants (As)	2-3 (H)	Reinjection; water treatment
	5 Central North Island	6.1.4.1	Fish (Hg)	2-3 (H)	
	6 Waiohewa Str	6.2.5.2	Water (Hg)	2-3 (B,H)	
Industrial	7 Marsden Pt	6.2.1.2	Sediments	1	New water right
	8 Waiuku Est	6.2.2.2	Shellfish/sediments	1-2	New water right
	9 Tauhei Str	6.2.3.1	Water	2?	Plant management
	10 Topehahae	6.2.4.1	Sediments	2-3?	?
	11 Masterton	6.2.9.1	Groundwater	4 (H,St)	Plant management; bore water use discontinued
	12 Waiwhetu Str/Est	6.2.10.2	Sediments/shellfish	3-4 (B,H,Sh)	Industry sewered; sediments removed
	13 Heathcote R	6.2.13.2	Sediments/biota	3-4 (B,H,Sh)	Industry sewered
	14 Otago Harbour (Ravensbourne)	6.2.14.1/2	Water (Cu)/sediments	2	Cu discharge ceased
	15 Otago Harbour (Sawyer's Bay)	6.2.14.1/2	Water/sediments/biota (Cr)	3 (B?)	Diversion; treatment
	16 Otago Harbour (Upper)	6.2.14.2	Sediments (Cu)	2-3?	Nil
	17 Aparima R	6.2.15.1	Algae (Cr)	1?	Discharge ceased
Urban (with or without industrial input)	18 Taranaki Harbour	6.1.1.2	Water	2-3 (B)	Nil
	19 Whangarei Harbour	6.2.1.2	Sediments	2?	Under study
	20 Wellington Harbour	6.1.2/6.2.10.2	Sediments/shellfish/plants	2-3 (H)	Industry sewered
	21 Avon/Heathcote Est	6.2.13.2	Sediments/shellfish	2-3	Industry sewered
	22 New River Est	6.2.15.1	Sediments	2?	Nil

Urban or road runoff	23 Lake Taupo	6.2.3.2	Plants (Pb)	1	Nil
	24 Waitara R	6.2.7.2	Sediments (Pb)	1	Nil
	25 Hawke's Bay drains	6.2.8.1	Water	1-2	Under study
	26 Hamilton drains	4.4	Water	1-2	Under study
	27 Auckland drains	4.4	Water	1-2	Under study
	28 Pauatahanui	6.2.10.2	Sediments (Pb)	1-2	Nil
	29 Avon-Heathcote drains	6.2.13.2	Sediments	2	Nil
	30 Water of Leith	6.2.14.1	Sediments	1-2	Nil
	31 Kaikorai R	6.2.14.1	Sediments	1-2	Nil
Mining	32 Awaroa Str	6.2.3.1	Water (As)	1	Nil
	33 Tui/Tunakohoia Str	6.2.4.1/2	Water/sediments	4 (B,H)	Catchment control
	34 Comstock/Paroquet Str	6.2.4.2	Water/sediments	3?	Nil
	35 Middlemarch	6.2.14.1	Water/sediments (As)	4(St)	Under study
Sewage	36 Moa Point	6.2.10.2	Sediments	1-2	Nil
	37 Taieri R	6.2.14.1	Water	2-3?	Nil
Other natural (or no obvious source)	38 Firth of Thames (d)	6.1.2	Sediments	1	
	39 Tinline/Pelorus	6.2.12.1	Water (Cr)	1	
	40 Various	6.1.4.2	Fish (Hg)	3 (H)	
	41 Various	6.1.3/6.2.2.2	Shellfish (Cd)	3?	
Rubbish tips	42 Gisborne	6.2.6.1	Groundwater	3 (e)	Nil
Treated wood	43 Various	6.1.3	Shellfish (As)	3 (H)	Nil

Notes:

(a) Assume several metals are responsible for the impact unless otherwise indicated.

(b) The code given in brackets after the severity rating indicates a risk to:
aquatic biota (other than shellfish) (B)
humans (H)
stock (cattle) (St)
shellfish (Sh).
The code is used only if the rating is 3 or 4. The code (H) is used if human health is at risk either from consumption of water, shellfish, or other biota.

(c) A blank in this column indicates that remedial action is impossible or extremely difficult.

(d) Cause not established. Possibly some mining influence.

(e) Not a potable water supply.

Geothermal

The Hg content of central North Island trout sometimes exceeds the Food Regulations limit and this has resulted in cautions being given on their consumption (see for example Brooks *et al.* 1976). The Waikato River, and some of its tributaries, contain As concentrations which are close to those at which human and biotic health may be at some risk. Less than half of the As is due to natural inputs, but exploitation of geothermal resources has added to these. Reinjection of geothermal fluid will reduce this problem.

Uncontrolled Industrial Discharges

That uncontrolled industrial discharges can be a major source of metals is evident by the high sediment levels in the Waiwhetu Stream and estuary, Heathcote River and parts of the Otago Harbour. These discharges have now been sewered, diverted or treated and controlled by water rights. The main risk now is from accidental spillage and vandalism, exacerbated by poor site management.

Urban Stormwater Runoff

Investigations to date show that evidence for pollution from urban stormwater comes from levels of Pb and Zn found in drain sediments (Avon and Heathcote Rivers) and from shellfish, taken near stormwater outlets in Wellington Harbour, which have Pb levels above Food Regulation limits. High concentrations of Cd, Cu, Pb and Zn in stormwater (drains in Hamilton, Auckland, and Hastings) are a result of suspension of metal rich sediments, a large proportion of which is not likely to be biologically available. Levels of metals found in sediments and biota from urbanised estuaries (Invercargill and Christchurch) may show an impact, but these are judged to be low severity by the classification used here. This source, and its effects, are still under review by MWD Water Quality Centre staff.

Mining

Past mining activities have resulted in gross contamination of water and sediment in a few Coromandel streams. Biological stress or impoverishment has been observed in several Coromandel streams below discharges from past mining sites.

Arsenic contamination of waters and/or soils in Middlemarch, Otago seems to have caused the deaths of some cattle. This has resulted from a nearby arsenopyrite deposit which was once mined.

Large scale coal mining in the Waikato is not regarded as a significant potential heavy metal source.

Natural

Many sea fish have Hg concentrations close to or above the Food Regulation limit. This is considered to be natural. Shellfish taken from many areas around the New Zealand coast contain high Cd concentrations. The cause is not known but because of the isolation of many of the sampling sites from human activity, natural causes seem likely. There is no Food Regulation limit for Cd in shellfish.

7.2 Recommendations

The following recommendations are limited to requirements for managing heavy metals in the New Zealand aquatic environment. Because of New Zealand's limited scientific resources, the recommendations are restricted to matters which could reasonably be tackled in New Zealand. Information on topics such as standards and criteria development, toxicology, speciation, and analytical methods development where considerable research effort is required, will still need to be sought from overseas.

The recommendations presented here are those of the authors and must not be construed as necessarily being the policy of either the National Water and Soil Conservation Authority or the Ministry of Works and Development.

7.2.1 Sampling and Analysis

There are several technical matters that need to be considered before recommendations can be made.

The information available on heavy metals could be considerably enhanced if attention were paid to adopting adequate sampling procedures, more sensitive analytical techniques, and overcoming contamination problems. This is particularly true for analysis of metals in natural waters, where there is a distinct lack of credible data. Much of the methodology needed to improve analyses of sediment and biota is available in the literature and readily transferable to a competent laboratory. Analysis of metals in natural waters should only be performed by laboratories with proven capability in this skill.

Information on heavy metal concentrations would also be improved if more information were available on sample variance. A number of the studies reviewed here compared concentrations from different locations or followed changes in concentrations with time, but few were able to carry out statistically valid comparisons. Not only would this have been of value to the study itself, but would also allow more meaningful comparisons to be made with other work.

In research programmes on water, speciation of metals should be considered in order to assess the proportion of metal in free ionic (i.e., the most toxic) form. A minimum programme should consider water characteristics which are known to affect metal complexation and adsorption, e.g., pH, suspended solids, organic carbon, carbonate, and sulphate. Hardness should also be determined in instances where metal toxicity is hardness related.

For most water management purposes, the metal standards/criteria used will dictate the analytical methods and water characteristics to be assessed, but a general appreciation of the way water chemistry may affect metal speciation/toxicity is desirable.

In compiling this review, it was often difficult to compare concentrations in sediment and biota reported from different studies, because different digestion, extraction, or instrumental techniques were used. Future comparisons would be aided if a comparison of all commonly used analytical techniques were available, and if analysts defined the fraction of total metal their method determined. Analysis of sediments should also include those characteristics which affect metal concentrations, for instance, particle size distribution and organic carbon content.

Recommendation 1
Sampling and analysis of water for heavy metals should only be carried out by personnel and laboratories with demonstrable capability for this work.

Recommendation 2
Any monitoring programme should ensure that appropriate statistical and quality assurance requirements for sampling design and analysis are met.

Recommendation 3
A comparison of the commonly used analytical methods, especially digestion procedures, should be undertaken.

Recommendation 4
In reporting results, methods of sampling, sample preparation, and analysis should be given together with details of other characteristics which may assist in the interpretation of the results especially the form of the metal measured.

7.2.2 Water rights

There are two main problems in managing the release of heavy metals to aquatic ecosystems in New Zealand.

1. Deriving defensible water right conditions for the protection of aquatic life for the discharge of heavy metals.
2. Defining and controlling the effects of diffuse inputs of metals on aquatic life.

A major difficulty with each is knowing the appropriate dose/response relationships, i.e., the level at which heavy metals exert an undesirable biological effect. With the exception of the recent studies in Coromandel (Section 6.2.4.2) the New Zealand studies summarised in this review did not or could not define such dose/response relationships. However, there is no reason to suspect that the susceptibility of New Zealand aquatic ecosystems is substantially different from systems found in other parts of the world, so that overseas findings should be applicable here in a general sense, although not necessarily at a species level. The United States EPA criteria seek to provide ecosystem protection and appear to be the most extensively researched. At present, it seems appropriate to use them as the basis for environmental protection in New Zealand although it should be stressed that they are guideline values and not standards. Water right conditions for New Zealand discharges, developed from overseas criteria, should ideally include a provision for the detection and monitoring of defined changes in downstream biota. The monitoring results should be used to determine whether the water right conditions are appropriate. There is a lot of other useful information in the publications reviewed in Chapter 5 and these should also be considered. To be able to use overseas findings with confidence there is a need to evaluate the effects of similar metal levels in New Zealand. In this respect, many waste discharges (e.g., from New Zealand Refining Company at Marsden Point, New Zealand Steel Limited at Waiuku, petrochemical industries in Taranaki) are being monitored to assess biological effects although the contribution of metals may not be separable from other agents. Thus far, use of overseas metals criteria does not seem to have caused any ill-effects, but the data upon which this judgement is based are scarce.

Criteria are based on a large number of laboratory tests, where both the environment for the animals and the form of the metals may be irrelevant to natural systems. There seems little to be gained in repeating this exercise for New Zealand biota for individual metals, although such a case may be argued for a specific discharge with a complex mixture of toxicants. Further tests under realistic conditions (e.g., lake enclosures, laboratory macrocosm experiments) would be expensive if a wide range of metal toxicants and environmental conditions were tested.

It is difficult to evaluate new information on metal concentrations because at present there is little reliable information on, and experience with, heavy metal concentrations in New Zealand's fresh and coastal waters. There is a need to obtain a small dataset of credible heavy metal concentrations in these waters as an aid to national management decision making. The choice of sites should cover a wide range of waters draining areas of different land use and geology, although the dominant factors controlling metal concentrations are probably in-stream processes. It is recommended that a single synoptic survey be undertaken of one major river (e.g., the Waikato from headwater streams to the estuary), and a selection of coastal sites which receive runoff from a variety of catchment types and land uses. This exercise would enable comparison of typical New Zealand background levels with overseas situations and criteria, as well as provide a data base with which to compare new information.

Recommendation 5
An overview, preferably by a central agency (e.g., Water and Soil Directorate, MWD), needs to be kept on criteria and standards. Appropriate publications should be produced from time to time to guide those involved in the derivation of water right conditions. At present, the criteria for metals published by the US EPA seem to be the most appropriate to use as the basis for deriving water right conditions.

Recommendation 6
Evaluate, experimentally if possible, the field response of aquatic biota to metal inputs.
Suitable study areas would be:
- Coromandel streams (preliminary study completed),
- Urban streams,
- Geothermally impacted streams.

Recommendation 7
The appropriateness of water rights conditions should be assessed by long-term biological monitoring of receiving waters. Procedures for water and effluent sampling, preservation, and analysis should be agreed between the relevant agencies. Water rights conditions should contain maximum (or percentile) metal concentrations where appropriate and details of these conditions should be readily available to interested parties.

Recommendation 8
Conduct a single synoptic survey of heavy metals in a river such as the Waikato from its headwaters to its estuary, and in a selection of harbours and estuaries.

7.2.3 Diffuse sources

All major sources of heavy metals have been reviewed in chapter 4. The data show that there are several non-point source inputs of metals of possible concern for which there is insufficient information.

Recommendation 9
Evaluate the potential impact of heavy metal impurities, especially Cd, in superphosphate fertiliser, particularly during accidental application to streams and during the first runoff events after topdressing.

Recommendation 10
Evaluate the impact of antifouling paints from moored boats and boatyards on sediments and biota.

Recommendation 11
For studies involving metal budgets to large water bodies, evaluate the impact of metals from air-borne sources.

Recommendation 12
Ascertain the cause(s) of high Cd concentrations which are occasionally found in shellfish around the country.

7.2.4 Major inputs

Industrial discharges are now managed either by treatment followed by dilution in receiving waters or diversion to sewerage systems. The only major discharges of heavy metals not adequately evaluated in New Zealand are urban stormwater runoff and sewage discharges. Overseas, urban storm runoff is often regarded as a more serious potential pollution problem than municipal sewage. Sewage contains relatively low metal concentrations but large volumes may be discharged thereby producing proportionally large loads to some partially enclosed water bodies such as estuaries. In many cases sewage and stormwater are discharged to the same water body. These discharges are likely to continue for the foreseeable future and, because their effects are largely unknown, they should be evaluated.

Recommendation 13
Long-term low-intensity monitoring of the effects of sewage outfalls, especially those which discharge into partially enclosed water bodies such as estuaries, should be carried out.

Recommendation 14
The effects, especially on sediments and shellfish, of stormwater sewer outfalls in partially enclosed water bodies still needs to be evaluated.

7.3 Conclusions

At present, New Zealand does not appear to have a major heavy metals problem. However, in several parts of the country elevations of metal concentrations above expected background have occurred in waters, sediments and biota as the result of past uncontrolled industrial discharges, natural (mainly geothermal) inputs, natural inputs which have been increased by human activity (e.g. geothermal power development, mining), and urban stormwater discharges. In the main, the impacts produced to date are not widespread and it is rare for human or biotic health to have been obviously affected. In instances where remedial action can be taken, e.g., by diverting, treating, or limiting discharges, the effects will be reduced, although in some situations it may take a considerable period of time. Regional water boards appear to be aware of the problems that uncontrolled discharge of metals can cause, and are now severely limiting such discharges.

There are several potential problems not yet investigated, viz, effects due to superphosphate use, antifouling agents on boats in marinas and boat yards, and urban stormwater discharge. These should receive attention. Field research in New Zealand is required to derive sound, and defensible receiving water criteria. Long-term monitoring on sewage discharges into enclosed water bodies, e.g., estuaries, should be carried out. Evidence that contamination problems are a common source of error in heavy metal studies indicates that much more attention should be paid to analysis and sampling techniques.

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