THE UNIVERSITY OF THE SOUTH PACIFIC
LIBRARY

Author Statement of Accessibility

Name of Candidate	: **Shaneel Chandra**
Degree	: **Master of Science**
Department/School	: **Department of Chemistry / School of Pure and Applied Science**
Institution/University	: **University of the South Pacific**
Title of Thesis	: **Investigations into the Lami Municipal Dump as a source of heavy metal contamination**
Date of award	: **2002** (month, year)

This thesis may be:

1. consulted in the Library without the author's permission **YES** ☐
2. cited without the author's permission provided it is properly acknowledged **YES** ☐
3. photocopied in whole without the author's written permission **NO** ☐
   If you answered '**No**', select the percentage that may be photocopied

   20-40% ☐

I authorize The University of the South Pacific to:

4. produce a microfilm or microfiche copy for preservation purposes **YES** ☐
5. retain a copy in electronic format for archival and preservation purposes **YES** ☐
6. make this thesis available on the Internet
   YES ☐
7. make this thesis available on the USP Intranet
   YES ☐

Signed : ______________________

Date : April 6, 2018

Investigations into the Lami Municipal Dump
as a Source of Heavy Metal Contamination

By

Shaneel CHANDRA

A thesis submitted in partial fulfillment
of the requirements for the degree of Master of Science

Department of Chemistry
School of Pure and Applied Sciences
University of the South Pacific
Suva, Fiji Islands.

CERTIFICATE OF AUTHENTICITY

I, Shaneel Chandra hereby declare that this thesis is the result of my own original research and that any quotations that have been obtained from the literature or otherwise have been duly and appropriately acknowledged and referenced.

SHANEEL CHANDRA

ACKNOWLEDGEMENTS

I would like to acknowledge the following persons, without whom this thesis would not have reached this stage. Firstly, I am indebted to my supervisors, Dr Philomena Gangaiya and Dr Culwick Togamana for their support, suggestions, encouragement and guidance at all stages of the research project from the designing of the original pilot exercise in 1999 to the culmination of this project. It was difficult to continue my postgraduate study to the Masters level and this would have remained a dream had it not been for the funding secured by Dr Gangaiya for my accommodation, research expenses and tuition fees.

Secondly credit goes to Professor William Aalbersberg also for funding my postgraduate studies in 1999 and also towards the end of the the project in 2002. His assistance in providing the facilities at the Institute of Applied Sciences for analysis and completion of the thesis, together with suggestions and comments during proofreading of the subsequent draft versions of the thesis has been invaluable.

Thirdly, I wish to thank all other persons who have contributed overall to the final output – to Monica Swamy formerly of the South Pacific Applied Geoscience Commission for her assistance in obtaining the maps of the Lami dump and surrounding areas, Dr Rufus Chaney and Dr McLaren for kindly providing articles from literature at such short notices, Conway Pene at the Geographical Information Systems Unit at the University for providing necessary software for the mapping layout, and the technical staff and

colleagues at the Department of Chemistry. To my colleagues who could barely bear the stench at Lami, but plodded on nevertheless during the tedious sampling periods.

Finally, and most importantly, I wish to acknowledge my parents for their invaluable support and encouragement throughout the project. This thesis is the result of their faith in me and it is my honour to dedicate it to them.

ABSTRACT

The Lami dump, which is the depository for almost all of Suva's domestic and industrial wastes, has been suggested by researchers to be a significant source of contamination in the harbour area. There is lack of conclusive data to verify this suggestion which prompted this study. It was designed to determine the extent of contamination at the dump and investigate the possibility of remediating any contamination that could be found using the concept of an emerging new technology – phytoremediation.

Phytoremediation is the technique of remediating contaminated sites by cultivating plants on the sites. The contaminants tend to be absorbed in various sections of the plant, which can then be harvested and the contaminants removed. In this way, contaminants are removed from the soil.

Phytoremediation was considered as a possible remediation option for this study due to its relatively low cost, applicability to shallow soils and non-destructive impact on the soil, which are common concerns usually associated with other remediation methods. The investigation was limited to assessing the metal accumulating capacity of the natural vegetation at the site.

The study consisted of sampling three sites within the dump, selected on the basis of how long ago dumping had been discontinued at the site. Surface soil and the dominant plant species within nine blocks per site were obtained. In the soil, chemical characterisation was done prior to extraction of metals using: (a) a strong acid mixture consisting of concentrated nitric:perchloric:sulphuric acids (10:2:1) and (b) a dilute (0.05 M) solution of ethylenediamine tetraacetic acid. The plant samples were subjected to sample treatment followed by wet ashing using concentrated perchloric acid and 50 % (v/v) hydrochloric acid.

Considerable heterogeneity was found in metal levels in soil from within and across the sites. This was attributed to the indiscriminate dumping of materials at the dump as well as the piling of soils from various sites outside the Lami area to contain the odour. Due to the heterogeneity, there was absence of clear trends in the results. Hg and Cd were found to be in the lowest concentrations. Cu, Zn and Pb were found to be in significantly high amounts, while Cr and Ni levels tended to fluctuate. Overall, the levels were found to be exceeding many pollution standards used around the world.

Metal concentrations were too low in plants for them to be classified as hyperaccumulators. Despite this, levels were higher than those normally encountered in vegetation.

High heavy metal concentrations were also encountered in the bioavailable fraction of the soil. It was suggested that metals in this fraction, when in contact with the significantly high amount of rainfall that the Lami area receives could end up as organic-rich leachate. This leachate was suggested to have the potential to move into the marine environment.

The dependence of the local population on the marine resources of the Lami coastline, and the vegetation adjacent to and within the dump puts the population at risk of heavy metal enrichment and eventually toxicity from the dump. Recommendations were made to further and more detailed studies to evaluate the extent of contamination. Also, more planned and considerate dumping of materials in the dump as well as in the future site at Naboro, outside Lami was suggested, to avoid further degradation of the environment.

TABLE OF CONTENTS

LIST OF FIGURES AND PLATES

LIST OF TABLES

1.0 INTRODUCTION

The investigation of contamination of the marine coastal environment from anthropogenic sources is receiving considerable attention, particularly for small island countries that are surrounded by vast stretches of the ocean. This is because coastal environments serve as rich fishing grounds and recreational areas. A large proportion of the world's population is centred in coastal areas, and there is a continuing trend towards further concentration in these regions. The health, well being and the very survival of coastal populations are sometimes inextricably linked with the health and well being of coastal systems. It is therefore imperative that sustainable patterns of human activity are adopted in coastal areas. This is to maintain a productive marine environment, which in turn can allow humans to derive maximum benefits from it in a sustainable manner. However, this is often not the case, as human activities on land and immediately adjacent areas to coasts threaten the health, productivity and biodiversity of the marine environment.

Contaminants of major concern found in the marine coastal environment include heavy metals, persistent organic pollutants (POPS), oils (hydrocarbons), nutrients and radioactive substances. Most of these species largely emanate from land-based activities such as municipal, industrial and agricultural wastes, mining activities and runoff, as well as atmospheric deposition (UNEP, 1999).

Contamination of the environment, and in particular the marine environment by heavy metals has been receiving considerable attention. This is evidenced by a constant stream of publications appearing in the literature over the years (for example Li and Shuman, 1996; Sbriz *et al.*, 1998; Tabudravu, 1995; Zhang *et al.*, 1997). As pollutants, heavy metals present an entirely different problem and behaviour in the environment compared with volatile or biodegradable compounds. They are not easily decomposed, are toxic, persist and have a tendency to bioaccumulate and end up as permanent additions to the environment (Gangaiya, 1994; Lee *et al.*, 1998).

Heavy metal pollution has become a subject of great public interest as well because humans have been harmed by soil metal contaminants in the general environment. Two well-documented cases in history serve to illustrate this:

a) Industrial mercury (Hg) contamination on Minimata Bay in Japan caused severe health effects in consumers of fish and shellfish from the area (especially in developing children), and led to the identification of methyl mercury as a widespread food-chain and wildlife poison. Methyl mercury is now recognised as an important source of human risk when sediments are contaminated by inorganic mercury (Chaney *et al.*, 1999).

b) Cadmium (Cd) discharge from commercial mining upstream of the Jinzu River in Toyama Prefecture, Japan resulted in chronic Cd poisoning among locals whose water source was the river. Victims suffered from impaired kidney function and progressively developed oesteomalacia. Calcium deficiency, normally associated with hormone imbalance, pregnancy or breast-feeding also resulted in those affected (Chaney *et al.*, 2000).

Accordingly, in recent years, authorities in most developed countries have initiated programmes for the assessment of pollution, particularly that involving heavy metals. These include those focussing on aspects such as distribution in terrestrial (Lee *et al.*, 1997; McBride *et al.*, 2000; Rooney *et al.*, 1999) and the marine coastal environments (Chester and Voutsinou, 1981; Naidu and Morrison, 1994; Sbriz *et al.*, 1998; Virkanen, 1998), movement between different sectors of the environment (McGrath, 1987; Lee *et al.*, 1997; Romkens and Salomons, 1998), risk assessment (Chaney *et al.*, 2000) and various analytical protocols for the extraction of metals (Agemian and Chau, 1976; Martinez-Garcia *et al.*, 1999; Quevauviller *et al.*, 1999; Tessier *et al.*, 1979).

In urban estuarine environments, inputs of heavy metals such as lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni) and mercury (Hg) tend to be non-point in nature and include municipal and industrial discharges, urban runoff, atmospheric conditions and the presence of harbour facilities with heavy ship traffic (Meyerson *et al.*, 1981). Wastes produced in the urban and industrial areas provide one of the most likely sources of heavy metal contamination in the terrestrial environment, and these have the potential to contaminate large areas of land (McLaughlin *et al.*, 2000). When improperly-designed landfills are created to dispose of these wastes, they become a source of contaminants leaching into groundwater (Brodie and Morrison, 1984). In many countries, the problems associated with the disposal of wastes generated by population centres, both large and small, together with associated industrial activity, have become significant environmental issues (McLaren and Smith, 1996).

1.1 HEAVY METAL CONTAMINATION IN THE SOUTH PACIFIC

Outsiders often view the South Pacific as an unspoiled tropical paradise. They are also led to believe that the climate and available resources permit a quality of life traditionally better than many other subsistence societies. Even such communities are limited by their environmental resources, and development and changes have led to an increasing number of environmental problems (Dahl & Baumgart, 1983). Pacific island nations are undergoing a phase of rapid urbanisation, especially around the coastal regions. This is mainly due to the development of ports as points of entry of goods and services. The increasing tendency of rural dwellers to migrate to urban centres causes population imbalance, tipped towards the urban areas. This gives rise to the issue of disposal of wastes such as domestic refuse and sewage. Limited amount of development would suggest that contamination particularly from heavy metals is not of major concern. While this might be true of some countries, in others because of inadequate controls on waste disposal, cases of contamination have been detected.

Information on heavy metals in the South Pacific environment is limited. In general, however, heavy metal pollution in the region tends to vary with site. Morrison (1990) and Tabudravu (1995) mention that levels found in one country usually tend to reflect the degree of development and industrialisation. However, this may not always be the case.

The changing lifestyles of Pacific Islanders means moving away from traditionally subsistence lifestyles to cash-based, consumer goods societies, where the volume and complexity of waste products have increased. The biodegradable content of the waste has been decreasing, and has been accompanied by increased amounts of non-biodegradable matter, such as nicad and lithium batteries, waste oil and food and drink cans. All these contribute to heavy metal burdens in the environment (UNEP, 1999).

Fiji has been highlighted as one of the countries where elevated levels of heavy metals have been reported close to urban centres and mining sites (Naidu *et al.*, 1991). In particular, the largest urban centre, Suva, has largely been the focus of pollution studies in recent times, for example in the studies of Dougherty (1988), Naidu and Morrison (1994), Stewart and deMora (1990) and Tabudravu (1995).

1.2 HEAVY METAL CONTAMINATION AROUND SUVA, FIJI

Suva, the capital of Fiji, has been experiencing a population growth rate, which is more than 1.5 times the national average. The coastal zone in the Suva area is of vital importance to a significant proportion of the population. It brings together a unique assemblage of resources such as mangroves, water and seafood, on which there is great dependence for sustenance. The rapid increase in population, coupled with the associated increase in industries, port activities and waste disposal problems has led to coastal management problems in the area (Naidu *et al.*, 1991). It is generally believed that rapid economic growth is often achieved at the expense of the environment (Tabudravu, 1995), and Suva is no exception. The literature suggests that the Suva Harbour has the highest levels of tributyl tin from many others investigated around the world (Stewart and deMora, 1990) and also levels of heavy metals (Dougherty, 1988; Naidu *et al.*, 1991; Naidu and Morrison, 1994) that could be of significant concern.

A report by Watling and Chape (1993), for example, indicated severe marine pollution in the Suva area, with the suggestion that the consumption of seafood from the coastline would be a human health hazard. The edible species of mangrove oyster, *Crassostrea mordax*, was found to contain high levels of heavy metals (Naidu and Morrison, 1994).

1.3 THE LAMI RUBBISH DUMP

Although there are several potential sources of contamination in the Suva harbour area, a significant source is thought to be the rubbish dump at Lami. It is located directly on top of a reclaimed mangrove area, is unlined and is a repository for all kinds of waste including those from industries. Leachates from the site can move into the harbour waters (Lisk, 1991), dispersing the contaminants over a much larger area. Figure 1 shows an aerial representation of the dump and its immediate surroundings.

Until this study was carried out, there was only one other study that provided some information on the dump (Naidu and Morrison, 1994). This study included only one site from the dump area and therefore it was difficult to assess the magnitude of its effect and to ascertain whether or not the operation of the dump posed a health hazard to the surrounding environment. The fact that the dump has reached its capacity is evidenced

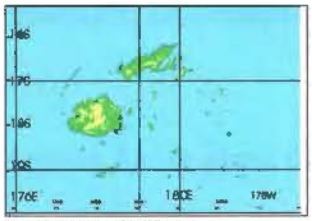


Figure 1 (a) Location of the Fiji Group

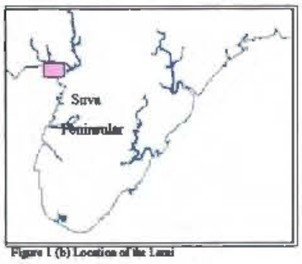


Figure 1 (b) Location of the Lami dump relative to Suva Peninsular

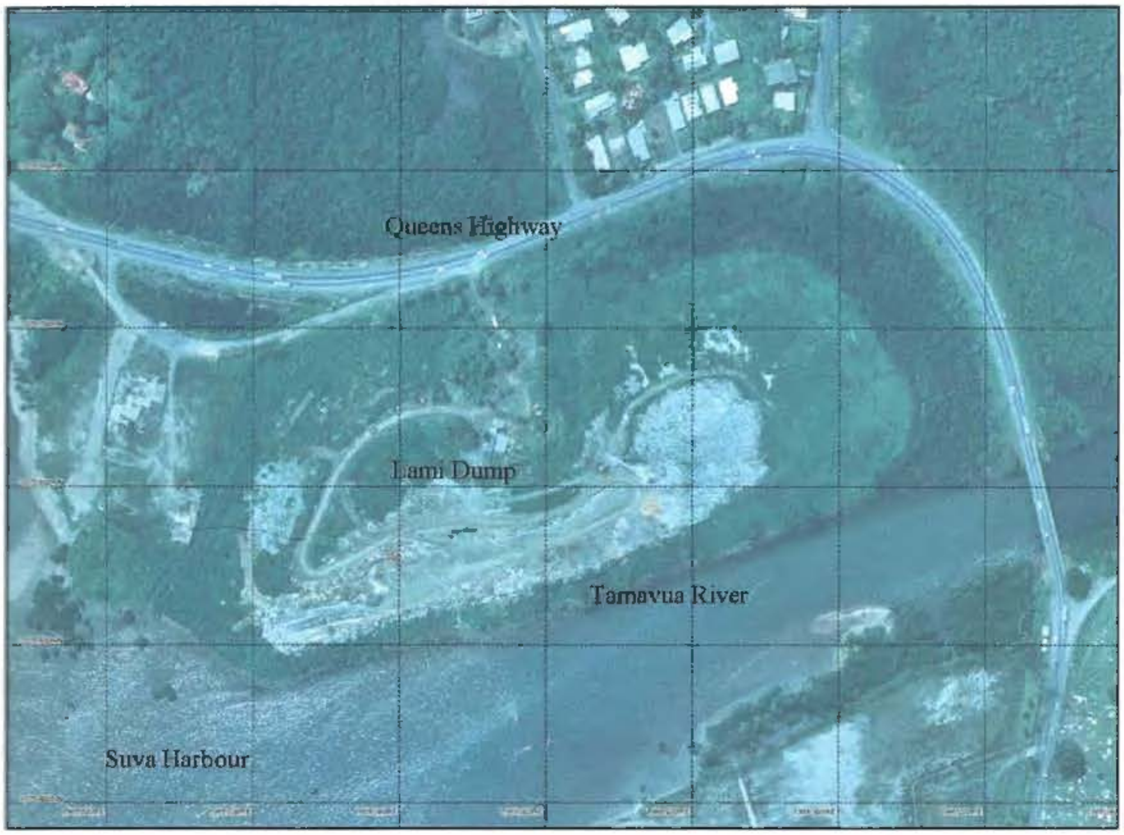


Figure 1 (c) Aerial photograph of the Lami Dump depicting study sites.

by the continual spillage of material into the nearby coastal waters. This has prompted authorities to seek an alternative disposal site away from the Lami area. The latter, when completed, is expected to be a completely lined landfill.

There are no definite future plans for the Lami dumpsite once the new site becomes operational. Due to its prime location adjacent to the Walu Bay industrial area and close proximity to the city itself, there is a lot of potential for it to become an extension to an already rapidly expanding industrial area. However, it would be prudent to determine the environmental status of the site, which would have implications for its future management. If significant amounts of contamination were detected, it is certain that before any development can be done, extensive site remediation may also be necessary so the site does not pose a hazard in the future. Various remediation methods are possible, however, a simple option would be phytoremediation, which is both inexpensive and less intensive than commercial methods currently in use in other parts of the world (Schnoor, 1997). Briefly, the technique employs plants with high capacities for absorbing heavy metals in their tissues to be planted in contaminated sites and later harvested. Such plants are referred to as hyperaccumulators. In this manner, the site is rid of heavy metals, and the harvested plants can be treated as metal ores. Site remediation using phytoremediation is discussed in detail in Chapter 2.

This study was designed to provide the kind of information that would help determine the extent of contamination at the dump and possibilities for remediation if found to be significantly contaminated. The results will also be informative in sustainably managing the new site so as to avoid any contamination-related problems.

1.4 OBJECTIVES OF THE PROJECT

The objectives of this study are to assess the extent of heavy metal contamination at the Lami dump, the potential for contamination of the surrounding marine environment, and the viability of native plants for phytoremediation of the site. The heavy metals to be investigated include Cu, Zn, Pb, Ni, Cd, Cr and Hg. More specific objectives are:

(i) characterisation of the physical and chemical nature of the mineralised waste material in the dump. This is important since the fate of heavy metals in the environment depends on the nature of the particles with which they are associated with and the mechanism of their association;

(ii) assessment of the spatial distribution of the heavy metals Cd, Cr, Cu, Hg, Ni, Pb and Zn in the dump. This is necessary because preliminary studies carried out by the author have shown that the dump is very heterogeneous with respect to heavy metal concentrations. Thus it would be vital to obtain approximate locations of the hotspots at the site;

(iii) investigation of the potential for metals to be mobilised into the surrounding marine environment, by determining the proportion of the total levels that is present as the bioavailable fraction. The unlined nature of the dump and its location atop a mangrove area could be factors leading to heavy metals emanating from the site into the nearby coastal environment. This objective would help determine the potential for such leaching, as well as the amount of metals likely to be leached;

(iv) assessment of the metal accumulating capacity of selected plants growing at the dumpsite. This is necessary to screen for any metal-hyperaccumulating plants that may be present in the vegetation of the dump; and,

(v) investigation of the feasibility of using phytoremediation for site clean-up.

2.0 BACKGROUND ON HEAVY METAL CONTAMINATION AND REMEDIATION STRATEGIES

This section provides an in depth discussion of the speciation of heavy metals, the chemical characteristics associated with each form and the chemical fate of the metals in soil. In addition, the various criteria used to determine polluted areas, which vary considerably around the world is examined and their applicability to the Lami dump is also discussed. Finally, the various options for remediating polluted sites are reviewed and compared, with phytoremediation (a rapidly emerging new technology with significant advantages over other presently existing options) being examined in more detail.

As indicated in the introductory chapter, substantial amounts of discharges containing toxic heavy metals are released into the environment by anthropogenic activities (Huamain *et al.*, 1999; McLaren and Smith, 1996; Naidu and Morrison, 1994). If released into the soil environment, they tend to get strongly bound to soil particles and accumulate to fairly high concentrations (Swift and McLaren, 1991; Li and Shuman, 1996). This is because in comparison with air and water, soil functions as a sink for the metals. It generally acts as a filter which retards the passage of chemicals to groundwater and therefore its occurrence at the land-atmosphere interface makes soil the recipient of a diverse range of heavy metals (Alloway, 1996).

When present at high enough concentrations, heavy metals can cause adverse effects on plants, soil organisms, wildlife, livestock and humans through pathways which involve soil ingestion, ingestion of foods grown on the soil, secondary consumption and from leaching of metals to drinking water bodies such as rivers and streams (Chaney *et al.*, 2000). The behaviour of these metals in soil differ according to the variables affecting long-term metal solubility, leachability and bio availability at any site, which include soil physical and chemical characteristics, climate and the vegetation in the area. Therefore, there is no one characteristic behaviour of even the same metal in different sites (McBride *et al.*, 2000).

It is important to study these characteristics in order to obtain a greater understanding of the environmental fate of these species in terms of their mobility, retention and availability. Understanding these will provide insight into their solubility, transformation, chemical reaction and pools of bioavailable fraction (Zhang *et al.*, 1997), phases of existence and mobility.

2.1 CONTAMINATION OR POLLUTION?

In scientific discussions, the word "polluted" should be distinguished from the word "contaminated" to help bring more precision into the debate about addition of contaminants to the environment. Elements are naturally present in all geological materials. On the one hand, almost all environments on earth have become somewhat contaminated by industrial and domestic emissions of inorganic contaminants. Contaminants are detectable if one uses analytical methods with low enough detection limits. On the other hand, the contaminant levels may be so high that the environment they are present in should be labelled "polluted", because the contaminants may harm exposed organisms. Modern science uses risk assessment as a tool, developed to identify the level at which areas should be labelled "polluted" and/or "contaminated".

The initial aim of many environmental monitoring programmes for heavy metals is simply to establish the degree (if any) of contamination. An approach which may be used to interpret the extent of anomalous trace metal in soil and sediments is to assess their magnitude in relation to baseline (also referred to as normal, natural or background) levels. A potentially rewarding technique to achieve this is to directly compare the non-residual trace metal fractions of "polluted" and "non-polluted" samples. If the initial aim of the investigation is simply assessing whether or not a soil/sediment population has suffered trace metal pollution, this method has the great advantage that the mineral compositions of both populations do not have to be similar. In such a case, the only information sought is how polluted the actual material is (Chester and Voutsinou, 1981).

Once a technique is formulated, the next logical step is to determine the background levels. Such concentrations are usually at trace level, and are related to the geochemistry of the parent material (Karathanasis and Seta, 1993). McLaughlin *et al.*, (2000) have argued however, that the background concentration is not always a well-defined condition due to contaminant movement through erosion and atmospheric accession of contaminants to seemingly unpolluted soils. Secondly, confining a set of background levels to particular regions is difficult due to variations in major soil parameters that control metal retention, such as soil pH, soil organic matter content, and cation exchange capacity. Such variations tend to be reflected in the background concentrations of metals. Concentrations of heavy metals that are described as being the background levels in Australia and New Zealand for instance are listed in Table 2.1.

Table 2.1 Environmental soil quality guidelines (mg/kg)

Heavy metal	**Background**[*]	**Environmental Investigation**[Ψ]
Cu	1 - 790	60
Zn	2 - 180	200
Pb	< 2 - 200	300
Ni	2 - 400	60
Cd	0.04 - 2	3
Cr	0.5 - 110	50
Hg	0.001 - 0.1	1

[*] Variable over different regions in each country

[Ψ] Health-based investigation levels for potential exposure of humans to metal through dermal contact, inhalation, soil-plant transfer, soil-plant-animal-human transfer and soil-human transfer (soil ingestion)

Source: McLaughlin *et al.*, 2000

These guidelines were developed by the Australia and New Zealand Environment and Conservation Council (ANZECC) and the National Health and Medical Research Council (NH&MRC) of Australia.

A more practical method for determining whether a soil population is polluted would be to compare the levels present in an area with set guidelines for polluted sites. Numerous such guidelines exist around the world, the most frequently referred to being the Dutch quality standards (Chen, 2000; McLaughlin *et al.*, 2000; Romkens and Salomons, 1998), Environmental Soil Quality Guidelines for Australia and New Zealand and the United States Environmental Protection Agency (USEPA) guidelines (McLaughlin *et al.*, 2000).

The primary rationale for establishing regulations for metal levels in soils is to limit or prevent the exposure of organisms to unacceptable hazards. While this may appear to be a straightforward objective, there are three complicating factors: (1) organisms differ in their sensitivity to different metals, (2) exposure pathways to metals vary, and (3) soil properties and properties of the material contaminated with metals strongly affect the degree of exposure (bioavailability) at any given concentrations of metals in soil. In addition, other environmental factors such as climate should not be ignored (McLaughlin *et al.*, 2000). These are some of the reasons why soil pollution criteria tend to vary around the world, and adapting them or comparing them should be done with caution.

Table 2.2 lists the regulations governing the maximum permitted levels in a number of developed countries. The data presented are confined to the metals of interest to this study.

Table 2.2 Contamination-defining levels (mg/kg) of trace elements in rural soils of the world

Country	Cu	Zn	Pb	Ni	Cd	Cr	Hg
Australia	100	1000	100	60	2	100	2
Belgium	750	2500	600	100	12	750	10
China[a]	250	500	300	100	5	250	15
China[b]	500	1000	1000	20	20	500	-
Denmark[c]	1000	4000	120	30	0.8	1000	0.8
France	100	300	100	50	2	100	1
Italy	100	300	100	75	1.5	100	1
Netherlands	190	720	530	210	12	190	10
Norway[d]	50	150	50	30	1	50	1
Norway[c]	1000	1500	100	80	4	100	5
South Africa	100	185	56	15	2	100	0.5
Sweden	40	75	40	30	0.4	40	0.3
UK[e]	100	250	300	60	3	100	1
USA[c]	750	1400	150	210	20	750	8
USA	1500	2800	300	420	39	1500	17
Canada	150	600	375	150	3	150	0.8
Germany	200	600	1000	200	5	200	50
Japan[f]	125	150	400	100	-	125	0.5
Taiwan	150	300	100	120	4	150	1

Notes:
a: pH < 6.5
b: pH > 6.5
c: After applying sewage sludge to the soil.
d: Before applying sewage sludge to the soil.
e: The concentration of Cu, Ni and Zn at pH < 6; other elements are the concentration at pH ≥ 5.0.
f: As extracted by 1M HCl, Cu and Ni; extracted by 0.1M HCl, Hg, Pb, and Zn total concentration.

Source: Chen (2000)

Overall, levels defined as polluted for Zn are the highest of all the metals, thus suggesting that Zn may be among the more ubiquitous and/or the lesser toxic metals. Permissible levels of Cu and Cr are almost similar in magnitude. However, the greatest emphasis is on regulating Hg and Cd, for which the threshold levels are the lowest. The general trend depicting the concentration of metals defined to be the threshold between polluted and non-polluted is, in the order of more permissible to less: Zn, Cu, Cr, Pb, Ni, Cd, Hg.

Most governments who have not developed their own formal guidelines follow the "Dutch Standard" to support their decisions in assessing and monitoring sites. Dutch authorities are improving their soil quality criteria in light of new scientific work (Chen, 2000). Table 2.3 lists their guidelines according to a risk-based approach.

Table 2.3 Dutch reference values and intervention values (all mg/kg) for contaminants in soil based on ecotoxicity and human health considerations

Element	Reference Value Model	Reference Value for Standard Soil[A]	Ecotoxicity Intervention Value[B]	Human Health Intervention Value[C]
Cu	$15 + 0.6 \times (L + H)$	36	190	16,000
Zn	$50 + 1.5 \times (2L + H)$	140	720	56,000
Pb	$50 + (L + H)$	85	290	300
Ni	$10 + L$	35	210	6,600
Cd	$0.4 + 0.007 \times (L + 3H)$	0.8	12	35
Cr	$50 + 2L$	100	230	2,250
Hg	$0.2 + 0.0017 \times (2L + H)$	0.3	10	200

L: Clay content (%)
H: Organic matter content (%)
[A] Standard soil of 25% clay, 10% organic matter
[B] Maximum permissible risk levels beyond which the metal species is expected to be toxic to species present in the environment excluding humans
[C] Maximum permissible risk levels beyond which the metal species is expected to be toxic to human beings

Source: McLaughlin *et al.,* (2000)

The so called "reference values" or "target values" represent soils with negligible risks, while intervention values represent the maximum permissible risk levels due to contamination and which warrant cleanup.

2.2 ANTHROPOGENIC SOURCES OF METALS IN THE SOIL ENVIRONMENT

Bulk of the potentially contaminated soils are likely to be in the vicinity of urban and/or industrial areas. However, rural areas are also affected as a result of transportation of the contaminant (McLaughlin *et al.*, 2000). The major sources of heavy metals in the environment and their modes of dispersion are discussed in more detail below.

2.2.1 Urban sewage applications

Sewage sludge contains a wide range of heavy metals, some of which can be present in very high concentrations. The bulk of the metals entering a sewage treatment plant are retained in the sludge, the most common being Cd, Cr, Cu, Ni, Pb, Zn, and Hg (McLaren and Smith, 1996). In Suva, the treated sewage outflow empties into the Laucala Bay which is part of the lagoon also comprising the Suva Harbour. No published data can be found in the literature to determine if heavy metals are also being released through this source.

Composted urban waste applied to agricultural land for waste disposal and to improve soil fertility is a popular practice world-wide. The compost is rich in organic compounds and therefore suited to improve soil fertility (Giusquiani *et al.*, 1992).

Application of chemicals and sewage sludge to agricultural soils may result in accumulation of heavy metals in soils (Zhang *et al.*, 1997; Luo and Christie, 1998). Studies have shown that high levels of metals in soils can reduce plant growth and furthermore, the concentrations of some metals in plants can be increased substantially by sludge applications to the soil (McLaren and Smith, 1996).

2.2.2 Leaching and spillage

Soil can be contaminated as a result of spills or direct contact with contaminated waste streams such as airborne emissions, process solid wastes or leachate from waste materials (Evanko and Dzombak, 1997). Hazardous wastes from many sources can contain varying amounts of many different metals (Alloway, 1996).

Landfills are a major source of leachate, especially in urban centres. Uncontrolled fermentation reactions within a landfill decompose solid wastes resulting in the formation of leachate. The chemical composition of leachate is highly variable and site specific due to the diverse chemical composition of the deposited materials. However, a common characteristic is high organic strength and in many ways, this characteristic makes leachate resemble sewage (McLaren and Smith, 1996)

2.2.3 Metalliferous mining

This is an important source of contamination by a wide range of metals, especially Cd, Cu, Ni, Pb and Zn because ore bodies generally include a range of minerals containing both economically exploitable metals (in ore minerals) and uneconomic elements (in gangue minerals). Wind blown tailings (finely ground particles of ore and country rock) and ions in solution from the weathering of ore minerals in heaps of tailings tend to be the major sources of pollution from abandoned mine sites. An example is the direct discharge of tailings (usually containing Cr, Hg, arsenic [As], Pb and Ni) into the sea (submarine) and rivers (Huamain *et al.*, 1999).

In Fiji, at the time this research was carried out, the only mine in operation was a goldmine in Vatukoula, on the western side of Viti Levu. Water bodies from this particular area enter the sea on the western coast. Therefore, any possible discharge of heavy metals from this source through rivers would not be expected to directly affect the survey of heavy metals in the Suva Harbour. However, no evidence in the literature exists yet to verify this.

2.2.4 Metal smelting

This process produces metals from mined ores, and can often be a source of many different metals. These metals are mainly transported in air, and can be in the form of fine particles of ore, aerosol-sized oxide particles (especially important in the case of the more volatile elements such as Cd and Pb).

2.2.5 Metal-using industries

Metals can be sourced in gaseous/particulate emissions to the atmosphere, effluents to drains and solid wastes. Industries using metals include the electronics industry where metals are used in semiconductor contacts, circuits, solders and batteries (Cd, Ni, Pb and

Hg); pigments and paints (Pb, Cr, Cd and Zn); the plastics industry using metals as polymer stabilisers (Zn, Cd and Pb) and the chemical industry which uses metals as catalysts and electrodes including Hg and Pb.

2.2.6 Other sources

Metals used for pulp processing in the timber industry, corrosion and chemical transformation of metals used in structures (for example Cu and Pb on roofs and in pipes, Cr and Ni in stainless steel, Cd and Zn in rust preventative coatings on steel, Cu and Zn in brass fittings and Pb and Cr in painted sources) often release these metals in the environment (Alloway, 1996; McLaren and Smith, 1996).

Trace elements present in coals and oils include Cd, Zn and Cu, and fossil fuels often include Pb (to prevent engine 'knocking'). These metals can be present in the ash or gaseous/particulate emissions from combustion (Alloway, 1996).

Anti-fouling paints, percussion caps and fireworks are other sources of metals, particularly tin. Anti-fouling paints are used on marine craft to prevent the growth of marine organisms. The biotoxic characteristics of anti-fouling paints in the marine environment prompted the United States Environmental Protection Agency (USEPA) to suspend the registration of 43 mercury-containing paints in 1972. Nevertheless, the accumulation of metals from past applications has left increased amounts sorbed onto marine sediments (Raine *et al.*, 1995).

2.3 CHEMICAL FATE AND MOBILITY

The chemical form and speciation of a metal is important when considering its chemical fate and mobility in soils (Allen *et al.*, 1994). This is because reactions such as sorption from soil solution onto soil particles (Swift and McLaren, 1991), retention by complexation onto soil organic matter (OM) and occlusion in mineral structures (Almås *et al.*, 2000) may hinder metal mobility in soil by preventing its dissolution (Evanko and Dzombak, 1997). As long as heavy metals remain tightly bound to soil constituents, there will generally be little effect on the environment. When soil conditions change in such a way that heavy metals go into solution, this poses a direct environmental hazard (Harmsen, 1977). Mobilisation into the solution phase is required before the metal poses a risk to other components of the environment, and this is affected by the soil and environmental conditions. Different metals may undergo similar reactions, however, the extent and nature of these reactions vary under different conditions.

In soil, the main factors influencing metal adsorption or mobility are pH, OM and content of Fe and Mn oxides (Ross, 1994c). By quantifying these characteristics in field soils, it can be predicted how metals may respond to different soil conditions. The following sections discuss these responses on a metal-by-metal basis.

2.3.1 Copper

The sources of Cu include iron and steel industries, metal finishing industries, microelectronic components, wood preservatives, refuse disposal, manure, pesticides, sewage sludge and coal ash (Ross, 1994b).

In soil, Cu is very strongly retained by many soil colloids (McBride *et al.*, 1997; Ross, 1994a). The reason for this is the high affinity of the metal for organic matter (Luo and Christie, 1998; Ross,1994a) and oxides of iron and manganese (Ross, 1994a). Cu tends to be present primarily as a moderately labile or non-labile species (Jeffery and Uren, 1983). The labile species is found in association with the organic fraction, which ultimately plays a more vital role in determining its chemical distribution (Luo and Christie, 1998). Humic and fulvic acids bind Cu strongly (Dzombak and Morel, 1990; Senesi *et al.*, 1989) and if water-soluble, such complexes increase Cu concentration in soil solution (Giusquiani *et al.*, 1992). Copper has low susceptibility to changes in pH (Jeffery and Uren, 1983) and especially in terms of sorption at low concentrations (Ross, 1994a).

Generally, the occurrence of Cu in various chemical fractions in soil depends on the total Cu content of the soil. As the total Cu concentration in soils increases, the percentage of total Cu in the water-soluble, carbonate, ferromanganese-oxide-oxide and organic fractions increases accordingly, whilst Cu in the exchangeable and residual fraction decreases. Therefore as the extent of Cu contamination in soils increases, more Cu gets associated in the non-residual fractions, which increases the potential for Cu mobility and bioavailability in these soils (Ma and Rao, 1997).

2.3.2 Zinc

Sources of Zn in the environment include textiles, microelectronic components, fossil fuel combustion, phosphatic fertilisers, fungicides, corroding metals and sewage sludge (Ross, 1994b).

For Zn, pH and OM all influence sorption to the solid phase. Increased pH increases Zn sorption (Evanko and Dzombak, 1997; Harter, 1983; Shuman, 1985). The solubility of Zn is directly related to pH, which in turn affects adsorption of the metal with inorganic and organic colloids. Sorption of Zn to sediments including hydrous ferromanganese-oxides, clay minerals and OM is the primary fate of Zn.

Increased organic matter is also reported to increase Zn adsorption (Li and Shuman, 1996; Shuman, 1985). Fulvates in particular are important Zn species in the soil solution (Geering and Hodgson, 1969). Strong complexation of Zn by humic acids at pH levels around 4.5 - 5.0, and particulate organics has been suggested as a possible mechanism for Zn movement downward in the profile, where the metal would be in an exchangeable organic form (Li and Shuman, 1996).

While there is agreement on the importance of pH on Zn speciation, varying information appears in the literature about the exact form of the metal at different pH values. For instance, Jeffery and Uren (1983) have found that soil of pH values less than about 5.5 had more than 90 % of the Zn in solution existing as free metal ions or as labile complexes, the remainder existing as moderately labile complexes. Between pHs of 5.5 - 7.5, there is a decrease in the percentage of total metal that is labile, although about 70 % still remains labile. A further 22 % Zn remains as moderately labile species. The small percentage of non-labile Zn which occurs in solutions of high pH may be present complexed with organic matter, or it may be associated with colloidal material such as hydrous oxides. The study concluded that Zn solubility in soil is directly related to pH, and the OM content of soil plays only a small part in determining the mobility of the metal.

In another study, Zhang *et al.* (1997), found that Zn in the labile form was predominant at $pH \leq 6.1$, while the organically-bound form was dominant in soils with pH varying from 6.5 - 7.4. At $pH > 7.4$, the amorphous form of Zn was dominant.

It has been established that the significantly high amount of Zn in the non-residual soil fractions remains potentially in the bioavailable form compared with other metals (Ma and Rao, 1997; Smith *et al.*, 1995).

2.3.3 Cadmium

Mine tailings, iron and steel industry, metal finishing plants, microelectronic components, fossil fuel combustion and sewage sludge are common sources of Cd in the environment (Ross, 1994b).

Soils have a range of natural Cd concentrations, with a typical value being approximately 0.8 mg/kg. Most of the Cd in soil is present as inorganic material species associated with the clay mineral phase of the soil (vanLoon and Duffy, 2000) or as the free metal ion.

Cd is less prone to form stable metal-organic complexes compared to Cu and Pb (Almås *et al.*, 2000; Stevenson, 1977). Despite this, the association of Cd with organics in soil solution is not insignificant, and the existence of Cd-organic complexes therefore should not be overlooked. It has been shown that the addition of organic matter often increases soluble Cd concentration (Almås and Singh, 2001).

Increasing pH and OM both serve to increase Cd sorption (Christensen, 1984; Eriksson, 1989; Harter, 1983; Levi-Minzi *et al.*, 1976; Naidu *et al.*, 1994). However, for highly Cd-retentive soils, there is little effect of pH on Cd sorption at low initial Cd concentrations, since most of the added Cd remains sorbed. At any fixed pH, the percentage sorption decreases with increasing initial Cd concentration, probably indicating gradual saturation of sorbing sites (Naidu *et al.*, 1994).

Plant uptake of Cd is more dependant on the soil solution properties (like pH and total organic carbon concentration) than for other metals. The uptake of the latter is controlled by soil pH, but even more than the total concentration of the metal in soil (Almås and Singh, 2001).

2.3.4 Lead

Sources of Pb in the environment include mine tailings, metal finishing, iron and steel industries, fossil fuel combustion, lime (agriculture), pesticides, corroding metals and sewage sludge (Ross, 1994b).

Pb has been found predominantly in the organic matter fraction (Li and Shuman, 1996). It forms strong complexes with surfaces and soluble organics which tends to make it less mobile in soils, and also provides a greater opportunity for facilitated transport by any present soluble organics (Camobreco *et al.*, 1996). Concentrations of Pb in the exchangeable fraction have been reported to be very low. With decreasing organic matter content and increasing clay content with depth, the amount of residual-based Pb increases, making it the main Pb-containing fraction (Li and Shuman, 1996).

Increased pH increases Pb retention in soil. This is believed to be mainly by precipitation as lead carbonate at high pH (Griffin and Shimp, 1976). Oxides of iron, manganese and aluminium all have strong affinity for Pb (Kinniburgh *et al.*, 1976; McKenzie, 1980). With increasing pH, there is stronger association of Pb with organic matter (Gregson and

Alloway, 1984), while the stability of humic and fulvic acid-Pb complexes are more stable at high pH (Schnitzer and Skinner, 1967).

Due to the extremely low solubility of Pb, the metal has a long residence time in soils. (Rooney *et al.*, 1999). The primary processes that influence the fate of Pb in soil include adsorption, ion exchange, precipitation and complexation with sorbed organic matter. These processes limit the amount of the metal that can be transported into the surface water or groundwater (Smith *et al.*, 1995).

2.3.5 Nickel

Nickel is found in the iron and steel industry, metal finishing plants, microelectronic components and sewage sludge (Ross, 1994b).

Sawhney *et al.* (1994), in a study of leachability of metals from a composting heap found that out of five metals, Cd, Cu, Pb, Zn and Ni, Ni was the most mobile. These results may suggest a low affinity of the metal for organic matter.

Generally, less than 70 to 75 % of Ni is retained in the soil at pH 7.0 or above in the surface soil. Rapid increase in soil retention of the metal does not occur until pH is at or greater than 7.0. Thus the amount of Ni retained by soil is strongly influenced by the soil pH (Harter, 1983).

In soil and sediments, the metal does not display any clearly discernible pattern, however, a high proportion of Ni has been found to be in the soluble/exchangeable forms (Förstner, 1986). In another study Ni was positively correlated to clay content in predominantly clay and clay loam soils. Distribution was also found to be dependant on soil horizonation. Furthermore, Ni does not bioaccumulate in soil surface horizons, and since it is a non-essential element, biogeochemical cycling also does not influence Ni levels in any way, as compared to essential elements like Cu and Zn (Lee *et al.*, 1997).

2.3.6 Chromium

There are relatively few sources of Cr. These include metal finishing, plastics and sewage sludge.

McGrath (1987) found soils amended with metal-containing manure have only a very small fraction (0.03 %) of Cr removed. An indicator of the very low mobility of the metal is its residence time as shown in Table 2.4.

Table 2.4 Residence times of metals

Metal	**Residence time* (years)**
Zn	3,700
Ni	5,700
Cd	7,500
Cu	13,100
Pb	35,000
Cr	70,000

*No. of years of same cropping regime required to remove 100 % of the added metals, given to the nearest 100 years.

Source: McGrath (1987)

At low pH (< 4), Cr (+3) forms soluble complexes with ammonia; the hydroxyl, chloride, fluoride, cyanide and sulphate anions, and soluble organic ligands. Major Cr (+6) species include chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), which precipitate readily in the presence of metal cations. Chromate and dichromate also adsorb on soil surfaces, especially on ferromanganese oxides (Smith *et al.*, 1995).

Cr mobility depends on sorption characteristics of the soil, including clay content, iron-oxide content and the amount of organic matter present. As pH increases, the leachability of Cr (+6) increases as well (Smith *et al.*, 1995).

2.3.7 Mercury

As was in the case of Cr, the sources of Hg are few and include, apart from geothermal activity (a major source) plastics, sewage sludge (Ross, 1994b) and mine tailings (Smith *et al.*, 1995; Ross, 1994b).

In soil, a Hg compound can be adsorbed by soil colloids, precipitated as insoluble compounds, leached to lower depths in the soil profile, lost to the atmosphere or absorbed by plants. Of these, the adsorption process is believed to dominate initially, and to a certain extent determines the amount of Hg remains in the soil solution. The remaining Hg in solution can be eventually precipitated, volatilised, leached or taken up by plant roots (Hogg *et al.*, 1978).

The redox potential and pH of the system determine the stable forms of Hg that will be present. When mildly reducing conditions exist, organic or inorganic mercury may be reduced to elemental mercury, which may then be converted to alkylated forms by biotic or abiotic processes (Smith *et al.,* 1995). Hg has a particularly high affinity for organic species which results in its accumulation in biota. The affinity of the metal for organic species and its transformation to alkylated forms strongly influence its environment effects (Preston and Chester, 1996).

Inorganic Hg may be methylated in the environment to monomethyl (+1)- and dimethylmercury (+2) species (Craig, 1986; Weiner, 2000). It is this ability of the various inorganic species to become transformed to the more toxic methylmercury (+2) cation which is the most important transformation of the metal. The cation strongly binds to sulphur residues in human tissues and tends to accumulate for up to 70 days (compared to 4 days for the inorganic species). Furthermore, the ability of methylmercury (+2) to solubilize in lipid media reduces its rate of elimination from organisms, compared to the inorganic forms (Craig, 1986).

The elemental (boiling point 39 ^{0}C) and alkylated forms of Hg are volatile (Craig, 1986; Weiner, 2000). Due to the low solubility of the element, atmospheric diffusion is an important dispersion route for alkylated Hg (Craig, 1986). The alkylated forms, which are the most toxic (Weiner, 2000), are not only soluble in water but also volatile in air (Craig, 1986; Smith *et al.*, 1995).

Sorption to soils, sediments and humic materials is an important mechanism for the removal of Hg from solution. Sorption is pH-dependant, and increases as pH increases. Hg may also be removed from solution by co-precipitation with sulfides (Smith *et al.*, 1995).

Under anaerobic conditions, both organic and inorganic forms of Hg may be converted to alkylated forms by microbial activity, such as by sulphur-reducing bacteria. In such conditions, the metal may often get reduced to its elemental form by demethylation of methyl mercury, or by reduction of Hg (+2). Acidic conditions ($pH < 4$) also favour the formation of methyl mercury, whereas higher pH leads to precipitation of Hg as solid

HgS. In soils, Hg is very strongly retained (McLaughlin *et al.*, 2000), and exists mostly as HgS, with a concentration range of 0.01 to 2.0 μg/g (Craig, 1986).

2.4 MECHANISM OF TOXICITY

It must be appreciated that metals may exert different effects on organisms depending on the element as well as the chemical form. Examination of this is beyond the scope of this discussion and interested readers are referred to other works in the literature (for example Chaney *et al.*, 1999; Ellis, 1989; Harrison, 1990; Weiner, 2000).

However, the general biochemical mechanism of toxic action arises from the strong affinity of the metal cations for sulphur. Thus, sulfhydryl groups, —**SH**, which occur commonly in enzymes that control the rate of critical metabolic reactions in the human body, readily attach themselves to ingested heavy metal cations or molecules containing the metals. The resultant metal-sulphur bonding affects the entire enzyme, preventing it from functioning normally. In this manner, human health is adversely affected, sometimes fatally (Baird, 1995).

In addition to the potentially toxic effects of metals on plant growth and their introduction into the food chain, current concern is focusing on the effects of high soil metal concentrations on soil biological activity. There is evidence which shows that long term exposure to elevated metal concentrations can reduce soil microbial biomass levels, inhibit N_2 fixation by both free-living and symbiotic organisms and reduce enzyme activities (McLaren and Smith, 1996).

2.5 REMEDIATION OF CONTAMINATED SOILS

Several technologies exist for the remediation of sites contaminated with metals. Of these, three major categories of general approaches to remediation are: *isolation*, *immobilisation*, and *toxicity reduction* (Evanko and Dzombak, 1997). As is usually the case, combinations of one or more of these approaches are often used for effective treatment of a contaminated site.

The major remediation techniques are discussed briefly in the following sections, followed by a more detailed discussion of phytoremediation which was considered in this study as a possible remediation method for the studied site.

2.5.1 Isolation

Isolation techniques attempt to prevent the transport of contaminants from the affected site by containing them within a designated area, thus preventing the spread of the contaminant. These technologies are employed when other treatment methods are not physically or economically feasible for a site. Capping and creation of barriers are two methods of isolating contaminants.

2.5.2 Immobilisation

Immobilisation techniques are designed to reduce or, where possible, eliminate the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. Most immobilisation technologies can be performed ex-situ or in-situ. Since the major form of contaminant transport is through groundwater, any possible mobility of the contaminant is usually decreased by physically restricting contact between the contaminant and the surrounding groundwater. Alternatively, the contaminant is chemically altered to make it more stable with respect to dissolution in groundwater. Therefore, the aqueous and solid phase chemistry of the metals of concern is important to immobilisation by these techniques.

Two methods which use the technique are solidification/stabilisation and vitrification. Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilisation usually utilises a chemical reaction to convert the waste to a less mobile form. The general approach to both solidification and stabilisation is to mix or inject treatment agents to the contaminated soils, followed by applying inorganic binders such as cement and fly ash and organic binders such as bitumen around the waste. The precipitation of metal hydroxides within the solid matrix immobilises the metals (Evanko and Dzombak, 1997).

Vitrification involves melting and fusion of materials at temperatures normally in excess of 1600 ^{0}C followed by rapid cooling into a non-crystalline amorphous form (LaGrega *et al.*, 1994). The high temperature may also volatilise and/or destroy organic contaminants or volatile metal species (such as Hg) that have to be collected for treatment or disposal. Most soils can be treated by vitrification and a wide variety of inorganic and organic contaminants can be targeted.

2.5.3 Toxicity and/or mobility reduction / detoxification

Chemical and/or biological processes can be used to alter the form of metal contaminants in order to decrease their toxicity or mobility (Evanko and Dzombak, 1997). Detoxification may be achieved by any mechanism that changes a chemical constituent into another less- or non-toxic form, such as the reduction of Cr (VI) to Cr (III) during stabilisation with cement-based materials. A number of fixation systems can be used to destroy the Cr (VI) by reducing its valence state, of which elemental iron has proved to be amongst the most effective (LaGrega *et al.*, 1994). Such low oxidation state chemical species can serve as electron donors for the reduction of higher oxidation-state contaminants (Evanko and Dzombak, 1997).

Metals may occur in different forms, and often the extent of toxicity differs among the forms, such as that for Hg (Craig, 1986; Preston and Chester, 1996; Smith *et al.*, 1995) and Cr (Craig, 1986; McLaughlin *et al.*, 2000; vanLoon and Duffy, 2000). The most appropriate method of treatment depends upon the form of the metal, its concentration, pH, the matrix of the waste material and the desired effluent standard.

The most commonly used technique in treating metal wastes is precipitation using pH adjustment. The optimum pH for precipitation varies depending on the metal, and where several metals are involved, a compromise pH (mostly in the range 8.0 - 9.0) is used. Following precipitation, normally separation of the liquid and solid phases is carried out (James and McDougall, 1996).

Metals-contaminated sites can be remediated using techniques designed to extract the contaminated fraction from the rest of the soil, either in-situ or ex-situ. Extraction is achieved by either contacting the contaminated soil with a solution containing an extracting agent or applying electrokinetic processes. The contaminated fraction of soil is separated from the remaining soil disposed or further treated if necessary (Evanko and Dzombak, 1997).

The solvents used in such techniques are usually too expensive for single-use, and often , the contaminants are too highly concentrated in the extract. Thus, the spent solvent from the operation almost always needs further treatment to reclaim the solvent for reuse and to further reduce the volume in which the contaminant is contained. Some solvent re-purification methods include the use of distillation or adsorption (James and McDougall, 1996).

Biological treatment technologies available for remediation of metals-contaminated sites exploit natural biological processes that allow certain plants and microorganisms to aid in the remediation process (Evanko and Dzombak, 1997; LaGrega *et al.*, 1994). Previously, these methods were restricted to the removal of organic chemicals only, but now have been successfully tried on metals as well (Schnoor, 1997). Microorganisms, particularly bacteria, have been known for a long time to obtain metabolic energy from oxidation-reduction reactions that they catalyse in the form of enzymatic attacks. Such activities in the environment have earlier been applied in the western United States to stimulate microbial leaching of Cu ores, a process termed bio-leaching. For instance, *Thiobacillus ferrooxidans* has been used for the transformation of Hg^{2+} ions to volatile elemental Hg, while vanadium (V) has been converted to the less-toxic vanadium (IV) in the environment by *Thiobacillus thiooxidans* (Olson, 1986).

Phytoremediation (also known as green remediation, botano-remediation, agroremediation and vegetative remediation) is another form of biological remediation. It can be defined as the use of plants to partially or substantially remediate selected contaminants in contaminated soil, sludge, sediment, ground water, surface water and waste water (Pivetz, 2001). Such plants, referred to as hyperaccumulators, have the ability and capacity to absorb unusually large amounts of metals in comparison to other plants (USEPA, 1998). The species to be absorbed does not necessarily have to be a component of the nutrient diet of the plant.

Since phytoremediation constitutes a major part of this discussion, it is treated as a separate section below.

2.6 THE HISTORY OF PHYTOREMEDIATION

The study of phytoremediation began with the work of three pioneering scientists. The first A. Baumann, who in 1885 analysed specimens of *Viola calaminaria* and *Thlaspi calaminare* growing over the calamine deposits of Aachen, Germany. He found over 1% (dry weight) Zn in these plants and recorded the first of the hyperaccumulators of any heavy metal. In the 1930s, O. A. Beath and his co-workers discovered hyperaccumulation of selenium in *Astragalus* plants from the Western USA. Finally, O. Vergnano Gambi from the University of Florence together with C. Minguzzi in 1948 discovered the unusual hyperaccumulation of nickel by the Tuscan serpentine plant *Alyssum bertolonii* (Brooks, 1998; Brown, 1995).

Phytoremediation has emerged as an alternative to the engineering and/or chemical-based remediation techniques. In this approach, plants are used to absorb contaminants from the soil and translocate them to the shoots. Pollutants are then removed by harvesting the above-ground tissue for subsequent volume reduction (for example by dry-ashing or composting) and storage (Chaney *et al.*, 2000; Ebbs *et al.*, 1997). The process of phytoremediation is cost-effective and can remediate a site without dramatically disturbing the landscape (Ebbs *et al.*, 1997). The overall process of phytoremediation takes advantage of the fact that a living plant can be compared to a solar-driven pump which can extract and concentrate particular substances from the environment, for example, heavy metals, nutrients and organic chemicals. The accumulation of the specific elements could also allow the ash of the plant bio-mass to be recycled as an ore. In that way, the value of the metals in the plant bio-mass could offset part of the cost of soil decontamination and support “phytomining” of some elements as a commercial venture (Chaney *et al.*, 2000).

The initial emphasis in phytoremediation research has been on a small number of wild plants, termed hyperaccumulators, that are able to accumulate high concentrations of metals (Klassen *et al.*, 2000). The term "hyperaccumulator" was coined by Brooks and his co-workers in 1977, to describe plants containing more than 1000 µg/g (0.1 %) nickel in dry material (Brooks, 1998).

Phytoremediation may be grouped into two categories: ex in-situ techniques, which require removal of the contaminated soil or groundwater to the treatment site; and in-situ methods, which remediate without excavation of contaminated soil or pumping off contaminated groundwater. In-situ techniques are favoured due to their low cost and reduced impact on the ecosystem.

Phytoremediation encompasses a number of different methods that can lead to contaminant degradation, removal (through accumulation or dissipation), or immobilisation. These are summarised in Table 2.5.

Table 2.5 Different methods within the phytoremediation technique

Principle	Method	Description
Degradation (for destruction or alteration of organic contaminants)	*Rhizodegradation*	Enhancement of biodegradation in the below-ground root zone by microorganisms.
	Phytodegradation	Contaminant uptake and metabolism above (within the root, stem or leaves), or below-ground.
Accumulation (for containment or removal of organic and/or metal contaminants)	*Phytoextraction*	Contaminant uptake and accumulation for removal.
	Rhizofiltration	Contaminant adsorption on roots for containment and/or removal.
Dissipation (for removal of organic and/or inorganic contaminants into the atmosphere)	*Phytovolatilisation*	Contaminant uptake and volatilisation.
Immobilisation (for containment of organic and/or inorganic contaminants)	*Hydraulic control*	Control of groundwater flow by plant uptake of water.
	Phytostabilisation	Contaminant immobilisation in the soil

Adapted from Pivetz (2001)

2.6.1 Methods directly applicable to metals-contaminated sites

Generally, the common strategies for phytoremediation of metal-contaminated soils are: phytoextraction, rhizofiltration and phytostabilization (Chaney *et al.*, 2000; USEPA, 1998). In addition to these, phytovolatilization appears to be relevant to remediation of soils rich in Hg. However, other elements do not readily form volatile chemical species in the soil environment or in plant shoots, so the process cannot be applied to these elements, thus limiting its overall application (Chaney *et al.,* 2000). Each of these is discussed below.

Phytoextraction, also called phytoaccumulation, refers to the uptake and translocation of metal contaminants in the soil by plant roots into the aboveground portions of the plants (USEPA, 1998). It has been known for well over a century that plants extract significant quantities of the major nutrients phosphorus and potassium from soils. Some time later, trace elements received that classification because most plants normally take them up in very small quantities.

In the phytoextraction technique, one or a combination of hyperaccumulators is selected and planted at a particular site based on the type of metals present and other site conditions. After the plants have been allowed to grow for some time, they are harvested and either incinerated or composted to recycle the metals. This procedure may be repeated as necessary to bring soil contaminant levels down to allowable limits. If plants are incinerated, the ash must be disposed of in a hazardous waste landfill, but the volume of ash will be less than 10% of the volume that would be created if the contaminated soil itself were dug up for treatment.

Metals such as nickel, zinc, and copper are the best candidates for removal by phytoextraction because it has been shown that they are preferred by a majority of the approximately 400 known plants that uptake and absorb unusually large amounts of metals. Plants that absorb lead and chromium are currently being studied and tested.

However, owing to the time needed for remediation and its associated costs (McGrath, 1998), phytoextraction may not be an acceptable technology for the Lami Dump.

The second strategy, rhizofiltration is the adsorption or precipitation onto roots, or absorption into roots, of contaminants that are in solution surrounding the root zone. The process is similar to phytoextraction, but in rhizofiltration, plant roots are used to clean up contaminated water, rather than soil (McGrath, 1998; USEPA, 1998). The heavy metals, Pb, Cu, Co and Zn are known to have been extracted from water (Raskin, 1997).

Phytostabilization, the third strategy uses certain plants to immobilise contaminants in the soil and groundwater into persistently non-bioavailable forms, thus rendering them harmless (Chaney *et al.*, 2000; Raskin, 1997; USEPA, 1998). This process reduces the bioavailability of the contaminants for entry into the food chain (USEPA, 1998).

The actual technique may incorporate soil amendments rich in iron, phosphate and limestone equivalent, which are used to transform metals into forms with lower bioavailability and/or phytoavailability (Chaney *et al.*, 2000).

Phytostabilization appears to have strong promise for two toxic elements, chromium and lead. Reduction of Cr^{6+}, which poses an environmental risk, to Cr^{3+}, which is highly insoluble and not shown to pose an environmental risk, by deep rooted plants can be very effective (James and McDougall, 1996). Chemical species of Pb in soil are usually somewhat bioavailable if the soil is ingested, while a Pb phosphate mineral, chloropyromorphite, is both extremely insoluble and non-bioavailable, but it is formed slowly, apparently because the reactants have low solubility. Roots of *Agrostis capillaris* growing in highly contaminated Pb/Zn mine wastes caused the formation of pyromorphite from soil Pb and phosphate (Chaney *et al.*, 1997).

Phytostabilization can be used to re-establish a vegetative cover at sites where natural vegetation is lacking due to high metal concentrations in surface soils, or physical disturbances to surface materials (USEPA, 1998). For Lami, this technique may be appropriate in controlling leaching, immobilising heavy metals and reducing erosion at the same time.

Plants that hyperaccumulate metals are ideal subjects for phytochemical studies, because their elemental concentrations are by definition so high, that milligram quantities of the target organometallic complexes can be isolated and studied outside the plant. Conventional methods of studying metals in plants that do not hyperaccumulate these elements have previously had to rely on use of radioactive tracers, or carrying out these studies within the plant, or by use of extracts that do not contain enough of the target material for actual separation and storage for future use (Brooks, 1998).

2.6.2 Characteristics of plants ideal for phytoremediation purposes

The main requirement of a plant to be used for phytoremediation is that it should be a hyperaccumulator (Brown, 1995; Miller, 1996). Tissues of hyperaccumulators can contain from 1,000 - 30,000 mg/kg of certain heavy metals (USDA-ARS, 1995). Secondly, the use of trees are preferable over small plants because tree roots penetrate more deeply into the ground, thus allowing the treatment of deeper contamination (USEPA, 1998).

A plant should have the ability to translocate an element from roots to shoots at high rates. Normally, root Zn, Cd or Ni concentrations are ten or more times higher than shoot concentrations, but in hyperaccumulators, the reverse occurs. There should also be a rapid uptake rate for the elements at levels that occur in soil solution. Often, hyperaccumulators experience toxicity at different concentrations for different metals. Thus prior to applying the technique at a site, the tolerance level of the plants should be determined or known (Chaney *et al.*, 1997).

To make phytoremediation viable, fast-growing trees/plants are needed. Since plants with naturally fast rates of growth are rare, attempts are now being made to create plants that grow fast. An example of such an exercise has been one carried out by scientists, which involved implanting genes from yeast into tobacco plants and the mouse-eared cress (Pearce, 1996). Tobacco has been found to be an ideal remover of strontium (Goetz, 1997).

2.6.3 Applications of phytoremediation

The low-squatting perennial plant penny cress (*Thlaspi caerulenscens*) is one of a few known plants that absorb heavy metals in large concentrations (Brown, 1995). Penny cress, as it is commonly known, is a wild herb found on Zn and nickel (Ni) rich soils in many countries. When tested at Pig's Eye Landfill in St. Paul, Minnesota, it proved especially good at removing Zn and Cd, accumulating 30,000 mg/kg of Zn in its leaves, without yield reduction. Most plants experience Zn toxicity by the time they contain 500 mg/kg Zn (USDA - ARS, 1995). *T. caerulenscens*'s natural survival in deadly territory has been attributed to its evolved ways to filter toxins (Brown, 1995).

In another research carried out by Robinson *et al.* (1998), *T. caerulenscens* was studied by pot trials in plant growth units and in populations of wild plants growing over Cd/Zn base metal mine wastes at Les Malines in Southern France. The trials on *T. caerulenscens* showed it would be entirely feasible for removal of low levels of Cd, where only a single crop would be needed to halve a Cd content of 10 μg/g in the soil. However, for Zn, the study concluded that to remediate elevated Zn concentrations within an economic time frame of 10 years would be impossible because of the lower bioaccumulation coefficient for this element.

Another study by Brown *et al.* (1994) at the University of Maryland confirmed that *T. caerulenscens* showed much greater tolerance to the metals than other plants (up to 18,455 mg/kg Zn and 1020 mg/kg Cd). The species was also more effective at translocating both Zn and Cd from soil to plant shoots.

However, the genus *Thlaspi*'s small size and relatively low growth rate are two drawbacks of using plants of this genus for phytoremediation purposes. In this regard, another genus, *Brassica* has been found to perform better. The broccoli and Indian mustard belong to this genus, and which have been part of numerous studies in removing heavy metals and radioactivity (USEPA, 1998; Raskin, 1997; Brown, 1995). They have the added advantage that they are faster growing and can take out more metals out of the soil.

The Indian mustard (*Brassica juncea*) has been employed to cleanup heavy metals and radionuclides from Trenton, New Jersey, and radionuclides from Upton, New York. Both areas were subjected to phytoextraction (USEPA, 1998). Another member of the same genus, *Brassica nigra*, has shown considerable promise in hyperaccumulating Zn and Ni (Brown, 1995).

In any case, it is *Brassica juncea* has been commonly used around the world for phytoremediation applications. This species alone can absorb Pb, Cr, Cd, Ni, Zn and Cu in relatively high amounts. In lab experiments, the most efficient cultivar accumulated 3.5% of its dry body weight in lead (Brown, 1995). These plants have also been used to cleanup the 1986 Chernobyl nuclear accident site, particularly to radioactive metals such as strontium and caesium. The results showed a lot of promise and measurable decreases in soil pollution.

In the United States, the possibility of using *Brassica juncea* for removing naturally occurring selenium from soil is being explored. Once leached into groundwater, this nutrient can poison wildlife and livestock. Laboratory research has demonstrated that *Brassica juncea* not only takes up selenium, but converts it into dimethyl selenide, a non-toxic gas (Raskin, 1997).

2.6.4 Limitations of Phytoremediation

Many hyperaccumulators are slow-growing, and have a low biomass. Therefore, the technique suffers from an inability to assure clean-up below action levels in a short period of time (Miller, 1996; Schnoor, 1997).

Another significant disadvantage of phytoremediation is the depth limitation due to the generally shallow nature of plant roots. Effective phytoremediation generally requires that the contaminants be within 3 feet from the soil surface. Thus sites where the contamination is deeper than 3 feet may not be appropriate for complete remediation by the phytoremediation process (Miller, 1996; Pivetz, 2001; Schnoor, 1997).

A phytoremediation system can lose its effectiveness with season, such as winter (when plant growth slows or stops), the occurrence of extreme events such as droughts or floods as well as diseases and/or pests which damage vegetation. In anticipation of such events, a backup remedial technology may be necessary. However, in the Pacific, given its warm tropical climate, this problem is expected to be of relatively minor significance.

As far as plants are concerned, noxious or invasive hyperaccumulators can negatively impact the local ecosystem by escaping the phytoremediation site and then out-competing and eliminating local species. Other potential problems include allergy-causing pollen, plant debris such as fallen leaves or released seeds (Pivetz, 2001).

Potential transfer of contaminants via food chains is also possible. Bio-concentration in plants and subsequent ingestion of the metals by ecosystem consumers is a concern, especially as the levels are expected to be magnified along the food chains due to the bio-accumulative nature of the metals.

Plant species or varieties of one species can vary significantly in their efficacy for phytoremediation. This may arise from their response to a metal, the concentration of the contaminant metal, in the plant's uptake of the metal or the ability of the plant to grow under specific soil and climatic conditions. For example, *Brassica juncea* only hyperaccumulates Pb if ethylenediaminetetraacetic acid (EDTA) is added to the soil (Huang and Cunningham, 1996). However, in adding EDTA to induce hyperaccumulation in this manner, there is an accompanying risk of contaminating groundwater with the EDTA-mobilised heavy metals. Due to these factors, phytoremediation may not be an "off-the-shelf" technology. Rather, site-specific studies may always be necessary prior to its implementation (Pivetz, 2001; Schnoor, 1997).

2.6.5 Advantages of phytoremediation

Phytoremediation costs indicate substantial savings over the cost of traditional technologies, especially for large areas having low to moderately contaminated surface soils. The technique has been perceived to be a more environmentally-friendly and low-tech alternative to more active and intrusive remedial methods. Remediation goals are achieved without resorting to the use of other (often toxic) chemicals for cleanup.

Phytoremediation can be applied in-situ to remediate shallow soils, which can be left at site after contaminant removal, rather than having to be disposed or isolated.

The technique does not have the destructive impact on soil fertility and structure that the more vigorous traditional technologies have. Instead, the presence of plants is likely to improve the overall condition of the soil. The topsoil is left in a usable condition and may be reclaimed for agricultural use (Miller, 1996; Pivetz, 2001).

2.7 REMEDIATION FOR THE LAMI DUMP

The remediation methods that have been examined in the preceding sections are relatively expensive to implement and often pose other accompanying demands. For instance, if the cost of isolating, chemically immobilising, decomposing at high heat or modifying to less-toxic forms could be met, the disposal of chemicals that have been used for techniques such as chemical modification often poses another challenge. In the case of Lami, where the site may possibly require remediation, the costs of such techniques could exceed the benefits. In this regard, phytoremediation offers a less expensive and easier-to-implement solution. It is worthwhile to examine this technique for Lami, since it is both inexpensive and not restricting in size.

2.8 CHAPTER CONCLUSION

It is difficult to ascertain whether a site containing heavy metals is polluted and/or contaminated without first considering the geology of the area concerned, which determines what the natural or background concentrations are at the site. It means therefore, the adoption of numerous criteria world-wide which prescribe threshold values for contamination must be treated with caution.

It is important to note that pollution is not solely determined by the total amounts of metals present from a site. Metal toxicity often depends on the species of the metal. In turn, the form of existence and mobility of the metal is determined to a large extent by the prevalent soil conditions such as soil pH, temperature, moisture, mineralogy and composition. Thus, overall, the soil conditions present are among the most important factors controlling metal toxicity.

When a site is classified as contaminated, the magnitude of the affected area, the depth to which the contaminant has infiltrated and the metals involved should be the major considerations when undertaking a cost-benefit analysis to select an appropriate remediation procedure.

In developing island states of the South Pacific, where the extent of pollution and accompanying remediation resources are low, phytoremediation may offer a feasible option. Like any other remediation technique, it has its advantages and limitations, but for this still-emerging new technology, further research may eliminate current shortcomings and possibly elevate phytoremediation to be amongst the most viable technology for the future.

3.0 METHODOLOGY

3.1 DESCRIPTION OF STUDY AREA

The Lami dump is located one kilometre to the west of Suva, the capital of the Fiji Islands, in the southern part of Viti Levu, the largest island in the archipelago. The position of the dump in the Suva area has already been given in Figure 1 (Section 1.3). The dump surroundings and the location of the sampling sites within the dump, labelled as **A, B,** and **C** are shown in Figure 3.1.

3.1.1 Climate

Figure 3.2(a) shows the mean monthly temperatures for the Lami area over the 2000 - 2001 period. July - September were the cooler months, while January - April defined the warm season. The difference between the highest mean monthly temperature and lowest mean monthly temperature was 10.9 ^{0}C. Overall, temperatures at lower altitudes around Fiji are usually fairly uniform. On the windward side of the islands, temperatures are lower by 1 - 2 ^{0}C than on the leeward side (Watling and Chape, 1993). The Lami area, being located on the windward side is usually cooler, and displays wide variation between the summer and winter temperatures as shown in Figure 3.2(a).

Rainfall is highly variable over the group. It is plentiful between December to April especially over the larger islands, but in May to October, it is often deficient. In the dry season, the heaviest rainfall occurs on the windward (south-east) sides of the mountainous islands. This includes the Lami area. In the Navua-Suva area, places have

Figure 3.1 Sketch of sampling sites in the dump

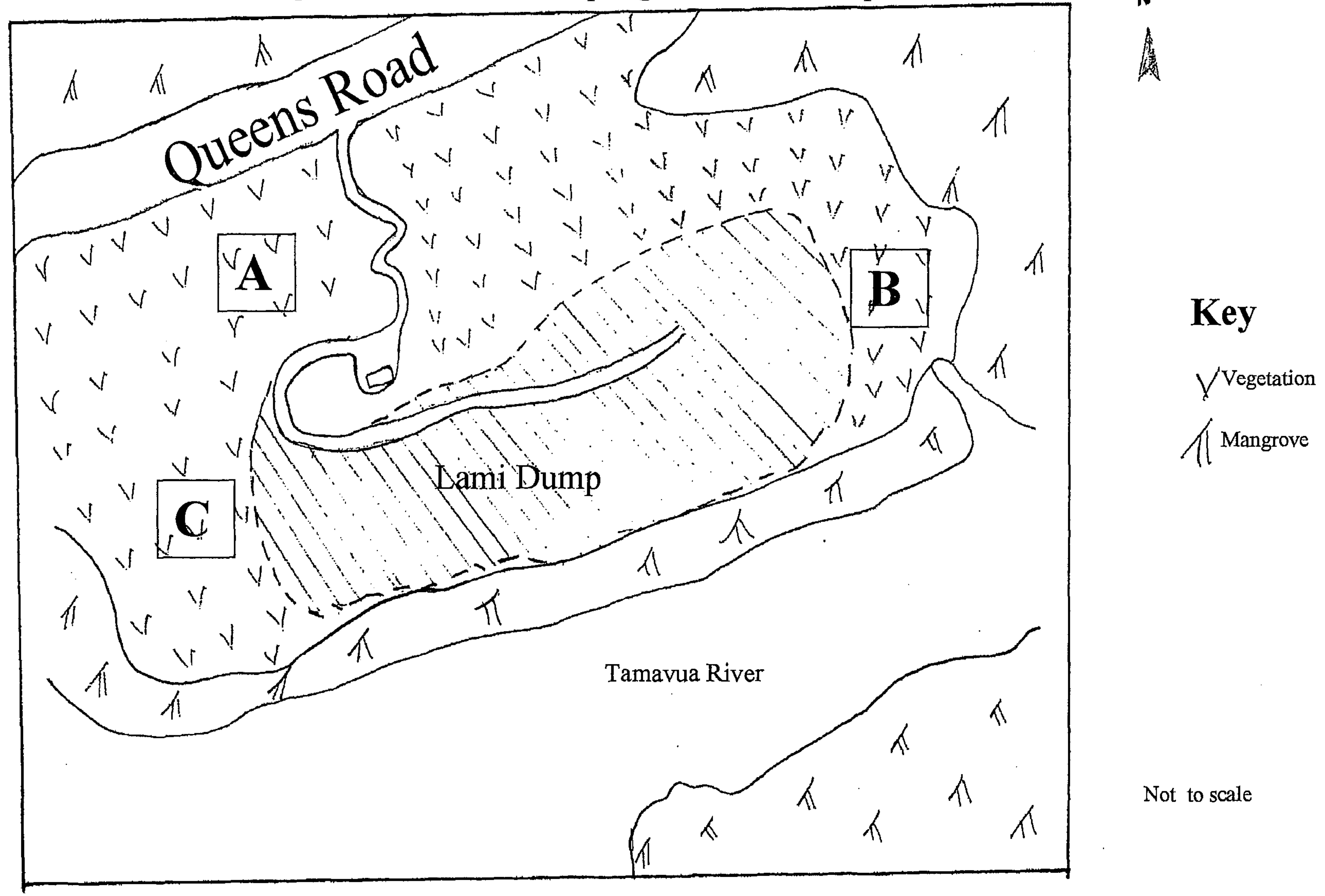


Figure 3.2(a) Air temperature data

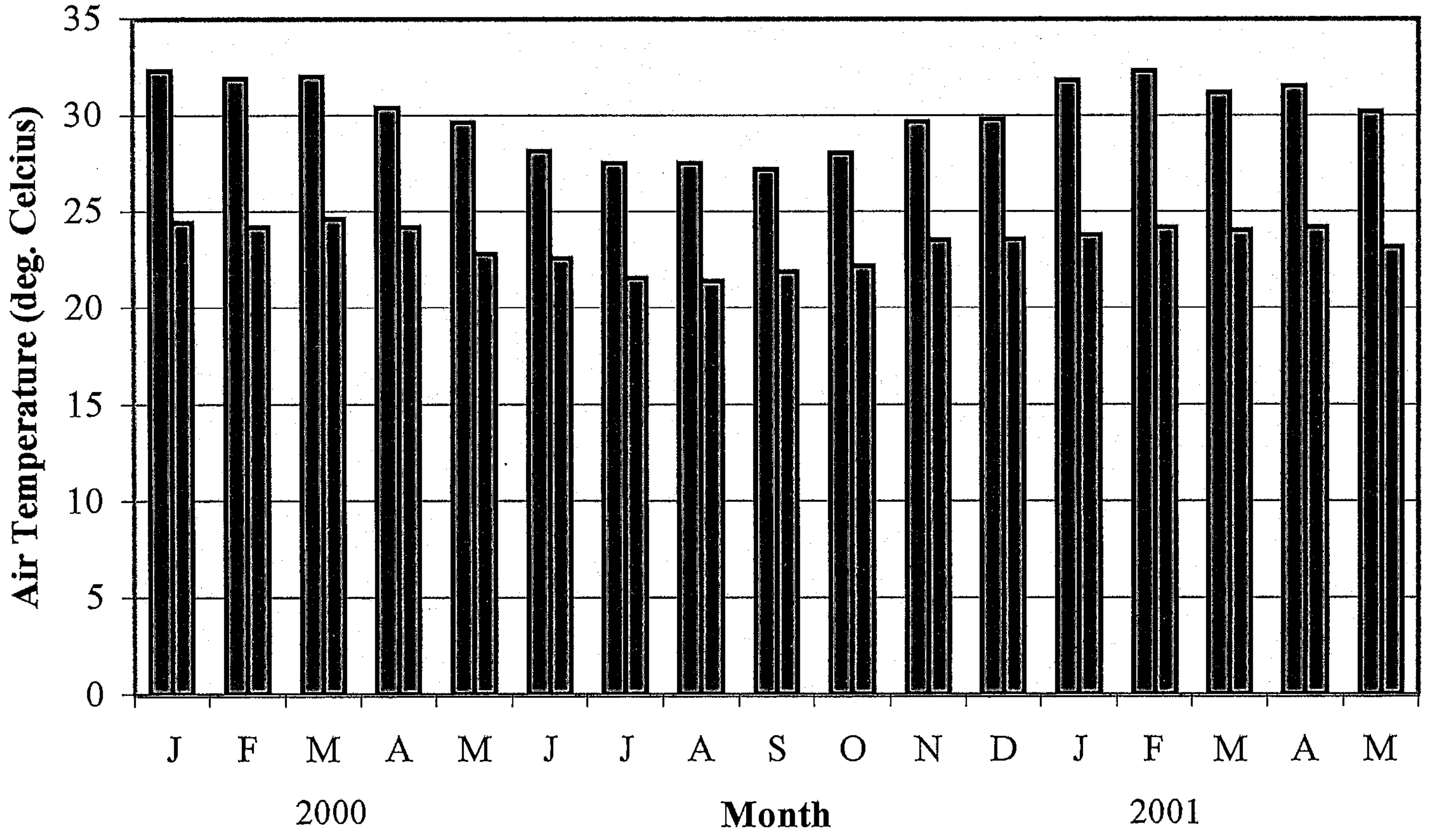


Figure 3.2(b) Rainfall data

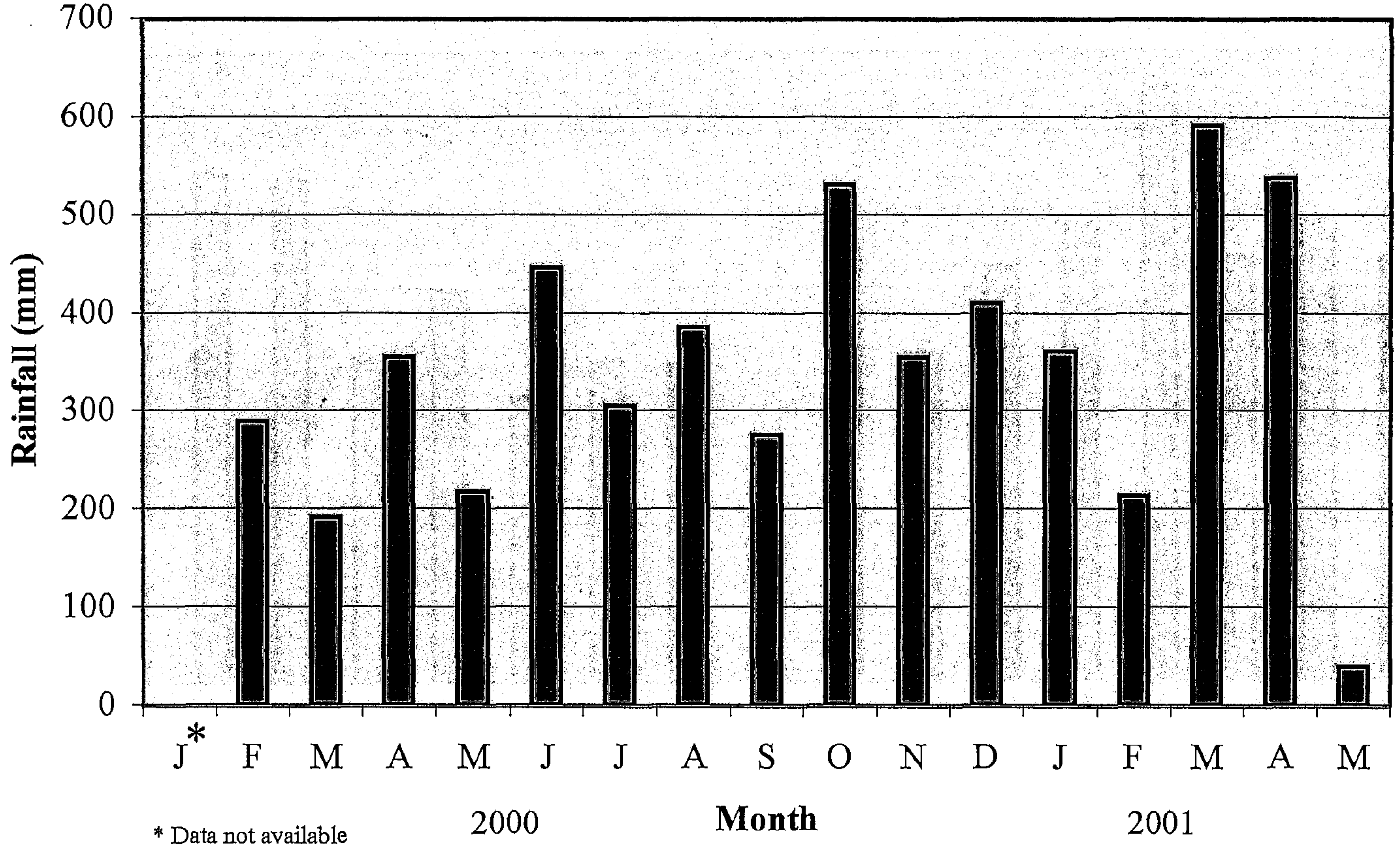
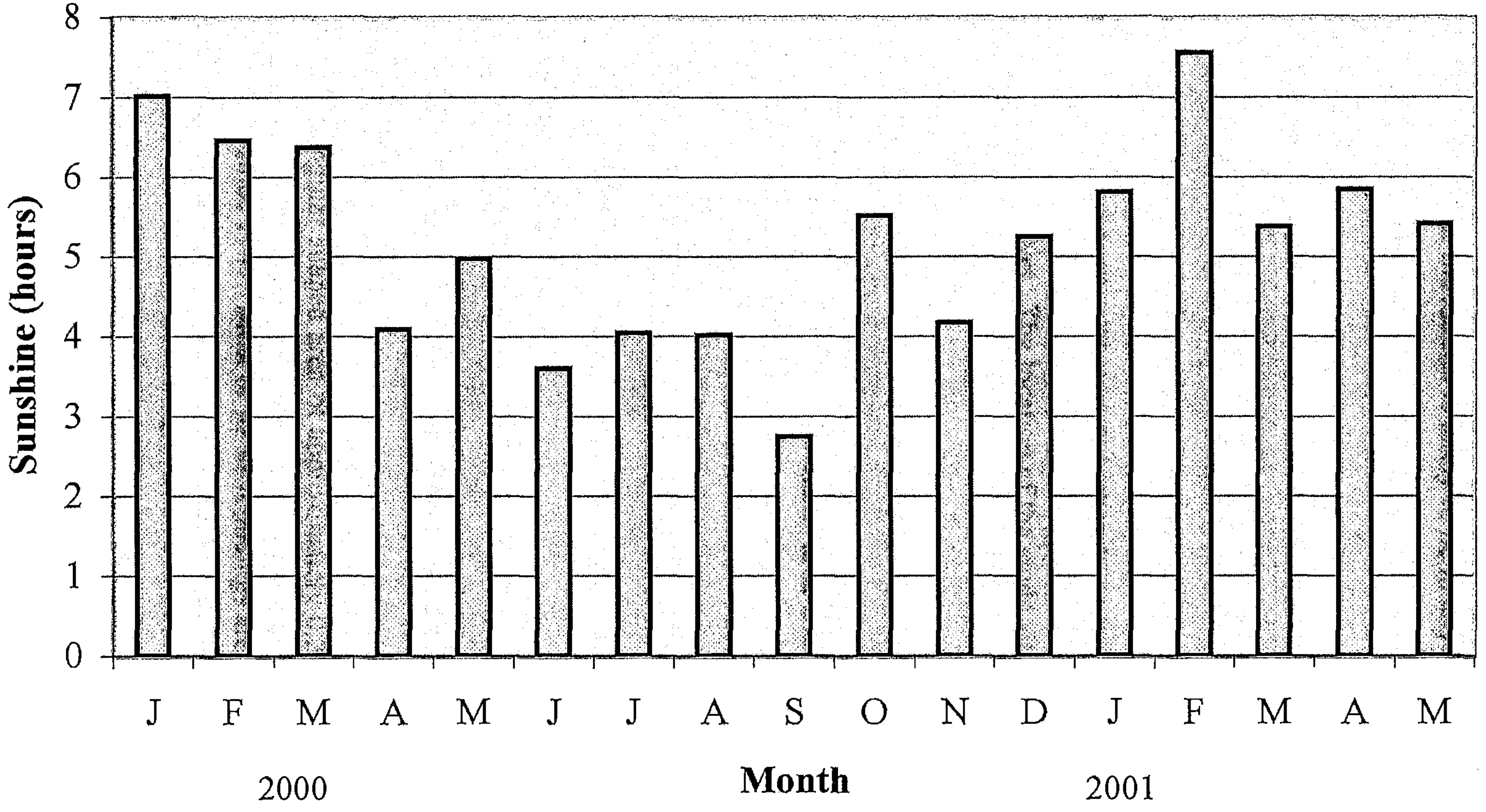


Figure 3.2(c) Sunshine data



heavy rain on five to six days out of ten, amounting to an average of 1000 - 2000 mm for the year. However, because of the great variability of rainfall in the region, averages have little value as indicators of what the rainfall is likely to be in any particular month or season (Watling and Chape, 1993).

Figure 3.2(b) shows the rainfall for the Lami area. There is considerable variation in the levels, which is attributed to the combination of both the prevailing trade winds and the geographical structure of the main islands. The result is that the eastern and southeastern parts of the main islands are usually wet. The location of the study site is within this wet region.

Figure 3.2(c) shows the mean sunshine hours in the Lami area over the 2000 - 2001 period. The largest amount of sunshine hours are found in the January to May period. The remaining period sees considerably less sunshine compared to the January - May period.

3.2 THE LAMI RUBBISH DUMP

The Lami Rubbish is a rectangular shaped area of approximately 0.2 km^2 (Figure 3.1). The site has been in operation since 1947. Most of its surroundings are mangrove forests, with the southern side being on the coastline fronting the Suva Harbour. The dumpsite is the recipient of all of Suva's domestic and industrial wastes, which are dumped together irrespective of composition. Parts of the dump that are still in use are the southern, western and central areas. Here, all the material deposited are levelled with the means of a bulldozer (Plate 1), and eventually layers of soil are piled on the dumped matter to allow for containment of odour and to facilitate transport of dump trucks on the area while another section is utilised for dumping. There is no sorting of materials, hence the area is heterogeneous in composition, and can contain anything ranging from domestic refuse to industrial chemicals (Plates 2, 3 and 4).

The far north (facing the Queens Highway) and east of the dump have not been in use and are now covered with dense vegetation (Plate 5). Proper soil cover has also begun to develop in these areas, especially in the northern section. As a result of this, occupants of nearby villages have established gardens, comprising root crops and vegetables.

The Suva City Council is the authority charged with managing the dumpsite. Their staff who are based at the site levy a fee for usage of the site, however it is doubtful that the content of the materials are inspected. Leachates that emanate from the materials are channelled by means of small drains that ultimately end up in the mangrove areas along the dumpsite (Plate 6). In addition, the material that is piled along the south of the dump often spills over into the ocean nearby (Plate 7). No attempts appear to have been made to prevent this, and as the pile of dumped materials gets higher, the incidences of spillover increase.

Plate 1 A Suva City Council bulldozer disperses materials. Towards the right, a private vehicle is leaving the dump after dumping its load.

Plate 2 Chemical matter dumped at the site (arrowed)

Plate 3 Scrap iron metal (displayed in the foreground) is facing the eastern end of the Lami Dump. Such scraps are common sights throughout the dump.

Plate 4 South end of the Lami Dump facing the Suva Harbour. Towards the left are the remains of automobile parts and a rusting drum - both made of iron.

Plate 5 The mineralised area of the dump, with dense vegetation cover

Plate 6 Leachate movement from the dumped material into the lower parts of the dump (mineralised area)

Plate 7 Plate showing the immediate location of the dump to the marine environment

Plate 8 A scavenger collecting materials from the dump. The Suva City Council has since implemented security measures to curb this practice.

Throughout the past, there have been numerous scavengers frequenting the site foraging through the materials. At the time of commencement of this project, this activity was on the rise (Plate 8). The Council has been consistently trying to put a stop to this in light of the health risks involved. Security guards based on-site managed to curb the practice temporarily, but the scavengers began to approach the dump from the harbour end by means of small punts. This practice was eventually stopped recently when Council employees started patrolling all the possible points of entry to the dump. At the completion of the project, scavenging had ceased.

3.3 SAMPLING

The characteristics of the sampling site are described in detail below. Sampling was carried out at three sites within the dump area, namely Sites A, B and C. The locations of these sites are shown in Figure 3.1. The sites were chosen on the basis of the discontinued dumping period at each site. Site A had not been in use for at least five years as suggested by workers at the site. As such, it represented an area that had the opportunity of the greatest degree of mineralisation.

Site B was located on the boundary of an area of discontinued dumping, and a dumping area. The choice of this site enabled a comparison of whether the vicinity of the dumped materials to the site resulted in any higher metal levels within the site. Site C was a recently (1 year) discarded former dumping site, and was selected since it represented an intermediate between a long-discarded (Site A) and a still-active site (Site B). A study of this site would be expected to show temporary metal distribution patterns in the dump prior to long-term speciation.

3.3.1 Sampling sites

Site A was north-west of the present dumping site, currently unused and covered with up-to-waist-height vegetation. The soil cover was not uniform, and appeared to be a mixture of different soils. There were small channels and drains bisecting the area. Overall, the soil was loamy, with sandy texture and was very easy to dig out.

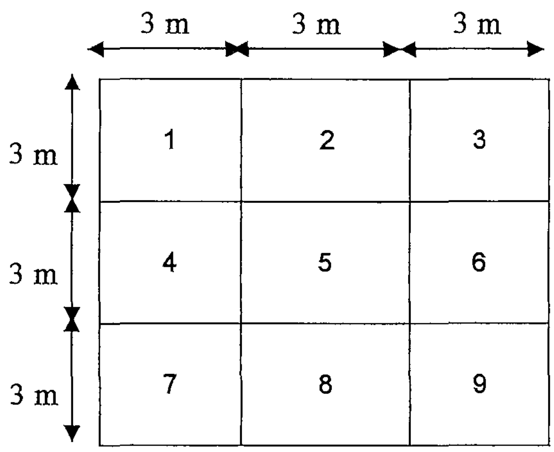
Site B was north-east of the present dumpsite, and was only accessible by crossing the dumped material. The area was being rapidly covered with dense vegetation, and appeared to have been up till recently, been used, and then left to allow vegetation colonisation. This was evidenced from the presence of PET (polyethylene tetraphtalate) soft drink bottles in the subsurface layer. The soil cover was very thin, with most of the substrate being just decaying matter. The soil present was characterised by organic matter, and was largely loamy. This site was at an elevated height compared to Site A, but not higher than that of the dumped material immediate to it.

The location of Site C was just west of the dumping area. Up till early 1999, this was an active dumping site, but during the time of sampling, a small part of it was being used to pile rubbish. Vegetation growth here mostly comprised creepers and weeds. The soil here was thin as well, similar to that in Area B. Where soil was present, it was sandy and had a significant amount of gravel in it.

3.3.2 Sampling Strategy

Within each site, a 9m × 9m area was marked and this area was divided into 3m × 3m blocks (Figure 3.3). From each block, surface soil was collected to make a composite sample for that block of about 1 kg, which was placed into an acid pre-washed and labelled plastic bag. While it is equally important to sample below-surface soil to study heavy metal movement with depth, the absence of proper soil horizons and layers in Sites A and B made this impossible and as such, for consistency, all soil sampled was from the surface. It is also noteworthy that in some instances, especially at sites B and C, what is referred as soil was not strictly soil, but more soil-like material. The material was a combination of many different materials such as soil together with humus, and decaying vegetation. In such cases, the material was dark in colour, often with a soot-like appearance.

Figure 3.3 Schematic representation of sampling quadrant.



For the investigation of phytoremediation potential of plants, various plants were selected. Plants growing at the site were selected because their mere presence suggested that they may be tolerant to relatively high levels of heavy metals, which is a requirement of phytoremediation.

For plant samples, in each block, after the soil sample was obtained, the dominant plant species was selected, and leaves were removed from plants of this dominant species. Up to approximately 1kg of plant leaf per sample was taken and placed into acid pre-washed plastic bags. The list of plants obtained in the dump appears in Table 3.1. Photographs of the plant species are given in the Appendix (Plates A1 - A11). Identification of each plant species was done at the South Pacific Regional Herbarium, based at the University.

Table 3.1 Plant species obtained in the Lami dump

	Plant species		
Block	**Site A**	**Site B**	**Site C**
1	*Crassocephalum crepidiodes*	*Meremia peltata*	*Echinochloa colonumm*
2	*Brachiara mutica*	*Commelina diffusa*	*Lagenaria siceraria*
3	*Mikania micrantha*	*Commelina diffusa*	*Curcurbita pepo*
4	*Brachiara mutica*	*Kyllinga polyphylla*	*Commelina diffusa*
5	*Brachiara mutica*	*Lagenaria siceraria*	*Echinochloa colonumm*
6	*Brachiara mutica*	*Commelina diffusa*	*Lagenaria siceraria*
7	*Brachiara mutica*	*Wedelia trilobata*	*Commelina diffusa*
8	*Kyllinga polyphylla*	*Mikania micrantha*	*Manihot esculenta*
9	*Kyllinga polyphylla*	*Commelina diffusa*	*Manihot esculenta*

The sampling procedures for both soil and plant matter were conducted at each of the three sites, resulting in a total of 27 plant and 27 soil samples.

3.3.3 Sample Treatment

For soils, any visible litter was physically removed from the samples, and the soil was left to air-dry in a soil laboratory for 14 days. Once air-dried, the samples were ground using a mortar and pestle and the ground material was sieved through a 0.5 mm nylon sieve. The sieved samples were then manually homogenised by shaking and later placed into acid pre-washed plastic bags and sealed, for analysis later.

The leaf samples were washed under running tap water to remove any traces of wind-borne matter that may have settled onto them. After washing, they were left to air-dry.

The dried plant leaves were ground up by means of an electric blender (Waring Commercial Blender - Model number 35BL64) to powder size, and stored in sealed acid pre-washed plastic sachets.

3.4 EXPERIMENTAL PROCEDURE

3.4.1 General procedure

All glassware and other materials used in all analyses were soaked in 5 % nitric acid for a minimum of 12 hours, and then rinsed with distilled water prior to use. Drying of glassware was carried out in an oven at a temperature of 50 ^{0}C.

The reagents used were of analytical grade except where specified. Analysis of heavy metals and other metals (Cu, Zn, Pb, Ni, Cd, Cr, Mn, Fe, Mg and Ca) was carried out using atomic absorption spectrophotometry (AAS) on a Perkin Elmer instrument (Model

Number 3110). Analysis for Hg was carried out using the cold-vapour atomic absorption spectrophotometry method, on a Perkin Elmer instrument (Model Number 2380).

Metal concentrations were determined using a 5-point calibration curve containing composite standards. The calibration standards were prepared from dilutions of 1000 mg/dm^3 stock solutions that in turn were prepared from pure metal powder. Instrument conditions utilised were those specified in the instrument manual by Perkin Elmer (1982), using high purity acetylene as fuel.

For quality assurance, all samples were digested (for metals) and analysed (for metals and organic carbon) in triplicate. Secondly, samples for total metals were also analysed at the Institut de recherche pour le développement (IRD) in Noumea, for inter-laboratory comparison. An Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) instrument (model not specified) was used for the IRD analyses. Thirdly, as part of quality control measures to minimise possible contamination of samples from reagents, reagent blanks were subjected to the same treatment and digestions as the samples underwent and the resulting concentrations determined from each analysis were corrected using the blank concentration.

Detection limits for the various metals were determined following the method described by the American Public Health Association (1992). Briefly, the standard deviation, *s*, for seven replicates of a blank sample containing the digestion-acid-mixture only was obtained. This value of *s* is referred to as the theoretical instrument detection limit (IDL)

The theoretical method detection limit (MDL) is related to the IDL in the ratio 4:1. Seven replicates of a standard solution having a metal concentration near the MDL were prepared. These standard solutions, treated as those having unknown concentrations were analyzed and using the respective calibration graph, the exact concentration for each solution was obtained. The standard deviation for the concentrations of the seven replicate solutions was obtained. From a table of the one-sided t distribution, the value of t at the 99 % confidence level was found to be 3.14, and this value, multiplied by the standard deviation is the experimental MDL.

3.4.2 Percentage organic carbon

The methods for the determination of organic carbon content vary from manual to instrumental techniques. The former include two commonly used techniques, namely the loss-on-ignition method and the Walkley-Black Titration method. For this study, the percentage organic carbon was determined according to the Walkley-Black procedure as outlined by Nelson and Sommers (1982). Accurately weighed soil material (1 g) was transferred to a 500-cm^3 wide-mouth Erlenmeyer flask. To this, 10 cm^3 of 0.1667 mol dm^{-3} potassium dichromate ($K_2Cr_2O_7$) was added and the flask was swirled to disperse the soil. Then, 20 cm^3 of concentrated sulphuric acid (H_2SO_4) was rapidly added. The flask was swirled until sediment and reagents were mixed, and more vigorous swirling was done for 1 minute. The flask was then allowed to stand on an asbestos sheet for 30 minutes, after which, 200 cm^3 of deionised water was added.

To the contents of the flask, 10 drops of Ferroin indicator were added and excess dichromate ($Cr_2O_7^{2-}$) was titrated with 0.4 mol dm^{-3} ferrous sulphate heptahydrate [$Fe(SO_4).7H_2O$]. A blank determination was done in the same manner, but without sediment, to standardise the $Cr_2O_7^{2-}$. A correction factor of 1.15 was used. The reason for correction is that the Walkley-Black method does not utilise supplemental heating during the analysis and therefore only up to 86 % of the organic carbon is recovered. The correction factor accounts for the incomplete oxidation of the organic carbon in the reaction (Nelson and Sommers, 1982).

3.4.3 Particle-size analysis

The particle-size distribution of a soil expresses the proportions of the various sizes of particles which the soil contains. These proportions are commonly represented by the relative numbers of particles within stated size classes. The determination of a particle-size distribution is commonly referred to as particle-size analysis.

There are two classical methods of particle-size determination, namely the pipette method and the hydrometer method. The theory behind these two methods has been extensively discussed in the literature and as such is not discussed here. The method of choice for the analysis was the hydrometer method (Day, 1965), and it is described below.

Soil (40 g) was weighed and oven dried overnight at 105^0C for determination of the oven-dry weight. In the procedure by Day, a separate, but equal amount is to be used for the analysis. However, in this case, the particle analysis was carried out after the percentage organic carbon and total and mobile-extractable heavy metal content analyses had been completed. As a result, most of the soil samples that remained were in insufficient amounts. There were ten samples from the first and third sites that were slightly less than 70 g. These were thus used, with the oven-dried soil also being used for the particle-size analyses. The soil was placed in a 600 cm^3 beaker, to which 100 cm^3 of 5 % sodium hexametaphosphate [$Na(PO_3.2H_2O)_6$] was added, followed by the addition of approximately 400 cm^3 of distilled water. The sample was allowed to soak for at least 10 minutes.

The suspension was transferred into the mixing jug of a commercial blender (Waring Commercial Blender - Model number 35BL64) using a stream of water to complete the transfer quantitatively. The suspension was mixed for 5 minutes with the motor mixer, and then transferred to the sedimentation cylinder using a stream of water. The level of the liquid was brought to the 1000 cm^3 mark with distilled water. The sedimentation cylinder was then moved into a disturbance-free fume cupboard.

The temperature of the suspension was recorded when the former had become constant. The plunger was then inserted, and moved up and down to thoroughly mix the contents. Caution had to be exercised when moving the plunger towards the surface to avoid spillage of the contents. Any sediment remaining was dislodged by inclining the rod slightly and rotating it to impart a spinning motion to the disk.

Agitation of the contents was completed with three strokes, then the plunger was removed after tipping it slightly to remove adhering drops. The time was immediately recorded at this point. A drop of amyl alcohol had to be added to remove the foam forming at the surface. The hydrometer was then carefully lowered into the suspension, and after 30 seconds, the scale at the top of the meniscus was read. Another reading was again taken at the end of one minute. After this and each subsequent reading, the hydrometer was carefully removed, the surface rinsed and wiped with soft tissue.

Other hydrometer readings were taken at 3, 10, 30, 120 and 300 minutes respectively. In each case, the hydrometer was carefully lowered into the suspension about 10 seconds before each measurement. Care was taken to avoid re-mixing of the suspension between measurements. Processing of the readings taken at the different time intervals to obtain particle-size distribution was done according to the method described in detail by Day (1965).

3.4.4 Total heavy metal content

Numerous methods can be found in the literature on metal extraction schemes (Agemian and Chau, 1976; Quevauviller *et al.*, 1999; Tessier *et al.*, 1979; Virkanen, 1998). Extraction methods involving fusion or acid dissolution have been well documented, with the latter technique having several advantages. Mineral acids are available in analytical grade and their use does not introduce impurities into the solution. In addition, while fusion techniques are limited to the determination of total metal content of silicates only, by varying the acid concentrations, selective dissolution of several components of sediments can be determined (Agemian and Chau, 1976). Accordingly, acid dissolution is the most commonly used method.

The method of choice for this investigation had to be the strongest acid mixture to efficiently extract metals from all possible fractions of soil. Ideally, a mixture of HF, HNO_3 and $HClO_4$ should have been used, but owing to a lack of adequate protection facilities in the laboratory for HF, this acid could not be used. Therefore the method of extraction selected was that of Virkanen (1998), which included a large amount of HNO_3 and $HClO_4$ and H_2SO_4 in smaller proportions. The (10:2:1) ratio of HNO_3: $HClO_4$: H_2SO_4 ensured that the metals in the organic fraction of soil would be completely extracted, while the other two acids would attack the other fractions.

For the digestion, soil (1 g) was accurately weighed into a 100-cm^3 beaker, and 25 cm^3 of a HNO_3-$HClO_4$-H_2SO_4 acid mixture (10:2:1) was added. The contents of the beaker were subjected to wet digestion on a hotplate at a temperature of 190 ^{0}C. Heating was continued until most of the acid had evaporated in each sample, in a total time range of approximately 45 to 60 minutes. At this point, 20 cm^3 of deionized water was added to each sample, and the mixture was further boiled for 15 minutes before being allowed to cool to room temperature. Upon cooling, the mixture was filtered through Whatman™ No. 541 (12 cm) filter paper and diluted to a final volume of 50 cm^3 (Virkanen, 1998). Ten-fold dilutions were done to each sample to account for the possibility of metal levels in the samples being beyond the calibration range.

3.4.5 Bioavailable fraction

Fractional determination of metals in soil is necessary since the behaviour of heavy metals in the environment (mobility, bioavailability to plants and re-mobilisation ability) depends strongly on their specific chemical forms or ways of binding (Ma and Rao, 1997; Quevauviller *et al.*, 1999). Consequently, the determination of these forms are sometimes more useful than the total element content (Quevauviller *et al.*, 1999).

In this study, the mobile fraction was determined with EDTA, using a slight modification of the method of Agemian and Chau (1976). While EDTA has been found to often attack the organic fractions in soil (Agemian and Chau, 1976; Chester and Voutsinou, 1981), it also enables complete extraction to be achieved from the bio-available fractions and mimics the mobility of heavy metals from soils (Quevauviller *et al.*, 1999). Therefore, it presents the analyst with a more valid picture of the amounts of metals that can be leached into the environment via complexation with these acids.

The experimental procedure involved weighing 4 g soil samples into centrifuging tubes. To each sample, 40 cm^3 of 0.05 mol dm^{-3} EDTA solution (pH adjusted to 4.8) was added and the weight of the tube and contents was taken. The tubes were placed in an end-to-end mechanical shaker and the spaces between the shaker container and the tubes tightly packed to avoid movement of the tubes. This is necessary because any movement of the tube during the shaking process reduces the effectiveness of the agitation of the contents within. The samples were shaken for three hours at room temperature.

After shaking, the samples were centrifuged at 2000 revolutions/minute for a period of 20 minutes, after which the tubes were opened and the contents quantitatively transferred to 50-cm^3 volumetric flasks. In some cases the samples had to be filtered due to excess turbidity. All samples were acidified to 10 % nitric acid content, and the flasks made up to volume. These were later analysed.

3.4.6 Plant total metal extraction

The Association of Analytical Chemists (AOAC) Method 975.03 was used to extract metals from the plant leaf tissues. The procedure is referred to as *wet ashing*, and is commonly used for the determination of metals in plants around the world. Dried and ground plant material (1 g) was accurately weighed into a 100-cm^3 Pyrex beaker. Concentrated nitric acid (10 cm^3) was added to the sample and allowed to soak thoroughly. $HClO_4$ (3 cm^3 of 60 % concentration) was then added, and the beaker was heated on a hotplate at 140 ^{0}C, until the frothing ceased. This temperature is desirable, as it allows the contents of the beaker to rapidly heat up without excessive frothing and thus avoids sample loss.

After the frothing had subsided, the hotplate temperature was increased to 160 ^{0}C. At this temperature, boiling of the contents began. The boiling process normally takes between 40 - 50 minutes before the nitric acid is completely evaporated and white fumes of $HClO_4$ are seen. At this point, the beakers were taken off the hotplate and cooled to room temperature. A small amount (10 cm^3) of dilute HCl (1+1) was added to the contents, which were transferred quantitatively to 50-cm^3 volumetric flasks. To the solutions in the flasks, 10 cm^3 of 5% lanthanum solution was added, and the volumes were made up to the mark.

4.0 RESULTS AND DISCUSSION

Tabulated raw data are provided as appendices and are arranged according to the order in which they are discussed in this chapter. An "A" in front of a table number, for example Table A4.1 denotes a table in the Appendix. In-text tables, which are included in this chapter contain summarised versions of the data listed in the Appendices, and serve to facilitate the discussion of trends.

4.1 PERCENTAGE ORGANIC CARBON IN SOILS

The range of values obtained for each site is presented in Table 4.1. The detailed results are given in Table A.4.1.

Table 4.1 Range of percentage organic carbon in the Lami Dump

	Percentage organic carbon content
Site A	0.630 - 5.01
Site B	12.7 - 19.0
Site C	2.49 – 25.2

On the basis of these data, Site A appears to have the lowest amounts of organic carbon. Levels were greatest in Site B, followed by those at Site C. Overall, the levels are lower than what would normally be expected to be present in a dumpsite, where large amounts of organic material can accumulate. This can be attributed to two reasons: firstly, what is referred to as soil in the dump may not be soil, but soil-like matter such as humus and materials from the dumping pile itself. In case of this, parameters such as organic carbon content, particle-size distribution and even the heavy metal content cannot be expected to conform to patterns of distribution that are normally observed in proper soils. This is most important and must be kept in mind, especially in the case of Sites B and C when these parameters are discussed in later sections. Secondly, recovery of organic carbon by the Walkley-Black method can often range from 57 % - 114 %, with an average recovery of 102 %, even after correction (Nelson and Sommers, 1982). It is therefore likely that the results are appearing to be lower than what may actually be present.

Organic matter often contributes from <1 - 5 % weight percent to the soil mass (vanLoon and Duffy, 2000). By contrast, the levels at Lami are variable, with the lowest levels in site A, the highest in the second and with the third site having levels mainly in between these. In terms of variability within the blocks at each site (for results, see Table A4.1), the percentage organic carbon levels do not differ extensively within a site, possibly due to the organic matter being relatively rapidly mineralised at each site. The organic carbon content of soils is often the net result of processes that release dissolved organic matter, such as leaching from litter or desorption from the solid phase, and processes that remove dissolved organic matter such as adsorption or decomposition. Therefore, the study of the organic matter content and its fluxes gives an appreciation of the fluxes of the organic carbon content. The processes that release and /or remove organic matter are dependent on environmental factors such as temperature and precipitation, and the physical and chemical characteristics of the soil itself (Kalbitz *et al.*, 2000).

Sites A and C were sections of the Lami dump that had previously been used extensively for dumping, but apparently had recently been left relatively untouched. At these sites, some semblance of proper soil cover had developed, allowing dense vegetation to colonise them. In contrast, Site B, being immediately adjacent to an active rubbish pile, was still subject to disturbances, compared to the other two sites. The swampy characteristics of Site B had resulted in poor drainage, which may possibly be a contributing factor to the build-up of organic carbon at the site. Soil drainage is an important factor in controlling the organic carbon content of soils. In poorly-drained soils, dissolved organic carbon concentrations, particularly in surface horizons often reach very high levels (Kalbitz *et al.*, 2000). This appears to have been the case at Site B, where the soil was waterlogged and at the time of sampling, much of the soil was wet.

In addition, the dump being a heterogeneous pile of dumped material, has a large organic-source base, mainly in the form of organic refuse from households, discarded organic products such as food from canning and processing factories and leather scraps from footwear industries. This, coupled with the humid and moist environment, created by continuous piling of materials may lead to very rapid breakdown of organic matter by microorganisms. The leachate emanating from these materials is therefore expected to be highly rich in organic compounds such as humic acids. Percolation of this leachate into the adjacent soil could be the major reason for the elevated concentrations of organic content of the soils at site B, which is the nearest out of all sites to the dumped material. Equally possible is the presence of organic rubbish which itself can be a source of organic matter.

In the case of Lami, it appears that the percentage organic carbon content values obtained does not represent those that would normally be expected from an organic-rich municipal dumpsite. This is because there is no proper soil cover in certain sections of the dump, and the substrate that is present is largely soil-like material, often composed of the rubbish itself. This also explains the large variability in percentage organic carbon results for the second and third sites.

The importance of soil organic matter has been discussed by many researchers (for example, Almås and Singh, 2001; Almås *et al.*, 2000; Leita and De Nobili, 1991; Romkens and Salomons, 1998; Zhang *et al.*, 1997). Many have obtained significantly positive correlation between the organic carbon content and concentrations of metals such as copper, zinc and manganese, suggesting that the metals have strong affinity for the organic matter, via formation of organic matter-metal complexes.

Organic matter can act either to mobilise or immobilise metals in the soil. The solubility of metals that are structural components of organic matter, or that form strong complexes with it, is determined by the solubility of the associated organic matter. Often, decomposition to form products that are smaller and more soluble is an important factor in increasing the solubility of such metals. Organic acids, formed by the degradation of organic litter in soil act as ligands for many metals, enhancing movement in percolating water down through the soil profile (vanLoon and Duffy, 2000).

4.2 PARTICLE SIZE DISTRIBUTION

The particle size determines the soil texture, which refers to the relative size distribution of the primary particles in a soil (Kettler *et al.*, 2001; White, 1997). The soil texture is one of the most stable of soil properties, and a useful index of soil structure, leaching, erosion potential, organic matter dynamics, nutrient storage, water movement and aeration (Kettler *et al.*, 2001; Pitty, 1979; Radojević and Bashkin, 1999; White, 1997).

Figure 4.1 shows the distribution of particles in four different size groups (very coarse sand, fine sand, silt and clay). The clay fraction appears to be the most dominant for most soils tested (with the exception of two samples). This confirms that the overall texture of the soil is largely clay.

The method used for classifying and naming of the different fractions is arbitrary, and a number of different systems are used. That adopted by the International Society of Soil Science is shown in Table 4.2.

Table 4.2 International Scheme of particle-size classification

Fraction	Particle diameter range (mm)	Classification
I	2. 0 - 0. 2	Very coarse sand
II	0. 2 - 0. 02	Fine sand
III	0. 02 - 0. 002	Silt
IV	< 0. 002	Clay

Source: Day (1965).

Figure 4.1 Particle-size-distribution

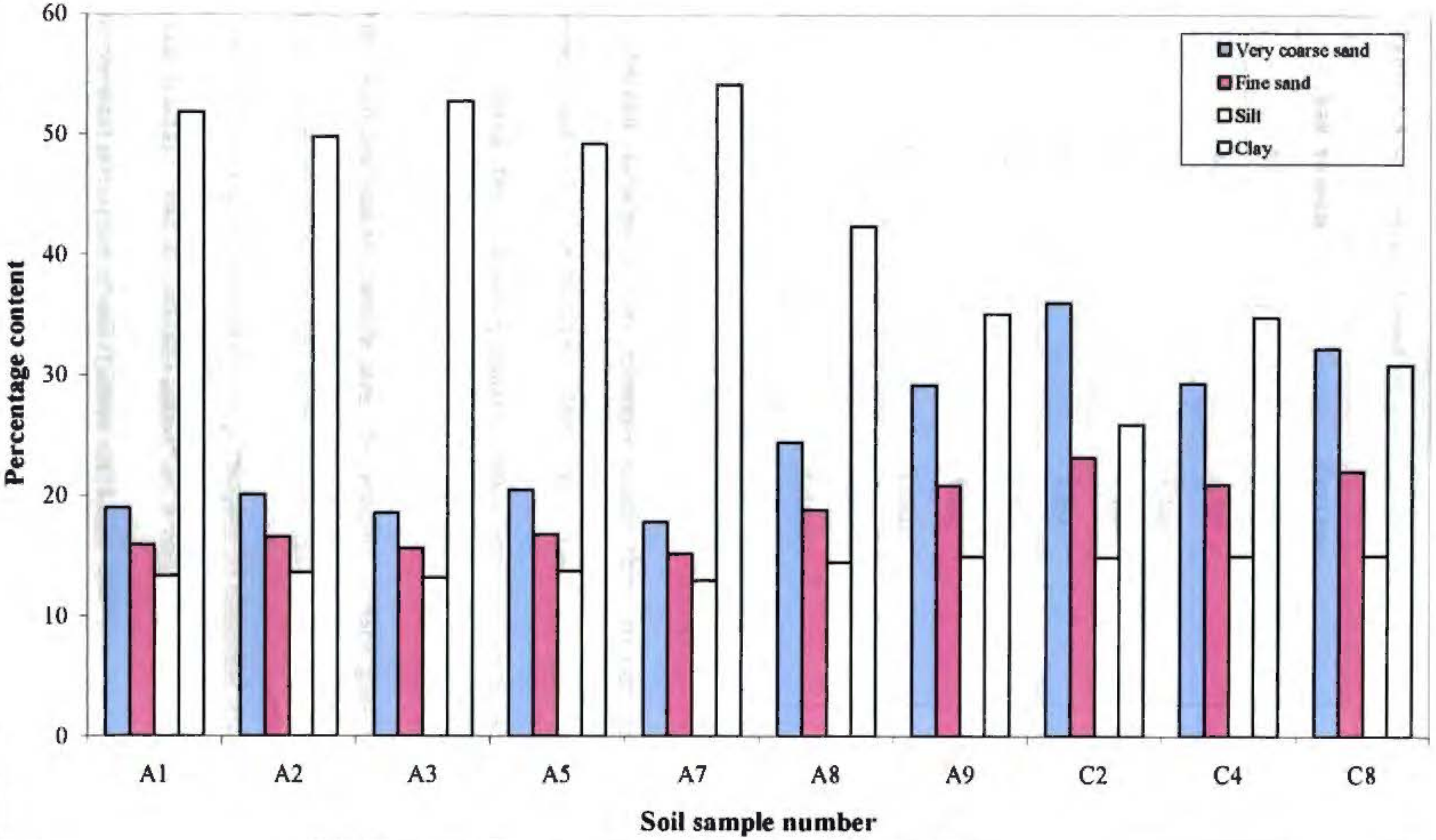


Table 4.3 lists the texture of the soil with the respect to the different particle sizes present.

Table 4.3 Soil texture based on particle-size distribution

Soil Sample	Texture
A1	Clay
A2	Clay
A3	Clay
A5	Clay
A7	Clay
A8	Clay
A9	Clay
C2	Loam
C4	Clay
C8	Loam

The electrically-charged surfaces of clay minerals enable them to participate in ion-exchange processes (Radojević and Bashkin, 1999). It is these ion-exchange processes that are of interest to researchers, for heavy metal retention onto clay surfaces is common.

As a general rule, with decreasing particle size, the specific surface area of a particle increases. This in turn results in an increase in the proportion of the potentially reactive surfaces in the sample, making it more likely to participate in chemical reactions. For this reason, the clay fraction, with its colloidal properties is very important in determining the chemical and physical properties of soil (Leeper and Uren, 1993).

4.3 MAJOR CATIONS

Table 4.4 lists the average concentration of the major cations, iron (Fe), aluminium (Al), magnesium (Mg), manganese (Mn) and calcium (Ca) in the soil samples at the three sites.

Soil cover material has a major influence on levels of major cations. In this, the nature of the soil is very important. In the Lami dump, piling of soil carted from outside the Lami and Suva areas to cover the refuse is a common practice. The input of such soil, often having different chemical and physical characteristics and thus metal content, can result in varied increases in the metal concentrations in the area over which it is piled. This is manifested in large variations in metal concentrations that are obtained from each site.

Table 4.4 Average concentrations of major cations at the three sites at the dump

	Concentration (mg/kg)		
Metal	**Site A**	**Site B**	**Site C**
Fe	55,500	67,100	48,300
Al	48,400	23,100	27,500
Mg	9,150	7,040	6,830
Mn	1,000	634	509
Ca	8,360	20,100	36,100

Figures 4.2(a) and 4.2(b) show the range of concentrations obtained for each metal across the three sites. Each bar on the graph denotes the range for each metal in each site. On average, Fe was found to be present at the highest concentration among all the major cations determined. The largest variability occurred at Site C, possibly due to its

Figure 4.2(a) Range of Mn and Mg values in soil at the three sites

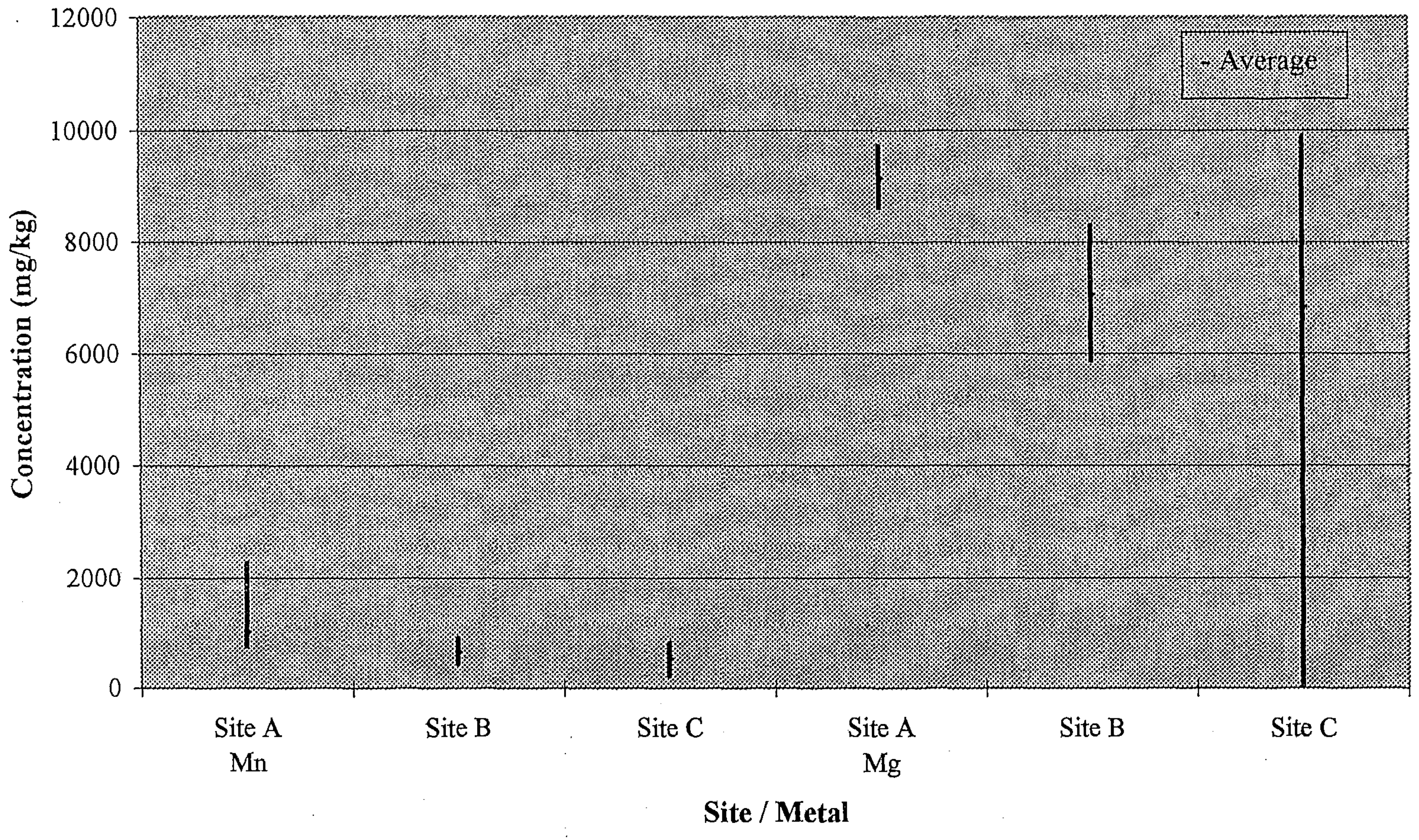
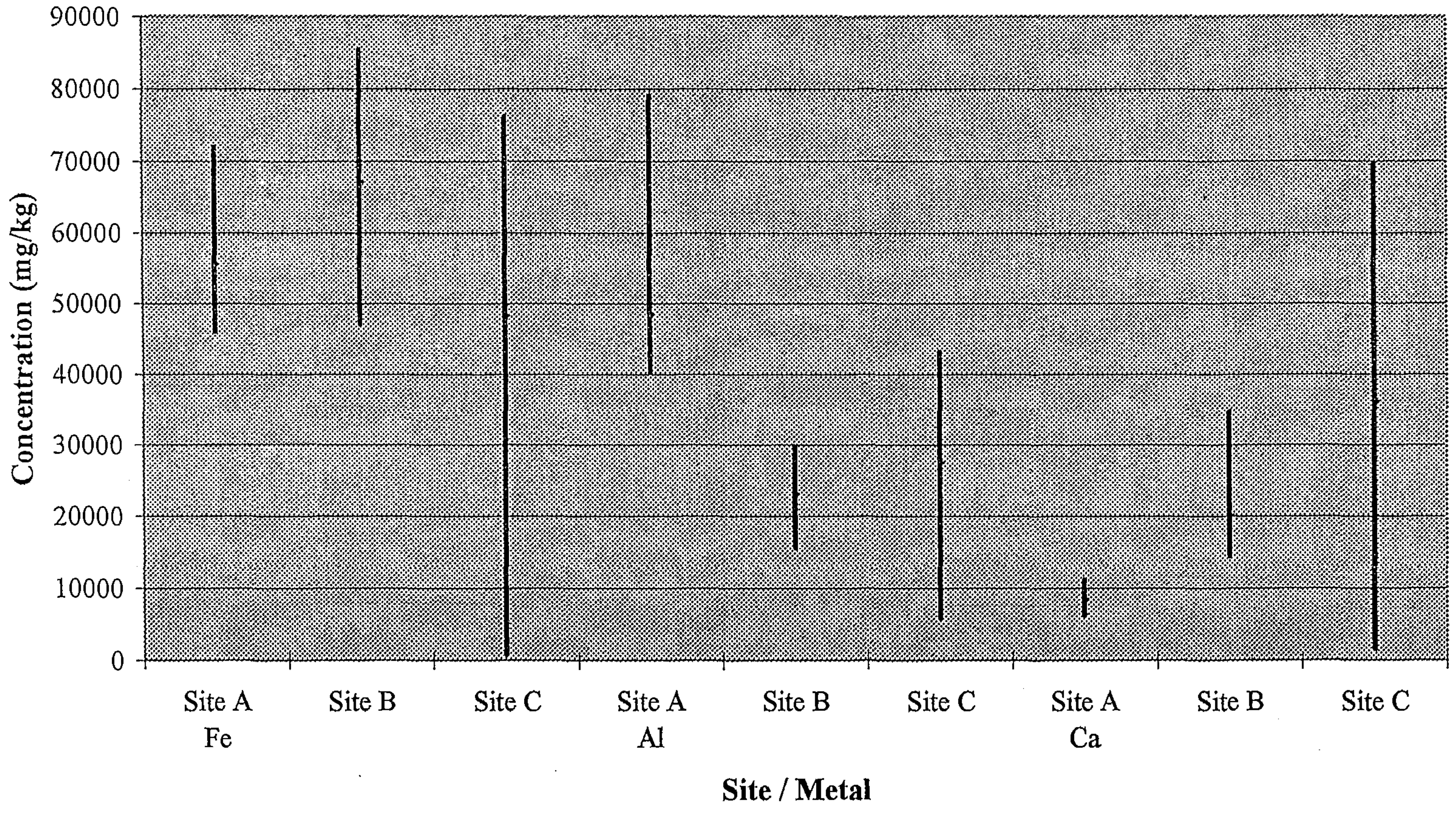


Figure 4.2(b) Range of Fe, Al and Ca values in soil at the three sites



relatively recent abandonment as a dumping area, and/or as a consequence of its lack of proper soil cover.

Mitchell (1964) and Pitty (1979) suggest the Fe content of soils to be in the range of 5,000 mg/kg to 100,000 mg/kg. The levels at the Lami municipal dumpsite fall within this range. The Fe content of the dump is greater than those of other cations, possibly due to the overwhelming range of Fe-containing materials. These materials include besides contributions from the soil used as cover, food cans, metal scraps and automobile parts (see Plates 1 - 8).

Site A contains the highest amounts of Al of all three sites. The levels tended to decrease from Site A to Site B, only to increase slightly at site C. It is possible that soil cover may have an influence on the distribution of the metal at site A. The establishment of a somewhat thicker soil cover could be facilitating greater incorporation of Al as part of mineral matrices.

The levels of Ca tended to be lower than that for Fe, Al and Mg at site A, with increasing concentrations at sites B and C. Overall, the highest concentration of the metal was at site C, with a mean concentration of 36000 mg/kg.

The Ca concentrations presented are from the IRD laboratory data, since the concentrations obtained using the facilities at the University of the South Pacific seemed too low (based on comparison of the data from the two laboratories). This could be due to reduced sensitivity of Ca with the presence in the digest of elements that give rise to stable oxysalts. These elements include Al, beryllium, phosphorus, silicon, vanadium, titanium and zirconium. The addition of strontium can often reduce the effect (Perkin Elmer, 1982) but not completely remove it. This could be the reason why addition of 0.5 % strontium chloride ($SrCl_2$) to the digests before dilution did not lead to significantly improved results.

The soils around the Suva peninsular contain extensive amounts of fine and medium sized marl particles throughout, and as such are expected to contain extremely high amounts of exchangeable Ca (Twyford and Wright, 1965). Therefore the levels of Ca are expected to be higher than that found, especially at Site A. It appears that deposition of soil of non-calcareous origin to compact the dumped material is being used rather than nearby soil. Overall, the use of sulphuric acid in the digestion procedure may have caused some Ca to precipitate out as the relatively insoluble calcium sulphate, hence lowering the overall concentration in solution. On the other hand, the high proportion of nitric acid also present in the digestion mixture may have minimised this loss to some extent (Radojević and Bashkin, 1999).

Mg levels showed relatively little variation across the dump. The levels were lower than 1000 mg/kg, with the concentration ranging in the order of the highest - lowest: Site A > Site B > Site C. The species was found to be amongst the lowest concentrated out of the rest of the major cations in the dump.

Mn was found to be in fairly constant amounts throughout the three sites, and present in low amounts. The levels ranged from 208 mg/kg to 2390 mg/kg. The highest occurrence of the metal was found in Block 4 at Site A, where all the replicates analysed contained similar levels. This suggests the presence of a Mn-rich substrate in the location, possibly a Mn-containing material.

It was noted that as the relative length of the mineralisation period increased between sites, the degree of variability decreased, suggesting that metals may have gradually become assimilated in soil with time.

Overall, the levels of Fe, Al and Ca were high in the dumpsite, while those for Mg and Mn were the lowest. The range of values for these species usually present in the mineral portion of soils are depicted in Table 4.5.. It is important to note that these specified values are the total concentrations, which is not necessarily equivalent to those obtained by strong-acid digestions such as that used in this study.

Table 4.5 Range of values for total major cations in the mineral component of soils

Metal	Concentration (mg/kg)
Al	24000 – 74000
Fe	12000 – 43000
Ca	1000 – 39000
Mg	1000 – 16000
Mn	Approximately 400

(vanLoon and Duffy, 2000)

In comparison to the values in Table 4.5, in the dump, Fe concentrations were the highest, followed by Al (with the exception of Site C, where Mn concentrations were higher than that for Al). The concentration of Mg was the lowest out of all the other cations. The possible reasons for deviations from the trends in Table 4.5 have been discussed earlier in the section.

4.4 HEAVY METAL CONTENT

4.4.1 Quality control of data

The analyses in this study have been performed without the inclusion of standard reference materials. This is not an oversight, but an omission resulting from the limited research budget. Nevertheless, other quality control methods, namely method of standard additions, analyses of blank samples, analyses in triplicate and an inter-laboratory comparison have been included to ensure the output of quality data. The results of these are discussed in the following.

The results of the recovery by standard addition method, used to evaluate the extent of matrix interference, are summarised in Table 4.6. Briefly, the method used to test these recoveries involved taking five sub-samples from a soil sample, in this case, **A4**. To each except one sub-sample, aliquots of a metal solution containing increasing amounts of the analyte were added. This is referred to as *spiking*. The amount spiked is referred to as the *theoretical yield*. The sub-samples were then digested using the procedure outlined in Section 3.4.4. The metal concentration in each sub-sample was then determined, and the difference between this concentration and the concentration in the unspiked sub-sample was established as the experimental yield. The experimental yield as a percentage of the theoretical yield is the percentage recovery.

Table 4.6 Percentage recovery for heavy metals

Metal	Percentage recovery	Acceptable percentage recovery*
Cu	104	100 ± 20
Zn	72	100 ± 20
Pb	110	100 ± 20
Ni	41	100 ± 20
Cd	102	100 ± 20

*According to the American Public Health Association (1992) guidelines.

Cu, Pb and Cd showed good results, confirming that there is no significant matrix interference for these metals in the samples. However, for Zn and Ni, the lower than acceptable value suggests that the sample matrix may be causing problems. Such matrix interference appears to be present in both the EDTA and strong acid digestions. Common type of interference from within the matrix is from both cations and anions, with the anions resulting in the formation of compounds of low volatility, which reduce the rate at which the analyte is atomised in AAS. Low results are the consequence (Skoog *et al.*, 1998). Any of these factors, in isolation or in conjunction, could possibly have suppressed the results for these metals, especially for Ni. This finding suggests that it is likely the values of Zn and Ni obtained in this study could actually be 1.4 and 2.5 times higher respectively.

Tables A4.4 (a) - A4.4 (c) compare the results of analysis obtained at the IRD laboratory using an ICPOES set-up, with those obtained at the University of the South Pacific using AAS. These results show significant agreement ($P = 0.05$), thereby confirming the accuracy of other results (plant metal content and bioavailable fraction content). The ICPOES determination is not affected by matrix-related problems that are frequently encountered in AAS analyses. Therefore, some variations in the data of the two laboratories is to be expected, with that of IRD exhibiting greater precision. In the case of Ni and Zn, there is overall considerable variation between the data from USP and IRD. As was discussed earlier in the section, matrix effects appear to be suppressing the results for these two metals in the AAS analysis, and therefore, their levels as obtained at IRD would be higher. An examination of the data in Table A 4.4(b) shows that this is indeed the case for Zn, especially for Site B. For Ni, however, the levels in either set of results do not follow any such trend. No explanations can be found in the literature to account for this.

The method detection limits obtained for each metal was the criterion for determining the detectable and non-detectable concentrations. These limits are shown in Table 4.7. Detection limits for Hg are not listed in the table due to lack of analytical facilities at the time of determination.

Table 4.7 Method detection limits for the heavy metals

Metal	Detection limit (mg/kg)
Cu	1.25
Zn	0.70
Pb	7.80
Ni	4.30
Cd	1.95
Cr	4.95

4.4.2 Heavy metal content in soils

Total heavy metal contents in individual samples can be found in Tables A4.3(a) - A4.3(c), while Table 4.8 (below) gives the average value per site.

Table 4.8 Average concentrations of heavy metals within each site

	Concentration (mg/kg)		
Metal	**Site A**	**Site B**	**Site C**
Cu	156	223	373
Zn	313	1180	494
Pb	174	485	4910
Ni	28. 4	163	32. 7
Cd	0.968	7.84	3.24
Cr	38. 9	1.17	59. 2
Hg	0.489	18. 1	3.56

Overall, Hg and Cd were the only metals that were found to be present in the lowest amounts, and these were sometimes below the respective method detection limits. The reasons for the low concentrations obtained for Hg and Cd could be that the species were already present in very low amounts in the dumpsite, hence the low concentrations detected. Also, the method of open-beaker digestion could have resulted in loss of Hg through volatilisation, given the volatile nature of the metal. Due to the largely undetectable amounts of Hg, analysis of the metal was confined to total concentrations in soil only, and no further analysis was performed on the plant and dilute acid digests respectively.

The consistently low and largely undetectable levels of Cd present suggest that the metal may be present naturally in very low amounts. This is reinforced by the low background concentrations usually associated with Cd as has been shown in Section 2.1. It also seems that there is low input of the metal from the dumped material. As in the case of Hg, no correlation was done between Cd and organic carbon and Ca, owing to the unreliability of Hg data for statistical analysis.

The precision of metal levels between the three replicates in which each analysis was done was low, and this is seen in the variation of results per sample in Tables A4.2 (a) - A4.2 (d). The low precision occurs despite vigorous homogenisation of the soil sample in each case prior to digestion. Also, the composition of soil is often dominated by foreign materials from past dumping pits, on which the current soils are piled. These materials, many of which are of metallic nature appear to be strongly influencing the heavy metal results.

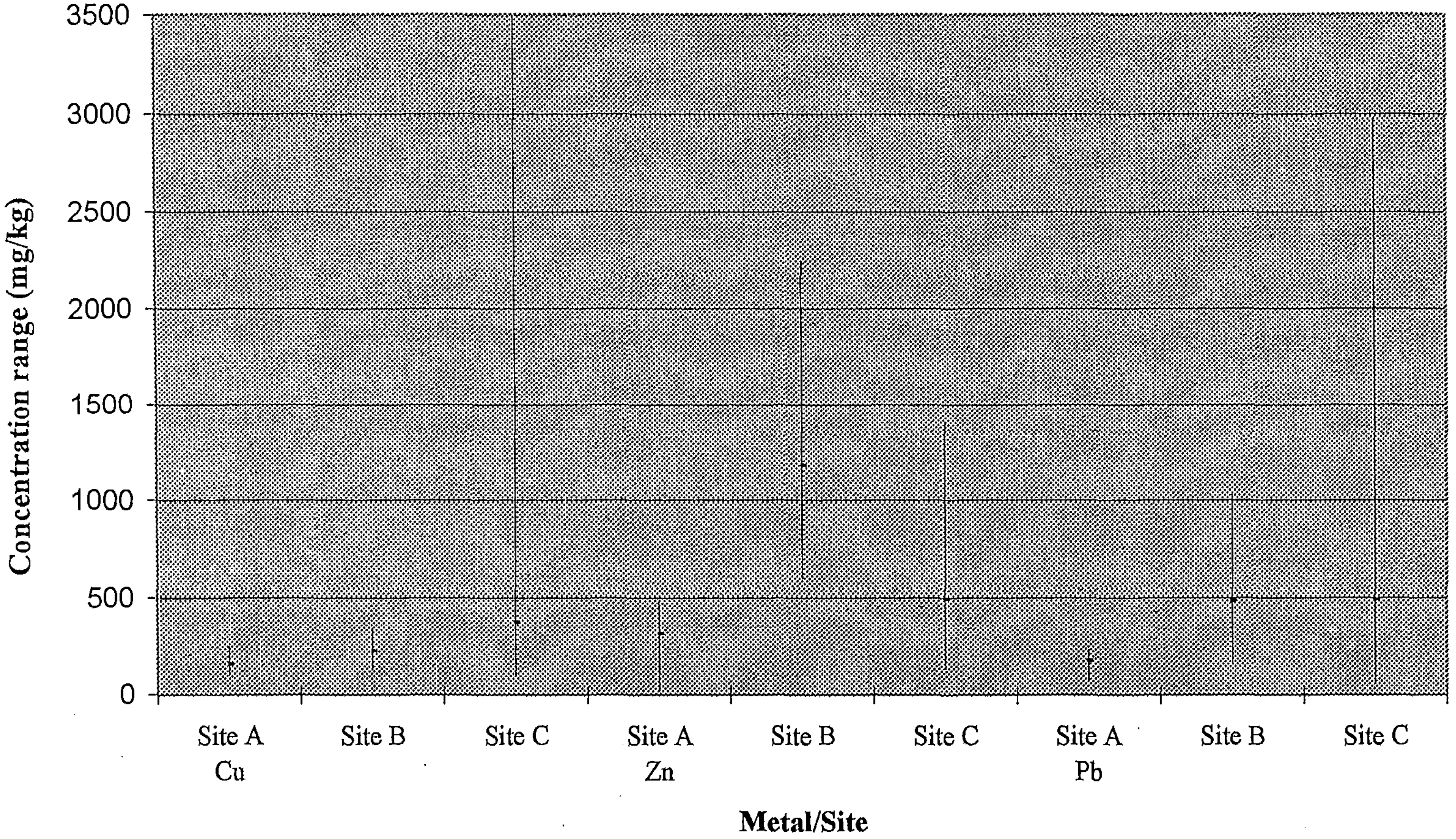
Distribution patterns

Figures 4.3(a) and 4.3(b) present the range of concentrations obtained for each metal at the three sites. Also marked is the average concentration for each range (information presented in Table 4.8).

Site A had the lowest concentration of all heavy metals. At this site, Zn was present in the highest amounts of all the heavy metals, and the amount did not exceed 487 mg/kg. Cu and Pb were in almost similar amounts, as were Ni and Cr, while Cd and Hg were largely at trace levels.

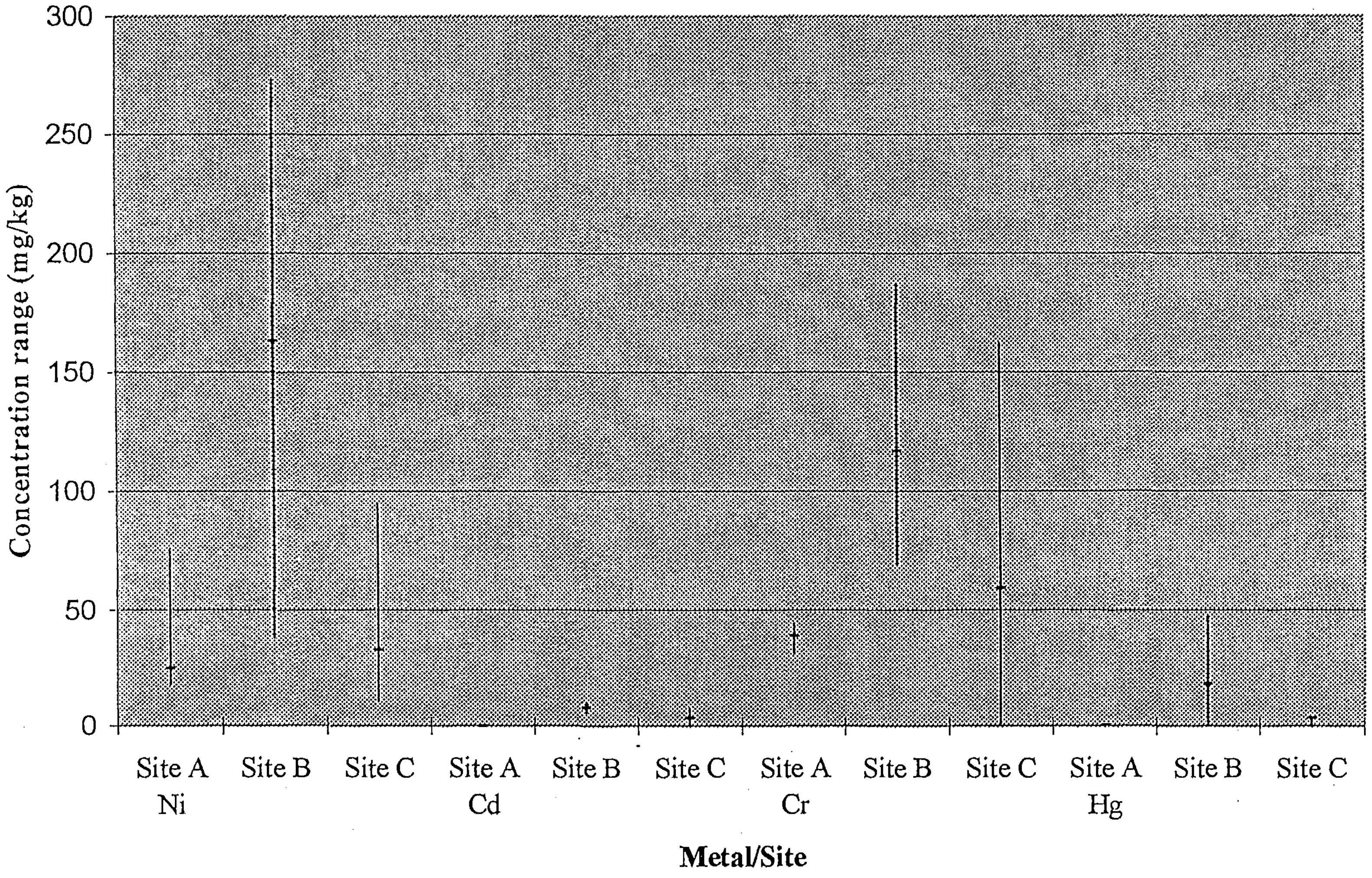
At Site B, there was less consistency in the distribution of the metals. In order of decreasing concentrations, the metals were ranked as follows: Zn>Pb>Cu>Ni>Cr>Hg>Cd. At Site C, the levels of all the metals were generally high, with the concentrations ranging in the following order from highest to lowest: Cr>Zn>Pb>Cu>Ni>Hg>Cd. At this site, Cr increased almost six-fold compared to Site B, and was the most abundant metal present. The relative and collective distribution of the metals suggests that Site A contains low amounts of heavy metals, Site B in slightly higher amounts, while Site C is fairly enriched in all metals studied.

Figure 4.3(a) Concentration range of total Cu, Zn and Pb at the three sites



Note: Cu range in Site C exceed the maxima of the scale

Figure 4.3(b) Concentration range of total Ni, Cd, Cr and Hg at the three sites



One of the reasons for variation in the distribution of metals appears to be the duration of the stabilisation period that each site has undergone. Stabilisation in this sense refers to degradation of the various different waste components into a homogenous soil-like material. Since Site A had a longer stabilisation period, greater metal concentrations would be expected at this site.

Alternatively, metals could be leached out of the organic-rich surface layer. McBride *et al.* (2000) have studied the leaching of metals in this manner, and suggested that metal-organic complexes could be a possible pathway for removal of metals, especially from surface soil.

Secondly, the soil cover at site A is more developed, and could contain a higher proportion of organisms. Correspondingly, there would be high organism activity in this site. Organisms, especially earthworms usually tend to remove organic particles high in heavy metal content and transfer them to lower soil horizons by defecation. This process explains the relatively low organic matter content and consistent reduction of all heavy metal concentrations in the surface (McBride *et al.*, 2000). Moreover, metals unavailable for root uptake may be liberated through microbial decomposition of large organo-metallic complexes (Almås and Singh, 2001).

It is also possible that metal bearing wastes may not have been dumped at Site A in the first place. This cannot be ascertained since there are no definite dumping patterns at the dump. It is also likely that at the time the site was in use, highly-metals-contaminated wastes were not being dumped at all.

However most importantly, the fact is that what is referred to as soil may be actually soil-like material. This possibility has been explored and discussed in Section 4.1. However, the implication of it on the results obtained cannot be quantified. It is certain that in case of Site B (which is in the immediate vicinity of the dumped materials) and Site C (which has only recently been discarded as a dumping spot), there is no definite proper soil cover, and what is referred to as soil may actually be metal-containing materials instead that have physically been broken down and appear like soil. The high level of Cu and Pb in Block 4 at Site C suggest that this is a strong possibility.

Correlation analysis

Table 4.9 shows the product-moment correlation coefficient, *r* for the heavy metals and organic carbon content.

Table 4.9 Correlation coefficient, *r*, among heavy metals, major cations and organic carbon content (OC)

	Cu	**Zn**	**Pb**	**Ni**	**Cd**	**Cr**	**Hg**
Zn	0.3						
Pb	0.8	0.4					
Ni	0.05*	0.4	0.2*				
Cd	0.4	0.8	0.5	0.7			
Cr	-0.01*	0.4	0.2*	0.6	0.4		
Hg	0.003*	-0.01*	-0.02*	-0.007*	0.01*	-0.002*	
Ca	0.4	0.07*	0.3	-0.07*	0.2*	-0.1*	0.003*
Mn	-0.1*	-0.3	-0.2*	0.0009*	-0.2*	-0.06*	-0.02*
Fe	-0.03*	0.4	0.1*	0.3	0.3	0.5	0.01*
Mg	0.09*	-0.06*	0.06*	-0.1*	-0.1*	0.1*	0.03*
Al	0.04*	-0.4	-0.08*	-0.3	-0.4	-0.3	0.003*
% OC	-0.01*	0.5	0.1*	0.6	0.6	0.4	0.02*

* Not statistically significant at $P = 0.05$

According to Table 4.9, the organic carbon content exerts an influence in the association of Zn, Ni, Cd and Cr in the soil. These metals correlated positively to the organic carbon content. Pb and Cu did not show any such correlation.

The lack of correlation between Cu and Pb and organic carbon content is contrary to what has been reported in the literature (Ross, 1994[a]). However, these results cannot be effectively compared with those that have been obtained in areas with proper soil covers. Generally, Cu and Pb both have been found to be largely associated with the organic carbon content, and the latter has been identified as one of the most important components for trace metal retention (Almås *et al.*, 2000; Luo and Christie, 1998). This association continues until the organic matter decomposes over time, thus liberating the metals (Camobreco *et al.*, 1996; Zhang *et al.*, 1997). At site A, where there was proper soil cover, it is possible that the metals were associated in fractions other than the organic such as the carbonate. Strong metal retention can often be attributed in part to the presence of free calcium carbonate, pH and organic matter content (McBride *et al.*, 2000). In general, the pH of the Lami Dump area is constant at 5.8 (as measured in the leachates in and around the sites) in the dump. Therefore, considering the high correlation between Cu and Pb and Ca, the importance of calcium carbonate as a parameter controlling the retention of the metals is a strong possibility. The two metals also have the highest degree of correlation with Ca.

As metal redistribution occurs, more metals tend to be associated with clay minerals and oxides (Han *et al.*, 2001). Gomes *et al.* (2001) have found that apart from the organic fraction, Cu can often be associated with minerals such as clay. The adsorption of Cu is mostly due to complexation by organic matter and specific adsorption by Fe and/or Al. Pb was found to depend more on CEC than organic matter.

Zn, Ni, Cd and Cr showed moderate correlation with organic carbon (0.5, 0.6, 0.6 and 0.4 respectively). The similarity of these correlation values suggests that the extent of association of these metals with organic carbon is similar. The positive correlation obtained among the metals usually suggests that those positively correlated have similar dissolution-precipitation characteristics (Zhang *et al.*, 1997). In the case of Zn, high pH can often reduce the concentration of the metal in the non-organic fractions, such as the exchangeable. Zn immobilisation has been reported to occur due to sorption on organic and mineral colloidal surfaces (Luo and Christie, 1998). It is possible that preferential sorption to the organic fraction over others is occurring in the Lami dump. Trace metal complexation by organics has been found to be particularly important for Ni (Almås *et al.*, 2000; Dudley *et al.*, 1986), and Hg (Almås *et al.*, 2000).

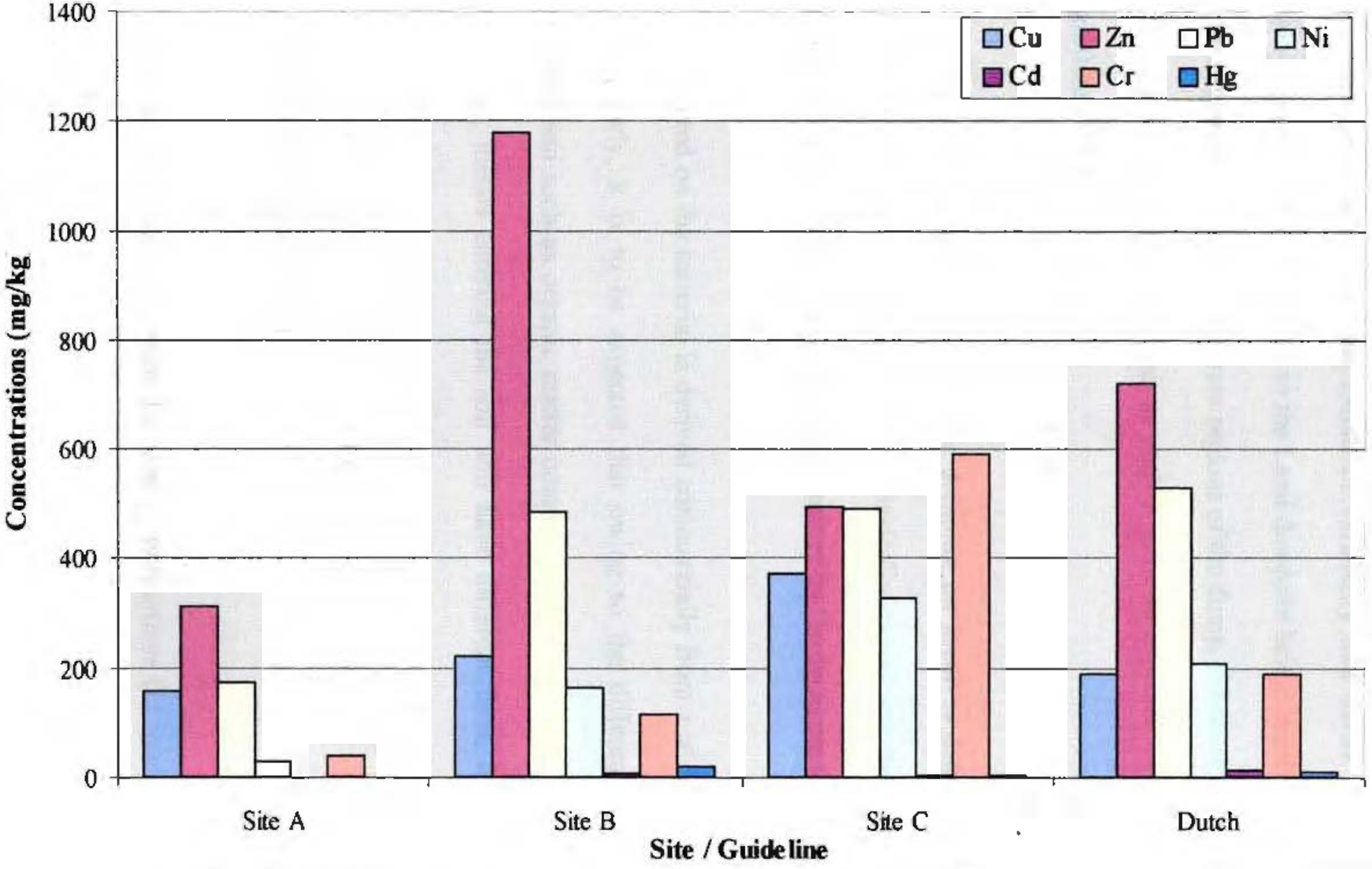
Al showed slightly negative correlation with Zn, Ni, Cd and Cr, suggesting that these heavy metals did not have any significant association with Al, but the same metals correlated positively with Fe. This could mean that either the metals have significant association with the ferrous oxides present in soil, or that the Fe-containing substances present in the dump are also contributing to the levels of these four heavy metals. The same four heavy metals showed negative correlation with Al, suggesting that if soil ferrous oxides control the association of these metals in the dump, then there is possible movement of these metals between the oxides and hydroxides of Fe and Al.

Mg did not have any significant correlation with the heavy metals, while Mn showed slightly negative correlation with Zn and Cd. These two cations appear to be the least involved in associating with the heavy metals.

Comparison of metal levels in Lami with international guidelines

Figure 4.4 shows the comparison of the metals present in the dump with the 'Dutch Standard', which is recognised, adopted and therefore established internationally (Chen, 2000). Compared to the Dutch guidelines, Site A contains metals within acceptable limits although Cu does almost border on the polluted side. At Site B, the levels of Cu

Figure 4.4 Heavy metals in the dump compared with the Dutch pollution guidelines



Zn and Hg exceed the pollution-defining levels while the rest (Pb, Ni, Cr and Cd) are within the acceptable range. At Site C, Cu, Ni and Cr do exceed the guidelines.

These mixed results are indicative of the extent of variability that exists within the dumpsite. The variability can be attributed to the Lami dumpsite being largely unsorted, giving rise to heterogeneity within the different regions of the dump. There is no defined pattern of utilisation of the dumping pit and as such it is to be expected that different areas yield significantly different results.

Furthermore, treatment of the material within the dumping pit involves dispersing the material across the dumping section, followed by mechanically compacting the matter by piled soil. The latter also serves to contain the odour emitted by the decaying vegetation.

The soil that is deposited on the material is derived commercially from a wide selection of areas. Consequently, it is to be expected that owing to the differences in the characteristics of the soil such as organic matter content, particle-size distribution, pH and mineral structure, metals entering the soil will have different fates, in terms of speciation and retention. This, coupled with different amounts of metals already present in each soil type would be expected to substantially contribute to the overall heterogeneity of metal levels in the dump.

Furthermore it was not possible to estimate the relative proportions (in terms of actual soil and rubbish) constituting the material tested. This is due to the continuous working of the soil to disperse it over the dumped material. As a result, it is difficult to quantify the contribution of each proportion to the overall heavy metal content.

As a final point, it must be emphasised that mobilisation of metals in soil is still not well understood. The roles of preferential flow paths and soluble organic matter are especially unclear (Camobreco *et al.,* 1996). Therefore, no fixed scenario could be assigned to any metal, especially keeping in mind the fact that the different soil types inculcate different behaviour onto metals.

4.4.3 Extractable amounts (bioavailable amounts)

The bioavailable fraction of metals in soil is that amount that can be mobilised into groundwater or be available for uptake by plants, and therefore is that fraction that is of most concern from an environmental standpoint. Various associations within soil can be included in this amount. There is some suggestion that the water-soluble and the organic fractions are plant-available forms (Shuman, 1991; Petruzzelli, 1989). It is important to consider these fractions since metal toxicity is not always directly correlated with the total amounts of heavy metals in soil (Leita and De Nobili, 1991; McLaughlin *et al.*, 2000). Solubility equilibria and mobility of heavy metals in soils are fundamental factors in determining metal availability to plants (Leita and De Nobili, 1991).

Tables A4.5(a) - A4.5(c) give the concentrations of heavy metals present in the bioavailable fraction of soil. The means of these results are presented in Table 4.10.

Table 4.10 Average concentrations of heavy metals within the bioavailable fraction

	Concentration (mg/kg)		
Metal	**Site A**	**Site B**	**Site C**
Cu	112	92. 1	656
Zn	31. 9	551	207
Pb	109	192	160
Ni	2.12	8.49	4.88
Cd	0.333	0.931	0.00889
Cr	0.824	1.48	1.37

The levels of Cu in samples A1, C8 and C9, and Pb in samples B7, C4, C5 and C6 were found to be extremely high, surpassing the total metal concentrations for the samples (section 4.4.1). Statistical tests on the values using the International Standards Organisation preferred Grubb's test (Miller and Miller, 2000) showed that only two of the values could be considered as outliers with 95% confidence. These values were discarded since they exceeded the total concentrations obtained for that particular sample, and are denoted as such. The rest of the values were retained. The source of such high values could possibly be due to the large amount of heterogeneity within each soil sample.

Figure 4.5 shows the relative proportions of the bioavailable and non-bioavailable amounts of each metal as a percentage value at the three sites. The dominant form of Cu was in the bioavailable fraction (although the figure has been exaggerated with the inclusion of the high Cu value in sample A1). Pb was also present largely in the bioavailable fraction. The high values of these two metals (even after excluding the anomaly for Cu) in the bioavailable fraction, together with a lack of significant correlation between them and organic carbon (as shown in Table 4.11) supports the suggestion that these two metals are not in association with organic carbon at site A. It is possible that they possibly exist in their free forms or in association with other soil fractions that do not bind them as firmly as organic matter would.

Generally the dilute acid-extracted digests showed that the levels of Cu, Zn and Pb in the bioavailable fraction of the soil were relatively high. Figures 4.6(a) and 4.6(b) show the distribution of the metals with site, which is based on the data in Table 4.10. At Site A, overall metal levels were the lowest in comparison to the other two sites. This was also the trend for total metal levels, and it is possibly due to the same reasons as discussed in Section 4.4.1.

At site C, Cu levels were the highest, followed closely by those for Pb and then Zn levels. The levels of Ni, Cr and Cd were the lowest (Cd being the least abundant metal in all three sites). Zn levels in the bioavailable fraction of Site A were lower than those for both Cu and Pb, suggesting that Zn is largely present in the residual or non-bioavailable fractions in soil of Site A. This is consistent with the findings of Luo and Christie (1998) who have found up to 72 % of Zn present in the residual fraction of soil. Sawhney *et al.* (1994) have found Zn to be in the highest concentrations in leachate-simulation studies,

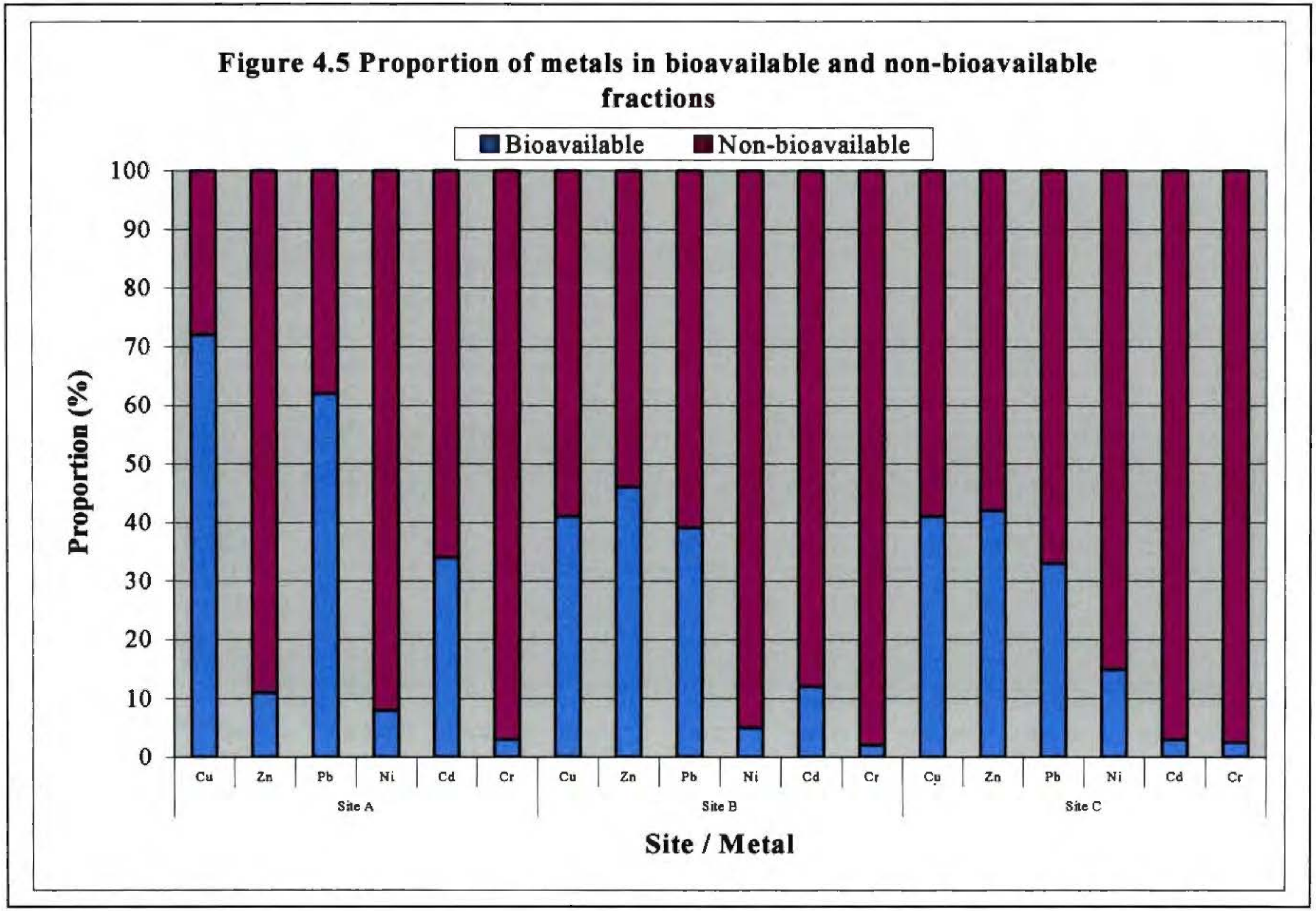


Figure 4.5 Proportion of metals in bioavailable and non-bioavailable fractions

Figure 4.6(a) Distribution of Cu, Zn and Pb in the bioavailable fraction of soil

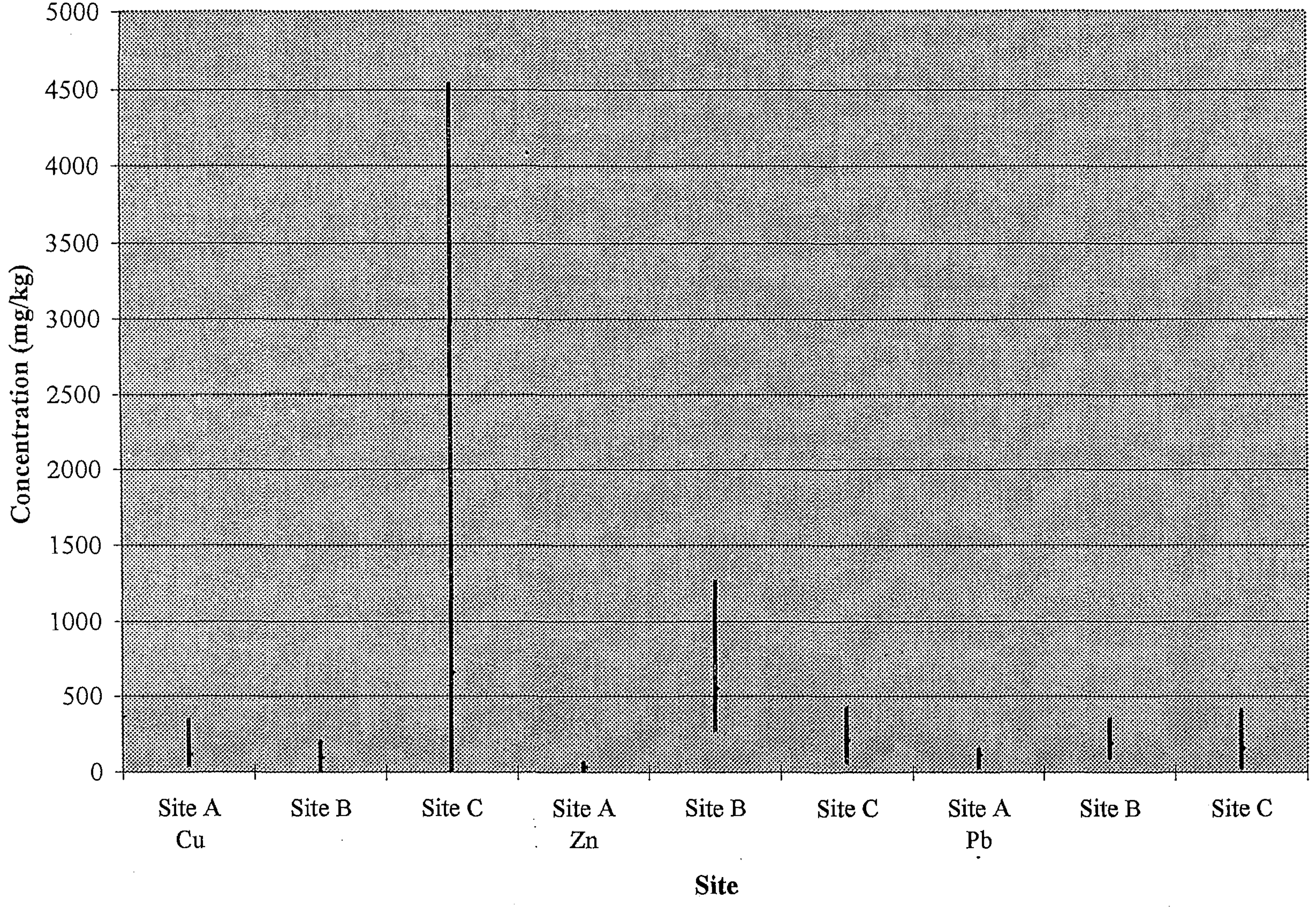
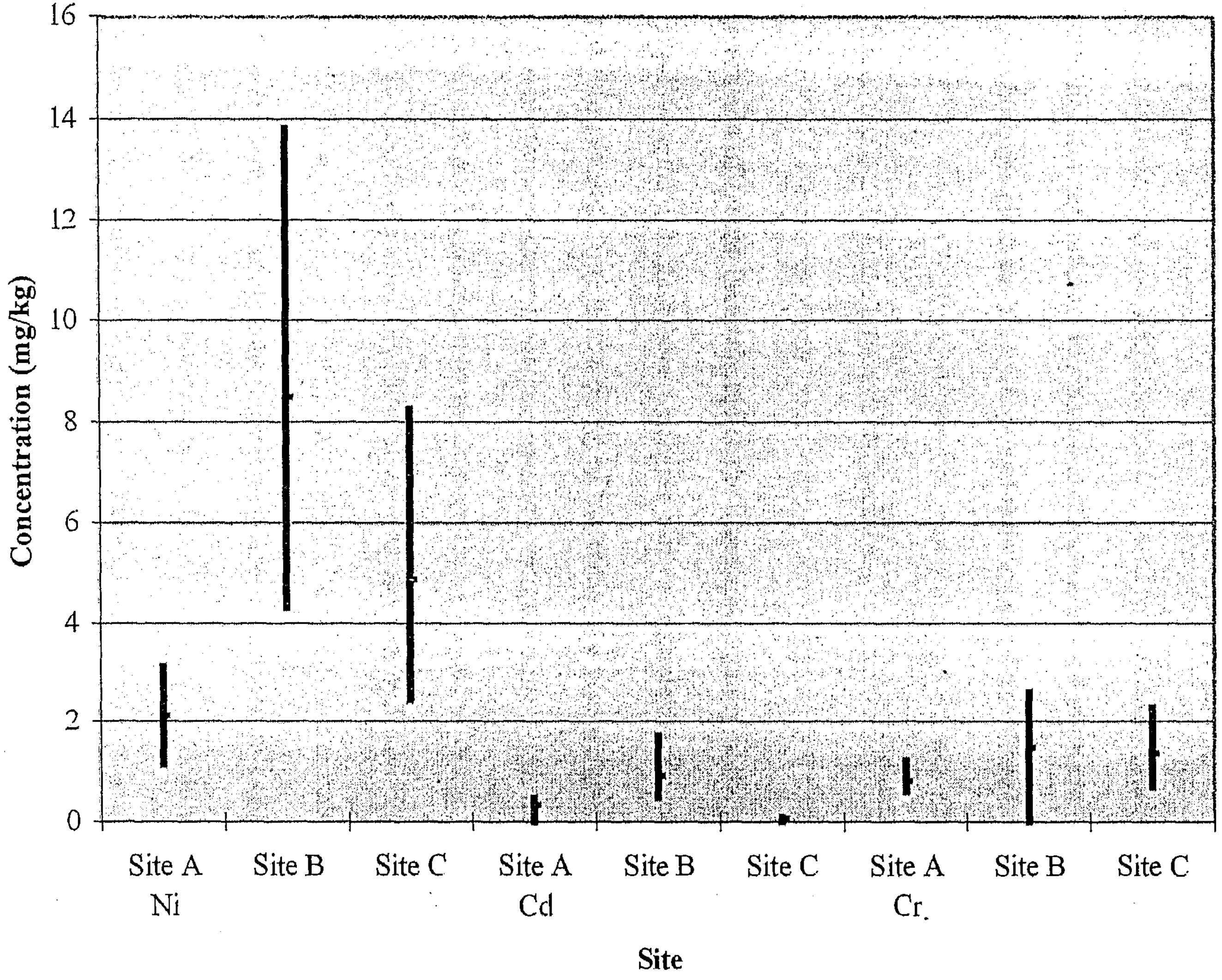


Figure 4.6(b) Distribution of Ni, Cd and Cr in the bioavailable fraction of soil



thereby confirming the high potential for the metal to be leached. Such a comparison with literature is possible for the metal levels in this site since it had a definite soil cover.

At Site B, the amount of Zn in the bioavailable fraction was larger than that for other metals (Figure 4.6[a]); followed by that of Pb and Cu. Ni Cd and Cr were present in lower concentrations, with Cd being the lowest. A comparison of Figure 4.5 with Figure 4.3 (distribution for total metal concentrations) shows a matching pattern of distribution of metals in both the bioavailable fraction and the total amounts. Therefore, it is possible that at site B, the factors influencing the total metal distribution also play an important part in that of the metals in the bioavailable fraction.

The high amount of Zn can be attributed to the immediate vicinity of the site to the active dumping pit boundary, from where leachates rich in complexed Zn could be readily emanating into the site. Due to the piling of materials at a considerable height, there is extensive leachate movement from the materials into the soil. Plate 6 shows leachate streams from the piled material into the mineralised area of the dump. This, together with the high mobility and leachability of Zn and the wet soil environment of Site B could be a factor resulting in elevated Zn levels. The significant correlation of Zn and organic carbon content in Table 4.11 (later in the section) supports this suggestion. At site C, the level of Cu was at its maximum, which also surpassed those of other metals. This is largely due to the extremely high concentration of the metal in Sample A4, which appeared to have very high concentrations of both Cu and Pb (although the latter was discarded due to statistical recognition as an anomaly). The digest from sample A4 was also deep blue in colour, similar to that of copper sulphate solution. Thus it appears that there is a Cu and Pb "hotspot" in this region, caused by dumped chemical matter, and over 40 % of the Cu and 30 % of Pb present due to the hotspot is bioavailable. For Zn, Pb and Ni, the consistency of the relative amounts they are present in (especially Pb and Ni) suggests that their respective distributions are controlled by factors already discussed. For Zn and Pb, however, the amounts in the bioavailable fraction also decreased, suggesting that these metals could be gradually being incorporated into the non-bioavailable fractions. On the other hand, the increases in the respective concentrations of Ni, Cd and Cr could mean that these metals are more in the bioavailable fractions of the soil at site C. In soil, long-term studies of metal movements in soil by Han *et al.*, (2001) have found that Cr has a tendency to move into the residual fraction of the soil by isomorphous substitution with Mg ions. Cr has an ionic radius of 0.64×10^{-10} m, which is similar in size to Mg (ionic radius of 0.65×10^{-10} m) and Fe (0.65×10^{-10} m). Thus, the suggestion is that Cr substitutes for Mg in silicates and Fe in Fe-oxides, thus reducing its overall bioavailability. This does not appear to be occurring at the third site in the dump, possibly as a result of the complex composition of the soil-like material at the site.

In Table 4.11, the correlation between heavy metals in the bioavailable fraction and organic carbon and the major cations are shown based on the product-moment correlation coefficients ($P = 0.05$).

Table 4.11 Correlation among heavy metals in the bioavailable fraction and organic matter and major cations

	Cu	**Zn**	**Pb**	**Ni**	**Cd**	**Cr**
% OC	-0.05$^{\varphi}$	0.6	0.1$^{\varphi}$	0.6	0.4	0.2$^{\varphi}$
Ca	0.4	0.04$^{\varphi}$	0.4	0.09$^{\varphi}$	-0.3	-0.03$^{\varphi}$
Mn	-0.2$^{\varphi}$	-0.3	-0.2$^{\varphi}$	-0.3$^{\varphi}$	-0.06$^{\varphi}$	-0.07$^{\varphi}$
Fe	-0.03$^{\varphi}$	0.4	0.03$^{\varphi}$	0.4$^{\varphi}$	0.4	0.2$^{\varphi}$
Mg	0.1$^{\varphi}$	-0.1$^{\varphi}$	0.1$^{\varphi}$	-0.2$^{\varphi}$	0.1$^{\varphi}$	0.1$^{\varphi}$
Al	0.06$^{\varphi}$	-0.4	0.0002$^{\varphi}$	-0.5	-0.1$^{\varphi}$	-0.1$^{\varphi}$

$^{\varphi}$ Statistically insignificant at all confidence levels.

Based on the data from Table 4.11, Cu and Pb appeared to be associated with the calcium-containing fractions of the soil. This could be especially possible at Site A where there was extensive soil cover. Zn correlated positively with the organic carbon and Fe, suggesting that the metal could be complexed with organic acids as well as the oxides and hydroxides of Fe in the leachate that is present at site B. The negative correlation of Zn with Al could also mean that there is possible movement of Zn between the oxides and hydroxides Al and Fe. A similar pattern was observed for Cd, which could be having similar chemical associations to Zn.

It is important to note that each site within the dump has different characteristics in terms of soil cover, land-use and soil characteristics. As a result, effective comparisons cannot be made between the metal levels in each site. It is also difficult to evaluate trends in the distribution of metals in the dump, since the parameters controlling metal availability and association in each site may not be as significant as in others. Therefore, soil parameters such as the different chemical and mineral fractions may be important in controlling metal distribution at site A, where there is ample soil cover, but may not be as significant at site B, where there is greater leachate movement from the rubbish pile, and what is referred to as soil is largely a mixture of some soil and dumped material from the adjacent pile. As a result, while correlation has been made between heavy metal concentrations and major cations and the organic carbon content and explanations given accordingly, it is important that the heterogeneity between the sites also be considered.

Secondly, bioavailability is a dynamic process that can be better understood and quantified if monitoring of a particular site of interest is carried out over a period of time. While the amount that is extracted in a single equilibration can yield useful information on the bioavailability of a metal at any given point in time, it is equally likely that a second equilibration would remove the same amount. Therefore, the amounts that have been extracted in this research could well be just a minor fraction of what is constantly being added and removed from the dump into the surrounding environment.

4.4.4 Heavy metal concentration in Lami foreshore area

Other studies that have been done on the marine foreshore area have found elevated concentrations of metals in the immediate vicinity of the Lami dump. Table 4.12 gives these results.

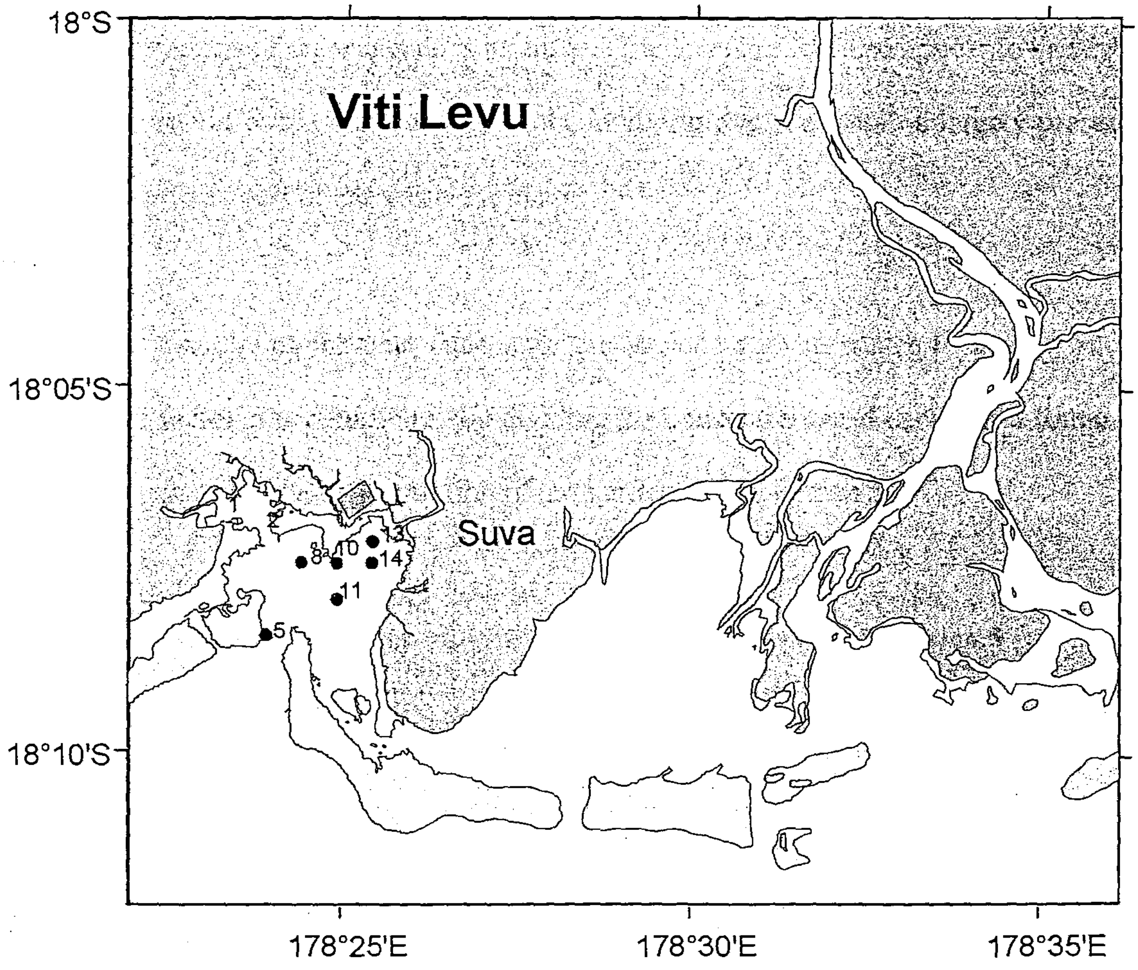
Table 4.12 Levels of metals in the Suva Harbour in the vicinity of the Lami dump

	Concentration of metal (µg/g)				
Station	**Cu**	**Cr**	**Fe**	**Mn**	**Ni**
5	49.5	30.8	31.9×10^3	45.1×10^1	13.5
8	34.7	26.7	35.9×10^3	60.1×10^1	13.4
10	51.8	24.8	32.1×10^3	47.6×10^1	13.2
11	49.4	37.2	26.5×10^3	39.9×10^1	16.8
13*	102	29.4	55.0×10^3	44.9×10^1	13.0
14*	95.2	26.1	41.6×10^3	48.7×10^1	12.9

*Highlighted rows contain data for sites that are in the immediate vicinity of the dump.
after Fichez (pers. comm.)

The sampling stations are projected in Figure 4.7. Station 5 is in the passage of the barrier reef, and represents a relatively unpolluted site, while Stations 8 - 11 are located within the Suva Harbour but further away from the dumpsite. Stations 13 and 14 (highlighted) are those fronting the dump. The levels of Cu and Fe are considerably higher in Stations 13 and 14 than others, suggesting that there may be influence of the dump on the levels of these metals. Cu and Fe are also the most common constituents of metallic materials present in the dump. The levels of Cr and Ni appear to be uniform for

Figure 4.7 Map of sampling stations for Lami foreshore sediment study



Key

▨ Location of Lami

▨ Land

□ Reef

□ Waterbody (sea /

● Sampling

(After Fichez (pers. comm.)

all stations. This could be due to the relatively low amounts that these metals are present in, both at natural levels as well as in the dump, therefore the contribution of the dump to the concentrations of these metals is minimal. The levels of Mn also appear to be within the range present in the harbour sediments, implying that the metal is largely present in the oxide form as part of the sediment matrix.

Table 4.13 lists the enrichment factors for the stations with reference to Station 5. The enrichment factor was determined by dividing the concentration of each metal found at a particular station by the concentration of the same metal at Station 5.

Table 4.13 Enrichment factor of metals with reference to Station 5

	Enrichment factor				
Station	**Cu**	**Cr**	**Fe**	**Mn**	**Ni**
8	0.70	0.87	1.1	1.3	0.99
10	1.0	0.81	1.0	1.1	0.98
11	0.99	1.2	0.83	0.88	1.2
13*	2.0	0.95	1.7	0.99	0.96
14*	1.9	0.85	1.3	1.09	0.96

*Highlighted rows contain data for sites that are in the immediate vicinity of the dump.

The data in Table 4.13 shows that Stations 13 and 14 have considerably higher degrees of enrichment for Cu and Fe compared to the other three stations. For station 13 especially, which is nearest to the dump, the enrichment factor is more than two-fold for Cu while the figure for Fe is also higher compared to the other stations. Enrichment of Mn, Ni and

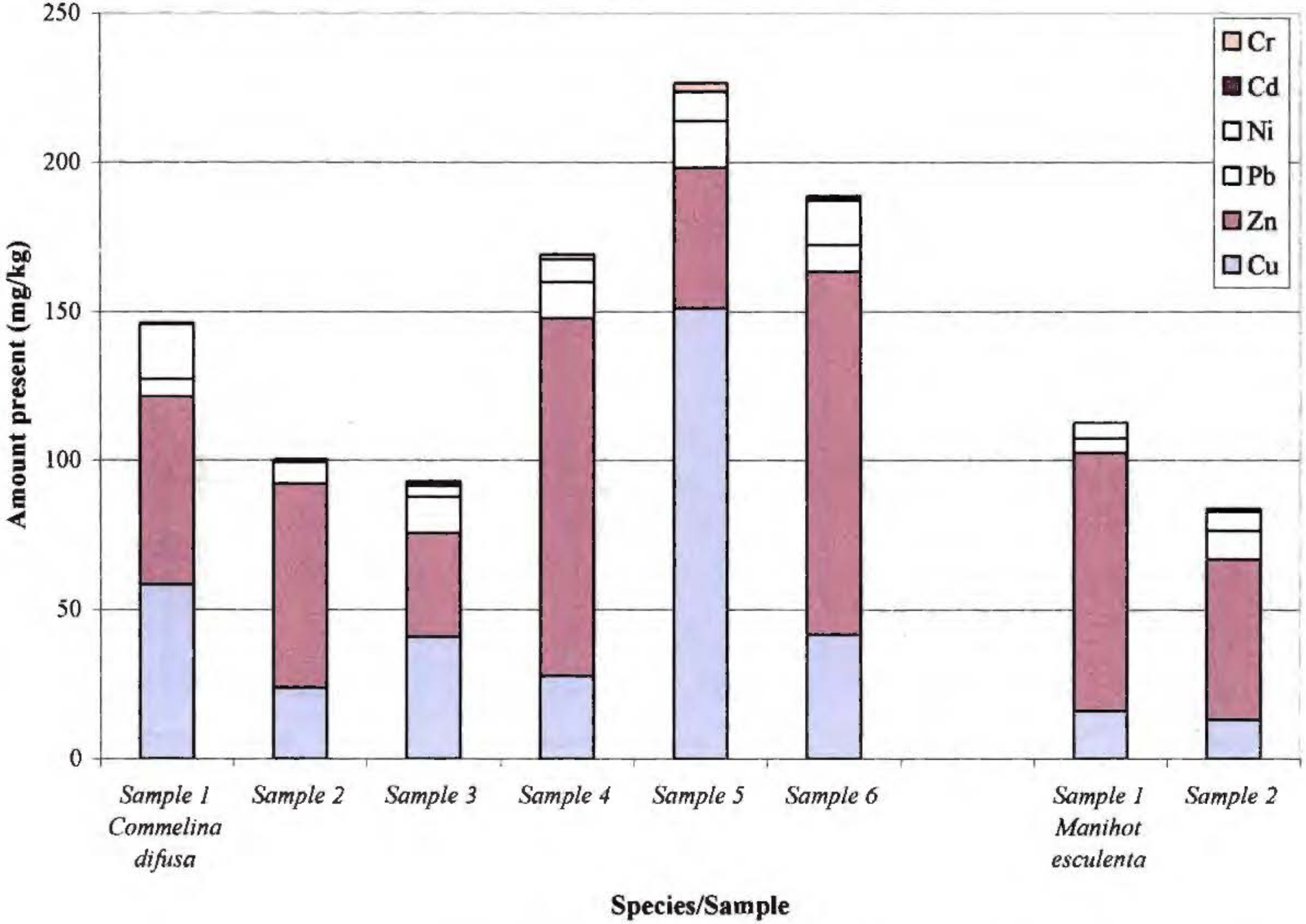
Cr is similar in all five stations. From the results, the sediments surrounding the dump are significantly enriched with respect to Cu and Fe. These two metals were also found to be present at high concentrations within the dump, with a large fraction of Cu present in the bioavailable fractions. These observations confirm that the dump may be a source for these two metals emanating into the harbour sediments.

In summary, detailed pathways of transformations depend primarily on the nature of the metal and soil properties (Han *et al.*, 2001; Shuman and Hargrove, 1985). In Lami, soil properties are very important. It has to be emphasised that many of the metals in the Lami dump are present in concentration levels that do not follow the expected pathways of distribution that is outlined in the literature. This is mainly due to the fact that the soil in the dump is not contaminated soil in the strict sense, however, it has been subjected to chemical input, which has increased its metal content. This, together with the fact that the soil itself is derived from a wide variety of areas and as a result is very heterogeneous itself, puts into context the absence of definite patterns of distributions of the metals.

4.4.5 Heavy metal content in plants

The amounts of metals present in each plant species sampled are shown in Figures 4.8 (a) - (d). In some sites there may be more than one sample of a particular plant species, for example, five blocks in Site A containing the species *Brachiara mutica*. This is due to that plant being the dominant species in the blocks concerned.

Figure 4.8 (a) Accumulated heavy metals in *C. diffusa* and *M. esculenta*



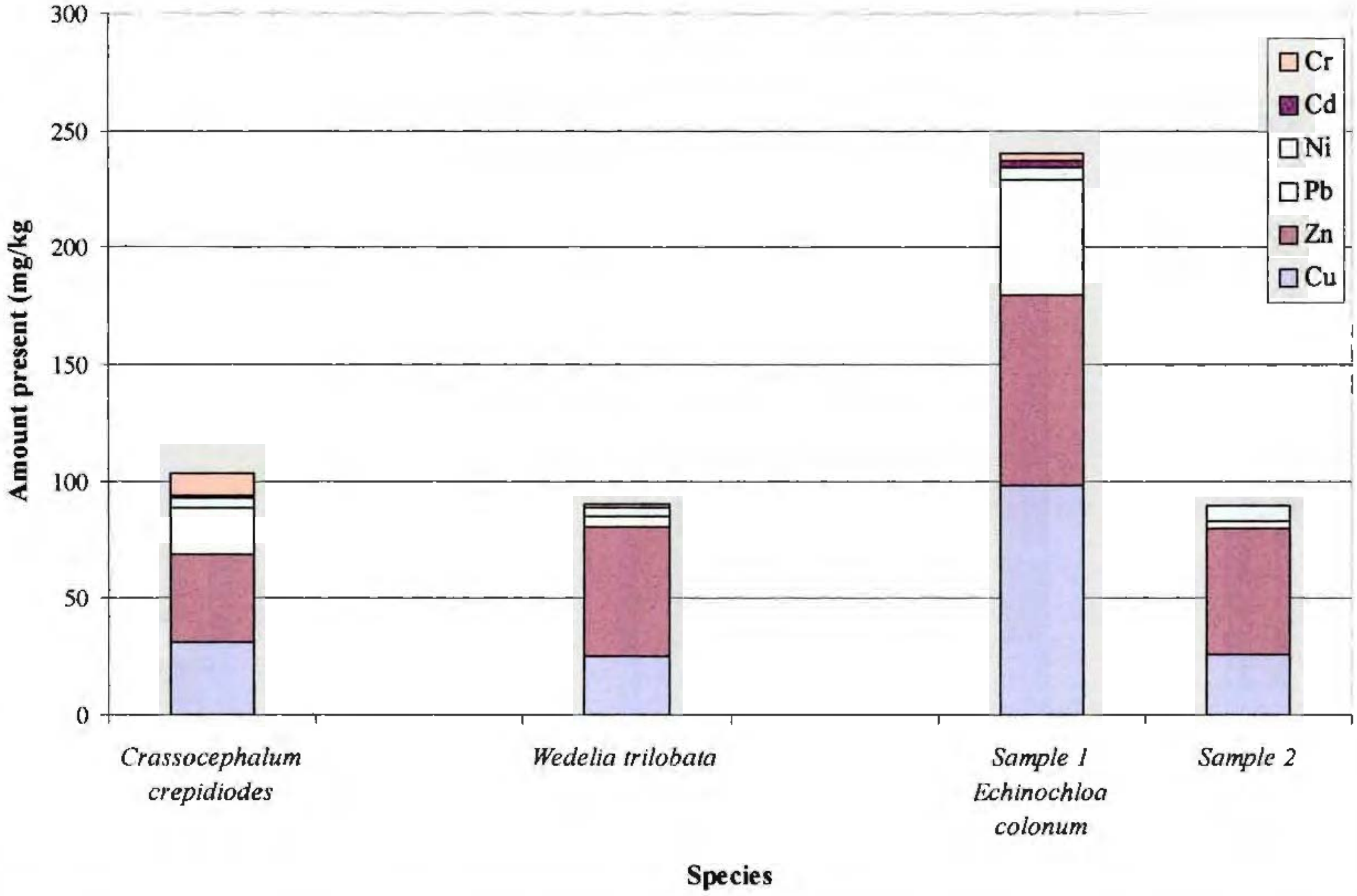


Figure 4.8 (b) Accumulated heavy metals in *C. crepidiodes, W. trilobata* and *E. colonumm*

Figure 4.8 (c) Accumulated heavy metals in *B. mutica, M. micrantha* and *C. pepo*

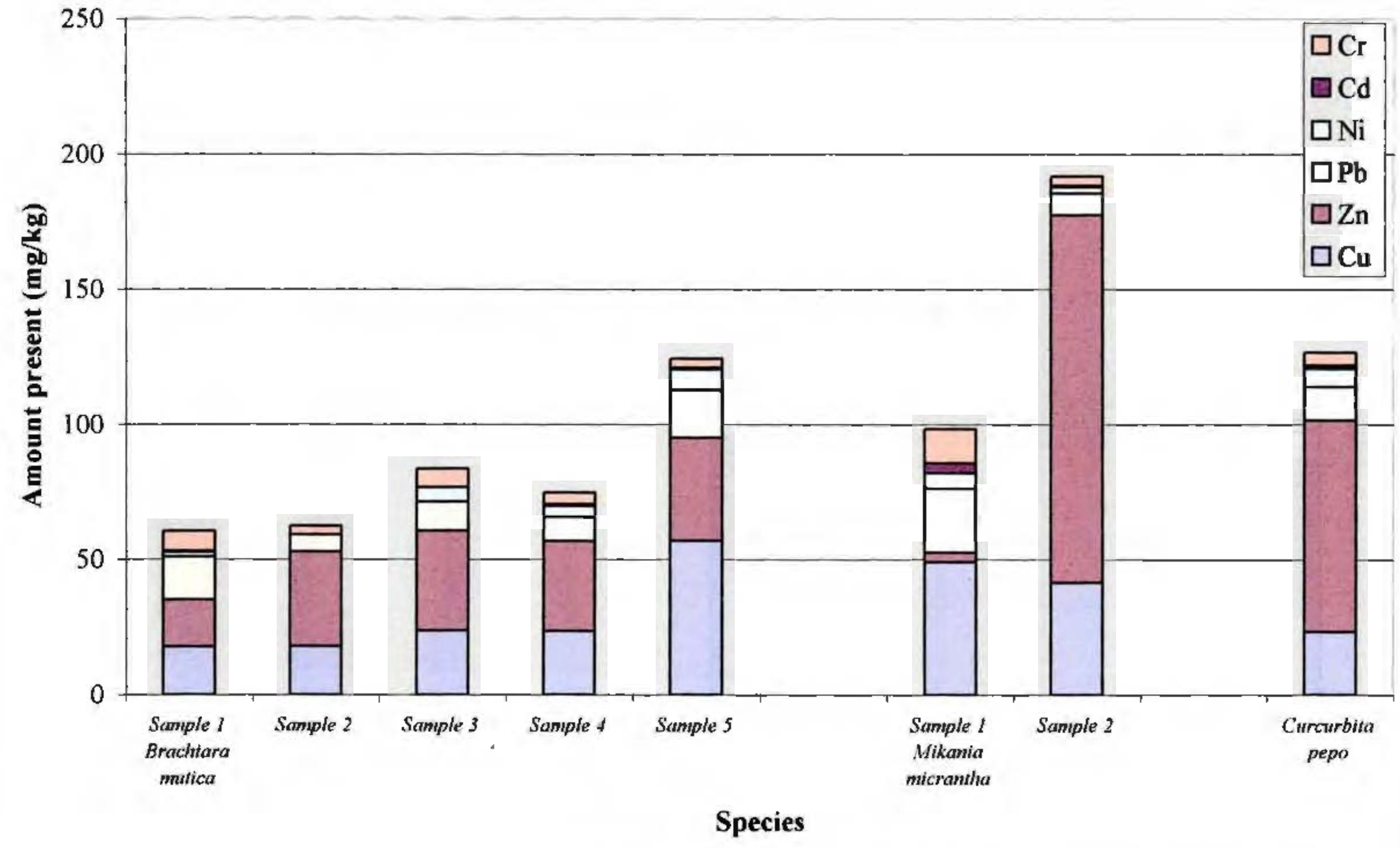
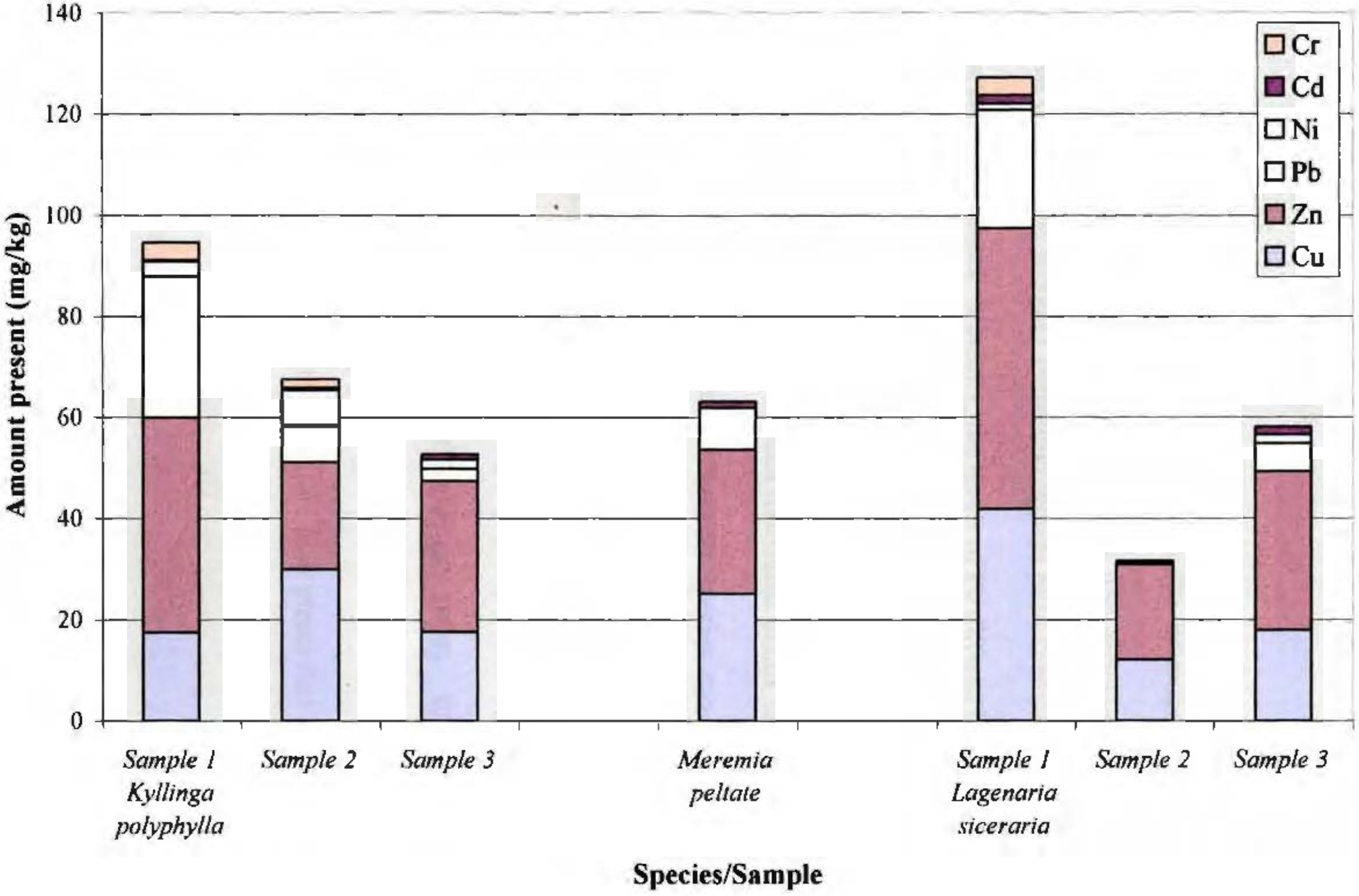


Figure 4.6 (d) Accumulated heavy metals in *K. polyphylla, M. peltata* and *L. siceraria*



Cu and Zn were the most abundant of all metals present, while the concentrations of Pb, Ni, Cd and Cr were variable, both in and within different species. Cu, Zn and Ni (for plants with nitrogen-fixing symbionts) are essential micronutrients to plants (Streit and Stumm, 1993), and as such, they are expected to be present in background concentrations.

Variations within the same species can arise due to the heterogeneous nature and composition of the soil like material on which the plant was germinating. For instance, the concentration of Ni in the second *Commelina diffusa* plant (Sample 2) was very low compared to the other five plants. Similarly, the levels of Pb differed by a factor of 25 in *Echinochloa colonumm*, while that of Zn differed by a factor of 45 in *Mikania micrantha.* Inhomogeneous soil structures (microedaphic differences within a very small area) can result in different elemental composition between individual plants of the same species even within a closely limited stand. Variation between species can result from many factors. Owing to genetic variability between species each plant has a different capacity for metal absorption compared to others (Markert, 1993). Also plants may not all be at the same growth stage during the time of sampling. This often renders the task of effective comparisons among them difficult (Qian *et al.*, 1999). While this criterion should be adhered to at all times, to ensure that these conditions are met during plant sampling is practically difficult. In this investigation, only plants that were at maximum growth stage were selected, based on common knowledge of maximum attainable growth sizes.

Furthermore, metal storage varies in different plant parts. For instance, the root section generally accumulates the most and often serves as the storage site preventing toxic dosages from reaching the stem, as is the case of Cd hyperaccumulation by *Chrysanthenum morifolium* (Grifferty and Barrington, 2000; Kirkham, 1978; Rooney *et al.*, 1999). Similiarly, young sunflower plants (*Helianthus annuus* L.) grown in a water culture supplemented with Cu, Cd, Pb and Zn accumulated heavy metals especially in the roots instead of the stem (Kastori *et al.*, 1992). Keeping this in mind, it is recommended to analyse the plant in its entirety by section, to obtain the levels absorbed by the plant as a whole. Therefore, the analysis of only leaves in this investigation is not representative of the entire plants, and this could possibly be another reason as to why metal levels are low and show wide variability.

The highest concentrations of metals were present among three plant species. This is shown in Table 4.14. Detailed data on the concentration of each metal in each plant species are presented in Tables A4.6 (a) – A4.6 (k).

Table 4.14 Species containing maximum concentrations of heavy metals

Metal	Species	Amount present (mg/kg)
Cu	*Commelina diffusa*	151
Zn	*Mikania micrantha*	136
Pb	*Echinochloa colonumm*	50.1
Ni	*Commelina diffusa*	18. 3
Cd	*Mikania micrantha*	3.71
Cr	*Mikania micrantha*	12. 5

Of particular significance are *Commelina diffusa* and *Mikania micrantha*, which contain two and three metals in the highest concentrations respectively. The remaining species contained moderate levels of heavy metals. Among the poorest accumulators of metals were *Wedelia trilobata*, *Meremia peltata* and *Manihot esculenta*.

Commelina diffusa, being a wetland plant would not be expected to have high levels of metals. Studies by Qian *et al.* (1999) have shown that wetland plants tend to accumulate very little Cu in their tissues. Investigations by their team itself found Cu present at a concentration of 95 mg/kg in smartweed (*Polygonum hydropiperoids* L.), thus confirming that wetland plants are not ideal hyperaccumulators. The levels of Cu in *Commelina diffusa* (151 mg/kg) are also quite low in accordance with the earlier (Section 2.6) definition of hyperaccumulators which should contain more than 0.1% of each metal in dry material.

Literature on metal-hyperaccumulating plants tends to focus more on hyperaccumulators which contain metals in far greater concentrations than those found in the vegetation from Lami. By definition, hyperaccumulators are plants that can accumulate over 1 % (> 10,000 mg/kg) of any particular metal (Chaney *et al.*, 1997). This paucity of data on non-hyperaccumulators makes it difficult to draw comparisons between other non-hyperaccumulating plants that do contain metals in higher than background concentrations. The levels of metals in some of these plants, as well as those from Lami are compared in Table 4.15.

Table 4.15 Concentration range of metals in non-hyperaccumulating, hyperaccumulating and Lami plants

Metal	Metal concentration (mg/kg)		
	Non-hyperaccumulator	Hyperaccumulator*	Lami
Cu	10	5,000	13.1 - 151
Zn	70	10,000	Nd - 122
Pb	2.1 - 2.5‡	-	Nd - 50.1
Ni	3	5,000	Nd - 18.3
Cd	0.1	100	Nd - 3.71
Cr	-	-	Nd - 12.5

* Not the highest concentration that can be encountered in hyperaccumulators
- Not provided
after Brooks, (1998)
‡ after Rooney *et al.* (1999)

The results show that plants from Lami contain heavy metals in too low concentrations to be classified as hyperaccumulators, yet the amounts that are present exceed the background concentrations normally found in plants growing on non-contaminated sites. (unfortunately data on metal content on plants growing in Fiji is not available in the literature). Therefore, it is possible that some translocation of metals from soil to plant shoots is occurring. Furthermore, the results also indicate that the heterogeneity in trace metal concentrations that was observed in soils of the dump is also reflected in the plants. To evaluate if there is any relationship between metals in these two matrices, correlation analyses were done. Table 4.16 shows the product-moment correlation coefficient, *r* (P = 0.01) for total trace metal content in soil and plant tissue, and bioavailable levels and plant tissue on a sample-by-sample basis. The metal levels are used from plant varieties which contained the respective metal in the highest concentration.

Table 4.16 Correlation between heavy metals in plants and in soil

Metal	Bioavailable and plant content	Strong acid-digested and plant content
Cu	0.8	0.8
Zn	0.4*	0.4*
Pb	0.0*	Nil
Ni	-0.1*	Nil
Cd	-0.1*	0.6
Cr	-0.5	-0.5

* Statistically insignificant at P = 0.01

Only Cu and Cr showed significant correlation (P = 0.01) between the bioavailable amounts and plant content, although for Cr, the correlation is negative whereas for Cu it is positive. For Cu, this could be interpreted as the metal being taken up by plants when in bioavailable forms, rather than being leached. The reason for the negative correlation for Cr is not immediately obvious. There was no significant correlation between the other metals in the bioavailable fraction and the plant leaves.

For the metals extracted from soil (by strong-acid digestion) and plants, good correlation was obtained for Cu and Cd, suggesting that increased levels of both metals in soil is accompanied by corresponding increases in the concentrations of the metals in the plant tissues growing on the same soil. This is consistent with the literature, where plant uptake of metals has been found to be related directly to soil availability (Grifferty and Barrington, 2000; Rooney *et al.*, 1999). For Cu, this is consistent with the significant correlation between the bioavailable fraction and the plant metal content.

Plant Zn showed insignificant correlation with soil Zn (r = 0.4). The reason for the relatively low r value could be the mobility of the metal within plants, whereby the metal is in a state of flux, from the soil system to plant tissues (Grifferty and Barrington, 2000).

The correlation between Cd in soil and plants was significant (r = 0.6). In the literature, Cd has been found to have an equilibrium process regulating its concentration in soil. As plant uptake of the metal increases, the equilibrium Cd concentration in soil is maintained from the input of Cd from the particulate-bound fraction. Thus, the concentration of Cd in soil is controlled by the nature of the particulate-bound form of Cd in the soil (Krishnamurti and Naidu, 2000). A correlation of 0.6 therefore would normally suggest that Cd may be present in soil as the free ion, whose uptake by plants may be dependant on the concentration of the metal in this free ionic state in soil. However, since there is insignificant correlation between Cd in the bioavailable fraction and in plants, there appears to be no equilibrium Cd concentration in the soil here. This may either be a consequence of the soil characteristics in the area, or a result of the lack of proper soil cover, or a combination of both.

The negative correlations of Cr in both fractions of soil with plant Cr means that the concentrations of the metal in the soil and plants were inversely related. There are two possible scenarios which could result in this: with increasing soil concentration of the metal, a decrease in the plant concentration, or vice-versa. Calculated ratios of the metal concentration in plant to metal concentration in soil did not yield any significant trends and therefore are not discussed here. Thus, the only possibility remaining is decreased plant Cr concentration with respect to soil Cr concentration. Should this be the case, then it suggests that the plants sampled are not accumulators of Cr and are largely unaffected by any increase in soil Cr concentration, irrespective of whether the increase is in the bioavailable or non-bioavailable fractions. This therefore renders their hyperaccumulating potential (see following section) as null.

Both Ni and Pb levels in plants did not show significant (P = 0.1) correlation with the levels in soil. This is consistent with literature on Ni concentrations in plants and soil (Severne, 1972). Pb occurs naturally in plants, but it is generally agreed that soil Pb concentration of 100 - 500 mg/kg and plant Pb concentration of several hundred mg/kg are considered as excessive (Kabata Pendias and Pendias, 1992). It is possible that the plants are non-accumulators of these two metals.

The purpose of the investigation of metal levels in plants was to screen for potential hyperaccumulators among the dominant plant species within the sampling sites. The results show that while the levels are above the background concentrations, they are too low to be considered as hyperaccumulators. Hence assessing only the shoot may not be the best method in deciding whether a plant is suitable for phytoremediation. Further research on this subject, using all section of the plants sampled (including those in this study) is recommended for possibly more successful outcomes.

5.0 GENERAL DISCUSSION

The Lami dump does not have any defined pattern of utilisation. A selected area within the site is used for dumping of materials for a given period. During the utilisation of the dumping area materials are dispersed with the help of a bulldozer, and soil brought in from different areas around and outside Suva is piled on the materials. This serves to contain the odour emitted by the degradable matter within the pit, and also serves as a new surface which can be used to pile another layer of materials. This also leads to a great degree of heterogeneity in the composition of the dump.

5.1 TOTAL HEAVY METAL CONTENT WITHIN SOIL

The total heavy metal content in soil showed considerable variation over the three sites. The reasons for this are, firstly, the heterogeneous nature of the soil present in the dump: the collective piling of soil from a wide variety of areas has resulted in differential soil characteristics within the dump. These characteristics, such as soil percentage organic carbon content, major cation content and soil particle-size distribution in turn appear to manifest themselves in the differential levels of heavy metals in the soil.

Secondly, due to the possibly insufficiently strong acid digestion mixture, any metals that may have been present in the silicate-mineral matrix of soil would have effectively remained unaffected by the acids. Therefore, the metals released in the first site could be from the non-silicate fractions which are available for leaching. Generally, remineralisation of organic carbon in soils would result in lower values for the percentage organic carbon, and this was seen in the results.

In terms of total concentrations, the levels of three metals, Cu, Zn and Pb were predominant in the dump, while Cr and Ni tended to show fluctuations, due to either differential soil characteristics, hotspots of these metals due to dumped materials or both. The levels of Cd and Hg were the lowest in all three sites. For Cd, the only plausible reason for such results is that the levels of the metal in the dump are very low as it is. There are not as many sources of Cd in the dump as there are for other metals. For Hg, the low levels could be due to the same reason. In addition to this, the digestion being performed in open beakers could have caused the volatilisation of the metal, hence leading to its low concentrations.

Overall, the levels of metals in the Lami dump are a cause for major concern, since they exceed the guidelines of many pollution standards around the world. Among the three sites, with the exception of Cd and Hg, all metals exceed the Dutch Standard, which is relatively lenient in terms of the permissible concentrations.

5.2 TOTAL HEAVY METAL CONTENT OF PLANTS

The total heavy metal content of the plants (on a species basis) was too low for the plants to be considered as hyperaccumulators. Despite this, however, the amounts of the metals in the shoots were higher than the background levels normally encountered in vegetation.

This should be a cause for concern, since there are many well-cultivated plantations of neighbouring villagers consisting of root crops and vegetables within the dump where active dumping is not occurring (including Site A). Considering the accumulative tendency of heavy metals, consumption of any produce from the dump should be avoided to avoid serious health consequences. To this end, the Suva City Council has in the past attempted to keep the dump guarded from scavengers, with relatively good success. Currently, there have been no reported incidences of scavengers, and prior permits are required before non-authorised personnel are permitted inside the area.

Plants have been known to hyperaccumulate heavy metals in roots, which often serve to exclude the metals from the shoots. Thus, it is possible that analysis of complete plant portions would have yielded higher concentrations in the plants sampled. Furthermore, sampling was confined to the dominant plant species within each site. This is justified by the fact that usually, hyperaccumulators are identified by their tendency to grow selectively in large numbers in contaminated sites, especially where the metal that the plant is a hyperaccumulator of is present. However, it may be worthwhile to screen *all* the plants present in Lami.

5.3 HEAVY METALS IN THE BIOAVAILABLE FRACTION

The high levels of metals obtained as the bioavailable fraction should also be a cause for concern, since it means that most of these metals can be readily released. Despite the variability, the metal concentrations in this fraction were generally high. The results of a study on the metal concentrations in the sediments of the harbour also showed that the levels of Cu and Fe were higher towards the foreshore of the dump, thereby insinuating that the dump could be contributing to the high concentrations.

In the dump, the levels of Cu and Zn in the mobile fraction of soil alone exceeded the total metal guidelines prescribed under the Dutch Standard, while Pb was present in higher than background concentrations. The other metals were present both within the Dutch Standard and the background concentrations. However, comparisons with background values should be attempted with caution, since the background concentrations vary with soil type, and as such, will be different for different sections of the dump.

It appears that the significantly high amount of precipitation that the Lami area receives makes it very likely that percolating rainwater ends up as organic-rich leachate, which has the potential to move into the adjacent marine environment, carrying with it its metal-rich load. This should be a cause for concern for the authorities managing the site, as well as for those who rely extensively on the Lami foreshore, and the vicinity of the dump area for subsistence.

6.0 CONCLUSION AND RECOMMENDATIONS

The mineralised waste at the Lami Dump is not significantly rich in organic matter content. There are high levels of Mn, Fe, Ca, Mg and Al. These metal species could be interacting with heavy metals, especially Fe and Mn with Zn, Ni, Cd and Cr. It also appears that there may be metal movement between the oxides and hydroxides of Al and Fe. Cu and Pb appeared to be existing largely in the non-residual fractions of the soil. Overall, the Lami dump is significantly enriched with heavy metals. Levels of Cu, Zn, Pb and Ni are especially of concern, since their concentrations in the dump were higher than the internationally-accepted pollution standards.

The levels of all heavy metals studied showed high variation, which indicated the extent of heterogeneity within the dump. This heterogeneity results from both the varied composition of the dump, as well as the different types of soil present, which have different physical (texture) and chemical (mineral composition, organic carbon content and pH) characteristics. These characteristics in turn play a major part in determining the heavy metal content. In many blocks that were sampled, especially in the second and third sites, the soil was actually soil-like matter that was heterogeneous in its composition, which was pointed out as another cause for the high variability in the data. Because of all these factors, many trends normally observed in metal-soil associations were not found in the dump.

Land-use within the dump also appears to be influencing metal distribution horizontally across the dump. The sites that had been disturbance-free for a longer time contained lesser concentrations of all metals extracted, in both total and residual amounts. The development of a proper soil profile allows the residual silicate fraction to develop as well. As a result, more metal movement would be expected to occur into the silicate fractions.

The amounts of heavy metals present as the bioavailable fraction were also high. Cu, Zn and Pb were the most abundant species present in the bioavailable fraction, suggesting that they have potential to be mobilised into the adjacent environment and cause problems. A study of metal amounts in the sediments of the harbour immediately in the vicinity of the dump showed elevated Cu and Fe concentrations, possibly a sign that metal leaching is already occurring.

Although the metal levels in the plants studied were higher than background concentrations normally found in plants, their concentrations were not high enough for these plants to be classed as hyperaccumulators. Thus, these plants were identified as unsuitable for phytoremediation. It is also equally possible, however, that the metal levels in the Lami dump are not sufficiently high enough to induce plant translocation. The dump contains metal-rich materials, but not actually metal-contaminated soils, as have been in cases around the world where phytoremediation has been successfully trialed.

A number of recommendations were identified as well, which would help obtain a clearer picture of the pollution status of the dump, especially in the long-term. These are listed in the following.

1. Firstly, there is a need to conduct more studies in the vicinity of the dump to determine the extent to which the pollution has spread. In the form of regular monitoring, this information would help identify the hazardous areas.

2. A study of the heavy metal profile with depth in the dump soils would be ideal, since it would provide knowledge on whether metal movement is occurring vertically as well. It is expected that there may be some vertical movement of metals with leachate movement, and only a proper study can put this speculation to rest. Additionally, any such study involving strong-acid digestion should also address the problem of matrix interference during the analysis.

3. For phytoremediation of the dump, other plants could be analysed to screen for hyperaccumulators, and should such a plant be identified, trials could be done to evaluate the success of the technique in Lami. Equally importantly, the screening of any plant (including those in this study) should include all sections of the plant to accommodate for any sectional differential in heavy metal accumulation.

4. Finally, but perhaps most importantly, planned and considerate dumping of materials in the dump is long overdue. Indiscriminate dumping since the dump's inception has

resulted in a wide variety of substances ranging from domestic to industrial wastes being present. This practice needs to be curbed, and industrial and chemical wastes should be diverted for treatment possibly within industry, rather than dumping at Lami, which is already showing signs of a hazard area as far as metals are concerned. Consideration of the environment should also be incorporated into the cost-benefit-analysis of the new potential site at Naboro, since a well lined and proper landfill with recycling capabilities seems to be a viable solution to cater for the growing population of Suva, without compromising the very environment that sustains it.

7.0 REFERENCES

Agemian, H. and **Chau, A. S. Y.** 1976. Evaluation of extraction techniques for the determination of metals in aquatic sediments. *Analyst,* **101**: pp. 761 – 767.

Allen, H. E., Perdue, E. M. and **Brown, D. S.** 1994, cited in C.R.Evanko and D.A.Dzombak. 1997. *Remediation of Metals-Contaminated Soils and Groundwater.*Technology Evaluation Report TE-97-01. Groundwater Remediation Technologies Analysis Center (GWRTAC), Pittsburgh.

Alloway, B. J. 1996. Soil pollution and land contamination. In Harrison, R. M. (ed.), *Pollution: Causes, Effects and Control* (3rd edition). The Royal Society of Chemistry, Cambridge: pp. 318 - 339.

Almås, Å. R. and **Singh, B. R.** 2001. Heavy metals in the environment: plant uptake of cadmium-109 and zinc-65 at different temperature and organic matter levels. *Journal of Environmental Quality*, **30**: pp. 869 - 877.

Almås, A. R., McBride, M. B. and **Singh, B. R.** 2000. Solubility and lability of cadmium and zinc in two soils treated with organic matter. *Soil Science*, **165** (3): pp. 250 - 259.

American Public Health Association, American Water Works Association and **Water Environment Federation**. (Greenberg, A. E., Clesceri, L. S. and Eaton, A. D., eds.). 1992. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, Washington D.C.

Baird, C. 1995. *Environmental Chemistry*. W. H. Freeman and Company, New York.

Brodie, J., and **Morrison, J**. 1984. The management and disposal of hazardous wastes in the Pacific Islands. *Ambio*: pp. 331 - 333.

Brooks, R. R. 1998. Geobotany. In Brooks, R. R. (ed.), *Plants that Hyperaccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining*.Cab International, Wallingford, United Kingdom: pp. 55 - 94.

Brown, K. S. 1995. The Green Clean: The emerging field of phytoremediation takes root. *Bioscience* [online], **45** (9). [WWW]

http://www.aibs.org/biosciencelibrary/vol45/greenclean.html

(17 October 2000).

Brown, S. L., Chaney, R. L., Angle, J. S. and **Baker, A. J. M.** 1994. Phytoremediation potential of *Thlaspi caerulescens* and bladder campion for zinc-and-cadmium-contaminated soil. *Journal of Environmental Quality*, **23** (6): pp. 1151 - 1157.

Camobreco, V. J., Richards, B. K., Steenhuis, T. S., Peverly, J. H. and **McBride, M. B.** 1996. Movements of heavy metals through undisturbed and homogenized soil columns. *Soil Science*, **161** (11): pp. 740 - 750.

Chaney, R. L., Brown, S. L., Li, Y., Angle, S., Stuczynski, T. I., Daniels, W. L., Henry, C. L., Siebielec, G., Malik, M., Ryan, J. A. and **Compton, H.** 2000. Progress in Risk Assessment for Soil Metals and In-Situ Remediation and Phytoextraction of Metals from Hazardous Contaminated Soils. *USEPA Conference on Phytoremediation: State of the Science Conference*. May 1-2, 2000, Boston.

Chaney, R. L., Malik, M., Li, Y. M., Brown, S. L., Brewer, E. P., Angle, J. S. and **Baker, A. J. M.** 1997. Phytoremediation of soil metals. *Current Opinions in Biotechnology*, **8**: pp. 279 - 284.

Chaney, R. L., Ryan, J. A. and **Brown, S. L.** 1999. Environmentally acceptable endpoints for soil metals. In Anderson, W. C., Loehr, R. C. and Smith, B. P. (eds.), *Environmental Availability in Soils: Chlorinated Organics, Explosives, Metals.* American Academy of Environmental Engineering, Annapolis: pp. 111 - 154.

Chen, Z. S. 2000. *Relationship between heavy metal concentration in soils of Taiwan and uptake by crops.* FFTC/ASPAC Technical Bulletin No. 149. Food and Fertilizer Technology Center for Asia and the Pacific (FFTC/ASPAC), Taipei.

Chester, R. and **Voutsinou, F. G.** 1981. The initial assessment of trace metal pollution in coastal sediments. *Marine Pollution Bulletin,* **12** (3): pp. 84 - 91.

Christensen, T. H. 1984.Cadmium sorption at low concentrations. I-Effect of time, cadmium load, pH and calcium. *Water, Air and Soil Pollution,* **21**: pp.105 – 114.

Craig, P. J. 1986. Chemical species in industrial discharges and effluents. In Bernhard, M., Brinckman, F. E. and Sadler, P. J. (eds.), *The Importance of Chemical "Speciation" in Environmental Processes.* Report of the Dahlem Workshop on the Importance of Chemical "Speciation" in Environmental Processes. Springer-Verlag, Berlin: pp. 443 - 464.

Dahl, A. L. and **Baumgart, I. L.** 1983. *The state of the environment in the South Pacific.* UNEP Regional Seas Reports and Studies No. 31.

Day, P. R. 1965. Particle fractionation and particle-size analysis. In Black, C. A., Evans, D. D., White, J. L., Ensminger, L. E. and Clark, F. E. (eds.), *Methods of Soil Analysis Part 1: Physical, and mineralogical properties, including statistics of measurements and sampling.* Agronomy Series (9). American Society of Agronomy, Inc, Madison, Wisconsin: pp. 545 - 566.

Dougherty, G. 1988. Heavy metal concentrations in bivalves from Fiji's coastal waters. *Marine Pollution Bulletin,* **9** (2): pp. 81 - 88.

Dudley, L. M., McNeal, B. L. and **Baham, J. E.** 1986. Time-dependant changes in soluble organics, copper, nickel, and zinc from sludge-amended soils. *Journal of Environmental Quality,* **15** (2): pp. 188 - 192.

Dzombak, D. A. and **Morel, F. M. M.** 1990, cited in C. R. Evanko and D. A. Dzombak, 1997; *Remediation of Metals-Contaminated Soils and Groundwater.* Technology Evaluation Report TE-97-01. Groundwater Remediation Technologies Analysis Center (GWRTAC), Pittsburgh.

Ebbs, S. D., Lasat, M. M., Brady, D. J., Cornish, J., Gordon, R. and **Kochian, L. V.** 1997. Heavy metals in the environment: Phytoextraction of cadmium and zinc from a contaminated soil. *Journal of Environmental Quality*, **26**: pp. 1424 - 1430.

Ellis, D. 1989. *Environments at Risk: Case histories of impact assessment.* Springer-Verlag, New York.

Eriksson, J. E. 1989. The influence of pH, soil type and time on adsorption and uptake by plants of Cd added to soil. *Water, Air and Soil Pollution.*

Evanko, C. R. and **Dzombak, D. A.** 1997. *Remediation of Metals-Contaminated Soils and Groundwater.* Technology Evaluation Report TE-97-01. Groundwater Remediation Technologies Analysis Center (GWRTAC), Pittsburgh.

Fichez, R. 2001. Researcher. Institut de recherche pour le développement, Noumea. Personal communication.

Förstner, U. 1986. Chemical forms and environmental effects of critical elements in solid-waste materials: Combustion residues. In Bernhard, M., Brinckman, F. E. and Sadler, P. J. (eds.), *The Importance of Chemical "Speciation" in Environmental Processes*. Report of the Dahlem Workshop on the Importance of Chemical "Speciation" in Environmental Processes. Life Sciences Research Report 33. Springer-Verlag, Berlin: pp. 465 - 492.

Gangaiya, P. 1994. *Land-based Pollution Sources in Kiribati: A Case Study.* SPREP Series No. 80. South Pacific Regional Environmental Programme, Apia, Western Samoa.

Geering, H. R. and **Hodgson, J. H.** 1969. Micronutrient cation complexes in soil solution. III. Characterisation of soil solution ligands and their complexes with Zn^{2+} and Cu^{2+}. *Soil Science Society of America,* **33** (1): pp. 54 – 59.

Giusquiani, P. L., Giovanni, G. and **Businelli, D.** 1992. Heavy metals in the environment: Mobility of heavy metals in urban waste-amended soils. *Journal of Environmental Quality*, **21**: pp. 330 - 335.

Goetz, R. (1997). *Purdue Researchers Prod Plants to Clean up Pollution* in PURDUE NEWS April, 1997 [WWW] http://www.purdue.edu/uns/html4ever/9704.Goldsbrough.phyto.html (24 March 2000).

Gomes, P. C., Fontes, M. P. F., da Silva, A. G., Mendonca, E. D. and **Netto, A. R.** 2001. Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Science Society of America Journal*, **65** (4): pp. 1115 - 1121.

Gregson, S. K. and **Alloway, B. J.** 1984. Gel permeation chromatography studies on the speciation of lead in solutions of heavily polluted soils.*Journal of Soil Science*, **35** (1): pp. 55 – 61.

Grifferty, A. and **Barrington, S.** 2000. Zinc uptake by young wheat plants under two transpiration regimes. *Journal of Environmental Quality*, **29**: pp. 443 - 446.

Griffin, R. A. and **Shimp, N. F.** 1976. Effect of pH on exchange-adsorption or precipitation of lead from landfill leachates by clay minerals. *Environmental Science and Technology*, **10**: 1256 - 1261.

Han, F. X., Banin, A. and **Triplet, G. B.** 2001. Redistribution of heavy metals in arid-zone soils under a wetting-drying cycle soil moisture regime. *Soil Science*, **116** (1): pp. 18 - 28.

Harmsen, K. 1977. *Behaviour of heavy metals in soils.* Agriculture Research Reports 866. Centre for Agricultural Publishing and Documentation, Wageningen, Holland.

Harrison, R. M. 1990. *Pollution: Causes, effects, and control* (2nd Edition).Royal Society of Chemistry, Cambridge.

Harter, R. D. 1983 Effects of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Science*, **47** (1): pp. 47 – 51.

Hogg, T. J., Stewart, J. W. B. and **Bettany, J. W. R.** 1978. Influence of the chemical form of mercury on its adsorption and ability to leach through soils. *Journal of Environmental Quality*, 7 (3): pp. 440 – 444).

Huamain, C., Chunrong, Z., Cong, T. and **Yongguan, Z.** 1999. Heavy metal pollution in soils in China: status and countermeasures. *Ambio*, **28** (2): pp. 130 - 134.

Huang, J. W. and **Cunningham, S. D.** 1996. Lead phytoextraction: Species variation in lead uptake and translocation. *New Phytologist*, **134** (1): pp. 75 – 84.

James, A. and **McDougall, F. R.** 1996. The treatment of toxic wastes. In Harrison, R. M. (ed.), *Pollution: Causes, Effects and Control* (3rd edition). The Royal Society of Chemistry, Cambridge: pp. 123 - 143.

Jeffery, J. J. and **Uren, U. C.** 1983. Copper and zinc species in the soil solution and the effects of soil pH. *Australian Journal of Soil Research*, **21**: pp. 479 - 488.

Kabata Pendias, A. and **Pendias, H.** 1992, cited in **C. P. Rooney, R. G. McLaren** and **R. J. Cresswell.** 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water, Air and Soil Pollution*, **116**: pp. 535 - 548.

Kalbitz, K. Solinger, S., Park, J. H., Michalzik, B. and **Matnez, E.** 2000. Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Science*, **165** (4): pp. 277 - 304.

Karathanasis, A. D. and **Seta, A. K.** 1993, cited in B. D. Lee, B. J. Carter, N. T. Basta and B. Weaver. 1997. Factors influencing heavy metal distribution in six Oklahoma benchmark soils. *Soil Science Society of America Journal*, **61**: pp. 218 - 223.

Kastori, R., Petrovic, M. and **Petrovic, N.**1992, cited in A.Grifferty and S.Barrington 2000. Zinc uptake by young wheat plants under two transpiration regimes. *Journal of Environmental Quality*, **29**: pp. 443 - 446.

Kettler, T. A., Doran, J. W. and **Gilbert, T. L.** 2001. Simplified method for soil particle-size determination to accompany soil-quality analyses. *Soil Science Society of America Journal*, **65**: pp. 849 - 852.

Kinniburgh, D. G., Jackson, M. L.and Syers, J. K. 1976. Adsorption of alkaline, transition and heavy metal cations by hydrous gels of iron and aluminium. *Soil Science Society of America Journal*, **40** (5): pp. 796 – 799.

Kirkham, M. B. 1978. Water-relations of cadmium-treated plants. *Journal of Environmental Quality*, 7(3): pp. 334 - 336.

Klassen, S. P., McLean, J. E., Grossl, P. R. and **Sims, R. C.** 2000. Heavy metals in the environment: Fate and behavior of lead in soils planted with metal-resistant species (river birch and small wing sedge). *Journal of Environmental Quality*, **29**: pp. 1826 - 1834.

Krishnamurti, G. S. R. and Naidu, R. 2000. Speciation and phytoavailability of cadmium in selected surface soils of South Australia. *Australian Journal of Soil Research*, **38**: pp. 991 - 1004.

LaGrega, M. D., Buckingham, P. L. and **Evans, J. C.** 1994. *Hazardous Waste Management*. McGraw-Hill Series in Water Resources and Environmental Engineering. McGraw-Hill Inc., New York.

Lands and Survey Department. 1989. Fiji Map series 31. *Topographic map of Suva*. Sheet 29 (Edition 1). Government of Fiji.

Lee, B. D., Carter, B. J., Basta, N. T. and **Weaver, B**. 1997. Factors influencing heavy metal distribution in six Oklahoma benchmark soils. *Soil Science Society of America Journal*, **61**: pp. 218 -223.

Leita, L. and **Nobili, M. D**. 1991. Water-soluble fractions of heavy metals during Composting of Municipal Soils Waste. *Journal of Environmental Quality* (20): pp. 73 - 78.

Lee, C., Fang, M. and **Hsieh, M**. 1998. Characterization and distribution of metals in surficial sediments in southwestern Taiwan. *Marine Pollution Bulletin*, **36** (6): pp. 464 - 471.

Leeper, G. W. and **Uren, N. C.** 1993. *Soil Science: An Introduction* (5th Edition). Melbourne University Press, Victoria.

Levi-Minzi, R., Soldatini, G. F., and **Riffadi, R.**1976.Cadmium sorption by soils.*Journal of Soil Science*, **27** (1): pp.10 – 15.

Li, Z. and **Shuman, L. M**. 1996. Heavy metal movement in metal-contaminated soil profiles. *Soil Science*, **161** (10): pp. 656 - 666.

Lisk, D. J. 1991, cited in S. D. Naidu and R. J. Morrison. 1994. Contamination of Suva Harbour, Fiji. *Marine Pollution Bulletin* Vol. 29 (1-3): pp. 126 - 130.

Luo, Y. M. and **Christie, P.** 1998. Bioavailability of copper and zinc in soils treated with alkaline stabilized sewage sludges. *Journal of Environmental Quality* (27): pp. 335 - 342.

Ma, L. Q. and **Rao, G. N.** 1997. Heavy metals in the environment: Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. *Journal of Environmental Quality*, **26**: pp. 259 - 264.

Markert, B. 1993. Instrumental analysis of plants.In Markert, B.(ed.), *Plants as Biomonitors: Indicators for heavy metals in the terrestrial environment.* VCH Publishers Incorporated, New York: pp.65 - 104.

Martinez-Garcia, M. L., Carlosena, A., Lopez-Mahia, P., Muniategui, S. and Prada, D. 1999. Determination of mercury in estuarine sediments by flow injection-cold vapour atomic absorption spectrometry after microwave extraction. *Analusis*, **27**: pp. 61 - 65.

McBride, M. B., Martinez, C. E., Topp, E. and **Evans, L.** 2000. Trace metal solubility and speciation in a calcareous soil 18 years after no-till sludge application. *Soil Science*, **165** (8): pp. 646 - 656.

McBride, M. B., Sauvé, S. and **Henderson, W. H.** 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soil. *Journal of Soil Science*, 48: pp. 337 - 346.

McGrath, S. P. 1987. Long-term studies of metal transfers following application of sewage sludge. In Coughtrey, P. J., Martin, M. H. and Unsworth, M. H. (eds.), *Pollutant Transport and Fate in Ecosystems*. Blackwell Scientific Publications, Oxford: pp. 301 - 317.

McGrath, S. P. 1998. Phytoextraction for soil remediation. In Brooks, R. R. (ed.), *Plants that Hyperaccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining*. Cab International, Wallingford, United Kingdom: pp. 261 - 289.

McKenzie, R. M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Australian Journal of Soil Research*, **18** (1): pp. 61 – 73.

McLaren, R. G. and **Smith, C. J.** 1996. Issues in the disposal of industrial and urban wastes. In Naidu *et. al.* (eds.), *Contaminants and the Soil Environment in the Australasia-Pacific Region*. Kluwer Academic Publishers, Great Britain: pp. 183 - 212.

McLaughlin, M. J., Hamon, R. E., McLaren, R. G., Speir, T. W. and **Rogers, S. L.** 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research*, **38**: pp. 1037 – 1086.

Miller, J. N. and **Miller, J. C.** 2000. Statistics and Chemometrics for Analytical Chemistry (4th edition). Prentice Hall, New York.

Miller, R. R. 1996. *Phytoremediation.* Technology Overview Report TO-96-03. Groundwater Remediation Technologies Analysis Center, Pittsburgh.

Mitchell, R. L. 1964, cited in B. D. Knezek and B. G. Ellis. 1980. Essential micronutrients IV: Copper, iron, manganese and zinc. In Davies, B. E. (ed.), *Applied Soil Trace Elements.* John Wiley and Sons Ltd, Chichester: pp. 259 - 286.

Morrison, R. J. 1990. *Assessment and Control in Coastal and Open Oceans of the SPREP Convention Region.* South Pacific Regional Environmental Programme, SPREP POL Progress Report prepared for the third inter-governmental meeting held in Noumea, New Caledonia. 24 - 28 September, 1990.

Naidu, R., Bolan, N. S., Kookana, R. S. and **Tiller, K. G.** 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European Journal of Soil Science*, **45**: pp. 419 - 429.

Naidu, S., Aalbersberg, W. G. L., Brodie, J. E., Fuavao, V. A., Maata, M., Naqasima, M., Whippy, P. and **Morrison, R. J.** 1991. *Water quality studies on selected South Pacific lagoons*. UNEP Regional Seas Reports and Studies No. 136, SPREP Reports and Studies No 49.

Naidu, S. D. and **Morrison, R. J.** 1994. Contamination of Suva Harbour, Fiji. *Marine Pollution Bulletin*, **29** (1-3): pp. 126 - 130.

Nelson, D. W., and **Sommers, L. E.** 1982. Total carbon, organic carbon and organic matter. In Page, A. L., Miller, R. H. and Keeney, D. R. (eds.), *Methods of Soil Analysis*. American Society of Agronomy, Inc. and Soil Science Society of America, Inc, Madison, Wisconsin. 2nd Edition (9): pp. 539 - 579.

Olson, G. J. 1986. Microbial intervention in trace-element-containing industrial process streams and waste products. In Bernhard, M., Brinckman, F. E. and Sadler, P. J. (eds.), *The Importance of Chemical "Speciation" in Environmental Processes*. Report of the Dahlem Workshop on the Importance of Chemical "Speciation" in Environmental Processes. Life Sciences Research Report 33. Springer-Verlag, Berlin: pp. 493 - 512.

Pearce, J. 1996. Plants may help reclaim 'brownfields' from industrial pollution. *Detroit News* (February 12): pp. 1.

Perkin Elmer. 1982. *Analytical methods for atomic absorption spectrophotometry.* Perkin Elmer Corporation.

Petruzzelli, G. 1989, cited in **Z. Li** and **L. M. Shuman** 1996. Heavy metal movement in metal-contaminated soil profiles. *Soil Science*, **161** (10): pp. 656 - 666.

Pitty, A. F. 1979. *Geography and Soil Properties.* Methuen & Co. Ltd, London.

Pivetz, B. E. 2001. *Phytoremediation of Contaminated Soil and Ground Water at Hazardous Waste Sites.* USEPA Ground Water Issue EPA/540/S-01/500. Superfund Technology Support Center for Groundwater, Ada, Oklahoma.

Preston, M. R. and **Chester, R.** 1996. Chemistry and pollution of the marine environment. In Harrison, R. M. (ed.), *Pollution: Causes, Effects and Control* (3rd edition). The Royal Society of Chemistry, Cambridge: pp. 26 - 51.

Qian, J-H., Zayed, A., Zhu, Y-L., Yu, M. and **Terry, N.** 1999. Phytoaccumulation of trace elements by wetland plants: III. Uptake and accumulation of ten trace elements by twelve plant species. *Journal of Environmental Quality*, 28: 1448 - 1455.

Quevauviller, Ph., Rauret, G., López-Sánchez, J. F., Ure, A., Barahona, E., Lachica, M. and **Muntau, H.** 1999. EDTA-, DTPA- and Acetic Extraction Protocols for the Determination of the Extractable Contents of Heavy metals in Sewage Sludge- Amended Soils. *Collaborative Report to the European Commission Standards, Measurements and Testing Programme*. European Commission, Brussels.

Radojević, M. and **Bashkin, V. N.** 1999. *Practical Environmental Analysis.* The Royal Society of Chemistry, Cambridge.

Raine, L. R. Siegel, B. Z. and **McMurty, G. M.** 1995. Mercury accumulation in sediments of the Ala Wai Canal and in soils and stream sediments of the central Honolulu watershed. *Pacific Science*, **49** (4): pp. 511 - 525.

Raskin, I (1997) Phytoremediation: Using plants to remove pollutants from the environment [WWW] http://www.aspp.org/pubaff/phytorem.htm (12 September 2000).

Robinson, B. H., Leblanc, M., Petit, D., Brooks, R. R., Kirkman, J. H. and **Gregg, P. E. H.** 1998. The potential of *Thlaspi caerulescens* for phytoremediation of contaminated soils. *Plant and Soil*, **203** (1): pp. 47 - 56.

Romkens, P. F. A. M. and **Salomons, W.** 1998. Co, Cu and Zn solubility in arable and forest soils: Consequences of land use changes for metal mobility and risk assessment. *Soil Science* Vol. 163 (11): pp. 859 - 871.

Rooney, C. P., McLaren, R. G. and **Cresswell, R. J.** 1999. Distribution and phytoavailability of lead in a soil contaminated with lead shot. *Water, Air and Soil Pollution*, **116**: pp. 535 - 548.

Ross, S. M. 1994a. Retention, transformation and mobility of toxic metals in soils. In Ross, S. M. (ed.), *Toxic metals in soil plant systems.* John Wiley and Sons, Chichester: pp. 63 – 152.

Ross, S. M. 1994b. Sources and forms of potentially toxic metals in soil-plant systems. In Ross, S. M. (ed.), *Toxic metals in soil plant systems.* John Wiley and Sons, Chichester: pp. 3 – 27.

Ross, S. M. 1994c. Toxic metals: Fate and distribution in contaminated ecosystems. In Ross, S. M. (ed.), *Toxic metals in soil plant systems.* John Wiley and Sons, Chichester: pp. 189 – 244.

Sawhney, B. L., Bugbee, G. J. and **Stilwell, D. E.** 1994. Leachability of heavy metals from growth media containing source-separated municipal solid waste compost. *Journal of Environmental Quality* (23): pp. 718 - 722.

Sbriz, L., Aquino, M. R., De Rodriguez, N. M. A., Fowler, S. W. and **Sericano, J. L.** 1998. Levels of chlorinated hydrocarbons and heavy metals in bivalves and nearshore sediments from the Dominican Republic. *Marine Pollution Bulletin*, **36** (12): pp. 971 - 979.

Schnitzer, M. and **Skinner, S. I. M.** 1967. Organo-metallic interactions in soils. 7. Stability constants of Pb^{2+} Ni^{2+}, Mn^{2+}, Cd^{2+}, Cu^{2+} and Mg^{2+} fulvic acid complexes. *Soil Science*, **103**: pp. 247 – 252.

Schnoor, J. L. 1997. *Phytoremediation.* Ground-Water remediation Technologies Analysis Center (GWRTAC) Technology Evaluation Report TE-98-01. GWRTAC, Pittsburgh.

Senesi, N., Sposito, G., Holtzclaw, K. M. and **Bradford, G. R.** 1989. Chemical properties of metal-humic acid fractions of a sewage sludge-amended aridisol. *Journal of Environmental Quality*, **18** (2): pp. 186 – 194.

Severne, B. C. 1972, cited in R. R. Brooks. Biogeochemistry and hyperaccumulators. In Brooks, R. R. (ed.), *Plants that Hyperaccumulate Heavy Metals: Their Role in Phytoremediation, Microbiology, Archaeology, Mineral Exploration and Phytomining.* Cab International, Wallingford, United Kingdom: pp. 95 - 118.

Shuman, L. M. 1985. Fractionation method for soil microelements. *Soil Science*, **140**: pp. 11 - 22.

Shuman, L. M. 1991, cited in **Z. Li** and **L. M. Shuman.** 1996. Heavy metal movement in metal-contaminated soil profiles. *Soil Science*, **161** (10): pp. 656 - 666.

Shuman, L. M. and **Hargrove, W. L.** 1985. Effects of tillage on the distribution of manganese , copper, iron and zinc in soil fractions. *Soil Science Society of America Journal*, **49** (5): pp. 1117 - 1121.

Skoog, D. A., Holler, F. J. and **Nieman, T. A.** 1998. *Principles of Instrumental Analysis* (5th edition). Saunders College Publishing, Philadelphia.

Smith, L. A., Means, J. L., Chen, A., Alleman, B., Chapman, C. C., Tixier, J. S., Jr., Brauning, S. E., Gavaskar, A. R. and Royer, M. D. 1995, cited in **C. R. Evanko** and **D. A. Dzombak.** 1997. *Remediation of Metals-Contaminated Soils and Groundwater*. Technology Evaluation Report TE-97-01. Groundwater Remediation Technologies Analysis Center (GWRTAC), Pittsburgh.

Stevenson, F. J. 1977. Nature of divalent transition metal complexes of humic acids as revealed by a modified potentiometric titration method. *Soil Science*, **123**: pp. 10 – 17.

Stewart, C. and **deMora, S. J.** 1990. A review of the degradation of tri (n-butyl) tin in the marine environment. *Environmental Technology*, **11**: pp. 565 - 570.

Streit, B. and **Stumm, W.** 1993. Chemical properties of metals and the process of bioaccumulation in terrestrial plants. In Markert, B. (ed.), *Plants as Biomonitors: Indicators for heavy metals in the terrestrial environment.* VCH Publishers Incorporated, New York: pp. 29 - 62.

Swift, R. S. and **McLaren, R. G.** 1991. Micronutrient adsorption by soils and soil colloids. In Bolt, G. H. *et. al.*, (eds.) *Interactions at the Soil Colloid-Soil Solution* Interface. Kluwer Academic Publications, Dodrecht, The Netherlands: pp. 257 - 292.

Tabudravu, J. N. 1995. *Experimental and field evaluation of Etemorpha flexuosa as an indicator of heavy metal pollution by zinc lead and copper in coastal waters of Lami, Fiji.* M.Sc. thesis. University of the South Pacific, Suva.

Tessier, A., Campbell, P. G. C. and **Bisson, M.** 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51** (7): pp. 844 – 851.

Twyford, I. T. and **Wright, A. C. S.** 1965. *The Soil Resources of the Fiji Islands* (Volume 1). Government of Fiji, Suva.

United Nations Environment Programme (UNEP). 1999. *Guidelines for Municipal Solid Waste Management: Planning in small island developing states in the Pacific Region.* South Pacific Regional Environment Programme, Apia.

United States Environmental Protection Agency (USEPA) (1998) A Citizen's Guide to Phytoremediation [WWW] http://clue-in.org/products/citguide/phyto2.htm (18 September 2001).

USDA-ARS, 1995. Metal-Scavenging Plants to Cleanse the Soil. *Agricultural Research* [online]. USDA-ARS [WWW] http://bob.soils.wisc.edu/~barak/soilscience326/agres.htm (11 December 2000).

vanLoon, G. W. and **Duffy, S. J.** 2000. *Environmental Chemistry: A global perspective.* Oxford University Press, Oxford.

Virkanen, J. 1998. Effect of urbanization on metal deposition in the Bay of Toolonlahti, southern Finland. *Marine Pollution Bulletin*, **36** (9): pp. 729-738.

Watling, D. and **Chape,** S. 1993. The National Environment Strategy. Government of Fiji and World Conservation Union. World Conservation Union, Switzerland.

Weiner, E. R. 2000. *Applications of Environmental Chemistry: A practical guide for environmental professionals.*Lewis Publishers, Boca Raton.

White, R. E. 1997. *Principles and Practice of Soil Science: The soil as a Natural Resource* (3rd edition). Blackwell Sciences Ltd, London.

Zhang, M., Alva, A. K., Li, Y. C. and **Calvert, D. V**. 1997. Chemical association of Cu, Zn, Mn and Pb in selected sandy citrus soils. *Soil Science*, **162** (3): pp. 181 - 188.

APPENDIX 1 Organic Carbon Data

Table A4.1 Percentage Organic Carbon at all sites

Site	Mean Percent Organic Carbon	± Variation
A1	2.11	0.327
A2	3.47	0.0990
A3	2.62	0.0320
A4	6.30	0.113
A5	2.91	0.0630
A6	2.98	0.0940
A7	2.59	0.149
A8	2.71	0.229
A9	5.01	0.229
B1	14.3	0.464
B2	17.9	0.832
B3	19.0	0.0690
B4	15.2	0.401
B5	17.9	0.997
B6	15.2	0.790
B7	13.5	0.222
B8	12.6	0.346
B9	16.9	0.685
C1	24.2	0.837
C2	7.58	0.120
C3	7.87	0.365
C4	9.18	1.74
C5	8.83	0.413
C6	13.8	1.59
C7	9.73	0.0710
C8	2.49	0.113
C9	10.6	0.524

The figures are averaged representations of the three replicates for analysis, with the variation describing the range. The variation was determined by calculating the range (lowest value subtracted from the highest) and dividing the range by 2. This is the method of expression of results in Appendices 1 – 6.

APPENDIX 2 Major Cation Concentrations in Soil

Table A4.2 (a) Manganese and Magnesium levels at all three sites

Site	Metal Concentration ± Variation (mg/kg)			
	Manganese		Magnesium	
	Mean	Variation	Mean (x 10^2)	Variation (x 10^2)
A1	809	34.5	88.4	2.69
A2	844	19.6	93.4	3.76
A3	865	19.9	86.2	6.60
A4	2280	91.9	90.9	9.31
A5	865	36.5	94.5	1.68
A6	755	20.6	88.9	5.53
A7	894	59.1	97.3	3.64
A8	909	13.1	97.1	1.01
A9	791	23.9	86.7	5.67
B1	736	13.1	81.2	2.30
B2	908	11.2	83.1	2.54
B3	595	23.9	71.1	0.758
B4	606	14.0	58.7	18.90
B5	433	28.9	64.5	10.70
B6	598	21.6	67.4	8.00
B7	828	29.1	73.8	2.39
B8	509	6.64	68.8	9.85
B9	489	38.4	65.0	5.67
C1	208	20.2	58.9	0.0296
C2	447	35.7	82.6	11.60
C3	606	23.6	90.3	2.77
C4	421	27.2	89.2	1.93
C5	419	34.9	0.543	0.0167
C6	569	23.9	77.5	0.948
C7	325	17.9	87.2	2.26
C8	765	18.9	99.0	2.72
C9	819	26.7	87.4	3.21

Table A 4.2(b) Iron and Aluminium levels at all three sites

Site	Metal Concentration ± Variation (mg/kg)			
	Iron		Aluminium	
	Mean (x 10^3)	Variation (x 10^3)	Mean (x 10^3)	Variation (x 10^3)
A1	46.1	4.76	40.3	0.487
A2	63.5	3.34	43.1	1.23
A3	47.1	6.24	46.0	0.472
A4	72.0	3.21	79.1	2.06
A5	47.9	4.99	41.6	0.989
A6	48.9	5.46	45.7	0.687
A7	57.4	2.31	51.5	2.05
A8	50.9	1.62	47.7	0.811
A9	65.1	11.4	41.0	1.30
B1	63.4	6.98	29.9	0.315
B2	47.1	26.5	28.7	0.311
B3	71.9	33.1	23.7	2.11
B4	70.8	28.4	22.7	0.727
B5	55.7	29.1	15.6	0.446
B6	68.0	0.675	24.2	0.454
B7	85.5	4.45	23.1	1.31
B8	68.2	9.63	17.7	3.28
B9	72.8	5.60	21.8	0.491
C1	0.758	0.0267	5.76	0.0681
C2	51.4	2.03	29.8	0.173
C3	68.4	2.08	32.9	0.0561
C4	53.1	5.79	36.9	1.76
C5	2.07	0.102	18.7	1.01
C6	76.3	3.92	20.9	0.329
C7	55.8	1.94	29.1	1.11
C8	69.3	2.69	43.3	0.335
C9	57.3	3.69	30.1	1.70

Table A4.2(c) Calcium levels at all three sites

	Metal Concentration ± Variation (mg/kg)	
Site	**Mean (x 10^3)**	**Variation (x 10^3)**
A1	7.62	0.531
A2	10.3	0.227
A3	7.43	0.115
A4	6.22	0.168
A5	9.90	0.117
A6	8.23	0.184
A7	11.3	0.135
A8	8.66	0.149
A9	8.27	0.429
B1	21.6	4.48
B2	18.5	3.75
B3	14.5	0.521
B4	14.6	2.90
B5	20.9	0.416
B6	19.3	0.644
B7	21.7	1.42
B8	34.8	5.29
B9	14.9	0.499
C1	44.3	3.77
C2	40.9	2.09
C3	27.4	4.01
C4	51.8	10.6
C5	69.6	7.06
C6	25.5	1.58
C7	17.7	0.124
C8	15.3	0.237
C9	31.9	4.52

APPENDIX 3 Heavy Metal Concentrations in Soil

Table A4.3 (a) Copper and Zinc levels in soil from all three sites

Site	Metal Concentration ± Variation (mg/kg)			
	Copper		Zinc	
	Mean	Variation	Mean	Variation
A1	98.0	0.498	345	7.34
A2	190	12.1	487	12.7
A3	246	11.2	294	5.22
A4	169	6.01	156	4.27
A5	179	2.52	377	8.93
A6	146	1.57	251	9.83
A7	89.5	5.23	330	2.46
A8	135	3.62	293	12.5
A9	149	9.11	288	11.8
B1	243	20.2	844	5.65
B2	183	20.2	1030	35.6
B3	142	1.85	892	20.2
B4	344	23.4	1710	56.2
B5	125	11.9	836	35.8
B6	204	11.3	599	27.2
B7	316	23.6	1100	48.8
B8	189	7.84	1340	40.1
B9	269	50.9	2250	108
C1	399	1.63	129	5.53
C2	372	8.68	365	6.07
C3	191	5.55	794	7.73
C4	12600	47.1	1410	34.6
C5	355	10.9	244	6.19
C6	443	2.77	586	9.50
C7	144	20.2	278	3.78
C8	95.4	5.82	309	6.66
C9	94.7	10.5	329	13.9

Table A4.3 (b) Lead and Nickel levels in soil from all three sites

Site	Metal Concentration ± Variation (mg/kg)			
	Lead		Nickel	
	Mean	Variation	Mean	Variation
A1	201	10.6	20.1	1.38
A2	179	39.0	22.0	0.453
A3	165	10.7	27.5	2.29
A4	68.6	6.21	75.6	2.56
A5	219	31.9	21.4	0.830
A6	148	7.50	24.8	0.537
A7	146	2.43	27.6	0.449
A8	208	4.26	17.9	2.29
A9	230	8.51	18.4	3.31
B1	296	18.4	187	28.9
B2	235	17.4	273	19.8
B3	157	82.9	184	16.2
B4	809	8.57	200	34.8
B5	530	34.6	202	27.2
B6	484	48.9	240	30.9
B7	1040	223	89.9	12.9
B8	468	40.3	52.5	5.98
B9	346	68.8	38.2	25.0
C1	61.3	5.22	10.9	2.19
C2	458	208	26.3	1.94
C3	216	30.7	53.9	3.53
C4	2980	1470	94.8	2.57
C5	108	25.7	13.8	1.22
C6	208	8.95	31.4	2.23
C7	87.3	2.28	21.3	2.53
C8	221	12.0	22.0	0.919
C9	80.2	5.96	19.7	0.781

Table A4.3(c) Cadmium and Chromium levels in soil from all three sites

Site	Metal Concentration ± Variation (mg/kg)			
	Cadmium		Chromium	
	Mean	Variation	Mean	Variation
A1	Nd*	0	37.3	2.89
A2	Nd	0	44.1	0.539
A3	Nd	0	42.6	4.39
A4	Nd	0	56.7	0.666
A5	Nd	0	33.4	1.51
A6	Nd	0	38.6	2.32
A7	Nd	0	32.9	1.26
A8	Nd	0	31.4	1.74
A9	Nd	0	32.9	3.65
B1	8.92	1.61	187	8.56
B2	10.1	2.38	125	10.5
B3	7.77	1.58	77.2	8.81
B4	7.08	1.29	112	12.3
B5	5.80	1.68	89.7	10.3
B6	8.10	2.56	143	11.8
B7	6.31	1.36	183	15.3
B8	7.98	3.34	70.5	10.1
B9	8.47	2.90	69.2	12.7
C1	Nd	0	13.6	1.38
C2	Nd	0	35.1	1.85
C3	1.96	0.245	64.4	2.46
C4	11.1	1.55	64.8	5.85
C5	Nd	0	21.1	1.81
C6	Nd	0	96.6	3.18
C7	Nd	0	162	1.11
C8	Nd	0	46.3	1.55
C9	7.44	0.383	41.4	0.350

[*] Not detected

Table A4.3 (d) Mercury levels in soil from all three sites

	Metal Concentration ± Variation (mg/kg)	
Site	**Mean**	**Variation**
A1	Nd	0
A2	Nd	0
A3	Nd	0
A4	Nd	0
A5	Nd	0
A6	Nd	0
A7	0.489	0.0124
A8	Nd	0
A9	Nd	0
B1	47.4	6.50
B2	7.74	2.84
B3	Nd	0
B4	Nd	0
B5	Nd	0
B6	Nd	0
B7	11.2	4.76
B8	9.74	2.27
B9	14.4	5.84
C1	Nd	0
C2	Nd	0
C3	Nd	0
C4	3.73	1.94
C5	Nd	0
C6	3.38	1.08
C7	Nd	0
C8	Nd	0
C9	Nd	0

APPENDIX 4 Interlaboratory Comparison Results

Table A 4.4 (a) Comparative results from USP and IRD

	Metal concentration in acid-digests (mg/L)					
Site	**Nickel**		**Lead**		**Copper**	
	USP	**IRD**	**USP**	**IRD**	**USP**	**IRD**
A1	0.760	0	0.480	2.00	2.06	2.33
A2	0.800	0	4.36	1.67	4.08	5.33
A3	0.920	0	4.14	2.00	5.15	6.33
A4	2.03	1.33	1.87	0	3.54	4.00
A5	0.900	0	4.87	2.00	3.70	4.00
A6	0.970	0.500	3.44	1.50	3.03	3.50
A7	104	1.00	3.07	1.00	1.90	2.00
A8	0.840	0	4.38	2.33	2.86	3.00
A9	0.840	0	4.72	2.33	3.07	4.00
B1	0.560	6.70	1.70	3.00	0.730	6.00
B2	0.650	6.70	1.43	1.33	0.480	3.00
B3	0.530	3.30	1.33	1.00	0.450	3.00
B4	0.590	1.00	2.26	5.33	1.00	6.67
B5	0.530	0	1.37	3.00	0.380	2.33
B6	0.650	1.00	1.30	2.00	0.590	4.00
B7	0.640	0.100	3.29	6.00	0.840	6.33
B8	0.550	0.100	1.91	3.00	0.530	4.00
B9	0.510	1.00	1.56	3.00	0.690	5.00
C1	0.180	0	1.44	1.00	0.910	1.00
C2	0.500	0	9.57	9.33	7.71	9.67
C3	1.09	1.00	4.71	3.33	4.08	4.33
C4	1.92	1.00	59.4	56.3	2.54	3.61
C5	0.280	0	2.31	2.00	7.30	7.33
C6	0.650	0	4.42	3.33	9.27	8.67
C7	0.430	0	1.99	1.00	2.96	2.67
C8	0.450	0	4.71	3.67	2.03	2.00
C9	0.400	0	1.83	1.00	2.00	2.00

Table A 4.4 (b) Comparative results from USP and IRD

	Metal concentration in acid-digests (mg/L)					
Site	**Chromium**		**Zinc**		**Magnesium**	
	USP	**IRD**	**USP**	**IRD**	**USP**	**IRD**
A1	0.790	1.00	7.03	8.00	199	188
A2	0.940	1.00	9.96	10.3	201	191
A3	0.910	1.00	6.10	6.00	179	176
A4	1.31	1.33	3.24	2.00	191	212
A5	0.820	1.00	7.64	8.00	193	173
A6	0.930	1.00	5.10	4.50	191	164
A7	0.780	1.00	6.77	7.76	214	215
A8	0.760	1.00	6.07	6.00	199	185
A9	0.770	1.00	5.81	6.00	184	160
B1	0.580	3.67	2.29	21.0	168	131
B2	0.350	2.00	2.28	23.3	169	135
B3	0.280	1.00	2.38	24.3	154	115
B4	0.340	1.67	4.63	70.3	128	105
B5	0.250	1.00	2.05	19.3	133	74.0
B6	0.400	2.00	1.53	13.7	139	102
B7	0.550	4.00	2.70	26.0	154	119
B8	0.280	1.00	3.24	33.7	141	92.8
B9	0.260	1.00	5.16	100	137	103
C1	0.800	1.00	2.59	3.00	1.48	99.9
C2	0.770	1.00	7.45	9.00	169	159
C3	1.40	1.33	16.6	20.3	188	165
C4	1.23	1.33	28.6	38.3	180	152
C5	1.24	1.00	5.01	7.00	1.31	81.9
C6	1.93	2.00	12.2	15.0	161	114
C7	3.17	3.33	5.67	7.00	178	146
C8	0.810	1.00	6.28	7.00	202	188
C9	0.700	1.00	6.64	8.33	176	147

Table A 4.4 (c) Comparative results from USP and IRD

	Metal concentration in acid-digests (mg/L)					
Site	**Iron**		**Manganese**		**Aluminium**	
	USP	**IRD**	**USP**	**IRD**	**USP**	**IRD**
A1	1040	1010	18.3	16.0	909	813
A2	1370	1080	18.4	16.3	932	872
A3	978	1030	18.2	16.3	958	908
A4	1510	1210	48.2	34.7	1670	161
A5	978	995	17.8	16.0	849	781
A6	1050	1020	16.4	15.0	982	894
A7	1270	1070	19.8	16.7	1130	1040
A8	1040	1030	18.7	16.7	974	862
A9	1380	1010	16.9	14.3	869	756
B1	1310	994	15.3	13.3	621	526
B2	962	761	18.6	17.0	589	491
B3	1560	1150	12.9	11.7	517	544
B4	1550	1250	13.3	11.3	501	515
B5	1150	599	8.98	7.67	328	324
B6	1410	1130	12.4	11.3	506	531
B7	1790	964	17.4	14.7	486	470
B8	1390	778	10.5	0.900	366	385
B9	1540	964	10.4	8.33	467	495
C1	16.5	137	4.28	4.00	120	118
C2	1050	761	9.25	8.33	613	613
C3	1430	937	12.8	10.7	693	702
C4	1070	514	8.52	7.33	753	759
C5	42.8	389	8.56	7.33	387	377
C6	1590	1110	11.9	9.33	442	444
C7	1140	724	6.65	8.00	598	596
C8	1410	999	15.6	14.0	888	883
C9	1150	695	16.5	15.7	611	610

APPENDIX 5 Heavy Metals in the Bioavailable Fraction of Soil

Table A4.5 (a) Copper and Zinc concentrations in the bioavailable fraction

Site	**Metal Concentration ± Variation (mg/kg)**			
	Copper		**Zinc**	
	Mean	**Variation**	**Mean**	**Variation**
A1	3.49	25.3	62.5	0.870
A2	79.8	13.6	55.9	0.377
A3	140	1.94	28.7	4.31
A4	44.3	0.445	7.92	0.872
A5	105	2.94	23.2	0.382
A6	81.3	2.39	10.0	1.66
A7	44.7	4.04	23.7	2.79
A8	59.7	8.79	38.0	1.33
A9	98.8	3.80	37.1	6.05
B1	99.9	6.63	367	23.0
B2	94.7	12.8	548	76.6
B3	84.5	2.79	346	71.5
B4	206	2.72	799	38.1
B5	50.2	20.2	559	39.1
B6	91.1	1.47	278	50.9
B7	149	3.59	415	26.7
B8	42.6	3.27	381	30.3
B9	10.1	2.98	1260	100.9
C1	917	0.642	66.3	2.83
C2	181	5.48	77.3	4.65
C3	74.7	1.81	355	26.2
C4	4540	469	427	51.8
C5	118	9.88	67.3	4.07
C6	219	12.2	358	50.5
C7	76.6	4.49	154	54.5
C8	479	12.7	218	9.74
C9	204	79.8	137	12.2

Table A4.5 (b) Lead and Nickel concentrations in the bioavailable fraction

Site	Metal Concentration ± Variation (mg/kg)			
	Lead		Nickel	
	Mean	Variation	Mean	Variation
A1	152	12.5	1.76	0.658
A2	132	4.27	1.86	0.277
A3	109	3.86	2.29	0.418
A4	30.6	3.17	3.11	0.443
A5	143	10.4	2.54	0.258
A6	82.8	1.77	2.36	0.892
A7	90.7	2.19	1.13	0.199
A8	103	2.25	1.74	0.514
A9	134	2.59	2.30	0.384
B1	194	24.6	4.32	0.00800
B2	173	14.6	5.62	1.30
B3	95.7	7.16	8.30	0.830
B4	353	6.28	10.4	1.21
B5	230	9.02	12.3	1.36
B6	108	4.41	13.8	1.35
B7	Discarded	0	5.17	0.622
B8	167	10.1	5.70	0.388
B9	214	23.1	10.9	1.11
C1	29.3	2.79	2.43	0.118
C2	413	8.85	2.53	1.02
C3	171	11.2	7.53	0.730
C4	Discarded	0	7.07	1.39
C5	123	6.87	3.83	1.18
C6	212	10.2	8.25	1.03
C7	77.9	10.9	4.30	1.35
C8	187	2.57	5.02	0.562
C9	69.7	8.41	2.95	0.419

Table A4.5 (c) Cadmium and Chromium concentrations in the bioavailable fraction

Site	Metal Concentration ± Variation (mg/kg)			
	Cadmium		Chromium	
	Mean	Variation	Mean	Variation
A1	0.440	0.106	0.640	0.0390
A2	0.470	0.124	0.610	0.0200
A3	0.240	0.122	0.610	0.0180
A4	Nd	0	0.850	0.329
A5	0.420	0.0620	1.03	0.358
A6	0.460	0.0450	0.630	0.00700
A7	0.310	0.0130	1.21	0.601
A8	0.290	0.156	0.810	0.275
A9	0.370	0.0810	1.03	0.337
B1	0.850	0.170	1.74	0.755
B2	0.800	0.0330	2.59	0.756
B3	0.730	0.0570	1.64	0.826
B4	1.72	0.0340	0.680	0.0460
B5	1.62	0.0766	0	0
B6	1.40	0.0850	1.73	0.383
B7	0.980	0.0830	2.18	0.192
B8	0.480	0.130	0.600	0.0190
B9	1.20	0.231	2.12	1.11
C1	Nd	0	0.700	0.0340
C2	0.0800	0.0730	1.01	0.334
C3	Nd	0	1.73	0.340
C4	Nd	0	0.830	0.280
C5	Nd	0	1.10	0.359
C6	Nd	0	1.54	0.152
C7	Nd	0	2.27	0.754
C8	Nd	0	1.95	0.603
C9	Nd	0	1.24	0.452

APPENDIX 6 Heavy Metal Concentrations in Plants

Table A4.6 (a) Metal levels in *Crassocephalum crepidiodes*

Metal	Site / Block	Metal Concentration ± Variation (mg/kg)	
		Mean	Variation
Cu	A/1	30.7	9.16
Zn	A/1	38.1	5.86
Pb	A/1	20.1	3.25
Ni	A/1	4.35	1.94
Cd	A/1	0.790	0.354
Cr	A/1	9.76	2.33

Table A4.6 (b) Metal levels in *Brachiara mutica*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**A/2**	17.8	1.12
	A/4	18.0	3.17
	A/5	23.8	0.500
	A/6	23.5	2.17
	A/7	57.1	2.52
Zn	**A/2**	17.2	1.19
	A/4	34.8	0.482
	A/5	36.9	1.03
	A/6	33.3	3.84
	A/7	37.9	11.8
Pb	**A/2**	15.9	6.26
	A/4	6.32	3.25
	A/5	10.6	4.95
	A/6	8.92	2.47
	A/7	17.6	1.42
Ni	**A/2**	4.35	1.94
	A/4	Nd	0
	A/5	5.38	1.76
	A/6	4.18	0.913
	A/7	7.64	1.79
Cd	**A/2**	0.320	0.00600
	A/4	Nd	0
	A/5	Nd	0

	A/6	Nd	0
	A/7	0.430	0.154
Cr	**A/2**	7.52	0.140
	A/4	3.35	1.36
	A/5	6.84	2.56
	A/6	4.27	1.32
	A/7	Nd	0

Table A4.6 (c) Metal levels in *Mikania micrantha*

Metal	Site / Block	Metal Concentration ± Variation (mg/kg)	
		Mean	**Variation**
Cu	**A/3**	48.9	8.79
	B/8	41.4	0.747
Zn	**A/3**	3.60	0.706
	B/8	Nd	0
Pb	**A/3**	23.7	4.29
	B/8	8.05	1.16
Ni	**A/3**	5.84	1.83
	B/8	2.37	0.904
Cd	**A/3**	3.71	0.419
	B/8	0.650	0.328
Cr	**A/3**	12.5	2.29
	B/8	3.40	2.55

Table A4.6 (d) Metal levels in *Kyllinga polyphylla*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**A/8**	17.4	0.701
	A/9	29.9	12.4
	B/4	17.6	1.75
Zn	**A/8**	42.5	2.87
	A/9	21.2	1.29
	B/4	29.7	1.75
Pb	**A/8**	28.1	6.78
	A/9	7.27	2.40
	B/4	2.44	0.0280
Ni	**A/8**	2.95	0.909
	A/9	7.13	2.72
	B/4	Nd	0
Cd	**A/8**	Nd	0
	A/9	0.430	0.329
	B/4	1.09	0.154
Cr	**A/8**	3.38	1.29
	A/9	1.70	1.29
	B/4	Nd	0

Table A4.6 (e) Metal levels in *Meremia peltata*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**B/1**	25.1	2.98
Zn	**B/1**	28.5	17.1
Pb	**B/1**	8.22	3.66
Ni	**B/1**	Nd	0
Cd	**B/1**	1.21	0.649
Cr	**B/1**	Nd	0

Table A4.6 (f) Metal levels in *Commelina diffusa*

Metal	Site / Block	Metal Concentration ± Variation (mg/kg)	
		Mean	Variation
Cu	B/2	58.3	1.61
	B/3	23.7	1.68
	B/6	40.8	10.9
	B/9	27.8	1.34
	C/4	151	23.7
	C/7	41.4	4.17
Zn	B/2	42.5	2.87
	B/3	21.1	1.29
	B/6	34.9	2.27
	B/9	Nd	0
	C/4	47.3	5.86
	C/7	122	19.2
Pb	B/2	5.79	3.09
	B/3	7.17	2.25
	B/6	12.1	6.32
	B/9	12.0	4.02
	C/4	15.6	1.79
	C/7	8.93	1.29
Ni	B/2	Nd	0
	B/3	Nd	0
	B/6	3.56	2.75
	B/9	7.65	2.73
	C/4	9.58	3.49
	C/7	14.9	3.70

Cd	**B/2**	Nd	0
	B/3	0.760	0.336
	B/6	1.60	0.279
	B/9	Nd	0
	C/4	Nd	0
	C/7	0.550	0.167
Cr	**B/2**	Nd	0
	B/3	Nd	0
	B/6	Nd	0
	B/9	1.66	1.29
	C/4	Nd	0
	C/7	Nd	0

Table A4.6 (g) Metal levels in *Lageneria siceraria*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**B/5**	17.9	0.977
	C/2	41.9	17.1
	C/6	12.0	1.08
Zn	**B/5**	31.3	0.615
	C/2	55.4	17.2
	C/6	18.8	0.421
Pb	**B/5**	5.61	2.44
	C/2	23.5	6.13
	C/6	Nd	0
Ni	**B/5**	Nd	0
	C/2	Nd	0
	C/6	Nd	0
Cd	**B/5**	1.40	0.173
	C/2	1.63	0.817
	C/6	Nd	0
Cr	**B/5**	Nd	0
	C/2	3.41	1.29
	C/2	Nd	0

Table A4.6 (h) Metal levels in *Wedelia trilobata*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**B/7**	25.3	0.247
Zn	**B/7**	54.1	2.50
Pb	**B/7**	4.74	0.22
Ni	**B/7**	3.54	1.89
Cd	**B/7**	Nd	0
Cr	**B/7**	1.71	1.29

Table A4.6 (i) Metal levels in *Echinochloa colonumm*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	C/1	98.4	3.41
	C/5	25.6	3.22
Zn	C/1	80.8	0.724
	C/5	54.4	5.62
Pb	C/1	50.1	4.31
	C/5	Nd	0
Ni	C/1	4.69	1.88
	C/5	7.09	2.55
Cd	C/1	3.08	0.220
	C/5	0.220	0.163
Cr	C/1	Nd	0
	C/5	Nd	0

Table A4.6 (j) Metal levels in *Curcurbita pepo*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	**C/3**	23.3	0.237
Zn	**C/3**	78.1	2.36
Pb	**C/3**	12.4	5.39
Ni	**C/3**	6.87	4.09
Cd	**C/3**	1.06	0.490
Cr	**C/3**	4.96	2.56

Table A4.6 (k) Metal levels in *Manihot esculenta*

Metal	**Site / Block**	**Metal Concentration ± Variation (mg/kg)**	
		Mean	**Variation**
Cu	C/8	15.9	5.19
	C/9	13.1	1.99
Zn	C/8	86.6	6.46
	C/9	53.8	5.48
Pb	C/8	4.85	2.39
	C/9	9.52	2.38
Ni	C/8	5.38	1.86
	C/9	6.41	0.849
Cd	C/8	Nd	0
	C/9	Nd	0
Cr	C/8	Nd	0
	C/9	Nd	0

APPENDIX 7 Plant Specimens

Plate A1 ***Crassocephalum crepidiodes***

Plate A2 ***Curcurbita pepo***

Plate A3 *Commelina diffusa*

Plate A4 *Meremia peltate*

Plate A5 ***Brachiara mutica***

Plate A6 ***Kyllinga polyphylla***

Plate A7 *Wedelia trilobata*

Plate A8 *Mikania micrantha*

Plate A9 ***Manihot esculenta***

Plate A10 *Lagenaria siceraria* *(Leeward Community College, The University of Hawaii)*

[***Lagenaria siceraria*** **Ipu, or gourd**. (Digital image) Leeward Community College, The University of Hawaii.

http://alaike.lcc.hawaii.edu/millen/bot130/learning_objectives/lo03/list/yaif/ipu.leaves.jpg

(Accessed 11 November, 2001)].

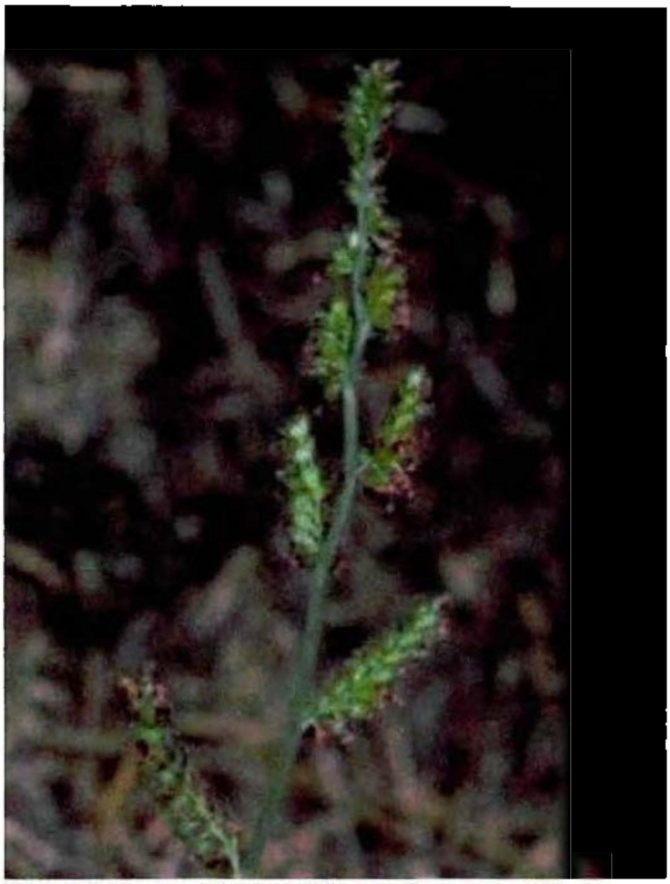


Plate A11 ***Echinochloa colonumm*** (*Viarural*)

[**Echinochloa** colona (digital image) The Argentine Agribusiness Portal. http://www.viarural.com.ar/viarural.com.ar/agricultura/malezas/echinochia-colonum03.htm (Accessed 11 November, 2001)].

APPENDIX 8 Map projections used in Figure 1

The geo-referencing projection of the map of the Fiji Group is in the **Latitude/Longitude** scale, whilst that of the Lami dump aerial photograph is in the Transverse Mercator Projection, referred to as the Fiji Mercator Grid (FMG). The FMG is a false projection in metres, used to take into account the small size of the Fiji Group, and when used can show extensive detail. It originates at 17^0 00' South Latitude and 178^0 45' East Longitude, and has coordinates at 20000,000 m East and 40000,000 m North (Lands and Survey Department, 1989).