Natural and anthropogenic influences upon trace metal geochemistry in sediments of Cleveland Bay and adjacent areas of the Great Barrier Reef Lagoon

Thesis submitted by

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Abstract

Processes that influence variations in trace metal concentration and their bioavailability in surface and subsurface sediments have been measured in sediments from Cleveland Bay and the adjacent shelf areas of the Great Barrier Reef lagoon from Upstart Bay to Rockingham Bay. The scope of work is consistent with strategies incorporated within the National Water Quality Management Strategy (e.g., the draft Australian and New Zealand Environment and Conservation Council (ANZECC) Guidelines for Fresh and Marine Water Quality). The results can be used as a guide for the management of sediment quality in the study region.

Statistical analysis (Principal Component Analysis, Multiple Regression Analysis) has been completed upon chemical and physical parameters from 1023 surface sediment samples collected in the central section of the Great Barrier Reef Lagoon. In conjunction with spatial analysis the results of statistical analysis have been used to identify influences upon the distribution of whole surface sediment strong acid soluble Cd, Co, Cu, Ni, Pb and Znoncentrations. The predominant influence upon their distribution is the distribution of fine-grained aluminosilicate rich terrigenous sediment. Subordinant natural influences include; changes in the concentration of Co, Cu and Ni in terrigenous sediment being supplied to the lagoon; increases in Cd and Co concentration in sediments due to post depositional early diagenetic processes; and nutrient like behaviour of Cd.

In oder to evaluate anthropogenic influences upon trace metal concentration In Cleveland Bay, statistical analysis (Multiple Regression Analysis, Principal Component Analysis, Linear Discriminant Analysis) and spatial analysis of 122 surface sediment samples and 124 sediment core samples have been supported by temporal analysis of samples from 5 sediment cores using ^{210}Pb radiochemistry. Anthropogenic influences in sediments of Cleveland Bay are distinguishable from natural variations in concentration at sites that have high rates of fine grained terrigenous sediment accumulation, are typically close to source, are limited in spatial extent, and are characterised by simultaneous increases of more than one trace metal.

Temporal trends in enhancement of metals exhibit associations with economic growth and the introduction of specific metal commodities to the region. Enhancement of metal concentrations above a statistically modelled background are generally less than 2 times the modelled background, and are typically less than the draft ANZECC guideline trigger values for the concentration of metals in sediment. The results indicate that identification of anthropogenic influences do not necessarily represent a decline in environmental quality but are diagnostic of urbanisation and industrial development.

To assist understanding processes that influence the bioavailability of trace metals in sediments a mass balance of dissolved and solid phase sulfur concentrations of 5 sediment cores collected from Cleveland Bay was completed. A model of the rate of organic matter decomposition explains between 82 to 90% of the variance observed in the sulfur accumulated in sediments of cores from Cleveland Bay. Therefore the rate of organic matter decomposition is the dominant influence upon sulfur accumulation within individual sediment cores. The mass balance indicates that typical muddy sediments in the intertidal zone are open to the resupply of sulphate, but probably have a high retention rate of authigenic sulphides due to abundant reactive Fe and high burial rates.

Speciation of trace metals in sediment profiles has been evaluated by two operationally defined methods. 1) Speciation determined by wet chemical analyses of metals. 2) Speciation determined by in situ passive sampling devices that use the theory of Diffusive Gradients in Thin-films (DGT). Interpretation of the influences upon metal speciation was found to be highly dependent upon the scale of sampling (e.g., vertical resolution, depth), and method of analysis.

In sediment cores sampled at 20mm intervals, the partitioning of trace metals into 1M HCl soluble (Cd, Pb and Zn) and 1M HCl insoluble (Co, Cu and Ni) species can be attributed to the predominantn early diagenetic process occurring in sediments, SO_4 reduction. However, in 300mm deep DGT probes sampled at intervals of 10mm strong vertical zonation of metals with apparent contrasting lability to that deterined by wet chemical analysis. Lability in DGT probes can be described as DGT available (Co, Ni, Pb and Zn) and DGT unavailable (Cd and Cu) metals. These patterns in speciation are interpreted to be created by interaction of metals with other early diageneitc processes including Fe, Mn and SO_4 reduction.

The comparison of operationally defined speciation methods indicates that the use of a single speciation method (e.g., 1M HCl soluble metals or ΣSEM/AVS > 1) to predict the bioavailability of Cd, Co, Cu, Ni, Pb and Zn may not adequately describe the speciation of some metals in near surface sediments. As a consequence methods used to assess metal bioavailability in sediments should not be used in isolation, or applied as generic indicators of sediment quality. The methods are tools that can be used for the assessment of sediment quality, and require to be evaluated before being integrated within sediment quality management strategies.

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Declaration

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from published or unpublished work of others has been acknowledged in the text and a list of references provided.

14/02/2006

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'*The only person who is educated is the one who has learned how to learn and change*'

Carl Rogers

Chapter 1

Introduction and thesis outline

1.1 Introduction

Declining quality of terrestrial run off entering the Great Barrier Reef lagoon is the most significant anthropogenic influence upon environmental quality to the lagoon (Brodie 1997). Increases in river sediment loads of 4 to 20 times pre European settlement (circa 1850) have been estimated (Arakel 1995; Moss *et al.* 1992; Neil & Yu 1996; Brodie 1997). The significance of these apparent increases, and the effect upon the wider lagoon, has been the subject of public scientific debate since at least 1987 (Brodie 1991; Bell & Gabric 1991; Hopley *et al.*1991; Furnas & Brodie 1996; Rayment & Neil 1997; Wasson 1997; Larcombe & Woolfe 1999a).

The regions of the lagoon that are threatened by declining quality of terrestrial run off are on the inner shelf, are close to a source and are limited in spatial extent (Kelleher 1987; Botto *et al.* 1987; Baldwin *et al.* 1987; Cosser 1987; Brodie 1997). Metals are not considered a threat to the lagoon relative to those threats posed by increased sediment and nutrient loads (e.g., Kelleher 1987; Baldwin *et al.* 1987).

However, sites close to urbanised areas, or areas of deliberate habitat destruction, where terrestrial water quality has diminished, are potentially at risk of deleterious effects of excess supply of metals (Zann 1995; Arakel 1995). Moreover, there is a perception by the public that metal contaminants do pose a risk to the lagoon (Brown 1973; Knauer 1977; Wallace 1992; Ormsby 1996; Walker & Brunskill 1996). These threats, whether real or perceived, are a management issue (Kinsey 1991). Therefore, localised anthropogenic enhancement of metals does constitute an issue to be addressed by those managing the environment.

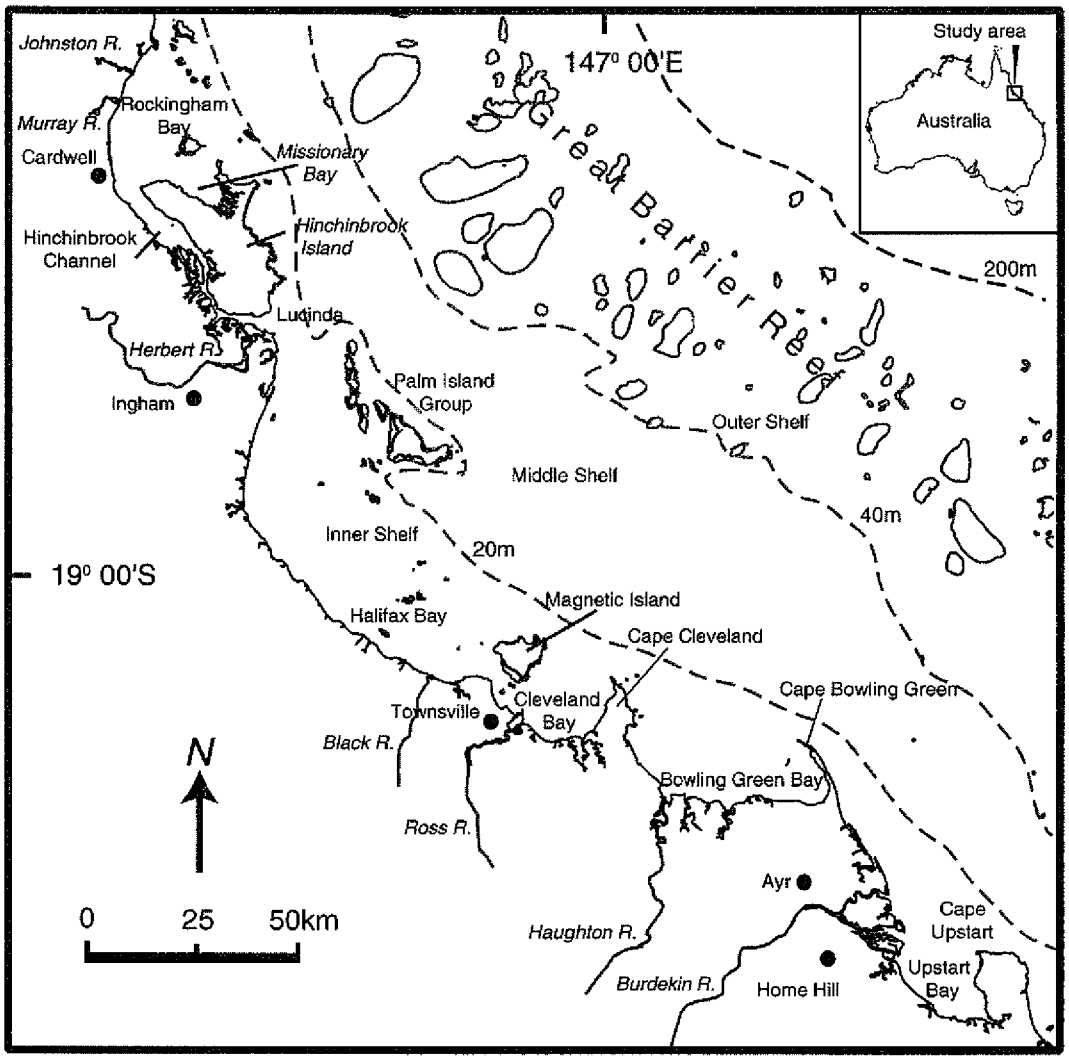


Figure 1.1 Location of geographic features and submerged reefs in the study region (central section of the Great Barrier Reef lagoon). Submerged reefs are shown in stippled grey. They occur on the inner shelf as free standing reefs, and on the margins of the majority of inner shelf islands. The inner shelf, middle shelf and outer shelf are defined by the 20m, 40m and 200m depth isobaths.

This thesis examines natural and anthropogenic influences upon sediment trace metal geochemistry in the central section of the Great Barrier Reef lagoon, with the focus of work in Cleveland Bay (Figure 1.1). It helps address the need to understand the processes that effect marine chemical oceanographic baseline data, and provides discriminatory methods to identify threats to the lagoon (e.g., Stark *et al.* 1975; Kelleher 1987; Larcombe *et al.* 1996; Johnson 1996; Jensen *et al.* 1999).

1.2 Trends in the supply of metals from anthropogenic sources

Metals derived from anthropogenic sources are supplied to the marine environment by diffuse and point source inputs (Zann 1995; Karuppiah & Gupta 1996). Diffuse sources include atmospheric fallout from combustion of fossil fuels and waste (Bricker 1993; Cochran *et al.* 1998; Kolak *et al.* 1998), and surface water run off from agricultural areas and mining districts (Cortesao & Vale 1995; Bervoets *et al.* 1998). Run off from agricultural and mining activities in catchments have been found to be a source of metals in the Great Barrier Reef lagoon (Tesiram 1995; Walker & Brunskill 1995).

Surface water run off from urban areas is also a source of metals, because of the high density of sources (Mason *et al.* 1999; Widianarko *et al.* 2000). Effluent discharges, from industrial and sewage discharge points in urbanised, areas have been a significant source of metals in northern hemisphere studies (Bricker 1993; Mayer & Johnson 1994; Karuppiah & Gupta 1996; Bothner *et al.* 1998; Kahkonen *et al.* 1998; Grousset *et al.* 1999). Trends in the supply rate of metals from anthropogenic sources over time display an increase with the onset of industrialisation, and a decrease associated with more recent environmental awareness and legislation (Bricker 1993; Alexander *et al.* 1993; Zwolsman *et al.* 1996; Kolak *et al.* 1998; Cochran *et al.* 1998; Brannvall *et al.* 1999). Shorter term spatial and temporal variance have also been identified (Birch *et al.* 1998).

There is a positive correlation between economic growth (Huh & Chen 1999) and urbanisation (Callender & Rice 1999). An 'urban environmental gradient' was recognised by Callender & Rice (1999), where the gradient reflects a positive correlation between rate of supply of metals to sediments from anthropogenic activities, and size of the population.

The land region adjacent the study area to Cleveland Bay has experienced economic growth and urbanisation since settlement mid last century. The city of Townsville has historically been a focus of trade, and was initially established in 1864 as a port to service pastoral holdings (wool and beef) located in the hinterland. It was

connected by rail to agricultural and mineral resources in other regions of Queensland by 1915 (Taylor 1980; TMI 1999; TPA 1999).

Since 1945, heavy industry has stimulated population growth in Townsville (TTSP 2000). These industries support mining and rural activities in regional areas of North Queensland and include; the copper refinery in 1957, sugar terminal in 1959, Yabulu nickel refinery in 1974, nickel laterite imports in 1986, and a zinc refinery in 1999. At present, Townsville has a population of over 130 000, and combined with the city of Thuringowa, forms the largest urbanised area located adjacent to the Great Barrier Reef lagoon. The region has an annual economy of over $5.7 Billion, forecast to double by 2017, and is growing faster than other regions of Queensland (AEC 1999).

Given sustained economic and population growth in the region, we might expect to see increases in rate of supply of metals to the lagoon. Trends in the supply rate of metals from anthropogenic sources over time can be identified by comparing variations in metal concentration over time in radio chemically dated sediments (e.g., Bricker 1993; Alexander *et al.* 1993). The risk that such trends pose to the environment, if any, is an important issue to resolve.

1.3 Thesis outline and sediment quality assessment strategies

A tiered risk assessment strategy (Figure 1.2) is recommended for the management of metals in sediments (Arakel 1995; ANZECC 1999; Chapman & Mann 1999; IMO 1999). The work completed in this thesis uses methods that are compatible with the Australian National Water Quality Management Strategy, which is described in the Draft Australian and New Zealand Environment and Conservation Council Guidelines for Fresh and Marine Water Quality (ANZECC 1999). The guidelines are driven by the philosophy of the Australian National Strategy for Ecologically Sustainable Development (ESD) (ANZECC 1999).

The initial stage of the risk assessment strategy is to define management goals and the level of protection of the environment. Three categories are recommended as; 1) high conservation ecological value systems (pristine); 2) slightly to moderately disturbed systems, and; 3) highly disturbed systems.

The Great Barrier Reef lagoon is a multi-use Marine Park, and a World Heritage Listed area (Valentine *et al.* 1997). It accommodates a variety of industries operating directly in the lagoon, such as military training grounds, merchant shipping, commercial fishing and tourism. It also receives run off from rural and urbanised regions located inland of and adjacent to the coast, as well as waste discharges from sewage and industries situated along the coast. It contains regions that qualify within all three categories of pristine, slightly disturbed and highly disturbed.

The tiered sediment quality assessment strategy in Figure 1.2 advocates the measurement of metal concentrations followed by comparison to trigger values specified in the guidelines, or interim sediment quality values (ISQVs). ISQVs are the trigger mechanism to initiate further action, and the setting of appropriate SQVs is recognised as a controversial issue (Chapman *et al.* 1999a). At present, ISQVs are set at two levels, low (ISQV-low) and high (ISQV-high). The values are adapted from the effects range low (ERL) and effects range median (ERM) criteria respectively of Long *et al.* (1995). The ERL and ERM represent the 10 and 50th percentiles of a statistical analysis of a biological effects database, and indicate at what concentration metals concentrations, derived from whole sediment total acid digestion, will have an affect upon test organisms.

If the management objective for a region is to remain pristine it is recognised by the ANZECC guidelines that the ISQV-low should be replaced with the background concentration. In slightly to highly disturbed areas, if metal concentrations fall between the ISQV-low and ISQV-high, it is also recommended that background concentrations of metals be identified before proceeding with examination of bioavailability. Identification of background metal concentrations, and their variation, is a significant step in the tiered assessment strategy.

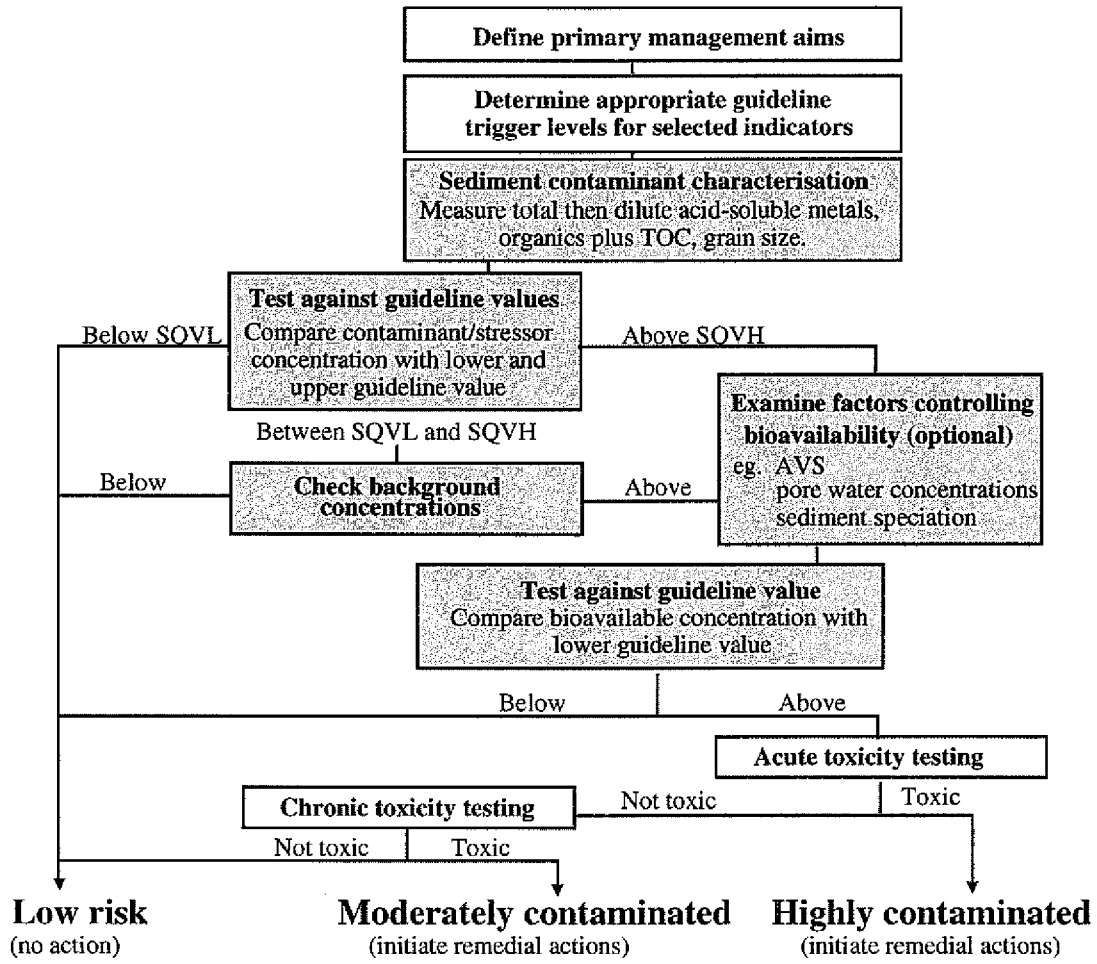


Figure 1.2 Tiered risk assessment strategy for sediment quality assessment, adapted from ANZECC (1999). Subjects shaded are those addressed in this study.

Chapter 2 of this thesis examines the influences of sediment sources, sediment transport mechanisms, early diagenetic processes, and anthropogenic sources upon metal concentrations in the central section of the Great Barrier Reef lagoon between Upstart Bay to Rockingham Bay. The aim is to identify influences upon variation in natural metal concentrations at different locations in the study area. This is done using a combination of multi-element mapping and exploratory statistical analysis, which have been found to be valuable tools for regional resource assessment (e.g., Burenkov *et al.* 1999; Cocker 1999; Grunsky & Smee 1999).

Chapter 3 examines the capacity of statistical methods to identify background variation, and to discriminate metals derived from anthropogenic sources in sediments of Cleveland Bay. This includes the use of a hierarchy of statistical tests, coupled with radiochemical sedimentation history, to identify natural and anthropogenic influences upon sediment composition (e.g., Ragland *et al.* 1997; Kilby & Bately 1993; Zwolsman *et al.* 1996; Grousset *et al.* 1999).

Factors that influence bioavailability are a function of sediment organism interactions (Stark 1998), and it is the chemical form of metals that determines risk to organisms by toxic metals (Allen & Hansen 1996). This thesis deals specifically with wet chemical methods of measuring metal speciation in sediments, and does not attempt to directly measure bioavailability.

Chapters 4, 5 and 6 examine influences upon speciation of metals, and interpretation of methods used to measure metal speciation, in intertidal and near shore sediments of Cleveland Bay. The kinetics of decomposition of organic matter, and the processes that affect accumulation of authigenic iron sulfides, are the most important early diagenetic processes in shallow marine sediments (Berner 1980) and are explored in chapter 4. The results of chapter 4 are used in chapter 5, to examine the interactions between measures of wet chemical trace metal speciation commonly used in environmental surveys and authigenic sulfides. Chapter 6, compares a new method (diffusive gradients in thin films) to with wet chemical speciation methods.

1.4 Identifying natural concentrations of trace metals in sediments

1.4.1 Natural influences upon trace metal concentrations

Unlike some compounds sourced from anthropogenic activities, such as PCBs and DDT, trace metals occur naturally in sediments and over a range of concentrations. Natural concentrations of metals are influenced by differences in source of bulk sediment, transport regime and post depositional regime. These influences do not operate in isolation, and consequently natural metal concentrations in sediments are a function of several influences that can occur over different time scales (e.g., seasonal variations, Birch & Davey 1995).

The source of sediment being supplied to a region can be influenced by catchment geology (Loring 1990), weathering processes (Hirst 1962) and mineralisation (Moss & Costanzo 1998, Langston *et al.* 1999), and several sources can contribute to a single region (e.g. Basaham & El-Sayed 1998; Rosales-Hoz *et al.* 1999).

Sediment transport mechanisms (e.g., waves, currents) result in physical sorting and partitioning of sediment of different physical properties. These processes result in mineralogical and particle size differences between sites (e.g., Calvert *et al.* 1993; Loring 1991).

Post depositional changes in sediment composition can be attributed to a combination of biological, physical and chemical processes. Physical redistribution of elements occurs by bioturbation or through wave-current particle mixing (Berner 1980; Rhoads & Boyer 1982). Chemical redistribution can occur during early diagenesis, and are typically related to the decomposition of organic matter (e.g., Rae & Allen 1993; Van Cappellen & Wang 1995).

These processes create variation in natural concentrations of metals in sediments. The natural variations can obscure the addition of metals from anthropogenic sources. In the context of providing guidelines for the management of sediment quality, it is important to identify these natural processes and their effects upon metal concentrations.

1.4.2 Statistical analysis of trace metal concentrations in sediments and their interpretation

1.4.2.1 Standardisation and regression analysis

In marine sediments, the greatest source of natural variation in sediment trace metal concentration is differences in particle size and mineralogical composition between samples (e.g., de Groot *et al.* 1982; Klamer *et al.* 1990; Loring 1990). This natural variation in trace metal composition can be removed by dividing the measured value by a conservative (one that is not affected by anthropogenic influences) parameter(s) that is proportional to the grain size or mineralogical variations of the sediment samples. Measurements of sediment grain size can be used to remove grain size variations and elemental analyses can be used to remove both grain size and mineralogical variations (e.g., lithium, Loring 1990; aluminium, Summers *et al.* 1996; iron, Negrel 1997). In this thesis, this is referred to as standardisation (normalisation) of trace metal concentrations. It is done to remove natural variation in their concentration so that measured values are standardised to common natural criteria, and it is easier to observe the variance created by anthropogenic influences upon metal concentrations.

Regression analysis methods can be used remove natural variation in sediment trace metal composition. Regression methods include linear regression (Summers *et al.* 1996), non-linear regression (Bervoets *et al.* 1998), robust regression (Grant & Middleton 1998), semi parametric regression (Shively & Sager 1999) and multiple regression (Schneider & Davey 1995). These methods represent similar, yet distinct, methods that enable standardisation of trace metal concentrations (dependent variable) to a conservative numeric parameter (independent variable), and allow direct comparison of trace metal concentrations between sites in an overall gradient of bulk sediment types.

All linear regression methods have limitations that include the assumptions of existence, independence, linearity, homoscedasticity and normality (Kleinbaum *et al.* 1998). If results are to be used in a tiered sediment quality assessment strategy, the limitations of models have significant implications upon the appropriateness of the decisions that can be made using the models. Ultimately, models can only determine similarity or differences between samples at a statistical significance determined by the user. The reason why a sample is different from other samples is a function of the regression model parameters.

Some mathematical limitations of methods can be overcome by transformation of data and selection of methods that suit the distribution of the data (e.g., robust regression, semi-parametric regression). However, most limitations are inherent to the method and cannot be removed. From the author's experience, the limitation of regression models, to identify anthropogenic influences upon trace metal concentrations in sediment geochemical data sets, is centred on the assumption that the relationship between dependent and independent variable(s) is constant for all samples (conservative behaviour).

This above assumption often results in 'confounding'. Confounding is when meaningfully different interpretations of a relationship occur when an extraneous variable is ignored or included in the analysis (Kleinbaum *et al.* 1998). If a significant independent variable is excluded from a model, a component of the variance of the model will be in response to that variable. Similarly, if the relationship between the independent and dependent variable changes between sites, some of the variance of the model will be in response to these changes.

Non-conservative behaviour, between dependent and independent variables, can be created by changes in geochemical composition of sediment being supplied to a region (e.g., Loring 1991). This can result in variance in the regression model that is created by spatial and temporal differences in sediment supply. Similarly, post-depositional changes to sediment geochemical composition can also affect the consistency of relationships. The use of a single regression model to suit all samples is therefore unlikely to satisfy all assumptions of the method.

1.4.2.2 Multivariate statistical analysis

The interpretation of what causes standardised metal values to be different and the associated significance requires testing and support. Multi-element signatures have been used to discriminate samples that have terrigenous and biogenic sources (Rosales-Hoz *et al.* 1999), and to discriminate between specific anthropogenic sources (e.g. Krumgalz 1993; Cortesao &Vale 1995). This information is essential to the interpretation of regression data to explain why samples or groups of samples are geochemically and statistically different.

Principal Component Analysis (PCA) allows the observation of multivariate data in fewer dimensions (McArdle 1999). It can be used to identify groups of sediment samples that have similar geochemical composition (e.g. Ragland *et al.* 1997; Emmerson *et al.* 1997). The resultant grouping of data can assist the understanding of why groups of sediment samples respond differently to regression models.

PCA is not a hypothesis testing tool, it is a hypothesis generation tool (McArdle 1999). Multivariate classification techniques are required to classify or determine differences between groups of samples. Linear discriminant analysis is one such method, which allocates a probability of group membership to each sample based upon user-specified categories. Discriminant analysis can be used to classify samples into groups based on the patterns observed in PCA (e.g., Calvert *et al.* 1993; Ragland *et al.* 1997).

The combination of multivariate analysis methods such as regression, PCA and discriminant analysis is similar to methods known as redundancy analysis and correspondence analysis. The greatest difference between the methods is data pre-treatment, or standardisation (McArdle 1999). The advantage of these multivariate methods is that they can be integrated with a variety of numeric or classification variables, and they are not restricted to chemical analysis to identify changes to sediment properties (e.g., Krantzberg *et al.* 2000).

1.5 Metal speciation and 'bioavailability'

Metal speciation refers to the chemical and mineralogical form that metals occur as. In sediments, metals may occur in a variety of forms, including; as dissolved metals

in interstitial pore waters, adsorbed to particles, as discrete mineral phases or held within crystalline lattice structures of solid phases (e.g., Ruby *et al.* 1999). The factors that influence metal speciation in sediments are related to sources of metals and post depositional modification to sediments. Metals bound in crystalline lattice structures rarely undergo change during burial. Metals that are sorbed to small reactive particles, or held within particles that undergo changes during early diagenesis, are labile and will undergo changes in speciation during burial.

Post-depositional changes to metal speciation in sediments is driven by biogeochemical processes that are related to the decomposition of organic matter, and are most intense near the surface (Van Cappellen & Wang 1995; Veeh *et al.* 1999). Sulfate reduction is one of several processes occurring in sediments that result in oxidation of organic carbon and results in the formation of authigenic iron sulfide minerals (e.g. Berner 1980; Goldharber & Kaplan 1982). The interaction between authigenic iron sulfides and trace metals has been found to result in the formation of insoluble, and less labile, metal sulfide mineral species (Ferguson *et al.* 1983; Davies-Colley *et al.* 1985; Di Toro *et al.* 1990; Huerta-Diaz & Morse 1992; Morse & Arakaki 1993; Brennan & Lindsay 1996). This is environmentally significant because it can result in a decreased risk of exposure of organisms to high concentration of dissolved metals in sediment interstitial waters (Morse & Luther 1999).

In contrast to metal speciation, 'bioavailability' is a function of organism sediment interaction (Stark 1998). It is dependent upon organism-specific exposure routes and sensitivity (e.g., Hare *et al.* 1994; Mayer *et al.* 1996; Lee *et al.* 2000). Because of these complications, simple and cost effective methods of determining metal concentrations available to organisms, dependent upon metal speciation, are desired for use in tiered sediment quality assessment strategies (e.g., Chapman & Mann 1999).

Operationally defined wet chemical sediment metal speciation methods are one option to producing cost effective measures that may approximate bioavailability. 1M HCl soluble metals, or methods that liberate weakly bound metals in sediments, are often considered bioavailable (e.g., Bervoets *et al.* 1998; Langston *et al.* 1999). Other speciation methods include; direct measurement of dissolved metal concentrations in pore waters of sediment and sequential digestion schemes that provide operationally defined metal categories (e.g., Tessier *et al.* 1979; Huerta-Diaz & Morse 1990).

Speciation methods also include mechanistic methods, based upon equilibrium partitioning of metals between different host minerals in sediments (Chapman *et al.* 1999b). This includes the ratio of the sum of metals extracted simultaneously with acid volatile sulfides (Di Torro *et al.* 1990) and the distribution coefficient (K_d). These methods rely on the measured partitioning between solid phase and dissolved phase (pore water) metals. Metals in the dissolved phase are considered to represent a higher risk of exposure to organisms (greater bioavailability).

A new approach to speciation measurements is in situ passive sampling devices that use the theory of Diffusive Gradients in Thin-films, or DGT (Zhang & Davison 1995). This method uses a thin membrane of known diffusive properties to constrain the mass transport of metals to a collecting medium such as Chelex® resin. The resin accumulates only metals capable of diffusing across the membrane. It accumulates only dissolved metals in waters and metals capable of exchange between solid phase and the Chelex® resin. The method offers provides high spatial resolution and in situ preconcentration of metals within the range of atomic adsorption spectrometry analytical methods and offers significant advantages over traditional sampling methods.

1.6 Conclusions

Metals derived from anthropogenic sources pose a subordinate risk to the lagoon, relative to those posed by increased sediment and nutrient loadings in terrestrial run off. However, locations close to sources, such as urbanised regions, mining and agricultural districts, are at greater risk of receiving deleterious concentrations of metals from anthropogenic sources.

A tiered risk assessment strategy is advocated for the assessment of metal concentrations in sediments by ANZECC (1999), and this is broadly followed by this thesis. In this thesis, mapping and multivariate statistical analysis are initially used to identify natural influences upon metal concentrations in sediments and then determine background metal concentrations. This work is then supplemented with examination of the processes that effect metal speciation in sediments of Cleveland Bay and comparison of methods used to measure metal speciation.

Chapter 2

Influences upon spatial variation in sediment geochemical composition in the Great Barrier Reef lagoon between Upstart Bay and Rockingham Bay

2.1. Introduction

The need to understand processes that effect marine chemical oceanographic baseline data in the lagoon has been advocated by Stark *et al.* (1975), Kelleher (1987), Larcombe *et al.* (1996), Johnson (1996) and more generally within Australian marine jurisdiction by Jensen *et al.* (1999).

There have been numerous chemical oceanographic studies completed in the study region (Figure 2.1). The studies include; The Three Bays Study (Bowling Green Bay, Cleveland Bay and Halifax Bay) that involved mainly baseline biota and water data collection (Stark *et al.* 1975; Burdon-Jones *et al.* 1982); Cd inputs to Hinchinbrook Channel from fertiliser usage in the Herbert River catchment (Tesiram 1995; Valente 1998); Hg in sediment from Bowling Green Bay derived from gold mining activities in the Charters Towers region (Walker & Brunskill 1995); Ni in sediments of Halifax Bay derived from Ni refinery operations (Knauer 1977; Carey 1981); the potential effects of dredging in Cleveland Bay (Gibbs 1993; Reichelt & Jones 1994); monitoring programs in place by the Townsville Port Authority (Anderson & Roche 1999), Queensland Government monitoring (Moss & Costanzo 1998); and more general small scale research studies (e.g. Esselmont 1997; Inglis & Kross 1999).

Despite this apparent wealth of information there is relatively little work undertaken in the lagoon dedicated to identifying and understanding influences upon natural variation in sediment geochemical composition on a shelf scale or at a local scale. Maxwell (1968) undertook the largest study that has dealt specifically with natural variations in sediment composition. This work included mapping and classification of the Great Barrier Reef lagoon based on the variation in acid soluble carbonate concentrations, combined with mineralogical and granulometric examination

of the surface sediments. Since that time, there have been numerous other studies of surface sediment grain size distributions within the study area (Orme & Flood 1980; Miller 1982; Belperio 1983; Davidson 1985; Carter *et al.* 1993; McIntyre 1996; Orpin & Ridd 1996; Lambech & Woolfe 1999; Woolfe *et al.* 2000). The only published studies to examine the natural variability of sediment geochemical compositions in the region are that of Ward (1994), Ward *et al.* (1995) and Ward & Larcombe (1996). This work compared the geochemical signature of Holocene mangrove sediments with recent mangrove sedimentary deposits located in the south of Halifax Bay and in Cleveland Bay.

It is essential to understand natural influences upon variations in sediment trace metal composition if influences of anthropogenic activities are to be recognised and the risk to the environment evaluated. This chapter describes spatial variations in sediment geochemical composition for 1023 surface sediment grab samples collected in the Great Barrier Reef lagoon between Upstart Bay and Rockingham Bay (Figure 2.1). It provides the first images of regional scale variation in geochemical properties that are coupled with multivariate statistical analysis of sediment major element and trace element composition. These methods have been found to be useful tools in regional resource assessment (e.g., Burenkov *et al.* 1999; Cocker 1999; Grunsky & Smee 1999).

The aim of this chapter is to identify influences upon the variation in surface sediment trace metal composition at a regional scale. A secondary objective is to develop multivariate statistical methods that can be used to identify influences upon trace metal concentration in sediments.

2.1.1 Study Site

In the study region, the central section of the Great Barrier Reef lagoon, the continental shelf is between 50 to 100 km wide (Figure 2.1). It has been subdivided by Belperio (1983) on the basis of water depth into; inner shelf (0-20 m), middle shelf (20-40 m) and outer shelf (40-80 m). The Great Barrier Reef is situated on the outer shelf, and is up to 100 km from the coast.

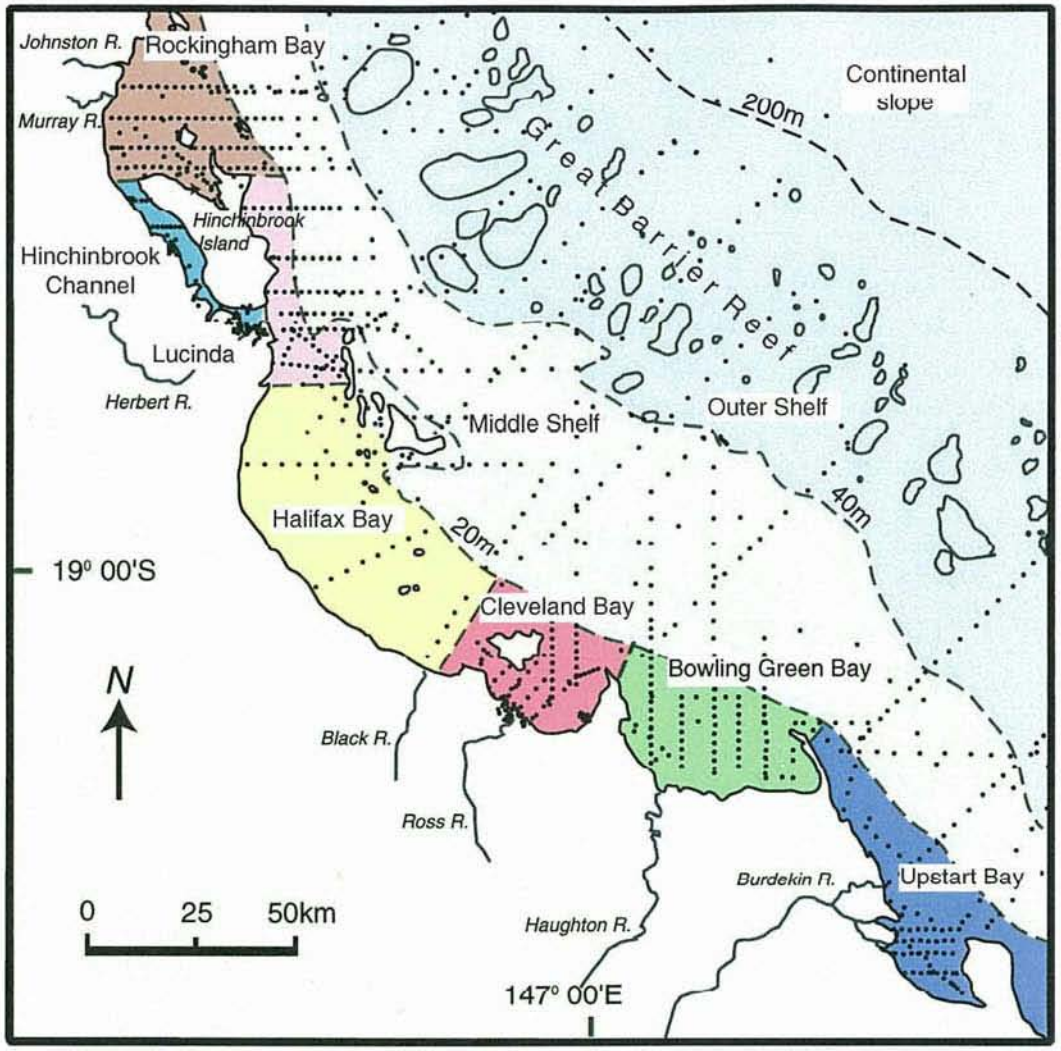


Figure 2.1 Location and boundaries of geographic subdivisions made within the lagoon (coloured), and surface sediment grab samples (●). The 20 m and 40 m isobaths have been used to subdivide the inner shelf, middle shelf and outer shelf.

2.1.1.1 Climate

The climate of the study region ranges from dry tropical to wet tropical. The average annual rainfall of locations in the study region is highly variable. For example, the Herbert River region has an average annual rainfall of 2100 mm (Clough 1998), relative to the Ross River region that has a rainfall of only 1160 mm (Carter *et al.* 1993). Most rain occurs during the summer months of December to March. Cyclones also occur during summer months and are highly significant short term rainfall, wind, wave and current generating events (e.g., Orpin *et al.* 1999). South east winds prevail between April to November and are characterised by speeds of 10-30 km h-1 (Carter *et al.* 1993).

2.1.1.2 Sediment supply

Sediment supplied to the lagoon is derived from two predominant sources. These sources can be characterised as; 1) aluminosilicate rich terrigenous sediment that is supplied to the inner shelf by riverine discharges, and; 2) calcium carbonate rich biogenic sediment that is supplied shelf wide by biogeochemical processes (e.g., Maxwell 1968; Maxwell & Swinchatt 1970; Orme & Flood 1980; Belperio 1983).

Terrigenous sediments in the region are muddy quartz rich fine-medium grained sands, with lesser amounts of feldspar, mica and carbonate materials (Belperio 1978; Carter *et al.* 1993; Ward *et al.* 1995; Woolfe *et al.* 2000). The clay mineral assemblage is predominantly kaolinitic (Orpin & Woolfe 1999). The Burdekin River is the principal source of terrigenous sediment to the study region (Table 2.1). The suspended and dissolved load of the Burdekin River comprises 85% of the entire sediment yield and within its region of influence terrigenous mud is the dominant fraction of sediment on the inner shelf (Belperio 1983).

Differences in the geochemical composition of terrigenous sediment supplied from different catchments have not been documented. Each catchment contains a large variety of Palaeozoic rock types and an extended history (up to 36 million years old) of soil formation and landform development (e.g., Isbell & Murtha 1970; Grimes 1980; Coventry *et al.* 1980; Pringle 1986; Bain *et al.* 1990).

The catchment areas of the Burdekin and the Herbert can be characterised as dry tropical and wet tropical respectively (Mitchell & Furnas 1996). Climate is the main determinant of sediment yield from rivers in the region (Neil & Yu 1996). This is because rainfall effects both run off and the vegetation cover with the dry catchments having significantly greater sediment yield (t km^{-2}) due to low vegetation cover (Table 2.1).

In contrast to riverine terrigenous sediment, marine biogenic sediment is supplied across the lagoon by natural biogeochemical processes. On the outer shelf, reef flat sediments are > 80% $CaCO_3$ and are derived from corals, coralline algae, molluscs, Halimeda and foraminifera (Maxwell 1968; Orme & Flood 1980), while Halimeda dominated sediments occur between reefs (Harris *et al.* 1990).

Table 2.1 Properties of inner shelf geographic subdivisions of the central section of the Great Barrier Reef lagoon. Catchment, rainfall and run off data were compiled from Pulsford (1993); Belperio (1983); Moss *et al.* (1992);

Inner Shelf Subset	Climate	Inner Shelf Area (km^2)	Rivers	Catchment Area (km^2)	Run off ($ML\ yr^{-1}$)	Estimated Sediment Load ($Mt\ yr^{-1}$)
Upstart Bay	Dry tropical	257	Burdekin	129 860	10 100 000	5
Bowling Green Bay	Dry tropical	714	Haughton	3 650	756 000	< 0.5 *
Cleveland Bay	Dry tropical	350	Ross	1 815	372 000	0.3
Halifax Bay	Dry tropical	1 500	Bohle/Black	1 075	509 000	< 0.5 *
Lucinda	Wet tropical	173	Herbert	10 131	4 991 000	0.62
Hinchinbrook Channel	Wet tropical	300	Herbert	as above	as above	as above
Rockingham Bay	Wet tropical	700	Herbert/Murray/Tully	2825	5 301 000	0.66

* *This study approximated*

The bioclastic components of the middle shelf sediments are comprised of bryzoans, Halimeda, foraminifera and sponges whereas the principle contributors to the bioclastic components of inner shelf sediments are bivalves, gastropods and foraminifera (Belperio 1983). Coralline debris can form a significant portion of the bioclastic debris adjacent to inner shelf coral reefs.

2.1.1.3 Sediment transport processes

The Great Barrier Reef protects the lagoon from the open ocean currents and waves. Within the lagoon, currents and waves are predominantly north-westerly directed, and are driven by the predominant southeast winds (Maxwell 1968; Orme & Flood 1980; Belperio 1983). Wave heights of 1 m are typical (Woolfe *et al.* 2000), with waves up to 3 m generated during stronger wind periods (Orme & Flood 1980).

Wind-induced wave generated bed stress and northerly-directed (along-shelf) currents are the dominant sediment transport energy within the Great Barrier Reef lagoon (Orpin *et al.* 1999). Wind forcing of currents results in almost total decoupling of the outer shelf and the inner shelf, with little mixing of waters by across-shelf tidal excursions (King & Wolanski 1992). This results in strong across-shelf partitioning of sediment composition (Maxwell 1968; Orme & Flood 1980; Belperio 1983) and the physical sorting and redistribution of sediment along-shelf into facies that have characteristic grain size and composition sediments (e.g., Orpin & Woolfe 1999; Lambeck & Woolfe 1999).

Across-shelf partitioning of sediment is characterised by trapping of terrigenous sediment within the inner shelf, with terrigenous sediment forming a wedge against the coast, typically up to 5 m thick. Along-shelf distribution of sediments is characterised by the maximum thickness (30 m) of terrigenous sediment occurring in low energy environments, which are created on the leeward side of geographic features (Belperio 1983; Johnson & Searle 1984; Larcombe & Woolfe 1999b). In regions exposed to the effects of the south east trade winds on the inner shelf (e.g., Halifax Bay), the fine grained terrigenous sediments are resuspended and advected northwards by wind induced currents (Orpin & Ridd 1996).

2.1.1.4 Post depositional processes

Physical mixing of sediments through bioturbation is considered to be a significant post-depositional modification that results in homogenisation of surface sediments to 20-30cm depth (Belperio 1978; Larcombe & Ridd 1994; Carter *et al.* 1993). This work is predominantly observational and published sediment mixing rates using chemical tracers has not been completed. Sorting of sediments during periodic cyclonic or storm events have been documented by Gagan *et al.* (1990).

Diagenetic processes in shelf sediments have been documented by Alongi (1995) in the Herbert River delta and Hinchinbrook Channel region. Maximum rates of sulfate reduction occurred in Hinchinbrook Channel where there was an abundant supply of organic carbon in the form of mangrove and marine algal organic matter. Elsewhere on the shelf, studies of early diagenetic processes that effect sediment geochemical composition are scarce. Differences in sediment geochemical composition between cores collected from Halifax Bay and Cleveland Bay have been attributed to diagenetic processes by Ward *et al.* (1995).

2.2 Methods

2.2.1 Sampling

The Australian Institute of Marine Science, Department of Primary Industries and James Cook University collected samples (1023) periodically between 1993 to 1998. GPS, aerial photographs or topographic maps were used to locate sample sites. Samples were collected using either a ponar, frame mounted grab, or a modified van Veen grab with a top opening port in shallow waters, or plastic sampling tools for subaerial intertidal sediments. The use of these sampling devices allowed the collection of near surface sediment (0-100mm) without mixing with deeper sediment. Sample date, depth, latitude, longitude and geographic region are presented in Appendix 1.

At least 500 grams of surface sediment was collected, from which at least a 20 mL subsample was collected for analytical purposes. The remaining sediment was placed in containers for archive storage at the Australian Institute of Marine Science.

2.2.2 Chemical analysis

2.2.2.1 Strong acid digestion

All sediment samples have been subjected to a consistent strong acid digestion. It is a not a total digestion method. Whole (unsieved solids and water) sediment samples were dried at 70°C in an oven, then pulverised and homogenised in an agate mill for 3 minutes. An accurately weighed subsample of sediment (0.5-1 g) was digested in 4 mL of concentrated HNO_3 (AR grade) and 3 mL of concentrated $HClO_4$ (AR grade) at 120°C for 2 hours, then 180°C for 6 hours, within a computer controlled heating block. The solutions were made up to 50 mL with deionised water, mixed, and reheated to 90°C for 1 hour. Solutions were allowed to stand for at least 24 hours before analysis.

The concentration of Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, P, Pb, S and Zn extracted from the sediment were measured in the acid solution using a Varian Liberty 220 ICP Atomic Emission Spectrometer (ICP-AES). When the concentrations of Pb and Cd were below the detection limits of ICP-AES, the concentrations were measured using a combination of Varian Spectra 400 Zeeman Atomic Adsorption Spectrometer (ZGF-AAS) and Varian Ultramass Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

2.2.2.2 Total acid digestion

Total digestion of 23 selected surface sediment samples was completed to evaluate the capacity of the strong acid digestion method described above to dissolve metals in sediments of different composition. The recovery is expressed as Equation 2.1.

$$Recovery = \frac{Strong\ acid\ digestion}{Total\ acid\ digestion} \times 100\ (\%) \qquad \text{(Equation 2.1)}$$

Samples to be digested were selected such that they represented the range of possible grain size and mineralogical types (from predominantly sand to predominantly mud). These samples were dried, pulverised and homogenised by methods previously described. An accurately weighed subsample was digested overnight in 1.5 mL 30% HCl (AR grade), 0.5 mL 70% HNO_3 (AR grade) and 1.0 mL 30% HF (AR grade), at 60°C, in a sealed polyethylene bottle. The following day, solutions were cooled in ice

before adding 15 mL of boric acid solution (50 g/L), shaken to dissolve precipitated fluorides, then made up to 50 mL.

The concentration of Al, Ca, Cd, Cu, Fe, Ni, Pb and Zn in solution were measured by ICP-AES. When the concentrations of Pb were below the detection limits of ICP-AES the concentrations were determined using a combination of ZGF-AAS. The results of the chemical analyses are presented in Appendix 2.

2.2.2.3 Carbon

Carbon analyses were determined by combustion of samples at 950° in a Shimadzu SSM-500A solid sample module attached to a Shimadzu TOC-500A Total Organic Carbon Analyser (non dispersive infra red detector). Total carbon (TC) was determined by measuring CO_2 released upon combustion of an accurately weighed, pulverised and homogenised sediment sample. Organic carbon (OC) was determined similarly after acidification of the sample with weak HCl. Carbonate carbon (CC) was calculated by subtracting OC from TC.

2.2.3 Mineralogical analysis

X-ray diffraction (XRD) analysis of 8 samples, consisting of 4 sediment samples before and after digestion by the strong acid digestion procedure, was completed. Pulverised and homogenised samples were smear mounted on a glass slide. Analysis was completed over a range of 1.3° 2θ to 65°2θ using a Rigaku D-Max series A Diffractometer using Cu Kα radiation. XRD traces are presented in Appendix 3.

2.2.4 Grain size analysis

Grain size distributions were obtained using a Malvern MasterSizer-X long bed laser particle sizer, similar to the methods of Orpin & Woolfe (1999), for 20 surface grab samples that were also subjected to total acid digestion. The percentage of material in the less than 63 micron fraction (< 63 μm) is used to describe the proportion of mud (silt + clay) in the sample.

2.2.5 Statistical analysis

Statistical analysis is used in this chapter to identify processes that influence the spatial distribution of element concentrations in surface sediment grab samples. The analysis is completed on 2 subsets of data that originate from a single large database held at the Australian Institute of Marine Science. Analysis has been completed separately on two subsets, because over the 5 year period of sample collection the choice of elements to be determined varied between batches. For ease of statistical analysis and interpretation the data has been subdivided into 2 subsets that have a consistent suites of elements determined. 1) A subset of 762 surface samples that span the inner shelf, middle shelf and outer shelf, and have a consistent suite of Al, Ca, CC, Fe, Mn, OC, P and S determinations. 2) A subset of 264 surface sediment samples from the inner shelf that had analyses of Al, Ca, CC, Cd, Co, Cu, Fe, Mn, Ni, OC, P, Pb, S and Zn. All statistical analysis was completed in SPSS for Windows Version 6.1.3.

Prior to analysis all samples have been assigned to a geographic subdivision, which describes the general location across-shelf and along-shelf within the study region. Across-shelf subdivisions included outer shelf, middle shelf and inner shelf, which are based on the 20 m and 40 m depth isobaths (Figure 2.1). The inner shelf subdivision was further subdivided on the basis of along-shelf geographic location, which included; Upstart Bay, Bowling Green Bay, Cleveland Bay, Halifax Bay, Lucinda, Hinchinbrook Channel and Rockingham Bay (Figure 2.1).

2.2.5.1 Principal component analysis

Principal Component Analysis (PCA) is used here as an exploratory technique to explore groups of samples that have similar chemical properties and generate hypotheses upon the influences that create groups of samples. Observation of scree plots and plots of component scores were used to determine the number of significant components. The results of PCA are presented as component plots, which use colour coded symbols representing geographic subdivisions to demonstrate sample groupings.

PCA has been completed on the shelf wide subset of 764 samples and the inner shelf subset of 264 samples using raw concentration data as independent variables. PCA was also completed on the subset of 264 inner shelf sediment samples after they had been standardised to remove natural variation in concentration (described in 2.2.5.2).

The standardised trace metal values were then used as independent variables in PCA. The results of the PCA of standardised and unstandardised data are compared.

2.2.5.2 Standardisation of trace metal concentrations

Standardisation of trace metal has been undertaken to minimise the natural variation in concentration created by changes in sediment composition between sites. In doing so, trace metal concentrations of samples that have different composition may be compared equally, and other influences upon variation in trace metal concentrations (e.g., anthropogenic influences) can be more easily observed.

As described in section 1.4.2.1, natural variation in the concentration of trace metals can be predicted by regression models. In this chapter, elemental concentrations, water depth and distance along-shelf (approximated by Pythagoras Theorem) from the mouth of the Burdekin River have been used as independent variables to predict sediment trace metal concentrations in multiple regression models. These models have the form of Equation 2.3.

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 \ldots\ldots\ldots \beta_n x_n \qquad \text{(Equation 2.3)}$$

Where y is the dependent variable (trace metal concentration); x_1, $x_2 \ldots x_n$ are the independent variables (major element concentrations, distance, depth etc.); and β_1, $\beta_2 \ldots \beta_n$ are the partial correlation coefficients fitted to each independent variable.

Full stepwise regression has been used. This method works by adding and removing variables, according to a critical probability value, until no more variables are eligible for entry. All possible nonrecurring combinations of independent variables are considered (Balsillie & Tanner 1999). Critical probability values represent the significance of the partial correlation coefficient of each variable, and were set at 0.05 and 0.1 for entry and removal respectively for all models.

The optimum adjusted coefficient of determination (adjusted R^2) is a measure of the success of the predicting capabilities of the model (Balsille & Tanner 1999). However, the final combination of variables was determined by scrutiny of standardised predicted values plotted against studentised deleted residual values and so that colinearity did not occur between independent variables (e.g., Kleinbaum *et al.* 1998).

Colinearity was common between Al and Fe, and between Ca and CC. Al was selected in preference to Fe, because Al exhibits a linear relationship with the < 63 μm fraction of sediments (see Figure 2.2). Ca was selected in preference to CC, because all Ca analyses were above detection limit. Homogenous distribution of residuals, with constant variance, no colinearity between independent variables, and the absence of clusters or trends is the preferred selection criterion. Therefore the model with the greatest adjusted R^2 value was not necessarily selected.

All chemical parameters were log transformed prior to regression analysis. This ensured that all data approximated the assumptions of normality and ensured constant variance. Normal probability plots of the data before and after transformation are presented in Appendix 4. Samples that were below method detection limits were assigned a value of half the method detection limit. Outlying samples from the intertidal zone of western Cleveland Bay were removed before calculation of the regression model because samples have high metal concentrations as a consequence of anthropogenic influences (e.g., Reichelt & Jones 1994). Some samples from Hinchinbrook Channel were also edited from the model calculation because they contained distinctly different (high OC) sediment geochemical composition to the majority of the inner shelf sediment samples (see Table 2.2).

Trace metal concentrations have been standardised by dividing the measured concentration by the concentration predicted using a full stepwise regression model (Equation 2.2).

$$Standardised\ \ value = \frac{Strong\ acid\ digestion\ measured\ concentration}{Stepwise\ regression\ predicted\ concentration} \quad \text{(Equation 2.2)}$$

The standardised value is therefore a function of the parameters used in the regression model to predict a natural concentration. If parameters that have an influence upon trace metal concentration are not included in the regression model, their influence will be apparent in the variation of standardised values.

2.3 Results

2.3.1 Quality control and digestion recovery

Figures 2.2a and 2.2b demonstrate that the recovery of elements by the strong acid digestion is dependent upon the mineralogy (matrix) of the sediment (e.g., Tessier et al. 1979; de Groot et al. 1982; Cook et al. 1997). The recovery of Fe, Pb and Zn increases with strong acid soluble Al concentration. The increase in strong acid soluble Al is proportional to the percentage of material in the < 63 mm particle size fraction. The recovery of most metals increases in proportion with the amount of mud (silt +clay) in a sample. However, the recovery of Ni and Cu is near constant and is independent of the sediment matrix. The recovery of Cd could not be determined for this suite of samples because of the low concentration of Cd in the samples, and high detection limit of the total acid digestion method (due to the addition of boric acid).

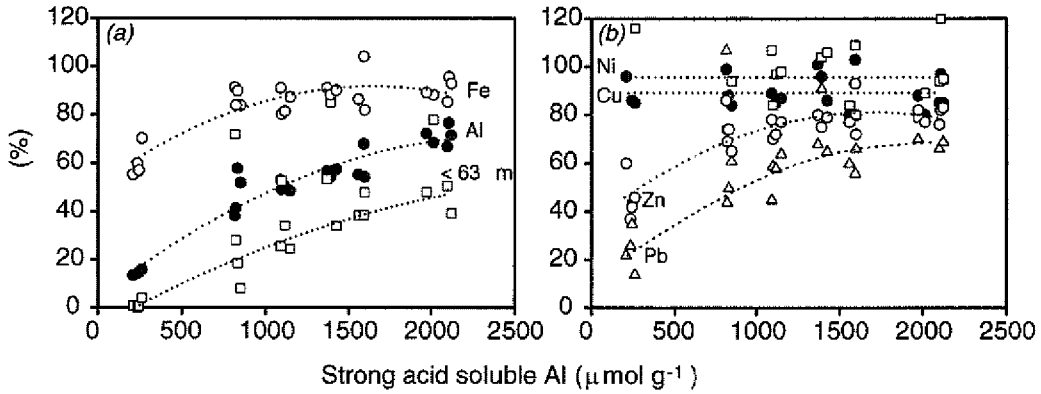


Figure 2.2 Recovery of elements by the strong acid digestion procedure. Increases in strong acid soluble Al are proportional to the % < 63μm (mud). Recovery of elements increases in muddy sediments relative to sandy sediments. (% recovery = strong acid digest/total digest x 100): (a) Recovery of Fe (○), recovery of Al (●), percentage < 63μm (□); (b) recovery of Cu (●), recovery of Ni (□), recovery of Pb (Δ), recovery of Zn (○); Trend line for each element (dashed line).

Recoveries of metals from certified reference material BCSS-1 by the strong acid digestion procedure and the total acid digestion procedure are presented in Table 2.2. The coefficient of variation (CV = standard deviation/mean x 100) between 50 batches of samples is typically between 5-10 % for all elements. This demonstrates that the strong acid digestion method provides consistent recovery of metals from samples that have a constant matrix. The average CV for the analysis of triplicate grab samples, from within a 5m x 5m area, is between 5 to 15% for most elements (Table 2.2), and is greater than the between batch error.

Table 2.2 Recovery of metals by the strong acid digestion procedure, variation in BCSS-1 between batches and sampling variance (C.V.). The recovery of elements from certified reference material BCSS-1 by the strong acid digestion procedure is less than the total digestion, and less than the certified values of BCSS-1. The between batch variation in analysis of BCSS-1 is less than 10% or 50 batches of samples. Precision of triplicate sample analysis is between 5 to 15% for most elements, and typically exceeds the between batch CV. (mean ± standard deviation; * n = 7).

	Al $\mu mol\ g^{-1}$	**Ca** $\mu mol\ g^{-1}$	**Cd** $nmol\ g^{-1}$	**Co** $nmol\ g^{-1}$	**Cu** $nmol\ g^{-1}$	**Fe** $\mu mol\ g^{-1}$	**Mn** $\mu mol\ g^{-1}$	**Ni** $nmol\ g^{-1}$	**P** $\mu mol\ g^{-1}$	**Pb** $nmol\ g^{-1}$	**S** $\mu mol\ g^{-1}$	**Zn** $nmol\ g^{-1}$
BCSS-1 Certified concentration	2320 ± 82	135 ± 13	2.2 ± 3.6	193 ± 36	291 ± 42	589 ± 18	4.2 ± 0.3	942 ± 61	22 ± 2	111 ± 6	112 ± 16	1820 ± 184
Total acid digestion BCSS-1 recovered concentration (n= 1)	2334	nd	2.4	nd	290	585	nd	891	nd	120	122	1750
Strong acid digestion BCSS-1 recovered concentration (n = 50)	1331 ± 89	107 ± 7	2.3 ± 0.2*	183 ± 7	224 ± 13	569 ± 34	3.8 ± 0.3	857 ± 77	22 ± 1	95 ± 4*	119 ± 12	1622 ± 168
Replication of BCSS-1 between batches (CV)	7	7	9*	4	6	6	8	9	5	4*	10	10
Triplicate grab sample analysis (mean CV, n= 9)	10	9	14	6	10	7	16	8	10	10	9	12

XRD analysis of samples, before and after the strong acid digestion method, indicates that the method causes the destruction of carbonates, mixed layer clays, kaolinite and probably Fe oxides, but does not result in dissolution of illite (mica), quartz and feldspar. This is demonstrated in Figure 2.3 by the loss of these mineral XRD trace peaks and a corresponding increase in the counts of other minerals that are not destroyed during digestion.

Combined, the results of XRD analysis and evaluation of recoveries indicates the strong acid digestion preferentially leaches minerals in the < 63 mm fraction. These minerals are predominantly clays. Rather than considering the digestion as a partial extraction, it should be considered as a preferential extraction of clay minerals.

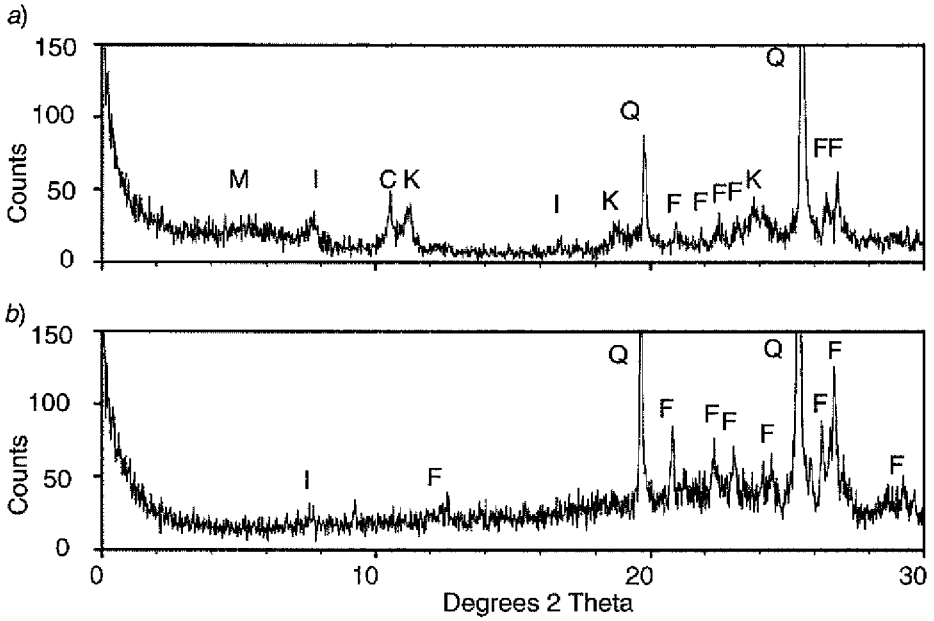


Figure 2.3 XRD trace of sample 1698 from 0 to 30° 2 Theta ; a) Pulverised whole sediment sample prior to digestion; b) residue remaining after the strong acid digestion procedure. Carbonate (C); feldspar (F); illite (I); kaolinite (K); mixed layer clays (M); quartz (Q).

2.3.2 Shelf wide trends in Al, Ca, CC, Fe, Mn, OC, P and S concentrations in sediments

Images of Al, Ca, CC, Fe, Mn, OC, P and S concentrations (Figure 2.4) demonstrate that the distribution of these elements is variable along-shelf and across-shelf. Across-shelf variations are characterised by a decline in Al, Fe, and Mn, and increases in Ca and CC towards the edge of the continental shelf. These changes are also characteristic of the changes in the average element concentration between inner shelf, middle shelf and outer shelf subdivisions (Table 2.3).

These relationships are identified by the PCA of 762 samples, using Al, Ca, CC, Fe, Mn, OC, P and S as independent variables (Table 2.4). Component 1 explains 49% of the total variation in concentration among elements in surface sediments. Component 1 is characterised by a positive correlation between Al, Fe, Mn, OC and S, and negative correlation of these elements with Ca and CC. Samples from the inner shelf have predominantly a positive component 1 score, whereas samples from the outer shelf have negative component 1 scores (Figure 2.5).

The components 2, 3 and 4 (Table 2.4) provide evidence for more subtle influences upon the concentrations of Mn, P, OC and S, which are subordinate to the influences measured by component 1. Component 2 is characterised by the coincidence of concentrations of OC, P and S with biogenic Ca and CC at some locations on the outer shelf and with Al and Fe at some locations on the inner shelf, which also coincide with low concentrations of Mn (Table 2.3). In contrast, OC and S are negatively correlated with CC, P and Mn in samples that are predominantly from Hinchinbrook Channel (component 3, Table 2.4). High concentrations of Mn occur on the inner shelf, and are independent upon other sediment parameters (Figure 2.4). The behaviour of Mn is recognised by component 4 (Table 2.4).

Table 2.3 Average major element and trace metal concentration of outer shelf, middle shelf and inner shelf geographic subdivisions. Average ± standard deviation (n).

Subset	Al (μmol g^{-1})	Ca (μmol g^{-1})	CC (μmol g^{-1})	Cd (pmol g^{-1})	Co (nmol g^{-1})	Cu (nmol g^{-1})	Fe (μmol g^{-1})
Upstart Bay	1632 ± 950 (73)	941 ± 1075 (73)	747 ± 824 (73)	267 ± 189 (43)	191 ± 77 (34)	256 ± 156 (73)	497 ± 249 (73)
Bowling Green Bay	1363 ± 798 (79)	1108 ± 951 (79)	1052 ± 947 (79)	159 ± 91 (53)	186 ± 66 (33)	191 ± 119 (79)	436 ± 218 (79)
Cleveland Bay*	914 ± 586 (70)	1277 ± 703 (70)	1047 ± 782 (70)	176 ± 107 (70)	86 ± 81 (70)	128 ± 133 (70)	345 ± 137 (70)
Halifax Bay	736 ± 277 (40)	3452 ± 2175 (40)	3805 ± 2450 (28)	189 ± 149 (32)	136 ± 54 (22)	107 ± 82 (40)	267 ± 94 (40)
Lucinda	1224 ± 655 (34)	1590 ± 1117 (34)	1464 ± 1093 (34)	309 ± 528 (25)	92 ± 35 (8)	173 ± 345 (34)	380 ± 154 (34)
Hinchinbrook Channel	1484 ± 806 (77)	346 ± 693 (77)	819 ± 920 (28)	340 ± 169 (29)	118 ± 42 (10)	180 ± 104 (77)	396 ± 208 (77)
Rockingham Bay	1133 ± 535 (89)	1835 ± 1239 (89)	1702 ± 1250 (89)	235 ± 223 (45)	118 ± 21 (23)	99 ± 41 (89)	378 ± 124 (89)
Middle Shelf	488 ± 332 (164)	4530 ± 1570 (164)	4453 ± 1655 (154)	166 ± 95 (67)	60 ± 34 (15)	53 ± 35 (164)	177 ± 93 (164)
Outer Shelf	149 ± 132 (74)	6971 ± 1527 (74)	7519 ± 2033 (74)	326 ± 425 (42)		49 ± 208 (74)	59 ± 47 (74)

Subset	Mn (μmol g^{-1})	OC (μmol g^{-1})	P (μmol g^{-1})	S (μmol g^{-1})	Ni (nmol g^{-1})	Pb (nmol g^{-1})	Zn (nmol g^{-1})
Upstart Bay	7 ± 2 (73)	598 ± 458 (73)	11 ± 4 (73)	66 ± 35 (73)	319 ± 184 (34)	66 ± 35 (73)	724 ± 381 (73)
Bowling Green Bay	9 ± 3 (79)	403 ± 238 (79)	10 ± 3 (79)	44 ± 24 (79)	303 ± 145 (33)	60 ± 31 (79)	626 ± 325 (79)
Cleveland Bay	10 ± 3 (70)	106 ± 132 (70)	247 ± 194 (70)	8 ± 2 (70)	51 ± 21 (70)	30 ± 16 (70)	385 ± 271 (70)
Halifax Bay	11 ± 23 (40)	269 ± 127 (40)	13 ± 16 (40)	42 ± 25 (40)	165 ± 51 (22)	48 ± 32 (40)	542 ± 431 (24)
Lucinda	7 ± 1 (34)	426 ± 325 (34)	10 ± 3 (34)	57 ± 42 (34)	141 ± 89 (8)	57 ± 32 (34)	390 ± 190 (8)
Hinchinbrook Channel	3 ± 2 (77)	3126 ± 2869 (42)	9 ± 4 (77)	207 ± 225 (77)	235 ± 142 (10)	84 ± 44 (77)	693 ± 239 (10)
Rockingham Bay	7 ± 2 (89)	811 ± 1178 (89)	10 ± 3 (89)	86 ± 103 (89)	151 ± 48 (23)	56 ± 21 (89)	502 ± 145 (23)
Middle Shelf	5 ± 2 (164)	245 ± 150 (164)	10 ± 3 (164)	48 ± 13 (164)	109 ± 51 (15)	24 ± 12 (164)	187 ± 133 (57)
Outer Shelf9	2 ± 2 (74)	201 ± 54 (74)	11 ± 3 (74)	63 ± 12 (74)		10 ± 8 (74)	68 ± 101 (18)

Intertidal zone samples removed due to strong anthropogenic influences

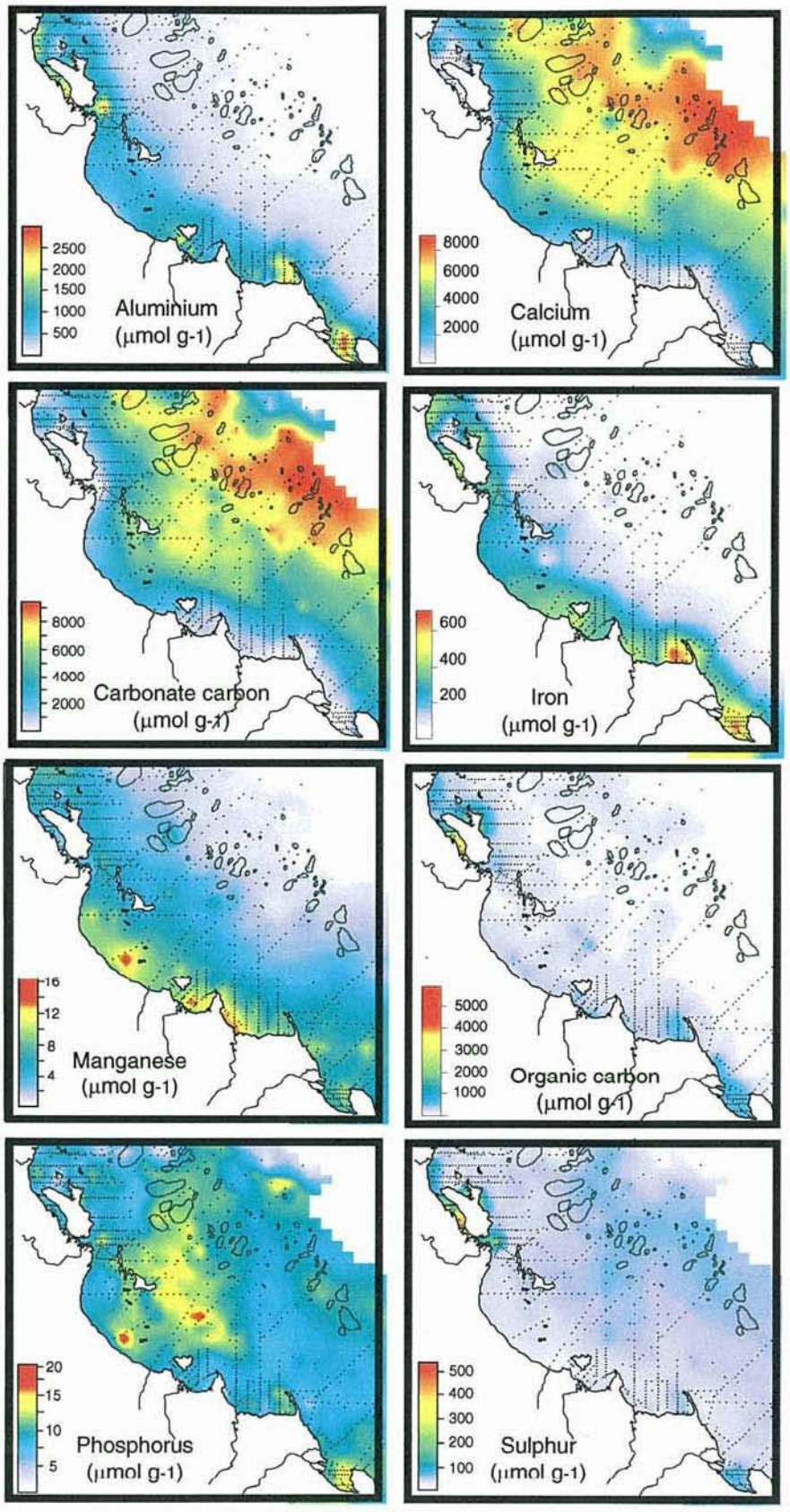


Figure 2.4 Images of Al, CC, Mn, OC, P and S concentration in surface sediments of the Great Barrier Reef lagoon. Surafce sample location (•).

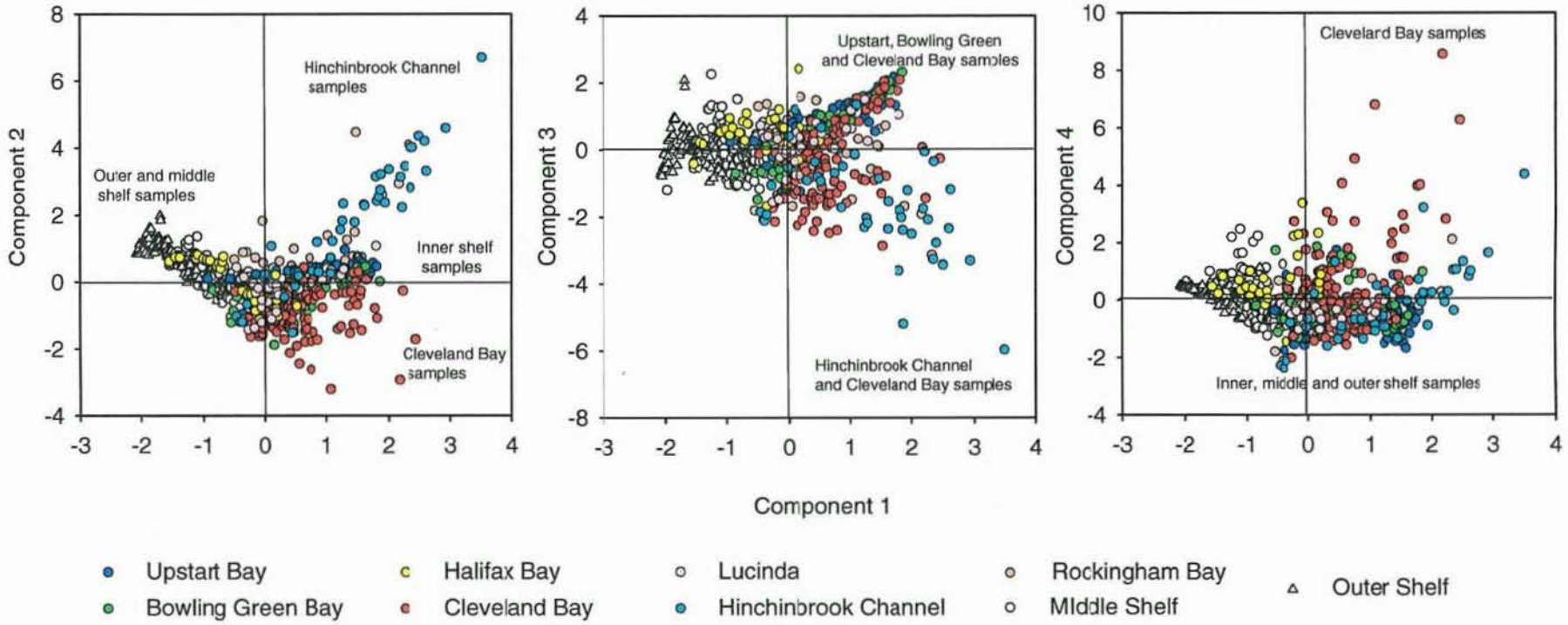


Figure 2.5 Component plots from PCA of Al, Ca, CC, Fe, Mn, OC, P and S for 762 surface sediment grab samples from the inner shelf, middle shelf and outer shelf.

2.3.3 Variations in sediment composition on the inner shelf

Variations in the distribution of trace metal concentration in Figure 2.6 display similar patterns to Al and Fe in Figure 2.4. This relationship is recognised in the PCA of 264 samples from the inner shelf, using major elements and trace metal concentration as independent variables, as component 1, and explains 40% of the total variance between elements (Table 2.5). Component 1 is characterised by a positive correlation between Al, Cd, Co, Cu, Fe, Mn, Ni, OC, Pb, S and Zn, which are negatively correlated with Ca and CC. This indicates that terrigenous sediments are enriched in trace metals relative to biogenic carbonate rich sediments.

Samples from the northern end of the study region (e.g., Rockingham Bay) have a more negative component 1 score (Figure 2.7) relative to samples form the southern end of the study region (e.g., Upstart Bay). The positive component 1 score of sample from the southern region indicates a distinctly more terrigenous composition of sediments relative to samples from the northern region. This is also demonstrated in Table 2.4 by the decline in the average concentration of Al, Fe and trace metals between geographic sub sets progressing northwards, and moving away from the mouth of the Burdekin River. These patterns recognise that there are changes in sediment geochemical composition along-shelf between geographic subsets.

Component 2 (Table 2.5) explains an additional 19% of the variance between elements. It is characterised by positive correlation between Cd, Cu, Pb and Zn, which are negatively correlated with Al and Fe. Samples from Cleveland bay are characterised by a strong positive component 2 score (Figure 2.7). Some samples from Cleveland Bay have trace metal concentrations that exceed the ANZECC ISQV-low, and this suggests the trend represents anthropogenic influences.

Components 3, 4 and 5 explain an additional 30.2% of the variance in the data. The variations are related to more complicated distributions of Mn, OC, P and S in sediments, previously described in the PCA f 764 samples from across the entire shelf. Where components 3, 4 and 5 in Table 2.5, are equivalent to component 2, 3 and 4 in Table 2.3, and will not be discussed further.

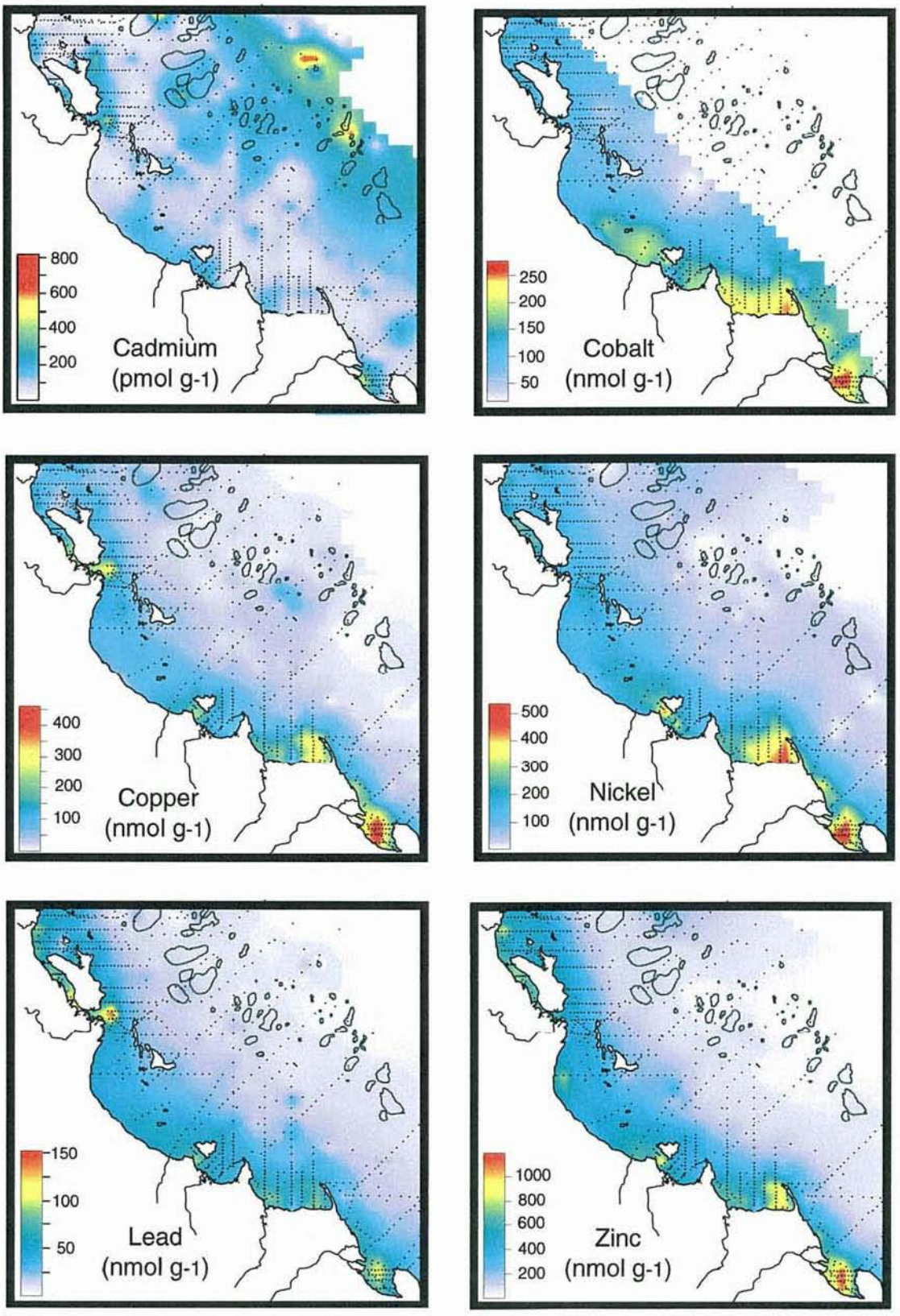


Figure 2.6 Images of Cd, Co, Cu, Ni, Pb and Zn in surface sediments of the Great Barrier Reef lagoon.

Table 2.5 Summary of principal component analysis of major element and trace metal concentrations for inner shelf surface sediment grab samples.

	Component 1	Component 2	Component 3	Component 4	Component 5
Aluminium	0.8331	-0.4493	0.1563	0.0520	-0.0183
Calcium	-0.5845	0.1293	0.6518	0.3908	0.1436
Carbonate carbon	-0.5892	0.1329	0.6486	0.3993	0.1342
Cadmium	0.5041	0.6595	0.0874	-0.0236	0.0407
Cobalt	0.7854	-0.4132	-0.1837	0.2330	0.0279
Copper	0.6624	0.4755	0.0639	0.2857	-0.2625
Iron	0.8591	-0.4429	0.1367	0.1429	-0.0008
Manganese	0.3003	0.0252	-0.4233	0.3952	0.7358
Nickel	0.7844	-0.4848	0.1027	0.2151	-0.0954
Organic carbon	0.6322	0.1601	0.4259	-0.5247	0.1997
Phosphorus	0.0553	-0.5080	0.6493	0.1994	-0.0600
Lead	0.6818	0.6497	0.0632	0.2138	-0.1253
Sulfur	0.4500	0.0330	0.4710	-0.6497	0.2597
Zinc	0.6432	0.6647	0.0931	0.1824	0.0153
Eigenvalue	5.62	2.65	1.96	1.49	0.79
Variance %	40.10	18.90	14.00	10.60	5.60
Cumulative %	40.10	59.10	73.10	83.70	89.30

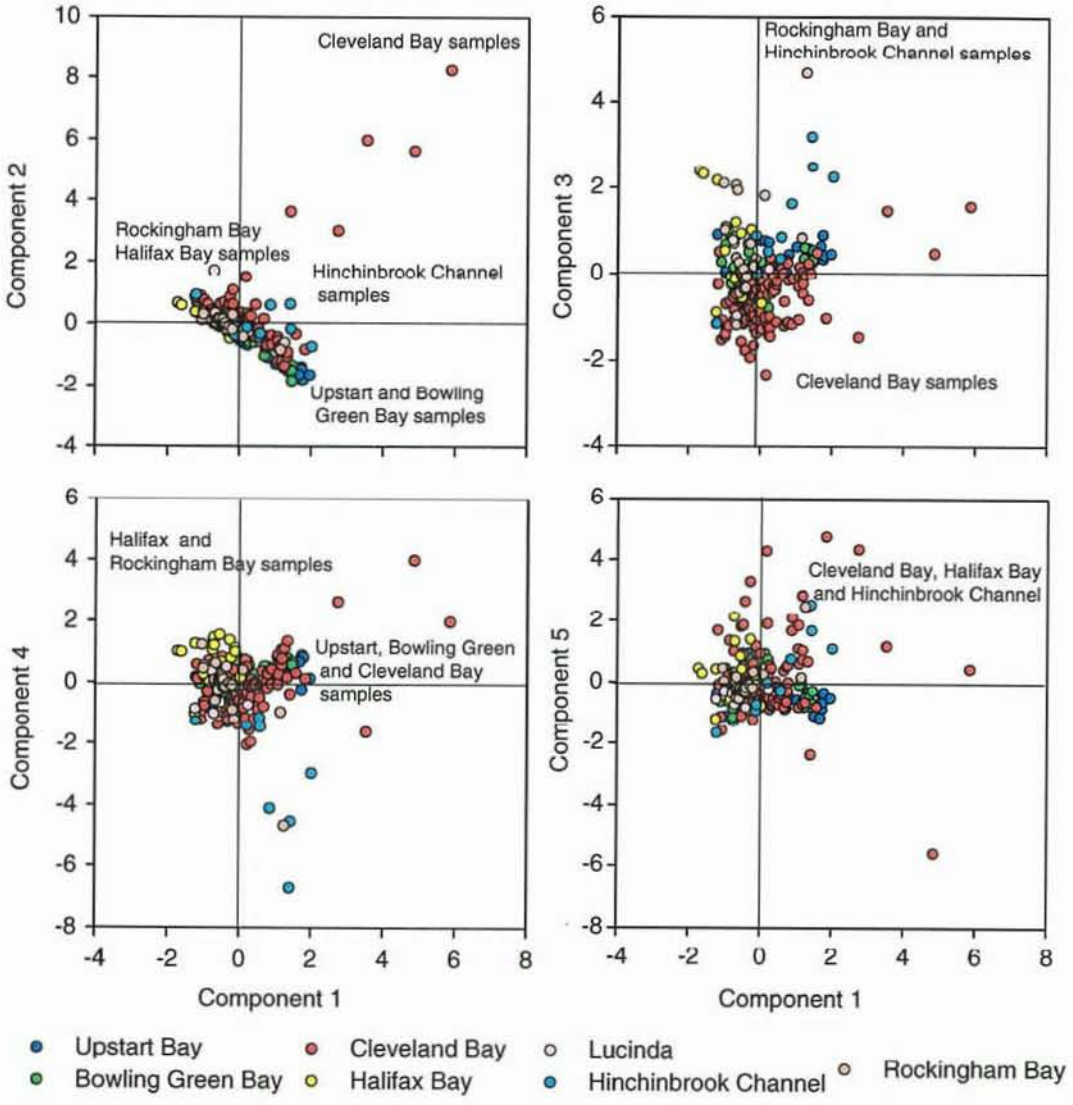


Figure 2.7 Plots of PCA component scores generated for 264 samples from the inner shelf using Al, Ca, CC, Cd, Co, Cu, Fe, Mn, Ni, OC, Pb, S and Zn as variables. Samples that have high component 1 score are relatively enriched in fine grained terrigenous sediment. Samples that have a low component 1 score are relatively enriched in biogenic carbonate rich sediment.

2.3.3.1 Standardisation and PCA of trace metal concentrations in sediments from the inner shelf

Standardisation of trace metal concentrations has been completed to remove these natural variations, and enhance changes in trace metal concentration along-shelf. Measured values were standardised by dividing the measured concentration by a value predicted by a full stepwise regression model (Equation 2.1). Models use major elements to predict a trace metal concentration. However, distance along-shelf from the mouth of the Burdekin River, and water depth have also been included to examine the affects of changes of metal concentration along-shelf and across-shelf.

The regression models (Table 2.6) of the natural concentration of Co, Cu, Ni, Pb and Zn, are strongly influenced by the positive correlation of trace metals with Al, Fe, Mn, OC and negative correlation with Ca and CC, and are consistent with results of PCA. Unlike the other trace metals, Cd does not form strong linear relationships with major elements. This is apparent by the greater variance, or standard error, of the regression model for Cd (Table 2.6).

Distance along-shelf is also a significant variable in the models of Co, Cu and Ni. The inclusion of distance along-shelf as a variable in regression models provides evidence for changes in standardised concentration of metals along-shelf. These changes are distinct from changes in the relative proportions of terrigenous and biogenic carbonate sediments, which should be removed (standardised) by the inclusion of Al, Fe, Ca and CC in regression models.

The significance of including or excluding distance along-shelf in each model has been evaluated by examining the effects upon the adjusted R^2 of each model, and comparing the significance of the partial correlation coefficient (Table 2.6). The large value of the test statistic (t) relative to the probability (p), and the improvement to the adjusted R^2 upon inclusion in the regression model for Co, Cu and Ni indicates that it is a more significant variable in the regression models than it is for Cd, Pb and Zn.

Table 2.6 Summary of multiple regression model results showing the significance and effect of including or excluding the distance along shelf from the mouth of the Burdekin River as a variable (n = number of samples in the model; t = test statistics; p = probability; adjusted R^2 = adjusted coefficient of determination)

Element	n	t	p	Excluded adjusted R^2	Included adjusted R^2	Optimum model equation
Cadmium	312	1.552	0.1218	0.3013	0.3044	LogCd = -0.170 logCa + 0.150 logOC + 0.000279 distance + 2.331
Cobalt	209	-8.765	0.0000	0.7693	0.8312	LogCo = 0.648 logFe + 0.252 logMn - 0.00067 distance + 0.343
Copper	392	19.723	0.0000	0.8269	0.9133	LogCu = 0.886 logAl - 0.032 logCC + 0.0411 logOC - 0.001 distance - 0.457
Nickel	208	12.082	0.0000	0.8795	0.9294	LogNi = 0.876 logAl + 0.047 logCa + 0.148 logMn - 0.0009 distance - 0.540
Lead	456	4.103	0.0000	0.8624	0.8659	LogPb = 0.541 logAl - 0.078 logCa +0.159 logMn- + 0.111 logOC + 0.00025 distance - 0.123
Zinc	314	1.013	0.3119	0.9225	0.9225	LogZn = 0.767 logAl - 0.038 logCa + 0.112 logMn + 0.018 logOC + 0.000071 distance-0.349

So that the effects of changes in distance along-shelf can be observed, standardised trace metal values, generated by regression models that do not include distane along-shelf, have been plotted against distance along-shelf as Figure 2.8. Standardised values of Co, Cu and Ni in the north of the study area are significantly lower than values in the south of the study area. The change in the standardised values between regions is characterised by a linear decline along-shelf, moving north of the Burdekin River delta (Figure 2.8).

PCA of standardised metal concentrations was completed using regression models that do not include distance along-shelf as a variable. Three components were identified that accommodate 74.7% of the variance in standardised trace metal values (Table 2.7). Component 1 is characterised by positive correlations between all metals, but most strongly between Cd, Cu, Pb and Zn, and explains 36.7% of the variance between standardised trace metal concentrations (Table 2.7). Samples from Cleveland Bay have strong positive component 1 scores, and in this respect are similar to component 2 of the PCA of raw data (Table 2.5).

Component 2 is characterised by positive correlations between Ni, Co and distance along-shelf (Table 2.7), and explains 27.5% of the variance in standardised trace metal concentrations. The clustering of samples from the different geographic subsets along the axis of this component indicates that statistically distinct differences in standardised trace metal values occur along-shelf (Figure 2.9). The clustering of samples is characterised by clear separation of samples in the northern part of the study region from those in the southern part.

Component 3 (Table 2.7) is characterised by increases in the standardised concentration of Cd, which is independent of the other elements. The source of this variation was not determined, and is complicated by the poor fit of the regression model. However, the plot of component 3 versus component 2 clearly separates samples from the north of the study area from those in the south. This suggests distinctly different influences upon Cd concentrations between the north and south of the study region.

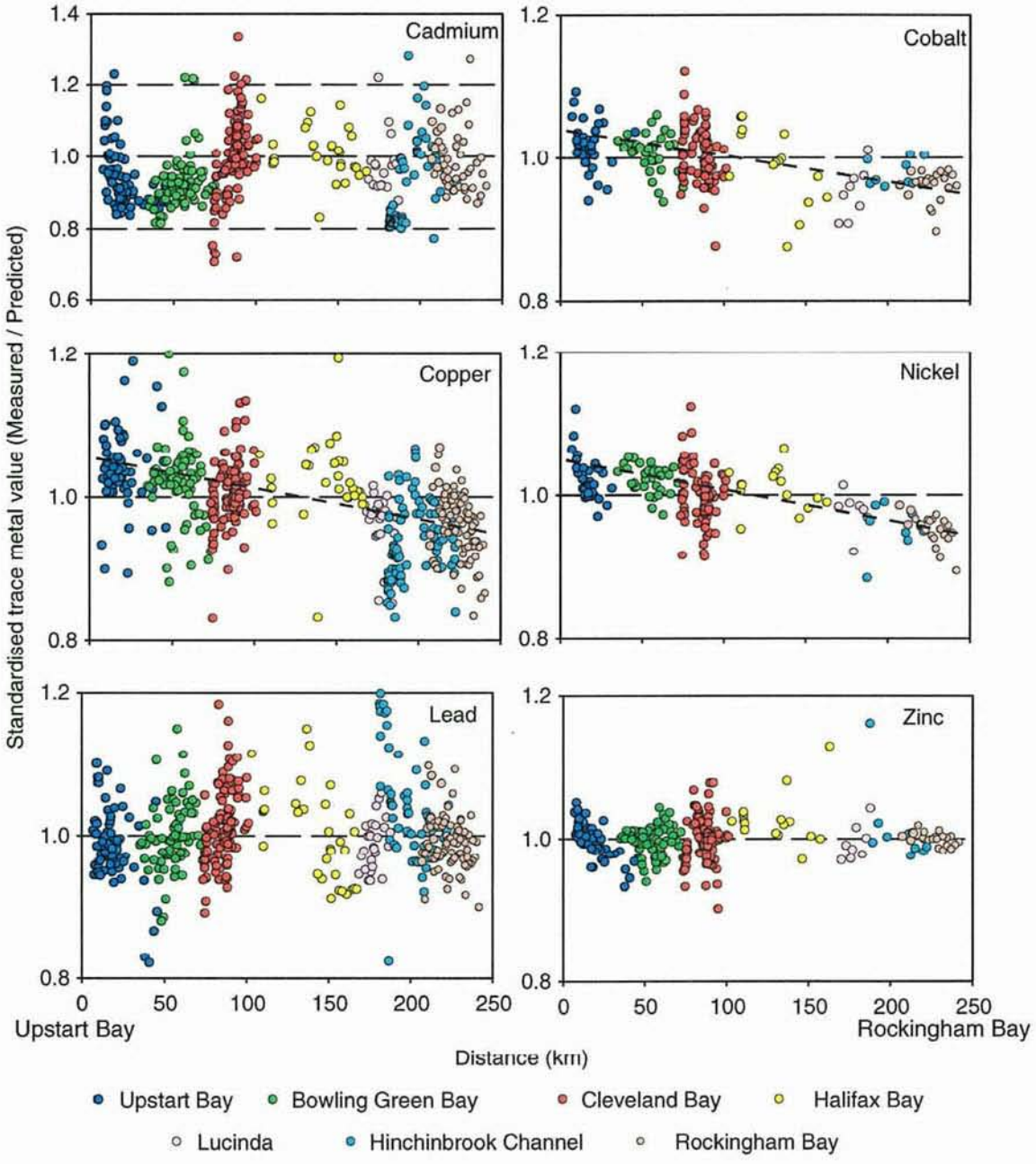


Figure 2.8 Plots of standardised trace metal values versus distance along-shelf. The decline in standardised values of Co, Cu and Ni with distance along-shelf (dashed line) are interpreted to indicate changes in the geochemical composition of terrigenous sediment supplied to regions of the inner shelf.

Table 2.7 Summary of principal component analysis of standardised trace metal concentrations for inner shelf surface sediment grab samples.

	Component 1	**Component 2**	**Component 3**
Cadmium	0.5913	0.2992	-0.6272
Cobalt	0.2529	-0.7551	0.0186
Copper	0.8559	-0.0058	-0.1012
Nickel	0.3159	-0.7083	0.2804
Lead	0.7256	0.3835	0.3441
Zinc	0.8464	0.2057	0.2308
Distance	-0.2772	0.7560	0.2914
Eigenvalue	2.97	1.92	0.74
Variance %	36.70	27.50	10.60
Cumulative %	36.70	64.10	74.70

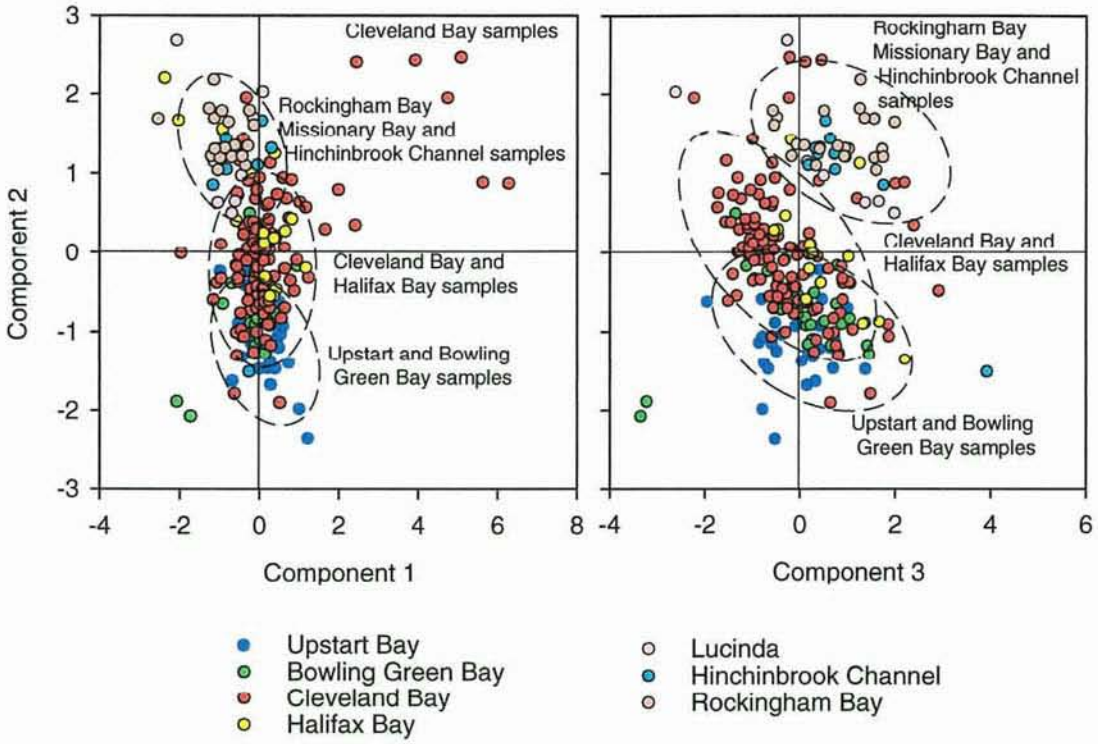


Figure 2.9 Plots of PCA component scores generated for 264 standardised trace metal concentrations from inner shelf surface sediment grab samples. Component 1 is characterised by simultaneous increases in Cd, Cu, Pb and Zn of samples from Cleveland Bay. Component 2 recognises changes in terrigenous sediment composition along-shelf. Samples with a more negative component 2 score are realtively enriched in Co, Cu and Ni. Component 3 recofnises variations in the standardised Cd values along-shelf. Samples with a more negative component 3 score are relativelty enriched in Cd.

2.4 Discussion

2.4.1 Shelf wide patterns and influences in the distribution of terrigenous and biogenic carbonate sediment

Strong across-shelf partitioning in sediment particle size and chemical composition is characteristic of the region (Maxwell 1968; Orme & Flood 1980; Belperio 1983, Woolfe *et al.* 2000). Partitioning is apparent in Figure 2.4 and 2.6 by the high concentrations of Al, Co, Cu, Fe, Ni, Pb and Zn on the inner shelf. This partitioning manifests within PCA as clustering of samples that are enriched in these elements on the inner shelf from samples located on the outer shelf and middle shelf (Figure 2.5).

Partitioning of sediment composition across-shelf occurs because the predominant influence to the distribution of fine grained terrigenous sediment is northerly directed wind induced waves and currents (Belperio 1983; King & Wolanski 1992; Orpin *et al.* 1999). These forces result in trapping of terrigenous sediments against the coast, with preferential accumulation of fine-grained terrigenous sediments in areas of low wave energy (Larcombe & Woolfe 1999a).

The same wind driven regime, which influences partitioning of sediment composition across-shelf, also influences the distribution of terrigenous sediment along-shelf on the inner shelf. In higher energy environments fine-grained terrigenous sediments are suspended by wind-wave induced bed stress and transported to the north by the prevailing currents (e.g., Lou & Ridd 1996; Orpin *et al.* 1999). Coarser grained more resilient minerals phases (e.g., quartz and feldspar) and biogenic carbonate sediments may accumulate in these environments (e.g., eastern side of Cape Bowling Green). Greater amounts of fine-grained terrigenous sediments are located in the lee of Cape Bowling Green (see Figure 1.1), in a low energy environment that is less effected by wind induced waves and currents (Figure 2.4).

Variation in sediment composition along-shelf on the inner shelf, from the south to the north of the study area, is characterised by a progressive decline in the amount of terrigenous sediment and increase in the amount of biogenic carbonate sediment.

Samples from Upstart Bay and Bowling Green Bay are more terrigenous in composition than samples from Halifax Bay and Rockingham Bay, which are relatively enriched in biogenic carbonate. Lambeck & Woolfe (1999) described the inner shelf as divided into discrete zones, which are characterised by the reduction in terrigenous sediment and increase in biogenic carbonate sediment towards the north of each zone. The start of each zone corresponds to the presence of a large source of terrigenous sediment, such as the Burdekin River.

The distribution of Ca and CC are indicative of the distribution of biogenic skeletal carbonate sediment, which is produced shelf wide by biogeochemical processes. The distribution of biogenic carbonate sediment is influenced the prevailing hydrodynamic regime, but is also influenced also by factors including; salinity, turbidity and substrate control (e.g., Larcombe & Woolfe 1999b; Hopley 1995). Regions of the inner shelf can have a strongly biogenic geochemical signature (e.g., Halifax Bay, Figure 2.4).

2.4.2 Variation in the distribution of Mn, P, S and organic carbon

The elements Mn, P and S and OC have spatial distribution patterns that are complicated by the supply of these elements from terrigenous sediment sources on the inner shelf, and biological processes that occur over the entire shelf. These relationships are further complicated by early diagenetic processes, which readily affect the concentration of Mn, OC, P and S in sediments (e.g., Berner 1984; Martens 1993; Anschutz *et al.* 1998).

The PCA of the 762 samples from the shelf wide subset and the 264 samples from the inner shelf subset, consistently identify 3 components that explain variance in concentrations of Mn, P and S and OC. In the PCA of 762 samples from all sections of the shelf, the individual variance explained by each of these components is less than 25% of the total variation measured. However, combined they represent 45.4% of the total variation in geochemical composition measured. Therefore, despite the subordinate role of each component in explaining variation in sediment geochemical composition, they constitute a significant influence upon sediment geochemical properties.

Within shallow marine sediments, the supply and metabolic properties of organic matter limits diagenetic processes that influence sediment geochemical composition (Veeh *et al.* 1999; Berner 1984). Hinchinbrook Channel has the highest average OC concentrations on the shelf (Table 2.2) due to the abundant supply of organic matter in the form of mangrove detritus (Alongi 1990). As a consequence, samples from Hinchinbrook Channel are strongly affected by post depositional diagenetic processes.

Highest rates of sulfate reduction and pyrite preservation on the shelf occur in Hinchinbrook Channel, where there is an abundant supply of reactive organic carbon (Alongi 1995). This is recognised in PCA as component 2, by a strong positive relationship between OC and S (Table 2.4). A similar, but weaker relationship between OC and S also occurs on the outer shelf and is apparent by the grouping of samples from the outer shelf in the plot of component 1 versus component 2 (Figure 2.5).

The components 2 and 3 also identify strongly negative correlations between high concentrations of OC and S with P and Mn in samples from the inner shelf. The negative correlation is interpreted to be a consequence of changes to sediment geochemical composition during diagenesis. The formation of iron sulfides has been found to promote poor burial efficiency of P by reducing the adsorption capacity of the sediment (e.g., Krom & Berner 1980). Similarly under reducing conditions, dissolution of Mn oxides and diffusion of reduced Mn across the sediment water interface will occur (e.g., Wersin *et al.* 1991).

2.4.2.1 Independent behaviour of Mn

While loss of Mn occurs at some locations on the inner shelf, anomalously high concentration of Mn also occurs at some locations on the inner shelf. The anomalously high concentrations are independent of other elements, and are identified in PCA by component 4 (Table 2.4). These samples are characterised by high concentrations of Mn at sites in Bowling Green Bay, Cleveland Bay and Halifax Bay that are exposed to wave energy (Figure 2.4).

There is no obvious detrital source for the high Mn concentrations at these sites. Therefore the high Mn concentrations are interpreted to represent the concentration of Mn, as Mn oxides at a redox interface. The formation of a specific Mn mineral phase is unlikely (e.g., $MnCO_3$, Fang & Hong 1999; Wartel *et al.* 1990) given the independence upon other geochemical parameters.

For these high concentrations to occur at surface would require erosion of sediment, to expose the redox interface. This is consistent with the location of these sites in areas of higher energy that would allow the resuspension and transport of sediment to expose buried and more reduced sediment.

Therefore the behaviour of Mn is strongly a function environment of deposition. In Hinchinbrook Channel, the very low energy environment will enhance the loss of solutes across the sediment water interface by allowing reducing conditions to occur very close to the sediment water interface (e.g., Anschutz *et al.* 1998).

This interpretation is consistent with sediment resuspension and erosion occurring in areas exposed to wave energy. Shallow buried redox interfaces would be periodically exposed as pulses of sediment are driven through these regions by the prevailing currents.

2.4.3 Nutrient like behaviour of Cd

The behaviour of Cd warrants separate discussion on a shelf scale because unlike other trace metals it has distinctive nutrient like behaviour. This behaviour is apparent by the high concentrations of Cd with Al and Fe on the inner shelf, and high concentrations on the outer shelf (Figure 2.4 and 2.6). The distribution is similar to patterns of OC and P distribution (Figure 2.4).

Nutrient-like behaviour of Cd in oceanic waters is not unusual and the ratio of Cd/PO_4 has been shown to increase with depth in most oceans as a function of natural biogeochemical cycling (Boyle 1976; de Baar *et al.* 1994). Enhanced concentrations of Cd have been found in sediments that underlie oceanic zones of Cd rich up welling water (Everaats & Nieuwenhuize 1995; Rosenthal *et al.* 1995a). For example, high concentrations of Cd in sediments of the outer shelf and continental slope in water

depths of 100 to 1000m (Figure 2.6) are derived from Cd enriched waters that periodically up-well from the Coral Sea (Valente 1998).

Biogeochemical cycling of Cd in waters of the inner shelf has been documented in Jones *et al.* (1986) and Jones (1992), but there is no work to indicate that this process is a significant source of Cd to sediments of the lagoon. The poor fit of regression models to Cd concentrations (Table 2.6) indicates factors other than supply from a single terrigenous or biological source is influencing Cd concentrations on the inner shelf. Post-depositional processes have been found to affect the retention or accumulation of Cd in sediments (e.g., Zwolsman *et al.* 1996; Rosenthal *et al.* 1995b). The results of this study indicate that Cd in sediment concentrations are not controlled only by terrestrial or biogenic carbonate sediment supply.

2.4.4 Variation in sediment trace metal composition along-shelf on the inner shelf

Variation in sediment geochemical properties along-shelf on the inner shelf has been examined by 2 methods: 1) PCA of major element and trace metal concentrations in a subset of 264 sediment samples form the inner shelf. 2) PCA of the same subset of sediment samples, where the trace metal concentrations have been standardised.

PCA of major element and trace metal concentrations indicates the predominant influence upon variation in trace metal concentration along-shelf are changes in the proportion of terrigenous sediment relative to biogenic carbonate sediments. Trace metals are positively correlated with major elements that are representative of terrigenous sediment in component 1 (Table 2.5), which explains 40.1% of the variance in concentration. This distribution of samples along the axis of component 1 in Figure 2.7 indicates sediments from the south of the study region are more terrigenous and contain high concentrations of trace metals than sediments in the north.

Standardisation of trace metal concentrations attempts to remove effects of these natural variations in sediment composition. This allows trace metal concentrations in sediments of different composition to be compared equally. However, standardisation is a function of the independent variables used in the regression model. If a variable that

has a significant influence is not included in the model, or the relationship between the dependent and independent variables is not linear (constant), the standardised value will exhibit variation in response to this influence.

This effect has been exploited in statistical analysis by using regression models that do not include distance along-shelf, even though it is a significant influence upon Co, Cu and Ni concentrations (Table 2.6). In this manner the differences in sediment composition between regions can be more clearly observed. The variations in Co, Cu and Ni concentrations along-shelf are recognised in the PCA of standardised metal concentrations by the distinct clustering of samples from different geographic subsets along the axis of component 2 (Figure 2.9). This component accounts for 27.5% of the variance in standardised trace metal concentration.

The linear nature of this change with distance along-shelf (Figure 2.8) suggests that the variations are related to progressive dilution of Co, Cu and Ni rich sediment supplied from the Burdekin River that is transported northwards, and mixed with sediment residing within successive bays. This indicates that not only does the proportion of terrigenous to biogenic skeletal carbonate sediment change, but the trace metal composition of the terrigenous sediment also changes.

Component 2 of the PCA of major and trace metals, identifies samples from Cleveland Bay that are affected by anthropogenic influences (Figure 2.7). These samples have Cu, Pb and Zn concentrations that exceed the Draft ANZECC ISQG-low. However, the PCA of standardised trace metal values more clearly distinguishes samples in Cleveland Bay relative to samples from other regions in Figure 2.9. Some samples from Cleveland Bay have a distinct positive component 1 score, which is characterised by samples that are influenced by anthropogenic activities.

The effect of having more than one influence upon Cd concentration on the inner shelf is recognised within regression analysis by; 1) The low value of the adjusted R^2, and the high standard error of models used to standardise Cd values (Table 2.6). 2) The inclusion of Cd values in more than 1 component of the PCA of standardised metal concentration.

The plot of component 3 versus component 2 (Figure 2.9) of the PCA analysis of standardised trace metal values, clearly separates the samples from the south of the study area (e.g., Upstart Bay and Bowling Green Bay), from those in the north (e.g., Lucinda and Rockingham Bay). Samples from Cleveland Bay and Halifax Bay occur within both groups of samples, and a large group of samples from Cleveland Bay have a distinctly negative component 3 scores (Figure 2.9). These results indicate that the influences upon Cd concentrations are variable along-shelf. The source of Cd in the north of the study region is probably influenced more by biogenic carbonate sediments than in the south, which are influenced by predominantly terrigenous sediment sources.

2.5 Conclusions

The predominant influence upon the distribution of the elements Al, Fe, Cu, Co, Mn, Ni, Pb and Zn are the processes that determine the distribution of fine-grained terrigenous sediments. Fine grained terrigenous sediments are trapped on the inner shelf by the prevailing wind-wave driven hydrodynamic regime, with maximum accumulation in areas protected from wind-wave induced energy, such as the leeward side of geographic features.

The distribution of Ca, Cd, P, organic carbon (OC) and carbonate carbon (CC) are influenced by supply from marine biological processes. On the outer shelf, where source of sediment is predominantly marine in origin, sediments are enriched in these elements. However, on the inner shelf, OC, Cd and P are influenced by the their supply from both terrigenous and marine sources and high concentrations of OC, Cd and P occur in association with fine grained terrigenous sediment. Unlike other trace metals, Cd has a distinctive nutrient like behaviour.

On the inner shelf, variation in sediment geochemical composition along-shelf is characterised by a decline from south to north in the amount of terrigenous sediment relative to marine biogenic sediment. Changes in the composition of terrigenous sediment also occurs and is characterised by a decline in Co, Cu and Ni concentrations from south to north. This is interpreted to indicate that the sediment derived from the Burdekin River is enriched in Co, Cu, and Ni relative to sediment sources located to the north of its mouth.

Early diagenetic effects upon sediment geochemical composition are characterised by the loss of Fe, Mn and P in sediments that have very high OC and S concentrations as a consequence of sulfate reduction, and the enrichment of Mn in locations where sediments are exposed to high wave energy.

Standardisation of measured trace metal concentrations to regression predicted concentration removes the majority of natural variation in concentration. This assists the identification of anthropogenic influences upon trace metal concentrations. Anthropogenic influences are apparent by the enhancement of Cu, Pb, Zn, Ni and Co in samples from western Cleveland Bay.

Chapter 3

Natural and anthropogenic influences upon trace metal concentrations in sediments of Cleveland Bay

3.1 Introduction

In this chapter, statistical methods and their interpretation used in the previous chapter are extended and applied to surface sediment grab samples and ^{210}Pb dated sediment core samples from Cleveland Bay. Statistical models are used to: 1) identify temporal and spatial variations in enhancement of trace metals created by natural and anthropogenic influences, and 2) quantify the enhancement of Cd, Co, Cu, Ni, Pb and Zn concentrations from anthropogenic influences above a common background. The aim of this chapter is to quantify increases in trace metal concentrations due to anthropogenic activities in Cleveland Bay.

3.1.1 Study site

Physical environment

Cleveland Bay is a coastal embayment located in the central section of the Great Barrier Reef lagoon (Figure 1.1). The bay has a northerly aspect and an area of 440 km^2, including the intertidal zone (Figure 3.1). The climate is dry tropical with an average annual rainfall of 1150 mm, 85% of which falls between December and March (Belperio 1983). It is protected from effects of the prevailing southeast trade winds by Cape Cleveland (Carter *et al.* 1993).

The intertidal zone covers an area of 120 km^2 and includes tidal flats, tidal creeks, salt flats and mangrove swamps. It is formed upon an extensive coastal plain of Holocene sediments. The coastal plain sediments represent the accumulation of predominantly terrigenous sediment since approximately 3 ka before present, and resulting in the progradation of the Cleveland Bay shoreline to its present position (Carter *et al.* 1993).

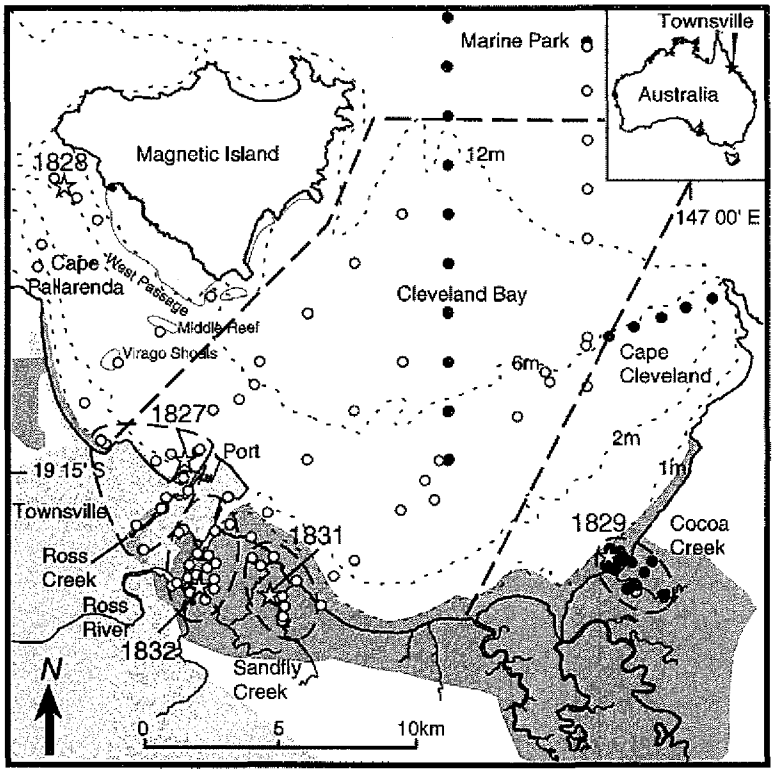


Figure 3.1 Location of sample sites and geographic subdivisions in Cleveland Bay: Urbanised areas (light shaded); intertidal zone (dark shaded); reef (light stippled areas in western bay); approximate boundary of Great Barrier Reef Marine Park (- - -); surface sediment grab sample (○); surface sediment grab used to generate regression models (model suite) (●); sediment core site (☆); depth contours (. . .).

The modern bay Holocene sediment is up to 6m thick in the eastern bay, thins both seaward and shoreward, and represents the accumulation of sediment since 6.5 ka before present, at a maximum average rate of 1 m/1 ka (Carter et al. 1993). The central region of the bay is characterised by a shallow (< 15 m deep) plain. Surface sediment consists of poorly sorted polymodal terrigenous muddy sand facies, which are composed of mud, sand and carbonate modes (Larcombe & Ridd 1994). This sediment is comprised of quartz (50%), feldspar (20%), clay minerals (20%) and carbonate (10%) (Ward et al. 1995). The carbonate content is predominantly molluscan (McIntyre 1996). The formation of this polymodal sediment was attributed to the mixing of successive layers of fine grained and coarse grained sediments by bioturbation (Larcombe & Ridd 1994). Coral reefs occur in the western bay between Magnetic Island (granitic) and the mainland as well as flanking Magnetic Island.

In Cleveland Bay, wave energy is the most significant influence upon sediment transport and sediment facies distribution. Wave energy, generated outside of the bay by south-easterly trade winds, and propagated into the bay, is the principle mechanism for suspension and transport of fine-grained sediments (Lou & Ridd 1996). Once suspended, sediment is available for redistribution by the prevailing currents. A counter clockwise residual tidal circulation of the bay was determined by Carter *et al.* (1993), who postulated that long-term maximum accumulation of sediment has occurred on the eastern side of the bay in areas protected from wave energy. However, Belperio (1978) concluded that at wind speeds greater than 15 knots, which would also coincide with the swell events responsible for suspension of sediment, results in the entire water column moving in a north west direction, and transport of sediment to the north west.

Supply of terrigenous sediment to the bay is from two sources: 1) Periodic flood related discharges by local estuaries (Carter *et al.* 1993; MacIntyre 1996); 2) Sediment that is advected along the coast under the prevailing hydrodynamic regime (Belperio 1983; Orpin *et al.* 1999). The amount of sediment supplied by estuaries directly into the bay is estimated by Belperio (1978) to historically have been 0.3 Mt a^{-1}, but since damming of the Ross River during the 1970s the total load is estimated to be less than 0.1 Mt a^{-1}. Orpin & Ridd (1996) estimate the amount of sediment supplied to the bay by advection to be in the order of 0.3Mt. Recent work by Orpin & Woolfe (1999) and Larcombe & Woolfe (1999b) indicate that the central bay (subtidal) acts more as a zone of sediment transfer than a zone of sediment accumulation. The poorly sorted polymodal central bay facies is postulated as a source of sediment to more well sorted facies in other regions of the bay, such as the intertidal zone.

Geography

The city of Townsville (population 130 000) is situated on the western side of Cleveland Bay (Figure 3.1). Since settlement in 1864 the city and surrounding region has experienced continuous economic and population growth (section 1.2). Changes over time to the population of Townsville and the total tonnes of cargo transhipped by the port (Port throughput) are presented in Figure 3.2, along with other events relevant to this chapter.

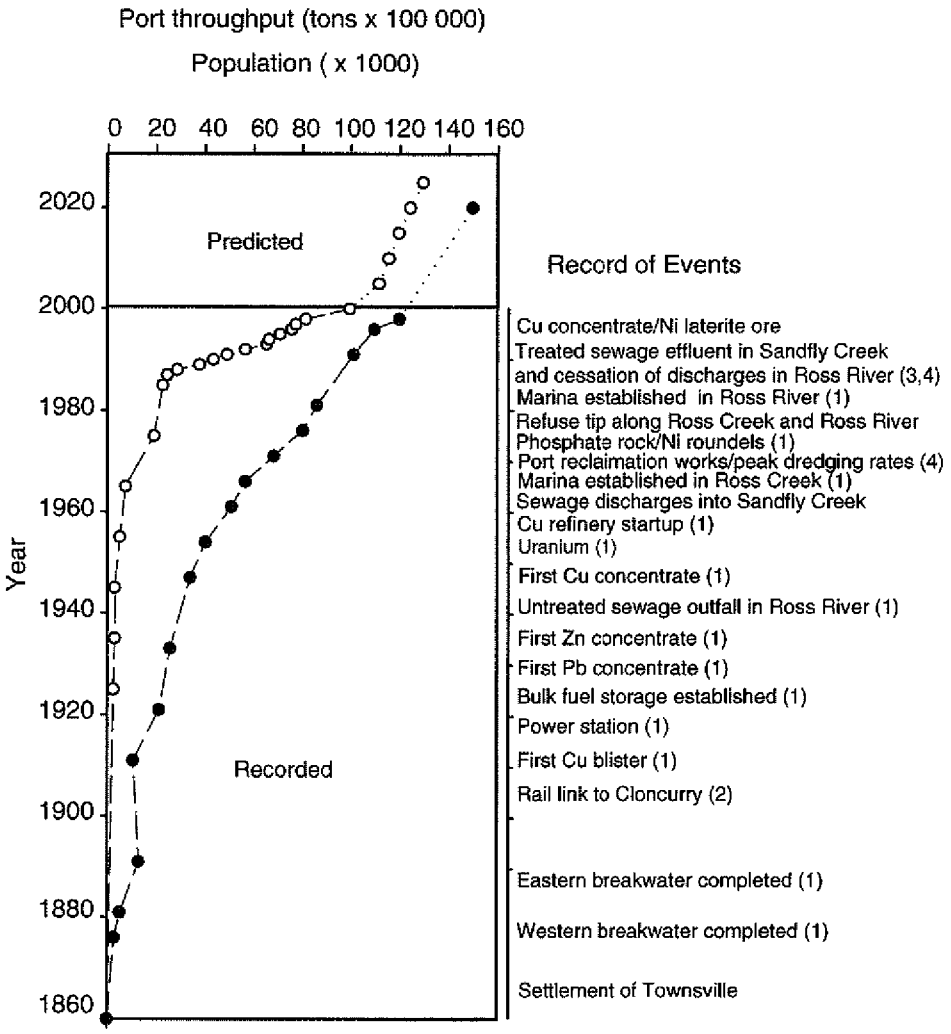


Figure 3.2 Summary of population growth, Port throughput and significant events in the Townsville region that could be recorded in the sedimentary record. Total Port throughput (O) is the total tonnes of cargo transhipped per year; Townsville population (●) data sourced from TTSP (2000), TPA (1996; 1998, 1999), TMI(1999), SKM (2000), Australian Bureau of Statistics census data, Queensland Government Statistician (1998). Events sourced from 1) Taylor, 1980, 2)Hoyle 1979; 3) Jones 1992; 4) Pringle 1989.

Previous investigations of sediment trace metal concentrations have identified increases in weak acid soluble trace metal concentrations in western Cleveland Bay, with maximum concentrations occurring in Ross Creek (Gibbs 1993; Reichelt & Jones 1994; Esselmont 1997). Changes in benthic community structure in Ross Creek relative to local control sites are positively correlated with trace metal and hydrocarbon concentrations (Inglis & Kross 1999).

In contrast to the western bay, the eastern side of the bay is situated within Bowling Green Bay National Park, and has been exposed to relatively little human development. However, dredge spoil from the western bay, removed to maintain shipping access to the port, has been dumped seaward at several locations in the bay (see Pringle 1989) and has been found to be redistributed into the eastern bay (Pringle 1989; Carter *et al.* 1993). Peak historical dredging rates of over 1 Mt a^{-1} occurred during the 1970s associated with development works to establish a shipping channel to the Port of Townsville, located at the mouth of Ross Creek. The bulk of this dredged sediment was buried below 1 m and would probably have been deposited prior settlement of Townsville. Therefore, the sediment disposed of during the peak rates of dredging is unlikely to contain metals derived from anthropogenic activities.

3.2 Methods

3.2.1 Surface sediment grab samples

Surface sediment grab samples (112) were collected periodically between late 1997 and early 1999. The 112 samples are part of the sample suite described in Chapter 2 from Cleveland Bay. Sampling and analytical methods are described in section 2.2.2.1. Sample locations and analytical results are presented in Appendix 1.

3.2.2 Sediment core samples

3.2.2.1 Sampling

Sediment cores were collected between August and December 1998 from R.V. The Harry Messel and small support craft. The sites chosen were intended to represent

sites that had rapidly accumulated fine-grained terrigenous sediments. These sites were determined by interpretation of changes in landforms and stream channel patterns identified by the comparison of historical and recent aerial photographs and topographic maps.

A clear 150 mm diameter polycarbonate tube gravity corer, fitted with a core catcher and topped by a 300 kg lead driving weight was used to collect cores 1827 and 1828 from R.V. The Harry Messel. A modified version of the corer was used, without the driving weight, to manually drive cores 1829, 1831 and1832 at intertidal sites.

Sediment was extruded from the top of the core tubes by a hydraulically driven piston, which was inserted into the base of the tube when the core catcher was removed. This method facilitates minimal disturbance of sediment at the sediment water interface and prevents the loss of water and sediment from the core during slicing.

The cores were cut into slices at accurate 2 cm intervals to 20 cm core depth. Between 20 cm and 60 cm depth sample slice thickness was increased to 4 cm, and either 4 or 8 cm intervals where below 60 cm depth. Slicing tools were stainless steel and plastic, and were scrubbed and washed in clean salt water between slices.

Cores were dissected within 24 hours of collection. A 50 mL and a 20 mL subsample of sediment was collected for analytical purposes, and were placed in clean plastic or glass containers. Sediment core chemistry described in this chapter was determined from the 20 mL subsample, while the 50 mL subsample was held for pore water and AVS determinations. The remaining sample (> 250 mL) was placed in plastic bags for radiochemical measurements.

3.2.2.2 Strong acid digestion and analysis

Sediment core samples have been subjected to the same preparation and analytical procedures as surface sediment grab samples. These methods are described in section 2.2.2.1. The analytical results are presented in Appendix 5.

3.2.2.3 Radiochemical analysis

Gamma spectrometric measurements of ^{210}Pb, ^{226}Ra, ^{137}Cs and ^{234}Th were undertaken at the Australian Institute of Marine Science. Samples were dried at 70°C in a fan forced oven, before being ground and mixed in a LM1 laboratory disk mill for 2 minutes. Between 50-150 grams of sediment was pressed under 1 tonne of weight, using a hydraulic ram, into gas-tight plastic containers.

Counts of ^{234}Th were completed within 2 weeks of sampling. After storage for 3-4 weeks, radon daughter in-growth allows direct estimation of ^{210}Pb and ^{226}Ra from gamma emissions (e.g., Robbins & Edginton 1975). Excess ^{210}Pb was estimated by subtraction of ^{226}Ra from total ^{210}Pb activity. Analytical results are presented in Appendix 6.

Planar germanium detectors and a well germanium detector were used inside 10 cm thick walled lead castles with steel liners. The energy spectra of gamma spectrometers were calibrated with Amersham and CANMET standards of known low activity added to cleaned silica sand of geometry and mass similar to the sediment samples. Counting errors of these sample measurements were less than 10%.

Based upon terrestrial soil profiles and rainfall collections, the atmospheric supply rates of ^{210}Pb and ^{137}Cs in North East Queensland are estimated to be 50 Bq ^{210}Pb m^{-2} y^{-1} and 400 Bq ^{137}Cs m^{-2} (Brunskill & Pfitzner 1999). These measurements have been used to calculate focussing factors of ^{210}Pb and ^{137}Cs by Equation 3.1. When the focussing factor > 1, this indicates accumulation of these particle bound tracers at rates greater than atmospheric supply. This is interpreted to represent the accumulation of particle bound isotopes from other locations, or focussing and trapping of sediment supplied from other areas that are characterised by erosion.

$$Focussing\ factor = \frac{Measured\ flux\ or\ inventory}{Atmospheric\ flux\ or\ inventory} \qquad \text{(Equation 3.1)}$$

3.2.3 Statistics

3.2.4.1 Data transformations

Transformation of geochemical variables was required to satisfy the assumptions of normality and ensure constant variance. Transformations were selected by scrutiny of normal probability plots to determine which transformation more closely resulted in normally distributed data and constant variance. Concentrations of elements that were below the method detection limit were attributed a value of half the detection limit. Similar approaches to data transformation were adopted by Summers *et al.* (1996) and Cocker (1999).

3.2.4.2 Standardisation of trace metal concentrations

Similar to chapter 2, trace metal concentrations are standardised in this chapter by dividing the measured concentration by a concentration predicted by a stepwise regression model. Standardisation is done to: 1) Remove the effects of natural variation in sediment composition between samples, so that anthropogenic influences can be more easily recognised. 2) Remove scaling effects created by different ranges in absolute concentrations between trace metals (e.g., Cd in pmol g^{-1} and Zn in μmol g^{-1}). Ideally standardisation allows the equal comparison of trace metal concentrations between sites of different sediment composition and between metals.

The suite of samples used to generate regression models (model suite) of the natural variation in trace metal concentrations are sediment cores slices and surface sediment grab samples collected from Cocoa Creek and subtidal samples from eastern Cleveland Bay (Figure 3.1). Samples from eastern Cleveland Bay were chosen because that side of the bay is flanked by Bowling Green Bay National Park, and because hydrodynamic models predict a predominantly north west direction of transport for terrigenous sediment discharged into the western side of the bay (e.g., Pringle 1989; Lou & Ridd 1996). Therefore these samples are probably less affected by anthropogenic activities than samples from the western bay.

Using the model suite samples, full stepwise regression models for Cd, Co, Cu, Ni, Pb and Zn were generated using Al, Ca, CC, Fe, Mn, OC and S as independent variables. The full stepwise regression method has been described in section 2.2.5.2. A predicted trace metal concentration was calculated for all samples by substituting the major element parameters into the regression model. Measured trace metal concentrations were then standardised by dividing by the value of the upper 95% prediction level of the regression model generated for the model suite of samples (Equation 3.2).

$$Enhancement = \frac{Measured\ concentration}{Model\ suite\ upper\ 95\%\ prediction\ level} \qquad \text{(Equation 3.2)}$$

This ratio is referred to as enhancement. Enhancement > 1 represents an increase in metal concentration above a limit tolerated by the model suite. It should be noted that this is distinct from the standardised metal value described in the previous chapter, where measured values were divided by the predicted concentration (Equation 2.2).

3.2.4.3 Multivariate analysis

Specific influences, such as point source discharges from industries or natural changes in source of sediment, can have a characteristic multielement signature (e.g., Krumgalz 1993; Negrel 1997; Shin & Fong 1999). The multielement signature may be characteristic of a source, e.g., Zn and Cd from zinc concentrates or Ni and Co from Ni laterite ore.

PCA is used here to examine the data for such multielement signatures. This has been done by using the value of enhancement for each trace metal, calculated by Equation 3.2, as the independent variables in PCA. The PCA method has been described in section 2.2.5.1. Plots of one component score versus another component score are used to identify grouping of samples. The grouping of samples represents samples that have a similar combination of trace metal enhancement values. The spatial distribution of samples from the same group, their trace metal signature and their relationships with other parameters, have been used to identify the source the influence.

The difference between samples in different groups has been quantified using linear discriminant analysis methods, as described by Vandeginste *et al.* (1998). Linear discriminant analysis uses the component scores calculated by PCA as independent variables and the geographic location of samples (see Figure 3.1) as categorical variables (e.g., Emmerson *et al.* 1997; Calvert *et al.* 1993).

Samples were subdivided into 2 categories; category 1 samples belonging to the Cocoa Creek suite of samples, which should be not be affected by increases in trace metals derived from anthropogenic sources; and, category 2 being all other samples. The probability of each sample belonging to category 1 and category 2 was then calculated based upon the PCA component scores. For a description of this method Vandeginste *et al.* (1998) should be consulted. The cumulative frequency distribution of the probability of group membership was used to select threshold probabilities that determine group membership (Figure 3.11).

3.2.4 Models of sediment mass accumulation rate and sediment mixing

The sediment dry Mass Accumulation Rate (MAR), and the depth of sediment mixing, was calculated using a combination of radiochemical, solid phase sediment chemistry and historical aerial photographic and mapping controls. This approach was adopted to provide a robust and consistent method of determining maximum age dates of recently accumulated sediments (e.g., Hancock 2000; Edgington *et al.* 2000).

Where appropriate, models of excess ^{210}Pb were used to calculate MAR (Robbins & Edgington 1975; Robbins 1986) and the distribution of ^{234}Th was used to identify depth of short term particle mixing. These are naturally occurring isotopes of the ^{238}U series with half-lives of 22.3 years and 24.2 days respectively (Weast 1977). The isotope ^{137}Cs is also used as a sedimentation and sediment mixing tracer and is supplied as a consequence of atmospheric nuclear bomb testing during 1950-80 and has a half-life of 30.7 years (Weast 1977). The presence of ^{137}Cs indicates sediments have been deposited post 1950. These isotopes are strongly bound to soil and aquatic sediment particles and they provide a known time dependant tracer to evaluate short-term sedimentation processes (Nittrouer *et al.* 1984).

The critical assumptions of radiochemical models of mass accumulation rate using excess ^{210}Pb decay profiles are; 1) the flux of the isotope to the sediment water interface is known; 2) the decadal average rate of sediment accumulation is constant; and 3) the surface sediment mixed layer thickness is constant over deposition time frames of 4 half lives of ^{210}Pb (about a century).

Where radiochemical data was not appropriate to estimate MAR, a maximum age of deposition of sediment in the base of the core, and a probable age of sediment deposition of sediment in the base of the core have been used to indicate the most likely interval of time when sediment was deposited.

When excess ^{210}Pb profiles were unsuitable to generate MAR, a maximum age of deposition was determined using recorded events. These events place constraints upon the maximum age when sediments may have been deposited. The events are recorded in historical aerial photography and maps and include stream capture processes resulting in ox bow lakes and construction of breakwaters. The presence of ^{137}Cs in sediments can also be used because it occurs only in sediments that are deposited after nuclear bomb testing commenced (1955). The maximum age of deposition provides a minimum MAR.

However, sediment may have been deposited at any stage after the maximum age of deposition up to the time of sampling. Therefore a probable age of deposition is also used to calculate a second maximum likely MAR. The probable age is the best estimate of sediment in the base of the core, given that it was deposited at some stage after the maximum age. MAR was calculated using both the maximum age of deposition and probable age of deposition, assuming constant flux of sediment, and constant mixed layer thickness.

Mixed layer thickness was interpreted from a combination of radiochemical data, whole sediment chemistry, pore water concentration profiles and logging of cores. These methods can identify near surface homogeneity of sediment parameters due to sediment mixing, or alternatively heterogeneity and layers of discrete chemical composition that indicate mixing. The average age of sediment contained in the mixed

layer was estimated using a box model that assumed homogenous mixing of sediment and the average porosity of the mixed layer (e.g., Berner 1980).

3.3 Results

3.3.1 Spatial distribution of element concentrations in surface sediments

In Figures 3.4 and 3.5 the spatial distributions of Al, Co, Cu, Fe, Mn, OC, P, Pb and Zn concentrations are similar. Based on the results of Chapter 2, this represents the distribution of fine-grained terrigenous aluminosilicate sediments. Average concentrations of each element, for each geographic region and sediment cores, are presented as Table 3.1 and 3.2.

The central facies of the bay (3-15 m water depth) is characterised by lower Al, Co, Cu, Fe, Mn, OC, P, Pb and Zn concentrations and higher Ca and CC concentrations compared to more shoreward sample locations. Maximum concentrations of Ca and CC occur in the western bay adjacent to coral reefs, and in the east of the bay in the lee of Cape Cleveland, within a sedimentary facies rich in mollusc shell fragments (Figure 3.4). The facies leeward of Cape Cleveland also has anomalously high Mn and Co concentrations relative to other locations in the bay (Figure 3.4).

In general, high concentrations of elements associated with terrigenous sediment occur shoreward, within the intertidal zone. However, maximum Al and Ni concentrations occur within an isolated muddy facies situated in West Passage (Figure 3.4 and 3.5). This muddy facies has Ni concentrations that exceed the Draft Australia and New Zealand Environment and Conservation Council (ANZECC) interim sediment quality value (ISQV)-low threshold value (Table 3.2).

Maximum concentrations of Cu, Pb, Zn and Cd occur within Ross Creek. In Ross Creek, the average concentration of Cu, Pb and Zn exceed the Draft ANZECC ISQV-low (Table 3.2) and are influenced by anthropogenic sources of metals (e.g., Gibbs 1993).

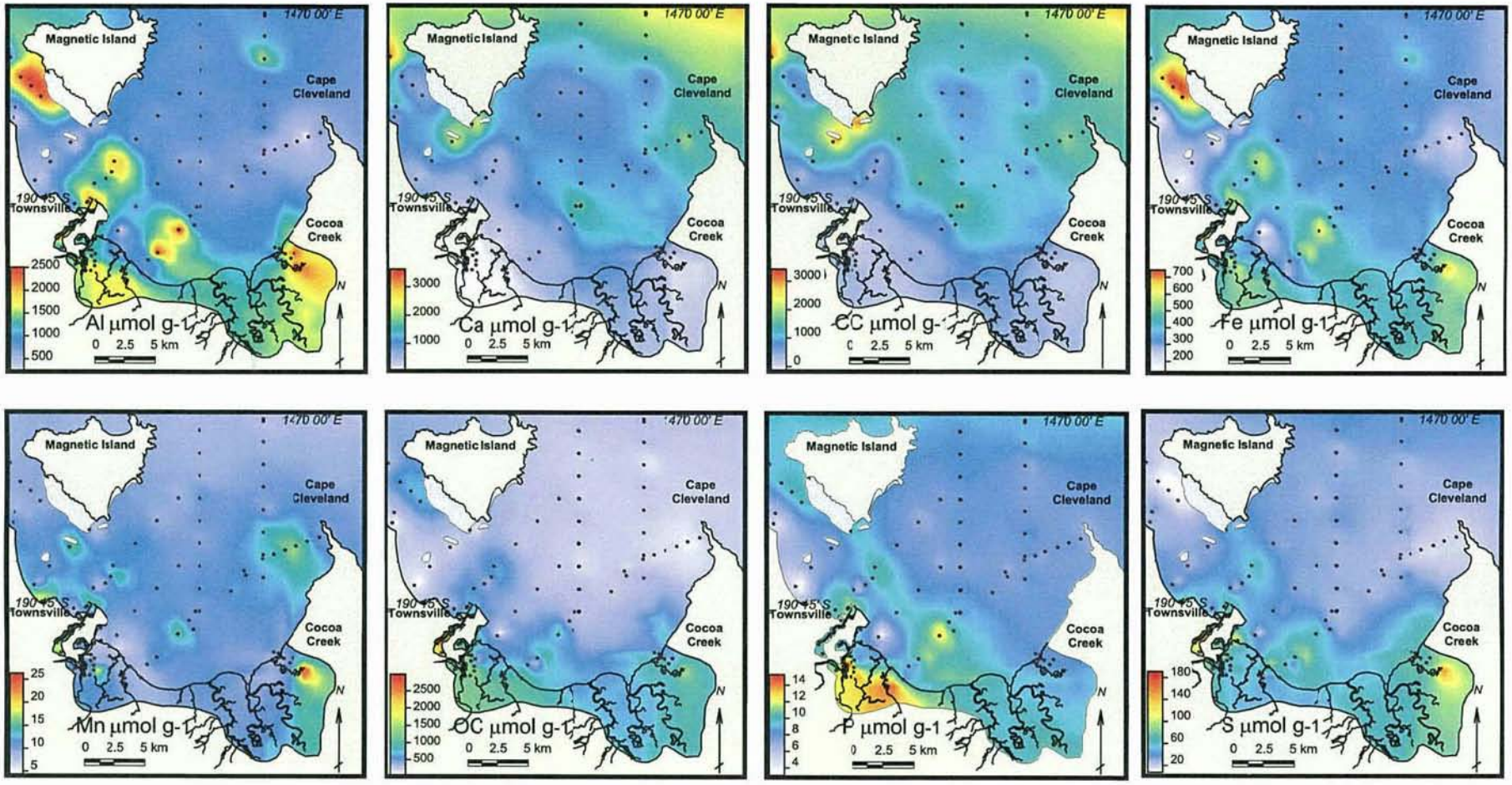


Figure 3.3 Images of Al, Ca, CC, Fe, Mn, OC, P and S concentration in surface sediments of Cleveland Bay. CC (carbonate carbon); OC (organic carbon); grab sample (●).

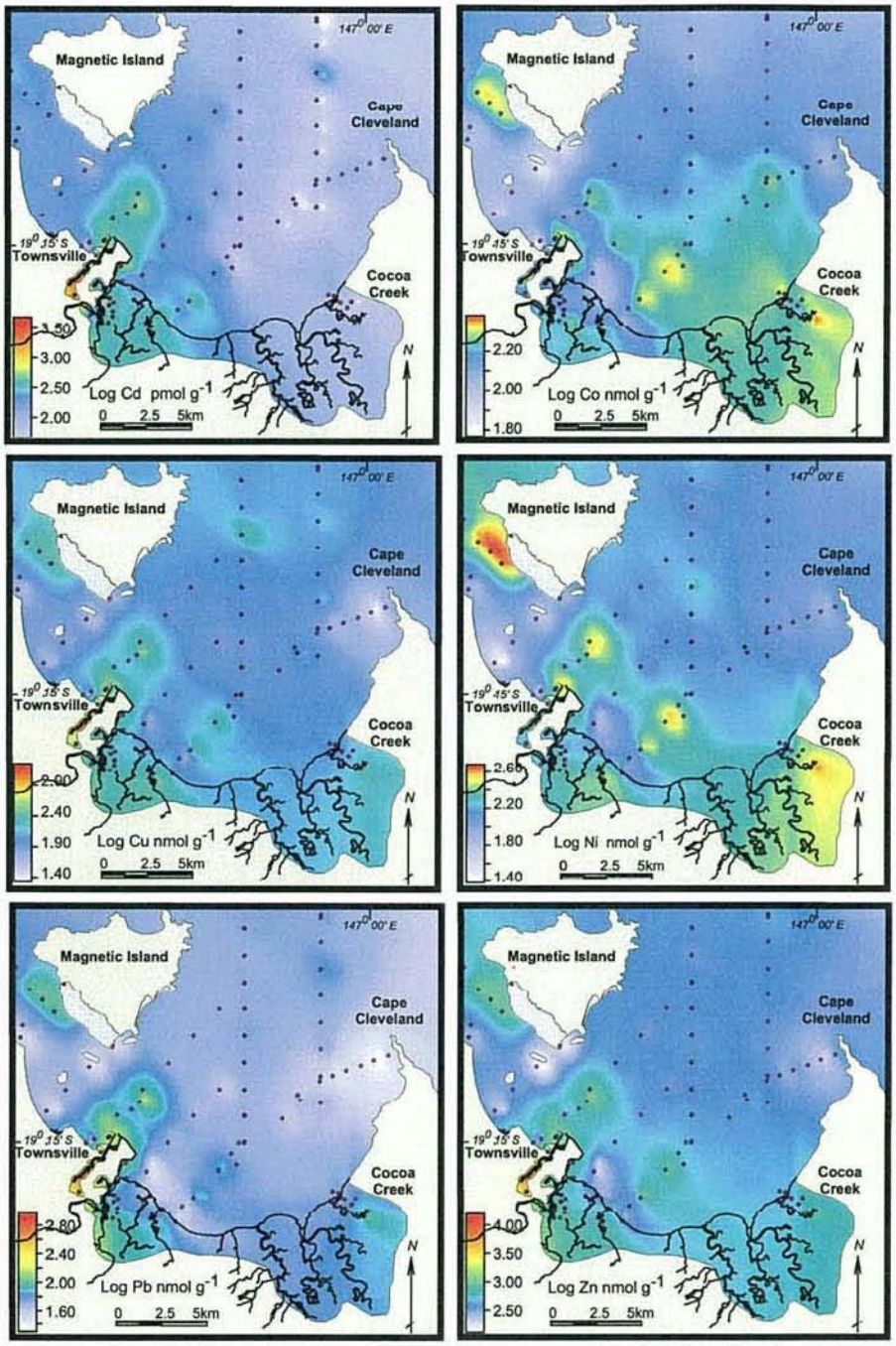


Figure 3.4 Images of log transformed concentrations of Cd, Co, Cu, Ni, Pb and Zn in surface sediments of Cleveland Bay. Grab sample (●).

Table 3.1 Comparison of average major element concentrations of geographic subsets in Cleveland Bay. Location of subsets are shown in Figure 3.1. Calcium carbonate (CC); organic carbon (OC); all samples in μmol g^{-1}, (mean ± standard deviation)

	Al	Ca	CC	Fe	Mn	OC	S
Cleveland Bay (n = 43)	782 ± 133	1419 ± 731	903 ± 742	312 ± 25	9 ± 1	208 ± 42	31 ± 6
Core 1828 (n = 24)	2158 ± 823	879 ± 518	982 ± 578	597 ± 214	8 ± 2	660 ± 170	124 ± 27
Cocoa Creek (n = 16)	1479 ± 641	440 ± 726	278 ± 525	437 ± 138	11 ± 7	908 ± 583	87 ± 34
Core 1829 (n = 25)	1132 ± 477	452 ± 102	365 ± 116	395 ± 107	13 ± 2	473 ± 332	104 ± 96
Sandfly Creek (n = 16)	1168 ± 537	236 ± 181	159 ± 134	362 ± 132	8 ± 3	799 ± 308	56 ± 28
Core 1831 (n = 18)	1560 ± 207	126 ± 32	26 ± 84	528 ± 57	5 ± 1	1525 ± 393	268 ± 86
Ross River (n = 29)	1379 ± 382	107 ± 87	104 ± 229	421 ± 107	9 ± 5	833 ± 491	66 ± 28
Core 1832 (n = 30)	1803 ± 349	121 ± 24	72 ± 108	600 ± 89	6 ± 1	1132 ± 186	175 ± 75
Townsville (n = 13)	1686 ± 752	336 ± 299	289 ± 318	512 ± 201	16 ± 11	1415 ± 1157	90 ± 56
Core 1827 (n = 27)	1676 ± 362	452 ± 92	372 ± 138	509 ± 93	11 ± 3	501 ± 170	82 ± 36

Table 3.2 Comparison of average trace metal concentration from geographic subsets in Cleveland Bay. Draft ANZECC ISQV-low and ISQV-high are the ANZECC (1999) trigger levels to initiate additional work within the tiered sediment quality assessment strategy. Values are in nmol g^{-1}, except Cd in pmol g^{-1} (mean)

	Cd	Co	Cu	Ni	Pb	Zn
Cleveland Bay (n = 43)	178 ± 44	146 ± 20	93 ± 17	155 ± 53	44 ± 5	361 ± 37
Core 1828 (n=24)	228 ± 52	205 ± 56	266 ± 97	369 ± 128	91 ± 33	963 ± 339
Cocoa Creek (n = 16)	80 ± 36	183 ± 36	156 ± 65	278 ± 90	67 ± 17	577 ± 165
Core 1829 (n=25)	124 ± 38	179 ± 25	132 ± 61	205 ± 76	54 ± 17	599 ± 159
Sandfly Creek (n = 16)	356 ± 107	141 ± 32	195 ± 99	196 ± 83	59 ± 23	532 ± 220
Core 1831 (n=18)	414 ± 54	225 ± 22	354 ± 41	288 ± 27	77 ± 6	873 ± 83
Ross River (n = 29)	383 ± 133	158 ± 29	206 ± 55	204 ± 55	84 ± 26	702 ± 182
Core 1832 (n=30)	374 ± 128	200 ± 19	284 ± 42	265 ± 41	91 ± 12	1040 ± 141
Townsville (n = 13)	1957 ± 2562	182 ± 61	1280 ± 1574	296 ± 133	507 ± 483	5660 ± 6578
Core 1827 (n=27)	327 ± 98	204 ± 18	297 ± 145	276 ± 74	108 ± 25	1145 ± 338
ANZECC ISQV-low	13345	not	1023	358	241	3059
ANZECC ISQV-high	88730	applicable	4249	886	1062	6272

3.3.2 Physical and chemical description of sediment cores

Five sediment cores have been collected, 1827, 1828, 1829, 1831 and 1832 (Figure 3.1). The analytical results of sediment samples from these cores are combined with those from surface sediment grab samples during statistical analysis in this Chapter 3 and are the focus of work in subsequent Chapters.

The core sites were chosen because the sites were identified as likely sites of high mass accumulation rates of fine-grained terrigenous sediments. This was determined from aerial photograph interpretation, review of historical records and review of sedimentological and hydrodynamic studies in the bay (Belperio 1978; Pringle 1989; Carter *et al.* 1993; Lou & Ridd 1996).

3.3.2.1 Core 1827

Core 1827 was collected from the leeward side of the western Port breakwater at 19° 14`11``S / 146° 49`40``E in 3 m of water (Figure 3.1). This north-south running breakwater was built between 1865 and 1890 (Taylor 1980) and an east-west running extension was built at the seaward end during the early 1980s. The region in the lee of the breakwater has formed an environment protected from wave energy and currents and has acted as a trap for fine-grained terrigenous sediments.

The core was 110 cm long, and comprised a fining upward sequence of terrigenous sand and mud. The core catcher contained a coarse grained subrounded sand that included quartz, feldspar and lithic grains with lesser mollusc fragments and could not be penetrated (Figure 3.5).

The surface 10 cm contained traces of sea grass root stems and laminated grey brown and black soft mud. The increase in Al and trace metal concentrations and decrease in Ca and CC concentrations towards surface reflect the progressive increase in terrigenous and simultaneous decline in biogenic carbonate sediment components towards surface (Figure 3.6).

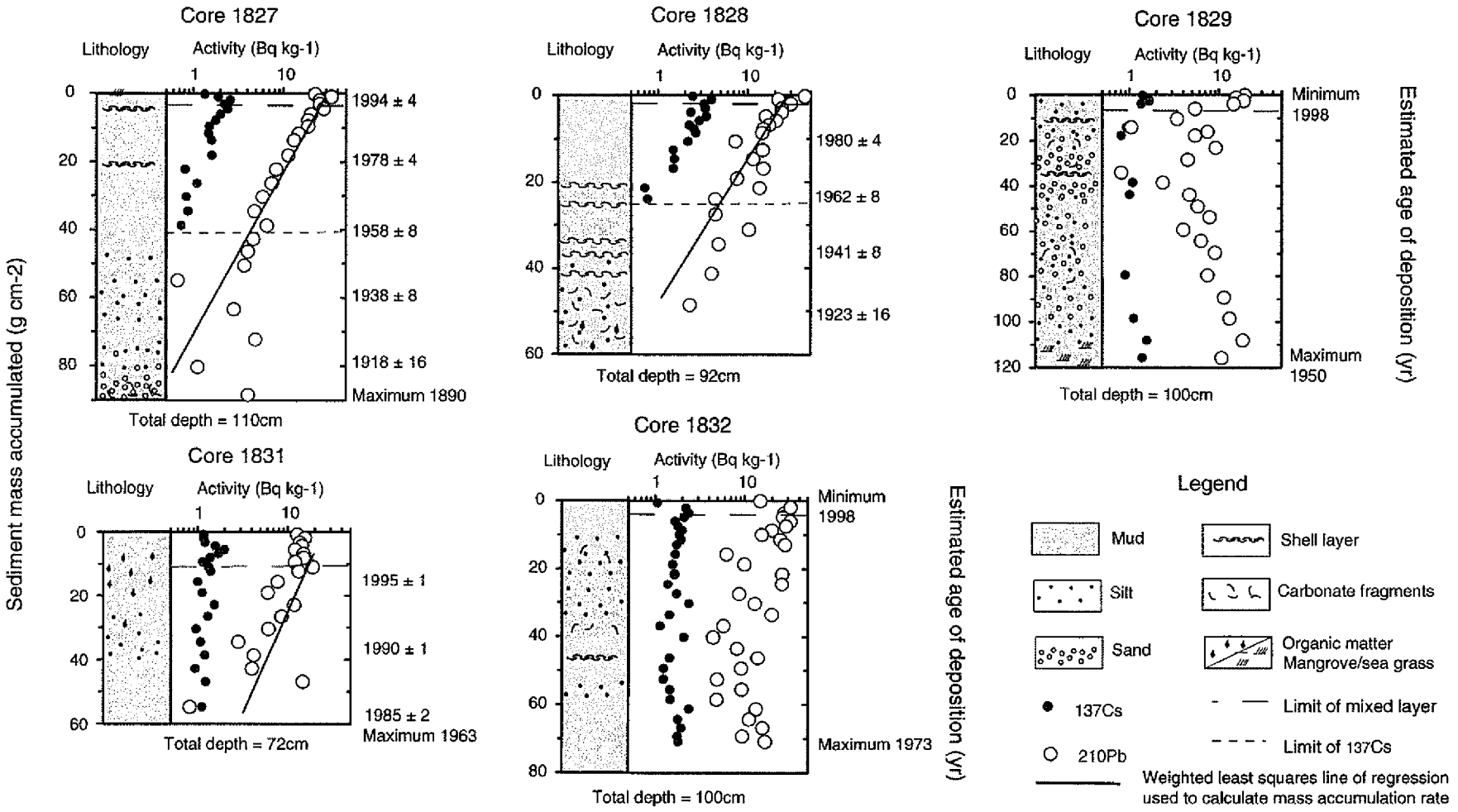


Figure 3.5 Sediment core lithological and radiochemical profiles. The length of each profile is proportional to the core depth.

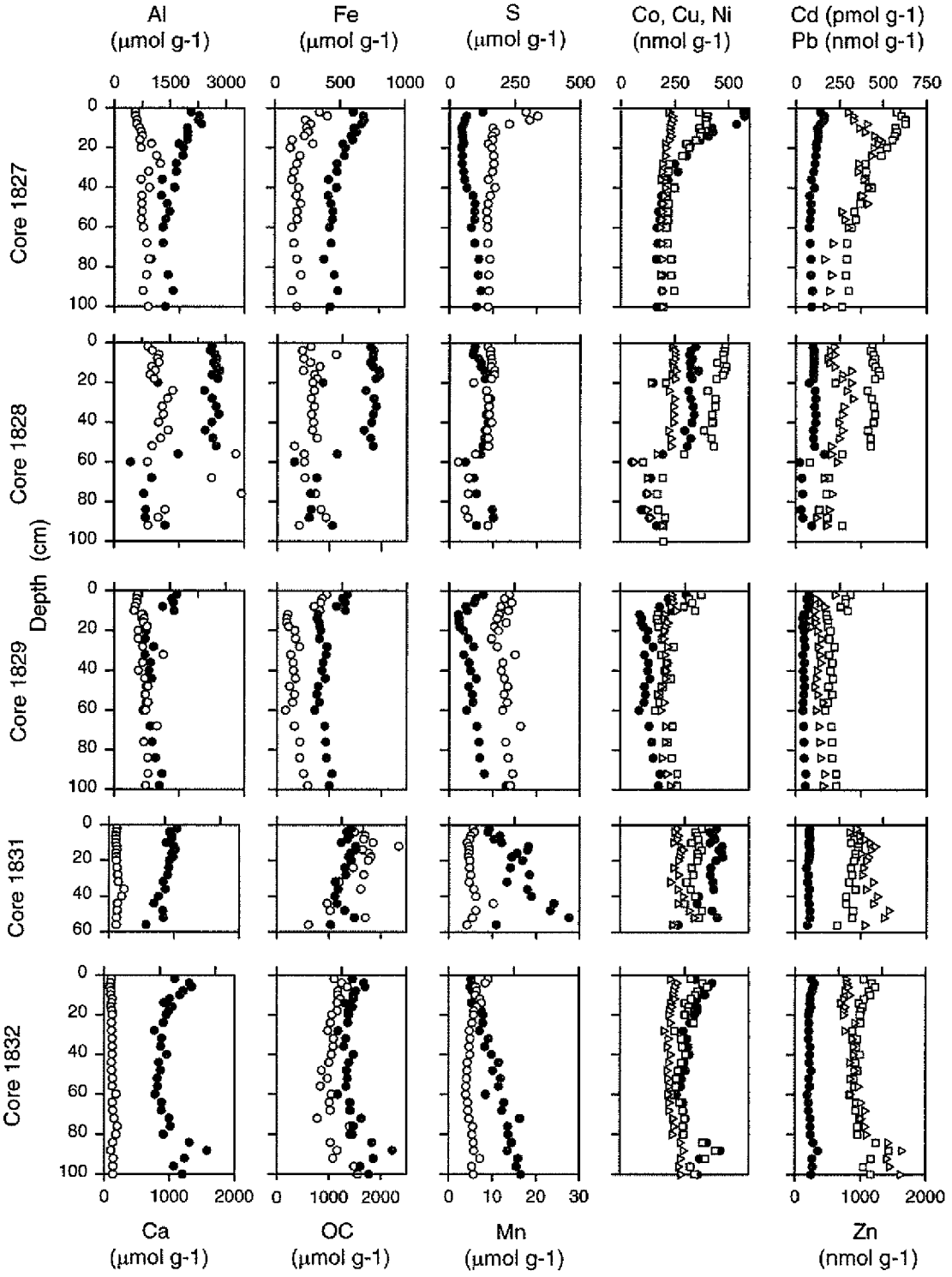


Figure 3.6 Sediment core profiles of major element and trace metal concentrations. Al (●); Ca (○); Cd (Δ); Co (Δ); Cu (●); Fe (●); Mn (○); Ni (□); OC (○); Pb (●); S (●); Zn (□).

Table 3.3 Summary of sediment core Mass Accumulation Rates (MAR) and average age of the Mixed Layer (MLA). The minimum time is the earliest possible age for sediments at the base of the core to have been deposited and is used to calculate minimum MAR and MLA for cores 1829, 1831 and 1832. The probable time of deposition is the most likely time of deposition of sediment in the base of these cores given the available data. The focussing factor is the ratio of the atmospheric supply of the isotope to that measured.

Core	Depth of ^{234}Th (m)	Mixed layer depth (m)	Minimum time of deposition (yr)	Minimum MAR (kg m^{-2} y^{-1})	Minimum MLA (y)	Probable time of deposition (yr)	Probable MAR (kg $m^{-2}y^{-1}$)	Probable MLA (y)	Excess ^{210}Pb flux (Bq m^{-2} y^{-1})	^{210}Pb Focussing factor	^{137}Cs inventory (Bq m^{-2})	^{137}Cs Focussing factor	Controls to MAR
1827	0.02	0.06	1900 ± 16##	10	5.4	1890##	10	3.8	186 ± 94	3.7	476 ± 149	1.2	^{210}Pb, ^{137}Cs, historical records
1828	0.02	0.06	1923 ± 24##	7.8	5	1923##	7.8	5	124 ± 50	2.5	347 ± 74	0.9	^{210}Pb, ^{137}Cs
1829	0.02	0.08	1950**	> 25	< 3	1975#	48	1.0	282 ± 83	5.6	190 ± 84*	> 0.5	^{137}Cs, aerial photographs
1831	0.02	0.10	1965**	> 35	< 7	1985##	47	1.3	136 ± 50	2.7	658 ± 215*	> 1.6	^{210}Pb, ^{137}Cs, aerial photographs
1832	0.02	0.06	1975**	> 28	3.2	1985#	53	0.7	275 ± 80	5.5	1019 ± 260*	> 2.5	^{137}Cs, aerial photographs

* incomplete inventory because limit of ^{137}Cs was not sampled; ** Based upon aerial photographic records; # average core deposition age; ## time based on excess ^{210}Pb.

Activities of excess ^{210}Pb demonstrate a decline from surface (Figure 3.5). Models of the decay of excess ^{210}Pb indicate that the base of the measured ^{137}Cs corresponds to a time of deposition of approximately 1950, supporting the application of this model to infer rates of sediment accumulation. Sediment at the base of the core has a ^{210}Pb estimated time of deposition of 1900 ± 16, which corresponds to the construction period of the breakwater (1870-1890). Depth of sediment mixing was interpreted from ^{210}Pb and ^{137}Cs activities to be less than 6 cm, and was supported by the lack of ^{234}Th below the surface slice. The focussing factor of the flux of ^{210}Pb, and inventory of ^{137}Cs, are greater than 1 (Table 3.3). This indicates accumulation of ^{210}Pb and ^{137}Cs radio labelled sediments from adjacent sites of sediment erosion. Combined, these data indicate the core site to represent the site of accumulation of fine-grained sediment since 1890 (Table 3.3).

3.3.2.2 Core 1828

Core 1828 was collected from a fine-grained terrigenous facies between Cape Palleranda and West Point at 19°09`25``S / 146°46`49``E in 8 m of water (Figure 3.1). The site is situated such that it is protected from the effects of wave energy and tidal currents (see Pringle 1989) and results in trapping of fine-grained terrigenous sediments.

The core was 92 cm long and bottomed in a coarse grained muddy sand, which was rich in large shell fragments and woody material up to 8 cm in diameter (Figure 3.5). Between 50 to 60 cm depth, the coarse-grained carbonate rich interval graded rapidly to a fine-grained, green-grey, muddy silt interval, which persisted to surface. This interval contained occasional silt and shell hash (< 1 cm diameter) layers. The change in sediment composition at 60 cm is reflected by the rapid change in Al, trace metal and CC concentrations at that depth (Figure 3.6). Above 60 cm depth are sediments that contain Al concentrations that exceed all other sediment core and surface sediment grab samples collected in the bay (Table 3.1).

Activities of excess ^{210}Pb exhibit a continuous decline from near surface to the bottom of the core, despite traversing a major change in sediment composition. The base of the measured ^{137}Cs corresponds to a ^{210}Pb estimated age of approximately 1950, supporting the application of this model to infer rates of sediment accumulation. The

profiles of ^{210}Pb and ^{137}Cs activities, and the absence of ^{234}Th below 0-2 cm depth, indicate depth of sediment mixing is less than 6 cm. The focussing factor of the flux of ^{210}Pb is greater than 1, but the inventory of ^{137}Cs is near 1 (Table 3.3). Combined, the radiochemical data are interpreted to indicate sediment accumulation from 1900 to present (Table 3.2).

3.3.2.3 Core 1829

Core 1829 was collected from the inside of a meander bend formed at the mouth of Cocoa Creek at 19°16`56``S / 146°38`37``E (Figure 3.1). The core was collected on an incoming tide in 30 cm of water. The channel at the mouth of Cocoa Creek is 30 m wide and cuts across a 500 m wide intertidal flat, which is exposed at low to mid tide. Aerial photographs indicate that the channel has maintained its current path since at least 1940.

The core was 100 cm long and bottomed at the limit of the core device, in a soft muddy organic rich interval. Above this horizon, the core contained grey-green interbedded silt and sand layers, which contained frequent shell hash bands and minor muddy intervals (Figure 3.5). Mud rich silts overlay coarser grained silts and sands surface to 8 cm depth. The changes in composition are also reflected in the major element chemistry by variation in Al and CC concentrations (Figure 3.6). Intervals of high Mn concentrations coincide with high $CaCO_3$ concentrations. The layering in sediment composition and grain size indicates that physical mixing of sediment is less than 8 cm thick (Figure 3.6).

The profiles of the activities of excess ^{210}Pb and ^{137}Cs do not allow estimation of MAR. Finer grained intervals (high Al concentration) have higher activities of excess ^{210}Pb than coarse grained (low Al concentration) intervals (Figure 3.5) and indicate activities are dependent upon grain size variation. The nature of the results also suggests that sediments have been deposited rapidly. The focussing factor of the flux of ^{210}Pb is the greatest of all cores, whereas the inventory of ^{137}Cs is the lowest of all cores (Table 3.3) and ^{137}Cs is present over the entire core length. These radiochemical data are interpreted to indicate rapid accumulation of sediment post 1950. Sediment in the base of the core has been assigned 1950 as the maximum date of deposition. However, because the base of soft mud was not reached and ^{137}Cs was present over the entire core

length, a probable age sediment deposition at the base of the core of 1975 is preferred. This is the average age of deposition of the core, assuming 1950 as the maximum and 1999 as the minimum sediment deposition ages (Table 3.3).

3.3.2.4 Core 1831

Core 1831 was located at 19°17`52``S / 146°51`12``E (Figure 3.1) within an oxbow (truncated stream meander bend) of Sandfly Creek. Aerial photographs indicate the oxbow was formed during 1963 when the main channel (25 m wide) of the creek was breached (Figure 3.7a). Within a period of 30 years the oxbow filled with sediment, to a point where it is now a mangrove forest, with a small creek channel navigable only by a small boat. The sediment core was collected from the middle of a narrow tidal channel (4 m wide) at the apex of the old meander bend, and is exposed at low tide.

The core was 72 cm long and bottomed in a stiff grey mud that could not be penetrated by hand (Figure 3.6). The core comprised grey to black laminated organic rich muddy sediment from 60 cm to surface. Minor mangrove root and leaf materials occurred in the sediment.

The activity of excess ^{210}Pb exhibits a decline from surface and ^{137}Cs activities are consistently high over the entire core length (Figure 3.6). The focussing factor of ^{210}Pb and ^{137}Cs exceed 1 (Table 3.3). These radiochemical data indicate the site is rapidly accumulating sediment. The mass accumulation rate derived from ^{210}Pb activities indicates that the base of the core to have a maximum age of deposition of 1985 ± 2. However, the reliability of this model is less than that for core 1827 and 1828, because it is not supported by aerial photographic history or the homogenous distribution of ^{137}Cs. Therefore, sediment at the base of the core has a probable age of deposition of 1985, but based a maximum age of deposition of 1965 is inferred from aerial photographic interpretation (Table 3.3).

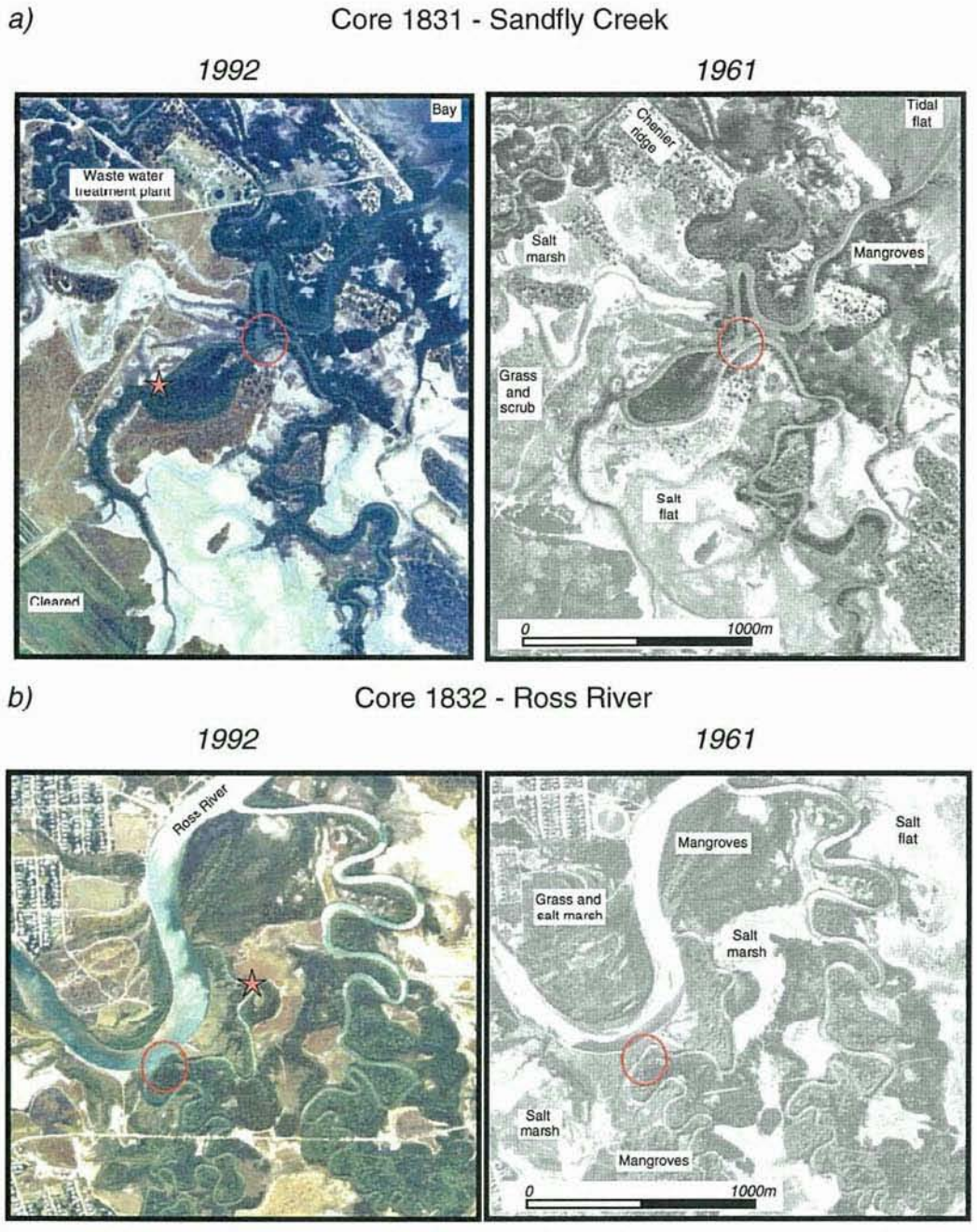


Figure 3.7 Aerial photographs of core sites 1831 and 1832 showing changes in stream channels between 1961 and 1992. a) Core 1831 - Sandfly Creek; b) Core 1832 - Ross River; Core site (☆). Photographs sources; Queensland State Government (Sunmap) Run 6, 188/Qc5084, 21/06/1992, Townsville 8259 (1:25 000) and Commonwealth of Australia (Department of National Development) Run 3, 5026 CAB 193, 11/06/1961, Townsville E55-14 (1:80 0000).

This core was collected during an unusual rainfall event during August of 1998 (> 150 mm in 24 hours). This resulted in flooding in the Townsville region and large quantities of fresh rainwater run off was occurring when the core was collected. The absence of ^{234}Th below the surface layer suggests low short-term particulate mixing rates.

3.3.2.5 Core 1832

Core 1832 was collected at 19°17`28``S / 146°49`76``E (Figure 3.1) during December 1998, from a mud bank located on a truncated meander of a mangrove creek that once flowed into Ross River (Figure 3.7b). The original mangrove creek was up to 30m wide, but has rapidly filled with sediment since being truncated by Ross River 1.5 km upstream from the mouth of the creek at some time after 1970.

The creek channel is presently 10 m wide and is navigable by small boats only at high tide. The mouth of the creek to the point of truncation has remained an isolated channel that forms a loop adjacent to the main Ross River Channel and has rapidly filled with sediment. The core site is exposed at low tide.

The core was 100 cm long and terminated in soft mud at the limit of the core device. The core contained brown to grey-black mud with minor silt intervals between 30 cm and 60 cm (Figure 3.5). Infrequent thin shell hash laminae, organic matter and thin silt rich layers were logged between 30 cm to 70 cm depth. These silt rich intervals are recognised by the decrease in Al and trace metal concentration over this interval (Figure 3.6).

Activities of ^{210}Pb and ^{137}Cs are high over the entire length of this core (Figure 3.5). The profile of ^{210}Pb decay exhibits a slight decline in activity, which is in part influenced by the presence of more silt rich intervals in the middle part of the core. The focussing factor of ^{210}Pb flux and ^{137}Cs exceed 1 (Table 3.3). These radiochemical data indicate rapid accumulation of sediment post 1950. Combined with the aerial photographic controls to sediment accumulation, the results are interpreted to indicate recent and rapid sediment accumulation since 1975. Therefore, the sediment at the base of the core was not deposited prior to 1975, which is used to calculate a minimum MAR. However, the base of the soft mud deposit was not reached, suggesting that the sediment was deposited after 1973. Therefore the probable age of deposition of

sediment at the base of the core is estimated to be 1985, which is the average age given the maximum age of 1975 and time of collection of 1998 (Table 3.3).

Physical mixing of sediment is not considered to be rapid because of the presence of discrete silt intervals observed during logging and absence of ^{234}Th below the surface interval. Depth of homogenous mixing is interpreted to be 6cm.

3.3.3 Standardisation of trace metal concentrations

To develop stepwise regression models it was necessary to log transform all variables to approximate assumptions of normality and provide constant variance. Normal probability plots of each element for the model suite of samples are presented in Appendix 7.

The stepwise regression models generated for the model suite of samples, located in the eastern bay, are presented in Table 3.4. These models are used to remove natural variation in sediment geochemical composition. All model calculations contain Al and this demonstrates that the changes between sites are driven predominantly by variation in the amount of fine-grained terrigenous sediment. Model equations for Cu, Ni, Pb and Zn have an adjusted coefficient of determination (R^2) > 0.9, whereas the R^2 of Cd and Co are substantially less (0.41 and 0.58 respectively).

Major element concentrations for each surface sediment and core sample have been substituted into the model equations in Table 3.4 to calculate a predicted concentration. There is a strong linear relationship between the measured value and the value predicted by the regression model for Cu, Ni, Pb and Zn (Figure 3.8). However, for Cd and Co, which have low adjusted R^2 values, the relationships between the measured value and the predicted values are non linear.

Table 3.4 Regression models generated for the model suite of samples (surface grabs and core samples) from eastern Cleveland Bay. n is the number of samples used to calculate the regression model.

	Adjusted R^2	Standard error	n	Regression model equation
Log Cd	0.4150	0.13501	55	= 0.490931 log Al + 0.403943 log Ca - 0.504377
Log Co	0.5815	0.04847	56	= 0.225326 log Al - 0.001449 log CC + 0.165298 log Mn + 1.411019
Log Cu	0.9641	0.04273	56	= 0.880423 log Al + 0.059808 log Mn + 0.118234 log OC - 0.938976
Log Ni	0.9183	0.04660	56	= 0.740578 log Al - 0.002427 log CC + 0.116869
Log Pb	0.9226	0.04204	56	= 0.636611 log Al - 0.040021 log Ca - 0.094559
Log Zn	0.9479	0.03359	57	= 0.380553 log Al - 0.078177 log Ca + 0.221075 log Mn + 0.1174 log OC + 1.250194

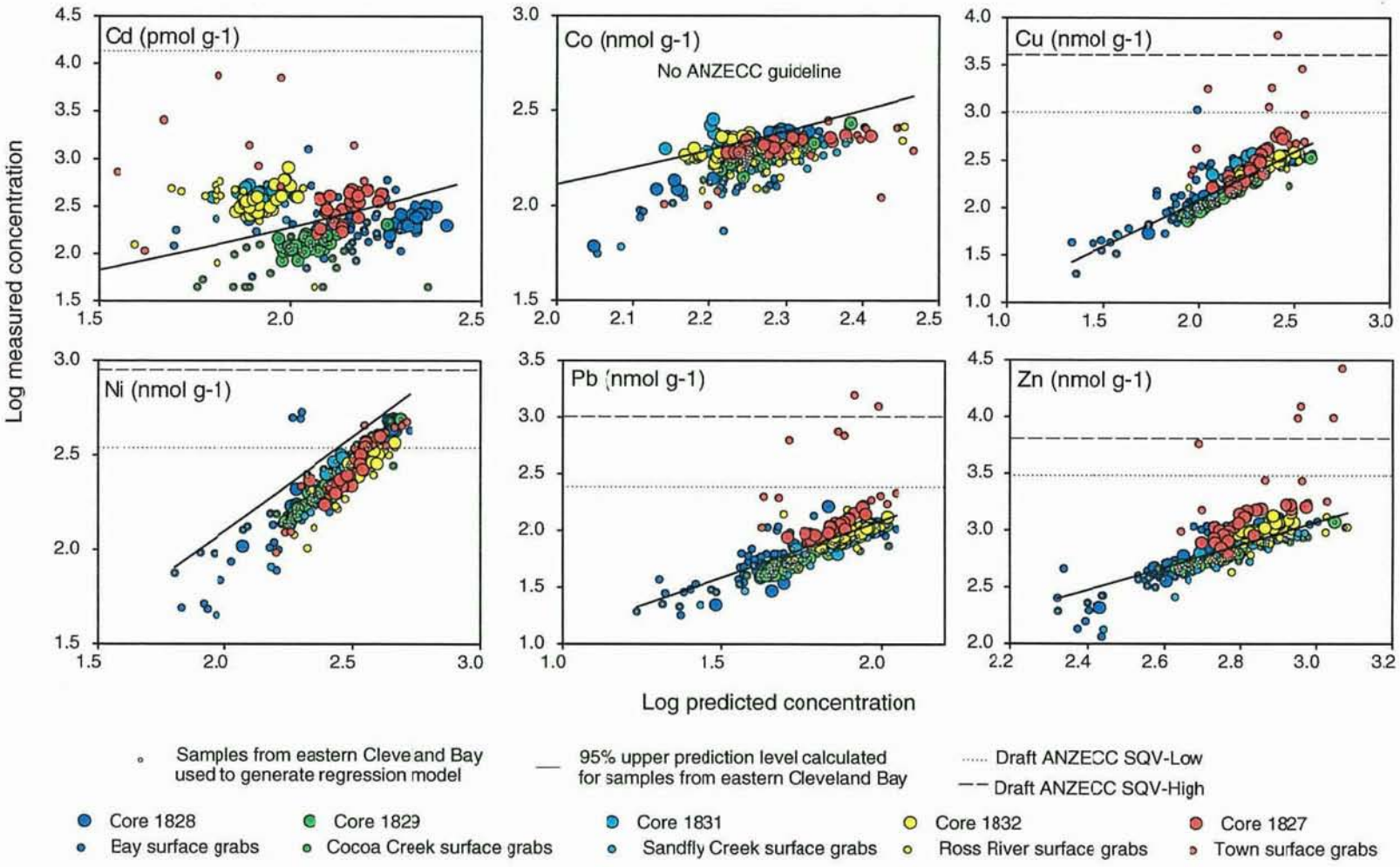


Figure 3.8 Plots of the concentration predicted by regression models against the measured concentration

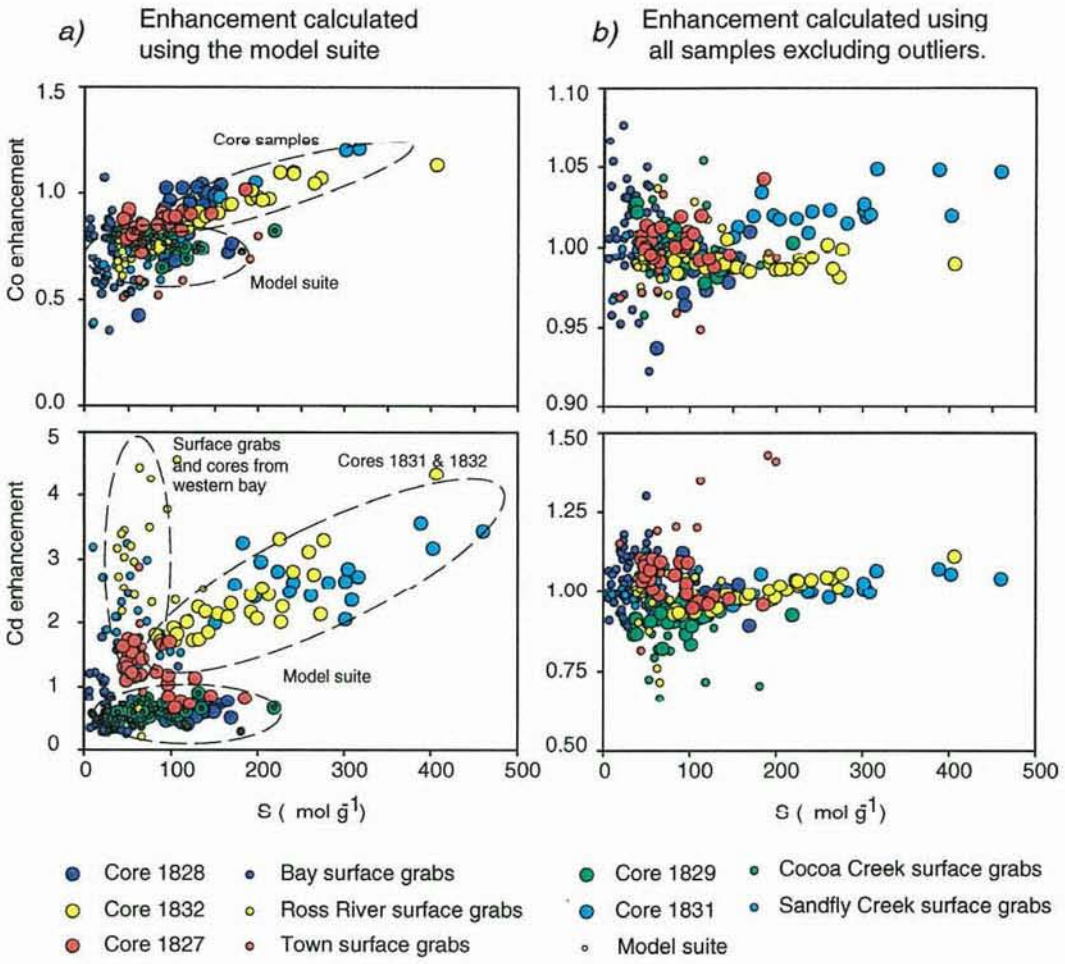


Figure 3.9 Plots of enhanced Cd and Co values versus S concentrations. There is a positive linear relationship between enhancement of Cd and Co in cores 1831 and 1832 a) Enhancement values calculated using the regression model generated by the model suite of samples from eastern Cleveland Bay; b) Enhancement calculated using the regression model generated by the entire data set with outliers from Ross Creek removed.

To further investigate these patterns in Cd and Co concentrations, a second regression model was generated. This model used all samples in Cleveland Bay, with outlying concentrations from Ross Creek removed. The enhancement of Cd and Co calculated for these models were found to have a positive linear relationship with S concentrations (Figure 3.9b).

These results indicate the relationships between Cd, Co and the variables used in regression models in Table 3.4 are not constant. The linear relationships of Cd and Co enhancement in some core samples with S concentrations suggests that these metals are influenced by post depositional processes resulting in the accumulation of authigenic sulfides.

3.3.4 Principal component analysis

PCA was completed using the enhancement values (Equation 3.1) of Cd, Co, Cu, Ni, Pb and Zn as independent variables. The enhancement values were calculated using stepwise regression models generated by the model suite. Three components were measured, which could explain 88.6% of the variance in enhancement of trace metals (Table 3.5). Component 1 explains 54.2% of the variance, and is characterised by samples that have simultaneously enhancement > 1 of Cd, Cu, Pb, Zn, and to a lesser extent Ni. Figure 3.10 shows that surface grab and core samples from Ross Creek, which exceed the Draft ANZECC ISQV-low, are characterised by being distributed along the axis of component 1. This suggests that sites that are influenced by anthropogenic increases in trace metal concentration have a high positive component 1 score and simultaneous enhancement > 1 of more than one metal.

Components 2 and 3 explain an additional 20.7% and 13.7% of the variance respectively (Table 3.5). Component 2 is characterised by a positive correlation between Co and Ni values. Some samples from West Passage and Sandfly Creek have strong positive component 2 scores (Figure 3.10). Component 3 is characterised by samples that have high Cd and Co standardised values and are inversely correlated with Ni standardised values. A plot of component 2 vs component 3 separates the samples from West Passage and Sandfly Creek (Figure 3.10). This suggests that the samples from these regions have different influences upon their trace metal chemistry.

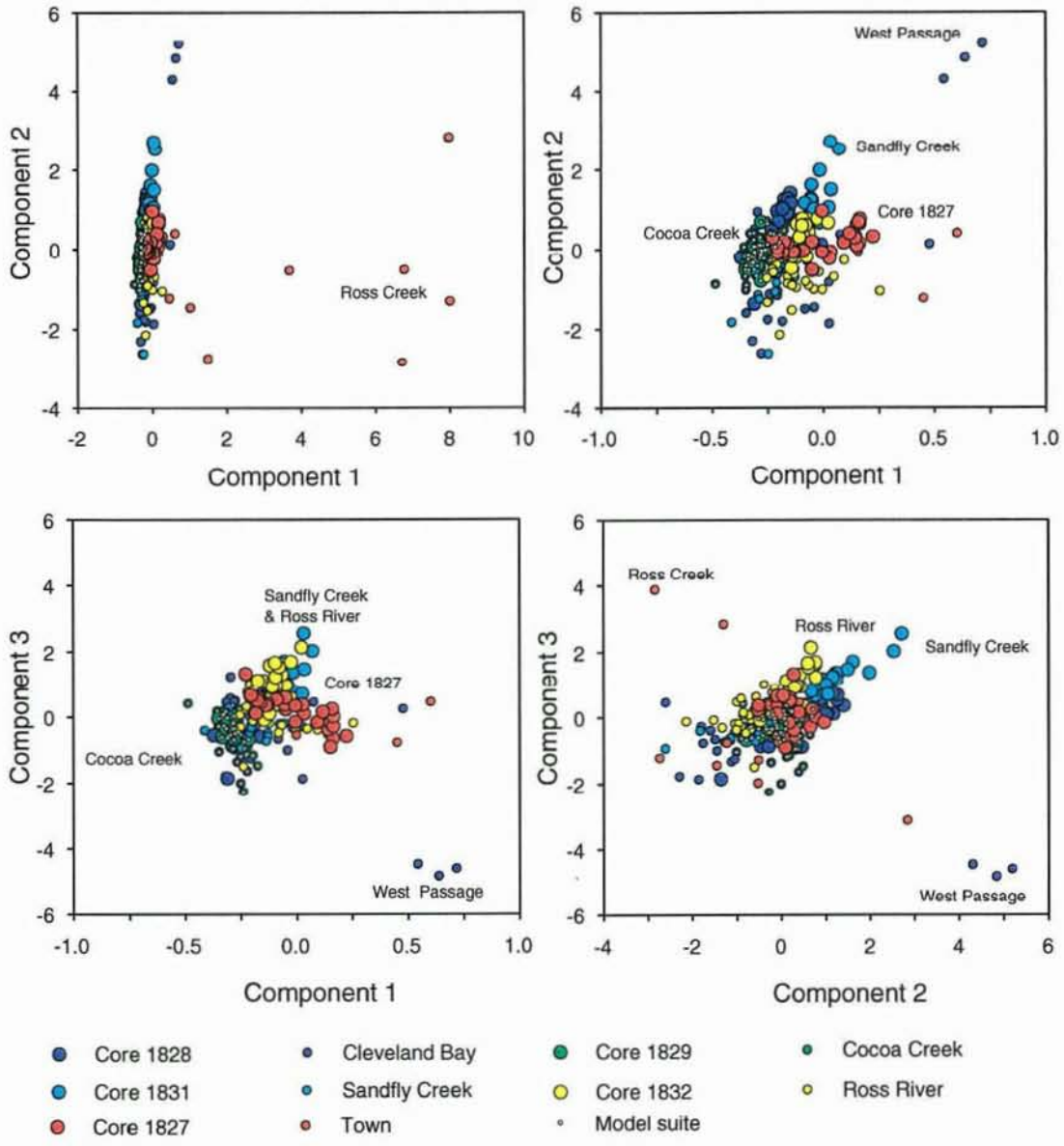


Figure 3.10 Plots of component scores generated by the PCA of standardised Cd, Co, Cu, Ni, Pb and Zn values for surface sediment grab samples and sediment core samples. Component 1 versus component 2 is presented twice to demonstrate the significance of outlying samples from Ross Creek that contain enhanced trace metal concentrations.

Table 3.5 Summary table of the results of PCA of standardised trace metal concentrations.

	Component 1	Component 2	Component 3
Cadmium	0.8016	-0.2109	0.2908
Cobalt	-0.0402	0.7438	0.6549
Copper	0.8623	0.1293	-0.1753
Nickel	0.1403	0.7906	-0.5055
Lead	0.9721	0.0023	-0.1009
Zinc	0.9486	-0.0271	0.1195
Eigenvalue	3.25	1.24	0.82
Variance %	54.20	20.70	13.70
Cumulative %	54.20	74.90	88.60

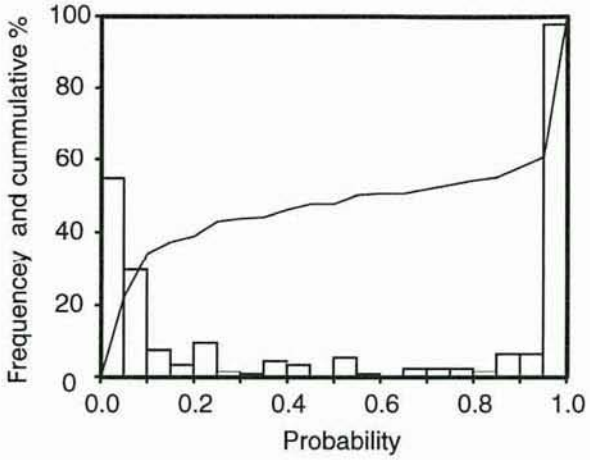
3.3.5 Linear discriminant analysis

Linear discriminant analysis was completed using PCA components 1 and 2 as independent variables, and 2 samples categories; 1) Cocoa Creek (part of model suite in eastern bay), and 2) all other samples. Component 1 and 2 were chosen as independent variables because they were found to identify samples that have patterns in trace metal enhancement that can be attributed to anthropogenic influences.

A plot of the cumulative frequency distribution of the probabilities of samples belonging to category 2 (not the same as Cocoa Creek) is presented as Figure 3.11a. The distribution is characterised by a large group of samples with a probability of < 0.25, and a second large group having a probability of > 0.9. Samples that have a probability of < 0.25 have patterns in enhancement values that are characteristic of samples from Cocoa Creek, which is considered to be not influenced by anthropogenic activities.

Samples that have a probability of > 0.25, have a greater probability having patterns in trace metal enhancement values that can be attributed to anthropogenic influences. The spatial distribution of probabilities for surface sediment samples is plotted as Figure 3.11b. The distribution of probabilities indicates there is a greater likelihood of anthropogenic influences upon trace metal concentrations in the western bay. This distribution supports the use of the 0.9 probability as the threshold criteria to indicate anthropogenic influences. The value of enhancement for samples that have a probability > 0.9 have been imaged and are presented as Figure 3.12.

a)



b)

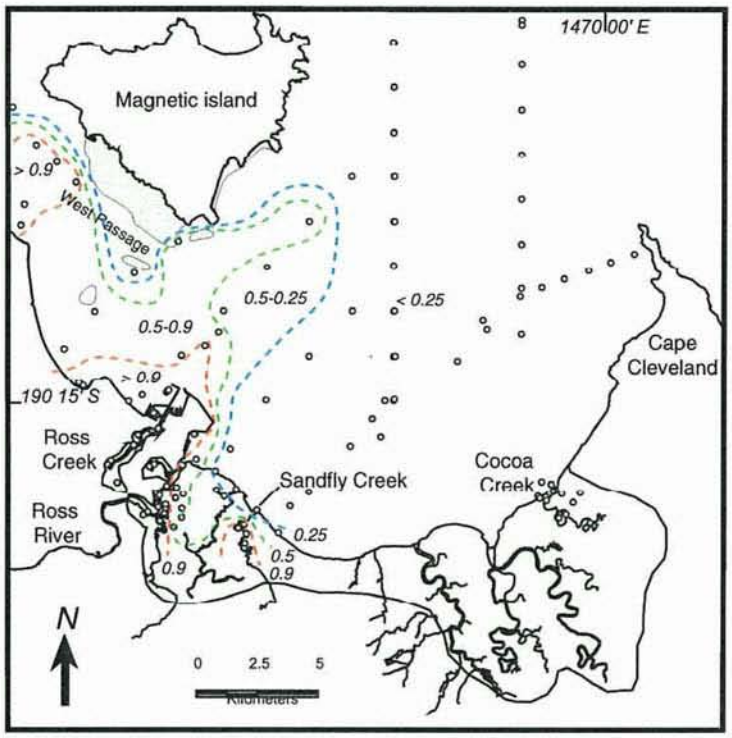


Figure 3.11 Distributions of the probability that trace metal concetrations are influenced by anthropogenic activites. a) Cumulative frequency distribution of probabilities. The threshold probability separating groups of samples are 0.25, 0.5 and 0.9 ; b) Contours of 0.25 (blue), 0.5 (green) and 0.9 (red) probability demonstrating the spatial distribution of probabilities in surface sediment grab samples of Cleveland Bay

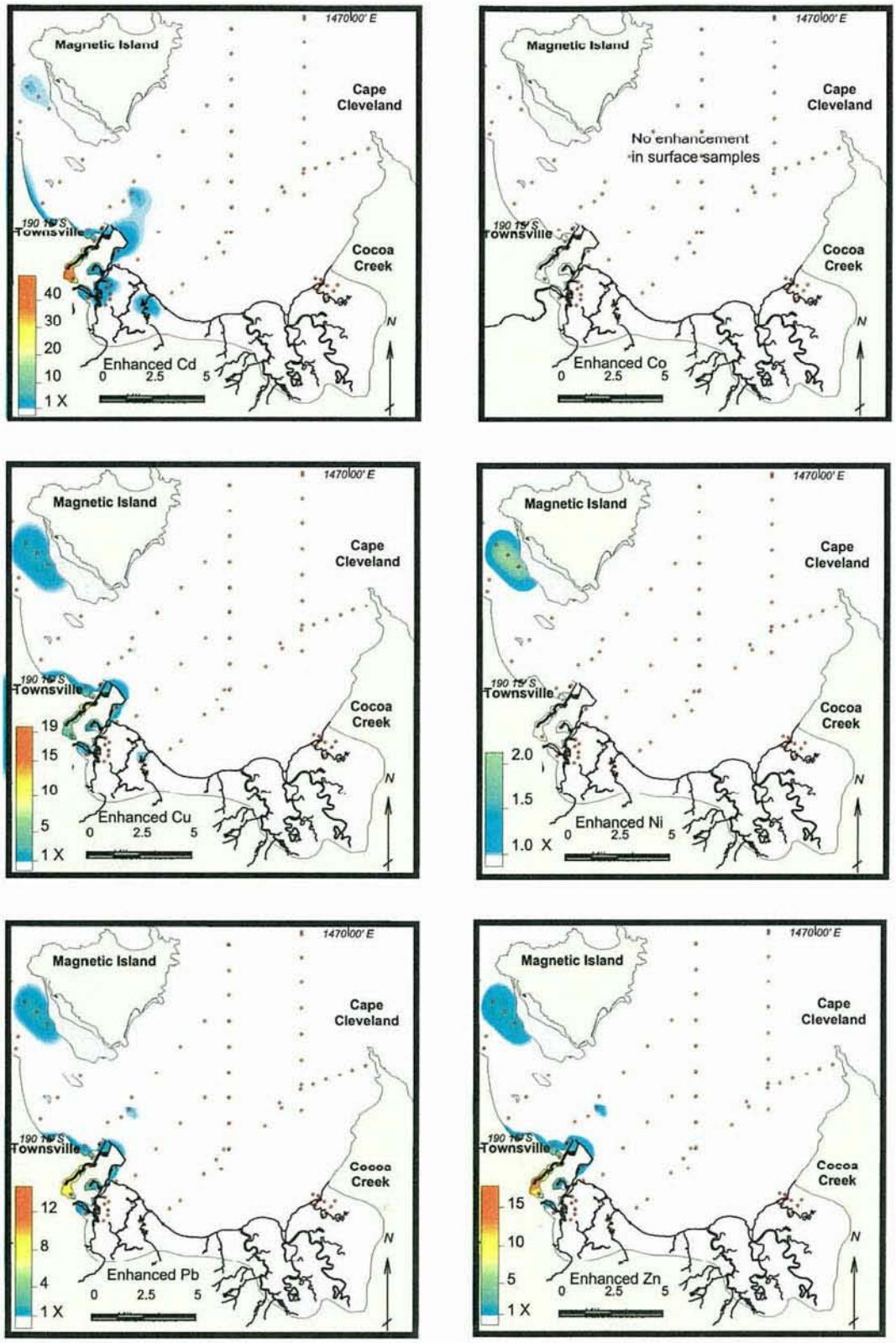


Figure 3.12 Images of enhanced trace metal values that concentrations that have a probability of > 0.9 of belonging to category 2. These enhancements are interpreted to represent anthropogenic influences upon trace metal concentrations

3.3.6 Temporal trends in enhancement

Temporal variations in the enhancement values of trace metals in sediment cores have been examined by combining the results of statistical models with models of mass accumulation rate. Enhancement of metals in cores 1831 and 1832 (Figure 3.13) includes weak enhancement of Cu, Pb and Zn in Core 1832 and weak enhancement of Cu, Ni and Zn in Core 1831. The sediment in these cores was deposited post 1965 and 1975 respectively, in the intertidal zone of the western bay. The period of deposition of these sediments is equivalent to the top 20 cm depth in cores 1827 and 1828.

Sediment in core 1827 was deposited post 1900 ± 16, and the increase and decrease in enhancement of some metals (Figure 3.13) can be correlated with events summarised in Figure 3.2. These trends include; the increase in enhancement of Cu post 1960 that correlates with increases in total port throughput and population growth; and, increases in enhancement of Zn and Cd post 1935 and decreases post 1985 that correlate with the introduction of Zn concentrates to the port and improvements to their storage and handing facilities.

Sediment in core 1828 was deposited post 1928 ± 24, and exhibits sustained enhancement of Zn near surface, in fine grained terrigenous sediment that overlies a calcium carbonate rich sediment. The change in sediment composition occurs post 1945, and indicates a change in the source of sediment supplied to the site.

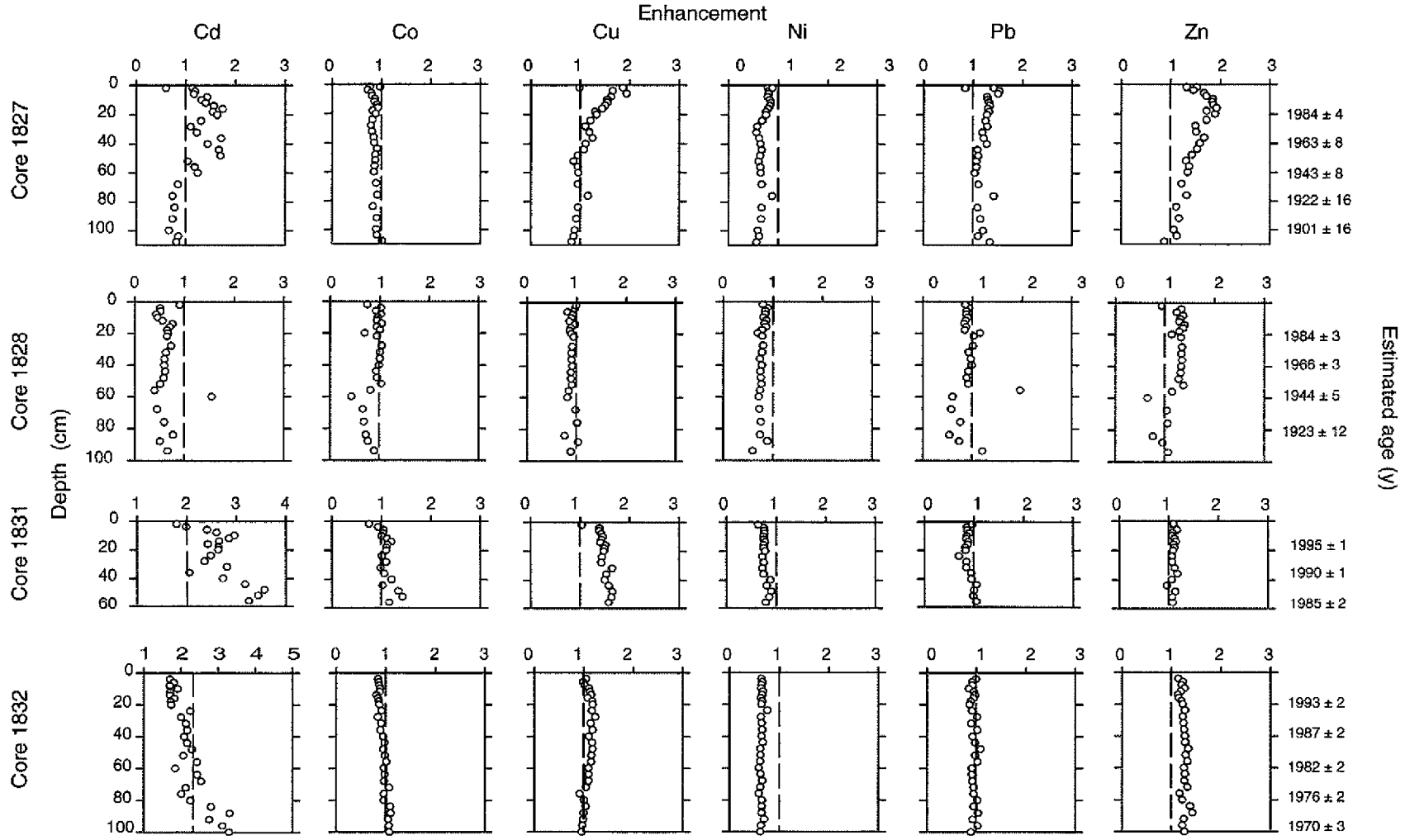


Figure 3.13 Sediment core profile showing trace metal enhancement above the upper 95% prediction level of the regression model. ^{210}Pb estimated time of deposition is shown on the right axis.

3.4 Discussion

3.4.1 Limitation of statistical methods

It is important to interpret the results of statistical analysis with a clear understanding of why the analysis was attempted and what the key limitations of the analysis are. Standardisation of sediment trace metal concentrations is undertaken here to remove the influence of natural variation in trace metal concentrations, so that anthropogenic influences can be identified. Principal component analysis of enhancement values is undertaken to identify groups of samples that have a characteristic multielement signature that may be related to a specific source (e.g., Krumgalz 1993; Negrel 1997). Linear discriminant analysis was then completed, using the PCA component scores, to quantify the trends identified by PCA.

The most critical step in this hierarchy of statistical analysis is standardisation of measured trace metal concentrations. The stepwise regression models used here to predict trace metal concentrations use chemical parameters to describe changes in sediment composition between a subset of samples (the model suite). The variance explained by the model is a function of the relationships between model equation parameters in samples from the eastern bay. Samples from the western bay are being classified as a function of modelled relationships generated for a group of samples from the east of the bay.

Enhancement (Equation 3.1) is a measure of the variance not explained by the regression. The variance is created by parameters not included in the model, which may be created by natural and anthropogenic influences. Enhancement of a sample, above the upper 95% prediction level of a regression model does not necessarily indicate that it is created by anthropogenic influences (e.g., Schropp *et al.* 1990). In this study, enhancement classifies a sample as being different to samples from the eastern bay.

The key assumption in this method is that that the relationships between the dependent (trace metals) and independent variables (major elements) is constant (see section 1.4.2.1). In this study, this assumption is required to hold for surface sediment samples from different locations in the bay (spatially constant) and with sub-surface

core samples of different ages of deposition (temporally constant). The extent to which these assumptions are breached or supported will be discussed in the following sections.

3.4.2 Natural influences upon sediment geochemical composition

3.4.2.1 Influences of sediment source and transport processes

The trends in spatial distribution of Al, Co, Cu, Fe, Mn, Ni, OC, P, Pb, S and Zn concentrations in sediment are characterised by greater concentrations occurring shorewards, as sediments become more terrigenous (Figure 3.4 and 3.5). Greater concentrations of Ca and CC occur seaward. In intertidal regions exposed to wave energy, sediments are characteristically low in both Al and CC, and indicate the presence of coarser grained silicate minerals that form terrigenous quartz rich sands (e.g., west of the Port). In regions that are protected from wave energy fine grained Al rich muddy terrigenous sediments accumulate (e.g., West Passage).

The sedimentary facies on the leeward side of Cape Cleveland is geochemically distinct from the central bay facies because it contains relatively high concentrations of CC, Mn and Co. This location was identified by McIntyre (1996) to be a discrete shell rich facies and was described by Belperio (1978) as a site where sediments where being resuspended and transported by strong tidal currents. The high Mn signature of this facies is consistent with interpretation of the regional data in the previous chapter - High Mn concentrations occur at sites of sediment resuspension, oxidation and erosion.

The presence of maximum Ca and CC concentrations west of Magnetic Island is due to the proximity to inshore coral reefs at these sites. Maximum concentrations of Al and high concentrations of trace metals also occur west of Magnetic Island, in West Passage. This is created by the presence of an isolated muddy facies that has formed in a relatively unique environment that is protected from wave and tidal influences (e.g., Pringle 1989).

The distribution of fine-grained terrigenous sediment and biogenic carbonate sediment correspond well with the distribution of surface sediment facies of Carter *et al.* (1993), McIntyre (1996) and grain size distributions of Belperio (1983). However, the presence of the Al rich muddy facies seaward of the Port and Sandfly Creek, in areas exposed to wave energy, was not expected. These muddy facies were not detected by

previous surveys and it is therefore presumed that they are either transient features that may have been formed by floods during early 1998, or exposure of older facies deposited during previous sea level stands (e.g., Carter *et al.* 1993).

Despite these large variations in sediment composition between sites in the bay, the relationship between dependent and independent variables are temporally and spatially constant across the bay. This is indicated by the similarity in patterns of trace metal enhancement values for samples from West Passage (Core 1828) to samples from Cocoa Creek (Figure 3.8).

This is in line with the concept of Orpin & Woolfe (1999) that sediments in Cleveland Bay are essentially derived from redistribution by physical processes of a well mixed but poorly sorted poly-modal facies located in the central bay. Therefore, despite the physical redistribution of sediment and presence of more than one source of sediment to the bay (see section 3.1.1), the relationship between dependent and independent variables is constant. This also supports the use of a model suite of samples from the eastern bay to compare samples with samples from the western bay.

3.4.2.2 Influence of post depositional processes

Post depositional early diagenetic changes to sediment composition have been found to confound regression models of trace metal concentration (e.g., Elderfield *et al.* 1979; Rae & Allen 1993; Douglas & Adeney 2000). This occurs because the relationship between dependent and independent variables may change during diagenesis and the changes are time dependent. Unless the change is constant and linear between all samples, it will manifest as variance in the regression model.

The strong linear relationship between the regression model predicted and measured Cu, Ni, Pb and Zn concentrations indicates that the majority of natural variation in metal concentrations is accommodated by the regression models. This does not imply that post depositional early diagenetic processes do not affect Cu, Ni, Pb and Zn, rather that affects are included within the model, or that the magnitude of the affects are insignificant relative to other influences.

In cores 1831 and 1832 post depositional changes to sediment composition have a measurable affect upon the concentrations of Cd and Co. These affects manifest in the

statistical analysis as the poor quality of fit of samples from these cores to regression models (Figure 3.8) and enhancement values of Cd and Co that increase in proportion to increases in S concentrations (Figure 3.9).

An increase in S concentration with depth occurs in all cores (Figure 3.6). These increases with depth are consistent with the formation of authigenic Fe sulfides as a consequence of sulfate reduction (e.g., Raiswell & Berner 1985). However, increases in Cd and Co concentrations are apparent only in cores 1831 and 1832.

The greatest difference between cores 1831 and 1832as well as surface sediment and cores samples, is the combined high OC concentrations (Table 3.1). In shallow marine sediments sulfate reduction is limited only by the concentration and metabolic properties of organic carbon (Berner 1980). This suggests that changes in Cd and Co concentrations are only significant in sediments that have high sulfate reduction rates. Cores 1831 and 1832 have average OC concentrations > 500 μmol g^{-1}.

To remove the natural variance in Cd and Co concentrations from regression models requires to account for a rate (time) dependent early diagenetic process, which can not be done for surface samples. Therefore, because the source of variance was identified and because the effect was only upon a minority of the samples, the regression models generated by the model suite of samples were used to standardise Cd and Co concentrations. A consequence of using these models is the presence of component 3 in PCA (Table 3.4). Samples from cores 1831 and 1832 have positive component 3 scores (Figure 3.10). This is interpreted to be a response to natural influences of early diagenetic processes that cause increases in Cd and Cu concentrations.

3.4.3 Anthropogenic influences upon trace metal concentrations

3.4.3.1 Spatial variation in anthropogenic influences

The simultaneous enhancement of several metals in Ross Creek is similar to the patterns in trace metal enhancement found in urban regions around the world (Cortesao & Vale 1995; Stark 1998; Callender & Rice 2000; Widianarko *et al.* 2000). Ross Creek runs through the historical centre of Townsville's rail, shipping and industrial activities. In Ross Creek the average concentration of Cu, Pb and Zn in sediments exceed the Draft ANZECC ISQVs (Figure 3.8) and enhancement values are > 20 (Figure 3.12).

It is this 'multielement signature' that is used to classify sites, using linear discriminant analysis, to determine if trace metal concentrations are influenced by anthropogenic activities. Classification of samples used PCA components 1 and 2 (Table 3.5). Component 1 is undoubtedly a consequence of anthropogenic influences, which have been found in Ross Creek (Gibbs, 1993; Reichelt & Jones 1994; Inglis & Kross 1999). Component 2 is also interpreted to represent anthropogenic influences upon trace metal concentrations. Component 2 is characterised by similar patterns in the enhancement of Ni, Co and Cu (Table 3.5), and samples from Sandfly Creek and West Passage have high component 2 scores (Figure 3.10).

Enhancement of Cu and Ni in sediments from Sandfly Creek is probably a consequence of anthropogenic influences because the catchment of the creek hosts a sewage treatment plant and industrial areas that include a Cu refinery, meat works, power station and refuse tip. Samples from West Passage are also considered to have trace metal concentration influenced by anthropogenic activities. Ni concentrations in surface sediment samples exceed the natural range in concentration, and in core 1828 (West Passage) erratic enhancement of trace metals occurs after approximately 1945. The location of West Passage is also down current of Townsville (e.g., Pringle 1989), given a predominantly north west direction water circulation in the western bay.

Classification of sites using these characteristic multielement signatures identifies samples in the western bay to have a greater probability of having trace metal concentrations being affected by anthropogenic influences than the eastern bay (Figure 3.11b). This probability increases towards Townsville and samples from the intertidal zone around Townsville have a probability of > 0.9. This region is characterised by

simultaneous enhancement of < 2 times the modelled background and to have enhancement of more than one trace metal (Figure 3.12). This indicates that anthropogenic influences upon trace metal concentrations are typically < 2 times the modelled background concentration.

3.4.3.2 Temporal variations in anthropogenic influences

Events that affect the supply of metals over time from anthropogenic sources can be recorded in sediments. (e.g. Bricker 1993; Kolak *et al.* 1998; Cochran *et al.* 1998; Lauenstein & Daskalakis 1998; Brannvall *et al.* 1999; Huh & Chen 1999). This requires both appropriate identification of metals from anthropogenic sources and estimation of the sediment deposition age.

In general, cores examined here are characterised by high mass accumulation rates and represent sediment accumulated within the last 100 years. The focussing factors of ^{210}Pb and ^{137}Cs are typically > 1 for all cores (Table 3.3). This indicates core sites have a high sediment trapping efficiency on a 20-100 year time scale. The mass accumulation rates measured in the cores (> 5 kg m^{-2} y^{-1}) are an order of magnitude greater than sediment accumulation rates described by Carter *et al.* (1993) in Cleveland Bay (1 mm y^{-1}). The low rate of accumulation described by Carter *et al.* (1993) is due to a low sediment trapping efficiency of the central bay, where the majority of sediment (> 90%) entering the bay is resuspended or entrained and transported elsewhere (Woolfe & Larcombe 1998). This rate represents average sediment rates of the entire bay over the Holocene (6000y time scale).

The methods used to estimate deposition age of sediment, use the sediment mass accumulation rate and mixed layer thickness. These parameters are based upon ^{210}Pb and other supporting information, including ^{137}Cs, ^{234}Th, aerial photograph interpretation and sediment geochemistry. Cores 1827 and 1828 exhibit the most reliable ^{210}Pb based models of mass accumulation rate and these are corroborated by ^{137}Cs and historical information (Figure 3.5). This is because the 1950 time interval predicted by the ^{210}Pb model of mass accumulation rate coincides with the base of ^{137}Cs activities. For core 1827, the ^{210}Pb based model is further supported by constraints placed upon sediment deposition by construction of the breakwater.

Core 1827 is interpreted to represent the accumulation of sediment on the leeward side of the breakwater since at least 1900. Situated at the mouth of Ross Creek (Figure 3.1), it is an ideal site to trap and accumulate particulate materials discharged from the creek and provides a record of historical events affecting sediment trace metal concentrations.

The profile of enhancement of Cu in Core 1827 (Figure 3.13) exhibits a sustained increase after 1960. This increase not only corresponds to the construction of marina facilities in Ross Creek and the start up of a Cu refinery but is also sympathetic with the total Port throughput and population growth (Figure 3.2). Therefore there are a variety of potential anthropogenic sources of Cu. The transhipment of Cu products at the port is probably not a significant source because Cu commodities (blister Cu) were first introduced to Townsville in 1914 (Taylor 1980).

Enhancement of Cd above 60 cm depth coincides with the introduction of Zn concentrates to Port in 1936 (Taylor 1980). The decline in enhancement of Cd and Zn above 20 cm depth coincides with improvements made to the Zn concentrate handling facilities during the 1980s. The presence of weakly enhanced Pb and Zn at the base of the core indicates the presence of other sources of these metals prior to the introduction of concentrates to the port.

Ni has been exported from the port since 1975 in the form of roundels and Ni laterite ore (< 1% Ni) has been imported since the early 1990s. Nickel laterite ore was > 70% of the total tonnage of all commodities imported in 1887 (TPA 1998) yet no strong enhancement of Ni occurs in Core 1827 or in surface sediment grab samples in the bay. These results indicate that the form that a metal commodity is in and the handling processes will have a significant affect upon its recognition in the sedimentary record.

In core 1828 the transition in sediment composition, from calcium carbonate rich sediment to predominantly terrigenous muddy sediments, corresponds to approximately 1945 (post war) (Figure 3.5). The transition indicates a distinct change in the composition of sediment accumulating at the site. Changes in sediment composition to this site could occur by natural progradation of sedimentary facies. However, the coincidence of Zn enhancement with this change in composition and erratic enhancement of metals above this interval, suggests that it is related to anthropogenic

influences. Weak enhancement of Ni occurs in near surface samples that have been deposited within the last 20 years.

Estimation of mass accumulation rate for cores 1829, 1831 and 1832 are based upon controls to the maximum age of sediment deposition from interpretation of aerial photography and the presence of ^{137}Cs over the entire length of each core. Cores 1831 and 1832 represent sediment that has been deposited within the last 35 and 25 years respectively and contain sustained weak enhancement of Cu, Zn and erratic enhancement of Pb.

These results provide evidence for anthropogenic sources of metals at locations other than Ross Creek. Core 1831, from Sandfly Creek, has distinctive enhancement of Cu, whereas Core 1832 (Ross River) has lower levels of Cu enhancement and more erratic Pb enhancement. Potentially the most important trend in the data is that the period of deposition of cores 1831 and 1832 corresponds to the top 20 cm of cores 1827 and 1828. This demonstrate a consistent trend among cores, whereby recently deposited (< 30 years) sediments are influenced by anthropogenic activities and are characterised by enhancement of several metals that do not exceed the Draft ANZECC ISQV-low.

3.4.4 Relationships between enhancement and the Draft ANZECC Guidelines ISQVs

The Draft ANZECC Guidelines recommend a tiered risk assessment strategy for sediment quality assessment. The context within which the strategy is to work is as critical as the process itself. For example, the use of ISQVs as trigger levels are recommended only in areas that are moderately disturbed. In areas to be maintained pristine background is the preferred trigger level.

Cleveland Bay contains regions that are moderately disturbed. However, it is also within a World Heritage Area and parts of the bay are also within the Great Barrier Reef Marine Park (Figure 3.1). Therefore, dependent upon the management strategy for a specific region of the bay, ISQVs or background may be appropriate trigger levels. The relationships between enhancement, probability of anthropogenic influences and the ISQVs is therefore relevant.

The Draft ANZECC ISQV-low and ISQV-high are presented where relevant for each trace metal in Figure 3.8. The most significant difference between the ISQVs and the modelled background is that the ISQVs are a single threshold applied to all sediment types. In contrast, regression models of the natural range in concentration recognise that background is variable and ranges from low to high concentration.

The ISQVs represent threshold concentrations were biological effects within sediments have been determined to occur within a large database of experimental results (e.g., Chapman & Mann 1999). The individual ISQVs have been adapted from the Long *et al.* (1995). The data used to compile the ISQVs is based on a whole sediment, total acid digestion and was based predominantly on North American and European (temperate climates) data.

The ISQVs are set above natural concentrations because no statistically significant effects have been determined to occur at lower concentrations. Therefore, the majority of trace metal enhancements in surface sediments and cores are not enough to trigger a response within the Draft ANZECC Guidelines using the ISQVs as trigger levels. Ni is one exception to this, where the natural range in concentration appears to exceed ISQV-low. This is apparent in Figure 3.8, where Ni concentrations from Cocoa Creek situated in the eastern bay (Figure 3.1), exceed the ANZECC ISQV-low. The Draft ANZECC guidelines accommodate this circumstance by recommending that background concentrations be checked if the trigger levels are exceeded.

If the ISQVs are reliable indicators of sediment quality, then the value of enhancement and the probability of samples being influenced by anthropogenic activities are diagnostic only of anthropogenic activities. The results of the statistical modelling alone cannot be used to provide indications of sediment quality.

3.5 Conclusions

Anthropogenic influences upon trace metal values have been discriminated from natural influences using a hierarchy of statistical methods. The hierarchy includes three steps: Step 1 is standardisation of trace metal concentrations for variation in natural concentration. This is done by dividing measured values by the upper 95% prediction level of the stepwise regression model generated for a model suite of samples located in

the eastern bay. Step 2 is identification of groups of samples that have similar enhancement values using PCA. Step 3 is calculation of the probability that a sample belongs to a group of samples that have a specific multielement signature, by linear discriminant analysis, of the component scores generated by PCA.

Samples that contain metals from anthropogenic sources are characterised by simultaneous enhancement of Cd, Cu, Ni, Pb and Zn as well as having a probability of > 0.9 of being different to the model suite of samples. Maximum enhancement of sediment trace metal concentration occurs within Ross Creek and are up to 20 times the modelled background concentration. Outside of Ross Creek, enhancement is less than 2 times the modelled background concentration.

Temporal trends in enhancement of metals exhibit associations with economic growth and the introduction of specific metal commodities to the region. Combined with spatial trends in enhancement, the results indicate that recently accumulated sediments in the western bay are characterised by simultaneous enhancement of metals, which have concentrations that are less than the ANZECC ISQV-low. This is consistent with the supply of metals from several anthropogenic sources located in an urbanised region.

Chapter 4

Influences upon sulfur accumulation in recent and rapidly accumulating sediments of Cleveland Bay

4.1 Introduction

The decomposition of organic matter is the single most important early diagenetic process (Berner 1980) and is responsible for the majority of post-depositional changes to sediment geochemical properties. The most intense biogeochemical reactions involving organic matter decomposition occur near surface, and follow a well described series of microbially mediated processes including; aerobic respiration, denitrification, Mn reduction, Fe reduction, sulfate reduction and methanogenesis (Martens 1993; Stumm & Morgan 1996).

Sulfate reduction is a significant post depositional, early diagenetic process in shallow marine sediments (Berner 1980). It is responsible for changes to sediment geochemical properties that have significant environmental consequences. For example, the interaction of trace metals with authigenic iron sulfide has been found to reduce the bioavailability of some trace metals (e.g., Di Toro *et al.* 1990). The processes that influence the accumulation of sulfur in sediments are therefore important to understand.

In shallow marine environments that have high rates of sediment accumulation, sulfate reduction often dominates the oxidation of organic matter (Middelburg 1991; Canfield 1994; Tromp *et al.* 1995; Morse & Berner 1995). This is due to the relatively high concentration of sulfate (~28.2 mmol L^{-1}) in sea water relative to oxygen (> 0.2 mmol L^{-1}), which has the capacity to oxidise at least 100 times more carbon than oxygen (Crill & Martens 1987). The process is bacterially mediated and involves several interacting communities of microorganisms. The overall process can be described as one in which 2 moles of carbon are oxidised for every 1 mole of sulfate reduced (after Berner 1980):

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

The hydrogen sulfide (H_2S) produced by sulfate reduction may react with reactive iron minerals and form insoluble authigenic iron sulfides (e.g., amorphous iron monosulfide [FeS], pyrite [FeS_2]). If the authigenic sulfide minerals are not oxidised they will progressively accumulate in the sediment over time, until the supply of sulfate, reactive Fe or metabolisable organic matter is exhausted. Therefore, in shallow marine environments, where the supply of reactive Fe and sulfate is not limited, the concentration and metabolic properties of organic matter limit the reduction of sulfate to form sulfide (Berner 1980).

The retention rate of the sulfide produced during sulfate reduction has been found to be highly variable (e.g. Lord & Church 1983; King *et al.* 1985; Berner & Westrich 1985; Chanton *et al.* 1987; Middelburg 1991; Henneke *et al.* 1997). This is because H_2S and authigenic sulfides may be oxidised to form sulfate, or if there is no reactive iron to form insoluble authigenic Fe sulfides, the H_2S will be available to diffuse through the sediment. The rate of retention of the sulfate reduced is a function of the environment of deposition. The environment of deposition determines factors such as; burial rates (Morse & Berner 1995); Fe limitation (Berner 1980); bioturbation (Goldharber *et al.* 1977; Lin & Morse 1991); vegetation (Silva *et al.* 1990); and seasonal and diurnal oscillations in salinity and temperature (Casey & Lasaga 1987; Chanton *et al.* 1987; Alongi 1995; Vandenberg *et al.* 1998).

Because of these environmental interactions, the amount of sulfide accumulated in the sediment is not a simple function of the amount of organic matter decomposed (e.g. Murray *et al.* 1978), where 1 mole of sulfate is reduced for every 2 moles of organic carbon oxidised. The effect of environmental influences can be examined by the relationships between carbon, sulfur and iron in sediments relationships (Raiswell & Berner 1985; Middelburg 1991). These relationships are often explained in terms of ratios such as; organic carbon to sulfur in sediments (C/S ratio) (Berner & Raiswell 1983; Leventhal 1983; Berner & Raiswell 1984); the degree of pyritisation (DOP) (Raiswell & Berner 1985); and, the degree of sulfidation (DOS) (Boesen & Postma 1988). DOP and DOS are defined in subsequent sections.

The processes that influence sulfur accumulation in 4 sediment cores from Cleveland Bay have been investigated. The core sites (Figure 4.1) represent environments of very high accumulation rates of fine-grained terrigenous sediment (> 10 kg m-2 y-1), which have been deposited within the last 100 years. The sites are best described as unvegetated subtidal (core 1827) and intertidal (core 1829, 1831 and 1832) mud flats. They are sites that are protected from the effects of waves and currents, and have shallow mixed layers.

In this chapter, the influences upon sulfur accumulation will be evaluated by sulfur mass balances, and reconciliation between the sulfur accumulated in sediments with an estimate of sulfate reduced predicted by models of organic matter decomposition. The objective was to identify the predominant influences upon sulfur accumulation in recently deposited sediments of Cleveland Bay.

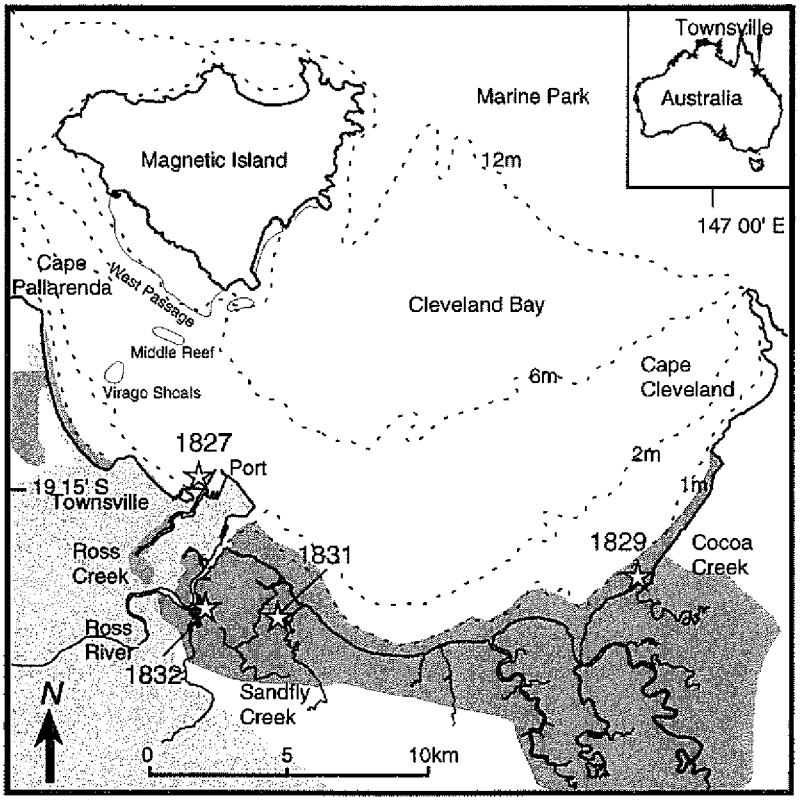


Figure 4.1 Location of sediment cores: Urbanised areas (□); intertidal zone (▩); reef (□); sediment core site (☆); depth contours (. . .).

4.2 Methods

4.2.1 Sampling

Samples from sediment cores 1827, 1829, 1831 and 1832 are described in this chapter. The location of cores and collection methods has been described in section 3.2.2.

Additional analyses completed in this chapter were performed on a 50 mL whole sediment subsample that was collected from each core slice and placed in air tight polycarbonate containers. Containers were filled to the top to minimise exposure of sediment to oxygen and refrigerated (< 24 hours) until they were centrifuged to remove pore water.

To remove pore waters, the 50 mL sub samples were spun at 5000 rpm for 15 minutes. The separated water was immediately extracted through a nitrogen purged 0.45 μm cellulose acetate filter into a 10 mL acid washed syringe, acidified with 0.1 mL concentrated HNO_3 (AR grade) and refrigerated until analysis. The remaining sediment was immediately resealed and frozen for later determination of acid volatile sulfide and simultaneously extracted metals.

4.2.2 Eh and pH

Eh and pH measurements were collected to provide a semi quantitative understanding of the changes in redox potential and alkalinity with depth. Eh measurements were made in freshly sliced sediment held in plastic bags (not to be used for trace metal analysis) by inserting a Pt electrode and measuring its potential relative to a standard calomel electrode. pH was measured simultaneously with Eh, using a Radiometer combination pH electrode. Prior to field measurements the Eh electrode was calibrated in a 1:1 mole ratio $Fe(CN)_6^{2+}/Fe(CN)_6^{3+}$ solution and the pH electrode was calibrated at 2 points using commercially available ionic standard pH solutions. Electrodes were allowed to equilibrate in the sample before measurements were taken and were washed and stored in fresh seawater between samples to monitor and correct for any drift in the instrument calibration.

4.2.3 Chemical Analysis

Analysis methods of whole sediment sample, major element, trace element and radiochemistry have been described previously in section 3.2.2. Additional analyses completed in this chapter include the extraction of 1M HCl soluble Fe and acid volatile sulfide using the method of Allen *et al.* (1991). This method involves cold acid (room temperature) distillation of AVS and simultaneous extraction of metals in 1M HCl from 2 to 10 gm of wet sediment under nitrogen for 1 hour. These analyses were completed using a thawed subsample of the 50 mL sediment sample, subsequent to the pore waters being removed.

The Fe simultaneous extracted with AVS was measured in the filtered 1M HCl solution, using a Varian Liberty 220 ICP Atomic Emission Spectrometer (ICP-AES). The liberated H_2S, operationally defined as AVS, was trapped in NaOH and measured by colorimetric methods described by Allen *et al.* (1991). The concentration of total dissolved sulfur (assumed to be SO_4^{2-}) and dissolved Fe was measured directly in the acidified pore waters by ICP-AES.

4.2.4 Sulfur mass balance

A sulfur mass balance is undertaken to provide information on processes affecting sulfur accumulation in sediments (e.g., Chanton *et al.* 1987; Middelburg 1991; Aller & Blair 1996). The simplest sedimentary mass balance approach is to balance inputs of sulfur into the sediment column with outputs at the limit of sampling. Inputs include the diffusive flux of sulfur across the sediment water interface, and the addition of sulfur in detrital form. Outputs include the loss of sulfur by diffusion across the sediment water interface, and burial below the zone of investigation.

Two methods of calculating sulfur mass balance have been used. The first follows methods of Chanton *et al.* (1987) and Middelburg (1991) and balances the diffusive flux of sulfate across the sediment water interface with the burial flux of sulfur at the base cores. The second method follows methods of Berner (1980) and Aller & Blair (1996) and balances the total amount of sulfate reduced, calculated from profiles of pore water sulfate concentration, with the concentration of sulfur accumulated since burial at base of cores. Because of the uncertainties in obtaining reliable dates of sediment deposition for cores 1829, 1831 and 1832, both mass balance methods have

been calculated using the minimum mass accumulation rate (MAR) and probable MAR (Table 3.3).

4.2.4.1 Method 1 - Diffusive flux of sulfate versus burial flux of sulfur

The diffusive flux of sulfate across the sediment water interface (J_0) can be calculated using a modified version of Fick's first law by Equation 4.1 (e.g., Chanton *et al.* 1987, Middelburg 1991). In equation 4.1 the first term represents the diffusive flux across the sediment water interface. The second term represents the burial flux of sulfate in pore water at the base of the core.

$$J_0 = -\phi_0 D_s \left(\frac{\partial [SO_4]}{\partial x} \right)_0 + \phi_\infty w_\infty [SO_4] \text{ (mol cm}^{-2}\text{ y}^{-1}\text{)} \qquad \text{(Equation 4.1)}$$

In Equation 4.1, ϕ_0 is the porosity at the sediment water interface, and ϕ_∞ is the porosity at the base of the core. D_s is the bulk sediment diffusion coefficient of SO_4, which was calculated from Equation 4.2.

$$D_s = \frac{D_o}{\theta^2} \qquad (\text{cm}^2\text{ y}^{-1}) \qquad \text{(Equation 4.2)}$$

Where D_0 is the diffusion coefficient of SO_4 in seawater, which is 10.7 cm^2 y^{-1} at 25^{0}C (Li & Gregory 1974), and θ is the tortuosity of the sediment. The tortuosity of the sediment was approximated by Equation 4.3.

$$\theta^2 = \phi F \qquad \text{(Equation 4.3)}$$

Where F, the formation factor is given by Equation 4.4, after Boudreau (1997).

$$F = 1 - ln(\phi^2) \qquad \text{(Equation 4.4)}$$

$(\partial SO_4 / \partial x)_0$ is the concentration gradient in SO_4 across the sediment water interface, which was calculated from polynomial lines fitted to the measured SO_4 concentration versus depth; x is the depth (cm); and w_∞ is the burial velocity (cm y^{-1}) at the base of the core, which has been obtained from the estimates of MAR.

The burial flux of sulfur at the base of each core can be calculated by multiplying the concentration of sulfur accumulated in the sediments since deposition (S_{acc}; mol g^{-1}) by MAR (g cm^{-2} y^{-1}).

Sulfur burial rate = S_{acc} x MAR (mol cm^{-2} y^{-1}) (Equation 4.5)

To calculate S_{acc}, whole sediment strong acid soluble S measurements (ΣS; mol g^{-1}) are corrected for the sulfur contained in the dissolved phase (SO_4 mol mL^{-1}) and organic matter (OC; mol g^{-1}). This was calculated by Equation 4.6,

$$S_{acc} = \Sigma S(1-\phi)\rho - SO_4\phi\rho - OC0.008(1-\phi)\rho \text{ (mol cm}^{-3}) \quad \text{(Equation 4.6)}$$

in which; ϕ is the porosity, and was calculated using the dry mass of material collected within a slice of known volume, less the mass of solids in the water. ρ is the specific gravity, assuming a specific gravity of 2.5 for the dry solids and 1.03 for the water. Organic sulfur, hosted within particulate organic matter, was assumed to be 0.8% by weight of organic carbon (OC μmol g^{-1}) (Middelburg 1991).

Equation 4.6 does not account for solid phase sulfur containing minerals that may be deposited in detrital form. The amount of detrital (solid phase) sulfur deposited at the sediment water interface upon burial was not considered to be significant because sites are intertidal and are periodically exposed during low tide. Periodic exposure would result in the oxidation of sulfide exposed at the sediment water interface.

4.2.4.2 Method 2 - Integrated sulfate reduction rate versus sulfur accumulated

Under steady state diagenesis, and high sulfide retention rates, the amount of sulfur accumulated in sediments since burial at any depth (S_{acc}) should be equal to the sum of sulfate reduced during burial to that depth (ΣS_{red}) (Berner 1980). Under steady state conditions of porosity and burial rate, the rate of sulfate reduction (R_{SO_4}) can be described by Equation 4.7 (Berner 1980).

$$D_s \frac{\partial^2 SO_4}{\partial x^2} - w\frac{\partial\ SO_4}{\partial x} = R_{SO_4} \text{ (mol mL}^{-1}\text{ y}^{-1}) \qquad \text{(Equation 4.7)}$$

In Equation 4.7, SO_4 is the concentration of sulfate in the pore water (mol mL^{-1}), x is the depth (cm). $\partial SO_4 / \partial x$ and $\partial^2 SO_4 / \partial x^2$ were calculated from 4th or 5th order polynomial lines fitted to plots of measured SO_4 concentration versus depth (e.g., Chanton *et al.* 1987). w is the average burial rate of the core (cm y^{-1}) that is estimated from MAR.

However, changes in porosity and burial rate with depth were found to occur in all cores (see Figure 4.4) and this indicates non steady state conditions with respect to

these parameters. Under non steady state conditions of porosity and burial rate sulfate reduction rates can be calculated by Equation 4.8 after Murray *et al* (1978).

$$\frac{\partial\left(\phi^3 D_0 \frac{\partial SO_4}{\partial x}\right)}{\partial x} - \phi_x \omega \frac{\partial SO_4}{\partial x} = \phi R_{SO_4} \text{ (mol mL}^{-1}\text{ y}^{-1}\text{)} \quad \text{(Equation 4.8)}$$

In Equation 4.8, ϕ is predicted by a polynomial curve fit to the porosity data versus depth and ϕ_x is the porosity at the bottom of the core. Equation 4.7 and Equation 4.8 have been used to calculate sulfate reduction rates to examine if changes in porosity are a significant influence upon the models.

The total amount of sulfate reduced (ΣS_{red}) during burial of a layer to depth x=0 to its present depth can be calculated using Equation 4.9 (Berner 1980). If sediments are undergoing steady state diagenesis, and all sulfate reduced in the sediment is retained $\Sigma S_{red} = S_{acc}$. Variations in this relationship can be used to identify processes affecting the accumulation of sulfur in the cores.

$$\Sigma S_{red} = \int_0^x \frac{R_{SO_4}}{w} dx \text{ (mol cm}^{-3}\text{)} \quad \text{(Equation 4.9)}$$

4.2.5 Models of organic carbon decomposition and sulfate reduction

If sulfate reduction is the dominant process resulting in decomposition of organic matter, and there are high retention rates of sulfide, the amount of sulfur accumulated in an interval will be in proportion to the organic matter decomposed. This will be at a rate of approximately 1mole of sulfide for every 2 moles of organic carbon oxidised (Berner 1980). An estimate of the amount of sulfate reduced (*ESR*) in any sediment interval since burial to depth x due to the decomposition of organic carbon can be obtained by Equation 4.10.

$$ESR = \frac{OC_0 - OC_x}{2} \text{ (μmol g}^{-1}\text{)} \quad \text{(Equation 4.10)}$$

OC_x is the concentration of organic carbon remaining in the sediment at depth x, which has been measured. OC_0 is the initial concentration of organic carbon deposited at the sediment water interface, now buried to depth x, and was not directly measured. However, OC_0 can be estimated using published rates for the decomposition of organic matter.

The model of Middelburg (1989) recognises that the decay constant for organic carbon (k_t) is a function of time and decreases over time with a power type decay (Equation 4.11). The decay constant is claimed to be predictable over several orders of magnitude and is relatively invariant upon the environment of deposition.

$$k_t = 0.16(a+t)^{-0.95} \qquad \text{(Equation 4.11)}$$

In Equation 4.11, a is the apparent initial age of the organic carbon upon deposition. It is required to be approximated and the effect of varying a upon the model outcome have been evaluated. As a starting point, the minimum value of a is assumed to be the average age of the mixed layer, which was calculated using the probable age of sediment deposition (Table 3.3). The parameter t is the time since deposition of the sediment and is derived from models of MAR, using the probable age of sediment core slice deposition (Table 3.3).

By assuming first order kinetics for the oxidation of organic matter (Equation 4.12), and by combining Equations 4.11 and 4.12 followed by integration, the concentration of organic carbon remaining (OC_x) at any depth below the sediment water interface is given by Equation 4.13 (Middelburg 1989).

$$\frac{dOC_x}{dt} = -k_t OC_0 \qquad \text{(Equation 4.12)}$$

$$OC_x = OC_0 \, exp\left[3.2(a^{0.05} - (a+t_x)^{0.05})\right] \qquad \text{(Equation 4.13)}$$

OC_0 can be calculated by arranging Equation 4.13 into Equation 4.14.

$$OC_0 = \frac{OC_x}{exp\left[3.2(a^{0.05} - (a+t_x)^{0.05})\right]} \qquad \text{(Equation 4.14)}$$

The estimate of sulfate reduced (*ESR*) can then be calculated by combining Equation 4.10 with Equation 4.14 to form Equation 4.15. This equation assumes that 1 mole of sulfate is reduced for every 2 moles of organic carbon oxidised.

$$ESR = \frac{\left\{\frac{OC_x}{exp\left[3.2(a^{0.05} - (a+t_x)^{0.05})\right]}\right\} - OC_x}{2} \qquad \text{(Equation 4.15)}$$

The ratio ESR/S_{acc} is a measure of the sulfate reduced, under modelled conditions relative to the actual sulfur accumulated in the sediment. The difference in this ratio among cores and within cores can be used to evaluate the influences of the rate of organic carbon decomposition upon sulfur accumulation. This ratio will also be compared with the ratio of organic carbon to sulfur, the degree of pyritisation (DOP) and the degree of sulfidation (DOS). These measures have been approximated by Equations 4.16 and 4.17. The pyrite concentration is estimated to be half the residual concentration of S_{acc} after AVS has been subtracted ($0.5[S_{acc}\text{-}AVS]$). This assumes that the residual sulfur species is FeS_2, and that AVS is FeS.

$$DOP = \frac{0.5(S_{acc} - AVS)}{Whole\ sediment\ strong\ oxidising\ acid\ soluble\ Fe} \quad \text{(Equation 4.16)}$$

$$DOS = \frac{0.5(S_{acc} - AVS) + SEM\ Fe}{Whole\ sediment\ strong\ oxidising\ acid\ soluble\ Fe} \quad \text{(Equation 4.17)}$$

4.3 Results

4.3.1 Bulk sediment geochemistry

Significant variation in the concentration of Al, OC and Ca are created by variations in grain size and mineralogical composition within and among cores (Figure 4.2). Muddy fine-grained sediments (Cores 1831 and 1832) contain higher concentrations of Al than do coarser grained sandy sediments (Cores 1827 and 1829). High concentrations of OC in cores 1831 and 1832 are influenced by the location of these cores in small mangrove fringed creeks, whereas higher concentrations of Ca in cores 1827 and 1829 are influenced by the presence of more calcium carbonate sedimentary materials and are indicative of more marine source of sediment at these locations.

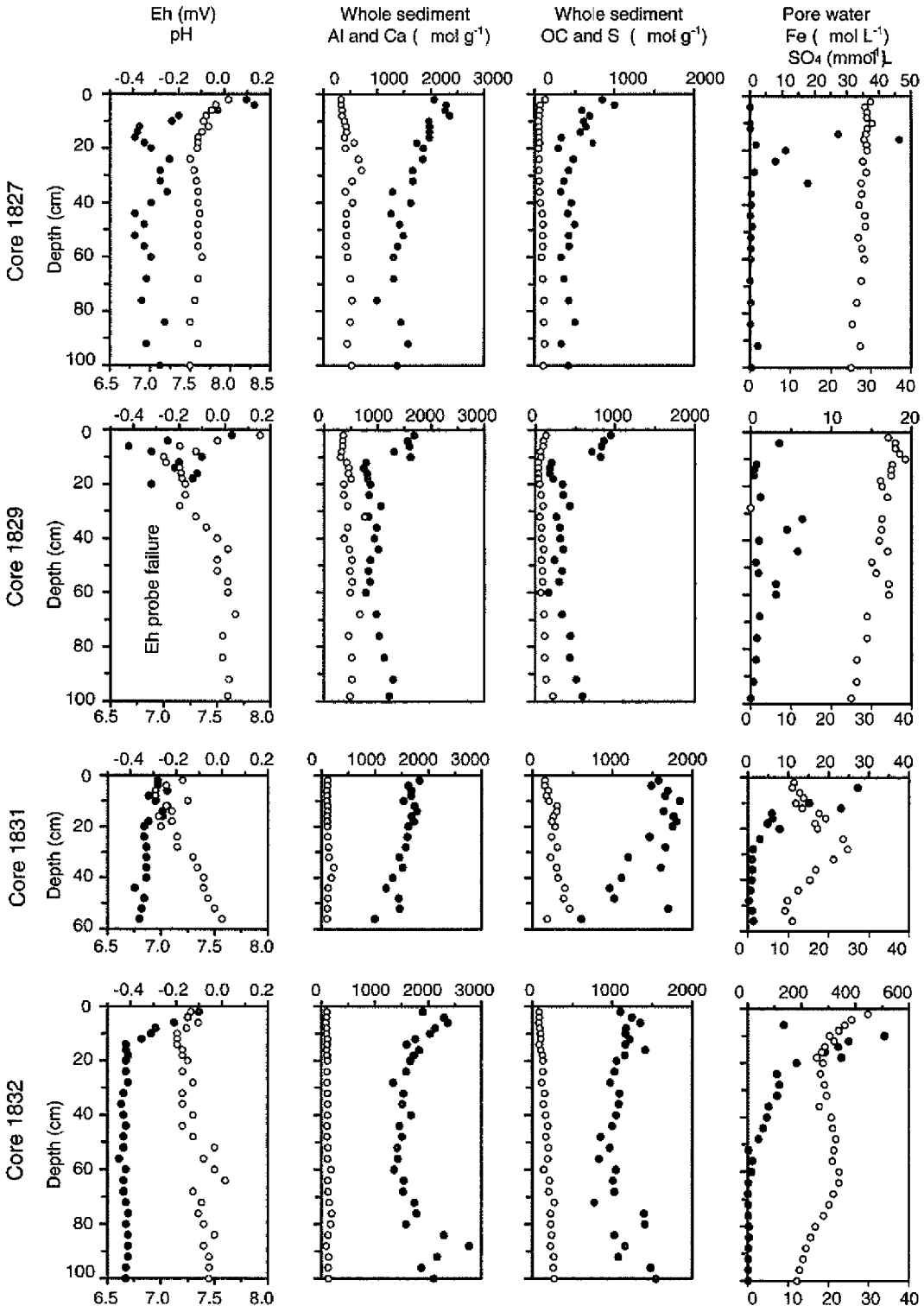


Figure 4.2 Sediment core profiles of Eh, pH, whole sediment strong acid soluble elemental concentrations and dissolved elemental concentrations in pore waters. Cores 1831 and 1832 are enriched in OC relative to cores 1827 and 1829, which are relatively enriched in Ca. Eh (●), pH (○), whole sediment Al (●), whole sediment Ca (○), whole sediment OC (●), whole sediment S (○), Pore water Fe .(●), Pore water SO4 (○).

A plot of 1M HCl soluble Fe against *Sacc* (Figure 4.3) indicates a general trend within cores of declining 1M HCl soluble Fe concentrations with increasing *Sacc*. This is most apparent within core 1832 (Figure 4.3) that has samples distributed perpendicular to the trend of increasing 1M HCl soluble Fe with increasing *Sacc*. The plot of strong acid soluble Fe versus *Sacc* indicates that strong acid soluble Fe concentrations greatly exceed *Sacc* concentrations (Figure 4.3). Therefore, Fe does not limit accumulation of sulfur.

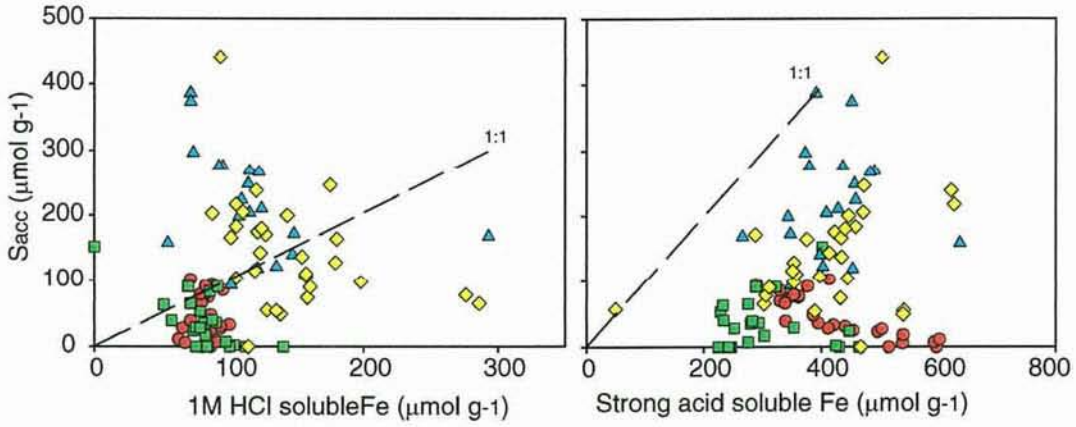


Figure 4.3 Relationships between *Sacc*, 1M HCl soluble Fe and strong acid soluble Fe. Strong acid soluble Fe exceeds the *Sacc* in all cores. Core 1827 (●); Core 1829 (■); Core 1831 (▲); Core 1832 (◆).

Profiles of Eh and pH are used to demonstrate qualitative trends in sediment geochemical properties. Cores exhibit more positive Eh potentials near the surface and grade to more negative as well as constant potentials by 20 cm depth (Figure 4.2). The values of pH are near 7.5 and constant at the base of each core. These trends in Eh and pH are best demonstrated by cores 1827 and 1832 that are Al rich fine-grained terrigenous muds.

The trends in Eh and pH in core 1829 are complicated by changes in sediment composition (Figure 4.2), where reduced, fine-grained and Al rich sediments overlay more oxidising coarser grained sediments. The trends in Eh, pH and pore water SO_4 in core 1831 are complicated by a significant rain event (> 150 mm in 24 hours) that occurred during the sample period. This resulted in freshwater infiltration in core 1831 and is responsible for the decay in pore water SO_4 concentrations towards surface and pH values less than 7 near surface.

For mass balance calculations in core 1831 the pore water SO_4 concentrations were substituted with values that were considered to be representative of normal tidal influences (Figure 4.4). These values were obtained by assuming surface water SO_4 concentrations are between 30 to 35 mmol L^{-1} and fitting a polynomial curve to a surface concentration of 32.5 mmol L^{-1} and measured SO_4 concentrations below 30 cm. The high SO_4 concentrations (> 30 mmol L^{-1}) in surface waters are characteristic of the region during the dry season (e.g., Walker 1981). Within the intertidal zone they are further enhanced by the presence of hypersaline salt flats adjacent the creeks. This effect is most obvious in core 1829 where pore water concentrations are > 35 µmol mL^{-1} below 10 cm depth.

4.3.2 Sulfur mass balance

The sulfur mass balance attempts to reconcile the diffusive flux of sulfate, based upon the decline in the pore water SO_4 concentrations with depth, with the measured increase in S_{acc} concentrations with depth (Figure 4.4). Methods 1 and 2 indicate a greater rate of sulfur burial at the base of each core relative to the flux of sulfate across the sediment water interface, and the total sulfate reduced (Table 4.1). This indicates that the decline in concentration of pore water SO_4 with depth is insufficient to account for the sulfur that has accumulated in each core since burial.

The difference between using Equation 4.7 relative to Equation 4.8 to calculate the total sulfate reduced is negligible. The similarity of both these results (Table 4.1) indicates that changes in porosity and burial rate are not a source of the observed imbalance between of ΣS_{red} with S_{acc}. This suggests that the pore water SO_4 concentration profiles are non steady state and are prone to fluctuations.

The low rate of decline in pore water SO_4 concentrations suggests that the pore waters are open to the resupply of sulfate. Processes other than simple diffusive resupply of sulfate are implicated in the resupply process by the presence of a sub surface peak in pore water SO_4 concentrations at depth in core 1832 (Figure 4.4). This interval corresponds to a more silt rich interval. Similarly, steep profiles of pore water SO_4 concentrations also occur in core 1827 and 1829, which have intervals of silt to sand rich sediments. This suggests that resupply is enhanced in coarser grained sediments, probably by flow through more permeable sediment.

Table 4.1 Summary of the results of sulfur mass balance calculations for sediment cores from Cleveland Bay. Methods 1 and 2 have been calculated using parameters determined by the minimum MAR and probable MAR. The sulfur burial flux is calculated for the base of each core (98cm depth for 1827, 1829 and 1832, *60cm depth for 1831)

	Minimum MAR				Probable MAR			
Method 1	**1827**	**1829**	**1831***	**1832**	**1827**	**1829**	**1831***	**1832**
Sulfate flux (mol m^{-2} y^{-1}) (Equation 4.1)	0.41	0.24	1.52	1.95	0.41	0.12	1.25	1.10
Sulfur burial flux (mol m^{-2} y^{-1}) (Equation 4.5)	1.05	2.78	8.48	7.69	1.05	4.5	21.56	12.88
Sulfate flux/sulfur burial (%)	40	9	18	27	40	3	6	8
Method 2								
Total sulfate reduced (ΣS_{red} µmol cm^{-3}) (Equations 4.7/4.8)	3.4/11.9	20.8/31.2	77/117	47.1/43.5	3.4/11.9	15.2/23.0	41.4/57.3	32.9/24.1
Sulfur accumulated (S_{acc} µmol cm^{-3}) (Equation 4.6)	105	91	440	194	105	91	440	194
ΣS_{red} /S_{acc} (%)	3/11	23/34	18/27	24/22	3/11	17/25	9/12	17/12

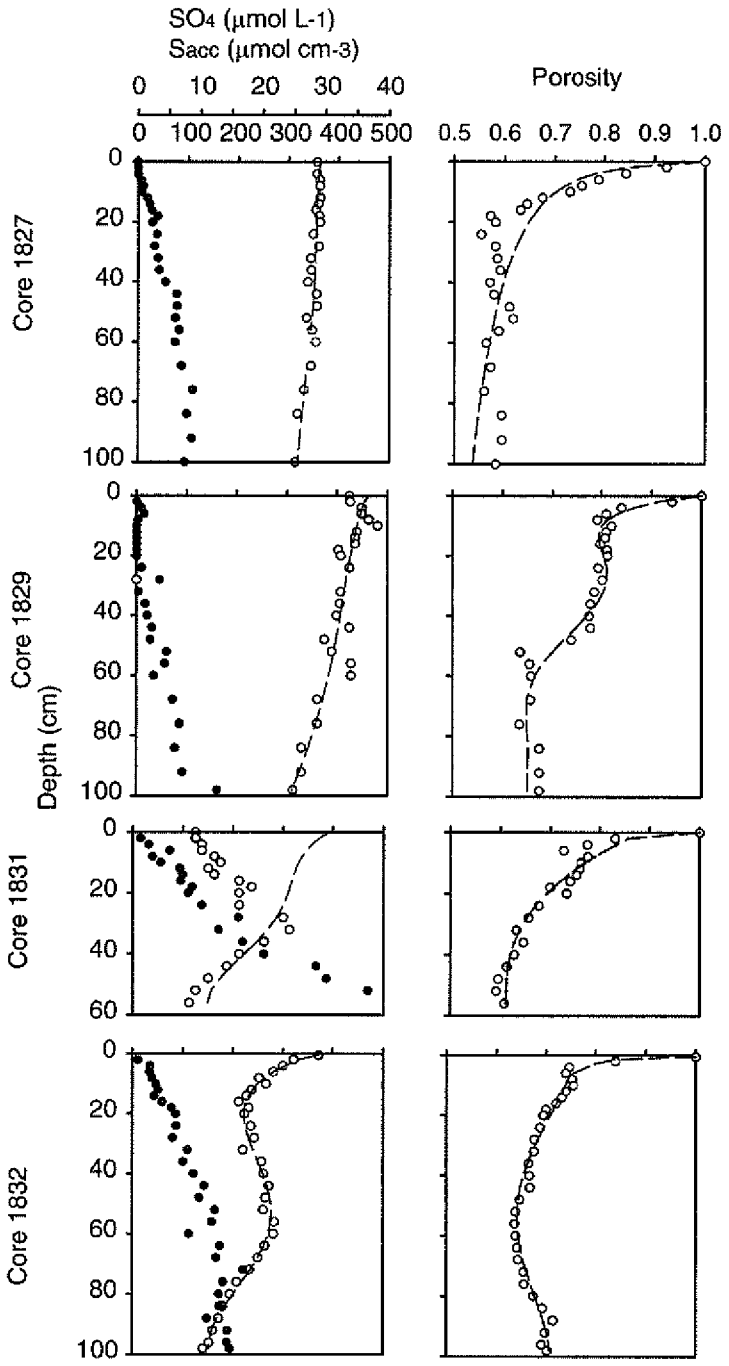


Figure 4.4 Sediment core profiles of *Sacc*, *SO4* and porosity used to calculate the sulfur mass balance. *Sacc* (●); *SO4* (○); porosity (○) polynomial fitted to *SO4* and porosity profiles (- - -).

4.3.4 Influence of organic carbon decomposition upon sulfur accumulation

The estimate of sulfate reduced (*ESR*) was calculated by Equation 4.13 using parameters based upon the probable MAR (Table 3.3). In these calculations the initial age parameter (*a*) is assigned the average age of the mixed layer. The plot of S_{acc} versus *ESR* for each core is presented as Figure 4.5. The trends displayed are characterised by a positive linear relationship, with a coefficient of determination (R_2) greater than 0.8, except core 1831 ($R_2 = 0.61$). If the bottom four samples are removed from core 1831 the R_2 value increases to 0.88. This indicates that the *ESR*, which is based upon a model of the kinetics of organic carbon decomposition, can explain the majority of the variation in S_{acc} among and within cores.

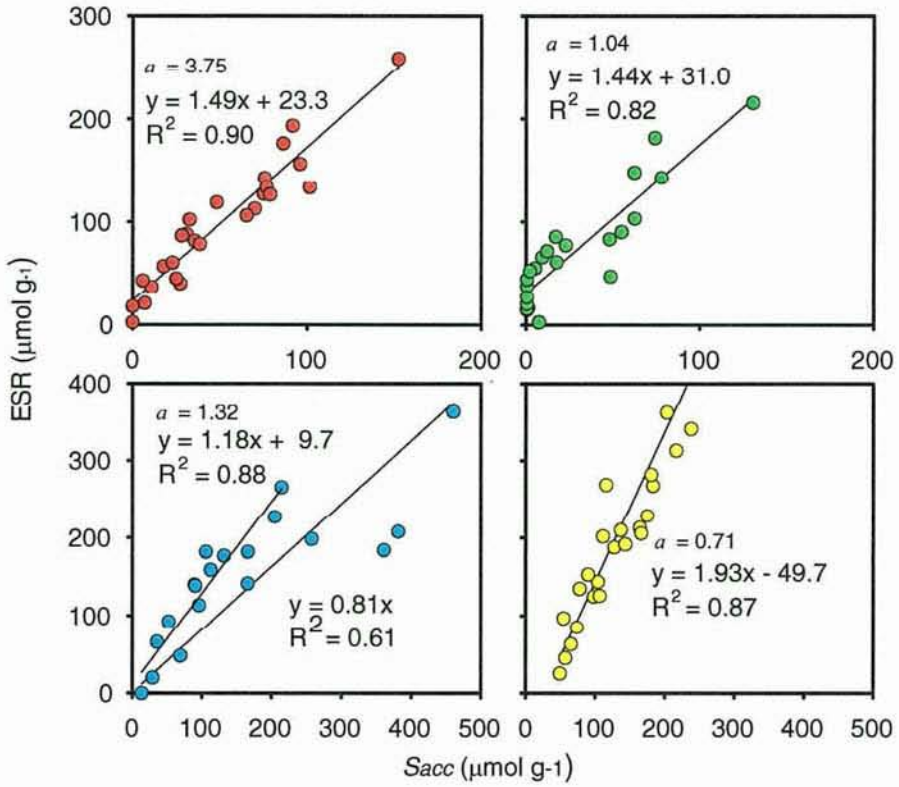


Figure 4.5 Plots of S_{acc} versus *ESR* for cores 1827, 1829, 1831 and 1832. The line of regression and coefficient of determination (R_2) is presented for each core. *a* is the value of the initial age parameter used in calculation of Equation 4.13. Two lines of regression are presented for core 1831, where one excludes 4 samples from the base of the core. Core 1827 (●); core 1829 (●); core 1831 (●); core 1832 (○).

The slope of the line of regression formed for cores 1827, 1829 and 1832 is characterised by a value that is > 1 (Figure 4.5). This indicates that Equation 4.13, used to calculate the *ESR*, consistently predicts more organic matter is decomposed during burial than can be accounted for by the sulfur accumulated since burial. Assuming that the rate constant of Middelburg (1989) is correct, either a constant portion of the sulfate reduced is lost, or some of the organic matter in the mixed layer does not undergo decomposition by sulfate reduction.

Core 1831 has a distinctly lower slope than other cores, which is influenced by at least 4 outlying samples, which come from the lower 4 sample intervals (Figure 4.5). If these samples are removed from the regression the core still has a lower slope than other cores. This indicates that this core retains a greater amount of the sulfate reduced (high sulfide retention rate), or that more organic matter undergoes decomposition by sulfate reduction relative to other sites.

Adjusting the slope of the relationship between S_{acc} and *ESR*, can be used to estimate differences in the relative amounts of organic carbon undergoing decomposition, or the retention rate of sulfide. Changes in slope can be made by multiplying the value of *ESR* by a correction factor (r), or by changing the value of *a*. The correction factor (r), which results in parity between *ESR* and S_{acc}, is different for each core, and ranges between 0.55 to 0.85, where 1832 (0.55) < 1827 (0.68) < 1829 (0.74) < 1831 (0.85). This correction does not result in changes to the R^2 value between *ESR* and S_{acc} (Figure 4.6*a*). Increasing the value of *a* in Equation 4.13 can also result in parity between *ESR* and S_{acc} (Figure 4.6*b*). Core 1827, which has the lowest MAR is required to have the largest increase in the value of *a* to achieve parity (Figure 4.6*b*).

The intercept of the line of regression for each core is variable. Cores 1827 and 1829 have a distinct non-zero intercept that is created by very low S_{acc} near surface (Figure 4.4). This suggests significant loss of sulfide from the top of these cores. In contrast Core 1832 has a strong positive intercept. This suggests the input of sulfide into the sediment near surface

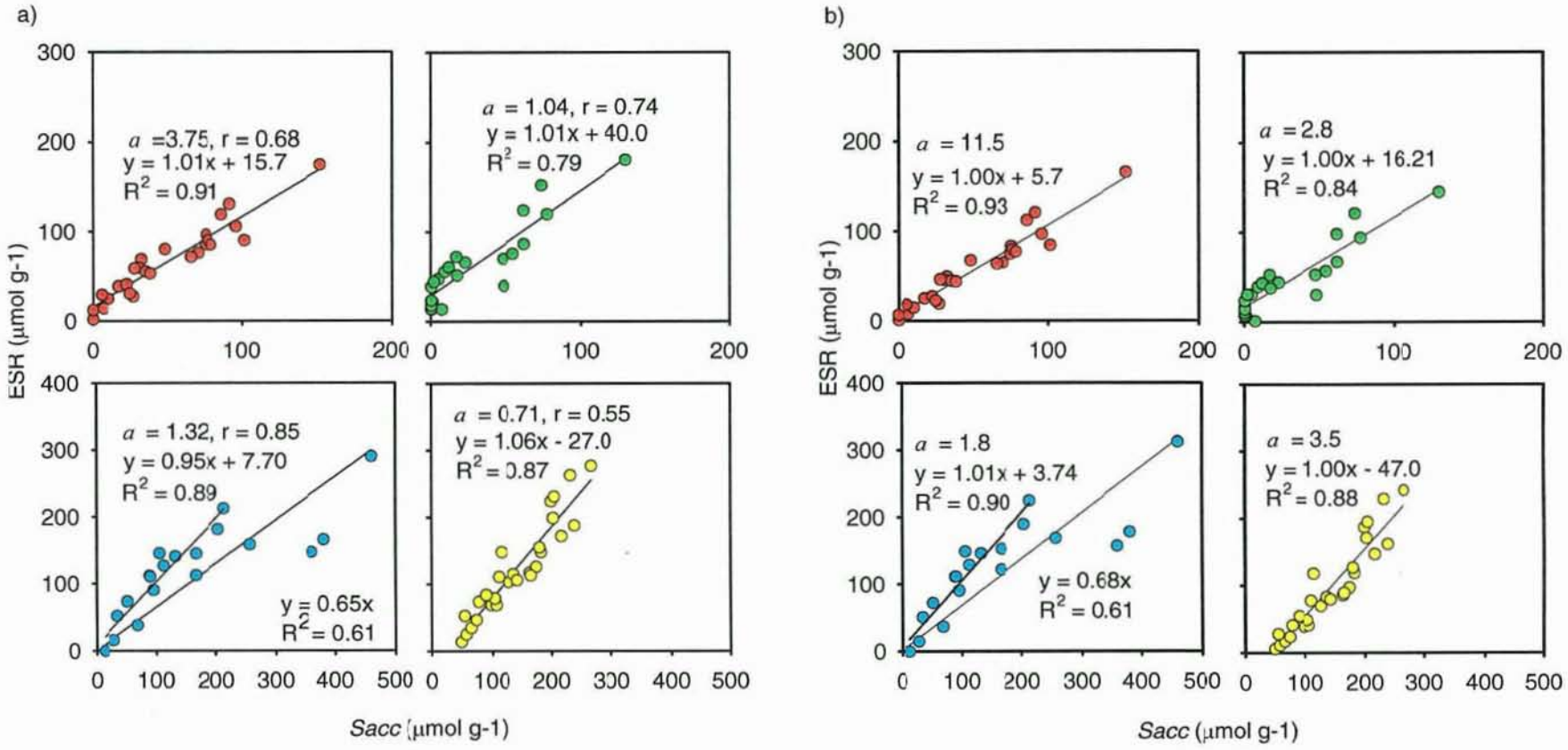


Figure 4.6 Plots of S_{acc} versus adjusted *ESR* values. a) *ESR* adjusted by multiplying by a correction factor (r), using the initial age parameter (*a*) set as the average age of the mixed layer. b) *ESR* adjusted by changing the a to create parity with S_{acc} . The line of regression and coefficient of determination (R_2) is presented for each core. Two lines of regression are presented for core 1831, where one excludes 4 samples from the base of the core. Core 1827 (●); core 1829 (●); core 1831 (●); core 1832 (○).

4.4 Discussion

4.4.1 Identifying influences upon sulfur accumulation from mass balances

Mass balance approaches can be applied to assess influences upon sulfur dynamics in marine sediments (e.g., Casey & Lasaga 1987; Chanton 1987; Aller & Blair 1996). However, the environment of deposition of the cores in this study are unusual, in respect of the very high mass accumulation rates of terrigenous sediments and time frames of deposition (typically < 30 years).

Measuring sediment accumulation rates over short time scales is essential if the rates of early diagenetic processes are to be estimated. The short period of deposition of sediment makes the application of ^{210}Pb radiochemistry to constrain mass accumulation rates (MAR) and infer rates of early diagenetic processes problematic. Based upon near homogenous radio tracer distributions (Figure 3.5), sediments in cores 1829, 1831 and 1832 could be interpreted to be near homogenously mixed, or a consequence of a single sediment deposition event.

If sediments were homogenously mixed, or were a result of single depositional event, the profiles of S_{acc} (Figure 4.4) would not exhibit a consistent and smooth increase with depth. This feature, which is apparent in all cores, supports the assumption of continuous flux of sediment to each site, with a fixed and shallow (< 10 cm) mixed layer depth (Table 3.3). Significant breaks in sedimentation, or sedimentation events, would be marked by irregular profiles of S_{acc} with depth. Other evidence supporting that the cores are not homogenously mixed include, the absence of ^{234}Th below 2 cm depth (Table 3.3) and distinct changes in sediment composition in cores (e.g., 1829, Figure 4.2). The homogenous distribution of radioisotopes is therefore a function of the relatively long half-life of the isotopes measured (~25 years), relative to the short time intervals being examined (< 30 years). The apparent mixing is entirely a function of the behaviour and half-life of the parameter being used as a tracer of mixing.

The flux of particulate materials to the sediment water interface is variable in composition over time (Figure 4.2). Surface water and pore water concentrations are

variable (Figure 4.2) and the sediments undergo significant compaction and porosity changes during burial (Figure 4.4). The changes in these parameters with depth indicate that sediments in cores 1827, 1829, 1831 and 1832 are undergoing non steady state diagenesis.

Because of non steady state conditions, sulfur mass balances have been calculated using two methods. Method 1 (Equation 4.7) assumes a steady state burial rate, no compaction and steady state pore water sulfate concentration profiles. Method 2 (Equation 4.8) takes into account changes in porosity and burial rate. Furthermore, because of the uncertainties in estimating the time of deposition of sediments in cores 1829, 1831 and 1832, calculations have been undertaken using both the minimum MAR and probable MAR (Table 4.2).

Both mass balance methods indicate pore water sulfate profiles underestimate the amount of sulfate being reduced. There is also little difference in the total sulfate reduced calculated using Equation 4.7 relative to Equation 4.8 (Table 4.2). This indicates that changes in burial rate and sediment porosity within cores have little influence upon the total amount of sulfate reduced (Table 4.2). The effect of using the probable MAR, rather than the minimum MAR, is to increase the burial rate of sulfur at the base of each core. However, using both the minimum MAR and probable MAR, the rate of sulfur burial is greater than can be accounted for by the diffusive resupply of SO_4 based upon the decline with depth in concentration of pore water sulfate (Table 4.2).

The sulfur burial rates, calculated at 20 cm depth for each core using the probable MAR, are 0.27 (1827), 0.47 (1829), 11.82 (1831) and 3.14 (1832) mol m^{-2} y^{-1}. These rates are of a similar order of magnitude to the depth integrated (18-20 cm) sulfate reduction rates measured in Hinchinbrook Channel of 8.7-11.2 mol m^{-2} y^{-1} by Alongi (1995). The similarity of these rates suggests that the sulfur burial rates approximate real sulfate reduction rates. This also supports the conclusion that the decline in pore water sulfate is anomalously low. This is interpreted to indicate that the resupply of pore water sulfate is much greater than the rate of sulfate reduction.

The high burial rate and short time scales being investigated result in incomplete early diagenetic processes (e.g., Berner 1980). In all cores the reactive Fe is not exhausted, metabolisable organic carbon is available over the entire core length, sulfate

supply is unlimited, and the limit of sulfate reduction is not reached. Therefore the accumulation of sulfur is not limited by the supply of sulfate.

4.4.2 Influences upon sulfur accumulation identified by models of organic matter decomposition.

ESR is an estimate of the sulfate reduced that is predicted by a model of organic matter decomposition (Equation 4.15). For each core the rate of decay of organic matter is held constant and the initial age parameter (a) is determined by constraints placed upon average age of the mixed layer by models of MAR (described in chapter 3). Examining the relationships between *ESR* and S_{acc}, where S_{acc} is the measured amount of sulfur accumulated in sediments, can identify influences upon sulfur accumulation related to changes in rate of decay of organic matter.

A linear relationship between *ESR* and S_{acc} indicates that sulfur is accumulating in sediments in proportion to the rate of decomposition of organic matter. Parity between *ESR* and S_{acc} indicates that all the organic matter is oxidised by sulfate reduction, and all sulfate reduced is retained in the sediment as authigenic sulfide minerals.

The linear and positive correlation between *ESR* and S_{acc} in Figure 4.5 indicates Equation 4.15 explains between 82% and 90% of the variation in S_{acc} concentration within each core. This relationship also indicates that the rate of organic matter decomposition is the predominant influence upon the changes in S_{acc} with depth in each core.

The slope of the relationship between *ESR* and S_{acc} is dependent upon the value of a, and parity can be achieved by increasing the value of a (Figure 4.6b). The value of a in Figure 4.5 is set as the average age of the mixed layer and the *ESR* predicted by this value consistently exceeds the measured S_{acc} (slope > 1). This suggests that the true value of a is greater than the average age of the mixed layer used to calculate *ESR* in Figure 4.5. The reasons why increasing the value of a results in parity between *ESR* and S_{acc} requires a greater understanding of what a represents.

The initial age parameter a

The parameter a is introduced to Equation 4.13 as a time variable, that is a function of the MAR. It is used to recognise that not all of the initial concentration of organic matter that is oxidised goes towards the formation of authigenic iron sulfides. Organic matter may undergo decomposition prior to burial (Middelburg 1989), or during burial by processes that include: oxic degradation, nitrate reduction; Mn oxide reduction, Fe oxide reduction and sulfate reduction (e.g. Murray *et al.* 1978; Goldharber & Kaplan 1982;Veeh *et al.* 1999).

The net effect of these processes is to degrade the metabolisable portion of organic matter, so that the organic matter available for sulfate reduction is more refractory. Increasing the value of a, or the period of oxidation of organic matter prior to burial, reduces the amount of metabolisable organic matter that is available for sulfate reduction, and lower values of *ESR* are predicted by Equation 4.15. The parameter a determines the metabolic properties of the organic carbon that is buried.

The value of a used to calculate *ESR* in Figure 4.5 is the average age of the mixed layer. It represents the minimum possible age of the organic matter because it assumes that; 1) the initial age of the organic matter is the depositional age of the sediment (i.e., organic matter is pristine and not reworked detrital material); and 2) that oxidation of organic matter occurs only by sulfate reduction during burial.

Using the average age of the mixed layer as the value of a, the correction factor (r) required to multiply *ESR* by to achieve parity with S_{acc}, is a measure of the portion of organic matter that is consumed by sulfate reduction and retained in the sediment as authigenic iron sulfide. For core 1831, $r = 0.85$, which indicates that at least 85% of the available organic matter is consumed by sulfate reduction, and the sulfate reduced is retained in the sediment as authigenic sulfide. All other cores have lower values of r (Figure 4.6a), with core 1832 having the lowest value (55%).

Assuming sulfate reduction is the predominant process resulting in oxidation of organic matter, would indicate that between 15 to 45% of the sulfide formed is lost from the sediment. Alternatively, assuming no loss of sulfide, 15 to 45% of organic matter may be oxidised by processes other than sulfate reduction during burial. However, a combination of loss of sulfide and oxidation by other processes probably occurs.

Loss of sulfide and sulfide retention

Sulfide retention refers to the ability of sediments to retain the sulfide produced by sulfate reduction. If sulfate reduction is the predominant process oxidising organic matter, the values of r can be considered representative of sulfide retention rates. The value of r ranges from 55 to 85%, and is high when compared to other published sulfide retention rates. Berner & Westrich (1985) have found sulfide retention rates of up to 75 %. However, retention rates are more commonly described to be less than 15% (e.g., Chanton *et al.* 1987; Aller & Blair 1996 Henneke *et al.* 1997).

No independent measurements of sulfide retention rate have been made in this study. However, high retention rates of sulfide are supported in the cores being studied considering that; 1) All cores have high rates of burial (Table 3.3), which is known to increase sulfide retention (Morse & Berner 1995). 2) All cores have shallow mixed layers (Table 3.3) that limits the oxidation of newly formed sulfide by exposure to oxic conditions (e. g. Goldharber *et al.* 1977, Lord & Church 1983). 3) All cores have an abundance of reactive Fe (Figure 4.3*)* which will react with H_2S to form insoluble sulfides and trap the sulfide in the sediment (e.g. Chanton *et al.* 1987; Martens 1993; Gagnon *et al.* 1995). 4) No H_2S odours were noticed during sampling of cores, indicating very low concentrations of free H_2S in the sediments.

Loss of sulfide from cores 1827 and 1829 is evident by the positive intercept on the *ESR* axis of the line of regression formed by between S_{acc} and *ESR* (Figure 4.5). The positive intercept, and poor fit of near surface samples, which have low S_{acc} values, indicates that there is a fixed amount of S_{acc} lost from each interval relative to the *ESR*. The linear relationship for samples that have higher S_{acc} values, and are located at lower depth intervals, indicates that there is no loss of sulfide at depth. Rates of loss should be greater near surface, due to the enhanced supply of oxygen created by bioturbation and exposure of sediment during low tide (e.g., Goldharber *et al.* 1977; Casey & Lasaga 1987; Martens 1993). Therefore, the non-zero intercept on the *ESR* axis for cores 1827 and 1829 is consistent with the oxidative loss of sulfide from near surface sediments.

In contrast to cores 1827 and 1829, a positive intercept occurs on the S_{acc} axis for core 1832. This suggests there is more sulfide in the sediment that can be accounted

for by the *ESR*. This is probably due to the presence of detrital sulfides, but other sources such as diffusion of sulfide cannot be excluded (e.g., Murray *et al.* 1978).

These data indicate that the oxidative loss of sulfide occurs near surface. However, the amount lost, which is given by the intercept of the line of regression between *ESR* and S_{acc} in Figure 4.5, is a fixed amount, and is less than the 15 to 45% indicated by the value of *r*. This suggests that other processes are creating a deficit in the measured amount of S_{acc} relative to the modelled *ESR*.

Oxidation of organic matter

Oxidation of organic matter, by biogeochemical processes, during burial results in degradation of the metabolic properties of organic matter. The metabolic properties of organic matter have been found to be a function of burial rate (e.g., Berner 1980). At higher rates of burial, greater amounts of metabolisable organic matter is buried before it can be fully degraded. Cores that have high MAR require lower values of *a* because more organic matter is preserved. This is supported in the four cores from Cleveland Bay by the larger increase in the value of *a* required to achieve parity in core 1827, which also has the lowest MAR (Figure 4.7). However, the relationships between burial rate and the value of *a* can not be measured in the four cores examined because of the limited range of MARs in cores 1829, 1831 and 1832 (all very high).

Differences in the metabolic properties of organic matter among cores can also be created by differences in source of organic matter. The organic matter contained in the mixed layer is derived from several sources, including detrital terrigenous and marine sources, as well as being produced in situ (e.g., Middelburg 1991). Detrital organic matter may be reworked and it may be more refractory than pristine organic matter. Terrestrial organic matter, in particular mangrove detritus, has also been found to be highly refractory relative to organic matter supplied from marine sources (e.g. Alongi 1990; Kristensen *et al.* 1992; Woolfe *et al.* 1995). The intertidal location of sites, situated in mangrove dominated environments, suggests that the predominant source of organic matter to the sites is relatively refractory mangrove detritus.

If sulfide retention rates are high and sulfate reduction is the predominant process oxidising organic matter, then 15 to 45% of the organic matter could be

refractory. A 10% residual organic phase, which does not undergo decomposition, was used by Tromp *et al.* (1995) in global models for the decomposition of organic carbon.

A higher residual portion of organic matter is probably justified in the cores of this study, because the dominant supply of organic matter is dominantly mangrove detritus. This would require modifying the power rate of decay model of Middelburg (1989), to form two discrete pools of metabolisable and refractory organic matter. The concept of a pool of organic matter that is not metabolisable is in line with several discrete pools of organic matter undergoing decomposition at different rates, which is the basis of the multi G model of organic carbon decomposition (Berner 1980; Westrich & Berner 1984). However, the power rate of decay of organic matter of Middelburg (1989) attempts to rationalise several pools of organic matter undergoing different rates of decomposition, into a single pool undergoing time dependent rate of decomposition. Therefore the presence of a separate pool of refractory organic matter should not be necessary.

These data indicate that the metabolic properties of organic matter are degraded during oxidation by processes other than sulfate reduction. The source of the degradation is probably due to reworking of organic matter prior to burial or degradation by other biogeochemical processes.

4.4.3 Application of models to identify different influences upon sulfur accumulation

The relationships between Fe, OC and S in sediments can be used to generate models that can identify the environment of deposition (e.g., Aller & Blair 1996; Gerritse 1999). This is because environments can be characterised by processes that influence sediment geochemical properties. For example, the ratio of OC and S can be used to discriminate between marine and freshwater environments of deposition (Berner & Raiswell 1983).

This is possible because in fresh water environments, where there may be an abundance of organic matter, sulfate reduction is limited by the supply of sulfate. In Figure 4.7*a*, the OC/S ratios have a range of between 2.5-15 and have a near zero intercept. The range of this ratio includes normal marine conditions (1.5-4; Berner & Raiswell 1984), but is also within the range of saline to freshwater conditions (4-17; Woolfe *et al.* 1995). The large range in ratios is created by incomplete degradation of organic matter in the upper parts of the cores. This is indicated by changes in the OC/S ratios from 10-15 at the top of the core to 2.5-4.0 at the base (Figure 4.7a).

The ratios DOP and DOS are referred to as the degree of pyritisation (Raiswell & Berner 1985) and the degree of sulfidation (DOS) (Boesen & Postma 1988). DOS is used where the formation of Acid Volatile Sulfides (AVS) in sediments is significant. The benefit of this ratio can be observed for core 1831 in Figure 4.8 where the plot of OC/DOP appears to identify core 1831 as having very high DOP values relative to other cores. However, the plot of OC/DOS indicates the sediment does contain sulfidation ratios similar to other cores. This is because AVS is a more significant authigenic sulfide phase in core 1831. In Figure 4.8, the DOP and DOS ratios fall between 0 to 0.3 and 0 to 0.6 respectively and are typical of marine sediments (Raiswell *et al.* 1988). These ratios indicate that sulfide in the cores is greatly exceeded by the reactive Fe, and therefore the formation of authigenic iron sulfide minerals is not limited by the supply of reactive Fe.

Similar to the ratios OC/S, DOP and DOS, the ratio of *ESR* to S_{acc} can be used to identify differences between sites. It can be used to identify changes in the source of organic matter, if the changes are associated with changes in the metabolic properties of organic matter. This can be demonstrated by comparing the differences in the slope of the line of regression between *ESR* to S_{acc} among cores.

Core 1831 has the lowest slope of 1.18 (Figure 4.5), and the correction factor (r) of this slope to achieve parity is 0.85 (Figure 4.6). This indicates that 85% of the organic matter is available for sulfate reduction at this site compared to other core sites (55-75%). If the outlying four points at the base of core 1831 are included, the amount of available organic matter is even greater (Figure 4.5). The outlying points at the base of core 1831 indicate a distinctly more metabolisable organic matter source at depth.

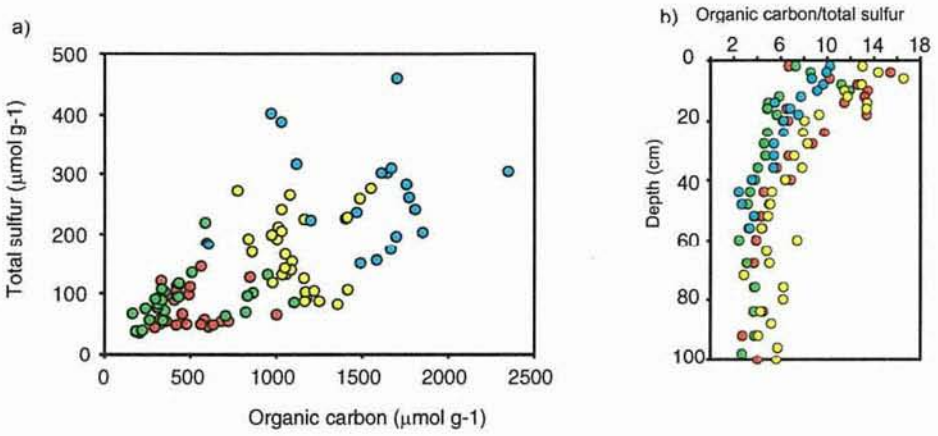


Figure 4.7 Plots of organic carbon and sulfur relationships in cores from Cleveland Bay. a) Plot of organic carbon versus total sulfur in sediment samples ;b) Plot of the ratio of organic carbon/sulfur versus depth. Core 1827 (●); Core 1829 (●); Core 1831 (●); Core 1832 (●).

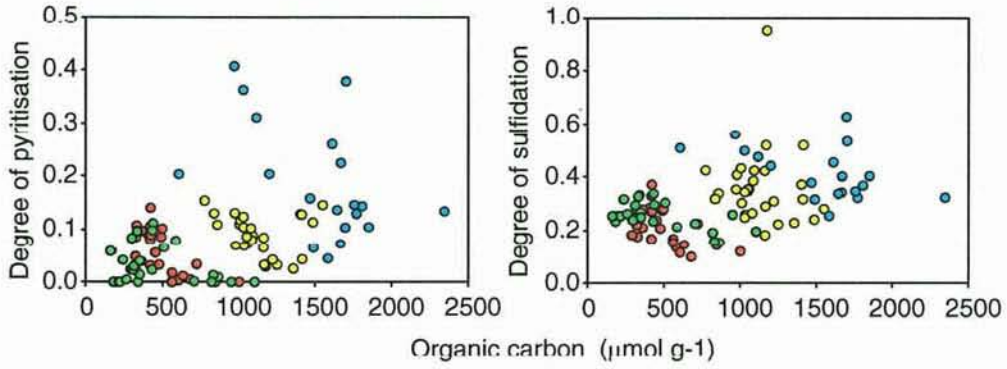


Figure 4.8 Plots of DOP and DOS versus Organic carbon concentration. Among cores there is a general trend of increasing DOP and DOS with increasing Organic carbon concentration. Within cores, samples are aligned perpendicular to the trend observed among cores. Core 1827 (●); Core 1829 (●); Core 1831 (●); Core 1832 (●)

This suggests that the organic matter supplied to the site is more metabolisable than other sites, and has changed over time

This interpretation is consistent with the location of core 1831 in Sandfly Creek, which also contains a treated sewage effluent outfall. This supports the hypothesis that that the organic matter supplied to this site has more favourable metabolic properties than that supplied to other sites. Similarly the outlying points at the base of core 1831 indicate a change in metabolic properties of organic matter over time that may be related to upgrading of the facilities during the late 1980s (Pringle 1989).

4.5 Conclusions

Mass balance of dissolved and solid phase sulfur concentrations indicates that all cores are open to the resupply of sulfate. Despite being open to resupply of sulfate, sediments probably have a high retention rate of the sulfide due to abundant reactive Fe and high burial rates.

A model of the rate of organic matter decomposition explains between 82 to 90% of the variance observed in the sulfur accumulated in sediments of cores from Cleveland Bay. Therefore the rate of organic matter decomposition is the dominant influence upon sulfur accumulation within individual sediment cores.

However, the model indicates that either 15-45% of the organic matter does not undergo decomposition via sulfate reduction, or that 15-45% of the sulfate reduced by decomposition of organic matter is not retained in the sediment. A combination of these two possibilities occur, where the deficit between the measured S_{acc} and predicted ESR is more a consequence of the degradation of organic matter by biogeochemical processes other than sulfate reduction in near surface sediments, rather than oxidative loss of sulfide.

The ratio of the estimate of sulfate reduced, based upon the model for the decomposition of organic matter, versus the sulfur accumulated in sediments since burial can be used to identify differences in the source of organic matter if sources have different metabolic properties. Core 1831 has organic matter that is more metabolisable than other sites. The source of this organic matter is probably from a sewage treatment plant.

Chapter 5

Influence of authigenic sulfides upon trace metal speciation - implications for the interpretation of ΣSEM/AVS ratios

5.1 Introduction

Sediments are not passive recipients of particulate materials, they are biogeochemical reactors that are fuelled by the decomposition of organic matter (Van Cappellen & Wang 1995). These biogeochemical processes result in changes to sediment geochemistry that have environmental implications. The most significant of these is the interactions of authigenic sulfide minerals with trace metals.

The interaction of authigenic sulfide minerals with trace metals results in partitioning of metals into different sulfide mineral phases, which have different chemical properties (e.g., Morse 1995). The properties of each phase can have significant consequences upon sediment quality by determining the 'bioavailability' of metals (Di Toro *et al.* 1990).

Interaction between authigenic sulfide mineral species and trace metals is generally described to occur within two operationally defined pools: 1) acid volatile sulfides (amorphous FeS, mackinawite [FeS], greigite [Fe_3S_4]); and 2) pyrite (FeS_2) (e.g., Morse 1995). This interaction is typically found to result in the formation of insoluble metal sulfide mineral species that reduce the 'bioavailability' of metals (e.g., Di Torro *et al.* 1990). The interaction of metals and polysulfide species has been theoretically found to result in the formation of soluble metal sulfide species, resulting in an increase in bioavailability (Davies-Colley *et al.* 1985). However, a non theoretical response between polysulfide and trace metals has been observed in simulations by Simpson *et al.* (1998), where polysulfide were not found to increase trace metal bioavailability.

The interaction of trace metals with Acid Volatile Sulfide (AVS) can be described by the molar ratio ΣSEM/AVS. Where ΣSEM is the sum of all 'simultaneously extracted metals', whose sulfide species solubility product (K_{sp}) is less soluble than that of Fe, extracted in 1 hour by 1M HCl simultaneously with AVS (Allen *et al.* 1991). Trace metal sulfide species are predicted to precipitate in order of their K_{sp}, i.e., Mn < Fe < Co < Ni < Zn < Pb < Cd <Cu (e.g., Hare *et al.* 1994).

In anoxic sediments, if ΣSEM/AVS > 1, trace metals are interpreted to be in excess of the sulfides binding capacity. Trace metals are then capable of being present in the dissolved phase and pose a greater risk of uptake by organisms. Conversely, if ΣSEM/AVS < 1, metals are predicted to form insoluble metal sulfide species (MeS), with a consequent reduced risk of exposure (e.g., Mikac *et al.* 2000). The method represents a simple mechanistic approach that uses measured partitioning, between dissolved and solid phases, to predict toxicity of metals in sediments (Chapman & Mann 1999).

However, this simple interpretation is often confounded by numerous other influences upon metal speciation, including the presence of other metal binding sites (sulfides, organics matter, Fe and Mn oxides and clays). Kinetic and thermodynamic constraints have been used to explain preferential incorporation of metals into sulfide mineral phases (e.g., Jacobs *et al.* 1985; Brennan & Lindsay 1996; Morse & Luther 1999).

Interaction of metals with pyrite (FeS_2) has been described by Morse (1995) as the Degree of Trace Metal Pyritisation (DTMP, Equation 5.1). The ratio uses operationally defined categories made by the three step sequential acid digestion procedure of Huerta-Diaz & Morse (1990). The three steps in this procedure are: 1) Liberation of the reactive phase by cold 1M HCl digestion over 16 hours; 2) Liberation of silicate phases by HF digestion, and; 3) Liberation of metals bound in pyrite by concentrated HNO_3. Preferential incorporation of trace metals into pyrite phase by this method has been found to follow the order Cu = Fe > Co > Ni >> Mn > Zn > Pb > Cd (Morse & Luther 1999).

$$DTMP = \frac{metal\ in\ pyrite\ phase}{metal\ pyrite\ phase + metal\ in\ reactive\ phase} \qquad \text{(Equation 5.1)}$$

The concentration and speciation of authigenic sulfide mineral species in sediments therefore has a significant influence on the speciation of trace metals as either AVS or pyrite. AVS is often described as a metastable precursor to pyrite formation (Wilkin & Barnes 1997) and pyrite is often the predominant end product of sulfate reduction in marine sediments (King *et al.* 1985; Henneke *et al.* 1997). Exceptions to this do occur, where sulfide minerals are not preserved during burial, or predominantly AVS accumulates (e.g., Gagnon *et al.* 1995, Ferdelman *et al.* 1997).

The mechanism of pyrite formation occurs by two pathways: The first is the relatively rapid and direct formation of pyrite (no Fe monosulfide precursor), described by the reaction (Equation 5.2) of Fe^{2+} with thiosulfate (Rickard 1975). This reaction is the path of pyrite formation in salt marsh sediments (Howarth & Teal 1979; Giblin & Howarth 1984) and when pH is > 7 (Morse & Wang 1997).

$$Fe^{2+} + 4S_2O_3^{2-} \rightarrow FeS_2 + 3S^0 + 3SO_4^{2-} \qquad \text{(Equation 5.2)}$$

The second path is distinct from the former because Fe monosulfide precursors are required. It is considered to be a slower reaction (Equation 5.3) between Fe monosulfides and hydrogen sulfide (Berner 1984). This reaction has been attributed to the formation of pyrite in subtidal sediments (Rickard 1997).

$$FeS + H_2S \rightarrow FeS_2 + H_2 \qquad \text{(Equation 5.3)}$$

Equation 5.3 was found by Rickard (1997) to be the rate limiting step in a sequence of steps leading to pyrite formation. The rate of pyrite formation is dependent upon AVS concentration and hydrogen sulfide concentration given by Equation 5.4.

$$\frac{d(FeS_2)}{dt} = k`(FeS)(H_2S) \qquad \text{(Equation 5.4)}$$

Where; FeS_2 is the concentration of pyrite in mol L^{-1}, FeS is the concentration of AVS in mol L^{-1}, H_2S is the concentration of hydrogen sulfide in solution in mol L^{-1} and

the second order rate constant k` = 1.03 x 10^{-4} L mol^{-1} s^{-1} at 25°C. This implies that pyrite concentrations are a function of AVS concentrations and time (t).

In the previous chapter, the influences upon the sulfur accumulation have been identified in 4 sediment cores from Cleveland Bay (Figure 4.1). In this chapter, the influences upon speciation authigenic sulfide and their interaction with trace metals in these cores are described. Two operationally defined pools of sulfide species are evaluated jointly with trace metals. These results have been used to interpret ΣSEM/AVS ratios, and statistically modelled enhancement of metal concentrations from anthropogenic sources. The aim is to demonstrate that individual metals are incorporated at different rates into different mineral species. It will also be demonstrated that in isolation from other sediment parameters, simple interpretation of ΣSEM/AVS > 1 is not an ideal method to determine metal toxicity in sediments.

5.2 Methods

5.2.1 Sampling and analysis

In this chapter, chemical results from Cores 1827, 1829, 1831 and 1832 are examined. The methods of collection, analysis of Strong Acid Soluble (SAS) metals, Simultaneously Extracted Metals (SEM) and Acid Volatile Sulfides (AVS) have been described in previous sections (2.2.2.1 and 4.2.3). Models of accumulated sulfur (S_{acc}) and Mass Accumulation Rates (MAR) have also been determined in previous chapter sections (4.2.3 and 3.2.5 respectively).

In addition to the previously described measures, concentrations of Al, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn simultaneously extracted with acid volatile sulfide (SEM) were obtained using the method of Allen *et al.* (1991). This method has been described previously in section 4.2.3.

5.2.2 Speciation

5.2.2.1 Sulfide speciation and morphology

Two separate determinations of sulfur concentration have been made that are used to provide two operationally defined sulfur species, pyrite and AVS. The concentration of sulfur as AVS has been defined by direct measurement of AVS. The concentration of sulfur as pyrite is defined as Equation 5.5. Where S_{acc} ($\mu mol\ g^{-1}$) is the solid phase sulfur accumulated since burial. This assumes that the stoichiometry of the residual sulfur species is FeS_2.

$$Pyrite = \frac{S_{acc} - AVS}{2} \quad (\mu mol\ g^{-1}) \qquad \text{(Equation 5.5)}$$

The rate of pyrite formation was calculated using Equation 5.6. Pyrite concentrations were obtained by fitting a third or fourth order polynomial curve fitted to the plot of pyrite concentration with depth. Difference in age was calculated using the probable mass accumulation rate (MAR, Table 3.3).

$$Rate\ of\ pyrite\ formation = \frac{\Delta pyrite}{\Delta time} (\mu mol\ g^{-1}\ y^{-1}) \qquad \text{(Equation 5.6)}$$

The sulfur burial rate was calculated from Equation 5.7, using the probable MAR (Table 3.3), and calculated concentrations of S_{acc} (Equation 4.6).

$$sulphur\ burial\ rate = S_{acc} \times MAR\ (\mu mol\ cm^{-2}\ y^{-1}) \qquad \text{(Equation 5.7)}$$

Morphology and density of sulfide minerals were examined in fresh sediment samples under low vacuum conditions in a Jeol JSM-5000LV scanning electron microscope in back scatter mode. Samples were prepared by smearing a small amount of fresh sample on paper covered glass microscope slides. This method was chosen to limit the amount of sample preparation that could result in oxidation of sulfide species. Because samples are not polished, and contain some residual moisture, the resolution of images is less than optimal.

5.2.2.2 Trace metal speciation

Two operationally defined trace metal species have been measured, Strong Acid Soluble (SAS) metal, and metals simultaneously extracted in 1M HCl with Acid Volatile Sulfides (SEM). SAS metals represent near total digestion of metals, and the recovery is dependent upon sediment composition (Section 2.3.1). This extraction would include metals from the pyrite phase, reactive phase and probably some of the silicate phase according to Huerta-Diaz & Morse (1990).

SEM represents metal extracted with 1M HCl, and the digestion should include only some of the metals in the reactive phase of Huerta-Diaz & Morse (1990). The digestion method of Huerta-Diaz & Morse (1990) also used 1M HCl, but for a duration of 16 hours rather than 1 hour.

The ratio SEM/SAS is operationally defined as the 'lability' of a metal and ideally should range between 0 and 1. Where lability ≥ 1 sediments have 100% of trace metals soluble in 1M HCl.

5.3 Results

5.3.1 Sulfide speciation and morphology

In cores 1827, 1831 and 1832, the ratio AVS/pyrite is greatest at surface (Figure 5.1a) and declines with depth. The decline in the ratio is driven predominantly by increases in pyrite concentrations with increasing depth. Below a near surface maximum, AVS concentrations are relatively constant or exhibit a weak decline with depth.

There is a positive linear relationship between rate of pyrite formation and AVS concentration (Figure 5.1b). The consistency of this relationship suggests that there is a single mechanism controlling the AVS/pyrite ratio among these cores. The concentration of AVS exceeds, or approaches, the concentration of pyrite only in near surface sediments of cores or in sediment that has high rates of pyrite formation (Figure 5.1a).

Scanning electron microscope examination of fresh mud smears indicate that the unoxidised sulfide mineral morphology is dominated by disseminated euhedral individual crystals (< 1 μm in width). Lesser amounts of amorphous aggregates (< 5 μm width) and spherical clusters (< 5 μm in width) occur (Figure 5.2). Euhedron, aggregates and framboids are present throughout the core, and no changes in density of euhedron or morphological form were apparent with depth.

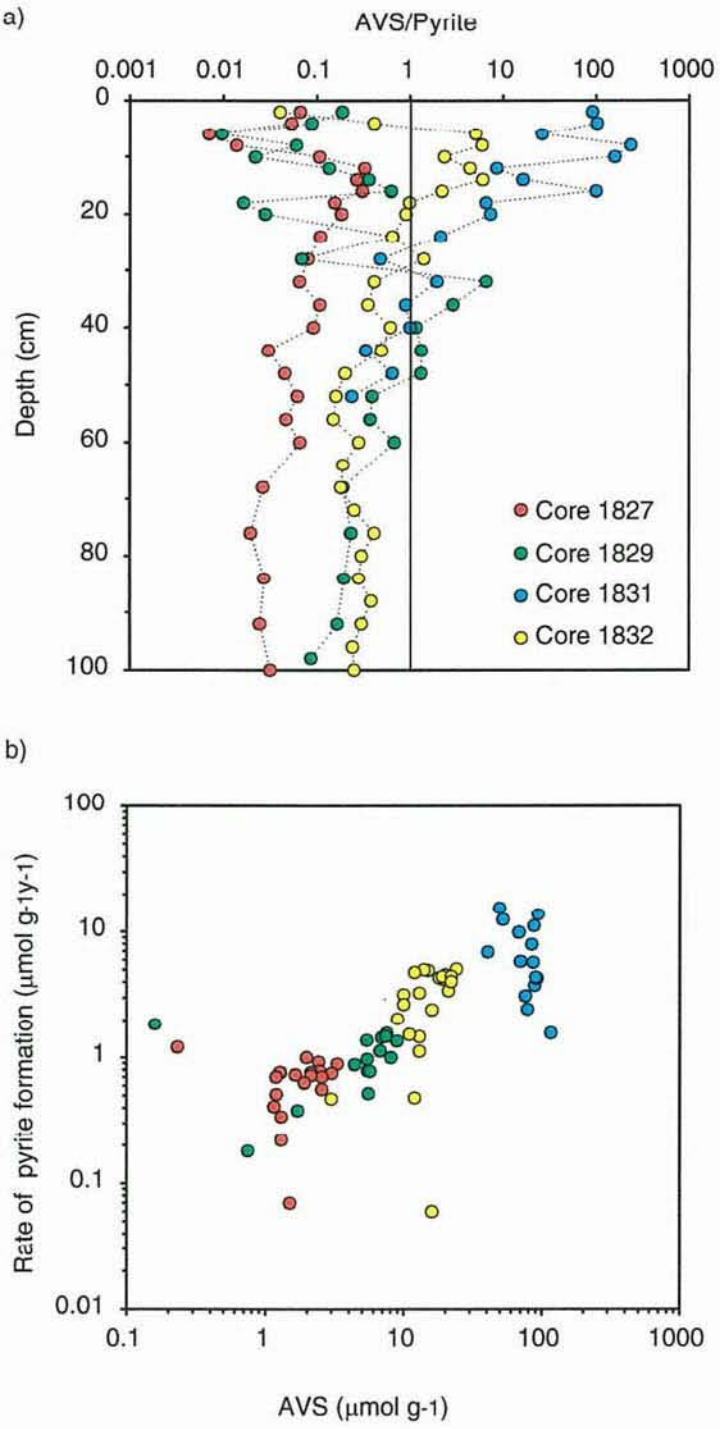


Figure 5.1 Acid volatile sulfide and pyrite relationships within and among cores. *a*) Plot of AVS/pyrite versus depth for sediment core samples; *b*) Plot of AVS concentration versus the rate of pyrite formation

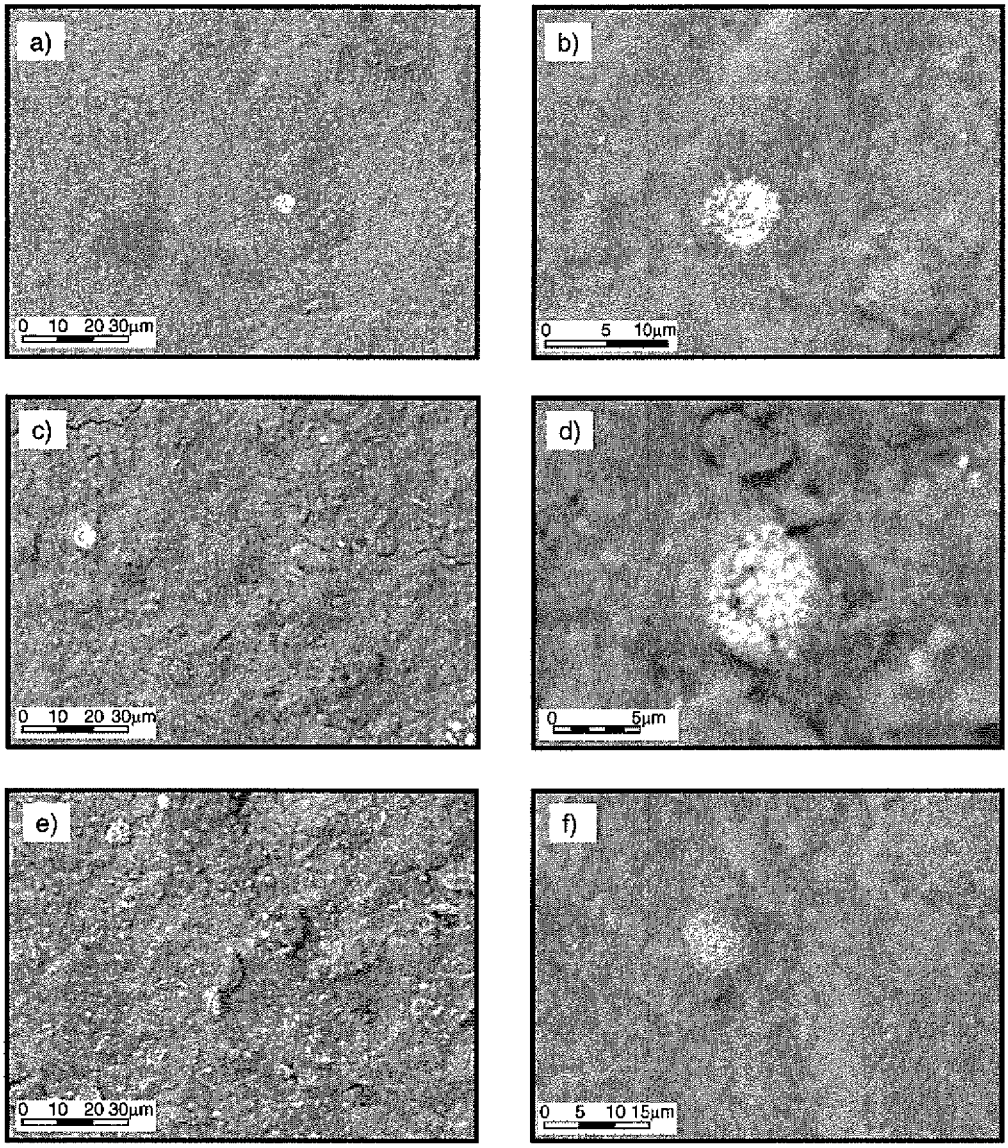


Figure 5.2 Images of Fe sulfide minerals at core site 1832 (Ross river). *a*) Disseminated euhedron in clay matrix at 2-4 cm depth with circular aggregate near middle of view. *b*) Enlargement of circular aggregate . *c*) Circular aggregate in left of view with disseminated euhedron in clay matrix at 8-10 cm depth. *d*) Enlargement of circular aggregate showing distinct spherical/framboidal morphology. *e*) Disseminated euhedron in clay matrix at 14-16 cm depth. *f*) Well formed framboid comprised of euhedron in a clay matrix at 16-18 cm depth.

5.3.2 SEM and SAS metal relationships

The order of average lability of metals (SEM/SAS), calculated for all core samples from lowest to highest lability is; Al (0.06) << Ni (0.17) < Cu (0.22) = Fe (0.22) < Co (0.30) < Zn (0.50) < Mn (0.70) < Pb (0.85) < Cd (1). A rapid change in lability of most metals occur in all cores near surface, but is strongest for Co and Cu, which exhibit a persistent decline with increasing depth in all cores. (Figure 5.3).

Variation in lability of some metals correlate with patterns in OC and S concentrations (Figure 5.3). Cores 1831 and 1832, which have high OC and S concentrations compared to cores 1827 and 1829 (Figure 4.2), have distinctly lower Co lability. Cores 1831 and 1832 also exhibit greater lability of Cd and Ni relative to other cores.

The elements Pb and Zn exhibit a consistent lability of between 0.5 and 1 among cores. A weak decline in lability of Pb and Zn does occur in some cores, but the amount of labile metal is higher than Cu, Ni and Co. This suggests that the processes that are affecting the lability of Cu, Ni and Co are not influencing the lability of Pb and Zn.

5.3.3 Trace metal and sulfide species relationships

The molar ratio of ΣSEM (Cd + Co + Cu + Ni + Pb + Zn = ΣSEM in nmol g^{-1}) to AVS plotted against depth (Figure 5.4a) indicates that the ΣSEM exceeds AVS in near surface sediments of Core 1827 and Core 1829. The variation in ΣSEM/AVS between cores displays a strong negative relationship with the sulfur burial rate (Figure 5.4b).

Pyrite burial rate is compared to metal lability in Figure 5.5. There is a progressive decline in metal lability with increasing pyrite burial rate for Co, Cu, and Mn. In contrast to these metals, Ni exhibits a weak trend of increasing lability. The changes in lability of Cd, Pb and Zn is variable, and exhibit weak increases in lability within cores 1827 and 1829, while decreases occur in 1831 and 1832.

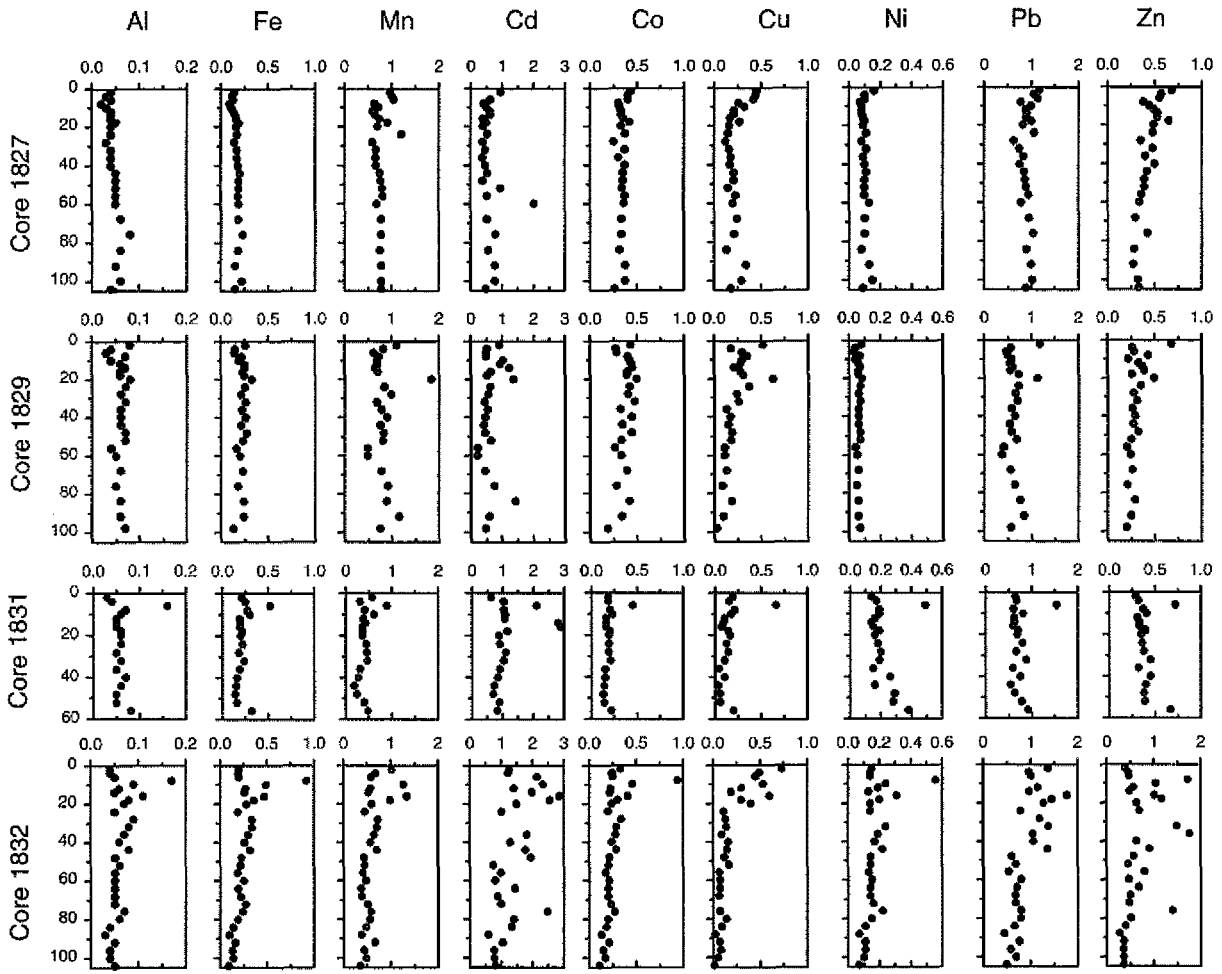


Figure 5.3 Plots of lability (SEM/SAS) / versus depth in each core. The increase in Co lability and the decrease in Cd and Ni increase in Cores 1831 and 1832 compared to 1827 and 1829 is related to increases in OC and S concentration.

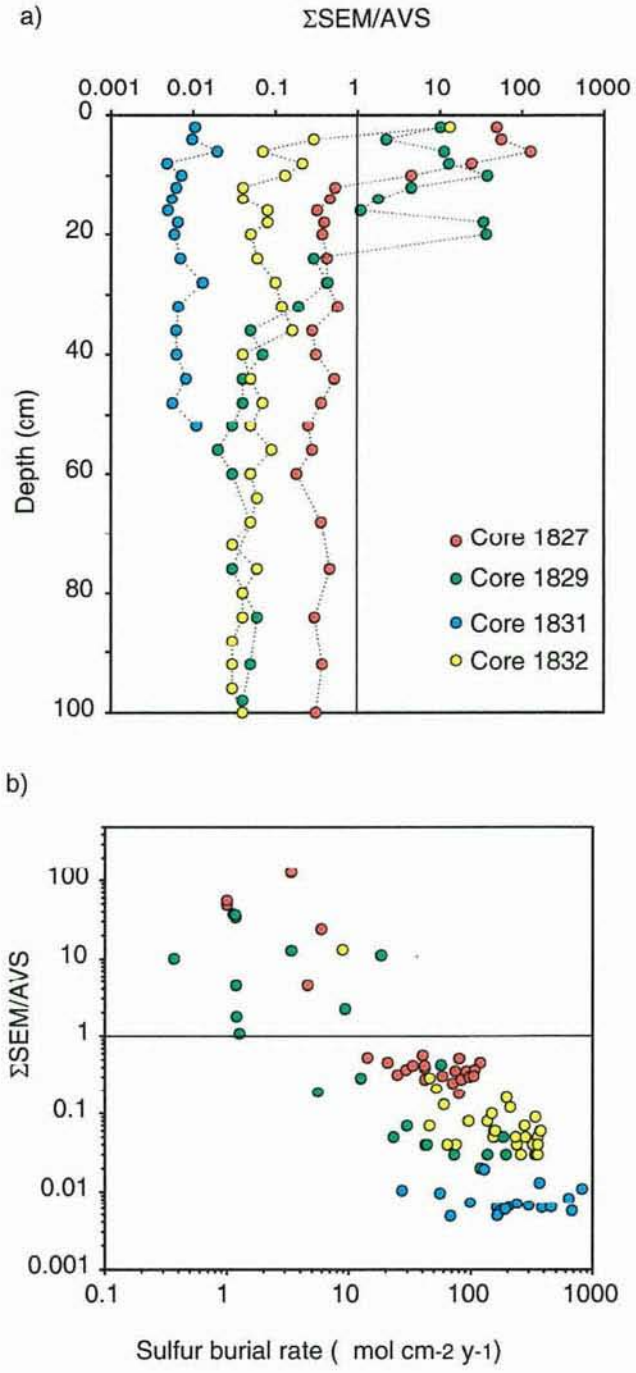


Figure 5.4 Simultaneously extracted metals (SEM) and acid volatile sulfide (AVS) relationships within and among cores. *a*) Plot of the ratio ΣSEM/AVS with depth for sediment cores; *b*) Plot of sulfur burial rate versus SEM/AVS.

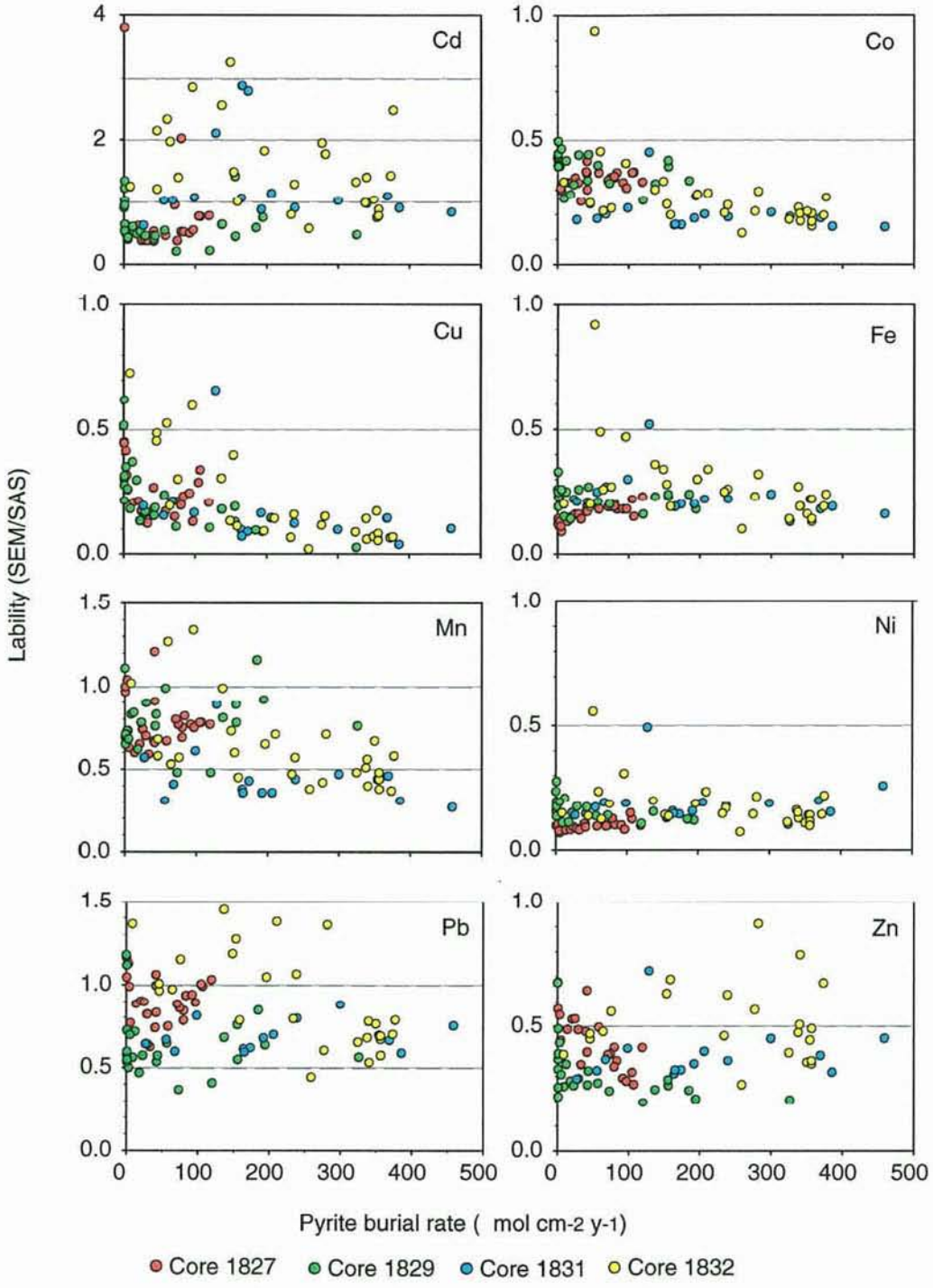


Figure 5.5 Plots of pyrite burial rate versus lability (SEM/SAS). Co, Cu, Fe and Mn display distinct reduction in lability with increasing pyrite burial flux. Cd, Pb and Zn also display weak reduction in lability with increases in pyrite burial rate. Ni exhibits a weak increase in lability with increasing pyrite burial rate.

5.4 Discussion

5.4.1 Influence of sulfur burial rate upon authigenic iron sulfide speciation

The relationships between AVS, pyrite and sulfur burial rate have been examined to determine why some cores have very high AVS concentrations relative to pyrite concentration. The accumulation of authigenic sulfide as either AVS or pyrite is significant when considering ΣSEM/AVS ratios in sediment quality assessment strategies (e.g., ANZECC 1999). In Cleveland Bay, the ΣSEM/AVS ratios among cores range over 5 orders of magnitude and have a linear relationship with sulfur burial rate, plotted on log log axes (Figure 5.4b). At low sulfur burial rates (< 10 μmol cm^{-2} y^{-1}) low AVS concentrations occur, and ΣSEM/AVS exceed 1.

Low AVS/pyrite ratios occur in each core at surface (Figure 5.1a). The low value can be explained in terms of more oxidising conditions near surface, which would result in the preferential oxidation of AVS minerals and preservation of pyrite (e.g., Morse 1995). Oxidative loss of sulfide from near surface sediments has been described in cores 1827 and 1829, in Chapter 4. The amount of sulfur undergoing oxidation has not been measured. However, from the results it appears that the amount of sulfur oxidised is sufficient to impact upon trace metal speciation near surface but not the crude sulfur mass balances completed in Chapter 4.

However, changes in the ratio AVS/pyrite among cores can be described in terms of the kinetics of pyrite formation. The increase in the rate of pyrite formation with increasing AVS concentration (Figure 5.1b), agrees with kinetic constraints upon the rate of pyrite formation described by Rickard (1997), as Equation 5.4. The limitation of the rate of pyrite formation in Equation 5.4 is transport controlled and has been attributed to the rate of diffusion of colloidal FeS and H_2S to the surface of pyrite (Rickard & Luther 1997). This limitation results in the accumulation of greater concentrations of AVS at high rates of sulfur burial, because AVS formation is more rapid than the formation of pyrite.

Alternative hypotheses regarding limitation of pyrite formation include; high burial rates result in preservation of AVS at depth (Berner 1964; Fergusson 1983); thermodynamic constraints cause the precipitation of metastable AVS in preference to more stable pyrite under high rates of sulfate reduction (Brennan & Lindsay 1996); acidic conditions result in more AVS converting to pyrite (Morse & Wang 1997); inhibition of pyrite nucleation by organic carbon (Morse & Wang 1997); slower reduction of a more refractory Fe oxide phase at depth subsequent to exhaustion of more reactive Fe (Lord & Church 1985; Henneke *et al.* 1997); high concentrations of reactive Fe inhibit the formation of pyrite by limiting the supply of newly reduced S species (Gagnon *et al.* 1995). Each of these hypotheses could be argued within the 4 cores examined.

However, further evidence for Equation 5.3 as the dominant reaction path, can be derived from the second order rate constant (k`) for the reaction in Equation 5.4. Under experimental conditions k` was found by Rickard (1997) to be 1.03×10^{-4} L mol^{-1} s^{-1} at 25°C. The rate of change of pyrite formation with increasing AVS concentration in Figure 5.1b has a slope of 0.107 (y^{-1}). This is a first order rate constant that assumes a constant concentration of H_2S. No H_2S measurements have been made in this study, but assuming maximum likely H_2S concentrations of 0.1 to 100 μmol L^{-1}, we can place limits upon the second order rate constants by Equation 5.8.

$$k` = \frac{k}{H_2S} \text{ (L mol}^{-1}\text{ y}^{-1}\text{)} \qquad \text{(Equation 5.8)}$$

Where H_2S is the estimated concentration of H_2S dissolved in the pore water in mol L^{-1}. The concentration of H_2S in the pore waters has been estimated by 2 methods. Firstly, because no H_2S was smelt during core dissection, the concentration in the gas phase can be assumed to be less than 1 μmol L^{-1} and by using Henry's Law the concentration in solution must be < 0.1 μmol L^{-1}. Secondly, it has been asserted in Chapter 4 that the total pore water sulfur concentrations represent dominantly SO_4. Hence other S species can be assumed to be less than < 1% of the total S concentrations (100-300 μmol L^{-1}). Using Equation 5.4 the range of the second order rate constant k` is

therefore between 3.39×10^{-2} and 1.13×10^{-5} L mol^{-1} s^{-1}, or within two orders of magnitude of the rate experimentally determined by Rickard (1997).

Pyrite end products of the reaction Equation 5.3 were described as mixtures of individual cubes (up to 0.8 μm in size) and subspherical aggregates up to 1.4 μm in diameter (Rickard & Luther 1997). However, Luther *et al.* (1982) considered the presence of near identical sulfide morphologies in salt marsh sediments to be a function of rapid pyrite formation by Equation 5.2. The morphology of the sulfide minerals in Core 1832 fit this description (Figure 5.2). The amount, size and shape of pyrite morphologies observed are constant with depth, and indicate the method of formation of these products is not depth dependent and very rapid (< 30 years).

In summary, the slower rate of pyrite formation, relative to AVS formation, results in high AVS concentrations in sediments that have high sulfur burial rates. Evidence for this is the linear relationship of the rate of pyrite formation and concentration of AVS among cores in Figure 5.3b. Discussion will now be directed towards the interaction of AVS and pyrite with trace metals.

5.4.2 Trace metal partitioning and interaction with authigenic iron sulfides

Partitioning of metals in sediments refers to the preferential incorporation of metals into operationally defined categories (species), which are based on their recovery from wet chemical extractions (e.g., Tessier *et al.* 1979; Huerta-Diaz & Morse 1990; Scancar *et al.* 2000). In this study, two operationally defined species have been measured, metals simultaneously extracted in 1M HCl with AVS (SEM) and strong acid soluble metals (SAS). The operational nature and limitations of the methods used to classify metal sulfide species, and partitioning, requires discussion before proceeding.

Speciation methods

Because acid digestion schemes cannot determine trace metal species (Van den Berg *et al.* 1998; Cooper & Morse 1999). For example, mineral phases soluble in 1M HCl are not limited to AVS, and include clays and oxides. Moreover, the recovery of

MeS phases by 1M HCl has also been found to be highly variable, where the recovery of CuS, NiS, and HgS are less than CdS, FeS, PbS and ZnS (Cooper & Morse 1998a).

In this study, it is the interaction between the operationally defined categories of metals and authigenic sulfide that are used to infer metal sulfide speciation. The term lability is used to describe the changes in recovery of metals from the SEM and SAS phases. Changes in lability represent changes in the acid soluble properties of trace metals. These changes are influenced by interactions with authigenic sulfides as well as other potential metal binding phases, which may be determined by source of the metals (e.g., Simpson *et al.* 2000).

Rapid changes in lability occur in most near surface samples (Figure 5.3), and some changes in lability are not related to authigenic sulfides. This is emphasised here because of the potentially misleading similarity in the order of lability (Al << Ni < Cu = Fe < Co < Zn < Mn < Pb < Cd) compared to the order of DTMP (Cu = Fe > Co > Ni >> Mn > Zn > Pb > Cd) of Morse (1995). To demonstrate this Al has been included with other metals, and it has an average lability of 0.06. This low lability does not imply that Al is in a pyrite phase, and similarly the low lability of other metals such as Ni, Co and Cu should not be used to infer pyrite speciation. The operationally defined 'lability' is influenced by metal concentrations derived from silicate phases, whereas DTMP requires the removal of silicate phases before nitric acid digestion to recover the pyrite phase (Huerta-Diaz & Morse (1990).

The plot of DTMP versus degree of pyritisation (DOP) has been used to describe the interaction between pyrite and trace metals (Morse 1995). In this study the plot of pyrite burial rate versus lability (Figure 5.5) is used to examine relationships. If there are correlations between changes in metal lability and pyrite formation, these changes may be related to pyritisation of sediments and metals. The trends displayed by metals should not be treated as true speciation as other factors (e.g., source) will also influence the acid soluble properties of metals.

In Cleveland Bay, partitioning of metals is characterised by 2 trends. 1) The metals Cd, Pb and Zn exhibit consistently higher lability than Co, Cu and Ni, and suggest preferential formation of SEM species (Figure 5.4). This has environmental

significance because 1M HCl soluble metals (SEM) are often referred to as bioavailable (e.g., Langston *et al.* 1990, Reichelt & Jones 1994). 2) The metals Co, Cu and Mn exhibit a decline in lability that is a function of pyrite burial rate (Figure 5.5). This represents a transition during burial from a SEM phase to a SAS phase.

Trace metal sulfide interactions

The partitioning among metals can be argued to be a consequence of the interactions between trace metals and authigenic sulfide species (AVS and pyrite). Interaction between AVS and trace metals in anoxic marine sediments and waters occurs via precipitation of metal sulfide species (Jacobs *et al.* 1985; Di Toro *et al.* 1990; Brennan & Lindsay 1996) and adsorption with and coprecipitation onto amorphous to poorly crystalline FeS (Morse & Arakaki 1993; Coles *et al.* 2000). The partitioning of metals into MeS phases based upon thermodynamic constraints (e.g., order of K_{sp}, Mikac *et al.* 2000) does not explain the observed partitioning of metals into MeS phases (e.g., Jacobs *et al.* 1985). Both thermodynamic and kinetic constraints are required to explain partitioning the observed partitioning of metals into authigenic sulfide phases (Morse & Luther 1999).

Kinetic constraints have been found to result in Pb, Zn and Cd preferentially forming MeS phases because they have faster water exchange reaction kinetics than Fe^{2+}. These metals form MeS phases prior to FeS formation and subsequent to pyrite formation (Morse & Luther 1999). In the samples from Cleveland Bay, on average 50% of Zn, 85% of Pb and 100% of Cd is held in the 1M HCl extract (SEM). This indicates that the majority of these metals are held in a labile 1M HCl soluble phase. The high lability of these metals and poor correlation between Cd, Pb and Zn with pyrite burial rate (Figure 5.5), is consistent with these metals being affected to a lesser extent by pyritisation.

Cd lability remains near 100% in core samples and in surface sediment grab samples. It is therefore most strongly partitioned into the 1M HCl soluble phase. Cd concentrations have also been found to increase in proportion to strong acid soluble S concentrations in cores 1831 and 1832. The increases in sulfur are driven by the accumulation of authigenic iron sulfides as pyrite rather than AVS (chapter 4).

Therefore, the Cd is accumulating in sediments as a consequence of pyrite formation, but is accumulating in a 1M HCl soluble phase. This behaviour has been attributed to Cd having only a single redox divalent state (Cd^{2+}), making it less suitable to incorporate into a pyrite phase (Rosenthal *et al.* 1995).

In contrast to Cd, Pb and Zn, the elements Co, Cu, Mn and Ni are held predominantly in a non 1M HCl soluble phase and undergo changes in lability with depth. The decline in lability of Cu, Co and Mn indicates that these metals are preferentially pyritised with depth. There is a distinct non-linear behaviour of Cu lability versus pyrite burial rate, relative to trends displayed by Co and Mn lability (Figure 5.5). Morse & Luther (1999) attributed the noise in plots of DTMP versus DOP attributed to more than one Cu species being present. This may also be responsible for the trends in Cu lability where a more labile species is present near surface.

The significant difference between the trends observed in the DTMP by Morse & Luther (1999) and lability in sediments from Cleveland Bay is the weak increase in the lability of Ni with increasing pyrite burial rate. The low lability reflects that Ni is held predominantly in a phase that is not soluble in 1M HCl, which could be a variety of more resistant mineral fractions, including pyrite and silicate phases. The increase in lability suggests that a small portion of the SAS soluble Ni is incorporated within a 1M HCl soluble phase of sediments that have high pyrite burial rates. A specific mechanism for this to occur has not been identified.

5.4.3 Interpretation of ΣSEM/AVS ratios

The ratio ΣSEM/AVS is recommended as a tool to be used in tiered sediment quality assessment strategies (e.g., Arakel 1995; Van der Hoop *et al.* 1997; ANZECC 1999; Porebski *et al.* 1999). Generic application of apparently simple and cost effective methods, to assess metal bioavailability are desirable during sediment quality assessment (e.g., Chapman *et al.* 1999). However, simple interpretation of ΣSEM/AVS ratios (e.g., > or < 1) do not lend themselves to generic application for the assessment of sediment quality.

This is best demonstrated by ΣSEM/AVS ratios > 1 at the top of cores 1827 and 1829 (Figure 5.4a). Both core sites are accumulating measurable amounts of authigenic sulfide (Figure 5.1), indicating sediments are reducing and sulfate reduction is occurring. Core 1827 is situated at the mouth of Ross Creek (Figure 4.1), and has been identified in Chapter 3 to contain enhancement of SAS trace metal concentrations, which are < 2 times the modelled background and are less than the ANZECC ISQV-low. In contrast, core 1829 is located in the east of the bay and was used in Chapter 3 along with other samples from the eastern bay to model background concentrations, and is not affected by anthropogenic influences upon trace metal concentrations.

Both cores have low rates of sulfur burial in near surface sediments (< 10 μmol m^{-2} y^{-1}), relative to cores 1831 and 1832 (Figure 5.3). The ratio is discriminating between sites that have high rates of sulfur burial from those that do not, rather than discriminating differences in sediment quality. The low rates of sulfur burial result in low AVS concentrations in near surface sediments. Conditions favour the preservation authigenic sulfide as pyrite due to the low burial rate, and probably more oxidising conditions near surface (e.g., Morse 1995). High sulfur burial rates in cores 1831 and 1832 result in very low ΣSEM/AVS ratios and occur because such conditions favour the preservation of AVS rather than pyrite.

These results indicate that the ratio ΣSEM/AVS discriminates between sediments that have concentrations of AVS sufficient to allow the partitioning of labile metals into insoluble phases. Where ΣSEM/AVS < 1 dissolved metals will form an insoluble AVS phase, and where ΣSEM/AVS > 1 metals are capable of being present in the dissolved phase. The influences upon the ratio can be anthropogenic or natural.

Differences in sulfur burial rate are the most significant influence upon the ratio in 4 sediment cores from Cleveland Bay. These results indicate that the can only be used effectively to identify anthropogenic influences upon sediment quality if used in conjunction with other methods, such as proposed in tiered sediment quality assessment strategy (e.g., Chapman *et al.* 1999). Dependent upon the management strategy for the location the next tier of assessment, involving toxicity testing, may be warranted where ΣSEM/AVS > 1.

5.5 Conclusions

During burial, interactions of Cu and Co with authigenic sulfides result in incorporation of these metals into a non 1M HCl soluble phase. The rate of incorporation of Cu into a non 1M HCl soluble phase is non-linear, and indicates that samples that have low pyrite burial flux will have disproportionately higher liabilities of Cu. In contrast, Ni exhibits a weak increase in lability with increasing pyrite burial flux.

The elements Cd, Pb and Zn are preferentially incorporated within a 1M HCl soluble phase, and undergo only minor changes into non 1M HCl soluble phases with depth. Cd concentration increases in proportion to pyrite formation in cores that have high burial rates of sulfur. Despite these changes in concentration Cd remains almost 100% soluble in 1M HCl.

In Cleveland Bay, the predominant influence upon the ratio ΣSEM/AVS are processes that determine AVS concentrations. In near surface sediments, AVS concentrations are influenced by oxidation, and can result in very low concentrations of AVS. Below the effects of oxidation, AVS concentration is dependent upon the rate of pyrite formation. High AVS concentrations occur in sediments that have high sulfur burial rates, because the rate of pyrite formation from AVS precursors is slower than the rate of AVS formation.

In the cores examined the ratio of ΣSEM/AVS discriminates between sites that have high and low concentrations of AVS. The method does not distinguish between natural and anthropogenic influences. The method requires to be used in conjunction with other methods in a tiered risk assessment strategy if it is used as an indicator of sediment quality.

Chapter 6

DGT measured metal fluxes: Interpretation and relevance to environmental surveys

6.1 Introduction

Post depositional biogeochemical processes influence speciation of trace metals and can influence the risk of exposure of organisms to toxic metal concentrations (Allen & Hansen 1996; Lam *et al.* 1997; Fernandes 1997; Chapman *et al.* 1998). Rapid vertical changes in metal speciation can occur (Luther 1995; Zhang *et al.* 1995; Davison *et al.* 1997; Lam *et al.* 1997). The vertical patterns in metal speciation are related to processes that result in the oxidation of organic matter (Bertolin *et al.* 1995; Morse 1994; Veeh *et al.* 1999). These processes follow a well recognised sequence with increasing depth of aerobic oxidation, denitrification, Mn reduction, Fe reduction, sulfate reduction and methanogenesis (Berner 1984; Stumm & Morgan 1996).

Biogeochemical cycling of trace metals at the sediment water interface at sub millimetre scale has been demonstrated by Davison *et al.* (1997), using sampling devices that employ the technique of Diffusive Gradients in Thin-Films (DGT). DGT devices work by quantifying in situ fluxes of labile (or exchangeable) metal across a diffusive layer (thin film typically < 1 mm thickness) of known diffusive properties, where the diffusing ions are accumulated in a chelating resin located at the rear of the diffusive layer. The method offers three distinct advantages over other in situ passive sampling methods (such as dialysis membranes). 1) The diffusive layer places constraints upon mass transport to the chelating resin so that concentrations may be predicted. 2) High vertical spatial resolution (< 1 mm) of sample intervals are possible. 3) Metals are preconcentrated, in situ by the chelating resin, to allow detection by routine atomic adsorption spectroscopy.

In this study, the DGT devices use a diffusive layer comprised of a 0.45 μm filter membrane overlaying a macroporous polyacrylamide hydrogel. The diffusive

layer overlies a second polyacrylamide hydrogel containing Chelex resin on one surface, which acts as a collection media for diffusing metal ions. The gels are mounted on acrylic housings that expose a window (of known area) of the diffusive layer to a solution (Figure 6.1).

The time averaged diffusive flux of an ion through the diffusive gel layer (J_t) can be calculated by Equation 6.1.

$$J_t = \frac{m}{at} \text{ (mol cm}^{-2}\text{ hr}^{-1}\text{)} \qquad \text{(Equation 6.1)}$$

Where, m (mol) is the number of ions accumulating in the Chelex resin, behind the diffusive layer, a (cm^2) is the area of the gel exposed to the solution and, t (hours) is the time of deployment.

Ficks first law of diffusion (Equation 6.2) may also be used to calculate the time average diffusive flux of metal.

$$J_t = D\ \frac{\partial C}{\partial x} \text{ (mol cm}^{-2}\text{ h}^{-1}\text{)} \qquad \text{(Equation 6.2)}$$

Where D ($cm^2\ hr^{-1}$) is the diffusion coefficient of an ion in the diffusive medium, and $\partial C / \partial x$ (mol cm^{-1}) is the gradient in concentration. If the diffusion coefficient of the DGT device diffusive layer (D_g) is known, the thickness of the diffusive layer (Δx; cm) is small and is significantly greater than the diffusive boundary layer (Figure 6.1*c*), J_t may also be calculated from Equation 6.3.

$$J_t = D_g \frac{C_b - C_0}{\Delta x} \text{ (mol cm}^{-2}\text{ h}^{-1}\text{)} \qquad \text{(Equation 6.3)}$$

In Equation 6.3 the concentration of dissolved ions at the rear of the diffusive gel layer (C_0) is 0, because of uptake of dissolved ions by the Chelex resin. The difference in concentration across the diffusive layer is therefore equal to C_b, which can be calculated by combining Equations 6.1 and 6.3 to form Equation 6.4.

$$C_b = \frac{m\Delta x}{D_g at} \quad \text{(mol cm}^{-3}\text{)} \qquad \text{(Equation 6.4)}$$

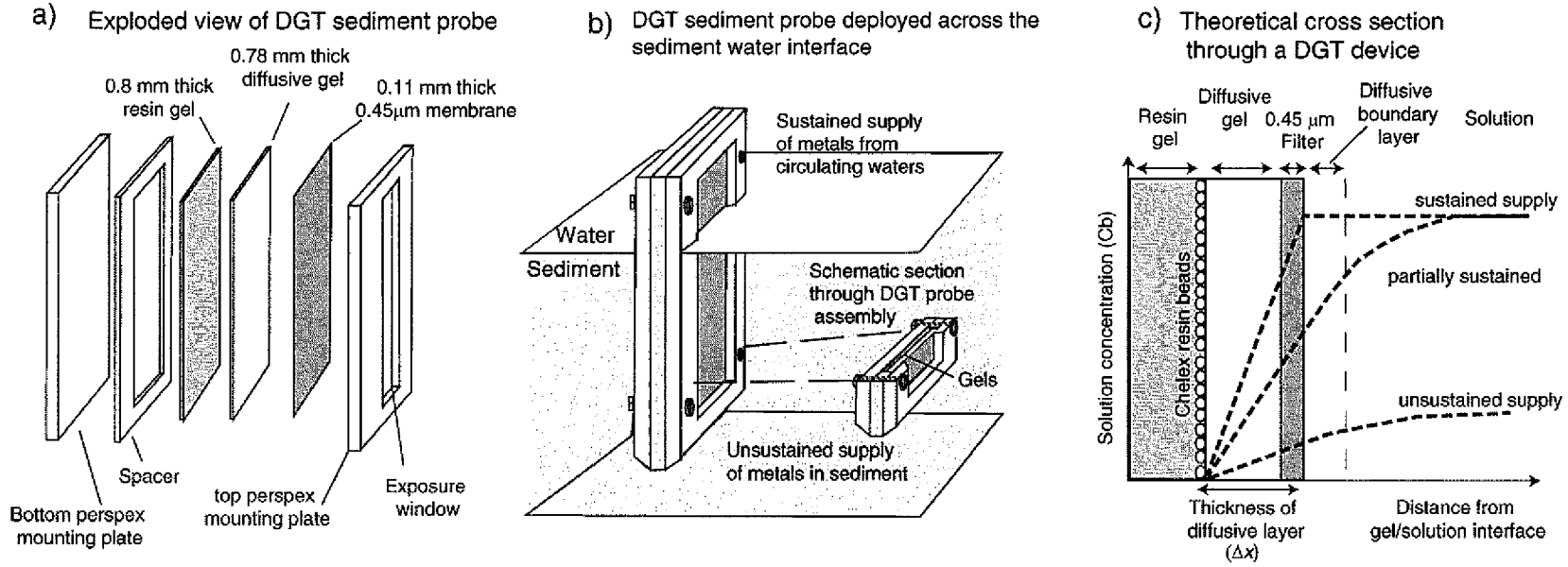


Figure 6.1 Schematic illustration and cross sections of diffusive gradients in thin-films (DGT) sediment probe devices (adapted from Zhang & Davison 1995). a) Exploded view of sediment probe. Two layers of gel are held between perspex plates that are separated by a spacer. The spacer maintains the gel thickness and acts as a seal to prevent water flow between the plates. Plates are held together with nylon bolts. b) The sediment probe can be inserted across the sediment water interface to allow simultaneous measurement of metal fluxes in water and sediment. c) Theoretical cross section through a DGT device showing effects of sustained and unsustained supply of metals on metal concentration in the solution adjacent a DGT device. Low rates of resupply of metals taken up by the DGT device result in unsustained (depleted) concentrations adjacent to the probe.

A critical assumption of Equation 6.4 is that C_b remains constant during the time of deployment. In buffered and well mixed waters, C_b can be assumed to be constant because of fast resupply of the ions depleted by uptake into the DGT device by natural circulation of water (e.g., Zhang & Davison 1995).

In sediments, uptake by the DGT probe can lower the concentration of dissolved metals in pore water and disrupt the equilibrium between dissolved and solid phase concentrations (Zhang *et al.* 1995). Resupply of pore water metal concentrations is by diffusive flux of metals across a gradient in concentration from adjacent pore waters, and by desorption of metals from particulate phases into the dissolved phase. Therefore, DGT fluxes measured by sediment probes are a function of the diffusive resupply of metals and the kinetics of resupply of metals between the solid and dissolved phase. Prediction of concentrations using flux measurements is not possible without knowledge of the kinetics of resupply between the dissolved and solid phase (Harper *et al.* 1998).

DGT fluxes are used here to provide information on near surface metal speciation. DGT metal flux is also compared to other operationally defined metal speciation measures (dissolved metal, 1M HCl soluble metal) made in sediment cores collected adjacent to the DGT probes. This information is used to provide evidence for incorporation of metals into biogeochemical cycles and has implications for the determination of trace metal bioavailability to be used in sediment quality assessment.

6.1.1 Study site

An intertidal mud bank situated in Ross Creek was chosen as the study site (Figure 6.2*a*). It is typical of mud rich intertidal deposits of the region and is situated in an urbanised region that is used for recreational purposes. The area was also of interest because it is known to contain metal concentrations that exceed the ANZECC ISQV-low (Table 3.2).

a)

b)

Figure 6.2 Photographs of the location and character of DGT sediment probe deployment site. a) Location of site in Ross Creek (red circle, aerial photograph from Townsville City Council, 07/12/1995, Run 4, #080); b) Close up view of sediment probes deployed in intertidal mud bank at low tide. Sediment core location is marked in left of view. DGT probes are 10 cm wide with an exposure window that is 1 cm wide.

The intertidal mud bank is located at the mouth of a small mangrove fringed creek (< 4 m wide, < 30 m long) that drains an area of reclaimed land, now occupied by railway yards (Figure 6.2*a*). The mud bank forms part of the base of the Ross Creek stream bed. It is near horizontal, is located below the extent of mangrove root systems and is exposed at low tide (Figure 6.2*b*). The surface is covered in small pits < 20 mm deep, probably due to biological activity.

6.2 Methods

6.2.1 Sediment core sampling and analysis

6.2.1.1 Sampling

Two shallow (< 0.3 m) sediment cores were collected within 1 m of where the DGT probes were deployed. A 150 mm diameter clear polycarbonate core tube fitted with a stainless steel core catcher was used to collect cores. The core was extruded within 2 hours of collection, using a tight fitting piston. This equipment allows the clean and rapid sampling of undisturbed sediment at cm scale accuracy. One core was used for determination of dissolved metals in sediment interstitial pore waters. The second core was used for the measurement of Eh, pH, porosity and analysis of strong acid soluble metals, acid volatile sulfides and simultaneously extracted metals.

6.2.1.2 Surface water and pore water sampling and analysis

Upon extrusion of sediment intervals, sediment was immediately loaded into 60 mL syringes. Syringes were placed under pressure using clamps, and pore waters were squeezed over a 4 hour period, through a 0.45 µm filter into a container spiked with 1 µL of concentrated HNO_3 (ultrapure).

Pore water samples were photolized for 18 hours in an Aceglass UV photolizer. Metal concentrations in the pore water samples after photolysis were determined on a Metrohm 746 VA Trace Analyser potentiostat using a Metrohm 747 VA hanging mercury drop electrode after adjustment of the pH. 8 mL of each sample was buffered with 0.05M HEPES and 0.02M HCl. Cu, Pb, Cd were analysed by ASV according to the methods described by Colombo & van den Berg (1997). Zn was analysed by ASV

using the standard ASV Method No. 231/1 a e (Metrohm 1997). The elements Fe, Mn and S were measured in the remaining sample by inductively coupled plasma atomic emission spectroscopy. Analytical results of pore water analyses are presented in Appendix 9.1.

6.2.1.3 Porosity, Eh, pH, Strong acid soluble metals, SEM and AVS

The procedures for the determination of Eh, pH, strong acid soluble metals (Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, Pb, S, Zn), organic carbon (OC), calcium carbonate (CC), SEM (Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) and AVS have been described in chapters 2, 4 and 5. All analytical results are presented in Appendix 9.2 and 9.3.

Porosity was determined calculating the difference between the wet and dry weight of samples using Equation 6.5, assuming a density (ρ in g cm^{-3}) of 2.5 and 1.03 for sediment and 35 ppt salinity water respectively.

$$\phi = \frac{volume\ of\ water}{total\ volume} = \frac{\frac{wet\ weight - dry\ weight}{\rho_{water}}}{\frac{dry\ weight}{\rho_{sediment}} + \frac{wet\ weight - dry\ weight}{\rho_{water}}} \qquad \text{(Equation 6.5)}$$

Porosity was then used to convert concentrations (mol g^{-1}) of solid phase and dissolved phase (mol mL^{-1}) metals into moles per unit volume (mol cm^{-3}) of sediment by Equation 6.6 and 6.7 respectively. This is necessary to enable comparison of sediment and pore water concentrations with the number of moles of metal accumulated over the deployment period per unit area of the DGT device (mol cm^{-2}).

$$Solid\ phase\ (mol\ cm^{-3}) = concentration \times (1-\phi)\rho_{sediment} \qquad \text{(Equation 6.6)}$$

$$Dissolved\ phase\ (mol\ cm^{-3}) = concentration \times \phi \qquad \text{(Equation 6.7)}$$

6.2.1.4 Operational speciation definitions and other categories

Three operationally defined metal species have been determined: dissolved metals in pore waters (dissolved); simultaneously extracted metals (SEM); and residual metals. The concentration of residual metal was calculated by subtracting the moles of dissolved metals and SEM contained within 1 cm^3 of whole sediment from the amount

of metal held within 1 cm^3 recovered by the strong acid soluble metals (SAS) of a whole sediment sample.

Other operationally defined values used in this chapter include; the distribution coefficient (K_d), pyrite and lability. K_d was calculated by Equation 6.8, using concentrations converted to volumetric units, and is dimensionless. Pyrite was calculated by Equation 6.9, and is half the molar concentration of S remaining when the concentration of S in pore water (S_{pw}), S in organic matter (assumed to be 0.8% by weight) and concentration of AVS are subtracted from the strong acid soluble S concentration (see section 5.2.2.1). This assumes that residual authigenic iron sulfide species are FeS_2. The ratio of metal simultaneously extracted with AVS in 1M HCl (SEM), to the metal extracted by the strong acid digestion method (SAS) is operationally defined as lability (Equation 6.10).

$$Distribution\ coefficient\ (K_d) = \frac{SAS\ metal\ concentration}{Pore\ water\ metal\ concentration} \qquad \text{(Equation 6.8)}$$

$$Pyrite = \frac{SAS\ S(1-\phi)2.5 - 0.008OC - \phi S_{pw} - AVS(1-\phi)2.5}{2} \qquad \text{(Equation 6.9)}$$

$$Lability = \frac{SEM\ concentration}{SAS\ concentration} \qquad \text{(Equation 6.10)}$$

6.2.2 DGT device manufacturing, calibration and deployment

6.2.2.1 Gel manufacturing

All equipment was acid washed prior to use in 10% HNO_3 (AR grade), and rinsed and soaked in distilled deionised (DDI) water (Continental Modulab Pure 1). Diffusive gel layers and resin gel layers were made by methods described by Zhang & Davison (1995). A gel solution was made up containing 30% acrylamide gel solution, and 15% AcrylAide ™ (BioProducts). Diffusive gel layers were made by mixing 10 mL of the gel solution with 75 µL of ammonium persulfate (APS) and 25 µL of tetramethylenediamine (TMED). Diffusive gels were cast by injecting the solution between two glass plates separated by a 0.5 mm spacer, and allowed to set in an oven at 40° C.

Diffusive gels were hydrated in DDI for 24 hours, and stored in 100 mL of 0.05M $NaNO_3$. After 24 hours residence time in the DDI gels swell to a new and stable dimension. The final thickness of the gel was measured using a 10 μm graduated reference scale bar observed with a transmitted light microscope. The average thickness of the diffusive gel was found to be 0.78 mm. Measurement of 0.45 μm cellulose nitrate membranes (Whatmann), that were soaked in DDI, were also measured by microscope and had an average thickness of 0.11 mm. Diffusive gels and 0.45 μm filter membranes were stored in DDI, with the water changed regularly to eliminate electrical charge build up within the gel, which could impede the diffusion of ions through the gel (e.g., Zhang & Davison 1995).

The resin gel was made as described by Zhang & Davison (1995) using 2.5 gm of Chelex 100 ® (Bio Rad) 200-400 mesh, sodium form in 10 mL of gel solution mixed with 60 μL of APS and 20 μL of TMED. Prior to incorporation into the gel, the Chelex was washed twice in 2 bed volumes of 2M HNO_3 (Ultrapure) and regenerated in 2 bed volumes of 1M NaOH (Aristar), followed by extended flushing in DDI water to lower pH to less than 10.

Resin gels were injected between glass plates separated by 0.5 mm spacers. The lower volumes of APS and TMED provide a longer setting time of the gel. That allows the Chelex resin, which is negatively buoyant, to accumulate on one side of the gel when the casting assembly is laid flat. Resin gels were allowed to set at room temperature. Resin gels were immersed in DDI and the water was changed regularly.

6.2.2.2 Calibration of DGT devices

The diffusive properties of the gels, prepared as described above, have been found by Zhang & Davison (1995) to be similar to seawater. The diffusive coefficient of an ion in seawater (D_0) can be obtained from literature (e.g., Li & Gregory 1974). However, Alfaro-De la Torre *et al.* (2000) have found the diffusive properties of the gel to be $< D_0$. Therefore, the diffusive properties of the DGT device (D_g) have been measured directly.

The diffusive layer of the DGT devices comprised a 0.78 mm thick diffusive gel layer and a 0.11 mm thick 0.45 μm cellulose nitrate filter membrane, which overlay a 0.80 mm thick resin gel (Figure 6.1*a*). The resin gel and diffusive layer were mounted on a 25 mm diameter acid washed acrylic gel holder that has a 20 mm diameter exposure window.

Measurement of D_g was completed in the laboratory, by measuring the uptake of low concentrations of metals from seawater. Triplicate DGT devices were placed into metal spiked seawater solutions for 21.5 hours. During that time the solution was stirred continuously and the pH and temperature monitored. This was done to ensure that constant equilibrium between dissolved and adsorbed metal phases in the experimental apparatus was maintained.

Experiments were completed in 10 L of 4 μm filtered seawater (pH 8.2, 35 ppt salinity) stirred continuously at 25° C. Seawater solutions were spiked with small volumes of standard Cu and Pb solutions to provide a concentration < 100 nmol L^{-1}. The solutions were stirred for 48 hours prior to inserting DGT devices, to ensure that equilibrium between the metals introduced to the solutions and the surfaces of the container had been achieved.

A 10 mL subsample of the seawater solutions was collected and acidified with 10 μL of concentrated HNO_3 (Ultrapure) 15 minutes after insertion and immediately prior to removal of the DGT devices. The concentrations of Cu and Pb were measured in these solutions by ASV methods described in section 6.2.1.2. These measurements are required to ensure the concentration remained constant during the experiment.

Upon removal, the gel assembly was rinsed in DDI water and dismantled. A 20 mm resin gel slice was cut from the exposure window, rinsed in DDI water, padded dry to remove excess water and placed in an acid washed 6 mL tube. The weight of the 5 mL tube was measured prior to and after inserting the gel. Assuming that the density of the resin gel is near 1, the volume of the gel can be calculated by difference in weight. Metals were leached from the resin gel by adding 2 mL of 2M HNO_3 to the 6 mL tube. After at least 24 hours, 4 mL of DDI was added, and the solution analysed by inductively coupled plasma - mass spectroscopy (ICP-MS).

The concentration of a metal in the seawater solutions (C_b) can be calculated by modification of Equation 6.4, to accommodate analytical procedures, to form Equation 6.11. Where; m is the concentration of metal measured in the elutent, v is the volume of elutent, w is the weight of the resin gel eluted, Δx is the diffusive layer thickness, D_g is the diffusion coefficient of an ion in the gel, a is the area of the gel undergoing elution, t is the period of deployment; f is the elution factor (recovery).

$$C_b = \frac{m(v+w)\Delta x}{D_g atf} \qquad \text{(Equation 6.11)}$$

D_g can be calculated by arranging Equation 6.11 to form 6.12.

$$D_g = \frac{m(v+w)\Delta x}{C_b atf} \qquad \text{(Equation 6.12)}$$

Where D_g was not measured, published diffusion coefficients of metal ions in seawater were substituted (e.g., Li & Gregory 1974). A nominal elution factor of 0.8 (80%) was used (e.g., Zhang & Davison 1995).

6.2.2.3 DGT sediment probe deployment

DGT sediment probes comprised a 0.8 mm thick resin gel layer overlain by a diffusive layer comprised of a 0.78 mm thick diffusive gel layer and a strip of 0.11 mm thick cellulose nitrate 0.45 µm membrane layer (Hybondextra C®-Amersham-Life products). Gels were mounted between two acrylic plates (Figure 6.1). The plates are separated by a spacer, which maintains the gel thickness and ensures no solutions enter the device between the plates. The upper plate has an exposure window of 10 mm x 270 mm. Once gels were loaded into the probes they were placed in DDI water and deoxygenated by bubbling with nitrogen for 48 hours prior to deployment.

Three DGT sediment probes were deployed in a 1 m x 1 m area. The probes were removed from the nitrogen purged DDI and pushed vertically into the sediment, so that at least 70 mm of the probe was above the sediment, and about 200 mm below the surface. They were deployed within 1 m of sediment core sample sites. The gels were deployed at low tide and were retrieved 72 hours later at low tide.

Once removed from the sediment DGT probes were washed in seawater to remove mud, rinsed thoroughly in DDI water, padded dry, and sealed in plastic bags. Within 4 hours of collection, probes were dismantled, and a 10 mm x 270 mm resin gel strip, which was located beneath the exposure window was removed by cutting with a scalpel. The resin gel strip was rinsed thoroughly in DDI and padded dry to remove excess water. This resin gel was dissected using a scalpel on an acid washed glass cutting board at 5 mm or 10 mm intervals. Narrower sampling intervals were made over the area of gel that straddled the sediment water interface.

Gel slices were placed in 6 mL pre weighed acid washed tubes and the weight of the gel determined by the difference in the weight of the tube and gel. Metals were eluted from the resin gel in 2 mL of 2M HNO_3 for 24 hours at 25°C, before being diluted with 4 mL of DDI, and analysed for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn by ICP-MS.

The total number of moles of metal accumulated in the resin gel are presented in Appendix 10 as the time average flux (J_t) in mol cm^{-2} hr^{-1}. For samples that were located below the sediment water interface a deployment period of 72 hours has been used. Gel samples that were above the sediment water interface and exposed at low tide, have been assigned a deployment period of 62 hours.

6.2.2.4 Resupply coefficient

Using ASV measured pore water concentrations (C_{pw}) it is possible to calculate a time averaged DGT flux assuming sustained resupply of metals as Equation 6.13. This flux is referred to as the initial flux (J_0) because it should closely approximate the real time average flux not long after inserting the DGT probe.

$$J_0 = D_g \frac{C_{pw}}{\Delta x} \qquad \text{(Equation 6.13)}$$

The ratio of J_0 to the DGT probe measured time average flux (J_t) can be used to identify differences in the resupply rate of metals. This ratio is referred to as the resupply coefficient (R), Equation 6.14.

$$R = \frac{J_1}{J_0} \qquad \text{(Equation 6.14)}$$

If R is near 1, this indicates high rates of resupply of metals. If R is less than 1, this indicates that pore water concentrations are not sustained. The relative differences in the value of R can be used to qualitatively assess changes in resupply of metals.

The concept of R was introduced by Harper *et al.* (1998) who found during modelling studies that after 5 hours deployment in sediments the time average DGT flux closely approximates the actual flux. However, the ratio of Harper *et al.* (1998) used a concentration predicted by Equation 6.11 divided by an independent measure of pore water concentration. In this study, R is based upon flux measurements because it should not be inferred that DGT measured fluxes represent dissolved concentrations of ions adjacent the diffusive layer.

R has been calculated for each metal for 9 sediment sample intervals, where dissolved metal concentrations were also available. A depth average DGT flux value was used in calculations because there was typically 4 DGT flux measurements for each interval where pore water was recovered.

6.3 Results

6.3.1 Sediment core chemistry

6.3.1.1 Sediment core description and major element chemistry

Sediment cores were 30 cm deep and collected within 1 m of the DGT probe deployments (Figure 6.2b). A near surface brown coloured oxidised layer was present and was less than 20 mm thick. Below this interval, the sediment was a homogenous soft grey to black, poorly sorted muddy silt. It contained minor gravel sized lithic fragments, and skeletal calcium carbonate fragments were rare. The homogenous nature of the core is demonstrated by the relatively constant concentrations of strong acid soluble major element, organic carbon and carbonate carbon concentrations (Table 6.1).

Sediment porosity is near 80% in surface intervals and declines to 65% by 5 cm depth (Figure 6.3). Sediment Eh exhibits a similar rapid decline over the top 5 cm of the core. The pH has an abrupt step from 7.1 to 7.4 at 8 cm depth (Figure 6.3).

Table 6.1 Whole sediment chemical analyses of major elements from a shallow core collected adjacent to DGT sediment probe deployments in Ross Creek.

Depth (cm)	**Al** $\mu mol\ g^{-1}$	**Ca** $\mu mol\ g^{-1}$	**CC** $\mu mol\ g^{-1}$	**Fe** $\mu mol\ g^{-1}$	**Mn** $\mu mol\ g^{-1}$	**OC** $\mu mol\ g^{-1}$
0-2	1620	179	89	476	9.1	1170
2-4	1718	87	4	473	4.1	1015
4-6	1982	78	117	513	3.9	1113
6-8	1891	97	23	529	4.4	1063
8-10	1739	98	28	530	4.1	1102
10-12	1682	98	62	513	4.6	933
12-14	1798	93	49	560	4.2	1074
14-16	1616	100	54	504	4.4	1059
16-18	1806	97	47	563	4.1	935
Average	1761	103	53	518	4.8	1052

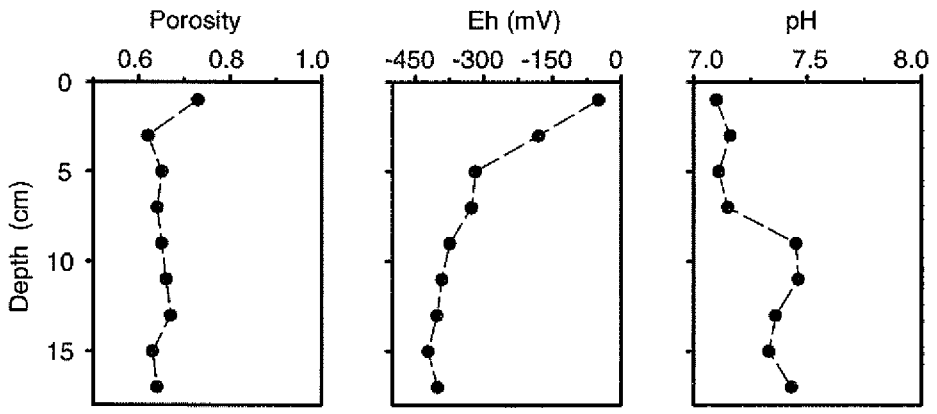


Figure 6.3 Profiles of porosity, Eh and pH from a shallow core in Ross Creek located adjacent DGT sediment probe deployments. Porosity and Eh decline with depth. The pH profile is characterised by a step from 7.1 to 7.4 at 8 to 10 cm depth.

6.3.1.2 Solid phase trace metals

Concentrations of strong acid soluble Cd, Cu, Pb and Zn in whole sediment samples exceed the modelled natural background (Table 6.2). The models used to determine background have been described in Chapter 3. The average enhancement above background (measured/upper 95% prediction level) is presented in Table 6.2. The average concentration of Cu, Pb and Zn also exceeds the Draft ANZECC ISQV-low (Table 6.2).

Increases in the concentration of SEM and residual phase metals below surface in Figure 6.4 are influenced by the decline in porosity with depth (Figure 6.3). Below 5 cm depth, Co, Cu, Ni, Pb and Zn exhibit relatively constant concentrations of SEM and residual metal. However, Cd exhibits a distinct increase in SEM concentrations and decline in residual metal concentrations.

The average lability (Equation 6.9) of individual metals is; Co (0.01) < Ni (0.06) < Cu (0.10) = Fe (0.12) < Mn (0.21) < Pb (0.34) = Cd (0.34) < Zn (0.63). These results are in line with the order of lability found in Chapter 5. Cd exhibits a distinct increase in lability with depth and Cu a likely decline in lability with depth (Figure 6.5).

The increase in lability of Cd with depth is proportional to the increases in the concentration of pyrite and AVS (Figure 6.6). Pore water sulfate concentrations are constant with depth, despite these increases in authigenic sulfide concentration. The ΣSEM/AVS exceeds 1 between 0 to 6 cm depth, but typically exhibits a decline with depth (Figure 6.6).

Table 6.2 Whole sediment strong acid soluble metal concentrations from a shallow core collected adjacent DGT sediment probe deployments in Ross Creek. Average enhancement above background is based upon regression models developed in Chapter 3. The average enhancement above the Draft ANZECC ISQV-low is the ratio of measured value/ANZECC ISQV-low. Not applicable (n.a.).

Depth (cm)	**Cd** pmol g^{-1}	**Co** nmol g^{-1}	**Cu** nmol g^{-1}	**Ni** nmol g^{-1}	**Pb** nmol g^{-1}	**Zn** nmol g^{-1}
0-2	4213	137	1209	252	2042	7832
2-4	6915	175	1460	279	1604	10559
4-6	8600	184	1650	302	1616	12652
6-8	7044	186	1499	313	1681	11403
8-10	6668	168	1309	243	1589	10625
10-12	6327	165	1101	244	1617	9484
12-14	5972	158	1308	238	1660	10179
14-16	6326	164	1131	232	1610	9618
16-18	6155	160	1294	269	1610	10075
Average concentration	6469	166	1329	264	1670	10270
Average enhancement above modelled background (measured/upper 95% prediction level)	82	1.1	6.4	0.8	21.5	2.0
Average enhancement above Draft ANZECC ISQV-low (measured/ISQV-low)	0.5	n.a.	1.3	0.7	6.9	3.4

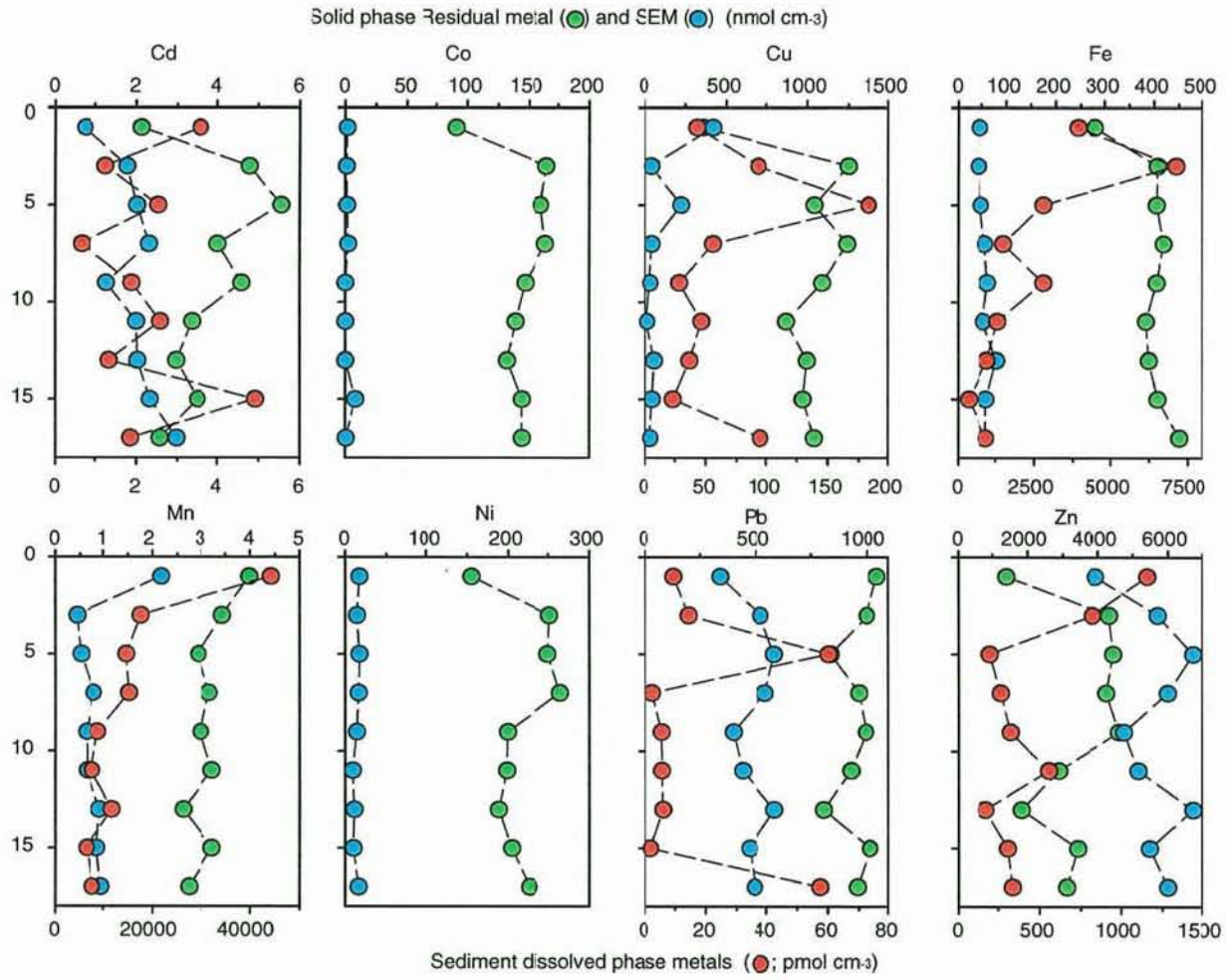


Figure 6.4 Sediment core profiles of dissolved phase metals, simultaneously extracted metals and residual phase metals from a shallow sediment core located adjacent to DGT sediment probe deployments in Ross Creek.

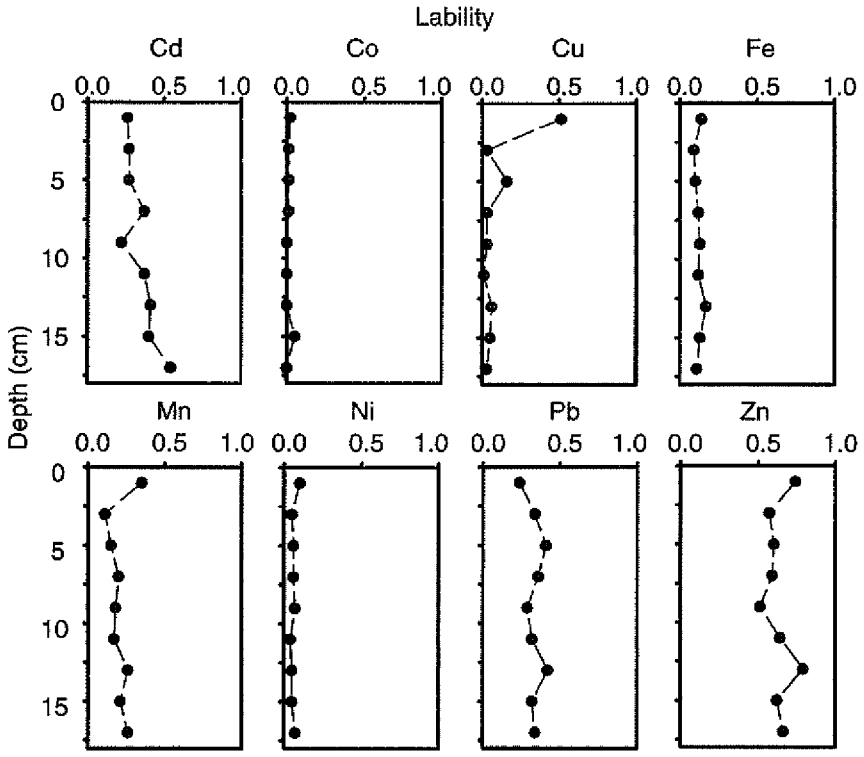


Figure 6.5 Profiles of lability (SEM/SAS) from a shallow core located adjacent to DGT deployment sites in Ross Creek. Cd exhibits an increase in lability with increasing depth. Whereas Cu exhibits a decrease in lability with increasing depth.

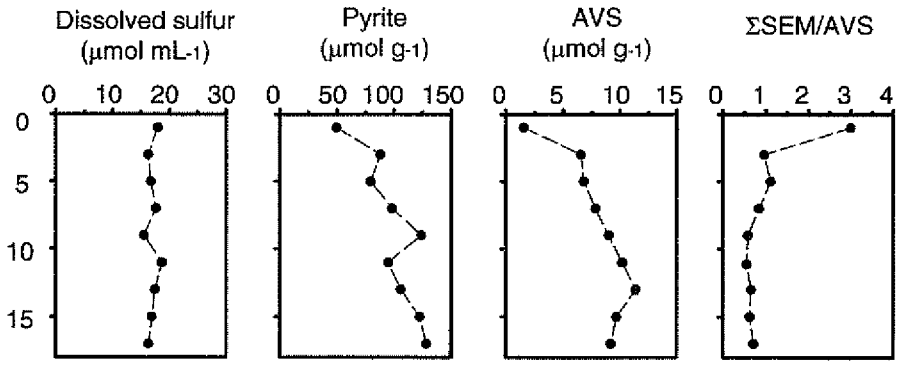


Figure 6.6 Profiles of dissolved sulfur in sediment pore waters, pyrite, acid volatile sulfide (AVS), and the ratio of the sum of simultaneously extracted metals to acid volatile sulfides (ΣSEM/AVS) from a shallow sediment core located adjacent to DGT deployments in Ross Creek.

6.3.1.3 Pore waters

Between 5 to 10 mL of water was squeezed from each core slice over a 4 hour period. Initial attempts to directly measure dissolved Cd, Cu, Pb and Zn concentrations by ASV failed to detect any metal. After UV irradiation metal concentrations could be detected. This suggests that metals were complexed with dissolved or colloidal organic compounds. The concentration of metals in sediment pore waters (mol mL^{-1}) exceeds the Draft ANZECC guidelines trigger levels for Cu, Pb, Mn and Zn (Table 6.3) in marine waters. Profiles of 'dissolved' phase metals are presented in Figure 6.4. A decline in dissolved metal concentration per unit volume of sediment (mol cm^{-3}) with depth in Figure 6.4 is due to declining porosity with depth.

Table 6.3 Surface water and pore water concentrations from a shallow core collected adjacent DGT sediment probe deployments in Ross Creek. Cd, Cu, Pb and Zn were determined by ASV. Fe, Mn and S were determined by ICP-AES. Draft ANZECC water quality trigger levels are the interim guideline levels used to trigger a response (follow up) in marine waters. Not applicable (n.a.); not determined (n.d.).

Depth (cm)	**Cd** nmol L^{-1}	**Cu** nmol L^{-1}	**Fe** µmol L^{-1}	**Mn** µmol L^{-1}	**Pb** nmol L^{-1}	**Zn** nmol L^{-1}
Surface water	5.9	111	1.07	0.73	13	646
0-2	4.9	59	5.37	60.61	n.d.	1589
2-4	2	n.d.	11.46	28.21	23.2	1324
4-6	3.9	283	4.29	22.57	92.7	306
6-8	1	87	2.33	23.66	3.9	413
8-10	2.9	44	4.29	13.47	8.7	n.d.
10-12	3.9	70	1.97	11.28	8.7	840
12-14	2	55	1.43	17.47	9.2	257
14-16	7.8	37	0.547	10.19	2.9	488
16-18	2.9	148	1.43	11.65	89.8	526
Draft ANZECC water quality trigger levels	15	5	n.a.	0.855	3.8	43

6.3.2 DGT device calibration

The diffusion coefficients of Cu and Pb for the DGT device (D_g) were calculated to be 4.75 and 5.0 x 10^{-6} cm^2 sec^{-1} respectively. These D_g values are 64% and 53% less than published D_0 values, of 7.33 and 9.45 x 10^{-6} cm^2 sec^{-1} for Cu and Pb respectively (Li & Gregory 1974). A summary of the experimental results used to derive D_g, and the effects of using D_0, are presented as Table 6.4. The average of the initial and final ASV measured concentration of Cu and Pb has been used to calculate D_g (Table 6.4).

Table 6.4 Calibration of DGT device diffusion coefficient (D_g) for Cu and Pb. Concentration of the bulk solution is under estimated using the published diffusion coefficients of Cu and Pb in seawater (D_0) (Li & Gregory 1974).

		ASV measured concentration (nmol mL^{-1})		**DGT measured concentration (nmol mL^{-1})**	
		Initial t = 0.25h	Final t = 20.5h	$D_g = D_0 = 7.33$ (10^{-6} cm^{-2} sec^{-1})	$D_g = 4.75$ (10^{-6} cm^{-2} sec^{-1})
Cu	blank	17.0 ± 1.6	15.6 ± 1.6	12.5 ± 4.4	18.5 ± 6.5
	addition 1	19.5 ± 3.1	31.0 ± 4.7	21.2 ± 1.9	31.4 ± 2.8
	addition 2	49.6 ± 3.1	63.4 ± 7.9	36.6 ± 2.7	54.1 ± 4.1
	addition 3	98.2 ± 3.1	74.8 ± 12.6	59.4 ± 5.0	87.7 ± 7.4
		Initial t = 0.25h	Final t = 20.5h	$D_g = D_0 = 9.45$ (10^{-6} cm^{-2} sec^{-1})	$D_g = 5.00$ (10^{-6} cm^{-2} sec^{-1})
Pb	blank	3.9 ± 1.0	3.9 ± 1.0	1.5 ± 0.6	2.8 ± 1.2
	addition 1	4.3 ± 0.5	8.7 ± 0.5	4.9 ± 0.6	9.3 ± 1.0
	addition 2	18.8 ± 0.5	18.8 ± 1.4	11.3 ± 0.5	21.4 ± 1.0
	addition 3	26.5 ± 3.9	29.9 ± 1.9	15.0 ± 0.6	28.4 ± 1.2

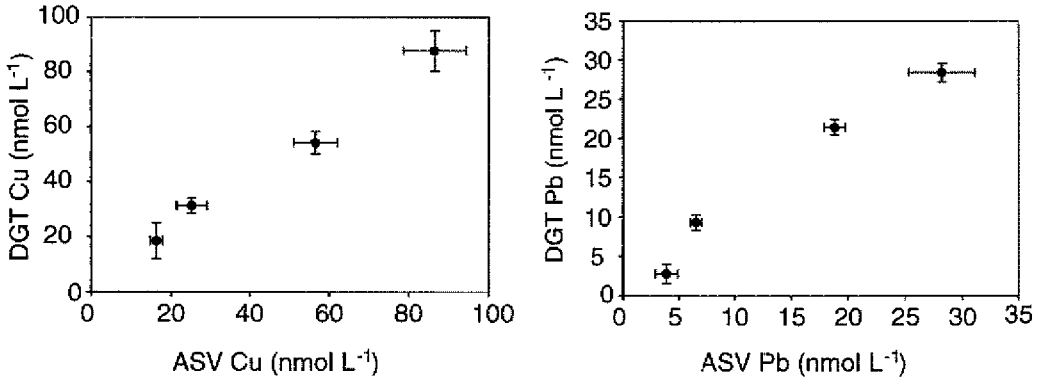


Figure 6.7 Calibration of DGT devices for Cu and Pb in seawater. Triplicate DGT devices were immersed in 10 L of 4 μm filtered seawater at 25°C and stirred continuously for 21.5h. Error bars represent 1 standard deviation.

Despite $D_g \gg D_0$, the positive linear increase in DGT predicted metal concentration versus ASV measured metal concentration occurs in Figure 6.7. These data indicate that with calibration of the diffusive properties, the DGT method can be used to measure low concentrations of metals in well mixed waters. The D_g for all metals could not be determined because insufficient diffusive gel was available to allow calibration for all metals in the laboratory and replication of DGT probes in the field.

6.3.3 DGT Deployment

6.3.3.1 DGT measured fluxes

Depth profiles of the minimum and maximum DGT flux measured for Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn, from three DGT probes, located within a 1 m x 1 m area, are presented in Figure 6.8. The variation in minimum and maximum value of the time average flux measurements of individual metals, made at equivalent depth from the seidment water interface, is typically within 1 order of magnitude. This indicates that within 1 m2 the variation in time averaged DGT flux of metals will be less than 1 order of magnitude. Therefore, the *average of three*, time averaged DGT flux measurements, at equivalent depths relative to the surface water interface, are used herein to describe the measured time average flux from this site (DGT flux or J_t).

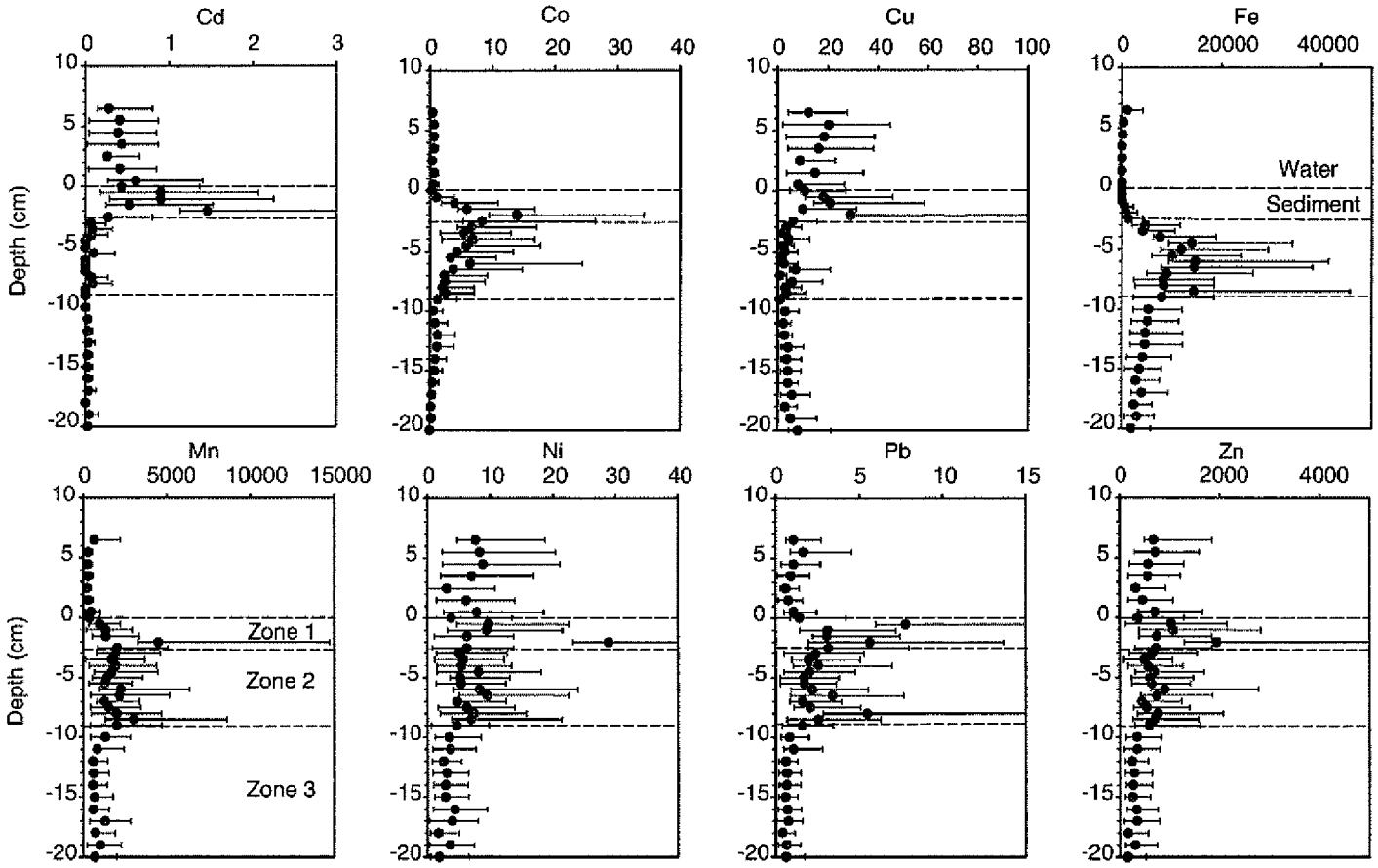


Figure 6.8 DGT time averaged metal fluxes (J_t) from a triplicate sediment probes deployed in Ross Creek. All results in pmol cm^{-2} h^{-1}. Black circles are the average of three time averaged DGT flux measurements within 1 m^2. Horizontal bars represent minimum and maximum time averaged flux. Probes straddle the sediment water interface at 0 cm depth. Dashed lines represent limits of vertical zonation of DGT available metals described in the text.

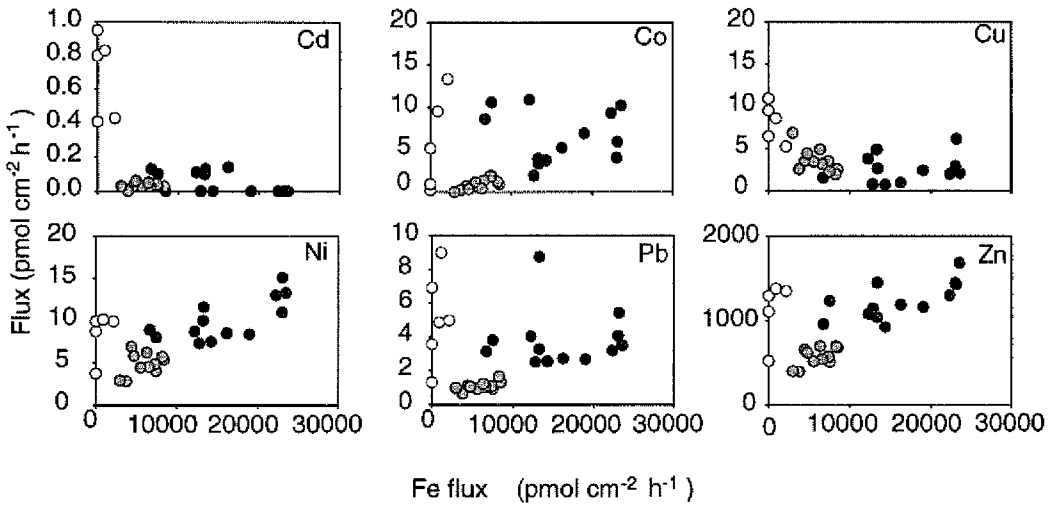


Figure 6.9 Plots of average time averaged DGT flux (J_t) of Fe versus average time averaged DGT metal flux. Symbol codes represent sample depth. 0 - 2.5 cm (○); 2.5 - 9 cm (●); 9 - 20 cm (⊜).

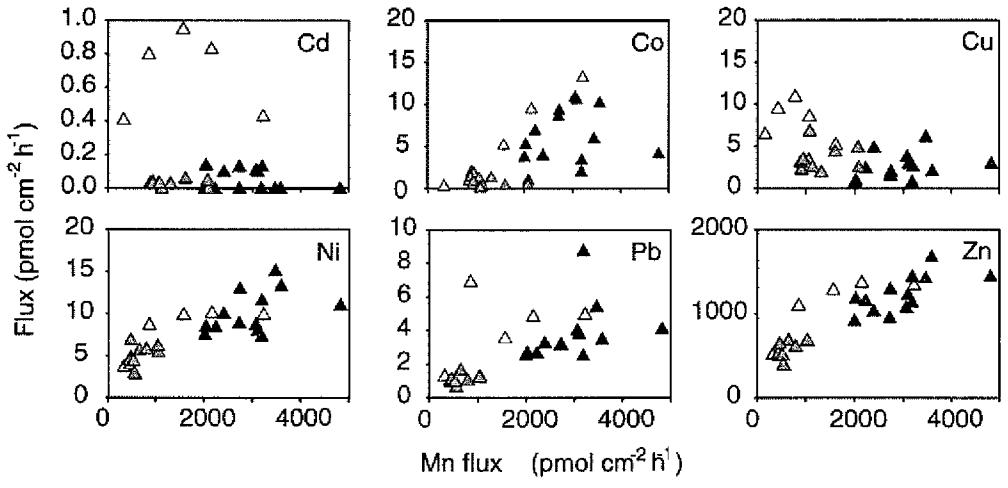


Figure 6.10 Plots of average time averaged DGT flux (J_t) of Mn versus average time averaged DGT metal flux. Symbol codes represent sample depth. 0 - 2.5 cm (△); 2.5 - 9 cm (◬); 9 - 20 cm (▲).

In Figure 6.8, at least three discrete vertical zones in DGT metal flux can be distinguished. The 3 zones can be classified on the basis of relationships of Fe and Mn with trace metal fluxes (Figures 6.9 and 6.10). Zone 1 is characterised by an overall decrease in trace metal DGT flux towards surface, above a maximum DGT flux of trace metals at 2.5 cm. In this zone the DGT flux of Co, Ni, Pb and Zn has a positive linear correlation with Mn DGT flux (Figure 6.10).

Zone 2 occurs from 2.5 cm to 9 cm, and is characterised by consistently high DGT flux of Co, Fe, Mn, Ni, Pb and Zn (Figure 6.8). The DGT fluxes of Co, Ni, Pb and Zn exhibit a positive linear correlation with DGT flux of Fe and Mn over this interval (Figure 6.9 and 6.10). In contrast, Cd and Cu display distinctly different DGT flux profiles characterised by rapid decline in flux from the near surface peak at 2.5 cm. The peak Fe flux occurs in this interval near 5 cm depth, below the peak flux of other metals at 2.5cm.

Zone 3 occurs below 9 cm depth and is characterised by a decline in DGT flux of all metals. The slope of the relationships between Fe and trace metals in Figure 6.8 also changes. This suggests a distinct change in the rate of DGT flux of trace metals relative to Fe and Mn in this zone.

6.3.3.2 Constraints upon metal resupply

Among metals, a high R value indicates greater resupply rates of metals from the solid phase. This can be demonstrated by the linear relationships between R and K_d for each metal (Figure 6.11) when plotted on log axes. This relationship occurs because the DGT devices have been deployed for an extended (> 24 hours) period of time. This resulted in pore water concentrations being depleted and resupply is predominantly a function of the rate of resupply of metals from the solid to the dissolved phase.

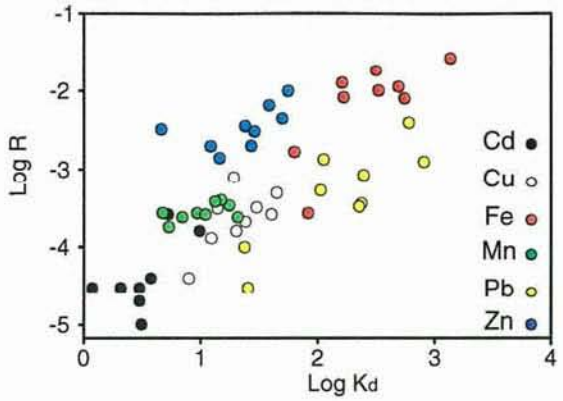


Figure 6.11 Relationship of distribution coefficient (*Kd*) and the resupply coefficient (*R*), for Cd, Cu, Fe, Mn, Pb and Zn. *R* and *Kd* values for Ni and Co could not be calculated because dissolved phase concentrations were not measured. The relationship indicates that metals with a high resupply rate from the solid phase to the dissolved phase have high *Kd*.

For Cd, the value of *R* is lower than other metals and indicates low rates of resupply from the solid phase to the dissolved phase. Changes in *R* for Cd, are characterised by a rapid decline with depth (Figure 6.12), similar to porosity and Eh (Figure 6.3). The profiles of *R* for Fe and Mn increase with depth and indicate greater rates of resupply from the solid phase at depth than at surface. The profiles of *R* for Pb and Zn exhibit a weak decline with depth below 6 cm. The high values of *R* for Fe and Zn are consistent with high rates of these elements from the solid phase.

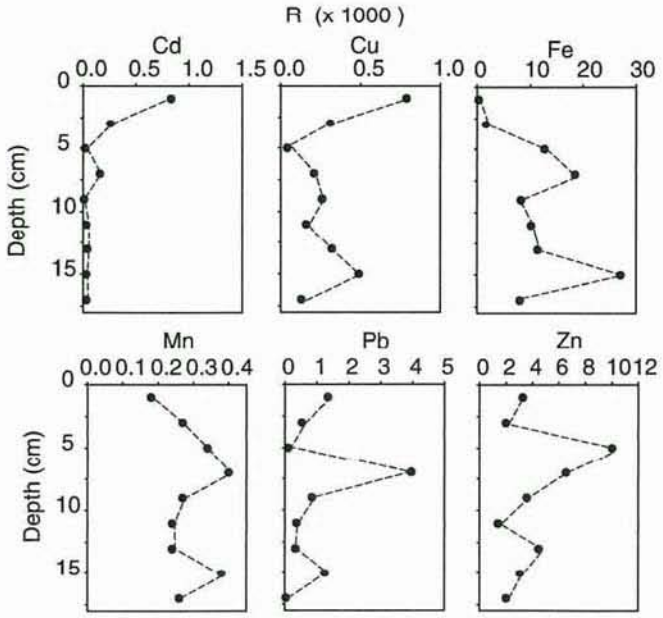


Figure 6.12 Profiles of the resupply coefficient (*R*), for Cd, Cu, Fe, Mn, Pb and Zn.

6.4 Discussion

6.4.1 Relationships between DGT flux and concentration

Conversion of DGT flux measurements (mol cm^{-2} hr^{-1}) to concentrations (mol cm^{-3}, mol g^{-1}) is desirable if measurements are to be compared directly with other metal speciation measures (e.g., pore water concentration). It is possible to calculate dissolved metal concentrations in well buffered circulating waters using Equation 6.10 (Zhang & Davison 1995; Denney *et al.* 1999; Alfaro-De la Torre *et al.* 2000). Under such circumstances, the metals depleted from solution adjacent to the DGT device, by uptake into the device, are replenished by relatively fast resupply of metals by water circulation. The concentration of metals adjacent the DGT device is constant and Fickian diffusive properties, assumed by Equation 6.11, are maintained.

In sediments, uptake of metals from pore waters by the DGT probe, results in depletion of dissolved pore water metal concentrations adjacent the DGT probe (Zhang *et al.* 1995). The depletion disrupts the equilibrium between dissolved and solid phase metals and results in desorption of metals from the solid phase to the dissolved phase (e.g., Zhang *et al.* 1995). The efficiency of resupply is dependent upon the response time of the exchange process (Harper *et al.* 1998). If there is a large pool of exchangeable metal and the rate of exchange is rapid to sustain pore water concentrations, Equation 6.11 can be used to predict pore water concentrations.

The resupply coefficient (R) for all metals is less than 1 and this indicates that pore water metal concentrations are not sustained during the deployment period. Therefore the rate of resupply of all metals is insufficient to maintain the pore water concentration at the initial concentration. Because the concentration of metals in pore water is not constant, Equation 6.11 cannot be used to calculate pore water metal concentrations. The linear relationship between R and K_d in Figure 6.12 indicates that the time average diffusive flux is more representative of the resupply of metals from the solid phase rather than the metals hosted in the dissolved phase.

Alternative methods for calculating metal concentrations, under conditions where the concentration adjacent the diffusive layer is not constant, have been

developed and are based upon models of diffusive and desorptive resupply rates during deployment (e.g., Zhang *et al.* 1995; Harper *et al.* 1998). These methods are computationally arduous and are beyond the scope of this study.

In this study, only a single deployment period and diffusive layer thickness has been used and the diffusion coefficients of all metals have not been determined for the DGT device. Quantitative calculation of sediment pore water concentrations is therefore not possible. However, qualitative limits to the volume of sediment affected by DGT uptake can be made. The limits can be based upon the relationship between the number of moles of a metal accumulated by the DGT sediment probe per unit area (mol cm^{-2}), and the number of moles of a metal held in different operationally defined phases of 1 cm^3 of sediment (Figure 6.13).

In Figure 6.13*a*, the total moles of each metal accumulated by the DGT probe per cm^2 (mol cm^{-2}) over the 72 hour deployment period is greater than the number of moles of each metal contained in the dissolved phase in 1 cm^3 of sediment. The ratio of mol cm^{-2} to mol cm^{-3} yields a value with units of cm. This value can be interpreted as the distance (cm) from the diffusive layer into the sediment required to host the equivalent number of moles accumulated by the DGT device. Therefore, if resupply is only from the dissolved phase, the distance into the sediment affected by depletion over a 72 hour deployment, is greater than 1 cm for most metals.

In Figure 6.13*b*, the number of moles of each metal accumulated by the probe is typically less than the 10% of the number of moles of each metal contained in the dissolved and SEM phases of 1 cm^3 of sediment (Figure 6.13*b*). This suggests that if resupply is from the dissolved phase and all of the metal in the SEM phase is exchangeable, the distance away from the diffusive layer affected by resupply is less 0.1 cm for most metals.

Therefore the metals accumulated by the DGT device during a 72 hour deployment represent the entire dissolved phase and only a small portion (< 10%) of the SEM phase contained in 1 cm^3 of sediment. This is in line with modelling by Harper *et al.* (1998) who found that the region of influences to be less than 1 mm thick for a deployment of 24 hours.

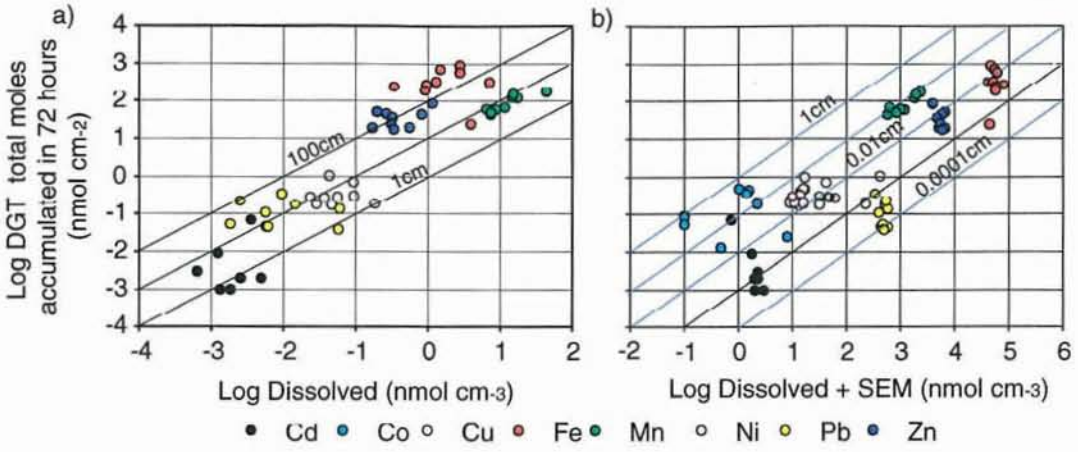


Figure 6.13 Thickness of the zone of depletion adjacent to the DGT device. a) Plot of the mass of metal contained within 1 cm3 of sediment in the dissolved phase versus the mass of metal accumulated in 1 cm2 of resin gel in 72 hours. b) Plot of the mass of metal contained within 1 cm3 of sediment in the dissolved phase and SEM phases versus the mass of metal accumulated in 1 cm2 of resin gel in 72 hours.

6.4.2 Significance of DGT flux and metal speciation to environmental surveys

Despite the complications of converting single or replicate DGT probe flux measurements to concentration under conditions of low resupply rate, the measurements can provide valuable information on metal speciation (Harper *et al.* 1998; Denney *et al.* 2000; McNee & Robertson 2000). DGT flux measurements are time dependent operationally defined speciation values, for which the properties can be standardised (e.g., device diffusive properties, diffusive layer thickness, time of deployment). Metals available for uptake by DGT devices in this study are capable of diffusing through the diffusive layer and are dissolved ionic species. The metals are capable of being collected by Chelex resin, which has a high affinity for trace metals cations.

DGT fluxes are measured in situ, with minimum disruption of sediment redox status. Redox status has been found to be an important influence upon the preservation of metastable Fe monosulfides (AVS), which are easily oxidised (Vandenberg *et al.* 1998)

The oxidation of AVS can result in the liberation and increased bioavailability of metals bound in the AVS phase (e.g., Simpson *et al.* 2000; Morse 1995). The time dependent uptake of metals across a membrane by the DGT device is also consistent with models of metal uptake by organisms (e.g., Van Leeuwen 1999). Such models recognise that the kinetics of resupply of metals is also critical to determining metal bioavailability.

Therefore the metals collected by DGT probes are potentially a more meaningful measure of bioavailability than concentration based parameters measured in sediment core intervals. However, it has been found that Chelex available metals in surface waters overestimate the amount of some metals available for uptake by organisms (e.g., Apte & Batley 1995).

DGT fluxes can also be measured at high spatial resolution (e.g., Zhang *et al.* 1995; Davison *et al.* 1997; Shuttleworth *et al.* 1999). In this study, the high vertical spatial resolution of sampling has enabled three vertical zones to be identified (Figure 6.8), which can be discriminated on the basis of the relationships between Fe, Mn and trace metals (Figure 6.9 and 6.10). The high spatial resolution allows collection of several samples from each of these zones and more clearly identifies the relationships among metals within each zone.

The zones identified are present in each of 3 sediment probes deployed within a 1 m^2 area. The processes creating the zonation are therefore laterally persistent over larger areas. However, within the 1 m^2 area, the DGT measured fluxes vary by up 1 order of magnitude for individual metals.

Sediment core speciation measurements

The significance of DGT speciation and the vertical zonation of fluxes to environmental surveys can be demonstrated by comparing the results with operationally defined speciation measures made in sediment cores adjacent to the DGT deployments and the Draft ANZECC interim sediment/water quality values. Operationally defined speciation measures assumed to represent bioavailable metals made in this study are dissolved metals in pore waters, 1M HCl soluble metals (SEM) and ΣSEM/AVS.

In the sediment cores, collected adjacent to the DGT deployments, there is no strong vertical zonation in solid phase SEM and residual phase metal concentration (Figure 6.4). The average concentration of strong acid soluble (SAS) Cd, Cu, Ni, Pb and Zn in whole sediment samples (mol g^{-1}) exceed the modelled (described in Chapter 3) natural variation in sediment concentration (Table 6.2). The average concentrations of SAS Cd, Cu, Pb and Zn in whole sediment samples exceed the Draft ANZECC ISQV-low threshold (Table 6.2) and this suggests that concentrations may have a deleterious effect upon sediment quality.

The trends in acid soluble lability (SEM/SAS) of metals in sediment cores are characterised by high lability of Cd, Pb and Zn and low lability of Co, Cu and Ni (Figure 6.5). Cd is the only metal to exhibit distinct changes in lability with depth and is characterised by an increase in lability with depth. These results indicate that Cd, Pb and Zn are preferentially incorporated into a more 'bioavailable' phase than Co, Cu and Ni. This is in line with the patterns of lability of trace metals described in Chapter 5 from sediment cores located in other parts of the intertidal zone of Cleveland Bay.

ΣSEM/AVS ratios > 1 occur to 6 cm depth (Figure 6.6) and this indicates that in the absence of other binding sites, trace metals could occur in the dissolved phase in this interval. This would increase the risk of organisms being exposed to metals in near surface sediment.

The pore water concentrations of Mn and Zn (nmol L^{-1}) exhibit an increase in concentration towards surface (Table 6.3). Other metals do not exhibit distinct vertical zonation in concentration. The concentration of Cu, Pb and Zn in the dissolved phase (mol L^{-1}) exceeds the ANZECC water quality guidelines trigger levels (Table 6.3). This suggests that the concentrations of these metals in the pore water of sediments are potentially harmful.

In summary, the parameters measured in the sediment cores at 2 cm intervals indicate that there are no strong patterns in vertical zonation in the concentration of metals in the solid (Table 6.2) or dissolved phases (Table 6.3). The concentrations measured in the dissolved phase and solid phase exceed the Draft ANZECC guideline trigger levels, and suggests that there is potential for the concentrations to adversely

effect sediment quality. The ΣSEM/AVS ratios suggest metals are capable of being present in the dissolved phase from 0 to 6cm depth.

DGT speciation

In contrast, the DGT flux profiles identify strong vertical zonation of all metals. The zones can each be characterised on the basis of the relationships between the DGT available trace metals with DGT available Fe and Mn. These associations provide strong evidence that Fe and Mn reduction are influencing the availability of trace metals to the DGT probe near surface (e.g., Zhang *et al.* 1995). Trace metals are incorporated as passive participants in the reduction or oxidation of Fe and Mn (e.g., Klinkhammer *et al.* 1982; Sawlan & Murray 1983; Morse & Arakaki 1993; Douglas & Adeney 2000). This is due to the capacity of Fe and Mn oxide species to adsorb trace metals and release them upon reduction (e.g. Hem 1977; Morse 1995).

Zone 1 extends from the sediment water interface to 2.5 cm depth. It is characterised by high porosity and more oxidised conditions than deeper in the core (Figure 6.3). The availability of Cd, Co, Cu, Mn, Ni, Pb and Zn to the DGT probe over this zone typically declines towards surface, above a sub surface maximum at 2.5 cm depth. The changes among metals correlate positively with the DGT available Mn (Figure 6.9). This suggests that metal lability in this interval is related to the reductive dissolution of Mn oxides, with trace metals becoming more labile with the reduction of Mn oxides (e.g., Yu *et al.* 2000).

This relationship suggests that despite ΣSEM/AVS > 1 in the 0 to 2 cm interval, metals are probably less bioavailable nearer the sediment water interface due to the presence of Mn oxides. The maximum amount of DGT available metals occur at 2.5 cm below surface, which probably also represents the interval of peak metal bioavailability.

Interpretation of this near surface interval is critical to determine if the sediment behaves as a source or a sink for metals (e.g., Cheevaporn *et al.* 1995; Anshutz *et al.* 1997). The patterns in DGT available metals do not support or exclude the diffusive fluxes of metals across the sediment water interface. The trends do suggest that the

behaviour of Mn in this near surface interval probably regulate diffusive fluxes of trace metals. Therefore fluxes will be dependent upon the redox status of this interval.

Zone 2 occurs from 2.5 to 9 cm depth. Interpretation of this zone is critical to understanding bioavailability of metals, because the majority of sediment organism interactions occur in the top 10 cm of sediments (Boudreau 1998). The presence of a peak in the amount of DGT available Cd, Cu, Ni, Pb and Zn at 2.5 cm (Figure 6.8), indicates that a portion of all trace metals in this interval are periodically available for redistribution and concentration at a redox interface (e.g., Rosenthal *et al.* 1995; Clark *et al.* 1997).

The zone is characterised by a positive linear correlation between DGT available Co, Ni, Pb and Zn with Fe and Mn, and declining DGT available Cd and Cu (Figure 6.8). The correlation between DGT available Co, Ni, Pb and Zn with Fe and Mn in this interval indicates that DGT availability is determined by Fe and Mn reduction. This interval is also the peak interval of Fe and Mn reduction, which is supported by the separation of the peak DGT available Fe and Mn within this zone. The separation with depth represents classical separation of their reduction peaks over a redox gradient (e.g., Stumm & Morgan 1996).

In contrast to Co, Ni, Pb and Zn, the rapid decline with depth in DGT available Cd and Cu is independent of Fe and Mn DGT availability (Figure 6.8). The changes in DGT available Cd and Cu are proportional to increases in both AVS and pyrite concentrations measured at 2 cm intervals (Figure 6.6). This suggests that the interaction with authigenic Fe sulfide is the predominant influence upon Cd and Cu availability to the DGT probe. Cd is progressively partitioned into a 1M HCl soluble authigenic sulfide phase with depth and Cu partitioned into a non 1M HCl soluble authigenic sulfide phase (Figure 6.5).

Below 9 cm there is a distinct break in sediment pH and availability of metals to the DGT probe. The break is characterised by a decline in the DGT availability of all metals to values, which are at least half the values occurring between 2.5 to 9 cm. The slope of the relationship between DGT available trace metals and Fe also changes, relative to the interval from 2.5 to 9 cm (Figures 6.8 and 6.9). The change in metal DGT

availability is also associated with a marked step in the pH from 7.1 to 7.4 (Figure 6.3). The progressive decline in DGT availability is associated with a progressive increase in pyrite and AVS. This suggests that the amount of metal that is available for exchange with the DGT probe below 9 cm depth is decreased by the interactions with authigenic sulfides.

The vertical zonation of DGT metal flux indicates that Mn, Fe and sulfate reduction each play a highly significant role in determining the availability of metals to the DGT probe. The effects of Fe and Mn reduction are not apparent within the wet chemical speciation methods used to analyse sediment core samples at 2 cm intervals. The processes observed are entirely a function of the sample interval spacing and the speciation method (e.g., Zhang *et al.* 1995).

At 2 cm sample intervals, the trends with depth in acid lability (SEM/SAS) of metals indicate significant changes in Cd and Cu lability only (Figure 6.5) and pore water concentrations do not identify the interval of high DGT available metal from 2.5 to 9 cm depth (Table 6.3). The partitioning of metals based on patterns in DGT availability, into DGT available (Co, Ni, Pb and Zn) and non DGT available (Cd and Cu), is in contrast to the partitioning based on the solubility of metals in 1M HCl.

Partitioning of metals based upon acid 1M HCl soluble properties (Figure 6.5) indicate partitioning of Cd, Pb, Zn into 'bioavailable' 1M HCl soluble phases relative to Co, Cu, Ni (Figure 6.5). If 1M HCl soluble metals are considered to be bioavailable (e.g., Langston *et al.* 1999), then the DGT speciation provides very different measures of bioavailability to sediment core samples.

These results suggest that concepts of metal bioavailability in sediments based upon 1M HCl solubility and the capacity of some metals to form insoluble AVS or pyrite phases, may not be relevant in near surface sediments due to other interactions. In this study Fe and Mn reduction greatly influences the availability of Co, Ni, Pb and Zn to exchange with the DGT probes between 0 to 9 cm depth.

The partitioning of Cd and Cu into non DGT exchangeable sulfide phases in preference to other metals is not adequately explained by the kinetic and

thermodynamic constraints described by Morse & Luther (1998) and described previously in Chapter 5. The data presented here suggests that Cd and Cu have a greater affinity to form sulfide phases between 2.5 to 9 cm depth than Co, Ni, Pb and Zn, which are affected by Fe and Mn reduction.

The mechanism behind the observed partitioning has not been resolved. As such the observed DGT partitioning may be as much a function of the source of the metals as the interaction with early diagenetic processes (e.g., Simpson *et al.* 2000). More work is required to confirm the mechanisms that result in the observed partitioning of trace metals by DGT.

6.5 Conclusions

DGT fluxes, measured in triplicate sediment probes, differ by up to an order of magnitude within 1 m^2. Despite this large variation in absolute flux, the patterns in vertical zonation of DGT trace metal flux created by Fe, Mn and SO_4 reduction are consistent between probes. This indicates these processes are laterally extensive and each play a major role in determining the amount of trace metal available to exchange with the DGT device.

Quantitative measurements of pore water concentrations cannot be derived from DGT probe deployments used in this study. However, the flux measurements can be considered as operationally defined, time dependent, metal speciation values. The speciation data can be integrated with other measurements to provide a greater understanding of the behaviour of trace metals in sediments.

DGT flux measurements indicate that from 0 to 2.5 cm depth the DGT available metal is regulated by the presence of Mn oxides. The maximum DGT flux of all trace metals occurs at 2.5 cm and combined with the results of ΣSEM/AVS ratios, which are > 1 at this interval, suggests that this represents the interval of maximum bioavailability of trace metals.

From 2.5 to 9 cm, high DGT availability of Co, Ni, Pb and Zn are influenced by Fe and Mn reduction and declining DGT availability of Cd and Cu are influenced by the

interaction with authigenic sulfides. Below 9 cm depth, all trace metals exhibit a decline in DGT availability, probably due to the interactions with authigenic sulfides. The partitioning of metals, into DGT available (Co, Ni, Pb and Zn) and unavailable (Cd and Cu), from 2.5 to 9 cm depth indicates that interactions with authigenic sulfide are less significant for Co, Ni, Pb and Zn than for Cd and Cu. However, below 9 cm depth the interaction with authigenic sulfides is significant for all metals.

The results indicate that the application of ΣSEM/AVS theory and partitioning of metals into bioavailable and non bioavailable phases based upon 1M HCl properties, are potentially confounded by interactions with other processes occurring within near surface sediments. DGT speciation provides an alternative tool for the determination of the behaviour of metals in near surface sediments. Further work is required to determine; 1) the mechanisms that determined preferential interaction between Cd and Cu with authigenic sulfide relative to Co, Ni, Pb and Zn; 2) if the patterns in DGT speciation represent bioavailability.

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Appendix 1 Surface sediment grab samples - location data and strong acid digestion analytical results

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
301	Inner Shelf	Halifax Bay	-18.6117	146.4850	28-Aug-93	7.00	493	6487	6338	< D. L.	-	48.79	167	4.73	-	287	12.37	22.20	60.82	6625	-
302	Inner Shelf	Halifax Bay	-18.6100	146.4667	28-Aug-93	18.00	667	6262	6114	< D. L.	-	66.10	202	4.42	-	270	12.33	25.58	57.08	6383	-
303	Inner Shelf	Halifax Bay	-18.6083	146.4483	28-Aug-93	20.00	845	4990	4819	106.76	-	81.84	236	3.90	-	294	10.59	28.96	49.59	5113	-
304	Inner Shelf	Lucinda	-18.6067	146.4317	28-Aug-93	18.00	1071	4516	4394	97.86	-	100.72	304	4.97	-	310	12.21	37.16	47.10	4704	-
305	Inner Shelf	Lucinda	-18.6050	146.4133	28-Aug-93	16.00	875	3842	3562	124.56	73.83	80.26	304	5.26	143.33	251	10.46	36.68	36.18	3812	333.64
306	Inner Shelf	Lucinda	-18.6033	146.3967	28-Aug-93	15.00	930	2203	2053	97.86	-	92.85	290	4.30	-	255	8.04	39.58	28.76	2308	-
307	Inner Shelf	Lucinda	-18.6017	146.3800	28-Aug-93	12.00	1342	2645	2547	< D. L.	113.05	147.94	394	6.81	257.11	410	10.36	61.78	43.04	2956	549.33
308	Inner Shelf	Lucinda	-18.6000	146.3633	28-Aug-93	5.00	482	1205	1124	97.86	-	45.64	249	8.06	-	167	9.20	33.30	23.61	1291	-
309	Inner Shelf	Lucinda	-18.5983	146.3433	28-Aug-93	1.00	193	634	561	< D. L.	36.87	< D. L.	88	6.86	18.13	58	2.91	15.93	18.50	619	116.87
310	Inner Shelf	Lucinda	-18.5833	146.3667	28-Aug-93	3.00	545	1113	997	< D. L.	-	51.94	283	5.99	-	185	10.11	34.75	21.99	1181	-
311	Inner Shelf	Lucinda	-18.5700	146.3750	28-Aug-93	5.00	2342	778	625	< D. L.	-	204.60	637	10.34	-	749	13.85	99.42	91.08	1374	-
312	Inner Shelf	Lucinda	-18.5533	146.3817	28-Aug-93	8.00	1605	1310	1109	115.66	-	155.81	458	7.15	-	460	10.07	74.81	48.66	1569	-
313	Inner Shelf	Lucinda	-18.5367	146.3867	28-Aug-93	12.00	1168	1524	1312	< D. L.	-	116.46	353	6.46	-	365	9.01	52.12	37.43	1678	-
314	Inner Shelf	Lucinda	-18.5183	146.3900	28-Aug-93	15.00	1412	1275	1089	< D. L.	-	143.22	408	6.26	-	500	9.95	68.53	58.33	1589	-
315	Inner Shelf	Lucinda	-18.5000	146.3800	28-Aug-93	10.00	2828	364	208	444.84	-	335.22	763	8.66	-	1600	13.92	159.27	207.11	1808	-
316	Inner Shelf	Lucinda	-18.5000	146.3600	28-Aug-93	3.00	2224	277	153	373.67	-	2093.17	587	7.44	-	1241	10.36	139.48	147.85	1395	-
317	Inner Shelf	Lucinda	-18.5000	146.3950	28-Aug-93	17.00	1560	1834	1579	106.76	-	155.81	462	7.77	-	460	11.53	67.08	46.79	2038	-
318	Inner Shelf	Lucinda	-18.5000	146.4117	28-Aug-93	18.00	982	3169	2876	< D. L.	-	100.72	319	5.93	-	297	10.59	41.99	34.62	3173	-
319	Mid Shelf	Mid Shelf	-18.5000	146.4283	28-Aug-93	21.00	982	3368	3045	< D. L.	-	99.15	308	6.86	-	321	11.27	39.09	42.73	3366	-
320	Mid Shelf	Mid Shelf	-18.5000	146.4467	28-Aug-93	22.00	741	3393	3159	< D. L.	-	50.36	245	4.68	-	270	9.91	30.89	38.68	3429	-
321	Mid Shelf	Mid Shelf	-18.5000	146.4683	28-Aug-93	23.00	634	3842	3464	< D. L.	-	62.95	211	4.42	-	222	9.88	26.54	42.42	3687	-
322	Mid Shelf	Mid Shelf	-18.5000	146.4850	28-Aug-93	25.00	612	3693	3390	< D. L.	-	64.53	201	3.31	-	241	9.75	24.13	43.67	3632	-
323	Mid Shelf	Mid Shelf	-18.5000	146.5033	28-Aug-93	25.00	430	4217	3884	< D. L.	-	44.07	177	4.66	-	206	11.20	22.20	40.55	4090	-
324	Mid Shelf	Mid Shelf	-18.5000	146.5383	28-Aug-93	27.00	378	3069	3274	< D. L.	-	34.62	127	2.51	-	182	7.52	17.37	33.69	3456	-
325	Mid Shelf	Mid Shelf	-18.5000	146.5733	28-Aug-93	31.00	337	5414	5766	< D. L.	-	29.90	132	3.24	-	204	12.79	16.41	54.27	5970	-
326	Mid Shelf	Mid Shelf	-18.5250	146.5967	28-Aug-93	33.00	393	5589	5862	< D. L.	-	33.05	122	3.62	-	256	15.56	15.44	52.09	6119	-
327	Mid Shelf	Mid Shelf	-18.5483	146.6200	28-Aug-93	33.00	356	5015	5209	< D. L.	-	28.33	113	4.24	-	205	12.56	14.96	54.90	5413	-
328	Mid Shelf	Mid Shelf	-18.5733	146.6450	28-Aug-93	33.00	311	5389	5703	< D. L.	-	26.75	104	4.24	-	199	12.17	14.96	54.90	5902	-
329	Mid Shelf	Mid Shelf	-18.5967	146.6700	28-Aug-93	31.00	285	5539	5860	< D. L.	-	25.18	98	4.10	-	206	11.43	13.51	58.33	6066	-
330	Mid Shelf	Mid Shelf	-18.6133	146.6867	28-Aug-93	31.00	315	5714	5884	< D. L.	-	31.48	109	4.86	-	219	11.20	15.93	59.26	6104	-
331	Mid Shelf	Mid Shelf	-18.6133	146.6500	28-Aug-93	29.00	345	6038	6320	< D. L.	-	31.48	116	4.28	-	216	11.88	14.96	58.64	6536	-
332	Mid Shelf	Mid Shelf	-18.6133	146.6150	28-Aug-93	28.00	415	5714	5993	97.86	-	37.77	127	3.93	-	240	12.98	17.37	55.83	6233	-
333	Mid Shelf	Mid Shelf	-18.6133	146.5783	28-Aug-93	27.00	430	4716	4907	< D. L.	-	40.92	140	4.62	-	218	11.08	16.89	46.16	5125	-
334	Mid Shelf	Mid Shelf	-18.6150	146.5450	28-Aug-93	23.00	545	4516	4582	< D. L.	-	51.94	168	3.71	-	251	11.08	20.27	46.48	4834	-
335	Mid Shelf	Mid Shelf	-18.6133	146.5217	28-Aug-93	22.00	793	4117	4168	142.35	-	75.54	231	5.26	-	351	11.24	25.10	47.41	4518	-
336	Mid Shelf	Mid Shelf	-18.6517	146.5233	28-Aug-93	42.00	808	5813	5734	115.66	-	77.12	211	3.55	-	329	10.62	22.20	64.25	6063	-
337	Mid Shelf	Mid Shelf	-18.6850	146.5383	28-Aug-93	26.00	274	7660	7437	275.80	-	34.62	213	9.16	-	209	20.28	22.20	43.04	7646	-
338	Inner Shelf	Halifax Bay	-18.7150	146.5533	28-Aug-93	20.00	574	6287	6274	< D. L.	-	62.95	172	3.73	-	286	12.66	27.99	66.13	6560	-
339	Inner Shelf	Halifax Bay	-18.7400	146.5667	28-Aug-93	5.00	133	7136	7129	< D. L.	-	20.46	45	2.42	-	223	8.81	13.51	71.74	7352	-
340	Inner Shelf	Halifax Bay	-18.7400	146.5200	28-Aug-93	20.00	682	5739	5713	115.66	-	70.82	208	4.82	-	295	12.79	25.10	56.14	6008	-
341	Mid Shelf	Mid Shelf	-18.5950	146.4667	29-Aug-93	27.00	467	6013	5821	< D. L.	-	51.94	163	3.95	-	213	10.72	20.27	47.72	6034	-
342	Mid Shelf	Mid Shelf	-18.5850	146.4533	29-Aug-93	22.00	567	5065	4902	< D. L.	-	53.51	209	7.86	-	222	9.27	23.17	46.79	5124	-
343	Mid Shelf	Mid Shelf	-18.5750	146.4383	29-Aug-93	23.00	782	4541	4483	< D. L.	-	89.71	244	4.82	-	307	10.40	29.92	49.91	4791	-
344	Inner Shelf	Lucinda	-18.5650	146.4250	29-Aug-93	20.00	941	3743	3585	124.56	-	105.45	328	4.99	-	315	10.66	36.20	38.68	3900	-
345	Inner Shelf	Lucinda	-18.5533	146.4100	29-Aug-93	20.00	1372	2206	2225	462.63	-	138.50	379	6.45	-	363	10.04	45.37	55.65	2588	-
346	Inner Shelf	Lucinda	-18.5450	146.3967	29-Aug-93	16.00	1212	1471	1422	106.76	-	130.63	349	5.37	-	329	8.50	47.30	32.53	1751	-
347	Inner Shelf	Lucinda	-18.5350	146.3833	29-Aug-93	14.00	1844	915	784	151.25	-	184.14	544	8.96	-	644	11.09	76.74	115.56	1428	-
348	Inner Shelf	Lucinda	-18.5350	146.3650	29-Aug-93	3.00	222	80	44	2758.01	55.89	23.61	122	5.79	31.49	42	3.59	25.10	15.32	87	170.03
349	Inner Shelf	Lucinda	-18.5333	146.4000	29-Aug-93	17.00	1261	1555	1483	< D. L.	107.05	111.74	370	5.35	199.37	325	9.13	46.33	33.09	1808	497.40

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
350	Inner Shelf	Lucinda	-18.5333	146.4183	29-Aug-93	19.00	1009	2459	2406	< D. L.	-	105.45	308	5.24	-	295	8.97	36.68	42.11	2701	-
351	Mid Shelf	Mid Shelf	-18.5333	146.4367	29-Aug-93	21.00	914	3303	3214	< D. L.	73.82	94.43	282	4.93	157.47	284	10.09	32.34	41.08	3498	355.97
352	Mid Shelf	Mid Shelf	-18.5333	146.4533	29-Aug-93	23.00	783	4047	3889	355.87	-	73.97	267	4.51	-	277	11.50	28.96	46.79	4166	-
353	Mid Shelf	Mid Shelf	-18.5333	146.4700	29-Aug-93	25.00	472	3441	3240	< D. L.	41.08	47.21	167	3.36	79.59	225	8.36	21.24	39.08	3464	190.30
354	Mid Shelf	Mid Shelf	-18.5333	146.4883	29-Aug-93	39.00	292	5636	5134	177.94	-	33.05	179	11.61	-	152	16.33	19.31	30.96	5286	-
355	Mid Shelf	Mid Shelf	-18.5350	146.5067	29-Aug-93	30.00	520	3573	3389	204.63	-	51.94	166	3.19	-	256	9.25	19.79	44.45	3644	-
356	Mid Shelf	Mid Shelf	-18.5333	146.5233	29-Aug-93	26.00	511	2700	2643	< D. L.	-	51.94	177	6.29	-	248	8.47	21.72	41.24	2892	-
357	Mid Shelf	Mid Shelf	-18.5333	146.5583	29-Aug-93	31.00	349	5986	5956	< D. L.	-	36.20	157	4.17	-	241	15.09	17.37	52.37	6197	-
358	Mid Shelf	Mid Shelf	-18.5350	146.5917	29-Aug-93	33.00	363	5793	5945	< D. L.	-	34.62	121	3.38	-	263	12.87	13.03	57.89	6208	-
359	Mid Shelf	Mid Shelf	-18.4583	146.5933	29-Aug-93	36.00	356	4406	4448	106.76	-	36.20	138	2.75	-	246	9.71	14.48	48.63	4694	-
360	Mid Shelf	Mid Shelf	-18.4600	146.5583	29-Aug-93	32.00	335	4049	4122	115.66	-	31.48	123	2.70	-	235	8.82	14.48	41.36	4357	-
361	Mid Shelf	Mid Shelf	-18.4583	146.5233	29-Aug-93	26.00	344	2272	2239	< D. L.	-	34.62	121	3.55	-	195	6.53	16.89	32.69	2434	-
362	Mid Shelf	Mid Shelf	-18.4600	146.5067	29-Aug-93	26.00	353	3119	3110	< D. L.	-	34.62	134	4.31	-	190	7.86	18.34	40.11	3300	-
363	Mid Shelf	Mid Shelf	-18.4583	146.4883	29-Aug-93	26.00	463	3181	3119	97.86	-	42.49	169	4.47	-	226	8.69	18.34	39.39	3344	-
364	Mid Shelf	Mid Shelf	-18.4583	146.4717	29-Aug-93	24.00	492	4044	3947	151.25	39.96	48.79	174	3.85	81.44	223	9.23	17.86	43.23	4170	183.11
365	Mid Shelf	Mid Shelf	-18.4583	146.4533	29-Aug-93	23.00	828	3648	3584	< D. L.	-	70.82	258	4.56	-	322	10.44	25.58	45.91	3906	-
366	Mid Shelf	Mid Shelf	-18.4583	146.4367	29-Aug-93	22.00	726	2695	2615	97.86	60.59	69.25	235	3.98	132.18	261	10.08	28.47	38.96	2877	284.69
367	Mid Shelf	Mid Shelf	-18.4583	146.4183	29-Aug-93	21.00	943	2715	2605	115.66	-	83.41	292	4.61	-	317	9.62	33.30	39.99	2922	-
368	Inner Shelf	Lucinda	-18.4583	146.4017	29-Aug-93	20.00	1024	3086	2947	124.56	87.66	62.95	321	5.66	167.26	296	10.15	37.16	37.24	3244	399.11
369	Inner Shelf	Lucinda	-18.4583	146.3833	29-Aug-93	17.00	2254	1191	1062	177.94	-	111.74	648	8.40	-	691	13.44	96.04	92.70	1753	-
370	Inner Shelf	Lucinda	-18.4583	146.3667	29-Aug-93	11.00	1488	543	428	195.73	144.70	133.77	456	7.14	227.64	827	9.90	85.91	104.68	1255	686.71
371	Inner Shelf	Lucinda	-18.4583	146.3483	29-Aug-93	7.00	646	322	232	106.76	-	72.40	258	7.04	-	326	6.46	43.44	43.64	559	-
372	Inner Shelf	Lucinda	-18.4583	146.3317	29-Aug-93	10.00	481	399	316	< D. L.	113.28	44.07	226	8.47	82.93	218	6.24	38.61	34.19	534	369.13
373	Inner Shelf	Hinchinbrook Channel	-18.4850	146.2967	29-Aug-93	-	3159	94	t	355.87	-	380.86	806	4.01	-	3947	13.99	192.08	383.03	3947	-
374	Inner Shelf	Hinchinbrook Channel	-18.4883	146.2967	29-Aug-93	-	2595	103	t	364.77	-	369.85	891	6.12	-	4355	13.00	175.68	552.40	4355	-
375	Inner Shelf	Hinchinbrook Channel	-18.4900	146.2883	29-Aug-93	-	1701	77	t	364.77	-	234.50	516	2.64	-	3530	8.44	117.76	455.08	3530	-
376	Inner Shelf	Hinchinbrook Channel	-18.4867	146.2817	29-Aug-93	-	2945	108	t	329.18	184.83	295.88	794	5.85	345.26	3788	13.63	178.09	294.57	3788	1184.79
377	Inner Shelf	Hinchinbrook Channel	-18.4867	146.2367	30-Aug-93	1.00	1582	77	t	613.88	94.26	226.63	401	2.43	187.62	2864	6.76	150.10	356.83	2864	810.00
378	Inner Shelf	Hinchinbrook Channel	-18.4850	146.1900	30-Aug-93	-	2666	94	t	293.59	-	335.22	618	2.48	-	5822	11.87	166.99	369.00	5822	-
379	Inner Shelf	Hinchinbrook Channel	-18.4733	146.1800	30-Aug-93	2.00	3056	108	t	533.81	-	355.68	587	2.25	-	7227	13.09	166.02	495.32	7227	-
380	Inner Shelf	Hinchinbrook Channel	-18.4733	146.1800	30-Aug-93	2.00	2898	146	t	418.15	-	368.27	544	2.26	-	6083	11.78	162.64	425.76	6083	-
381	Inner Shelf	Hinchinbrook Channel	-18.4700	146.1817	30-Aug-93	1.00	2170	112	t	498.22	-	350.96	585	2.36	-	5592	9.94	147.68	674.36	5592	-
382	Inner Shelf	Hinchinbrook Channel	-18.4667	146.1817	30-Aug-93	1.00	2246	164	262	943.06	-	336.80	634	2.58	-	5504	9.81	128.86	762.94	5766	-
383	Inner Shelf	Hinchinbrook Channel	-18.4483	146.1933	30-Aug-93	1.00	2855	100	228	364.77	-	316.34	657	2.46	-	2523	9.90	139.48	454.46	2751	-
384	Inner Shelf	Hinchinbrook Channel	-18.4367	146.1850	30-Aug-93	1.00	2151	112	415	364.77	-	250.24	587	2.37	-	3322	9.99	106.18	671.87	3737	-
385	Inner Shelf	Hinchinbrook Channel	-18.3583	146.1433	30-Aug-93	1.00	1952	532	549	258.01	-	195.15	590	3.48	-	3430	10.29	109.56	395.82	3979	-
386	Inner Shelf	Hinchinbrook Channel	-18.2783	146.0917	30-Aug-93	2.00	1318	804	811	< D. L.	-	119.61	359	3.72	-	1351	7.59	72.88	130.32	2162	-
387	Inner Shelf	Hinchinbrook Channel	-18.2800	146.0833	30-Aug-93	12.00	1998	406	332	142.35	148.87	140.07	542	6.14	248.34	1050	8.69	92.66	148.38	1382	752.18
388	Inner Shelf	Hinchinbrook Channel	-18.2800	146.0733	30-Aug-93	17.00	413	1805	1803	< D. L.	-	34.62	220	4.54	-	364	5.14	32.34	33.56	2166	-
389	Inner Shelf	Hinchinbrook Channel	-18.2800	146.0617	30-Aug-93	2.00	1572	2174	2082	< D. L.	-	89.71	816	8.51	-	1455	15.81	80.60	182.41	3537	-
390	Inner Shelf	Hinchinbrook Channel	-18.2800	146.0550	30-Aug-93	3.00	962	2844	2724	< D. L.	-	70.82	444	4.69	-	586	11.05	50.68	52.28	3310	-
391	Inner Shelf	Hinchinbrook Channel	-18.2800	146.0517	30-Aug-93	1.00	1172	461	416	< D. L.	-	62.95	307	3.62	-	657	5.90	60.33	55.05	1073	-
392	Inner Shelf	Hinchinbrook Channel	-18.2850	146.0533	30-Aug-93	1.00	1417	687	654	142.35	119.21	103.87	361	3.91	163.60	745	6.47	69.98	102.46	1400	564.48
393	Inner Shelf	Hinchinbrook Channel	-18.2750	146.0483	30-Aug-93	1.00	532	557	531	< D. L.	-	28.33	384	13.85	-	210	5.28	50.19	25.74	741	-
394	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1600	30-Aug-93	1.00	1266	545	252	329.18	-	111.74	394	3.00	-	4230	10.81	83.98	375.55	4482	-
395	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1517	30-Aug-93	5.00	1368	850	859	< D. L.	146.07	97.58	486	4.99	166.67	1594	7.87	63.71	129.73	2453	639.67
396	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1417	30-Aug-93	4.00	1030	1406	1315	< D. L.	-	78.69	631	5.53	-	774	11.97	59.85	58.86	2090	-
397	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1333	30-Aug-93	9.00	2112	608	609	142.35	132.66	180.99	530	4.48	219.21	1690	10.15	106.18	144.85	2299	725.03
398	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1250	30-Aug-93	6.00	1756	290	263	222.42	-	121.18	476	4.04	-	1398	8.37	89.77	116.87	1661	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
399	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1167	31-Aug-93	1.00	992	2251	2274	< D. L.	102.66	73.97	311	3.29	560.98	960	8.24	44.88	66.94	3234	461.60
400	Inner Shelf	Hinchinbrook Channel	-18.3333	146.1067	31-Aug-93	3.00	1309	4152	3904	< D. L.	-	75.54	505	5.90	-	1181	15.25	57.92	87.37	5085	-
401	Inner Shelf	Hinchinbrook Channel	-18.3333	146.0967	31-Aug-93	2.00	2191	246	394	231.32	133.72	176.27	598	3.59	260.35	3580	9.44	117.28	439.18	3974	826.07
402	Inner Shelf	Rockingham Bay	-18.0567	146.0367	01-Sep-93	2.00	715	110	103	< D. L.	92.15	23.61	242	7.97	77.38	85	4.85	32.34	22.67	187	388.01
403	Inner Shelf	Rockingham Bay	-18.0583	146.0550	01-Sep-93	7.00	2460	669	616	142.35	-	132.20	648	8.06	-	1046	14.34	103.28	127.11	1662	-
404	Inner Shelf	Rockingham Bay	-18.0567	146.0717	01-Sep-93	9.00	1316	1504	1481	< D. L.	135.06	103.87	405	7.38	176.72	528	10.02	57.43	62.73	2009	565.00
405	Inner Shelf	Rockingham Bay	-18.0583	146.0900	01-Sep-93	10.00	1176	1116	1137	< D. L.	-	119.61	381	7.86	-	365	9.09	52.61	58.98	1503	-
406	Inner Shelf	Rockingham Bay	-18.0567	146.1067	01-Sep-93	10.00	931	975	950	97.86	126.76	78.69	334	8.00	140.27	330	9.20	45.85	37.80	1280	473.54
407	Inner Shelf	Rockingham Bay	-18.0583	146.1250	01-Sep-93	11.00	834	1018	1021	< D. L.	-	75.54	315	8.17	-	221	9.08	41.51	32.94	1241	-
408	Inner Shelf	Rockingham Bay	-18.0583	146.1417	01-Sep-93	12.00	994	1391	1399	142.35	123.64	97.58	346	7.78	153.38	255	9.84	43.92	35.43	1653	479.19
409	Inner Shelf	Rockingham Bay	-18.0583	146.1600	01-Sep-93	13.00	1039	2026	2059	< D. L.	-	100.72	344	7.77	-	334	10.77	45.37	41.73	2393	-
410	Inner Shelf	Rockingham Bay	-18.0583	146.1767	01-Sep-93	14.00	1156	2099	2142	< D. L.	-	113.31	363	7.47	-	306	11.31	48.75	37.96	2449	-
411	Inner Shelf	Rockingham Bay	-18.0567	146.1950	01-Sep-93	15.00	1119	2794	2871	< D. L.	-	103.87	348	7.67	-	309	11.37	41.99	43.33	3180	-
412	Inner Shelf	Rockingham Bay	-18.0567	146.2117	01-Sep-93	18.00	1002	2837	2915	< D. L.	-	94.43	323	8.21	-	276	11.04	40.06	44.88	3190	-
413	Mid Shelf	Mid Shelf	-18.0583	146.2300	01-Sep-93	19.00	1130	3006	3145	142.35	-	108.59	341	7.24	-	296	11.06	40.06	46.07	3440	-
414	Mid Shelf	Mid Shelf	-18.0567	146.2467	01-Sep-93	20.00	856	3603	3707	106.76	-	99.15	275	5.95	-	219	10.51	31.85	40.52	3926	-
415	Mid Shelf	Mid Shelf	-18.0567	146.2650	01-Sep-93	21.00	738	3650	3628	< D. L.	-	72.40	248	5.25	-	175	10.01	27.99	41.36	3802	-
416	Mid Shelf	Mid Shelf	-18.0567	146.3000	01-Sep-93	24.00	543	3685	3722	< D. L.	-	51.94	191	5.34	-	196	10.01	22.68	43.48	3918	-
417	Mid Shelf	Mid Shelf	-18.0583	146.3350	01-Sep-93	25.00	365	3500	3405	< D. L.	-	34.62	138	3.45	-	125	7.98	15.93	38.33	3530	-
418	Inner Shelf	Rockingham Bay	-18.1783	146.1383	01-Sep-93	3.00	967	2094	2008	< D. L.	106.39	83.41	316	6.11	144.95	370	8.19	42.95	57.27	2379	450.01
419	Inner Shelf	Rockingham Bay	-18.1783	146.1217	01-Sep-93	3.00	540	1333	1266	< D. L.	-	42.49	258	6.25	-	182	6.15	30.89	35.59	1447	-
420	Inner Shelf	Rockingham Bay	-18.1783	146.1050	01-Sep-93	5.00	711	3782	3613	< D. L.	85.54	61.38	317	6.17	101.69	359	9.97	35.71	44.35	3971	351.14
421	Inner Shelf	Rockingham Bay	-18.1783	146.0867	01-Sep-93	6.00	680	5374	5113	< D. L.	-	69.25	332	5.87	-	322	12.25	38.13	47.07	5435	-
422	Inner Shelf	Rockingham Bay	-18.1783	146.0700	01-Sep-93	6.00	852	5536	5236	< D. L.	90.97	75.54	419	6.64	110.54	421	14.20	46.33	48.28	5657	369.97
423	Inner Shelf	Rockingham Bay	-18.1783	146.0517	01-Sep-93	5.00	1107	5212	4990	< D. L.	-	100.72	423	5.87	-	567	15.01	57.43	61.51	5557	-
424	Inner Shelf	Rockingham Bay	-18.1783	146.0333	01-Sep-93	5.00	1422	4828	4511	< D. L.	105.71	108.59	433	4.96	146.91	716	11.36	58.88	74.77	5227	524.50
425	Inner Shelf	Rockingham Bay	-18.1783	146.0167	01-Sep-93	4.00	2485	762	648	< D. L.	-	190.43	640	7.57	-	1147	9.89	106.18	234.97	1795	-
426	Inner Shelf	Rockingham Bay	-18.1783	146.0117	01-Sep-93	1.00	591	162	58	< D. L.	-	37.77	168	4.46	-	391	3.31	32.82	65.28	450	-
427	Inner Shelf	Rockingham Bay	-18.1783	146.0250	01-Sep-93	5.00	1745	3678	3443	< D. L.	-	135.35	456	5.49	-	894	10.33	69.50	96.44	4338	-
428	Inner Shelf	Rockingham Bay	-18.1783	146.1833	02-Sep-93	13.00	1350	3151	3000	< D. L.	-	132.20	405	6.83	-	461	13.69	56.95	52.96	3461	-
429	Inner Shelf	Rockingham Bay	-18.1783	146.2017	02-Sep-93	12.00	1017	1860	1753	< D. L.	120.72	94.43	373	7.54	151.25	327	9.57	48.26	36.28	2081	479.74
430	Inner Shelf	Rockingham Bay	-18.1783	146.2183	02-Sep-93	13.00	1260	1530	1422	< D. L.	-	114.89	401	7.56	-	433	9.94	55.50	42.61	1855	-
431	Inner Shelf	Rockingham Bay	-18.1783	146.2367	02-Sep-93	13.00	1514	1011	911	< D. L.	-	135.35	466	8.24	-	568	10.98	64.67	56.96	1479	-
432	Inner Shelf	Rockingham Bay	-18.1783	146.2550	02-Sep-93	15.00	1865	1252	1117	177.94	-	168.40	550	7.84	-	656	12.09	74.81	72.96	1773	-
433	Inner Shelf	Rockingham Bay	-18.1783	146.2717	02-Sep-93	18.00	1543	1933	1826	115.66	-	133.77	450	6.68	-	464	10.75	58.40	49.53	2290	-
434	Inner Shelf	Rockingham Bay	-18.1783	146.2883	02-Sep-93	19.00	1293	2507	2381	115.66	-	121.18	396	6.45	-	396	10.71	47.30	46.51	2777	-
435	Mid Shelf	Mid Shelf	-18.1783	146.3067	02-Sep-93	23.00	1474	2562	2441	106.76	-	141.64	445	7.23	-	459	11.84	48.75	50.69	2900	-
436	Mid Shelf	Mid Shelf	-18.1783	146.3233	02-Sep-93	25.00	968	3738	3652	204.63	-	92.85	355	6.44	-	267	13.85	33.30	40.92	3919	-
437	Mid Shelf	Mid Shelf	-18.1783	146.3417	02-Sep-93	27.00	728	3952	3872	213.52	-	77.12	280	4.73	-	231	11.56	26.06	36.40	4103	-
438	Mid Shelf	Mid Shelf	-18.1783	146.3600	02-Sep-93	29.00	485	4733	4751	< D. L.	-	45.64	206	4.49	-	183	11.15	18.34	42.17	4934	-
439	Mid Shelf	Mid Shelf	-18.1783	146.3783	02-Sep-93	29.00	519	4137	4473	142.35	-	45.64	192	3.97	-	219	11.44	17.86	46.76	4692	-
440	Mid Shelf	Mid Shelf	-18.1783	146.4117	02-Sep-93	31.00	284	4890	5349	< D. L.	-	28.33	111	3.30	-	162	9.93	13.51	51.72	5512	-
441	Mid Shelf	Mid Shelf	-18.1783	146.4467	02-Sep-93	33.00	286	6500	6383	< D. L.	-	26.75	108	3.19	-	197	11.09	12.55	64.10	6581	-
442	Mid Shelf	Mid Shelf	-18.1217	146.4300	02-Sep-93	34.00	301	4993	5012	< D. L.	-	33.05	140	2.99	-	177	10.10	14.48	52.03	5189	-
443	Mid Shelf	Mid Shelf	-18.1217	146.3950	02-Sep-93	31.00	385	5654	5681	106.76	-	33.05	184	4.15	-	239	12.22	17.37	52.25	5920	-
444	Mid Shelf	Mid Shelf	-18.1217	146.3600	02-Sep-93	28.00	397	5886	6030	< D. L.	-	39.35	192	4.33	-	206	12.15	19.31	47.44	6236	-
445	Mid Shelf	Mid Shelf	-18.1217	146.3433	02-Sep-93	27.00	433	3174	3246	< D. L.	-	42.49	171	3.88	-	168	8.41	18.82	37.27	3414	-
446	Mid Shelf	Mid Shelf	-18.1217	146.3250	02-Sep-93	26.00	507	3857	3921	< D. L.	-	51.94	214	5.08	-	195	10.46	21.24	35.34	4115	-
447	Mid Shelf	Mid Shelf	-18.1217	146.3083	02-Sep-93	26.00	756	3204	3226	204.63	-	70.82	253	5.17	-	240	9.62	27.03	36.93	3466	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
448	Mid Shelf	Mid Shelf	-18.1217	146.2900	02-Sep-93	23.00	1295	3124	3081	97.86	-	80.26	382	5.92	-	373	11.66	38.61	60.70	3454	-
449	Mid Shelf	Mid Shelf	-18.1217	146.2733	02-Sep-93	16.00	798	3745	3615	204.63	-	73.97	280	6.29	-	244	10.12	29.92	42.79	3859	-
450	Inner Shelf	Rockingham Bay	-18.1217	146.2550	02-Sep-93	17.00	847	3810	3721	< D. L.	-	53.51	260	5.45	-	316	10.30	34.27	45.73	4037	-
451	Inner Shelf	Rockingham Bay	-18.1217	146.2383	02-Sep-93	15.00	784	2680	2513	< D. L.	-	69.25	264	5.32	-	247	9.10	30.89	32.56	2760	-
452	Inner Shelf	Rockingham Bay	-18.1217	146.2200	02-Sep-93	14.00	894	2175	2094	97.86	-	89.71	301	5.87	-	306	8.72	36.68	35.43	2400	-
453	Inner Shelf	Rockingham Bay	-18.1217	146.2017	02-Sep-93	13.00	725	2337	2252	< D. L.	-	69.25	257	5.56	-	246	9.07	36.68	30.86	2499	-
454	Inner Shelf	Rockingham Bay	-18.1217	146.1850	02-Sep-93	11.00	1038	2221	2125	115.66	-	61.38	351	6.85	-	352	10.02	51.64	36.21	2477	-
455	Inner Shelf	Rockingham Bay	-18.1217	146.1683	02-Sep-93	10.00	935	1598	1514	97.86	119.03	72.40	346	7.68	146.91	311	9.50	50.68	32.97	1825	462.71
456	Inner Shelf	Rockingham Bay	-18.1217	146.1500	02-Sep-93	9.00	865	1164	1155	< D. L.	-	72.40	341	7.73	-	286	8.38	47.78	34.19	1441	-
457	Inner Shelf	Rockingham Bay	-18.1217	146.1333	02-Sep-93	8.00	795	1119	1044	258.01	123.31	59.80	339	8.00	132.52	286	8.27	43.44	37.37	1330	435.26
458	Inner Shelf	Rockingham Bay	-18.1217	146.1150	02-Sep-93	7.00	837	1236	1163	< D. L.	-	61.38	339	7.48	-	331	8.19	50.19	42.05	1494	-
459	Inner Shelf	Rockingham Bay	-18.1217	146.0983	02-Sep-93	7.00	967	1441	1370	106.76	131.30	70.82	368	7.56	140.69	398	8.63	53.09	52.84	1768	478.84
460	Inner Shelf	Rockingham Bay	-18.1217	146.0800	02-Sep-93	7.00	1102	1856	1864	< D. L.	-	88.13	357	7.16	-	499	8.56	55.50	57.80	2363	-
461	Inner Shelf	Rockingham Bay	-18.1217	146.0633	02-Sep-93	6.00	1382	2283	2311	< D. L.	125.66	105.45	397	6.52	178.76	683	9.86	66.12	72.52	2994	569.22
462	Inner Shelf	Rockingham Bay	-18.1217	146.0450	02-Sep-93	6.00	1752	2695	2619	< D. L.	-	99.15	466	5.54	-	800	9.57	73.36	119.99	3419	-
463	Inner Shelf	Rockingham Bay	-18.1217	146.0283	02-Sep-93	5.00	2728	422	328	240.21	177.46	169.97	700	7.46	304.80	1290	11.69	136.10	174.77	1618	1001.47
464	Inner Shelf	Rockingham Bay	-18.1217	146.0117	02-Sep-93	3.00	1721	283	192	< D. L.	-	99.15	476	7.74	-	917	8.85	89.77	119.81	1110	-
465	Inner Shelf	Rockingham Bay	-18.1417	146.0617	02-Sep-93	6.00	1381	3161	3025	< D. L.	-	113.31	394	6.04	-	714	9.71	64.67	70.09	3739	-
466	Inner Shelf	Rockingham Bay	-18.1567	146.0817	02-Sep-93	6.00	1152	3623	3498	< D. L.	-	99.15	365	6.40	-	607	10.31	55.02	57.49	4105	-
467	Inner Shelf	Missionary Bay	-18.2967	146.2483	03-Sep-93	1.00	2397	196	0	320.28	-	185.71	683	3.64	-	4001	10.16	97.97	520.90	4001	-
468	Inner Shelf	Missionary Bay	-18.2967	146.2450	03-Sep-93	1.00	1690	1600	1456	409.25	125.70	119.61	547	3.69	234.20	3813	27.28	73.36	549.28	5269	713.26
469	Inner Shelf	Missionary Bay	-18.2817	146.2367	03-Sep-93	3.00	2192	291	475	355.87	-	146.36	664	3.93	-	3547	10.11	96.04	475.67	4021	-
470	Inner Shelf	Missionary Bay	-18.2783	146.2233	03-Sep-93	-	2064	282	223	240.21	-	140.07	591	4.12	-	2190	10.37	95.08	244.29	2413	-
471	Inner Shelf	Missionary Bay	-18.2700	146.2317	03-Sep-93	-	1074	4411	4169	275.80	-	110.17	312	2.69	-	2481	11.86	55.98	208.23	6651	-
472	Inner Shelf	Missionary Bay	-18.2583	146.2167	03-Sep-93	2.00	1069	4568	4300	329.18	90.51	107.02	356	3.96	141.46	1127	11.51	57.43	92.95	5427	457.94
473	Inner Shelf	Missionary Bay	-18.2450	146.2083	03-Sep-93	1.00	905	1115	1126	231.32	123.66	84.99	344	7.12	148.87	1298	8.20	58.40	120.43	2424	481.80
474	Inner Shelf	Missionary Bay	-18.2283	146.1983	03-Sep-93	2.00	868	1066	999	< D. L.	-	77.12	334	7.76	-	475	7.92	55.50	55.27	1474	-
475	Inner Shelf	Rockingham Bay	-18.2167	146.1867	03-Sep-93	3.00	826	1114	1061	115.66	-	75.54	325	7.99	-	353	7.83	52.12	42.05	1414	-
476	Inner Shelf	Rockingham Bay	-18.2067	146.1717	03-Sep-93	5.00	895	1842	1864	< D. L.	114.30	97.58	333	7.34	136.09	348	8.74	55.02	34.68	2212	441.97
477	Inner Shelf	Rockingham Bay	-18.1983	146.1567	03-Sep-93	7.00	1216	2237	2216	142.35	-	136.92	366	6.35	-	578	9.56	65.64	56.14	2794	-
478	Inner Shelf	Rockingham Bay	-18.1917	146.1467	03-Sep-93	5.00	1162	2276	2229	204.63	-	113.31	355	6.23	-	430	9.32	65.64	41.20	2659	-
479	Inner Shelf	Rockingham Bay	-18.2150	146.2183	04-Sep-93	2.00	569	1314	1196	97.86	-	59.80	228	5.14	-	500	5.65	41.02	94.79	1696	-
480	Inner Shelf	Rockingham Bay	-18.2167	146.2017	04-Sep-93	6.00	758	2378	2360	115.66	108.11	83.41	309	7.39	123.66	455	9.23	49.23	47.10	2814	427.15
481	Inner Shelf	Rockingham Bay	-18.2167	146.1667	04-Sep-93	5.00	940	1280	1290	302.49	-	96.00	328	7.83	-	317	8.24	55.02	36.24	1608	-
482	Inner Shelf	Rockingham Bay	-18.2167	146.1500	04-Sep-93	5.00	893	1830	1733	97.86	119.74	96.00	317	7.54	136.09	362	8.69	53.57	36.93	2095	463.15
483	Inner Shelf	Rockingham Bay	-18.2167	146.1317	04-Sep-93	4.00	1055	1334	1258	< D. L.	-	116.46	345	7.16	-	667	9.11	59.36	70.15	1925	-
484	Inner Shelf	Rockingham Bay	-18.2150	146.1133	04-Sep-93	3.00	902	1131	1031	409.25	119.76	110.17	347	8.09	133.03	1077	8.57	58.40	96.23	2107	460.42
485	Inner Shelf	Rockingham Bay	-18.2150	146.0967	04-Sep-93	4.00	550	1289	1209	< D. L.	-	59.80	278	8.39	-	440	8.00	40.54	33.72	1649	-
486	Inner Shelf	Rockingham Bay	-18.2150	146.0783	04-Sep-93	7.00	634	906	840	< D. L.	98.19	70.82	358	7.18	101.26	301	8.47	53.09	24.01	1141	340.88
487	Inner Shelf	Rockingham Bay	-18.2150	146.0617	04-Sep-93	9.00	482	1628	1614	97.86	-	53.51	474	10.57	-	241	16.68	50.68	29.41	1855	-
488	Inner Shelf	Rockingham Bay	-18.2167	146.0433	04-Sep-93	7.00	1799	3256	3249	364.77	154.36	176.27	560	6.73	220.49	915	15.54	80.12	105.40	4164	734.28
489	Inner Shelf	Rockingham Bay	-18.2167	146.0267	04-Sep-93	4.00	2241	1017	932	169.04	-	180.99	570	7.38	-	1252	10.36	101.83	144.10	2184	-
490	Inner Shelf	Hinchinbrook Channel	-18.3717	146.1333	04-Sep-93	-	2854	125	0	195.73	-	234.50	718	3.32	-	6744	9.89	121.62	717.09	6744	-
492	Inner Shelf	Halifax Bay	-18.7950	146.2917	12-Sep-93	7.00	756	1060	1045	< D. L.	-	83.41	262	9.76	-	318	7.89	48.26	53.93	1363	-
493	Inner Shelf	Halifax Bay	-18.7950	146.3267	12-Sep-93	9.00	673	1165	1209	115.66	113.57	83.41	317	11.87	135.84	178	8.53	47.78	26.73	1387	795.59
494	Inner Shelf	Halifax Bay	-18.7950	146.3617	12-Sep-93	12.00	810	2093	2160	124.56	-	96.00	275	7.28	-	227	9.98	39.58	38.62	2387	-
495	Inner Shelf	Halifax Bay	-18.7950	146.3967	12-Sep-93	13.00	688	1813	1904	< D. L.	93.06	78.69	252	6.15	124.68	179	7.94	36.20	25.38	2083	343.66
496	Inner Shelf	Halifax Bay	-18.7950	146.4317	12-Sep-93	14.00	607	3064	3137	< D. L.	-	81.84	238	14.30	-	165	9.12	30.89	32.56	3301	-
497	Inner Shelf	Halifax Bay	-18.7950	146.4667	12-Sep-93	18.00	715	2862	2942	115.66	74.87	97.58	241	5.66	119.66	195	9.11	33.78	30.87	3137	354.05

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
498	Inner Shelf	Halifax Bay	-18.7950	146.5017	12-Sep-93	20.00	801	4873	5073	< D. L.	-	100.72	248	5.74	-	276	14.76	34.27	46.10	5348	-
499	Inner Shelf	Halifax Bay	-18.7950	146.5367	12-Sep-93	23.00	920	5736	5964	151.25	71.61	129.05	272	6.23	144.18	328	12.35	33.78	51.34	6292	351.78
500	Inner Shelf	Halifax Bay	-18.7950	146.5717	12-Sep-93	23.00	667	6143	6541	115.66	-	72.40	230	6.38	-	243	13.32	28.47	52.03	6784	-
501	Mid Shelf	Mid Shelf	-18.7950	146.6067	12-Sep-93	22.00	503	6282	6586	< D. L.	50.97	53.51	207	6.26	94.11	218	12.91	25.10	54.43	6804	207.26
502	Mid Shelf	Mid Shelf	-18.7950	146.6417	12-Sep-93	23.00	460	6362	6711	106.76	-	45.64	195	6.39	-	205	12.80	23.65	51.72	6916	-
503	Mid Shelf	Mid Shelf	-18.7950	146.6767	12-Sep-93	24.00	503	6791	7330	151.25	-	56.66	191	7.52	-	210	15.09	28.47	56.05	7540	-
504	Mid Shelf	Mid Shelf	-18.7967	146.7117	12-Sep-93	25.00	453	6906	7511	< D. L.	-	44.07	180	4.87	-	206	15.70	23.17	53.71	7717	-
505	Mid Shelf	Mid Shelf	-18.7950	146.7467	12-Sep-93	29.00	456	6397	6884	115.66	-	45.64	174	7.94	-	258	15.79	23.65	58.39	7142	-
506	Mid Shelf	Mid Shelf	-18.7950	146.7817	12-Sep-93	28.00	311	6801	7218	177.94	-	33.05	123	4.65	-	199	12.84	16.41	63.13	7417	-
507	Mid Shelf	Mid Shelf	-18.7950	146.8183	12-Sep-93	30.00	311	7108	7630	124.56	-	42.49	120	4.28	-	241	13.41	15.93	61.60	7871	-
508	Mid Shelf	Mid Shelf	-18.7950	146.8517	12-Sep-93	32.00	272	6213	6815	< D. L.	-	26.75	100	3.21	-	197	11.58	13.51	63.07	7013	-
509	Mid Shelf	Mid Shelf	-18.7033	146.7750	12-Sep-93	32.00	284	5843	6345	< D. L.	-	26.75	116	4.03	-	172	11.08	14.48	56.77	6517	-
510	Mid Shelf	Mid Shelf	-18.7033	146.7383	12-Sep-93	32.00	450	7206	7550	< D. L.	-	44.07	209	4.11	-	243	15.73	18.34	61.29	7793	-
511	Mid Shelf	Mid Shelf	-18.7017	146.7033	12-Sep-93	32.00	553	7333	7340	169.04	-	53.51	226	3.84	-	275	16.27	21.72	64.00	7615	-
512	Mid Shelf	Mid Shelf	-18.7017	146.6683	12-Sep-93	30.00	618	6198	6151	160.14	-	61.38	225	5.44	-	252	12.90	21.72	62.26	6403	-
513	Mid Shelf	Mid Shelf	-18.7033	146.6333	12-Sep-93	25.00	624	5771	5792	97.86	-	59.80	196	3.73	-	266	12.01	21.72	55.86	6058	-
514	Mid Shelf	Mid Shelf	-18.7017	146.6167	12-Sep-93	21.00	550	6028	6155	151.25	-	61.38	164	3.23	-	391	11.30	19.79	69.37	6546	-
515	Inner Shelf	Halifax Bay	-18.7050	146.5633	12-Sep-93	20.00	263	7038	7006	213.52	-	48.79	119	2.41	-	139	11.29	20.27	50.50	7145	-
516	Inner Shelf	Halifax Bay	-18.7167	146.5650	12-Sep-93	16.00	283	7021	7318	124.56	-	36.20	120	4.03	-	189	10.92	19.79	75.14	7507	-
517	Inner Shelf	Halifax Bay	-18.7083	146.4867	12-Sep-93	20.00	741	5257	5383	186.83	-	75.54	229	4.85	-	246	11.68	27.03	54.05	5630	-
518	Inner Shelf	Halifax Bay	-18.6667	146.4700	12-Sep-93	23.00	1049	5479	5514	115.66	-	105.45	288	4.21	-	386	12.68	32.34	59.92	5900	-
519	Inner Shelf	Halifax Bay	-18.6800	146.4933	12-Sep-93	17.00	731	5888	5929	169.04	-	78.69	211	3.65	-	304	11.60	26.06	56.99	6233	-
520	Mid Shelf	Mid Shelf	-18.3917	146.5483	13-Sep-93	34.00	213	3386	3476	< D. L.	-	25.18	107	1.99	-	142	7.47	14.00	43.29	3618	-
521	Mid Shelf	Mid Shelf	-18.3933	146.5117	13-Sep-93	29.00	220	3114	3267	< D. L.	-	23.61	107	3.58	-	168	7.39	15.44	42.70	3434	-
522	Mid Shelf	Mid Shelf	-18.3933	146.4783	13-Sep-93	28.00	490	4748	4821	< D. L.	-	50.36	195	3.43	-	252	11.38	21.24	48.41	5074	-
523	Mid Shelf	Mid Shelf	-18.3933	146.4600	13-Sep-93	26.00	504	3099	3150	< D. L.	-	50.36	210	3.62	-	206	9.60	22.20	36.46	3356	-
524	Mid Shelf	Mid Shelf	-18.3933	146.4433	13-Sep-93	25.00	595	2740	2778	115.66	-	64.53	212	3.28	-	221	8.67	23.65	38.27	3000	-
525	Mid Shelf	Mid Shelf	-18.3933	146.4250	13-Sep-93	24.00	666	2887	2912	97.86	-	66.10	246	4.04	-	211	9.77	26.54	35.53	3123	-
526	Mid Shelf	Mid Shelf	-18.3933	146.4067	13-Sep-93	23.00	884	2345	2384	97.86	-	91.28	286	4.03	-	230	8.84	32.34	33.44	2613	-
527	Mid Shelf	Mid Shelf	-18.3933	146.3900	13-Sep-93	22.00	901	1806	1902	186.83	-	97.58	290	4.32	-	240	8.12	34.75	29.48	2142	-
528	Inner Shelf	Hinchinbrook Shelf	-18.3933	146.3733	13-Sep-93	20.00	2208	1438	1402	151.25	-	226.63	643	7.96	-	639	12.64	82.53	111.70	2041	-
529	Inner Shelf	Hinchinbrook Shelf	-18.3933	146.3550	13-Sep-93	14.00	2056	704	609	142.35	-	210.89	561	7.60	-	751	11.20	83.49	112.04	1360	-
530	Inner Shelf	Hinchinbrook Shelf	-18.3933	146.3383	13-Sep-93	8.00	385	706	630	560.50	-	34.62	196	8.09	-	76	5.30	29.44	26.17	705	-
531	Inner Shelf	Hinchinbrook Shelf	-18.2933	146.2867	13-Sep-93	10.00	529	623	536	< D. L.	-	45.64	252	8.82	-	116	7.80	31.85	25.72	652	-
532	Inner Shelf	Hinchinbrook Shelf	-18.2933	146.3050	13-Sep-93	12.00	772	1734	1619	302.49	-	72.40	302	8.38	-	240	8.68	38.61	40.80	1858	-
533	Inner Shelf	Hinchinbrook Shelf	-18.2933	146.3217	13-Sep-93	16.00	1230	1954	1832	418.15	-	127.48	389	6.73	-	353	9.93	54.05	44.14	2185	-
534	Inner Shelf	Hinchinbrook Shelf	-18.2933	146.3400	13-Sep-93	19.00	1138	2236	2026	213.52	-	111.74	363	5.89	-	335	10.02	45.37	34.00	2361	-
535	Mid Shelf	Mid Shelf	-18.2933	146.3567	13-Sep-93	20.00	708	2036	1959	284.70	-	75.54	247	5.52	-	237	8.29	30.41	29.78	2196	-
536	Mid Shelf	Mid Shelf	-18.2933	146.3750	13-Sep-93	22.00	652	2522	2364	204.63	-	61.38	230	4.13	-	214	8.91	24.61	34.40	2578	-
537	Mid Shelf	Mid Shelf	-18.2933	146.3917	13-Sep-93	23.00	484	3004	2897	< D. L.	-	44.07	194	3.53	-	183	8.65	24.13	31.32	3081	-
538	Mid Shelf	Mid Shelf	-18.2933	146.4100	13-Sep-93	25.00	448	3486	3341	< D. L.	-	39.35	201	3.47	-	189	9.99	21.24	36.34	3530	-
539	Mid Shelf	Mid Shelf	-18.2933	146.4267	13-Sep-93	26.00	398	3438	3313	< D. L.	-	39.35	180	3.45	-	195	9.71	20.27	35.93	3508	-
540	Mid Shelf	Mid Shelf	-18.2933	146.4450	13-Sep-93	27.00	308	4037	3998	97.86	-	28.33	149	3.44	-	184	9.63	17.86	44.88	4182	-
541	Mid Shelf	Mid Shelf	-18.2933	146.4600	13-Sep-93	28.00	207	4421	4429	< D. L.	-	22.03	101	3.37	-	154	8.86	15.93	54.05	4583	-
542	Mid Shelf	Mid Shelf	-18.2933	146.4800	13-Sep-93	28.00	197	3286	3364	97.86	-	20.46	74	2.77	-	155	6.73	13.03	47.32	3518	-
543	Mid Shelf	Mid Shelf	-18.2933	146.5150	13-Sep-93	32.00	133	4736	4806	< D. L.	-	< D. L.	74	3.21	-	177	8.21	13.03	62.51	4984	-
544	Mid Shelf	Mid Shelf	-18.2933	146.5500	13-Sep-93	34.00	140	5289	5429	186.83	-	< D. L.	86	2.56	-	178	10.06	13.03	56.58	5607	-
545	Mid Shelf	Mid Shelf	-18.2167	146.5000	13-Sep-93	33.00	184	6170	6234	177.94	-	18.89	72	2.74	-	230	10.01	12.55	66.28	6464	-
546	Mid Shelf	Mid Shelf	-18.2167	146.4650	13-Sep-93	30.00	218	5524	5615	177.94	-	25.18	85	3.58	-	231	10.22	15.44	61.17	5845	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
547	Mid Shelf	Mid Shelf	-18.2183	146.4267	13-Sep-93	29.00	327	5397	5525	115.66	-	31.48	139	3.51	-	251	11.89	18.82	58.27	5776	-
548	Mid Shelf	Mid Shelf	-18.2183	146.3950	13-Sep-93	27.00	376	4461	4557	97.86	-	37.77	160	3.75	-	185	10.03	19.79	45.98	4741	-
549	Mid Shelf	Mid Shelf	-18.2183	146.3767	13-Sep-93	26.00	497	3099	3085	< D. L.	-	50.36	185	4.48	-	209	8.76	22.68	38.24	3294	-
550	Mid Shelf	Mid Shelf	-18.2183	146.3600	13-Sep-93	26.00	845	3523	3837	231.32	-	86.56	285	4.70	-	306	11.75	30.89	40.46	4144	-
551	Mid Shelf	Mid Shelf	-18.2183	146.3417	13-Sep-93	26.00	1052	2989	3117	169.04	-	107.02	332	4.98	-	379	10.56	37.64	48.44	3495	-
552	Mid Shelf	Mid Shelf	-18.2167	146.3250	13-Sep-93	24.00	961	3191	3274	320.28	-	100.72	322	6.13	-	331	9.96	39.09	35.53	3605	-
553	Mid Shelf	Mid Shelf	-18.2167	146.3067	13-Sep-93	25.00	2913	890	859	774.02	-	295.88	779	7.49	-	849	14.04	105.21	128.51	1708	-
554	Inner Shelf	Rockingham Bay	-18.2167	146.2900	13-Sep-93	10.00	122	982	951	< D. L.	-	37.77	59	1.93	-	85	3.00	15.44	12.86	1036	-
555	Inner Shelf	Rockingham Bay	-18.2167	146.2717	13-Sep-93	8.00	178	273	245	< D. L.	-	28.33	57	1.52	-	111	1.93	16.89	15.70	356	-
556	Inner Shelf	Rockingham Bay	-18.2183	146.2550	13-Sep-93	7.00	487	517	485	195.73	-	56.66	215	5.78	-	174	5.41	30.89	27.26	659	-
557	Inner Shelf	Rockingham Bay	-18.2167	146.2367	13-Sep-93	6.00	484	655	602	142.35	-	55.08	253	7.92	-	154	6.89	31.37	28.19	756	-
558	Inner Shelf	Rockingham Bay	-18.1783	146.1750	14-Sep-93	15.00	1581	1894	1942	195.73	-	173.12	492	6.39	-	551	11.95	66.12	75.64	2493	-
559	Inner Shelf	Rockingham Bay	-18.1350	146.1633	14-Sep-93	11.00	814	2116	2181	186.83	-	97.58	329	6.28	-	324	10.42	43.44	34.93	2505	-
560	Inner Shelf	Rockingham Bay	-18.1583	146.2900	14-Sep-93	20.00	775	1689	1723	< D. L.	-	89.71	260	3.92	-	229	7.73	35.71	27.51	1952	-
561	Inner Shelf	Rockingham Bay	-18.1550	146.2800	14-Sep-93	20.00	1040	1394	1383	106.76	-	111.74	321	4.81	-	331	8.02	41.99	33.72	1714	-
562	Inner Shelf	Hinchinbrook Channel	-18.4733	146.1800	27-Oct-93	-	1570	159	0	391.46	86.46	242.37	433	1.77	181.29	5495	7.47	89.29	530.57	5495	676.27
563	Inner Shelf	Hinchinbrook Channel	-18.4983	146.2917	28-Oct-93	-	204	98	196	160.14	32.80	25.18	79	1.80	20.48	82	2.45	18.34	11.42	277	286.56
564	Inner Shelf	Hinchinbrook Channel	-18.4983	146.2683	28-Oct-93	-	171	27	0	< D. L.	-	18.89	58	0.95	-	88	1.95	18.34	13.70	88	-
565	Inner Shelf	Hinchinbrook Channel	-18.3867	146.1450	30-Oct-93	1.00	2393	169	0	453.74	-	226.63	575	2.14	-	7693	12.04	87.84	455.40	7693	-
566	Inner Shelf	Hinchinbrook Channel	-18.3500	146.1267	30-Oct-93	1.00	138	247	197	< D. L.	-	< D. L.	45	1.03	-	95	3.66	14.00	16.51	291	-
567	Inner Shelf	Hinchinbrook Channel	-18.3683	146.1350	30-Oct-93	1.00	2065	106	0	373.67	-	188.86	524	2.70	-	4907	9.43	88.80	426.08	4907	-
568	Inner Shelf	Rockingham Bay	-18.2517	146.2783	31-Oct-93	1.00	1694	253	0	275.80	-	182.56	552	3.67	-	9058	12.66	68.53	410.79	9058	-
569	Inner Shelf	Missionary Bay	-18.2467	146.2250	31-Oct-93	1.00	2164	430	105	435.94	-	214.04	658	4.63	-	2706	13.46	90.73	198.60	2811	-
633	Inner Shelf	Rockingham Bay	-18.1500	146.0283	11-Feb-94	5.00	2036	2328	2450	1467.97	-	151.09	550	6.12	-	951	10.48	75.77	152.12	3401	-
635	Inner Shelf	Rockingham Bay	-18.0750	146.1167	11-Feb-94	9.00	922	959	952	< D. L.	-	72.40	365	7.68	-	351	8.77	47.30	32.84	1303	-
637	Inner Shelf	Missionary Bay	-18.2317	146.1867	12-Feb-94	3.00	738	1641	1635	< D. L.	-	69.25	335	7.10	-	376	8.99	41.02	43.76	2011	-
639	Inner Shelf	Rockingham Bay	-18.1950	146.1200	12-Feb-94	5.00	623	1689	0	169.04	-	50.36	321	6.98	-	433	8.26	43.92	39.80	433	-
641	Mid Shelf	Mid Shelf	-18.0833	146.2500	13-Feb-94	20.00	917	3718	3751	160.14	-	83.41	316	5.87	-	303	12.21	37.64	45.38	4054	-
643	Inner Shelf	Rockingham Bay	-18.2333	146.2633	13-Feb-94	6.00	338	709	651	195.73	-	28.33	163	5.13	-	152	4.13	25.58	28.28	803	-
646	Mid Shelf	Mid Shelf	-18.2067	146.3267	13-Feb-94	26.00	920	3256	3165	231.32	-	83.41	337	5.09	-	335	12.02	40.06	32.13	3499	-
648	Inner Shelf	Rockingham Bay	-18.1250	146.1183	14-Feb-94	9.00	827	1213	1208	685.05	-	67.67	365	7.48	-	391	8.37	45.37	47.47	1599	-
650	Inner Shelf	Rockingham Bay	-18.1917	146.0367	14-Feb-94	6.00	1299	3905	3890	< D. L.	-	113.31	463	5.54	-	744	12.49	65.15	53.46	4634	-
652	Inner Shelf	Bowling Shelf	-19.2683	147.3533	26-Mar-94	18.00	2562	849	908	186.83	239.66	373.47	761	7.02	497.84	719	13.09	79.73	76.64	1628	1090.26
653	Inner Shelf	Bowling Shelf	-19.2833	147.3533	26-Mar-94	15.00	2843	549	634	124.56	-	405.89	829	7.06	-	728	13.69	88.29	78.04	1362	1131.41
654	Inner Shelf	Bowling Shelf	-19.3000	147.3550	26-Mar-94	12.00	2476	300	397	160.14	268.04	385.74	786	8.17	533.51	826	12.84	98.77	80.04	1223	1114.88
655	Inner Shelf	Bowling Green Bay	-19.3183	147.3567	26-Mar-94	9.00	2325	185	267	186.83	-	367.01	763	8.07	-	798	12.86	80.29	80.72	1065	1083.07
656	Inner Shelf	Bowling Green Bay	-19.3350	147.3583	26-Mar-94	7.00	2411	178	252	< D. L.	270.34	382.44	772	7.94	532.45	739	13.05	97.43	79.63	992	1108.15
657	Inner Shelf	Bowling Green Bay	-19.3517	147.3567	26-Mar-94	7.00	1385	279	291	< D. L.	-	212.15	488	8.13	-	440	9.01	80.28	44.98	731	714.39
658	Inner Shelf	Bowling Green Bay	-19.3683	147.3567	26-Mar-94	5.00	2239	244	301	97.86	269.62	343.41	736	8.60	512.23	716	12.40	93.37	75.39	1017	1046.66
659	Inner Shelf	Bowling Green Bay	-19.3833	147.3567	26-Mar-94	4.00	1860	217	216	< D. L.	-	304.85	619	7.45	-	574	11.27	66.67	49.75	790	866.61
660	Inner Shelf	Bowling Green Bay	-19.4000	147.3550	26-Mar-94	4.00	2315	230	275	< D. L.	274.72	341.83	757	9.64	513.93	687	13.05	105.95	64.50	962	1071.13
661	Inner Shelf	Upstart Bay	-19.7267	147.6250	28-Mar-94	3.00	1432	141	249	427.05	257.51	292.89	524	6.15	362.19	697	12.73	60.58	79.41	996	863.70
662	Inner Shelf	Upstart Bay	-19.7267	147.6417	28-Mar-94	5.00	2624	111	219	293.59	-	466.95	808	8.71	-	963	15.64	90.21	75.92	1226	1201.16
663	Inner Shelf	Upstart Bay	-19.7250	147.6583	28-Mar-94	8.00	2807	130	213	195.73	296.32	493.55	828	9.37	581.33	807	14.54	89.01	75.55	1062	1219.52
664	Inner Shelf	Upstart Bay	-19.7250	147.6750	28-Mar-94	9.00	2923	216	240	204.63	-	439.09	856	8.08	-	750	14.44	86.16	77.82	1039	1231.45
665	Inner Shelf	Upstart Bay	-19.7267	147.6917	28-Mar-94	9.00	2583	589	632	160.14	251.26	367.80	744	9.48	506.07	715	14.02	84.23	88.15	1474	1104.18
666	Inner Shelf	Upstart Bay	-19.7267	147.7083	28-Mar-94	9.00	2023	1507	1160	< D. L.	-	284.07	599	6.66	-	616	14.10	78.06	81.35	2009	873.95
667	Inner Shelf	Upstart Bay	-19.7250	147.7250	28-Mar-94	9.00	1254	2410	1763	< D. L.	151.47	172.33	401	5.69	238.43	471	14.15	42.02	61.29	2589	584.37
668	Inner Shelf	Upstart Bay	-19.7250	147.7417	28-Mar-94	6.00	927	2402	1745	151.25	-	145.47	329	7.14	-	449	14.24	44.20	65.97	2545	463.21

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
669	Inner Shelf	Upstart Bay	-19.7883	147.6433	29-Mar-94	4.00	903	839	596	< D. L.	209.90	139.60	380	9.57	184.88	332	12.57	45.78	39.58	1048	576.41
670	Inner Shelf	Upstart Bay	-19.7867	147.6600	29-Mar-94	4.00	2034	1102	840	< D. L.	233.50	299.18	627	8.19	369.17	661	13.92	79.41	74.45	1670	946.00
671	Inner Shelf	Upstart Bay	-19.7883	147.6767	29-Mar-94	4.00	2209	923	726	115.66	-	298.55	679	8.44	-	731	14.01	72.66	80.88	1604	1002.45
672	Inner Shelf	Upstart Bay	-19.7867	147.6933	29-Mar-94	6.00	2301	837	714	< D. L.	233.21	307.37	688	7.17	413.17	792	14.28	73.25	95.54	1649	1033.35
673	Inner Shelf	Upstart Bay	-19.7883	147.7100	29-Mar-94	6.00	2198	1533	1134	< D. L.	-	282.81	598	6.89	-	643	13.39	65.80	87.74	2005	860.49
674	Inner Shelf	Upstart Bay	-19.7867	147.7267	29-Mar-94	6.00	1713	2297	1651	< D. L.	168.29	195.00	486	6.31	290.94	555	12.51	56.31	70.40	2539	685.79
675	Inner Shelf	Upstart Bay	-19.7883	147.7433	29-Mar-94	6.00	1075	3423	2402	< D. L.	-	119.66	321	4.86	-	427	11.42	37.35	58.36	3312	457.09
676	Inner Shelf	Upstart Bay	-19.7883	147.7500	29-Mar-94	5.00	470	3800	2653	< D. L.	70.71	31.48	201	4.81	76.61	271	12.08	26.29	40.21	3458	225.49
677	Inner Shelf	Upstart Bay	-19.8283	147.7617	29-Mar-94	2.00	852	806	643	151.25	115.62	225.06	272	3.41	154.17	624	6.15	38.74	125.05	1396	370.20
678	Inner Shelf	Upstart Bay	-19.8183	147.7517	29-Mar-94	2.00	229	721	542	< D. L.	-	31.48	92	2.42	-	114	2.92	18.89	24.81	765	156.65
679	Inner Shelf	Upstart Bay	-19.8117	147.7450	29-Mar-94	3.00	558	596	454	< D. L.	106.60	55.19	200	4.02	91.17	325	5.31	27.10	49.91	871	249.81
680	Inner Shelf	Upstart Bay	-19.7133	147.6250	29-Mar-94	4.00	2467	106	179	364.77	-	399.12	712	7.30	-	810	13.12	80.45	84.15	1025	1115.65
681	Inner Shelf	Upstart Bay	-19.7267	147.6417	29-Mar-94	6.00	2223	140	210	293.59	-	434.06	737	10.37	-	1231	13.97	83.32	114.19	1483	1109.84
682	Inner Shelf	Upstart Bay	-19.7367	147.6533	29-Mar-94	8.00	2780	130	222	266.01	-	439.88	815	10.91	-	859	13.73	103.28	75.17	1125	1201.47
683	Inner Shelf	Upstart Bay	-19.7500	147.6700	29-Mar-94	8.00	2887	295	313	822.06	275.97	402.27	829	9.64	557.99	707	13.42	100.87	85.03	1084	1186.63
684	Inner Shelf	Upstart Bay	-19.7583	147.6867	29-Mar-94	7.00	2766	712	567	171.71	235.81	396.76	740	8.97	460.51	747	13.58	91.65	95.32	1427	1055.68
685	Inner Shelf	Upstart Bay	-19.7733	147.6950	29-Mar-94	6.00	2599	914	740	194.84	-	339.94	693	8.21	-	715	13.86	100.10	92.45	1604	1008.57
686	Inner Shelf	Upstart Bay	-19.7850	147.7017	29-Mar-94	6.00	2341	1096	868	142.35	-	311.14	642	7.07	-	687	13.19	81.23	89.18	1729	933.61
687	Inner Shelf	Upstart Bay	-19.7983	147.7233	29-Mar-94	4.00	1699	1636	1225	98.75	-	222.69	482	6.09	-	614	12.35	61.87	84.93	2086	693.44
688	Inner Shelf	Upstart Bay	-19.8067	147.7383	29-Mar-94	4.00	918	687	523	130.78	-	108.12	292	4.94	-	578	8.49	42.18	76.61	1206	406.15
689	Inner Shelf	Upstart Bay	-19.7033	147.6200	30-Mar-94	4.00	461	114	17	145.91	104.47	55.92	200	4.36	102.06	53	5.22	29.05	18.77	73	324.00
690	Inner Shelf	Upstart Bay	-19.7033	147.6367	30-Mar-94	6.00	2345	104	183	599.64	-	415.96	678	6.00	-	678	11.95	97.30	88.93	898	1085.97
691	Inner Shelf	Upstart Bay	-19.7050	147.6533	30-Mar-94	10.00	2681	120	-619	324.73	304.75	452.63	792	8.47	607.58	1845	13.81	101.64	77.98	1102	1152.21
692	Inner Shelf	Upstart Bay	-19.7033	147.6700	30-Mar-94	12.00	2915	174	228	345.20	-	463.02	834	10.30	-	799	14.42	108.45	78.13	1072	1217.38
693	Inner Shelf	Upstart Bay	-19.7033	147.6867	30-Mar-94	13.00	2678	346	351	310.50	277.42	392.98	752	7.83	547.10	724	13.68	98.99	83.94	1146	1105.71
694	Inner Shelf	Upstart Bay	-19.7033	147.7033	30-Mar-94	14.00	2169	1259	1006	310.50	-	301.38	615	7.20	-	640	13.74	90.69	76.17	1848	910.66
695	Inner Shelf	Upstart Bay	-19.7050	147.7200	30-Mar-94	14.00	1606	1872	1456	201.96	182.92	221.28	482	5.94	325.09	541	13.98	62.07	67.47	2290	699.71
696	Inner Shelf	Upstart Bay	-19.7033	147.7367	30-Mar-94	16.00	1172	2472	1826	< D. L.	138.93	181.62	353	6.22	222.22	452	12.92	38.51	61.17	2644	492.58
697	Inner Shelf	Upstart Bay	-19.7500	147.7417	30-Mar-94	6.00	772	3575	2613	< D. L.	108.63	114.64	254	4.61	144.47	352	11.72	31.03	45.51	3491	342.21
698	Inner Shelf	Upstart Bay	-19.7500	147.7233	30-Mar-94	8.00	1592	2307	1646	< D. L.	166.52	221.28	447	5.80	266.31	518	13.10	51.79	68.03	2494	634.24
699	Inner Shelf	Upstart Bay	-19.7483	147.7067	30-Mar-94	9.00	2115	2175	1560	< D. L.	-	311.46	564	6.67	-	566	13.23	68.34	85.09	2440	808.02
700	Inner Shelf	Bowling Green Bay	-19.3517	147.4117	26-Mar-94	1.00	687	1296	1083	< D. L.	102.16	111.10	232	4.12	137.51	178	5.57	33.69	17.93	1261	343.58
701	Inner Shelf	Bowling Green Bay	-19.3717	147.4117	26-Mar-94	1.00	1834	338	322	151.25	-	282.81	563	7.60	-	497	10.82	74.71	43.48	818	873.80
702	Inner Shelf	Bowling Green Bay	-19.4083	147.4117	26-Mar-94	1.00	2403	277	320	110.32	269.01	342.15	687	9.52	498.68	641	12.48	92.62	68.75	961	1038.70
703	Inner Shelf	Bowling Green Bay	-19.4067	147.3900	26-Mar-94	1.00	2252	291	323	119.22	-	317.12	662	9.54	-	611	11.79	89.91	72.89	934	1007.50
704	Inner Shelf	Bowling Green Bay	-19.4083	147.3567	26-Mar-94	1.00	2333	202	281	111.21	-	308.47	701	12.28	-	711	13.55	89.62	119.49	992	1053.24
705	Inner Shelf	Bowling Green Bay	-19.3383	147.2500	26-Mar-94	5.00	267	124	84	< D. L.	-	31.48	97	6.91	-	54	3.29	17.47	9.48	138	133.29
706	Inner Shelf	Bowling Green Bay	-19.3550	147.2500	26-Mar-94	2.00	290	499	97	< D. L.	-	31.48	122	9.90	-	48	4.42	15.88	9.09	145	150.37
707	Inner Shelf	Bowling Green Bay	-19.3717	147.2500	26-Mar-94	2.00	332	380	241	96.98	-	104.06	146	9.10	-	45	4.11	21.67	8.75	286	181.58
708	Inner Shelf	Bowling Green Bay	-19.3883	147.2500	26-Mar-94	2.00	342	288	203	< D. L.	-	34.55	148	8.75	-	42	4.71	20.42	13.61	245	202.54
709	Inner Shelf	Bowling Green Bay	-19.3983	147.2500	26-Mar-94	1.00	217	3478	2939	< D. L.	-	31.48	106	11.74	-	42	4.79	18.05	18.33	2981	141.88
710	Inner Shelf	Bowling Green Bay	-19.3200	147.2500	27-Mar-94	14.00	2199	770	789	165.48	-	276.68	620	6.89	-	517	10.73	78.72	75.64	1305	918.16
711	Inner Shelf	Bowling Shelf	-19.3033	147.2517	27-Mar-94	15.00	2091	891	878	120.11	209.10	260.78	600	6.83	420.96	508	11.62	75.00	49.84	1385	849.01
712	Inner Shelf	Bowling Shelf	-19.2867	147.2500	27-Mar-94	17.00	1266	1417	1313	102.31	-	166.67	388	4.89	-	297	8.61	62.06	30.16	1610	552.39
713	Inner Shelf	Bowling Shelf	-19.2700	147.2500	27-Mar-94	17.00	1214	2458	2198	102.31	137.67	142.90	385	5.75	249.24	414	10.05	53.98	32.31	2612	530.67
714	Inner Shelf	Bowling Shelf	-19.2533	147.2500	27-Mar-94	18.00	944	2208	2063	120.11	-	110.47	285	4.73	-	264	7.08	42.95	28.62	2327	414.56
715	Inner Shelf	Bowling Shelf	-19.2350	147.2500	27-Mar-94	18.00	869	2234	2008	102.31	95.72	97.48	261	4.29	172.76	269	7.06	38.66	29.77	2277	350.31
716	Inner Shelf	Bowling Shelf	-19.2200	147.2500	27-Mar-94	19.00	612	2730	2573	< D. L.	71.31	44.48	184	4.40	121.93	211	6.60	28.72	31.09	2784	246.44
717	Inner Shelf	Bowling Shelf	-19.2033	147.2500	27-Mar-94	19.00	294	1757	1607	< D. L.	-	31.48	98	3.46	-	149	3.77	19.89	27.70	1756	166.59

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
718	Mid Shelf	Mid Shelf	-19.1683	147.2500	27-Mar-94	22.00	410	3139	3009	< D. L.	-	31.48	139	5.68	-	161	7.09	20.86	32.97	3170	226.25
719	Inner Shelf	Bowling Shelf	-19.1583	147.1200	27-Mar-94	20.00	741	3438	3213	< D. L.	86.87	72.71	245	6.63	152.28	219	8.98	35.52	35.87	3433	330.89
720	Inner Shelf	Bowling Shelf	-19.1750	147.1200	27-Mar-94	18.00	689	2078	1940	92.53	-	55.68	231	7.08	-	199	7.10	32.11	26.63	2139	298.00
721	Inner Shelf	Bowling Shelf	-19.1917	147.1200	27-Mar-94	17.00	701	1914	1771	< D. L.	93.37	54.03	232	6.78	143.88	202	6.12	35.16	24.69	1972	375.10
722	Inner Shelf	Bowling Shelf	-19.2083	147.1200	27-Mar-94	16.00	721	1871	1768	< D. L.	-	68.74	251	6.76	-	191	7.30	37.25	23.99	1959	340.83
723	Inner Shelf	Bowling Shelf	-19.2250	147.1200	27-Mar-94	16.00	952	1472	1392	< D. L.	140.04	98.80	344	5.80	203.78	226	7.97	52.05	22.02	1618	441.03
724	Inner Shelf	Bowling Shelf	-19.2417	147.1200	27-Mar-94	14.00	956	1425	1308	126.33	-	129.60	341	5.92	-	262	8.11	50.47	21.22	1570	462.44
725	Inner Shelf	Bowling Shelf	-19.2483	147.1217	27-Mar-94	13.00	955	1043	992	118.33	-	92.62	332	6.23	-	219	7.92	54.84	19.60	1211	466.57
726	Inner Shelf	Bowling Shelf	-19.2583	147.1200	27-Mar-94	12.00	1069	1301	1200	128.11	153.71	111.95	371	6.83	221.99	273	9.04	55.58	23.19	1473	485.08
727	Inner Shelf	Bowling Shelf	-19.2750	147.1200	27-Mar-94	11.00	954	1032	989	209.96	-	152.25	356	8.19	-	240	8.58	62.57	20.29	1230	589.11
728	Inner Shelf	Bowling Green Bay	-19.2917	147.1200	27-Mar-94	11.00	1156	1024	999	112.90	192.32	123.07	400	8.40	255.71	260	8.55	64.76	22.33	1260	618.17
729	Inner Shelf	Bowling Green Bay	-19.3100	147.1200	27-Mar-94	9.00	961	985	923	462.63	-	134.39	361	8.93	-	203	8.17	66.88	18.70	1126	579.47
730	Inner Shelf	Bowling Green Bay	-19.3250	147.1200	27-Mar-94	9.00	1158	1042	970	114.77	-	145.50	431	7.82	-	299	8.45	68.39	43.57	1269	669.88
731	Inner Shelf	Bowling Green Bay	-19.3417	147.1200	27-Mar-94	7.00	2913	208	293	221.53	-	414.54	822	15.17	-	849	14.93	108.40	82.84	1142	1212.79
732	Inner Shelf	Bowling Green Bay	-19.3583	147.1200	27-Mar-94	5.00	833	1374	1245	126.33	246.96	81.05	405	12.95	189.38	249	10.44	52.36	29.93	1494	575.65
733	Inner Shelf	Bowling Green Bay	-19.3767	147.1200	27-Mar-94	2.00	264	448	401	< D. L.	-	31.48	165	15.44	-	44	4.99	22.32	14.59	445	207.43
734	Inner Shelf	Upstart Bay	-19.7483	147.6900	30-Mar-94	5.00	2507	754	684	127.22	-	544.22	721	10.05	-	664	13.69	88.14	94.32	1485	1048.65
735	Inner Shelf	Upstart Bay	-19.7500	147.6733	30-Mar-94	9.00	3106	284	333	180.60	-	421.47	838	9.38	-	736	14.94	100.42	77.85	1136	1197.03
736	Inner Shelf	Upstart Bay	-19.7500	147.6567	30-Mar-94	9.00	1113	814	650	118.33	-	141.34	410	8.90	-	260	9.52	< D. L.	24.08	1042	624.90
737	Inner Shelf	Upstart Bay	-19.7517	147.6400	30-Mar-94	7.00	2815	138	237	225.08	301.34	449.48	817	10.26	570.64	950	15.40	99.33	84.50	1235	1192.29
738	Inner Shelf	Upstart Bay	-19.7500	147.6233	30-Mar-94	5.00	2105	98	373	545.37	317.01	493.55	700	4.86	609.03	1394	14.19	89.72	153.40	1842	1080.01
739	Inner Shelf	Upstart Bay	-19.7500	147.6167	30-Mar-94	3.00	458	102	45	101.42	-	49.76	184	7.74	-	37	5.49	31.97	18.68	91	281.78
740	Inner Shelf	Hinchinbrook Channel	-18.5433	146.3308	18-May-92	-	486	28	-	< D. L.	-	62.95	111	1.51	-	-	2.68	33.78	11.23	-	-
741	Inner Shelf	Hinchinbrook Channel	-18.5425	146.3283	18-May-92	-	1156	50	-	< D. L.	-	157.38	227	1.95	-	-	6.20	57.92	30.26	-	-
742	Inner Shelf	Hinchinbrook Channel	-18.5367	146.3233	18-May-92	-	1168	113	-	< D. L.	-	251.81	204	1.49	-	-	17.21	72.39	94.82	-	-
743	Inner Shelf	Hinchinbrook Channel	-18.5350	146.3250	18-May-92	-	1134	136	-	< D. L.	-	236.07	335	1.58	-	-	17.73	67.57	143.48	-	-
744	Inner Shelf	Hinchinbrook Channel	-18.5375	146.3225	19-May-92	-	756	31	-	< D. L.	-	110.17	179	2.33	-	-	4.39	53.09	19.34	-	-
745	Inner Shelf	Hinchinbrook Channel	-18.5433	146.3233	19-May-92	-	460	40	-	< D. L.	-	62.95	90	1.37	-	-	4.49	33.78	17.78	-	-
746	Inner Shelf	Hinchinbrook Channel	-18.5417	146.3142	19-May-92	-	1857	61	-	< D. L.	-	251.81	381	2.15	-	-	9.43	91.70	204.62	-	-
747	Inner Shelf	Hinchinbrook Channel	-18.5400	146.3117	19-May-92	-	511	40	-	< D. L.	-	62.95	107	1.27	-	-	3.87	43.44	27.76	-	-
748	Inner Shelf	Hinchinbrook Channel	-18.5317	146.3150	19-May-92	-	734	44	-	< D. L.	-	94.43	163	1.98	-	-	5.42	57.92	44.92	-	-
749	Inner Shelf	Hinchinbrook Channel	-18.5333	146.3083	19-May-92	-	901	44	-	< D. L.	-	125.90	206	2.20	-	-	6.01	62.74	19.34	-	-
750	Inner Shelf	Hinchinbrook Channel	-18.5283	146.3142	20-May-92	-	2939	62	-	53.38	-	361.98	666	6.21	-	-	13.69	130.31	91.08	-	-
751	Inner Shelf	Hinchinbrook Channel	-18.5275	146.3067	20-May-92	-	1182	66	-	< D. L.	-	173.12	247	1.98	-	-	7.65	77.22	52.71	-	-
752	Inner Shelf	Hinchinbrook Channel	-18.5292	146.2900	20-May-92	-	1297	90	-	< D. L.	-	220.33	288	3.13	-	-	9.01	101.35	106.99	-	-
753	Inner Shelf	Hinchinbrook Channel	-18.5292	146.2933	20-May-92	-	437	63	-	< D. L.	-	78.69	104	1.73	-	-	4.68	33.78	38.68	-	-
754	Inner Shelf	Hinchinbrook Channel	-18.5325	146.3017	20-May-92	-	1256	64	-	< D. L.	-	204.60	269	2.31	-	-	8.56	77.22	47.72	-	-
755	Inner Shelf	Hinchinbrook Channel	-18.5233	146.2892	21-May-92	-	1079	53	-	< D. L.	-	110.17	297	2.40	-	-	6.10	77.22	56.14	-	-
756	Inner Shelf	Hinchinbrook Channel	-18.5200	146.2717	21-May-92	-	2324	62	-	< D. L.	-	361.98	517	3.93	-	-	11.72	125.48	86.71	-	-
757	Inner Shelf	Hinchinbrook Channel	-18.5358	146.2917	21-May-92	-	812	48	-	< D. L.	-	141.64	256	4.68	-	-	7.17	53.09	13.72	-	-
758	Inner Shelf	Hinchinbrook Channel	-18.5617	146.3033	22-May-92	-	1145	66	-	< D. L.	-	141.64	276	4.00	-	-	11.43	62.74	57.08	-	-
759	Inner Shelf	Hinchinbrook Channel	-18.5625	146.3025	22-May-92	-	1023	28	-	< D. L.	-	141.64	297	3.60	-	-	10.85	67.57	2.18	-	-
760	Inner Shelf	Hinchinbrook Channel	-18.5608	146.3042	22-May-92	-	1086	55	-	< D. L.	-	157.38	317	8.45	-	-	13.95	62.74	26.82	-	-
761	Inner Shelf	Hinchinbrook Channel	-18.5550	146.3083	22-May-92	-	1071	167	-	< D. L.	-	299.02	483	2.29	-	-	30.77	77.22	144.73	-	-
762	Inner Shelf	Hinchinbrook Channel	-18.5500	146.3150	22-May-92	-	638	81	-	< D. L.	-	125.90	118	1.06	-	-	8.88	24.13	134.12	-	-
763	Inner Shelf	Hinchinbrook Channel	-18.5417	146.2717	04-Aug-92	-	1064	68	-	< D. L.	-	173.12	206	2.07	-	-	8.56	53.09	52.09	-	-
764	Inner Shelf	Hinchinbrook Channel	-18.5317	146.2733	04-Aug-92	-	500	40	-	< D. L.	-	78.69	115	1.82	-	-	3.58	24.13	28.07	-	-
765	Inner Shelf	Hinchinbrook Channel	-18.5317	146.2767	04-Aug-92	-	1431	56	-	< D. L.	-	236.07	365	2.82	-	-	8.10	82.05	38.05	-	-
766	Inner Shelf	Hinchinbrook Channel	-18.5400	146.2733	04-Aug-92	-	2476	65	-	< D. L.	-	393.45	627	11.59	-	-	14.79	115.83	62.07	-	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
767	Inner Shelf	Hinchinbrook Channel	-18.5083	146.2633	05-Aug-92	-	2468	78	-	< D. L.	-	346.24	523	5.68	-	-	9.01	120.66	112.91	-	-
768	Inner Shelf	Hinchinbrook Channel	-18.5208	146.2583	05-Aug-92	-	259	25	-	< D. L.	-	47.21	52	0.86	-	-	1.23	14.48	26.82	-	-
769	Inner Shelf	Hinchinbrook Channel	-18.5250	146.2733	05-Aug-92	-	337	33	-	< D. L.	-	62.95	68	1.38	-	-	2.78	9.65	25.27	-	-
770	Inner Shelf	Hinchinbrook Channel	-18.5383	146.2633	05-Aug-92	-	1238	73	-	< D. L.	-	173.12	249	2.48	-	-	6.97	67.57	72.68	-	-
771	Inner Shelf	Hinchinbrook Channel	-18.5333	146.2642	05-Aug-92	-	830	39	-	< D. L.	-	141.64	242	5.61	-	-	5.72	48.26	16.22	-	-
772	Inner Shelf	Hinchinbrook Channel	-18.5133	146.2533	06-Aug-92	-	1112	50	-	< D. L.	-	157.38	220	2.49	-	-	6.20	67.57	31.50	-	-
773	Inner Shelf	Hinchinbrook Channel	-18.5200	146.2483	06-Aug-92	-	2524	62	-	< D. L.	-	330.50	509	4.37	-	-	11.46	120.66	67.69	-	-
775	Inner Shelf	Hinchinbrook Channel	-18.5150	146.2267	06-Aug-92	-	960	43	-	< D. L.	-	125.90	292	1.80	-	-	4.36	62.74	83.59	-	-
884	Mid Shelf	Mid Shelf	-19.1317	147.1200	01-Sep-94	21.00	598	4436	4283	< D. L.	-	47.56	195	4.69	-	227	11.18	24.37	46.97	4510	245.37
885	Mid Shelf	Mid Shelf	-19.1150	147.1200	01-Sep-94	23.00	616	5287	5186	< D. L.	-	57.77	197	4.49	-	243	10.49	23.87	54.40	5429	248.28
886	Mid Shelf	Mid Shelf	-19.0983	147.1200	01-Sep-94	23.00	682	5262	5040	171.71	-	76.02	220	4.26	-	405	11.77	28.59	58.80	5444	287.59
887	Mid Shelf	Mid Shelf	-19.0667	147.1200	01-Sep-94	26.00	452	4830	4684	< D. L.	-	134.04	162	4.19	-	258	10.36	22.06	45.54	4942	204.68
888	Mid Shelf	Mid Shelf	-19.0317	147.1200	01-Sep-94	26.00	255	6801	7184	< D. L.	-	31.48	107	3.90	-	229	12.06	15.42	68.59	7413	114.82
889	Mid Shelf	Mid Shelf	-18.9983	147.1200	01-Sep-94	27.00	373	5911	6081	< D. L.	-	31.48	134	2.88	-	342	11.65	15.15	63.01	6422	161.24
890	Mid Shelf	Mid Shelf	-18.9483	147.1200	01-Sep-94	30.00	170	6599	6901	< D. L.	-	31.48	92	3.07	-	223	11.42	13.59	60.57	7124	75.91
891	Mid Shelf	Mid Shelf	-18.9000	147.1200	01-Sep-94	32.00	223	6098	6380	< D. L.	-	31.48	73	2.28	-	245	9.61	12.36	63.69	6625	102.97
891	Mid Shelf	Mid Shelf	-18.9000	147.1200	01-Sep-94	32.00	188	5906	6151	< D. L.	-	31.48	70	2.50	-	223	8.89	10.26	61.63	6374	88.76
892	Mid Shelf	Mid Shelf	-18.8483	147.1200	01-Sep-94	35.00	99	7707	8229	< D. L.	-	31.48	56	1.44	-	195	10.64	10.00	68.15	8424	46.50
893	Mid Shelf	Mid Shelf	-18.8150	147.1550	01-Sep-94	37.00	92	6465	6888	< D. L.	-	31.48	38	1.48	-	155	8.36	12.25	59.26	7044	44.41
894	Outer Shelf	Outer Shelf	-18.7817	147.1900	01-Sep-94	40.00	113	4918	5031	< D. L.	-	31.48	56	1.85	-	174	7.27	8.36	54.24	5204	53.53
895	Outer Shelf	Outer Shelf	-18.7467	147.2283	01-Sep-94	45.00	123	4586	4629	< D. L.	-	31.48	80	1.87	-	190	9.16	8.24	46.97	4820	61.40
896	Outer Shelf	Outer Shelf	-18.7433	147.2617	01-Sep-94		9	8952	9360	< D. L.	-	31.48	2	0.11	-	225	6.66	< D. L.	60.23	9585	15.30
897	Outer Shelf	Outer Shelf	-18.7467	147.2633	01-Sep-94		9	8795	9332	< D. L.	-	31.48	3	0.11	-	237	6.51	< D. L.	63.41	9570	15.30
898	Outer Shelf	Outer Shelf	-18.7500	147.2667	01-Sep-94		6	8832	9334	< D. L.	-	31.48	2	0.12	-	238	6.61	18.62	66.50	9571	15.30
899	Outer Shelf	Outer Shelf	-18.7533	147.2717	01-Sep-94		69	8650	9318	< D. L.	-	31.48	17	0.25	-	142	7.31	< D. L.	56.92	9460	29.65
900	Outer Shelf	Outer Shelf	-18.7567	147.2750	01-Sep-94		7	8603	9383	< D. L.	-	1787.85	3	0.21	-	296	8.40	< D. L.	65.66	9679	15.30
901	Outer Shelf	Outer Shelf	-18.8017	147.2483	02-Sep-94	43.00	80	5162	5248	< D. L.	-	31.48	40	2.36	-	167	6.34	7.63	44.95	5414	34.88
902	Outer Shelf	Outer Shelf	-18.8500	147.2483	02-Sep-94	40.00	139	5384	5544	< D. L.	-	31.48	80	2.26	-	226	8.45	9.46	53.71	5770	61.05
903	Mid Shelf	Mid Shelf	-18.9000	147.2483	02-Sep-94	37.00	167	3847	3827	225.08	-	31.48	78	1.99	-	196	6.54	45.94	50.90	4023	82.58
904	Mid Shelf	Mid Shelf	-18.9500	147.2483	02-Sep-94	32.00	173	3850	3808	< D. L.	-	31.48	69	2.20	-	180	7.81	11.16	44.51	3988	64.62
905	Mid Shelf	Mid Shelf	-18.9950	147.2483	02-Sep-94	30.00	224	3268	3207	< D. L.	-	31.48	88	2.12	-	157	6.09	37.34	38.83	3364	86.83
906	Mid Shelf	Mid Shelf	-19.0333	147.2483	02-Sep-94	28.00	228	4237	4212	< D. L.	-	31.48	80	2.70	-	182	6.67	14.64	41.45	4393	90.41
907	Mid Shelf	Mid Shelf	-19.0667	147.2483	02-Sep-94	26.00	240	3550	3541	< D. L.	-	38.54	92	2.56	-	172	6.24	64.71	40.95	3713	102.89
908	Mid Shelf	Mid Shelf	-19.1000	147.2483	02-Sep-94	25.00	280	3533	3215	< D. L.	-	40.49	103	2.15	-	224	6.14	17.68	40.67	3439	115.22
909	Mid Shelf	Mid Shelf	-19.1333	147.2483	02-Sep-94	23.00	317	4202	4015	< D. L.	-	40.73	140	8.69	-	217	8.70	41.52	38.18	4233	144.70
910	Mid Shelf	Mid Shelf	-19.1333	147.3533	02-Sep-94	27.00	297	2530	2589	< D. L.	-	31.48	113	2.14	-	204	6.24	16.77	35.50	2793	125.39
911	Mid Shelf	Mid Shelf	-19.1667	147.3533	02-Sep-94	23.00	352	2779	2904	< D. L.	-	39.82	137	4.65	-	215	7.51	49.51	36.24	3119	165.37
912	Mid Shelf	Mid Shelf	-19.2000	147.3533	02-Sep-94	22.00	352	2735	2932	< D. L.	-	116.82	126	3.97	-	203	6.69	20.48	39.15	3135	153.28
913	Inner Shelf	Bowling Shelf	-19.2167	147.3533	02-Sep-94	19.00	275	3663	4123	< D. L.	-	49.40	103	4.19	-	213	7.20	22.33	39.49	4336	128.24
914	Inner Shelf	Bowling Shelf	-19.2333	147.3533	02-Sep-94	18.00	881	3194	3531	< D. L.	90.58	116.90	256	3.89	182.79	356	9.56	38.50	43.20	3887	370.97
915	Inner Shelf	Bowling Shelf	-19.2500	147.3533	02-Sep-94	17.00	971	3171	3523	< D. L.	-	125.79	285	6.04	-	375	10.20	39.65	43.45	3898	420.99
916	Inner Shelf	Bowling Green Bay	-19.2917	147.0733	03-Sep-94	8.00	1284	982	882	< D. L.	230.94	183.51	462	11.86	255.63	463	10.72	64.39	46.94	1345	702.31
917	Inner Shelf	Bowling Green Bay	-19.3033	147.0883	03-Sep-94	8.00	1322	662	605	< D. L.	-	187.44	482	13.25	-	416	11.08	80.55	35.50	1022	705.06
918	Inner Shelf	Bowling Green Bay	-19.3150	147.0850	03-Sep-94	7.00	1128	794	712	124.56	-	153.67	447	14.75	-	359	10.37	59.25	34.56	1071	660.39
919	Inner Shelf	Bowling Green Bay	-19.3267	147.1167	03-Sep-94	7.00	1050	689	605	548.04	221.04	164.46	421	14.46	227.09	303	9.69	92.19	28.06	908	597.52
920	Inner Shelf	Bowling Green Bay	-19.3700	147.1300	03-Sep-94	7.00	1102	962	859	106.76	216.08	163.99	426	15.04	228.61	343	10.17	60.48	32.88	1202	598.59
921	Inner Shelf	Bowling Green Bay	-19.3483	147.1433	03-Sep-94	7.00	1279	1069	940	124.56	-	192.79	464	8.84	-	363	10.27	108.66	37.40	1303	695.58
922	Inner Shelf	Bowling Green Bay	-19.3617	147.1567	03-Sep-94	5.00	796	460	394	97.86	207.22	128.12	334	13.45	188.54	265	8.10	44.52	25.67	659	469.94
923	Inner Shelf	Bowling Green Bay	-19.3833	147.1833	03-Sep-94	3.00	1407	439	342	177.94	221.56	214.20	476	9.56	288.75	455	10.87	85.38	53.77	798	713.94

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
924	Inner Shelf	Bowling Green Bay	-19.3667	147.1833	03-Sep-94	5.00	1654	661	577	142.35	-	253.86	526	7.90	-	502	11.32	83.45	60.85	1079	813.37
925	Inner Shelf	Bowling Green Bay	-19.3500	147.1833	03-Sep-94	7.00	2193	488	420	119.22	-	306.74	662	9.87	-	647	14.19	120.77	70.15	1067	985.16
926	Inner Shelf	Bowling Green Bay	-19.3333	147.1833	03-Sep-94	9.00	2389	516	470	177.94	247.27	329.24	691	8.53	489.46	721	13.88	99.02	75.39	1191	1037.33
927	Inner Shelf	Bowling Green Bay	-19.3167	147.1833	03-Sep-94	7.00	748	510	533	115.66	139.90	115.01	309	10.95	180.94	230	8.46	45.34	22.37	763	374.48
928	Inner Shelf	Bowling Green Bay	-19.3000	147.1833	03-Sep-94	10.00	1658	1134	1032	< D. L.	-	259.68	529	7.62	-	493	12.54	73.83	48.13	1524	761.21
929	Inner Shelf	Bowling Shelf	-19.2833	147.1833	03-Sep-94	11.00	1020	1697	1560	160.14	133.88	155.59	370	13.47	214.75	316	10.15	58.40	34.44	1876	479.88
930	Inner Shelf	Bowling Shelf	-19.2667	147.1833	03-Sep-94	12.00	973	1778	1797	< D. L.	-	126.96	341	7.43	-	305	9.24	46.40	35.78	2101	445.01
931	Inner Shelf	Bowling Shelf	-19.2500	147.1833	03-Sep-94	14.00	1379	1847	1693	222.42	135.05	173.59	404	14.05	245.01	388	11.66	57.71	45.82	2081	533.27
932	Inner Shelf	Bowling Shelf	-19.2500	147.2133	03-Sep-94	15.00	1117	2058	1896	124.56	-	135.14	317	7.84	-	326	9.14	40.47	37.06	2222	447.61
933	Inner Shelf	Bowling Shelf	-19.2500	147.2733	03-Sep-94	14.00	993	4022	4024	176.16	-	127.89	266	7.03	-	373	9.27	39.66	53.56	4397	372.65
934	Inner Shelf	Bowling Shelf	-19.2500	147.3000	03-Sep-94	17.00	1218	2167	2007	105.87	121.77	162.26	339	9.17	211.17	411	9.04	43.79	49.06	2419	473.31
935	Inner Shelf	Bowling Shelf	-19.2667	147.3000	03-Sep-94	15.00	1536	1636	1409	153.91	145.68	195.15	427	7.58	269.64	568	10.32	58.27	48.22	1977	608.23
936	Inner Shelf	Bowling Shelf	-19.2833	147.3000	03-Sep-94	15.00	2907	687	591	144.13	-	393.45	767	8.52	-	836	14.15	94.10	77.67	1428	1098.52
937	Inner Shelf	Bowling Shelf	-19.3000	147.3000	03-Sep-94	13.00	2917	469	363	126.33	252.36	391.72	799	9.62	530.93	903	15.08	< D. L.	83.84	1266	1121.46
938	Inner Shelf	Bowling Green Bay	-19.3167	147.3000	03-Sep-94	11.00	2857	309	234	149.47	-	412.97	791	9.55	-	920	14.02	89.15	91.05	1154	1151.29
939	Inner Shelf	Bowling Green Bay	-19.3333	147.3000	03-Sep-94	6.00	334	130	63	< D. L.	-	31.48	131	7.90	-	84	4.48	18.80	12.88	147	180.66
940	Inner Shelf	Bowling Green Bay	-19.3500	147.3000	03-Sep-94	6.00	984	321	267	131.67	162.57	169.03	348	9.46	196.81	224	9.06	< D. L.	28.13	490	489.52
941	Inner Shelf	Bowling Green Bay	-19.3667	147.3000	03-Sep-94	5.00	2729	258	258	162.81	257.61	392.04	743	8.83	498.82	743	13.45	175.15	77.20	1001	1103.26
942	Inner Shelf	Bowling Green Bay	-19.3833	147.3000	03-Sep-94	5.00	2239	307	271	171.71	248.81	332.70	646	11.25	439.98	639	12.37	82.10	61.48	911	972.31
943	Inner Shelf	Alva Shelf	-19.3000	147.4167	04-Sep-94	5.00	317	181	119	115.66	-	41.96	125	5.81	-	40	3.51	< D. L.	9.59	159	172.40
944	Inner Shelf	Alva Shelf	-19.3000	147.4333	04-Sep-94	10.00	368	76	30	< D. L.	74.94	78.61	131	5.33	68.36	31	3.66	18.25	12.17	61	193.36
945	Inner Shelf	Alva Shelf	-19.3000	147.4667	04-Sep-94	18.00	2751	444	367	151.25	-	439.88	753	7.87	-	1044	14.47	130.23	100.06	1410	1123.15
946	Mid Shelf	Mid Shelf	-19.3000	147.5000	04-Sep-94	23.00	312	1299	1181	< D. L.	-	31.48	136	7.31	-	59	6.51	21.91	18.11	1240	149.11
947	Mid Shelf	Mid Shelf	-19.3000	147.5333	04-Sep-94	24.00	391	2280	2123	< D. L.	-	72.91	144	6.98	-	140	6.53	28.85	29.73	2263	171.94
948	Mid Shelf	Mid Shelf	-19.3000	147.5667	04-Sep-94	27.00	996	3144	2956	< D. L.	-	118.81	266	5.28	-	344	9.25	30.36	58.36	3300	376.01
949	Mid Shelf	Mid Shelf	-19.3283	147.5567	04-Sep-94	23.00	387	2465	2402	< D. L.	-	62.86	145	5.90	-	146	7.37	24.88	26.29	2548	162.15
950	Inner Shelf	Alva Shelf	-19.3550	147.5483	04-Sep-94	20.00	338	2440	2198	< D. L.	-	31.48	137	9.93	-	140	6.96	19.84	25.75	2338	145.51
951	Inner Shelf	Alva Shelf	-19.3833	147.5400	04-Sep-94	20.00	1084	1611	1465	< D. L.	-	156.83	331	5.62	-	371	9.38	50.74	33.09	1837	443.17
952	Inner Shelf	Alva Shelf	-19.4117	147.5317	04-Sep-94	13.00	786	503	457	< D. L.	127.18	103.98	303	8.46	156.70	209	8.11	37.15	20.32	666	365.76
953	Inner Shelf	Alva Shelf	-19.4383	147.5250	04-Sep-94	10.00	748	751	687	< D. L.	137.51	121.78	347	15.43	152.60	217	9.59	50.71	21.13	904	368.67
954	Inner Shelf	Alva Shelf	-19.4700	147.5167	04-Sep-94	6.00	307	207	163	< D. L.	-	52.93	131	9.30	-	27	3.57	20.48	13.57	190	169.50
955	Inner Shelf	Alva Shelf	-19.4867	147.5700	04-Sep-94	10.00	711	122	52	< D. L.	144.48	100.91	272	7.07	151.04	169	6.78	56.79	21.10	221	396.21
956	Inner Shelf	Alva Shelf	-19.5033	147.5633	04-Sep-94	13.00	2603	142	104	160.14	273.42	427.92	751	6.45	516.57	992	14.45	102.23	77.20	1096	1141.96
957	Inner Shelf	Alva Shelf	-19.5217	147.5833	04-Sep-94	12.00	1016	782	738	115.66	134.31	147.99	340	8.91	195.58	331	8.54	60.12	35.15	1069	452.65
958	Inner Shelf	Alva Shelf	-19.5400	147.6083	04-Sep-94	12.00	554	1424	1341	< D. L.	-	90.68	208	6.02	-	187	7.14	28.29	21.38	1528	234.97
959	Inner Shelf	Alva Shelf	-19.5583	147.6317	04-Sep-94	16.00	1183	1595	1491	< D. L.	120.79	160.21	366	6.25	205.45	356	9.82	56.11	40.70	1847	490.13
960	Inner Shelf	Alva Shelf	-19.5750	147.6550	04-Sep-94	16.00	531	2107	1975	< D. L.	74.75	87.35	222	6.55	103.95	179	8.76	26.03	28.60	2154	225.94
961	Inner Shelf	Alva Shelf	-19.5933	147.6333	04-Sep-94	14.00	2911	311	291	240.21	267.72	471.99	810	6.69	569.42	867	15.08	132.66	79.60	1158	1181.58
962	Inner Shelf	Alva Shelf	-19.6133	147.6100	04-Sep-94	7.00	2997	115	37	302.49	-	461.91	814	6.55	-	977	15.47	88.30	46.97	1014	1189.38
963	Inner Shelf	Alva Shelf	-19.6200	147.6033	04-Sep-94	5.00	670	107	19	97.86	128.71	113.82	272	6.91	151.49	62	7.67	51.58	19.62	81	438.58
964	Inner Shelf	Upstart Bay	-19.6500	147.6133	04-Sep-94	2.00	629	126	219	613.88	-	176.74	306	5.93	-	3029	8.98	59.44	90.67	3292	509.26
965	Inner Shelf	Upstart Bay	-19.6617	147.6417	04-Sep-94	8.00	1908	157	113	204.63	253.21	353.79	668	10.93	422.61	815	13.99	131.00	88.05	951	953.95
966	Inner Shelf	Upstart Bay	-19.6733	147.6683	04-Sep-94	12.00	3051	263	155	169.04	-	468.05	847	10.48	-	995	15.33	113.24	89.64	1181	1208.81
967	Inner Shelf	Upstart Bay	-19.6850	147.6967	04-Sep-94	14.00	2721	746	559	< D. L.	240.81	370.16	738	9.66	471.79	833	14.84	149.87	86.90	1504	1056.45
968	Inner Shelf	Upstart Bay	-19.7033	147.7550	05-Sep-94	10.00	221	5579	4450	< D. L.	-	35.60	131	7.24	-	176	11.27	16.61	52.84	5521	132.92
969	Mid Shelf	Mid Shelf	-19.6900	147.7617	05-Sep-94	20.00	1357	2727	2444	< D. L.	-	186.02	396	6.19	-	519	14.45	58.18	57.05	2962	543.98
970	Mid Shelf	Mid Shelf	-19.6767	147.7733	05-Sep-94	24.00	1034	3119	2749	< D. L.	-	141.03	324	6.63	-	371	12.01	30.90	44.67	3120	411.50
971	Mid Shelf	Mid Shelf	-19.6483	147.7967	05-Sep-94	24.00	919	2471	2189	< D. L.	-	105.29	293	6.85	-	326	9.75	56.55	38.37	2515	355.82
972	Mid Shelf	Mid Shelf	-19.6183	147.8183	05-Sep-94	26.00	506	3463	3141	< D. L.	-	46.32	194	5.55	-	229	9.61	19.88	37.55	3370	199.48

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
973	Mid Shelf	Mid Shelf	-19.5900	147.8417	05-Sep-94	29.00	310	4860	4620	< D. L.	-	31.48	176	5.65	-	166	11.74	31.55	34.78	4786	128.06
974	Mid Shelf	Mid Shelf	-19.5483	147.8717	05-Sep-94	33.00	312	4122	3890	< D. L.	-	36.51	139	6.69	-	183	9.26	17.26	43.23	4073	124.29
975	Mid Shelf	Mid Shelf	-19.5067	147.9033	05-Sep-94	35.00	196	4359	4166	< D. L.	-	31.48	122	7.46	-	133	8.47	33.64	42.55	4299	79.09
976	Outer Shelf	Outer Shelf	-19.4667	147.9350	05-Sep-94	40.00	157	4496	4412	< D. L.	-	31.48	90	7.35	-	116	7.48	10.67	40.83	4528	62.75
977	Outer Shelf	Outer Shelf	-19.4250	147.9667	05-Sep-94	41.00	121	5467	5416	< D. L.	-	31.48	90	5.05	-	115	10.62	16.01	39.21	5531	51.31
978	Outer Shelf	Outer Shelf	-19.3950	147.9917	05-Sep-94	37.00	94	6816	6940	< D. L.	-	31.48	59	2.31	-	160	9.20	5.98	51.25	7099	40.20
979	Outer Shelf	Outer Shelf	-19.3733	148.0067	05-Sep-94	46.00	102	5432	5697	< D. L.	-	31.48	55	2.54	-	156	8.86	12.65	44.01	5854	56.89
980	Outer Shelf	Outer Shelf	-19.3533	148.0233	05-Sep-94	46.00	66	7415	8249	< D. L.	-	31.48	37	0.91	-	206	10.23	< D. L.	57.83	8456	30.14
981	Outer Shelf	Outer Shelf	-19.3467	147.9900	06-Sep-94	51.00	102	5549	5916	< D. L.	-	31.48	67	4.47	-	142	9.35	12.66	41.64	6058	55.47
983	Outer Shelf	Outer Shelf	-19.3600	147.9017	06-Sep-94	39.00	143	3860	3957	< D. L.	-	31.48	69	8.54	-	182	7.42	10.89	39.52	4139	58.79
984	Mid Shelf	Mid Shelf	-19.3633	147.8600	06-Sep-94	16.00	4	8668	9311	< D. L.	-	31.48	2	0.11	-	654	5.17	6.28	73.52	9966	15.30
985	Mid Shelf	Mid Shelf	-19.3617	147.8200	06-Sep-94	38.00	114	4945	5336	< D. L.	-	31.48	64	6.19	-	126	8.25	12.54	55.21	5462	50.85
986	Mid Shelf	Mid Shelf	-19.3600	147.7783	06-Sep-94	36.00	137	3975	4225	< D. L.	-	31.48	70	5.45	-	101	6.93	16.51	41.64	4326	63.44
987	Mid Shelf	Mid Shelf	-19.3583	147.7250	06-Sep-94	32.00	184	3219	3320	< D. L.	-	32.64	86	7.68	-	114	7.09	13.64	42.89	3434	74.84
988	Mid Shelf	Mid Shelf	-19.3583	147.6733	06-Sep-94	27.00	200	3323	3447	< D. L.	-	38.26	97	5.08	-	175	7.31	15.43	40.67	3622	84.73
989	Mid Shelf	Mid Shelf	-19.3583	147.6200	06-Sep-94	23.00	212	4366	4114	< D. L.	-	52.74	107	7.93	-	199	8.40	14.33	37.71	4314	90.42
990	Mid Shelf	Mid Shelf	-19.3550	147.5850	06-Sep-94	22.00	243	1927	1618	< D. L.	-	31.48	100	5.53	-	129	5.05	14.92	27.02	1747	103.04
991	Inner Shelf	Alva Shelf	-19.3533	147.5117	06-Sep-94	9.00	271	137	77	< D. L.	-	43.81	125	7.27	-	47	4.32	13.40	9.35	124	146.46
992	Inner Shelf	Alva Shelf	-19.3333	147.4833	06-Sep-94	11.00	240	80	23	< D. L.	-	67.22	93	4.60	-	60	3.30	12.35	8.08	82	123.50
993	Inner Shelf	Alva Shelf	-19.3133	147.4533	06-Sep-94	9.00	273	83	13	103.20	-	68.76	109	4.08	-	74	3.74	15.10	12.25	87	151.35
994	Inner Shelf	Bowling Shelf	-19.2967	147.2167	06-Sep-94	10.00	552	456	335	< D. L.	-	103.08	225	8.19	-	231	5.79	31.50	19.14	566	264.65
994	Inner Shelf	Bowling Shelf	-19.2967	147.2167	06-Sep-94	10.00	570	500	494	< D. L.	-	93.55	224	8.87	-	191	6.40	33.33	19.32	684	268.17
994	Inner Shelf	Bowling Shelf	-19.2967	147.2167	06-Sep-94	10.00	557	756	737	495.55	-	106.94	223	7.66	-	187	6.79	35.19	19.97	924	268.62
995	Mid Shelf	Mid Shelf	-19.1567	147.0583	07-Sep-94	21.00	732	1234	1177	< D. L.	-	110.95	270	10.04	-	232	7.78	34.36	26.58	1410	315.44
1240	Inner Shelf	Bowling Green Bay	-19.3083	147.1200	17-Jan-95	8.00	1060	966	920	< D. L.	-	174.06	382	8.18	-	255	9.13	58.10	21.59	1176	611.29
1242	Inner Shelf	Bowling Green Bay	-19.3667	147.3550	17-Jan-95	4.00	2373	249	219	< D. L.	-	347.03	714	10.55	-	800	14.16	101.09	77.17	1019	1043.45
1243	Inner Shelf	Bowling Shelf	-19.2350	147.2517	18-Jan-95	16.00	560	1869	1715	< D. L.	-	87.72	186	5.86	-	254	6.84	29.90	29.95	1969	255.01
1244	Outer Shelf	Outer Shelf	-18.7450	147.2267	18-Jan-95	47.00	169	4536	4452	< D. L.	-	41.39	90	1.92	-	178	7.93	9.73	51.43	4630	105.57
1245	Mid Shelf	Mid Shelf	-18.8983	147.3033	18-Jan-95	39.00	194	6487	6860	< D. L.	-	31.48	61	1.73	-	261	8.25	9.17	60.64	7122	76.21
1246	Inner Shelf	Upstart Bay	-19.6767	147.6367	19-Jan-95	6.00	1416	189	115	705.52	-	317.91	486	7.20	-	552	9.60	108.18	116.41	690	882.51
1247	Inner Shelf	Upstart Bay	-19.6750	147.6367	19-Jan-95	6.00	1901	146	153	776.69	-	435.79	617	12.22	-	993	11.37	105.67	182.10	1177	1030.14
1249	Inner Shelf	Upstart Bay	-19.7867	147.6983	19-Jan-95	6.00	2260	1436	1096	< D. L.	-	303.59	612	7.07	-	779	12.84	74.60	114.25	2095	915.10
1251	Inner Shelf	Cleveland Bay	-19.2233	146.9533	20-Jan-95	4.00	781	1223	1092	< D. L.	-	135.69	326	11.51	-	299	7.27	47.34	24.73	1391	443.17
1252	Inner Shelf	Cleveland Bay	-19.2200	146.9517	20-Jan-95	4.00	635	961	965	< D. L.	-	94.00	301	11.78	-	130	6.96	35.04	19.10	1095	399.88
1253	Inner Shelf	Cleveland Bay	-19.2350	146.9417	20-Jan-95	3.00	605	1194	1106	< D. L.	-	92.92	309	12.11	-	198	7.59	37.26	21.25	1304	413.03
1255	Inner Shelf	Cleveland Bay	-19.2500	146.9133	21-Jan-95	3.00	664	2111	2008	< D. L.	-	70.08	316	9.84	-	208	7.87	40.94	21.01	2216	437.97
1256	Inner Shelf	Cleveland Bay	-19.2567	146.9083	21-Jan-95	3.00	887	1626	1464	< D. L.	-	108.45	380	10.12	-	256	9.49	51.68	25.74	1720	543.98
1257	Inner Shelf	Cleveland Bay	-19.2633	146.9117	21-Jan-95	3.00	765	1465	1300	< D. L.	-	116.87	366	10.36	-	232	9.30	56.75	22.83	1532	513.84
1259	Inner Shelf	Bowling Shelf	-19.2983	147.3517	21-Jan-95	14.00	2814	343	473	169.93	-	396.29	812	9.04	-	721	14.76	95.60	79.38	1194	1174.54
1261	Inner Shelf	Hinchinbrook Channel	-18.4083	146.1717	03-Jun-95	5.00	2434	121	103	338.08	-	253.86	535	2.72	-	505	10.50	140.06	479.73	608	-
1264	Inner Shelf	Hinchinbrook Channel	-18.3883	146.1500	03-Jun-95	3.00	1504	1108	498	< D. L.	-	151.29	372	2.84	-	1792	7.28	70.32	316.59	2290	-
1265	Inner Shelf	Hinchinbrook Channel	-18.3783	146.1400	04-Jun-95	3.00	844	63	408	115.66	-	89.49	279	5.04	-	9891	4.53	59.56	362.76	10299	-
1267	Inner Shelf	Hinchinbrook Channel	-18.3800	146.1383	04-Jun-95	3.00	2200	154	558	382.56	-	220.96	637	3.02	-	12455	9.27	116.41	845.91	13013	-
1268	Inner Shelf	Hinchinbrook Channel	-18.3850	146.1300	04-Jun-95	3.00	1734	120	143	249.11	-	161.47	452	2.05	-	823	7.72	139.33	543.98	966	-
1269	Inner Shelf	Hinchinbrook Channel	-18.3717	146.1367	04-Jun-95	3.00	2133	139	160	275.80	-	217.03	618	4.02	-	889	8.55	133.64	712.73	1049	-
1271	Inner Shelf	Missionary Bay	-18.2533	146.2167	05-Jun-95	3.00	1401	1856	531	< D. L.	-	183.19	441	6.25	-	2666	8.66	110.23	314.41	3197	-
1273	Inner Shelf	Missionary Bay	-18.2300	146.1467	05-Jun-95	4.00	794	1276	371	< D. L.	-	75.51	308	7.89	-	1527	7.97	51.21	48.97	1898	-
1274	Inner Shelf	Missionary Bay	-18.2233	146.1667	05-Jun-95	4.00	708	1128	321	< D. L.	-	71.12	298	8.21	-	1194	7.50	70.37	40.92	1515	-
1275	Inner Shelf	Missionary Bay	-18.2400	146.2017	05-Jun-95	4.00	1089	1413	250	< D. L.	-	106.59	340	6.78	-	1207	8.87	68.24	77.39	1457	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1277	Mid Shelf	Mid Shelf	-18.0383	146.3933	07-Jun-95	29.00	285	4518	2394	< D. L.	-	25.18	103	2.01	-	179	8.26	27.82	50.75	2573	-
1278	Outer Shelf	Outer Shelf	-18.0200	146.4433	07-Jun-95	31.00	243	6791	6989	< D. L.	-	18.89	73	1.74	-	209	8.87	12.07	67.90	7198	-
1279	Outer Shelf	Outer Shelf	-18.0000	146.4917	07-Jun-95	34.00	220	7293	7563	< D. L.	-	17.31	68	1.63	-	232	11.41	18.34	67.81	7795	-
1280	Outer Shelf	Outer Shelf	-17.9800	146.5400	07-Jun-95	41.00	235	7575	7960	< D. L.	-	17.31	66	1.36	-	268	11.46	9.17	72.18	8228	-
1281	Outer Shelf	Outer Shelf	-17.9567	146.5883	07-Jun-95	51.00	325	7550	7828	< D. L.	-	26.75	88	1.49	-	354	13.62	15.93	74.17	8182	-
1282	Outer Shelf	Outer Shelf	-17.9417	146.6383	08-Jun-95	54.00	220	7068	7311	< D. L.	-	< D. L.	88	2.11	-	217	12.34	8.69	64.07	7528	-
1283	Outer Shelf	Outer Shelf	-18.0100	146.6400	08-Jun-95	50.00	245	7967	8580	2758.01	-	17.31	93	1.45	-	278	14.36	12.07	65.94	8858	-
1284	Outer Shelf	Outer Shelf	-18.0917	146.6217	08-Jun-95	50.00	203	6053	6210	< D. L.	-	< D. L.	96	1.84	-	198	12.06	8.69	49.19	6408	-
1285	Outer Shelf	Outer Shelf	-18.1467	146.5733	08-Jun-95	41.00	203	6964	7323	< D. L.	-	291.78	71	1.80	-	211	10.55	12.07	61.38	7534	-
1286	Outer Shelf	Outer Shelf	-18.1433	146.6317	08-Jun-95	43.00	176	7510	7913	< D. L.	-	< D. L.	59	1.37	-	212	13.11	7.24	63.13	8125	-
1287	Outer Shelf	Outer Shelf	-18.1450	146.6883	08-Jun-95	47.00	135	7647	8123	< D. L.	-	< D. L.	52	2.06	-	222	14.70	8.69	68.50	8346	-
1288	Outer Shelf	Outer Shelf	-18.1433	146.7433	08-Jun-95	55.00	185	7864	8645	97.86	-	17.31	62	1.11	-	291	12.55	5.79	74.05	8935	-
1289	Outer Shelf	Outer Shelf	-18.1450	146.8017	08-Jun-95	58.00	190	7789	8584	< D. L.	-	20.46	62	1.06	-	287	13.44	9.17	74.77	8871	-
1290	Outer Shelf	Outer Shelf	-18.1467	146.8583	08-Jun-95	60.00	167	7650	8422	< D. L.	-	22.03	50	0.99	-	279	11.56	5.79	74.30	8700	-
1291	Outer Shelf	Outer Shelf	-18.2550	146.8900	08-Jun-95	35.00	29	8421	9502	< D. L.	-	< D. L.	12	0.34	-	163	10.27	7.72	72.02	9665	-
1292	Outer Shelf	Outer Shelf	-18.2683	147.3750	10-Jun-95	35.00	10	8575	9591	< D. L.	-	< D. L.	3	0.12	-	170	7.27	< D. L.	66.53	9761	-
1293	Outer Shelf	Outer Shelf	-18.2867	147.3383	10-Jun-95	92.00	115	8076	9087	400.36	-	28.33	27	0.57	-	272	11.80	25.10	67.06	9360	-
1294	Outer Shelf	Outer Shelf	-18.3233	147.2983	10-Jun-95	68.00	65	8338	9240	355.87	-	< D. L.	16	0.41	-	340	10.14	< D. L.	66.31	9580	-
1295	Outer Shelf	Outer Shelf	-18.3617	147.2600	10-Jun-95	70.00	73	8059	9126	266.90	-	< D. L.	43	0.98	-	215	11.14	6.76	73.49	9341	-
1296	Outer Shelf	Outer Shelf	-18.3983	147.2200	10-Jun-95	63.00	53	7725	9115	97.86	-	< D. L.	25	0.57	-	163	7.36	< D. L.	74.17	9278	-
1297	Outer Shelf	Outer Shelf	-18.4367	147.1800	10-Jun-95	55.00	70	7595	8601	240.21	-	< D. L.	28	0.69	-	212	8.75	7.24	72.80	8813	-
1298	Outer Shelf	Outer Shelf	-18.4750	147.1400	10-Jun-95	46.00	39	8116	9229	222.42	-	< D. L.	13	0.41	-	181	9.00	< D. L.	73.52	9411	-
1299	Outer Shelf	Outer Shelf	-18.5133	147.1000	10-Jun-95	28.00	27	8303	9565	258.01	-	< D. L.	12	0.25	-	148	10.53	9.65	72.05	9714	-
1300	Outer Shelf	Outer Shelf	-18.5517	147.0600	10-Jun-95	50.00	101	7375	8286	240.21	-	< D. L.	39	0.96	-	188	11.15	< D. L.	72.74	8474	-
1301	Outer Shelf	Outer Shelf	-18.5883	147.0200	10-Jun-95	45.00	120	6475	7217	160.14	-	< D. L.	50	1.85	-	143	9.07	13.51	66.31	7360	-
1302	Outer Shelf	Outer Shelf	-18.6083	146.9683	10-Jun-95	41.00	122	6939	7697	213.52	-	< D. L.	48	2.87	-	169	10.91	8.20	69.37	7865	-
1303	Outer Shelf	Outer Shelf	-18.6100	146.9150	10-Jun-95	40.00	135	6539	7370	195.73	-	< D. L.	56	3.38	-	157	10.58	13.03	65.00	7527	-
1304	Mid Shelf	Mid Shelf	-18.6117	146.8567	10-Jun-95	38.00	171	6517	7398	213.52	-	< D. L.	65	3.49	-	165	10.99	9.17	59.45	7563	-
1305	Mid Shelf	Mid Shelf	-18.6117	146.8000	10-Jun-95	41.00	219	6372	7045	213.52	-	< D. L.	87	3.13	-	160	12.62	17.37	58.67	7205	-
1306	Mid Shelf	Mid Shelf	-18.6133	146.7433	10-Jun-95	36.00	245	5971	6715	231.32	-	29.90	91	3.62	-	165	12.29	12.07	54.68	6880	-
1307	Outer Shelf	Outer Shelf	-18.2417	147.3833	01-Aug-95	199.00	95	7897	9297	800.71	-	< D. L.	70	1.20	-	128	15.86	9.65	66.31	9425	-
1308	Outer Shelf	Outer Shelf	-18.2167	147.3083	01-Aug-95	127.00	116	7857	9103	693.95	-	18.89	56	1.04	-	141	16.37	6.27	68.47	9244	-
1309	Outer Shelf	Outer Shelf	-18.1867	147.2133	01-Aug-95	210.00	172	7465	8581	640.57	-	25.18	120	1.28	-	161	22.67	12.07	71.02	8742	-
1310	Outer Shelf	Outer Shelf	-18.1650	147.1667	01-Aug-95	195.00	175	7378	8459	569.40	-	23.61	99	1.56	-	191	21.68	9.65	66.44	8650	-
1311	Outer Shelf	Outer Shelf	-18.1883	147.1417	01-Aug-95	110.00	84	8209	9180	738.43	-	18.89	37	0.78	-	144	12.95	8.20	71.77	9324	-
1312	Outer Shelf	Outer Shelf	-18.2250	147.1000	01-Aug-95	66.00	73	8101	9245	106.76	-	< D. L.	21	0.36	-	171	7.27	< D. L.	77.11	9416	-
1313	Outer Shelf	Outer Shelf	-18.2783	147.0600	01-Aug-95	78.00	129	6138	6446	249.11	-	28.33	62	1.33	-	151	11.53	9.65	54.93	6597	-
1314	Outer Shelf	Outer Shelf	-18.2950	147.0200	01-Aug-95	71.00	138	7488	8110	151.25	-	< D. L.	49	0.99	-	215	11.89	5.31	68.00	8325	-
1315	Outer Shelf	Outer Shelf	-18.3283	146.9783	01-Aug-95	72.00	142	7552	8142	< D. L.	-	31.48	44	1.07	-	227	11.40	8.20	70.62	8368	-
1316	Outer Shelf	Outer Shelf	-18.3650	146.9417	01-Aug-95	67.00	160	6751	7266	142.35	-	17.31	54	1.17	-	207	11.21	6.76	62.91	7473	-
1317	Outer Shelf	Outer Shelf	-18.4000	146.9000	01-Aug-95	63.00	159	5659	5718	< D. L.	-	17.31	61	1.20	-	172	9.68	9.65	49.19	5890	-
1318	Outer Shelf	Outer Shelf	-18.4333	146.8600	01-Aug-95	66.00	163	7128	7531	124.56	-	31.48	60	1.51	-	188	15.06	7.72	71.21	7720	-
1319	Outer Shelf	Outer Shelf	-18.4567	146.8133	01-Aug-95	53.00	176	6816	7136	62.28	-	17.31	66	1.73	-	181	12.79	11.10	65.00	7317	-
1320	Outer Shelf	Outer Shelf	-18.4567	146.7583	01-Aug-95	50.00	213	4726	4727	97.86	-	< D. L.	75	1.84	-	160	9.98	10.62	46.07	4887	-
1321	Outer Shelf	Outer Shelf	-18.4567	146.7000	01-Aug-95	45.00	162	6248	6327	115.66	-	34.62	72	1.61	-	119	12.09	14.00	50.75	6447	-
1322	Outer Shelf	Outer Shelf	-18.4567	146.6467	01-Aug-95	42.00	253	5631	5587	169.04	-	22.03	118	2.44	-	172	11.51	13.03	43.26	5759	-
1323	Outer Shelf	Outer Shelf	-18.1333	146.9117	02-Aug-95	64.00	118	7909	8614	195.73	-	< D. L.	39	0.89	-	240	10.75	9.17	76.23	8854	-
1324	Outer Shelf	Outer Shelf	-18.1000	146.9533	02-Aug-95	67.00	113	8056	8923	169.04	-	< D. L.	33	0.65	-	226	11.15	5.79	74.55	9149	-
1325	Outer Shelf	Outer Shelf	-18.0650	146.9967	02-Aug-95	65.00	40	8306	9484	240.21	-	< D. L.	16	0.32	-	128	7.75	6.27	76.01	9612	-

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1326	Outer Shelf	Slope	-18.0350	147.0367	02-Aug-95	200.00	162	7735	9502	355.87	-	22.03	43	0.88	-	163	13.27	6.27	71.80	9665	-
1327	Outer Shelf	Slope	-17.9817	146.9817	02-Aug-95	200.00	152	7924	9591	373.67	-	17.31	39	0.79	-	170	14.63	14.48	72.08	9761	-
1328	Outer Shelf	Slope	-17.9400	146.9367	02-Aug-95	190.00	159	7802	9087	266.90	-	17.31	43	0.92	-	272	16.63	5.79	71.71	9360	-
1329	Outer Shelf	Slope	-17.9083	146.8983	02-Aug-95	170.00	140	7909	9240	338.08	-	17.31	42	0.86	-	340	16.48	7.72	70.90	9580	-
1330	Outer Shelf	Outer Shelf	-17.9083	146.8467	02-Aug-95	70.00	77	8066	9123	204.63	-	< D. L.	26	0.56	-	169	11.60	< D. L.	77.01	9291	-
1331	Outer Shelf	Outer Shelf	-17.9133	146.7967	02-Aug-95	65.00	64	8256	9425	471.53	-	< D. L.	40	0.72	-	133	12.39	9.65	70.12	9559	-
1332	Outer Shelf	Outer Shelf	-17.9183	146.7417	02-Aug-95	63.00	174	7201	7726	160.14	-	< D. L.	70	1.68	-	226	13.35	8.20	66.09	7952	-
1333	Outer Shelf	Outer Shelf	-17.9317	146.6900	02-Aug-95	57.00	219	6684	7206	115.66	-	< D. L.	86	1.93	-	181	11.87	14.00	66.25	7387	-
1430	Inner Shelf	Cleveland Bay	-19.2250	146.9667	29-Jul-96	4.00	724	953	771	< D. L.	-	97.58	353	12.50	-	310	8.20	48.26	40.95	1081	-
1431	Inner Shelf	Cleveland Bay	-19.2083	146.9667	29-Jul-96	5.00	746	1505	1222	< D. L.	-	97.58	330	12.30	-	201	9.01	43.92	29.68	1423	-
1432	Inner Shelf	Cleveland Bay	-19.1917	146.9667	29-Jul-96	7.00	1011	1256	1337	< D. L.	-	151.09	388	13.96	-	0	8.63	54.05	33.62	1337	-
1433	Inner Shelf	Cleveland Bay	-19.1750	146.9667	29-Jul-96	9.00	891	1153	812	< D. L.	-	100.72	331	8.45	-	217	7.46	51.64	30.90	1028	-
1434	Inner Shelf	Cleveland Shelf	-19.1583	146.9667	29-Jul-96	11.00	900	971	968	< D. L.	-	124.33	338	10.80	-	250	7.44	49.23	26.76	1218	-
1435	Inner Shelf	Cleveland Shelf	-19.1417	146.9667	29-Jul-96	13.00	1604	1488	1219	391.46	-	160.53	447	9.33	-	102	6.92	73.36	24.36	1321	-
1436	Inner Shelf	Cleveland Shelf	-19.1250	146.9667	29-Jul-96	15.00	1054	1966	1664	< D. L.	-	124.33	361	7.95	-	264	9.25	52.61	38.71	1928	-
1437	Inner Shelf	Cleveland Shelf	-19.1083	146.9667	29-Jul-96	17.00	947	2366	1967	< D. L.	-	122.76	321	8.09	-	245	9.23	46.33	38.33	2212	-
1438	Inner Shelf	Cleveland Shelf	-19.0917	146.9667	29-Jul-96	19.00	933	2954	2577	< D. L.	-	125.90	308	7.26	-	240	9.53	44.40	43.08	2817	-
1439	Inner Shelf	Cleveland Shelf	-19.0750	146.9667	29-Jul-96	21.00	915	4155	3520	< D. L.	-	108.59	301	7.30	-	259	10.75	39.58	49.00	3779	-
1440	Mid Shelf	Mid Shelf	-19.0083	146.9667	29-Jul-96	22.00	569	6259	5567	< D. L.	-	55.08	213	4.83	-	247	14.00	40.06	71.37	5814	-
1441	Mid Shelf	Mid Shelf	-18.9417	146.9667	29-Jul-96	23.00	353	6491	4712	< D. L.	-	51.94	133	5.23	-	207	10.35	25.58	69.25	4920	-
1442	Mid Shelf	Mid Shelf	-18.8750	146.9667	29-Jul-96	28.00	306	6256	5370	< D. L.	-	17.31	168	4.05	-	210	13.44	26.06	67.09	5581	-
1443	Mid Shelf	Mid Shelf	-18.8083	146.9667	29-Jul-96	32.00	238	6602	6533	< D. L.	-	26.75	90	2.80	-	221	11.70	14.96	77.67	6755	-
1444	Mid Shelf	Mid Shelf	-18.7417	146.9667	29-Jul-96	37.00	297	6041	5343	< D. L.	-	29.90	145	9.76	-	229	12.88	22.68	79.38	5572	-
1445	Mid Shelf	Mid Shelf	-18.6750	146.9667	29-Jul-96	39.00	154	5850	5070	< D. L.	-	22.03	75	2.48	-	150	10.36	11.58	72.49	5220	-
1446	Outer Shelf	Outer Shelf	-18.6083	146.9667	29-Jul-96	41.00	120	6805	6366	< D. L.	-	29.90	51	2.72	-	173	10.90	7.24	81.97	6539	-
1447	Outer Shelf	Outer Shelf	-18.5417	146.9667	29-Jul-96	49.00	183	5531	3704	< D. L.	-	20.46	65	1.35	-	234	9.32	10.14	68.75	3939	-
1448	Outer Shelf	Outer Shelf	-18.5350	146.9667	30-Jul-96	4.00	760	298	285	160.14	-	97.58	233	5.16	-	280	4.31	53.57	59.83	564	-
1486	Inner Shelf	Cleveland Shelf	-19.1583	146.9667	08-Aug-96	12.00	818	981	714	< D. L.	-	116.46	320	9.10	-	199	7.06	62.26	23.07	913	399.42
1487	Inner Shelf	Cleveland Shelf	-19.1100	146.9667	08-Aug-96	17.00	1025	2364	1662	< D. L.	-	121.18	326	6.34	-	279	8.81	61.29	31.38	1940	457.55
1489	Inner Shelf	Cleveland Shelf	-19.0833	146.9167	08-Aug-96	18.00	1521	2529	1696	< D. L.	-	185.71	452	8.42	-	368	11.29	77.70	48.53	2064	648.00
1490	Inner Shelf	Cleveland Shelf	-19.1000	146.9167	08-Aug-96	16.00	1045	2349	0	< D. L.	-	135.35	353	8.28	-	0	9.77	63.22	34.44	0	457.55
1491	Inner Shelf	Cleveland Shelf	-19.1167	146.9167	08-Aug-96	14.00	967	1946	1301	< D. L.	-	124.33	353	8.68	-	245	9.02	62.26	33.13	1546	455.25
1492	Inner Shelf	Cleveland Shelf	-19.1333	146.9167	08-Aug-96	12.00	897	1308	931	< D. L.	-	198.30	352	7.55	-	200	8.27	59.85	24.70	1131	444.39
1493	Inner Shelf	Cleveland Bay	-19.1500	146.9167	08-Aug-96	11.00	910	1398	1059	< D. L.	-	1070.19	363	8.91	-	185	8.80	59.85	26.25	1244	458.77
1494	Inner Shelf	Cleveland Bay	-19.1667	146.9167	08-Aug-96	9.00	664	935	687	< D. L.	-	80.26	325	12.64	-	141	7.64	53.09	24.23	828	383.82
1495	Inner Shelf	Cleveland Bay	-19.1833	146.9167	08-Aug-96	7.00	723	1256	921	< D. L.	-	89.71	339	11.22	-	168	7.92	53.09	26.86	1089	402.94
1496	Inner Shelf	Cleveland Bay	-19.2000	146.9167	08-Aug-96	6.00	778	1149	870	< D. L.	-	107.02	354	9.56	-	160	7.89	53.09	26.02	1030	437.97
1497	Inner Shelf	Cleveland Bay	-19.2167	146.9167	08-Aug-96	5.00	623	1391	1030	< D. L.	-	89.71	329	10.37	-	110	7.58	47.30	22.03	1139	398.81
1498	Inner Shelf	Cleveland Bay	-19.2333	146.9167	08-Aug-96	4.00	726	1235	832	< D. L.	-	73.97	368	14.31	-	256	8.80	55.50	26.94	1088	461.07
1499	Inner Shelf	Cleveland Bay	-19.2500	146.9167	08-Aug-96	3.00	790	1494	1034	< D. L.	-	84.99	384	11.70	-	241	9.82	58.88	24.79	1276	497.48
1681	Inner Shelf	Cleveland Bay	-19.2916	146.9838	28-Oct-97	-	949	102	8	53.38	136.26	101.83	329	7.21	250.21	208	0.00	69.50	53.03	216	419.31
1682	Inner Shelf	Cleveland Bay	-19.2933	146.9810	28-Oct-97	-	1768	240	150	115.66	223.15	227.89	566	17.21	358.71	1141	0.00	85.42	77.98	1290	692.21
1683	Inner Shelf	Cleveland Bay	-19.2878	146.9872	28-Oct-97	-	1968	67	0	53.38	198.20	194.05	553	12.16	340.32	516	0.00	83.49	65.50	516	724.80
1684	Inner Shelf	Cleveland Bay	-19.2841	146.9900	28-Oct-97	-	2721	57	17	-0.44	203.97	150.93	562	12.33	277.64	500	0.00	73.36	77.98	516	764.11
1685	Inner Shelf	Cleveland Bay	-19.2934	146.9815	29-Oct-97	-	1282	115	33	97.86	162.23	127.32	397	6.34	259.07	724	0.00	62.74	59.26	758	528.68
1686	Inner Shelf	Cleveland Bay	-19.2934	146.9815	29-Oct-97	-	1368	127	67	115.66	173.60	158.48	421	6.88	292.11	716	0.00	67.57	62.38	783	560.81
1687	Inner Shelf	Cleveland Bay	-19.2935	146.9816	29-Oct-97	-	1193	182	108	124.56	157.64	173.59	383	8.82	265.71	541	0.00	62.74	74.86	649	497.02
1688	Inner Shelf	Cleveland Bay	-19.2825	146.9797	29-Oct-97	-	1086	322	266	151.25	152.38	121.34	337	4.94	224.15	1957	0.00	59.36	127.89	2223	448.37
1689	Inner Shelf	Cleveland Bay	-19.2832	146.9803	29-Oct-97	-	971	2877	2015	-0.44	122.01	98.84	297	12.12	243.40	366	0.00	52.12	46.79	2381	401.56

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1690	Inner Shelf	Cleveland Bay	-19.2845	146.9827	29-Oct-97	-	2016	77	25	-0.44	209.91	207.90	564	12.30	357.52	450	0.00	66.12	90.46	475	739.79
1691	Inner Shelf	Cleveland Bay	-19.2734	146.8223	29-Oct-97	-	1764	90	108	240.21	181.91	310.83	501	5.48	284.11	1532	0.00	153.47	40.55	1640	1055.84
1692	Inner Shelf	Cleveland Bay	-19.2734	146.8230	29-Oct-97	-	1420	82	42	409.25	168.00	197.36	417	13.30	225.17	283	0.00	114.38	53.03	325	795.01
1693	Inner Shelf	Cleveland Bay	-19.2622	146.8386	30-Oct-97	0.10	1319	327	291	1272.24	196.16	293.36	414	9.53	242.21	408	0.00	135.62	49.91	699	964.66
1694	Inner Shelf	Cleveland Bay	-19.2623	146.8389	30-Oct-97	0.10	1268	359	275	524.91	208.04	220.65	399	9.92	226.03	341	0.00	98.46	49.91	616	757.84
1695	Inner Shelf	Cleveland Bay	-19.2624	146.8386	30-Oct-97	0.10	1001	364	275	400.36	182.08	203.65	347	8.99	213.59	366	0.00	96.04	37.43	641	681.81
1696	Inner Shelf	Cleveland Bay	-19.2801	146.8085	30-Oct-97	-	1568	70	50	7455.52	184.63	1004.56	471	9.12	216.32	4204	0.00	748.65	190.27	4254	10831.42
1697	Inner Shelf	Cleveland Bay	-19.2720	146.8061	30-Oct-97	-	2513	100	125	7081.85	255.22	2542.81	772	16.34	354.62	3089	0.00	1247.57	199.63	3214	23437.97
1698	Inner Shelf	Cleveland Bay	-19.2444	146.7951	30-Oct-97	-	738	444	383	516.01	119.46	197.99	274	7.59	123.32	466	0.00	106.66	62.38	849	857.58
1699	Inner Shelf	Cleveland Bay	-19.2626	146.8167	30-Oct-97	-	886	62	25	2571.17	101.82	1560.59	303	2.87	216.15	1157	0.00	627.57	112.29	1182	5072.97
1700	Inner Shelf	Cleveland Bay	-19.2742	146.8212	30-Oct-97	-	815	45	33	124.56	144.75	144.63	274	13.40	119.91	133	0.00	139.96	53.03	167	784.92
1701	Inner Shelf	Cleveland Bay	-19.2807	146.9785	04-Nov-97	1.00	1060	1200	841	151.25	175.46	113.63	353	9.28	175.44	366	0.00	56.47	53.03	1207	480.34
1702	Inner Shelf	Cleveland Bay	-19.2807	146.9786	04-Nov-97	1.00	956	1694	1166	169.04	174.61	98.21	312	9.83	173.56	375	0.00	48.26	59.26	1540	428.79
1703	Inner Shelf	Cleveland Bay	-19.2808	146.9786	04-Nov-97	1.00	1045	1450	1016	124.56	177.67	111.58	335	9.93	180.89	391	0.00	52.61	65.50	1407	453.42
1704	Inner Shelf	Cleveland Bay	-19.2798	146.9748	04-Nov-97	2.00	1179	1492	1074	106.76	247.75	138.81	415	17.46	209.85	616	0.00	59.85	49.91	1690	546.43
1705	Inner Shelf	Cleveland Bay	-19.2854	146.9734	04-Nov-97	1.00	1045	1073	774	< D. L.	203.97	107.02	371	9.96	175.27	433	0.00	55.02	53.03	1207	504.21
1706	Inner Shelf	Cleveland Bay	-19.2802	146.8087	03-Nov-97	-	652	45	0	729.54	110.81	221.91	231	31.98	96.41	774	0.00	199.81	18.71	774	2410.43
1707	Inner Shelf	Cleveland Bay	-19.2925	146.8188	03-Nov-97	-	1390	80	0	80.07	208.55	209.79	415	10.72	164.54	341	0.00	85.91	62.38	341	699.71
1708	Inner Shelf	Cleveland Bay	-19.2603	146.8245	03-Nov-97	-	1920	100	0	845.20	279.82	5763.30	723	9.62	454.61	2148	0.00	1566.49	68.62	2148	8554.38
1709	Inner Shelf	Cleveland Bay	-19.2863	146.9741	04-Nov-97	0.50	667	1300	916	106.76	171.56	84.20	247	5.26	154.49	833	0.00	40.06	115.41	1748	400.64
1710	Inner Shelf	Cleveland Bay	-19.2844	146.9779	04-Nov-97	1.00	867	796	574	< D. L.	180.72	86.87	328	9.45	170.33	450	0.00	50.68	56.14	1024	434.76
1711	Inner Shelf	Cleveland Bay	-19.2835	146.9793	04-Nov-97	0.50	1090	237	0	62.28	181.23	119.45	353	6.90	201.67	2115	0.00	55.50	118.53	2115	469.33
1712	Inner Shelf	Cleveland Bay	-19.2871	146.9767	04-Nov-97	-	964	92	0	-0.44	172.07	96.95	322	4.58	178.33	1174	0.00	49.71	68.62	1174	457.70
1713	Inner Shelf	Cleveland Bay	-19.2953	146.9939	04-Nov-97	-	2646	217	150	71.17	258.61	308.78	731	30.06	478.79	1665	0.00	105.69	180.91	1815	931.31
1714	Inner Shelf	Cleveland Bay	-19.2922	146.9844	04-Nov-97	-	2109	235	117	-0.44	223.32	234.50	596	17.88	402.83	1124	0.00	89.77	99.81	1241	753.10
1715	Inner Shelf	Cleveland Bay	-19.2716	146.8394	05-Nov-97	-	1016	499	416	< D. L.	140.51	146.99	312	14.98	207.29	400	0.00	54.05	65.50	816	478.05
1716	Inner Shelf	Cleveland Bay	-19.2661	146.8149	06-Nov-97	-	1720	100	125	1396.80	195.32	1598.05	616	38.20	343.89	1382	0.00	690.16	84.22	1507	8625.36
1717	Inner Shelf	Cleveland Bay	-19.2663	146.8150	06-Nov-97	-	782	55	17	106.76	100.46	370.95	233	4.76	124.34	724	0.00	195.46	43.67	741	1323.85
1718	Inner Shelf	Cleveland Bay	-19.2502	146.8130	06-Nov-97	-	208	85	83	-0.44	55.66	37.77	100	4.83	49.23	42	0.00	37.16	9.36	125	221.05
1719	Inner Shelf	Cleveland Bay	-19.2431	146.7935	06-Nov-97	-	615	908	708	177.94	128.12	114.10	218	22.15	102.37	183	0.00	62.74	53.03	891	484.63
1720	Inner Shelf	Cleveland Bay	-19.2432	146.7933	06-Nov-97	-	682	704	558	151.25	138.81	119.29	244	25.25	99.81	167	0.00	69.02	68.62	724	475.14
1721	Inner Shelf	Cleveland Bay	-19.2433	146.7934	06-Nov-97	-	667	968	749	< D. L.	127.95	96.79	213	17.71	77.67	133	0.00	59.85	56.14	883	421.91
1722	Inner Shelf	Cleveland Shelf	-19.0998	146.9166	05-Feb-98	18.00	939	1674	2196	201.25	108.20	96.60	299	7.87	174.74	250	8.80	43.53	40.71	2446	348.37
1723	Inner Shelf	Cleveland Shelf	-19.1165	146.9163	05-Feb-98	15.00	892	1452	1795	177.05	120.60	110.61	310	7.37	167.92	228	8.06	47.70	44.55	2023	361.03
1724	Inner Shelf	Cleveland Shelf	-19.1334	146.9166	05-Feb-98	13.00	622	1127	1330	130.96	114.89	71.97	255	8.50	121.43	150	8.18	36.89	24.31	1480	268.47
1725	Inner Shelf	Cleveland Bay	-19.1501	146.9166	05-Feb-98	12.00	831	1132	1386	263.88	130.90	93.71	303	7.89	159.46	184	8.02	45.19	31.30	1570	333.52
1726	Inner Shelf	Cleveland Bay	-19.1667	146.9170	05-Feb-98	10.00	886	738	828	105.87	135.98	93.94	321	9.31	156.11	213	7.84	49.05	37.48	1041	367.80
1727	Inner Shelf	Cleveland Bay	-19.1833	146.9170	05-Feb-98	9.00	1061	728	817	214.15	151.94	121.10	366	9.79	203.34	306	8.17	55.62	43.75	1123	422.14
1728	Inner Shelf	Cleveland Bay	-19.1996	146.9166	05-Feb-98	8.00	873	888	1023	178.02	168.61	99.94	340	9.05	177.96	210	7.72	47.99	26.82	1233	387.18
1729	Inner Shelf	Cleveland Bay	-19.2166	146.9170	05-Feb-98	6.00	579	826	919	156.58	164.04	67.73	290	10.90	124.52	149	6.60	44.48	26.26	1068	319.83
1730	Inner Shelf	Cleveland Bay	-19.2332	146.9173	05-Feb-98	5.00	713	1015	1187	84.34	167.21	93.31	327	9.60	154.07	220	8.00	39.46	28.36	1407	381.79
1731	Inner Shelf	Cleveland Bay	-19.2495	146.9170	05-Feb-98	4.00	762	1258	1477	164.15	164.74	87.86	330	9.39	160.00	234	8.72	38.66	24.02	1711	404.98
1732	Inner Shelf	Cleveland Bay	-19.2668	146.8997	05-Feb-98	3.00	2489	514	494	284.25	226.15	289.43	690	15.94	413.51	868	13.60	82.12	69.54	1362	964.43
1733	Inner Shelf	Cleveland Bay	-19.2838	146.8835	05-Feb-98	2.00	2747	348	236	475.71	228.56	325.48	686	12.99	388.83	1059	12.45	94.11	107.67	1295	1022.59
1734	Inner Shelf	Cleveland Bay	-19.2891	146.8761	05-Feb-98	1.50	524	566	537	204.63	190.11	46.58	276	12.05	122.94	70	8.36	36.89	22.21	607	356.04
1735	Inner Shelf	Cleveland Bay	-19.2678	146.8528	05-Feb-98	0.90	234	260	207	121.09	82.37	36.65	130	8.68	44.06	24	2.95	16.29	12.74	231	114.96
1736	Inner Shelf	Cleveland Bay	-19.2498	146.8666	05-Feb-98	4.00	958	1114	1195	163.52	186.47	106.43	379	10.10	201.72	252	9.75	44.59	30.81	1447	491.71
1737	Inner Shelf	Cleveland Bay	-19.2332	146.8835	05-Feb-98	6.00	746	1267	1634	243.68	164.44	89.10	317	10.68	130.43	189	8.10	42.29	26.52	1823	388.21
1738	Inner Shelf	Cleveland Bay	-19.2166	146.9004	05-Feb-98	7.00	621	1223	1452	154.27	158.18	71.34	287	9.67	138.35	183	6.58	36.39	30.13	1635	323.42

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1739	Inner Shelf	Cleveland Bay	-19.1667	146.9001	05-Feb-98	10.00	849	759	851	193.95	152.70	105.80	333	8.14	170.33	244	7.19	45.09	23.71	1096	370.10
1740	Inner Shelf	Cleveland Bay	-19.1833	146.8835	05-Feb-98	9.00	683	946	1211	230.07	137.65	99.85	293	8.59	152.02	216	6.70	45.92	30.17	1427	348.98
1741	Inner Shelf	Cleveland Bay	-19.2003	146.8669	05-Feb-98	8.00	667	1243	1505	170.02	154.93	89.10	304	11.87	138.75	193	7.56	46.42	28.38	1698	380.65
1742	Inner Shelf	Cleveland Bay	-19.2166	146.8500	05-Feb-98	6.00	2100	412	390	450.27	184.41	251.86	590	10.81	374.74	624	10.12	86.61	62.64	1014	887.32
1743	Inner Shelf	Cleveland Bay	-19.2329	146.8335	05-Feb-98	4.00	1054	973	1045	388.70	110.23	119.14	345	7.06	143.84	480	5.77	69.70	19.28	1525	461.66
1744	Inner Shelf	Cleveland Bay	-19.2479	146.8183	05-Feb-98	2.30	1004	510	486	397.78	135.80	178.78	334	9.08	167.55	253	9.37	81.42	36.63	740	821.89
1745	Inner Shelf	Cleveland Bay	-19.2306	146.7877	05-Feb-98	3.50	242	256	179	177.58	81.05	39.39	138	7.97	17.39	45	2.95	26.07	20.25	224	167.95
1746	Inner Shelf	Cleveland Bay	-19.2169	146.7996	05-Feb-98	4.00	532	1316	1543	251.78	104.88	64.84	247	9.53	99.25	134	6.67	43.59	23.03	1677	311.44
1747	Inner Shelf	Cleveland Bay	-19.2026	146.8151	05-Feb-98	6.00	226	2407	3151	104.36	63.93	37.46	187	15.76	47.00	136	7.28	25.50	27.86	3287	98.03
1748	Inner Shelf	Cleveland Bay	-19.1900	146.8303	05-Feb-98	5.00	318	2480	3309	179.98	75.38	52.76	205	6.49	78.40	103	9.72	30.75	52.72	3412	134.24
1749	Inner Shelf	Cleveland Bay	-19.1846	146.7707	05-Feb-98	2.00	278	720	740	172.51	96.60	45.94	159	11.05	62.71	65	4.03	27.57	23.53	805	226.65
1750	Inner Shelf	Cleveland Bay	-19.1770	146.7721	05-Feb-98	3.00	758	1566	1967	143.59	103.04	104.60	261	7.56	151.78	288	6.70	56.81	33.02	2255	399.29
1751	Inner Shelf	Cleveland Bay	-19.2830	146.8473	12-Feb-98	-	889	160	99	253.91	132.88	136.51	318	6.61	172.65	537	9.33	50.31	37.25	636	455.72
1752	Inner Shelf	Cleveland Bay	-19.2856	146.8504	12-Feb-98	-	762	236	180	447.42	128.61	109.89	288	9.17	137.14	560	9.03	45.89	52.21	740	399.99
1753	Inner Shelf	Cleveland Bay	-19.2826	146.8551	12-Feb-98	1.50	261	45	55	183.81	52.69	44.74	107	2.22	40.88	265	3.54	20.11	10.63	319	113.24
1754	Inner Shelf	Cleveland Bay	-19.2759	146.8470	12-Feb-98	-	644	142	104	234.07	108.19	87.73	224	4.23	120.14	689	7.00	37.43	25.40	793	312.44
1755	Inner Shelf	Cleveland Bay	-19.3046	146.8582	12-Feb-98	-	1835	100	41	368.24	166.48	302.81	504	9.10	277.20	1195	14.71	79.38	35.05	1236	745.45
1756	Inner Shelf	Cleveland Bay	-19.3045	146.8581	12-Feb-98	-	2014	100	93	428.29	182.24	318.17	537	7.89	308.03	1223	15.68	84.88	42.33	1316	810.16
1757	Inner Shelf	Cleveland Bay	-19.3045	146.8582	12-Feb-98	-	1946	102	72	338.35	185.79	318.98	546	9.72	305.13	1301	16.20	88.36	37.19	1374	809.67
1758	Inner Shelf	Cleveland Bay	-19.3029	146.8584	12-Feb-98	-	1608	97	75	330.07	158.53	312.62	470	11.25	271.10	517	12.54	79.78	71.40	591	741.72
1759	Inner Shelf	Cleveland Bay	-19.2994	146.8590	12-Feb-98	-	1506	91	39	421.44	160.43	236.46	471	8.29	257.66	885	11.63	84.80	21.14	924	699.81
1760	Inner Shelf	Cleveland Bay	-19.2971	146.8554	12-Feb-98	-	1644	81	78	337.46	161.06	340.76	492	8.16	277.09	523	11.88	83.93	61.30	600	811.78
1761	Inner Shelf	Cleveland Bay	-19.2974	146.8560	12-Feb-98	1.00	1294	166	132	545.28	148.89	228.59	405	9.26	243.94	1082	12.75	66.68	71.82	1213	585.69
1762	Inner Shelf	Cleveland Bay	-19.2960	146.8582	12-Feb-98	1.00	887	204	111	537.19	139.38	183.00	321	6.08	167.63	682	9.83	58.88	48.60	793	505.63
1763	Inner Shelf	Cleveland Bay	-19.2908	146.8631	12-Feb-98	1.50	1008	435	420	352.67	136.44	146.52	325	12.78	163.13	984	11.50	56.19	87.32	1404	452.06
1764	Inner Shelf	Cleveland Bay	-19.2908	146.8632	12-Feb-98	1.50	822	506	447	353.29	135.07	121.32	280	6.30	143.51	568	8.33	37.18	98.73	1015	384.24
1765	Inner Shelf	Cleveland Bay	-19.2907	146.8631	12-Feb-98	1.50	1060	407	234	362.90	148.55	154.80	329	7.15	165.85	662	9.94	44.85	110.43	896	477.91
1766	Inner Shelf	Cleveland Bay	-19.2990	146.8716	12-Feb-98	0.50	510	533	357	227.49	100.05	73.74	175	5.42	73.73	1084	6.31	26.72	63.17	1441	220.24
1767	Inner Shelf	Cleveland Bay	-19.2914	146.8206	12-Feb-98	2.00	1265	62	320	527.49	146.52	193.25	392	6.84	168.84	613	8.38	89.34	75.95	933	680.61
1768	Inner Shelf	Cleveland Bay	-19.2896	146.8245	12-Feb-98	1.00	2282	110	84	495.02	200.41	335.22	640	13.73	316.41	1284	15.34	103.26	57.41	1368	1124.77
1769	Inner Shelf	Cleveland Bay	-19.2947	146.8249	12-Feb-98	-	1597	63	70	477.05	150.78	257.73	467	5.48	242.11	1812	11.82	101.06	45.32	1882	813.03
1770	Inner Shelf	Cleveland Bay	-19.2945	146.8249	12-Feb-98	-	1633	68	147	438.70	156.51	260.65	498	7.44	261.79	1460	12.46	101.87	45.17	1606	844.07
1771	Inner Shelf	Cleveland Bay	-19.2947	146.8252	12-Feb-98	-	1751	77	932	399.38	163.43	259.81	487	7.45	247.51	538	12.26	91.43	44.65	1470	840.85
1772	Inner Shelf	Cleveland Bay	-19.2899	146.8275	12-Feb-98	-	1560	73	375	458.99	149.74	231.20	459	6.15	228.94	1170	11.91	85.89	37.23	1545	781.19
1773	Inner Shelf	Cleveland Bay	-19.2886	146.8275	12-Feb-98	-	852	85	-3	408.19	104.54	157.60	279	4.81	118.79	461	7.90	42.92	74.59	458	471.46
1774	Inner Shelf	Cleveland Bay	-19.2853	146.8250	12-Feb-98	-	1279	65	0	581.32	140.31	223.85	358	2.97	193.10	1568	10.83	77.14	106.06	1568	700.54
1775	Inner Shelf	Cleveland Bay	-19.2970	146.8307	12-Feb-98	-	1775	140	212	432.74	191.87	225.35	648	20.15	225.12	1565	16.20	92.72	42.73	1777	819.29
1776	Inner Shelf	Cleveland Bay	-19.2934	146.8337	12-Feb-98	-	2123	84	15	409.79	227.73	272.13	617	23.77	287.96	1365	13.41	98.09	77.39	1380	910.28
1777	Inner Shelf	Cleveland Bay	-19.2901	146.8338	12-Feb-98	-	1130	136	45	222.24	150.32	191.97	340	7.79	177.89	300	9.14	61.33	56.59	345	488.62
1778	Inner Shelf	Cleveland Bay	-19.2863	146.8313	12-Feb-98	-	778	67	0	457.12	107.41	97.18	267	8.79	92.51	533	6.19	50.01	62.94	533	366.21
1779	Inner Shelf	Cleveland Bay	-19.2847	146.8343	12-Feb-98	-	1096	74	17	368.51	135.84	146.01	349	8.45	170.57	230	8.06	70.45	56.79	247	552.86
1780	Inner Shelf	Cleveland Bay	-19.2820	146.8315	12-Feb-98	-	1025	41	51	492.26	130.87	169.74	369	6.86	180.29	659	7.71	73.93	39.06	711	518.73
1781	Inner Shelf	Cleveland Bay	-19.2820	146.8316	12-Feb-98	-	1593	69	24	391.19	176.44	216.82	499	8.31	232.86	676	10.39	63.97	38.88	700	731.75
1782	Inner Shelf	Cleveland Bay	-19.2820	146.8318	12-Feb-98	-	1352	57	19	419.57	157.88	202.18	440	7.74	199.34	703	9.03	68.53	42.41	722	651.17
1783	Inner Shelf	Cleveland Bay	-19.2814	146.8278	12-Feb-98	-	1115	73	8	471.26	134.92	165.68	360	4.61	154.58	692	7.63	62.41	95.22	700	559.81
1784	Inner Shelf	Cleveland Bay	-19.2739	146.8339	12-Feb-98	-	1284	109	59	318.15	157.81	181.53	369	4.80	196.64	824	9.53	66.67	119.61	883	627.75
1785	Inner Shelf	Cleveland Bay	-19.2738	146.8342	12-Feb-98	-	1148	100	7	334.16	156.66	154.10	341	4.37	179.83	739	8.43	73.23	104.88	746	574.39
1786	Inner Shelf	Cleveland Bay	-19.2737	146.8340	12-Feb-98	-	1425	139	-383	451.16	171.29	199.67	412	6.10	226.21	1014	10.06	75.02	136.34	631	680.10
1787	Inner Shelf	Cleveland Bay	-19.2470	146.8277	12-Feb-98	6.00	1973	461	1107	602.05	192.78	253.69	522	9.29	314.89	498	10.26	93.02	62.90	1605	881.23

Appendix 1

Surface sediment grab samples - location data and strong acid digestion analytical results

AIMS catalogue	Shelf position	Geographic region	Decimal Latitude	Decimal Longitude	Sample date	Water depth m	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1788	Inner Shelf	Cleveland Bay	-19.2293	146.8427	12-Feb-98	6.00	1302	525	350	447.24	148.74	162.42	384	9.68	215.78	341	8.76	70.10	51.56	691	617.48
1789	Inner Shelf	Cleveland Bay	-19.2466	146.8281	12-Feb-98	3.00	2278	300	151	496.53	205.31	419.12	626	15.92	403.39	738	11.79	184.09	66.68	889	1496.52
1790	Inner Shelf	Cleveland Bay	-19.2244	146.8481	12-Feb-98	3.00	2060	311	495	587.46	194.59	408.46	596	17.28	378.20	734	11.25	169.28	63.82	1229	1403.77
1791	Inner Shelf	Cleveland Bay	-19.2462	146.8286	12-Feb-98	3.00	2485	369	72	321.44	224.17	436.43	633	24.95	411.96	721	12.64	157.16	67.16	793	1536.46
1792	Inner Shelf	Cleveland Bay	-19.2559	146.8228	12-Feb-98	4.00	2644	198	199	1394.13	206.11	831.66	674	8.65	432.25	813	12.50	195.24	108.73	1012	2322.20
1793	Inner Shelf	Cleveland Bay	-19.1688	146.7922	28-Aug-98	8.50	2446	582	589	181.03	212.85	272.92	744	8.64	493.30	730	9.80	100.60	5.93	1319	1018.07
1794	Inner Shelf	Cleveland Bay	-19.1613	146.7848	28-Aug-98	8.50	2618	590	587	206.99	224.80	297.17	793	9.76	533.26	740	10.55	108.57	6.20	1327	1093.30
1795	Inner Shelf	Cleveland Bay	-19.1547	146.7767	28-Aug-98	8.00	2578	678	638	267.10	233.03	275.62	767	9.24	498.97	662	9.94	106.95	6.59	1300	1082.38
1796	Inner Shelf	Halifax Bay	-19.1408	146.7635	28-Aug-98	8.00	773	3789	3561	287.63	124.10	106.69	333	8.89	182.60	230	9.12	60.47	22.47	3791	444.98
1797	Inner Shelf	Cleveland Bay	-19.1953	147.0110	29-Aug-98	3.50	621	1520	1468	119.91	138.32	78.39	300	9.27	155.16	249	6.70	33.62	14.28	1717	379.32
1798	Inner Shelf	Cleveland Bay	-19.1983	147.0017	29-Aug-98	4.50	193	1496	1473	57.44	103.04	20.15	211	11.47	75.26	71	7.63	19.24	12.82	1544	193.27
1799	Inner Shelf	Cleveland Bay	-19.2017	146.9932	29-Aug-98	6.00	264	2128	1960	97.49	133.18	35.38	230	15.38	96.26	85	7.61	22.47	14.98	2045	228.67
1800	Inner Shelf	Cleveland Bay	-19.2048	146.9835	29-Aug-98	7.00	449	1256	1189	119.98	170.95	63.32	277	19.09	127.28	152	7.63	30.15	9.35	1341	322.86
1801	Inner Shelf	Cleveland Bay	-19.2080	146.9747	29-Aug-98	7.00	314	1667	1730	108.14	165.76	32.68	239	13.92	95.10	106	6.77	21.36	10.69	1836	264.13
1802	Inner Shelf	Cleveland Bay	-19.2112	146.9662	29-Aug-98	7.00	471	1118	1037	70.64	192.66	66.99	282	14.26	132.35	130	6.54	28.69	7.26	1167	368.42
1803	Inner Shelf	Halifax Bay	-19.1690	146.6612	30-Aug-98	4.50	1249	385	275	243.68	188.66	169.51	428	7.55	169.24	385	9.07	59.93	3.03	659	737.18
1804	Inner Shelf	Halifax Bay	-19.1390	146.6820	30-Aug-98	8.00	1076	2425	2207	129.52	231.48	135.46	418	10.27	221.31	259	9.94	58.44	16.71	2466	644.93
1805	Inner Shelf	Halifax Bay	-19.1095	146.7002	30-Aug-98	11.00	1141	2386	2097	138.47	222.29	134.97	421	8.82	235.96	269	9.75	59.68	16.36	2366	614.00
1806	Inner Shelf	Halifax Bay	-19.0830	146.7163	30-Aug-98	12.00	1055	2212	2010	141.17	204.71	113.48	388	8.16	216.33	267	9.17	56.89	16.34	2276	562.38
1807	Inner Shelf	Halifax Bay	-19.0547	146.7397	30-Aug-98	16.00	913	1939	2186	102.59	164.92	101.34	331	7.84	185.58	46	8.52	47.21	16.00	2231	459.44
1808	Inner Shelf	Halifax Bay	-19.0340	146.4317	01-Sep-98	5.00	184	764	628	69.68	30.80	< D. L.	109	3.42	33.59	208	3.12	25.75	11.35	836	137.60
1809	Inner Shelf	Halifax Bay	-19.0185	146.4633	01-Sep-98	9.00	317	3182	3063	129.71	181.44	42.07	276	17.93	109.50	192	9.83	45.60	22.44	3255	325.46
1810	Inner Shelf	Halifax Bay	-19.0035	146.4950	01-Sep-98	12.00	815	3246	2586	192.34	181.54	104.86	384	15.02	201.32	758	20.52	60.44	24.38	3344	494.17
1811	Inner Shelf	Halifax Bay	-18.9862	146.5277	01-Sep-98	15.00	869	3919	3952	229.68	163.62	115.05	381	11.55	222.42	189	12.56	58.31	28.50	4140	503.36
1812	Inner Shelf	Halifax Bay	-18.9733	146.5588	01-Sep-98	16.00	753	4146	4099	215.50	148.22	93.81	316	13.23	196.12	296	11.37	48.88	31.00	4395	408.07
1813	Inner Shelf	Halifax Bay	-18.9567	146.5898	01-Sep-98	19.00	992	4097	4130	192.09	132.34	94.35	335	8.26	220.10	235	11.89	53.77	35.69	4365	480.20
1814	Mid Shelf	Mid Shelf	-18.9377	146.6222	01-Sep-98	21.00	772	4177	4711	61.63	111.73	93.04	299	9.58	188.73	274	11.76	30.73	33.73	4985	393.58
1815	Mid Shelf	Mid Shelf	-18.9238	146.6568	01-Sep-98	24.00	841	3594	4086	125.80	115.15	100.06	286	7.11	183.59	484	12.45	40.25	34.07	4569	402.29
1816	Outer Shelf	Outer Shelf	-18.0272	146.7610	01-Sep-98	20.00	890	2622	2954	136.82	147.36	114.09	326	7.70	206.90	248	11.97	52.22	24.43	3202	461.16
1817	Mid Shelf	Mid Shelf	-18.9975	146.7808	02-Sep-98	22.00	837	3380	3558	93.62	124.81	99.58	292	7.60	190.08	271	11.12	44.30	30.68	3829	403.73
1818	Mid Shelf	Mid Shelf	-18.9678	146.8023	02-Sep-98	23.00	475	5149	5089	59.06	77.20	68.92	206	7.06	116.82	497	12.09	32.06	39.20	5586	233.86
1819	Mid Shelf	Mid Shelf	-18.9428	146.8202	02-Sep-98	25.00	382	5764	5669	33.35	57.66	40.69	168	5.77	100.87	195	12.96	27.84	42.98	5864	207.03
1820	Mid Shelf	Mid Shelf	-18.9145	146.8387	02-Sep-98	25.00	342	6793	6550	75.33	55.36	26.38	149	5.30	94.53	209	12.83	25.61	51.81	6759	166.39
1821	Mid Shelf	Mid Shelf	-18.8895	146.8568	02-Sep-98	28.00	209	8098	6603	113.47	36.66	21.22	160	7.93	64.23	1757	17.06	24.68	51.23	8360	123.14
1822	Mid Shelf	Mid Shelf	-18.8547	146.8787	02-Sep-98	29.00	189	7986	7663	59.99	24.68	24.24	90	3.97	51.87	179	11.61	21.79	55.63	7842	680.66
1823	Mid Shelf	Mid Shelf	-18.8262	146.8938	02-Sep-98	32.00	245	6751	6869	105.38	21.33	< D. L.	121	3.79	69.61	206	11.94	20.21	50.31	7075	119.58
1824	Mid Shelf	Mid Shelf	-18.7947	146.9165	02-Sep-98	34.00	200	6390	7140	86.31	16.05	23.59	115	3.04	34.77	181	12.74	20.67	55.65	7322	130.51

Less than method detection limits (< D.L.)

Detection limits for trace metals are; Cd 89 pmol/g; Co 17 nmol/g; Cu 16 nmol/g; Ni 17 nmol/g; Pb 5 nmol/g; Zn 0.4 nmol/g

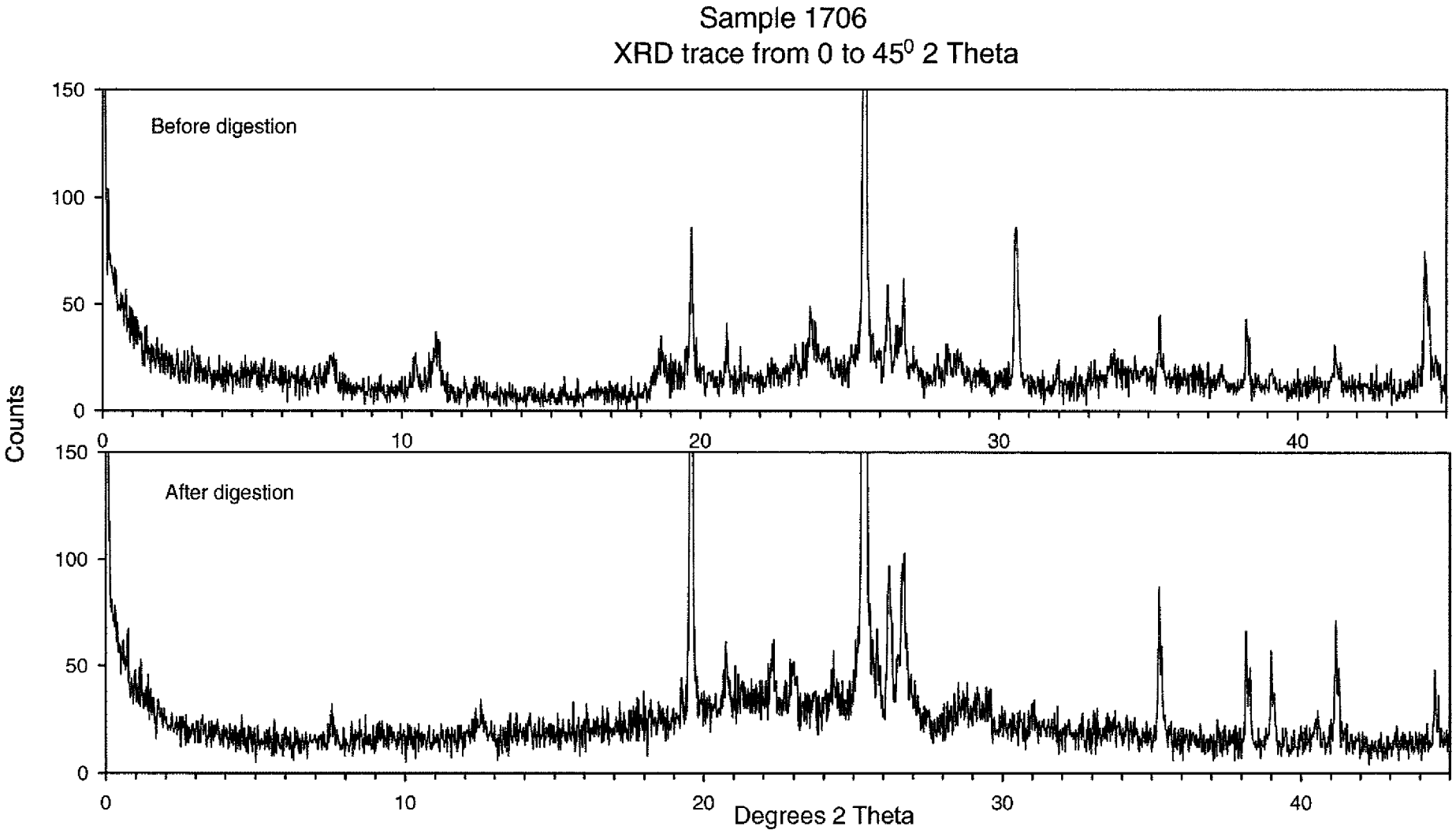
Appendix 2 Surface sediment total acid digestion analytical results

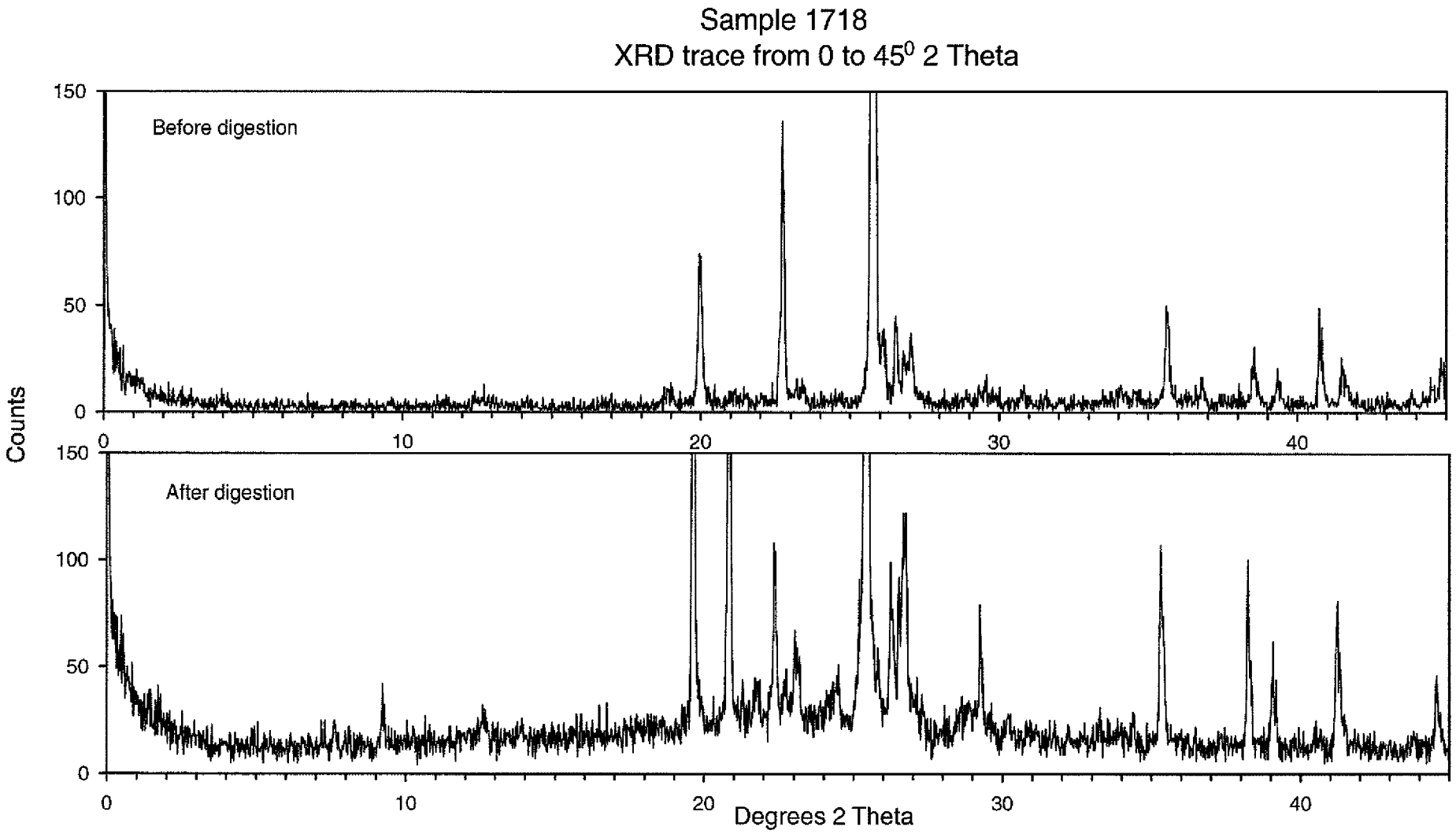
Appendix 2
Surface sediment total acid digestion analytical results

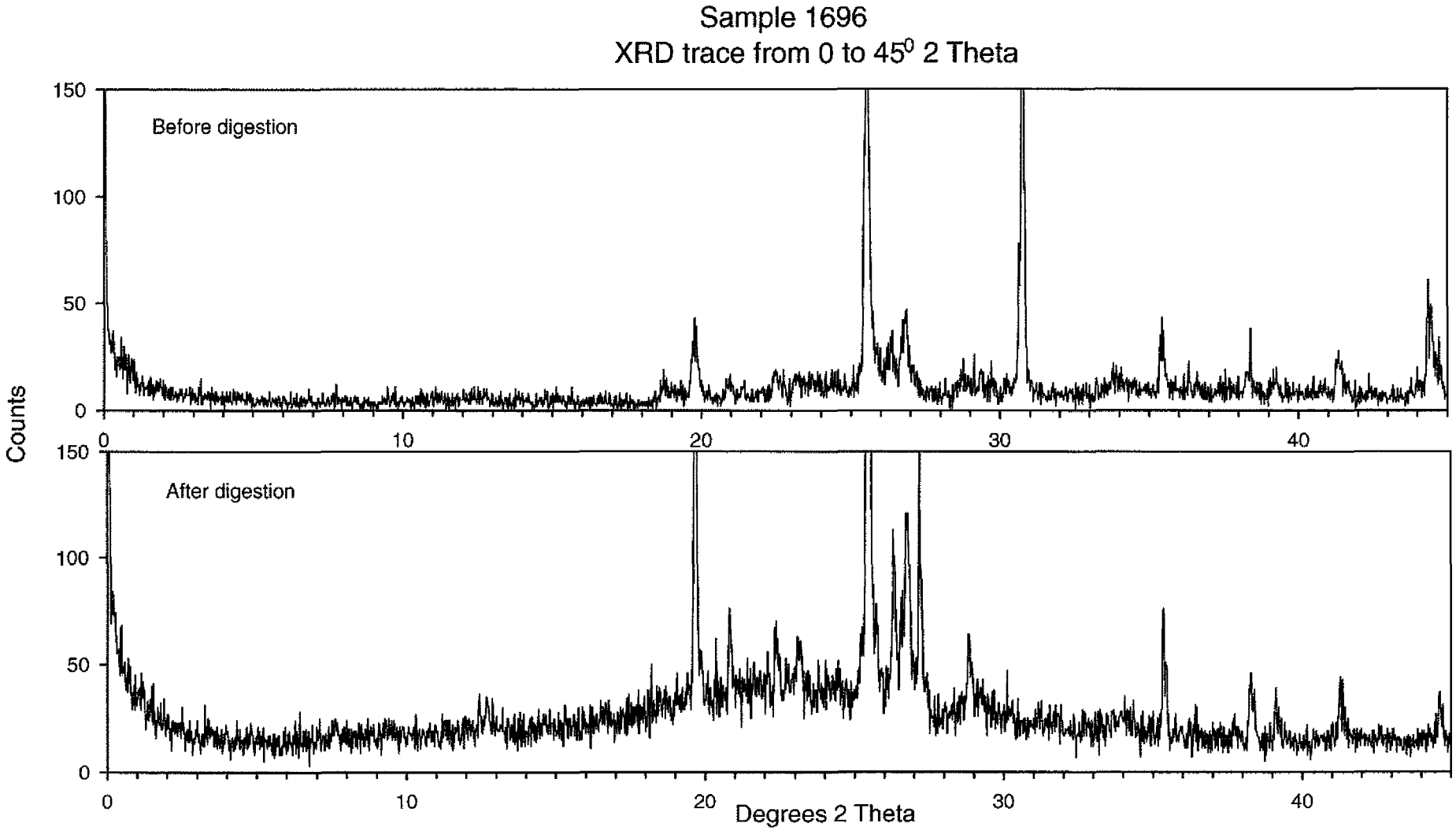
AIMS Catalogue	Al µmol/g	Cd pmol/g	Cu nmol/g	Fe µmol/g	Ni nmol/g	Pb nmol/g	S µmol/g	Si µmol/g	Zn nmol/g
1686	2416	< D. L.	152	462	199	100	77	11131	702
1700	2136	< D. L.	142	300	77	131	48	12361	917
1707	2559	< D. L.	213	471	137	94	60	10634	929
1711	2056	< D. L.	131	387	162	124	123	11342	599
1714	2754	543	234	623	290	79	101	10363	913
1718	1553	< D. L.	38	181	21	171	13	14611	366
1725	1440	587	103	337	159	90	30	11703	452
1735	1656	< D. L.	23	217	29	63	19	14098	311
1739	1635	< D. L.	123	398	157	74	24	12145	567
1742	3147	379	287	691	345	132	75	9518	1167
1745	1662	< D. L.	44	242	35	75	21	13675	399
1753	1649	< D. L.	51	152	30	139	16	14484	247
1756	2943	< D. L.	385	608	299	71	43	10813	1050
1764	1984	< D. L.	160	334	142	85	104	12341	561
1769	2940	< D. L.	312	570	262	153	55	10999	1132
1772	2818	< D. L.	282	531	235	143	39	11463	1021
1776	2972	< D. L.	311	664	261	142	84	10897	1091
1779	2232	< D. L.	202	435	175	120	64	11636	791
1781	2348	1581	205	479	185	114	36	12668	790
1783	2218	< D. L.	190	443	137	107	97	12748	776
1785	2363	< D. L.	172	391	157	115	105	12602	749
1786	2487	< D. L.	226	457	184	115	138	11744	856
1787	2731	452	281	585	343	133	64	10666	1078

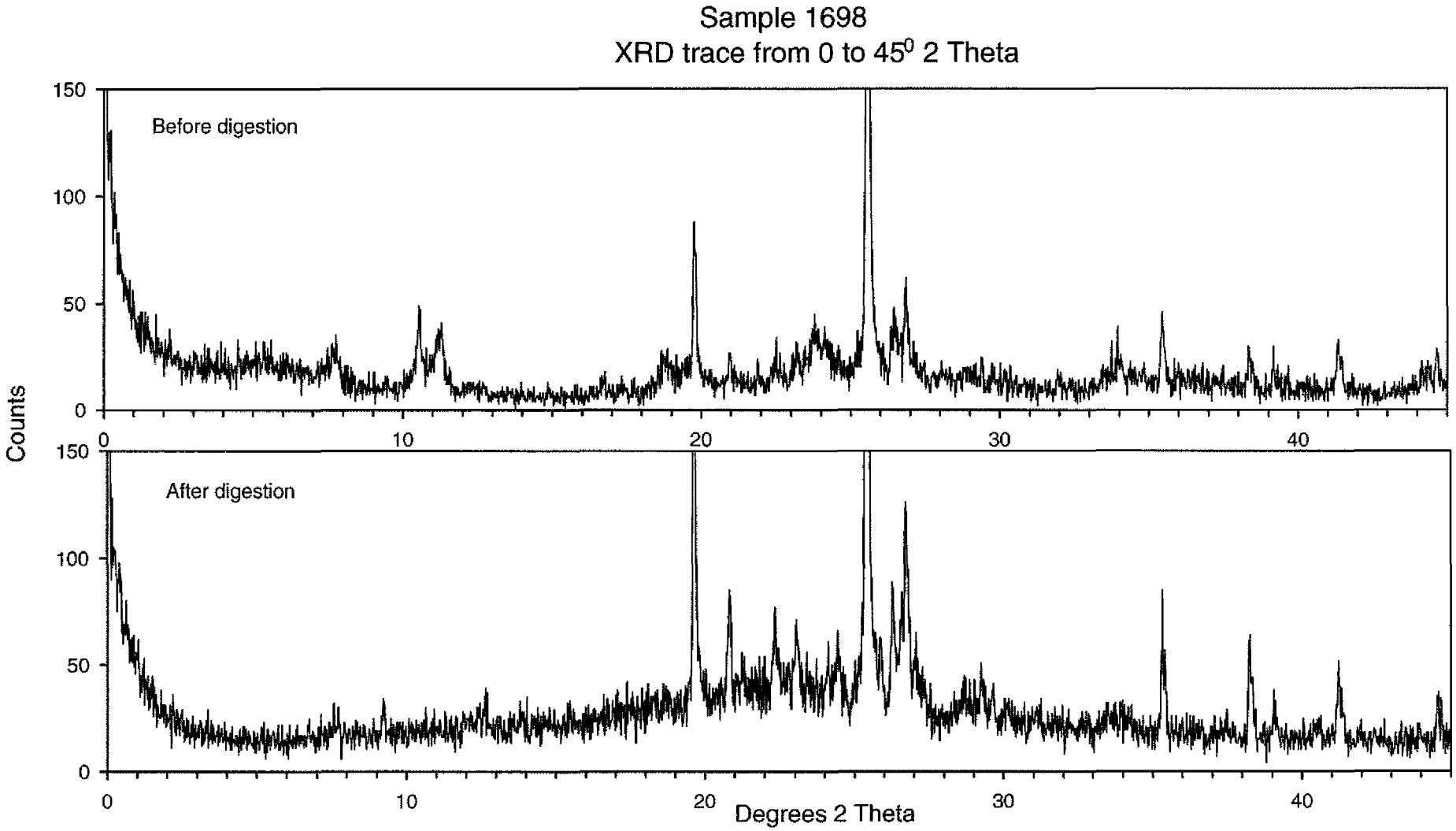
< D. L. = below detection limit
Detection limit of Cd = 300 pmol/g

Appendix 3 XRD profiles of sediment samples prior to and after digestion


Sample 1706
XRD trace from 0 to 45⁰ 2 Theta
Before digestion
After digestion
Counts
Degrees 2 Theta
150
100
50
0
0
10
20
30
40


Sample 1718
XRD trace from 0 to 45⁰ 2 Theta
Before digestion
After digestion
Counts
Degrees 2 Theta
150
100
50
0
0
10
20
30
40


Sample 1696
XRD trace from 0 to 45⁰ 2 Theta
Before digestion
After digestion
Counts
Degrees 2 Theta
150
100
50
0
0
10
20
30
40


Sample 1698
XRD trace from 0 to 45⁰ 2 Theta
Before digestion
After digestion
Counts
Degrees 2 Theta
150
100
50
0
0
10
20
30
40

XRD Raw data from selected samples before and after digestion

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
0.02	313	321	315	260	321	252	363	365
0.04	223	222	266	206	176	198	318	288
0.06	190	176	173	158	155	110	245	247
0.08	156	155	134	98	143	92	187	191
0.1	109	124	110	74	125	50	141	169
0.12	118	99	90	56	69	50	127	140
0.14	84	92	89	45	75	37	90	118
0.16	81	64	69	49	73	37	122	108
0.18	75	104	63	42	84	31	128	117
0.2	81	98	81	39	82	33	97	130
0.22	75	71	63	41	73	32	105	116
0.24	71	74	75	41	72	27	102	131
0.26	73	70	70	39	65	28	104	99
0.28	68	67	60	31	74	33	103	99
0.3	78	68	74	31	58	37	90	88
0.32	76	66	49	18	55	27	75	78
0.34	70	62	73	25	56	32	90	89
0.36	61	62	66	39	56	19	88	102
0.38	70	59	46	19	57	24	92	85
0.4	62	67	57	23	49	20	98	91
0.42	56	55	48	33	45	16	84	92
0.44	60	66	60	21	67	25	93	85
0.46	56	62	48	28	46	25	89	64
0.48	59	52	74	22	68	21	65	78
0.5	46	47	42	28	45	23	70	83
0.52	51	49	46	18	48	25	60	64
0.54	53	48	51	30	46	19	65	66
0.56	59	50	65	15	48	20	69	73
0.58	62	47	51	17	51	34	64	64
0.6	51	47	46	10	42	20	64	66
0.62	55	55	35	18	38	24	80	62
0.64	53	53	44	18	38	15	71	60
0.66	48	48	43	31	46	30	62	64
0.68	50	54	50	12	37	29	69	51
0.7	51	46	43	12	53	19	68	52
0.72	66	40	43	8	46	19	64	59
0.74	43	50	45	14	41	26	51	62
0.76	67	48	40	18	49	16	62	56
0.78	39	57	38	17	36	8	53	52
0.8	39	47	39	15	37	15	52	58
0.82	35	37	33	14	29	26	63	49
0.84	36	40	52	19	29	23	51	46
0.86	44	43	45	19	37	16	52	53
0.88	41	39	27	18	31	13	64	61
0.9	40	49	27	13	40	17	49	47
0.92	32	32	40	12	29	24	54	38
0.94	37	41	37	17	45	23	46	47
0.96	46	48	32	12	37	18	56	43
0.98	48	35	38	13	31	14	55	56
1	40	47	33	17	33	24	55	54
1.02	33	43	32	15	34	19	52	42
1.04	41	29	36	9	38	13	62	43
1.06	37	38	33	9	36	8	46	38
1.08	33	44	27	18	39	11	44	42
1.1	32	37	30	20	33	18	35	34
1.12	49	31	34	12	29	11	45	38
1.14	31	44	34	15	46	11	43	32
1.16	40	31	21	16	34	12	37	44
1.18	53	42	33	16	35	11	48	40
1.2	36	37	20	11	42	7	49	30
1.22	38	35	31	14	34	13	53	46
1.24	31	33	35	16	38	13	31	27
1.26	30	34	37	13	27	13	38	42
1.28	37	37	20	14	20	16	43	46
1.3	31	35	29	13	23	11	39	42
1.32	31	27	30	16	24	13	41	39
1.34	40	21	23	9	32	7	34	32
1.36	35	26	28	13	33	10	45	28
1.38	31	28	37	9	24	10	29	46
1.4	29	21	30	7	31	11	37	31
1.42	46	39	39	7	26	10	30	41
1.44	25	27	31	9	34	11	41	34
1.46	33	29	22	8	28	12	34	44
1.48	37	40	39	5	40	7	35	33
1.5	39	24	23	11	26	14	45	33
1.52	28	28	23	9	22	12	43	37
1.54	27	30	21	5	41	7	26	31
1.56	29	28	22	2	30	16	40	29
1.58	35	29	21	11	25	12	30	27
1.6	35	18	29	7	21	8	33	34
1.62	27	27	18	9	16	10	36	30
1.64	23	31	34	6	24	12	29	32
1.66	26	23	28	10	21	5	21	28
1.68	16	30	19	7	30	10	31	25
1.7	26	29	18	13	23	11	27	27
1.72	27	24	41	11	25	8	27	22

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
1.74	34	23	27	9	22	12	25	45
1.76	33	20	24	6	26	14	27	34
1.78	31	23	26	6	32	10	25	25
1.8	26	31	37	6	20	9	38	29
1.82	27	34	25	8	22	13	27	34
1.84	27	25	18	7	20	9	26	29
1.86	30	22	25	7	22	10	31	27
1.88	25	29	22	5	29	15	23	25
1.9	21	21	28	12	34	11	31	26
1.92	24	18	22	5	22	11	29	32
1.94	30	23	21	10	18	10	31	30
1.96	25	30	18	9	17	7	21	27
1.98	25	31	25	5	25	14	22	27
2	23	21	19	9	20	6	27	27
2.02	26	18	28	9	27	10	25	16
2.04	23	25	14	4	26	5	23	26
2.06	21	27	26	8	26	12	25	33
2.08	20	20	20	6	15	10	25	29
2.1	21	17	29	6	20	8	31	24
2.12	22	28	20	4	18	6	21	21
2.14	21	27	11	4	10	6	11	27
2.16	20	25	23	3	22	10	24	31
2.18	22	18	24	14	24	5	36	24
2.2	28	21	14	6	19	7	30	38
2.22	24	27	15	5	23	11	29	28
2.24	21	21	23	6	23	5	25	33
2.26	20	25	20	6	18	9	19	23
2.28	19	15	25	3	20	10	18	21
2.3	20	26	20	10	23	11	17	22
2.32	23	26	14	5	20	5	29	23
2.34	21	17	22	11	17	6	28	26
2.36	26	22	9	4	22	6	23	22
2.38	18	17	13	5	23	7	20	22
2.4	23	16	18	5	19	9	25	26
2.42	20	19	18	4	19	8	17	21
2.44	23	20	16	3	23	4	24	25
2.46	26	22	20	6	16	7	27	26
2.48	26	22	22	7	19	7	26	28
2.5	12	29	18	5	30	8	29	23
2.52	18	23	29	8	20	5	19	19
2.54	26	16	16	8	23	10	24	24
2.56	21	13	10	9	18	7	24	20
2.58	26	13	9	10	18	8	14	25
2.6	25	19	21	2	10	9	21	20
2.62	22	18	14	7	15	10	16	12
2.64	18	23	22	12	19	4	25	20
2.66	13	19	20	3	15	6	16	20
2.68	27	17	18	7	20	6	19	19
2.7	14	14	12	4	14	6	24	24
2.72	22	22	22	3	19	8	16	23
2.74	19	28	14	7	14	7	18	15
2.76	14	15	21	5	24	10	13	23
2.78	21	13	20	6	15	7	15	18
2.8	16	16	20	2	16	7	22	16
2.82	20	17	16	6	19	7	16	23
2.84	17	23	12	3	8	7	18	19
2.86	18	28	17	8	11	8	26	19
2.88	22	13	18	6	15	11	15	26
2.9	23	19	18	5	16	3	20	13
2.92	21	16	22	11	13	7	11	21
2.94	18	22	25	9	17	5	22	21
2.96	20	20	14	2	20	10	15	20
2.98	14	30	13	7	17	5	18	16
3	19	26	17	3	24	8	16	28
3.02	24	27	18	4	22	7	18	19
3.04	21	27	18	3	14	8	22	22
3.06	24	23	18	5	18	4	16	27
3.08	14	24	20	6	15	7	18	24
3.1	24	14	12	4	11	6	24	26
3.12	14	14	19	7	9	6	21	26
3.14	20	15	12	5	13	3	23	17
3.16	14	26	18	6	17	7	12	23
3.18	24	25	11	4	18	11	14	20
3.2	25	22	13	4	12	8	20	18
3.22	23	13	18	3	17	7	13	18
3.24	27	17	20	3	12	15	14	17
3.26	18	26	14	4	31	3	15	26
3.28	20	18	16	2	24	3	20	21
3.3	22	21	12	6	16	3	24	13
3.32	20	18	11	2	21	7	18	21
3.34	23	14	17	4	13	5	19	22
3.36	12	19	22	1	25	6	29	15
3.38	15	20	11	6	25	8	11	31
3.4	17	14	8	2	23	7	18	20
3.42	16	20	13	2	16	6	17	17
3.44	19	15	8	4	17	5	15	13
3.46	24	21	13	4	17	7	19	19
3.48	17	16	6	1	21	9	24	29
3.5	18	13	9	2	18	9	15	18

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
3.52	12	16	23	6	18	5	13	29
3.54	24	21	8	2	20	6	22	16
3.56	23	25	8	1	12	8	15	21
3.58	20	19	13	7	13	1	18	24
3.6	15	18	12	4	19	11	14	23
3.62	22	15	9	2	12	6	17	19
3.64	17	17	14	3	18	5	17	22
3.66	19	10	12	4	21	8	19	21
3.68	22	17	10	6	11	4	19	18
3.7	18	11	11	1	18	4	12	18
3.72	25	19	13	3	14	3	22	23
3.74	20	19	12	1	15	9	14	13
3.76	23	12	8	3	11	5	14	18
3.78	16	17	16	8	17	8	18	26
3.8	19	14	9	2	12	4	17	28
3.82	13	19	14	5	20	7	20	17
3.84	15	18	13	4	9	4	16	20
3.86	15	14	16	5	11	6	14	18
3.88	20	17	14	5	13	6	14	15
3.9	16	26	13	6	18	6	15	15
3.92	12	16	14	4	13	7	23	32
3.94	22	13	15	3	15	3	19	19
3.96	16	17	14	11	22	9	10	18
3.98	19	11	13	3	18	3	19	21
4	17	16	13	7	18	3	14	22
4.02	21	21	15	8	19	7	15	21
4.04	16	9	12	4	18	1	16	17
4.06	20	20	10	4	11	6	15	29
4.08	11	17	13	3	10	4	13	17
4.1	15	20	11	5	15	9	18	19
4.12	12	9	19	5	6	5	10	15
4.14	23	23	18	2	11	4	18	16
4.16	23	13	5	9	12	7	10	25
4.18	17	19	13	3	16	4	21	21
4.2	14	14	7	2	14	5	14	13
4.22	16	12	11	5	10	9	14	18
4.24	20	19	13	3	11	5	15	10
4.26	13	22	6	1	16	4	12	22
4.28	18	18	10	4	11	4	13	19
4.3	15	16	19	1	17	3	17	21
4.32	22	21	15	3	13	7	17	17
4.34	10	8	14	3	24	10	12	15
4.36	21	13	16	2	16	5	16	19
4.38	18	17	10	4	16	9	13	19
4.4	18	17	16	2	14	5	8	21
4.42	11	16	15	3	11	4	17	20
4.44	15	18	8	5	20	3	20	10
4.46	19	13	13	1	11	9	15	19
4.48	20	12	14	4	15	5	10	25
4.5	11	15	10	4	15	8	16	33
4.52	17	19	16	3	15	8	13	24
4.54	27	16	16	6	8	5	21	24
4.56	21	13	11	2	9	5	13	20
4.58	14	15	13	4	16	7	21	24
4.6	13	11	10	2	11	4	15	15
4.62	21	17	13	3	16	8	18	21
4.64	20	23	7	1	15	8	20	17
4.66	12	20	14	2	21	5	10	23
4.68	16	17	16	3	11	5	13	24
4.7	10	11	11	4	15	5	14	17
4.72	14	20	17	6	12	3	19	26
4.74	18	15	12	3	18	4	13	20
4.76	9	16	9	2	13	5	17	18
4.78	22	26	11	3	17	9	16	28
4.8	16	15	8	3	23	3	14	22
4.82	21	11	17	1	18	6	12	26
4.84	21	16	15	3	19	6	13	19
4.86	14	20	21	1	17	8	13	22
4.88	13	17	13	4	14	4	11	23
4.9	10	19	18	2	11	8	19	20
4.92	19	11	9	5	8	7	18	16
4.94	13	13	22	3	11	5	9	23
4.96	13	16	18	2	16	1	16	24
4.98	21	23	13	2	15	6	9	22
5	12	15	12	1	17	5	13	20
5.02	5	17	11	2	13	3	18	24
5.04	14	20	8	1	21	2	13	21
5.06	15	22	24	2	14	2	14	24
5.08	22	17	10	4	19	3	10	32
5.1	13	19	11	3	11	3	12	23
5.12	15	23	11	5	15	6	17	14
5.14	11	22	10	2	12	4	17	18
5.16	15	12	12	1	17	4	21	26
5.18	13	16	12	6	12	5	14	25
5.2	16	11	14	2	16	3	13	27
5.22	15	20	11	2	21	3	20	24
5.24	13	15	5	2	5	4	23	19
5.26	14	10	13	2	16	5	9	17
5.28	14	16	19	2	15	7	12	21

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
5.3	19	22	16	2	15	5	6	20
5.32	11	17	11	2	15	3	17	23
5.34	16	9	13	5	12	6	9	32
5.36	14	21	16	6	11	2	20	24
5.38	20	21	13	1	17	4	19	32
5.4	12	25	10	2	16	6	12	25
5.42	16	16	11	4	12	3	17	19
5.44	20	14	12	1	17	5	16	22
5.46	11	16	14	4	13	2	10	18
5.48	21	11	20	2	14	2	14	29
5.5	14	17	16	1	11	5	15	21
5.52	17	14	13	2	8	5	18	17
5.54	8	17	12	3	14	9	18	26
5.56	14	13	9	3	18	4	19	24
5.58	9	19	11	5	7	4	17	22
5.6	21	16	16	4	18	2	14	33
5.62	8	20	10	4	8	3	11	19
5.64	25	21	9	2	16	6	15	18
5.66	14	24	13	4	16	5	12	25
5.68	10	19	10	2	12	4	18	21
5.7	9	13	6	2	13	5	13	17
5.72	19	15	14	1	17	4	22	17
5.74	17	13	11	5	17	3	10	21
5.76	18	23	16	2	8	6	13	19
5.78	13	18	8	7	8	5	10	23
5.8	12	14	13	6	9	2	14	18
5.82	14	16	13	2	12	3	12	23
5.84	11	14	16	2	8	7	22	14
5.86	11	15	8	1	11	6	22	16
5.88	12	13	11	1	14	6	8	19
5.9	18	15	12	1	19	2	9	14
5.92	8	12	12	4	12	3	12	26
5.94	8	21	10	5	15	4	15	14
5.96	14	12	9	6	21	1	12	15
5.98	19	18	11	5	9	3	13	18
6	21	21	12	2	14	7	8	27
6.02	21	9	16	3	10	7	18	17
6.04	12	20	10	1	18	5	15	19
6.06	13	12	7	1	11	6	6	24
6.08	17	18	5	2	19	3	14	16
6.1	16	13	15	3	15	5	22	15
6.12	14	21	10	2	13	3	14	27
6.14	11	13	16	3	14	1	13	23
6.16	19	15	19	2	13	3	12	26
6.18	15	4	13	3	10	4	15	19
6.2	10	12	15	6	8	3	11	18
6.22	7	14	13	2	17	4	17	22
6.24	13	19	13	3	14	4	13	21
6.26	14	11	6	3	13	9	16	16
6.28	6	14	14	3	24	1	14	17
6.3	12	14	15	3	15	2	11	24
6.32	21	18	8	4	9	3	20	22
6.34	13	17	8	5	19	3	13	21
6.36	13	16	12	2	17	6	22	13
6.38	14	15	14	3	13	6	16	15
6.4	20	17	5	4	7	3	17	13
6.42	17	17	13	3	14	2	12	16
6.44	13	15	14	3	28	2	17	20
6.46	9	7	13	1	15	8	17	22
6.48	16	14	12	2	12	2	13	21
6.5	15	20	8	2	13	3	15	16
6.52	9	13	17	1	14	4	17	21
6.54	10	21	14	1	10	1	15	15
6.56	18	13	17	5	19	4	15	24
6.58	15	5	14	2	16	6	11	24
6.6	16	8	16	3	12	2	17	19
6.62	11	16	15	3	16	7	13	7
6.64	12	12	12	5	20	2	12	13
6.66	12	12	15	1	10	4	12	19
6.68	16	17	9	4	16	5	15	20
6.7	19	7	10	3	11	6	22	20
6.72	13	16	9	3	19	3	20	15
6.74	7	19	16	2	19	2	19	18
6.76	14	21	19	1	3	5	25	20
6.78	15	11	9	2	11	3	16	20
6.8	14	11	11	1	16	5	14	17
6.82	16	12	17	1	14	4	17	19
6.84	18	15	15	9	15	5	15	21
6.86	15	7	12	5	22	10	17	17
6.88	14	14	14	2	15	5	19	12
6.9	15	14	9	1	9	6	15	18
6.92	14	12	7	4	12	4	12	17
6.94	16	10	12	3	14	7	17	19
6.96	16	15	11	4	12	4	9	13
6.98	18	16	11	1	11	2	14	14
7	15	15	13	2	21	4	16	13
7.02	14	17	17	5	18	3	12	13
7.04	15	17	8	1	15	4	12	16
7.06	16	20	9	2	17	3	21	16

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
7.08	11	21	13	4	17	4	10	16
7.1	17	12	9	1	25	2	21	15
7.12	14	13	12	2	13	1	12	19
7.14	16	16	14	5	10	3	27	19
7.16	17	9	13	3	13	6	17	23
7.18	18	11	25	1	15	5	18	17
7.2	12	8	12	1	16	4	18	11
7.22	11	18	14	2	17	2	17	16
7.24	16	22	12	2	15	3	12	17
7.26	19	22	14	3	10	4	21	19
7.28	18	18	16	1	14	4	14	24
7.3	12	13	25	3	18	3	20	17
7.32	13	12	14	2	14	8	19	21
7.34	14	13	12	1	12	4	10	19
7.36	12	16	13	1	12	4	11	17
7.38	11	18	13	3	16	2	13	21
7.4	11	11	10	2	21	3	18	14
7.42	23	21	14	2	11	3	23	16
7.44	14	17	6	2	18	2	16	22
7.46	16	14	14	3	14	4	16	22
7.48	17	13	16	2	17	6	21	29
7.5	27	23	12	2	18	6	16	16
7.52	22	23	10	2	24	4	17	25
7.54	25	17	14	2	17	2	16	15
7.56	32	18	18	3	22	3	31	17
7.58	17	20	17	3	17	3	32	22
7.6	26	26	24	2	24	3	22	18
7.62	19	24	25	4	25	7	18	30
7.64	22	26	23	6	23	4	21	31
7.66	13	23	21	1	19	8	19	25
7.68	13	22	15	1	23	7	21	29
7.7	16	21	15	2	21	1	20	22
7.72	20	27	11	3	17	2	30	26
7.74	17	24	19	1	17	7	21	22
7.76	16	17	13	1	17	12	23	35
7.78	15	13	12	3	13	12	20	27
7.8	13	24	11	1	10	6	17	23
7.82	13	17	7	2	18	3	6	22
7.84	11	13	10	3	13	4	11	23
7.86	13	13	8	1	20	6	14	23
7.88	11	9	12	3	14	4	17	19
7.9	11	11	13	4	14	4	18	25
7.92	15	18	11	2	21	5	23	19
7.94	21	8	15	5	14	2	18	13
7.96	17	9	14	5	14	1	19	12
7.98	8	14	20	3	13	6	16	10
8	16	14	16	4	24	4	13	17
8.02	15	18	10	1	20	4	13	8
8.04	13	5	14	5	13	4	18	13
8.06	14	8	9	1	12	6	18	21
8.08	13	14	14	4	20	7	20	7
8.1	12	17	22	5	12	5	19	21
8.12	10	9	14	2	16	2	15	13
8.14	12	8	20	2	9	6	15	13
8.16	14	13	11	4	20	2	10	21
8.18	18	8	8	2	11	4	16	8
8.2	24	15	6	2	16	2	21	15
8.22	20	10	10	1	18	4	19	10
8.24	8	11	8	2	19	6	18	6
8.26	18	8	19	5	19	3	10	20
8.28	18	12	7	5	12	1	17	8
8.3	11	13	7	1	12	1	24	12
8.32	13	5	16	4	19	4	17	18
8.34	20	11	8	1	14	4	17	12
8.36	15	7	10	5	11	5	23	14
8.38	16	12	18	3	17	7	17	16
8.4	16	10	11	1	23	4	15	4
8.42	19	7	16	6	21	6	12	6
8.44	18	10	13	2	14	6	21	7
8.46	11	11	19	3	9	3	16	10
8.48	25	13	13	3	22	6	17	7
8.5	18	8	8	4	16	4	17	11
8.52	17	11	11	2	15	3	16	12
8.54	20	12	18	3	18	3	17	14
8.56	13	10	14	4	12	1	22	14
8.58	12	11	15	4	14	2	16	8
8.6	16	12	10	1	12	3	21	14
8.62	9	9	15	3	20	1	18	9
8.64	14	9	11	3	15	1	12	5
8.66	27	9	13	2	15	4	10	14
8.68	15	11	12	3	23	1	13	8
8.7	13	15	12	2	25	6	13	12
8.72	17	15	15	2	12	3	15	12
8.74	16	5	17	1	10	4	20	12
8.76	13	3	14	1	19	4	19	8
8.78	18	9	12	4	17	5	18	7
8.8	13	8	7	1	21	4	13	8
8.82	18	9	11	3	18	2	13	12
8.84	16	7	16	2	17	6	17	9

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
8.86	11	7	6	2	17	2	11	18
8.88	13	16	14	6	22	3	25	7
8.9	11	10	11	3	20	4	22	10
8.92	22	10	7	2	14	1	20	9
8.94	14	10	11	4	14	4	16	10
8.96	9	6	12	1	15	2	14	10
8.98	17	12	11	4	12	3	19	10
9	10	10	8	1	16	1	19	8
9.02	13	10	11	1	11	4	14	17
9.04	20	11	13	3	12	4	10	18
9.06	23	3	16	2	17	2	16	10
9.08	14	10	17	2	23	3	19	3
9.1	23	13	17	1	19	1	19	11
9.12	16	9	12	5	18	2	15	9
9.14	24	10	14	5	8	3	18	8
9.16	15	5	21	1	13	1	26	11
9.18	21	13	22	3	18	4	23	12
9.2	16	5	25	2	16	3	27	10
9.22	24	11	42	1	23	4	34	8
9.24	17	9	29	3	20	4	32	10
9.26	16	16	20	3	16	3	24	9
9.28	12	9	21	3	25	3	31	9
9.3	20	17	32	2	23	7	14	10
9.32	16	9	18	2	24	3	18	7
9.34	15	11	12	4	15	4	19	13
9.36	12	8	16	4	20	5	19	9
9.38	14	12	15	1	16	6	17	9
9.4	23	7	15	1	25	3	18	16
9.42	19	9	22	2	21	5	20	13
9.44	11	6	11	1	17	5	15	15
9.46	14	6	13	3	20	3	13	6
9.48	22	7	16	3	20	11	25	16
9.5	17	4	12	5	24	7	19	14
9.52	20	12	21	5	15	6	12	11
9.54	21	7	12	3	19	4	16	11
9.56	14	10	13	4	16	2	22	9
9.58	19	11	13	5	24	3	16	9
9.6	18	4	11	3	20	4	17	9
9.62	19	10	12	7	15	7	9	10
9.64	15	11	20	3	18	5	21	9
9.66	16	14	10	4	16	8	13	8
9.68	15	8	9	6	21	7	23	10
9.7	13	11	16	2	13	3	23	13
9.72	11	9	9	4	19	6	23	13
9.74	17	7	18	3	9	11	15	5
9.76	19	9	13	1	13	2	21	11
9.78	13	12	13	2	21	2	23	13
9.8	15	6	10	1	14	4	20	9
9.82	16	12	18	5	18	4	21	4
9.84	23	7	16	1	19	1	13	7
9.86	15	10	13	3	21	4	23	8
9.88	18	11	14	2	21	3	23	13
9.9	9	9	11	1	21	6	13	13
9.92	18	14	16	4	16	4	17	13
9.94	18	12	15	2	17	5	19	12
9.96	20	9	18	3	16	7	17	10
9.98	15	7	15	2	12	4	21	11
10	11	16	12	3	16	3	11	12
10.02	5	9	11	3	13	4	15	6
10.04	17	8	25	1	17	2	16	19
10.06	11	8	12	5	21	3	12	10
10.08	23	4	19	3	20	4	25	9
10.1	13	16	14	6	18	4	20	11
10.12	19	13	12	1	18	4	18	17
10.14	20	9	11	2	17	6	20	10
10.16	22	7	16	4	18	4	23	11
10.18	13	6	13	1	15	5	15	16
10.2	21	11	17	5	16	4	22	11
10.22	19	10	13	3	19	5	17	10
10.24	13	14	22	1	21	4	20	18
10.26	11	11	19	3	17	1	14	19
10.28	17	18	21	3	11	2	20	13
10.3	11	11	17	3	27	6	14	13
10.32	21	11	10	1	13	2	24	16
10.34	7	13	10	1	25	4	15	17
10.36	19	11	17	3	10	2	20	24
10.38	17	25	4	3	16	1	18	19
10.4	17	14	15	2	17	2	22	22
10.42	20	23	15	1	18	7	20	17
10.44	10	26	18	1	20	4	16	30
10.46	23	27	7	6	11	5	19	29
10.48	15	22	16	2	14	3	13	31
10.5	18	21	7	3	16	7	23	37
10.52	14	18	14	2	17	6	20	39
10.54	12	14	18	4	20	3	16	49
10.56	19	13	13	2	19	8	24	34
10.58	13	11	13	4	18	2	24	47
10.6	13	17	18	1	17	10	19	29
10.62	18	10	16	2	14	7	15	27

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
10.64	18	11	9	1	13	4	30	23
10.66	16	9	27	4	12	8	25	24
10.68	15	14	14	2	19	3	16	25
10.7	12	11	8	2	17	7	16	22
10.72	11	11	13	4	20	6	18	24
10.74	16	10	16	2	16	2	12	17
10.76	17	20	20	4	21	1	20	11
10.78	20	17	15	5	23	4	18	29
10.8	22	16	23	1	20	8	20	25
10.82	14	9	10	4	14	6	23	16
10.84	11	14	14	3	15	2	12	16
10.86	14	14	19	2	19	2	25	18
10.88	11	11	15	1	17	4	17	19
10.9	13	27	12	4	14	4	16	26
10.92	12	21	9	1	19	6	29	21
10.94	20	15	17	3	12	7	13	18
10.96	13	11	20	2	22	8	16	22
10.98	17	23	13	3	21	9	21	26
11	16	17	13	1	19	3	21	22
11.02	14	19	10	4	18	2	20	19
11.04	14	25	15	5	19	6	18	18
11.06	18	29	15	5	14	5	21	27
11.08	18	23	14	3	12	8	17	25
11.1	16	25	16	1	14	11	24	33
11.12	12	28	17	3	12	4	24	27
11.14	16	37	10	2	11	8	20	35
11.16	10	31	10	8	19	3	17	33
11.18	17	21	16	6	14	4	16	38
11.2	23	33	13	3	27	6	16	29
11.22	17	33	12	3	16	8	16	28
11.24	16	33	18	1	23	4	19	37
11.26	20	19	10	5	22	5	16	34
11.28	16	32	8	2	24	5	28	41
11.3	12	17	16	2	17	9	14	39
11.32	15	12	12	5	21	5	26	33
11.34	14	18	13	6	24	5	19	26
11.36	18	19	16	4	15	3	18	30
11.38	20	12	15	2	16	4	14	21
11.4	10	14	17	2	24	8	15	14
11.42	21	13	17	6	13	7	19	24
11.44	20	9	14	1	24	1	24	18
11.46	18	14	22	8	20	3	21	12
11.48	16	8	10	6	19	2	16	16
11.5	15	17	22	3	13	8	26	12
11.52	18	4	13	3	11	5	19	16
11.54	7	18	12	7	22	1	14	12
11.56	21	4	15	1	10	6	21	20
11.58	17	7	12	4	18	4	21	18
11.6	17	5	15	4	14	4	19	18
11.62	18	12	12	2	21	2	9	7
11.64	13	11	14	3	18	4	23	12
11.66	20	12	15	1	20	8	26	12
11.68	16	8	6	3	19	2	23	11
11.7	14	9	22	5	20	4	25	10
11.72	13	11	14	2	24	4	15	7
11.74	10	6	19	5	15	6	16	11
11.76	22	4	19	3	21	1	18	4
11.78	12	9	20	1	13	6	19	11
11.8	15	5	14	2	14	7	11	11
11.82	22	5	20	2	14	8	23	7
11.84	18	4	10	4	17	5	18	10
11.86	16	8	19	1	20	2	13	10
11.88	22	11	17	2	25	3	28	7
11.9	14	8	18	4	23	6	23	8
11.92	17	3	18	2	11	5	25	6
11.94	8	10	19	4	23	5	27	9
11.96	19	10	16	2	26	5	20	7
11.98	15	6	19	3	26	5	20	9
12	12	9	15	3	18	5	22	10
12.02	19	9	15	2	24	10	25	13
12.04	18	9	14	3	19	5	25	6
12.06	20	8	17	2	15	6	24	12
12.08	19	9	20	5	25	4	25	7
12.1	19	16	19	1	23	4	19	11
12.12	17	11	21	3	24	8	26	11
12.14	22	13	19	3	17	6	28	12
12.16	17	11	21	1	22	4	27	8
12.18	14	9	20	2	21	5	20	13
12.2	19	2	11	5	19	3	26	13
12.22	17	8	18	6	24	8	20	13
12.24	25	8	19	1	16	6	19	8
12.26	16	5	11	2	19	3	23	10
12.28	20	5	21	1	12	10	21	13
12.3	25	7	16	1	20	5	20	9
12.32	15	10	20	1	20	7	24	9
12.34	26	9	13	8	19	7	18	12
12.36	30	8	20	4	22	5	30	13
12.38	19	6	14	4	16	11	25	10
12.4	22	11	22	7	27	5	30	7

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
12.42	25	13	26	10	30	7	28	11
12.44	21	6	23	5	36	5	25	10
12.46	21	16	15	4	27	4	32	10
12.48	21	5	21	6	26	3	24	12
12.5	22	15	20	5	26	7	17	5
12.52	23	8	24	4	19	11	16	12
12.54	34	11	23	7	18	6	25	13
12.56	29	11	23	6	24	3	29	4
12.58	23	14	32	3	20	9	29	14
12.6	26	16	25	3	26	6	26	8
12.62	27	9	21	5	22	6	31	10
12.64	19	13	24	5	26	5	39	7
12.66	22	9	30	7	28	3	32	10
12.68	21	11	20	5	35	6	17	13
12.7	24	7	26	5	33	10	37	12
12.72	18	5	19	13	32	6	20	10
12.74	21	14	24	6	30	7	23	10
12.76	15	9	20	3	28	7	20	11
12.78	18	9	20	5	24	9	22	7
12.8	17	9	20	3	25	10	22	11
12.82	18	7	9	3	21	5	22	7
12.84	19	13	14	3	18	6	19	8
12.86	19	6	16	7	18	6	17	5
12.88	24	2	10	7	34	6	17	4
12.9	17	8	15	8	29	2	25	7
12.92	18	6	24	2	19	4	16	4
12.94	15	9	17	3	24	5	18	6
12.96	19	7	15	1	17	3	15	4
12.98	15	7	16	7	22	8	22	9
13	22	6	21	4	20	7	24	5
13.02	13	6	19	5	26	2	23	8
13.04	13	8	21	8	19	2	26	8
13.06	12	6	6	4	20	4	13	6
13.08	16	5	20	2	19	2	21	8
13.1	6	9	24	4	19	6	20	6
13.12	18	6	15	4	19	5	26	6
13.14	8	8	9	7	22	3	26	6
13.16	15	5	10	5	21	2	22	9
13.18	17	13	17	1	21	3	18	8
13.2	22	6	21	1	19	7	14	3
13.22	11	8	15	4	30	5	19	7
13.24	12	3	15	2	19	2	15	6
13.26	9	7	13	2	19	4	24	9
13.28	21	2	15	2	19	9	15	7
13.3	17	11	15	3	14	4	19	6
13.32	19	11	21	6	21	5	18	7
13.34	12	8	13	3	18	1	13	11
13.36	21	9	13	4	11	1	18	6
13.38	18	7	19	2	25	4	14	4
13.4	10	8	18	2	25	3	17	9
13.42	14	3	19	2	23	6	25	5
13.44	24	6	18	2	23	6	16	4
13.46	8	10	17	5	15	6	28	7
13.48	14	9	20	5	17	2	14	4
13.5	24	2	14	3	16	5	13	11
13.52	28	9	18	3	22	1	25	7
13.54	19	8	14	1	16	6	22	8
13.56	15	8	14	4	15	2	21	9
13.58	15	6	12	2	14	8	22	9
13.6	14	13	21	4	26	4	27	9
13.62	17	11	18	4	27	2	19	6
13.64	23	5	15	4	13	1	20	6
13.66	17	9	12	1	19	3	20	10
13.68	21	6	13	1	14	2	18	7
13.7	15	12	22	2	19	6	24	8
13.72	28	4	17	5	10	1	20	3
13.74	27	6	24	4	25	3	18	7
13.76	13	8	16	3	21	10	23	1
13.78	20	7	17	3	15	2	21	6
13.8	15	10	18	1	28	5	33	10
13.82	18	4	18	2	20	7	21	4
13.84	22	1	22	5	12	5	25	5
13.86	23	8	21	1	12	5	24	9
13.88	19	7	19	3	24	9	28	3
13.9	19	4	26	1	14	7	23	6
13.92	16	6	20	3	27	3	28	7
13.94	20	4	23	2	25	4	21	5
13.96	21	8	15	1	12	6	14	13
13.98	19	5	17	3	18	5	25	6
14	15	5	18	6	19	8	20	8
14.02	13	6	16	4	19	2	16	9
14.04	23	5	18	2	18	5	35	9
14.06	15	4	17	4	13	5	14	5
14.08	19	7	16	5	15	4	15	7
14.1	15	4	15	2	22	5	17	6
14.12	24	11	9	4	21	6	13	4
14.14	26	8	19	5	25	4	15	5
14.16	22	2	13	5	12	4	23	4
14.18	28	7	22	8	20	4	17	6

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
14.2	22	5	16	2	26	8	27	10
14.22	22	10	18	2	21	4	20	7
14.24	17	11	15	2	18	5	20	8
14.26	18	8	8	4	23	3	22	5
14.28	11	7	17	6	15	4	26	9
14.3	18	11	17	1	20	3	23	7
14.32	19	9	21	6	22	1	17	8
14.34	23	11	7	5	14	4	25	4
14.36	17	5	18	1	15	3	16	5
14.38	14	5	10	3	21	2	20	11
14.4	12	8	16	2	25	1	30	4
14.42	19	4	20	3	29	2	17	5
14.44	19	11	14	2	19	2	21	4
14.46	17	4	20	4	16	8	23	5
14.48	26	10	12	3	23	4	12	7
14.5	15	4	16	5	18	2	26	6
14.52	12	6	18	2	22	3	13	7
14.54	18	7	19	2	17	4	21	6
14.56	16	9	21	2	24	5	22	5
14.58	17	4	16	2	27	6	28	7
14.6	18	6	14	2	23	5	20	8
14.62	26	6	23	1	22	3	24	4
14.64	21	2	23	1	24	6	26	4
14.66	12	8	13	1	27	4	21	6
14.68	15	10	21	1	22	2	23	6
14.7	16	7	13	7	19	5	24	8
14.72	21	4	11	3	22	3	19	5
14.74	21	2	10	2	18	5	19	2
14.76	18	8	13	1	21	10	25	5
14.78	17	13	17	3	26	5	30	5
14.8	22	7	19	3	29	7	20	8
14.82	23	4	14	2	18	5	24	5
14.84	13	5	19	1	23	9	22	6
14.86	23	4	12	1	23	1	22	13
14.88	23	5	22	2	23	2	19	8
14.9	16	8	24	1	22	2	23	8
14.92	22	8	14	3	15	4	21	10
14.94	14	7	22	4	25	7	29	6
14.96	22	3	16	1	20	3	17	6
14.98	18	9	20	1	22	5	22	6
15	14	6	12	1	17	8	17	8
15.02	14	10	18	6	18	1	16	9
15.04	19	6	14	3	19	4	18	2
15.06	17	8	19	4	18	7	24	7
15.08	17	8	13	1	28	4	23	5
15.1	28	4	9	2	16	4	21	4
15.12	11	6	23	2	21	11	20	5
15.14	18	4	17	1	24	7	21	8
15.16	21	3	15	1	22	4	13	4
15.18	15	6	19	1	15	8	18	8
15.2	11	3	13	1	23	4	22	6
15.22	18	3	13	3	19	4	18	6
15.24	21	8	15	1	12	7	26	5
15.26	17	9	16	3	22	5	25	3
15.28	25	4	17	2	24	4	27	4
15.3	21	11	24	3	31	5	17	11
15.32	18	7	15	2	30	3	20	8
15.34	15	3	11	5	22	6	23	7
15.36	15	8	15	1	25	7	16	7
15.38	19	11	19	3	19	5	32	2
15.4	14	8	10	3	16	4	28	9
15.42	18	7	16	2	25	2	18	6
15.44	15	16	12	3	21	4	23	1
15.46	25	12	12	2	25	3	33	7
15.48	18	7	21	5	25	1	30	8
15.5	23	5	14	1	17	3	28	7
15.52	16	8	22	3	18	7	19	6
15.54	16	8	19	1	21	4	24	7
15.56	15	3	15	5	22	7	18	6
15.58	22	5	22	1	25	4	29	7
15.6	18	6	14	4	27	3	27	7
15.62	33	7	21	1	17	5	23	5
15.64	16	5	21	2	24	11	20	4
15.66	21	9	19	1	21	6	24	9
15.68	10	5	18	2	23	4	20	5
15.7	12	7	17	2	15	3	23	4
15.72	14	5	28	7	25	5	22	3
15.74	22	7	13	1	19	4	24	7
15.76	21	2	8	1	30	1	18	12
15.78	22	2	15	1	15	3	24	9
15.8	26	5	15	1	19	4	24	6
15.82	19	10	12	1	15	3	23	5
15.84	8	4	24	3	16	7	19	12
15.86	20	10	20	2	15	3	21	6
15.88	16	15	28	3	30	3	15	3
15.9	22	6	25	1	27	1	27	7
15.92	13	4	12	1	20	3	27	7
15.94	12	6	18	4	28	4	13	4
15.96	24	8	18	6	21	2	22	10

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
15.98	23	7	20	1	22	3	27	5
16	25	6	14	1	18	4	30	3
16.02	16	5	17	1	23	5	20	7
16.04	10	5	18	2	22	3	18	7
16.06	32	2	24	4	22	2	23	2
16.08	24	8	18	5	18	4	31	5
16.1	28	6	15	1	22	5	22	4
16.12	19	6	13	1	23	3	15	9
16.14	25	6	20	2	31	6	26	7
16.16	16	8	9	1	11	3	15	7
16.18	15	7	14	2	17	3	27	5
16.2	21	9	17	3	30	2	20	4
16.22	21	9	13	1	30	6	18	4
16.24	20	7	22	3	20	6	24	8
16.26	18	10	25	3	18	1	29	11
16.28	19	7	14	1	26	2	23	7
16.3	25	11	11	4	21	6	29	9
16.32	17	6	19	1	23	5	23	11
16.34	20	6	18	5	20	2	23	6
16.36	24	10	17	2	27	5	24	8
16.38	24	10	18	6	22	7	25	11
16.4	18	9	21	1	22	4	17	5
16.42	26	8	15	3	19	3	27	7
16.44	25	10	21	1	23	3	25	6
16.46	21	5	17	1	23	3	22	6
16.48	17	10	32	1	26	2	25	10
16.5	22	9	24	1	33	3	28	11
16.52	21	14	15	7	25	6	27	5
16.54	22	5	20	4	28	7	22	9
16.56	21	12	15	1	22	3	29	9
16.58	14	9	13	2	30	4	21	8
16.6	31	10	19	3	27	8	36	9
16.62	25	10	16	4	22	5	17	15
16.64	15	7	14	4	23	4	25	7
16.66	25	11	20	2	32	3	19	16
16.68	18	8	11	8	30	6	27	10
16.7	23	8	17	2	28	3	27	13
16.72	19	10	16	5	24	3	34	12
16.74	23	8	33	5	18	4	21	15
16.76	30	8	14	3	33	4	31	18
16.78	16	3	19	2	22	9	24	12
16.8	28	11	17	7	24	4	20	5
16.82	13	10	15	2	21	3	23	8
16.84	19	11	16	1	28	3	23	6
16.86	21	4	18	5	21	3	24	9
16.88	21	10	21	4	22	3	24	8
16.9	19	5	20	5	24	8	33	12
16.92	17	6	17	1	23	3	28	10
16.94	19	4	15	6	27	7	29	8
16.96	21	14	15	5	14	2	29	7
16.98	18	9	18	5	24	3	19	6
17	18	12	16	9	22	3	20	9
17.02	22	5	24	1	23	2	36	12
17.04	22	3	19	4	18	1	21	5
17.06	26	11	17	3	28	1	38	3
17.08	19	10	14	1	27	6	24	8
17.1	20	5	19	1	23	4	27	6
17.12	24	9	13	6	18	7	23	4
17.14	20	7	18	4	22	2	32	6
17.16	18	12	22	4	30	3	31	6
17.18	33	5	18	2	20	1	17	12
17.2	24	8	17	2	23	1	32	11
17.22	15	13	15	2	28	2	31	6
17.24	19	1	14	4	29	7	29	8
17.26	24	7	10	3	26	8	25	12
17.28	14	9	15	2	26	1	29	12
17.3	22	6	21	1	18	1	31	8
17.32	28	8	26	1	25	1	19	16
17.34	19	3	25	2	28	5	15	11
17.36	25	7	22	1	17	2	23	7
17.38	19	11	17	5	34	2	42	12
17.4	21	7	13	1	18	5	22	8
17.42	16	5	23	1	25	5	27	12
17.44	19	9	22	1	36	3	31	9
17.46	15	12	22	4	22	5	30	10
17.48	25	6	20	6	26	8	31	10
17.5	29	7	21	3	22	4	24	8
17.52	28	1	18	1	32	1	34	10
17.54	15	7	27	1	21	4	26	5
17.56	29	7	17	5	27	3	37	3
17.58	23	4	18	3	30	1	31	7
17.6	20	7	22	2	22	7	25	6
17.62	18	9	10	1	30	4	25	7
17.64	31	4	20	5	23	3	30	6
17.66	22	6	18	1	26	5	18	14
17.68	28	16	14	3	29	4	13	9
17.7	21	7	26	1	31	5	25	6
17.72	30	8	19	3	26	1	35	8
17.74	15	9	28	4	21	4	24	15

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
17.76	35	5	22	3	38	2	30	8
17.78	16	5	20	2	18	1	29	8
17.8	15	7	24	2	20	3	28	6
17.82	34	6	21	1	31	3	29	6
17.84	17	6	19	2	24	3	20	10
17.86	26	1	21	1	25	1	31	9
17.88	27	8	25	5	30	5	39	11
17.9	27	9	18	3	28	4	31	2
17.92	22	13	17	4	23	2	28	5
17.94	20	6	22	2	31	2	23	5
17.96	20	8	15	2	35	3	33	3
17.98	38	8	26	8	28	4	18	10
18	15	6	24	3	19	2	27	7
18.02	28	8	18	3	26	4	37	11
18.04	31	6	20	3	21	2	22	5
18.06	20	9	19	1	26	3	26	2
18.08	25	6	21	4	38	4	41	10
18.1	8	9	28	2	35	2	26	7
18.12	20	10	23	3	27	2	32	9
18.14	27	13	27	2	16	4	27	12
18.16	29	12	16	4	34	4	31	7
18.18	26	9	14	5	31	3	35	6
18.2	26	4	21	1	50	1	24	12
18.22	34	9	28	4	23	6	30	13
18.24	17	6	18	1	32	4	35	12
18.26	29	10	24	1	24	2	33	9
18.28	26	7	19	2	33	2	33	9
18.3	23	5	12	3	27	4	32	5
18.32	22	10	27	2	26	2	37	16
18.34	22	16	17	3	28	5	30	14
18.36	26	12	20	5	23	1	25	11
18.38	25	15	18	4	40	6	35	15
18.4	23	18	27	6	33	4	38	11
18.42	18	12	22	1	26	7	33	6
18.44	20	21	21	3	31	9	23	13
18.46	23	18	21	4	39	5	24	10
18.48	33	12	18	1	38	1	26	8
18.5	25	19	23	2	35	5	29	12
18.52	31	14	25	5	31	6	33	14
18.54	29	21	22	5	30	5	24	21
18.56	23	19	25	2	26	7	26	19
18.58	24	17	16	4	31	7	32	16
18.6	28	29	27	5	34	4	41	12
18.62	30	26	26	4	34	14	27	10
18.64	20	21	22	6	38	7	33	20
18.66	28	17	22	6	25	11	35	28
18.68	22	35	25	5	40	9	40	12
18.7	26	23	14	8	33	10	28	24
18.72	15	28	21	1	34	19	35	26
18.74	24	25	19	2	29	15	38	22
18.76	21	24	22	12	28	11	31	24
18.78	31	18	17	6	30	7	25	18
18.8	16	16	15	6	35	12	37	25
18.82	24	26	16	7	35	15	32	20
18.84	20	18	20	4	31	10	35	22
18.86	22	23	20	11	24	6	30	29
18.88	23	13	22	10	24	11	26	14
18.9	20	17	22	11	27	6	29	20
18.92	26	14	17	10	22	6	27	20
18.94	27	22	16	4	33	9	22	22
18.96	24	10	20	3	26	6	34	19
18.98	30	6	16	14	33	13	34	23
19	18	27	14	5	37	8	23	19
19.02	24	16	18	5	36	10	28	12
19.04	26	9	25	12	31	9	25	15
19.06	23	15	26	9	46	9	37	21
19.08	28	23	22	7	35	6	35	15
19.1	27	16	22	5	31	12	36	18
19.12	26	10	19	6	35	9	25	8
19.14	25	21	17	3	29	9	28	17
19.16	27	24	23	3	36	4	33	26
19.18	23	19	16	3	31	5	38	21
19.2	21	16	20	4	28	10	27	11
19.22	32	17	14	2	36	10	24	17
19.24	44	10	23	6	39	7	21	20
19.26	44	20	32	1	29	7	25	11
19.28	35	20	22	4	31	8	25	10
19.3	28	23	31	10	29	14	35	19
19.32	33	10	28	1	33	5	28	12
19.34	23	21	19	6	37	5	40	16
19.36	29	11	31	2	31	8	38	22
19.38	25	14	24	4	39	12	21	21
19.4	41	16	18	4	46	2	34	19
19.42	27	18	27	4	36	4	39	19
19.44	43	15	28	5	41	10	41	16
19.46	57	10	34	3	38	9	42	24
19.48	57	27	29	7	40	5	41	17
19.5	100	29	21	4	40	7	44	15
19.52	164	23	28	4	29	7	33	25

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
19.54	259	30	49	4	38	8	50	15
19.56	369	17	86	6	43	6	62	15
19.58	326	25	131	3	70	9	99	21
19.6	268	25	253	4	83	12	145	26
19.62	222	33	327	7	116	14	219	20
19.64	138	48	355	8	173	20	236	15
19.66	79	56	285	2	220	23	209	25
19.68	65	77	219	5	261	26	152	26
19.7	43	86	162	7	219	32	126	39
19.72	50	75	75	6	171	29	71	56
19.74	43	48	66	3	121	25	76	78
19.76	35	44	42	10	68	43	52	88
19.78	45	32	52	7	60	23	53	73
19.8	26	29	35	11	45	36	58	75
19.82	36	19	44	10	57	39	53	70
19.84	27	16	44	15	48	30	49	58
19.86	32	34	27	24	51	24	42	32
19.88	34	25	35	29	56	20	42	23
19.9	32	14	30	44	46	20	39	29
19.92	37	20	36	49	47	19	37	24
19.94	32	16	31	74	40	14	47	19
19.96	31	17	27	67	32	11	33	17
19.98	22	22	31	73	31	14	39	22
20	38	13	22	60	33	14	34	15
20.02	36	19	19	51	33	9	48	16
20.04	26	20	23	47	41	12	46	18
20.06	23	19	21	31	36	7	34	11
20.08	29	19	20	28	41	9	26	16
20.1	35	21	27	15	47	4	31	11
20.12	26	12	19	14	29	7	36	19
20.14	30	10	24	11	27	6	41	15
20.16	30	7	20	12	38	9	26	15
20.18	36	13	22	9	39	9	34	14
20.2	30	11	25	4	32	5	34	16
20.22	19	13	20	10	30	7	27	12
20.24	25	15	24	12	31	12	29	12
20.26	32	18	25	9	33	10	39	18
20.28	29	17	20	5	24	7	31	19
20.3	30	18	26	9	35	5	37	13
20.32	29	18	36	5	43	6	34	19
20.34	32	14	24	3	35	6	29	11
20.36	30	14	22	5	62	6	39	10
20.38	32	16	18	6	27	3	35	11
20.4	37	19	21	1	47	5	38	12
20.42	28	17	26	4	32	6	31	15
20.44	26	13	27	7	42	7	33	6
20.46	27	11	18	13	26	4	41	15
20.48	29	15	23	3	38	5	41	9
20.5	30	16	19	7	26	8	24	15
20.52	28	11	31	6	44	7	41	10
20.54	30	15	30	2	40	2	44	11
20.56	27	16	27	4	32	7	36	13
20.58	36	8	25	7	30	7	39	12
20.6	30	8	26	4	40	6	30	12
20.62	38	7	29	6	35	6	35	11
20.64	31	14	31	4	37	2	32	12
20.66	48	19	34	2	33	3	28	14
20.68	43	13	28	2	35	4	44	12
20.7	35	18	30	3	39	7	38	14
20.72	58	11	62	3	32	10	54	16
20.74	61	15	75	2	27	6	57	13
20.76	49	12	76	5	43	5	60	5
20.78	51	12	133	7	52	9	64	11
20.8	45	23	185	1	72	6	79	14
20.82	41	19	244	8	76	15	85	13
20.84	44	18	234	5	64	11	74	16
20.86	36	28	256	3	66	12	78	14
20.88	43	41	206	3	56	10	65	14
20.9	35	22	141	6	57	11	40	18
20.92	31	33	109	4	39	15	40	24
20.94	35	20	59	10	49	11	31	27
20.96	26	19	48	6	40	17	43	27
20.98	31	17	32	4	42	9	34	25
21	32	11	34	10	43	13	28	21
21.02	38	15	28	9	30	11	37	13
21.04	29	16	30	5	45	12	46	18
21.06	50	17	29	9	38	11	40	19
21.08	23	15	32	3	39	8	40	9
21.1	34	8	28	10	43	7	45	21
21.12	34	8	25	10	36	6	42	15
21.14	28	21	36	10	39	3	35	15
21.16	46	10	26	11	48	7	31	18
21.18	34	19	27	3	35	10	42	14
21.2	35	8	26	4	37	5	42	11
21.22	28	12	20	8	21	6	41	15
21.24	40	13	26	4	44	6	56	14
21.26	41	15	33	8	43	8	46	14
21.28	42	12	36	3	37	6	42	12
21.3	43	10	44	2	37	7	45	12

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
21.32	31	18	30	9	43	8	54	18
21.34	42	30	33	5	38	11	35	8
21.36	30	19	25	6	38	10	38	13
21.38	40	13	17	5	35	10	44	9
21.4	37	10	21	3	41	11	31	16
21.42	30	9	32	5	53	11	37	17
21.44	36	7	21	12	32	14	34	10
21.46	30	12	19	6	43	6	44	13
21.48	39	18	30	7	35	7	32	13
21.5	36	14	25	8	31	5	34	12
21.52	31	15	34	7	48	6	43	14
21.54	37	14	26	9	25	8	33	10
21.56	28	18	24	6	41	7	49	18
21.58	30	17	22	9	36	6	41	9
21.6	44	21	24	1	40	6	29	10
21.62	28	13	29	7	50	4	43	9
21.64	28	13	29	4	51	6	42	8
21.66	34	17	39	4	50	7	37	15
21.68	39	16	33	2	36	4	49	9
21.7	39	15	29	6	40	10	45	11
21.72	28	17	45	5	35	8	33	10
21.74	39	14	36	5	44	4	46	13
21.76	41	11	34	4	43	4	35	11
21.78	29	15	43	2	39	6	42	16
21.8	37	15	39	4	36	6	29	7
21.82	36	14	43	1	45	9	54	7
21.84	35	17	28	4	47	8	45	13
21.86	28	15	29	8	42	5	36	15
21.88	43	15	44	3	43	10	25	24
21.9	36	11	30	6	34	4	34	21
21.92	25	18	24	5	40	7	38	17
21.94	37	15	25	5	35	9	49	15
21.96	43	13	22	4	41	9	29	12
21.98	31	8	24	5	46	9	41	16
22	35	16	30	6	39	8	54	11
22.02	33	19	29	9	27	10	38	12
22.04	30	12	26	7	45	10	27	16
22.06	35	14	26	6	45	11	44	12
22.08	43	16	28	7	41	7	32	14
22.1	31	9	27	8	56	10	43	8
22.12	30	13	29	3	44	4	43	13
22.14	25	12	15	5	46	8	39	8
22.16	51	12	38	7	45	4	29	8
22.18	32	11	33	8	30	5	41	10
22.2	36	16	30	4	37	9	41	15
22.22	46	16	41	3	31	11	44	11
22.24	51	17	39	6	32	4	52	15
22.26	47	22	36	4	40	12	50	9
22.28	60	13	49	3	26	5	61	15
22.3	56	20	42	6	48	10	55	16
22.32	47	20	68	5	67	10	75	20
22.34	62	11	108	3	52	6	77	18
22.36	38	17	93	3	60	13	69	18
22.38	38	25	88	14	70	16	50	13
22.4	40	17	104	4	55	13	58	22
22.42	43	21	64	6	62	18	50	15
22.44	28	22	65	6	50	16	48	25
22.46	30	12	59	4	47	16	58	22
22.48	30	18	32	4	55	19	49	18
22.5	35	22	36	6	53	18	43	34
22.52	27	18	30	6	43	17	51	19
22.54	35	17	30	3	36	13	36	15
22.56	33	15	23	15	33	14	39	15
22.58	33	20	34	23	38	10	42	19
22.6	27	12	37	23	36	14	40	13
22.62	34	14	28	36	33	16	51	27
22.64	31	17	32	38	34	16	43	19
22.66	29	16	39	41	41	11	36	19
22.68	40	18	44	53	38	12	38	15
22.7	37	11	40	102	53	6	44	16
22.72	43	17	36	136	45	9	49	16
22.74	29	17	49	89	41	19	37	11
22.76	42	20	45	113	43	12	46	22
22.78	29	19	30	72	50	12	51	14
22.8	28	16	32	68	40	10	46	13
22.82	31	14	34	32	37	7	48	17
22.84	31	21	29	23	39	8	31	13
22.86	41	17	36	14	37	3	37	9
22.88	53	18	27	9	43	3	29	12
22.9	36	22	38	11	43	6	43	11
22.92	38	19	36	6	44	7	53	11
22.94	51	17	29	11	46	15	47	12
22.96	45	12	35	10	36	2	49	18
22.98	46	22	38	7	48	7	50	19
23	52	17	48	9	49	9	53	14
23.02	49	26	61	7	47	8	61	26
23.04	41	26	67	9	42	13	71	14
23.06	41	22	56	8	58	13	65	27
23.08	41	19	44	8	63	14	61	15

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
23.1	45	19	59	7	63	16	57	19
23.12	45	21	54	8	52	17	59	24
23.14	36	26	47	10	60	12	52	20
23.16	22	31	52	11	52	13	48	32
23.18	35	24	46	11	61	17	40	32
23.2	20	26	55	16	59	14	36	26
23.22	37	22	34	8	55	16	51	22
23.24	22	22	28	7	49	13	38	25
23.26	31	20	30	7	42	18	30	27
23.28	31	12	26	6	47	11	34	17
23.3	33	22	25	12	25	16	41	23
23.32	30	20	27	11	37	12	37	18
23.34	33	18	28	7	39	6	28	16
23.36	24	15	20	10	45	15	35	18
23.38	37	16	23	16	46	11	43	12
23.4	36	21	31	11	33	14	56	24
23.42	32	32	29	9	35	16	41	28
23.44	23	19	26	13	47	13	40	20
23.46	37	24	19	10	35	8	36	30
23.48	28	24	22	12	42	12	47	21
23.5	32	19	28	4	45	13	45	25
23.52	36	31	32	7	34	13	30	24
23.54	21	16	26	8	32	12	45	24
23.56	34	21	24	5	27	7	33	25
23.58	32	32	32	7	32	12	37	18
23.6	28	34	23	5	34	18	36	25
23.62	31	30	29	3	41	16	44	33
23.64	37	36	18	3	30	10	28	21
23.66	33	49	17	1	33	14	29	25
23.68	37	45	31	4	37	17	40	27
23.7	36	41	32	5	38	15	40	38
23.72	38	43	26	7	34	15	53	33
23.74	38	31	24	7	28	12	35	35
23.76	29	29	21	2	32	12	41	31
23.78	20	33	28	9	52	9	26	45
23.8	35	24	21	6	38	14	36	31
23.82	18	42	21	2	38	9	30	36
23.84	36	37	31	2	37	12	41	32
23.86	33	39	31	3	34	11	34	37
23.88	29	23	32	3	41	18	37	28
23.9	26	31	34	6	37	15	45	38
23.92	29	25	28	3	32	9	26	35
23.94	20	31	21	4	39	10	30	29
23.96	35	25	29	2	30	17	39	31
23.98	35	24	31	4	35	11	37	30
24	28	24	20	5	34	7	41	24
24.02	34	23	24	10	52	14	41	27
24.04	35	26	29	4	29	9	41	26
24.06	37	22	34	2	48	8	47	30
24.08	39	27	26	3	41	6	45	32
24.1	24	27	39	8	40	7	49	31
24.12	26	29	32	8	45	15	61	39
24.14	37	23	36	2	38	9	45	29
24.16	27	26	31	4	42	18	45	33
24.18	34	25	37	6	33	6	31	32
24.2	37	28	25	5	34	12	39	25
24.22	34	25	30	6	38	11	45	33
24.24	33	30	39	6	39	9	50	30
24.26	48	19	26	3	45	10	33	24
24.28	38	29	40	5	43	11	36	30
24.3	32	30	41	4	36	10	47	32
24.32	43	25	43	5	42	15	41	24
24.34	57	23	28	7	36	11	51	15
24.36	40	16	37	9	33	19	48	31
24.38	40	20	39	4	48	10	42	27
24.4	35	20	38	1	44	14	50	19
24.42	36	18	38	3	38	9	66	27
24.44	44	15	46	6	52	17	65	14
24.46	30	17	40	5	39	18	47	25
24.48	37	15	37	8	45	11	50	21
24.5	42	17	51	11	48	12	54	18
24.52	32	22	41	3	31	8	48	17
24.54	27	25	37	5	33	11	45	28
24.56	37	19	29	5	41	19	41	19
24.58	31	22	28	7	37	11	26	30
24.6	27	21	21	5	42	9	45	25
24.62	28	16	30	7	25	8	49	28
24.64	43	22	22	9	33	14	30	17
24.66	27	16	28	5	30	7	35	23
24.68	34	18	26	7	39	9	45	14
24.7	27	24	24	4	41	10	38	17
24.72	34	22	22	10	43	10	32	20
24.74	25	12	27	4	39	9	38	16
24.76	29	14	25	3	35	11	30	23
24.78	27	15	28	5	30	17	30	15
24.8	39	26	23	2	38	10	26	19
24.82	37	24	27	3	33	13	27	19
24.84	25	14	21	7	24	11	21	20
24.86	30	15	21	5	25	8	32	16

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
24.88	43	17	27	6	42	9	29	14
24.9	30	21	24	7	30	7	30	21
24.92	27	23	20	2	31	6	41	18
24.94	35	11	21	4	37	11	31	9
24.96	37	14	22	4	33	10	34	25
24.98	32	25	27	2	38	10	40	15
25	48	22	29	2	34	7	38	18
25.02	47	23	34	2	34	11	52	22
25.04	46	31	30	7	37	13	46	16
25.06	38	27	31	2	40	11	32	20
25.08	62	25	39	5	34	21	38	19
25.1	45	26	46	4	35	6	38	15
25.12	57	23	40	6	47	13	50	21
25.14	56	22	43	6	44	10	54	27
25.16	68	29	63	4	41	10	45	22
25.18	59	21	52	8	58	9	50	20
25.2	69	31	91	3	64	17	41	24
25.22	81	28	64	2	62	13	55	37
25.24	98	26	73	5	54	8	74	20
25.26	158	24	79	3	67	19	79	24
25.28	244	37	84	8	66	22	64	32
25.3	488	27	107	7	54	17	80	31
25.32	893	41	140	7	70	18	106	20
25.34	1291	35	253	5	84	21	169	34
25.36	1159	48	457	6	108	18	317	30
25.38	926	53	811	9	195	35	577	28
25.4	750	108	1223	10	311	46	840	40
25.42	681	152	1338	12	609	93	805	40
25.44	442	240	1154	9	881	114	666	55
25.46	190	304	895	11	918	126	563	89
25.48	130	263	727	21	749	136	528	118
25.5	83	250	562	11	599	153	390	195
25.52	74	236	265	21	503	170	184	272
25.54	69	196	163	24	356	193	118	358
25.56	79	148	101	20	179	185	80	336
25.58	74	88	86	36	114	140	91	287
25.6	46	63	72	44	81	126	71	246
25.62	59	60	81	68	87	102	65	204
25.64	62	50	70	139	63	90	58	146
25.66	51	35	63	204	55	67	64	121
25.68	54	38	65	210	71	55	56	93
25.7	48	23	55	261	60	38	65	84
25.72	41	33	43	242	78	46	61	64
25.74	35	33	39	291	64	44	49	56
25.76	53	36	38	305	69	28	43	57
25.78	56	36	48	309	66	34	47	41
25.8	67	27	44	429	45	22	38	38
25.82	59	23	59	241	47	29	46	39
25.84	47	25	56	165	37	27	62	36
25.86	41	25	41	145	47	26	63	30
25.88	44	20	44	115	45	31	61	32
25.9	50	28	35	105	48	25	58	27
25.92	36	27	35	34	44	22	51	27
25.94	30	26	35	37	44	16	42	32
25.96	35	24	29	31	46	25	38	26
25.98	36	29	22	37	27	29	37	29
26	26	24	35	23	31	17	40	20
26.02	26	24	31	24	30	17	34	16
26.04	28	28	28	31	38	13	26	25
26.06	25	13	31	33	49	18	27	30
26.08	39	19	28	38	38	15	32	31
26.1	45	21	30	31	48	24	30	21
26.12	48	16	29	39	48	12	37	14
26.14	70	23	28	34	34	12	30	24
26.16	86	29	37	21	45	20	33	18
26.18	88	32	45	34	43	23	43	21
26.2	97	28	50	22	44	29	54	21
26.22	93	40	60	12	53	19	59	17
26.24	80	50	85	16	57	31	59	12
26.26	74	59	99	6	73	23	89	17
26.28	71	54	72	13	71	19	86	17
26.3	70	42	73	13	113	22	79	20
26.32	46	44	77	14	101	34	73	29
26.34	43	39	68	9	100	27	61	39
26.36	33	30	57	4	91	27	59	28
26.38	38	27	53	13	65	37	58	38
26.4	41	20	53	12	69	18	47	31
26.42	33	18	40	9	52	26	55	28
26.44	41	22	48	8	55	24	50	48
26.46	53	21	35	18	55	23	51	34
26.48	54	25	51	33	38	18	50	44
26.5	55	25	67	41	46	15	57	41
26.52	53	28	88	45	69	24	57	32
26.54	54	40	92	38	69	19	71	39
26.56	50	30	71	40	81	18	67	26
26.58	60	25	60	32	58	11	84	36
26.6	69	40	74	26	84	18	76	26
26.62	94	31	85	14	67	23	68	31
26.64	87	27	94	15	69	24	61	31

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
26.66	98	37	97	15	63	26	81	30
26.68	90	39	122	13	84	34	83	36
26.7	102	30	98	15	99	27	116	33
26.72	103	34	107	9	99	42	126	13
26.74	65	31	112	12	121	38	121	26
26.76	58	45	122	23	116	27	108	39
26.78	65	50	93	29	113	42	97	37
26.8	65	62	94	22	121	40	92	40
26.82	48	49	63	27	97	46	65	57
26.84	48	32	41	23	96	41	70	55
26.86	34	30	45	20	80	47	72	62
26.88	39	26	40	18	74	35	51	41
26.9	37	28	36	22	54	32	43	46
26.92	45	18	29	24	43	20	34	31
26.94	46	20	42	23	56	25	47	33
26.96	37	15	35	20	56	30	39	38
26.98	35	21	38	26	50	18	50	24
27	35	15	35	32	45	17	52	21
27.02	30	22	31	35	38	13	53	24
27.04	34	21	34	37	50	21	47	22
27.06	43	20	31	26	53	18	65	23
27.08	31	22	37	31	41	18	38	20
27.1	27	19	37	24	50	21	44	32
27.12	27	30	28	20	52	12	53	23
27.14	33	18	45	18	94	13	36	20
27.16	36	23	28	12	101	11	46	27
27.18	28	20	29	8	165	17	35	17
27.2	28	22	22	11	90	18	45	27
27.22	30	23	19	12	95	17	34	25
27.24	26	24	30	9	91	13	30	17
27.26	20	21	16	10	66	7	44	15
27.28	24	20	30	6	75	15	49	18
27.3	28	14	37	9	43	6	37	15
27.32	21	19	31	6	40	14	34	22
27.34	28	16	27	10	37	12	35	21
27.36	19	18	28	10	40	7	43	15
27.38	31	20	29	6	44	7	34	13
27.4	23	14	26	6	39	10	36	20
27.42	30	11	24	8	39	9	21	18
27.44	22	19	11	9	46	5	27	19
27.46	26	16	16	7	30	6	31	21
27.48	29	6	26	4	38	6	27	23
27.5	27	16	16	2	38	9	25	15
27.52	26	14	21	6	18	4	31	10
27.54	29	14	15	7	29	11	41	11
27.56	27	11	19	8	27	9	26	16
27.58	18	18	16	4	25	9	15	15
27.6	24	17	26	6	25	6	18	14
27.62	16	17	7	10	26	5	29	10
27.64	24	12	16	2	26	10	28	12
27.66	14	14	8	4	21	9	29	8
27.68	14	17	14	5	35	9	18	8
27.7	19	13	13	7	26	11	25	15
27.72	25	16	25	4	17	6	31	16
27.74	19	13	13	4	25	4	22	16
27.76	20	12	24	1	20	9	21	17
27.78	17	14	22	5	18	10	26	18
27.8	17	14	17	3	36	4	21	15
27.82	26	22	19	5	34	6	29	17
27.84	19	20	14	3	21	11	19	11
27.86	19	12	15	5	24	5	14	16
27.88	21	18	18	2	25	7	27	13
27.9	27	20	21	4	22	3	29	10
27.92	18	21	21	4	23	10	25	16
27.94	26	27	21	3	29	4	31	11
27.96	27	25	17	1	20	4	22	17
27.98	28	15	20	6	24	13	21	14
28	15	21	20	2	27	6	27	18
28.02	23	15	23	5	31	6	26	18
28.04	32	18	14	2	32	3	20	23
28.06	15	11	32	3	28	6	28	15
28.08	16	20	13	6	30	8	22	19
28.1	20	18	20	7	18	7	22	17
28.12	21	14	24	7	23	7	28	17
28.14	31	15	26	2	25	7	24	16
28.16	33	12	18	11	27	15	18	14
28.18	19	13	12	4	28	8	25	15
28.2	26	23	15	1	25	7	28	19
28.22	29	31	27	2	27	7	24	17
28.24	24	23	15	6	29	6	32	12
28.26	29	17	18	3	31	9	21	13
28.28	31	31	18	3	24	8	26	16
28.3	26	27	15	2	32	5	27	16
28.32	18	24	13	5	30	1	28	20
28.34	26	25	17	1	39	7	37	11
28.36	20	27	20	4	26	7	25	9
28.38	37	17	18	1	17	6	25	14
28.4	32	18	24	5	27	1	23	17
28.42	33	20	19	4	25	12	33	14

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
28.44	22	17	20	7	32	4	22	14
28.46	28	16	30	2	23	9	27	14
28.48	23	20	20	2	26	9	24	14
28.5	22	27	27	3	35	10	33	6
28.52	42	26	25	9	33	13	27	11
28.54	31	22	29	5	22	9	30	8
28.56	29	17	20	5	34	6	29	17
28.58	30	24	31	1	36	14	38	16
28.6	26	28	29	9	37	13	27	17
28.62	34	29	30	3	31	11	39	14
28.64	34	20	36	2	34	10	42	17
28.66	29	25	17	4	24	9	29	18
28.68	38	23	16	4	35	19	45	17
28.7	34	23	26	6	28	13	32	10
28.72	25	27	32	6	34	15	44	14
28.74	27	22	22	7	33	14	26	9
28.76	35	17	32	2	41	24	29	17
28.78	33	23	31	6	41	9	29	20
28.8	31	20	25	3	56	9	34	18
28.82	42	16	33	6	64	17	27	18
28.84	33	12	28	7	62	15	31	20
28.86	21	16	29	7	63	9	43	16
28.88	27	14	34	6	44	10	27	13
28.9	28	13	32	11	45	11	26	20
28.92	25	21	31	7	51	16	33	20
28.94	31	17	31	5	46	12	27	20
28.96	24	14	28	7	48	11	26	18
28.98	30	20	24	5	38	13	22	13
29	22	19	20	9	35	8	34	18
29.02	28	17	30	5	26	15	43	20
29.04	33	15	30	4	29	7	42	13
29.06	29	12	27	3	36	7	21	12
29.08	37	9	31	3	30	8	31	18
29.1	27	13	34	4	41	13	34	14
29.12	32	14	27	7	43	14	27	21
29.14	24	17	26	1	26	26	34	12
29.16	40	16	28	3	33	7	31	21
29.18	36	20	31	9	37	9	27	14
29.2	37	18	31	6	34	10	35	22
29.22	36	11	37	3	39	8	38	11
29.24	27	19	79	7	37	11	51	11
29.26	25	18	64	3	35	10	45	14
29.28	25	16	65	3	31	9	42	15
29.3	29	16	51	11	43	14	35	16
29.32	33	19	38	13	35	18	43	15
29.34	25	12	54	9	29	17	39	11
29.36	32	18	32	10	28	19	28	17
29.38	32	24	25	7	35	18	40	25
29.4	26	14	23	8	28	17	27	21
29.42	24	13	29	7	27	9	32	24
29.44	29	20	19	10	17	18	25	19
29.46	40	16	19	5	36	6	20	8
29.48	29	13	18	12	33	12	27	14
29.5	24	20	26	9	27	6	34	10
29.52	36	12	28	15	31	12	24	8
29.54	38	19	21	10	29	10	29	9
29.56	32	18	24	13	30	13	27	10
29.58	26	12	29	18	21	4	33	14
29.6	39	11	25	7	33	16	33	10
29.62	39	19	15	3	37	13	38	8
29.64	26	17	33	9	24	14	37	16
29.66	18	11	21	8	33	4	41	12
29.68	14	17	19	9	38	7	34	8
29.7	25	13	24	4	30	23	28	15
29.72	26	8	18	7	20	13	26	21
29.74	24	10	19	5	28	11	23	22
29.76	18	7	20	10	27	15	25	13
29.78	19	11	24	12	23	15	24	15
29.8	19	11	14	5	22	7	17	17
29.82	20	9	16	5	30	14	21	20
29.84	18	12	11	8	32	10	26	14
29.86	20	8	21	6	28	13	19	12
29.88	17	18	14	6	26	11	19	13
29.9	27	11	9	9	22	6	27	14
29.92	19	15	14	5	18	8	17	13
29.94	20	17	18	8	27	3	29	14
29.96	22	11	11	3	26	4	21	7
29.98	31	13	22	4	27	4	26	15
30	28	18	15	6	29	9	28	13
30.02	17	19	18	12	31	11	25	22
30.04	20	13	17	2	19	4	34	10
30.06	23	13	25	5	28	8	19	7
30.08	29	18	21	2	28	4	28	8
30.1	27	17	17	3	23	8	31	11
30.12	20	11	20	2	47	9	29	15
30.14	19	15	22	1	24	15	32	16
30.16	21	11	26	3	29	12	26	19
30.18	16	20	26	5	30	8	34	13
30.2	23	18	28	4	27	8	27	14

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
30.22	21	10	26	5	26	17	24	18
30.24	23	20	27	4	26	14	25	16
30.26	25	18	19	4	30	11	21	4
30.28	20	10	28	6	27	14	33	14
30.3	15	12	17	1	33	11	25	8
30.32	23	23	16	7	23	8	20	9
30.34	28	12	20	3	27	10	19	21
30.36	17	12	20	1	24	11	24	19
30.38	24	12	19	3	20	7	30	15
30.4	27	17	22	5	15	8	16	13
30.42	20	15	20	6	25	11	24	6
30.44	21	18	13	7	16	10	26	6
30.46	19	21	11	6	25	15	18	10
30.48	18	30	16	5	34	14	28	9
30.5	28	43	14	6	20	13	25	14
30.52	13	71	14	1	24	13	23	12
30.54	26	84	21	5	17	14	19	14
30.56	21	86	12	4	23	18	21	16
30.58	29	85	16	3	24	26	28	7
30.6	24	81	16	7	23	31	17	10
30.62	25	56	20	4	24	59	26	6
30.64	25	48	20	2	18	78	22	12
30.66	21	50	9	7	24	58	22	11
30.68	15	37	12	5	25	89	32	9
30.7	15	27	16	6	19	141	21	8
30.72	28	19	17	11	25	190	19	12
30.74	21	16	13	7	15	221	13	12
30.76	11	16	14	10	16	150	16	11
30.78	21	18	23	6	19	166	18	12
30.8	16	13	25	10	25	103	15	12
30.82	18	11	17	13	16	107	28	15
30.84	16	15	19	11	20	84	18	14
30.86	29	12	22	8	24	52	19	13
30.88	20	15	20	4	21	28	26	6
30.9	17	15	17	2	24	13	19	6
30.92	25	15	25	8	22	14	20	13
30.94	27	14	13	2	22	19	30	11
30.96	26	17	24	8	21	17	25	9
30.98	32	13	15	4	20	14	24	11
31	20	8	21	3	25	9	22	13
31.02	32	9	16	6	24	14	25	14
31.04	31	8	18	8	18	14	23	4
31.06	34	17	20	4	29	13	28	11
31.08	20	7	16	5	26	13	27	12
31.1	27	16	21	6	21	4	30	6
31.12	25	15	22	2	23	10	27	13
31.14	25	12	23	4	27	8	20	15
31.16	17	10	18	4	32	9	22	11
31.18	23	14	20	3	26	9	31	11
31.2	14	10	18	4	20	10	24	5
31.22	24	8	20	3	29	13	22	7
31.24	20	11	16	6	26	8	34	7
31.26	18	11	10	2	33	7	21	2
31.28	17	16	13	3	25	5	18	12
31.3	22	12	9	3	19	8	16	12
31.32	23	16	16	1	17	13	23	8
31.34	24	9	20	6	19	7	14	8
31.36	21	14	12	2	20	3	22	11
31.38	25	15	12	8	25	13	18	8
31.4	20	6	18	9	25	9	18	11
31.42	21	11	11	5	21	9	17	11
31.44	21	11	20	3	24	6	20	8
31.46	17	19	21	1	21	8	22	9
31.48	17	3	8	3	27	7	28	9
31.5	22	16	17	6	15	7	20	9
31.52	23	4	15	8	21	7	19	14
31.54	25	9	13	6	31	5	23	13
31.56	22	10	16	7	21	6	22	6
31.58	17	10	25	11	22	4	17	6
31.6	18	11	17	2	23	9	16	9
31.62	23	9	15	3	18	9	27	13
31.64	22	11	12	7	24	5	17	7
31.66	25	14	14	3	26	5	21	14
31.68	16	8	16	6	28	7	18	10
31.7	20	9	17	4	19	5	30	8
31.72	18	12	20	3	27	9	26	8
31.74	28	7	17	3	31	11	23	7
31.76	21	12	25	4	21	9	21	10
31.78	17	9	18	4	25	13	18	4
31.8	22	8	11	1	27	5	26	10
31.82	14	17	17	2	27	9	14	9
31.84	31	10	15	3	27	10	24	7
31.86	14	14	18	3	21	2	19	7
31.88	9	12	13	2	13	8	26	14
31.9	17	14	13	2	26	8	19	14
31.92	20	20	11	5	31	7	23	15
31.94	19	18	9	3	24	9	16	19
31.96	14	22	10	4	23	8	31	16
31.98	19	15	17	4	18	8	28	11

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
32	11	24	17	7	17	6	21	12
32.02	21	8	14	6	17	7	17	11
32.04	21	14	9	6	18	9	8	18
32.06	18	14	9	4	20	9	16	16
32.08	23	14	15	7	18	6	20	5
32.1	10	14	9	5	19	6	25	7
32.12	22	11	14	4	20	5	16	11
32.14	17	3	15	5	20	7	17	13
32.16	20	13	19	6	21	8	25	13
32.18	22	12	16	7	18	7	29	10
32.2	22	15	23	3	18	11	20	8
32.22	25	15	20	1	17	8	20	10
32.24	18	11	22	3	24	5	23	5
32.26	23	8	15	1	17	4	18	9
32.28	19	11	15	1	19	6	20	10
32.3	18	14	14	4	16	9	22	11
32.32	17	10	17	4	15	9	19	15
32.34	19	14	15	2	27	10	21	10
32.36	16	5	13	1	23	8	18	14
32.38	19	7	12	4	21	8	17	9
32.4	16	16	16	7	14	9	20	9
32.42	19	7	15	8	7	10	18	15
32.44	11	10	16	1	17	4	15	11
32.46	20	9	13	3	17	6	21	14
32.48	17	14	12	3	18	7	14	6
32.5	19	5	17	9	17	7	17	9
32.52	19	16	12	2	23	1	24	4
32.54	11	18	16	4	19	13	16	13
32.56	22	21	10	4	14	6	20	5
32.58	19	15	18	4	19	10	25	8
32.6	23	5	20	4	15	5	20	3
32.62	17	6	13	3	20	11	28	10
32.64	16	13	19	4	29	3	18	14
32.66	26	7	18	6	26	9	25	8
32.68	28	16	17	4	17	9	24	11
32.7	17	17	15	4	28	5	20	4
32.72	21	14	17	5	25	9	16	10
32.74	12	10	19	1	27	10	18	11
32.76	13	8	24	4	17	3	28	10
32.78	15	16	14	1	23	12	18	8
32.8	10	11	14	8	23	7	20	8
32.82	20	10	17	1	21	7	22	5
32.84	15	7	8	2	25	9	27	15
32.86	21	10	18	6	20	9	26	10
32.88	25	9	10	6	23	13	13	10
32.9	17	15	13	3	18	6	24	8
32.92	11	3	12	6	12	8	21	8
32.94	14	12	12	2	22	8	20	8
32.96	21	18	15	5	24	7	11	8
32.98	9	12	17	6	16	4	20	5
33	19	21	18	5	12	12	13	11
33.02	14	14	14	4	16	1	9	13
33.04	29	17	23	4	18	7	21	10
33.06	18	10	11	2	28	6	20	12
33.08	20	23	12	3	23	8	21	15
33.1	28	13	11	1	16	4	18	11
33.12	9	12	15	6	14	7	24	7
33.14	21	12	16	5	15	7	17	8
33.16	13	14	24	3	28	4	18	15
33.18	30	18	17	1	24	6	21	10
33.2	16	24	15	6	8	10	28	11
33.22	17	19	15	5	29	15	15	12
33.24	19	11	26	4	18	13	22	8
33.26	21	16	24	3	27	13	17	9
33.28	16	17	31	6	25	9	25	11
33.3	13	16	15	4	24	5	22	12
33.32	18	12	25	5	16	6	18	8
33.34	15	6	20	2	22	6	26	14
33.36	21	17	8	6	15	8	28	12
33.38	20	19	17	6	21	6	19	13
33.4	16	15	20	4	12	12	20	18
33.42	17	14	15	4	17	12	26	19
33.44	22	17	15	7	27	8	32	10
33.46	16	15	16	6	23	11	18	21
33.48	26	17	17	11	22	6	31	17
33.5	15	14	13	8	26	15	32	16
33.52	28	11	17	3	21	13	26	15
33.54	25	17	26	3	19	8	25	19
33.56	19	12	15	8	19	9	22	18
33.58	26	17	13	8	19	12	22	9
33.6	15	11	24	6	16	7	28	12
33.62	24	21	14	3	28	9	27	20
33.64	21	18	18	6	27	10	22	13
33.66	22	21	17	4	27	13	20	18
33.68	18	19	16	4	29	10	31	14
33.7	25	21	14	6	24	10	19	12
33.72	20	20	20	10	20	12	25	19
33.74	26	25	14	3	19	18	32	32
33.76	21	27	16	8	26	14	21	13

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
33.78	29	17	16	10	21	22	27	18
33.8	12	25	21	7	23	12	25	13
33.82	21	22	14	4	22	17	16	17
33.84	21	24	18	3	21	8	22	17
33.86	22	29	26	2	25	14	21	14
33.88	22	16	19	6	26	21	19	24
33.9	24	22	16	6	26	17	32	13
33.92	18	24	20	11	28	15	25	23
33.94	23	11	20	11	27	9	26	39
33.96	20	22	18	9	28	16	28	21
33.98	18	25	22	3	24	10	33	23
34	15	18	24	12	25	17	13	19
34.02	13	19	14	7	23	9	23	19
34.04	21	17	12	9	29	11	31	26
34.06	14	15	20	12	35	20	19	23
34.08	19	24	8	13	22	16	19	24
34.1	18	14	22	12	27	10	22	19
34.12	17	10	18	9	17	14	26	20
34.14	24	24	17	8	29	13	19	17
34.16	27	18	20	5	24	9	20	16
34.18	20	17	18	8	28	10	30	14
34.2	25	17	15	9	19	13	22	16
34.22	19	21	11	8	20	13	24	12
34.24	11	11	16	10	30	15	25	16
34.26	19	20	18	10	17	10	21	7
34.28	20	11	13	7	17	9	31	16
34.3	24	17	24	4	17	4	16	16
34.32	20	21	13	7	23	14	21	19
34.34	17	7	20	8	33	11	14	15
34.36	14	17	22	2	25	13	24	14
34.38	17	19	29	6	25	12	18	23
34.4	24	19	22	7	22	8	24	15
34.42	17	20	28	6	16	10	20	12
34.44	26	15	22	5	17	14	16	19
34.46	18	18	16	3	17	10	23	18
34.48	19	13	14	8	23	12	14	15
34.5	21	14	10	11	22	15	17	12
34.52	19	20	13	10	17	11	11	20
34.54	14	24	20	10	20	12	24	19
34.56	11	26	15	9	12	7	22	15
34.58	10	20	10	10	7	14	17	13
34.6	17	15	19	10	26	7	20	11
34.62	13	19	6	3	15	9	21	13
34.64	16	15	10	10	14	6	15	14
34.66	16	19	18	6	28	11	17	18
34.68	12	15	13	11	17	13	26	17
34.7	21	14	10	6	13	7	14	16
34.72	17	15	13	4	21	10	13	16
34.74	19	19	10	11	16	9	16	13
34.76	14	19	7	7	19	9	18	13
34.78	14	18	11	4	14	9	21	19
34.8	14	17	11	5	16	10	16	17
34.82	24	20	9	7	16	11	20	17
34.84	22	17	22	5	22	9	11	22
34.86	13	21	24	2	18	12	20	13
34.88	17	20	10	6	26	10	12	13
34.9	19	19	10	4	13	8	22	16
34.92	14	21	11	6	25	12	26	9
34.94	19	19	19	2	12	9	22	12
34.96	21	12	18	4	23	13	19	11
34.98	15	18	15	7	24	7	10	14
35	10	15	16	6	28	7	21	15
35.02	12	14	15	6	19	7	19	12
35.04	14	16	14	2	15	10	16	13
35.06	17	14	20	10	13	6	10	9
35.08	21	21	13	5	16	8	23	16
35.1	22	10	17	6	18	8	17	10
35.12	15	16	18	2	16	11	15	8
35.14	21	20	19	5	21	12	20	16
35.16	16	14	14	4	25	7	14	9
35.18	31	16	18	4	12	9	24	14
35.2	34	8	16	5	24	9	25	14
35.22	54	17	29	2	15	6	27	16
35.24	81	12	25	7	27	9	20	15
35.26	87	18	45	4	21	9	37	15
35.28	70	24	80	3	27	15	51	8
35.3	46	21	85	7	29	8	56	10
35.32	50	27	107	6	62	15	85	11
35.34	59	27	80	4	75	27	53	15
35.36	46	44	75	6	76	35	38	20
35.38	29	37	68	6	65	24	43	32
35.4	26	45	74	7	35	23	57	29
35.42	25	21	66	9	51	43	51	41
35.44	27	22	50	7	50	23	36	46
35.46	21	20	41	11	49	37	37	37
35.48	20	24	30	7	47	28	17	37
35.5	20	27	21	12	23	22	23	30
35.52	16	18	20	11	17	24	23	28
35.54	12	19	24	23	27	16	15	27

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
35.56	19	16	14	27	10	16	17	23
35.58	22	17	15	32	16	17	9	20
35.6	18	12	16	50	14	15	16	13
35.62	18	16	15	42	13	11	19	14
35.64	18	16	16	43	16	12	26	20
35.66	24	15	23	47	14	13	20	12
35.68	12	17	15	36	20	6	15	14
35.7	15	19	16	39	16	8	14	15
35.72	6	14	17	15	19	14	19	11
35.74	20	11	17	16	20	8	17	6
35.76	12	11	15	22	27	10	17	10
35.78	21	16	17	9	17	13	26	14
35.8	15	13	19	13	14	5	18	7
35.82	12	16	14	8	17	13	16	10
35.84	16	13	9	7	16	9	18	9
35.86	11	17	18	9	14	9	11	24
35.88	19	15	16	7	18	16	17	10
35.9	20	22	13	13	19	9	22	9
35.92	16	11	19	7	21	9	14	16
35.94	10	17	19	5	21	10	18	16
35.96	9	8	16	5	18	10	22	15
35.98	21	18	16	3	21	10	22	22
36	11	21	18	6	18	9	25	17
36.02	17	13	21	6	16	6	18	18
36.04	6	9	7	7	16	9	15	11
36.06	21	11	17	4	12	11	13	5
36.08	18	18	14	5	11	8	16	19
36.1	14	12	12	9	15	8	15	14
36.12	14	16	9	6	11	5	19	11
36.14	18	15	18	2	18	10	27	17
36.16	20	12	12	6	11	17	12	16
36.18	17	14	14	4	18	5	19	13
36.2	16	20	15	8	23	7	17	15
36.22	13	18	19	7	25	10	17	11
36.24	10	16	15	9	17	10	26	10
36.26	13	12	13	5	23	11	21	10
36.28	20	15	8	11	19	7	10	13
36.3	16	13	13	3	7	14	20	19
36.32	13	18	11	4	14	23	13	18
36.34	18	8	11	6	12	13	12	16
36.36	18	15	12	10	22	13	26	15
36.38	19	16	9	6	18	13	15	10
36.4	18	18	13	8	21	9	14	10
36.42	15	18	15	7	31	9	17	13
36.44	14	17	18	8	14	6	20	18
36.46	13	12	15	3	30	7	22	14
36.48	18	21	22	5	14	6	20	19
36.5	12	9	6	4	10	12	15	8
36.52	15	22	14	5	22	7	20	9
36.54	12	10	13	6	14	13	24	21
36.56	16	21	14	4	19	11	15	8
36.58	15	9	11	13	16	14	17	13
36.6	12	19	12	6	16	18	17	16
36.62	23	16	17	9	20	9	21	14
36.64	18	18	10	8	11	12	24	13
36.66	16	12	9	2	19	11	19	17
36.68	10	21	14	8	12	13	19	14
36.7	16	15	16	7	17	7	20	12
36.72	10	22	11	8	11	11	8	14
36.74	18	8	8	7	19	7	17	8
36.76	15	20	13	17	11	6	17	12
36.78	9	19	13	11	18	12	12	19
36.8	14	16	7	16	18	10	11	22
36.82	14	10	10	17	17	5	12	11
36.84	16	19	10	11	9	6	14	8
36.86	16	7	13	11	12	13	14	10
36.88	10	11	8	6	17	5	17	9
36.9	13	12	9	10	19	6	10	13
36.92	16	13	17	8	9	9	18	10
36.94	11	11	8	6	13	5	21	19
36.96	18	14	11	5	17	11	15	13
36.98	17	22	15	7	10	9	21	7
37	17	23	14	3	23	8	17	18
37.02	14	12	10	2	17	4	13	9
37.04	10	8	9	1	20	7	18	9
37.06	6	6	13	3	16	12	26	9
37.08	18	16	16	4	11	4	17	11
37.1	7	9	12	2	19	6	15	4
37.12	13	15	15	7	12	7	19	14
37.14	15	11	10	4	13	6	7	15
37.16	14	15	6	2	20	7	19	17
37.18	8	12	13	5	10	8	17	12
37.2	25	17	10	1	20	10	15	11
37.22	20	10	18	3	16	9	19	15
37.24	21	14	20	5	19	7	15	16
37.26	16	10	11	5	23	9	25	12
37.28	10	15	16	5	12	8	17	12
37.3	18	12	17	1	12	12	23	15
37.32	19	15	17	4	18	13	17	13

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
37.34	10	18	19	5	9	8	14	11
37.36	8	17	17	5	21	7	20	13
37.38	13	12	14	9	11	16	14	10
37.4	20	18	12	5	17	8	18	16
37.42	11	20	11	3	12	12	24	7
37.44	22	16	13	8	14	5	20	19
37.46	18	22	22	9	17	13	18	16
37.48	18	17	6	3	11	7	29	21
37.5	11	14	16	4	16	11	27	11
37.52	13	17	15	3	9	4	17	11
37.54	9	15	18	9	18	19	16	12
37.56	17	15	16	7	20	14	18	7
37.58	13	13	9	6	12	5	20	10
37.6	20	11	12	4	18	7	13	10
37.62	13	14	13	5	19	11	15	13
37.64	14	11	13	2	11	11	16	12
37.66	14	9	15	6	23	10	16	12
37.68	18	11	18	8	17	15	23	14
37.7	18	13	13	5	25	5	16	9
37.72	14	9	9	3	20	14	17	11
37.74	20	10	14	4	27	6	16	9
37.76	13	13	12	3	18	11	21	15
37.78	6	12	13	8	17	8	14	14
37.8	22	10	16	2	21	9	13	7
37.82	13	10	18	5	19	12	13	15
37.84	11	13	11	3	11	8	13	6
37.86	18	8	10	9	21	8	14	7
37.88	19	13	15	5	19	8	15	16
37.9	7	12	14	7	16	8	18	14
37.92	16	12	12	3	16	6	17	12
37.94	10	8	12	3	14	13	15	11
37.96	21	11	15	7	18	6	11	7
37.98	16	9	14	3	19	16	15	7
38	7	15	12	2	18	5	11	18
38.02	16	10	16	2	13	6	16	10
38.04	14	10	15	14	12	8	13	8
38.06	15	10	7	3	10	9	19	7
38.08	21	12	16	3	13	8	22	13
38.1	16	15	19	10	11	9	9	12
38.12	26	11	13	2	16	6	15	6
38.14	51	11	23	5	10	9	12	12
38.16	66	11	25	3	14	10	20	11
38.18	56	15	33	8	24	11	28	11
38.2	44	14	56	3	22	11	42	13
38.22	31	18	84	6	28	16	61	6
38.24	44	15	100	2	40	18	59	17
38.26	36	29	72	3	37	16	64	17
38.28	36	43	57	5	46	18	42	15
38.3	49	37	45	5	45	17	41	14
38.32	29	35	50	6	32	17	41	30
38.34	21	30	53	6	28	14	44	29
38.36	19	17	32	9	28	25	36	23
38.38	16	23	41	5	33	38	25	24
38.4	14	34	18	7	38	33	21	24
38.42	14	17	14	7	27	15	22	13
38.44	13	10	16	7	20	15	29	23
38.46	12	5	17	20	19	6	16	19
38.48	15	15	8	22	17	13	12	22
38.5	11	9	16	16	17	14	9	17
38.52	13	13	15	18	16	12	15	17
38.54	12	7	16	31	16	8	15	7
38.56	21	10	17	17	13	10	15	13
38.58	12	18	14	16	10	7	18	16
38.6	14	14	16	19	14	13	15	10
38.62	16	11	14	11	11	13	13	12
38.64	7	16	17	8	15	8	15	14
38.66	12	14	8	10	18	8	18	13
38.68	15	17	18	15	10	5	13	6
38.7	13	11	14	10	14	13	22	11
38.72	13	14	10	8	18	8	16	3
38.74	12	10	12	8	5	3	23	10
38.76	17	11	22	4	21	12	12	11
38.78	11	9	8	6	8	6	16	7
38.8	14	13	7	8	12	9	4	8
38.82	21	10	15	5	18	9	20	8
38.84	18	11	16	6	15	3	13	7
38.86	18	12	17	4	15	8	17	6
38.88	16	12	7	3	13	5	16	10
38.9	18	8	7	5	11	7	9	17
38.92	18	15	15	4	23	5	21	5
38.94	21	15	24	5	14	10	18	9
38.96	29	11	16	5	15	7	17	9
38.98	36	11	25	1	13	2	19	10
39	57	11	27	1	10	14	17	12
39.02	43	9	42	2	18	6	26	7
39.04	31	13	36	2	15	15	38	12
39.06	34	18	52	5	24	7	22	9
39.08	34	17	62	3	32	8	29	6
39.1	37	17	28	1	31	13	33	15

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
39.12	27	19	35	2	39	12	19	19
39.14	22	20	23	8	23	19	21	18
39.16	22	19	31	3	22	10	25	30
39.18	15	13	44	8	18	13	21	20
39.2	15	14	29	5	29	13	20	17
39.22	9	14	15	5	30	12	18	13
39.24	12	16	16	7	21	20	14	11
39.26	15	10	17	10	19	15	16	10
39.28	14	11	8	10	16	13	11	18
39.3	13	13	18	14	25	12	20	21
39.32	9	10	7	21	12	11	16	10
39.34	8	10	7	13	12	7	17	13
39.36	12	8	15	11	11	7	13	11
39.38	21	10	6	15	15	12	14	15
39.4	12	15	15	6	16	8	10	12
39.42	13	12	12	15	23	6	19	6
39.44	17	9	12	13	16	8	15	17
39.46	17	9	11	7	19	4	22	4
39.48	21	9	17	7	13	5	17	9
39.5	21	11	7	7	13	7	16	8
39.52	11	11	14	7	15	6	8	7
39.54	10	12	12	5	18	6	12	16
39.56	13	12	13	4	15	15	15	5
39.58	13	10	9	2	19	8	12	16
39.6	8	12	10	4	11	6	10	14
39.62	11	10	11	4	14	7	19	12
39.64	11	5	8	5	12	13	13	15
39.66	9	14	16	2	12	4	19	21
39.68	17	11	6	8	16	9	15	9
39.7	10	6	9	2	16	11	17	5
39.72	12	10	15	1	10	7	10	13
39.74	11	8	17	1	18	5	19	11
39.76	20	7	15	4	16	8	13	7
39.78	13	13	11	3	14	8	14	9
39.8	12	6	19	7	15	7	18	8
39.82	12	10	12	1	8	13	17	9
39.84	12	8	17	7	11	7	15	7
39.86	12	11	13	1	10	7	16	9
39.88	8	15	10	5	13	8	10	5
39.9	8	8	8	3	18	9	19	6
39.92	18	13	8	6	13	9	19	9
39.94	16	9	22	3	14	10	14	7
39.96	11	7	17	3	11	8	10	14
39.98	19	13	12	6	14	4	11	6
40	22	20	10	2	12	5	18	13
40.02	15	15	11	6	10	12	15	5
40.04	19	5	13	5	17	7	25	6
40.06	9	11	14	3	15	9	12	12
40.08	14	15	8	2	11	7	21	13
40.1	10	7	20	8	13	7	13	10
40.12	21	7	13	3	12	8	10	10
40.14	11	9	9	5	20	9	15	13
40.16	11	7	11	3	22	6	13	7
40.18	22	13	13	8	8	6	16	10
40.2	15	12	11	3	11	5	14	13
40.22	13	12	9	4	13	6	18	12
40.24	16	16	14	2	14	10	19	4
40.26	15	9	7	5	10	10	12	7
40.28	21	7	11	4	6	6	22	15
40.3	10	14	11	5	10	12	12	16
40.32	11	6	10	5	12	10	12	13
40.34	18	14	14	3	15	6	11	5
40.36	16	7	10	1	16	9	17	8
40.38	17	17	11	3	20	9	24	13
40.4	19	10	13	3	15	6	19	15
40.42	17	9	16	3	15	10	22	8
40.44	20	8	14	4	11	9	18	6
40.46	22	16	22	5	19	5	22	11
40.48	25	12	10	3	14	13	16	6
40.5	23	15	15	2	15	16	24	4
40.52	20	9	25	2	17	9	17	9
40.54	16	12	15	4	12	6	20	17
40.56	29	21	12	2	13	9	25	8
40.58	24	10	16	4	14	9	22	7
40.6	21	15	17	4	16	6	17	5
40.62	22	14	12	5	17	8	21	14
40.64	19	10	15	15	16	9	26	13
40.66	12	16	19	3	17	6	17	12
40.68	14	11	21	18	15	13	10	5
40.7	12	9	16	23	14	12	17	11
40.72	16	4	11	49	15	8	17	6
40.74	16	16	16	39	18	14	15	11
40.76	19	14	16	25	10	9	11	8
40.78	17	11	18	28	16	8	11	7
40.8	13	12	5	20	10	7	14	10
40.82	9	14	14	40	11	11	16	8
40.84	12	11	8	14	19	12	19	9
40.86	14	10	10	24	14	8	13	5
40.88	12	7	17	16	19	14	20	4

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
40.9	12	8	6	11	11	15	18	10
40.92	17	14	9	13	17	8	11	8
40.94	14	12	10	6	11	8	13	12
40.96	22	9	9	9	10	7	17	15
40.98	9	10	14	9	22	6	16	9
41	25	6	8	6	17	11	21	4
41.02	19	14	16	7	23	9	22	10
41.04	16	9	6	3	18	8	15	10
41.06	15	14	18	3	15	5	14	10
41.08	23	13	19	3	15	8	18	9
41.1	24	14	13	4	12	9	13	12
41.12	40	16	19	5	16	10	22	15
41.14	46	14	27	5	23	8	29	9
41.16	65	18	37	7	15	4	31	14
41.18	71	16	52	7	16	7	30	7
41.2	37	17	67	4	26	10	40	15
41.22	37	16	69	5	25	13	52	14
41.24	36	31	81	3	32	22	40	15
41.26	48	29	63	5	42	24	40	17
41.28	49	22	38	5	44	20	35	19
41.3	33	23	47	5	38	23	25	28
41.32	17	21	57	3	19	22	39	31
41.34	12	20	48	4	31	28	28	33
41.36	24	15	43	5	43	23	25	27
41.38	17	17	26	4	30	20	26	25
41.4	20	20	23	9	20	19	27	24
41.42	15	15	27	14	17	19	26	19
41.44	18	23	22	17	30	22	18	25
41.46	18	19	18	9	21	23	13	24
41.48	21	9	28	26	23	7	16	23
41.5	16	12	20	18	15	14	13	14
41.52	9	14	21	20	21	11	18	13
41.54	23	7	23	21	25	17	15	11
41.56	14	14	18	16	11	9	7	12
41.58	11	11	9	8	20	8	13	8
41.6	14	11	14	18	18	13	19	9
41.62	10	9	9	15	18	8	19	8
41.64	13	14	11	12	16	13	10	10
41.66	18	9	15	13	17	11	13	13
41.68	16	9	16	13	13	14	12	5
41.7	18	11	14	13	13	9	12	13
41.72	13	16	14	12	20	8	15	7
41.74	9	11	15	6	20	7	14	7
41.76	15	10	10	7	20	9	11	13
41.78	13	12	15	6	9	7	12	10
41.8	11	7	17	10	18	4	11	17
41.82	14	12	21	4	11	5	13	8
41.84	17	17	12	5	20	4	13	6
41.86	15	12	10	6	11	7	20	15
41.88	15	8	12	4	16	10	13	7
41.9	16	13	16	3	18	14	19	7
41.92	15	15	13	7	14	1	17	10
41.94	19	5	19	5	19	2	21	8
41.96	14	11	13	5	12	3	14	7
41.98	7	12	12	2	20	6	24	5
42	9	11	14	10	15	8	14	10
42.02	9	14	7	7	15	4	18	7
42.04	13	10	8	5	16	3	13	9
42.06	19	10	12	4	16	11	11	11
42.08	10	18	11	3	18	8	18	12
42.1	11	8	10	3	12	4	17	9
42.12	14	13	19	3	12	10	18	9
42.14	17	9	15	3	17	7	11	6
42.16	10	13	9	6	15	6	12	2
42.18	13	10	10	3	15	5	13	12
42.2	17	5	15	4	16	5	9	6
42.22	12	13	10	2	12	7	15	5
42.24	9	13	15	6	16	8	15	10
42.26	13	12	18	6	17	4	18	8
42.28	4	13	10	1	14	9	14	7
42.3	7	12	6	1	13	7	18	11
42.32	13	11	9	2	12	5	8	10
42.34	12	11	19	2	11	6	12	2
42.36	7	13	7	1	19	17	14	5
42.38	15	8	10	7	19	8	15	12
42.4	15	11	9	1	9	8	17	12
42.42	11	10	15	3	19	10	20	10
42.44	10	8	10	2	13	11	19	7
42.46	10	18	14	2	17	5	19	9
42.48	13	10	20	1	16	7	16	7
42.5	15	18	9	7	14	9	14	9
42.52	10	5	13	1	12	6	13	7
42.54	11	10	10	3	15	7	16	3
42.56	8	6	13	2	15	10	12	9
42.58	7	14	7	2	22	6	16	8
42.6	15	5	10	1	15	9	11	4
42.62	15	7	7	2	19	10	18	9
42.64	16	22	11	7	21	5	20	9
42.66	10	10	13	6	21	7	13	2

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
42.68	19	10	7	4	13	2	16	5
42.7	11	12	15	8	17	8	16	10
42.72	10	6	10	5	12	6	14	6
42.74	6	5	9	6	13	4	11	4
42.76	12	13	13	3	15	8	24	4
42.78	14	8	15	1	17	6	13	5
42.8	10	13	13	4	17	4	15	6
42.82	7	10	12	4	17	9	12	5
42.84	12	10	12	8	9	5	14	5
42.86	9	7	14	4	20	8	11	9
42.88	17	10	7	6	17	7	15	11
42.9	7	13	8	1	13	8	9	13
42.92	17	14	10	1	17	8	16	5
42.94	12	10	9	1	18	6	12	7
42.96	11	10	13	5	10	6	15	6
42.98	11	13	15	2	16	3	10	6
43	14	18	14	4	13	5	7	8
43.02	11	10	16	10	12	5	13	8
43.04	8	13	10	2	20	5	11	8
43.06	10	9	11	5	15	7	8	8
43.08	15	11	7	3	20	5	10	6
43.1	11	13	10	7	14	7	10	7
43.12	16	17	13	4	17	7	12	10
43.14	15	20	8	3	16	9	18	6
43.16	19	3	15	6	15	12	12	7
43.18	13	11	13	5	9	4	12	10
43.2	12	8	14	3	14	10	12	10
43.22	22	8	8	2	16	6	8	13
43.24	17	15	11	4	16	5	12	9
43.26	12	8	7	6	16	6	18	5
43.28	6	8	6	6	12	4	15	6
43.3	15	8	8	4	13	5	12	8
43.32	14	5	8	3	15	10	15	11
43.34	11	5	8	4	12	7	23	7
43.36	17	7	14	2	10	4	7	8
43.38	16	9	11	3	10	7	11	8
43.4	12	8	11	4	10	6	12	13
43.42	19	6	8	1	15	8	11	9
43.44	11	15	13	1	16	10	14	6
43.46	12	12	6	3	13	5	20	7
43.48	18	10	11	3	15	7	17	6
43.5	17	7	7	2	8	5	20	15
43.52	11	9	12	1	16	6	14	5
43.54	11	9	11	5	11	5	7	9
43.56	15	7	14	4	17	6	17	7
43.58	10	6	8	5	11	2	16	11
43.6	15	14	14	3	11	8	10	10
43.62	7	7	18	4	16	3	6	7
43.64	19	10	12	2	7	6	21	3
43.66	19	9	12	5	12	9	8	10
43.68	16	14	9	6	12	3	19	7
43.7	12	13	10	3	15	9	12	12
43.72	10	14	18	3	12	9	20	7
43.74	17	10	17	7	17	8	12	12
43.76	13	15	13	1	11	11	12	9
43.78	9	6	14	2	13	15	15	12
43.8	11	13	20	6	13	8	10	10
43.82	10	11	16	9	15	9	11	9
43.84	19	10	18	11	12	7	16	16
43.86	13	12	15	7	12	7	9	9
43.88	18	19	13	8	20	7	22	7
43.9	11	9	8	4	10	6	10	10
43.92	16	11	19	7	13	8	21	16
43.94	9	18	6	7	17	12	22	9
43.96	12	11	16	4	18	12	20	11
43.98	19	11	7	5	14	20	19	13
44	14	9	16	4	12	9	15	7
44.02	15	9	8	3	19	12	16	9
44.04	6	22	8	3	12	14	14	10
44.06	18	16	16	3	18	9	13	8
44.08	9	16	8	4	15	14	13	13
44.1	16	17	16	2	19	14	17	19
44.12	17	12	13	3	17	12	14	10
44.14	12	21	15	3	14	6	15	22
44.16	10	13	13	5	9	13	11	23
44.18	18	12	12	4	18	13	18	17
44.2	14	33	18	5	14	11	9	17
44.22	13	20	17	10	12	7	16	11
44.24	23	34	5	6	22	14	18	13
44.26	13	75	15	5	19	17	15	13
44.28	10	52	9	7	16	16	11	20
44.3	12	71	13	5	20	43	6	18
44.32	15	63	17	8	14	43	9	9
44.34	15	64	6	7	18	45	18	23
44.36	12	43	14	4	14	61	13	22
44.38	13	44	12	3	16	24	9	20
44.4	13	40	11	8	11	45	15	20
44.42	14	49	18	7	17	43	11	14
44.44	24	46	14	6	13	48	20	14

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
44.46	22	30	21	5	23	49	9	21
44.48	29	15	12	17	13	32	16	12
44.5	48	26	18	11	27	35	22	13
44.52	38	24	20	11	20	32	26	11
44.54	28	19	42	11	16	20	35	14
44.56	20	19	33	11	18	27	31	8
44.58	19	16	46	11	35	16	37	18
44.6	23	22	38	13	33	27	22	20
44.62	36	24	33	5	37	26	20	19
44.64	21	26	24	6	29	24	14	29
44.66	18	25	23	7	29	16	34	25
44.68	12	19	22	6	21	12	32	27
44.7	21	17	29	8	27	21	24	25
44.72	20	23	21	12	31	34	20	18
44.74	14	20	15	12	22	14	10	12
44.76	14	15	16	7	19	19	21	11
44.78	12	16	21	21	12	21	18	19
44.8	19	22	16	15	14	19	17	14
44.82	13	4	16	26	19	13	8	15
44.84	13	8	10	18	16	10	16	14
44.86	14	12	14	20	17	13	22	9
44.88	17	12	9	20	9	10	18	11
44.9	20	10	10	17	16	11	10	14
44.92	10	9	12	24	11	5	16	11
44.94	14	17	12	7	18	7	19	10
44.96	18	8	11	13	13	8	17	11
44.98	12	9	7	13	14	8	10	14
45	14	17	16	14	15	8	13	6
45.02	17	10	9	10	13	11	24	8
45.04	9	12	6	6	10	3	18	16
45.06	9	11	14	9	13	8	13	12
45.08	13	11	10	5	17	14	7	10
45.1	15	5	11	10	15	9	14	4
45.12	15	12	9	8	17	11	11	6
45.14	14	7	10	1	13	12	13	11
45.16	13	7	10	11	23	9	19	4
45.18	13	9	21	2	12	8	9	8
45.2	16	19	8	6	9	4	10	8
45.22	14	10	8	5	18	7	11	10
45.24	14	5	11	4	13	6	17	5
45.26	14	10	15	4	9	5	10	6
45.28	13	4	8	8	13	6	12	8
45.3	11	11	6	3	18	1	21	9
45.32	15	10	7	4	11	1	18	2
45.34	12	14	15	4	13	8	12	6
45.36	19	14	16	4	12	10	10	8
45.38	12	5	10	3	19	7	12	11
45.4	18	7	9	7	8	9	5	8
45.42	11	11	10	3	11	4	12	5
45.44	10	9	13	3	9	4	10	5
45.46	9	15	12	5	12	6	14	7
45.48	16	9	11	4	13	8	13	8
45.5	10	4	9	6	13	7	11	8
45.52	12	8	9	5	10	4	10	8
45.54	14	9	12	7	19	4	8	11
45.56	10	8	11	1	15	7	13	9
45.58	9	10	6	1	11	6	16	7
45.6	12	9	7	6	10	8	9	9
45.62	10	8	19	7	17	2	14	4
45.64	12	12	9	3	11	8	15	8
45.66	11	9	16	3	13	8	17	9
45.68	15	10	11	6	19	4	19	4
45.7	16	6	8	3	7	4	14	7
45.72	17	8	11	2	14	5	10	10
45.74	8	9	9	5	10	9	12	4
45.76	11	11	14	3	22	7	22	8
45.78	7	7	12	5	13	10	6	7
45.8	14	15	18	3	12	9	15	10
45.82	16	8	9	3	9	6	11	5
45.84	14	7	13	6	6	6	11	9
45.86	19	6	20	3	15	12	15	5
45.88	15	13	15	2	11	4	14	7
45.9	13	9	12	2	11	9	20	6
45.92	10	12	9	7	13	7	13	10
45.94	19	12	12	1	21	13	13	4
45.96	18	10	12	6	15	11	15	10
45.98	11	4	5	6	14	9	15	11
46	11	11	9	4	8	6	14	6
46.02	12	13	11	5	28	10	19	9
46.04	13	8	11	4	11	9	17	3
46.06	15	14	13	3	11	6	12	8
46.08	16	6	15	3	16	6	10	11
46.1	14	5	8	9	7	3	13	14
46.12	10	10	10	4	12	11	12	5
46.14	18	10	15	6	12	5	19	11
46.16	10	14	9	7	10	9	16	2
46.18	10	8	11	5	18	4	16	7
46.2	12	7	15	2	20	6	5	5
46.22	14	9	18	4	18	6	12	8

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
46.24	9	9	12	3	9	5	11	7
46.26	14	13	15	2	16	9	14	11
46.28	16	20	16	2	13	5	16	10
46.3	14	11	9	6	5	7	11	7
46.32	15	16	14	1	14	10	14	14
46.34	14	8	15	4	10	4	12	7
46.36	12	13	13	2	11	5	10	12
46.38	12	11	12	4	19	11	15	7
46.4	5	11	15	6	15	7	14	13
46.42	19	9	16	2	19	7	11	4
46.44	15	13	7	7	13	8	14	13
46.46	7	11	16	2	12	10	15	8
46.48	10	8	5	9	13	5	9	13
46.5	10	13	11	3	12	4	9	6
46.52	14	12	6	3	21	9	21	8
46.54	11	14	12	6	15	2	20	12
46.56	10	9	10	9	16	2	15	6
46.58	15	13	11	3	17	7	11	5
46.6	14	9	6	3	11	4	22	7
46.62	12	10	16	3	8	5	5	4
46.64	13	6	2	1	14	2	13	11
46.66	13	13	11	5	16	10	25	13
46.68	14	12	6	4	14	9	15	2
46.7	13	10	11	5	20	7	13	3
46.72	14	8	8	6	17	10	16	12
46.74	10	16	16	6	6	13	12	7
46.76	12	9	11	4	18	8	10	16
46.78	7	10	12	9	17	6	13	8
46.8	15	8	15	4	17	8	16	11
46.82	10	10	15	4	10	7	11	10
46.84	10	11	12	3	10	11	16	16
46.86	11	11	3	9	11	9	13	8
46.88	10	12	16	4	13	7	20	11
46.9	17	15	10	5	17	5	6	9
46.92	8	12	14	5	10	8	8	5
46.94	20	12	12	5	13	6	15	16
46.96	11	11	17	3	8	7	17	7
46.98	13	10	21	6	17	9	13	12
47	9	7	22	1	14	9	10	9
47.02	12	8	17	3	16	10	10	8
47.04	14	11	19	4	12	11	16	9
47.06	17	9	22	6	17	4	16	9
47.08	19	18	28	4	12	11	12	7
47.1	16	9	19	4	18	5	10	13
47.12	7	15	17	6	10	8	21	9
47.14	9	11	18	9	12	11	14	1
47.16	16	9	20	5	7	5	10	4
47.18	8	11	13	3	12	5	15	5
47.2	17	14	17	7	10	6	14	9
47.22	4	17	15	3	7	8	15	9
47.24	9	10	13	9	15	4	6	11
47.26	14	10	8	5	19	14	16	7
47.28	8	10	14	10	18	4	19	6
47.3	10	9	9	10	9	10	15	8
47.32	14	8	6	11	14	9	15	11
47.34	13	6	13	19	15	9	10	10
47.36	10	10	9	17	14	5	14	5
47.38	18	11	11	24	16	12	11	8
47.4	9	9	9	26	14	3	11	9
47.42	8	10	12	23	14	4	19	8
47.44	9	7	11	21	12	7	16	7
47.46	10	12	12	10	9	7	9	6
47.48	6	11	12	14	14	4	14	4
47.5	14	8	15	6	14	5	15	10
47.52	14	4	16	15	15	8	16	8
47.54	9	8	15	12	9	4	10	10
47.56	11	12	11	8	11	6	9	6
47.58	12	10	10	4	9	6	11	7
47.6	10	8	17	7	12	6	14	5
47.62	15	5	13	2	17	3	15	6
47.64	7	16	15	10	11	7	12	8
47.66	15	6	15	4	16	9	11	7
47.68	11	5	9	5	15	10	15	12
47.7	13	4	9	3	11	10	12	7
47.72	11	16	15	3	15	4	15	6
47.74	15	12	9	7	18	6	12	2
47.76	9	11	21	3	9	10	17	11
47.78	6	8	22	4	9	8	15	7
47.8	15	9	14	4	6	10	11	5
47.82	8	11	13	3	12	10	14	6
47.84	16	9	11	5	20	9	15	5
47.86	15	7	11	1	18	3	11	6
47.88	11	17	8	3	13	7	14	5
47.9	19	15	14	4	11	8	13	7
47.92	21	5	15	1	17	7	11	4
47.94	16	10	21	5	14	11	14	9
47.96	8	12	15	3	15	6	17	1
47.98	18	8	15	2	16	5	20	7
48	11	7	21	5	18	9	18	11

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
48.02	16	13	17	8	17	8	8	5
48.04	15	13	14	4	15	8	10	11
48.06	17	9	15	5	11	9	17	12
48.08	13	9	12	6	12	6	13	8
48.1	9	15	14	3	12	9	13	7
48.12	10	12	18	3	10	15	16	7
48.14	18	16	8	3	15	13	18	5
48.16	6	16	7	3	13	9	10	10
48.18	18	4	10	2	21	5	14	5
48.2	18	11	3	3	8	3	18	5
48.22	9	3	16	6	11	4	17	7
48.24	17	7	17	14	13	6	12	9
48.26	6	5	4	6	19	7	11	9
48.28	13	7	11	6	13	3	11	8
48.3	11	11	13	6	15	9	11	7
48.32	20	8	12	5	11	6	10	4
48.34	17	7	9	4	15	8	24	3
48.36	12	4	16	6	11	9	15	7
48.38	17	8	18	3	10	8	7	10
48.4	21	9	13	6	15	8	16	8
48.42	15	11	8	6	18	3	16	5
48.44	13	7	15	5	16	6	10	3
48.46	10	7	15	3	13	3	16	6
48.48	13	12	11	3	12	4	22	6
48.5	18	10	17	3	18	6	16	4
48.52	12	9	11	3	11	10	15	8
48.54	14	11	14	3	12	8	12	7
48.56	14	6	15	3	15	12	19	8
48.58	17	8	20	7	17	6	16	9
48.6	14	7	19	4	13	16	20	12
48.62	18	6	22	5	16	5	27	7
48.64	24	11	32	4	18	6	17	3
48.66	25	8	16	3	29	10	16	11
48.68	10	7	19	7	24	12	26	16
48.7	24	8	18	2	21	8	19	13
48.72	20	13	27	6	16	10	21	3
48.74	24	7	24	5	24	11	14	11
48.76	19	10	19	6	16	12	11	10
48.78	32	9	25	6	14	13	22	6
48.8	47	4	31	6	15	11	20	9
48.82	90	11	15	8	15	10	32	10
48.84	116	10	35	10	16	15	26	8
48.86	107	16	80	15	26	12	43	4
48.88	91	13	117	12	32	11	66	22
48.9	46	26	181	10	42	28	101	15
48.92	41	16	159	9	64	31	64	18
48.94	40	40	125	8	70	34	66	25
48.96	66	35	76	7	70	29	48	27
48.98	64	26	65	11	60	45	33	29
49	62	39	61	10	42	37	45	41
49.02	39	23	93	9	36	36	55	51
49.04	27	14	87	14	26	42	48	54
49.06	16	20	83	21	42	36	53	35
49.08	12	33	68	21	49	39	45	46
49.1	18	27	46	26	33	34	37	31
49.12	18	18	27	41	39	18	14	36
49.14	10	17	14	41	28	21	22	32
49.16	14	15	15	45	18	36	19	26
49.18	16	9	10	65	13	18	20	30
49.2	14	12	13	55	21	19	13	19
49.22	15	9	23	49	18	23	18	30
49.24	11	15	12	39	13	9	12	20
49.26	22	18	15	40	12	10	21	12
49.28	22	6	11	34	14	10	16	10
49.3	13	12	18	46	15	3	18	8
49.32	23	9	12	24	15	10	15	12
49.34	19	8	18	19	18	15	12	5
49.36	18	7	17	29	11	8	11	7
49.38	28	12	17	15	11	8	13	9
49.4	22	10	15	10	11	12	17	9
49.42	17	7	20	6	16	11	21	12
49.44	9	9	17	7	19	15	18	13
49.46	16	10	18	8	22	14	11	17
49.48	15	8	19	6	10	14	17	13
49.5	22	14	15	5	19	10	17	9
49.52	20	5	24	5	20	8	17	15
49.54	18	10	22	5	15	18	22	12
49.56	14	10	28	6	16	17	28	20
49.58	16	11	19	8	19	17	22	10
49.6	17	11	9	4	21	10	20	11
49.62	12	12	17	4	15	11	17	16
49.64	8	16	12	5	11	13	10	13
49.66	15	6	16	6	20	17	14	14
49.68	14	9	12	6	8	13	16	16
49.7	19	12	17	4	13	19	18	11
49.72	7	7	14	6	14	10	17	10
49.74	13	16	14	4	14	14	13	11
49.76	8	12	19	7	15	14	12	5
49.78	12	11	6	5	15	12	18	8

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
49.8	23	4	9	5	7	7	14	6
49.82	13	12	12	6	13	6	10	12
49.84	21	7	9	3	18	5	18	17
49.86	9	13	7	8	10	3	18	4
49.88	11	9	6	6	20	9	15	10
49.9	7	5	15	6	20	6	13	12
49.92	18	9	16	6	14	8	25	11
49.94	13	13	8	7	11	8	18	11
49.96	18	6	26	8	19	8	20	7
49.98	5	5	16	4	15	15	5	9
50	11	8	13	7	20	13	18	7
50.02	9	8	17	7	23	5	19	16
50.04	14	12	21	1	17	4	16	6
50.06	13	12	15	1	18	7	12	7
50.08	11	8	20	4	19	3	17	13
50.1	15	11	17	5	18	6	13	9
50.12	13	7	18	5	19	5	14	6
50.14	12	5	22	5	12	2	13	7
50.16	18	10	16	4	21	5	12	7
50.18	10	11	15	3	14	15	12	5
50.2	15	10	13	4	20	12	19	6
50.22	9	5	15	5	14	9	17	12
50.24	6	5	13	4	10	6	13	9
50.26	9	6	7	4	20	9	11	6
50.28	20	11	13	9	16	7	12	1
50.3	9	9	12	5	17	7	12	4
50.32	11	5	7	3	12	14	9	7
50.34	22	7	13	8	11	8	11	7
50.36	8	12	9	4	16	5	12	9
50.38	10	10	7	4	9	4	8	2
50.4	8	5	13	2	11	4	17	6
50.42	9	8	7	3	13	13	10	6
50.44	9	6	8	1	11	13	11	6
50.46	11	8	13	3	16	8	16	7
50.48	12	12	11	5	14	7	12	3
50.5	14	7	10	7	12	5	12	9
50.52	13	6	14	4	9	7	10	2
50.54	13	7	9	4	17	5	8	8
50.56	9	6	8	6	15	8	8	6
50.58	11	6	7	2	6	7	10	3
50.6	14	4	11	5	11	5	15	6
50.62	7	4	10	5	14	7	12	3
50.64	16	4	9	3	9	4	7	10
50.66	12	12	9	5	17	2	19	3
50.68	7	9	14	7	17	4	8	5
50.7	7	4	9	4	16	4	13	3
50.72	6	5	9	3	18	5	9	7
50.74	7	11	5	6	14	5	11	3
50.76	12	8	6	2	14	8	10	6
50.78	9	7	12	1	17	7	9	3
50.8	13	11	14	4	12	5	10	8
50.82	15	11	6	3	17	5	8	9
50.84	7	4	12	3	12	6	13	5
50.86	10	8	8	2	18	4	12	6
50.88	14	8	13	2	9	7	10	4
50.9	12	9	5	3	15	8	9	7
50.92	11	3	16	3	8	5	12	6
50.94	7	8	14	2	18	6	13	5
50.96	10	8	12	7	12	6	17	2
50.98	8	11	13	2	10	9	15	6
51	11	8	12	1	11	4	13	13
51.02	13	4	10	1	11	3	8	6
51.04	14	7	11	6	14	11	14	10
51.06	11	8	20	6	13	8	13	10
51.08	13	7	12	3	12	6	13	7
51.1	16	7	9	2	14	3	12	3
51.12	14	9	14	5	11	4	8	6
51.14	7	12	7	4	12	9	10	8
51.16	8	7	9	6	14	5	9	6
51.18	8	5	16	2	11	7	12	5
51.2	18	9	10	3	17	8	17	7
51.22	6	11	12	3	18	6	16	3
51.24	6	9	7	2	19	7	13	10
51.26	13	10	12	3	21	6	14	9
51.28	9	10	14	2	14	5	7	6
51.3	12	8	7	1	11	11	10	10
51.32	5	12	13	5	9	6	11	5
51.34	9	13	7	6	10	8	15	3
51.36	15	3	12	3	6	7	16	6
51.38	11	10	12	3	21	11	13	8
51.4	10	13	14	1	4	6	8	5
51.42	11	12	5	3	10	6	7	6
51.44	13	9	11	4	10	11	14	6
51.46	11	9	10	4	17	5	11	9
51.48	21	7	12	6	14	3	19	9
51.5	9	11	9	1	17	7	11	7
51.52	11	9	10	3	14	8	10	13
51.54	12	6	9	4	12	7	12	8
51.56	10	7	14	5	5	9	15	7

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
51.58	14	7	20	4	21	6	12	8
51.6	17	6	16	3	12	13	13	4
51.62	13	7	18	2	10	9	12	7
51.64	12	6	11	4	12	7	5	4
51.66	12	8	11	6	16	6	14	8
51.68	8	11	9	2	4	2	18	7
51.7	5	4	9	2	13	6	8	6
51.72	21	4	11	2	17	9	13	6
51.74	10	11	7	4	12	12	9	7
51.76	14	9	10	5	15	7	15	7
51.78	12	10	17	6	13	6	28	6
51.8	14	8	11	3	13	9	11	4
51.82	15	21	10	3	17	10	15	8
51.84	13	8	12	5	20	9	9	10
51.86	9	5	9	2	12	6	16	6
51.88	12	6	19	3	16	8	20	6
51.9	9	10	10	2	17	6	11	6
51.92	13	12	13	4	12	7	9	7
51.94	11	9	9	1	8	9	14	12
51.96	10	16	10	4	11	9	16	4
51.98	11	8	12	5	20	4	17	3
52	12	10	14	4	19	9	11	6
52.02	9	11	14	3	16	6	17	11
52.04	12	5	13	4	15	5	17	9
52.06	10	8	5	4	18	13	14	5
52.08	5	12	15	5	11	6	15	11
52.1	12	13	10	2	10	9	11	4
52.12	9	6	16	3	11	6	12	11
52.14	13	17	17	3	12	3	18	12
52.16	11	13	16	4	18	7	16	6
52.18	10	9	6	4	10	9	14	7
52.2	12	8	20	2	17	6	17	13
52.22	16	9	8	7	14	10	15	7
52.24	9	8	9	7	17	3	9	9
52.26	9	18	8	6	11	3	13	11
52.28	9	8	12	6	14	6	15	8
52.3	8	8	11	9	12	5	11	9
52.32	9	14	7	5	7	5	10	6
52.34	12	11	3	7	11	6	11	5
52.36	10	10	11	7	15	8	14	4
52.38	12	4	4	2	14	2	18	4
52.4	10	9	8	3	13	5	14	7
52.42	10	15	11	7	9	9	8	5
52.44	5	8	13	5	16	11	13	13
52.46	6	10	12	5	17	6	15	9
52.48	6	8	14	4	15	7	6	2
52.5	10	17	12	3	14	6	7	6
52.52	6	5	13	1	16	5	16	11
52.54	9	15	1	7	18	8	13	9
52.56	9	10	12	6	14	5	12	9
52.58	6	9	9	2	20	3	11	9
52.6	15	12	7	4	10	3	11	5
52.62	23	10	15	3	7	6	9	11
52.64	13	11	12	1	21	11	19	4
52.66	7	11	18	3	5	9	11	12
52.68	9	14	12	4	12	4	12	10
52.7	6	7	10	4	13	5	14	11
52.72	8	11	10	3	17	14	10	8
52.74	9	16	13	3	11	7	13	11
52.76	11	11	13	3	13	5	6	4
52.78	14	6	14	2	20	10	13	10
52.8	19	11	6	3	8	10	10	11
52.82	7	9	6	4	11	4	9	9
52.84	11	11	7	7	6	14	16	5
52.86	17	10	11	2	16	7	10	8
52.88	12	17	10	7	8	7	12	7
52.9	6	13	12	9	20	6	17	7
52.92	10	14	10	4	13	12	7	7
52.94	12	9	12	5	13	6	14	6
52.96	5	9	11	7	16	13	11	5
52.98	7	11	13	4	7	10	12	9
53	19	14	14	7	10	8	13	9
53.02	11	15	11	6	17	15	6	10
53.04	12	9	13	5	10	7	12	12
53.06	11	13	14	3	13	12	13	7
53.08	10	13	11	1	13	5	17	14
53.1	7	7	12	5	16	10	14	9
53.12	14	11	13	6	7	12	13	10
53.14	9	6	13	6	10	10	11	10
53.16	13	8	5	3	15	5	17	13
53.18	10	10	11	13	8	5	12	11
53.2	14	8	15	3	9	8	12	5
53.22	10	15	15	8	10	12	14	12
53.24	5	10	13	1	19	8	17	7
53.26	14	10	10	4	13	5	12	10
53.28	11	17	11	8	12	9	14	13
53.3	10	13	12	6	10	8	9	6
53.32	21	12	10	2	12	14	15	7
53.34	13	10	12	7	8	7	13	8

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
53.36	10	12	8	1	9	5	18	3
53.38	7	9	8	4	13	10	15	9
53.4	9	17	10	2	17	6	8	8
53.42	15	11	14	5	12	7	12	8
53.44	14	7	6	3	16	8	11	9
53.46	14	12	10	5	16	7	10	11
53.48	11	16	14	9	9	8	13	8
53.5	13	9	8	3	17	7	18	8
53.52	20	10	16	5	12	10	12	11
53.54	26	15	8	8	10	6	12	9
53.56	29	8	11	2	8	9	14	10
53.58	38	13	21	8	12	15	31	9
53.6	38	13	26	6	10	9	23	12
53.62	32	16	42	1	19	10	27	12
53.64	23	23	49	2	28	10	28	14
53.66	21	15	38	6	21	11	33	13
53.68	13	28	29	4	29	16	29	19
53.7	27	17	23	3	28	23	23	22
53.72	30	18	19	7	26	13	17	22
53.74	27	14	17	7	22	11	20	26
53.76	27	11	25	4	10	19	21	17
53.78	17	20	28	4	14	13	22	18
53.8	11	13	35	3	15	14	19	24
53.82	13	11	13	18	26	21	22	17
53.84	14	13	22	9	30	14	19	20
53.86	14	17	14	14	10	22	17	18
53.88	12	17	18	13	12	11	13	19
53.9	9	13	10	15	16	11	9	17
53.92	10	21	12	18	12	13	13	16
53.94	13	12	14	9	19	16	9	19
53.96	5	14	11	22	16	16	7	16
53.98	9	13	13	16	13	7	12	10
54	19	16	11	41	12	10	9	14
54.02	22	22	18	15	15	12	12	13
54.04	27	11	18	21	11	13	15	12
54.06	14	17	14	6	14	12	15	20
54.08	23	12	22	4	12	5	23	17
54.1	11	16	21	9	13	13	21	12
54.12	11	14	18	7	15	14	25	16
54.14	9	17	23	18	16	16	10	12
54.16	14	15	13	13	21	17	18	20
54.18	16	18	12	5	18	10	10	15
54.2	14	18	22	7	8	17	10	16
54.22	17	9	29	11	20	4	16	23
54.24	17	10	20	12	22	18	15	23
54.26	12	11	18	3	17	9	26	18
54.28	12	23	13	9	11	9	18	21
54.3	15	13	18	14	10	12	14	20
54.32	13	13	12	9	5	9	17	14
54.34	14	12	26	7	10	6	7	14
54.36	9	20	15	6	14	13	19	14
54.38	20	6	11	8	13	8	15	11
54.4	7	10	13	8	10	11	13	9
54.42	9	16	21	8	16	12	15	15
54.44	7	14	16	4	10	9	16	16
54.46	5	14	9	9	12	10	14	13
54.48	11	16	11	12	16	7	9	7
54.5	11	15	12	5	9	10	14	14
54.52	11	7	14	4	12	6	11	8
54.54	13	6	17	3	5	6	10	9
54.56	12	14	7	5	11	11	16	8
54.58	6	10	8	4	18	8	8	6
54.6	13	13	8	9	17	11	10	9
54.62	12	17	11	2	11	10	9	13
54.64	11	17	6	5	12	7	8	9
54.66	7	8	12	5	16	4	6	13
54.68	8	15	8	1	11	8	11	14
54.7	8	16	10	3	12	10	6	11
54.72	10	13	5	1	8	13	13	6
54.74	15	14	9	7	14	6	9	8
54.76	10	11	6	6	9	5	8	9
54.78	9	12	13	4	14	8	9	10
54.8	11	12	8	5	19	6	12	11
54.82	14	8	15	3	6	7	11	6
54.84	14	12	11	3	9	9	13	13
54.86	6	4	10	5	19	7	15	9
54.88	12	13	9	6	15	12	13	13
54.9	8	11	9	5	15	9	10	10
54.92	8	10	6	4	16	5	11	13
54.94	12	11	12	6	12	8	16	10
54.96	16	12	11	9	10	5	10	12
54.98	8	7	7	5	9	6	19	14
55	12	9	10	5	12	5	10	9
55.02	13	12	10	5	12	8	11	12
55.04	8	9	15	5	9	8	16	11
55.06	15	17	10	5	17	12	15	17
55.08	6	12	5	9	18	13	14	11
55.1	9	10	7	4	14	6	7	12
55.12	8	11	5	5	13	13	10	19

Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
55.14	15	13	9	8	13	10	7	11
55.16	13	11	10	5	17	7	17	12
55.18	8	16	12	10	11	13	16	10
55.2	16	16	9	4	25	7	10	14
55.22	5	16	9	9	14	10	17	9
55.24	10	20	4	7	14	22	19	14
55.26	14	29	8	5	9	17	12	9
55.28	7	35	11	3	17	39	18	15
55.3	15	28	11	6	11	23	9	17
55.32	12	70	11	3	8	34	15	10
55.34	16	88	9	1	11	25	17	7
55.36	10	56	8	3	11	24	12	18
55.38	13	52	2	2	9	19	20	9
55.4	9	23	10	1	11	35	14	3
55.42	14	24	8	7	10	27	8	13
55.44	10	36	16	8	16	26	13	12
55.46	5	30	13	4	13	24	12	11
55.48	5	38	8	6	12	16	11	15
55.5	6	43	12	8	15	20	16	8
55.52	13	32	7	5	11	11	13	13
55.54	13	20	11	7	9	20	7	9
55.56	4	18	11	5	15	8	10	7
55.58	7	23	13	7	10	11	15	9
55.6	19	13	13	4	5	10	12	7
55.62	17	22	8	7	11	6	11	10
55.64	6	15	10	12	14	9	15	8
55.66	10	12	14	12	14	3	19	9
55.68	12	13	9	10	9	9	8	10
55.7	11	12	6	7	16	9	15	8
55.72	8	10	6	10	14	10	9	13
55.74	10	15	12	6	19	11	18	13
55.76	8	9	11	8	17	6	12	11
55.78	8	12	8	4	15	3	12	4
55.8	12	11	8	13	14	2	8	9
55.82	4	11	10	4	14	12	18	7
55.84	11	7	6	6	18	7	15	9
55.86	11	3	13	7	14	2	12	10
55.88	7	7	11	5	10	8	21	11
55.9	12	13	7	2	12	2	15	10
55.92	9	12	11	3	12	4	7	12
55.94	15	10	11	5	30	7	7	7
55.96	17	11	6	4	11	3	14	8
55.98	7	6	12	3	15	5	15	7
56	12	9	14	2	7	7	13	11
56.02	7	3	10	5	11	6	9	10
56.04	8	15	13	3	13	9	11	5
56.06	10	11	13	5	11	5	11	7
56.08	14	7	13	5	15	6	10	12
56.1	20	9	14	2	9	11	11	8
56.12	10	5	14	1	7	7	13	3
56.14	9	13	11	7	16	7	7	13
56.16	11	6	12	8	14	5	12	13
56.18	15	7	15	2	14	5	14	15
56.2	8	13	12	4	17	5	13	13
56.22	7	9	12	3	7	4	11	7
56.24	15	7	11	2	17	5	14	12
56.26	16	8	10	5	12	6	9	6
56.28	11	9	14	4	8	9	12	8
56.3	7	9	4	3	22	8	18	10
56.32	10	10	14	3	13	4	11	5
56.34	14	12	6	5	15	6	13	15
56.36	12	13	13	2	16	9	15	6
56.38	10	13	8	3	16	6	10	10
56.4	8	8	15	2	18	9	9	8
56.42	13	10	9	4	7	9	14	7
56.44	10	14	6	4	6	8	9	9
56.46	9	7	19	2	11	7	9	4
56.48	11	8	14	1	12	12	13	6
56.5	19	9	8	4	17	9	10	8
56.52	7	16	7	3	7	4	18	9
56.54	10	12	7	5	17	5	8	5
56.56	14	8	12	1	16	9	11	8
56.58	12	7	6	6	15	9	12	8
56.6	12	9	13	4	17	7	11	6
56.62	13	8	12	4	7	8	13	11
56.64	8	6	12	3	14	6	12	8
56.66	7	5	10	2	14	6	11	6
56.68	11	13	12	3	14	12	11	9
56.7	13	10	7	4	9	7	14	8
56.72	12	15	7	3	5	6	17	9
56.74	10	13	12	1	11	7	9	9
56.76	8	8	9	4	15	8	13	10
56.78	10	8	20	1	9	8	10	10
56.8	17	14	5	5	10	7	9	5
56.82	13	9	12	5	12	8	10	8
56.84	9	7	12	2	10	4	9	7
56.86	9	8	13	5	12	10	10	9
56.88	8	10	14	6	14	6	15	4
56.9	9	10	9	7	10	9	12	6

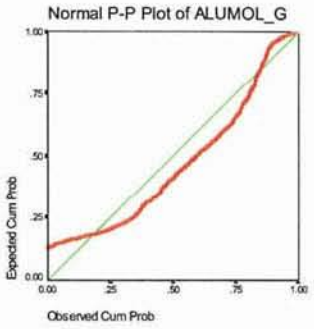
Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
56.92	7	8	13	6	5	2	11	6
56.94	10	10	5	6	9	4	9	7
56.96	10	8	14	3	12	6	17	7
56.98	7	12	9	4	14	7	14	7
57	9	12	9	3	11	5	9	10
57.02	8	7	9	2	14	8	10	7
57.04	22	6	14	2	14	1	14	4
57.06	13	8	7	5	20	6	13	8
57.08	6	10	8	6	15	7	9	2
57.1	18	2	10	3	20	10	15	6
57.12	16	2	15	4	13	5	15	7
57.14	7	7	15	2	15	5	8	12
57.16	19	7	11	3	7	11	14	8
57.18	8	6	11	2	11	7	9	6
57.2	9	5	7	6	8	11	9	4
57.22	12	7	12	3	17	3	7	8
57.24	7	15	12	6	12	5	11	5
57.26	9	6	11	1	8	7	17	7
57.28	9	13	12	5	16	6	11	9
57.3	16	8	11	3	13	4	14	8
57.32	10	11	8	3	12	8	11	7
57.34	15	3	10	1	24	10	13	5
57.36	14	9	12	5	14	7	15	5
57.38	7	10	10	3	12	10	13	4
57.4	9	9	12	3	10	6	12	12
57.42	15	11	12	4	17	3	14	9
57.44	19	10	14	5	9	6	17	4
57.46	21	11	9	5	11	4	11	9
57.48	17	10	20	3	17	6	13	7
57.5	15	10	11	5	15	7	14	10
57.52	8	7	8	4	16	4	23	10
57.54	16	3	14	2	14	5	12	9
57.56	8	11	8	2	15	8	18	6
57.58	15	7	13	3	16	10	13	3
57.6	11	18	10	8	11	7	17	7
57.62	14	8	13	6	13	7	13	6
57.64	19	7	8	5	12	14	9	9
57.66	17	16	6	11	9	8	21	7
57.68	13	9	11	7	14	4	13	7
57.7	14	11	13	10	12	3	14	13
57.72	9	12	14	6	11	8	18	5
57.74	12	6	16	4	12	9	18	4
57.76	18	10	15	12	13	10	8	9
57.78	10	5	10	4	12	6	16	5
57.8	6	6	9	6	8	8	11	5
57.82	9	11	11	8	11	7	5	3
57.84	9	10	9	5	15	6	13	2
57.86	11	6	6	3	9	4	10	7
57.88	9	12	9	5	18	5	8	11
57.9	9	10	6	5	9	7	15	11
57.92	12	7	6	4	13	4	8	9
57.94	11	7	11	4	17	5	11	14
57.96	11	8	7	3	8	9	12	6
57.98	15	12	9	7	12	9	9	7
58	11	7	8	2	10	5	21	6
58.02	8	7	6	1	10	7	8	11
58.04	14	5	10	1	13	13	12	4
58.06	11	18	9	2	14	13	13	7
58.08	16	9	12	4	14	12	17	8
58.1	12	14	12	3	16	6	12	8
58.12	13	9	11	4	15	7	10	6
58.14	16	14	9	1	12	7	9	8
58.16	15	6	12	2	15	11	10	8
58.18	16	11	12	4	15	9	16	7
58.2	7	13	18	2	13	11	13	6
58.22	12	15	11	6	17	9	21	10
58.24	11	9	8	2	14	7	15	5
58.26	5	9	7	3	14	7	10	7
58.28	12	5	9	3	17	10	15	4
58.3	13	9	4	7	12	7	13	3
58.32	14	10	14	1	16	7	7	6
58.34	8	11	6	6	15	4	12	10
58.36	10	11	11	4	16	6	11	16
58.38	9	6	17	3	4	8	6	9
58.4	10	12	14	3	9	6	9	11
58.42	12	12	16	5	12	10	16	7
58.44	12	16	20	3	14	4	17	6
58.46	14	10	12	2	13	9	8	7
58.48	14	10	14	4	15	10	12	10
58.5	10	7	20	5	15	8	19	12
58.52	22	12	16	5	18	8	12	5
58.54	12	15	11	2	14	5	16	12
58.56	17	6	8	8	13	7	10	8
58.58	16	12	21	1	19	8	11	10
58.6	31	9	17	1	16	6	19	9
58.62	32	14	20	5	17	8	14	7
58.64	40	14	23	3	11	7	23	5
58.66	67	13	42	2	14	5	32	9
58.68	77	11	29	8	16	14	44	9

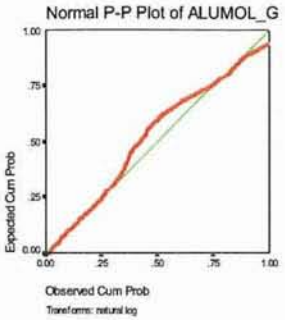
Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
58.7	76	22	69	6	25	10	45	7
58.72	37	28	85	4	30	17	46	13
58.74	22	26	83	5	55	22	62	13
58.76	24	29	80	3	63	35	36	18
58.78	15	41	53	10	57	44	30	22
58.8	27	38	30	4	58	19	30	25
58.82	44	28	37	10	42	26	28	33
58.84	34	12	27	7	23	31	29	46
58.86	38	8	49	11	21	33	19	28
58.88	22	17	38	17	19	24	43	38
58.9	22	20	59	16	33	21	32	24
58.92	18	17	35	29	21	17	37	22
58.94	16	20	33	39	40	26	34	23
58.96	14	17	27	57	35	22	26	24
58.98	8	17	25	59	32	26	18	27
59	13	17	10	47	16	21	17	32
59.02	15	13	8	42	18	12	11	29
59.04	12	11	12	35	17	19	9	20
59.06	16	7	17	27	12	21	16	12
59.08	9	10	9	25	11	15	18	15
59.1	5	17	10	30	14	11	13	14
59.12	7	8	19	26	9	17	9	13
59.14	12	10	10	38	19	8	19	12
59.16	12	9	14	35	11	3	13	10
59.18	13	10	15	21	8	8	14	10
59.2	10	9	11	17	13	6	8	11
59.22	7	13	6	8	15	10	8	12
59.24	7	10	12	14	15	8	12	9
59.26	15	9	10	9	20	11	14	11
59.28	9	9	14	10	7	3	14	5
59.3	11	10	13	9	13	9	7	12
59.32	11	13	17	7	16	8	18	11
59.34	15	10	8	7	10	11	9	14
59.36	8	5	8	5	12	11	14	6
59.38	12	15	13	12	13	9	17	8
59.4	17	12	9	3	10	9	13	13
59.42	9	8	14	6	9	9	11	9
59.44	17	14	13	6	13	7	17	5
59.46	9	11	9	7	15	8	6	6
59.48	8	11	9	7	14	10	9	10
59.5	13	12	14	6	11	5	10	11
59.52	9	13	13	6	21	13	18	13
59.54	6	11	7	5	23	7	9	8
59.56	8	7	15	2	18	9	15	9
59.58	9	11	16	4	14	7	8	8
59.6	18	8	11	8	10	5	10	10
59.62	12	10	13	6	9	8	12	11
59.64	11	12	5	5	12	5	11	5
59.66	8	11	16	3	16	8	18	13
59.68	13	7	8	3	19	2	19	10
59.7	17	11	11	7	16	5	14	17
59.72	14	8	16	6	16	11	6	9
59.74	6	10	14	3	7	10	11	13
59.76	6	14	12	5	15	6	13	11
59.78	12	8	10	3	17	10	9	8
59.8	11	7	10	2	12	3	12	3
59.82	12	13	10	3	16	9	17	9
59.84	8	12	6	4	16	9	6	7
59.86	18	14	10	4	10	6	11	8
59.88	10	14	11	2	12	9	16	8
59.9	11	8	11	6	13	8	18	4
59.92	14	10	12	8	19	2	10	7
59.94	8	9	4	5	15	16	9	6
59.96	11	14	14	2	18	5	13	5
59.98	15	9	9	3	17	6	7	4
60	10	13	16	7	11	9	8	11
60.02	9	10	11	6	17	13	14	9
60.04	12	11	15	5	8	10	11	8
60.06	11	11	8	3	14	6	11	4
60.08	11	10	6	4	10	6	12	7
60.1	6	7	12	7	10	4	17	11
60.12	9	11	12	2	8	5	10	17
60.14	9	5	13	6	16	8	16	9
60.16	18	16	16	4	7	2	8	8
60.18	10	18	10	3	12	5	9	9
60.2	10	10	17	6	14	4	15	11
60.22	5	11	6	3	14	7	5	10
60.24	6	12	14	5	10	9	16	7
60.26	15	10	17	8	8	5	16	6
60.28	10	12	14	2	9	9	7	9
60.3	14	11	7	6	9	5	15	6
60.32	6	12	12	4	9	10	8	11
60.34	3	16	11	3	10	5	7	8
60.36	18	10	9	5	15	12	10	14
60.38	16	15	11	2	10	11	10	12
60.4	15	12	11	1	12	11	16	11
60.42	9	11	11	6	15	8	8	11
60.44	13	12	15	4	8	9	9	10
60.46	19	12	10	2	6	7	14	17

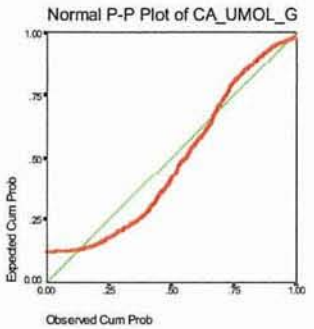
Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
60.48	12	8	16	3	8	9	14	11
60.5	7	10	9	13	17	8	12	10
60.52	19	7	5	2	7	12	15	6
60.54	11	18	16	5	13	9	16	11
60.56	20	10	12	9	19	7	14	16
60.58	14	15	11	4	9	12	13	13
60.6	10	14	15	5	11	12	8	8
60.62	19	10	13	7	16	6	19	15
60.64	11	8	12	6	13	10	5	12
60.66	10	18	13	5	9	12	16	16
60.68	17	8	11	6	13	8	1	11
60.7	15	9	12	3	14	8	16	9
60.72	14	8	11	4	17	8	20	15
60.74	12	10	8	5	12	10	15	13
60.76	12	17	12	1	10	8	12	11
60.78	10	19	12	7	11	6	12	14
60.8	12	10	12	3	7	10	12	10
60.82	8	19	11	4	14	6	11	15
60.84	8	5	6	4	13	13	15	13
60.86	14	21	12	5	23	4	16	18
60.88	13	17	20	7	16	5	19	14
60.9	16	9	10	3	19	18	11	16
60.92	14	12	11	3	16	15	10	11
60.94	8	9	11	8	14	8	11	11
60.96	12	12	16	3	15	9	16	13
60.98	11	9	11	7	18	7	13	5
61	16	9	13	4	19	6	16	8
61.02	17	10	13	3	15	10	12	14
61.04	6	12	13	5	9	9	11	12
61.06	14	14	15	7	7	15	20	8
61.08	12	11	13	4	19	9	14	6
61.1	16	15	11	6	13	7	15	16
61.12	13	5	9	2	12	8	11	16
61.14	14	11	8	5	13	11	14	10
61.16	12	12	5	9	14	11	16	9
61.18	5	14	6	2	12	8	9	13
61.2	11	11	4	5	13	12	13	8
61.22	10	13	14	8	15	6	15	13
61.24	13	7	17	6	17	7	11	13
61.26	14	12	7	4	11	12	11	5
61.28	18	19	11	9	15	6	12	8
61.3	10	10	5	4	11	4	19	9
61.32	8	9	8	5	22	11	7	12
61.34	13	10	10	9	18	12	11	6
61.36	10	7	18	10	21	13	11	11
61.38	12	10	15	3	13	7	17	10
61.4	18	7	10	3	16	7	14	11
61.42	12	10	16	6	9	7	11	8
61.44	13	7	11	6	13	11	10	9
61.46	15	6	9	3	12	9	13	9
61.48	11	6	10	5	10	6	9	5
61.5	9	15	11	4	17	10	12	8
61.52	12	11	10	5	7	11	16	8
61.54	12	17	10	2	12	7	9	9
61.56	14	10	11	2	23	12	10	5
61.58	12	9	9	3	7	6	11	4
61.6	6	8	9	6	11	9	17	6
61.62	11	6	9	5	10	8	16	10
61.64	16	8	16	4	17	10	13	7
61.66	7	9	11	4	8	7	14	8
61.68	10	11	7	1	13	16	19	9
61.7	16	6	14	5	17	8	9	9
61.72	12	6	12	9	14	7	10	4
61.74	7	10	6	2	17	2	16	3
61.76	12	14	5	3	9	2	11	12
61.78	14	12	9	5	11	8	7	4
61.8	14	12	8	5	16	8	12	5
61.82	8	13	13	3	12	10	11	7
61.84	14	10	10	6	8	7	5	6
61.86	15	13	11	3	11	9	6	8
61.88	11	8	14	2	14	7	15	8
61.9	10	12	9	3	9	6	15	5
61.92	13	5	5	3	12	5	12	8
61.94	9	10	9	2	13	7	19	12
61.96	13	6	7	6	11	8	10	7
61.98	14	8	11	5	10	4	18	7
62	15	11	7	5	8	5	12	8
62.02	11	8	14	1	17	5	6	4
62.04	8	10	10	9	12	5	11	6
62.06	11	14	8	7	16	7	10	6
62.08	12	12	11	4	16	7	14	5
62.1	10	13	5	1	9	7	7	7
62.12	14	10	13	4	13	6	11	9
62.14	15	10	11	5	16	9	15	7
62.16	7	10	16	6	13	6	19	10
62.18	4	16	8	4	18	6	5	14
62.2	15	5	15	3	9	4	7	3
62.22	9	9	9	6	16	5	11	10
62.24	11	8	13	7	13	5	21	4

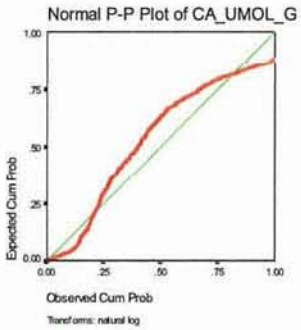
Degrees 2 Theta	1706 After digestion	1706 Before digestion	1718 After digestion	1718 Before digestion	1696 After digestion	1696 Before digestion	1698 After digestion	1698 Before digestion
62.26	7	7	21	7	14	9	11	5
62.28	8	7	18	2	22	7	10	2
62.3	13	8	18	2	13	10	11	10
62.32	11	7	9	2	15	12	16	6
62.34	19	5	13	3	15	8	8	9
62.36	9	11	14	4	7	9	14	10
62.38	9	17	9	4	12	12	9	8
62.4	14	14	18	4	10	16	16	8
62.42	11	8	15	4	15	10	19	9
62.44	7	10	22	2	16	3	12	5
62.46	8	7	15	6	17	10	19	7
62.48	11	11	17	1	18	7	15	5
62.5	13	16	19	6	9	7	19	8
62.52	11	9	9	3	12	8	16	8
62.54	15	12	9	5	11	10	13	13
62.56	14	9	13	10	16	7	17	9
62.58	17	7	14	1	10	15	14	12
62.6	21	8	15	7	9	7	18	9
62.62	13	7	14	9	17	8	11	2
62.64	12	7	9	4	15	1	22	8
62.66	13	7	14	4	9	7	14	13
62.68	20	5	12	2	9	9	5	12
62.7	15	9	14	5	17	11	14	12
62.72	29	10	22	4	14	10	21	6
62.74	19	12	11	5	21	6	17	4
62.76	31	7	18	7	15	7	18	14
62.78	24	10	26	8	9	12	13	9
62.8	16	10	21	5	27	4	17	7
62.82	18	11	20	4	14	15	24	7
62.84	20	12	14	2	17	12	19	8
62.86	10	13	13	8	18	9	26	5
62.88	13	8	14	3	14	13	10	15
62.9	12	12	11	10	11	18	20	13
62.92	16	8	14	10	17	7	13	11
62.94	19	7	16	8	11	17	13	8
62.96	19	13	21	6	12	8	23	14
62.98	15	13	16	10	12	13	15	14
63	14	12	19	3	15	15	18	7
63.02	9	16	15	7	14	8	12	12
63.04	11	5	13	11	16	11	10	18
63.06	7	14	8	14	10	11	14	15
63.08	9	9	14	7	20	11	10	13
63.1	18	10	8	10	19	6	14	9
63.12	19	4	15	13	11	7	11	7
63.14	16	13	14	1	16	8	13	9
63.16	14	9	14	8	9	9	6	9
63.18	6	9	11	8	16	6	8	8
63.2	11	10	13	9	11	5	8	17
63.22	11	15	13	7	10	7	12	4
63.24	5	10	10	2	15	4	11	4
63.26	14	11	8	7	13	6	12	8
63.28	8	6	8	2	10	6	11	5
63.3	7	7	8	4	18	9	14	4
63.32	10	8	11	4	12	6	13	8
63.34	10	10	8	2	18	8	16	6
63.36	19	6	13	3	12	6	18	10
63.38	21	7	18	2	20	9	15	6
63.4	16	11	12	3	15	6	14	6
63.42	15	11	10	3	20	2	12	6
63.44	16	9	10	1	15	6	15	10
63.46	8	10	10	1	8	5	10	8
63.48	13	9	14	5	16	6	10	10
63.5	8	14	12	5	17	5	9	8
63.52	7	6	14	4	11	6	10	6
63.54	8	9	6	2	15	7	11	9
63.56	15	7	14	2	15	7	8	8
63.58	13	8	10	1	17	13	17	13
63.6	8	13	9	3	13	9	11	6
63.62	16	11	13	3	10	6	6	7
63.64	13	10	10	3	18	11	13	10
63.66	10	13	7	7	12	10	10	6
63.68	8	8	12	4	12	7	12	6
63.7	19	7	4	3	13	9	20	9
63.72	13	7	10	1	8	7	15	8
63.74	10	9	8	5	13	9	10	8
63.76	17	8	10	6	9	8	11	8
63.78	13	15	11	4	19	8	9	6
63.8	14	15	12	1	9	4	8	8
63.82	15	10	20	2	8	8	15	8
63.84	11	6	8	2	10	9	14	5
63.86	7	10	10	5	12	6	13	10
63.88	12	8	15	2	11	9	11	8
63.9	14	17	7	5	10	8	10	4
63.92	13	10	15	4	13	9	17	8
63.94	12	10	11	5	12	5	14	4
63.96	16	12	14	4	14	9	11	9
63.98	11	8	9	4	14	7	16	9
64	8	11	16	7	17	6	16	11
64.02	8	10	10	5	10	6	8	5

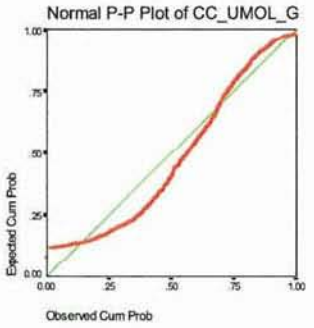
Appendix 4 Normal probability plots of chemical parameters determined in surface sediment samples

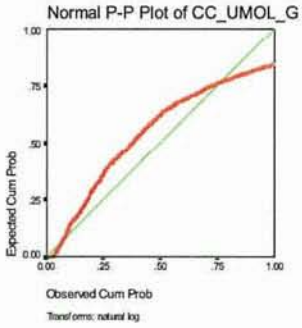

Normal P-P Plot of ALUMOL_G
Expected Cum Prob
Observed Cum Prob

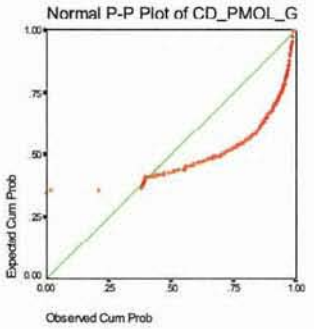

Normal P-P Plot of ALUMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

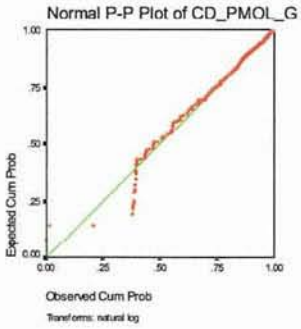

Normal P-P Plot of CA_UMOL_G
Expected Cum Prob
Observed Cum Prob

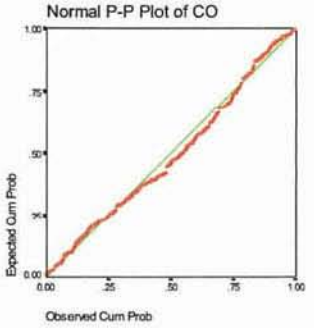

Normal P-P Plot of CA_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

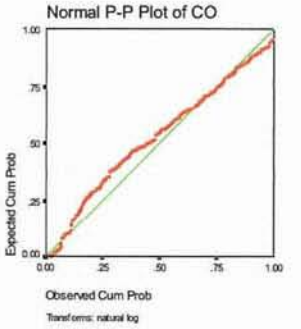

Normal P-P Plot of CC_UMOL_G
Expected Cum Prob
Observed Cum Prob

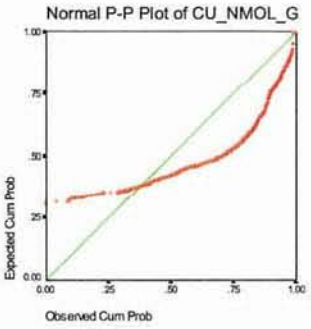

Normal P-P Plot of CC_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

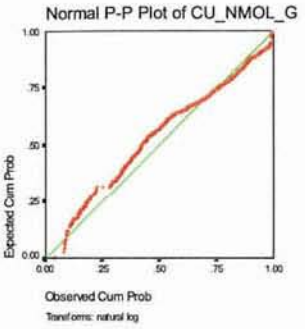

Normal P-P Plot of CD_PMOL_G
Expected Cum Prob
Observed Cum Prob

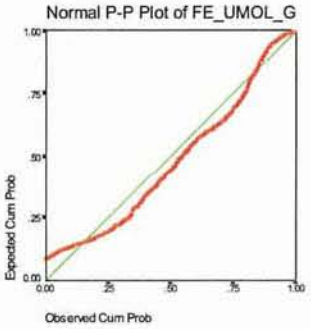

Normal P-P Plot of CD_PMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

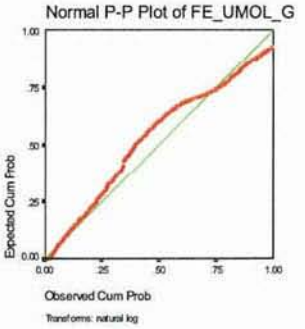

Normal P-P Plot of CO
Expected Cum Prob
Observed Cum Prob

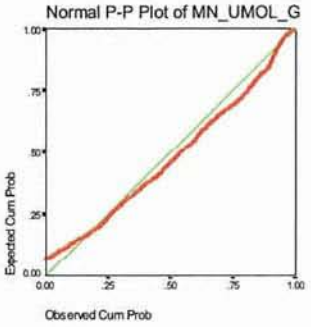

Normal P-P Plot of CO
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

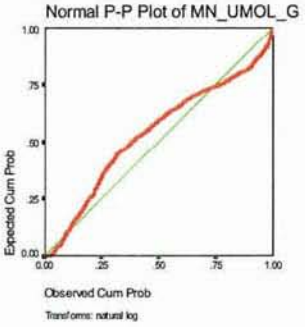

Normal P-P Plot of CU_NMOL_G
Expected Cum Prob
Observed Cum Prob

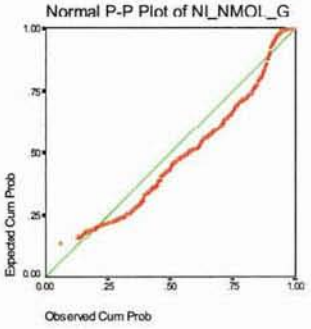

Normal P-P Plot of CU_NMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

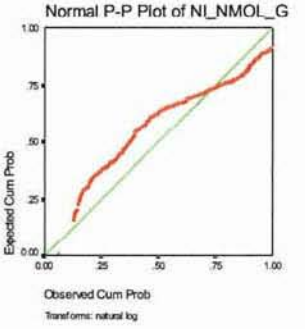

Normal P-P Plot of FE_UMOL_G
Expected Cum Prob
Observed Cum Prob

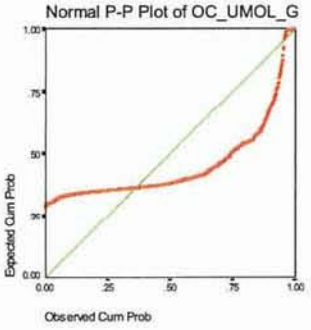

Normal P-P Plot of FE_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

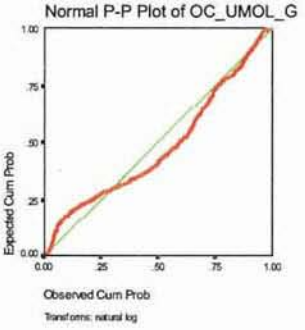

Normal P-P Plot of MN_UMOL_G
Expected Cum Prob
Observed Cum Prob

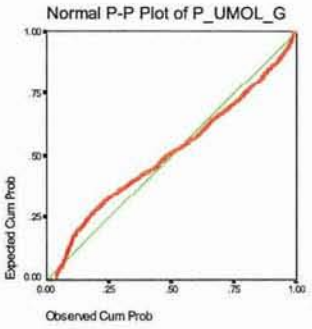

Normal P-P Plot of MN_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

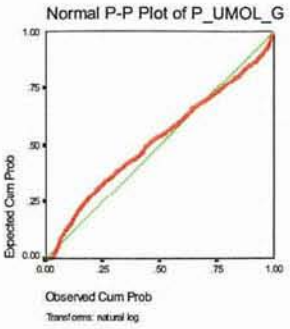

Normal P-P Plot of NI_NMOL_G
Expected Cum Prob
Observed Cum Prob

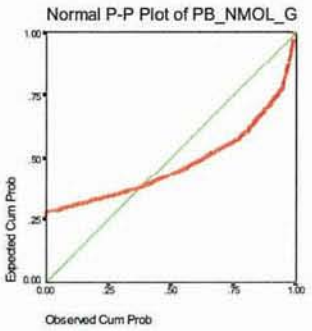

Normal P-P Plot of NI_NMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

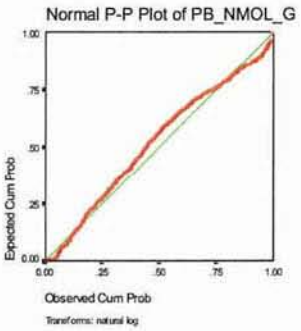

Normal P-P Plot of OC_UMOL_G
Expected Cum Prob
Observed Cum Prob

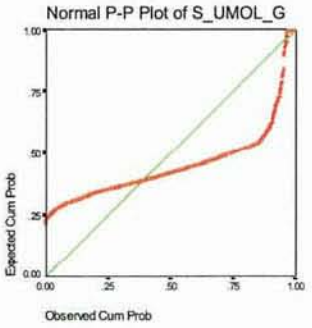

Normal P-P Plot of OC_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

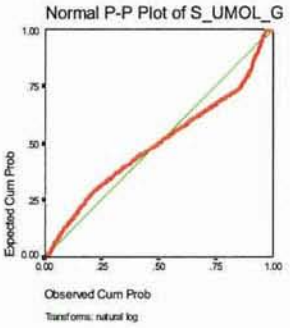

Normal P-P Plot of P_UMOL_G
Expected Cum Prob
Observed Cum Prob

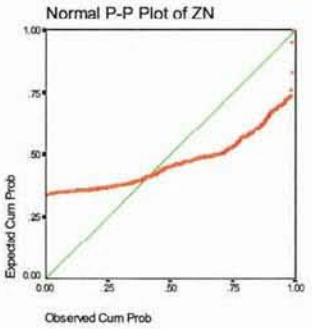

Normal P-P Plot of P_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

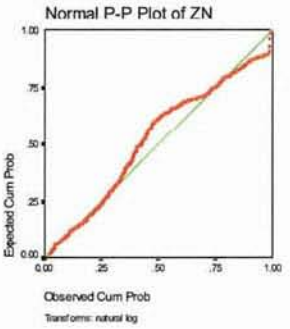

Normal P-P Plot of PB_NMOL_G
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of PB_NMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log


Normal P-P Plot of S_UMOL_G
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of S_UMOL_G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log


Normal P-P Plot of ZN
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of ZN
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

Appendix 5 Sediment core samples - location and strong acid digestion analytical results

Appendix 5

Sediment core samples - Location and strong acid digestion analytical results

Core Number	From cm	To cm	Collar Decimal Latitude	Collar Decimal Longitude	Water depth m	Sample date	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1827	0	2	-19.2352	146.8233	3	27/08/1998	2062.40	319.76	< D. L.	293.69	218.70	573.91	601.66	17.51	362.52	846.91	12.87	142.37	127.18	811.39	1541.70
1827	2	4	-19.2352	146.8233	3	27/08/1998	2286.30	321.96	32.36	324.19	233.39	575.12	677.87	20.20	403.35	1001.69	14.59	164.28	64.60	1034.05	1611.21
1827	4	6	-19.2352	146.8233	3	27/08/1998	2266.77	344.49	383.01	325.05	235.58	622.56	682.84	18.35	394.36	580.52	13.98	160.58	57.26	963.54	1677.22
1827	6	8	-19.2352	146.8233	3	27/08/1998	2349.50	337.66	254.58	404.97	228.97	539.00	664.69	13.68	397.16	680.41	14.19	139.85	53.69	935.00	1676.28
1827	8	10	-19.2352	146.8233	3	27/08/1998	1963.12	383.75	269.48	358.24	222.79	423.60	605.79	9.94	364.31	606.47	13.07	125.39	45.00	875.95	1527.10
1827	10	12	-19.2352	146.8233	3	27/08/1998	1974.57	410.98	237.49	393.40	223.65	427.79	624.11	10.49	373.86	633.38	12.40	128.00	48.04	870.87	1543.33
1827	12	14	-19.2352	146.8233	3	27/08/1998	1975.69	426.34	304.66	447.26	228.80	408.49	584.92	9.77	367.28	561.71	12.35	129.30	49.16	866.37	1511.07
1827	14	16	-19.2352	146.8233	3	27/08/1998	1973.13	387.56	519.76	477.70	220.21	369.23	597.00	9.89	349.29	325.98	11.41	126.08	50.05	845.75	1481.61
1827	16	18	-19.2352	146.8233	3	27/08/1998	1740.38	567.06	251.24	466.58	201.85	324.15	520.61	8.87	302.81	722.05	11.17	116.53	54.40	973.29	1313.33
1827	18	20	-19.2352	146.8233	3	27/08/1998	1859.98	404.32	508.65	442.50	206.48	316.53	541.59	9.69	318.31	290.81	10.96	119.13	44.01	799.46	1393.13
1827	20	24	-19.2352	146.8233	3	27/08/1998	1849.12	646.67	512.56	429.20	203.19	304.17	533.78	10.11	283.83	476.56	10.59	114.02	48.82	989.12	1304.19
1827	24	28	-19.2352	146.8233	3	27/08/1998	1667.00	703.90	552.99	356.12	190.36	248.56	476.71	10.14	223.02	417.93	8.86	109.29	47.76	970.92	1066.14
1827	28	32	-19.2352	146.8233	3	27/08/1998	1671.60	526.86	443.35	350.34	188.32	263.85	476.62	9.86	217.91	359.66	10.03	101.89	54.19	803.00	1075.62
1827	32	36	-19.2352	146.8233	3	27/08/1998	1287.89	403.68	338.41	386.22	181.83	216.28	410.72	8.89	198.24	321.08	10.36	89.25	57.24	659.49	1063.02
1827	36	40	-19.2352	146.8233	3	27/08/1998	1625.46	537.14	405.41	410.61	202.50	248.28	472.90	10.42	246.63	452.35	11.01	107.79	66.35	857.76	1158.42
1827	40	44	-19.2352	146.8233	3	27/08/1998	1263.90	418.57	364.90	377.35	197.24	188.61	409.67	9.33	210.82	405.76	10.45	79.25	89.13	770.66	997.65
1827	44	48	-19.2352	146.8233	3	27/08/1998	1420.75	418.87	363.67	408.70	192.12	188.53	431.11	8.84	219.53	490.81	9.97	86.17	97.79	854.49	981.01
1827	48	52	-19.2352	146.8233	3	27/08/1998	1490.32	423.51	314.06	256.78	189.19	174.76	446.17	8.57	216.75	418.73	10.24	85.80	95.98	732.79	895.18
1827	52	56	-19.2352	146.8233	3	27/08/1998	1380.52	410.16	379.63	275.87	184.94	180.96	443.03	8.66	217.03	423.28	10.20	82.00	96.29	802.91	914.42
1827	56	60	-19.2352	146.8233	3	27/08/1998	1309.87	443.86	374.48	292.39	179.13	168.38	418.53	8.72	210.17	323.52	10.21	76.55	82.77	698.00	846.85
1827	60	68	-19.2352	146.8233	3	27/08/1998	1312.38	495.71	445.15	207.86	188.22	169.65	432.80	8.77	216.40	360.56	10.55	81.80	96.50	805.71	776.11
1827	68	76	-19.2352	146.8233	3	27/08/1998	994.87	529.79	465.67	161.31	190.44	164.99	377.69	9.28	232.61	421.17	9.26	87.43	112.79	886.84	775.44
1827	76	84	-19.2352	146.8233	3	27/08/1998	1448.91	495.22	383.96	201.07	181.76	193.83	458.35	9.03	233.73	496.98	10.91	85.70	110.67	880.95	765.76
1827	84	92	-19.2352	146.8233	3	27/08/1998	1583.58	439.80	548.95	188.97	191.44	192.21	484.67	9.10	247.12	329.28	10.43	95.95	121.41	878.23	804.91
1827	92	100	-19.2352	146.8233	3	27/08/1998	1376.31	522.30	510.17	170.92	191.53	167.77	425.55	8.89	198.99	418.51	9.88	91.30	103.69	928.68	700.01
1827	100	104	-19.2352	146.8233	3	27/08/1998	1903.25	444.44	436.74	242.24	209.11	228.88	549.20	9.98	265.29	562.24	10.74	103.39	145.33	998.98	901.36
1827	104	108	-19.2352	146.8233	3	27/08/1998	1209.84	443.60	444.01	184.27	223.14	147.66	386.49	10.75	173.14	595.47	8.67	94.53	184.95	1039.48	602.43
1828	0	2	-19.1542	146.7748	8	28/08/1998	2643.07	519.55	632.83	214.18	236.01	350.50	716.53	8.82	486.09	637.70	14.74	97.15	97.52	1270.53	1171.80
1828	2	4	-19.1542	146.7748	8	28/08/1998	2596.69	588.35	820.58	191.62	247.05	328.30	740.84	9.42	483.03	479.92	14.11	105.81	93.36	1300.50	1145.20
1828	4	6	-19.1542	146.7748	8	28/08/1998	2724.74	688.08	194.84	215.30	247.47	321.43	734.34	9.36	476.74	1129.52	14.72	102.45	91.19	1324.36	1183.43
1828	6	8	-19.1542	146.7748	8	28/08/1998	2774.48	669.18	785.08	177.00	248.73	333.58	735.68	9.63	480.45	507.72	14.55	103.49	111.71	1292.80	1210.75
1828	8	10	-19.1542	146.7748	8	28/08/1998	2688.93	691.17	686.45	189.31	236.98	324.34	715.07	9.69	449.05	630.70	13.79	104.16	120.86	1317.14	1170.57
1828	10	12	-19.1542	146.7748	8	28/08/1998	2762.71	578.94	408.16	215.57	240.71	326.93	736.99	9.58	491.18	814.66	14.28	102.18	120.13	1222.82	1214.57
1828	12	14	-19.1542	146.7748	8	28/08/1998	2855.63	635.40	797.39	313.12	254.31	363.08	780.69	10.37	482.20	497.81	14.86	101.08	134.26	1295.19	1267.76
1828	14	16	-19.1542	146.7748	8	28/08/1998	2647.14	555.66	490.54	262.03	235.07	323.57	788.76	10.35	474.85	712.86	12.56	100.71	144.20	1203.40	1278.87
1828	16	18	-19.1542	146.7748	8	28/08/1998	2798.62	614.67	516.23	259.31	250.48	332.73	758.05	9.61	447.17	761.33	13.83	100.65	136.93	1277.55	1204.72
1828	18	20	-19.1542	146.7748	8	28/08/1998	1180.69	2536.69	590.30	312.85	139.41	152.15	350.48	5.51	208.51	677.91	9.62	74.59	92.02	1268.21	596.14
1828	20	24	-19.1542	146.7748	8	28/08/1998	2440.35	905.65	729.95	286.76	222.46	316.48	681.02	8.52	405.05	706.42	13.35	110.07	142.32	1436.37	1097.15
1828	24	28	-19.1542	146.7748	8	28/08/1998	2649.54	827.28	884.80	322.98	244.64	327.26	743.34	8.77	442.15	648.37	13.53	115.05	156.21	1533.17	1157.26

Appendix 5

Sediment core samples - Location and strong acid digestion analytical results

Core Number	From cm	To cm	Collar Decimal Latitude	Collar Decimal Longitude	Water depth m	Sample date	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1828	28	32	-19.1542	146.7748	8	28/08/1998	2751.81	742.57	677.41	268.51	242.25	337.97	760.80	9.11	441.29	707.31	14.07	108.35	150.25	1384.73	1193.13
1828	32	36	-19.1542	146.7748	8	28/08/1998	2831.16	760.15	756.40	262.21	242.17	343.23	740.39	9.14	426.69	652.58	13.75	115.23	141.40	1408.98	1207.58
1828	36	40	-19.1542	146.7748	8	28/08/1998	2645.83	688.39	733.99	240.86	241.23	332.02	727.38	9.70	427.70	691.62	13.91	112.66	148.94	1425.61	1188.96
1828	40	44	-19.1542	146.7748	8	28/08/1998	2465.25	832.81	848.41	261.92	218.77	298.44	667.49	8.64	388.52	674.06	12.74	99.71	136.99	1522.47	1102.47
1828	44	48	-19.1542	146.7748	8	28/08/1998	2670.41	717.33	990.08	241.78	230.28	326.77	717.58	8.97	422.56	763.27	13.13	101.23	136.03	1753.35	1141.15
1828	48	52	-19.1542	146.7748	8	28/08/1998	2754.69	587.14	2449.25	197.63	231.12	310.21	737.46	8.99	434.00	329.49	13.01	108.02	128.76	2778.74	1142.94
1828	52	56	-19.1542	146.7748	8	28/08/1998	1729.50	1875.27	1911.47	199.45	164.63	196.01	463.23	6.00	295.10	516.29	10.45	163.91	118.59	2427.76	702.44
1828	56	60	-19.1542	146.7748	8	28/08/1998	444.89	513.11	1707.20	230.77	60.98	53.94	132.54	2.02	104.17	519.31	3.30	22.16	61.52	2226.52	207.48
1828	60	68	-19.1542	146.7748	8	28/08/1998	1019.47	1506.16	2068.46	155.66	119.53	140.86	304.12	4.44	195.39	527.78	7.01	34.42	94.23	2596.24	495.93
1828	68	76	-19.1542	146.7748	8	28/08/1998	798.16	1959.98	1725.40	201.76	121.96	121.45	255.06	4.32	170.40	730.88	6.38	38.45	104.07	2456.28	465.79
1828	76	84	-19.1542	146.7748	8	28/08/1998	854.15	785.59	1572.73	185.76	122.22	96.86	260.10	3.55	174.66	838.01	4.06	29.45	164.97	2410.73	357.28
1828	84	88	-19.1542	146.7748	8	28/08/1998	846.66	682.29	1054.34	113.74	136.03	133.82	245.88	4.25	208.64	936.06	3.76	40.32	168.98	1990.40	478.02
1828	88	96	-19.1542	146.7748	8	28/08/1998	1376.31	522.30	510.17	170.92	191.53	167.77	425.55	8.89	198.99	418.51	9.88	91.30	103.69	928.68	700.01
1829	0	2	-19.2760	146.6395	0.3	29/08/1998	1687.06	354.74	203.05	220.80	196.45	254.68	542.36	13.76	312.87	949.91	12.13	75.30	131.20	1152.96	833.81
1829	2	4	-19.2760	146.6395	0.3	29/08/1998	1556.84	343.27	214.62	111.17	197.11	185.82	504.43	12.70	266.55	864.47	12.13	62.38	101.46	1079.10	757.51
1829	4	6	-19.2760	146.6395	0.3	29/08/1998	1594.53	346.31	227.74	135.95	199.94	192.29	523.06	14.37	278.36	832.28	12.51	78.42	95.80	1060.02	747.40
1829	6	8	-19.2760	146.6395	0.3	29/08/1998	1307.79	320.00	215.67	161.02	193.03	151.25	456.97	11.84	246.22	706.04	11.79	69.50	63.35	921.71	677.39
1829	8	10	-19.2760	146.6395	0.3	29/08/1998	1618.41	302.55	207.65	106.62	213.84	200.19	525.14	13.58	288.54	821.10	12.96	77.45	68.64	1028.75	790.85
1829	10	12	-19.2760	146.6395	0.3	29/08/1998	784.87	420.27	317.19	84.47	171.26	75.40	313.24	11.47	145.45	205.43	9.86	43.96	35.39	522.62	468.80
1829	12	14	-19.2760	146.6395	0.3	29/08/1998	737.81	459.70	365.08	105.11	166.95	81.95	306.20	11.03	140.80	182.87	9.83	40.23	37.31	547.95	471.90
1829	14	16	-19.2760	146.6395	0.3	29/08/1998	804.59	452.18	337.44	108.17	179.43	80.92	321.85	13.11	145.25	184.47	10.27	46.00	38.13	521.91	494.07
1829	16	18	-19.2760	146.6395	0.3	29/08/1998	813.12	506.34	398.64	85.00	171.00	90.42	326.56	10.38	149.04	220.23	10.50	40.13	38.59	618.87	490.85
1829	18	20	-19.2760	146.6395	0.3	29/08/1998	863.41	365.94	321.21	119.90	167.22	107.32	336.50	11.27	168.59	338.85	10.26	46.74	54.99	660.06	525.13
1829	20	24	-19.2760	146.6395	0.3	29/08/1998	842.14	364.94	286.35	144.52	164.93	102.08	324.35	9.75	161.56	349.28	9.67	47.05	72.03	635.63	506.19
1829	24	28	-19.2760	146.6395	0.3	29/08/1998	1064.58	436.88	371.28	125.59	179.79	127.17	384.34	11.02	206.45	430.02	10.39	53.42	93.75	801.30	589.37
1829	28	32	-19.2760	146.6395	0.3	29/08/1998	827.93	756.96	701.41	134.38	169.75	93.19	377.25	15.14	158.53	262.13	13.72	40.49	56.08	963.54	506.20
1829	32	36	-19.2760	146.6395	0.3	29/08/1998	984.83	437.16	337.93	137.91	177.86	109.54	353.80	12.34	179.25	306.65	10.46	48.97	75.94	644.58	557.34
1829	36	40	-19.2760	146.6395	0.3	29/08/1998	940.87	371.32	275.63	119.11	174.29	105.82	342.77	11.99	172.16	310.82	9.85	41.82	82.24	586.45	526.48
1829	40	44	-19.2760	146.6395	0.3	29/08/1998	1015.48	469.41	556.78	111.53	171.27	114.76	371.36	12.66	194.27	349.23	10.38	46.83	102.82	906.01	566.91
1829	44	48	-19.2760	146.6395	0.3	29/08/1998	861.02	520.07	413.29	103.94	154.31	93.30	315.58	13.44	164.90	238.28	9.26	49.70	74.81	651.57	496.38
1829	48	52	-19.2760	146.6395	0.3	29/08/1998	827.76	480.50	417.96	121.63	141.30	98.45	305.38	12.63	150.05	334.02	8.88	46.18	88.61	751.97	557.00
1829	52	56	-19.2760	146.6395	0.3	29/08/1998	861.68	522.50	418.27	151.18	166.94	91.70	326.22	13.34	151.87	297.05	9.34	40.56	91.03	715.32	486.25
1829	56	60	-19.2760	146.6395	0.3	29/08/1998	778.67	485.52	391.00	111.24	153.92	73.33	289.45	12.30	135.83	162.62	8.72	40.20	66.77	553.62	452.33
1829	60	68	-19.2760	146.6395	0.3	29/08/1998	976.90	663.54	549.56	128.43	172.40	112.12	368.27	16.38	200.58	332.28	10.08	44.99	107.18	881.85	544.74
1829	68	76	-19.2760	146.6395	0.3	29/08/1998	1030.19	456.20	387.66	133.96	170.07	123.38	373.56	13.04	182.38	436.53	9.88	47.19	114.51	824.20	550.64
1829	76	84	-19.2760	146.6395	0.3	29/08/1998	1126.20	515.83	431.30	139.24	159.36	127.52	379.53	13.57	199.33	432.37	10.08	47.76	116.67	863.67	556.97
1829	84	92	-19.2760	146.6395	0.3	29/08/1998	1295.64	520.03	411.00	161.27	178.31	153.93	424.06	14.58	220.49	508.49	11.09	57.04	134.68	919.49	615.74
1829	92	98	-19.2760	146.6395	0.3	29/08/1998	1221.29	483.15	384.26	154.65	191.09	149.00	402.02	14.09	220.05	585.91	10.29	55.40	218.71	970.17	621.73
1829	98	102	-19.2760	146.6395	0.3	29/08/1998	2998.07	391.80	358.09	204.57	271.78	339.56	774.95	22.37	490.23	1650.59	14.69	111.39	532.53	2008.68	1188.77

Appendix 5

Sediment core samples - Location and strong acid digestion analytical results

Core Number	From cm	To cm	Collar Decimal Latitude	Collar Decimal Longitude	Water depth m	Sample date	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1831	0	2	-19.2920	146.8520	0.5	31/08/1998	1835.97	116.32	16.47	346.54	217.23	374.45	574.82	5.47	316.52	1583.56	22.06	81.03	155.18	1600.03	925.83
1831	2	4	-19.2920	146.8520	0.5	31/08/1998	1631.85	111.87	< D. L.	303.62	205.59	347.94	538.06	5.82	292.15	1489.24	25.00	77.34	150.04	1477.42	935.63
1831	4	6	-19.2920	146.8520	0.5	31/08/1998	1688.38	102.98	54.22	361.96	222.27	361.63	558.96	5.02	299.03	1696.90	20.81	80.01	196.32	1751.13	987.47
1831	6	8	-19.2920	146.8520	0.5	31/08/1998	1681.84	106.60	< D. L.	395.61	218.11	368.45	544.99	4.80	302.08	1665.55	18.79	83.50	173.04	1664.79	893.67
1831	8	10	-19.2920	146.8520	0.5	31/08/1998	1541.38	101.52	< D. L.	424.53	203.05	349.02	496.17	4.17	276.05	1849.86	13.74	74.66	203.16	1788.07	845.13
1831	10	12	-19.2920	146.8520	0.5	31/08/1998	1746.16	114.90	< D. L.	453.71	231.95	395.08	605.88	4.52	305.69	2346.89	14.63	79.32	304.28	1936.56	960.58
1831	12	14	-19.2920	146.8520	0.5	31/08/1998	1790.37	115.70	363.27	429.12	241.08	382.79	606.18	4.60	316.47	1645.32	14.38	84.33	301.20	2008.59	954.73
1831	14	16	-19.2920	146.8520	0.5	31/08/1998	1697.20	108.61	< D. L.	373.33	229.39	394.66	568.01	4.56	298.96	1772.49	14.44	80.80	261.32	1766.14	909.25
1831	16	18	-19.2920	146.8520	0.5	31/08/1998	1737.16	113.03	4.33	416.47	225.58	398.29	553.35	4.48	302.78	1807.23	14.61	77.62	240.66	1811.57	925.05
1831	18	20	-19.2920	146.8520	0.5	31/08/1998	1629.52	113.09	< D. L.	403.88	222.92	372.23	570.89	4.77	300.09	1756.56	14.32	74.67	281.73	1725.27	889.58
1831	20	24	-19.2920	146.8520	0.5	31/08/1998	1613.74	118.85	< D. L.	386.50	203.82	351.79	524.64	4.71	276.84	1467.31	13.83	62.14	236.46	1413.38	847.29
1831	24	28	-19.2920	146.8520	0.5	31/08/1998	1583.72	133.02	< D. L.	379.33	222.59	349.78	532.08	5.02	282.85	1668.79	13.10	74.44	308.57	1630.00	862.45
1831	28	32	-19.2920	146.8520	0.5	31/08/1998	1462.37	139.00	< D. L.	443.11	193.14	359.66	450.76	4.62	257.40	1200.64	10.90	70.19	222.85	1152.71	817.49
1831	32	36	-19.2920	146.8520	0.5	31/08/1998	1525.42	228.87	< D. L.	401.23	219.75	363.38	472.03	5.73	273.97	1611.09	12.88	78.88	301.31	1186.65	915.87
1831	36	40	-19.2920	146.8520	0.5	31/08/1998	1338.21	190.74	56.73	466.60	240.96	304.79	445.88	6.17	291.47	1116.81	10.75	73.50	316.21	1173.54	775.00
1831	40	44	-19.2920	146.8520	0.5	31/08/1998	1213.75	128.29	< D. L.	445.61	220.71	299.09	461.66	10.21	250.20	968.81	10.77	77.92	402.26	961.82	770.54
1831	44	48	-19.2920	146.8520	0.5	31/08/1998	1451.77	122.60	< D. L.	533.82	265.50	357.16	523.31	6.20	318.26	1028.40	12.55	83.46	388.18	1014.19	879.46
1831	48	52	-19.2920	146.8520	0.5	31/08/1998	1468.61	114.00	< D. L.	504.10	284.44	377.01	596.56	5.43	306.40	1702.21	13.78	82.61	459.89	1664.60	863.90
1831	52	56	-19.2920	146.8520	0.5	31/08/1998	1000.07	110.30	< D. L.	395.60	199.79	225.37	414.13	4.16	211.36	605.93	16.37	69.05	182.48	589.38	629.96
1832	0	2	-19.2880	146.8293	0.3	20/11/1998	1898.93	105.22	39.58	287.44	190.71	293.31	581.89	9.08	274.33	1104.92	15.70	96.50	84.99	1144.51	1049.91
1832	2	4	-19.2880	146.8293	0.3	20/11/1998	2293.51	98.32	33.13	291.41	216.83	356.53	668.24	8.42	319.80	1249.51	16.95	112.23	86.81	1282.64	1177.13
1832	4	6	-19.2880	146.8293	0.3	20/11/1998	2365.30	87.52	< D. L.	298.71	209.33	341.41	678.01	6.24	336.52	1356.45	17.03	106.23	81.68	1331.68	1228.25
1832	6	8	-19.2880	146.8293	0.3	20/11/1998	2127.07	98.74	48.72	280.23	205.19	314.39	605.99	6.37	300.34	1175.63	15.78	99.10	90.52	1224.35	1127.43
1832	8	10	-19.2880	146.8293	0.3	20/11/1998	2039.14	97.71	42.28	308.45	202.23	329.60	588.62	6.09	290.79	1170.17	15.35	88.88	102.37	1212.45	1152.46
1832	10	12	-19.2880	146.8293	0.3	20/11/1998	1762.32	115.70	< D. L.	274.92	206.58	298.45	591.05	7.16	274.77	1220.53	15.82	89.99	103.60	1209.69	1051.96
1832	12	14	-19.2880	146.8293	0.3	20/11/1998	1603.93	110.28	< D. L.	257.11	192.91	279.74	524.49	7.52	250.89	1166.42	15.24	87.32	87.38	924.78	973.77
1832	14	16	-19.2880	146.8293	0.3	20/11/1998	1832.33	99.68	< D. L.	280.67	197.16	299.63	582.27	6.49	266.42	1414.85	14.70	91.89	106.37	1259.10	1040.99
1832	16	18	-19.2880	146.8293	0.3	20/11/1998	1733.94	112.67	18.10	271.34	187.97	300.17	552.03	5.77	263.91	1160.89	13.47	83.29	124.70	1179.00	1005.20
1832	18	20	-19.2880	146.8293	0.3	20/11/1998	1669.48	117.01	31.95	272.68	186.33	289.31	554.84	5.74	250.94	1058.85	13.34	78.91	131.56	1090.80	993.48
1832	20	24	-19.2880	146.8293	0.3	20/11/1998	1592.33	110.44	37.68	337.41	190.86	270.60	549.29	5.33	286.09	1033.87	13.19	80.86	130.85	1071.55	998.56
1832	24	28	-19.2880	146.8293	0.3	20/11/1998	1349.10	109.84	18.66	279.10	167.76	244.83	472.14	4.76	210.33	978.89	12.07	81.13	117.62	997.54	877.32
1832	28	32	-19.2880	146.8293	0.3	20/11/1998	1543.23	116.29	46.59	322.81	184.05	259.11	532.76	4.92	237.41	1092.46	12.81	78.07	153.34	1139.04	950.26
1832	32	36	-19.2880	146.8293	0.3	20/11/1998	1518.53	119.06	51.36	328.91	179.81	263.46	514.99	4.68	238.80	1085.76	12.76	87.79	139.20	1137.12	940.08
1832	36	40	-19.2880	146.8293	0.3	20/11/1998	1683.85	116.92	68.15	329.59	191.85	268.97	589.01	4.87	252.69	1051.79	13.41	84.51	165.02	1119.94	994.63
1832	40	44	-19.2880	146.8293	0.3	20/11/1998	1469.07	105.59	75.74	308.42	184.94	249.20	555.88	4.25	236.91	1004.57	12.44	82.39	191.89	1080.31	922.44
1832	44	48	-19.2880	146.8293	0.3	20/11/1998	1516.26	109.49	247.80	336.49	179.25	254.02	537.39	4.22	224.29	858.23	12.67	93.73	168.62	1106.02	957.22
1832	48	52	-19.2880	146.8293	0.3	20/11/1998	1427.40	125.24	101.20	309.80	183.33	238.44	544.59	4.10	216.58	973.26	12.21	80.32	198.97	1074.46	896.23
1832	52	56	-19.2880	146.8293	0.3	20/11/1998	1438.38	117.99	283.94	358.06	185.29	235.31	534.99	3.99	215.19	836.72	12.61	85.16	192.11	1120.67	906.57
1832	56	60	-19.2880	146.8293	0.3	20/11/1998	1367.43	178.68	< D. L.	311.23	182.72	219.04	470.13	3.92	198.39	1049.57	11.93	71.86	142.49	906.54	834.02

Appendix 5

Sediment core samples - Location and strong acid digestion analytical results

Core Number	From cm	To cm	Collar Decimal Latitude	Collar Decimal Longitude	Water depth m	Sample date	Al µmol/g	Ca µmol/g	CC µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	OC µmol/g	P µmol/g	Pb nmol/g	S µmol/g	TC µmol/g	Zn nmol/g
1832	60	64	-19.2880	146.8293	0.3	20/11/1998	1546.96	120.07	122.98	373.90	186.04	245.41	563.96	4.38	229.98	1011.30	14.38	78.97	212.17	1134.28	936.17
1832	64	68	-19.2880	146.8293	0.3	20/11/1998	1535.61	128.34	44.17	398.01	186.17	244.72	564.73	4.43	242.01	1029.56	15.24	78.89	204.53	1073.73	922.81
1832	68	72	-19.2880	146.8293	0.3	20/11/1998	1746.94	146.05	510.12	372.60	201.02	254.21	648.64	4.69	248.87	773.97	14.29	88.26	272.44	1284.09	985.52
1832	72	76	-19.2880	146.8293	0.3	20/11/1998	1784.04	194.43	< D. L.	397.14	203.82	246.49	589.47	5.53	243.11	1402.91	13.81	88.23	226.49	1127.32	951.99
1832	76	80	-19.2880	146.8293	0.3	20/11/1998	1591.63	175.82	< D. L.	405.36	199.37	243.26	582.33	5.38	246.39	1412.35	14.21	88.72	228.25	1114.48	958.03
1832	80	84	-19.2880	146.8293	0.3	20/11/1998	2294.77	126.58	153.90	528.64	230.38	336.54	732.02	5.67	319.49	1030.16	16.48	105.76	240.60	1184.06	1242.37
1832	84	88	-19.2880	146.8293	0.3	20/11/1998	2770.84	94.27	41.74	607.98	243.00	387.74	889.60	5.78	368.96	1163.28	18.67	132.48	224.70	1205.02	1438.16
1832	88	92	-19.2880	146.8293	0.3	20/11/1998	2165.81	137.40	155.14	521.92	231.48	309.94	742.79	7.17	331.38	1078.61	18.83	99.15	264.68	1233.75	1165.53
1832	92	96	-19.2880	146.8293	0.3	20/11/1998	1878.42	129.91	< D. L.	538.97	223.49	274.12	640.43	5.29	272.44	1484.94	13.98	100.68	258.64	1259.29	1047.98
1832	96	100	-19.2880	146.8293	0.3	20/11/1998	2103.67	130.20	< D. L.	602.42	233.24	302.13	708.50	5.72	290.08	1549.80	15.13	94.18	275.96	1252.92	1158.31
1832	100	104	-19.2880	146.8293	0.3	20/11/1998	2240.55	128.01	50.11	811.30	231.16	355.13	721.55	5.71	284.91	1098.24	13.87	104.79	406.10	1148.35	1345.81

Carbonate carbon was calculated by subtracting Organic carbon from totla carbon. < D.L. indicates a negative carbonate carbon value.

Appendix 6 Sediment core radiochemistry analytical results

Appendix 6

Sediment core radiochemistry analytical results

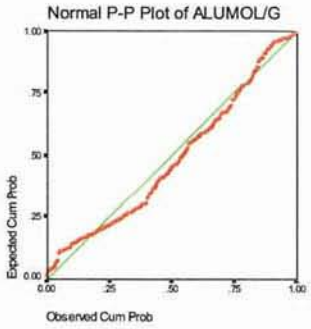
Core Number	to cm	Ra226 Bq/kg	Ra226 error Bq/kg	Pb210 Bq/kg	Pb210 error Bq/kg	Cs137 Bq/kg	Cs137 error Bq/kg	U238 Bq/kg	U238 error Bq/kg	Ra228 Bq/kg	Ra228 error Bq/kg	Th228 Bq/kg	Th228 error Bq/kg	K40 Bq/kg	K40 error Bq/kg
1827	2	21.59	1.11	44.17	7.03	1.34	0.64	36.83	5.07	32.10	2.15	37.87	1.47	516.14	21.55
1827	4	22.19	0.48	56.52	2.95	1.89	0.34	34.01	2.06	39.04	1.36	43.11	1.13	506.69	11.28
1827	6	24.61	0.96	49.91	4.59	2.57	0.49	39.10	3.59	40.33	1.62	44.97	1.49	516.64	24.58
1827	8	24.39	0.79	49.84	4.54	2.22	0.48	39.51	3.81	43.52	1.84	47.36	1.46	525.95	20.03
1827	10	24.38	0.78	52.45	4.24	2.41	0.38	36.63	2.96	42.08	1.62	44.31	1.47	543.98	18.89
1827	12	23.27	0.76	43.53	3.87	2.00	0.42	44.73	8.12	42.28	1.53	42.97	1.12	542.79	27.21
1827	14	25.03	0.78	43.98	3.80	1.78	0.40	42.61	7.75	40.76	1.45	41.47	1.07	530.43	26.41
1827	16	24.71	0.78	43.63	4.13	1.51	0.42	44.21	7.91	42.17	1.76	41.72	1.29	538.99	20.06
1827	18	27.02	1.01	41.90	4.06	1.48	0.43	42.94	7.93	44.23	1.64	42.55	1.41	535.15	25.13
1827	20	25.27	0.79	38.44	3.58	1.59	0.35	37.66	2.92	45.36	1.67	44.15	1.46	545.85	18.68
1827	24	29.97	0.93	41.38	3.95	1.61	0.38	39.93	3.22	51.26	1.87	49.25	1.62	539.58	19.01
1827	28	31.69	1.19	40.06	4.16	0.81	0.48	52.34	9.33	51.18	1.89	50.68	1.65	511.34	24.55
1827	32	28.37	0.90	35.83	4.28	1.10	0.48	37.83	8.14	51.89	2.10	50.49	1.56	541.36	20.95
1827	36	25.02	0.82	30.97	3.61	0.83	0.43	37.70	7.95	52.07	1.73	50.25	1.27	514.80	26.24
1827	40	23.72	0.71	28.54	2.76	0.87	0.28	38.13	2.64	52.53	1.68	50.09	1.53	521.29	16.97
1827	44	23.10	0.85	29.70	3.03	0.73	0.36	45.14	7.33	50.93	1.64	50.65	1.56	519.68	23.72
1827	48	23.90	0.70	28.58	3.17	-	-	37.32	6.73	53.32	1.84	52.32	1.50	545.94	19.14
1827	52	22.17	0.67	26.23	2.75	-	-	37.60	6.69	54.15	1.47	50.97	1.19	526.23	25.40
1827	56	21.40	0.65	25.11	2.71	-	-	39.61	6.79	53.92	1.47	53.17	1.22	514.30	24.87
1827	60	21.26	0.65	21.93	2.88	-	-	28.62	5.95	51.20	1.75	49.08	1.41	505.15	17.82
1827	68	22.05	0.75	24.89	3.64	-	-	35.04	7.53	54.36	2.08	52.05	1.57	533.06	20.23
1827	76	22.34	0.76	27.27	3.75	-	-	44.73	8.17	51.55	2.02	52.84	1.58	537.43	20.39
1827	84	20.97	0.71	22.09	3.05	-	-	33.21	6.24	56.36	1.94	53.99	1.71	529.93	18.43
1827	92	24.23	0.95	28.31	3.50	-	-	46.01	8.44	58.02	2.02	58.46	1.84	546.28	25.86
1827	98	22.97	0.77	22.30	3.26	-	-	37.20	7.84	57.91	1.79	54.68	1.35	559.42	28.00
1828	2	21.64	1.14	64.55	7.67	2.43	0.69	37.85	5.24	34.88	2.25	37.64	1.51	534.93	22.37
1828	4	19.46	0.72	41.23	4.57	3.92	0.66	37.79	3.57	31.99	1.78	36.62	1.16	518.52	22.69
1828	6	20.70	0.71	50.64	4.20	3.25	0.42	38.97	3.04	40.39	1.61	40.14	1.36	554.08	19.41
1828	8	21.22	0.76	44.97	3.68	3.38	0.34	38.17	2.88	43.04	1.35	41.01	1.26	527.43	23.59
1828	10	21.93	0.78	45.65	4.22	2.31	0.49	40.36	3.71	46.80	1.71	45.12	1.19	543.66	27.78
1828	12	20.65	0.62	36.46	3.80	3.44	0.54	46.41	7.18	43.86	1.70	45.35	1.25	553.95	21.74
1828	14	21.78	0.81	42.41	3.70	2.88	0.38	40.74	6.79	48.50	1.56	46.83	1.45	534.66	24.25
1828	16	20.99	0.63	38.15	3.13	2.22	0.35	46.36	7.20	50.27	1.38	48.96	1.13	529.47	25.44
1828	18	18.92	0.75	33.75	4.42	2.51	0.67	46.83	8.93	46.45	2.07	47.93	1.43	535.86	23.62
1828	20	19.92	1.01	34.32	3.40	2.63	0.60	41.36	8.57	49.53	1.90	47.17	1.29	547.46	19.56
1828	24	22.16	0.73	29.46	3.32	2.15	0.41	37.65	7.56	54.94	1.68	52.30	1.29	535.88	26.77
1828	28	21.19	0.70	35.85	3.48	1.47	0.36	37.29	2.98	56.33	1.93	52.75	1.67	529.50	18.33
1828	32	18.85	0.66	30.32	3.35	1.51	0.36	34.96	2.95	58.73	2.00	54.24	1.72	526.06	18.40
1828	36	27.02	1.01	41.90	4.06	1.48	0.43	42.94	7.93	44.23	1.64	42.55	1.41	535.15	25.13
1828	40	22.63	0.76	30.26	3.85	-	-	40.50	7.95	56.25	2.13	53.51	1.61	536.17	20.40
1828	44	19.82	0.61	33.34	4.22	0.71	0.44	42.93	7.38	47.53	1.87	49.05	1.41	511.47	14.86
1828	48	16.79	0.88	21.14	3.62	0.76	0.76	38.25	7.71	42.85	1.70	44.88	1.20	491.13	17.51
1828	52	14.22	0.62	18.61	4.45	-	-	34.32	7.47	34.25	1.70	34.99	1.09	455.48	20.28
1828	56	13.91	0.61	24.25	3.56	-	-	31.16	8.15	34.65	1.72	35.71	1.03	423.69	16.75
1828	60	13.57	0.50	18.33	2.86	-	-	43.78	7.21	32.26	1.44	34.60	0.93	428.48	14.60
1828	68	13.97	0.67	17.94	2.68	-	-	37.20	6.16	35.89	1.31	36.76	0.94	460.64	14.75
1828	76	12.81	0.50	15.08	3.45	-	-	35.35	6.09	30.02	1.37	31.22	0.93	462.32	18.49
1829	2	24.28	0.77	43.65	3.86	1.40	0.41	35.41	3.30	48.97	1.61	49.28	1.22	542.48	27.01
1829	4	24.68	0.67	40.19	3.19	1.46	0.30	31.49	2.71	46.51	1.53	48.03	1.34	530.93	17.77
1829	6	27.29	1.03	46.15	4.33	1.66	0.44	40.00	3.60	50.56	1.79	53.12	1.70	524.02	24.64
1829	8	26.65	0.82	41.23	3.68	1.35	0.35	41.25	3.10	54.44	1.86	55.76	1.75	530.91	18.20
1829	10	24.86	0.95	30.26	2.67	-	-	27.84	6.67	49.42	1.62	49.61	1.22	505.23	16.14
1829	12	25.29	0.57	30.63	2.57	0.96	0.36	32.62	2.40	52.58	1.74	48.91	1.31	483.53	12.10
1829	14	24.52	0.68	27.94	3.22	-	-	38.38	3.09	52.33	2.02	47.33	1.40	486.87	14.73
1829	16	22.82	0.77	23.87	4.14	0.93	0.64	46.16	8.69	50.43	2.13	47.29	1.39	478.30	21.67
1829	18	21.16	0.73	28.59	3.18	-	-	39.96	9.12	47.06	2.05	45.86	1.26	502.13	19.08
1829	20	22.51	1.05	27.92	3.24	0.81	0.56	34.25	8.39	45.82	1.85	45.07	1.25	500.60	18.50
1829	24	19.93	0.98	29.11	3.16	-	-	32.86	8.08	43.68	1.78	43.05	1.19	505.98	18.42
1829	28	21.93	0.65	26.42	3.21	-	-	30.26	2.98	48.42	1.93	46.39	1.38	514.64	15.31
1829	32	21.14	0.72	21.95	3.05	-	-	31.44	8.85	41.31	1.95	42.10	1.19	469.73	18.26
1829	36	20.27	0.75	22.65	4.10	1.09	0.63	22.25	8.13	41.65	1.99	42.65	1.30	498.65	22.51
1829	40	20.78	0.70	25.47	3.83	1.01	0.58	34.43	7.80	45.09	1.90	43.52	1.27	488.81	21.12
1829	44	17.50	0.63	23.30	2.78	-	-	31.83	8.14	37.80	1.76	36.07	1.03	482.65	17.57
1829	48	17.17	0.54	25.02	2.69	-	-	27.75	2.46	35.20	1.53	34.69	1.07	497.79	13.83
1829	52	17.78	0.87	21.81	2.78	-	-	23.76	7.07	36.79	1.56	36.42	1.02	505.51	17.56
1829	56	17.04	0.58	23.34	2.99	-	-	28.28	6.81	32.89	1.59	33.32	1.08	508.07	15.16
1829	60	18.92	0.72	27.96	2.81	-	-	33.33	5.99	39.48	1.35	37.04	1.19	511.44	23.26
1829	68	19.72	0.61	27.18	2.67	0.90	0.32	38.85	6.55	44.96	1.30	42.67	1.01	516.92	24.89
1829	76	18.25	0.66	29.66	3.30	-	-	22.59	6.58	40.18	1.50	38.60	1.04	524.13	26.41
1829	84	19.97	0.82	33.16	3.67	1.12	0.46	35.94	7.36	45.06	1.71	43.44	1.45	534.02	25.38
1829	92	11.57	0.54	30.12	3.14	1.57	0.39	28.20	5.84	28.71	1.23	28.74	1.01	299.99	15.19
1829	98	35.10	0.93	45.88	4.00	1.40	0.64	50.93	10.86	78.77	2.85	76.53	1.90	873.91	27.43
1831	2	22.90	1.11	35.63	3.61	1.17	0.62	32.57	3.51	46.67	1.95	46.81	1.31	536.84	20.10
1831	4	24.63	0.81	40.22	3.86	1.16	0.43	38.50	3.56	49.07	1.68	49.55	1.26	548.02	27.62
1831	6	25.30	0.97	38.95	3.94	1.21	0.44	39.58	3.58	48.95	1.75	50.85	1.63	525.87	24.77

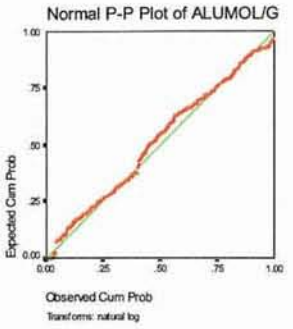
Appendix 6

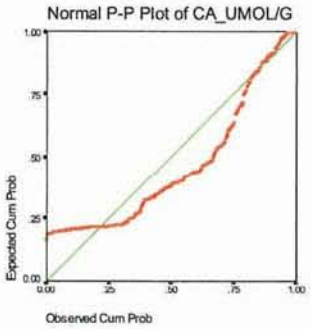
Sediment core radiochemistry analytical results

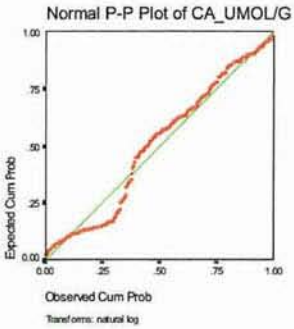
Core Number	to cm	Ra226 Bq/kg	Ra226 error Bq/kg	Pb210 Bq/kg	Pb210 error Bq/kg	Cs137 Bq/kg	Cs137 error Bq/kg	U238 Bq/kg	U238 error Bq/kg	Ra228 Bq/kg	Ra228 error Bq/kg	Th228 Bq/kg	Th228 error Bq/kg	K40 Bq/kg	K40 error Bq/kg
1831	8	24.71	0.72	39.16	3.51	1.57	0.36	35.95	3.18	45.65	1.66	50.39	1.44	546.09	19.09
1831	10	23.00	0.69	35.12	2.98	1.98	0.29	36.39	2.55	45.90	1.51	48.29	1.49	541.53	17.48
1831	12	23.69	0.71	38.72	3.60	1.71	0.38	43.41	7.22	47.17	1.73	46.85	1.37	525.03	18.75
1831	14	21.46	0.67	36.61	2.83	1.38	0.36	46.62	7.52	44.85	1.38	44.15	1.08	517.06	25.24
1831	16	22.76	0.85	34.86	3.36	1.14	0.37	46.22	7.50	43.47	1.50	44.94	1.41	522.15	23.99
1831	18	21.10	0.65	40.05	3.25	1.33	0.29	40.55	6.01	46.44	1.55	43.95	1.39	532.20	17.45
1831	20	20.94	0.68	34.19	3.43	1.39	0.32	41.91	6.47	47.59	1.67	43.79	1.41	525.35	17.90
1831	24	23.14	0.73	30.91	2.95	1.00	0.38	51.00	8.19	43.40	1.47	43.97	1.11	507.66	25.28
1831	28	22.14	0.71	28.18	3.45	1.12	0.39	40.16	7.25	44.35	1.73	44.60	1.35	528.16	19.37
1831	32	23.13	0.89	34.97	3.62	1.53	0.43	42.32	7.64	46.87	1.68	46.08	1.48	521.59	24.42
1831	36	24.09	0.93	32.66	3.55	1.30	0.43	45.34	8.00	48.57	1.73	46.13	1.51	478.63	22.76
1831	40	23.54	0.75	29.69	3.48	0.96	0.34	32.69	6.12	50.26	1.77	49.03	1.57	511.93	17.75
1831	44	24.67	0.78	27.51	3.60	1.08	0.41	37.18	7.44	51.10	1.94	47.18	1.43	491.52	18.76
1831	48	24.76	0.78	28.99	3.04	1.20	0.39	33.35	7.21	46.86	1.55	47.75	1.19	511.19	25.62
1831	52	25.77	0.98	29.81	3.44	0.94	0.44	42.29	7.83	51.77	1.81	49.36	1.59	513.36	24.15
1831	56	22.07	0.71	36.83	3.52	1.23	0.33	41.18	6.49	49.28	1.71	48.50	1.55	535.06	18.18
1831	64	29.63	0.88	30.45	3.74	1.12	0.42	35.89	7.54	55.64	2.04	54.13	1.61	520.86	19.43
1831	72	27.38	0.84	33.44	3.21	1.37	0.41	48.12	8.40	53.48	1.68	53.67	1.31	520.91	26.14
1832	2	20.43	0.74	36.38	3.43	1.06	0.58	35.62	3.54	43.45	2.05	48.29	1.33	520.37	19.85
1832	4	23.54	0.78	54.16	5.38	2.20	0.44	36.63	3.53	50.23	1.68	52.79	1.33	561.65	28.19
1832	6	24.31	0.96	51.43	5.18	2.38	0.50	39.64	3.77	47.01	1.81	54.79	1.77	556.10	26.42
1832	8	23.48	0.86	49.84	4.42	2.10	0.38	43.83	3.42	48.44	1.58	52.31	1.60	569.18	25.78
1832	10	23.97	0.70	56.03	4.59	1.67	0.36	39.72	3.06	48.34	1.38	51.88	1.20	585.95	28.00
1832	12	22.50	0.69	51.02	4.54	1.79	0.37	39.90	3.15	48.60	1.43	51.15	1.20	560.17	27.11
1832	14	23.88	0.89	43.69	4.22	1.99	0.40	42.69	3.46	48.46	1.63	51.41	1.60	566.88	25.91
1832	16	23.42	0.93	38.83	4.01	1.85	0.47	42.08	3.76	48.15	1.79	51.35	1.66	561.53	26.44
1832	18	23.41	0.77	48.06	5.03	1.94	0.44	37.54	3.49	47.56	1.62	49.25	1.24	581.51	28.94
1832	20	23.19	0.77	50.99	5.15	1.73	0.43	35.97	3.45	48.09	1.64	49.62	1.25	554.85	27.87
1832	24	23.79	0.94	30.06	3.59	1.67	0.46	37.15	7.66	47.83	1.78	46.87	1.55	533.45	25.34
1832	28	24.29	0.94	34.19	3.70	1.56	0.46	37.77	7.57	50.09	1.80	49.11	1.59	571.03	26.74
1832	32	23.10	0.76	48.96	4.97	1.64	0.42	37.25	7.58	48.64	1.62	48.38	1.21	541.19	27.03
1832	36	23.11	0.69	48.85	4.26	1.38	0.35	35.39	6.56	50.80	1.41	49.41	1.16	562.98	27.00
1832	40	22.55	0.83	31.23	3.12	1.73	0.37	43.95	7.16	49.24	1.60	47.96	1.48	546.50	24.84
1832	44	23.31	0.85	36.21	3.36	2.37	0.38	39.22	6.77	50.75	1.62	50.21	1.54	573.17	25.92
1832	48	22.58	0.68	42.38	4.08	1.44	0.35	46.04	7.37	52.61	1.45	52.34	1.21	570.30	27.34
1832	52	23.63	0.94	29.42	3.55	1.13	0.48	41.44	8.03	53.74	1.92	50.83	1.65	607.10	28.42
1832	56	23.79	0.79	28.22	3.89	2.08	0.47	46.31	8.42	52.92	2.08	52.97	1.60	584.87	21.91
1832	60	20.52	0.73	28.71	4.19			41.18	9.29	47.38	2.09	48.99	1.34	539.37	20.02
1832	64	19.71	0.68	33.60	3.74	1.44	0.37	39.53	6.70	58.15	1.99	54.52	1.73	578.77	19.92
1832	68	21.27	0.62	30.39	4.32	1.23	0.44	39.05	7.46	48.11	1.88	48.21	1.40	532.52	15.20
1832	72	24.26	0.88	29.17	2.97	1.23	0.36	40.66	6.90	57.62	1.78	55.80	1.69	566.15	25.58
1832	76	21.83	1.05	31.07	4.30	1.45	0.60	40.19	8.69	52.72	1.98	52.44	1.39	577.63	20.03
1832	80	24.08	0.70	28.93	3.12	1.47	0.36	38.97	6.70	59.29	1.94	57.56	1.62	554.35	19.13
1832	84	21.68	0.80	34.96	5.72	2.36	0.69	48.08	9.31	53.36	2.28	57.05	1.62	576.45	25.12
1832	88	21.68	0.65	32.83	2.66	1.78	0.35	48.13	7.46	62.63	1.58	61.12	1.36	563.79	26.97
1832	92	21.24	0.75	36.88	4.39	1.93	0.59	51.36	9.83	55.07	2.28	53.16	1.43	530.28	19.91
1832	96	22.91	0.68	32.27	2.95	1.76	0.30	43.03	6.14	60.88	1.86	58.51	1.74	561.73	17.97
1832	100	21.17	0.63	37.87	4.32	1.79	0.47	43.22	7.52	52.17	1.95	53.92	1.51	539.23	15.08

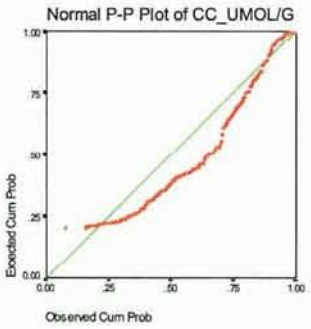
Appendix 7 Normal probability plots of chemical parameters determined in surface sediment samples and sediment core samples in Cleveland Bay

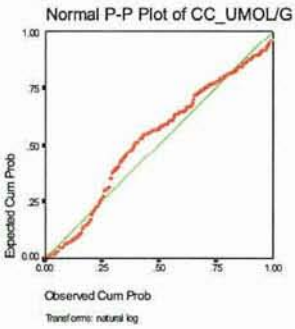

Normal P-P Plot of ALUMOL/G
Expected Cum Prob
Observed Cum Prob

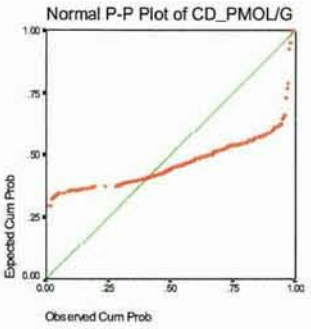

Normal P-P Plot of ALUMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

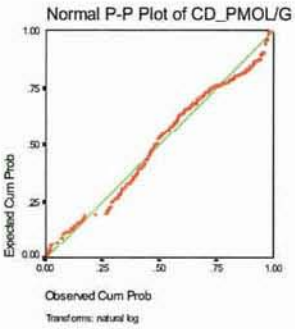

Normal P-P Plot of CA_UMOL/G
Expected Cum Prob
Observed Cum Prob

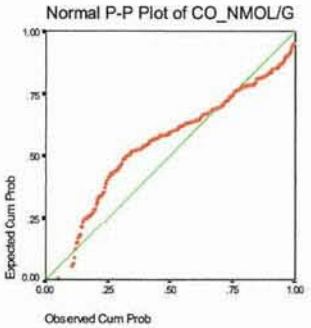

Normal P-P Plot of CA_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

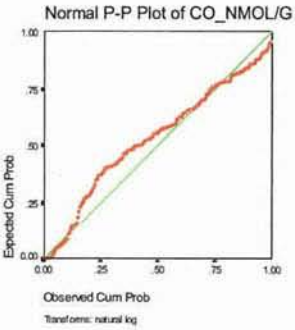

Normal P-P Plot of CC_UMOL/G
Expected Cum Prob
Observed Cum Prob

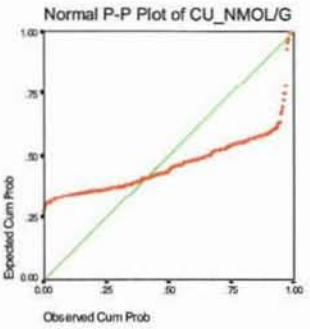

Normal P-P Plot of CC_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

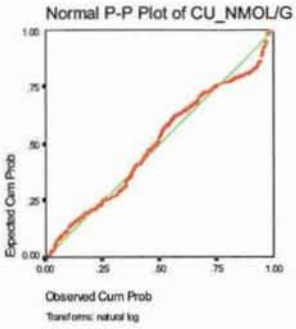

Normal P-P Plot of CD_PMOL/G
Expected Cum Prob
Observed Cum Prob

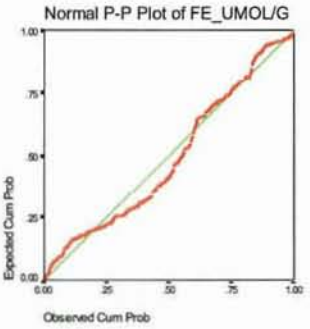

Normal P-P Plot of CD_PMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

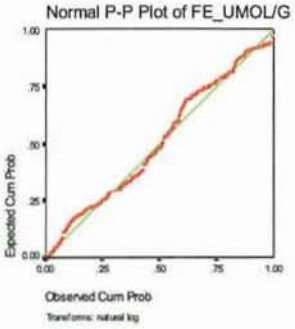

Normal P-P Plot of CO_NMOL/G
Expected Cum Prob
Observed Cum Prob

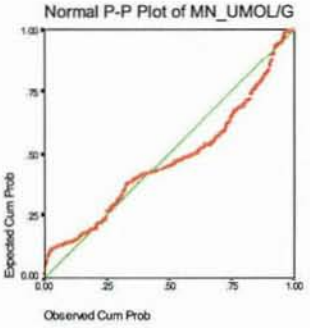

Normal P-P Plot of CO_NMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

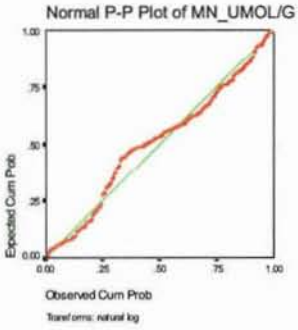

Normal P-P Plot of CU_NMOL/G
Expected Cum Prob
Observed Cum Prob

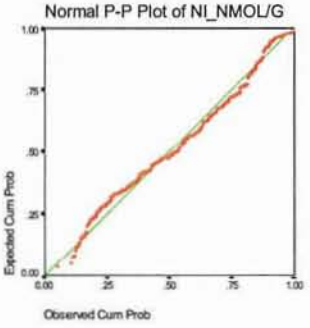

Normal P-P Plot of CU_NMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

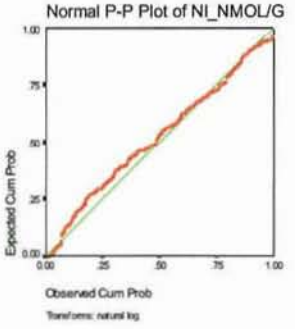

Normal P-P Plot of FE_UMOL/G
Expected Cum Prob
Observed Cum Prob

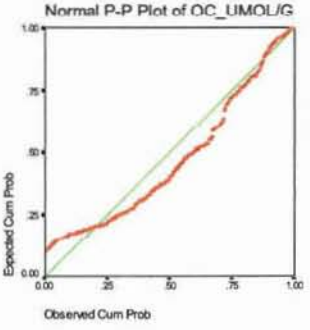

Normal P-P Plot of FE_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

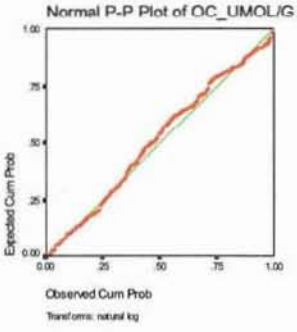

Normal P-P Plot of MN_UMOL/G
Expected Cum Prob
Observed Cum Prob

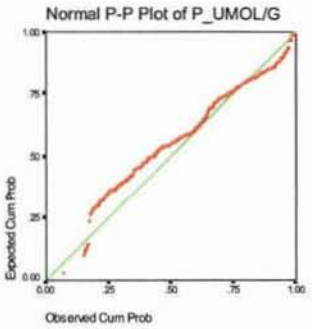

Normal P-P Plot of MN_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

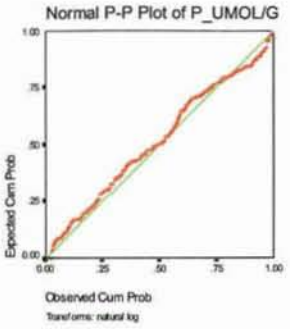

Normal P-P Plot of NI_NMOL/G
Expected Cum Prob
Observed Cum Prob

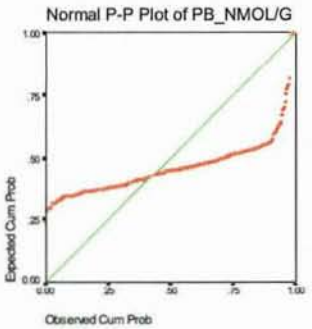

Normal P-P Plot of NI_NMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

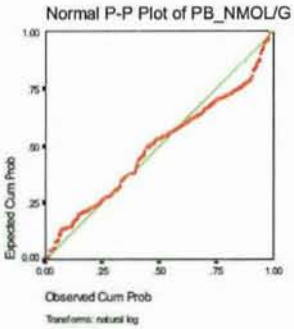

Normal P-P Plot of OC_UMOL/G
Expected Cum Prob
Observed Cum Prob

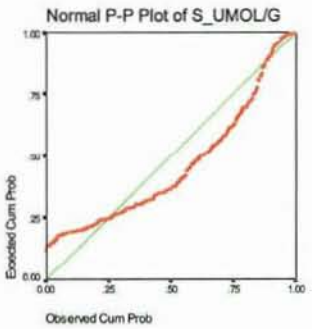

Normal P-P Plot of OC_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

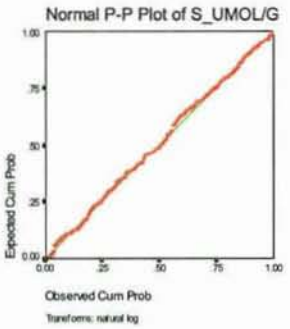

Normal P-P Plot of P_UMOL/G
Expected Cum Prob
Observed Cum Prob

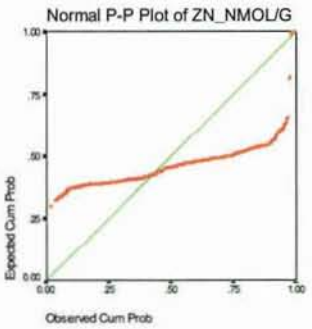

Normal P-P Plot of P_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

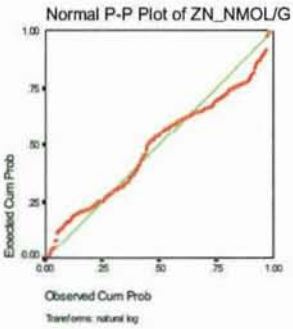

Normal P-P Plot of PB_NMOL/G
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of PB_NMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log


Normal P-P Plot of S_UMOL/G
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of S_UMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log


Normal P-P Plot of ZN_NMOL/G
Expected Cum Prob
Observed Cum Prob


Normal P-P Plot of ZN_NMOL/G
Expected Cum Prob
Observed Cum Prob
Transforms: natural log

Appendix 8 Sediment core acid volatile sulfide (AVS) and simultaneously extracted metal (SEM) analytical results

Appendix 8

Sediment core acid volatile sulphide (AVS) and simultaneously extracted metal (SEM) analytical results

Core Number	Depth to cm	Al µmol/g	AVS nmol/g	Ca µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	P µmol/g	Pb nmol/g	Zn nmol/g
1827	2	83.61	33.12	377.12	278.50	93.92	258.38	85.96	16.90	57.28	7.44	165.72	1047.10
1827	4	78.29	26.59	367.60	1233.18	93.02	255.75	80.43	20.23	39.61	7.11	171.80	917.74
1827	6	81.51	11.74	368.14	200.81	94.67	258.46	89.76	19.11	40.88	7.30	181.33	915.47
1827	8	53.83	40.73	299.24	164.15	68.67	139.63	62.40	8.55	27.71	5.71	107.38	635.92
1827	10	56.44	232.20	276.16	175.94	68.74	134.52	67.13	7.29	27.88	5.73	124.13	678.03
1827	12	71.54	1983.20	330.92	237.64	74.24	88.78	83.66	6.26	29.80	6.21	113.20	752.12
1827	14	79.93	2430.85	360.81	278.88	76.31	87.40	87.92	6.34	30.11	6.80	116.79	798.71
1827	16	83.83	3312.46	433.77	184.26	76.92	63.26	93.11	7.34	32.64	6.53	112.81	784.83
1827	18	90.12	3019.30	480.01	226.93	84.10	86.76	99.88	8.09	30.66	7.72	116.21	849.08
1827	20	78.22	2464.85	365.21	171.77	68.03	50.73	86.44	6.76	27.56	6.20	97.75	678.38
1827	24	79.14	2149.52	435.86	228.72	74.77	46.49	93.25	12.21	30.27	5.91	121.05	620.92
1827	28	58.19	1284.64	523.46	136.41	48.32	30.58	64.95	6.03	18.03	4.68	68.23	370.87
1827	32	67.15	1266.92	419.97	161.88	70.54	42.83	81.95	6.64	23.07	7.13	75.31	514.50
1827	36	56.63	2140.29	379.63	144.11	55.05	38.61	70.94	5.87	18.23	5.60	74.10	422.53
1827	40	66.19	2559.38	367.90	190.11	74.94	42.26	86.21	6.95	23.91	7.98	80.65	574.76
1827	44	66.99	1192.12	493.59	199.04	69.00	39.57	79.96	7.04	23.14	7.77	66.70	415.57
1827	48	70.93	1649.91	410.60	155.30	67.30	40.07	81.20	6.80	22.30	7.00	74.04	383.45
1827	52	73.20	2129.15	475.36	244.88	64.17	26.14	84.06	6.88	20.87	7.03	75.89	346.20
1827	56	74.45	1910.97	424.48	143.51	68.51	42.08	80.86	7.07	22.14	7.42	76.83	331.94
1827	60	69.70	2559.68	415.42	591.53	63.72	33.03	79.13	6.05	26.60	6.88	60.00	287.49
1827	68	74.24	1198.10	505.52	104.39	62.25	41.54	78.41	6.77	21.65	7.84	77.02	227.40
1827	76	80.53	1152.06	499.53	126.06	63.39	34.12	87.20	7.17	23.04	7.81	90.18	322.53
1827	84	84.67	1299.61	477.85	110.70	56.07	25.17	81.70	6.77	19.42	7.40	76.43	215.95
1827	92	78.43	1300.00	539.52	144.77	71.17	64.94	71.16	7.07	30.99	8.31	95.19	216.06
1827	100	86.27	1499.44	475.46	132.14	70.98	48.50	95.20	6.97	29.82	8.13	91.79	221.51
1827	104	81.64	1142.10	432.56	113.55	55.32	42.03	83.74	7.77	23.24	7.10	90.47	297.02
1829	2	128.04	93.10	349.97	199.82	84.52	131.60	140.20	15.23	74.51	8.49	88.90	564.89
1829	4	57.02	157.25	333.76	57.15	52.25	33.69	73.28	10.50	29.52	6.13	34.99	196.91
1829	6	55.41	35.02	462.24	66.13	56.50	57.24	75.35	8.94	31.51	5.89	36.87	210.64
1829	8	88.52	39.34	281.65	78.08	76.41	53.02	102.71	8.67	45.97	6.90	34.83	294.64
1829	10	65.49	10.93	330.89	109.53	90.50	60.53	100.47	9.37	39.28	7.50	44.87	173.28
1829	12	49.49	67.33	332.90	79.52	74.86	20.92	79.69	8.05	25.76	7.09	23.55	154.03
1829	14	51.23	179.52	326.61	129.30	74.43	17.60	77.72	7.20	27.76	7.33	24.00	173.53
1829	16	49.48	313.19	406.43	69.06	71.60	22.40	75.21	9.28	25.43	8.02	25.26	193.06
1829	18	46.80	8.20	350.80	45.29	67.47	28.45	83.03	20.87	26.05	7.68	29.11	125.86
1829	20	72.41	13.89	378.42	161.13	82.76	66.60	111.68	20.67	46.77	8.54	52.28	257.24
1829	24	63.05	1231.42	370.90	87.21	68.93	37.83	82.11	8.20	33.95	7.18	33.71	176.71
1829	28	60.32	752.38	379.25	68.41	71.89	30.16	80.98	10.88	28.30	8.05	34.56	161.12
1829	32	61.42	1709.01	437.05	57.23	78.96	24.44	96.93	10.37	30.98	8.31	28.20	155.71
1829	36	55.64	5474.09	434.58	72.53	57.32	14.56	77.69	9.64	26.89	6.65	28.07	147.22
1829	40	60.88	4401.49	357.56	54.46	76.88	17.79	90.48	10.81	30.22	7.63	26.70	153.54
1829	44	57.40	6728.32	384.39	45.13	58.00	17.73	77.61	9.66	28.46	6.69	25.03	151.13
1829	48	61.77	6916.82	506.85	47.02	68.38	17.26	86.73	11.20	28.58	7.39	28.45	159.77
1829	52	60.06	8929.94	430.57	77.89	45.92	17.67	70.91	10.25	23.28	6.20	31.47	137.97
1829	56	33.94	7537.71	284.19	33.28	43.06	9.72	50.58	6.40	16.25	4.47	16.60	94.98
1829	60	38.98	7407.22	231.90	23.23	50.38	8.11	56.61	5.93	19.13	4.80	14.86	109.52
1829	68	59.56	5409.70	553.80	57.45	67.77	14.36	84.83	12.81	25.86	7.00	24.70	143.99
1829	76	55.20	8077.96	480.99	100.61	46.88	11.08	68.96	12.05	21.86	6.78	30.07	115.26
1829	84	67.85	5539.94	484.41	197.20	66.74	24.29	90.70	12.09	26.52	7.89	36.20	159.65
1829	92	76.65	5679.33	454.21	94.63	60.23	14.72	101.29	16.86	27.37	8.16	48.18	151.07
1829	98	84.08	5433.32	222.93	73.46	36.66	3.96	54.16	10.69	22.71	5.59	31.20	127.31
1829	104	165.91	12980.29	692.24	128.60	115.60	32.47	137.62	31.73	58.14	15.22	60.39	302.36
1831	2	63.59	45458.87	44.18	216.22	39.13	72.27	121.17	3.12	44.59	19.00	52.06	268.20
1831	4	68.74	50996.12	38.21	312.26	37.81	53.57	135.20	1.79	50.51	12.04	51.61	302.25
1831	6	264.72	68356.48	91.20	761.32	100.44	238.45	292.71	4.47	147.37	31.80	123.60	715.71
1831	8	121.61	116472.57	44.45	408.76	44.01	78.82	146.83	1.99	58.32	11.96	49.83	328.81
1831	10	97.20	78819.93	47.83	457.77	45.99	57.89	148.09	2.53	52.49	16.58	60.64	348.44
1831	12	85.91	76048.86	44.51	485.78	36.72	38.58	114.95	1.72	47.89	9.86	48.61	298.68
1831	14	87.87	88493.79	53.31	1202.87	38.31	34.59	121.88	1.97	45.77	11.23	52.22	311.47
1831	16	82.10	92643.86	52.75	1078.24	36.76	28.23	109.45	1.64	43.80	9.13	47.95	296.42
1831	18	103.04	90294.33	48.31	476.90	45.49	57.61	124.04	1.63	58.35	9.43	54.23	370.54
1831	20	96.74	86324.40	61.24	355.45	41.38	61.08	114.07	1.74	47.09	8.59	50.61	312.06
1831	24	89.52	70173.96	53.04	350.47	38.84	43.19	115.38	2.07	49.58	9.87	49.49	307.59
1831	28	77.25	40668.98	63.37	416.67	41.36	50.30	94.87	2.30	56.38	9.32	49.47	330.72
1831	32	90.02	84196.19	77.13	454.76	40.41	35.14	107.10	2.17	48.54	10.67	61.67	368.57
1831	36	70.36	68265.56	97.82	363.61	33.35	13.97	91.64	1.77	41.94	9.17	46.38	290.19
1831	40	88.46	87440.07	102.60	392.43	36.10	30.99	73.08	1.66	75.68	12.59	55.28	350.36
1831	44	77.79	52237.93	144.31	318.65	30.90	8.71	70.85	1.87	38.81	12.89	42.39	308.27
1831	48	78.19	94075.01	85.46	365.69	34.76	16.33	71.02	1.47	91.86	11.61	52.41	335.64
1831	52	80.65	49468.18	76.46	437.76	41.14	17.83	92.63	2.15	85.61	16.78	64.10	334.92
1831	56	81.74	96589.65	56.58	317.08	42.62	42.18	126.57	1.99	79.41	16.08	63.31	417.88
1832	2	67.83	64.91	40.08	361.13	63.44	213.48	114.16	9.22	40.85	7.38	131.73	406.48
1832	4	86.31	3154.30	50.63	354.21	52.84	173.48	127.50	5.72	44.70	8.86	108.14	529.44
1832	6	106.54	13147.54	49.68	640.61	51.85	155.12	137.76	3.64	46.34	8.78	106.94	577.50
1832	8	361.76	15655.81	193.55	1422.83	192.77	528.92	556.21	15.54	167.51	33.97	403.89	1938.97

Appendix 8

Sediment core acid volatile sulphide (AVS) and simultaneously extracted metal (SEM) analytical results

Core Number	Depth to cm	Al µmol/g	AVS nmol/g	Ca µmol/g	Cd pmol/g	Co nmol/g	Cu nmol/g	Fe µmol/g	Mn µmol/g	Ni nmol/g	P µmol/g	Pb nmol/g	Zn nmol/g
1832	10	188.61	12901.36	99.23	717.86	92.03	173.19	285.50	7.71	68.96	17.29	189.68	1194.52
1832	12	104.29	20834.09	52.60	384.77	46.77	89.88	157.82	4.05	51.33	8.96	103.73	588.23
1832	14	82.13	19314.08	44.14	507.01	41.55	54.33	135.00	4.00	31.50	7.51	85.00	466.61
1832	16	197.98	20000.00	86.91	803.61	80.36	178.72	276.48	8.70	82.16	15.57	162.27	1051.29
1832	18	134.04	18000.00	74.46	692.07	56.82	91.46	197.56	5.69	52.43	11.27	120.89	1178.42
1832	20	113.30	19000.00	52.74	405.39	44.99	115.20	156.60	3.43	35.87	8.30	100.61	630.10
1832	24	86.95	15382.00	64.32	340.29	38.00	30.41	104.71	2.37	39.13	8.81	63.46	688.75
1832	28	123.81	24485.70	99.38	909.63	56.24	32.64	159.84	3.48	215.48	10.45	96.32	2035.69
1832	32	127.89	14416.33	72.61	3388.83	52.99	36.75	178.98	3.51	56.08	10.05	107.72	1419.65
1832	36	105.16	11643.62	82.69	600.17	50.86	24.28	157.03	3.05	45.09	9.84	91.89	1652.21
1832	40	109.27	22323.00	66.47	425.65	45.79	42.43	153.56	2.79	42.66	8.48	89.93	625.23
1832	44	124.47	22236.97	72.52	547.71	54.53	37.38	179.90	3.02	51.16	9.63	112.02	841.04
1832	48	78.37	10098.79	57.14	656.05	38.22	29.25	123.21	1.76	32.39	8.37	56.66	541.48
1832	52	81.04	10451.71	64.51	232.57	36.65	40.88	121.44	1.79	30.52	10.69	55.81	398.95
1832	56	68.49	9475.63	93.91	351.24	32.28	13.86	100.75	1.60	27.44	9.23	45.33	714.27
1832	60	73.79	11448.07	67.44	249.31	37.82	14.50	118.58	1.83	29.15	12.98	57.04	385.51
1832	64	72.25	13118.56	73.16	533.82	36.56	15.96	104.62	1.60	32.90	10.07	55.32	632.17
1832	68	77.52	11655.85	65.23	350.18	38.01	14.15	124.05	1.69	33.98	9.84	52.95	452.68
1832	72	89.56	20974.65	100.63	368.44	45.77	-6.42	175.41	2.40	39.97	12.07	60.02	467.41
1832	76	125.32	25666.94	96.90	981.62	55.01	16.80	142.81	3.22	53.53	9.05	69.31	1320.27
1832	80	94.44	17605.72	72.49	568.27	40.73	34.49	109.99	3.00	37.11	8.97	69.10	485.09
1832	84	94.90	15856.57	71.03	701.99	41.64	29.68	105.41	2.71	35.91	9.68	69.08	490.38
1832	88	77.57	16506.60	51.02	350.96	30.57	7.71	87.16	2.20	27.05	9.62	58.91	384.37
1832	92	108.00	18088.57	111.46	543.79	49.15	21.76	120.46	4.80	35.97	13.74	75.56	415.34
1832	96	78.05	15556.55	74.37	415.55	34.44	22.46	81.50	2.31	31.28	8.86	57.83	367.10
1832	100	90.94	15599.92	80.92	469.96	40.05	16.19	95.66	2.76	28.47	9.59	64.98	420.20
1832	104	103.74	11521.94	68.76	656.34	25.17	5.31	65.22	2.08	19.43	7.51	50.88	477.84

Appendix 9 DGT site sediment core analytical results

Appendix 9.1

Dissolved metal concentrations in surface waters and pore waters

from a shallow sediment core adjacent to DGT probe deployments in Ross Creek

Depth		*ASV determination			**ICP determination								
from	**to**	**porosity**	**pH**	**Eh**	**Cd***	**Co**	**Cu***	**Fe****	**Mn****	**Ni**	**Pb***	**S****	**Zn***
cm	cm			mv	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	nmol/l	umol/ml	nmol/l
surface water			8.2		5.9	n.d.	111	1074	728	n.d.	13	24	646
0	2	0.73	7.1	-200	4.9	n.d.	59	5372	60612	n.d.	n.d.	25	1589
2	4	0.62	7.16	-420	2	n.d.	n.d.	11459	28213	n.d.	23.2	26	1324
4	6	0.65	7.11	-740	3.9	n.d.	283	4297	22570	n.d.	92.7	26	306
6	8	0.64	7.15	-760	1	n.d.	87	2328	23662	n.d.	3.9	27	413
8	10	0.65	7.45	-870	2.9	n.d.	44	4297	13469	n.d.	8.7	24	n.d.
10	12	0.66	7.46	-910	3.9	n.d.	70	1970	11285	n.d.	8.7	28	840
12	14	0.67	7.36	-935	2	n.d.	55	1432	17474	n.d.	9.2	26	257
14	16	0.63	7.33	-980	7.8	n.d.	37	537	10193	n.d.	2.9	27	488
16	18	0.64	7.43	-920	2.9	n.d.	148	1432	11649	n.d.	89.8	26	526

Appendix 9.2

Whole sediment strong acid soluble metals, organic carbon and carbonate carbon

from a shallow sediment core adjacent to DGT probe deployments in Ross Creek

Depth from	to	Al	Ca	CC	Cd	Co	Cu	Fe	Mn	Ni	OC	Pb	P	S	Zn
cm	cm	umol/g	umol/g	umol/g	pmol/g	nmol/g	nmol/g	umol/g	umol/g	nmol/g	umol/g	nmol/g	umol/g	umol/g	nmol/g
0	2	1620	179	89	4213	137	1209	476	9.11	252	1170	2042	3.5	178	7832
2	4	1718	87	4	6915	175	1460	473	4.10	279	1015	1604	4.4	213	10559
4	6	1982	78	117	8600	184	1650	513	3.95	302	1113	1616	5.7	211	12652
6	8	1891	97	23	7044	186	1499	529	4.41	313	1063	1681	5.0	251	11403
8	10	1739	98	28	6668	168	1309	530	4.14	243	1102	1589	4.5	314	10625
10	12	1682	98	62	6327	165	1101	513	4.59	244	933	1617	3.8	261	9484
12	14	1798	93	49	5972	158	1308	560	4.23	238	1074	1660	4.6	291	10179
14	16	1616	100	54	6326	164	1131	504	4.42	232	1059	1610	4.0	298	9618
16	18	1806	97	47	6155	160	1294	563	4.09	269	935	1610	4.5	316	10075

Appendix 9.3

Simultaneously extracted metals (SEM) and acid volatile sulphide (AVS)

from a shallow sediment core adjacent to DGT probe deployments in Ross Creek

Depth from	to	AVS	Al	Ca	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	ΣSEM	ΣSEM/AVS
cm	cm	umol/g	umol/g	umol/g	nmol/g	nmol/g	nmol/g	umol/g	umol/g	nmol/g	nmol/g	nmol/g	umol/g	
0	2	2.31	87	79	1.1	2.31	616	65	3.19	25	499	5771	6.91	3.0
2	4	6.90	60	31	1.9	1.09	44	44	0.46	14	548	6006	6.62	1.0
4	6	7.72	92	54	2.3	1.59	256	53	0.59	20	664	7616	8.56	1.1
6	8	8.75	69	41	2.6	2.50	51	61	0.87	18	606	6673	7.35	0.8
8	10	10.23	56	42	1.4	0.00	36	69	0.73	16	454	5395	5.90	0.6
10	12	12.05	61	46	2.4	0.00	16	60	0.77	10	520	6080	6.63	0.6
12	14	13.55	83	63	2.4	0.00	73	95	1.09	13	698	7999	8.79	0.6
14	16	10.50	63	52	2.5	8.70	52	63	0.92	11	511	5922	6.51	0.6
16	18	10.19	67	52	3.3	0.53	35	63	1.05	18	550	6633	7.24	0.7

Appendix 10 DGT sediment probe time averaged fluxes

Appendix 10

DGT probe deployment time (72h) averaged flux

Probe #	Sample #	Depth cm	Depth cm	Cd pmol/cm2/h	Co pmol/cm2/h	Cu pmol/cm2/h	Fe pmol/cm2/h	Mn pmol/cm2/h	Ni pmol/cm2/h	Pb pmol/cm2/h	Zn pmol/cm2/h
1	501	7.5	6.5	0.52	0.58	9.62	< M. D. L.	263	11.08	1.02	1173
1	502	6.5	5.5	0.46	0.50	11.46	< M. D. L.	275	12.14	0.75	885
1	503	5.5	4.5	0.46	0.61	12.60	< M. D. L.	256	12.32	0.70	708
1	504	4.5	3.5	0.44	0.65	8.89	< M. D. L.	271	9.93	1.11	642
1	505	3.5	2.5	0.39	0.62	7.63	< M. D. L.	284	7.82	0.66	497
1	506	2.5	1.5	0.42	0.68	6.99	< M. D. L.	296	7.81	0.62	477
1	507	1.5	0.5	0.80	< M. D. L.	3.35	< M. D. L.	558	10.66	1.39	826
1	508	0.5	0	0.94	< M. D. L.	3.64	< M. D. L.	626	9.80	2.77	916
1	509	0	-0.5	1.17	2.94	7.17	< M. D. L.	1244	11.27	4.70	1112
1	510	-0.5	-1	0.61	6.89	6.55	< M. D. L.	1592	6.34	3.51	679
1	511	-1	-1.5	0.27	5.54	< M. D. L.	1712	1209	7.54	3.87	773
1	512	-1.5	-2	0.33	4.40	< M. D. L.	2317	1195	5.71	3.67	646
1	513	-2	-2.5	< M. D. L.	2.98	< M. D. L.	2856	1176	5.50	3.32	631
1	514	-2.5	-3	< M. D. L.	2.22	< M. D. L.	2616	1140	3.62	2.90	456
1	515	-3	-3.5	0.24	3.69	< M. D. L.	856	1555	4.50	3.09	552
1	516	-3.5	-4	0.20	4.92	< M. D. L.	1403	1570	3.93	4.44	573
1	517	-4	-4.5	< M. D. L.	< M. D. L.	< M. D. L.	4578	1060	7.78	2.74	692
1	518	-4.5	-5	< M. D. L.	< M. D. L.	< M. D. L.	4159	871	1.63	2.09	585
1	519	-5	-5.5	< M. D. L.	< M. D. L.	< M. D. L.	4193	933	4.01	1.92	778
1	520	-5.5	-6	< M. D. L.	< M. D. L.	< M. D. L.	5453	1264	5.15	1.93	539
1	521	-6	-6.5	< M. D. L.	< M. D. L.	13.94	6626	1739	13.03	3.39	790
1	522	-6.5	-7	< M. D. L.	< M. D. L.	0.00	5594	1204	6.83	2.33	483
1	523	-7	-7.5	0.196	< M. D. L.	12.03	5831	1102	7.71	2.19	501
1	524	-7.5	-8	0.243	< M. D. L.	6.48	5751	1508	5.34	3.11	595
1	525	-8	-8.5	< M. D. L.	< M. D. L.	< M. D. L.	5800	1692	3.16	2.05	442
1	526	-8.5	-9	< M. D. L.	< M. D. L.	< M. D. L.	5660	1609	4.60	1.70	474
1	527	-9	-10	< M. D. L.	< M. D. L.	1.17	3051	887	2.25	0.49	213
1	528	-10	-11	0.052	0.26	3.04	3331	847	2.78	0.56	254
1	529	-11	-12	0.060	0.24	3.18	2963	808	2.87	0.72	289
1	530	-12	-13	0.077	0.23	6.33	2821	931	3.53	0.82	337
1	531	-13	-14	0.065	0.28	5.91	3043	869	3.56	0.72	298
1	532	-14	-15	0.058	0.25	5.10	2851	873	3.82	0.62	270
1	533	-15	-16	0.060	0.29	4.32	220	938	4.31	0.72	394
1	534	-16	-17	0.085	0.22	5.04	2118	929	4.19	0.68	349
1	535	-17	-18	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.
1	536	-18	-19	0.117	0.21	10.41	2399	761	3.62	0.66	311
1	537	-19	-20	0.052	< M. D. L.	3.35	1678	680	2.11	0.54	183
2	538	7.5	6.5	0.187	0.41	12.97	3168	1579	8.83	1.67	667
2	539	6.5	5.5	0.402	0.62	18.17	790	234	6.00	2.89	827
2	540	5.5	4.5	0.364	0.48	14.95	550	225	7.57	1.59	636
2	541	4.5	3.5	0.443	0.43	12.21	< M. D. L.	219	4.88	0.83	654
2	542	3.5	2.5	0.379	0.39	13.95	< M. D. L.	232	5.14	0.81	598
2	543	2.5	1.5	0.440	0.46	13.40	< M. D. L.	266	4.67	0.82	613
2	544	1.5	0.5	0.656	0.92	0.00	< M. D. L.	485	7.34	1.20	957
2	545	0.5	0	< M. D. L.	< M. D. L.	9.17	< M. D. L.	26	< M. D. L.	0.90	< M. D. L.
2	546	0	-0.5	0.719	< M. D. L.	27.73	< M. D. L.	639	5.10	16.82	1067
2	547	-0.5	-1	1.348	2.73	37.86	< M. D. L.	1168	9.86	4.10	1755
2	548	-1	-1.5	1.007	10.77	21.41	< M. D. L.	1993	6.23	4.41	1102
2	549	-1.5	-2	0.872	16.87	15.31	< M. D. L.	2044	6.81	5.11	1002
2	550	-2	-2.5	0.527	18.14	9.44	1210	3069	7.59	4.84	1125
2	551	-2.5	-3	0.182	10.35	6.03	6908	2680	3.70	2.36	902
2	552	-3	-3.5	< M. D. L.	7.49	2.78	6401	1970	6.62	1.01	528
2	553	-3.5	-4	< M. D. L.	9.95	4.61	10257	2484	7.96	1.49	709
2	554	-4	-4.5	< M. D. L.	11.81	4.37	17171	2731	9.97	1.73	996
2	555	-4.5	-5	< M. D. L.	9.04	5.13	14096	2141	8.00	1.54	865
2	556	-5	-5.5	0.259	7.23	1.93	12285	1633	7.25	1.40	748
2	557	-5.5	-6	< M. D. L.	17.94	5.74	26631	4116	15.67	3.34	1885
2	558	-6	-6.5	< M. D. L.	11.05	2.27	23659	3008	10.99	2.49	1122
2	559	-6.5	-7	< M. D. L.	6.88	2.58	17348	2106	7.89	1.69	789
2	560	-7	-7.5	< M. D. L.	6.40	2.63	10268	1928	6.38	3.01	867
2	561	-7.5	-8	< M. D. L.	5.07	0.00	9221	2681	8.36	2.65	1306
2	562	-8	-8.5	< M. D. L.	2.09	2.08	6252	1764	2.96	1.84	790
2	563	-8.5	-9	< M. D. L.	3.15	1.46	10465	2715	5.20	1.84	1016
2	564	-9	-10	< M. D. L.	1.60	5.48	6742	1494	2.73	0.85	489
2	565	-10	-11	< M. D. L.	2.00	1.98	6209	< M. D. L.	4.12	0.80	457
2	566	-11	-12	< M. D. L.	2.85	2.78	7573	< M. D. L.	2.85	0.65	320
2	567	-12	-13	< M. D. L.	2.79	2.47	7627	< M. D. L.	3.31	0.73	356
2	568	-13	-14	< M. D. L.	1.90	2.59	5913	< M. D. L.	2.97	0.82	381
2	569	-14	-15	< M. D. L.	1.27	3.85	4379	< M. D. L.	2.81	0.74	353
2	570	-15	-16	< M. D. L.	1.01	3.83	4756	< M. D. L.	3.40	0.86	432
2	571	-16	-17	< M. D. L.	0.57	7.32	4427	1546	3.84	0.84	449
2	572	-17	-18	< M. D. L.	0.45	4.65	3678	1183	3.44	0.71	404
2	573	-18	-19	< M. D. L.	0.40	0.00	3436	1276	3.90	0.79	434
2	574	-19	-20	< M. D. L.	< M. D. L.	13.40	< M. D. L.	40	< M. D. L.	0.20	< M. D. L.
3	575	7.5	6.5	0.137	0.18	8.08	< M. D. L.	77	2.87	0.43	182
3	576	6.5	5.5	0.365	0.58	24.43	< M. D. L.	259	6.84	1.32	416
3	577	5.5	4.5	0.350	0.58	19.86	< M. D. L.	245	6.41	0.88	382
3	578	4.5	3.5	0.408	0.67	21.95	< M. D. L.	290	6.28	0.77	386

Appendix 10

DGT probe deployment time (72h) averaged flux

Probe #	Sample #	Depth cm	Depth cm	Cd pmol/cm2/h	Co pmol/cm2/h	Cu pmol/cm2/h	Fe pmol/cm2/h	Mn pmol/cm2/h	Ni pmol/cm2/h	Pb pmol/cm2/h	Zn pmol/cm2/h
3	579	3.5	2.5	< M. D. L.	< M. D. L.	< M. D. L.	< M. D. L.	40	< M. D. L.	0.30	< M. D. L.
3	580	2.5	1.5	0.379	0.65	19.39	< M. D. L.	299	5.71	0.83	287
3	581	1.5	0.5	0.334	0.65	18.48	< M. D. L.	330	5.33	0.55	336
3	582	0.5	0	0.357	0.71	16.47	< M. D. L.	348	5.15	0.56	315
3	583	0	-0.5	0.814	0.00	19.48	< M. D. L.	1011	12.84	1.79	923
3	584	-0.5	-1	0.739	2.11	17.70	< M. D. L.	1239	12.08	1.65	783
3	585	-1	-1.5	0.272	1.44	7.96	< M. D. L.	829	5.25	0.83	354
3	586	-1.5	-2	3.189	20.28	71.53	< M. D. L.	10216	74.15	8.07	4181
3	587	-2	-2.5	0.283	3.74	8.46	< M. D. L.	1793	5.53	1.16	422
3	588	-2.5	-3	< M. D. L.	7.28	4.08	4580	1992	7.71	1.87	589
3	589	-3	-3.5	< M. D. L.	4.93	2.53	5336	1565	5.55	1.80	414
3	590	-3.5	-4	< M. D. L.	5.66	8.31	11293	1688	4.34	1.63	396
3	591	-4	-4.5	< M. D. L.	5.72	2.43	20192	1327	6.59	1.52	382
3	592	-4.5	-5	< M. D. L.	3.84	3.03	17407	1171	6.09	1.38	377
3	593	-5	-5.5	< M. D. L.	2.59	1.43	13921	1234	4.61	1.76	391
3	594	-5.5	-6	< M. D. L.	1.18	1.36	12187	1340	4.19	1.28	272
3	595	-6	-6.5	< M. D. L.	< M. D. L.	4.76	13156	1746	4.37	4.28	323
3	596	-6.5	-7	< M. D. L.	< M. D. L.	< M. D. L.	3864	449	< M. D. L.	0.75	62
3	597	-7	-7.5	< M. D. L.	0.88	1.97	8813	1462	4.60	0.95	258
3	598	-7.5	-8	< M. D. L.	1.04	2.49	10128	1788	8.14	10.64	409
3	599	-8	-8.5	< M. D. L.	4.57	7.86	31206	5579	14.54	3.73	875
3	600	-8.5	-9	< M. D. L.	0.48	1.23	7893	1648	3.98	1.18	289
3	601	-9	-10	< M. D. L.	< M. D. L.	1.94	6157	1530	5.12	1.13	335
3	602	-10	-11	< M. D. L.	< M. D. L.	1.61	5971	1601	3.80	1.75	339
3	603	-11	-12	< M. D. L.	0.41	1.78	3535	876	1.81	0.38	149
3	604	-12	-13	< M. D. L.	0.31	3.17	3371	835	2.21	0.49	186
3	605	-13	-14	< M. D. L.	0.21	2.23	3367	781	1.87	0.43	134
3	606	-14	-15	< M. D. L.	0.51	2.77	3216	1107	1.69	0.39	158
3	607	-15	-16	< M. D. L.	< M. D. L.	3.66	3393	813	5.16	0.53	195
3	608	-16	-17	< M. D. L.	< M. D. L.	4.37	5368	1409	3.63	0.77	252
3	609	-17	-18	< M. D. L.	< M. D. L.	3.98	3415	935	3.11	0.52	180
3	610	-18	-19	< M. D. L.	< M. D. L.	4.71	3106	961	3.30	0.52	198
3	611	-19	-20	< M. D. L.	< M. D. L.	6.67	3922	1309	4.77	1.10	363