AN ASSESSMENT OF SELECTED METAL POLLUTANTS IN DURBAN HARBOUR

by

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DECLARATION OF CANDIDATE

I, Vimla Paul, declare that unless indicated, this dissertation is my own work and that it has not been submitted for a degree at another Technikon or Institution.

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ABSTRACT

The purpose of this study was to determine the concentration of selected metals in Durban Harbour water and sediments. Four sites were selected for the investigation. The water and sediment samples were collected from July 1998 to July 1999 to accommodate seasonal changes.

The water samples (collected from the surface of the harbour) and sediment samples (obtained from the bed of the harbour with a corer) were analysed immediately. Since the water samples generally contained relatively low amounts of analyte in a complex salt matrix, recourse to pre-concentrate was necessary. Sodium diethyldithiocarbamate was used as a chelating agent and chloroform as the extracting solvent. The corresponding sediment samples were completely digested with concentrated HNO_3 and HF using the microwave technique.

Preliminary studies showed that the atomic absorption spectroscopy was not sensitive enough for the determination of the selected metals in water. Graphite furnace atomic absorption spectrophotometer was therefore routinely used for the analysis of Cu, Ni and Pb in the harbour water and sediment samples. The inductively coupled plasma atomic emission spectrophotometer was used to determine the concentration of Zn, Fe, Ti, Al and Ca in the harbour sediment samples. These metals that can be toxic at elevated levels were randomly chosen to provide a profile of metals in the sediments.

The levels found in the water and sediments for Cu ranged from 0.34 to 4.83 $\mu g.L^{-1}$ and 100 to 252 $mg.kg^{-1}$; for Ni from 0.70 to 8.80 $\mu g.L^{-1}$ and 91 to 103 $mg.kg^{-1}$ and for Pb from 0.50 to 10.30 $\mu g.L^{-1}$ and 49 to 110 $mg.kg^{-1}$ respectively. The concentration of Zn, Fe, Ti, Al and Ca in the harbour sediment samples were approximately 2 %, 24 %, 1 %, 5 % and 2 % respectively. The results obtained in this study were compared to those reported for Botany Bay (Australia), Victoria Harbour (Hong Kong) and Puck Bay (Poland). The concentration of Cu in the water and the concentration of Cu, Ni, Pb and Zn in sediments were found to be lower than the corresponding values for the harbours mentioned above.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption Spectroscopy
APDC	ammomium pyrollidene dithiocarbamate
$CHCl_3$	chloroform
EPA	Environmental Protection Agency
EPD	Environmental Protection Department
GF-AAS	Graphite Furnace Atomic Absorption Spectroscopy
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
MIBK	methyl isobutyl ketone
NaDDC	Sodium diethyl dithiocarbamate

Chapter 1

INTRODUCTION

Pollution of the environment is a worldwide phenomenon and is of increasing concern to environmentalists all over the world (Ahlers, *et al.*, 1990). Durban Harbour is no exception to this phenomenon of pollution. In spite of the fact that Durban Harbour is susceptible to heavy pollution from sources such as marine traffic, industrial action and sporting activities, no recent studies have been done to ascertain the extent of the pollution. However there is an internal CSIR report (Hennig, 1985) on a study of pollution of selected sites along the South African coastline. The present study therefore is aimed at addressing the urgent need to assess the quality of water in the Durban Harbour with respect to the presence of pollutants.

A complete study of this nature necessitates the chemical analysis of all species in the water and those in contact with it (including flora and fauna). Due to time constraints, such a full evaluation was not possible and the study was therefore confined to the investigation of water and sediments samples for selected metals.

The quality of water is affected by disposal of waste into it (Förstner and Müller, 1973). Disposal of hazardous wastes often occurs by marine dumping because it is felt that dilution would minimise the hazard from waste substances; but in some cases localised "high" concentrations may occur due to poor mixing caused by the effects of stratification, winds, tides and currents. Hazardous wastes enter the bay from sources such as:

- harbour and port activities exemplified by entry and egress of ships, cargo handling and sporting activities involving boats and yachts)
- Oil discharged during the cleaning of oil tankers
- Effluents from industries in the vicinity of the harbour
- Ship repair activities in the dry dock
- Activities of line and boat fishermen
- Oil storage facilities at Island View

It should be noted that most of the sources mentioned above may contribute to metal pollution of bay water. Further, one study (Akhter, 1997) has shown that crude oil may also be a source of some heavy metals.

Contaminants in aquatic systems can be investigated by analysing the water, the suspended material or the sediments. Short-term measurements of pollutants in the water are (in most cases) not conclusive because of changes in water discharge, fluctuations in water currents and irregular local emissions (Förstner and Müller, 1973). Sediment analyses are used for selection of critical sites for routine water sampling for non-soluble contaminants that are rapidly adsorbed by particulate matter and may escape detection by water analysis (Förstner and Müller, 1973). Sediments are increasingly recognised as both a carrier and a possible source of contamination in aquatic systems (Förstner and Salomons, 1991). In the light of the fact that sediments are regarded as "sinks" for metals, it was decided to analyse sediments for a wider range of metals than the corresponding water samples.

Metals also accumulate in living organism such as fish, mussels and aquatic plants. These are considered good indicators for monitoring the contamination of their environment. Oysters have been shown to accumulate metals (Hayes *et al.*, 1997). In addition, marine bivalves (Burgess and McKinney, 1998), seaweeds, marine crustaceans and gastropods (Nott, 1991) have been found to be reliable bio-indicators of pollution. Metals that enter the environment from anthropogenic sources can contribute to the accumulation of metals from natural sources (Loring and Rantala 1992). It should also be noted that, to some degree, trace metals move through the environment independent of human activity (Stoker and Seager, 1976).

The Port of Durban is a natural resource of commercial and recreational activity in Kwa-Zulu-Natal. It can add value or detract from the importance of Durban as a prime destination for tourists from within and outside the country.

Pollution of the harbour can therefore have a negative impact on tourist trade and thus the economy of metropolitan Durban. Since it is anticipated that the number of tourists in the vicinity of the harbour will increase greatly once the Point Waterfront is developed, it is imperative for rehabilitation strategies and management options to be evaluated and implemented as soon as possible.

To conclude this brief introduction to the study, a list of the salient aspects of the project is given below:

- Review of literature with regard to previous studies and the method of analysis on what has been done elsewhere on the chemical quality of bay water
- Selection of the sites of interest in the Durban harbour with respect to marine traffic, industries along the harbour and recreational activities
- Development of an appropriate sample preparation procedure for the treatment of the samples before analysis
- Optimisation of analytical technique chosen for the determination of the selected metals
- Determination of the concentrations of selected trace metals in water
- Separation of sediments into three fractions according to grain size
- Analysis of each sediment grain fraction
- Correlations between concentration of metals in the water and sediment and between concentration of metals in different grain size fractions

Chapter 2

LITERATURE REVIEW

INTRODUCTION

Both water and suspended material or sediments can be analysed for contamination but it is noted that measurements in water are not conclusive (Förstener and Müller, 1973). Changes in water discharge, fluctuations in the predominance of certain source areas and irregular local emissions are contributors to the non-conclusive results obtained (Förstener and Müller, 1973). Sediments provide indications of the long-term pattern of pollution. Aerosol particles deposited into the water, either directly or washed off surfaces into watercourses either react with the constituents of the water or settle to the bottom where they react with the sediments. The solubility of the metal ions in solution will depend on the concentrations of the anions and chelating ligands present in the water, its pH and redox status, and the presence of adsorbant sediments (Alloway and Ayres, 1993). In the light of the above, it is clear that both water and the sediment have to be analysed concurrently.

This chapter will focus on sampling techniques, the pre-concentration or extraction techniques and the methods of analysis.

2.1 SAMPLING TECHNIQUES FOR WATER AND SEDIMENT

2.1.1 Sampling containers, Collection and Storage of Water Samples

For obvious reasons sampling containers must be scrupulously cleaned prior to use. The cleaning of the sample containers must eliminate or reduce contamination to an acceptable level. On the other hand the sample must be treated in order to minimize or prevent adsorption losses to the container wall. It is widely accepted (Laxen and Harrison, 1981) that adsorption losses may be reduced by acidifying the sample with 0.5 % HNO_3. This acidification step is, nevertheless, more likely to leach metals from an improperly cleaned container. Monitoring of water quality is generally hampered by contamination, either during sampling or sample treatment and analysis if the levels of pollutants are relatively low. The extent of leaching from the walls of the container will be affected by the length of time the sample is stored prior to analysis. The sample container must be carefully selected to avoid leaching of metals from the container into the sample and also to minimise losses of metal from the solution by adsorption onto the walls of the container. In this regard plastics have largely replaced metal and glass in the construction of samplers, storage containers and sample processing vessels (Grasshoff *et al.*, 1983). Materials that satisfy the high purity requirements are teflon, polyethylene, polypropylene and acrylic. Soft or soda lime glass is not suitable because of its high ion-exchange capacity and high levels of trace metal impurities (Grasshoff *et al.*, 1983).

The researchers involved in the National Marine Pollution Survey Programme in South Africa (Watling, 1981) used pre-cleaned high density polyethylene bottles to collect water samples from the surface of the harbours and/or oceans.

Moody and Lindstrom (1977) studied a number of plastic materials including bottles constructed of conventional polyethylene (CPE), linear polyethylene (LPE), polypropylene (PP), polymethylpentane (PMP), polycarbonate (PC), polyvinyl chloride (PVC) and several types of Teflon®. They used gravimetric techniques for determining the rate of loss of water from the bottles, isotope dilution mass spectrometry (IDMS) for analysing the impurities leached from a bottle during the cleaning process and neutron activation analysis (NAA) for determining the impurities contained within and leached from the plastics. For the gravimetric analysis CPE, PP, PVC and PC bottles were weighed and filled with water and re-weighed. The samples were re-weighed after 17 days and 66 days to establish the rate of moisture loss. They found that PP and CPE were suitable containers for long-term storage and PVC, PMP and PC for short-term storage of the aqueous samples. For the IDMS studies, lead was chosen as the model element, partly because lead is a common contaminant and partly because of the high accuracy obtainable by thermal source IDMS. In the above study Teflon and CPE bottles were found to be the least contaminating bottles (Moody and Lindstrom 1977). They also recommended the use of $HC\ell$ and HNO_3 as cleaning agents. However, despite its distinct advantages over glass, plastic also contains a number of additives (designed to stabilise the polymers) which may react with metals in seawater to cause negative contamination or interfere in subsequent analyses (Grasshoff *et al.*, 1983).

2.1.2 Collection and Storage of Sediment Samples

Two types of sampling techniques are used for collecting sediments from the sea or harbour floor, namely *grab sampling* which collects surface and near surface sediments and *coring* which collects a column of the subsurface sediment (Loring and Rantala, 1992).

2.1.2.1 Grab Sampling of Surface Sediments

Undisturbed surface sediment samples can provide an immediate assessment of the current levels of metal contamination in the area. The sampler used must therefore consistently collect relatively undisturbed samples at a selected depth below the sediment surface. Contamination of the sample can be minimised by using a stainless steel grab sampler. Special precautions can be taken by coating the stainless steel sampler with teflon and using polyethylene - coated lowering cables (Loring and Rantala, 1992). No loss of sample should take place if the sampler is well designed and it is especially important to avoid leakage of fine-grained sediments because erroneous grain size and compositional analysis will result.

The sediments contained in the grab sampler require special attention to ensure those essential components, observations and measurements are not lost due to improper handling (Loring and Rantala, 1992).

2.1.2.2 Core sub-surface Sediment Sampling

Sub-surface sediment samples are often taken using box corers (Loring and Rantala, 1992) to determine the changes in lithology and chemical composition with depth in order to determine the environmental changes in metal fluxes with time. The main types of corers having cylindrical barrels are *gravity* and *piston corers*. The former freefalls from the ship and penetrates the sea floor by gravity, while the latter is released from a set distance above the sea floor and collects the sediment into the core barrel by an upward moving piston as the core is retrieved. Plastic core liners are placed inside the core barrels to contain the sediment sample and to avoid contamination that may occur in unlined barrels.

The researchers involved in the National Marine Pollution Survey Programme in South Africa (Watling, 1981) collected surface sediment samples using a tube by the grab or drag technique. For core samples they used a PVC pipe which was manually pushed into the sediment.

2.2 ANALYSIS OF METALS IN MARINE WATER AND SEDIMENTS

Since marine water has a high concentration of salt and a very low concentration of metals the salt matrix has to be removed prior to analysis. An effective method is required to pre-concentrate the metals yet remove the matrix from a large quantity of sample before the analyte can be quantified. Many types of pre-concentration methods have been reported, such as co-precipitation, ion exchange, liquid-liquid extraction and solid-phase extraction (Liu and Huang, 1993).

A method to dissolve the sediment sample is essential in order to determine the total metals in the sediment (Schropp *et al.*, 1990). The selected method must dissolve all metals as well as silica, so that the total metal content in the sediment can be determined.

2.2.1 Methods for Determination of Trace Metals in Harbour Water

Direct and Indirect Methods

Metals in the seawater can be analysed both directly i.e. without pre-concentration and indirectly i.e. with pre-concentration. Direct determination by GF-AAS is difficult not only because of the presence of many trace metals in seawater, but also because the matrix of seawater may cause troublesome interferences. Most pollutants present in seawater are close to or slightly above the detection limit of the instrument being used [Lui and Huang (1993), Rasmussen (1980)]. Consequently many researchers (Slavin, 1980; Sturgeon *et al.,* 1981) have focussed on pre-concentration methods. For trace metal analysis of seawater, the analyte must be separated from an interfering matrix. Due to low concentrations of the analyte of interest, the analyte concentration in the seawater must be brought within a measurable range by the enrichment method of using liquid-liquid extraction.

Direct methods (Sturgeon *et al.,* 1980, Grobenski *et al.*, 1984) have been made possible by a number of factors. Among these are improvements in instrument design and the modification of the sample matrix to change its physical characteristics. With regard to instrument design, the direct method involves placement of a L'vov platform in the graphite furnace (Sturgeon *et al.*, 1980). Modification of the sample matrix requires the addition of an inorganic salt (large excess) to the sample and reference solution. The reagent causes either (i) the interferent to be become more volatile, or (ii) the analyte to be converted to a less volatile form. In both cases the matrix modification serves to make the volatilities of the analyte and interferents sufficiently different to permit easier separation during thermal pretreatment. In the first case the interferent can be removed before the atomisation of the analyte. In the second case the analyte forms thermally more stable salts, oxides, or metal compounds with the matrix modifier. This enables the use of higher pretreatment and atomisation temperatures.

An example of a chemical modifier is ammonium nitrate (NH_4NO_3).

Addition of NH_4NO_3 to the graphite furnace as a modifier assists in the removal of sodium chloride matrix during the charring cycle so that an extraction is not required (Lajunen, 1992).

NH_4NO_3	+	$NaC\ell$	=	$NaNO_3$	+	$NH_4C\ell$
Decomposes At 483 K		m.p. 1079K b.p. 1691 K		decomposes at 653 K		subl. 618 K b.p. 798 K

Sodium nitrate and ammonium chloride are formed, and these decompose or sublime at temperatures below 700 K. Excess of ammonium nitrate is also easily removed during the thermal treatment. The background interference can be minimised by volatilising the matrix components during the charring step to remove them before atomisation.

In the light of the special conditions required for the direct method, the indirect method using pre-concentration is the route that has to be adopted by researchers who do not have access to instruments with the updated technology.

The case studies of three pre-concentration techniques for trace metals in seawater; namely, solvent extraction, ion exchange and co-precipitation will be reviewed in this section. This will be followed by a description of methods for the digestion of sediments and techniques used for the analysis of the metals.

2.2.1.1 Solvent Extraction

Problems such as matrix effects exist when analysing seawater and sediments. Therefore the sample has to be treated in a special way before being analysed. Trace metals in marine water are often determined by solvent extraction, [(Sturgeon *et al.*, 1980); (Mcleod *et al.*, 1981); (Lo *et al.*, 1982)] which is accomplished by adding a chelating agent and extracting the metal chelate into an organic solvent which is not miscible with water. This separates the metals from the salt matrix and, at the same time, concentrates the trace metals.

Sodium diethyldithiocarbamate (NaDDC) followed by extraction with chloroform has been used (Watling, 1981) for the determination of copper, lead, zinc, iron, manganese, cobalt, nickel cadmium and chromium from marine water. The organometallic complex was dried and redissolved in 10 % nitric acid prior to analysis. This method is currently used for the determination of trace metals in South African coastline waters.

Slowey and Hood (1971) used diethyldithiocarbamate followed by extraction with chloroform for the determination of the total concentration of copper, manganese and zinc in the Gulf of Mexico. The organic matter was oxidised with peroxydisulphuric acid. The latter has the ability to destroy organic complexes in seawater. The extraction was followed by neutron activation analysis (NAA). The NAA was found to be a reliable method for the estimation of copper, manganese and zinc in seawater. Their results compared favourably with other researchers (Rona *et al.*, 1962). It was also suggested that a major portion of the copper, manganese and zinc existed in the divalent ionic form or in weakly bound complexes. A significant difference was observed between the concentrations determined by diethyldithiocarbamate extraction before and after peroxydisulphuric acid oxidation to indicate that a substantial amount of the metals might exist in an organic complex in the seawater.

Detailed studies of the ammonium pyrrolidene dithiocarbamate- methyl isobutyl ketone (APDC-MIBK) system were undertaken by Subramanian and Meranger (1979) and Tessier *et al.*, (1979). Although these studies involved fresh water, the extraction system could also be applied to saline water. A solution of ammonium citrate buffer was extracted with 1 % APDC and MIBK to remove any trace metal impurities. The method of standard addition was used to test the reliability of the APDC-MIBK-GF-AAS (graphite furnace atomic absorption spectroscopy) system. The recoveries for the extracted samples were within 100 ± 10 % for all the metals.

Bone and Hibbert (1979) focussed on the choice of chelating agents and the extracting solvent. They compared the results obtained from APDC and NaDDC extractions by using 2,6-dimethyl-4-heptanone (also known as diisobutyl ketone; DIBK) and 4-methyl-2-pentanone or commonly known as (MIBK). The seawater was shaken with an ammonium acetate buffer and with either APDC or NaDDC and with DIBK. After the phase separation the organic layer was analysed by flame AAS. The extraction properties of APDC and NaDDC were studied in the pH range 3-6. The extracted samples were found to be stable for 24 hours. They concluded that DIBK was superior to MIBK, as it possessed better combustion properties, a higher boiling point and lower miscibility with water than MIBK. The APDC-MIBK extraction system was recommended for samples containing less than 3 mg of iron. However if the sample to be extracted contained more than 3 mg of iron, then the NaDDC-DIBK system was recommended because NaDDC lessened the interference by iron. Results from interlaboratory tests done by AAS were in good agreement with each other.

Mcleod and co-workers modified the method of Bone and Hibbert by adding acetate buffer to a larger volume of seawater with the combined chelating agents (Mcleod *et al.*, 1981). The sample was extracted with chloroform and evaporated to dryness using an infrared lamp. The residue was dissolved in concentrated nitric acid and reduced to a small volume and reconstituted with water. An inductively coupled plasma - atomic absorption spectrophotometer (ICP-AES) was chosen to determine the metal concentrations. Seawater was spiked with known concentrations of standards and a recovery analysis was done. The percentage recovery for Cd was 100 %, Cu 101 %, Fe 95 %, Mo 92 %, Ni 104 % and Zn was 100 %.

A two-step pre-concentration method involving the extraction of metal-dithiocarbamate complexes into chloroform at pH 4.5 followed by back-extraction with a dilute solution of Hg^{2+} was investigated (Lo *et al.*, 1982). A mixture of APDC and NaDDC (1 % each) was used. This was added to the seawater sample and the pH adjusted to 4.0-4.5 with HNO_3. Chloroform was added to the above and shaken for 20 minutes. After 5 minutes the organic layer was pippetted and back-extracted with 1000-ppm mercury (II) solution. The aqueous layer was then analysed by AAS. Recoveries of greater than 90 % were achieved with this method that is applicable to most metals, except Hg, and noble metals such as Au, Pd and Pt. These metals have higher extraction constants than Hg.

In subsequent studies (Lo *et al.,* 1991) Pd^{2+} was used instead of Hg^{2+}, but these two studies were not correlated. The metals of interest were extracted at pH 3-5 with a mixture of NaDDC and APDC into a chloroform solution and, subsequently back-extracted into a Pd^{2+} solution. The aqueous phase was thereafter analysed by ICP-AES. Recoveries for the pure water samples and the seawater samples were found to be satisfactory (94 to 105 %) for a range of metals. More metals could be recovered and palladium caused no interference in the analysis of trace metals in seawater by ICP-AES. However, the need for using palladium made the method rather expensive. Furthermore, this method has the limitation of being applied to coastal polluted seawater but not for open ocean water as the concentration of metals is much lower in the open waters.

Brügman *et al.*, (1983) investigated two methods. The first method used APDC and MIBK as extractants. The organic extracts were evaporated to dryness and oxidised with concentrated nitric acid followed by analysis with AAS. The second method involved addition of acidified seawater to a mixed buffer complexing agent solution comprising acetic acid, ammonia, APDC (0.5 % w/v) and DDDC (0.5 % w/v). The sample was extracted twice with freon TF (1,1,2-trichloro-2,2,1-trifluoroethane). Concentrated nitric acid was added to the organic extract and thereafter shaken with water. The samples were analysed by AAS. It was concluded that the MIBK extraction for Zn gave almost twice the concentration found by the freon extraction. The freon extraction method gave about 30 % higher results for Ni as compared to the MIBK extraction and the MIBK extraction for Cu gave a higher result than the Freon extraction results. Freon is not frequently used because of its carcinogenic effects.

In summary, the most commonly used extraction procedure is liquid-liquid extraction using a combination of NaDDC and/or APDC with $CHCl_3$ and MIBK as the extracting solvent. The results or recoveries obtained for these methods were higher, indicating better extraction efficiencies and hence a more superior method than the others mentioned above.

2.2.1.2 Ion-Exchange Technique

Ion exchange is used when elements (lanthanide, actinides) that are difficult to separate from each other are to be determined (Lajunen, 1992). Ion exchange is a highly selective separation method and is used in AAS and AES for group separation and removal of interferences or removal of an excess of a particular matrix ion.

Metal chelating resins and immobilised (adsorbed or chemically bonded) chelates have found widespread application for the accurate determination of trace metals in seawater by pre-concentration and/or matrix separation (Nakashima *et al.*, 1988). Silica immobilised 8- hydroxyquinoline was used with an acid mixture of $HC\ell$ / HNO_3 to elute the trace metals from the column.

Sturgeon (1980) compared the APDC-MIBK solvent extraction to the pre-concentration of metals by use of the chelating resin Chelex-100. To the seawater, 5 % APDC and 2 % 8-hydroxyquinoline were added. The pH was adjusted to 4.0. The above solution was shaken for three minutes with MIBK. The MIBK extract was then back-extracted into concentrated HNO_3 .The acid extract was then reserved for analysis. The ion-exchange resin was prepared by slurry-loading the column with pre-cleaned NH_4^+ form resin. Seawater of pH 5 was loaded onto the column. The column was washed with ammonium acetate buffer followed by de-ionised water. The metals were then eluted with 2.5 M HNO_3. The recoveries for Fe, Cu, Pb, Cd, Zn, Ni, Mn, Co and Cr were from 90 to 100 %. They concluded that pre-concentration of trace metals on chelating ion exchange resin allows for rapid processing of large volumes of water. Chelation and solvent extraction with back – extraction was preferable to resin pre-concentration when only small volumes of seawater were available. They also concluded that neither technique was suitable for the simultaneous determination of all nine elements of interest.

Later in 1981, Sturgeon and other fellow workers used silica immobilized 8-hydroyquinoline (I-8-HOQ) for the pre-concentration of Cd, Pb, Zn, Cu, Fe, Mn, Ni and Co from seawater prior to analysis by GF-AAS. It was established that the I-8-HOQ was stable over a wide pH range of pH 0-9. The recovery for the metals (in %) were as follows: Cd = 94 ± 5; Pb = 92 ± 10; Zn = 94 ± 9, Cu = 96 ± 12; Fe = 96 ± 10; Mn = 115 ± 5; Ni = 96 ± 8; Co = 74 ± 1. These results were in good agreement with accepted values for the same samples (Sturgeon *et al.,* 1981).

Geen and Boyle (1990) automated the method of using sodium bis (2-hydroxyethyl) dithiocarbamate (NaHEDC) as a complexing agent and XAD-4 resin and were able to work with concentrations below 10^{-8} M. Analysis was done by GF-AAS on spiked and unspiked samples. Reproducibility on spiked samples improved from 6-9 % to 3-4 %. Recoveries ranged between 93 to 98 % for Cd, Cu, Ni and Zn. The trace metal concentrations were comparable to earlier determinations by different methods in their laboratory: Cd ≤ 1 pM; Cu = 0.83 nM; Ni = 1.95 nM; Zn <0.1 nM (Geen and Boyle, 1990). When these researchers modified this method, analyses of total metal was lowered by three orders of magnitude but the working pH range was narrowed. For Zn and Cd a L'vov platform was used for best reproducibility. Pyrocoated graphite tubes were used for the analysis. Since the pre-concentrated samples were introduced directly into the autosampler, complete analysis was achieved in a relatively short time.

In summary the most commonly employed chelating resin for the removal and pre-concentration of trace metals from seawater was the Chelex-100 resin. However, the technique is rather time-consuming (with flow rates of 1-2 mL/min). The resin has to be carefully washed prior to elution of some metals such as Ca and Mg. The preparation of the resin is considered tedious by researchers (Slavin, 1980).

2.2.1.3 Co-Precipitation Technique

In trace elemental analysis the analyte may be separated from the matrix by co-precipitation. The element of interest is collected on a " carrier-precipitate", which is sometimes dissolved in a much smaller quantity of solution. Direct precipitation, where the precipitate is analysed directly, is not possible because of the small concentrations of the analyte in the sample solution (Parker, 1972). Some suitable metal cation must usually be added to the solution to obtain sufficient precipitation. Compounds to be precipitated are often hydroxides, halides, sulphides or sulphates. Co-precipitation occurs during the precipitation of sparingly soluble compounds (Lajunen, 1992).

Wu and Boyle (1997) established a low blank value pre-concentration technique for the determination of lead, copper and cadmium in small volume seawater samples by co-precipitation with $Mg(OH)_2$. Acidified seawater was spiked with solutions enriched with isotopes ^{204}Pb, ^{65}Cu and ^{110}Cd. Aqueous NH_3 was mixed into the sample to precipitate $Mg(OH)_2$. The $Mg(OH)_2$ precipitate was dissolved in 5 % HNO_3 and analysed for the metals by ICP- MS. This method was simple, accurate and precise with detection limits of Pb = 1.3 pM, Cu = 39 pM, and Cd = 6.0 pM. Although it was claimed that the method was accurate, it was found that analyte loss affected the detection limit and excess residue sea salt and Mg matrix suppressed the ICP-MS signal.

Akagi *et al.*, (1985) studied co-precipitation with gallium hydroxide for the pre-concentration of trace metals in seawater prior to multi-element analysis by ICP-AES. Gallium hydroxide precipitates at pH 9 only when magnesium is present. Spectral interferences with gallium were found to be negligible and a concentration factor of more than 200 was obtained. Detection limits were in the range of a few ng l^{-1} to 150-ng l^{-1} for Al, Co, Cr, Fe, La, Mn, Ni, Ti, V, Zn, Y and Pb. This method has the limitation of being applied to fresh water because gallium does not co-precipitate without magnesium (more than 500-mg l^{-1} of magnesium is required for gallium to precipitate).

According to Parker (1972) co-precipitation techniques have a number of disadvantages:

i) Precipitations are lengthy and tedious.

ii) The total procedure is complex. With each extra step the possibility of loss of trace metals or contamination from the reagents can be a serious problem.

iii) A very large amount of "foreign" material must be added. Contamination from reagents can cause a serious problem.

iv) If the carrier precipitate cannot be destroyed by ashing, the final solution will contain large quantities of dissolved solids, with the potential for chemical and background absorption.

Since other concentration methods are comparatively simple and trouble-free, co-precipitation is not recommended for general use with AA analysis (Parker, 1972).

In considering the most convenient and efficient technique for the extraction of metals from seawater samples it is clear that liquid-liquid extraction far outweighs the ion exchange and co-precipitation techniques.

2.2.2 Extraction Methods for Trace Metals in Sediments

In order to determine metals in sediments by means of AAS, it is first necessary to bring them into solution. Extraction methods involve fusion or acid dissolution. The latter being more advantageous (Ageman and Chau, 1976). Mineral acids can be obtained in pure forms and do not introduce any appreciable impurities and acid decomposition methods. The fusion method has the drawback of having a high salt content that can cause instability and lead to high instrumental background reading.

Hydrofluoric, sulphuric, perchloric and hydrochloric acids are most frequently used for the digestion of metals in sediments (Agemian and Chau, 1976). Sulphuric acid is not suitable for the simultaneous extraction of a large number of metals as some insoluble sulphates are formed. Agemian and Chau's work involved the study of simultaneous extraction of a large number of metals from aquatic sediments to obtain a rapid but simple technique for measuring non-residual metal. Sediments were digested with various acid mixtures. The extraction efficiency of the methods for the metals studied was in the decreasing order of cold hydrofluoric- perchloric - nitric acid mixture, boiling perchloric-nitric acid mixture, boiling aqua regia, boiling nitric acid, cold 0.5 N hydrochloric acid and 0.5 N ethylenediaminetetraactic acid solution. Ageman and Chau confirmed that for complete dissolution of the silica matrix, hydrofluoric acid is necessary for total extraction of all metals of interest.

Trace metal determinations in soils and sediments commonly involve some type of mineral acid extraction that is reasonably rapid and inexpensive (Sinex *et al.*, 1980). For total metal determination the sediment must be totally dissolved. The use of HF is essential because it is the only acid that completely dissolves the silicate lattices and releases all the metals including associated metals such as aluminium, iron and lithium used for normalisation (Loring and Rantala, 1992). In addition, the HF decomposition procedures allow for verification of the results by the use of certified reference materials.

Sinex *et al.*, (1980) used boiling 90 % HNO_3 -10 % $HC\ell$ to remove trace metals from sediments followed by flame atomic absorption spectrometry (FAAS). They compared this method to one in which samples are fused with lithium metaborate, the resulting glass dissolved in nitric acid and analysed by using direct current argon plasma emission spectrometry. The former method had its limitation because trace metal concentrations were lower than that obtained by the lithium metaborate method. However this technique is not recommended for the following reasons:

i) Strong acid digestions without HF results in incomplete digestions because silicates and other refractory oxides are not completely dissolved.

ii) The proportion of metals dissolved is variable and depends on the sample type, matrix and element.

iii) Accuracy of the results cannot be determined since no reference materials are certified for strong acid digestions (Loring and Rantala, 1992).

iv) Metal data obtained from strong acid digestions are not intercomparable with total metal data and are subject to operationally defined bias.

Horowitz (1986) employed a wet digestion method for sediments using a combination of HF, $HC\ell O_4$ and HNO_3 in Teflon beakers, heated on a hot plate at 200^0C, followed by graphite furnace atomic absorption spectroscopy to quantify metals in sediments. Although complete digestion was achieved, the method was time consuming and was fraught with the danger of explosion.

Loring and Rantala (1992) used HF and aqua regia to release the total metal content from marine sediments into solution in a sealed teflon bomb.

From the above discussion it may be noted that hydrofluoric acid is necessary for the complete destruction of the silica matrix and for total metal determination.

2.3 ANALYTICAL TECHNIQUES

Direct comparisons of different methods used for analysing the same samples are rarely found in literature since most laboratories specialise in just one method.

Several analytical techniques have been used for trace metals in seawater. Anodic stripping voltammetry (ASV) methods are attractive because very little sample preparation is required. Many metals of analytical interest are detected by electroanalysis although sensitivity is low (Slavin, 1980). Interferences are often troublesome. ASV is a slower technique than graphite furnace and is therefore unsuitable for large scale routine work (Ashton and Chan, 1987)

X-ray fluorescence is becoming increasingly attractive as a tool for the determination of trace metals in water. Although the sensitivity obtained is barely sufficient for direct analysis, pre-concentration techniques have been developed to bring the concentrations of the required element well within the range of the technique (Jenkins, 1988).

Neutron activation analysis (NAA) has been used for the simultaneous determination of total trace metals in seawater. Slowey and Hood (1971) found that NAA was a reliable method for the estimation of the total elemental concentration of copper, manganese and zinc in seawater.

ICP-MS has gained considerable favour in marine analysis as it has proven to be a very powerful and versatile technique. A larger number of trace elements can be determined directly in freshwater and in concentrates prepared from seawater samples because of the far superior detection power of ICP-MS (McLaren *et al.*, 1990). ICP-MS also complements other sensitive techniques such as graphite furnace analysis.

ICP-AES is one of the most powerful analytical methods for determining trace metals in environmental matrices. However, this analytical method may be limited in use for samples with concentration in sub-ppm or lower levels, due to sensitivity limitations (Lo *et al.*, 1991). Although chemical interference from matrices is greatly reduced in most cases, sample matrix may cause problems concerning the kinetics of transporting trace elements in complex media into the ICP system.

Sturgeon *et al.*, (1980) compared three instrumental techniques: isotope dilution spark source mass spectrometry (ID SSMS); GF-AAS and ICP-AES. ID SSMS offers advantages of multi-element capability coupled with high sensitivity allowing for determinations to be carried out on less than 100 mL of seawater. The large capital outlay coupled with the fact that only a few samples can be processed in a day makes the method unsuitable for routine use. Although ICP-AES is a multi-element technique, its inferior detection limits (relative to GF-AAS) necessitates the processing of relatively large volumes of seawater. They found that direct GF-AAS was fast and accurate but only for concentrations higher than 0.2 μg/L of Fe and Mn, 0.4 μg/L Zn and 0.01 μg/L Cd. For lower levels chelation-solvent extraction methods were used and it was found that the GF-AAS technique was most reliable but unfortunately lacked the advantage of multi-element determination.

GF-AAS being a extremely sensitive analytical technique is widely used for simple, rapid and accurate method for determining low levels of trace metals in natural waters [(Nakashima *et al.*, 1988); (Slavin, 1980); (Mcleod, *et al.*, 1981]. Lo *et al.*, (1982) used GFAAS for the determination of trace metals in seawater as described in Section 2.2.1.1. Furnace AA methods are recommended because they are simple and rapid and are EPA approved (Voth, 1983). Spectral interferences are rare because of the specificity of AA technique. Physical interferences are more pronounced for flame AA since sample viscosity and surface tension play a role in sample nebulisation (Voth, 1983)

Thus the most widely used analytical technique for the determination of trace metals in seawater is graphite furnace atomic absorption spectrophotometry because of its accuracy, reliability and low detection limits.

2.4 THE RELATIONSHIP BETWEEN PARTICLE SIZE AND METAL CONCENTRATION IN MARINE SEDIMENTS

Sediments can be divided into seven grades: clay, silt, sand, granules, pebbles, cobbles and boulders. The chemical composition of marine sediments changes with the grain size and mineralogical composition. It is difficult to determine the proportion of natural and anthropogenic metals in sediment since they collectively accumulate (Loring and Rantala, 1992)

Anthropogenic activities related to 100 years of industrialisation in the metropolitan Detroit area have significantly enriched the bed sediment of the lower reaches of the Rouge River in Cr, Cu, Fe, Ni, Pb and Zn (Murray *et al.*, 1999). These researchers separated the sediments into different size fractions by wet sieving with the use of polyester mesh screens and compared the results to the bulk sediments. The samples were dried at 100^0C in a forced-air oven. Each size fraction was digested with 5:1 mixture of HF and $HC\ell O_4$ acids. The bulk sediments were digested similarly. The metal concentrations were determined by AAS. They concluded that total metal concentration in size-fractionated sediment samples display trends similar to those found in the bulk samples. The particle-size data suggested that the highest metal concentration was found in the fine sand fraction.

In another study (Loring and Rantala, 1992) sediment was wet sieved through a set of 500μm, 63μm and 37 μm stainless steel sieves. Each fraction from the different sieves was collected. Each fraction was carefully removed and dried at 105^0C and thereafter cooled and weighed. The samples were digested with HF and $HClO_4$. It was found that trace metal concentrations increase with decreasing grain size.

2.5 SUMMARY

From the literature review, it can be summarised that in order to determine low levels of metals in seawater, the sample has to be treated in a special way.

- The samples must be collected in polyethylene containers that are pre-cleaned by soaking them in HCℓ and/or HNO_3.
- For the accurate determination of trace metals in seawater, the samples must be pre-concentrated by liquid-liquid extraction in order to bring it within the range of detection of the instrument.
- HF is necessary for the complete digestion of sediments.
- GF-AAS is the most commonly chosen analytical tool for the determination of trace metals in seawater.

Chapter 3

SAMPLING AND SAMPLE PRE-CONCENTRATION

3.1 SAMPLING

3.1.1 Selection of Sampling Sites in the Durban Harbour

The Durban Habour is situated on the east coast of South Africa covering a distance of 21 km and total land and water area of 1 850 ha. Figure 3.1 shows an aerial map of the Durban Harbour. The water surface is approximately 890 ha at high tide and approximately 680 ha at low tide. Freight figures for the port continues to increase in all areas of traffic, from approximately 8 million tons in 1991 the Port of Durban handled nearly 15 million tons containerised throughput in 1998. Every month approximately 80 000 containers are handled at the Durban's container terminal.

Sampling sites were chosen with respect to the industries along the sites, the high concentration of traffic in the harbour and the recreational activities. The sites were also chosen were also on the assumption that they represent low, moderate and high levels of chemical contamination. Water and sediments were collected from four sites in the Durban Bay area namely the open channel (Site 1), opposite the Sugar Terminal (Site 2), opposite the dry docks near Dorbyl Shipping Repairs (Site 3) and the entrance of the Umhlatuzana Canal in the harbour (Site 4). These sampling points are shown in Figure 3.1.

The water and sediment samples were collected on a monthly basis for a period of one year from July 1998 to July 1999 to accommodate seasonal changes. Water and sediment samples were collected from the various sampling sites with an inflatable boat loaned from the Council for Scientific and Industrial Research (CSIR).

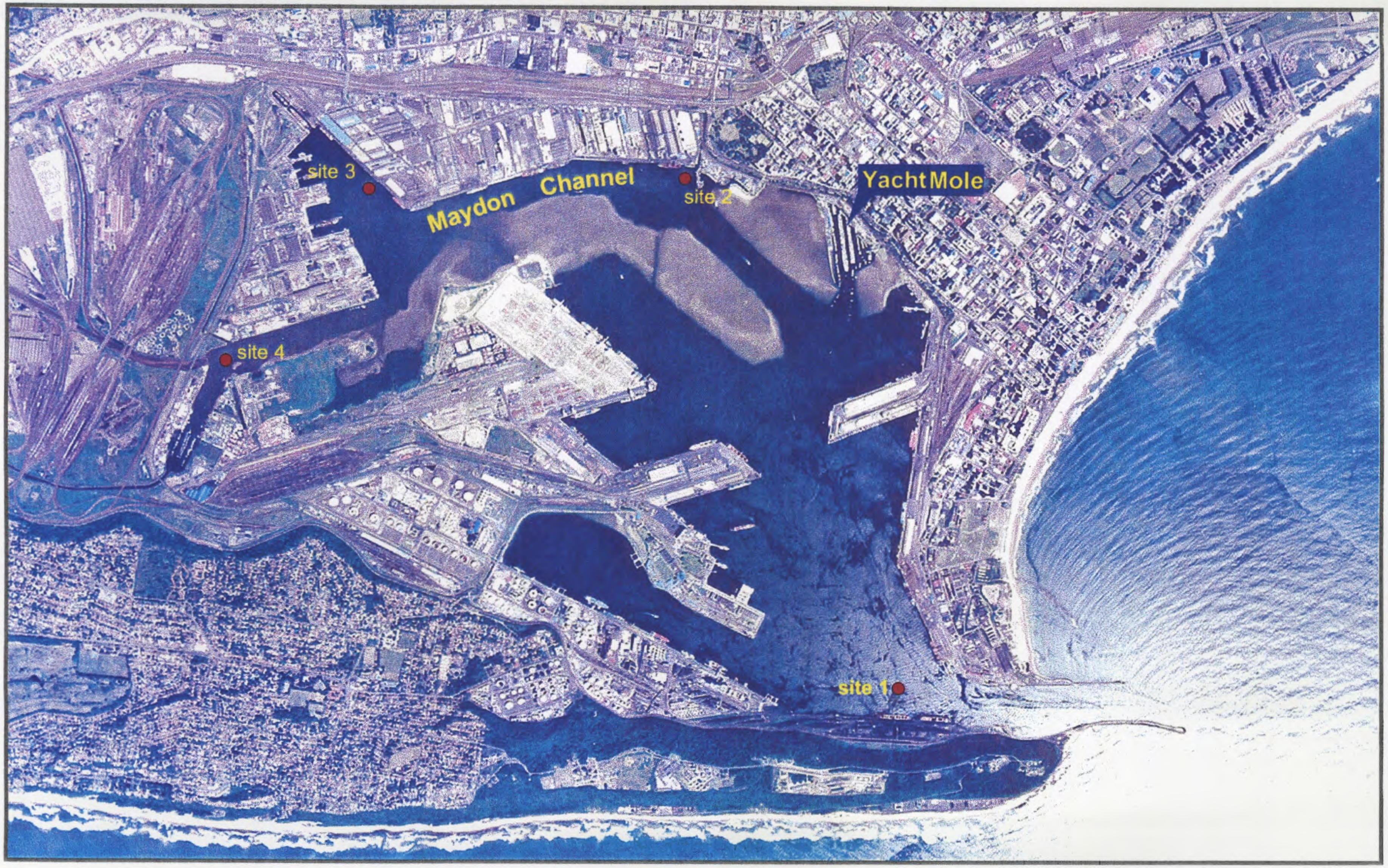


Figure 3.1. Aerial view of Durban Harbour.

Sub-surface water samples were collected by inverting a pre-cleaned high-density polyethylene bottle (Watling, 1981) under the surface of the water to a depth of approximately 0.5 m, turning the bottle mouth upwards and allowing it to fill up with water.

Samples of the marine sediments were collected from the harbour floor by the grab technique. This method collects the samples from the surface and near surface sediments. Sediment samples were collected using a stainless steel cone dredge attached to a 15 m long rope that was dropped off the boat until it settled on the bed of the harbour and dragged until the sample was collected into a pre-cleaned cone. This sample was thereafter transferred to a previously cleaned polyethylene container. These bottles were labeled with the date and sampling site number.

At all times the water sample was collected before the sediments to avoid the creation of a "bow wave" that would disturb the sediment-water interface (Loring and Rantala, 1992).

3.1.2 SAMPLING EQUIPMENT

In this study all glass and polyethylene containers were stored overnight in 25 % HNO_3 and rinsed in double deionised water before collecting the samples.

3.1.3 TREATMENT OF WATER SAMPLES

The temperature of the water was measured on site using a mercury thermometer calibrated to 1 ^{0}C. The pH and conductivity were measured as soon as the samples were brought into the laboratory. The pH was measured using a Metrohm pH meter with an Ag/AgCℓ pH electrode. The conductivity was measured with a Metrohm conductivity electrode attached to a Metrohm 660-conductivity meter. The results of pH, conductivity and temperature against concentration of Cu, Ni and Pb in the bay water are found in appendices A3-5, A3-7, A3-9, A3-13, A3-15, A3-17, A3-19, A3-21, A3-23, A3-25.

The water samples were analysed without filtration because the risk of contamination increases with sample handling (Slavin, 1980). In this study total metals in the water were reported. Once seawater is acidified prior to filtration, the final result could be ambiguous because the measured concentration cannot be classified as dissolved, total, or acid leachable (Pai *et al.*, 1990). The samples were extracted immediately (i.e. without pH alteration) as it was desirable to maintain the sample in its natural pH (Laxen and Harrison, 1981).

3.1.4 MATERIALS AND METHODS FOR SAMPLE PREPARATION

The following chemicals and reagents were used for the experimental work done.

Sodium acetate trihydrate (99.5-101.5 %), glacial acetic acid (99.5 %), NaDDC (99 %), MIBK (99 %) and chloroform (99.4 %) were obtained from Merck. Ammonium solution (25 %), 1000 ppm Cu, Ni, Pb, Fe, Zn, Ca, Al, Si and Ti were obtained from Saarchem. Nitric acid (70 %) was obtained from Riedel – de Haën. APDC (98 %) was obtained from Acros.

The MIBK was redistilled prior to being used.

All solutions were made in Milli-Q water (Millipore Corp).

3.1.5 SAMPLE PREPARATION

3.1.5.1 Water

Dithiocarbamate buffer (20 mL) was added to 200 mL of seawater contained in a 500 mL separating flask and shaken for 5 minutes using a Labcon mechanical shaker at a speed of 300 rpm. 20 mL of chloroform was added to the flask and shaken for 5 minutes. This extract was collected in a 150 mL stoppered Erlenmeyer flask. This step was repeated yielding 40 mL of chloroform. Concentrated nitric acid (2 mL) was added to the chloroform extract and slowly evaporated to dryness on a sand bath at 100 ^{0}C. Before analysis, 20.00 mL of 5 % nitric acid was added to the dry sample.

3.1.5.2 Sediment analysis

Extreme care was taken during the sample preparation. Sediment samples were mixed with a pre-cleaned glass rod to avoid any metal contamination and dried in an oven at 100°C for a period of 8 hours as soon as it was brought to the laboratory. Samples of 0.5 g of dried sediment (accurately weighed) were digested using 1 mL HF and 2 mL of HNO_3 in a Milestone MLS 1200 MEGA High Performance Microwave Digestion unit with a 6- vessel carousel using the operating parameters shown in Table 3.1.

Table 3.1 Programme showing the optimum conditions for the digestion of the sediments

STEP NO	**1**	**2**	**3**
TIME (min)	5	5	10
POWER (watts)	250	400	500
10 minutes were allowed for venting of any noxious fumes.			

The carousel with the vessels was removed from the digester and allowed to cool for approximately one hour. The samples were quantitatively transferred to 100-mL polyethylene volumetric flask with HF and HNO_3 as the blank solution. The blanks, standards and samples were analysed for copper, nickel and lead using a Varian AA 1275 model atomic absorption spectrophotometer attached to a graphite furnace model (GTA-95). The optimum operating conditions for Cu, Ni and Pb are shown in Table 4.1. The furnace and sampler operating parameters for Cu analysis were the same as those of water (cf Table 4.2 and 4.3). The furnace and sampler operating parameters for nickel and lead are shown in appendix table A1-1/2.

3.1.6 TOTAL METAL IN BULK SEDIMENTS BY ICP

Sediments were analysed before (referred to as bulk sediment) and after grain size separation. Dried sediment sample (0.2 g) was digested using the above method and made up to 100 ml with HF and HNO_3 as blank solution and analysed for Fe, Ti, Zn, Al and Ca by ICP-AES.

3.1.7 TOTAL METAL IN THE DIFFERENT GRAIN SIZE BY ICP

Forty-five (45) samples were divided into groups of 3 based on the period in which they were collected i.e. July-September, October-December, January-March, April-June and mixed well. A sediment sample (10 g) was transferred to a pre-weighed set of stainless steel sieves (355µm, 63µm and the pan). De-ionised water was used to wash the sediment through the sieves and thereafter dried in an oven at 100 ^{0}C for about 2-3 hours. The sieves were cooled and re-weighed and by mass difference the distribution of the sediments (see Table 5.8) in each sieve was calculated. Duplicate samples (0.2 g) of each fraction were digested by the above microwave method. The samples were made up to 50 ml and analysed for the same metals as the bulk sediments by ICP-AES.

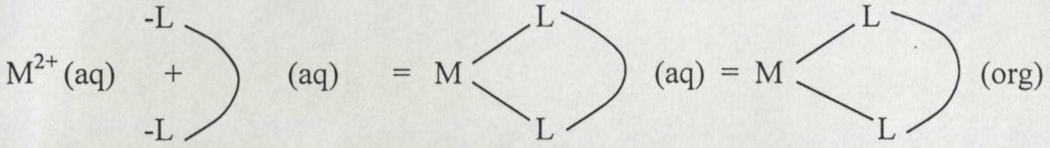
3.2 SAMPLE PRE- CONCENTRATION

As noted in 2.2.1.1 it is clear that the chelation and solvent extraction method is superior to other techniques such as ion-exchange (Sturgeon, *et al.,* 1979). Since trace metals in seawater are too low to be detected by the available instrumentation it was necessary to resort to pre-concentration. In view of their established efficacy (Sturgeon, *et al.,* 1979) it was therefore decided to pre-concentrate. Chelating agents, APDC and NaDDC with the extracting solvents, MIBK and $CHC\ell_3$ respectively were used for pre-concentration purposes. For the back extraction technique using NaDDC, the effect of pH, stability of the complex and extraction efficiency were also investigated. For the APDC investigation two solvents namely diethyl isobutyl ketone (DIBK) and MIBK were used. DIBK did not give satisfactory results and hence no results are reported.

A brief description of the theory on liquid-liquid extraction will be given in the next sub-section.

3.2.1 Liquid-Liquid Extraction

Liquid-liquid or solvent extraction is a procedure in which two immiscible liquids are shaken together so that one or more species in one liquid phase are transferred to the other due to the greater solubility of the species in the second liquid phase. One liquid phase is usually the aqueous sample solution and the other is an organic solvent. After solvent extraction, the analyte is separated from the salt matrix and an increase in the concentration is accompanied by a decrease in the effect of interfering substances. In order to get metal cations transferred from an aqueous phase to an organic phase they must be converted from the ionic form to a neutral compound. Chelating agents are used for this purpose as illustrated below:



A bidentate ligand anion a neutral metal chelate

In general other chelate complexes may be formed as shown by the reaction equations below.

M^{2+} (aq) + (L-L) (aq) = $M(L\text{-}L)^{2+}$ (aq)

A neutral bidentate ligand

a cationic meta chelate

$M(L\text{-}L)^{2+}$ (aq) + 2 X^- (aq) = $M(L\text{-}L)X_2$ (aq) = $M(L\text{-}L)X_2$ (org)

A neutral ion-pair

M^{2+} (aq) + 2 $(L\text{-}L)^{2-}$(aq) = $M(L\text{-}L)_2{}^{2-}$ (aq)

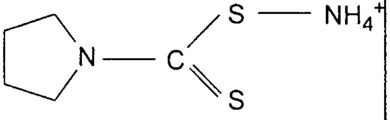
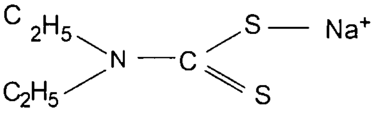
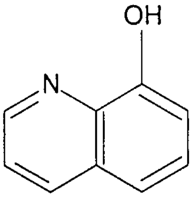
An anionic metal chelate

$M(L\text{-}L)_2{}^{2-}$ (aq) + 2Y^+ (aq) = $Y_2M(L\text{-}L)$ (aq) = $Y_2M(L\text{-}L)$ (org)

A neutral ion-pair

In order to transfer metal ions quantitatively into the organic phase, the extraction conditions (pH, reagent concentrations, and volume ratio of the liquid phases) must be optimised. Some commonly used chelating ligands and their structures are shown in Table 3.2 below.

Table 3.2. Some common chelating ligands used in the extraction of metals.

LIGAND	ABBREVIATION or TRIVIAL NAME	STRUCTURE
Ammonium-pyrrolidine dithiocarbamate	APDC	
Sodium diethyldithiocarbamate	NaDDC	
8- Hydroxyquinoline	Oxine	

All the ligands shown in the above table are polyprotic which means that the metal complex formation with these ligands depends on the pH of the solution (Lajunen, 1992).

3.2.2 Organic Solvents

In principle any organic solvent can be used in sample preparation for GF-AAS, and the best solvent for a particular separation can be employed in solvent extraction (Lajunen, 1992). One of the limitations is the difficulty of handling organic solvents with micropipettes. The pipetting precision or repeatability of non-aqueous solvents such as alcohols, ketones and chlorinated hydrocarbons are usually much poorer than that of aqueous solutions. The other limitation is when the organic solvent spreads within the graphite tube the reproducibility is usually worse than in aqueous solutions (Lajunen, 1992).

3.2.3 Back Extraction

The analyte in an organic medium may be back extracted into an aqueous phase with an acid. The pH of the solution must be low enough to ensure the quantitative decomposition of the metal complex. The pH required depends on the stability of the metal complex. Using back extraction it is possible to obtain complete separation of the analyte from the matrix components. The determination of the analyte is then carried out in an almost pure aqueous solution and there is hardly any interference.

From a comparison of the two extraction procedures, it was decided that back extraction would be the more feasible technique.

3.2.4 Determination of Appropriate Extraction Technique of Metals from Water

Two derivative structures of dithiocarbamate (DTC) shown in Fig. 3.2 (a), namely NaDDC (Fig. 3.2 (b)) and APDC (Fig. 3.2 (c)) were used for the extraction of metals from seawater.

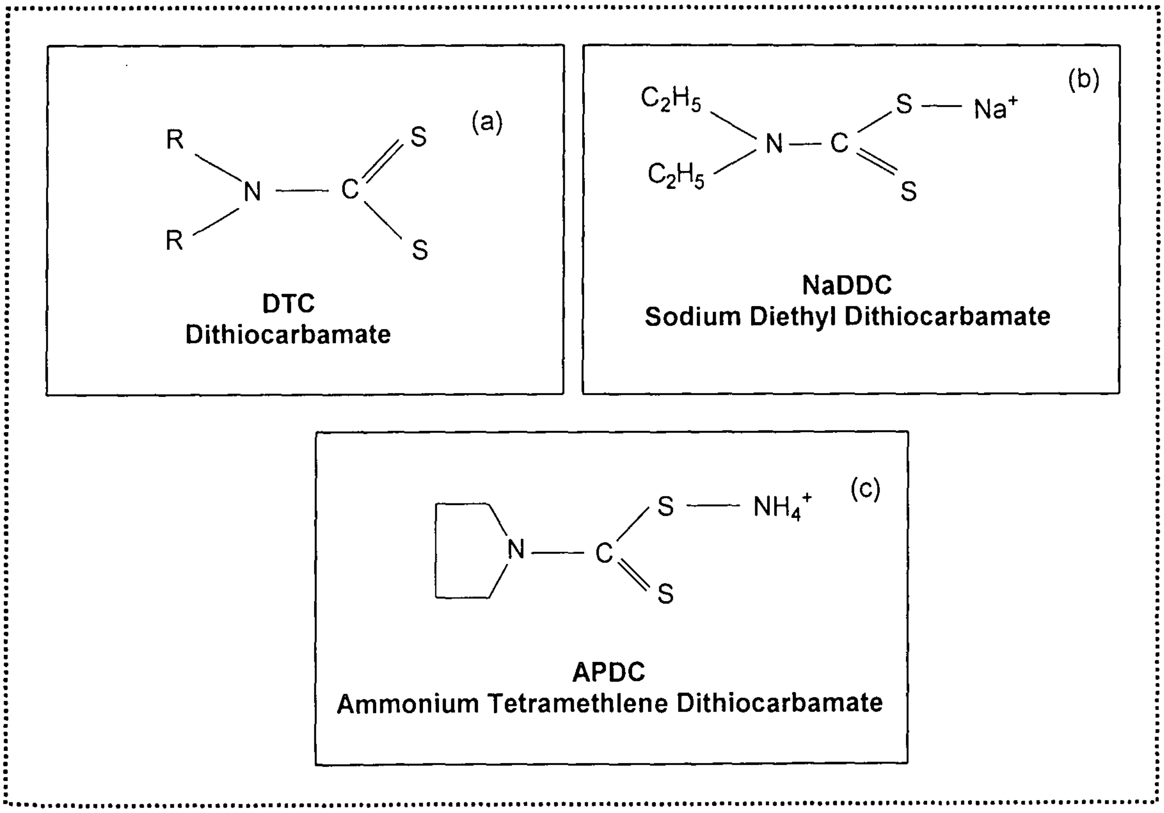


Figure 3.2 Derivatives of dithiocarbamate (a) DTC, (b) NaDDC and (c) APDC

Dithiocarbamate complexes are a group of chelating agents that form organometallic complexes with metal cations. Chloroform is used to extract the metal complexes into the organic solvent. HNO_3 is added to decompose the organometallic complex.

The decomposition of dithiocarbamate in an aqueous medium follows the mechanism shown in Figure 3.3 and Figure 3.4 (Subrammanian and Meranger, 1978).

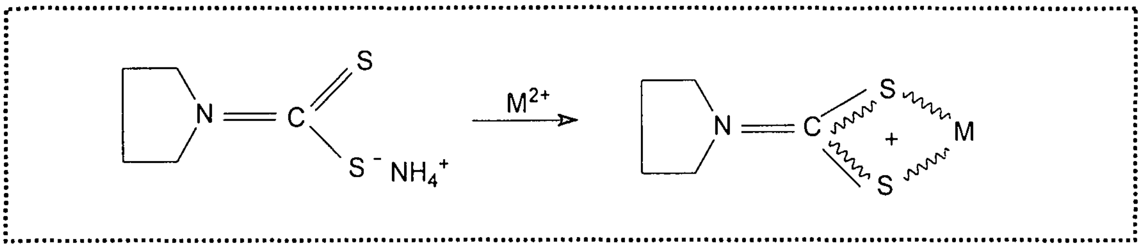


Figure 3.3 Mechanism of complex formation of a metal ion with APDC

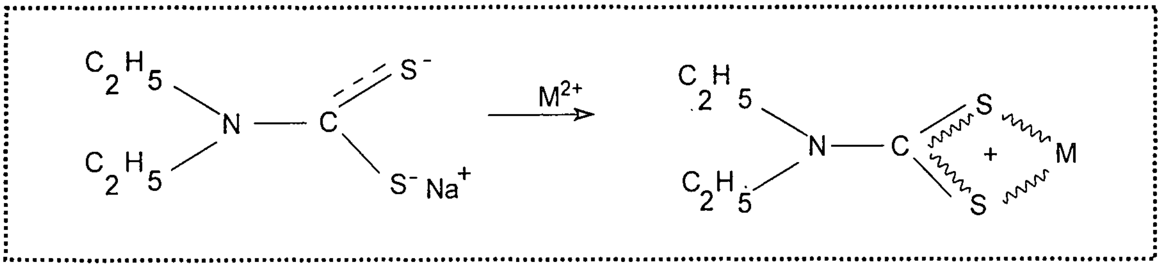


Figure 3.4 Mechanism of complex formation of a metal ion with NaDDC

3.2.5 NaDDC/$CHC\ell_3$ Extractions

3.2.5.1 Preparation of the NaDDC buffer

The buffer was prepared by dissolving 123 g of sodium acetate trihydrate in deionised water. Glacial acetic acid (5.5 mL) was added and the pH adjusted to ~9.5 with ammonia solution. NaDDC (25,0g) was dissolved in the above solution and made up to 500 mL with double deionised water. The buffer was extracted 3 times with 20 mL

$CHCl_3$ to remove any metals in it. The buffer was reported to be stable for one week (Watling, 1981). In this study a fresh buffer was prepared for each new set of extraction.

3.2.5.2 Preparation of stripped seawater (blank)

Dithiocarbamate buffer (20 mL) was added to 200 mL of seawater contained in a 500 mL separating flask and shaken for 5 minutes using a Labcon mechanical shaker at a speed of 300 rpm. Chloroform (20 mL) was added to the flask and shaken for 5 minutes. The organic phase was discarded, removing any metal impurities present. The aqueous phase was retained. This step was repeated three times. The aqueous phase was referred to as the **purified or stripped seawater.** Chloroform (20 mL) was added to the stripped seawater and shaken for 5 minutes. This extract was collected in a 150 mL stoppered Erlenmeyer flask. This step was repeated yielding 40 mL of chloroform. Concentrated nitric acid (2 mL) was added to the chloroform extract and slowly evaporated to dryness on a sand bath at 100 ^{0}C. Before analysis, 20,00 mL of 5 % nitric acid was added to the dry sample. This solution was called the **reagent blank.** Since the reagent blank gave an absorbance reading of 0.000, it was taken that no transitional metals were present.

3.2.5.3 Preparation of spiked standard

A large amount of stripped seawater was prepared in which the spiked standard was prepared. Dithiocarbamate buffer (20 mL) was added to 200 mL of stripped seawater spiked with 20 mL of 0,01 ppm Cu, Ni and Pb and shaken for 5 minutes. The spiked standards were serially diluted from 1000-ppm stock solution. The pH was adjusted to 9 with NH_4OH. Chloroform (20 mL) was added to the above and shaken for 5 minutes. The chloroform was extracted into a 150 mL Erlenmeyer flask. Another aliquot of 20 mL of chloroform was added to the stripped seawater and extracted again into the same Erlenmeyer flask. Concentrated nitric acid (2mL) was added to the chloroform extract which was brought to dryness on a sand bath at 100 ^{0}C. Before analysis 20 mL of 5%

nitric acid was added to completely dissolve the inorganic residue. This solution formed the **spiked standard.**

3.2.5.4 Preparation of standard

The standard was prepared by following the procedure used for preparing the reagent blank (**Section 3.2.5.2**) but the residue was dissolved in 20.00 mL of a solution, which contained 0.020 ppm Cu, Ni and Pb. This solution formed the **standard**. Recoveries were calculated for these solutions and were compared to those for APDC/MIBK extractions.

3.2.6 APDC/MIBK Extractions

A solution of 1 % APDC was prepared in double deionised water. The buffer (10 mL) was added to 200 mL of seawater and shaken on the Labcon shaker at 300 rpm for 5 minutes. The pH was adjusted to ~ 4.0 with ammonium hydroxide solution. The solution was shaken for a further 5 minutes to thoroughly mix the components and extract the metals. MIBK (10.0mL) was added and the mixture shaken for 5 minutes. The latter was allowed to stand for 10 minutes, during which time complete phase separation occurred. The lower aqueous layer was collected in a beaker and the organic layer was run into a stoppered 150-mL erlenmeyer flask. The seawater was then transferred back to the separating flask. MIBK(10 mL) was added and the above procedure repeated. The MIBK layer was analysed by GF-AAS. In the case where NaDDC was the chelating ligand chloroform was used as extracting solvent. Further the NaDDC/$CHC\ell_3$ mixture was back-extracted into 5 % nitric acid. The resulting solution was analysed by the same technique as used for the APDC/MIBK extracts. The recovery obtained by the two methods of extractions of Cu, Ni and Pb from seawater is shown in Table 3.3.

Table 3.3 Comparison of recoveries using NaDDC/$CHCl_3$ and APDC/MIBK as chelating agents

	NaDDC/$CHC\ell_3$			APDC/MIBK		
	% Cu	% Ni	% Pb	% Cu	% Ni	% Pb
1	95	70	84	74	74	75
2	96	73	79	73	70	70
3	100	84	79	75	69	77
4	96	76	80	74	68	78
5	98	81	88	76	70	65
6	100	83	96	75	71	69
7	99	75	99	73	73	70
8	97	79	89	78	75	61
9	94	78	90	79	68	71
10	90	80	92	80	65	76
Mean %	97	78	88	76	70	71
SD	3.1	4.4	7.0	2.5	3.1	5.4

It can be seen that higher mean recoveries were obtained for the extraction of Cu, Ni and Pb using the NaDDC/$CHC\ell_3$ than by using APDC/MIBK extractions. Therefore the NaDDC/$CHC\ell_3$ extraction procedure proved to be superior to the APDC/MIBK extraction. A possible explanation for this difference in recovery is as follows. Whereas the NaDDC/$CHC\ell_3$ was back extracted into 5 % HNO_3 (thus yielding an aqueous extract for analysis) the APDC/MIBK complex was extracted into an organic medium and analysed as such. MIBK, being an oxygenated solvent, is significantly soluble in water and is therefore not suitable for the extraction of low levels of metals from a large volume of harbour water. A significance test for the comparison of the means of the two methods was applied (See Appendix A1-1/2). Hence all future extractions were carried out using the NaDDC/$CHC\ell_3$ system.

Using certified reference material containing Cu, Ni and Pb further tested the efficiency of the chosen extraction system. The results of this experiment which show that this method was suitable is given in Appendix A1-3.

3.2.7 The effect of pH on NaDDC/CHCℓ_3 extraction

It has been shown that extraction efficiency depends on the pH of the aqueous phase (Lajunen, 1992). When the analyte is back extracted into the aqueous phase, the pH should be low enough to ensure the quantitative decomposition of the metal complex. The pH depends on the stability of the metal complex:

$$M(L\text{-}L)_2\ (org) + 2H^+ = \quad M^{2+}\ (aq) \quad + \quad HL\text{-}LH\ (org/aq)$$

In this way it is possible to obtain complete separation of the analyte from the matrix components. In this work the pH of the seawater was adjusted to 4 and 9 respectively after the buffer was added. The spiked metal (1 ppm Cu) was extracted as described in Section 3.2.5.3. These samples were analysed by the graphite furnace using the program in Table 4.2. The recoveries for each sample was calculated and compared. From the results in Table 3.4 it was concluded the pH 9 gave superior recoveries. The final pH was however acidic as 5 % HNO_3 was added to the inorganic residue prior to analysis.

Table 3.4 Recoveries of NaDDC/CHCℓ_3 extraction at pH 4 and 9 for Cu, Ni and Pb

ELEMENT	pH 4	pH 9
Cu	77 %	98 %
Ni	72 %	79 %
Pb	70 %	85 %
Recoveries = (absorbance of spiked sample/ absorbance of standard) × 100 %		

3.2.8 Determination of extraction efficiency

It has been shown that two extractions are sufficient to extract all the metals into the organic layer (Watling, 1981). The extraction was repeated 5 times to verify this. The NaDDC/$CHC\ell_3$ extraction procedure was performed twice with 20 mL of chloroform each to complex with the metals spiked in the seawater. This procedure was repeated three, four and five times with 60 mL, 80 mL and 100 mL of chloroform respectively. Table 3.5 shows the number of extractions and the respective absorbances. The first extraction was not done because it does not completely extract metals from the seawater.

Table 3.5 The number of extractions with the respective absorbances.

Extractions no.	Absorbance
2nd	0.215
3rd	0.213
4th	0.214
5th	0.212

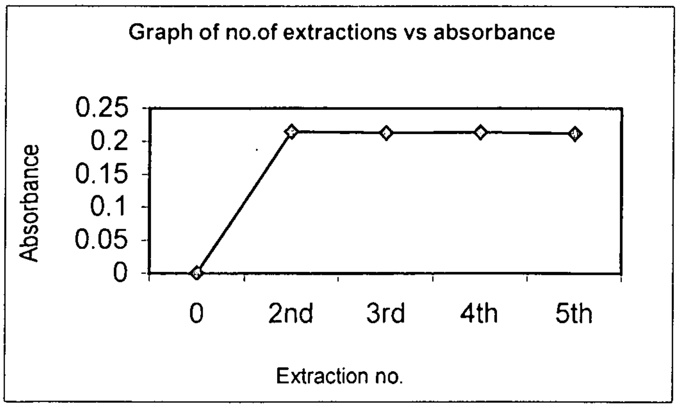


Figure 3.5 Graph of absorbance vs. number of extractions

From Figure 3.5, the graph shows that there is negligible difference between the absorbance values with the number of extractions after the second. Thus that all future extractions were performed twice.

3.2.9 Stability tests for extracted material

The metal complexes must remain stable in the extracted solvent (organic or aqueous) during the time necessary to perform a minimum of extractions (Tessier *et al.*, 1979). It was found that APDC/MIBK extracts are stable for approximately 3 hours (Brooks *et al.*, 1967). If analysis was not possible within this time these researchers preserved the extracts by freezing in acetone-dry ice or liquid nitrogen. It was also reported that samples extracted by the NaDDC/$CHC\ell_3$ procedure are stable up to 3 months in the inorganic form (Watling 1981). In this study water samples that were extracted from the same batch of samples and were stored in the solid form in the erlenmeyer flasks for a period of 5 months and analysed from March 1999 to July 1999 to verify this.

Table 3.6 Analysis data for same extract over a period

MONTH	CONCENTRATION (ppb)		
	Cu	Ni	Pb
MARCH ‘99	1.36	1.11	1.69
APRIL ‘99	1.35	1.10	1.69
MAY ‘99	1.37	1.10	1.71
JUNE ‘99	1.38	1.14	1.68
JULY’99	1.45	1.17	1.72

From the above table it can be seen that the concentrations for the water samples stored from March ‘99 to July ‘99 are almost the same. These results indicate that the metal concentrations of the water samples are unchanged for a period of three months.

3.3 CONCLUSION

From the results obtained, it was decided that seawater would be extracted using NaDDC as the chelating ligand and chloroform as the extracting solvent. The chloroform was back extracted into nitric acid to get the analyte into solution. The ideal pH to perform extractions was at 9 and since the pH of seawater was between 7 and 8, seawater was extracted without adjusting the pH. The extractions were performed twice so that all the analyte was extracted into the chloroform.

Chapter 4

INSTRUMENTS AND INSTRUMENTAL TECHNIQUES

INTRODUCTION

Two instruments were used for the analysis of metals. A graphite furnace atomic absorption spectrometer (GF-AAS) was used for the analysis of copper, nickel and lead in harbour water and sediment samples while an inductively coupled plasma atomic absorption spectrometer (ICP-AES) was utilised for the analysis of iron, zinc, titanium, aluminium and calcium in sediment samples. Prior to a discussion of the principles of these two instruments a brief description of the salient features of atomic spectroscopy will be given.

The science of atomic spectroscopy has yielded three techniques for analytical use, namely atomic emission, atomic absorption and atomic fluorescence (Beaty and Kerber, 1993).

During atomic absorption, energy of the right magnitude is supplied to an atom, the atom absorbs the energy and an outer electron is promoted to a higher energy level leading to a less stable configuration or "excited state". As this state is unstable, the atom will spontaneously return to its stable ground state configuration, and radiant energy equivalent to the amount of energy initially absorbed in the excitation process will be emitted. The absorption signal is directly proportional to the number of atoms present.

During atomic emission, a sample is subjected to a high energy, thermal environment in order to produce excited atoms, capable of emitting light of various wavelength. The energy source can be, inter alia, an electrical arc, a flame or more recently a plasma. This emission spectrum can be used for qualitative analysis (Beaty and Kerber, 1993). Emission techniques can also be used to determine how much of an element is present in a sample. For a quantitative analysis, the intensity of light emitted at a specific wavelength is measured. The emission intensity at this wavelength is directly proportional to the number of atoms present.

Atomic fluorescence incorporates aspects of both absorption and emission. Like atomic absorption, ground state atoms created in a flame are excited by focusing a beam of light at right angles into the atomic vapour. Instead of measuring the amount of light absorbed in this process the emission intensity resulting from the decay of atoms is determined. The intensity of this fluorescence increases with increasing atom concentration, providing the basis for quantitative analysis.

Figure 4.1 to Figure 4.3 below illustrates how the three techniques are implemented.

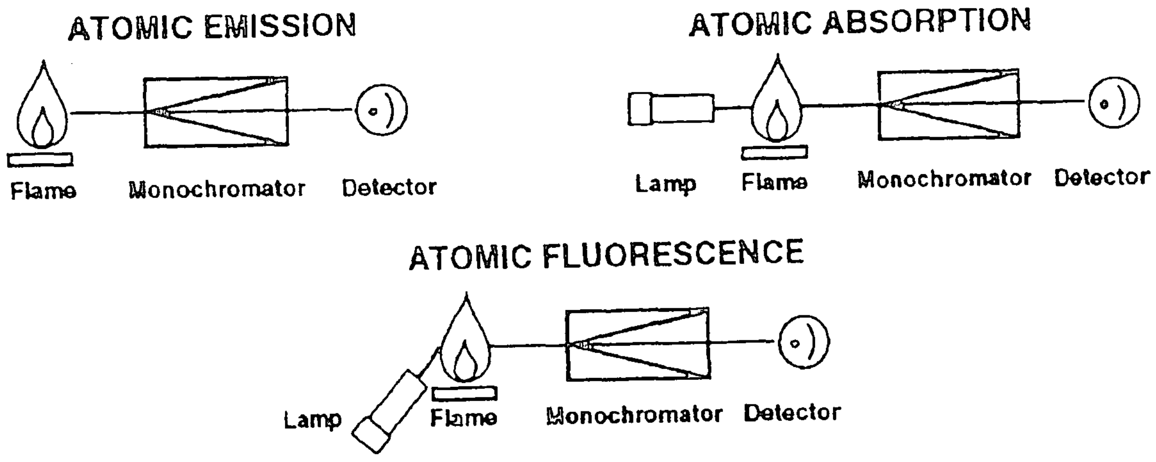


Figure 4.1 to 4.3 Atomic spectroscopy systems

4.1 PRINCIPLES OF OPERATION OF INSTRUMENTS

4.1.1 Graphite Furnace Analysis

Beaty and Kerber, (1993) and Ueda *et al.*, (1988) claim that the most advanced and widely used high sensitivity analytical technique for atomic absorption is the graphite furnace. The sensitivity of GF-AAS makes it the obvious choice for trace metals applications. Routine determinations of trace metals make it ideal for environmental applications [(Sturgeon *et al.*, 1980; Nakashima, 1988)].

4.1.1.1 Basic Principle of Operation

In GF-AAS, a graphite tube is placed in the sample compartment of an AA spectrophotometer, with light path from a hallow cathode lamp focussed into the tube. A small volume of sample is quantitatively introduced into the tube, through a sample injection hole located in the centre of the tube wall. The tube is heated through a programmed temperature sequence until the analyte present in the sample is dissociated into ground state atoms and atomic absorption occurs.

As atoms are created and diffuse out of the tube, the absorbance rises and falls in a peak- shaped signal. The peak height or integrated peak area is used as the analytical signal for quantification.

4.1.1.2 GF-AAS Parameters

The following parameters can be varied

i) Temperature	final temperature during step
ii) Ramp time	time for temperature increase
iii) Hold time	time for maintaining final temperature
iv) Internal gas	gas type and flow rate

In addition to the above, the following parameters can be controlled to give the optimum result.

Sample size

The absorbance signal is dependant on the sample volume and therefore varying the sample volume can therefore control the analytical range of furnace analysis. A convenient sample volume for most analysis is 20 μL.

The Drying Stage

This is the desolution stage. The sample must be dried in a controlled manner to avoid splattering, which causes sample loss. The time necessary for the drying process varies according to sample size e.g. a 20 μL of aqueous sample needs 30 to 40 s at 380 K to dry.

The Pyrolysis Stage

The purpose of the pyrolysis stage (sometimes referred to as ashing or char pre-treatment step) is to volatilise inorganic and/or organic matrix components selectively from the sample, leaving the analyte element in a less complex matrix for analysis. During this step, the temperature is increased as high as possible to volatilise matrix components but below the temperature at which analyte loss would occur. The temperature selected for the pyrolysis step will depend on the analyte and the matrix. The internal gas is left on to drive off volatilised matrix materials.

The Atomisation Stage

The purpose of this stage is to produce an atomic vapour of the analyte element, thereby allowing for the absorption to be measured. The temperature in this step is increased to the point where dissociation of the volatilised molecular species occurs. Care should be taken to avoid the use of an excessively high atomisation temperature, as the analyte residence time in the tube will be decreased and a loss of sensitivity will occur. Also, the use of high temperatures shortens the useful life of expensive graphite tubes.

For atomisation, the temperature should be increased rapidly since the maximum density of atom cloud can be achieved only when the atomisation time is shorter than the residence time of atoms in the graphite tube. Therefore, ramp times are normally set at minimum values to provide high heating rates. The internal gas flow is stopped in order to increase the residence time of the atomic vapour in the furnace thus maximising sensitivity.

The Clean Out and Cool Down Stages

After atomisation, the graphite tube has to be heated to a higher temperature to burn off any sample residue that may remain in the furnace tube thereby minimising memory effect.

4.1.1.3 Interferences in GF-AAS

Saline water containing large concentrations of dissolved salts present unusual demands in the form of interference on non-flame atomisation systems. Interference effects in GF-AAS may be categorised as being physical or chemical. Changes in sample introduction, background signals and memory effects may introduce physical interference effects. Chemical interferences are caused by reaction of the analyte with a matrix component, tube material or inert gas.

Physical Interference

Viscosity and surface tension of the sample solution affect the degree to which the sample solution spreads inside the graphite tube after injection. Background absorption is severe in saline samples because of the presence of large concentrations of sodium chloride and other salts. This interference can be minimised by volatilising the matrix components during the charring step to remove them before atomisation.

Memory effects are due to incomplete atomisation or ineffective subsequent tube cleaning and can result in enhancement of the analyte response in later analysis. This problem is worse with elements forming very stable refractory oxides. This effect may be minimised by using very high atomisation and tube cleaning temperatures, or longer times for these stages (Lajunen, 1992).

Chemical Interference

In GFAAS chemical interferences may be classified into two groups:

i) Volatile compound formation in which the analyte is wholly or partly lost from the graphite tube before the atomisation temperature has been reached

ii) Stable compound formation, where atomisation is either completely or partly prevented or retarded by the formation of analyte compounds that remain unatomised at the normal atomisation temperature.

These interferences can be minimised by matrix modification and by the use of pyrolytic graphite tubes (Lajunen, 1992).

Background Correction

Non-specific absorption is due to background absorption and scattering effects. In the graphite furnace, light scatter is caused by mist and smoke due to the recombination of sample matrices at the cooler ends of the tube or from carbon particles released from the tube walls. This is particularly true for samples containing alkali or alkali-earth halides. The amount of radiation absorbed or scattered must be measured and subtracted from the total measured absorbance in order to obtain net value for the analyte atoms only. The same absorbance readings were obtained for both harbour water and sediments with or without the use of background correction, indicating that no interferences were caused by smoke and mist (See Appendix A2-1). Consequently, deuterium background correction was not applied.

4.1.2 Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES)

Although (ICP) emission technique has only become commercially available since the mid-1970, it has become widely accepted for the analysis of most metals. It has the following features: i) high specificity; ii) high selectivity; iii) high sensitivity; iv) accuracy; v) precision; vi) capacity for multi-element determinations; vii) ease of operation and viii) is free of matrix effects (Mcleod et al., 1981).

4.1.2.1 Basic Operation

Inductively coupled plasmas are divided into two main groups namely high power, nitrogen-argon ICPs and low or medium-power argon ICPs. For this study, a medium power argon ICP was available for use.

ICP-AES is an atomic emission technique using argon plasma as an excitation source. The ICP consists of three concentric quartz tubes, Around the torch is a two or three turn induction coil, to which radio frequency (RF) energy is applied. Flowing gases are introduced into the torch and the RF is switched on. An intense oscillating magnetic field is developed. The magnetic field induces an electric field. When seed electrons and ions are introduced with a Tesla discharge, these start oscillating within the field and provided that the magnetic field is high enough, a plasma will form.

4.1.2.2 Interference

The interferences have been categorised into three groups:

- Spectral overlap (including continuum and background radiation)
- stray light, and
- matrix effects

Spectral and stray light interferences relate to the spectrometer since it originates from the argon spectrum, or from line and continuum spectra of atomic and molecular species entering the plasma.

The high temperatures of the ICP have one disadvantage. The plasma is so effective in generating excited species that the rich emission spectra produced increase the probability of spectral interference. ICP-AES detection sensitivity is known to deteriorate in highly acidic solutions (Beaty and Kerber, 1993).

Matrix effects are more closely related to the sample introduction and excitation part of the system. Changes in the acid concentration, and dissolved solid content from one solution to another will alter the efficiency of the nebulisation and hence the sensitivity. A peristaltic pump was use to regulate the flow of sample through the nebuliser into the spray chamber. This prevented any alteration of nebuliser efficiency and accuracy, precision and sensitivity were maintained. Matrix matching ensures that interferences are the same for the calibration standards and the samples being analysed.

4.2 OPTIMISATION OF INSTRUMENTS

4.2.1 Optimisation of GF-AAS

Preliminary work showed that FAAS was not suitable for analysis of bay water samples because the analyte concentration was below the detection limit (see Appendix A2-2/3). GF-AAS was used because of its excellent sensitivity for low concentration of metals.

The data for this study was obtained using the Varian 1275 Atomic Absorption Spectrophotometer attached to a graphite tube atomiser (GTA-95). The instrumental conditions for copper nickel and lead in water and sediments are shown in Table 4.2. Graphite furnace parameters for copper are shown in Table 4.3. Parameters for nickel and lead are in appendix A2-4/5. The parameters for the standards and the samples for copper are shown in Table 3.4 (see appendix A 2-4/5 for nickel and lead). The instrument was also fitted with an automatic sampler capable of handling 45 different samples for analysis. Nitrogen was used as a purge gas. The suggested program in the instrument manual was used as a guide to determine the optimum conditions for the analysis of a specific metal.

The AA was optimised as follows:

i) The wavelength is optimised for each metal,

iii) The lamp current is set for the respective metals and

iii) The hallow cathode lamp was aligned for maximum deflection of the galvanometer.

The automatic sample dispenser was adjusted so that the sample is dispensed in the middle of the pyrolytically coated graphite tube at a fixed height above the tube wall. The syringe on the automatic sample dispenser was bled prior to analysis to remove any air bubbles from the system. Thereafter furnace-operating parameters shown in Table 4.1 were adjusted to obtain an optimum program.

The following programs for Cu, Ni and Pb were used.

Note: Values in parenthesis are for sediments.

Table 4.1: **Experimentally determined optimum operating conditions for Cu, Ni and Pb in bay water and (sediments)**

ELEMENT	Cu	Ni	Pb
Wavelength (nm)	324.7	232.0	217
Slit width (nm)	0.5	0.2	0.5
Lamp Current (mA)	5	4	5
Standard conc. (ppm)	0.1 (1)	0.1 (1)	0.1 (1)
Signal measurement	Internal repeat	Internal repeat	Internal repeat
Background correction	off	Off	off
Furnace parameters	Table 4.2	Table A1	Table A 3
Sampler parameters	Table 4.3	Table A 2	Table A 4

Table 4.2: **Experimentally determined optimum graphite furnace parameters for Cu in water and sediments samples**

Step no.	Temp. (°C)	Time (s)	Gas flow	Gas type	Read command
1	75	5.0	3.0	NITROGEN	
2	90	40	3.0	NITROGEN	
3	1100	10	3.0	NITROGEN	
4	1100	2.5	0.0	NITROGEN	
5	2300	2.0	0.0	NITROGEN	read
6	2300	2.0	0.0	NITROGEN	read
7	2500	2.0	3.0	NITROGEN	

Table 4.3: **Volume of standards and blanks for a typical determination**

	STANDARD	BLANK	TOTAL VOL(μL)
Blank	0	20	20
Std 1	2	18	20
Std 2	5	15	20
Std 3	10	10	20
Std 4	15	5	20
Std 5	20	0	20

4.2.2 Optimisation of ICP-AES

The Perkin Elmer Plasma 40 Emission Spectrophotometer with AS 90 autosampler was used. The standard operating procedure for the ICP used during the analysis of the metals in the bulk sediments and in the various grain fractions are tabulated in Table 4.4.

Table 4.4 Standard operating parameters of the ICP

Gas : Nebuliser flow pressure	15 L min^{-1}
Auxiliary flow pressure	1.0 L min^{-1}
Frequency	40 MHz
Power	1 kW
Observation height	1 mm above coil
Sample uptake rate	1 mL min^{-1}

4.3 CALIBRATION OF INSTRUMENTS AND ANALYSIS OF METAL CONCENTRATION

4.3.1 Calibration of GF-AAS and Analysis of Metals in Water and Sediment

4.3.1.1 Water

The graphite furnace was calibrated using a standard solution of the metal to be analysed. The standards were prepared by serial dilution using double de-ionised water. The harbour water and the standards had to be matched with the samples because of matrix interferences. The instrument automatically diluted the standard with stripped seawater to achieve this.

Using the dilutions from Table 4.3 the calibration curve for copper in bay water was drawn as shown in Figure 4.4 below. Similar graphs were obtained for nickel and lead. Microsoft Excel was used to analyse the data.

Table 4.5 Graphite furnace calibration data for copper in harbour water

[Cu] in ppm	Absorbance
Blank	0.000
0.025	0.052 ± 0.001
0.050	0.095 ± 0.001
0.075	0.131 ± 0.001
0.1	0.167 ± 0.001

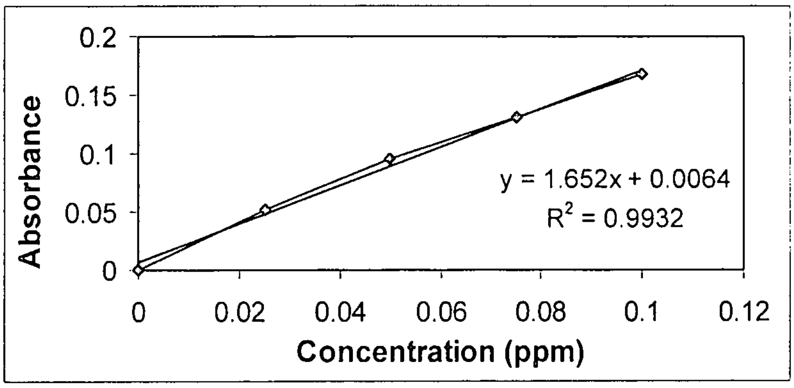


Figure 4.4 Calibration graph of absorbance versus concentration of Cu standards

The graph shown in Figure 4.4 was linear with a R^2 value of 0.9932 and was used to determine unknown concentrations of copper in water. Since harbour water samples were pre-concentrated, a pre-concentration factor of 20 was taken into consideration. By substituting a sample absorbance of 0.088 into the graph shown in Figure 4.4 the corresponding concentration was calculated to be 0.049 mg/L. 200 ml of the original seawater was extracted and dried into an inorganic residue. The dried sample was made up to 10 mL with 5 % HNO_3.

Example of calculation of [Cu] in harbour water samples (as used for all future calculations)

[Cu] in 10 mL = 0.049 mg/L

Therefore in 200 mL [Cu] = 0.049/20

= 0.00245mg/L

= 0.00245mg/L * 1000

= 2.45 μg/L (ppb)

The above calculation was used for the quantification of copper in all the harbour water samples analysed.

4.3.1.2 Sediments

Using the dilutions in Table 4.3 the calibration curve for copper in sediments was drawn as shown below. Similar graphs were obtained for nickel and lead. Microsoft Excel was used to analyse the data.

Table 4.6 Graphite furnace calibration data for copper in sediments

[Cu] in ppm	Absorbance
Blank	0.000
0.010	0.026 ± 0.001
0.025	0.058 ± 0.001
0.050	0.106 ± 0.001
0.075	0.141± 0.001

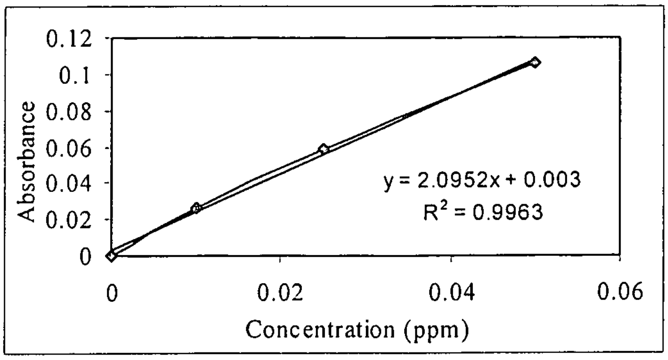


Figure 4.5 Calibration graph of absorbance versus concentration of Cu standards

The graph shown in Figure 4.5 was linear with a R^2 value of 0.9963 and was used to determine all unknown concentrations of copper in the sediments. The Excel data program determines the equation to evaluate the concentration of the analyte in the samples.

Table 4.7. Results from a typical analysis of copper in sediments

Sampling Date	Sampling Site	Run No	Abs. Value	Conc. of Unknown (ppm)
July 1998	1	01	0.041	0.018
		01	0.040	0.018
		01	0.039	0.017
		Mean	**0.040**	**0.018 ± 0.001**
August 1998	2	02	0.079	0.036
		02	0.080	0.037
		02	0.079	0.036
		Mean	**0.079**	**0.036 ± 0.001**

The concentration of unknown copper in the sediment sample 01 was calculated by substitution of the absorbance in the equation $y = 2.0952x + 0.003$ (refer to figure 4.5). The average concentration of sample 01 was 0.018 ± 0.001. The relative standard deviation calculated was 3.3 %.

Example of calculation of sediment concentrations

Concentration in100 ml = 0.0018 mg
Concentration in 0,5 g of sample = 0.0018 mg/ 0.5 g
Therefore concentration in 1 kg = 3.6 mg/kg

The above calculation was used for the quantification of copper in all the harbour sediments analysed.

4.3.2 Calibration of ICP-AES and Analysis of Metals in Sediment

Elements Ca, Al, Zn, Fe and Ti were grouped because of the closeness of the wavelengths required for their detection (see Table 4.8).

The instrument sequentially measures the emission intensity of each element starting from the lowest wavelength proceeding to the highest as individual runs and repeats the cycle if the instrument is set for multiple runs. It is therefore recommended that the elements that form a group have the emission lines as close as possible. This saves time, as there is no forward and backward movement of the grating.

The standards were prepared by serial dilution from 1000 ppm Univar stock standards. These standards were used for the bulk and grain-size analysis of the sediments. The calibration of the standards and the analysis of the samples were run using the Plasma 400 programme. This programme automatically analyses the standards and draws a calibration graph and thereafter determines the concentration of the unknown samples.

This instrument was calibrated daily with freshly prepared standards.

Table 4.8 Two sets of standards used for ICP calibration

STANDARDS		CONCENTRATION (ppm)	WAVELENGTH (nm)
SET 1	Zn	5, 10, 20	213.856
	Fe	5, 10, 20	238.204
	Ti	2, 5, 10	334.941
SET 2	Ca	10, 20, 30	393.366
	Al	10, 20, 50	396.152

In addition to the prepared standards used for calibration as described above, certified reference material were used to calibrate the instruments (For further details see Appendix A1-3).

RESULTS AND DISCUSSION

5.1 THE ANALYSIS OF Cu, Ni AND Pb IN WATER AND SEDIMENTS

Water and sediments samples from Durban Harbour were collected once a month from July 1998 to July 1999 from four different sites. Preliminary work revealed that the level of copper, nickel and lead in the harbour water were low and it was therefore decided that the analyses be done by GF-AAS. For comparison purposes the above metals in the harbour sediments were also analysed by GF-AAS. The concentration levels of these metals are discussed below in relation to temperature, conductivity, pH and seasonal changes of the water for the different sites.

5.1.1 Copper

Copper, a transition metal, is present in seawater in its divalent oxidation state. Copper is a fairly hard acceptor, displaying little affinity for chloride or bromide ions. The approximate concentration of copper in oceans is $\leq 3.0\ \mu g.L^{-1}$ (Scheinberg, 1988; Fifield and Haines, 1995) and in sediments concentrations ranges from 6000-60 000 $mg.kg^{-1}$ (Fifield and Haines, 1995).

Copper is biologically available as Cu (I) or Cu (II) in inorganic salts and in organic complexes. Water plants take up about three times more copper than land plants. Mussels and fish are capable of bio-accumulating large amounts of copper. However, this is not a problem for human nutrition (Scheinberg, 1988) because copper in its natural form is non-toxic. Soluble salts of copper are poisonous when they are ingested through misguided or suicidal intent or are used as topical medical treatment of extensively burned areas of the skin. In the former instances ingestion of small amounts of copper sulphate, also known as blue vitrol or bluestone, lead to nausea, vomiting, diarrhoea, sweating and in severe cases lead to convulsions, coma and death

(Scheinberg, 1988). Where copper salts have been applied to burned areas, high concentration of serum copper and toxic forms are present (Scheinberg, 1988). The dominant species of copper found in natural water are Cu^{2+}, $Cu(OH)$, $CuSO_4$ and $CuCO_3$, (Fifield and Haines, 1995).

The mean concentrations (of triplicate determinations) of copper in both harbour water and sediment samples collected from each of the four sites from July 1998 to July 1999 are shown in Table 5.1. The 95 % confidence limits for the concentration of copper in the harbour water and sediments are shown in Table 5.1. The variation in the results can be attributed to the dynamic nature of the harbour. The continuous tidal change, the different currents, sampling times and sites together with various other physical factors of the water and the sediments account for the large variation of the error limits. The small sample size also contributes to the large confidence limits (See appendix A3-1/2 for a typical analysis with the statistical analysis for confidence limits).

Table 5.1 The monthly mean [Cu] in water and sediment for the period July 1998 to July 1999 in Durban Harbour

MONTH	SITE	WATER (μg.L^{-1})	SEDIMENTS (mg.kg^{-1}) (dry weight)	MONTH	SITE	WATER (μg.L^{-1})	SEDIMENTS (mg.kg^{-1}) (dry weight)
Jul-98	1	2.47 ± 0.34	86.0 ± 5.69	Jan-99	1	2.71 ± 0.23	25.9 ± 3.20
	2	2.43 ± 0.30	213 ± 6.83		2	3.05 ± 0.42	190 ± 6.73
	3	2.39 ± 0.05	370 ± 6.81		3	3.80 ± 0.43	148 ± 6.78
	4	3.80 ± 0.14	180± 3.35		4	3.20 ± 0.18	115 ± 3.20
Aug 98	1	3.99 ± 0.29	90 ± 3.32	Feb-99	1	2.03 ± 0.25	95 ± 3.28
	2	4.10 ± 0.19	230 ± 8.64		2	0.41 ± 0.32	84 ± 3.30
	3	4.37 ± 0.44	432 ± 3.30		3	0.61 ± 0.12	127 ± 8.70
	4	3.76 ± 0.47	145 ± 5.86		4	0.91 ± 0.51	147 ± 8.53
Sep 98	1	1.12 ± 0.16	110 ± 3.32	Mar-99	1	0.97 ± 0.17	67.6 ± 5.68
	2	1.15 ± 0.16	270 ± 8.75		2	1.89 ± 0.18	16.8 ± 3.17
	3	1.54 ± 0.32	534 ± 3.32		3	1.04 ± 0.26	211 ± 3.42
	4	1.21 ± 0.33	534 ± 6.79		4	2.52 ± 0.22	130 ± 6.47
Oct-98	1	3.01 ± 0.61	164 ± 8.81	Apr-99	1	1.40 ± 0.27	9.88 ± 3.08
	2	2.44 ± 0.20	487 ± 5.58		2	0.69 ± 0.47	332 ± 3.21
	3	1.58 ± 0.21	279 ± 6.69		3	2.38 ± 0.22	137 ± 5.56
	4	2.11 ± 0.41	175 ± 3.42		4	1.70 ± 0.094	140 ± 3.64
Nov 98	1	1.09 ± 0.25	120 ± 3.35	May 99	1	1.56 ± 0.11	95.4 ± 3.13
	2	1.12 ± 0.13	310 ± 3.38		2	1.29 ± 0.54	113 ± 3.34
	3	1.19 ± 0.25	511 ± 5.89		3	1.19 ± 0.23	127 ± 5.56
	4	1.15 ± 0.08	224 ± 5.78		4	1.42 ± 0.37	143 ± 3.22
Dec 98	1	1.82 ± 0.16	153 ± 3.34	Jun-99	1	0.89 ± 0.17	59.2 ± 3.32
	2	2.34 ± 0.67	44.0 ± 3.22		2	0.34 ± 0.23	127 ± 3.29
	3	2.98 ± 0.14	334 ± 3.31		3	1.39 ± 0.41	21.8 ± 3.64
	4	3.05 ± 0.47	220 ± 3.31		4	2.43 ± 0.15	18.1 ± 3.93
				Jul-99	1	1.90 ± 0.12	223 ± 3.42
					2	2.44 ± 0.12	120 ± 3.26
					3	2.78 ± 0.18	33.7 ± 3.32
					4	4.83 ± 0.12	139 ± 3.40

5.1.1.1 Copper content in the water

As shown in Table 5.2 the average copper concentration in the harbour water at all four sites ranges from 0.34 to 4.83 $\mu g.L^{-1}$. The graphs in Figure 5.1 illustrate the range of copper concentration found at each site. The highest copper concentration in water for the entire sampling season was 4.83 $\mu g.L^{-1}$ at site 4. This "high" value at site 4 could be attributed to industrial effluent flowing from the Umhlatuzana Canal. These values are well within the range 0.57 to 27 $ug.L^{-1}$ as reported by Hennig on a study of Durban Bay in 1978 (Hennig, 1985). The mean value of copper in saline water in other parts of the world is 3 $\mu g.l^{-1}$ (Fifield and Haines, 1995).

5.1.1.2 Copper content in the sediment

Copper concentration in the sediment at all four sites is given in Table 5.2. It ranges from 9.88 to 534 $mg.kg^{-1}$. Figure 5.2 illustrates the mean concentration of copper in the sediments at each site for the entire sampling period. From Figure 5.2 it is observed that there is an increase in the mean copper concentration in the sediments from site 1 to 3 and then a slight decrease at site 4. The values obtained were higher than that reported by Hennig and McClurg and co-workers. The copper concentration in Durban Harbour sediments in 1978 ranged from 5.5 to 57 $mg.kg^{-1}$ (Hennig, 1985). McClurg and co workers reported the concentration of copper in sediments to be 5.8 to 257 $mg.kg^{-1}$ near the Yacht Mole and 2.67 to 5.00 $mg.kg^{-1}$ along the Maydon Channel in the Durban Harbour (McClurg *et al.,* 1990). Typical concentration of copper in sediments in other parts of the world ranges from 6000 to 60 000 $mg.kg^{-1}$ (Fifield and Haines, 1995). David (1999) reported copper concentration in the KwaZulu coastline to be in range from 0.47 to 48.53 $mg.kg^{-1}$ (David, 1999). Hennig (1981), McClurg *et al.,* (1990) and David (1999) used the experimental conditions described by Watling (1981) to digest sediments. Since this method used concentrated HNO_3 alone for digestion it is probable that digestion was not complete, hence giving lower results.

Table 5.2 Annual mean [Cu] in water and sediment in Durban Harbour

Month	**Site**	**[Cu] in Water** ($\mu g.L^{-1}$)	**Mean [Cu]** ($\mu g.L^{-1}$)	**[Cu] in Sediment** ($mg.kg^{-1}$) (dry weight)	**Mean [Cu]** ($mg.kg^{-1}$)
JULY 98- 99	1	0.89 to 3.99	1.92	9.88 to 223	99.9
JULY 98 -99	2	0.34 to 4.00	1.82	16.79 to 487	195
JULY 98 -99	3	0.61 to 4.37	2.10	21.83 to 534	252
JULY 98 -99	4	0.91 to 4.83	2.47	18.09 to 534	177

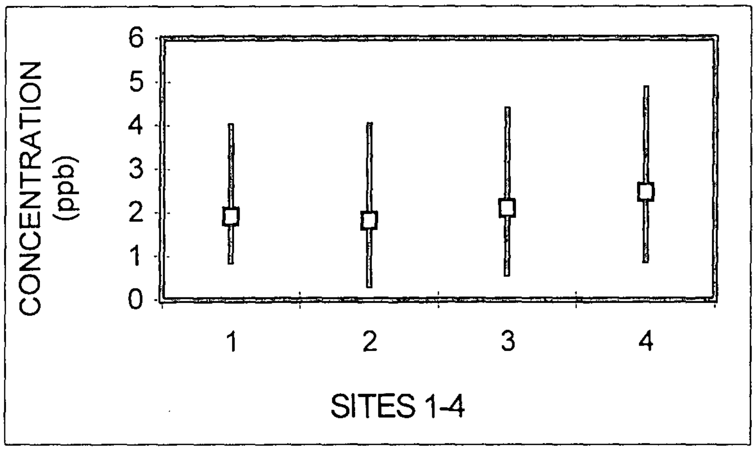


Figure 5.1 Graph of annual mean [Cu] in the water at each site in the harbour

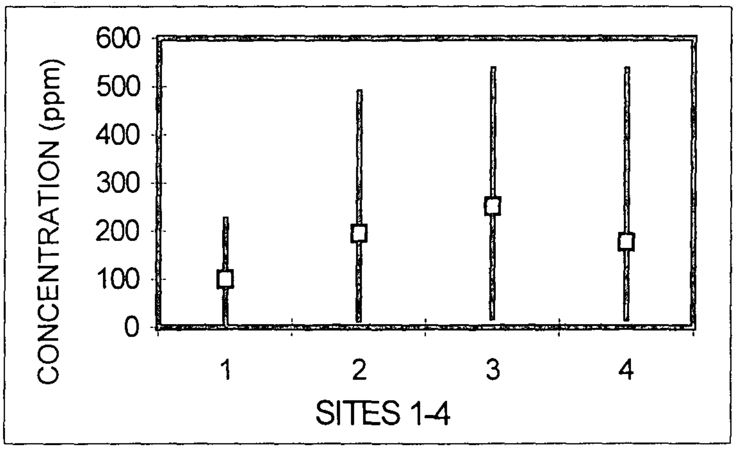


Figure 5.2 Graph of annual mean [Cu] in the sediment at each site in the harbour

5.1.1.3 Variation of copper concentration in the water and sediments with sampling sites

The sampling methods were the same for all four sites. Figures 5.3 and 5.4 illustrate the distribution of the level of copper for water and sediments respectively for the entire sampling season at the four sites. As seen in Figure 5.3 the level of copper at site 3 is generally higher than the other sites. Site 3 is opposite the dry docks where ships are brought in for repairs or maintenance procedures. There is little of a turbulence or disturbance of the water as there are boundary walls built to accommodate the repairs of ships. Metals stripped from the ships during repair contribute to the contamination of the water. Various sources contribute to the pollution of the water in this part of the harbour. Flakes of paint and compounds from antifouling paint, rust and dirt from the deck and an assortment of waste material thrown overboard enters the water (Grasshoff, 1988). The absence of turbulence prevents the distribution of the metals dumped in this part of the harbour resulting in the high levels of copper found at this site. Higher levels of Cu at all four sites were found in August 1998 and January 1999. It was also observed that during September 1998, November 1998, February 1999 and May 1999 the level of copper was low at all four sites. Copper levels are higher at the first part of the sampling season, i.e. from July to December 1998. This may be attributed to greater industrial activity and an increased flow of marine traffic into the harbour as a result of preparation for the annual market demands for the festive period.

Soils or sediments are considered as sinks for trace metals. They play an important role in the environmental cycling of elements because of the interaction between the water and sediment. Bacteria in the top water-sediment interface can strongly influence the chemical form and toxicity of the trace metals (Fifield, 1992). Likely sources of copper are industrial effluents emitted from industries around the harbour. One of the chemicals produced by chemical industries is copper sulphate that is used to supplement pastures deficient in the metal; as an algaecide and molluscicide in water, as a mordant; in electroplating and to estimate reducing sugars in urine (Scheinberg, 1988). Cupric oxide has been used as a component of paint for the bottom of ships. (Scheinberg, 1988). Ship repairs contribute significantly to the presence of metals in the water and copper could be deposited into the harbour from this action. Initially the copper would remain in solution and over a period of time accumulate in the sediment. Thus the sediment is a long-term indicator of pollutants that were and still maybe present in the water.

A Pearson product moment correlation test was performed to ascertain if a linear relationship did exist between the concentration of copper in the water with that in the sediment. At 95 % confidence level the null hypothesis was accepted which stated that the level of copper in the sediments was independent of the level of copper in the water. Statistics shown in Appendix A 4-2/3 also support this conclusion. The product moment correlation coefficient, $r = 0.005$ fell in the region of acceptance, which proved that there was no linear relationship between the concentration of copper in the water and the sediment (see Appendix A3-3/4 for interpretation of data).

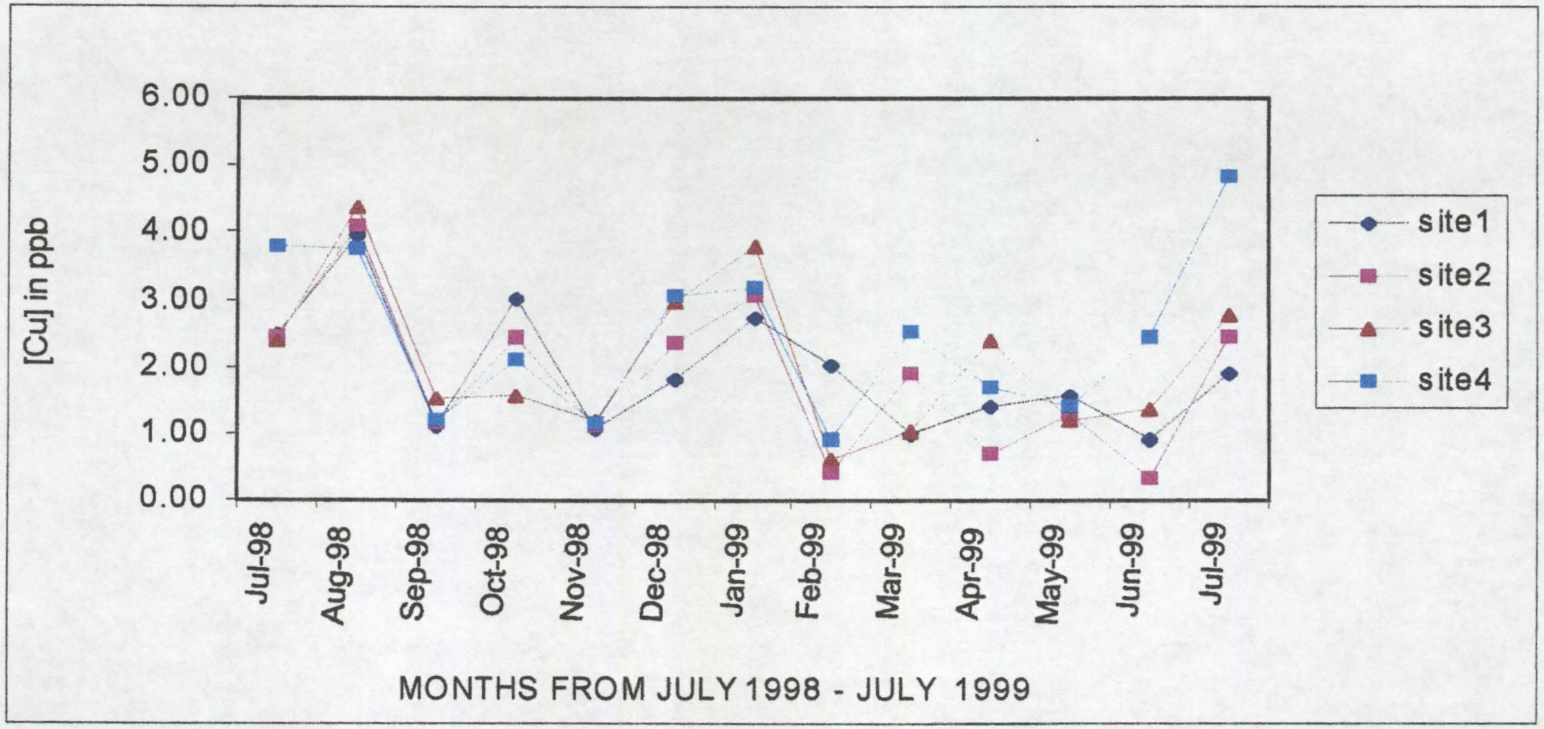


Figure 5.3 : Copper concentration in water at the four sites for the period July 1998 to July 1999

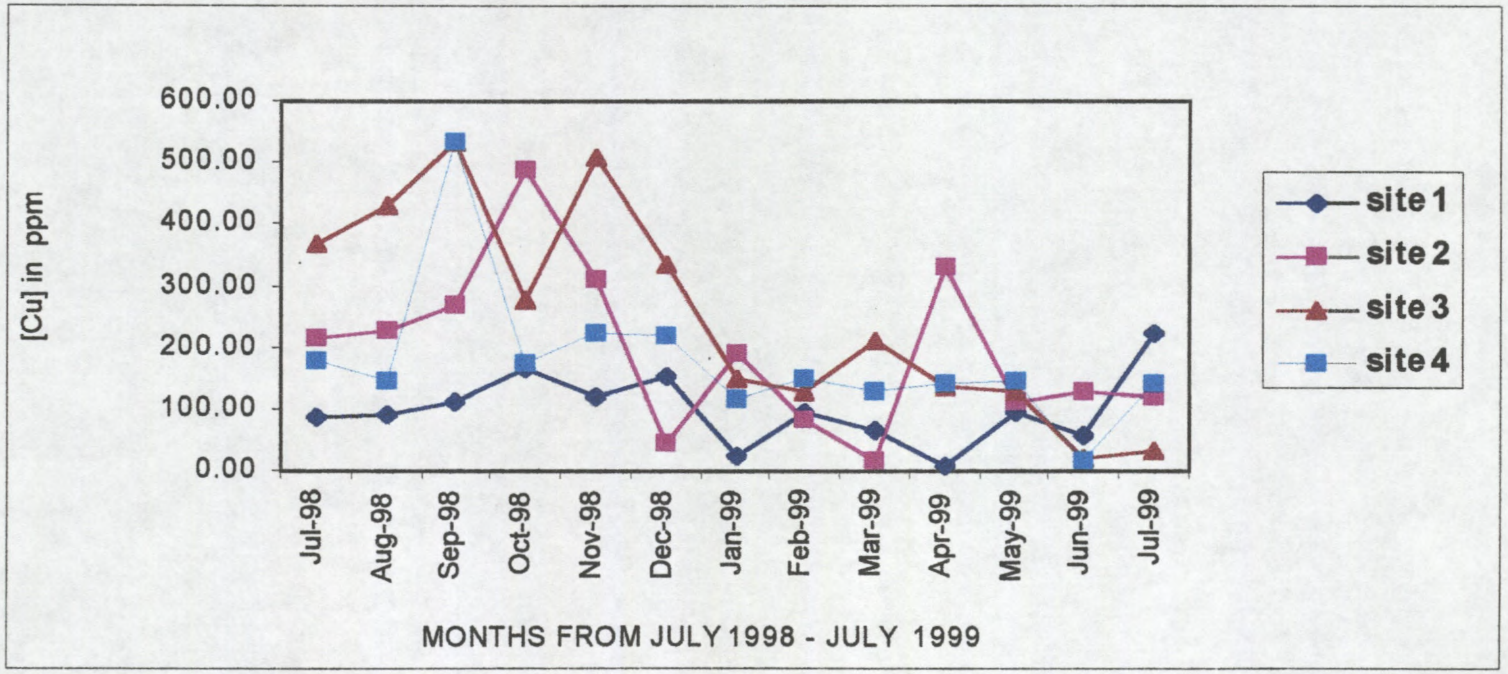


Figure 5.4 Copper concentration in sediments at the four sites for the period July 1998 to July 1999

5.1.1.4 Variation of [Cu] in Water with Temperature, Conductivity and pH

The possible effect of the variables temperature, conductivity and pH on the copper concentration in the water was investigated.

Figures 5.5 to 5.8 illustrate the variation of copper concentration with temperature for sites 1 to 4. Graphically in Figures 5.6 to 5.8 it can be observed that there is a very slight negative correlation between concentration of copper in the harbour water and temperature. This was verified by performing the least squared method test to ascertain if a linear relation ship did exist between the concentration of copper with temperature. The r-value at 95 % confidence level for site 1,2,3 and 4 was -0.1199, -0.2304, -0.2307 and –0.3944 respectively. These values fall within the accepted range of 0.553 from the Critical Values of r Table (see appendix A3-5/6). From this we may conclude that higher water temperatures tend to disperse the metals much more than cold water temperatures resulting in generally lower values at higher temperatures.

Figures 5.9 to 5.12 illustrate the variation of copper concentration with conductivity for sites 1 to 4. Graphically a slight positive correlation was observed at sites 1 to 3. This implies that with an increase in conductivity there is an increase in the concentration of copper in the water. No correlation was graphically observed at site 4. It is also observed that the conductivity values were lower at site 4 compared to the other sites. There is mixing of fresh water from the Umhlatazana canal with the harbour water that is saline. An increase in conductivity is an indication of the increase in concentration ions in solution. Consequently all ions, including copper, increases resulting in a higher conductivity. Although there is a very slight correlation graphically, this correlation may be inferred in the light of the r- values obtained statistically i.e. no real correlation between the concentration of copper and conductivity at the four sites. The r-value at 95 % confidence level for site 1, 2, 3 and 4 was 0.1756, 0.2700, 0.1921 and –0.0732 respectively. These values fall within the accepted range of 0.553 from the Critical Values of r Table. The interpretation of the data will be in Appendix A3-7/8.

Figures 5.13 to 5.16 illustrate the variations of copper concentration with pH for sites 1 to 4. The pH of the samples collected ranged from 7.64 to 8.27. Graphically it is observed that there is a positive correlation at all four sites implying that with higher pH values there is a greater concentration of copper ions. It is also possible that under more alkaline conditions more $Cu(OH)_2$ are found. It also could be noted that the concentration ranges from 1 to 5 ppb. This observation was statistically disproved. The r-value at 95 % confidence level for site 1, 2, 3 and 4 was 0.3108, 0.2449, 0.3777 and – 0.0102 respectively. These values fall within the accepted range of 0.553 from the Critical Values of r Table (see Appendix A3-9/10). It was therefore concluded that no correlation existed between pH and the concentration of copper in the water.

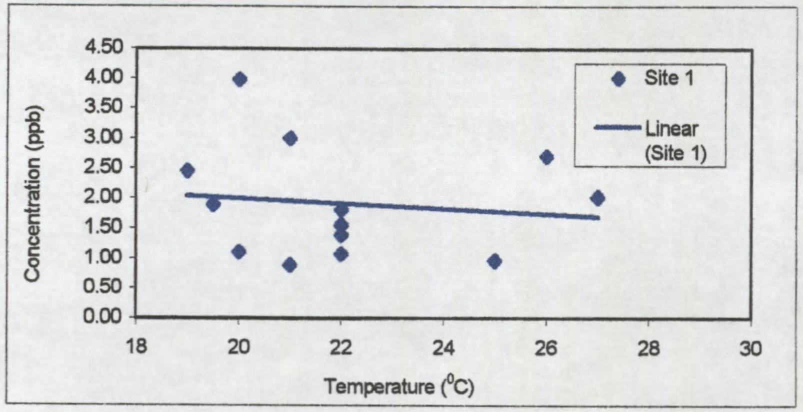


Figure 5.5 Graph of variation of [Cu] with temperature at site 1

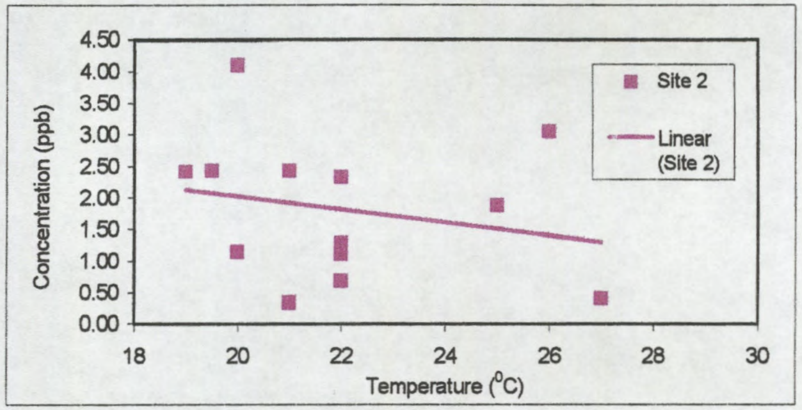


Figure 5.6 Graph of variation of [Cu] with temperature at site 2

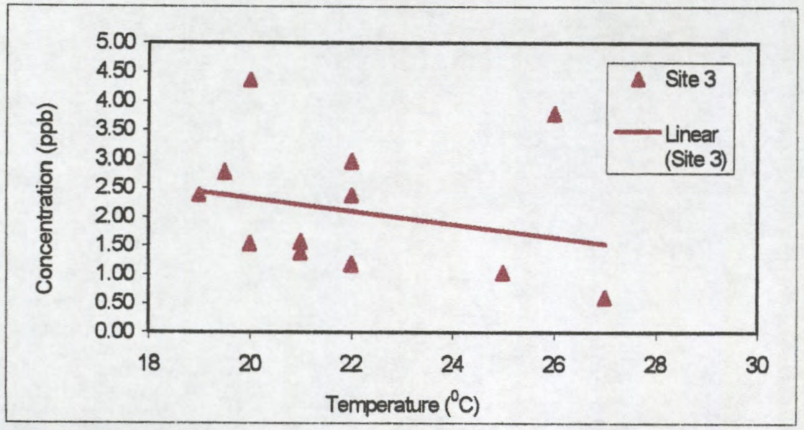


Figure 5.7 Graph of variation of [Cu] with temperature at site 3

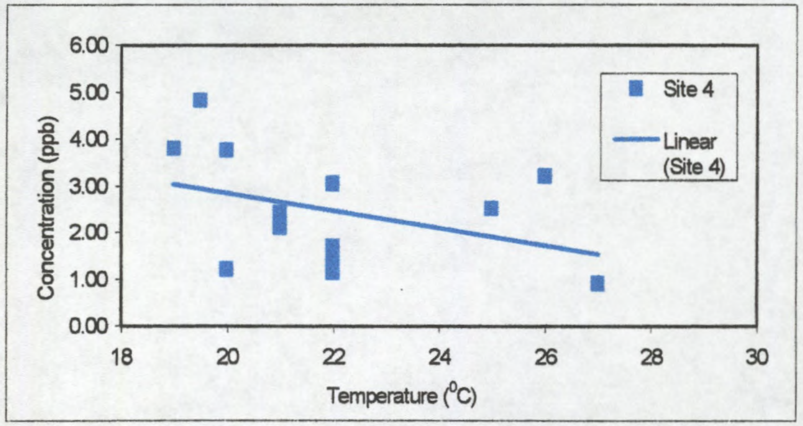


Figure 5.8 Graph of variation of [Cu] with temperature at site 4

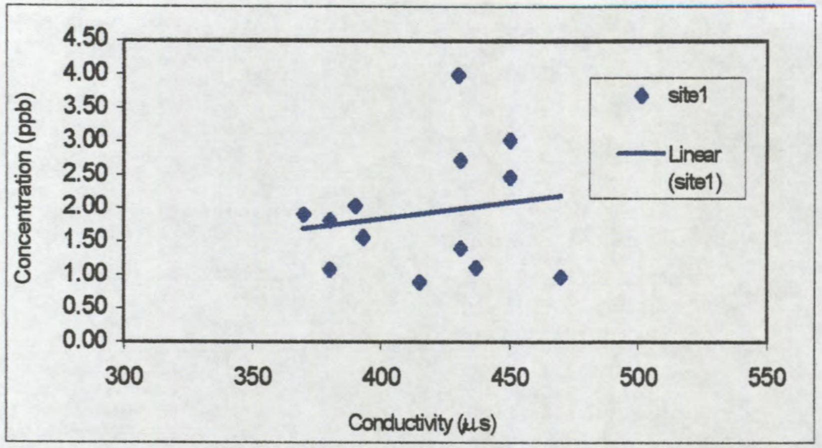


Figure 5.9 Graph of the variation of [Cu] with conductivity at site 1

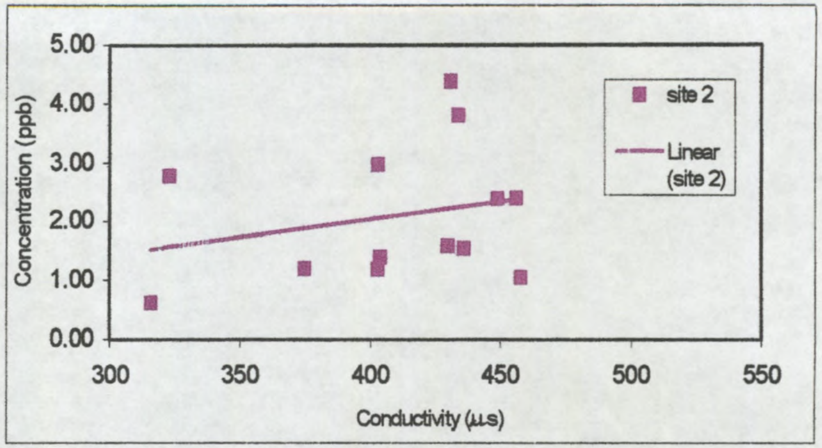


Figure 5.10 Graph of the variation of [Cu] with conductivity at site 2

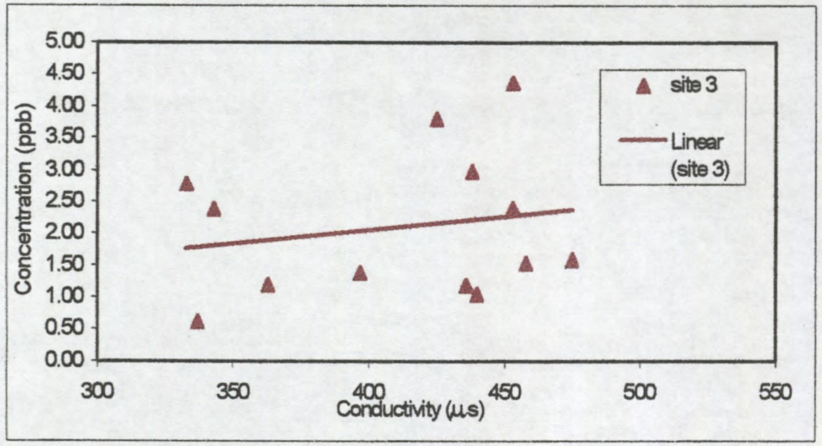


Figure 5.11 Graph of the variation of [Cu] with conductivity at site 3

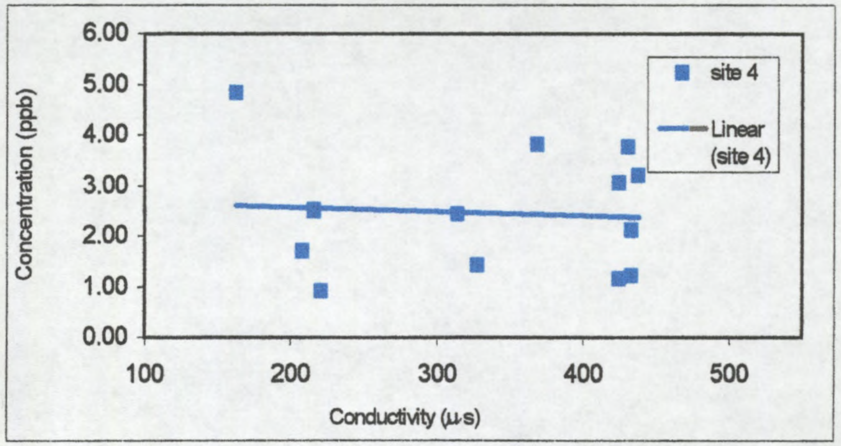


Figure 5.12 Graph of the variation of [Cu] with conductivity at site 4

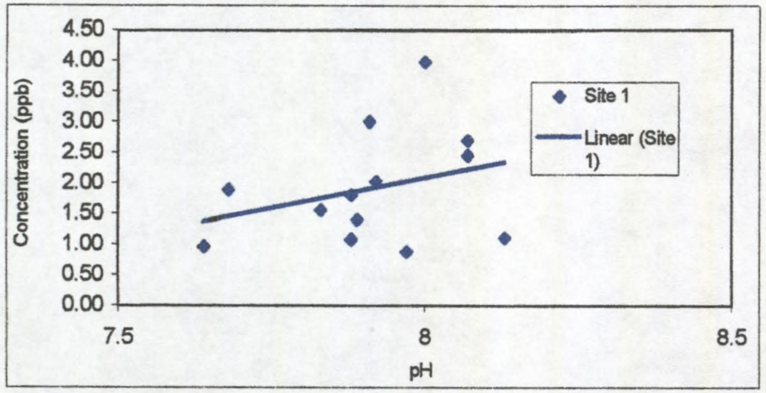


Figure 5.13 Graph of the variation of [Cu] with pH at site 1

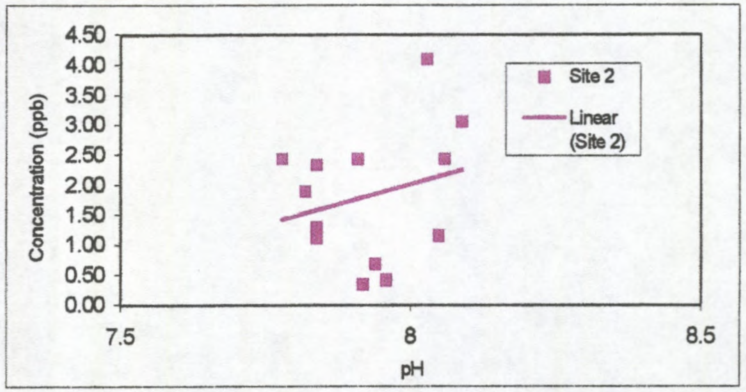


Figure 5.14 Graph of the variation of [Cu] with pHat site 2

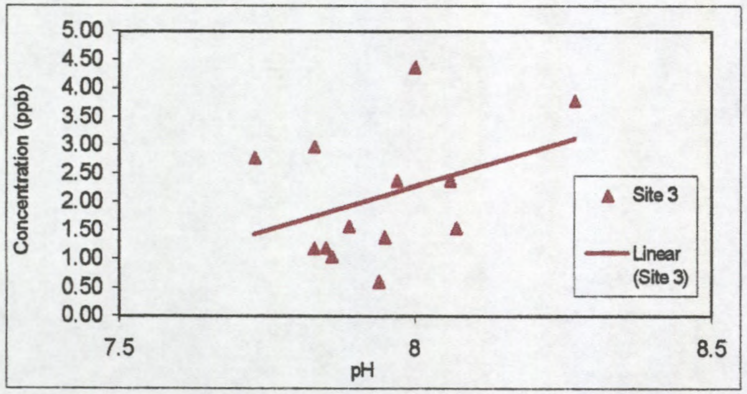


Figure 5.15 Graph of the variation of [Cu] with pH at site 3

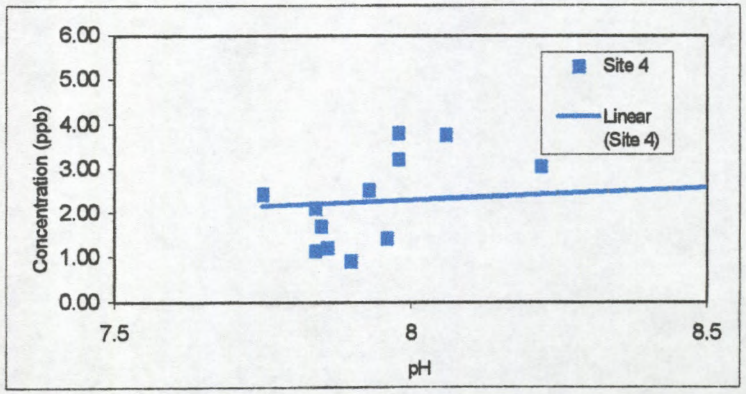


Figure 5.16 Graph of the variation of [Cu] with pH at site 4

5.1.2 NICKEL

Nickel, a transition metal, is present in seawater in its divalent oxidation state (Ahrland, 1988). At concentrations prevalent in natural waters, soils and foods, divalent nickel compounds are relatively nontoxic for plants, fishes, birds and mammals (Sunderman, 1991). In humans, adverse effects of inorganic, water-soluble nickel compounds occur after skin contact, which causes nickel dermatitis. Inhalation causes respiratory tract irritation and asthma in workers, such as electroplaters (Sunderman, 1991).

Aquatic species namely, shellfish and crustacea, generally contain higher concentration of nickel in their edible flesh than do other species of fish studied (Sunderman and Oskarsson, 1991). The toxicity of nickel in adult fish is generally low. The toxicity of nickel for embryonic and larval stages of fishes and amphibia varies widely. At a lethal concentration of 50 $\mu g.L^{-1}$ (LC_{50}) only 50 % of rainbow trout and narrow mouthed toad survived. Goldfish survived at 2.8 $mg.L^{-1}$ (Birge and Black, 1980).

In humans, oral intake of nickel is mainly through foods, since drinking water from public water supplies usually contains <20 $\mu g.L^{-1}$ (Sunderman, 1991).
The results of the concentration of nickel (of triplicate determination) in the water and sediments collected at the four sites are shown in Table 5.3.

The 95 % confidence limits for the concentration of nickel in the harbour water and sediments are shown in Table 5.3. The variation in the error can be attributed to the dynamic nature of the harbour. The continuous tidal change, the different currents, sampling times and sites together with various other physical factors of the water and the sediments account for the large variation of the error limits. The small sample size also contributes to the large confidence limits.

Table 5.3 The monthly mean [Ni] in water and sediments for the period July 1998 to July 1999 in Durban Harbour

MONTH	SITE	WATER (µg.L^{-1})	SEDIMENTS(mg.kg^{-1}) (dry weight)	MONTH	SITE	WATER (µg.L^{-1})	SEDIMENTS (mg.kg^{-1}) (dry weight)
Jul-98	1	0.95 ± 0.16	96.6 ± 6.90	Jan-99	1	1.15 ± 0.63	94.2± 6.72
	2	1.15 ± 0.094	90.5 ± 7.17		2	2.42 ± 0.63	94.1 ± 7.07
	3	1.55 ± 0.50	90.3 ± 7.16		3	1.91 ± 0.36	90.0 ± 7.13
	4	5.49 ± 0.16	84.0 ± 7.05		4	2.68 ± 0.63	84.8 ± 6.72
Aug-98	1	1.61 ± 0.094	93.1 ± 7.00	Feb-99	1	4.21 ± 0.64	63.0 ± 6.90
	2	1.94 ± 0.25	81.8 ± 6.86		2	6.25 ± 0.63	82.5 ± 6.92
	3	2.34 ± 0.25	136 ± 6.95		3	7.78 ± 0.11	77.5 ± 6.91
	4	4.11 ± 0.16	84.8 ± 7.11		4	7.53 ± 0.36	90.2 ± 6.78
Sep-98	1	1.52 ± 0.47	83.2 ± 6.98	Mar-99	1	1.34 ± 0.23	106.2 ± 6.89
	2	3.22 ± 0.47	107 ± 6.96		2	0.69 ± 0.23	70.1 ± 11.53
	3	2.46 ± 0.47	103 ± 6.98		3	1.75 ± 0.31	110 ± 12.44
	4	4.17± 0.27	110 ± 7.13		4	7.10 ± 0.11	81.0 ± 6.79
Oct-98	1	0.89 ± 0.63	88.3 ± 6.99	Apr-99	1	1.40 ± 0.63	68.1 ± 6.47
	2	1.40 ± 0.36	109 ± 6.77		2	2.68 ± 0.36	108 ± 6.73
	3	3.95 ± 0.36	93.6 ± 7.03		3	3.70 ± 0.63	99.2± 6.74
	4	1.40 ± 0.37	75.7 ± 7.19		4	5.74 ± 0.63	102 ± 7.66
Nov-98	1	1.15 ± 0.63	98.8 ± 7.05	May-99	1	1.42 ± 0.20	148 ± 6.59
	2	1.40 ± 0.36	109 ± 7.10		2	1.01 ± 0.11	103 ± 7.03
	3	2.17 ± 0.37	115 ± 7.14		3	1.26 ± 0.20	104 ± 6.75
	4	5.74 ± 0.96	93.3 ± 7.01		4	2.07 ± 0.030	104 ± 11.73
Dec-98	1	1.66 ± 0.36	73.9 ± 12.17	Jun-99	1	1.91 ± 0.36	92.8 ± 6.97
	2	1.66 ± 0.63	85.4 ± 6.77		2	2.42 ± 0.63	130 ± 11.98
	3	1.40 ± 0.63	112 ± 6.96		3	5.23 ± 0.63	118 ± 13.26
	4	1.15±0.37	102 ± 6.96		4	8.80 ± 0.73	116 ± 21.87
				Jul-99	1	1.84 ± 0.42	80.6 ± 19.00
					2	2.29 ± 0.27	120 ± 6.86
					3	2.29 ± 0.16	87.9 ± 6.96
					4	7.76 ± 0.42	85.1 ± 7.14

5.1.2.1 Nickel content in the water

The nickel content in the harbour water ranged from 1.62 to 4.0 ug.L^{-1} (Table 5.4). Hennig (1985) reports that the nickel concentration in Durban Harbour in 1978 ranged from 7 to 26 ug.L^{-1}.The values obtained in this study are were well below this range. Higher levels of nickel concentrations in South Africa have been reported around Richards Bay, Knysna, Green Point and the Olifants River (Hennig, 1985). Higher levels of nickel at the Olifants River were somewhat unusual but may be related to the fresh water run-off and organic matter. The fourth sampling site at the Durban Harbour also involves the mixing of fresh water from the Umhlatuzana Canal and the level of nickel is expected to be higher at this site. In addition to the mixing of fresh water, there are numerous industries upstream.

5.1.2.2 Nickel content in the sediments

Figure 5.18 illustrates that there is a relatively small change in the concentration of nickel in the sediments for the different sites. The mean nickel concentrations in the sediments ranged from 91 to 103 mg.kg^{-1} (Table 5.4). These values are higher than that reported by Hennig(1985) and McClurg *et al.*,(1990). Hennig (1985) reported that the nickel in 1978 ranged from 7 to 26 mg.kg^{-1}. McClurg and co workers reported the concentration of nickel in sediments to be 1.84 to 21.1 mg.kg^{-1} near the Yacht Mole and 1.31 to 2.00 mg.kg^{-1} along the Maydon Channel in the Durban Harbour (McClurg *et al.*, 1990). David (1999) reported that nickel in coastal sediments ranged from 1.11 to 43.74 mg.kg^{-1}. Hennig (1981), McClurg *et al.*, (1990) and David (1999) used the experimental conditions described by Watling (1981) to digest sediments. This method employs only concentrated HNO_3 for digestion and it is possible that incomplete digestion may have resulted in the lower values being obtained. Another reason for the variation could be due to the increase in industrial activities and greater marine traffic volume over the years.

Table 5.4 The mean annual [Ni] in water and sediment in the Durban Harbour

Month	Site	[Ni] In Water ($\mu g.L^{-1}$)	Mean [Ni] ($\mu g.L^{-1}$)	[Ni] in Sediment ($mg.kg^{-1}$)	Mean [Ni] ($mg.kg^{-1}$)
JULY 98- 99	1	0.89 to 4.21	1.62	75 to 148	91
JULY 98 -99	2	0.69 to 6.25	2.20	70 to 131	99
JULY 98 -99	3	1.26 to 7.78	2.91	88 to 136	103
JULY 98 -99	4	1.40 to 8.80	4.90	84 to 116	93

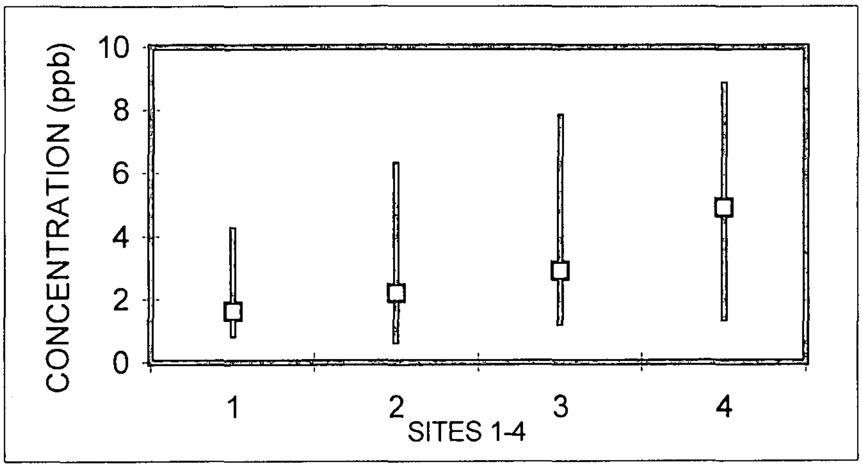


Figure 5.17 Graph of annual mean [Ni] in the water at each site in the harbour

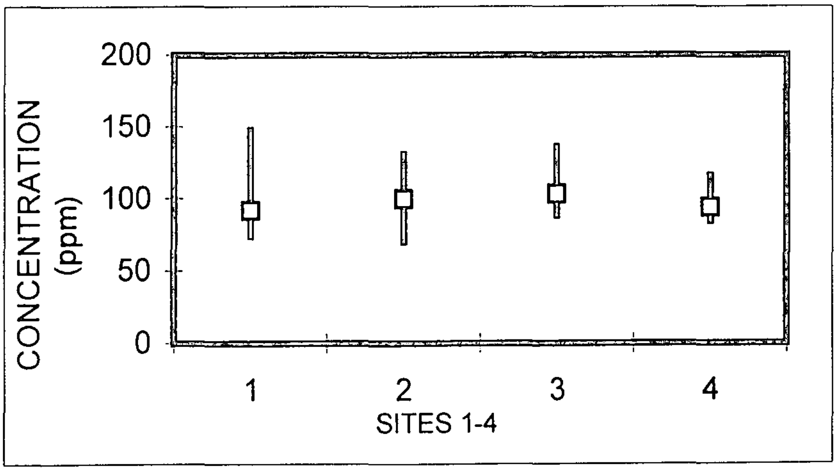


Figure 5.18 Graph of annual mean [Ni] in the sediment at each site in the harbour

5.1.2.3 Variation of Ni concentration in the water and sediments with sampling sites

Figure 5.17 illustrates that there is an increase in nickel concentration in water for sites 1 to 4. Site 1 is along the open channel. There are no industries at site 1 and pollution is expected to be low here. Site 2 is opposite the Sugar terminal and near a food industry. A possible source of nickel could be the effluent from a food industry using nickel as a catalyst in the manufacture of margarine. Site 3 is opposite the dry docks where ship repairs take place. During the cleaning process of decks there is rust and dirt overflowing into the harbour that can contribute to the increased level of nickel at this site. Site 4 is opposite the Umhlatuzana Canal and there are many industries upstream that dispose of their effluent in the canal. Figure 5.18 shows that the level of nickel is approximately the same in the sediments at all the sites. Sunderman explains that organic nickel complexes become adsorbed on silica particles at the bottom sediments of contaminated rivers, with gradual accumulation of nickel in the upper layers of mud (Sunderman, 1991).

A Product moment correlation test was performed to ascertain whether a linear relationship did exist between the concentration of nickel in the water with that in the sediment. At 95 % confidence level the null hypothesis was accepted which stated that the level of nickel in the sediments was independent of the level of nickel in the water. Statistically this was proven invalid. The product moment correlation coefficient, r = -0.1.031 fell in the region of acceptance, which proved that there was no linear relationship between the water and the sediment (see Appendix A3-11/12 for interpretation of data).

From Figure 5.19 it can be clearly seen that during almost every sampling month the level of nickel in the water was the highest at site 4 and the lowest at site 1. An increase in the level of nickel in the water was observed at all four sites during February 1999. No explanation is offered except the sampling for February was done after heavy rainfall. The water was visually dirty as a lot of debris was floating in the harbour. In figure 5.19 it is also observed that the level of nickel at site 4 takes a longer period to revert to the mean value as compared to the level at the other sites. In addition industries situated upstream that dispose their effluent into the canal may also contribute to high levels of nickel in the water at this site. Site 2 shows a higher concentration of nickel than sites 1 and 3 because of industries (such as a shipping company) at that site which may contribute to the increased levels of nickel. Figure 5.20 illustrates that the levels of nickel in the sediment at all the sites from July 1998 to July 1999 are fairly constant. Since sediments are long term indicators of pollution, this gives a good indication of the level of nickel in the harbour. It should also be noted that the texture of the sediment varied between the different sites. Sediment from site 1 was very course as compared to the sediment at site 4 that was very fine. Since metals accumulate more in the finer grain size (Murray, *et al.*, 1999), it is expected that the concentration of metals would be higher at site 4.

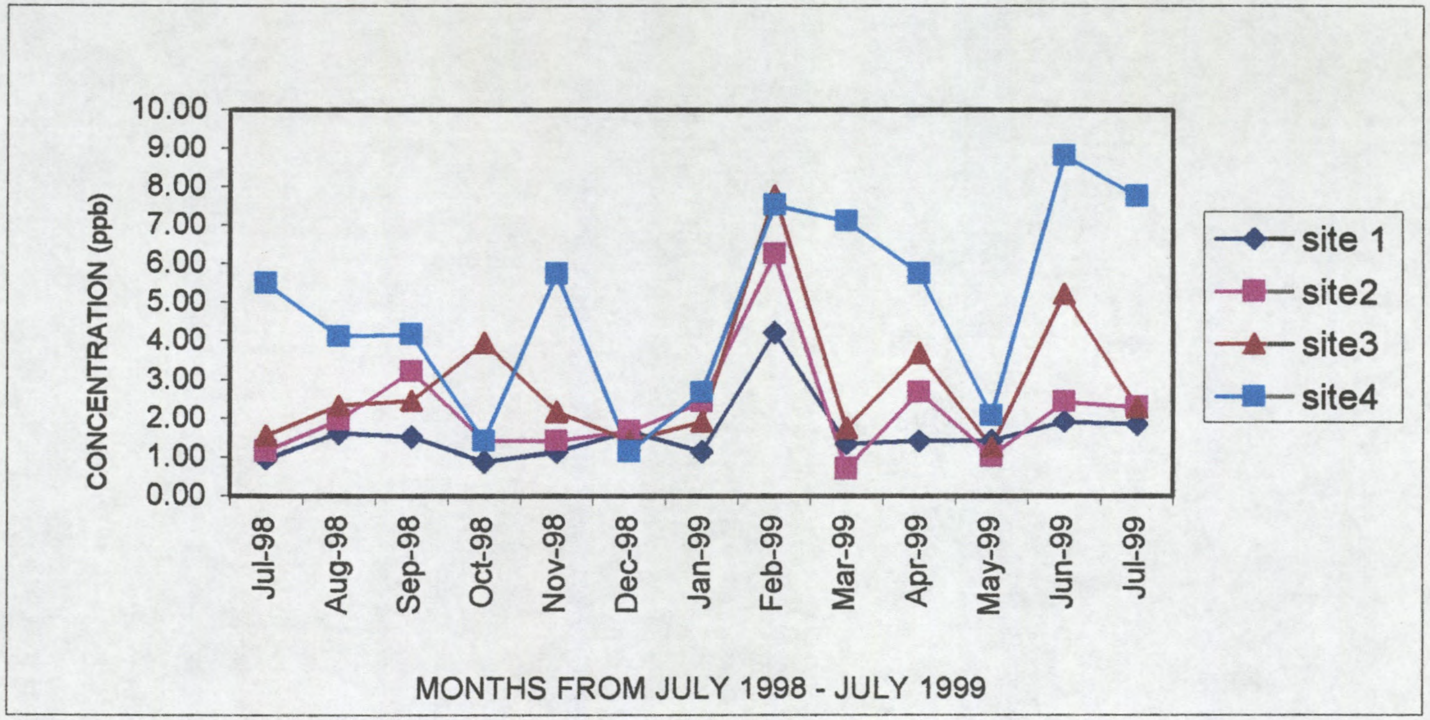


Figure 5.19 Nickel concentration in water at the four sites for the period July 1998 to July 1999

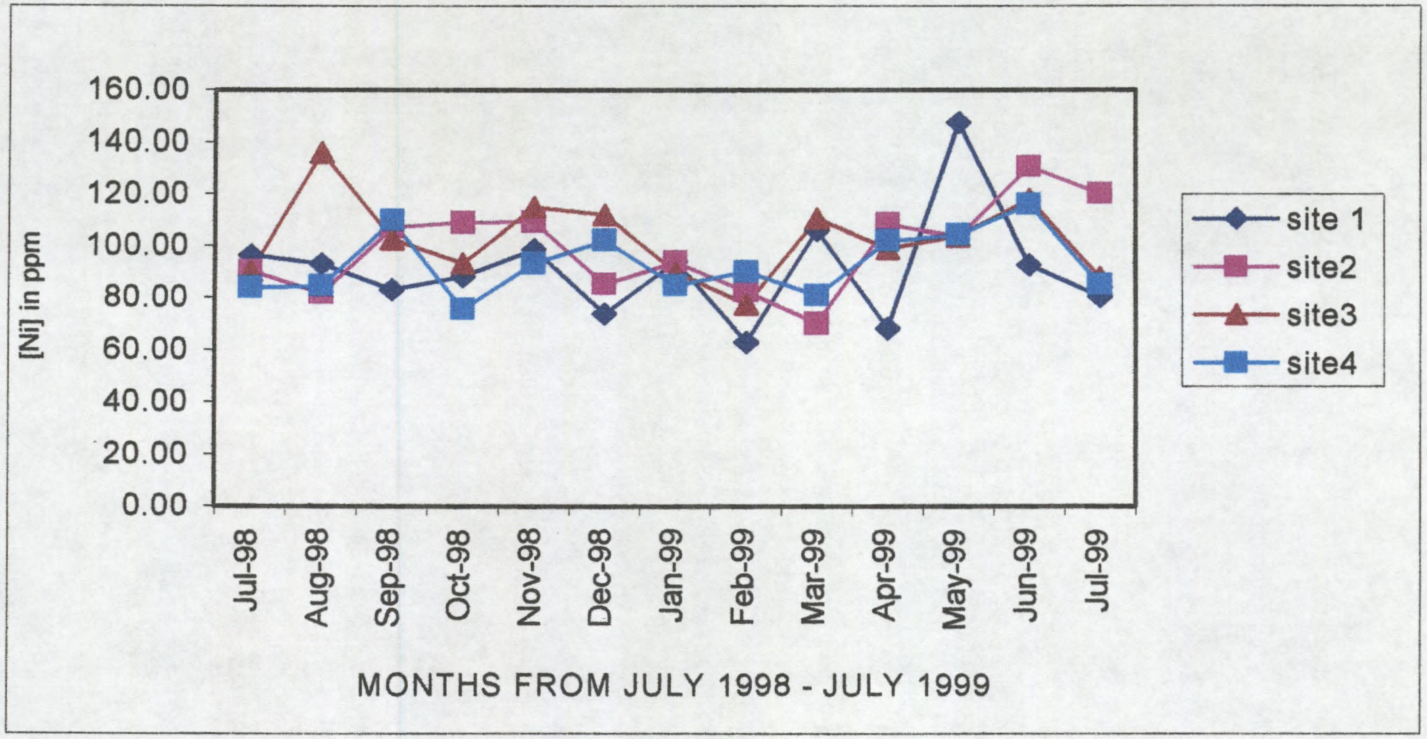


Figure 5.20 Nickel concentration in sediments at the four sites for the period July 1998 to July 1999

5.1.2.4 Variation of [Ni] in water with Temperature, Conductivity and pH

The possible effect of the variables temperature, conductivity and pH on the nickel concentration in the water was investigated.

Figures 5.21 to 5.24 illustrate the variation of the concentration of nickel with temperature. Graphically in Figures 5.21 to 5.24 it can be observed that there is a very slight positive correlation between concentration of nickel in the harbour water and the temperature. Statistically no correlation between concentration and temperature was found. The r-value of 0.4890, 0.4358, 0.3794 and 0.0598 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-13/14 for interpretation).

Figures 5.25 to 28 illustrate the relationship between nickel concentration and conductivity. Graphically it is observed that there is a negative correlation at all four sites implying that the level of nickel in the water decreases as conductivity increases. Statistical analysis proved that there was no correlation between the level of nickel in the water and conductivity. The r-value of –0.4138, -0.5449, -0.40739 and –0.6896 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-15/16 for interpretation). As an observation the conductivity measured at site 4 was generally lower than the other sites. In this case the increased conductivity may be due to other ions.

Figures 5.29 to 5.32 illustrates the variation of nickel with pH. In general Figures 5.29 to 5.32 show that there is no correlation between pH and the concentration of nickel in the water. Statistical analysis showed no correlation between the levels of nickel and pH at the four sites. The r-value of -0.0724, 0.2939, 0.00948 and -0.07578 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-17/18 for interpretation).

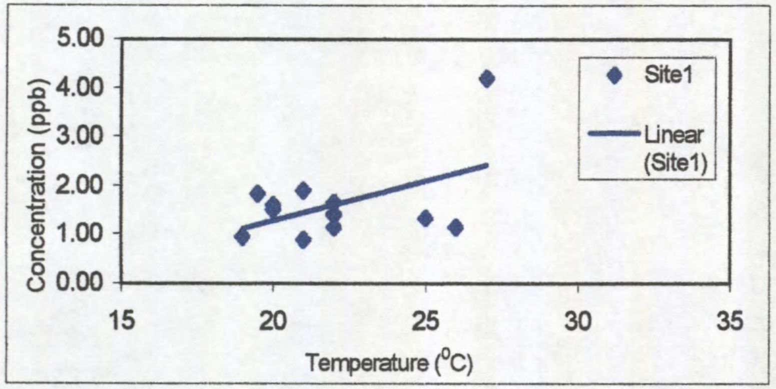


Figure 5.21 Graph of the variation of [Ni] with temperature at site 1

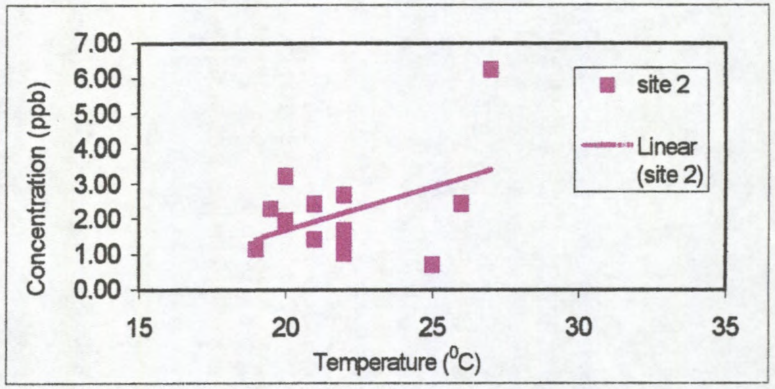


Figure 5.22 Graph of the variation of [Ni] with temperature at site 2

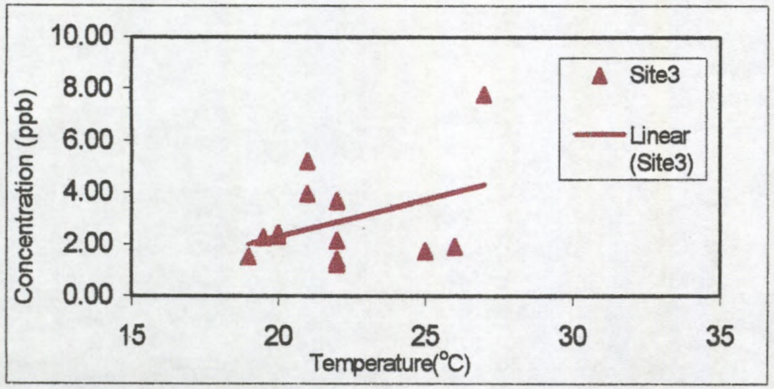


Figure 5.23 Graph of the variation of [Ni] with temperature at site 3

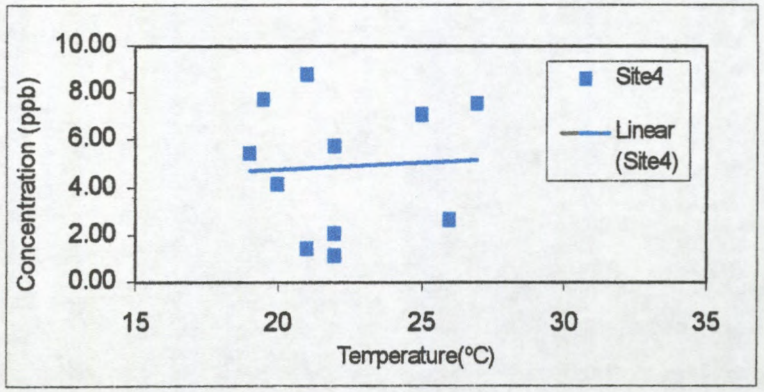


Figure 5.24 Graph of the variation of [Ni] with temperature at site 4

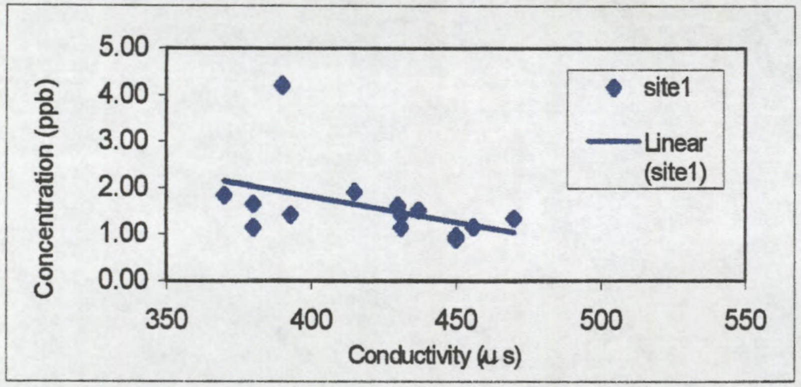


Figure 5.25 Graph of the variation of [Ni] with conductivity at site 1

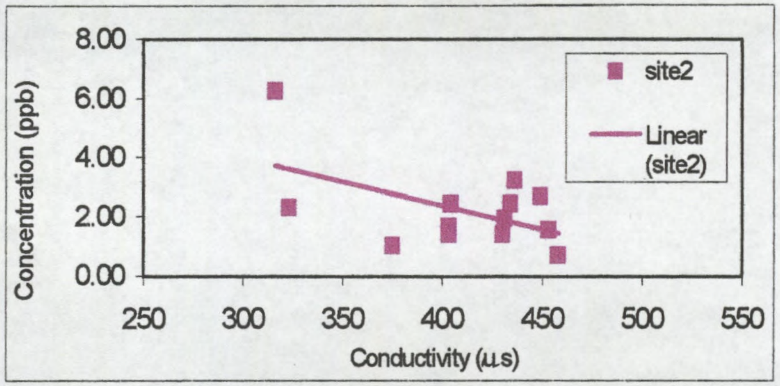


Figure 5.26 Graph of the variation of [Ni] with conductivity at site 2

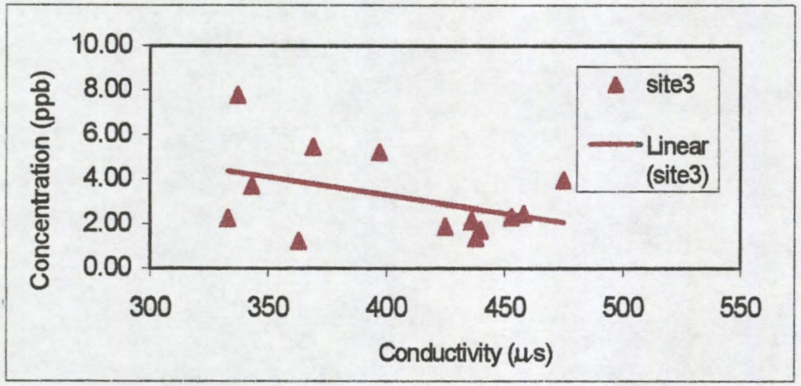


Figure 5.27 Graph of the variation of [Ni] with conductivity at site 3

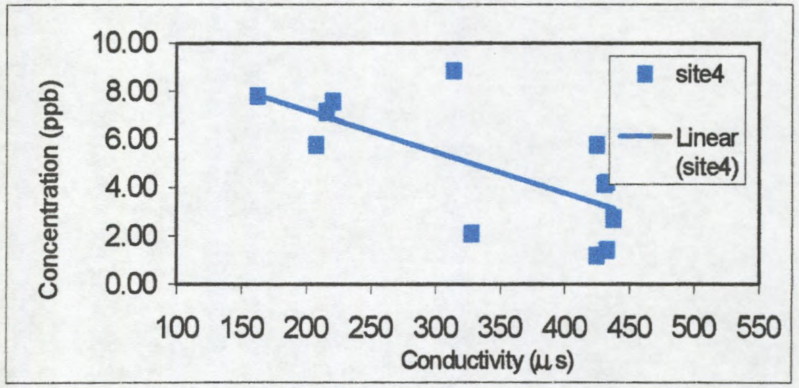


Figure 5.28 Graph of the variation of [Ni] with conductivity at site 4

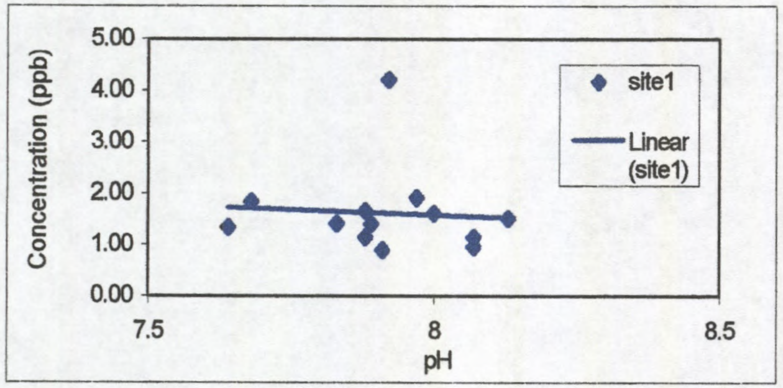


Figure 5.29 Graph of the variation of [Ni] with pH at site 1

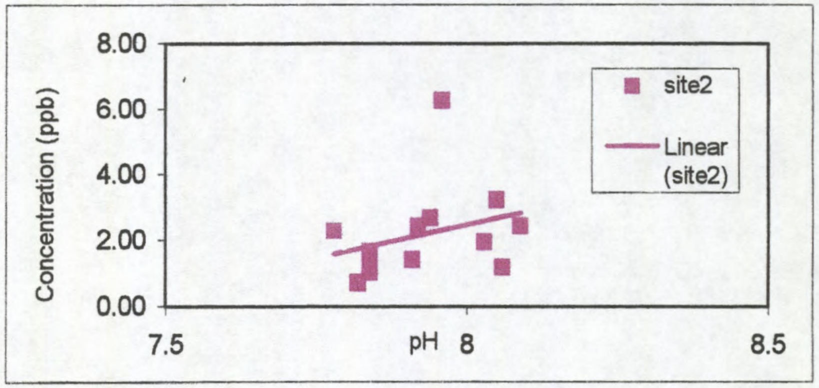


Figure 5.30 Graph of the variation of [Ni] with pH at site 2

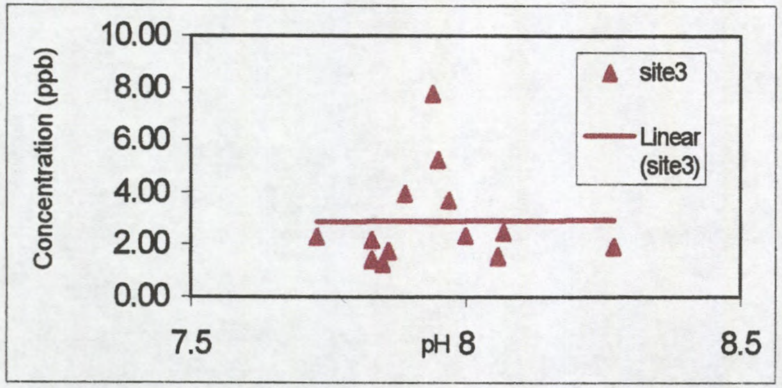


Figure 5.31 Graph of the variation of [Ni] with pH at site 3

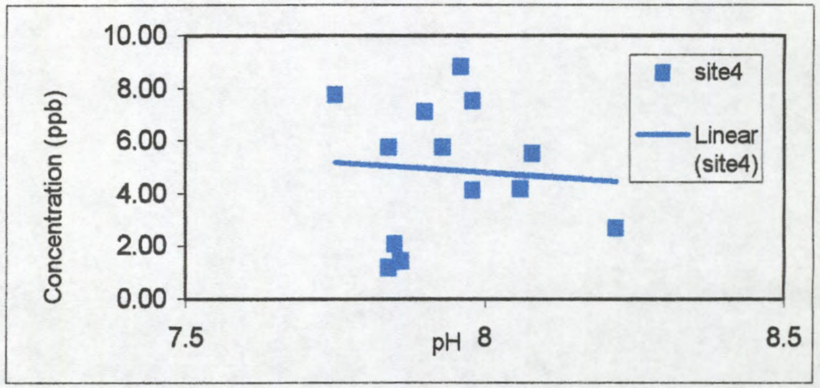


Figure 5.32 Graph of the variation of [Ni] with pH at site 4

5.1.3 LEAD

Lead is a naturally occurring element and is found in all environmental media (air, soil, rocks, sediments, and water) and in all components of the biosphere. Lead occurs primarily as the sulphide (galena) and in the form of oxides (Ewers and Schlipkoter, 1991). Lead and its compounds may enter the environment at any point during mining, smelting, processing, use, recycling, or disposal (Ewers and Schlipkoter, 1991). The average lead content in surface ocean water depends on emission and is about 0.01-0.03 $\mu g.L^{-1}$ (Ewers and Schlipkoter, 1991).

The releasing of lead into natural watercourses can pose long-term environmental problems. Sediments act as sinks for lead and recent evidence (Fifield and Haines, 1995) suggests that biomethylation takes place in the sediment-water interface producing the very toxic lead species $(CH_3)_3Pb^+$and $(CH_3)_4Pb$ (Fifield and Haines, 1995).

Lead is a serious cumulative poison. In adults symptoms of severe lead poisoning are abdominal pain, constipation, vomiting and diarrhoea (Ewers and Schlipkoter, 1991). Children exposed to mild forms of lead suffer effects to their central nervous systems shown by hypertension, irritability and impaired motor skills (Fifield and Haines, 1995).

The concentrations of lead (of triplicate determinations) in both harbour water and sediment samples collected from each of the four sites from July 1998 to July 1999 are shown in Table 5.5. The 95 % confidence limits for the concentration of lead in the harbour water and sediments are shown in Table 5.5. The variation in the error can be attributed to the dynamic nature of the harbour. The continuous tidal change, the different currents, sampling times and sites together with various other physical factors of the water and the sediments account for the large variation of the error limits. The small sample size also contributes to the large confidence limits.

Table 5.5 The monthly mean [Pb] in water and sediment for the period July 1998 to July 1999 in Durban Harbour

MONTH	SITE	WATER (μg.L^{-1})	SEDIMENTS(mg.kg^{-1}) (dry weight)	MONTH	SITE	WATER (μg.L^{-1})	SEDIMENTS(mg.kg^{-1}) (dry weight)
Jul-98	1	3.35 ± 0.43	79.1 ± 4.37	Jan-99	1	3.83 ± 0.51	17.8 ± 11.3
	2	2.78 ± 0.28	202 ± 9.08		2	3.56 ± 0.33	93.5 ± 7.75
	3	2.33 ± 0.56	123 ± 4.53		3	4.64 ± 0.51	84.9 ± 4.51
	4	2.78 ± 0.32	99.5 ± 8.92		4	2.89 ± 0.38	56.4 ± 4.26
Aug-98	1	3.92 ± 0.58	30.8 ± 7.67	Feb-99	1	8.53 ± 0.33	45.7 ± 7.57
	2	3.13 ± 0.28	169 ± 8.69		2	4.91 ± 0.33	51.9 ± 4.38
	3	3.69 ± 0.43	208 ± 4.39		3	2.76 ± 0.51	54.8 ± 11.6
	4	4.38 ± 0.43	132 ± 4.50		4	1.68 ± 0.51	92.6 ± 7.43
Sep-98	1	10.32 ± 0.41	142 ± 7.66	Mar-99	1	1.27 ± 0.42	33.4 ± 4.36
	2	5.38 ± 0.72	245 ± 4.40		2	1.16 ± 0.57	58.7 ± 14.6
	3	8.87 ± 0.19	206 ± 4.41		3	1.71 ± 0.27	110 ± 7.87
	4	3.05 ± 0.41	214 ± 7.82		4	1.71 ± 0.55	56.9 ± 4.30
Oct-98	1	8.17 ± 0.60	92.6 ± 8.85	Apr-99	1	0.50 ± 0.31	60.0 ±4 .09
	2	6.41 ± 0.39	140 ± 4.29		2	1.27 ± 0.55	134 ± 7.38
	3	8.97 ± 0.45	158 ± 4.44		3	0.94 ± 0.27	53.5 ± 7.39
	4	1.76 ± 0.39	69.7 ± 4.55		4	1.71 ± 0.42	87.8 ± 4.84
Nov-98	1	6.09 ± 0.60	21.7 ± 4.46	May-99	1	1.71 ± 0.16	20.4 ± 7.23
	2	6.25 ± 0.39	200 ± 7.78		2	1.83 ± 0.27	18.6 ± 4.44
	3	6.57 ± 0.61	142 ± 4.52		3	1.38 ± 0.57	47.6 ± 7.39
	4	3.85 ± 0.39	120 ± 4.43		4	2.38 ± 0.42	53.7 ± 4.28
Dec-98	1	1.14 ± 0.51	34.1 ± 4.44	Jun-99	1	1.16 ± 0.72	33.8 ± 7.64
	2	1.41 ± 0.51	47.8 ± 4.28		2	1.16 ± 0.27	45.8 ± 7.58
	3	1.28 ± 0.38	126 ± 8.81		3	1.71 ± 0.27	81.0 ± 4.84
	4	1.41 ± 0.51	117 ± 4.40		4	1.83 ± 0.31	54.7 ± 9.06
				Jul-99	1	1.71 ± 0.15	22.2 ± 7.87
					2	2.71 ± 0.47	33.3 ± 7.52
					3	5.70 ± 0.31	36.9 ± 7.06
					4	7.69 ± 0.42	50.4 ± 9.04

5.1.3.1 Lead Content in the Water

The average lead content in the harbour water ranged from 2.86 to 3.98 $\mu g.l^{-1}$ (Table 5.6). Hennig (1985) reported that the lead concentration in Durban Harbour in 1978 ranged from 18 to 117 $\mu g.l^{-1}$. The values obtained were well within this range. The average concentration of lead in unpolluted seawater averages 0.03 $\mu g.l^{-1}$ (Fifield and Haines, 1995). Figure 5.15 illustrates that the mean concentrations of lead in the water at all four sites are almost the same with little variation. The low levels of lead found is in keeping with Hennig's study (Hennig, 1985).

5.1.3.2 Lead content in sediment

Lead concentrations in the sediments ranged from 17.8 to 214 $mg.kg^{-1}$ (Table 5.6). The values obtained were higher than that reported by Hennig and closer in agreement with that of McClurg and co-workers (McClurg *et al.,* 1990). The lead concentration in Durban Harbour sediments in 1978 ranged from 18 to 117 $mg.kg^{-1}$ (Hennig, 1985). McClurg and co workers reported the concentration of lead in sediments to be 5.46 to 230$mg.kg^{-1}$ near the Yacht Mole and 1.21 to 7.33 $mg.kg^{-1}$ along the Maydon Channel in the Durban Harbour (McClurg *et al.,* 1990). Typical concentration of lead in sediments in other parts of the world ranges from 1.5 to 80 $mg.kg^{-1}$ (Fifield and Haines, 1995). David (1999) reported lead concentration in sediments in the Kwa-Zulu coastline to be in range from 0.57 to 127.77 $mg.kg^{-1}$ (David, 1999).

Table 5.6 Mean annual [Pb] lead in water and sediment in the harbour

MONTH	SITE	[Pb] IN WATER ($\mu g.l^{-1}$)	Mean [Pb] ($\mu g.l^{-1}$)	[Pb] IN SEDIMENT ($mg.kg^{-1}$)	Mean [Pb] ($mg.kg^{-1}$)
JULY 98- 99	1	0.51 to 10.32	3.98	17.8 to 142	48.7
JULY 98 –99	2	1.16 to 6.25	3.23	18.6 to 202	111
JULY 98 –99	3	0.94 to 8.97	3.89	36.9 to 208	110
JULY 98 –99	4	0.91 to 4.83	2.86	50.4 to 214	93.8

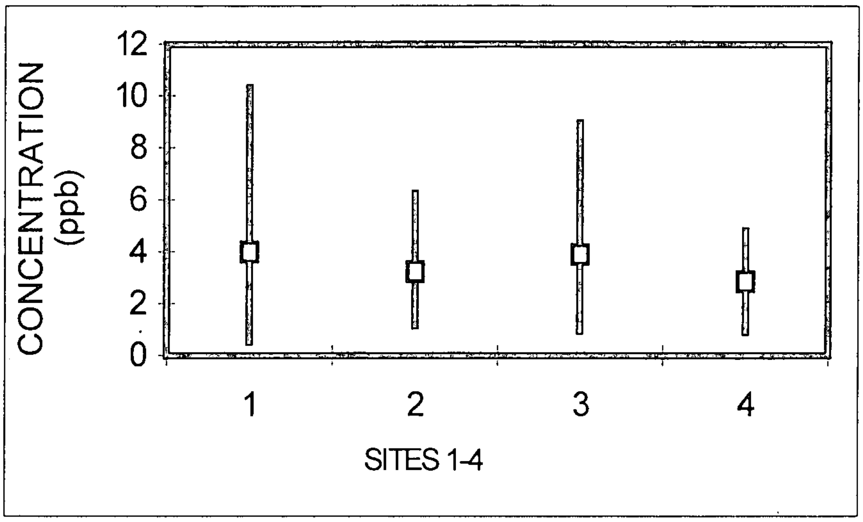


Figure 5.33 Graph of annual mean [Pb] in the water at each site in the harbour

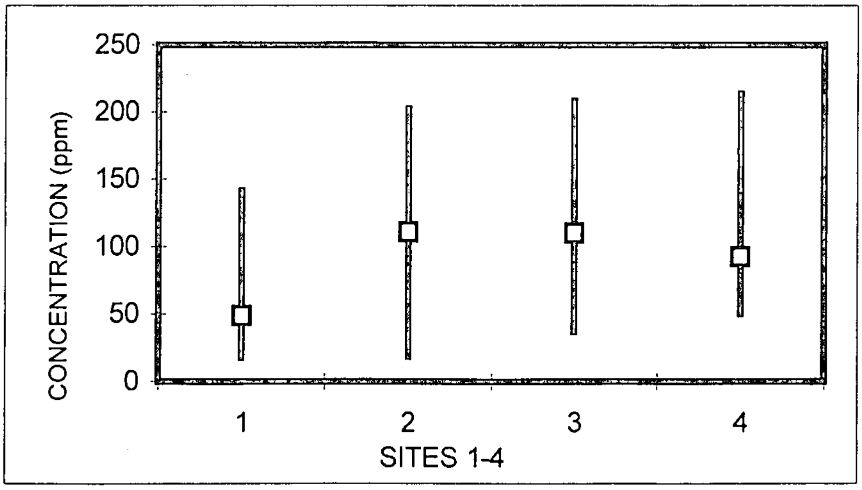


Figure 5.34 Graph of annual mean [Pb] in the sediment at each site in the harbour

5.1.3.3 Variation of lead concentration in the water and the sediments with sampling sites

From figure 5.33 it can be seen that there is an increase in the lead concentration in the sediments from sites one to three with a slight drop in level at site four. Site 3 has the expected highest concentration, as this site is the dry dock site. Here many ships are regularly docked with repairs taking place on a daily basis. Ships are generally coated with lead based paints and flaking of these paints accumulate in the water and/or sediments.

Standard correlation analysis was performed to ascertain if a linear relationship did exist between the concentration of lead in the water with that in the sediment. At 95 % confidence level the null hypothesis was rejected which stated that the level of lead in the sediments was independent of the level of lead in the water. Statistically this was proven invalid. The product moment correlation coefficient, $r = 0.34878$ fell in the region of rejection, which proved that there was a linear relationship between the water and the sediment (see Appendix A3-19/20 for interpretation of data). This meant that when the level of lead in the sediments increased then the level of lead in the water also increased and vice versa. One possible explanation for this is that concentration depends on the volume of the water and also the flow of water in the harbour (Einax *et al.*, 1997).

Figure 5.35 and 5.36 illustrates the distribution of lead in the water and sediments at all the sites for the entire sampling period. A general increase in lead levels can be observed for both water and sediments from the beginning to the middle of the sampling period. In Figure 5.35 the levels increase from July 1998 to November 1998, then a decrease in December 1998 and an increase in January and February 1999. Thereafter there is a decrease in the levels again. Here tidal changes can contribute to these fluctuating values. Also industrial activity and marine traffic increases during the second half of the year. Figure 5.36 illustrates an increase from July 1998 to December 1998 and thereafter there is a decrease in the levels of lead. Figure 5.36 shows that sites 2 and 3 have a higher lead content compared to sites

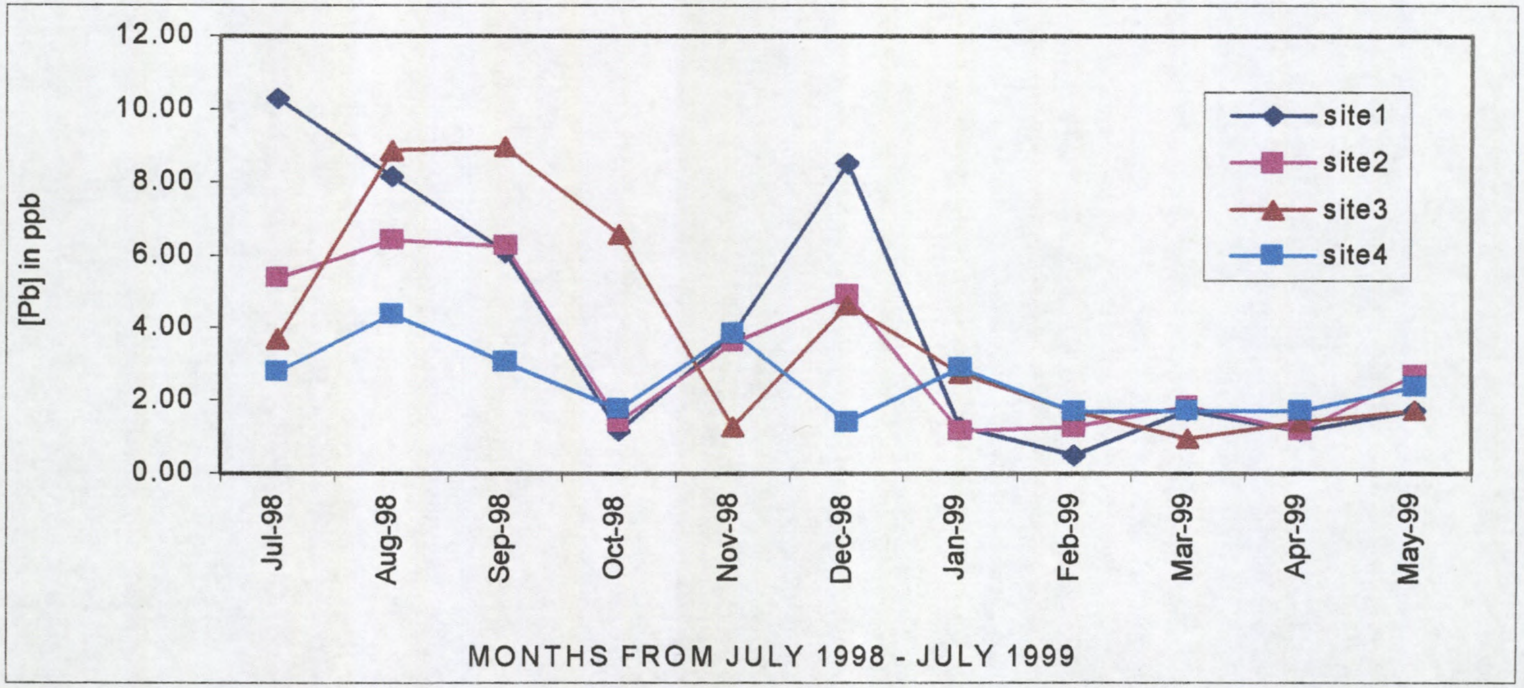


Figure 5.35: Pb concentration in water at the four sites from July 1998 to July 1999

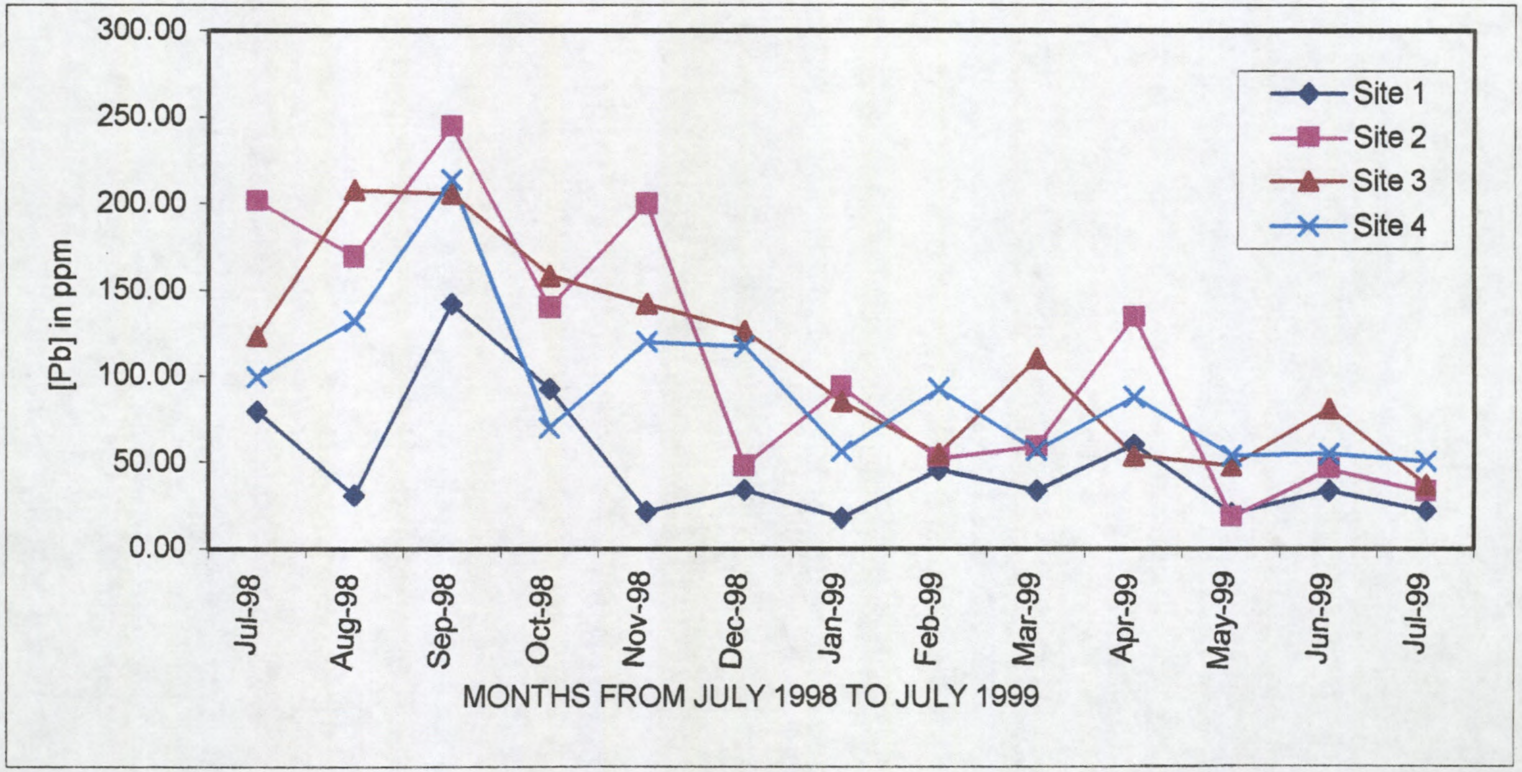


Figure 5.36 Pb concentration in sediments at the four sites from July 1998 to July 1999

5.1.3.4 Variation of [Pb] with Temperature, Conductivity and pH

The possible effect of the variables temperature, conductivity and pH on the lead concentration in the water was investigated.

Figure 5.37 to 5.40 illustrate the variation of lead concentration with temperature. Graphically no correlation was observed between concentration of lead in the water and temperature at site 1. A negative correlation was found at sites 2 to 4. Statistical analysis proved that there was no correlation between temperature and lead concentration at all the sites. The r-value of 0.0777, 0.01621, -0.2522 and -0.4338 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-21/22 for interpretation).

Figures 5.41 to 5.44 illustrate the variation of the level of lead with conductivity. Graphically no correlation was found at sites 1, 2 and 4. A positive correlation was observed in figure 5.43 implying that at site 3 the level of lead in the water increases as conductivity increases. Statistical analysis was done to ascertain if any correlation did exist between conductivity and the level of lead in water. The r-value of 0.0954, -0.1209, 0.4187 and -0.1746 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-23/24 for interpretation). Statistically no correlation was found.

Figures 5.45 to 5.48 illustrate the variation of lead concentration with pH. No correlation was graphically observed. Statistical analysis supported this conclusion. The r-value of 0.4734, 0.2317, 0.0726 and -0.2597 for sites 1, 2, 3 and 4 respectively fall within the acceptance range of ± 0.553 (from critical values of r table) (see Appendix A3-25/26 for interpretation).

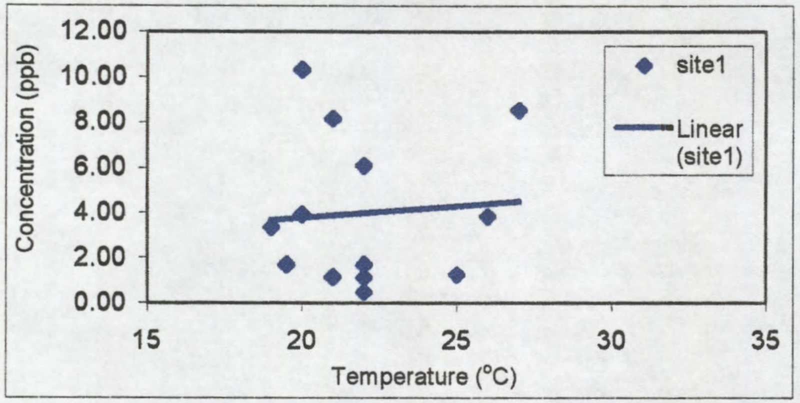


Figure 5.37 Graph of the variation of [Pb] with temperature at site 1

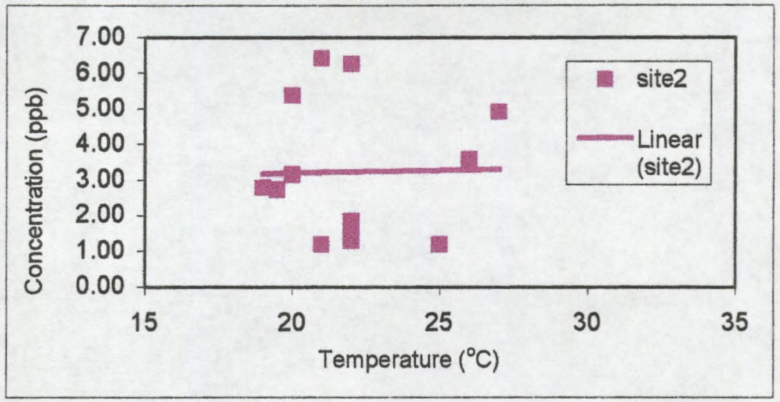


Figure 5.38 Graph of the variation of [Pb] with temperature at site 2

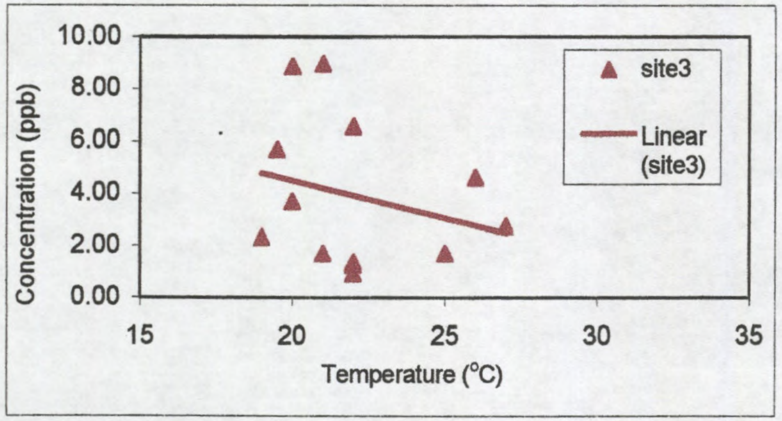


Figure 5.39 Graph of the variation of [Pb] with temperature at site 3

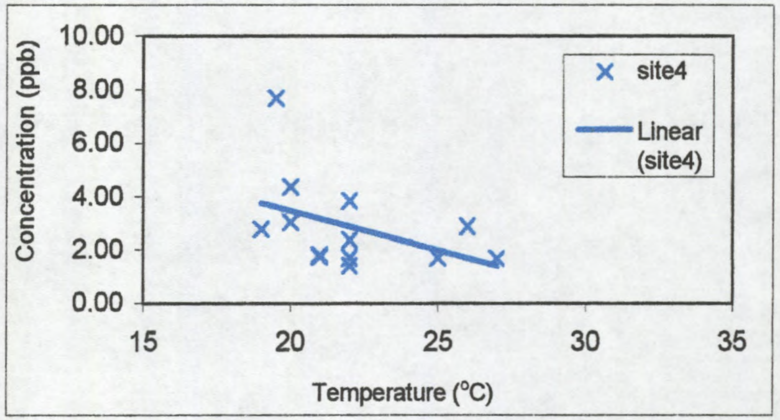


Figure 5.40 Graph of the variation of [Pb] with temperature at site 4

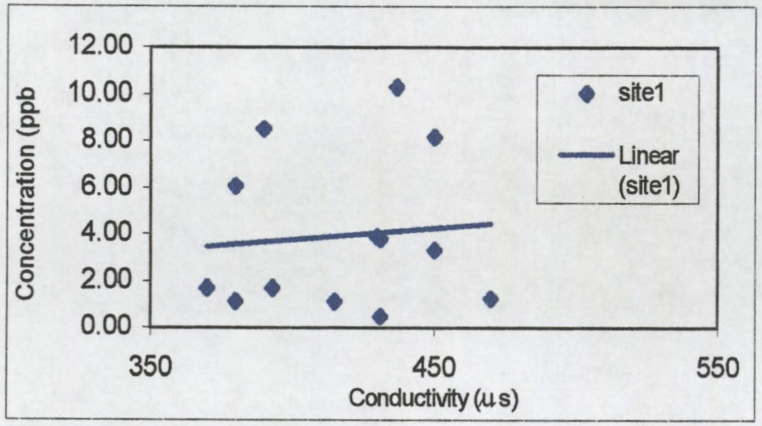


Figure 5.41 Graph of the variation of [Pb] with conductivity at site 1

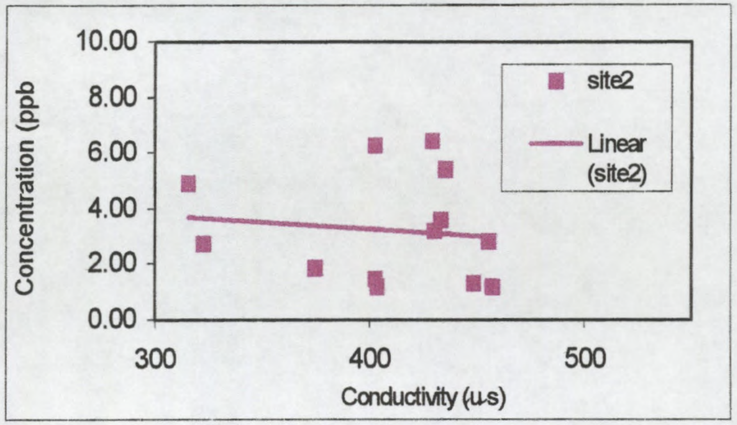


Figure 5.42 Graph of the variation of [Pb] with conductivity at site 2

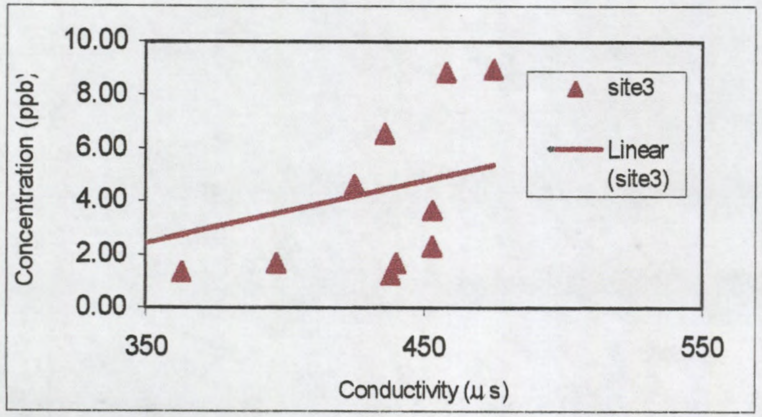


Figure 5.43 Graph of the variation of [Pb] with conductivity at site 3

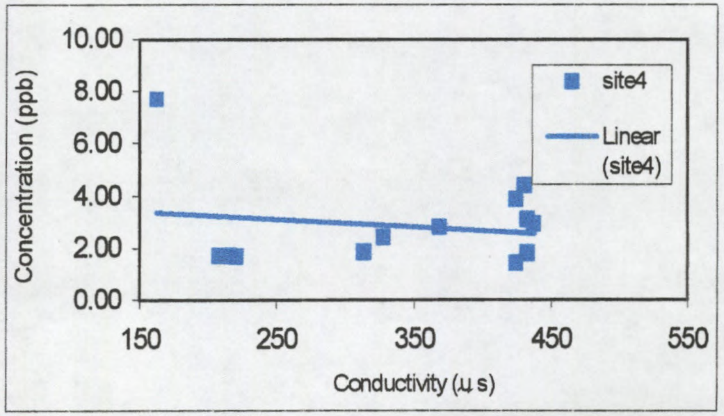


Figure 5.44 Graph of the variation of [Pb] with conductivity at site 4

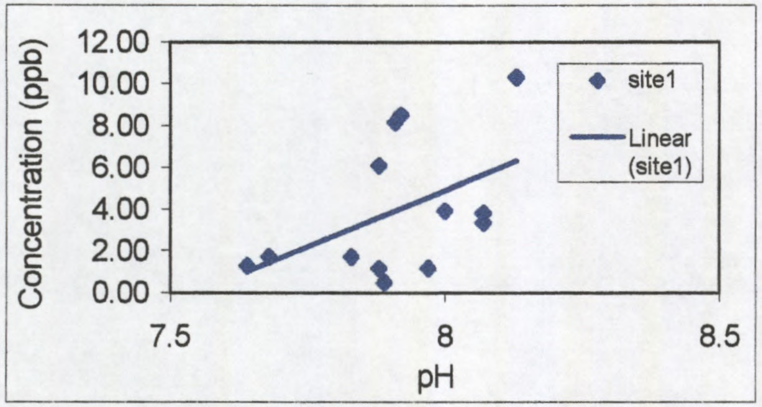


Figure 5.45 Graph of the variation of [Pb] with pH at site 1

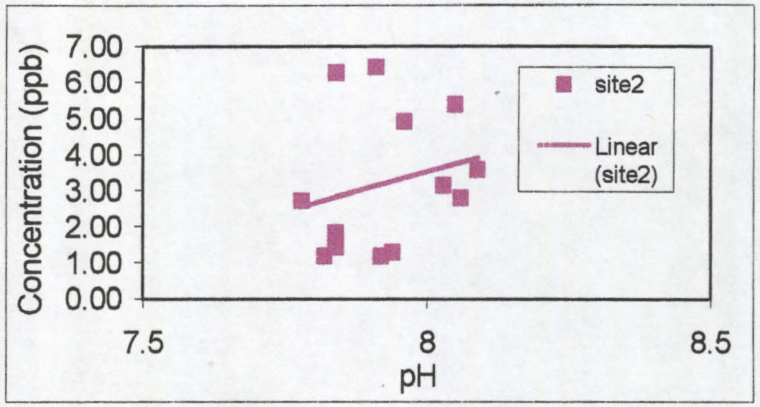


Figure 5.46 Graph of the variation of [Pb] with pH at site 2

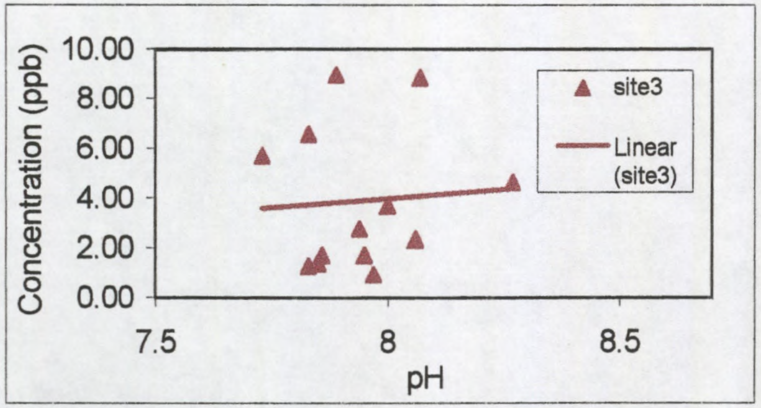


Figure 5.47 Graph of the variation of [Pb] with pH at site 3

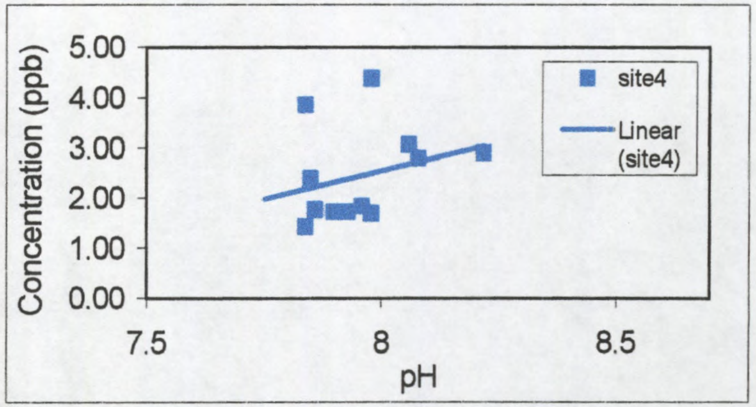


Figure 5.48 Graph of the variation of [Pb] with pH at site 4

5.2 THE DISTRIBUTION OF Zn, Fe, Al, Ti and Ca IN BULK SEDIMENTS AND IN THE VARIOUS GRAIN SIZES

Many trace elements do not exist in soluble forms for very long in water and therefore accumulate in bottom sediments (Fifield and Haines, 1995). Prolonged input of trace metals to coastal waters lead to accumulation in the aquatic system. As a consequence of long-term input, local sediments are enriched in these contaminants (Akhter and Al-Jowder, 1997). Mantei and Coonrod (1989) believed that the use of courser grain size gave a better indication of any trend of increasing quantities of metals in sediments because of limited transport and longer residence at a site. It was therefore decided to extend the study of sediments to obtain a profile of zinc, iron, aluminium, titanium and calcium in the sediments. This section focuses on the determination of the concentrations of these elements in the sediments prior to grain size separation (referred to as bulk sediments) and after grain sizes separation. These major elements in the sediments were analysed by the ICP-AES for ease of operation.

5.2.1 Bulk sediment analysis

The results of the mean concentration of zinc, iron, aluminium, titanium and calcium as per Table 5.7 will be discussed with respect to the metal distribution in the bulk sediments. Samples for all four sites were only available for the months of July, August, October, November 1998, January, March, April, June and July 1999. Comparisons of results will therefore be made where complete sets of samples were available. For the months when samples were not available a value of zero is assigned since the computer programme used requires a numerical value to draw the graphs. The digestion of the sediment was done in duplicate and the analysis was done in triplicate by ICP-AES. The data is given in Table 5.7 and the discussion is included in section 5.2.1.1 to 5.2.1.5.

At 95 % confidence and t = 12.71; the confidence limits were large since the number of samples were only two.

Table 5.7 Table of % Fe, Ti, Zn, Al and Ca in the bulk sediments

METALS IN BULK SEDIMENTS							
DATE	SITE	MASS(g)	Fe (%)	Ti (%)	Zn (%)	Al (%)	Ca (%)
Jul-98	1	0.5218	13.1 ± 6.07	1.64 ± 0.85	1.65 ± 0.22	2.41 ± 1.10	4.46 ± 0.12
Jul-98	2	0.5019	31.6 ± 3.45	2.23 ± 1.26	2.33 ± 1.26	3.96 ± 1.41	1.29 ± 0.25
Jul-98	3	0.5029	32.0 ± 6.15	2.33 ± 1.13	2.00 ± 1.55	5.05 ± 1.07	0.72 ± 0.25
Jul-98	4	0.5107	39.5 ± 24.5	2.32 ± 1.24	2.80 ± 1.22	4.75 ± 0.69	0.20 ± 0.01
Aug-98	1	0.5146	18.1 ± 9.07	1.82 ± 0.74	2.21 ± 0.23	3.29 ± 0.71	4.88 ± 1.39
Aug-98	2	0.5244	29.9 ± 9.23	2.10 ± 1.33	2.60 ± 1.28	5.80 ± 0.53	0.91 ± 0.25
Aug-98	3	0.5181	60.7 ± 19.2	2.34 ± 0.37	4.56 ± 1.59	7.75 ± 1.87	0.87 ± 0.19
Aug-98	4	0.5059	43.5 ± 3.88	2.70 ± 0.25	3.41 ± 1.00	5.32 ± 1.03	0.23 ± 0.01
Sep-98	1	0	0	0	0	0	0
Sep-98	2	0.5177	40.9 ± 4.18	2.30 ± 0.01	3.61 ± 1.02	5.80 ± 0.55	0.68 ± 0.67
Sep-98	3	0.5158	41.5 ± 2.46	2.33 ± 0.21	3.45 ± 1.09	5.19 ± 1.47	0.87 ± 0.98
Sep-98	4	0.5047	38.7 ± 1.26	1.62 ± 0.12	2.31 ± 1.75	6.64 ± 1.25	1.03 ± 0.15
Oct-98	1	0.5145	26.9 ± 16.1	2.13 ± 0.01	2.91 ± 0.42	4.73 ± 1.32	3.55 ± 0.72
Oct-98	2	0.5314	40.5 ± 9.56	2.11 ± 0.06	3.69 ± 1.57	4.96 ± 0.04	0.91 ± 0.23
Oct-98	3	0.5122	31.4 ± 6.20	2.12 ± 1.78	2.61 ± 1.07	3.67 ± 0.48	1.85 ± 0.53
Oct-98	4	0.5007	26.5 ± 6.34	2.00 ± 0.38	2.00 ± 1.42	3.76 ± 0.93	0.79 ± 0.18
Nov-98	1	0.5105	21.2 ± 4.98	2.13 ± 0.51	2.40 ± 0.74	3.86 ± 1.36	4.06 ± 0.17
Nov-98	2	0.507	37.8 ± 2.50	2.32 ± 0.42	3.61 ± 1.88	5.63 ± 2.03	0.89 ± 0.32
Nov-98	3	0.5038	42.8 ± 6.31	1.80 ± 0.34	3.11 ± 1.14	4.13 ± 0.64	0.68 ± 0.25
Nov-98	4	0.5137	36.6 ± 7.42	2.40 ± 1.11	3.14 ± 1.85	6.05 ± 1.18	0.46 ± 0.04
Dec-98	1	0	0	0	0	0	0
Dec-98	2	0.5316	21.9 ± 2.39	3.03 ± 0.59	1.30 ± 0.39	2.16 ± 0.56	2.64 ± 0.05
Dec-98	3	0.5173	38.4 ± 9.83	2.74 ± 0.42	3.32 ± 1.37	7.49 ± 0.27	0.68 ± 0.77
Dec-98	4	0.5174	33.6 ± 7.37	2.10 ± 0.37	3.44 ± 1.01	4.69 ± 0.06	0.46 ± 0.10
Jan-99	1	0.5354	9.90 ± 3.56	1.50 ± 0.70	1.83 ± 0.65	1.53 ± 0.39	5.35 ± 0.03
Jan-99	2	0.5092	36.4 ± 3.74	2.20 ± 1.28	2.50 ± 0.17	4.05 ± 0.55	0.48 ± 0.12
Jan-99	3	0.5047	33.6 ± 6.29	2.44 ± 0.84	3.12 ± 1.26	4.76 ± 0.11	0.32 ± 0.09
Jan-99	4	0.5353	23.0 ± 6.10	1.30 ± 0.97	1.70 ± 1.68	3.73 ± 0.16	0.93 ± 0.14
Feb-99	1	0	0	0	0	0	0
Feb-99	2	0	0	0	0	0	0
Feb-99	3	0.5209	24.6 ± 7.30	1.60 ± 0.63	1.82 ± 1.51	3.09 ± 1.10	0.83 ± 0.87
Feb-99	4	0	0	0	0	0	0
Mar-99	1	0.5224	14.9 ± 11.4	1.81 ± 0.70	1.92 ± 1.72	2.89 ± 0.20	5.00 ± 1.12
Mar-99	2	0.5405	5.58 ± 1.27	0.81 ± 0.65	1.00 ± 0.93	1.27 ± 0.31	3.67 ± 0.01
Mar-99	3	0.5012	40.4 ± 2.40	1.70 ± 0.36	2.03 ± 0.17	3.86 ± 0.21	2.66 ± 0.03
Mar-99	4	0.5299	24.4 ± 5.71	1.91 ± 0.21	1.30 ± 0.18	2.25 ± 0.26	0.15 ± 0.78
Apr-99	1	0.556	5.10 ± 0.11	0.96 ± 0.34	0.75 ± 0.51	1.11 ± 0.28	3.95 ± 0.22
Apr-99	2	0.5343	42.3 ± 0.36	2.13 ± 1.26	2.91 ± 0.84	6.46 ± 0.48	0.52 ± 0.37
Apr-99	3	0.5337	18.9 ± 6.76	2.10 ± 0.13	1.49 ± 0.98	2.79 ± 0.23	2.32 ± 0.05
Apr-99	4	0.47	32.5 ± 5.82	2.22 ± 0.98	2.32 ± 0.68	4.35 ± 0.43	0.33 ± 0.38
May-99	1	0.5458	9.80 ± 4.60	1.30 ± 0.86	1.86 ± 0.84	1.64 ± 0.37	6.78 ± 0.15
May-99	2	0	0	0	0	0	0
May-99	3	0	0	0	0	0	0
May-99	4	0.5318	21.1 ± 7.38	1.42 ± 1.08	1.76 ± 1.23	2.66 ± 0.41	0.43 ± 0.53
Jun-99	1	0.5166	6.60 ± 1.22	0.18 ± 0.39	1.44 ± 1.20	1.29 ± 0.68	4.64 ± 0.19
Jun-99	2	0.5205	7.54 ± 1.35	1.35 ± 0.28	1.17 ± 1.33	1.23 ± 1.22	3.64 ± 0.08
Jun-99	3	0.4704	26.3 ± 8.75	1.90 ± 1.50	2.30 ± 2.50	4.28 ± 0.48	0.51 ± 0.89
Jun-99	4	0.4355	28.8 ± 2.54	2.85 ± 0.61	3.00 ± 2.34	4.87 ± 0.52	0.50 ± 0.01
Jul-99	1	0.5012	7.10 ± 1.21	1.40 ± 0.02	1.10 ± 0.31	1.26 ± 0.91	3.81 ± 0.23
Jul-99	2	0.5244	18.3 ± 7.38	2.87 ± 0.48	1.51 ± 0.31	3.16 ± 0.30	3.81 ± 1.01
Jul-99	3	0.5167	19.1 ± 0.02	2.90 ± 0.79	1.15 ± 0.06	2.17 ± 0.37	2.47 ± 0.02
Jul-99	4	0.5038	22.7 ± 3.79	2.01 ± 0.01	0.77 ± 0.37	1.52 ± 1.04	0.45 ± 0.16

5.2.1.1 The distribution of % Zinc in the Bulk Sediments

The main ore of zinc contains zinc sulphide, ZnS. Zinc is widely used as a surface coating on iron and steel to prevent rusting. Ships are coated with zinc (Moody, 1969).

Figure 5.49 illustrates the distribution of zinc in the bulk sediments at the four sites for a period of one year. On inspection of Figure 5.49 the distribution of zinc is within a narrow range at each of the four sites. Although one would expect the level of zinc to be much higher at site 3, i.e. the dry dock site, there is little evidence from the graph to support the notion that zinc used during the maintenance or repair process contaminates the area. In this study the average value of zinc in the Durban Harbour was 1.94 %. In 1978 0.3 % of zinc was found in Durban Harbour (Hennig, 1985). He also found that industrialised areas showed higher concentrations than urban areas (Hennig, 1985).

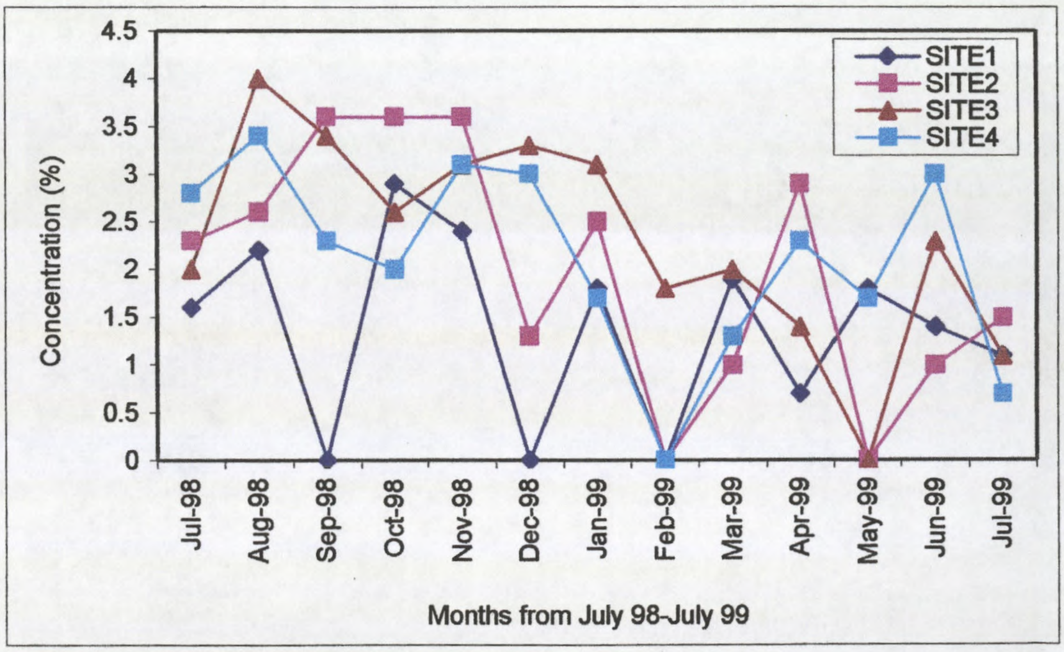


Figure 5.49 Distribution of Zn in the bulk sediments at the four sites

5.2.1.2 The distribution of % Fe in the Bulk Sediments

Iron is the fourth most abundant element and the second most abundant metal in the earth's crust. The principal ores of iron are haematite, Fe_2O_3 and limonite, $2Fe_2O_3.3H_2O$.

Figure 5.50 illustrates the distribution of iron in the bulk sediments at the four sites for a period of one year. On inspection of Figure 5.50 it is clear that the concentration of iron is generally much lower at site 1 that the other sites. Site 1 being an open channel has minimal industrial activity that accounts for the generally low values. It can also be observed that the concentration of iron at site 3 is at the highest for most of the months. At this site ship repairs take place on a regular basis. In this study the average value of iron was found to be 24 %. In 1978 40 % of iron was found in Durban Harbour (Hennig, 1985). This decrease in iron may be attributed to less rusting of ships due to better rust prevention methods.

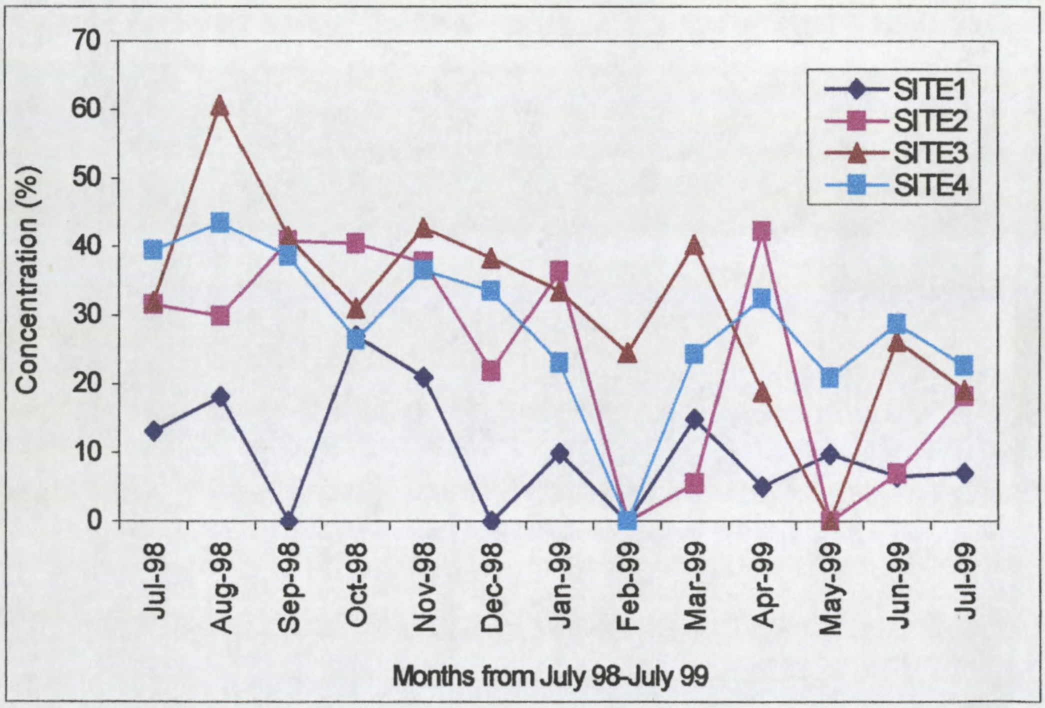


Figure 5.50 Distribution of Fe in the bulk sediments at the four sites

5.2.1.3 The distribution of % Ti in the bulk sediments

Titanium is the seventh most abundant metal and about the tenth most abundant element in the earth's crust (Moody, 1969). The principal ores are rutile, TiO_2 and ilmenite, $FeO.TiO_2$. Titanium is used in aircrafts, chemical and in electrochemical and nuclear engineering.

From Figure 5.51 the average amount of titanium in the sediments was found to be 1.69 %. From Figure 5.51 it is evident that titanium occurs within a very narrow range. The lowest value recorded was 0.1 % and the highest value was 3.1 %. Hennig or other researchers reported no values for titanium in Durban Bay sediments.

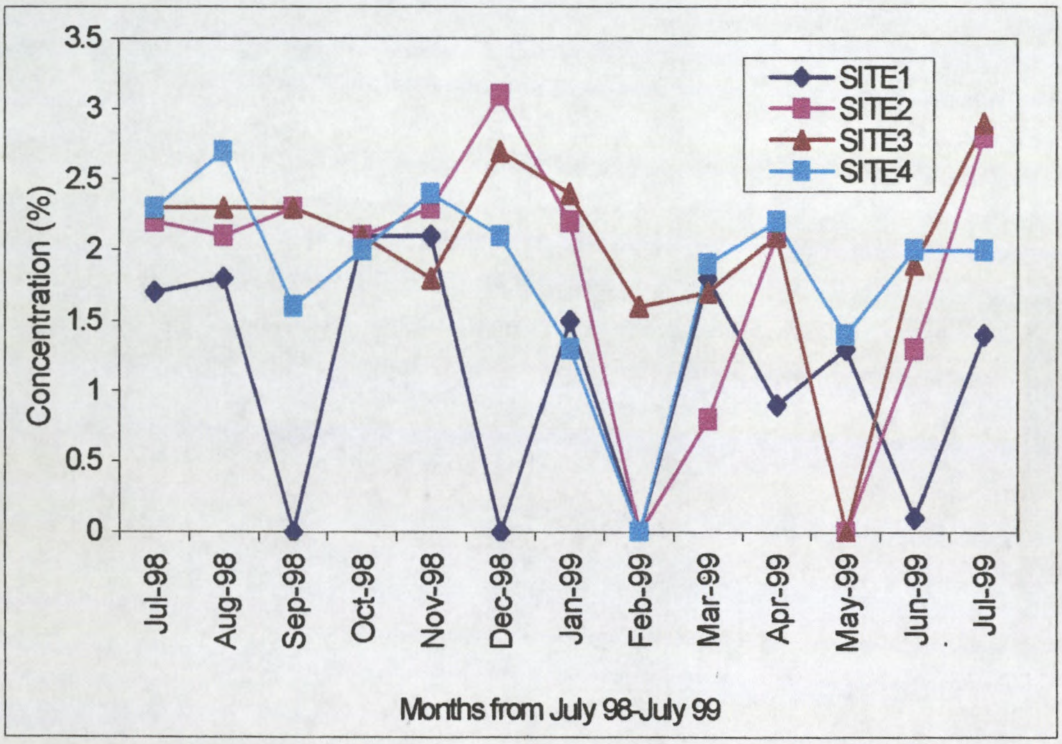


Figure 5.51 Distribution of Titanium in bulk sediments at the four sites

5.2.1.4 The distribution of % Aluminium in the bulk sediments

Aluminium is the third most abundant element in the earth's crust. In rocks, it occurs as alumino-silicate minerals, such as feldspar or clay minerals and as hydroxide, e.g. in bauxite. Deep clays and sediments can have levels of aluminium as high as 9.5 % (Fifield and Haines, 1995). In recent years aluminium has been cited as a possible toxin in the pathogenesis of various diseases (Fifield and Haines, 1995). Patients suffering from senile dementia of the Alzheimer type also have elevated levels of aluminium in the brain.

The average percentage of aluminium in the sediments was 3.33. The lowest value recorded was 1.1 % and the highest value was 7.75 %. Figure 5.52 shows sites 3 and 4 to have higher concentrations of aluminium than sites 1 and 2. This may be attributed to greater industrial activity and also repairing of ships. No values have been reported for aluminium by Hennig or other researchers.

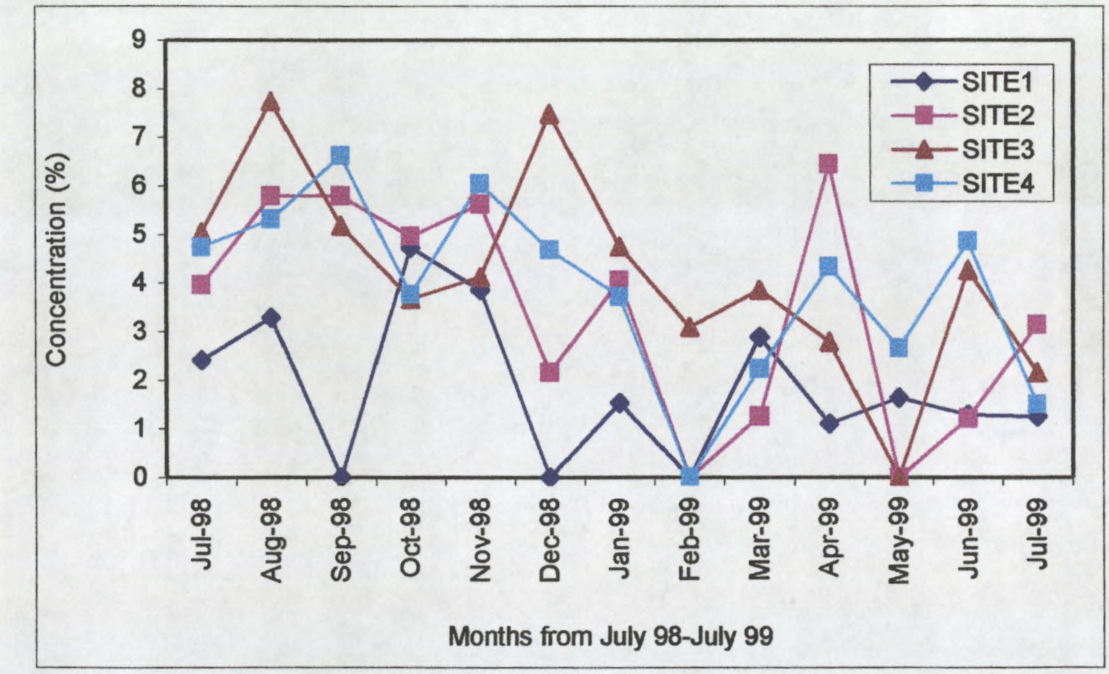


Figure 5.52 Distribution of Aluminium in bulk sediments at the four sites

5.2.1.5 The distribution of % Calcium in the bulk sediments

Calcium is found in limestone rock. Acid conditions result in the continuous dissolution of the limestone thus increasing the levels of calcium.

From Figure 5.53 an average of 1.67 % of calcium was found in the sediments. It is also observed from Figure 5.53 that the level of calcium was always higher at site 1. Site 1 is in the open channel and has minimum human activity compared to the other three sites. In addition seashells are found at this site and the wearing action of the waves on the seashells ca considerably add to the level of calcium in this area. According to Mantei and Coonrod, (1989) courser grain size gives a better indication of any trend of increasing quantities of metals in the sediments because of a limited transport and longer residence at a site. Thus the course grain sizes and limited activity helped in the accumulation of calcium over the years at this site resulting in the high values indicated on the graph.

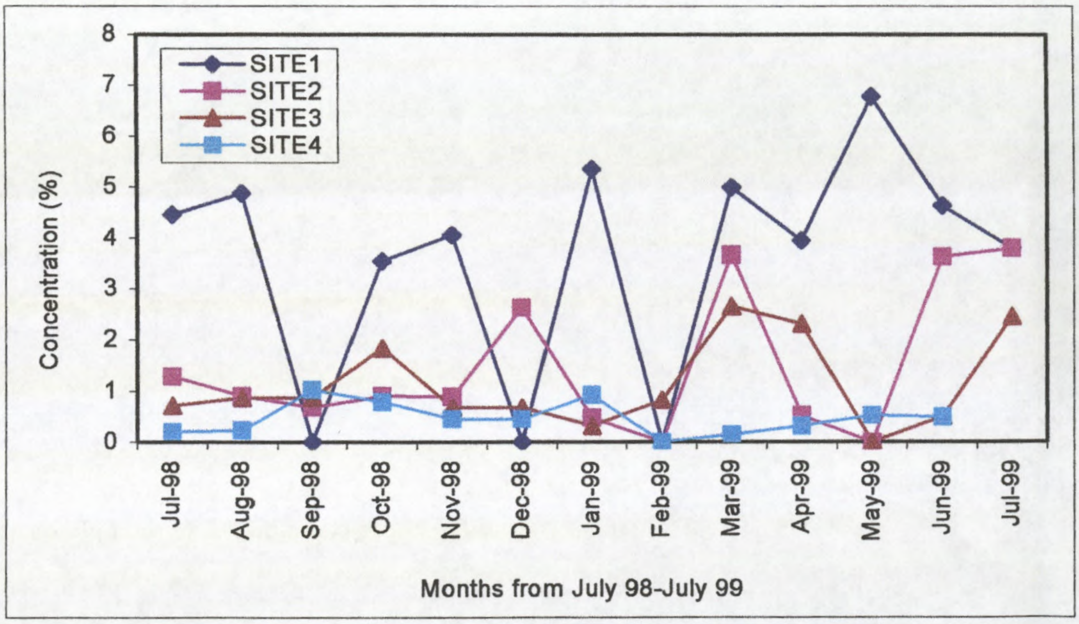


Figure 5.53 Distribution of Ca in bulk sediments at the four sites

CONCLUSION

From the above results it can be concluded that the levels of zinc, iron, titanium, aluminium and calcium gives a further indication of the metals in the bulk sediments. These metals occur naturally and are also contributed by anthropogenic effects.

5.2.2 Grain size analysis

Zn, Fe, Ti, Al, Ca were analysed by ICP for their levels in the different grain sizes. It is well known that higher quantities of metals accumulate on the smaller grain fractions because of the higher surface area to grain size ratio [(Mantei and Coonrod, 1989; Loring and Rantala, 1991; Windom *et al.*, 1989; Schropp *et al.*, 1990)]. As the grain sizes decrease the finer particles of sediments have a larger surface area for an increased metal adsorption. Anthropogenic trace metal contributions to marine sediments are often introduced initially to the environment in solution and accumulate on fine sediments and on inorganic and organic colloidal particles (Windom *et al.*, 1989). Trace metal contaminants from anthropogenic sources may also be introduced in large particles, (Windom *et al.*, 1989).

Table 5.8 indicates the results of zinc, iron, titanium, aluminium and calcium in the various grain sizes. The digestions of the sediments were done in duplicate and the analyses were done in triplicate by the ICP-AES. The data is given in Table 5.8 and the discussion in included in section 5.2.2.1 to 5.2.2.5. The results in Table 5.8 were generated from the various grain sizes of the sediment samples. Although the duplicate results were close the confidence limits were large because of a small sample size and the limits were therefore not calculated (at 95 % confidence, $n = 2$ and $t = 12.71$). It can be seen that From Table 5.8 the greatest percentage distribution of the sediment was in the 63 µm sieve. An example of the total % distribution as in Table 5.8 of the sediment was as follows [(1A (500-355µm) = 3 % + 1A(355-63 µm) = 90 % + 1A (63 µm) = 4 %] = 97 %. The particle size data, however, suggests that although the highest metal concentration typically occur in the < 63 µm size fraction, the 63 µm sieve contributes the largest percentage to the total metal concentrations to these samples (Murray, *et al.*,1999).

Table 5.8 Results of Zn, Fe, Ti, Al and Ca in the various grain sizes

ICP ANALYSIS OF METALS IN SEDIMENTS OF VARYING GRAIN SIZES								
SITE	GRAIN SIZE (µm)	MASS (g)	% DISTRIBUTION	Zn(%)	Fe(%)	Ti(%)	Al(%)	Ca(%)
1A	500-355µm	0.2572	3	0.06 ± 0.01	1.87 ± 0.02	0.52 ± 0.13	0.82 ± 0.16	0.33 ± 0.11
1B	500-355µm	0.2609	4	0.07 ± 0.01	0.10 ± 0.01	0	0.98 ± 0.11	1.41 ± 0.17
1C	500-355µm	0.2327	1	0.06 ± 0.05	0.42 ± 0.25	0.01 ± 0.01	1.35 ± 0.02	2.02 ± 0.21
2A	500-355µm	0.2547	14	0.09 ± 0.01	2.20 ± 0.12	0.82 ± 0.02	1.94 ± 0.05	0.35 ± 0.01
2B	500-355µm	0.2597	7	0.05 ± 0.01	0.41 ± 0.01	0.56 ± 0.04	0.67 ± 0.12	0.82 ± 0.17
2C	500-355µm	0.2566	3	0.05 ± 0.01	0.51 ± 0.01	0.23 ± 0.01	0.27 ± 0.01	0.36 ± 0.02
2D	500-355µm	0.2961	3	0.04 ± 0.01	0.11 ± 0.01	0	0.09 ± 0.01	0.38 ± 0.01
3A	500-355µm	0.2606	5	0.07 ± 0.01	2.47 ± 0.16	0.01 ± 0.02	0.12 ± 0.01	1.05 ± 0.06
3B	500-355µm	0.2598	4	0.05 ± 0.01	0.32 ± 0.18	0	0.29 ± 0.05	0.45 ± 0.02
3C	500-355µm	0.1578	3	0.05 ± 0.01	0.58 ± 0.03	0	0.42 ± 0.01	0.68 ± 0.07
3D	500-355µm	0.2922	4	0.04 ± 0.01	0.09 ± 0.11	0	0.12 ± 0.06	0.68 ± 0.03
4A	500-355µm	0.2143	4	0.05 ± 0.01	0.31 ± 0.17	0	0.31 ± 0.05	0.43 ± 0.09
4B	500-355µm	0.2368	4	0.05 ± 0.03	0.15 ± 0.12	0	0.23 ± 0.01	0.38 ± 0.04
4C	500-355µm	0.124	2	0.02 ± 0.01	0.18 ±0.34	0	0.15 ± 0.05	0.02 ± 0.03
4D	500-355µm	0.2321	2	0.06 ± 0.01	0.03 ± 0.06	0	0.18 ± 0.01	0.16 ± 0.07
1A	355-63 µm	0.2548	90	0.09 ± 0.01	0.60 ± 0.10	0.15 ± 0.08	1.29 ± 0.08	1.94 ± 0.01
1B	355-63 µm	0.272	92	0.08 ± 0.01	1.47 ± 0.16	0.49 ± 0.13	2.07 ± 0.24	0.17 ± 0.06
1C	355-63 µm	0.2703	95	0.08 ± 0.01	0.86 ± 0.18	0	0.81 ± 0.05	2.46 ± 0.07
2A	355-63 µm	0.2685	59	0.09 ± 0.01	1.77 ± 0.34	0.66 ± 0.02	1.14 ± 0.03	0.44 ± 0.09
2B	355-63 µm	0.2582	77	0.08 ± 0.01	1.56 ± 0.04	0.71 ± 0.02	0.97 ± 0.12	0.63 ± 0.05
2C	355-63 µm	0.2879	86	0.07 ± 0.01	0.49 ± 0.07	0.28 ± 0.09	0.33 ± 0.06	0.43 ± 0.03
2D	355-63 µm	0.2778	89	0.05 ± 0.01	0.91 ± 0.01	0.71 ± 0.04	0.58 ± 0.04	0.73 ± 0.09
3A	355-63 µm	0.2739	74	0.09 ± 0.01	2.61 ± 0.46	0.63 ± 0.02	1.16 ± 0.03	0.20 ± 0.13
3B	355-63 µm	0.2703	74	0.08 ± 0.01	1.76 ± 0.07	0.68 ± 0.11	1.43 ± 0.05	0.27 ± 0.01
3C	355-63 µm	0.2530	75	0.08 ± 0.01	0.84 ± 0.01	0.27 ± 0.12	0.26 ± 0.05	0.24 ± 0.01
3D	355-63 µm	0.2836	85	0.05 ± 0.04	0.74 ± 0.17	0.48 ± 0.01	0.14 ± 0.04	0.65 ± 0.08
4A	355-63 µm	0.2600	54	0.06 ± 0.02	0.38 ± 0.05	0.64 ± 0.05	0.24 ± 0.05	0.12 ± 0.01
4B	355-63 µm	0.2522	74	0.06 ± 0.02	0.95 ± 0.19	0.65 ± 0.05	0.32 ± 0.02	0.17 ± 0.03
4C	355-63 µm	0.2622	68	0.05 ± 0.02	0.88 ± 0.02	0.42 ± 0.06	0.14 ± 0.01	0.03 ± 0.01
4D	355-63 µm	0.2600	75	0.07 ± 0.01	0.79 ± 0.07	0.58 ± 0.06	0.45 ± 0.05	0.02 ± 0.01
1A	< 63µm	0.0768	4	0.24 ± 0.04	0.05 ± 0.01	0	0.74 ± 0.24	1.72 ± 0.05
1B	< 63µm	0.1241	2	0.09 ± 0.02	0.54 ± 0.04	0.30 ± 0.13	0.82 ± 0.07	1.88 ± 0.09
1C	< 63µm	0.0271	2	0.54 ± 0.02	2.69 ± 0.34	0.40 ± 0.04	2.29 ± 0.24	0.50 ± 0.01
2A	< 63µm	0.2596	22	0.13 ± 0.01	2.01 ± 0.33	0.76 ± 0.01	1.35 ± 0.04	0.25 ± 0.01
2B	< 63µm	0.1580	12	0.18 ± 0.01	2.30 ± 0.74	0.65 ± 0.07	2.15 ± 0.15	0.38 ± 0.01
2C	< 63µm	0.2774	8	0.08 ± 0.01	1.18 ± 0.10	0.70 ± 0.08	0.33 ± 0.02	0.49 ± 0.02
2D	< 63µm	0.1328	5	0.14 ± 0.01	1.86 ± 0.08	0.80 ± 0.26	0.99 ± 0.02	0.14 ± 0.13
3A	< 63µm	0.2506	18	0.12 ± 0.01	2.85 ± 0.09	0.83 ± 0.02	1.94 ± 0.01	0.24 ± 0.01
3B	< 63µm	0.2813	18	0.15 ± 0.01	2.03 ± 0.12	0.79 ± 0.08	2.01 ± 0.22	0.29 ± 0.01
3C	< 63µm	0.2618	19	0.08 ± 0.06	1.18 ± 0.09	0.67 ± 0.09	0.57 ± 0.05	0.45 ± 0.01
3D	< 63µm	0.2332	8	0.06 ± 0.01	0.91 ± 0.20	0.76 ± 0.13	0.29 ± 0.06	0.23 ± 0.01
4A	< 63µm	0.2604	41	0.06 ± 0.01	0.50 ± 0.17	0.79 ± 0.10	0.29 ± 0.06	0.09 ± 0.01
4B	< 63µm	0.2661	18	0.09 ± 0.02	1.42 ± 0.06	0.73 ± 0.08	0.36 ± 0.01	0.18 ± 0.02
4C	< 63µm	0.2528	28	0.07 ± 0.01	1.12 ± 0.13	0.87 ± 0.25	0.24 ± 0.06	0.04 ± 0.01
4D	< 63µm	0.258	21	0.09 ± 0.01	0.97 ± 0.01	0.64 ± 0.27	0.29 ± 0.01	0.06 ± 0.01

5.2.2.1 The distribution of % Zinc with grain size

From Figure 5.54 all sites showed an increase in the metal concentration of zinc as the grain size decreased. This is in keeping with the fact that metal concentration increases with decreasing grain size [(Loring and Rantala, 1991; Windom *et al.*, 1989; Schropp *et al.*, 1990)] Statistical analysis complimented this finding. Figure 5.55 illustrates a scatter plot of zinc against grain size. A negative correlation is observed. At 95 % confidence level the r - value of –0.3178 falls outside the region of acceptance. The alternate hypothesis that states that there is a linear relationship between grain size and concentration was accepted (See appendix A5-1/2 for detailed working of findings).

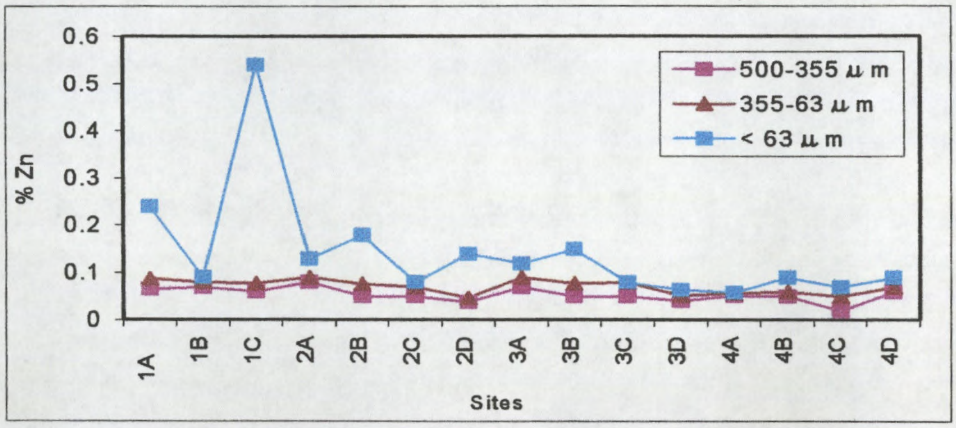


Figure 5.54 Distribution of % Zn with grain size

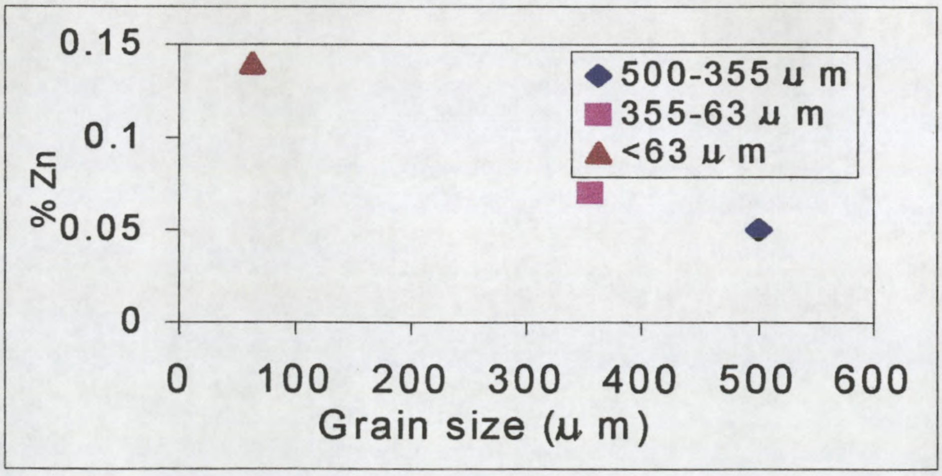


Figure 5.55 Plot of % Zn with different grain size

5.2.2.1 The distribution of % Fe with grain size

Figure 5.56 illustrates the distribution of iron with the various grain sizes. All sites besides sites 1A and 1B showed an increase in the metal concentration of iron as the grain size decreased. This is in keeping with the fact that metal concentration increases with decreasing grain size. Figure 5.57 shows a negative correlation between the level of iron and the different grain size. Statistical analysis proved the alternate hypothesis valid that states there is a linear relationship between grain size and concentration. At 95 % confidence level the r- value of –0.3689 falls outside the region of acceptance, hence accepting the alternate hypothesis. Appendix A5-3/4 shows a detailed working of the statistical analysis.

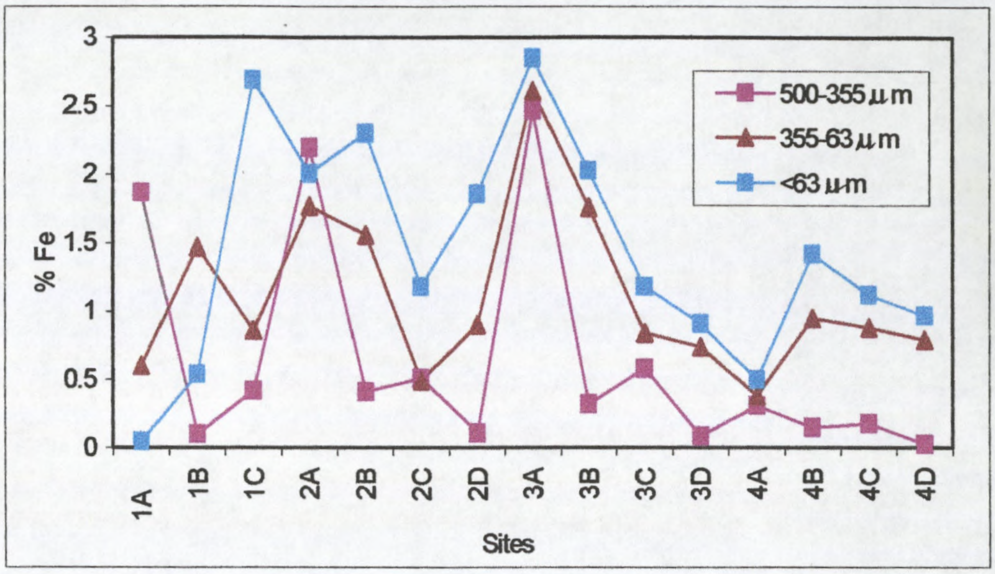


Figure 5. 56 Distribution of % Fe with grain fractions

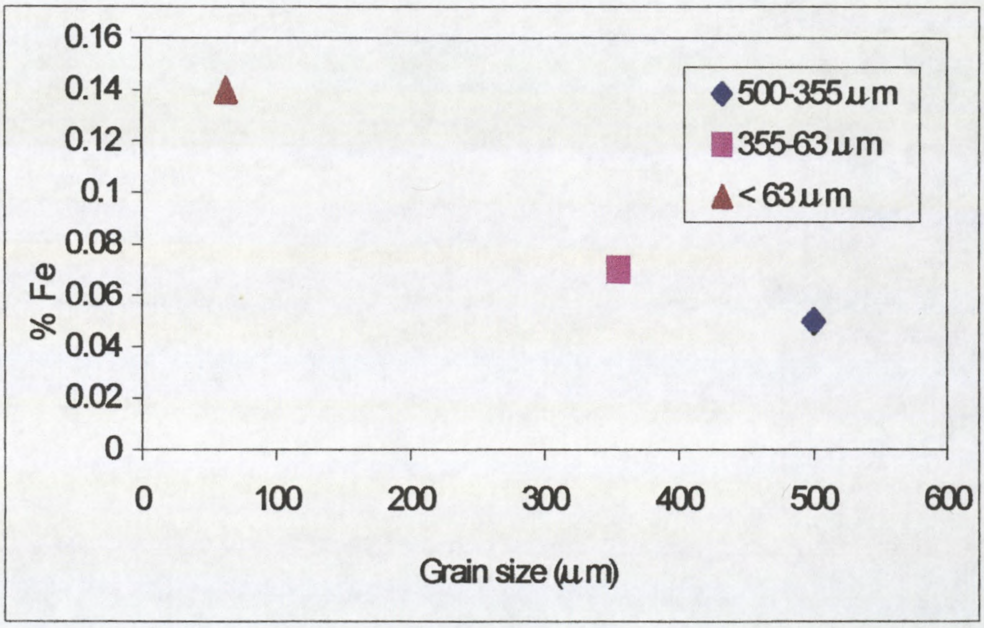


Figure 5.57 Plot of the mean % Fe with grain fractions

5.2.2.3 The distribution of % Ti with grain size

Figure 5.58 illustrates that for almost all analysis, titanium levels could only be determined in the grain fraction of 355-63 µm sieve and the < 63 µm pan. Negligible titanium was present in the very large grains. Again all sites showed that the finest grain size had the highest level of titanium. Statistical analysis (appendix 5-5/6) together with the scatter plot (Figure 5.59) confirms that concentration increases as grain size decreases.

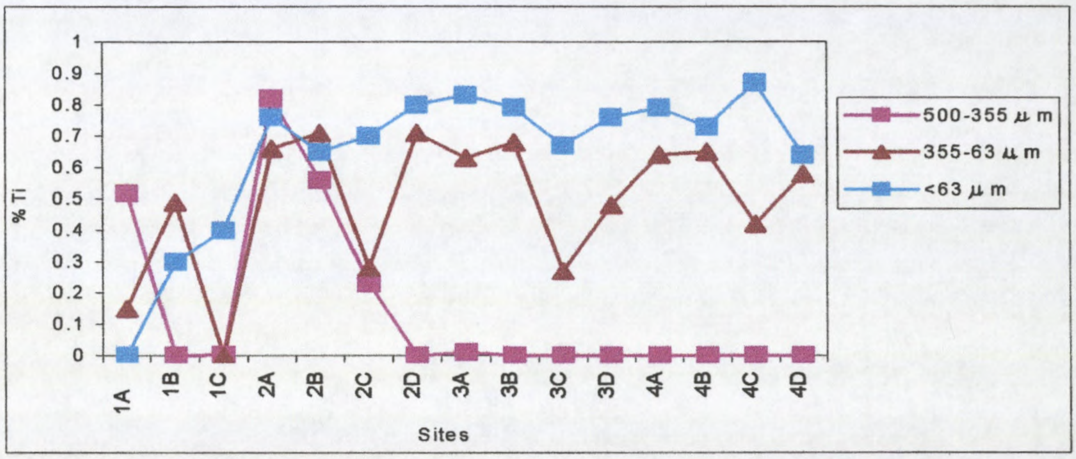


Figure 5.58 Graph of distribution of % Ti with grain fractions

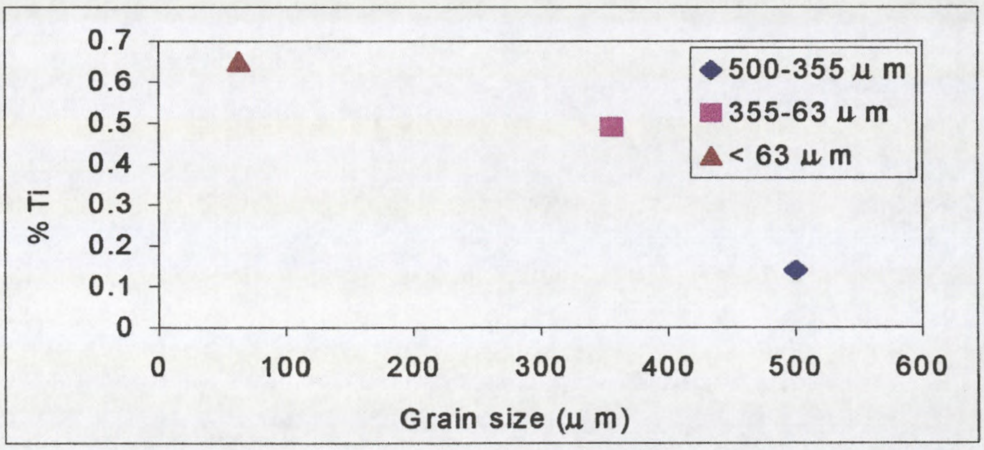


Figure 5.59 Plot of the mean % Ti with grain fractions

5.2.2.4 The distribution of % Al with grain size

Figure 5.60 illustrates that concentration of aluminium increases as grain size decreases. Figure 5.61 illustrates a scatter plot of the distribution of the % aluminium with grain size. A negative correlation is obtained which shows that with decreasing grain size the concentration of aluminium increases. Statistical analysis (appendix A5-7/8) compliments the above finding.

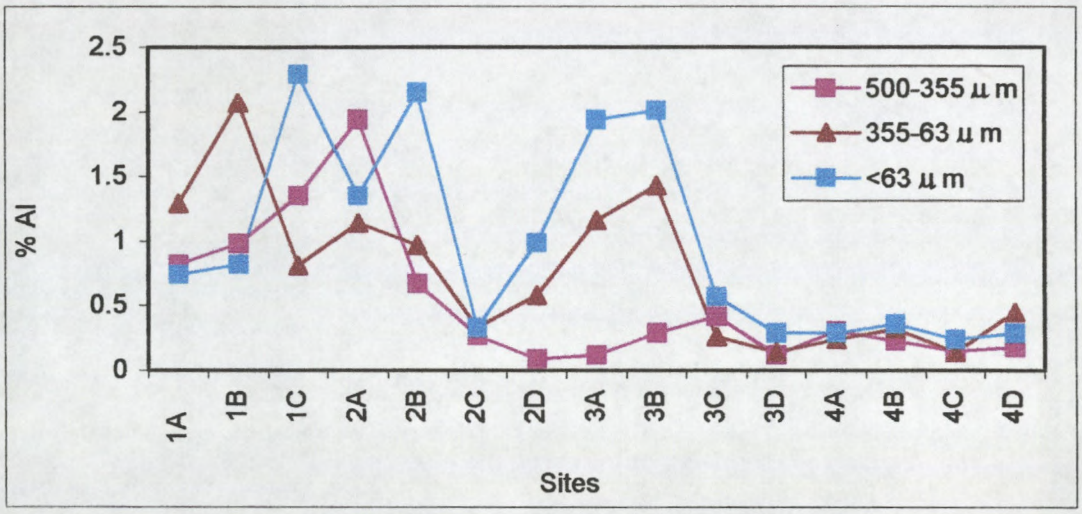


Figure 5.60 Graph of distribution of % Al with grain fractions

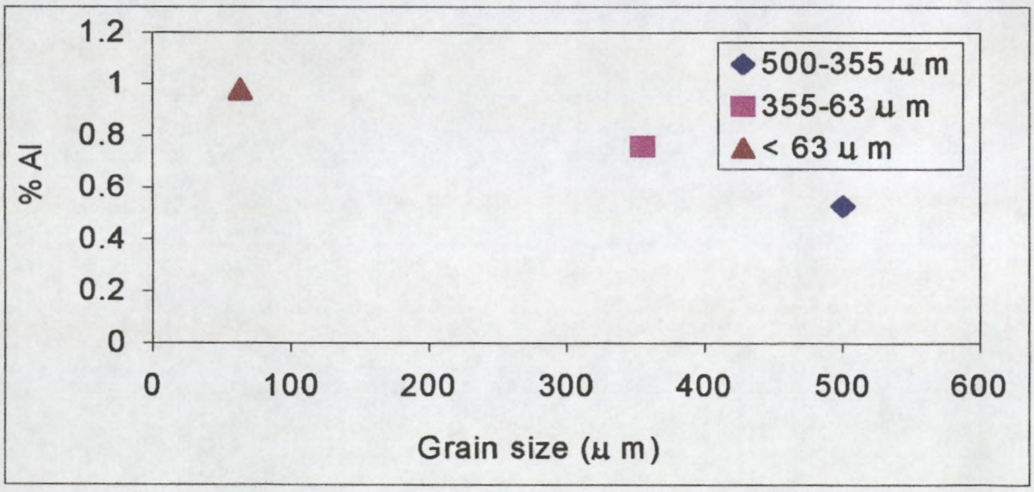


Figure 5.61 Plot of mean % Al with grain fractions

5.2.2.5 The distribution of % Ca with grain size

For the analysis of calcium in the various grain sizes the opposite trend was noticed. Here the concentration of calcium increased with increasing grain size. A higher level of calcium was found in the largest sediment particles. Seashells that were present in the sediment probably contributed to the high levels of calcium.

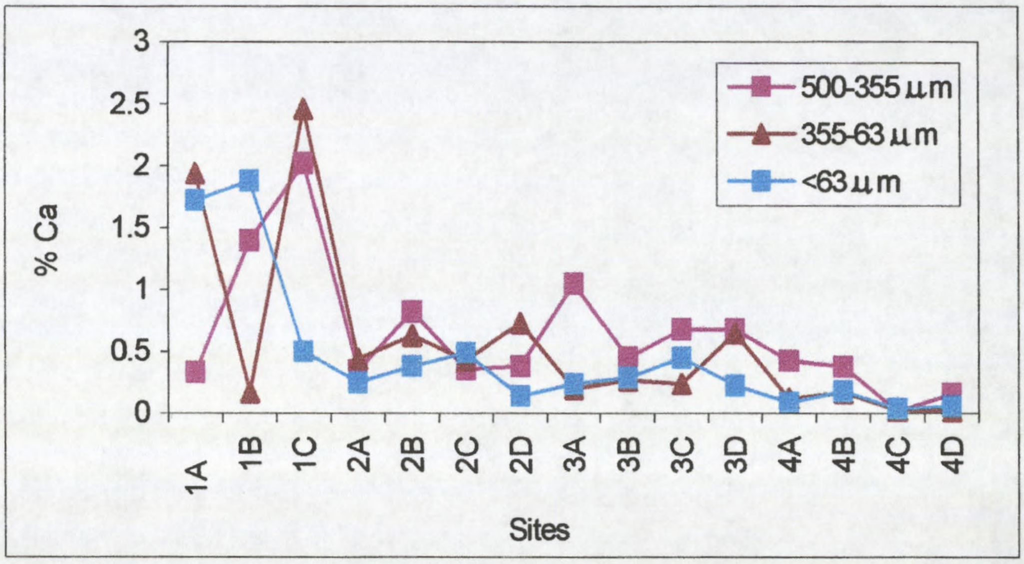


Figure 5.62 Graph of distribution of % Ca with size fraction

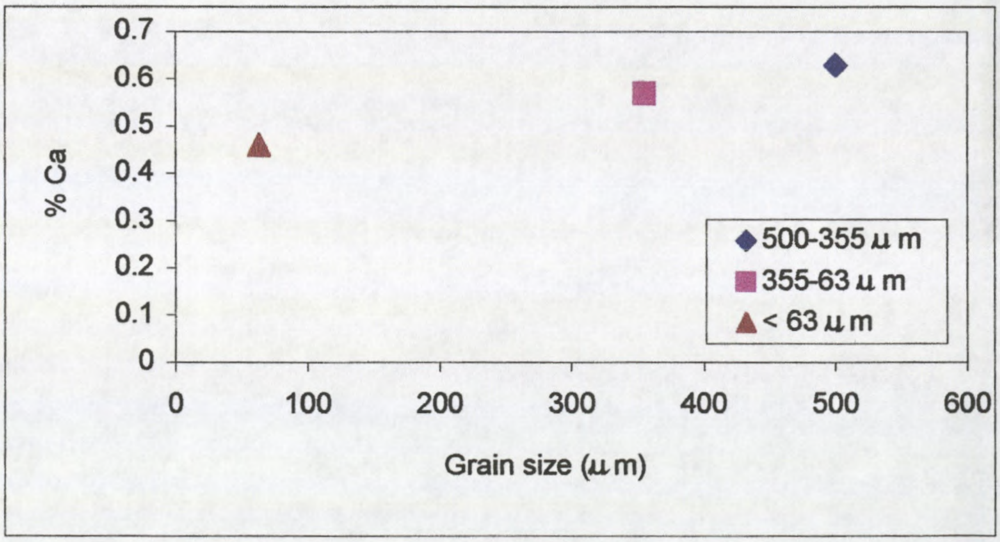


Figure 5.63 Plot of mean % Ca with grain fractions

CONCLUSION

In the size fractionated samples trace metal concentration generally increase with decreasing particle size. The accumulation of trace metals in bottom sediments occurs to a large extent by adsorption to sediment particle material, such as clays, minerals, hydrated iron oxides and planktonic organisms (Akhter and Al-Jowder, 1997). Therefore sediments may provide a reliable record of recent and long-term input of pollutants.

Chapter 6

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The main objectives of this research were: -

i) to determine concentrations of selected metals in the Durban Harbour water and compare them with those obtained for sediments

ii) to determine concentrations of metals in sediment fractions

iii) to infer the possible sources of metal pollutants

As there are no recent published reports of levels of metals in the Durban Harbour water and sediments; the results of this study are compared to a dated report compiled by Hennig (Hennig, 1985). However, it should be borne in mind that much has changed since Hennig's study. More industries have been developed over the years, marine traffic in and out of the harbour and recreational activities have increased substantially.

Analysis of the data indicates that the highest concentration of metal pollutants observed was at site 4 followed by sites 3, 2 and 1. It should be noted that site 4 is situated opposite the Umlatuzana canal and that the latter receives inputs from various sources. They are, inter alia, industries (textiles, cement, food industries, etc.) and runoff from agricultural and informal settlement areas.

In general, the levels of copper, nickel and lead in the harbour water are low with concentration being in the ppb levels. Likely sources of these metals are from effluents discharged from the surrounding industries and ships; flaking of paints and rust from ships. On the other hand, the concentrations of the same metals (copper, nickel and lead) are relatively higher in the sediment than in the water. Since sediments are regarded as sinks (Schropp, 1990) for metals, it is therefore reasonable to use sediments as a better long term indicator of pollution in the harbour.

Results for the different grain fractions of sediments in this study support the finding (Murray *et al.,* 1999) that the highest concentrations of heavy metals are found in the fraction with the smallest grain size.

Comparison of the results obtained for the Durban Harbour with those for other harbours or bays show that, overall, the level of heavy metals (copper, nickel, lead and zinc) pollution is generally less for Durban Harbour than for other harbours. The following table (Table 6.1) gives the values for sediment and in some cases for water for harbours and bays for which recent data are available.

Table 6.1 Comparison of concentrations of Cu, Ni, Pb and Zn in other harbour water and sediment samples with that of Durban Harbour

LOCATION	**WATER (ng.g^{-1})**			**SEDIMENT (mg.kg^{-1})**			
	Cu	Ni	Pb	Cu	Ni	Pb	Zn
Botany Bay [a] Australia	-	-	-	191-1113	-	599-4081	227-1472
Victoria Harbour [b] Hong Kong	12.82	0.26	-	>100	40	>50	150
Puck Bay [c] Poland	-	-	-	34 %	-	28 %	47 %
Durban Harbour	0.3-5.0	5.0-10.0	1.0-8.0	100-250	95-110	48-110	1-3 %

a – (Hayes *et al.*, 1998)

b – (Blackmore, 1998)

c – (Glasby and Szefer, 1998)

In terms of limits set by the environmental agencies (EPA and EPD) the concentrations of Cu, Ni , Pb and Zn in the sediments and in some instances water in the Durban Harbour are lower than those for Botany Bay (Australia), Victoria Harbour (Hong Kong) and Puck Bay (Poland). This is well illustrated by the values shown in Table 6.1.

In the light of the above comparisons, it is clear that this limited study assesses Durban Harbour as being less polluted than the other locations referred to in the comparisons. However, if the concentrations for Cu, Ni and Pb are compared with those from the 1985 study (Hennig, 1985) for Durban Harbour it is apparent that there is an increase in the levels of some of these metals. Thus, there should be constant monitoring for metals and other pollutants.

Recommendations for Future Work

1. A more comprehensive study to monitor the Durban Harbour for both inorganic and organic pollutants should be undertaken. In this study the scope for the monitoring of heavy metals was limited by the fact that the separation (from the salt-water matrix) and pre-concentration were both time- consuming and labour-intensive.

2. Use of analysis instruments with up-dated technology. One reason for recourse to the indirect method was the lack of GF-AAS with the requisite technology (platform atomiser and Zeeman background correction facility). If outright acquisition of such equipment is not possible, arrangements to lease such updated equipment should be urgently considered.

3. Future studies should include bioaccumulation as an indicator of metal pollutants. Uptake of heavy metals by bioaccumulators such as shellfish and seaweeds should be undertaken.

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APPENDIX A1

A significance test was applied to ascertain whether the difference between the means obtained by NaDDC/$CHCl_3$ or APDC/MIBK extraction methods were significant or not at the 95 % confidence level. The results below are discussed in section 3.2.5.

Table A1 Comparison of recoveries using NaDDC/$CHCl_3$ and APDC/MIBK as chelating agents

	NaDDC/$CHCl_3$			APDC/MIBK		
	Cu	Ni	Pb	Cu	Ni	Pb
1	95	70	84	74	74	75
2	96	73	79	73	70	70
3	100	84	79	75	69	77
4	96	76	80	74	68	78
5	98	81	88	76	70	65
6	100	83	96	75	71	69
7	99	75	99	73	73	70
8	97	79	89	78	75	61
9	94	78	90	79	68	71
10	90	80	92	80	65	76
Mean	97	78	88	76	70	71
SD	3.1	4.4	7.0	2.5	3.1	5.4

The null hypothesis adopted states that the means of the results given by the two methods of extraction for the determination of copper are equal.

Mean (x_1) (Cu) = 97 SD_1 (Cu) = 3.06

Mean (x_2) (Cu) = 76 SD_2 (Cu) = 2.50

$S^2 = (n_1-1)s_1^2 + (n_2-1)s_2^2 / (n_1+n_2-2)$
$= (9 \times 3.06^2) + (9 \times 2.5^2)/18$
$= 7.8$
$s = 2.79$
$t = (x_1-x_2)/S \sqrt{1/n_1+1/n_2}97-76)/2.76$
$= (97-76)/ \sqrt{1/10+1/10} = 3.35$

For 18 degrees of freedom $|t|$ $(P= 0.05)$ is 2.1 Since the experimental value is greater than 2.1 the difference between the two results is significant at 95 % confidence level and the null hypothesis is rejected.

ANALYSIS OF CERTIFIED REFERENCE MATERIALS

For checking the calibration of the instrument used for water samples certified reference materials for water (CRM 403) (Industrial Analytical (Pty) Ltd) were analysed by GF-AAS.

For the sediment samples certified reference material (SARM 51) (Industrial Analytical (Pty) Ltd). The analyses of Cu, Ni and Pb in CRM 403 and SARM 51 were done by GF-AAS whereas the analyses of Ti, Al and Ca in SARM 51 were done by ICP

Table 1 Certified results of Cu, Ni and Pb in sea water in CRM 403

METAL	CERTIFIED RESULT (ng/kg)	EXPERIMENTAL RESULT
Cu	247.8 ± 23.5	200.0
Ni	256.0 ± 21.2	210.5
Pb	24.24 ± 5.18	20.0

SEDIMENT

Table 2 Certified results of Fe, Al, Cu, Ni and Pb in sediments in CRM (SARM 51)

METAL	CERTIFIED RESULT	EXPERIMENTAL RESULT
Fe	18.36	16.5
Al (CRM 008-050)	22.24-27. 57	24.5
Cu (μg/g)	268	237
Ni (μg/g)	178	194
Pb %	0.52	0.47

APPENDIX A2-1

```
         A    0.003
         A    0.001
         A    0.001
MEAN     A    0.001
```

BLANK

```
ZERO     A    0.000

01       A    0.088
01       A    0.089
01       A    0.090
MEAN     A    0.089

02       A    0.085
02       A    0.085
02       A    0.084
MEAN     A    0.085
```

WITHOUT BACKGROUND CORRECTION

```
03       A    0.077    B
03       A    0.077    B
03       A    0.077    B
MEAN     A    0.077    B

04       A    0.082    B
04       A    0.081    B
04       A    0.082    B
MEAN     A    0.082    B
```

WITH BACKGROUND CORRECTION

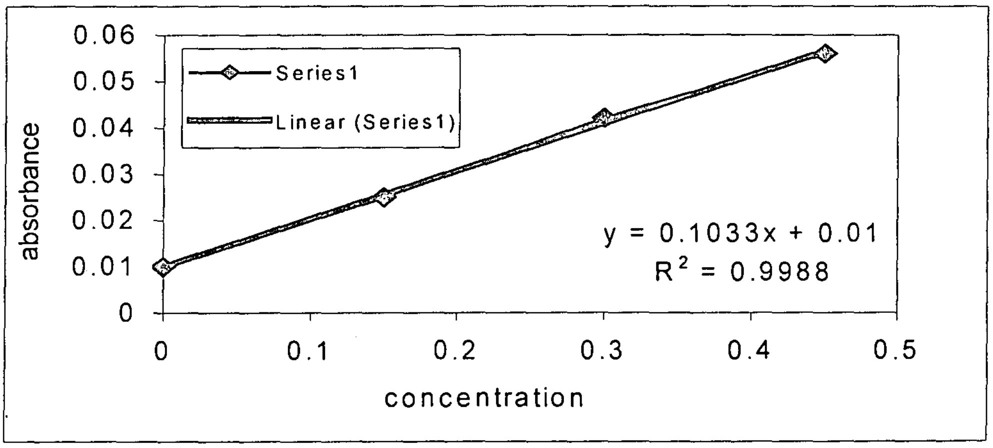
APPENDIX A2

Appendix 2 describes the preliminary work done to ascertain whether AAS could be used for the analysis of the samples collected for this project.

Harbour water was stripped of all metals by extracting thrice with NaDDC and $CHCl_3$ and discarding the organic layers. The final $CHCl_3$ layer was used as the blank. 2, 4 and 6 mL of 0.75 ppm of Cu were added to 500 mL of stripped seawater to give 0.002, 0.004 and 0.006 ppm of Cu respectively. All extractions were done in triplicate. All samples were extracted with 20 mL of buffer and 20 mL of $CHCl_3$. HNO_3 (2 mL) was added to the organic layer and thereafter evaporated on a sandbath at 100 ^{0}C to dryness. Samples were made up to 10 mL with 5% nitric acid to give a final concentration of 0.15, 0.30 and 0.45 ppm respectively. A triplicate set of seawater was treated in the same way. The samples were analysed by the GF-AAS and AA. Table A2.1 lists the absorbance values obtained by GF-AAS.

Table A2.1: Table of absorbance from the GFAAS

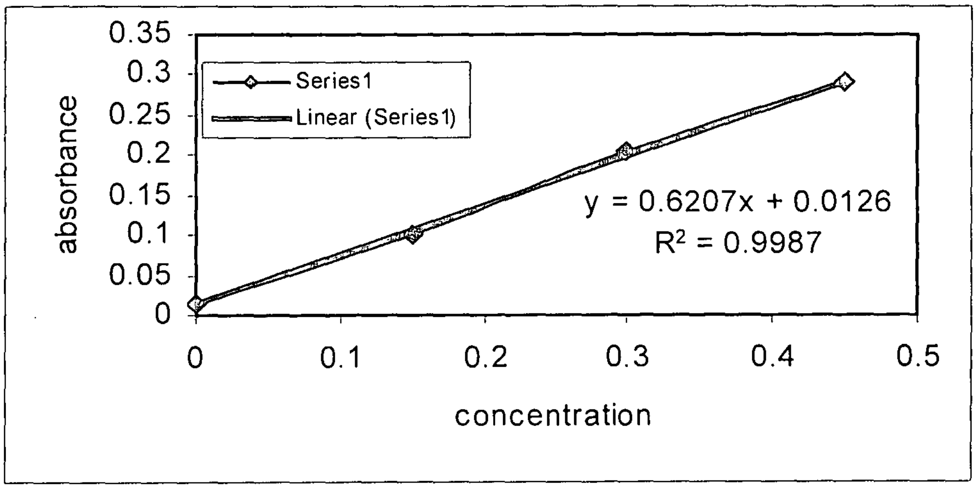
Sample	Absorbance			Average
Blank	0.012	0.015	0.013	**0.014**
Std 1	0.100	0.102	0.101	**0.101**
Std 2	0.205	0.202	0.205	**0.204**
Std 3	0.288	0.292	0.289	**0.290**
Seawater	0.150	0.146	0.144	**0.144**



Graph A 2.1 Graph of absorbance vs concentration for AAS

Table A 2.2 Table of absorbance for AAS

Sample	Absorbance			Average
Blank	0.012	0.010	0.008	**0.010**
Std 1	0.025	0.024	0.026	**0.025**
Std 2	0.042	0.040	0.043	**0.042**
Std 3	0.059	0.060	0.048	**0.056**
Seawater	0.012	0.009	0.010	**0.010**



Graph A 2.2 Graph of absorbance vs concentration for GFAAS

The above results indicate that GFAA is superior to AAS as the absorbance of the standards and the samples were higher for GFAAS than AAS. Although the R^2 values in both graphs in Figures A2.1 and A2.2 are almost the same the absorbances were higher for GFAAS.

Table A2- 3: **The graphite furnace parameters for Ni in water and sediments samples**

Step no.	Temp. (°C)	Time (s)	Gas flow	Gas type	Read command
1	75	5.0	3.0	NITROGEN	
2	90	40	3.0	NITROGEN	
3	900	10	3.0	NITROGEN	
4	900	1.5	0.0	NITROGEN	
5	2400	1.2	0.0	NITROGEN	*
6	2400	1.8	0.0	NITROGEN	*
7	2600	2.0	3.0	NITROGEN	

Table A2-4: **Sampler parameters for standards and samples for Ni in water and sediments**

SAMPLES AND STANDARDS			BLANK VOLUME(μL)
TYPE	LOCATION	VOLUME (μL)	
Blank	-	-	20
Std 1	51	5	15
Std 2	51	10	10
Std 3	51	15	5
Std 4	51	20	0
Std 5	51		
Samples	-	20	0
No of replicates = 3			

Table A2-5: The graphite furnace parameters for Pb in water and sediments samples

Step no.	Temp. (^{o}C)	Time (s)	Gas flow	Gas type	Read command
1	75	5.0	3.0	NITROGEN	
2	90	40	3.0	NITROGEN	
3	500	10	3.0	NITROGEN	
4	500	1.5	0.0	NITROGEN	
5	2300	2.0	0.0	NITROGEN	*
6	2300	2.0	0.0	NITROGEN	*
7	2500	2.0	3.0	NITROGEN	

Table A2-6: Sampler parameters for standards and samples for Pb in water and sediments

SAMPLES AND STANDARDS			BLANK
TYPE	LOCATION	VOLUME (μL)	VOLUME(μL)
Blank	-	-	20
Std 1	51	2 (8)	18 (12)
Std 2	51	5 (14)	15 (6)
Std 3	51	10 (16)	10 (4)
Std 4	51	15 (18)	5 (2)
Std 5	51	20	0
Samples	-	20	0
No of replicates = 3			

APPENDIX A3

```
        A    0.003    BLANK
        A    0.001
        A    0.001
MEAN    A    0.001

ZERO    A    0.000
        A    0.026
        A    0.026
        A    0.027
MEAN    A    0.026

STD 1   A    0.026

        A    0.060
        A    0.060
        A    0.059
MEAN    A    0.060

STD 2   A    0.060

        A    0.107
        A    0.106
        A    0.108
MEAN    A    0.107

STD 3   A    0.107

        A    0.142
        A    0.146
        A    0.144
MEAN    A    0.144

STD 4   A    0.144

        A    0.179
        A    0.180
        A    0.179
MEAN    A    0.180

STD 5   A    0.180

01      A    0.075    SITE 1
01      A    0.074
01      A    0.074
MEAN    A    0.074

02      A    0.070
02      A    0.072
02      A    0.071
MEAN    A    0.071
```

```
03      A    0.070    SITE 1
03      A    0.070
03      A    0.072
MEAN    A    0.071

04      A    0.085    SITE 2
04      A    0.085
04      A    0.085
MEAN    A    0.085

05      A    0.082
05      A    0.084
05      A    0.085
MEAN    A    0.084

06      A    0.096
06      A    0.098
06      A    0.098
MEAN    A    0.097

07      A    0.102    SITE 3
07      A    0.101
07      A    0.102
MEAN    A    0.102

08      A    0.099
08      A    0.100
08      A    0.099
MEAN    A    0.099

09      A    0.101
09      A    0.100
09      A    0.102
MEAN    A    0.101

10      A    0.104    SITE 4
10      A    0.105
10      A    0.104
MEAN    A    0.104

11      A    0.093
11      A    0.093
11      A    0.095
MEAN    A    0.094

12      A    0.097
12      A    0.098
12      A    0.098
MEAN    A    0.098
```

Typical example of calculation of confidence limits for water samples collected for the month of December 1998

MONTH	SITE	ABS	CONC (ppb)
Dec-98	1	0.074	1.927
		0.071	1.815
		0.071	1.815
		av	1.853
		sd	0.065
		error	**0.160**
	2	0.085	2.339
		0.084	2.302
		0.097	2.788
		av	2.320
		sd	0.271
		error	**0.670**
	3	0.102	2.975
		0.099	2.863
		0.101	2.938
		av	2.925
		sd	0.057
		error	**0.140**
	4	0.104	3.050
		0.094	2.676
		0.098	2.826
		av	2.851
		sd	0.188
		error	**0.470**

The 95 % confidence limits are given by

$$\mu = 1.853 \pm 4.3 \times 0.065 \sqrt{3}$$

$$= 1.853 \pm 0.160 \text{ ppb}$$

APPENDIX A3-3

Month	Site	Water	Sediments				
		Cu ppb	Cu ppm				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	2.47	86.03	6.10	7401.06	212.46	
	2	2.43	213.13	5.91	45426.40	518.26	
	3	2.39	369.40	5.73	136452.84	884.19	
	4	3.80	179.07	14.44	32066.57	680.36	
Aug-98	1	3.99	89.55	15.92	8019.77	357.26	
	2	4.10	229.03	16.84	52456.25	939.80	
	3	4.37	432.30	19.09	186881.00	1888.84	
	4	3.76	145.37	14.15	21132.88	546.80	
Sep-98	1	1.12	110.24	1.24	12152.99	122.97	
	2	1.15	268.90	1.32	72304.85	308.77	
	3	1.54	533.75	2.38	284893.53	823.05	
	4	1.21	533.67	1.47	284798.86	647.82	
Oct-98	1	3.01	163.83	9.07	26838.94	493.49	
	2	2.44	486.63	5.95	236810.23	1186.66	
	3	1.58	278.78	2.49	77715.90	439.87	
	4	2.11	175.49	4.45	30798.33	370.41	
Nov-98	1	1.09	120.67	1.18	14562.45	131.08	
	2	1.12	309.89	1.25	96033.45	346.97	
	3	1.19	510.92	1.41	261040.47	606.21	
	4	1.15	224.51	1.33	50403.63	258.87	
Dec-98	1	1.82	152.88	3.29	23371.45	277.49	
	2	2.34	44.02	5.47	1937.62	102.96	
	3	2.98	333.73	8.85	111372.58	992.93	
	4	3.05	218.29	9.30	47649.25	665.81	
Jan-99	1	2.71	25.87	7.36	669.09	70.19	
	2	3.05	188.98	9.30	35712.48	576.41	
	3	3.80	148.08	14.43	21928.49	562.51	
	4	3.20	115.08	10.24	13244.38	368.25	
Feb-99	1	2.03	95.29	4.13	9080.39	193.68	
	2	0.41	84.05	0.17	7063.98	34.17	
	3	0.61	127.43	0.37	16239.31	77.70	
	4	0.91	147.44	0.84	21737.93	134.85	
Mar-99	1	0.97	67.65	0.95	4576.19	65.79	
	2	1.89	16.79	3.56	281.81	31.65	
	3	1.04	211.05	1.09	44542.23	220.09	
	4	2.52	129.78	6.34	16841.62	326.72	
Apr-99	1	1.40	9.88	1.97	97.56	13.86	
	2	0.69	332.05	0.47	110253.89	227.94	
	3	2.38	137.80	5.68	18988.63	328.49	
	4	1.70	138.69	2.91	19236.06	236.46	
May-99	1	1.56	95.37	2.44	9095.63	149.02	
	2	1.29	113.28	1.66	12832.76	145.77	
	3	1.19	126.66	1.43	16043.19	151.34	
	4	1.42	142.78	2.03	20386.57	203.41	
Jun-99	1	0.89	59.16	0.80	3500.24	52.82	
	2	0.34	127.53	0.11	16264.28	43.19	
	3	1.39	21.83	1.92	476.42	30.24	
	4	2.43	18.09	5.92	327.37	44.01	
Jul-99	1	1.90	222.96	3.63	49711.43	424.58	
	2	2.44	119.75	5.96	14340.78	292.37	
	3	2.78	33.73	7.75	1138.03	93.89	
	4	4.83	138.87	23.37	19284.38	671.29	
	▯	108.00	9406.00	285.44	2626416.42	19574.04	0.005

Appendix A 3-4

Using the data from A 3-3

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{52*19574.04-108.00*9406.00}{\sqrt{[52*285.44-(108)^2]*[52*2626416.42-(9406.00)^2]}}$$

r = 0.005

Ho: $\rho = 0$ (There is no linear relationship between the concentration of copper in the water and the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = from table for critical values of r

n = 52

r-value is 0.005 which falls in region of acceptance. This implies that the null hypothesis is accepted ie there is no linear relationship between the concentration of copper in the sediment and the water.

APPENDIX A 3-5

Month	Site	Cu ppb	Temp(°C)				r-value
		X	Y	X^2	Y^2	XY	
Jul-98	1	2.47	19	6.10	361.00	46.92	
Aug-98	1	3.99	20	15.92	400.00	79.79	
Sep-98	1	1.12	20	1.24	400.00	22.31	
Oct-98	1	3.01	21	9.07	441.00	63.26	
Nov-98	1	1.09	22	1.18	484.00	23.90	
Dec-98	1	1.82	22	3.29	484.00	39.93	
Jan-99	1	2.71	26	7.36	676.00	70.55	
Feb-99	1	2.03	27	4.13	729.00	54.88	
Mar-99	1	0.97	25	0.95	625.00	24.32	
Apr-99	1	1.40	22	1.97	484.00	30.87	
May-99	1	1.56	22	2.44	484.00	34.38	
Jun-99	1	0.89	21	0.80	441.00	18.75	
Jul-99	1	1.90	19.5	3.63	380.25	37.13	
		24.97	286.5	58.08	6389.25	546.97	-0.119995
Jul-98	2	2.43	19	5.91	361.00	46.20	
Aug-98	2	4.10	20	16.84	400.00	82.07	
Sep-98	2	1.15	20	1.32	400.00	22.97	
Oct-98	2	2.44	21	5.95	441.00	51.21	
Nov-98	2	1.12	22	1.25	484.00	24.63	
Dec-98	2	2.34	22	5.47	484.00	51.46	
Jan-99	2	3.05	26	9.30	676.00	79.30	
Feb-99	2	0.41	27	0.17	729.00	10.98	
Mar-99	2	1.89	25	3.56	625.00	47.14	
Apr-99	2	0.69	22	0.47	484.00	15.10	
May-99	2	1.29	22	1.66	484.00	28.31	
Jun-99	2	0.34	21	0.11	441.00	7.11	
Jul-99	2	2.44	19.5	5.96	380.25	47.61	
		23.68	286.5	57.97	6389.25	514.08	-0.23039
Jul-98	3	2.39	19	5.73	361.00	45.48	
Aug-98	3	4.37	20	19.09	400.00	87.39	
Sep-98	3	1.54	20	2.38	400.00	30.84	
Oct-98	3	1.58	21	2.49	441.00	33.14	
Nov-98	3	1.19	22	1.41	484.00	26.10	
Dec-98	3	2.98	22	8.85	484.00	65.46	
Jan-99	3	3.80	26	14.43	676.00	98.76	
Feb-99	3	0.61	27	0.37	729.00	16.46	
Mar-99	3	1.04	25	1.09	625.00	26.07	
Apr-99	3	2.38	22	5.68	484.00	52.44	
May-99	3	1.19	22	1.43	484.00	26.29	
Jun-99	3	1.39	21	1.92	441.00	29.09	
Jul-99	3	2.78	19.5	7.75	380.25	54.27	
		27.24	286.5	72.61	6389.25	591.80	-0.251693
Jul-98	4	3.80	19	14.44	361.00	72.19	
Aug-98	4	3.76	20	14.15	400.00	75.23	
Sep-98	4	1.21	20	1.47	400.00	24.28	
Oct-98	4	2.11	21	4.45	441.00	44.32	
Nov-98	4	1.15	22	1.33	484.00	25.37	
Dec-98	4	3.05	22	9.30	484.00	67.10	
Jan-99	4	3.20	26	10.24	676.00	83.20	
Feb-99	4	0.91	27	0.84	729.00	24.70	
Mar-99	4	2.52	25	6.34	625.00	62.94	
Apr-99	4	1.70	22	2.91	484.00	37.51	
May-99	4	1.42	22	2.03	484.00	31.34	
Jun-99	4	2.43	21	5.92	441.00	51.08	
Jul-99	4	4.83	19.5	23.37	380.25	94.26	
		32.12	286.5	96.78	6389.25	693.51	-0.394479

APPENDIX A 3-6

Using data from A3-5 (Concentration of copper vs temperature)

SITE 1

$$r = \frac{n.\Sigma XY - \Sigma X.\Sigma Y}{\sqrt{[n.\Sigma X^2 - (\Sigma X)^2] * [n.\Sigma Y^2 - (\Sigma Y)^2]}}$$

$$r = \frac{13*546.97-24.97*286.50}{\sqrt{[13*58.08-(24.97)^2] * [13*6389.25-(286.50)^2]}}$$

r = -0.11199

Ho: ρ = 0 (There is no linear relationship between concentration of copper in water and temperature)

Ha: ρ ≠ 0 (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = -0.1199 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of copper and temperature of the water.

Using the above equation the r value at sites 2, 3 and 4 are –0.2304, -0.2517 and –0.3944 respectively.

APPENDIX A3-7							
Month	Site	Cu ppb	Conductivity				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	2.47	450	6.10	202500.00	1111.32	
Aug-98	1	3.99	430	15.92	184900.00	1715.43	
Sep-98	1	1.12	437	1.24	190969.00	487.47	
Oct-98	1	3.01	450	9.07	202500.00	1355.53	
Nov-98	1	1.09	380	1.18	144400.00	412.77	
Dec-98	1	1.82	380	3.29	144400.00	689.75	
Jan-99	1	2.71	431	7.36	185761.00	1169.44	
Feb-99	1	2.03	390	4.13	152100.00	792.68	
Mar-99	1	0.97	470	0.95	220900.00	457.13	
Apr-99	1	1.40	431	1.97	185761.00	604.75	
May-99	1	1.56	393	2.44	154449.00	614.06	
Jun-99	1	0.89	415	0.80	172225.00	370.54	
Jul-99	1	1.90	370	3.63	136900.00	704.59	
		24.97	5427	58.08	2277765.00	10485.45	0.175619
Jul-98	2	2.43	456	5.91	207936.00	1108.81	
Aug-98	2	4.10	431	16.84	185761.00	1768.54	
Sep-98	2	1.15	436	1.32	190096.00	500.66	
Oct-98	2	2.44	430	5.95	184900.00	1048.57	
Nov-98	2	1.12	403	1.25	162409.00	451.22	
Dec-98	2	2.34	403	5.47	162409.00	942.65	
Jan-99	2	3.05	434	9.30	188356.00	1323.76	
Feb-99	2	0.41	316	0.17	99856.00	128.46	
Mar-99	2	1.89	458	3.56	209764.00	863.57	
Apr-99	2	0.69	449	0.47	201601.00	308.23	
May-99	2	1.29	375	1.66	140625.00	482.54	
Jun-99	2	0.34	404	0.11	163216.00	136.82	
Jul-99	2	2.44	323	5.96	104329.00	788.57	
		23.68	5318	57.97	2201258.00	9852.40	0.270051
Jul-98	3	2.39	453	5.73	205209.00	1084.31	
Aug-98	3	4.37	453	19.09	205209.00	1979.29	
Sep-98	3	1.54	458	2.38	209764.00	706.23	
Oct-98	3	1.58	475	2.49	225625.00	749.49	
Nov-98	3	1.19	436	1.41	190096.00	517.31	
Dec-98	3	2.98	438	8.85	191844.00	1303.18	
Jan-99	3	3.80	425	14.43	180625.00	1614.43	
Feb-99	3	0.61	337	0.37	113569.00	205.49	
Mar-99	3	1.04	440	1.09	193600.00	458.85	
Apr-99	3	2.38	343	5.68	117649.00	817.65	
May-99	3	1.19	363	1.43	131769.00	433.73	
Jun-99	3	1.39	397	1.92	157609.00	550.03	
Jul-99	3	2.78	333	7.75	110889.00	926.81	
		27.24	5351	72.61	2233457.00	11346.80	0.192171
Jul-98	4	3.80	369	14.44	136161.00	1401.98	
Aug-98	4	3.76	431	14.15	185761.00	1621.16	
Sep-98	4	1.21	433	1.47	187489.00	525.62	
Oct-98	4	2.11	433	4.45	187489.00	913.91	
Nov-98	4	1.15	425	1.33	180625.00	490.06	
Dec-98	4	3.05	425	9.30	180625.00	1296.31	
Jan-99	4	3.20	438	10.24	191844.00	1401.53	
Feb-99	4	0.91	221	0.84	48841.00	202.13	
Mar-99	4	2.52	216	6.34	46656.00	543.79	
Apr-99	4	1.70	208	2.91	43264.00	354.62	
May-99	4	1.42	328	2.03	107584.00	467.28	
Jun-99	4	2.43	314	5.92	98596.00	763.73	
Jul-99	4	4.83	163	23.37	26569.00	787.94	
		32.12	4404	96.78	1621504.00	10770.07	-0.073169

APPENDIX A 3-8

Using data from A 3-7 (Concentration of copper vs conductivity)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*10485.45-24.97*5427}{\sqrt{[13*58.08-(24.97)^2]*[13*2277765.00-(5427)^2]}}$$

r = 0.1756

Ho: $\rho = 0$ (There is no linear relationship between concentration of copper in water and conductivity)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = 0.1756 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of copper and temperature of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.2700, 0.1921 and –0.0732 respectively.

APPENDIX A3-9

Month	Site	Cu ppb	pH				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	2.47	8.07	6.10	65.12	19.93	
Aug-98	1	3.99	8	15.92	64.00	31.91	
Sep-98	1	1.12	8.13	1.24	66.10	9.07	
Oct-98	1	3.01	7.91	9.07	62.57	23.83	
Nov-98	1	1.09	7.88	1.18	62.09	8.56	
Dec-98	1	1.82	7.88	3.29	62.09	14.30	
Jan-99	1	2.71	8.07	7.36	65.12	21.90	
Feb-99	1	2.03	7.92	4.13	62.73	16.10	
Mar-99	1	0.97	7.64	0.95	58.37	7.43	
Apr-99	1	1.40	7.89	1.97	62.25	11.07	
May-99	1	1.56	7.83	2.44	61.31	12.23	
Jun-99	1	0.89	7.97	0.80	63.52	7.12	
Jul-99	1	1.90	7.68	3.63	58.98	14.63	
		24.97	102.87	58.08	814.26	198.07	0.310806
Jul-98	2	2.43	8.06	5.91	64.96	19.60	
Aug-98	2	4.10	8.03	16.84	64.48	32.95	
Sep-98	2	1.15	8.05	1.32	64.80	9.24	
Oct-98	2	2.44	7.91	5.95	62.57	19.29	
Nov-98	2	1.12	7.84	1.25	61.47	8.78	
Dec-98	2	2.34	7.84	5.47	61.47	18.34	
Jan-99	2	3.05	8.09	9.30	65.45	24.68	
Feb-99	2	0.41	7.96	0.17	63.36	3.24	
Mar-99	2	1.89	7.82	3.56	61.15	14.74	
Apr-99	2	0.69	7.94	0.47	63.04	5.45	
May-99	2	1.29	7.84	1.66	61.47	10.09	
Jun-99	2	0.34	7.92	0.11	62.73	2.68	
Jul-99	2	2.44	7.78	5.96	60.53	18.99	
		23.68	103.08	57.97	817.47	188.07	0.244896
Jul-98	3	2.39	8.06	5.73	64.96	19.29	
Aug-98	3	4.37	8	19.09	64.00	34.95	
Sep-98	3	1.54	8.07	2.38	65.12	12.44	
Oct-98	3	1.58	7.89	2.49	62.25	12.45	
Nov-98	3	1.19	7.83	1.41	61.31	9.29	
Dec-98	3	2.98	7.83	8.85	61.31	23.30	
Jan-99	3	3.80	8.27	14.43	68.39	31.41	
Feb-99	3	0.61	7.94	0.37	63.04	4.84	
Mar-99	3	1.04	7.86	1.09	61.78	8.20	
Apr-99	3	2.38	7.97	5.68	63.52	19.00	
May-99	3	1.19	7.85	1.43	61.62	9.38	
Jun-99	3	1.39	7.95	1.92	63.20	11.01	
Jul-99	3	2.78	7.73	7.75	59.75	21.51	
		27.24	103.25	72.61	820.27	217.09	0.377752
Jul-98	4	3.80	8.08	14.44	65.29	30.70	
Aug-98	4	3.76	7.98	14.15	63.68	30.02	
Sep-98	4	1.21	8.06	1.47	64.96	9.78	
Oct-98	4	2.11	7.86	4.45	61.78	16.59	
Nov-98	4	1.15	7.84	1.33	61.47	9.04	
Dec-98	4	3.05	7.84	9.30	61.47	23.91	
Jan-99	4	3.20	8.22	10.24	67.57	26.30	
Feb-99	4	0.91	7.98	0.84	63.68	7.30	
Mar-99	4	2.52	7.9	6.34	62.41	19.89	
Apr-99	4	1.70	7.93	2.91	62.88	13.52	
May-99	4	1.42	7.85	2.03	61.62	11.18	
Jun-99	4	2.43	7.96	5.92	63.36	19.36	
Jul-99	4	4.83	7.75	23.37	60.06	37.46	
		32.12	103.25	96.78	820.23	255.06	-0.010204

APPENDIX A 3-10

Using data from A 3-9 (Concentration of copper vs pH)

SITE 1

$$r = \frac{n.\Sigma XY - \Sigma X.\Sigma Y}{\sqrt{[n.\Sigma X^2 - (\Sigma X)^2] * [n.\Sigma Y^2 - (\Sigma Y)^2]}}$$

$$r = \frac{13*198.07-24.97*102.87}{\sqrt{[13*58.08-(24.97)^2] * [13*814.26-(102.87)^2]}}$$

$r = 0.3108$

Ho: $\rho = 0$ (There is no linear relationship between concentration of copper in water and pH)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = 0.1756 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of copper and pH of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.2449, 0.3777 and –0.0102 respectively.

APPENDIX 3-11							
Month	Site	Water	Sediments				
		Ni ppb	Ni ppm				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	0.95	96.66	0.91	9343.88	92.21	
	2	1.15	90.50	1.33	8189.66	104.19	
	3	1.55	90.32	2.39	8157.13	139.63	
	4	5.49	84.02	30.18	7059.99	461.58	
Aug-98	1	1.61	93.14	2.60	8675.02	150.13	
	2	1.94	81.83	3.77	6695.92	158.81	
	3	2.34	136.10	5.45	18523.75	317.87	
	4	4.11	84.82	16.91	7194.59	348.77	
Sep-98	1	1.52	83.24	2.30	6929.12	126.12	
	2	3.22	107.12	10.37	11475.50	344.91	
	3	2.46	102.65	6.06	10537.69	252.74	
	4	4.17	109.88	17.36	12074.28	457.85	
Oct-98	1	0.89	88.28	0.80	7793.45	78.82	
	2	1.40	109.08	1.97	11899.38	153.05	
	3	3.95	93.58	15.63	8756.51	370.01	
	4	1.40	75.68	1.97	5727.20	106.18	
Nov-98	1	1.15	98.80	1.32	9762.12	113.42	
	2	1.40	109.38	1.97	11964.98	153.47	
	3	2.17	115.06	4.70	13238.87	249.49	
	4	5.74	93.30	32.95	8705.44	535.54	
Dec-98	1	1.66	73.96	2.75	5470.77	122.65	
	2	1.66	85.44	2.75	7300.13	141.67	
	3	1.40	112.06	1.97	12556.90	157.22	
	4	1.15	102.34	1.32	10472.62	117.48	
Jan-99	1	1.15	94.21	1.32	8875.21	108.15	
	2	2.42	94.13	5.87	8859.99	228.12	
	3	1.91	89.99	3.66	8099.05	172.18	
	4	2.68	84.85	7.17	7199.56	227.28	
Feb-99	1	4.21	63.07	17.72	3978.11	265.48	
	2	6.25	82.54	39.06	6812.33	515.86	
	3	7.78	77.56	60.54	6015.70	603.47	
	4	7.53	90.23	56.63	8141.30	679.02	
Mar-99	1	1.34	106.16	1.79	11269.94	142.18	
	2	0.69	70.11	0.48	4914.80	48.37	
	3	1.75	110.65	3.05	12243.51	193.10	
	4	7.10	80.98	50.44	6557.64	575.14	
Apr-99	1	1.40	68.15	1.97	4644.59	95.62	
	2	2.68	108.49	7.17	11770.56	290.60	
	3	3.70	99.21	13.68	9842.69	366.98	
	4	5.74	101.98	32.95	10399.55	585.33	
May-99	1	1.42	147.59	2.02	21781.43	209.64	
	2	1.01	103.37	1.03	10686.34	104.89	
	3	1.26	103.95	1.58	10805.85	130.78	
	4	2.07	104.28	4.28	10875.05	215.85	
Jun-99	1	1.91	92.78	3.66	8607.98	177.51	
	2	2.42	130.65	5.87	17070.27	316.63	
	3	5.23	117.90	27.35	13899.31	616.54	
	4	8.80	115.82	77.46	13414.03	1019.32	
Jul-99	1	1.84	80.61	3.39	6497.90	148.44	
	2	2.29	120.11	5.23	14426.65	274.81	
	3	2.29	87.90	5.23	7727.23	201.12	
	4	7.76	85.17	60.17	7254.70	660.67	
	Σ	151.12	5029.71	670.49	501176.16	14426.91	-0.10312

Appendix A 3-12

Using data from A 3-11([Ni] in water vs [Ni] in sediments)

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{52*14426.91-151.12*5029.71}{\sqrt{[52*670.49-(151.12)^2] * [52*501176.16-(5029.71)^2]}}$$

r = -0.1031

Ho: $\rho = 0$ (There is no linear relationship)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 52

r-value = -0.1031 falls in region of acceptance. This implies that the null hypothesis is accepted ie there no linear relationship between the concentration of Ni in the sediment and the water.

APPENDIX A 3-13							
Month	Site	Ni ppb	Temp(°C)				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	0.95	19	0.91	361.00	18.13	
Aug-98	1	1.61	20	2.60	400.00	32.24	
Sep-98	1	1.52	20	2.30	400.00	30.30	
Oct-98	1	0.89	21	0.80	441.00	18.75	
Nov-98	1	1.15	22	1.32	484.00	25.26	
Dec-98	1	1.66	22	2.75	484.00	36.48	
Jan-99	1	1.15	26	1.32	676.00	29.85	
Feb-99	1	4.21	27	17.72	729.00	113.65	
Mar-99	1	1.34	25	1.79	625.00	33.48	
Apr-99	1	1.40	22	1.97	484.00	30.87	
May-99	1	1.42	22	2.02	484.00	31.25	
Jun-99	1	1.91	21	3.66	441.00	40.18	
Jul-99	1	1.84	19.5	3.39	380.25	35.91	
		21.05	286.5	42.54	6389.25	476.33	0.489068
Jul-98	2	1.15	19	1.33	361.00	21.88	
Aug-98	2	1.94	20	3.77	400.00	38.82	
Sep-98	2	3.22	20	10.37	400.00	64.39	
Oct-98	2	1.40	21	1.97	441.00	29.46	
Nov-98	2	1.40	22	1.97	484.00	30.87	
Dec-98	2	1.66	22	2.75	484.00	36.48	
Jan-99	2	2.42	26	5.87	676.00	63.01	
Feb-99	2	6.25	27	39.06	729.00	168.75	
Mar-99	2	0.69	25	0.48	625.00	17.25	
Apr-99	2	2.68	22	7.17	484.00	58.93	
May-99	2	1.01	22	1.03	484.00	22.32	
Jun-99	2	2.42	21	5.87	441.00	50.89	
Jul-99	2	2.29	19.5	5.23	380.25	44.61	
		28.54	286.5	86.87	6389.25	647.66	0.435838
Jul-98	3	1.55	19	2.39	361.00	29.38	
Aug-98	3	2.34	20	5.45	400.00	46.71	
Sep-98	3	2.46	20	6.06	400.00	49.24	
Oct-98	3	3.95	21	15.63	441.00	83.04	
Nov-98	3	2.17	22	4.70	484.00	47.70	
Dec-98	3	1.40	22	1.97	484.00	30.87	
Jan-99	3	1.91	26	3.66	676.00	49.74	
Feb-99	3	7.78	27	60.54	729.00	210.08	
Mar-99	3	1.75	25	3.05	625.00	43.63	
Apr-99	3	3.70	22	13.68	484.00	81.38	
May-99	3	1.26	22	1.58	484.00	27.68	
Jun-99	3	5.23	21	27.35	441.00	109.82	
Jul-99	3	2.29	19.5	5.23	380.25	44.61	
		37.78	286.5	151.30	6389.25	853.88	0.379467
Jul-98	4	5.49	19	30.18	361.00	104.38	
Aug-98	4	4.11	20	16.91	400.00	82.24	
Sep-98	4	4.17	20	17.36	400.00	83.33	
Oct-98	4	1.40	21	1.97	441.00	29.46	
Nov-98	4	5.74	22	32.95	484.00	126.28	
Dec-98	4	1.15	22	1.32	484.00	25.26	
Jan-99	4	2.68	26	7.17	676.00	69.64	
Feb-99	4	7.53	27	56.63	729.00	203.19	
Mar-99	4	7.10	25	50.44	625.00	177.56	
Apr-99	4	5.74	22	32.95	484.00	126.28	
May-99	4	2.07	22	4.28	484.00	45.54	
Jun-99	4	8.80	21	77.46	441.00	184.82	
Jul-99	4	7.76	19.5	60.17	380.25	151.26	
		63.74	286.5	389.78	6389.25	1409.22	0.059853

Appendix A3-14

Using data from A3-13 (Concentration of nickel vs temperature)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*476.33-21.05*286.50}{\sqrt{[13*42.54-(21.05)^2] * [13*6389.25-(286.50)^2]}}$$

r = 0.4981

Ho: $\rho = 0$ (There is no linear relationship between concentration of nickel in water and temperature)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = 0.4981 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of Ni and temperature of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.4358, 0.3795 and 0.0598 respectively.

APPENDIX A 3-15							
Month	Site	Ni ppb	Conductivity				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	0.95	450	0.91	202500.00	429.28	
Aug-98	1	1.61	430	2.60	184900.00	693.09	
Sep-98	1	1.52	437	2.30	190969.00	662.12	
Oct-98	1	0.89	450	0.80	202500.00	401.79	
Nov-98	1	1.15	380	1.32	144400.00	436.22	
Dec-98	1	1.66	380	2.75	144400.00	630.10	
Jan-99	1	1.15	431	1.32	185761.00	494.77	
Feb-99	1	4.21	390	17.72	152100.00	1641.58	
Mar-99	1	1.34	470	1.79	220900.00	629.46	
Apr-99	1	1.40	431	1.97	185761.00	604.72	
May-99	1	1.42	393	2.02	154449.00	558.24	
Jun-99	1	1.91	415	3.66	172225.00	794.01	
Jul-99	1	1.84	370	3.39	136900.00	681.36	
		21.05	5427	42.54	2277765.00	8656.74	-0.413836
Jul-98	2	1.15	456	1.33	207936.00	525.00	
Aug-98	2	1.94	431	3.77	185761.00	836.48	
Sep-98	2	3.22	436	10.37	190096.00	1403.79	
Oct-98	2	1.40	430	1.97	184900.00	603.32	
Nov-98	2	1.40	403	1.97	162409.00	565.43	
Dec-98	2	1.66	403	2.75	162409.00	668.24	
Jan-99	2	2.42	434	5.87	188356.00	1051.79	
Feb-99	2	6.25	316	39.06	99856.00	1975.00	
Mar-99	2	0.69	458	0.48	209764.00	315.99	
Apr-99	2	2.68	449	7.17	201601.00	1202.68	
May-99	2	1.01	375	1.03	140625.00	380.48	
Jun-99	2	2.42	404	5.87	163216.00	979.08	
Jul-99	2	2.29	323	5.23	104329.00	739.01	
		28.54	5318	86.87	2201258.00	11246.28	-0.544954
Jul-98	3	1.55	453	2.39	205209.00	700.36	
Aug-98	3	2.34	453	5.45	205209.00	1057.99	
Sep-98	3	2.46	458	6.06	209764.00	1127.65	
Oct-98	3	3.95	475	15.63	225625.00	1878.19	
Nov-98	3	2.17	436	4.70	190096.00	945.41	
Dec-98	3	1.40	438	1.97	191844.00	614.54	
Jan-99	3	1.91	425	3.66	180625.00	813.14	
Feb-99	3	7.78	337	60.54	113569.00	2622.07	
Mar-99	3	1.75	440	3.05	193600.00	767.86	
Apr-99	3	3.70	343	13.68	117649.00	1268.75	
May-99	3	1.26	363	1.58	131769.00	456.70	
Jun-99	3	5.23	397	27.35	157609.00	2076.15	
Jul-99	3	2.29	333	5.23	110889.00	761.89	
		37.78	5351	151.30	2233457.00	15090.69	-0.407387
Jul-98	4	5.49	369	30.18	136161.00	2027.07	
Aug-98	4	4.11	431	16.91	185761.00	1772.20	
Sep-98	4	4.17	433	17.36	187489.00	1804.17	
Oct-98	4	1.40	433	1.97	187489.00	607.53	
Nov-98	4	5.74	425	32.95	180625.00	2439.41	
Dec-98	4	1.15	425	1.32	180625.00	487.88	
Jan-99	4	2.68	438	7.17	191844.00	1173.21	
Feb-99	4	7.53	221	56.63	48841.00	1663.14	
Mar-99	4	7.10	216	50.44	46656.00	1534.09	
Apr-99	4	5.74	208	32.95	43264.00	1193.88	
May-99	4	2.07	328	4.28	107584.00	678.90	
Jun-99	4	8.80	314	77.46	98596.00	2763.52	
Jul-99	4	7.76	163	60.17	26569.00	1264.34	
		63.74	4404	389.78	1621504.00	19409.34	-0.689693

Appendix A 3-16

Using data from A 3-15 (Concentration of nickel vs conductivity)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2]*[n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*8656.74-21.05*5427}{\sqrt{[13*42.54-(21.05)^2] * [13*2277765.00-(5427)^2]}}$$

r = -0.4138

Ho: $\rho = 0$ (There is no linear relationship between concentration of nickel in water and conductivity)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = -0.4138 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of nickel and conductivity of the water.

Using the above equation the r value at sites 2, 3 and 4 are -0.5449, -0.4074 and –0.6897 respectively.

APPENDIX A 3-17							
Month	Site	Ni ppb	pH				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	0.95	8.07	0.91	65.12	7.70	
Aug-98	1	1.61	8	2.60	64.00	12.89	
Sep-98	1	1.52	8.13	2.30	66.10	12.32	
Oct-98	1	0.89	7.91	0.80	62.57	7.06	
Nov-98	1	1.15	7.88	1.32	62.09	9.05	
Dec-98	1	1.66	7.88	2.75	62.09	13.07	
Jan-99	1	1.15	8.07	1.32	65.12	9.26	
Feb-99	1	4.21	7.92	17.72	62.73	33.34	
Mar-99	1	1.34	7.64	1.79	58.37	10.23	
Apr-99	1	1.40	7.89	1.97	62.25	11.07	
May-99	1	1.42	7.83	2.02	61.31	11.12	
Jun-99	1	1.91	7.97	3.66	63.52	15.25	
Jul-99	1	1.84	7.68	3.39	58.98	14.14	
		21.05	102.87	42.54	814.26	166.50	-0.072404
Jul-98	2	1.15	8.06	1.33	64.96	9.28	
Aug-98	2	1.94	8.03	3.77	64.48	15.58	
Sep-98	2	3.22	8.05	10.37	64.80	25.92	
Oct-98	2	1.40	7.91	1.97	62.57	11.10	
Nov-98	2	1.40	7.84	1.97	61.47	11.00	
Dec-98	2	1.66	7.84	2.75	61.47	13.00	
Jan-99	2	2.42	8.09	5.87	65.45	19.61	
Feb-99	2	6.25	7.96	39.06	63.36	49.75	
Mar-99	2	0.69	7.82	0.48	61.15	5.40	
Apr-99	2	2.68	7.94	7.17	63.04	21.27	
May-99	2	1.01	7.84	1.03	61.47	7.95	
Jun-99	2	2.42	7.92	5.87	62.73	19.19	
Jul-99	2	2.29	7.78	5.23	60.53	17.80	
		28.54	103.08	86.87	817.47	226.85	0.293973
Jul-98	3	1.55	8.06	2.39	64.96	12.46	
Aug-98	3	2.34	8	5.45	64.00	18.68	
Sep-98	3	2.46	8.07	6.06	65.12	19.87	
Oct-98	3	3.95	7.89	15.63	62.25	31.20	
Nov-98	3	2.17	7.83	4.70	61.31	16.98	
Dec-98	3	1.40	7.83	1.97	61.31	10.99	
Jan-99	3	1.91	8.27	3.66	68.39	15.82	
Feb-99	3	7.78	7.94	60.54	63.04	61.78	
Mar-99	3	1.75	7.86	3.05	61.78	13.72	
Apr-99	3	3.70	7.97	13.68	63.52	29.48	
May-99	3	1.26	7.85	1.58	61.62	9.88	
Jun-99	3	5.23	7.95	27.35	63.20	41.58	
Jul-99	3	2.29	7.73	5.23	59.75	17.69	
		37.78	103.25	151.30	820.27	300.11	0.009488
Jul-98	4	5.49	8.08	30.18	65.29	44.39	
Aug-98	4	4.11	7.98	16.91	63.68	32.81	
Sep-98	4	4.17	8.06	17.36	64.96	33.58	
Oct-98	4	1.40	7.86	1.97	61.78	11.03	
Nov-98	4	5.74	7.84	32.95	61.47	45.00	
Dec-98	4	1.15	7.84	1.32	61.47	9.00	
Jan-99	4	2.68	8.22	7.17	67.57	22.02	
Feb-99	4	7.53	7.98	56.63	63.68	60.05	
Mar-99	4	7.10	7.9	50.44	62.41	56.11	
Apr-99	4	5.74	7.93	32.95	62.88	45.52	
May-99	4	2.07	7.85	4.28	61.62	16.25	
Jun-99	4	8.80	7.96	77.46	63.36	70.06	
Jul-99	4	7.76	7.75	60.17	60.06	60.11	
		63.74	103.25	389.78	820.23	505.93	-0.075781

Appendix A 3-18

Using data from A 3-17 (Concentration of nickel vs pH)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*166.50-21.05*102.87}{\sqrt{[13*42.54-(21.05)^2]*[13*814.26-(102.87)^2]}}$$

r = -0.0724

Ho: $\rho = 0$ (There is no linear relationship between concentration of nickel in water and pH)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = -0.0724 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of nickel and pH of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.2939, 0.009488 and –0.07578 respectively.

APPENDIX A3-19							
Month	Site	Water	Sediments				
		Pb ppb	Pb ppm				
		X	Y	X^2	Y^2	XY	0.348781
Jul-98	1	3.35	79.12	11.24	6259.41	265.22	
	2	2.78	202.47	7.75	40994.00	563.69	
	3	2.33	123.13	5.43	15162.14	286.85	
	4	2.78	99.49	7.75	9898.35	276.99	
Aug-98	1	3.92	30.86	15.37	952.04	120.97	
	2	3.13	169.56	9.77	28750.50	529.87	
	3	3.69	208.40	13.64	43429.55	769.65	
	4	4.38	131.82	19.14	17376.56	576.71	
Sep-98	1	10.32	141.69	106.50	20074.88	1462.17	
	2	5.38	245.36	28.92	60203.03	1319.54	
	3	8.87	206.25	78.61	42538.45	1828.66	
	4	3.05	213.93	9.32	45766.31	652.99	
Oct-98	1	8.17	92.58	66.80	8571.69	756.69	
	2	6.41	140.43	41.09	19721.83	900.22	
	3	8.97	158.10	80.54	24995.16	1418.83	
	4	1.76	69.77	3.11	4867.26	122.98	
Nov-98	1	6.09	21.77	37.08	474.02	132.59	
	2	6.25	200.43	39.06	40173.41	1252.71	
	3	6.57	141.82	43.17	20114.23	931.86	
	4	3.85	120.55	14.79	14531.31	463.64	
Dec-98	1	1.14	34.09	1.31	1162.34	38.95	
	2	1.41	47.79	1.99	2283.83	67.44	
	3	1.28	125.85	1.63	15837.17	160.69	
	4	1.41	116.62	1.99	13599.06	164.58	
Jan-99	1	3.83	17.79	14.67	316.62	68.16	
	2	3.56	93.55	12.69	8751.05	333.20	
	3	4.64	84.94	21.50	7215.32	393.89	
	4	2.89	56.36	8.35	3176.20	162.86	
Feb-99	1	8.53	45.70	72.85	2088.18	390.02	
	2	4.91	51.92	24.07	2695.58	254.71	
	3	2.76	54.87	7.59	3010.45	151.18	
	4	1.68	92.66	2.82	8586.22	155.68	
Mar-99	1	1.27	33.43	1.62	1117.82	42.53	
	2	1.16	58.75	1.35	3451.94	68.24	
	3	1.71	110.88	2.94	12294.44	190.12	
	4	1.71	56.93	2.94	3241.26	97.62	
Apr-99	1	0.50	59.97	0.25	3596.53	29.85	
	2	1.27	133.73	1.62	17883.37	170.12	
	3	0.94	53.55	0.88	2867.78	50.35	
	4	1.71	87.84	2.94	7715.17	150.60	
May-99	1	1.71	20.36	2.94	414.69	34.92	
	2	1.83	18.60	3.33	345.95	33.95	
	3	1.38	47.62	1.91	2267.60	65.85	
	4	2.38	53.74	5.66	2888.30	127.82	
Jun-99	1	1.16	33.81	1.35	1143.07	39.27	
	2	1.16	45.76	1.35	2093.80	53.15	
	3	1.71	81.01	2.94	6562.70	138.90	
	4	1.83	54.69	3.33	2990.89	99.82	
Jul-99	1	1.71	22.18	2.94	491.78	38.02	
	2	2.71	33.31	7.35	1109.31	90.27	
	3	5.70	36.88	32.45	1359.82	210.08	
	4	7.69	50.43	59.11	2542.84	387.68	
	Σ	181.36	4713.12	949.73	609955.23	19093.34	

Appendix A 3-20

Using data from A 3-19 [Pb] in water vs [Pb] in sediment

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{52*19093.34-181.36*4713.12}{\sqrt{[52*949.73-(181.36)^2] * [52*609955.23-(4713.12)^2]}}$$

$r = 0.3488$

Ho: $\rho = 0$ (There is no linear relationship)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 52

r-value = 0.3488 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of Pb in the sediment and the water.

APPENDIX A 3- 21

Month	Site	Pb ppb	Temp(°C)				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	3.35	19	11.24	361.00	63.69	
Aug-98	1	3.92	20	15.37	400.00	78.41	
Sep-98	1	10.32	20	106.50	400.00	206.40	
Oct-98	1	8.17	21	66.80	441.00	171.63	
Nov-98	1	6.09	22	37.08	484.00	133.97	
Dec-98	1	1.14	22	1.31	484.00	25.13	
Jan-99	1	3.83	26	14.67	676.00	99.60	
Feb-99	1	8.53	27	72.85	729.00	230.44	
Mar-99	1	1.27	25	1.62	625.00	31.80	
Apr-99	1	0.50	22	0.25	484.00	10.95	
May-99	1	1.71	22	2.94	484.00	37.72	
Jun-99	1	1.16	21	1.35	441.00	24.39	
Jul-99	1	1.71	19.5	2.94	380.25	33.43	
		51.72	286.5	334.91	6389.25	1147.58	0.077783
Jul-98	2	2.78	19	7.75	361.00	52.90	
Aug-98	2	3.13	20	9.77	400.00	62.50	
Sep-98	2	5.38	20	28.92	400.00	107.56	
Oct-98	2	6.41	21	41.09	441.00	134.62	
Nov-98	2	6.25	22	39.06	484.00	137.50	
Dec-98	2	1.41	22	1.99	484.00	31.05	
Jan-99	2	3.56	26	12.69	676.00	92.61	
Feb-99	2	4.91	27	24.07	729.00	132.46	
Mar-99	2	1.16	25	1.35	625.00	29.04	
Apr-99	2	1.27	22	1.62	484.00	27.99	
May-99	2	1.83	22	3.33	484.00	40.15	
Jun-99	2	1.16	21	1.35	441.00	24.39	
Jul-99	2	2.71	19.5	7.35	380.25	52.85	
		41.96	286.5	180.33	6389.25	925.61	0.016211
Jul-98	3	2.33	19	5.43	361.00	44.26	
Aug-98	3	3.69	20	13.64	400.00	73.86	
Sep-98	3	8.87	20	78.61	400.00	177.33	
Oct-98	3	8.97	21	80.54	441.00	188.46	
Nov-98	3	6.57	22	43.17	484.00	144.55	
Dec-98	3	1.28	22	1.63	484.00	28.09	
Jan-99	3	4.64	26	21.50	676.00	120.56	
Feb-99	3	2.76	27	7.59	729.00	74.40	
Mar-99	3	1.71	25	2.94	625.00	42.87	
Apr-99	3	0.94	22	0.88	484.00	20.69	
May-99	3	1.38	22	1.91	484.00	30.42	
Jun-99	3	1.71	21	2.94	441.00	36.01	
Jul-99	3	5.70	19.5	32.45	380.25	111.09	
		50.55	286.5	293.24	6389.25	1092.58	-0.25229
Jul-98	4	2.78	19	7.75	361.00	52.90	
Aug-98	4	4.38	20	19.14	400.00	87.50	
Sep-98	4	3.05	20	9.32	400.00	61.05	
Oct-98	4	1.76	21	3.11	441.00	37.02	
Nov-98	4	3.85	22	14.79	484.00	84.62	
Dec-98	4	1.41	22	1.99	484.00	31.05	
Jan-99	4	2.89	26	8.35	676.00	75.13	
Feb-99	4	1.68	27	2.82	729.00	45.36	
Mar-99	4	1.71	25	2.94	625.00	42.87	
Apr-99	4	1.71	22	2.94	484.00	37.72	
May-99	4	2.38	22	5.66	484.00	52.32	
Jun-99	4	1.83	21	3.33	441.00	38.33	
Jul-99	4	7.69	19.5	59.11	380.25	149.92	
		37.12	286.5	141.25	6389.25	795.78	-0.43385

Appendix A 3-22

Using data from A 3-21 (Concentration of lead vs temperature)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*1147.58-51.72*286.50}{\sqrt{[13*334.91-(51.72)^2]*[13*6389.25-(286.50)^2]}}$$

$r = 0.0777$

Ho: $\rho = 0$ (There is no linear relationship between concentration of lead in water and temperature)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = 0.4981 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of lead and temperature of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.01621, -0.2523 and -0.4334 respectively.

APPENDIX A 3-23

Month	Site	Pb ppb	Conductivity(us)				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	3.35	450	11.24	202500.00	1508.52	
Aug-98	1	3.92	430	15.37	184900.00	1685.80	
Sep-98	1	10.32	437	106.50	190969.00	4509.74	
Oct-98	1	8.17	450	66.80	202500.00	3677.88	
Nov-98	1	6.09	380	37.08	144400.00	2314.10	
Dec-98	1	1.14	380	1.31	144400.00	434.14	
Jan-99	1	3.83	431	14.67	185761.00	1651.01	
Feb-99	1	8.53	390	72.85	152100.00	3328.63	
Mar-99	1	1.27	470	1.62	220900.00	597.90	
Apr-99	1	0.50	431	0.25	185761.00	214.55	
May-99	1	1.71	393	2.94	154449.00	673.84	
Jun-99	1	1.16	415	1.35	172225.00	482.02	
Jul-99	1	1.71	370	2.94	136900.00	634.40	
		51.72	5427	334.91	2277765.00	21712.53	0.09541
Jul-98	2	2.78	456	7.75	207936.00	1269.55	
Aug-98	2	3.13	431	9.77	185761.00	1346.88	
Sep-98	2	5.38	436	28.92	190096.00	2344.77	
Oct-98	2	6.41	430	41.09	184900.00	2756.41	
Nov-98	2	6.25	403	39.06	162409.00	2518.75	
Dec-98	2	1.41	403	1.99	162409.00	568.75	
Jan-99	2	3.56	434	12.69	188356.00	1545.83	
Feb-99	2	4.91	316	24.07	99856.00	1550.27	
Mar-99	2	1.16	458	1.35	209764.00	531.97	
Apr-99	2	1.27	449	1.62	201601.00	571.18	
May-99	2	1.83	375	3.33	140625.00	684.46	
Jun-99	2	1.16	404	1.35	163216.00	469.25	
Jul-99	2	2.71	323	7.35	104329.00	875.39	
		41.96	5318	180.33	2201258.00	17033.45	-0.120901
Jul-98	3	2.33	453	5.43	205209.00	1055.28	
Aug-98	3	3.69	453	13.64	205209.00	1673.01	
Sep-98	3	8.87	458	78.61	209764.00	4060.76	
Oct-98	3	8.97	475	80.54	225625.00	4262.82	
Nov-98	3	6.57	436	43.17	190096.00	2864.74	
Dec-98	3	1.28	438	1.63	191844.00	559.27	
Jan-99	3	4.64	425	21.50	180625.00	1970.77	
Feb-99	3	2.76	337	7.59	113569.00	928.56	
Mar-99	3	1.71	440	2.94	193600.00	754.42	
Apr-99	3	0.94	343	0.88	117649.00	322.51	
May-99	3	1.38	363	1.91	131769.00	501.94	
Jun-99	3	1.71	397	2.94	157609.00	680.70	
Jul-99	3	5.70	333	32.45	110889.00	1897.07	
		50.55	5351	293.24	2233457.00	21531.85	0.41874
Jul-98	4	2.78	369	7.75	136161.00	1027.33	
Aug-98	4	4.38	431	19.14	185761.00	1885.63	
Sep-98	4	3.05	433	9.32	187489.00	1321.66	
Oct-98	4	1.76	433	3.11	187489.00	763.30	
Nov-98	4	3.85	425	14.79	180625.00	1634.62	
Dec-98	4	1.41	425	1.99	180625.00	599.80	
Jan-99	4	2.89	438	8.35	191844.00	1265.73	
Feb-99	4	1.68	221	2.82	48841.00	371.30	
Mar-99	4	1.71	216	2.94	46656.00	370.35	
Apr-99	4	1.71	208	2.94	43264.00	356.64	
May-99	4	2.38	328	5.66	107584.00	780.09	
Jun-99	4	1.83	314	3.33	98596.00	573.12	
Jul-99	4	7.69	163	59.11	26569.00	1253.15	
		37.12	4404	141.25	1621504.00	12202.71	-0.174653

Appendix A 3- 24

Using data from A3- 23 (Concentration of lead vs conductivity)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2]*[n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*21712.53-51.72*5427}{\sqrt{[13*334.91-(51.72)^2] * [13*2277765.00-(5427)^2]}}$$

r = 0.0954

Ho: $\rho = 0$ (There is no linear relationship between concentration of lead in water and conductivity)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = 0.0954 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of lead and conductivity of the water.

Using the above equation the r value at sites 2, 3 and 4 are -0.1209, 0.4187 and –0.1746 respectively.

APPENDIX A 3-25							
Month	Site	Pb ppb	pH				
		X	Y	X^2	Y^2	XY	r-value
Jul-98	1	3.35	8.07	11.24	65.12	27.05	
Aug-98	1	3.92	8	15.37	64.00	31.36	
Sep-98	1	10.32	8.13	106.50	66.10	83.90	
Oct-98	1	8.17	7.91	66.80	62.57	64.65	
Nov-98	1	6.09	7.88	37.08	62.09	47.99	
Dec-98	1	1.14	7.88	1.31	62.09	9.00	
Jan-99	1	3.83	8.07	14.67	65.12	30.91	
Feb-99	1	8.53	7.92	72.85	62.73	67.60	
Mar-99	1	1.27	7.64	1.62	58.37	9.72	
Apr-99	1	0.50	7.89	0.25	62.25	3.93	
May-99	1	1.71	7.83	2.94	61.31	13.43	
Jun-99	1	1.16	7.97	1.35	63.52	9.26	
Jul-99	1	1.71	7.68	2.94	58.98	13.17	
		51.72	102.87	334.91	814.26	411.96	0.473441
Jul-98	2	2.78	8.06	7.75	64.96	22.44	
Aug-98	2	3.13	8.03	9.77	64.48	25.09	
Sep-98	2	5.38	8.05	28.92	64.80	43.29	
Oct-98	2	6.41	7.91	41.09	62.57	50.71	
Nov-98	2	6.25	7.84	39.06	61.47	49.00	
Dec-98	2	1.41	7.84	1.99	61.47	11.06	
Jan-99	2	3.56	8.09	12.69	65.45	28.82	
Feb-99	2	4.91	7.96	24.07	63.36	39.05	
Mar-99	2	1.16	7.82	1.35	61.15	9.08	
Apr-99	2	1.27	7.94	1.62	63.04	10.10	
May-99	2	1.83	7.84	3.33	61.47	14.31	
Jun-99	2	1.16	7.92	1.35	62.73	9.20	
Jul-99	2	2.71	7.78	7.35	60.53	21.09	
		41.96	103.08	180.33	817.47	333.24	0.231662
Jul-98	3	2.33	8.06	5.43	64.96	18.78	
Aug-98	3	3.69	8	13.64	64.00	29.55	
Sep-98	3	8.87	8.07	78.61	65.12	71.55	
Oct-98	3	8.97	7.89	80.54	62.25	70.81	
Nov-98	3	6.57	7.83	43.17	61.31	51.45	
Dec-98	3	1.28	7.83	1.63	61.31	10.00	
Jan-99	3	4.64	8.27	21.50	68.39	38.35	
Feb-99	3	2.76	7.94	7.59	63.04	21.88	
Mar-99	3	1.71	7.86	2.94	61.78	13.48	
Apr-99	3	0.94	7.97	0.88	63.52	7.49	
May-99	3	1.38	7.85	1.91	61.62	10.85	
Jun-99	3	1.71	7.95	2.94	63.20	13.63	
Jul-99	3	5.70	7.73	32.45	59.75	44.04	
		50.55	103.25	293.24	820.27	401.85	0.072696
Jul-98	4	2.78	8.08	7.75	65.29	22.50	
Aug-98	4	4.38	7.98	19.14	63.68	34.91	
Sep-98	4	3.05	8.06	9.32	64.96	24.60	
Oct-98	4	1.76	7.86	3.11	61.78	13.86	
Nov-98	4	3.85	7.84	14.79	61.47	30.15	
Dec-98	4	1.41	7.84	1.99	61.47	11.06	
Jan-99	4	2.89	8.22	8.35	67.57	23.75	
Feb-99	4	1.68	7.98	2.82	63.68	13.41	
Mar-99	4	1.71	7.9	2.94	62.41	13.55	
Apr-99	4	1.71	7.93	2.94	62.88	13.60	
May-99	4	2.38	7.85	5.66	61.62	18.67	
Jun-99	4	1.83	7.96	3.33	63.36	14.53	
Jul-99	4	7.69	7.75	59.11	60.06	59.58	
		37.12	103.25	141.25	820.23	294.17	-0.259763

Appendix A 3- 26

Using data from A3-25 (Concentration of lead vs pH)

SITE 1

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{13*411.96-251.72*102.87}{\sqrt{[13*334.91-(51.72)^2] * [13*814.26-(102.87)^2]}}$$

r = 0.4734

Ho: $\rho = 0$ (There is no linear relationship between concentration of lead in water and pH)

Ha: $\rho \neq 0$ (There is a linear relationship)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.553 from table for critical values of r

n = 13

r-value = -0.0724 falls in region of acceptance. This implies that the null hypothesis is accepted i.e. there is no linear relationship between the concentration of lead and pH of the water.

Using the above equation the r value at sites 2, 3 and 4 are 0.2317, 0.0727 and –0.2598 respectively.

site	(grain siz	y (% Zn)	x^2	y^2	xy	r-value
1A	355	0.065	126025	0.004	23.075	
1B	355	0.069	126025	0.005	24.495	
1C	355	0.060	126025	0.004	21.300	
2A	355	0.080	126025	0.006	28.400	
2B	355	0.050	126025	0.003	17.750	
2C	355	0.050	126025	0.003	17.750	
2D	355	0.038	126025	0.001	13.490	
3A	355	0.070	126025	0.005	24.850	
3B	355	0.050	126025	0.003	17.750	
3C	355	0.050	126025	0.003	17.750	
3D	355	0.041	126025	0.002	14.555	
4A	355	0.052	126025	0.003	18.460	
4B	355	0.050	126025	0.003	17.750	
4C	355	0.020	126025	0.000	7.100	
4D	355	0.060	126025	0.004	21.300	
1A	63	0.087	3969	0.008	5.481	
1B	63	0.080	3969	0.006	5.040	
1C	63	0.077	3969	0.006	4.851	
2A	63	0.090	3969	0.008	5.670	
2B	63	0.076	3969	0.006	4.788	
2C	63	0.070	3969	0.005	4.410	
2D	63	0.047	3969	0.002	2.961	
3A	63	0.090	3969	0.008	5.670	
3B	63	0.077	3969	0.006	4.851	
3C	63	0.080	3969	0.006	5.040	
3D	63	0.052	3969	0.003	3.276	
4A	63	0.057	3969	0.003	3.591	
4B	63	0.060	3969	0.004	3.780	
4C	63	0.050	3969	0.003	3.150	
4D	63	0.070	3969	0.005	4.410	
1A	62	0.240	3844	0.058	14.880	
1B	62	0.090	3844	0.008	5.580	
1C	62	0.540	3844	0.292	33.480	
2A	62	0.130	3844	0.017	8.060	
2B	62	0.180	3844	0.032	11.160	
2C	62	0.080	3844	0.006	4.960	
2D	62	0.140	3844	0.020	8.680	
3A	62	0.120	3844	0.014	7.440	
3B	62	0.150	3844	0.023	9.300	
3C	62	0.080	3844	0.006	4.960	
3D	62	0.064	3844	0.004	3.968	
4A	62	0.059	3844	0.003	3.658	
4B	62	0.090	3844	0.008	5.580	
4C	62	0.070	3844	0.005	4.340	
4D	62	0.090	3844	0.008	5.580	
sum	**7200**	**3.991**	**2007570**	**0.629**	**484.370**	**-0.31782**

Appendix A3-28 (grain size vs concentration of Zn)

Using data from A3-27

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{45*484.370-7200*3.991}{\sqrt{[45*2007570-(7200)^2] * [45*0.629-(3.991)^2]}}$$

$r = -0.3178$

Ho: $\rho = 0$ (There is no linear relationship between grain size and concentration of Zn in the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship between grain size and concentration of Zn in the sediments)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 45

The null hypothesis is rejected and the alternate hypothesis is accepted as r = -0.3178 falls outside the region of acceptance. There is a linear relationship between the concentration of zinc in the sediment and grain size.

Appendix A3-29

site	(grain siz	y (% Fe)	x^2	y^2	xy	r-value
1A	355	1.87	126025	3.497	663.850	
1B	355	0.1	126025	0.010	35.500	
1C	355	0.42	126025	0.176	149.100	
2A	355	2.2	126025	4.840	781.000	
2B	355	0.41	126025	0.168	145.550	
2C	355	0.51	126025	0.260	181.050	
2D	355	0.11	126025	0.012	39.050	
3A	355	2.47	126025	6.101	876.850	
3B	355	0.32	126025	0.102	113.600	
3C	355	0.58	126025	0.336	205.900	
3D	355	0.086	126025	0.007	30.530	
4A	355	0.31	126025	0.096	110.050	
4B	355	0.15	126025	0.023	53.250	
4C	355	0.18	126025	0.032	63.900	
4D	355	0.03	126025	0.001	10.650	
1A	63	0.6	3969	0.360	37.800	
1B	63	1.47	3969	2.161	92.610	
1C	63	0.86	3969	0.740	54.180	
2A	63	1.77	3969	3.133	111.510	
2B	63	1.56	3969	2.434	98.280	
2C	63	0.49	3969	0.240	30.870	
2D	63	0.9	3969	0.810	56.700	
3A	63	2.61	3969	6.812	164.430	
3B	63	1.76	3969	3.098	110.880	
3C	63	0.84	3969	0.706	52.920	
3D	63	0.74	3969	0.548	46.620	
4A	63	0.38	3969	0.144	23.940	
4B	63	0.95	3969	0.903	59.850	
4C	63	0.88	3969	0.774	55.440	
4D	63	0.79	3969	0.624	49.770	
1A	62	0.05	3844	0.003	3.100	
1B	62	0.54	3844	0.292	33.480	
1C	62	2.69	3844	7.236	166.780	
2A	62	2.01	3844	4.040	124.620	
2B	62	2.3	3844	5.290	142.600	
2C	62	1.18	3844	1.392	73.160	
2D	62	1.86	3844	3.460	115.320	
3A	62	2.85	3844	8.123	176.700	
3B	62	2.03	3844	4.121	125.860	
3C	62	1.18	3844	1.392	73.160	
3D	62	0.91	3844	0.828	56.420	
4A	62	0.5	3844	0.250	31.000	
4B	62	1.42	3844	2.016	88.040	
4C	62	1.12	3844	1.254	69.440	
4D	62	0.97	3844	0.941	60.140	
sum	**7200**	47.956	**2007570**	**79.786**	**5845.450**	**-0.36893**

Appendix A3-30 (grain size vs concentration of Fe)

Using data from A3-29

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2]*[n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{45*5845.45-7200*47.956}{\sqrt{[45*2007570-(7200)^2]*[45*79.786-(47.956)^2]}}$$

$r = -0.3689$

Ho: $\rho = 0$ (There is no linear relationship between grain size and concentration of Fe in the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship between grain size and concentration of Fe in the sediments)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 45

The null hypothesis is rejected and the alternate hypothesis is accepted as r = -0.3689 falls outside the region of acceptance. There is a linear relationship between the concentration of iron in the sediment and grain size.

Appendix A3-31

site	(grain siz	y (% Ti)	x^2	y^2	xy	r-value
1A	355	0.52	126025	0.270	184.600	
1B	355	0	126025	0.000	0.000	
1C	355	0.0021	126025	0.000	0.746	
2A	355	0.82	126025	0.672	291.100	
2B	355	0.56	126025	0.314	198.800	
2C	355	0.23	126025	0.053	81.650	
2D	355	0	126025	0.000	0.000	
3A	355	0.01	126025	0.000	3.550	
3B	355	0	126025	0.000	0.000	
3C	355	0	126025	0.000	0.000	
3D	355	0	126025	0.000	0.000	
4A	355	0	126025	0.000	0.000	
4B	355	0	126025	0.000	0.000	
4C	355	0	126025	0.000	0.000	
4D	355	0	126025	0.000	0.000	
1A	63	0.15	3969	0.023	9.450	
1B	63	0.49	3969	0.240	30.870	
1C	63	0	3969	0.000	0.000	
2A	63	0.66	3969	0.436	41.580	
2B	63	0.71	3969	0.504	44.730	
2C	63	0.28	3969	0.078	17.640	
2D	63	0.71	3969	0.504	44.730	
3A	63	0.63	3969	0.397	39.690	
3B	63	0.68	3969	0.462	42.840	
3C	63	0.27	3969	0.073	17.010	
3D	63	0.48	3969	0.230	30.240	
4A	63	0.64	3969	0.410	40.320	
4B	63	0.65	3969	0.423	40.950	
4C	63	0.42	3969	0.176	26.460	
4D	63	0.58	3969	0.336	36.540	
1A	62	0	3844	0.000	0.000	
1B	62	0.3	3844	0.090	18.600	
1C	62	0.4	3844	0.160	24.800	
2A	62	0.76	3844	0.578	47.120	
2B	62	0.65	3844	0.423	40.300	
2C	62	0.7	3844	0.490	43.400	
2D	62	0.8	3844	0.640	49.600	
3A	62	0.83	3844	0.689	51.460	
3B	62	0.79	3844	0.624	48.980	
3C	62	0.67	3844	0.449	41.540	
3D	62	0.76	3844	0.578	47.120	
4A	62	0.79	3844	0.624	48.980	
4B	62	0.73	3844	0.533	45.260	
4C	62	0.87	3844	0.757	53.940	
4D	62	0.64	3844	0.410	39.680	
sum	**7200**	**19.1821**	**2007570**	**12.645**	**1824.276**	**-0.6367**

Appendix A3-32 (grain size vs concentration of Ti)

Using data from A3-31

$$r = \frac{n.\Sigma XY - \Sigma X.\Sigma Y}{\sqrt{[n.\Sigma X^2 - (\Sigma X)^2] * [n.\Sigma Y^2 - (\Sigma Y)^2]}}$$

$$r = \frac{45*1824.276-7200*19.1821}{\sqrt{[45*2007570-(7200)^2] * [45*12.645-(19.1821)^2]}}$$

r = -0.6367

Ho: $\rho = 0$ (There is no linear relationship between grain size and concentration of Ti in the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship between grain size and concentration of Ti in the sediments)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 45

The null hypothesis is rejected and the alternate hypothesis is accepted as r = -0.6367 falls outside the region of acceptance. There is a linear relationship between the concentration of titanium in the sediment and grain size.

Appendix A3-33						
site	(grain siz	y (%Al)	x^2	y^2	xy	r-value
1A	355	0.82	126025	0.672	291.100	
1B	355	0.98	126025	0.960	347.900	
1C	355	1.35	126025	1.823	479.250	
2A	355	1.94	126025	3.764	688.700	
2B	355	0.67	126025	0.449	237.850	
2C	355	0.27	126025	0.073	95.850	
2D	355	0.09	126025	0.008	31.950	
3A	355	0.12	126025	0.014	42.600	
3B	355	0.29	126025	0.084	102.950	
3C	355	0.42	126025	0.176	149.100	
3D	355	0.12	126025	0.014	42.600	
4A	355	0.31	126025	0.096	110.050	
4B	355	0.23	126025	0.053	81.650	
4C	355	0.15	126025	0.023	53.250	
4D	355	0.18	126025	0.032	63.900	
1A	63	1.29	3969	1.664	81.270	
1B	63	2.07	3969	4.285	130.410	
1C	63	0.81	3969	0.656	51.030	
2A	63	1.14	3969	1.300	71.820	
2B	63	0.97	3969	0.941	61.110	
2C	63	0.33	3969	0.109	20.790	
2D	63	0.58	3969	0.336	36.540	
3A	63	1.16	3969	1.346	73.080	
3B	63	1.43	3969	2.045	90.090	
3C	63	0.26	3969	0.068	16.380	
3D	63	0.14	3969	0.020	8.820	
4A	63	0.24	3969	0.058	15.120	
4B	63	0.32	3969	0.102	20.160	
4C	63	0.14	3969	0.020	8.820	
4D	63	0.45	3969	0.203	28.350	
1A	62	0.74	3844	0.548	45.880	
1B	62	0.82	3844	0.672	50.840	
1C	62	2.29	3844	5.244	141.980	
2A	62	1.35	3844	1.823	83.700	
2B	62	2.15	3844	4.623	133.300	
2C	62	0.33	3844	0.109	20.460	
2D	62	0.99	3844	0.980	61.380	
3A	62	1.94	3844	3.764	120.280	
3B	62	2.01	3844	4.040	124.620	
3C	62	0.57	3844	0.325	35.340	
3D	62	0.29	3844	0.084	17.980	
4A	62	0.29	3844	0.084	17.980	
4B	62	0.36	3844	0.130	22.320	
4C	62	0.24	3844	0.058	14.880	
4D	62	0.29	3844	0.084	17.980	
sum	**7200**	**33.93**	**2007570**	**43.959**	**4441.410**	**0.709406**

Appendix A3-34 (grain size vs concentration of Al)

Using data from A3-33

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2]*[n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{45*4441.410-7200*33.93}{\sqrt{[45*2007570-(7200)^2]*[45*43.959-(33.93)^2]}}$$

$r = 0.7094$

Ho: $\rho = 0$ (There is no linear relationship between grain size and concentration of Al in the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship between grain size and concentration of Al in the sediments)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 45

The null hypothesis is rejected and the alternate hypothesis is accepted as r = 0.7094 falls outside the region of acceptance. There is a linear relationship between the concentration of aluminium in the sediment and grain size.

Appendix A3-35

site	(grain siz	y (%Ca)	x^2	y^2	xy	r-value
1A	355	0.33	126025	0.109	117.150	
1B	355	1.4	126025	1.960	497.000	
1C	355	2.02	126025	4.080	717.100	
2A	355	0.35	126025	0.123	124.250	
2B	355	0.82	126025	0.672	291.100	
2C	355	0.36	126025	0.130	127.800	
2D	355	0.38	126025	0.144	134.900	
3A	355	1.05	126025	1.103	372.750	
3B	355	0.45	126025	0.203	159.750	
3C	355	0.68	126025	0.462	241.400	
3D	355	0.68	126025	0.462	241.400	
4A	355	0.43	126025	0.185	152.650	
4B	355	0.38	126025	0.144	134.900	
4C	355	0.02	126025	0.000	7.100	
4D	355	0.16	126025	0.026	56.800	
1A	63	1.94	3969	3.764	122.220	
1B	63	0.17	3969	0.029	10.710	
1C	63	2.46	3969	6.052	154.980	
2A	63	0.44	3969	0.194	27.720	
2B	63	0.63	3969	0.397	39.690	
2C	63	0.43	3969	0.185	27.090	
2D	63	0.73	3969	0.533	45.990	
3A	63	0.2	3969	0.040	12.600	
3B	63	0.27	3969	0.073	17.010	
3C	63	0.24	3969	0.058	15.120	
3D	63	0.65	3969	0.423	40.950	
4A	63	0.12	3969	0.014	7.560	
4B	63	0.17	3969	0.029	10.710	
4C	63	0.03	3969	0.001	1.890	
4D	63	0.02	3969	0.000	1.260	
1A	62	1.72	3844	2.958	106.640	
1B	62	1.88	3844	3.534	116.560	
1C	62	0.5	3844	0.250	31.000	
2A	62	0.25	3844	0.063	15.500	
2B	62	0.38	3844	0.144	23.560	
2C	62	0.49	3844	0.240	30.380	
2D	62	0.14	3844	0.020	8.680	
3A	62	0.24	3844	0.058	14.880	
3B	62	0.29	3844	0.084	17.980	
3C	62	0.45	3844	0.203	27.900	
3D	62	0.23	3844	0.053	14.260	
4A	62	0.09	3844	0.008	5.580	
4B	62	0.18	3844	0.032	11.160	
4C	62	0.04	3844	0.002	2.480	
4D	62	0.06	3844	0.004	3.720	
sum	**7200**	**24.95**	**2007570**	**29.246**	**4341.830**	**0.860015**

Appendix A 3-36 (grain size vs concentration of Ca)

Using data from A3-35

$$r = \frac{n.\sum XY - \sum X.\sum Y}{\sqrt{[n.\sum X^2 - (\sum X)^2] * [n.\sum Y^2 - (\sum Y)^2]}}$$

$$r = \frac{45*4341.830-7200*24.95}{\sqrt{[45*2007570-(7200)^2] * [45*29.246-(24.95)^2]}}$$

$r = 0.8600$

Ho: $\rho = 0$ (There is no linear relationship between grain size and concentration of Ca in the sediments)

Ha: $\rho \neq 0$ (There is a linear relationship between grain size and concentration of Ca in the sediments)

α = 0.05 i.e. 95 % level of confidence

r = ± 0.279 from table for critical values of r

n = 45

The null hypothesis is rejected and the alternate hypothesis is accepted as r = 0.8600 falls outside the region of acceptance. There is a linear relationship between the concentration of calcium in the sediment and grain size.