THE APPLICATION OF DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY IN THE DETERMINATION OF TRACE METALS IN WET PRECIPITATION

By

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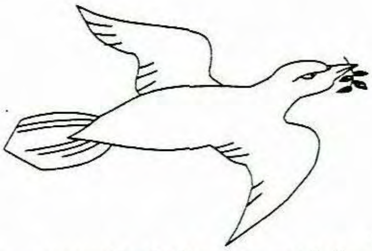
"I declare that

'THE APPLICATION OF DIFFERENTIAL PULSE STRIPPING VOLTAMMETRY IN THE DETERMINATION OF TRACE METALS IN WET PRECIPITATION'

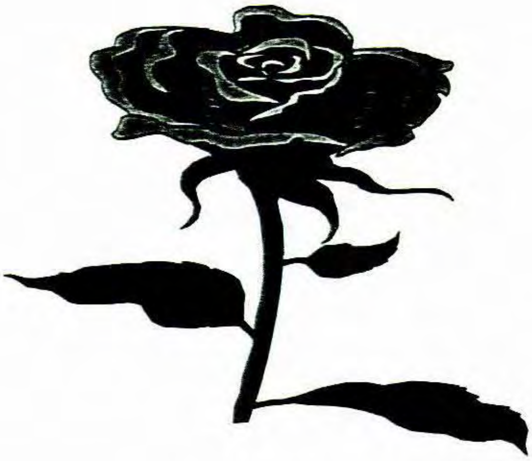
is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references".

SR LeRoux

Shirley Le Roux(Mrs)



Be careful for nothing; but in everything by prayer and supplication with thanksgiving let your requests be made unto God. And the peace of God, which passeth *all understanding, shall keep your hearts and minds* through Christ Jesus.



Philippians 4:6-7.

Abstract

Wet deposition of toxic trace metals is the dominant mode of deposition in terrestrial ecosystems and contributes very significantly to their pollution burden. Wet deposited metals are dissolved in rainwater. They reach the vegatation in a form most favourable for uptake. Reliable analysis of toxic trace metals in rainwater is important in order to determine the impact they make on the environment.

In this study, trace metals in rainwater and in dry deposition (as a control measure), have been analysed over a period of a year. These metals include cadmium, copper, cobalt, lead, nickel and zinc. The rainwater was filtered, acidified to pH2 and irradiated with UV-light. Dry deposition samples, were digested by heating in nitric acid before analysis. Differential-pulse anodic stripping voltammetry was used to determine cadmium, lead and zinc. Copper was determined by adsorptive cathodic stripping at pH7 after complexation with catechol. Cobalt and nickel were measured at pH9 by adsorptive cathodic stripping after formation of their dimethylglyoximes. Sampling was done on a daily basis from April 1996 to March 1997, on the campus of the Peninsula Technikon. The samples were collected over a 24-hour period. The total average concentration for the metals was 16.11μg/dm^3 for rainwater and 427μg/dm^3 for dry deposition. Meteorological factors such as wind speed, humidity and temperature affect the distribution of pollutants and thus the trace metal levels. The levels of the metallic pollutants were thus evaluated against meteorological data. Differential-pulse stripping voltammetry is shown to be applicable for heavy metal analysis of rainwater.

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GLOSSARY OF SYMBOLS

i	Current
i_p	Current peak height
E	Potential
E_p	Peak potential
AAS	Atomic Absorption Spectrometry
AC	Alternating current
DC	Direct current
DMG	Dimethylglyoxime
CSV	Cathodic stripping voltammetry
ASV	Anodic stripping voltammetry
ACSV	Adsorptive cathodic stripping voltammetry
ADPV	Adsorptive differential pulse voltammetry
M^{2+}	Metal ion
L	Ligand
ML	Metal-ligand complex
HMDE	Hanging mercury drop electrode
DME	Dropping mercury electrode
DOM	Dissolved organic material
DPCSV	Differential pulse cathodic stripping voltammetry

Key Terms

Bioaccumulation:	The process by which a toxic substance becomes more concentrated as it moves upward through the food chain.
Computer modeling:	A sophisticated computer mathematical program in which several parameters are considered such as concentration, humidity, rainfall, temperature, wind speed and any other factors that can have an influence on the final study.
Parts per million (ppm) and parts per billion (ppb).	Concentration units used to describe the composition of natural bodies of water or quality of air. It gives the number of milligrams per liter of solution ($mg.dm^{-3}$) for parts per million and micrograms per liter ($\mu g.dm^{-3}$) for parts per billion.
Speciation	The distribution of elements in different oxidation states.

CHAPTER 1

INTRODUCTION

1.1 Background to the study

It is becoming increasingly important to be able to analyse for extremely low levels of trace metals in the environmental and biomedical field (Schramel, 1993: 215).

Certain heavy metals are very toxic and can have a great impact on the environment. These harmful particulate matter are emitted by industrial processes as well as natural sources. Airborne particulates of natural origin include smoke and ash from forest fires and volcanic eruptions, dust, sea salt spray, pollen grains, bacteria and fungal spores. Industrial and other sources of particulate emissions include, amongst others, automobiles, solid-waste incineration, domestic wood stoves, agricultural activities, mining, ore processing, soot and ash from the incomplete combustion of coal. Toxic metal particulates, cement dust, and pesticide and fertilizer residues that are released in these activities are all potentially hazardous. Eventually all particulate matter is deposited on the earth's surface. Liquid aerosols and particulates are generally called mist and include fog and raindrops. Aerosols, acting as nuclei for the formation of droplets, reach the ground when the droplets condense and fall as rain and snow. Fine particulates can be transported considerable distances by winds before settling to the ground or being washed out by rain or snow (Buell & Girard, 1994: 408).

Heavy metals such as cadmium and lead are toxic to living organisms at very low levels. Other metals like copper, nickel and zinc are toxic with different threshold levels for different types of plants and organisms, including man. These metals are not biologically degradable and are bio-accumulators. They undergo a biochemical cycle in the environment, during which they are transformed into various chemical species. Of particular importance for the transfer of metals through the environment are all types of natural waters (rivers, lakes, ground water and the sea) as well as the atmosphere. From the atmosphere, the precipitates (rain and snow) are important ways in which heavy metals can be transferred into terrestrial and aquatic systems (Nurnberg, 1984: 1).

For the above-mentioned reasons, a reliable, accurate method of analysis of these trace metals is very important. Various methods for trace metal analysis are available, but because the concentrations of the metals are so low and close to the detection limits of most instruments, direct measurement is not possible. Development of new methods with increased sensitivity that can lower the detection limit is important for successful monitoring of toxic trace metals. Stripping voltammetry, usually in the differential pulse or alternatively the square-wave mode, has become an important method for the investigation of toxic heavy metals in aquatic systems and atmospheric precipitation. Voltammetry is especially suitable for the automated monitoring of the concentration and chemical speciation of trace elements in natural waters.

1.2 The problem statement

There are many environmental problems that are caused by pollution. In order to eliminate these problems we must understand the types and levels of pollutants. Toxic trace metals contribute to the pollution problem. It is difficult to analyse and monitor the metals because they occur at such low levels. There is a need for new improved analytical methods for monitoring toxic trace metals.

The purpose of this investigation is:

- to develop a novel voltammetric method; to study the complexation of trace metals with oxygen and nitrogen containing ligands such as amino acids; for the study of trace metals in wet precipitates; dry deposition was sampled and analysed as a control measure.
- to develop a low cost method of determining trace metals in rain water on a continuous basis in an industrial area;
- to determine the annual distribution and trends of these metals with meteorological parameters in order to establish interactions between the metals and climatic processes.

The following six amino acids were selected for voltammetric investigation of their complexing and absorptive ability: alanine, aspartic acid, cysteine, glutamic acid, glycine and valine.

The trace elements that are of interest due to their toxicity or their beneficial effect are the following: antimony, arsenic, beryllium, cadmium, copper, cobalt, fluorine, iron, lead, mercury, nickel, selenium and zinc. Six metals were chosen for analysis and these were cadmium, copper, cobalt, lead, nickel and zinc.

Long term monitoring is required to establish the role that rainwater plays in the distribution of metals that might be present in the atmosphere. An initial monitoring period of one year was selected for the purpose of this study.

To establish the role that meteorological parameters play in the distribution of these metals, the average monthly metal concentration was compared with meteorological data such as humidity, temperature and wind speed. Ideally computer based models should be employed together with long term monitoring. However in this investigation only monthly trends were considered for comparison.

1.3 Methods of trace analysis

The crucial factor in the choice of any method of analysis is dependent on the sample to be analysed. To make the correct choice the following has to be taken into account:

- the nature and complexity of the sample;
- the proportions of the components of the sample;
- the precision and accuracy required in the analysis.

When selecting methods for trace analysis, it is necessary to take into account their sensitivity, selectivity and reproducibility, as well as the accuracy of the results obtained (Kalvoda, 1985: 104). Reasonable rates of determination (eg. simultaneous determinations), convenience in operation, compactness of instrumentation and reasonable cost of analysis are further important features of any really useful method (Nurnberg, 1984: 4).

Many instrumental methods of determination are now available. Atomic Absorption (AAS), Inductively Coupled Plasma (ICP) and X-Ray Fluorescence spectroscopy (XRF), stripping analysis, or neutron activation has been used with varying degrees of success and convenience.

Determination of the smallest amounts of substances is the domain of radiochemical methods, especially of neutron activation analysis and tracer techniques, which are practically unrivalled in this field, since their detection limit is, in optimal cases, of the order 10^{-21}g, corresponding approximately to tens of atoms or molecules. These methods have a basic advantage in that their accuracy and precision is chiefly dependent on the number of disintegrations counted, and can be improved by prolonging the counting time. The sensitivity of these methods is, however, very variable: for example, for certain metals having low activation cross-sections (such as bismuth, lead, thallium and mercury), the sensitivity is rather low. A similar situation occurs with tracer methods in the case of nuclides with very long half-lives. After pre-concentration by freeze-drying, about fifty trace elements may be determined in natural fresh water, at ambient levels, by neutron activation analysis. A post-irradiation radiochemical separation normally has to be introduced before the radioactivity measurement. In most cases (for fresh water), the sample volume allowed for irradiation is only a few cm^3, restricting seriously the determination limits that can be achieved (Steinnes, 1988: 153).

Among physico-chemical analytical methods, fluorescence in ultra-violet light (detection limit about 10^{-15}g) and emission spectral analysis (with a limit of about 10^{-12}g) approach most closely the sensitivity of radiometric measurements. However, these methods suffer from rather low accuracy and precision and considerable matrix effects on the determination. For analysis in the range from about 10^{-6}g, or in the concentration range from about 10^{-6} to 10^{-10} mol dm^{-3} (M), a number of physico-chemical methods can be used, for example, atomic absorption, spectroscopy and fluorescence, kinetic and catalytic analytic methods and methods of stripping analysis. While the optical methods are usually more selective and have a broader range of application, electrochemical stripping methods are more sensitive for certain substances, the instrumentation is less costly and they are usually less sensitive to matrix effects than the optical methods. Their precision and accuracy are usually much better than optical methods (Vydra, Stulik & Julakova, 1976: 15).

Stripping analysis have the ability to measure 4 to 6 trace metals simultaneously at concentration levels down to the fractional parts per billion (sub-ppm), utilising relatively inexpensive instrumentation. Among its spectroscopic competitors only flameless atomic absorption has nearly the same sensitivity, but at a much higher cost (Abollino, Aceto, Sacchero, Sarzanini & Mentasti, 1995: 205). The potential of voltammetry, for simultaneous determination, balances the faster measurement rate of the AAS technique for a single element: moreover, if comparable precision is to be achieved, AAS need more test measurements than voltammetry. However, the AAS technique undoubtedly has the advantage that it is very sensitive for a greater number of metals (Nurnberg, 1984: 5).

There is considerable interest in speciation (the distribution of elements between various chemical forms as well as the total amount of the element present) (Behne, 1992: 555). The toxicity of elements is often significantly different for the different species (Marr & Cresser, 1983: 145). Speciation is also of prime importance in studies of the interaction of dissolved heavy metals with suspended particles, sediment surfaces and organisms, and hence is significant for concentration regulation in waters, and for toxic effects. Voltammetry has the advantage of being a species sensitive method, providing many opportunities for studies of heavy metal speciation (Estaban & Cassasas, 1994: 112).

Voltammetric determinations of trace metals require prior pre-concentration for very low levels of concentrations in the same way as other wet chemical instrumental methods (Abollino et al, 1995: 205). This is where the electrochemical approach provides its greatest inherent advantage because the pre-concentration can be done electrochemically in the same cell as the final measurement. There is therefore no risk of additional contamination (Nurnberg, 1984: 5). Common chemical pre-concentration procedures, for example, separation procedures such as solvent extraction, ion exchange, co-precipitation or co-crystallisation are both time consuming and open to additional contamination of samples.

There is an increasing appreciation of the power of stripping analysis (Thunus, 1996: 303; Bjorefors & Nyholm, 1996: 15). It is known that workers in the fields of toxicology, environment, clinical or material sciences, among other fields of study, have become increasingly aware of the unique properties of the technique (Nurnberg, 1985: 142).

1.4 Environmental perspective

Pollution affects the health of human beings and animals, damages vegetation and soils, deteriorates materials, affects climate, reduces visibility and solar radiation, contributes to safety hazards, and generally interferes with enjoyment of life and property (Sherman & Sherman, 1989: 254). Although some of these effects are specific and measurable, such as damage to vegetation and materials and reduced visibility, many are more difficult to measure, such as health effects on human beings. Pollutants can have an acute and chronic effect on human beings. An acute effect is a serious and rapid response to a high dosage of a toxic chemical. Acute poisons lead to a variety of severe symptoms and sometimes even to death. The effects are obvious and fairly consistent across individuals. Chronic effects occur when the toxic chemical dose is relatively low but prolonged. Chronic effects are more subtle effects and can lead to diseases like cancer (Spiro & Stigliano, 1996: 288).

Certain heavy metals have gained great significance in chemical and toxicological studies of the environment, because of their beneficial or toxic effect. Among those are metals such as cadmium, lead and mercury which are generally toxic even at low levels and other metals, for example, copper, zinc and nickel, that are considered to be potentially toxic (Nurnberg1984: 1). Cadmium, mercury and lead are major hazards to human health. All are cumulative poisons. Lead for example exhibits severe deleterious effects on humans. In particular, it strongly affects the mental and physical development of children (Wang, Lu & Yarnitzky, 1993: 61). Lead is abundant in dust and is deposited on food crops or on food as it is processed. Important sources of lead in dust are house paint and petrol. Lead salts are brightly coloured and have been widely used as pigments and as paint bases. Lead chromate, $PbCrO_4$, provides the yellow colouring for striping on roads, while the oxide Pb_3O_4, is the base for the corrosion-resistant paints on bridges and other metal structures. The hydrocarbonate, $Pb_3(OH)_2(CO_3)_2$, was widely used as the base of indoor paint, but has now been replaced by titanium oxide,TiO_2. Leaded paints have also been widely used on building exteriors, and weathering raises the lead levels in dust. The other major source of lead in dust is leaded petrol. Tetraethyl-or tetramethyl-lead is added to petrol to improve the octane rating by scavenging radicals and inhibiting pre-ignition. These compounds are very toxic; they are readily absorbed through the skin, and in the liver they are converted to trialkyl-lead ions, R_3Pb^+, which are neurotoxins. However, a much greater threat to public health is the lead that spews out of the tailpipes of vehicles and into the atmosphere. Most of the lead is emitted in small particles of PbX_2 (X = Cl or Br), formed by reaction with ethylene dichloride or dibromide, added to the petrol to prevent buildup of lead deposits inside the engine. (Spiro & Stigliano, 1996: 323). Copper is an essential element, but if it is present in excess, it can interfere with critical sites in proteins. Copper is generally present as Cu^{2+} and forms strong complexes with nitrogenous bases, including the histidine side chains of proteins. (Spiro & Stigliano, 1996: 311). Chronic exposure to cadmium has been linked to heart and lung disease, including lung cancer at high levels of exposure, to immune system suppression, and to liver and kidney disease (Spiro & Stigliano, 1996: 321). Zinc is not particularly harmful to man, but can be toxic to lower organisms, and can prove troublesome in food chains (Stephen, 1988: 21). Concerns and awareness about the accumulation of heavy metals in the human body have increased considerably over the last decade owing to the toxic or beneficial effects, which these elements have been known to cause. A thorough understanding of these effects depends largely on the ability to determine the rather low concentrations of heavy metals (Adeloju, Bond & Hughes, 1983: 55).

The natural bio-geochemical cycle of the metals has been greatly perturbed by human intervention. The scale of metals extracted from the ground has increased enormously since the Industrial Revolution. Evidence of a massive increase in the global environmental loading of lead can be found in the records provided by ice-cores from Greenland (Spiro & Stigliano, 1996:315). This ties in with the changes in lead concentrations found at varying depths in polar ice corresponding to atmospheric deposition from different historical periods, the levels increasing significantly at depths laid down since the beginning of the Industrial Revolution 200 years ago (Marr & Cresser, 1983: 6). These levels have significantly declined since 1970, due to the phasing of lead additives from gasoline. Large amounts of metals like cadmium, chromium, copper, lead, mercury, nickel and zinc are estimated to be dispersed into the environment and deposited on soils. In some cases (cadmium and mercury), the amounts deposited are actually greater than the amounts produced by extraction, because there are adventitious sources, such as ore processing for other metals or the burning of coal, which contain trace concentrations of many metals. In the case of cadmium, traces in phosphate rock, which is mined and incorporated into fertilizer, adds up to a significant fraction of the total (Spiro & Stigliano, 1996:313). Metals, because they are elements, cannot be broken down into simpler less toxic forms. They persist unchanged in the environment for many years and bio-accumulate through food chains. Metals undergo a biochemical cycle in the environment during which they are transformed into various chemical species (Nurnberg, 1984:1). Toxic metals can cause brain damage, kidney and liver disorders and bone damage. Many are carcinogens (Buell & Girard, 1994: 378).

Metals enter waterways from two main sources:

- Industrial waste discharges
- Particulates in the atmosphere that settle out and enter runoff in water (Buell & Girard, 1994: 378).

Metals pollutants are emitted into the atmosphere via numerous sources such as the burning of fossil fuels, from smelters and metal refineries, cement manufacturing and from incinerators. Metals and their metallic compounds occur in the atmosphere in three distinct physical forms, namely, solid particle matter, liquid droplets (mist) and vapours. Of these, airborne metal particles are by far the most common form found in the atmosphere. Eventually these metals will be deposited on the surface of the earth by natural fallout or the precipitates (rain and snow). In all types of natural waters the toxic heavy metal levels remain in the trace or ultra-trace range but, because they bio-accumulate, they constitute an important group amongst the chemicals of environmental importance (Nurnberg, 1984: 1).

1.5 Toxic heavy metals in wet precipitation

The availability of an adequate supply of water of suitable purity is essential to any community. Water plays a vital role in all ecological systems, both in the mobilization and transport of nutrients, and also in the photosynthetic production of dry matter by plant species (Marr & Cresser, 1983: 104).

Substantial emissions of ecotoxic metals into the atmosphere occur in the heavily industrialised and highly populated regions of the world. To a large extent the ecotoxic metals are bound to fine aerosol particles and therefore undergo mesoscalic transport and distribution with the wind or, after advection to the upper troposphere, even hemispherical transfer (Nurnberg, 1985: 136).

Rainwater plays an important role in the hydrological cycle, thus its analysis is essential in both environmental sciences and geochemistry. Heavy metals of ecotoxic significance exist in natural waters. The main pathways of input from natural and antropogenic sources are wet and dry deposition from the atmosphere, and run off water from land discharge of wastewater. Wet deposition of ecotoxic heavy metals in rain and snow is the dominant deposition mode in terrestrial ecosystems and contributes, therefore, very significantly to their pollution burden by ecotoxic metals via the atmospheric pathway. Rain in slightly to heavily polluted regions usually contains heavy metal levels between 0,1 and 1000$\mu g l^{-1}$ depending on the particular metal. Despite their occurrence at three levels, these toxic heavy metals constitute a group of prime significance among the chemicals of environmental importance in natural waters, because of their accumulation by aquatic organisms (Nurnberg & Mart, 1988: 125).

Wet deposited metals are dissolved in the rainwater. They reach the vegetation in a form most favourable for uptake. Reliable analysis of heavy trace metals in rainwater has thus become very important.

1.6 Meteorological factors influencing pollution

The variation in metal concentration with different seasons, or even from one day to the next, shows that there are factors that attribute towards this phenomenon. It is well known that the atmosphere uses metereological mechanisms that assist in the removal of pollutants. These mechanisms include stirring or turbulent diffusion, photochemical transformations, by rainfall or fallout (Lutgens & Tarbuck, 1995: 330). Pollutants emitted into the atmosphere travel through the atmosphere to reach people, animals, plants or things to have an effect. In water this carriage of pollutants is by water currents, while in air pollution, wind is the means of transport for pollutants. (Buell & Girard, 1994: 409).

The earth's atmosphere can be divided into easily recognisable strata. The troposphere, where most of our weather occurs, extends above the earth to a distance of 10–16 km. On top of the troposphere are the stratosphere followed by the mesosphere and thermosphere. Pollutants in the troposphere are moved by wind. Wind not only moves the pollutants horizontally, but it also causes the pollutants to disperse, reducing the pollutant concentration with distance away from the source (Buell & Girard, 1994: 397).

Normally, air temperature in the troposphere decreases with increasing altitude. Warm air at the earth's surface expands, becomes less dense and rises. As it does so, cooler air from above flows in to replace it. The cooler air is warmed and rises, and in this way the air is continually renewed and pollutants are dispersed by vertical currents and prevailing winds. Reversal of the usual temperature pattern, called a temperature inversion, sometimes occurs; after an initial decrease, the air temperature begins to increase instead of decrease. A lid of warm air forms over cooler air near the earth's surface. The cooler, denser layer cannot rise through the warm lid of air above it and becomes trapped, sometimes for days. There is no vertical circulation and pollutants accumulate (Buell & Girard, 1994: 413). In addition to inversions, serious air pollution episodes are almost always accompanied by fog. Fog sits in valleys and prevents the sun from warming the valley floor and breaking inversions, often prolonging air pollution episodes (Lutgens & Tarbuck, 1995: 332).

The temperature of the atmosphere depends upon the rate at which energy from the sun reaches the earth. Temperature is not a constant and hence it varies with factors such as height, latitude, season and time of day. During the day solar radiation is absorbed by the ground, and it results in warming of the earth's surface. At night, the radiation of energy by the earth's surface will result in its cooling and result in an inversion layer. As a consequence, pollutants accumulate during the night a few hundred meters above the ground. These pollutants are then carried to the ground in the morning as the earth's surface begins to warm; hence the pollution level will be increased at morning time and decrease as the day becomes warmer. Thus an increase in concentration with decreasing temperature can be expected due to the temperature inversion which occurs during the day (Lutgens & Tarbuck, 1995: 333).

1.7 Sources of errors in trace analysis

The possibility of sample contamination at trace levels is so great that it can easily result in large errors. Even low levels of contamination can lead to serious errors in trace analysis.

1.7.1 Errors arising during sampling

Sampling is one of the most critical stages in any practical analysis. Any systematic errors introduced at this stage will make the subsequent work unreliable and the final data will be useless (Nurnberg, 1984: 9).

It is important to be aware that all components of a sampling device are potential contaminants, and that devices suitable for certain needs may not be suitable for others with more stringent requirements for accuracy. Just as it is important to control contamination in analysis, contamination from sampling devices must be controlled too. There is no substitute for critical selection of all components of a sampling device, and for experimental tests of the degree of contamination caused by such a device.

Many processes (physical, chemical and biological) may occur within sample-collection devices with resultant effects on the concentrations of determinants. An example of a physical process is adsorption of surface-active substances, which leads to losses of determinants. Another important chemical process involves reactions between the sample and the sample-collection device (e.g. copper from copper pipes, organic compounds from plastic material). A problem can also occur when biological species settle on the surface of the sampling device and react with constituents of the sample.

Therefore certain general precautions to minimise contamination are useful; for example the contact time between sampler and sample become less important as the ratio decreases. Material for construction of the sampler must be chosen so that contamination is not expected to be a problem. Plastic materials are often suitable, particularly when trace amounts of metals are of interest; but they may need extensive preliminary cleaning to ensure that negligibly small concentrations of determinants are leached from them (Hunt & Wilson, 1986: 74).

Sample-collection devices should be kept clean, particularly with respect to undissolved solid materials and biological films on surfaces. The ability to maintain clean surfaces, are aided by a simple design, and smooth surfaces (Hunt & Wilson, 1986: 74).

1.7.2 Errors arising during analysis

The possibility of sample contamination is always present in trace analysis. The reliability of analytical data relies on the degree to which contamination can be minimised.

The choice whether the analytical method will be destructive or non-destructive depends on the nature of the sample. Non-destructive methods act directly upon the sample and they have the advantage of partly and with some precautions, totally eliminating the risk of contamination of the sample. When determination of trace components is done after a wet decomposition with water, acids etc. care must be taken to use clean vessels and pure reagents in order to minimise contamination risks.

Sources of contaminants are impurities in reagents, particulates in air and trace metals from container and cell walls. In order to minimise contamination, good laboratory practice must be observed, i.e. reagent purity, proper attention to glassware, cleanliness, and careful sample handling and storage.

The possibility of sample contamination by substances leached from the container is always present. Contamination is not only confined to the major constituents of the container material. Elements such as iron, manganese, zinc, boron and lead may be leached from glass containers. Contamination by a number of metals from plastic containers has also been reported. Cap or stoppers of bottles can be sources of contamination, e.g. zinc from rubber inserts in screwcaps, and organic compounds from cork. It is thus safer to ensure that caps and stoppers are made of the container material. One type of container is obviously more suitable for a certain type of analysis than another. Polyethylene containers are favoured, for analysis of trace metals. Before they are used all new containers should be thoroughly cleaned to minimise contamination and many detailed descriptions of recommended cleaning procedures exist. Diluted mineral acids are generally used when polyethylene bottles are used for trace metals (Hunt & Wilson, 1986: 94).

Losses of determinants may occur through adsorption by the sampler container or reaction with the container. Even weak attractive forces between surfaces and solute species give rise to losses from solution by adsorption, and for ionic species and inorganic surfaces ion–exchange may occur. Metal adsorption on to sampling containers has been studied, mainly by radiochemical methods. However, the effect of adsorption of metals on sample containers can be eliminated by the acidification of the sample (Marr & Cresser, 1983: 29).

General precautions to minimise contamination can thus be used when handling samples for trace analysis: samples to be analysed for trace metals should be acidified to prevent both ion-exchange and precipitation of hydroxides, and should be stored in plastic containers (polyethylene of Teflon) (Marr & Cresser, 1983: 29). Chemicals and water used for trace analysis must be of the highest purity. A clean, dust free laboratory environment or a laminar flow clean-air cupboard is very important for this type of work (Florence, 1986: 490). When all precautions are taken under consideration, it is possible to achieve high accuracy and low detection limits.

1.8 Sampling methods

Trace analysis presupposes an appropriate sampling procedure and dedicated high-purity reagents. In the case of atmospheric and water pollution, because of the uniqueness of individual samples, the sampling is complicated. Owing to diffusion and circulation processes, the composition of the samples differs practically from one moment to the next and special precautions have to be taken to ensure the reliability of the analytical information.

Regardless of their origin, samples should be collected under 'aseptic' conditions in order to prevent the risk of contamination. To achieve this, it is necessary for the sample to be collected either by an experienced operator or by a dedicated automated system.

In order that the conditions under which the sample is collected are kept constant, it is necessary to know its nature and then to choose the system most suitable for its collection, with minimal risk of contamination. The repeatability of the sample collection and storage system is an important factor of the reliability of the analytical information.

In analysis for environmental pollutants, the problem of the repeatability of the sample collection poses a difficulty. This is due to the special nature of such samples, which can vary in composition because of turbulent diffusion processes occurring both in air and water. The 'true' composition is itself variable and every sample must be regarded as unique, since its composition is a function of the period over which it was collected. By adopting the correct strategy, it is possible to get continuous information on the fluctuations occurring in the composition of the pollutants being analysed (Baiulescu, Dumitrescu & Zugravescu, 1991: 149).

Particulate matter consists of solid and liquid particles of greater than molecular size. The large particles are often visible in the air as dust and smoke. Smaller particles of 1mm or less in diameter called aerosols are often invisible. Particulate pollutants are emitted by a great variety of sources, both stationary and mobile. Metal pollutants are usually bound to particulate matter.

Particulate pollutants may be sampled either from suspension in air, for example, by filtration or by collection of deposited particles as they fall out from the atmosphere under gravitational influence, known as dustfall.

Samples of precipitation (rain, snow) may, by definition, be short interval, event or composite. Short interval refers to sampling for short periods of time, for example one to two hours during the precipitation event. Event sampling is when a single sample is taken over the entire precipitation period. However, the concentration of solutes in natural waters is not constant. Natural waters can be heterogeneous vertically, horizontally, and with time. This is not only due to man-made pollution but also natural phenomena such as erosion, thermoclines and precipitation washout of dust. Therefore, short interval and event sampling can lead to erroneous estimates of water composition. A series of such samples taken with time (composite sampling) may give a more useful result. Composite samples are obtained by combining a large number of samples that have been taken at different intervals and therefore an average composition can be obtained. These intervals may be either time or spatial or both. A distinct disadvantage of this approach is that any important compositional variation within the water system becomes undetectable (Van Loon, 1985: 229).

Reliable sampling procedures are available:

- Rainwater can be collected in $5dm^3$ beakers. During a rain period, the beakers can be emptied in fractions of $20\text{-}50cm^3$. This prevents contamination by dry fall-out.
- Rainwater can be collected in a $1dm^3$ Teflon bottle with a Teflon funnel that is covered with a polyethylene netting of 400μm meshes, to prevent large airborne particles contaminating the sample (Hiraide, Chen & Kawaguchi, 1995: 333).
- For reliable collection of rainwater an automated sample, that opens only when it rains, can be used. This will minimise the possibility of contamination of the rainwater by other particles e.g. dust particles. The opening and closing of the cover is controlled by an electromotor triggered by a humidity sensor. The sampler needs a normal electric power supply for its operation (Nurnberg & Mart, 1988: 128).

1.9 Voltammetric methods

Differential-pulse stripping voltammetry is especially suitable because of its high speed and multi-element character due to the large number of rainwater samples that a routine measurement program involves. For cadmium, copper, lead and zinc wet deposition is the prevailing transfer mode from the atmosphere into terrestrial and marine ecosystems. Reliable analysis of ecotoxic metals in rainwater has become a very important application of voltammetry (Nurnberg, 1985:137).

1.9.1 Theoretical principles

In voltammetry, current is measured as a function of potential under conditions that encourage polarisation of the working electrode. For this purpose electrodes have a surface area in the range between a few square millimeters and a few square micrometers. The field of voltammetry developed from polarography, which differs from other types of voltammetry in that the working microelectrode takes the form of a dropping mercury electrode (DME).

Techniques which comes under the general heading of voltammetry are:

- Polarography [Direct current (dc) and Alternating current (ac)].
- Stripping voltammetry
- Chronopotentiometry

In voltammetry, a variable potential excitation signal is impressed upon an electrochemical cell containing a microelectrode. This excitation signal elicits a characteristic current response upon which the method is based. The classical voltammetric excitation signal is the linear scan in which the dc potential applied to the cell increases linearly as a function of time. The current that develops in the cell is recorded as a function of time. Two pulse-type excitation signals are also employed. These procedures are termed differential pulse polarography and square wave polarography (Skoog, West & Holler, 1996: 461).

Voltammetric techniques are based on controlling the electrode potential and measuring the resulting current. When the applied potential becomes sufficiently negative or positive, it causes the chemical species present in the solution to become electrolysed (reduced or oxidised) at the surface of the electrode. This produces a current (i) that is recorded. This resulting current-potential plot is known as a voltammogram (or polarogram, in the case of polarography).

The current, resulting from a change in oxidation state of the electroactive species, is termed "Faradaic Current" following Faraday's law. According to this law, the electric charge involved in a redox reaction of l mole of substance is equivalent to 96485 C (coulomb). The Faradaic current is a direct measure of the rate of the redox reaction, taking place at the electrode. This depends mostly on the following:

- Mass transfer, which is the rate at which the species moves from the bulk of the solution to the electrode.
- Charge transfer, which is the rate at which the electron (e^-) is transferred from electrode to solution species and vice versa.

In voltammetry there are three common mass-transfer processes which occur. These are:

- Diffusion under the influence of a concentration gradient, that is the change in concentration as a function of distance;
- Migration of charged ions in an electric field; and,
- Convection currents due to the motion of the solution or the electrode.

The currents that arise due to convection and migration are suppressed. No stirring is permitted and an excess of supporting electrolyte is used. The supporting electrode may be an inorganic salt (KCl, KNO_3, NaCl etc.), a mineral acid or base (HCl or NaOH) or where pH control of the solution is essential, buffer systems such as citrate-citric acid or acetate-acetic acid can be used. This electrolyte must be inactive in the working range. When the concentration of the supporting electrolyte exceeds that of the analyte by 50 or 100-fold, the fraction of the total current due to migration carried by the analyte approaches zero. The rate at which the analyte reaches the electrode is thus due to diffusion only.

The diffusion current arises from a Faradaic process. The Ilkovic equation (equation 1) is derived from the theory that the electroactive material is transported to the surface of the DME by diffusion and not by other mass-transfer processes (Skoog et al, 1996: 482).

The maximum diffusion current is given by $(i_d)_{avg} = 607\, n\, C D^{1/2} m^{2/3} t^{1/6}$ ....(1)

where

i_d = the average current (in micro-amperes) flowing during the life of a drop,

n = the number of equivalents per mole of the electrode reaction,

D = the diffusion coefficients of the electroactive substance in square centimeters per second,

C = the concentration of the electroactive material in millimoles per litre,

m = the mass flow rate of mercury through the capillary in milligrams per second,

t = the drop time in seconds.

The diffusion current is proportional to the concentration of active species in solution. The potential at which the current is half the magnitude of the diffusion current is referred to as the half wave potential or $E_{1/2}$. The $E_{1/2}$ is independent of concentration and is a function of the oxidation-reduction characteristics of the species being evaluated. The $E_{1/2}$ can be related to the Standard Electrode Potential (E°) and can be used for identification of species (Bond, 1980: 10). For simple metal ion reductions the $E_{1/2}$ are reasonably close to the E^0 value, but usually not identical to that constant.

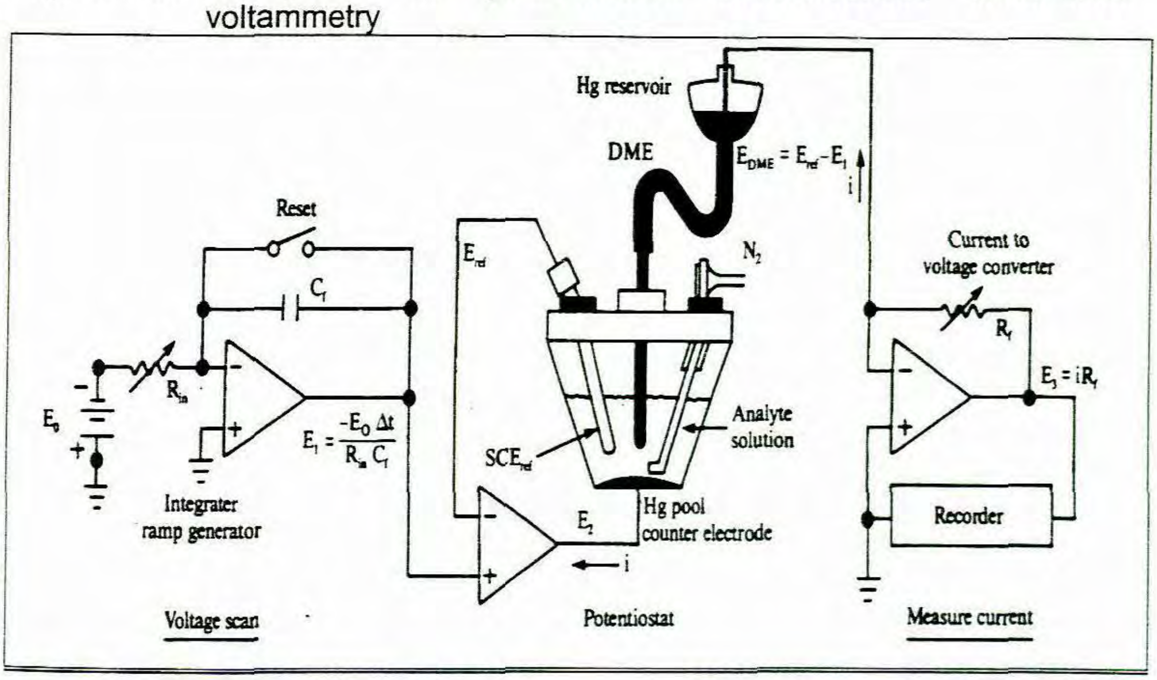
1.9.2 Instrumentation

Figure 1-1 shows a simplified diagram indicating the components of an apparatus for carrying out voltammetric measurements. The cell is made up of three electrodes immersed in a solution containing the analyte and the supporting electrolyte.

- The microelectrode, or working electrode, the potential of which is controlled at a fixed known value or varied linearly with time. Its dimensions are kept small in order to enhance its tendency to become polarized.
- A reference electrode, the potential of which remains constant throughout the experiment.
- A counter electrode, which is often a coil of platinum wire or a pool of mercury, that simply serves to conduct current from the source through the solution to the microelectrode (Skoog et al, 1996: 463).

Microelectrodes have a variety of forms and shapes. They are usually constructed from some inert, conducting material. The range of potentials that can be used with those electrodes in aqueous solutions varies and depends not only upon electrode material but also upon the composition of the solution in which it is immersed. The large currents that develop, because of the oxidation of water to give hydrogen, cause positive potential limitations.

Figure 1-1: A system for potentiostatic three-electrode linear-scan voltammetry



The figure above was extracted from Kennedy (1984,599). It is a schematic drawing that shows the components of a modern, three-electrode polarograph and cell.

Mercury microelectrodes have been widely employed in voltammetry for several reasons:

- Relatively large negative potentials can be tolerated with mercury electrodes owing to the high overvoltage of hydrogen on this metal.
- A fresh metallic surface is formed with every new drop.
- Many metal ions are reversibly reduced to amalgams at the surface of a mercury electrode, which simplifies the chemistry.

However, dissolved oxygen is readily reduced at the dropping mercury electrode and an aqueous solution, saturated with air, exhibits two distinct waves attributed to this element (O_2–H_2O_2-H_2O). Thus the presence of oxygen often interferes with the accurate determination of other species. The solution must be purged with an inert gas, usually N_2, prior to scanning in order to remove dissolved oxygen (Skoog et al, 1996: 475).

1.9.3 Differential pulse polarography

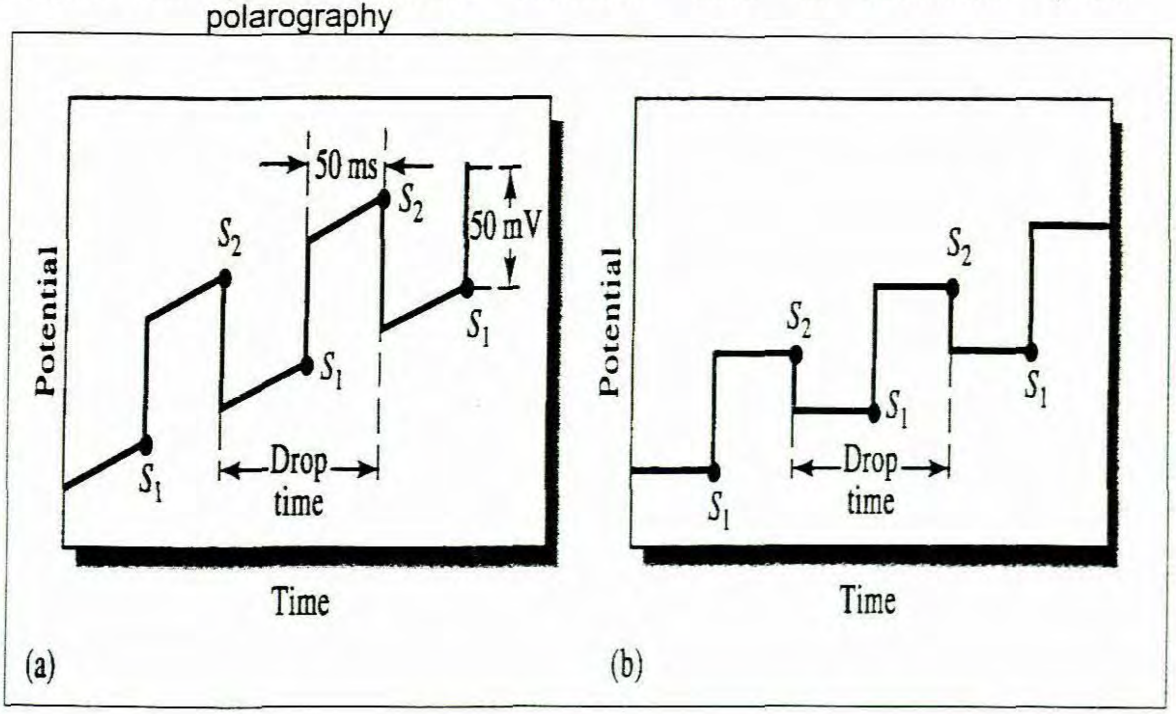
Pulse methods have currently supplanted the classical method (linear scan polarography) almost completely because of the greater sensitivity (Scarano & Morelli, 1996:15), convenience and selectivity (Tahan, Marcano & Romero, 1995: 90). The two most common excitation signals that are used for differential pulse polarography are obtained by:

- superimposing a periodic pulse on a linear scan;
- combining a pulse output with a staircase signal.

In either case, a 50mV pulse is applied during the last 50ms of the lifetime of the mercury drop. Two current measurements are made alternatively, one prior to the pulse and one at the end of the pulse, as illustrated in Figure 1-2. Figure 1-2 shows an applied potential waveform used in differential pulse polarography.

The difference in current per pulse is recorded as a function of the linearly increasing voltage. The resulting differential curve consists of a peak whose height is directly proportional to concentration.

Figure 1-2: Applied potential waveform used in differential pulse polarography



The figure above was reproduced from Skoog et al (1996:486), and shows the two most common excitation signals that are employed for differential pulse polarography. The first (a) was obtained by superimposing a periodic pulse on a linear scan. The second (b) involves the combination of a pulse output with a staircase signal.

Generally quantitative applications are based upon calibration curves or the standard addition method. In either case, it is essential that the composition of standards resemble as closely as possible the composition of the sample both as to electrolyte concentration and pH. If this is done, relative precision and accuracy in the 1-3% range can often be realised, for concentrations of 10^{-7}M and greater.

Pulse methods increase the sensitivity, and another advantage is that individual peak maxima can be observed for substances with half-wave potentials differing by as little as 0,04 to 0,05V. Classical polarography requires a difference of at least 0.2V for resolution of waves (Skoog et al, 1996: 486).

1.9.4 Stripping voltammetry

This technique has the lowest detection limit of any commonly used electroanalytical technique. All stripping methods involve a two step operation:

- The concentration or pre-electrolysis step; The analyte is first deposited on a microelectrode, usually from a stirred solution. The most popular electrode is the hanging mercury drop electrode (HMDE) which consists of a single drop of mercury in contact with a platinum wire.
- The stripping step; After an accurately measured period, the electrolysis is discontinued, the stirring stopped, and the deposited analyte is determined by any voltammetric procedure. During this second step in the analysis, the analyte is redissolved or stripped from the microelectrode. Each electrochemical species strips at a characteristic potential.

The concentration or deposition step amounts to an electrochemical preconcentration of the analyte, because the concentration of the analyte in the surface of the microelectrode is far greater than it is in the bulk solution.

Stripping methods are of prime importance in trace work because the electrochemical preconcentration step of the electrolysis permits the determination of minute amounts of an analyte with reasonable accuracy. Thus, the analysis of solution in the 10^{-6} to 10^{-9} mol dm^{-3} range becomes feasible by methods that are both simple and fast (Skoog et al, 1996: 492).

1.9.5 Anodic stripping voltammetry

In anodic stripping the microelectrode behaves as a cathode during the deposition step and an anode during the stripping step, with the analyte being oxidized back to its original form. Anodic stripping voltammetry is a two step technique. It involves a pre-concentration step and a stripping step (figure 1-3). In the pre-concentration step a controlled potential is applied at the HMDE, at a potential more negative than the half wave potential of the metal ion. This leads to the reduction of the metal ion, thus forming an amalgam with the mercury. The reduced reaction is allowed to take place over a fixed time period and under identical conditions. For the stripping step, the potential applied to the electrode is then reversed, i.e. to potentials more positive than the half-wave potential of the metal ion. As the applied potential reaches the half wave potential of the metal ion, oxidation of the amalgam occurs and the metal ion is stripped from the amalgam back into the solution.

Figure 1-3: Anodic stripping voltammetry

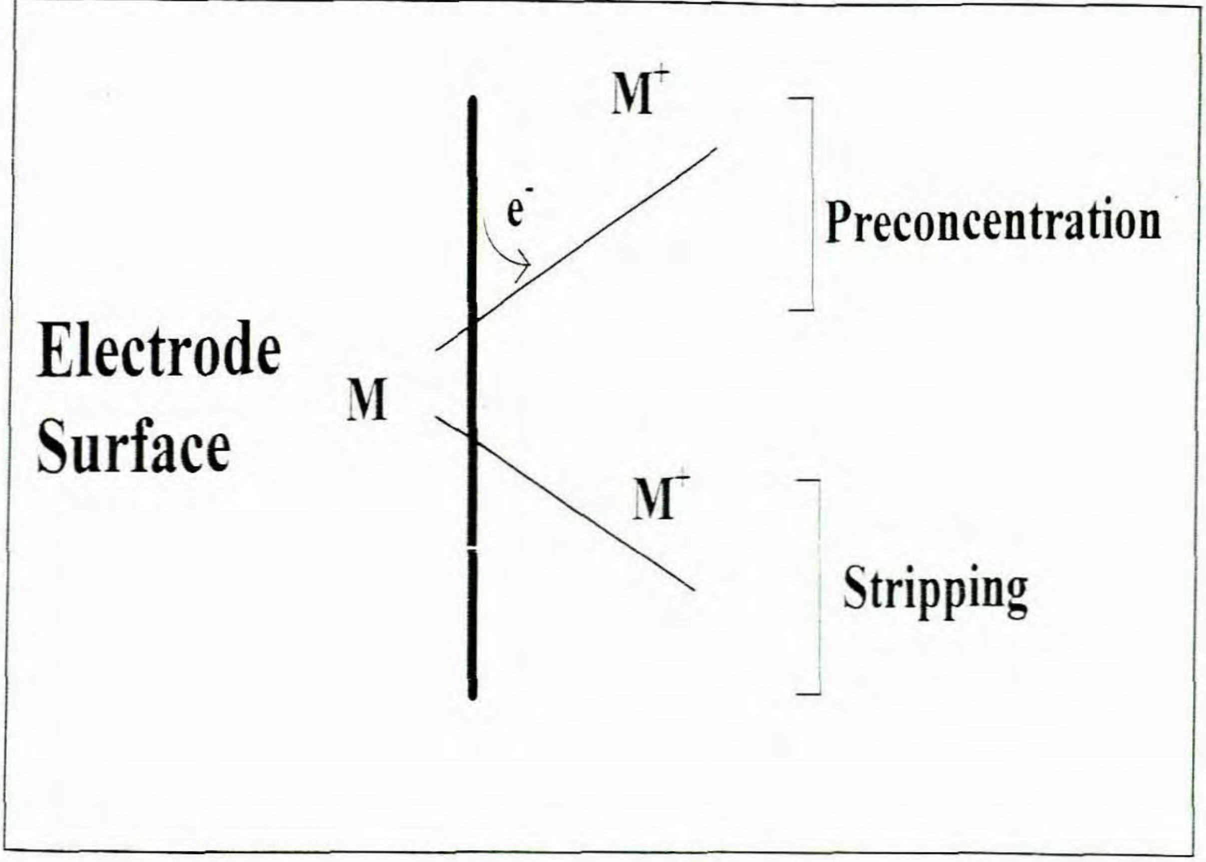


Figure 1-3 above illustrates the two step technique (preconcentration and stripping) of stripping voltammetry:

The stripping step is performed using any voltammetric technique. When the voltammetric technique is differential pulse polarography, the technique is known as differential pulse anodic stripping voltammetry (DPASV). The high sensitivity of the DPASV can be attributed to the high ratio of Faradaic to non-Faradaic currents generated in the electrochemical cell. (Skoog et al, 1996: 493).

The peak currents produced as the system reaches the oxidation potential of the metals are measured. The resulting voltammogram provides the analytical information of interest.

Some limitations exist in ASV, such as the requirement that the element be reduced to the elemental state and that the element be soluble in mercury. Four metals (cadmium, copper, lead, and zinc) can successfully be determined by ASV. The concentrations of the other elements are too low, or they suffer from interference such as those due to the formation of insoluble intermetallic compounds in mercury. When intermetallic compounds are present, the stripping peaks may be shifted, severely depressed or absent completely (Willard, Merritt, Dean & Settle, 1988: 721). ASV has undergone considerable progress and is applicable to far more elements. The main advance has been in the preconcentration step prior to the voltammetric scan. The preconcentration step, by deposition, is now done by adsorption instead of plating (Van Den Berg, 1991: 265).

1.9.6 Cathodic stripping voltammetry

Cathodic stripping voltammetry (CSV) is a very sensitive method for the determination of trace amounts of organic and inorganic substances, which can be accumulated and reduced at the mercury electrode. Cathodic stripping analysis consists of forming an insoluble layer at the electrode surface during an anode pre-electrolysis, and stripping it off by reverse electrolysis. Instead of deposition of an element in the elemental state as in ASV described above, the preconcentration step in CSV can consist of precipitation of an insoluble salt or adsorption of a surface active complex, prior to reduction of the deposited material (Estaban, Arino, Diaz-Cruz & Casassas, 1993: 277).

1.9.7 Adsorption stripping methods

Adsorption stripping methods are similar to the anodic and the cathodic stripping methods described above. The microelectrode, usually a HMDE is immersed in a stirred solution of the analyte for several minutes. Deposition of the analyte occurs by physical adsorption of the electrode surface rather than electrolytic deposition. The stirring is discontinued and the deposited material determined by linear-scan, or pulsed voltammetric measurements.

Adsorptive stripping voltammetry has been applied to the determination of a variety of inorganic cations at very low concentrations. The cations are complexed with surface-active complexing agents (ligands) such as dimethylglyoxime (DMG), catechol and bypyridine. Detection limits in the 10^{-10} to 10^{-11} M range have been reported (Skoog et al,1996: 493).

Figure 1-4: Preconcentration by adsorption of the metal-ligand complex at the surface of the electrode

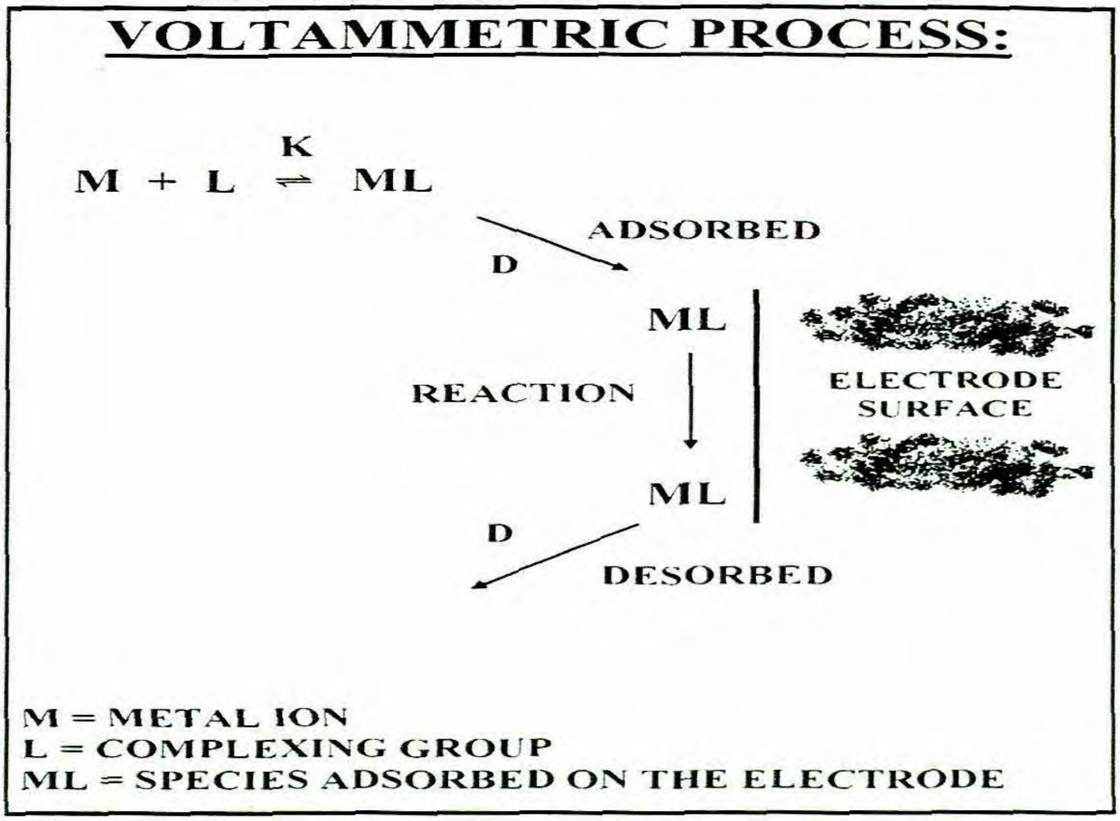


Figure 1-4 illustrates the complexation of metals with surface-active complexing agents (ligands) and the adsorption of the resulting metal-ligand complex on the mercury drop.

1.9.8 Complexation of metals with nitrogen-oxygen containing ligands

During preliminary investigation the complexes of trace metals (such as Cu, Pb, Zn, Ni, Cd and Co) with oxygen- and nitrogen-containing ligands, in particular amino acids, were studied. Amino acids such as alanine, aspartic acid, cystein, glutamic acid, glycine and valine were investigated for their complexing ability. Their adsorption at the surface of a HMDE was also studied.

Amino acids have both carboxylic acid groups as well as amino acid groups. In the zwitter-ionic state, complexation can therefore occur through the amino end and the carboxy end. When studying these molecules as ligands and especially their complexing ability, they are considered as nitrogen-oxygen bidentate ligands. Maximum complexation will occur at the isoelectric pH since the molecule is deprotonated at the carboxy end and the lone pair on the nitrogen is most available for binding since the N-end is positively charged. Voltammetry was done at the isoelectric pH of the ligand as well as pH 9. Both ASV (to see the decrease in the free metal concentration as the complex is formed) as well as CSV (to see the extent of adsorption by the complexes formed) was performed.

Lead and cadmium formed complexes with most of the ligands mentioned above, with the exception of cadmium with valine. Copper complexed with cystine and alanine. Nickel complexed with cystine and showed a cathodic response but at higher concentrations. Cathodic stripping voltammetry of the above metal-ligand complexes showed poor response. The complexes that were formed exhibited poor adsorptive qualities.

These investigations signalled no suitable method of analysis. In order to continue the study, it was decided to consult the literature and then use an established method of analysis to determine the concentrations of the rainwater and the dry deposition samples.

Cadmium, lead and zinc can be simultaneously determined by DPASV at the HMDE down to levels of 0.1-0.05μg kg^{-1} (Nurnberg, 1988:132). This has been successfully applied on rainwater by Vos et al. (1986:279). Due to the low detection levels and speed provided by the simultaneous determination, DPASV was used to determine cadmium, lead and zinc concentrations in the rainwater and dry deposition samples.

A substantial number of heavy metals do not form stable amalgams and therefore cannot be determined by the stripping approach. Adsorption voltammetry then becomes useful. It is based on the electrochemical preconcentration by adsorption of a suitable species of the substance to be determined. It has been successfully applied to the simultaneous determination of traces of nickel and cobalt. The sample solution is adjusted to pH 9.2 with ammoniacal buffer and enough DMG is added to complex the Ni(II) and Co(II) as $Ni(DMG)_2$ and $Co(DMG)_2$ Vos et al. (1986:279), Van den Berg,(1984,1069) and Nurnberg, (1988:137). The DMG complexes are surface-active and adsorb at the surface of a HMDE. To obtain optimal adsorption conditions, the electrode is held for several minutes at a potential of –0,7V(Ag/AgCl), while the solution is stirred to speed up mass transfer to the interface. Stirring is stopped and the potential is scanned in the negative direction past the reduction potentials of nickel and cobalt, using the differential-pulse mode. The method may then be termed adsorption differential-pulse voltammetry (ADPV). Detection limits are typically near 10^{-10}mol dm^{-3}. The amount of metals adsorbed is proportional to the overall bulk concentration of the metals. This adsorption approach provides very efficient electrochemical preconcentration and can be extended to many other cases (Esteban et al, 1994: 115). Copper was measured in the adsorptive mode after complexation with catechol (Van den Berg, 1984: 195). A reduction current is obtained when an aqueous solution of copper and catechol at a natural pH is subjected to differential pulse cathodic stripping voltammetry (DPCSV). This is due to the reduction of the copper (II)-catechol complex that adsorbs onto the hanging mercury drop electrode. The most likely form of the adsorbed complex ion is CuL_2^{2-} (L being catechol). Alternating current polarographic measurements showed that these complex ions adsorb more strongly onto the drop than free catechol ions. Analytically useful currents are obtained at very low metal concentration (Van den Berg, 1984: 195).

CHAPTER 2

EXPERIMENTAL PROCEDURES

2.1 The procedure

As a result of the study of relevant literature, which includes Vos et al. (1986:279), Van den Berg (1984,1069), Abollino, Aceto, Sacchero, Sarzanni & Mentasti (1995:200) and Esteban & Casassas (1993:110) and performing preliminary experiments, the following procedure was applied. DPSV was applied to measure zinc, cadmium and lead by anodic stripping in rainwater at pH2 (Nurnberg, 1988: 132). The pH was changed to 7 and copper was measured in the adsorptive mode after complexation with catechol (Van den Berg, 1984: 195). Cobalt and nickel were measured at pH 9,1 in the adsorptive mode after formation of their dimethylglyoximates.

2.2 Instrumentation

The voltammetric procedures were done with a polarographic analyser (Amel model 433A) linked to a x-y plotter and a printer (Epson model FX-850). The working electrode was a HMDE and a standard Ag/AgCl electrode filled with saturated KCl was used as the reference electrode; a platinum wire served as the counter or auxiliary electrode. The sample solution in the polarographic cell was de-aerated prior to the voltammetric determination by passing high purity nitrogen gas through the solution. A variable Gilson micropipet was used for adding the standard metal solutions into the electrochemical cell. Quantification was done by standard addition, using two spikes for each element.

The pH was measured with a Beckman 71 pH meter. For calibration, buffers of pH 4.00 and 7.00 (BDH) were used.

For weighing purposes the analytical balance, Mettler College 150 Analytical Balance, was used.

Caution was taken throughout the preparation steps to minimize any potential contamination.

2.3 Reagent preparation

2.3.1 Catechol

Catechol was obtained from Merck (analar grade). A fresh solution of catechol was prepared every day because it is known to be photosensitive and it reacts with oxygen. It was therefore also necessary to degas all solvents with oxygen-free nitrogen gas before adding any catechol sample (Van den Berg, 1986: 112).

2.3.2 Purification of water

Water was purified using a Millipore apparatus for reverse osmosis followed by ion exchange (Milli–Q). The Milli-Q system consists of a prefilter and a charcoal absorption column followed by 2 mixed-bed ion-exchanged columns. After deionisation, water was passed through a microfilter (0,22 μm) to remove particulates and could be drawn off into 10dm^3 polyethylene containers. When not in use, water in the ion-exchangers was circulated periodically for 1 minute every hour. This purified HPLC grade water was used for all experimental procedures.

2.3.3 Cleaning of glassware

Before use, all glassware and plastic containers were cleaned by washing with soap and water, rinsing with purified water, soaking in a 6 mol dm^{-3} nitric acid solution for two weeks and finally rinsing with high purity water.

2.3.4 Electrolyte solution (0,1 mol dm^{-3} HCl)

The electrolyte solution was prepared by diluting Merck Suprapure Hydrochloric acid (31-33%) with ultra high purity deionised water on a volume per volume basis.

2.3.5 Standard solutions

Standard solutions (atomic absorption standards, obtained from SMM Chemicals and Saarchem-Holpro) were prepared by diluting the atomic adsorption standard solutions with high purity deionised water. Concentrations ranged from 1ppm to 30ppm.

2.3.6 Ammonia– ammonium chloride buffer solutions

142cm^3 concentrated NH_3 (sp.gr. 0,88-0,90) was added to 17,5g NH_4Cl (Merck analar Grade) and diluted with de-ionised water to 250cm^3.

2.3.7 Dimethylglyoxime(DMG)

A 1% solution of analytical grade DMG (Merck analar grade) was prepared in analytical grade ethanol.

2.4 Sampling device

For the collection of samples, an automated sampler was used. When precipitation started, the sampler opened, and it closed once the rain stopped. In this manner reliable discrimination between wet deposition and dry deposition (by dust particles) was possible.

The bucket that remained closed during the precipitation period served as the control sample. Thus two samples, the rainwater sample and the control sample were taken on days that it rained. On days that it did not rain, two samples were also taken. The one bucket remained closed and the other open. One bucket served as the dry deposition sample (dust particles) and the other as the control. Samples were taken on a daily basis (every 24 hours) for a period of one year, from April 1996 to March 1997.

Figure 2-1: Rainwater sampler

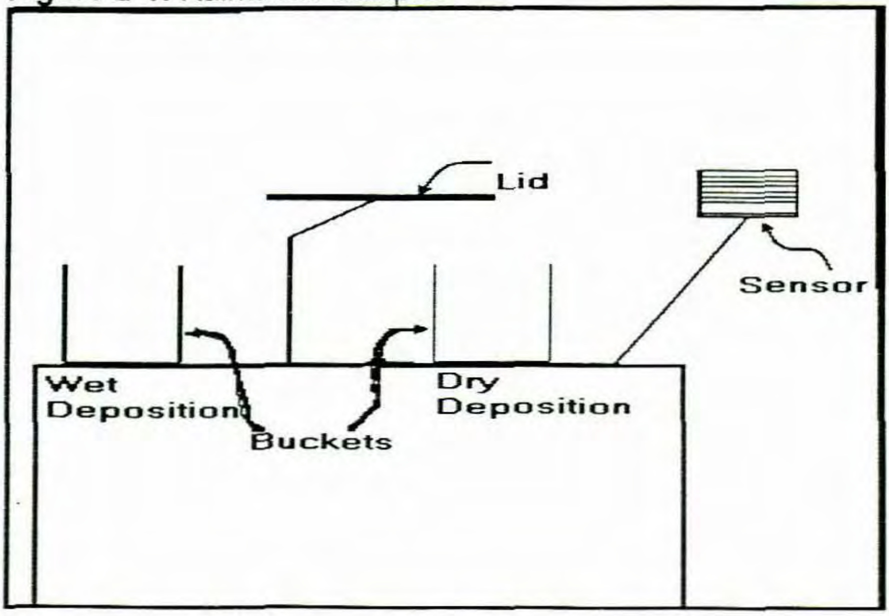


Figure 2-1 above is a schematic drawing of the rainwater sampler used. The sampler consisted of a sensor, a lid and two buckets. The sampler was battery driven. When water drops touched the sensor, the lid automatically moved over the dry deposition bucket and closed it. During the rainfall event, the wet deposition bucket was therefore open. After the rain, the lid moved over and again covered the wet deposition bucket.

2.5 Sample preparation

The rainwater samples and the dry deposition samples were treated and prepared differently, as is described below.

2.5.1 Rainwater samples

Before analysis, the samples were filtered to separate suspended matter from the water. Millipore filters, type HA pore size 0,45 mm were used.

The samples were acidified to pH 2 and were then irradiated for 15 minutes with an 800W ultraviolet lamp. It was necessary to take into account that samples might contain dissolved organic material (DOM). This material might bind, by complexation, a certain fraction of the dissolved heavy metals, forming species that are not accessible to differential-pulse stripping adsorption voltammetry. Significant DOM levels might also cause interferences because of adsorption at the electrode. Therefore, DOM had to be decomposed before voltammetric determination. This was achieved, without contamination risk, by uv irradiation, which photolytically decomposes DOM.

2.5.2 Dry deposition samples

These include dry deposition samples, dry deposition control samples and rainwater control samples. The buckets were rinsed with suprapure nitric acid and then with ultra pure water. The samples were then digested. Suprapure hydrochloric acid (0,1M) was added and the filtration was performed using Millipore filters (HA pore size 0,45mm). The samples were made up to 100 ml in an A-grade volumetric flask. The samples were stored in polyethylene bottles before they were analysed.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Introduction

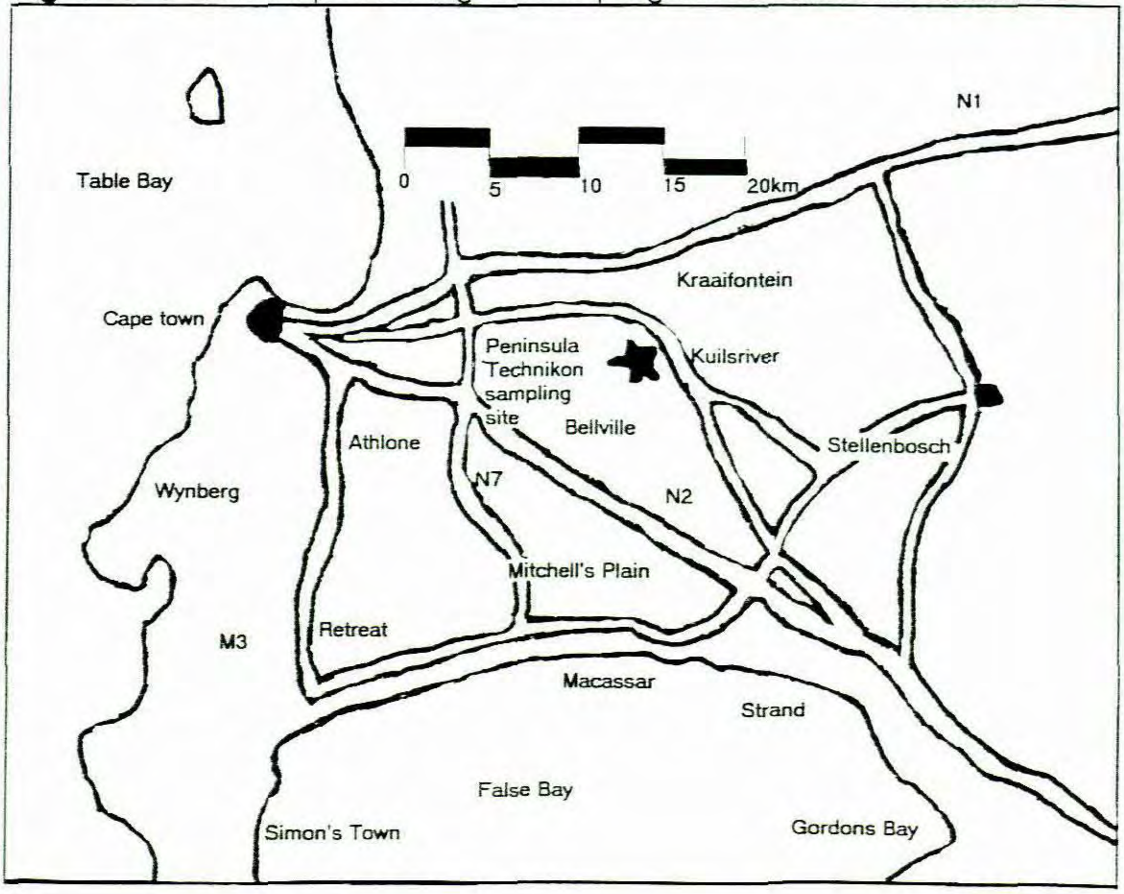
Analysis was performed on the samples, which were collected daily from April 1996 to the end of March 1997. The samples were collected once in a 24 hour period and thus reflected the daily averages of the metal detected. Exceptions to the daily sampling were:

- The festive season (including 16, 25, 26 December and 1, 2 January), when composite samples were collected.
- When the buckets cracked, after months of usage.
- Very windy days, when the buckets were blown away. Although the buckets were fastened to the sampler, on three occasions the wind was so strong it blew the buckets away.

The monitoring site is located close to the entrance gate of Peninsula Technikon. All vehicles entering or leaving the campus passed the monitoring site. The campus is situated next to Sacks Circle, an industrial area in Bellville, Cape.

For wet as well as dry deposition, cadmium, copper, cobalt, lead and zinc were detected. The concentrations of cadmium and cobalt detected were considerably lower than that of the other metals. Of all the metals analysed, the concentration of zinc was always higher. The concentrations of the metals, with the exception of cobalt, were always higher in the dry deposition sample than in the rainwater sample. This could be as a result of the rain causing a dilution effect.

Figure 3-1: Site map indicating the sampling site at Peninsula Technikon



The map in Figure 3-1 shows the sampling site at Peninsula Technikon. Peninsula Technikon is located in Bellville in the Province of Western Cape, South Africa. Bellville is an industrial as well as a residential area.

Due to the difference in concentration, two graphs had to be drawn in order to represent the dry deposition and wet deposition data. Although the graphs of these metals differ for the dry deposition representation they all have a peak during the time from February to mid-July. This could be due to the fact that the high rainfall removes pollutants from the atmosphere.

During filtration, heavy metals could be leached from the filters, resulting in higher curves for cadmium, copper, nickel, lead and zinc. Blank filter papers were analysed after subjection to the same dry digestion procedure and any other manipulations used for the samples.

Table 3-1 Concentrations of cadmium, copper, lead and zinc in Millipore nitrocellulose filter papers

Blank	Cu, ppb	Pb, ppb	Cd, ppb	Zn, ppb
1	1.94	1.00	-	55.41
2	0.86	2.70	-	40.97
3	4.25	4.34	-	33.18
4	6.62	3.18	-	26.92

These were found to contain small amounts of the elements of interest (Table 3-1). The concentrations measured in some samples were not much higher than that of the filter paper and therefore no background subtraction was done. In general, however, the matrix composition was always taken into account.

The ultra purified water used during sample preparation showed no traces of cadmium, copper, nickel, lead and zinc in the analytical range. However, the HNO_3 used for the digestion of filter papers contained trace amounts of the analytical elements.

Table 3-2: Maximum limits of impurities for cadmium, copper, nickel, lead and zinc from HNO_3 in μg/g

Acid	HNO_3 (65%) μg/g
Cu	0.001
Pb	0.001
Cd	0.001
Zn	0.005

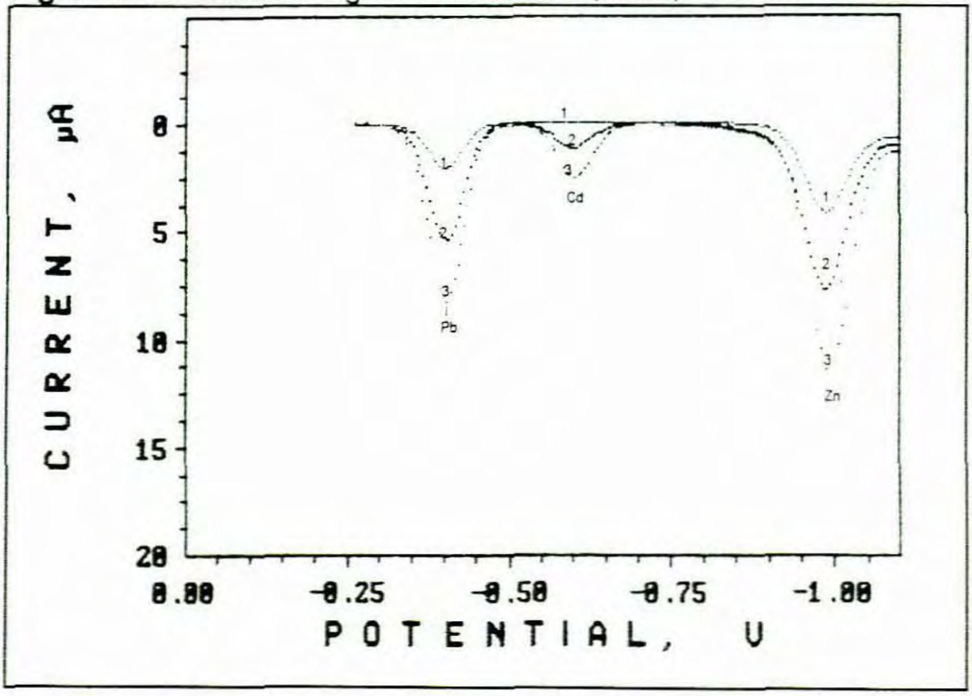
The contributions from acids added during digestions were accounted for in the concentrations reflected per filter paper in Table 3-2.

3.2 Voltammograms of the metals

3.2.1 Determination of cadmium, lead, and zinc by DPASV

The determination of cadmium, lead and zinc was performed by the DPASV technique.

Figure 3-2: Voltammogram of cadmium, lead, and zinc



A typical example of a DPASV voltammogram, for cadmium, lead and zinc is shown in Figure 3-2. Quantification was done by standard addition, using two spikes for each element. The peaks on the graph correspond to the following concentrations: (1) 10cm^3 sample solution, (2) 10cm^3 sample solution + 0.04mg/dm^{3}Pb + 0.02mg/dm^{3}Cd + 0.1mg/dm^3 Zn, (3) cm^3 sample solution + 0.08mg/dm^{3}Pb + 0.04mg/dm^{3}Cd + 0.2mg/dm^{3}Zn.

The metals were determined directly in a 10cm^3 portion of the sample. After de-aeration for 2 minutes; these elements were deposited at a negative potential of -1,2V with a deposition time of 2 minutes. During the deposition step, the solution was stirred automatically. After a rest interval of 30s, the HMDE was polarised in the differential-pulse mode in the anodic direction to 0,0V (Vos, et al, 1986:273).

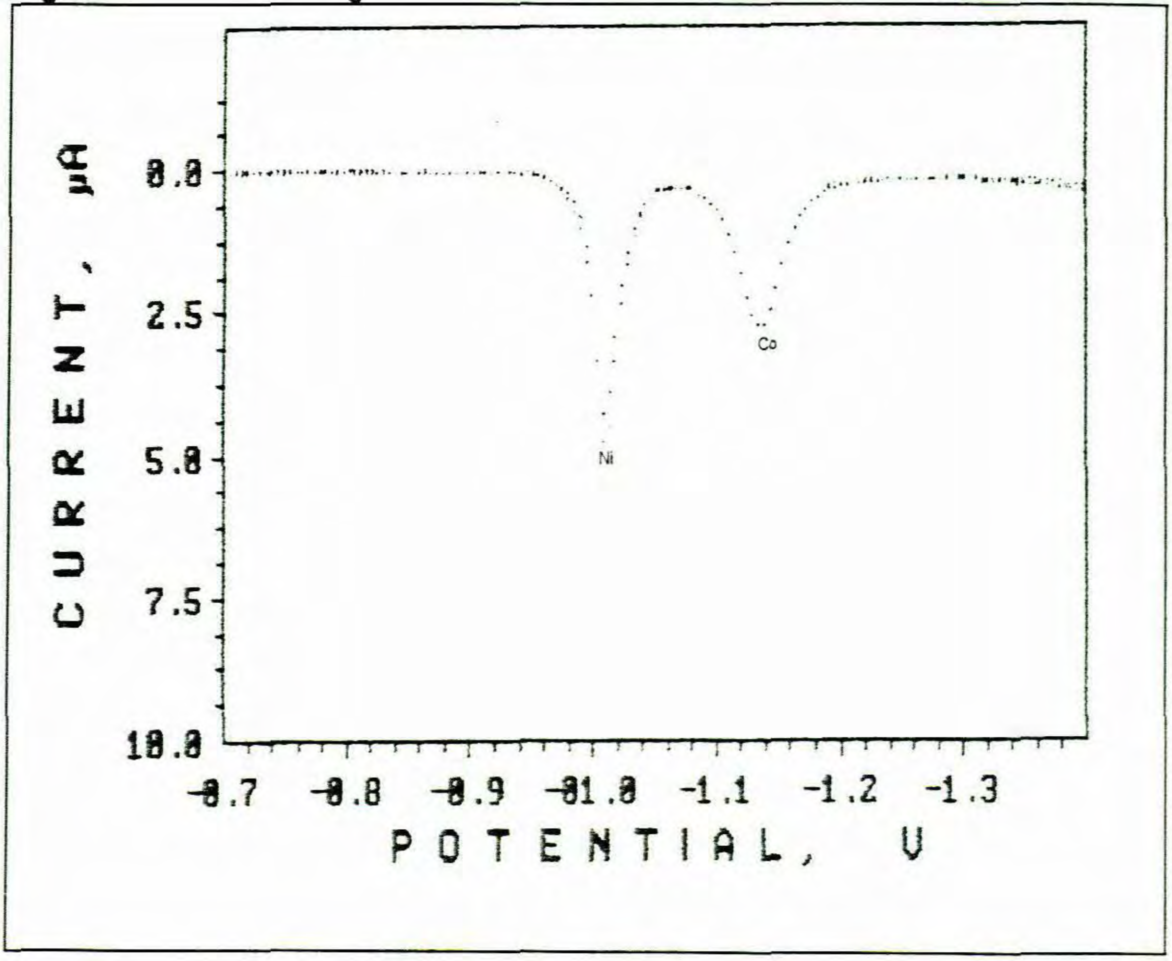
3.2.2 Determination of nickel and cobalt by CSV and ACSV

For the dry deposition samples, determination of nickel and cobalt was done by CSV. For CSV the deposition step was done at a potential of -0.7V and the voltammogram was recorded by scanning in the cathodic direction to –0.3V (Vos, et al, 1986:273).

However, in most cases it was found that CSV was not sensitive enough for rainwater samples. Thus for the determination of rainwater, ACSV was used. For ACSV, deposition was done at a voltage of –1,3V and then the potential was scanned in the negative direction (from 0V to –1300V).

The voltammogram of cobalt and nickel is obtained by deposition at a voltage of –1,3V and then scanning in the negative direction (from 0V to –1300V). After the determination of cadmium, lead and zinc by ASV, the pH was adjusted to 9.0-9.1 by adding 10M NH_3/NH_4Cl buffer and enough DMG to give a concentration of 10^{-4}M. The resulting complexes with DMG were adsorbed on the mercury drop at a potential of –0,7V for 2 minutes and the voltammogram (figure 3-3) was recorded by scanning in the cathodic direction of –1,3V.

Figure 3-3: Voltammogram of nickel and cobalt

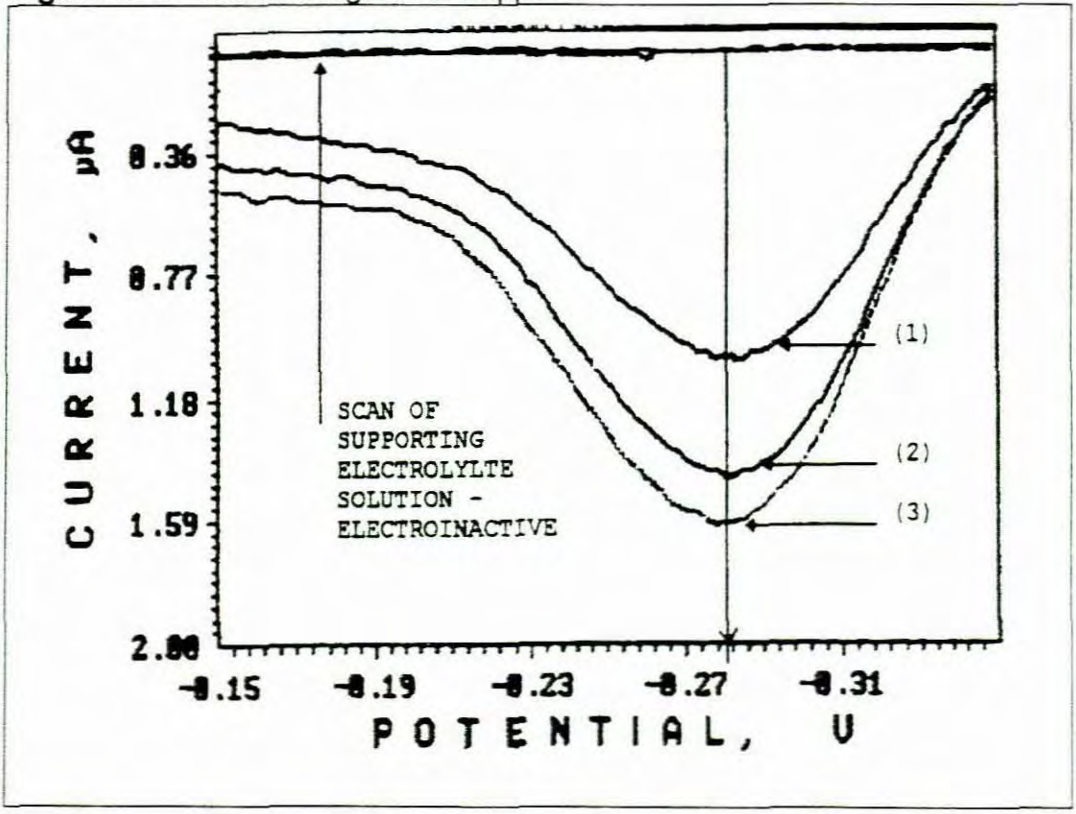


The voltammogram above is a typical example of cobalt and nickel determined by CSV. The voltammogram was obtained from the scan of 10 cm^3 dry deposition samples, after deposition at a potential of –0,7V for 2 minutes and then scanning in the cathodic direction of –1,3V.

3.2.3 Determination of copper by ACSV

The determination of copper was performed by the ACSV technique after complexation with catechol.

Figure 3-4: Voltammogram of copper



The voltammogram above is a typical one for copper, produced by scanning in the negative direction, from 0V to –0,8V. The peaks on the graph in Figure 3-4 is due to the following concentrations of copper: (1) 1.477 mg/dm^3 (2) 2.228mg/dm^3 and (3) 2.870 mg/dm^3.

In ASV the determination of copper is hampered by the oxidation wave of mercury. Copper was thus determined by ACSV. The pH was adjusted to 7 by adding 10M NH_3/NH_4C1 buffer; catechol was also added in order to complex the copper. The resulting complex with catechol was adsorbed on the mercury drop at a potential of –0,8V for 2 minutes and the voltammogram was recorded by scanning in the negative direction, from 0V to –0,8V (Van den Berg, 1984: 196).

3.3 Comparison of rainwater

The rainwater results, obtained in this study, were compared with studies done in Belguim, Germany and Japan. In Belguim the study was done using voltammetry. Sampling was done at Wilrijk on the university campus some 10km south of the center of Antwerp and at Maasmechelen in a rural zone in the northeast of Belguim. All three sampling sites are therefore close to residential as well as industrial areas. A graphite furnace atomic absorption spectrometer was used in the analysis done at Nagoya, Japan.

Table 3-3 Rainwater results obtained at Nagoya, Japan (elemental concentrations are in $\mu g.dm^{-3}$)

Co	Ni	Cu	Cd
3	13	59	4.1
13	25	65	5.5

The rainwater results in the table above were extracted from Hiraide, Chem & Kawaguchi, (1995: 335).

Table 3-4 Rainwater results at Wilrijk, Maasmechelen and Mechelen (elemental concentrations are in $\mu g.dm^{-3}$)

	Wilrijk		Maasmechelen		Mechelen	
	Mean	Max	Mean	Max	Mean	Max
Zn	66	163	73	347	33	71
Pb	47	110	41	180	19	72
Cu	15	58	5.5	18	5.3	14
Co	2.6	4.3	2.3	4.3	1.3	2.3
Ni	8.6	37	16	>500	5.6	21
Cd	3.5	22	1.3	4.3	0.9	2.6

The rainwater results in the table above were extracted from Vos et al, (1986: 279).

Table 3-5 Average daily wet deposition of heavy metals in rainwater in the Federal Republic of Germany from 1980 to 1982 (elemental concentrations are in $\mu g.dm^{-3}$)

	1980	1982	1980	1982	1980	1982
Cd	1.0	0.7	4.35	2.3	1.7	4.0
Pb	48	38	116	158	91	130

The rainwater results in the table above were extracted from Kalvoda & Parsons, (1984:137).

Table 3-6 Results of rainwater analysis done in this study at Peninsula Technikon
(elemental concentrations are in $\mu g.dm^{-3}$)

Metals	Mean	Max
Cd	2.5	43
Pb	4.0	14
Cu	25	114
Co	1.28	24.3
Zn	54	426
Ni	2.0	30

The metal concentrations found in the rainwater at Wilrijk and Maasmechelen (Table 3-4) is in the same minimum-maximum range as that found at Peninsula Technikon (Table 3-6). All three sampling sites are thus close to residential as well as industrial areas. The values of cadmium, nickel and zinc are of the same magnitude and a little higher than the concentrations found in the rainwater sampled at Mechelen. The values for lead found at Peninsula Technikon, were lower with a mean value of 4,0μgl^{-1} and a maximum value of 14$\mu g\ l^{-1}$. The mean found at Wilrijk for lead was 47$\mu g\ l^{-1}$ and the maximum value 110$\mu g\ l^{-1}$. For the measurement of lead done in North Holland values of 1.3$\mu g\ l^{-1}$ were reported by Slanina, Mols, Board, Van der Cloot & Raaphorst, (1979: 161) which was more in agreement with the values found at Peninsula Technikon. On average the Cu concentration of the rainwater sampled at Peninsula Technikon was higher with a mean value of 25$\mu g\ l^{-1}$ and a maximum value of 114μg l^{-1}. The mean value for the rainwater concentration of Cu found at Wilrijk was 15μ l^{-1} and the maximum value 58μg l^{-1}.

The values for the rainwater concentrations reported by Hiraide et al, (1995: 334) was of the same magnitude as the values found at Peninsula Technikon, except copper, which is higher. Thus the values agree well except for lead which was lower and the copper concentration values which were higher.

3.4 Concentration variations of the metals in rainwater

The average concentration of the wet deposition for cadmium is 2,5ppb and the highest concentration 43ppb. Many of the points on the graph (Figure A-1 in the appendix) fall below this average. There seem to be two peaks. One of these occurs towards the end of May to middle June and the second peak from middle January to February. During the heavy rainfall season from June to November, the concentration of cadmium is very low.

The average concentration for cobalt was 1,28ppb and the maximum concentration 24,3ppb. There were two peaks: one large peak occurring towards the end of May and a smaller one in October–November (Figure A-3 in the appendix). For most of the samples analysed very little or no cobalt was found. The two peaks occurred outside the heavier rainfall period, which suggests a dilution factor during the rainfall months.

The average concentration for copper was 25ppb and the maximum concentration was 114ppb. There were two peaks. One peak occurred in April–May and the other smaller one in January–February. Between those peak the concentrations were low, falling mostly below the average value for copper (Figure A-5 in the appendix). This decrease in concentration coincides with the heavy rainfall period and is thus due to the dilution effect of the rain.

The average concentration of lead is 4ppb and the maximum concentration reported 14ppb. There seem to be a decrease in concentration during the heavy rainfall months, with many values falling below average (Figure A-7 in the appendix). The decrease in concentrations could be due to the dilution effect because of the rain. This trend is less marked than that of cadmium.

The average concentration for nickel was 2ppb and the maximum concentration was 30ppb. There are no peaks or troughs (Figure A-9 in the appendix). The concentrations seem to be mostly constant except for a few points of higher concentrations.

The average concentration for zinc is 54ppb and the highest concentration 426ppb. There were peaks in June, September and October (Figure A-11 in the appendix). The trough seemed to be the periods April–June, July–August and December–March. There is thus no clear trend emerging.

3.5 Concentration variations of the metals in dry deposition

The average dry deposition concentration of cadmium was 29,2ppb. This is about ten times higher than that of the wet deposition. Concentrations of up to 800ppb have been measured. From the graph (Figure A-2 in the appendix), two peaks could be distinguished. One peak was from the end of May to July, and the other from December to mid February. From middle October to middle November the concentrations also increased. During the heavy rainfall period of mid-July to mid October, little or no cadmium was detected. This can be due to the high rainfall during this period that causes a dilution effect.

The average concentration for cobalt was 2,18ppb and the maximum concentration was 310,8ppb. There were three peaks on the graph (Figure A-4 in the appendix). The largest of these occur from April - June and two small ones in August and in December. Between the peaks there were only a few times cobalt was detected. Thus throughout most of the year little or no cobalt was detected.

The average concentration for the dry deposition of copper was 0,54ppm and the maximum concentration was 5,50ppm (Figure A-6 in the appendix). There was a big peak in the June-July period. The concentration then rapidly decreased with most points falling below the average value. This decrease in concentration may be because of the dilution effect of the heavy rainfall period.

The average concentration of lead was 0,2ppm and the maximum concentration reported was 5,6ppm (Figure A-8 in the appendix). The graph showed troughs in April, mid June-July, September, December and January. These periods coincide with the Technikon's vacation period. The monitoring site is located close to the entrance gate of Peninsula Technikon. All vehicles entering or leaving the campus pass the monitoring site, as it is the only way to enter or exit the campus. The emissions of motor vehicle exhaust systems could therefore have contributed to the concentration of lead (Spiro & Stigliano, 1996: 315). For the dry deposition samples the rainfall did not noticeably affect the concentration of lead.

The average concentration for nickel was 0,267ppm and the maximum concentration recorded was 7,18ppm. There were two peak areas (Figure A-10 in the appendix). One was in April and the other in June. After June the concentrations decreased rapidly, with most the points below the average value. The decrease in concentration coincided with the heavy rainfall period, and may thus be due to the dilution effect of the rain.

The average value for the dry deposition value for zinc was 2,48ppm and a maximum value of 97,28ppm was recorded. The wet and dry deposition graphs are alike. For the dry deposition, there were peaks in the period May–June, August-September and February (Figure A-12 in the appendix). No clear trend emerged.

3.6 Variation of metal concentration due to meteorological factors influencing pollution.

Meteorological factors affect pollution. Even when the quantities of contaminants emitted into the atmosphere remain relatively steady for extended periods, there often occur wide variations in air quality from one day to the next. When pollution episodes occur, they are generally not as a result of a drastic output of pollutants; instead they occur because of changes in certain atmospheric conditions.

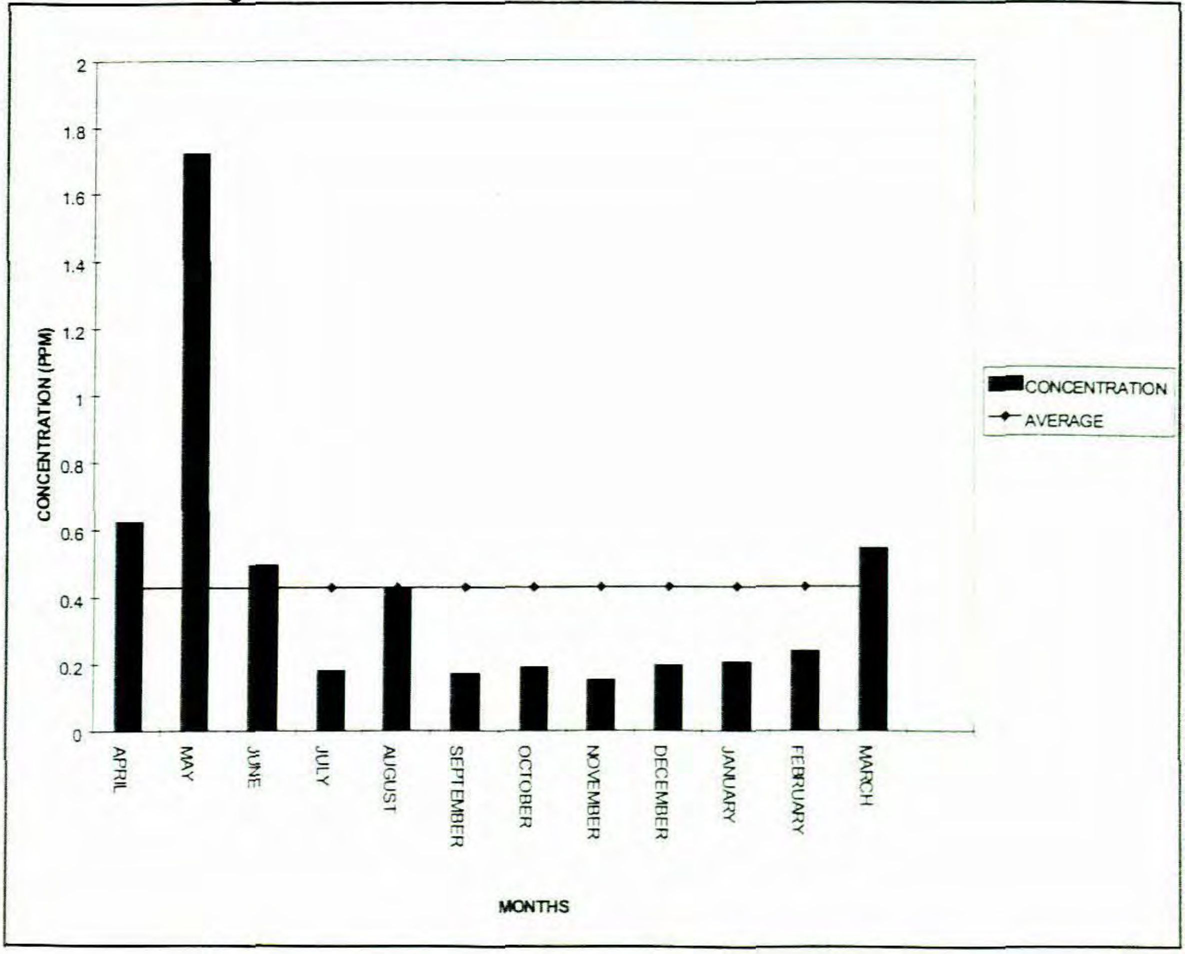
The annual distribution and trends of the metal concentration was compared, in the following section, with meteorological parameters, in order to establish interactions between the metals and climatic processes.

3.6.1 Monthly metal averages

The average monthly concentration of the metals, were given in Table A-1 for Dry Deposition and Table A-2 for Wet Deposition in the appendix. The monthly average concentration is represented graphically by the bar graphs in Figure 3-5 and Figure 3-6 below. For the dry deposition concentration, the concentrations of March, April, May and July were above the yearly average value. The total metal concentration was the highest for the month of May.

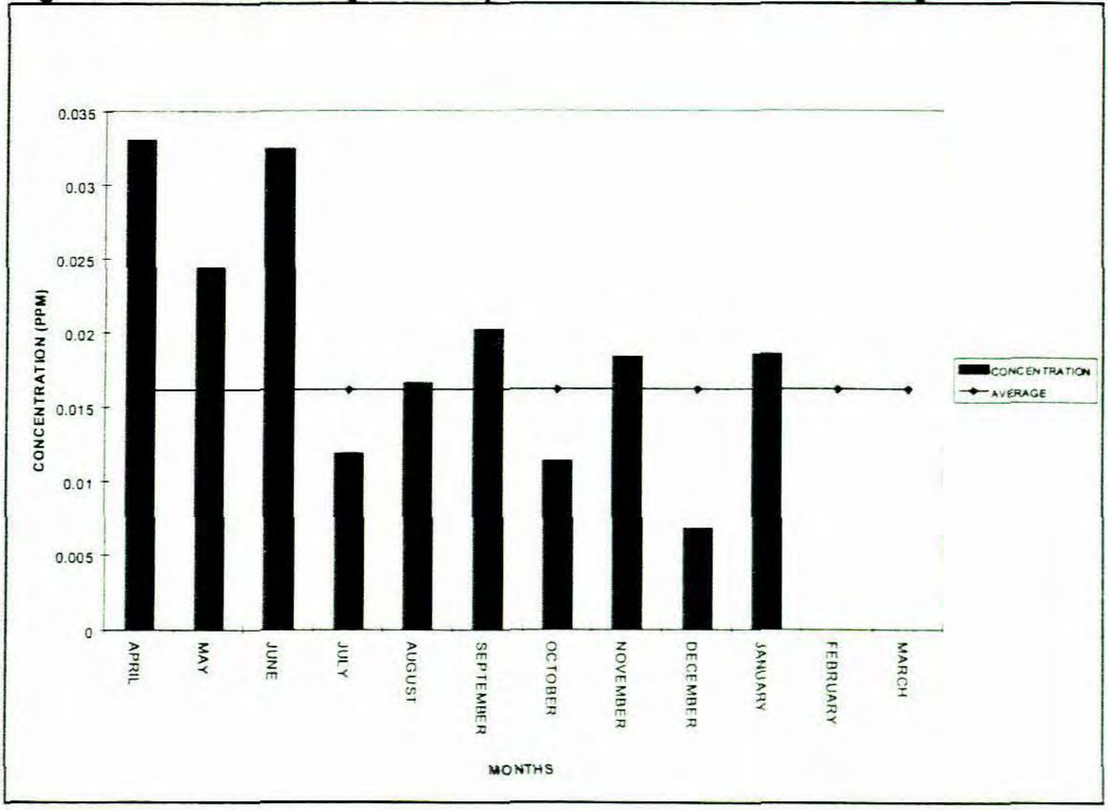
The average metal concentration for the dry deposition was 0,43 mg dm^{-3} and the highest total metal concentration in May was 1,7 mg dm^{-3}.

Figure 3-5: The average monthly dry deposition concentration in mg.dm^{-3}



The rainfall concentrations of July, October and December were below the yearly average (Figure 3-6). The total average metal concentration for the rainwater samples was 0,017mg dm^{-3}. The highest total metal concentration was in April with a value of 0,034mg dm^{-3}. The highest metal concentrations thus occur during the first half of the year and decrease from June to December as is shown in Figure 3-5 and Figure 3-6.

Figure 3-6: The average monthly rainwater concentration in $mg.dm^{-3}$

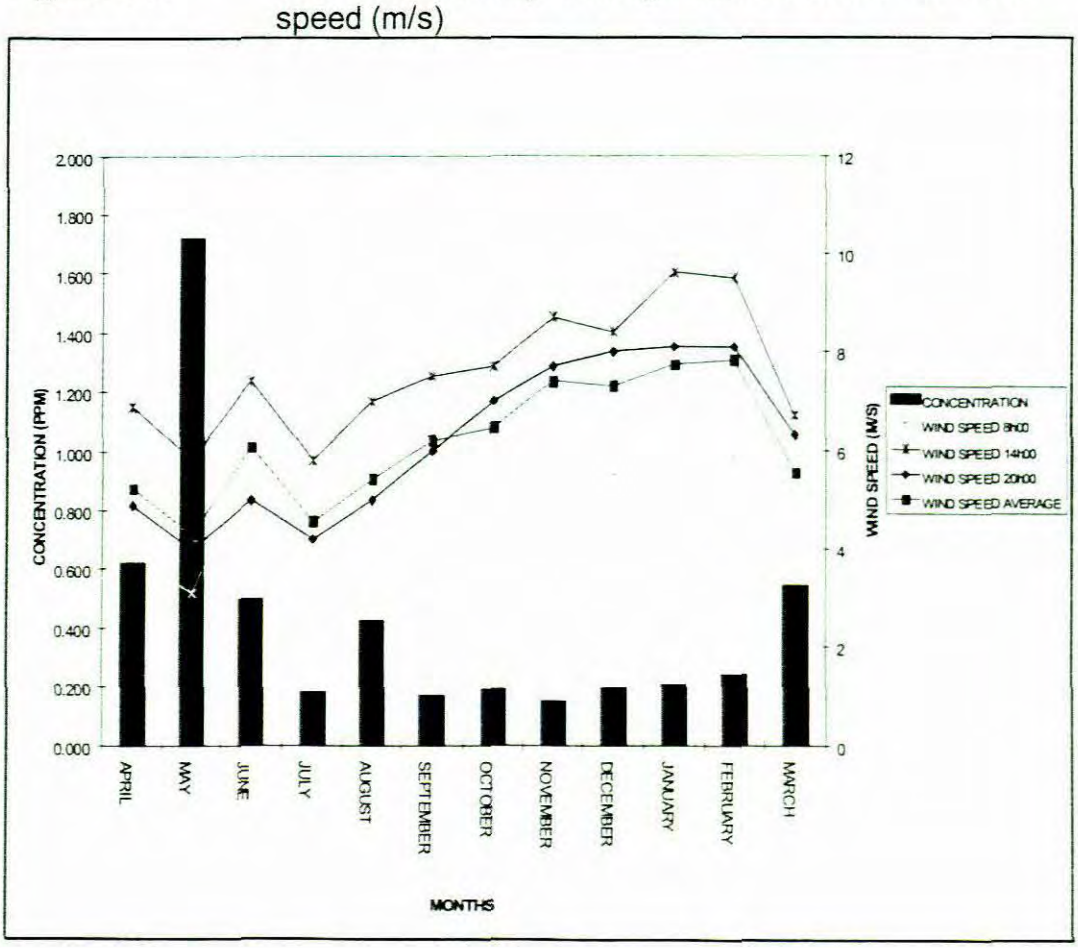


3.6.2 Wind speed

Wind strength is an important factor, which affects the dispersion of. pollutants. High wind speeds remove pollutants more rapidly away from the source and also cause the air to become more turbulent, thus diluting the pollutants with the surrounding air. This effect is illustrated in Figure 3-7 below where the concentration increased from March to

May with a corresponding decrease in wind speed. The converse is true for increasing wind speeds from July to February.

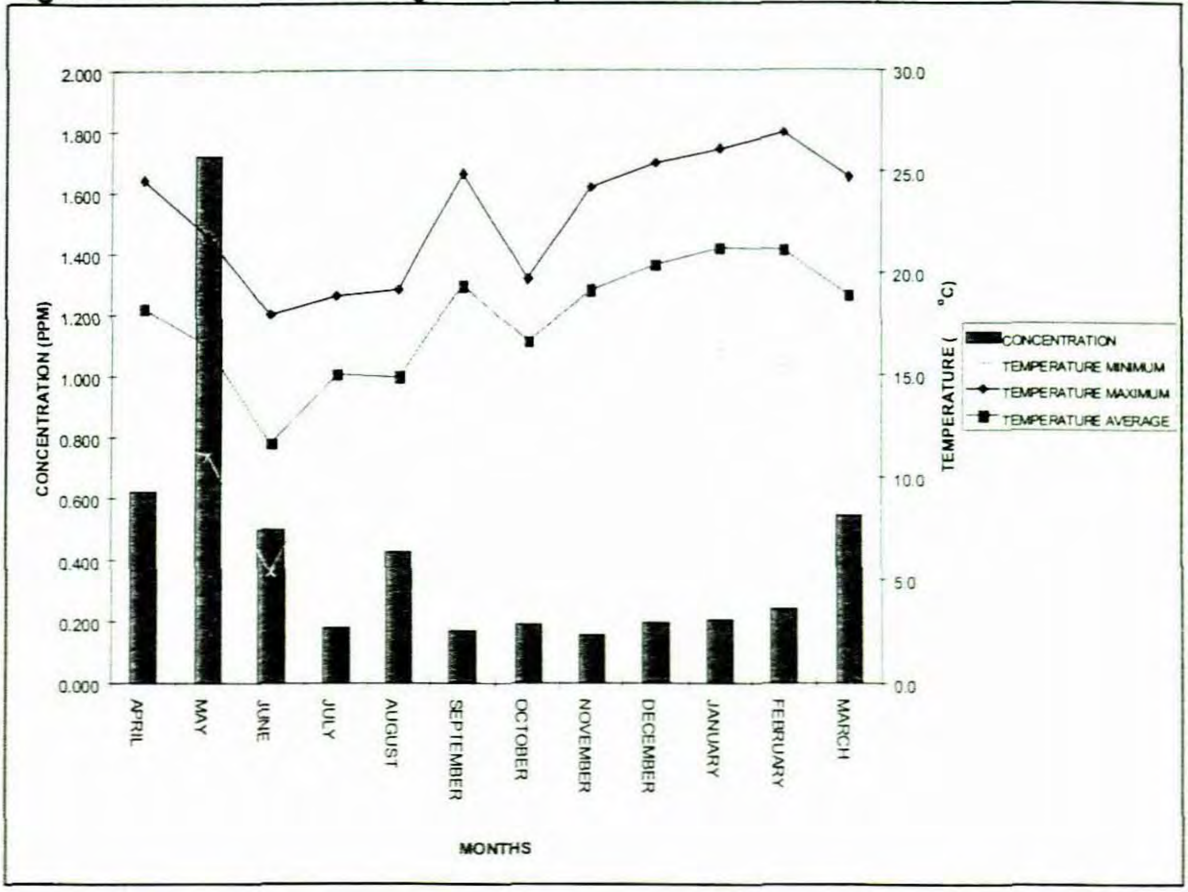
Figure 3-7: The total monthly average concentration vs wind speed (m/s)



3.6.3 Temperature and rainfall

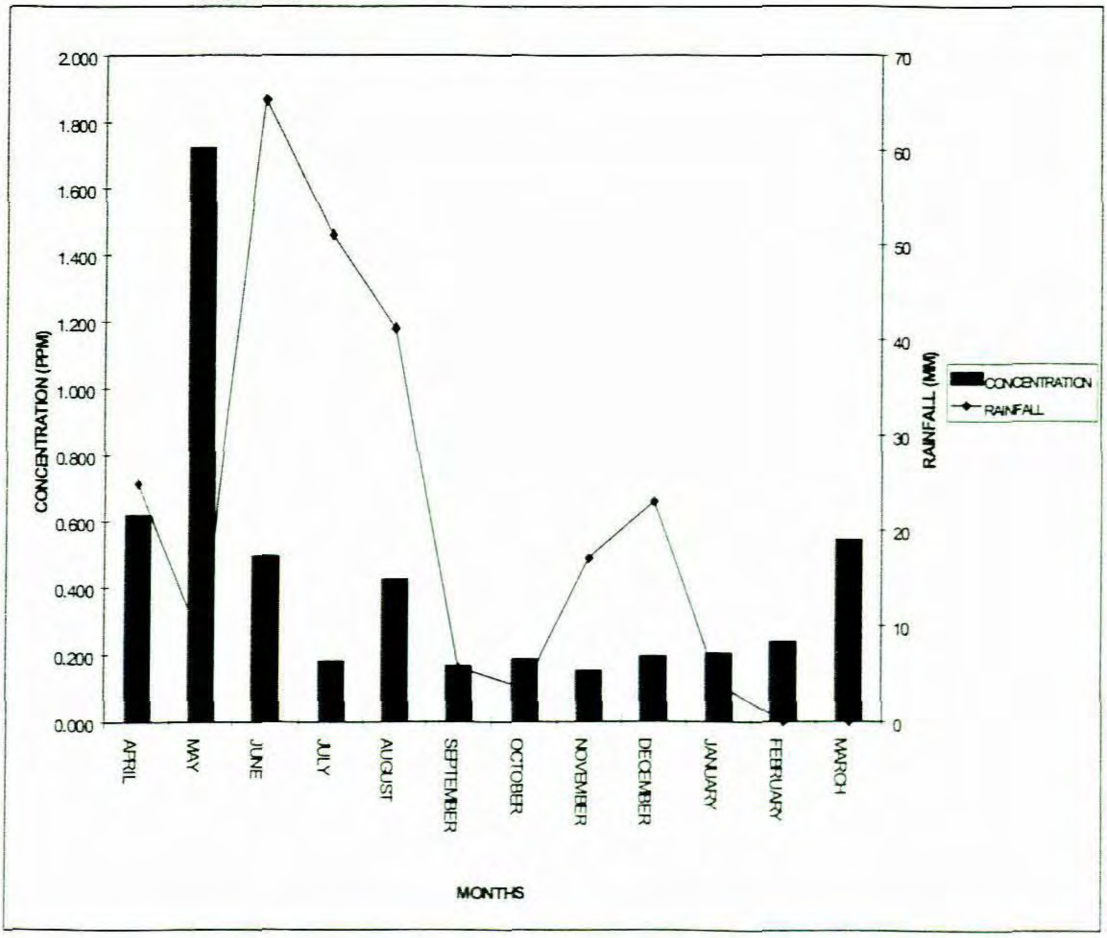
Generally, there was a decrease in concentration with an increase in temperature, from October to February, as is illustrated in Figure 3-8. Lower daytime temperature, and radiative heat loss during winter nights, combine to suppress trace metal conversion from particulate to gas phase. The increase in concentration with a decrease in temperature, as in the case of May, can be due to a temperature inversion, which occurred during the day.

Figure 3-8: The total average monthly concentration vs temperature



Rainfall results in pollutants being removed from the atmosphere. All the trace metals reached their maxima concentrations during the initial stages of the rainfall. During the months of higher rainfall the pollutants are lower. This is indicated from June to December in Figure 3-9.

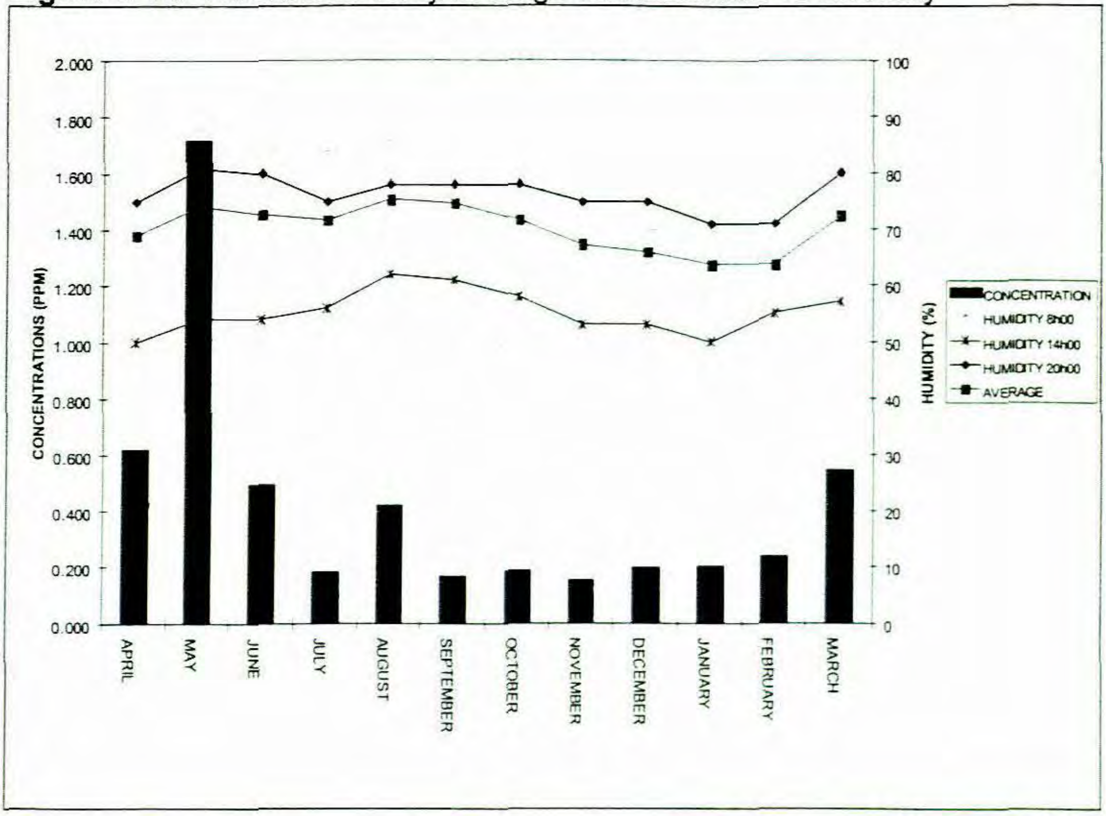
Figure 3-9: The average monthly concentration vs average monthly rainfall



3.6.4 Humidity

The relative humidity depends on the amount of water vapour required to saturate the air and is influenced by temperature. Generally a decrease in temperature increases the relative humidity, while an increase in temperature will result in a decrease in the relative humidity (Lutgens & Tarbuck, 1995:332).

Figure 3-10: The total monthly average concentration vs humidity



When the humidity is low, the concentration of suspended particulate pollutants increased. This accounts for the increase in pollutant concentration observed from March to June (in figure 3-10). August had the highest average humidity with a corresponding higher average metal concentration. High humidity also results in fog conditions, which can block solar heating of the ground surface, thus prolonging the life of inversion layers. Pollution concentration decreases from September to February as the relative humidity decreased, as is shown in Figure 3-10. The humidity can be expressed in several different ways. The values used in this study are relative humidity values expressed as percentages. The relative humidity is the ratio of the actual mixing ratio, to the saturation mixing ratio.

Weather conditions have a diluting effect on pollutants. When strong winds prevailed, there was a corresponding decrease in metal concentration. Rainwater also had a diluting effect. The highest metal concentrations were thus found in autumn and summer.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusion

In this study cadmium, cobalt, copper, lead, nickel, and zinc concentrations in rainwater and dry deposition were evaluated, based on one year of sampling. Analysis was done using ASV and adsorptive ACSV as an analytical tool. From these results certain trends emerged.

The trace metals showed strong seasonal dependence and manifested higher concentrations in the autumn/early winter months (March-July) than in the spring/summer period (September-February). Lead and zinc were the exceptions. The seasonal changes in trace metal concentrations were affected by the meteorological conditions. Concentrations of the trace metals were lowered by rainfall events with the exception of cobalt. In most wet deposition samples cobalt was detected, while none was found for most dry deposition samples. As rainfall can be a long-distance event, with its origin hundreds of kilometers away, the possibility exists that the cobalt can be from sources far away. Another reason might be that cobalt is only deposited during rainfall events and retained in the air at other times. The retention time of cobalt in air is unknown. The variation in metal pollutants with the meteorological data has emphasised the influence of meteorological factors such as wind speed, temperature and relative humidity in the cleansing of the atmosphere. The influence of climatic factors was treated on a qualitative basis therefore no quantitative mathematical model could be generated.

The intention of the study was to apply reliable sampling and to develop a suitable analytical technique for routine analysis of environmental samples especially rainwater. This was done in order to gain reliable and useful information on the behaviour of trace metals. It is important to study the effects of heavy metals in the atmosphere, hydrosphere and terrestrial ecosystems in order to gauge the effect on food, man and animals. The environmental burden caused by toxic heavy metals requires monitoring so that appropriate environmental protection regulations can be introduced.

Voltammetry was found to be suitable for routine analysis and monitoring of pollution levels in wet and dry analysis. Results of metal concentration in rainwater compared well with similar studies as is shown in the comparison done in this study. The metal concentrations were of the same magnitude. The exceptions were lead (the concentration was lower), and copper whose concentration was higher. A possible reason for the lower concentration of lead is that the lead adsorped on to the sample bottle during the storage period (Marr & Cresser, 1983: 35). It is thus important to do the analysis of lead immediately after sampling. The higher value for copper could be due to contamination although precautions were taken. These precautions include cleaning the electrodes thoroughly with acids and ensuring no carry over of metals between analysis runs. Blank samples were also routinely used to ensure that contamination was avoided.

For the dry deposition results, no suitable comparison could be found. The metal concentration evaluated in the dry deposition samples, were due to adsorption of these metals on dust particles. The particles that were looked at are relatively large (diameter greater than 10μm). These particles settle out under the influence of gravity within one or two days (Buell & Girard,1994: 409). This is important in order to pinpoint pollution point sources. However, this will involve a longer monitoring period as well as monitoring at a background site. A suitable computer model will also have to be used. Most studies involving atmospheric monitoring use filters and pumps. These studies thus look at finer particles. These fine particles may remain in the troposphere for several weeks or they can be transported considerable distances by wind.

Routine, reliable analysis of toxic heavy metals in rainwater is important. We must deepen our knowledge and understanding of toxic heavy metals and their role in the ecosystem.

4.2 Recommendations

Toxic trace metals in rainwater need to be carefully monitored on a regular long-term basis. Long term monitoring is necessary to establish pollution pathways and the role rainwater plays in the distribution of these metals. More sampling sites over a wider geographic region and over longer periods of time should be done. The results in this study could be statistically compared with studies done at other locations. This was outside the scope of the present study. This study was done in an industrial area so measurement at a background (non-industrial) area should also be looked at. There is also a need for the development of computer based models that can predict long-range transport, dispersion and associated impacts of pollution. It will also be able to identify point sources of pollution. This is important in order to determine pollution pathway from the source to man. If the levels prove to be exceptionally high, or continue to rise, action can then be taken. Speciation studies are also very important, as the toxicity of metals in their different oxidation states differs considerably.

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APPENDIX

Figure A-1

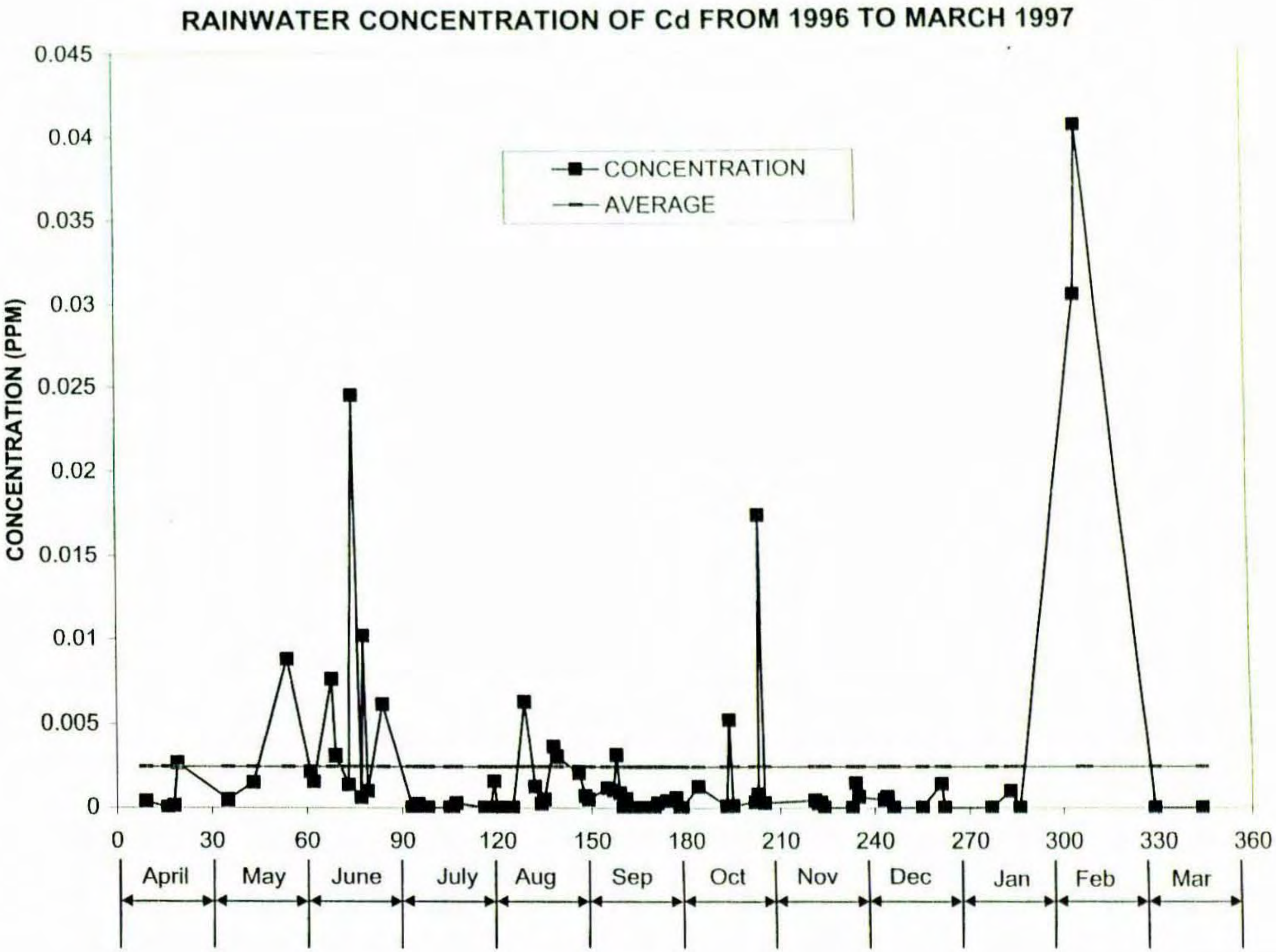
RAINWATER CONCENTRATION OF Cd FROM 1996 TO MARCH 1997
CONCENTRATION
AVERAGE
CONCENTRATION (PPM)
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
30
60
90
120
150
180
210
240
270
300
330
360
April
May
June
July
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar

Figure A-2

AVERAGE WEEKLY CONCENTRATION OF Cd FROM APRIL 1996 TO MARCH 1997

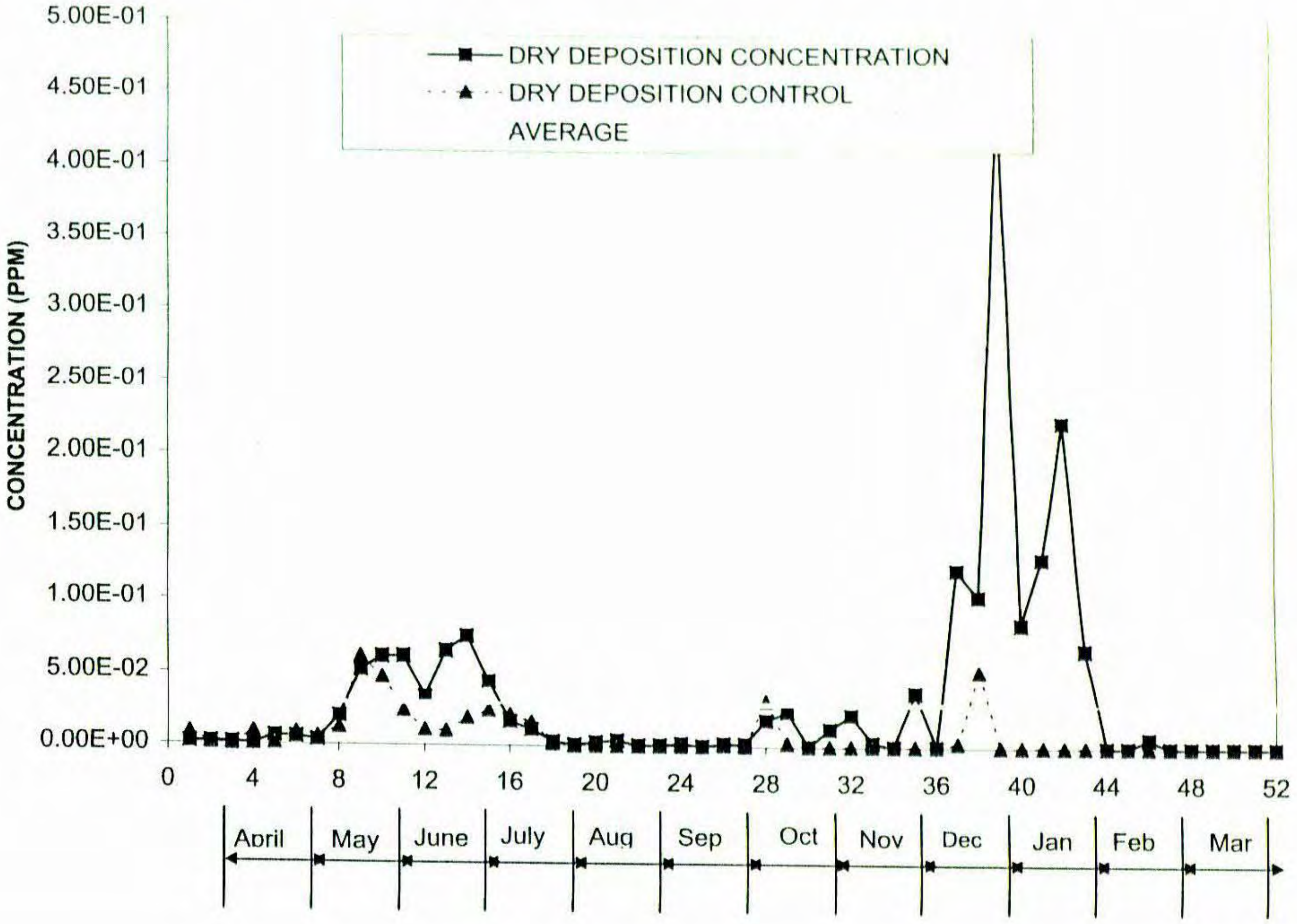

Figure A-3

Weekly average rainwater concentration of Co from April 1996-March 1997

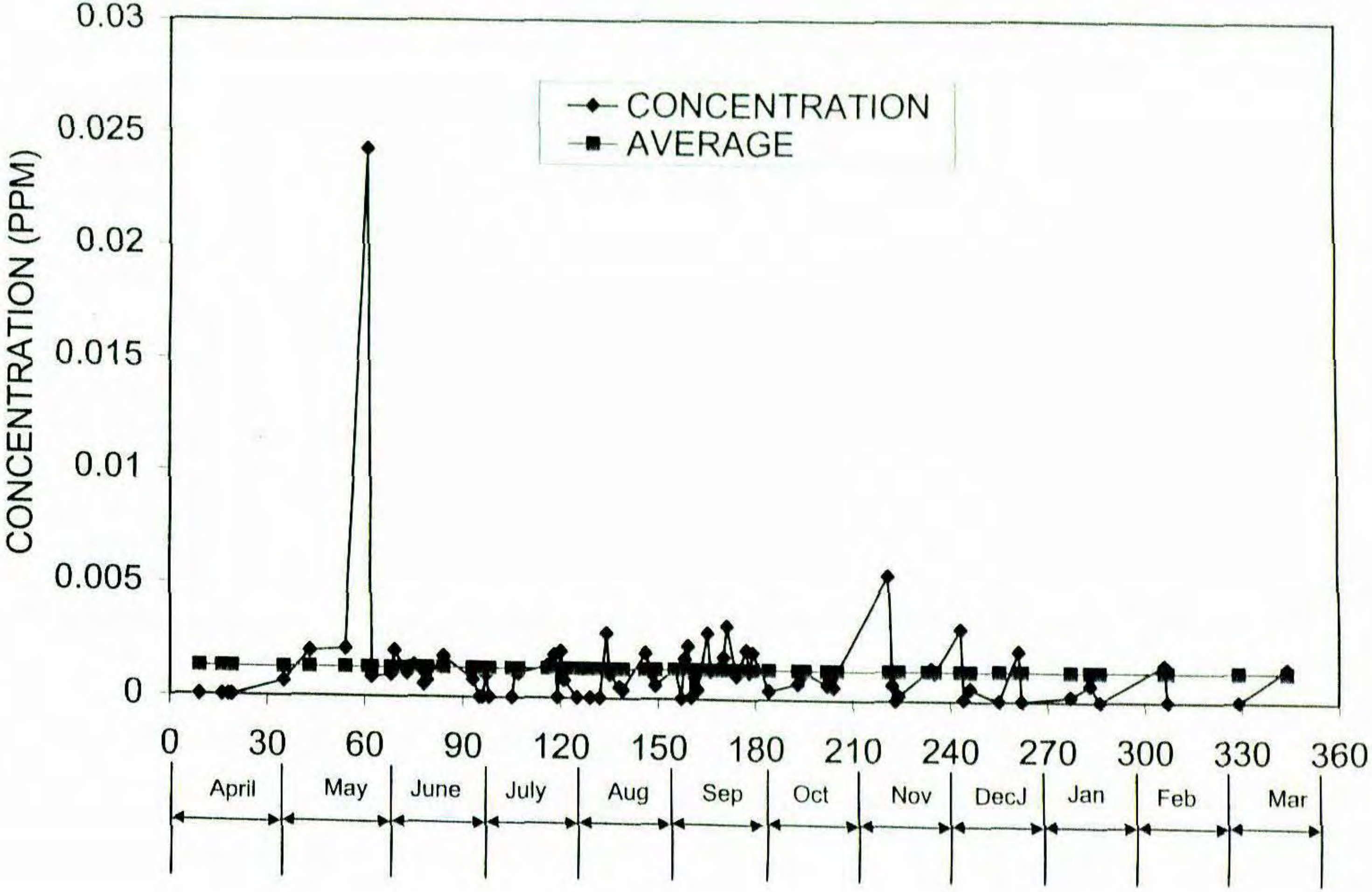

Figure A-4

WEEKLY AVERAGE CONCENTRATION OF Co FROM APRIL 1996 TO MARCH 1997

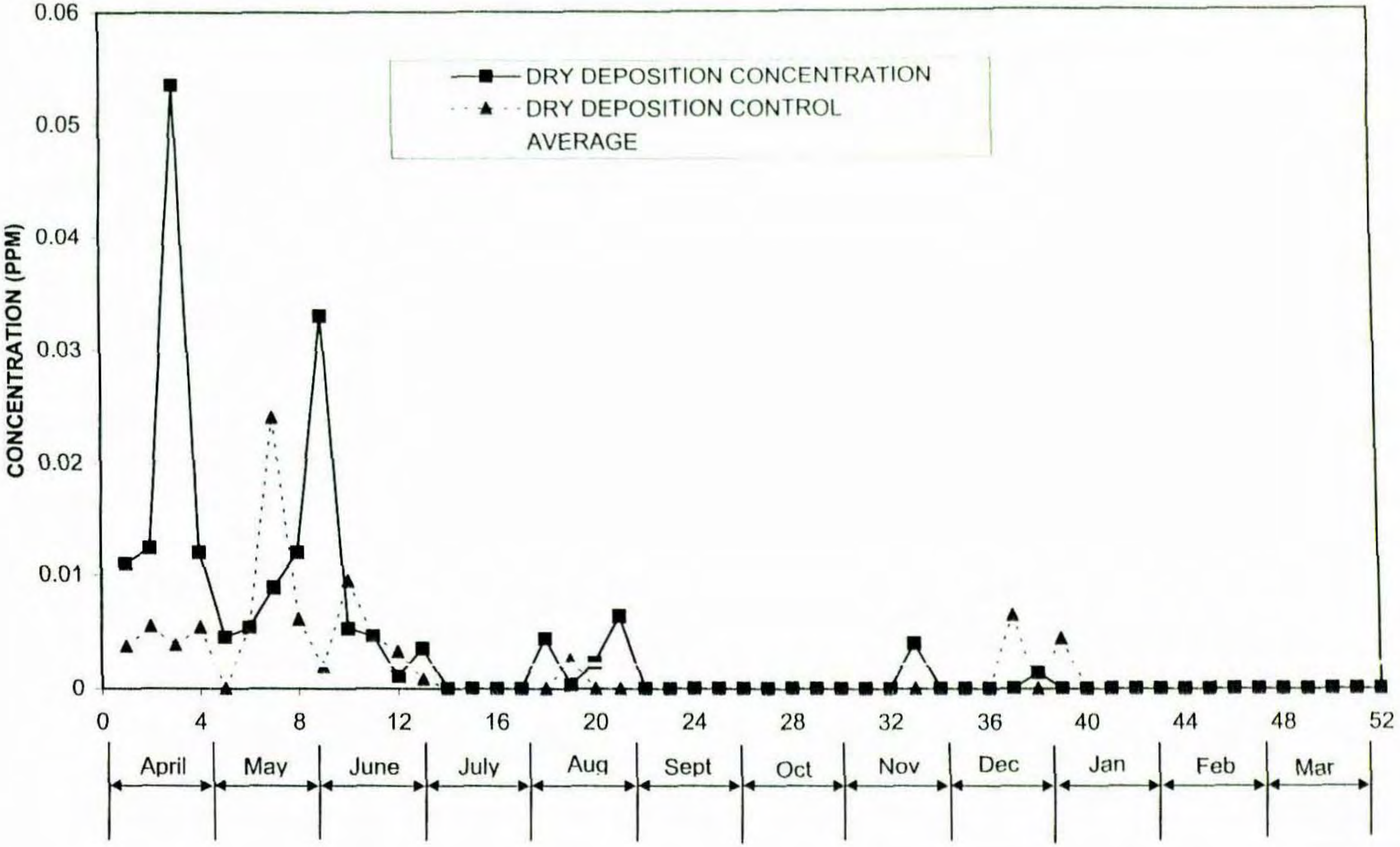

Figure A-5

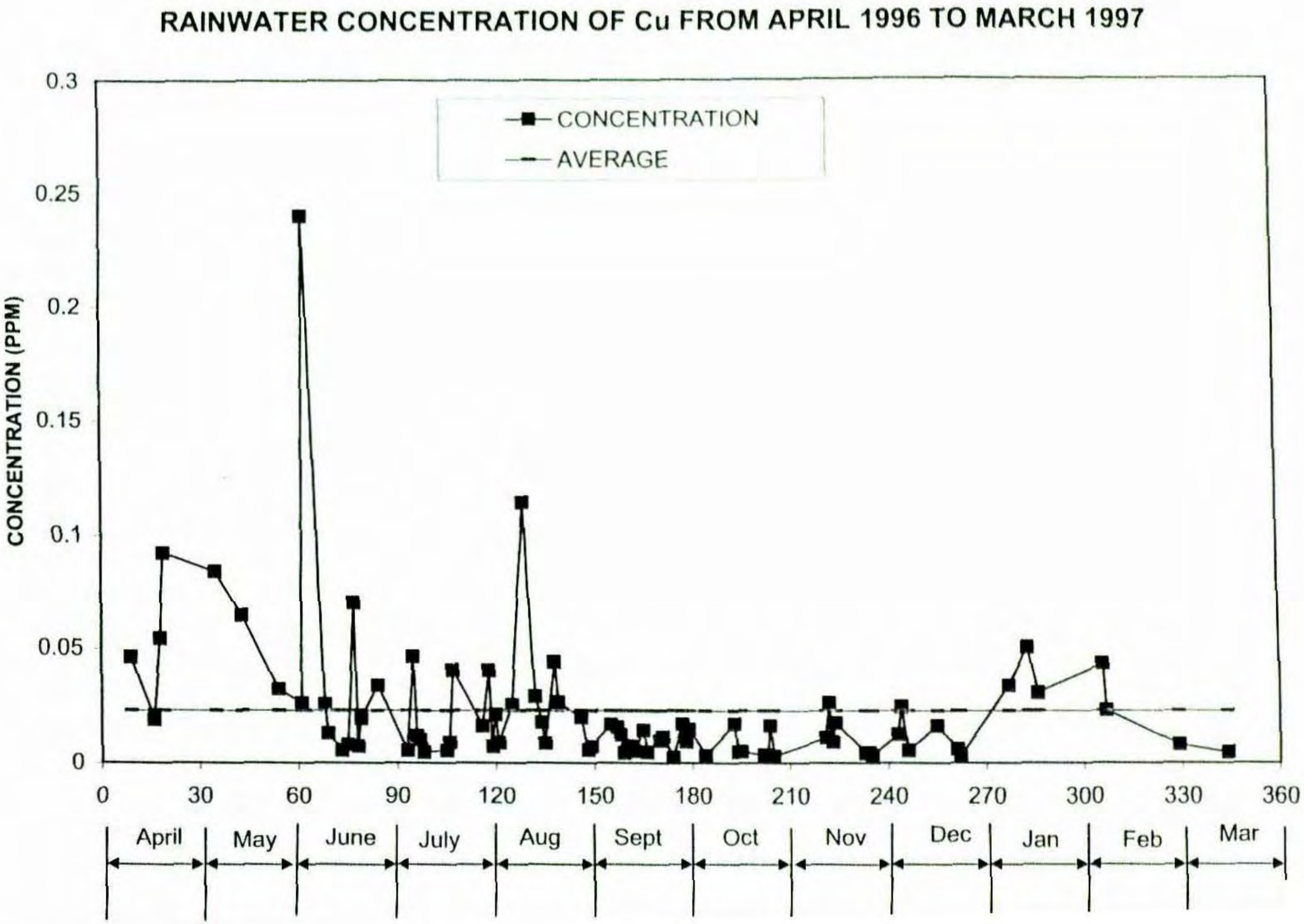
RAINWATER CONCENTRATION OF Cu FROM APRIL 1996 TO MARCH 1997
CONCENTRATION
AVERAGE
CONCENTRATION (PPM)
0.3
0.25
0.2
0.15
0.1
0.05
0
0
30
60
90
120
150
180
210
240
270
300
330
360
April
May
June
July
Aug
Sept
Oct
Nov
Dec
Jan
Feb
Mar

Figure A-6
WEEEKLY AVERAGE CONCENTRATION OF Cu FROM APRIL 1996 TO MARCH 1997

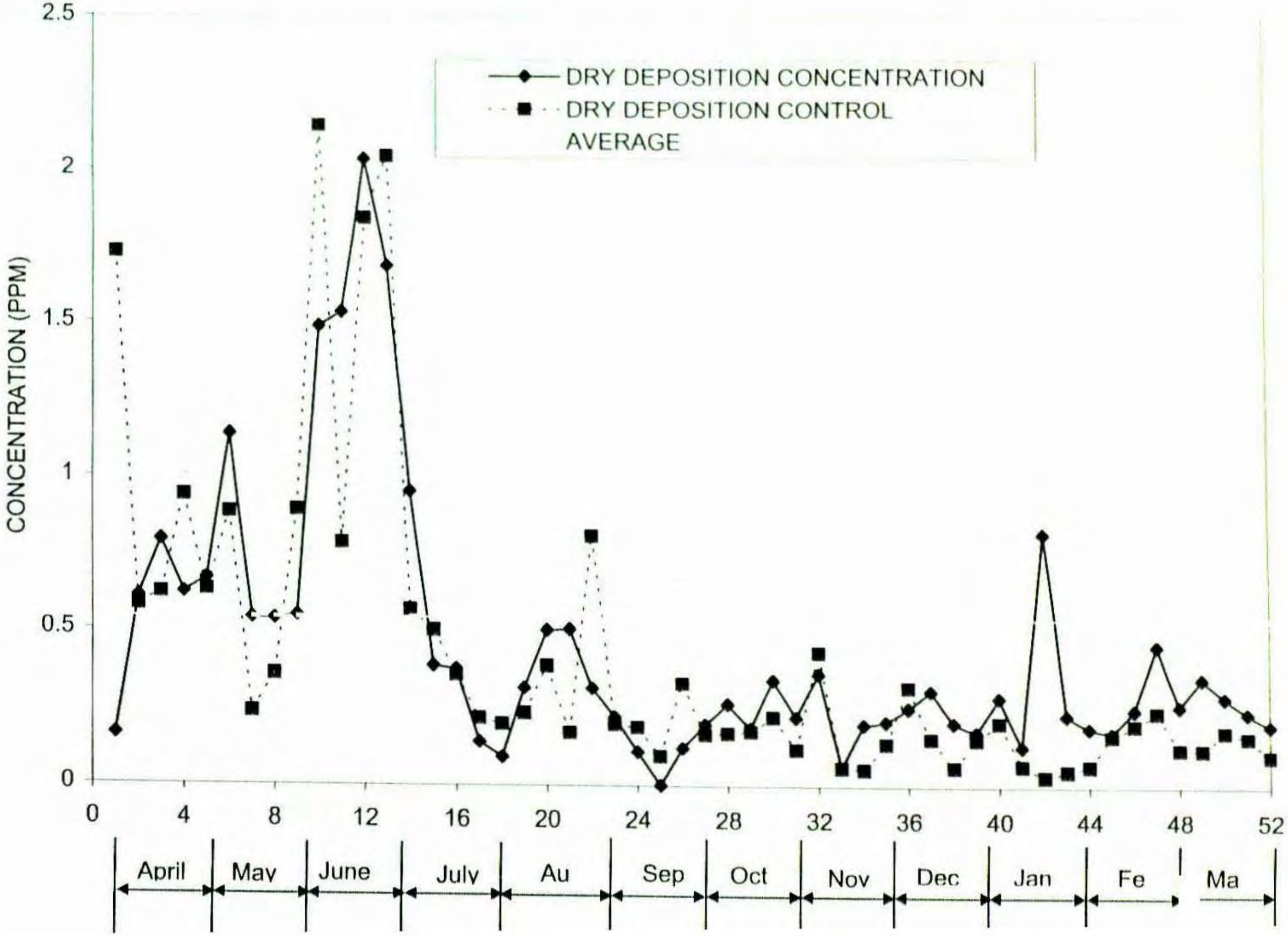

Figure A-7

RAINWATER CONCENTRATION OF Pb FROM APRIL 1996 TO MARCH 1997

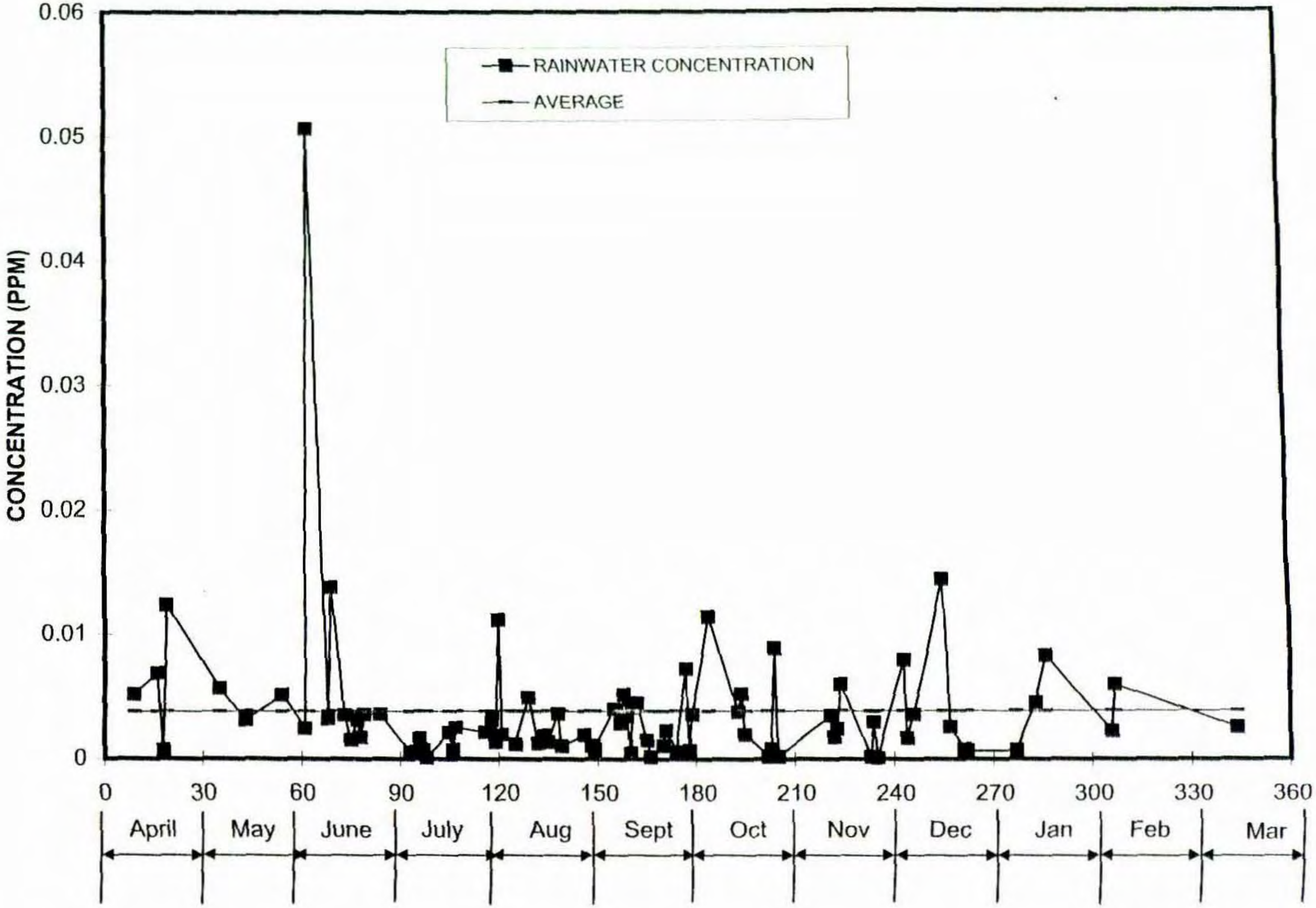

Figure A-8

WEEKLY AVERAGE CONCENTRATION OF Pb FROM APRIL 1996 TO MARCH 1997

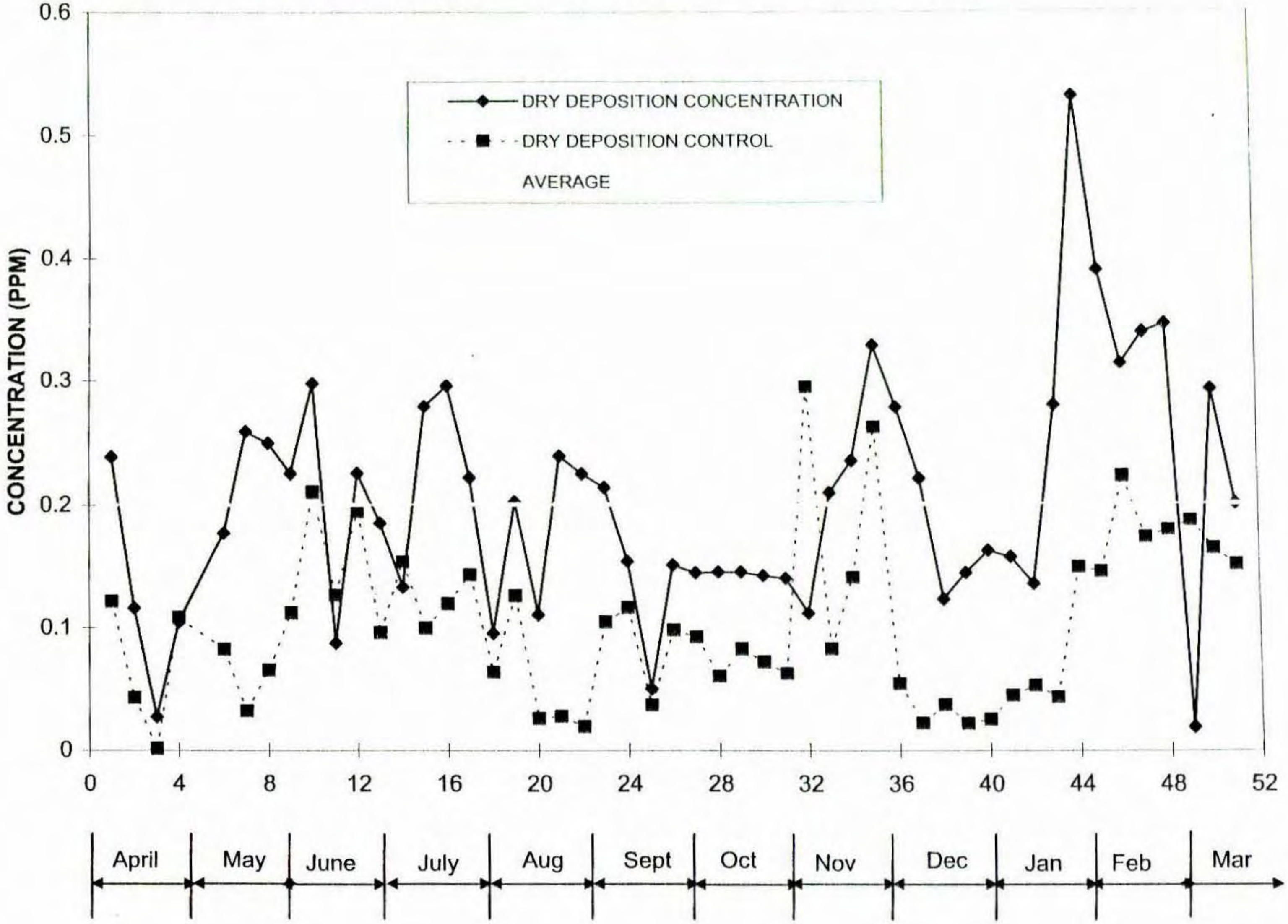

Figure A-9

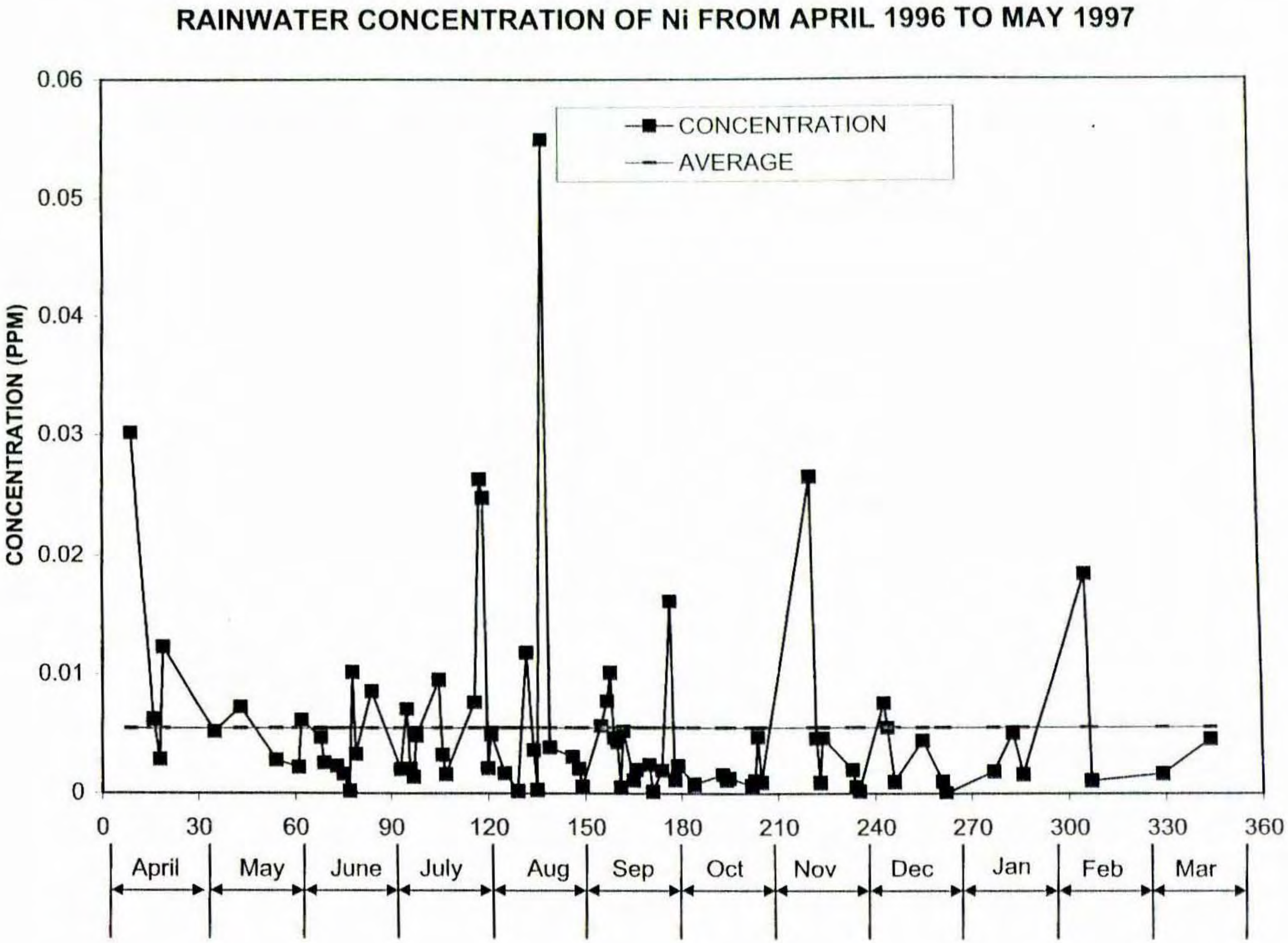
RAINWATER CONCENTRATION OF Ni FROM APRIL 1996 TO MAY 1997
CONCENTRATION
AVERAGE
CONCENTRATION (PPM)
0.06
0.05
0.04
0.03
0.02
0.01
0
0
30
60
90
120
150
180
210
240
270
300
330
360
April
May
June
July
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar

Figure A-10

AVERAGE WEEKLY CONCENTRATION OF Ni FROM ARRIL 1996 TO MARCH 1997

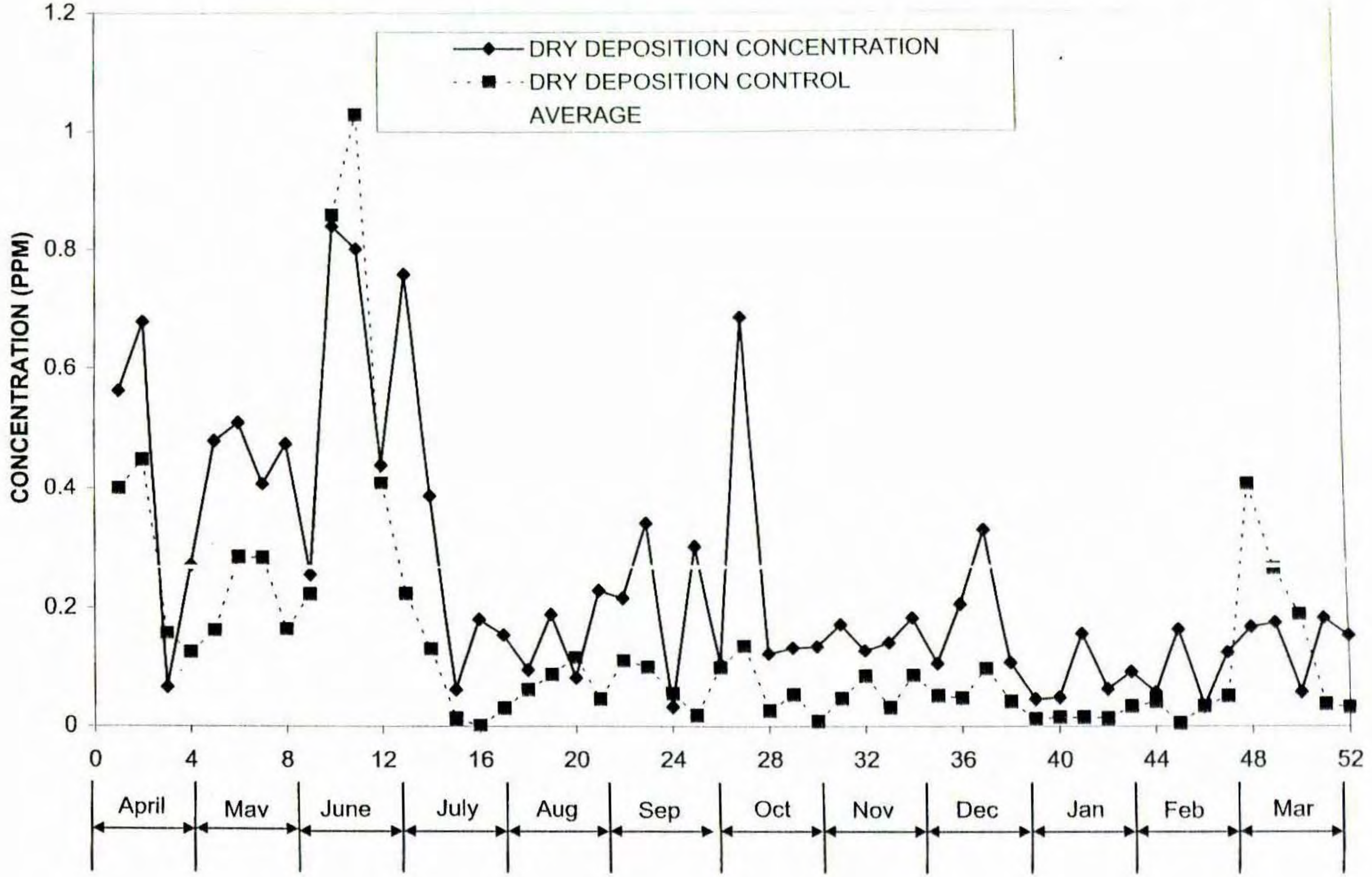

Figure A-11

RAINWATER CONCENTRATION OF Zn FROM APRIL 1996 TO MARCH 1997

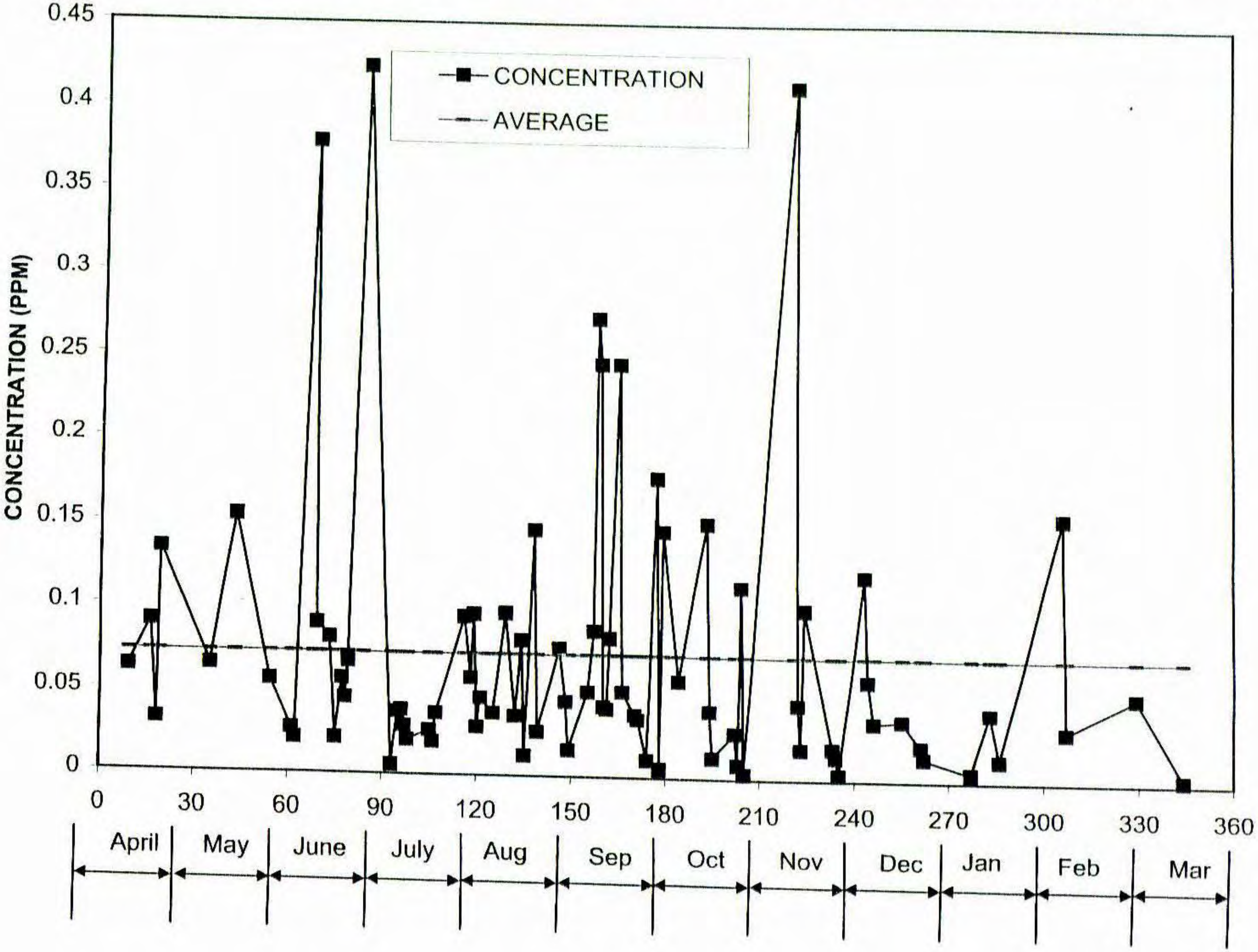

Figure A-12

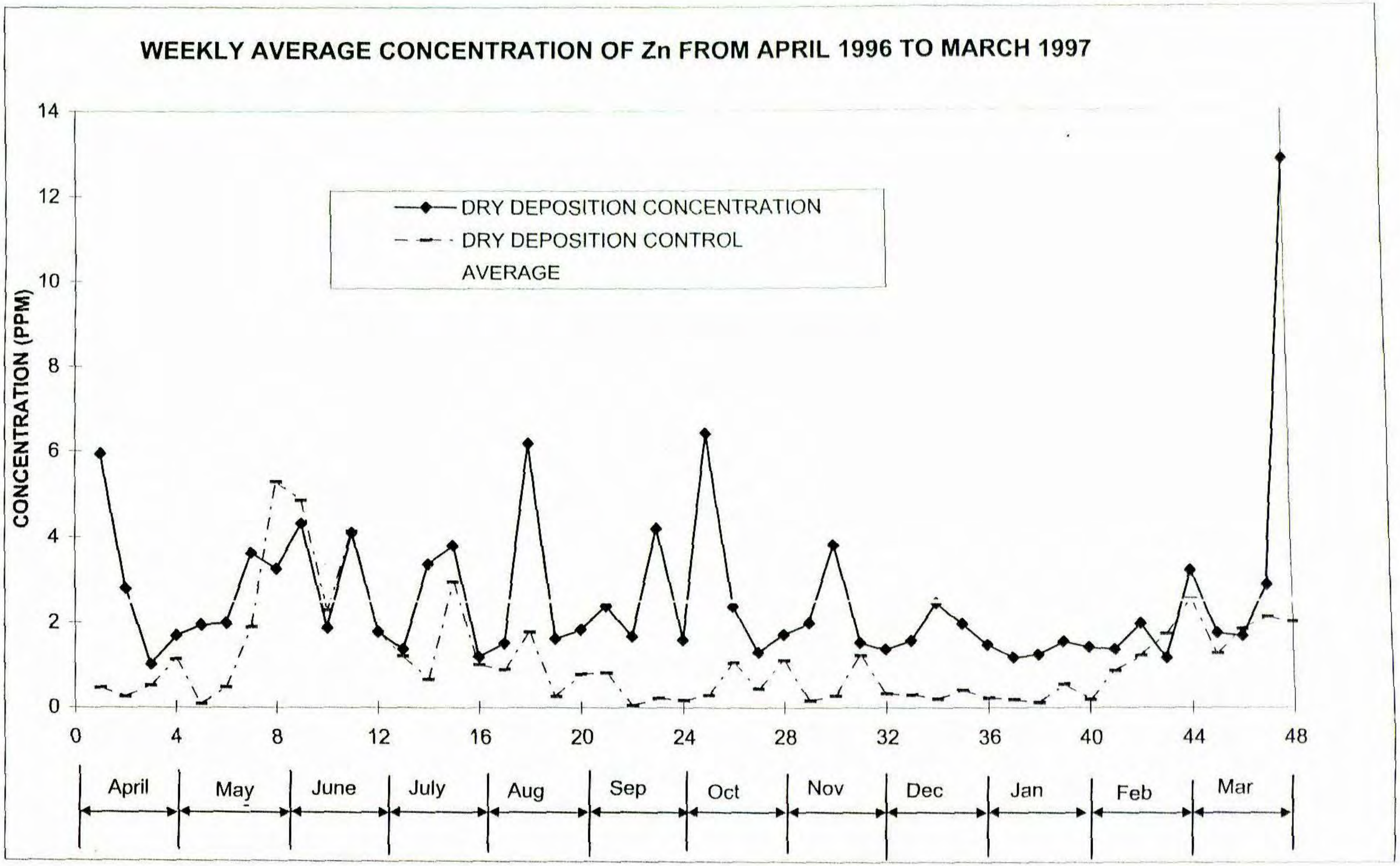
WEEKLY AVERAGE CONCENTRATION OF Zn FROM APRIL 1996 TO MARCH 1997
DRY DEPOSITION CONCENTRATION
DRY DEPOSITION CONTROL AVERAGE
CONCENTRATION (PPM)
0
2
4
6
8
10
12
14
0
4
8
12
16
20
24
28
32
36
40
44
48
April
May
June
July
Aug
Sep
Oct
Nov
Dec
Jan
Feb
Mar

Table A-1: Monthly averages in mg.dm^{-3} for dry deposition concentration

Month	Cu	Cd	Pb	Ni	Zn	Co	Total
April	0.493	1.83X10^{-3}	0.126	1.3	1.787	0.022	0.621
May	0.5	1.72X10^{-2}	0.397	0.306	9.097	0.0113	1.72
June	1.113	3.7X10^{-2}	0.111	0.62	1.087	0.003	0.495
July	0.122	2.04X10^{-2}	0.137	0.0107	0.794	0.003	0.181
August	0.247	1.66X10^{-3}	0.112	0.099	2.048	0.002	0.422
September	4.81X10^{-3}	2.35X10^{-4}	0.059	0.0022	0.777	6.5X10^{-4}	0.168
October	0.171	3.6X10^{-2}	0.101	0.087	0.73	2.2X10^{-4}	0.188
November	0.125	5.5X10^{-3}	0.22	0.0551	0.505	9.23X10^{-4}	0.152
December	0.172	7.05X10^{-2}	0.109	0.0605	0.855	1.34X10^{-4}	0.195
January	0.181	0.164	0.243	0.064	0.564	7.07X10^{-4}	0.203
February	0.146	2.4X10^{-3}	0.266	0.03	0.988	8X10^{-5}	0.238
March	0.300	1.3X10^{-3}	0.268	0.110	2.579	8.58X10^{-5}	0.543

Table A-2: Monthly average in mg dm^{-3} for the rainwater concentration

Month	Cu	Cd	Pb	Zn	Ni	Co	Total
April	0.0642	$1.05X10^{-3}$	$6.28X10^{-3}$	$7.98X10^{-2}$	$1.29X10^{-2}$	0	0.033
May	$5.17X10^{-2}$	$3.22X10^{-3}$	$4.10X10^{-3}$	$7.56X10^{-2}$	$4.33X10^{-3}$	$7.23X10^{-3}$	$2.44X10^{-2}$
June	$4.69X10^{-2}$	$6.22X10^{-3}$	$4.33X10^{-3}$	$1.32X10^{-1}$	$4.36X10^{-3}$	$1.15X10^{-3}$	$3.24X10^{-2}$
July	$1.84X10^{-2}$	$1.69X10^{-4}$	$1.53X10^{-3}$	$4.33X10^{-2}$	$7.19X10^{-3}$	$8.23X10^{-4}$	$1.19X10^{-2}$
August	$2.97X10^{-2}$	$1.81X10^{-3}$	$1.88X10^{-3}$	$5.74X10^{-3}$	$8.16X10^{-3}$	$7.72X10^{-4}$	$1.66X10^{-2}$
September	$9.93X10^{-3}$	$5.32X10^{-4}$	$2.75X10^{-3}$	$1.02X10^{-1}$	$4.30X10^{-3}$	$1.29X10^{-3}$	$2.02X10^{-2}$
October	$6.91X10^{-3}$	$2.53X10^{-3}$	$4.03X10^{-3}$	$5.19X10^{-2}$	$1.46X10^{-3}$	$8.24X10^{-4}$	$1.13X10^{-2}$
November	$1.25X10^{-2}$	$4.59X10^{-4}$	$2.91X10^{-3}$	$8.67X10^{-2}$	$5.76X10^{-3}$	$1.50X10^{-3}$	$1.83X10^{-2}$
December	$7.53X10^{-3}$	$3.51X10^{-4}$	$4.54X10^{-3}$	$2.59X10^{-2}$	$1.55X10^{-3}$	$6.83X10^{-4}$	$6.76X10^{-3}$
January	$3.96X10^{-2}$	$7.88X10^{-3}$	$3.90X10^{-3}$	$5.38X10^{-2}$	$5.75X10^{-3}$	$2.76X10^{-4}$	$1.85X10^{-2}$
February	-	-	-	-	-	-	-
March	-	-	-	-	-	-	-

Table A-3: Wind speed values in m/s

Month	8h00	14h00	20h00	Average
April	3.9	6.9	4.9	5.2
May	3.1	5.8	4.0	4.3
June	5.8	7.4	5.0	6.1
July	3.7	5.8	4.2	4.6
August	4.3	7.0	5.0	5.4
September	5.1	7.5	6.0	6.2
October	4.7	7.7	7.0	6.1
November	5.8	8.7	7.7	7.4
December	5.5	8.4	8.0	7.3
January	5.5	9.6	8.1	7.7
February	5.9	9.5	8.1	7.8
March	3.6	6.7	6.3	5.5

Table A-4: Temperature and rainfall

	Temperature (°C)		**Rainfall**
Month	**Minimum**	**Maximum**	**(mm)**
April	12.0	24.6	25.00
May	10.7	21.8	8.20
June	5.4	18.0	65.20
July	11.3	18.9	51.00
August	10.7	19.2	41.20
September	13.9	24.9	5.70
October	13.6	19.7	3.56
November	14.1	24.2	17.00
December	15.4	24.4	23.00
January	16.3	26.1	4.00
February	15.4	29.9	0
March	13.1	24.7	0

Table 3-5: Humidity values

	Humidity (%)			
Month	**8h00**	**14h00**	**20h00**	**Average**
April	82	50	84	48
May	88	54	88	52
June	84	54	84	54
July	84	56	86	55
August	86	62	87	62
September	85	61	88	60
October	79	58	81	58
November	74	53	85	53
December	70	53	89	50
January	70	50	76	48
February	65	55	87	51
March	80	57	87	57

Table A-6: Concentrations (ppm) of dry deposition samples for April 1996

CONCENTRATION (PPM) OF DRY DEPOSITION FOR APRIL 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	2.29E-02	6.59E-01	8.06E-01	6.52E+00	7.18E+00	0.00E+00
	2	0.00E+00	5.51E-01	2.85E-01	1.05E+00	3.14E+00	0.00E+00
	3	5.85E-03	2.40E-01	2.94E-01	3.47E+00	1.20E+00	0.00E+00
	6	9.48E-03	7.81E-01	2.70E-01	1.66E+01	1.13E+01	5.47E-02
	7	3.02E-03	4.94E-01	1.01E-01	2.50E+00	5.61E-01	0.00E+00
	8	7.24E-03	1.33E+00	1.05E-01	2.53E+00	1.32E+00	0.00E+00
RAIN	***9***	***3.66E-04***	***4.61E-02***	***5.22E-03***	***6.33E-02***	***3.01E-02***	***0.00E+00***
	10	0.00E+00	2.37E-01	7.12E-02	9.30E-01	2.04E+00	0.00E+00
	11	0.00E+00	1.08E+00	2.20E-01	7.92E-01	7.51E-01	0.00E+00
	12	0.00E+00	7.53E-02	9.77E-02	3.03E+00	3.72E-01	0.00E+00
	13	0.00E+00	3.06E-01	8.28E-02	5.32E-01	2.63E-01	6.22E-02
RAIN	***16***	***0.00E+00***	***1.90E-02***	***6.91E-03***	***9.02E-02***	***6.28E-03***	***0.00E+00***
RAIN	***18***	***1.18E-04***	***5.43E-02***	***7.12E-04***	***3.19E-02***	***2.80E-03***	***0.00E+00***
RAIN	***19***	***2.66E-03***	***9.23E-02***	***1.23E-02***	***1.34E-01***	***1.22E-02***	***0.00E+00***
	20	2.15E-03	1.20E+00	2.76E-03	6.67E-03	1.63E-02	7.65E-02
	21	0.00E+00	3.90E-01	2.50E-02	1.02E+00	1.13E-01	3.05E-02
	22	0.00E+00	8.39E-01	5.30E-02	3.15E-01	9.79E-01	2.52E-02
	23	1.16E-03	4.71E-01	5.95E-02	1.15E+00	1.44E-01	9.12E-02
	24	9.43E-05	1.38E-01	9.28E-02	2.99E-01	1.92E-01	4.04E-02
	25	0.00E+00	2.72E-01	9.33E-02	1.67E+00	7.83E-02	1.53E-02
	26	0.00E+00	8.01E-01	1.30E-01	2.46E+00	2.09E-01	8.29E-02
	27	0.00E+00	1.18E+00	9.57E-02	1.82E+00	2.40E-01	1.76E-01
	28	0.00E+00	6.36E-01	7.76E-02	1.39E+00	4.46E-02	0.00E+00
	29	0.00E+00	9.51E-01	1.81E-01	8.63E-01	3.07E+00	0.00E+00
	30	0.00E+00	5.13E-01	2.12E-01	1.71E+00	1.29E+00	0.00E+00
	29	0.00E+00	9.51E-01	1.81E-01	8.63E-01	3.07E+00	0.00E+00
	30	0.00E+00	5.13E-01	2.12E-01	1.71E+00	1.29E+00	0.00E+00

Table A-7: Concentrations(ppm) of dry deposition control samples for April 1996

CONCENTRATION(PPM) OF DRY DEPOSITION CONTROL FOR APRIL 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	9.73E-02	6.45E-01	3.63E+00	5.54E-01	7.93E-03
	2	0.00E+00	6.53E-01	1.50E-01	3.41E-01	6.24E-01	0.00E+00
	3	1.54E-02	9.88E-01	1.95E-01	7.31E-01	4.39E+00	6.22E-03
	6	0.00E+00	6.34E-01	7.32E-02	6.10E-01	4.68E-01	0.00E+00
	7	2.55E-02	1.77E+00	6.66E-02	1.91E-01	4.00E-01	4.79E-03
	8	1.01E-02	7.36E-01	7.94E-02	2.65E-01	8.08E-01	4.40E-03
	9	0.00E+00	1.08E+00	2.40E-01	2.50E-01	1.35E+00	9.96E-03
	10	0.00E+00	4.36E-01	1.57E-02	1.89E-01	4.13E-01	4.58E-03
	11	2.50E-02	7.03E-01	3.53E-02	4.16E-01	2.86E-01	7.34E-03
	12	0.00E+00	6.58E-01	2.31E-02	2.48E-01	2.60E-01	5.19E-03
	13	0.00E+00	3.69E-01	6.19E-02	5.61E-01	4.32E-01	6.55E-03
	16	4.88E-03	6.81E-02	9.65E-02	4.66E-01	1.51E-01	6.98E-03
	18	2.29E-03	2.24E-01	2.24E-01	2.61E+00	2.69E-01	7.04E-03
	19	1.21E-02	2.90E-01	4.55E-02	7.94E-01	1.89E-01	2.94E-03
	20	0.00E+00	2.46E-01	3.50E-02	8.10E-02	9.77E-02	2.73E-03
	21	0.00E+00	9.99E-01	5.16E-02	5.16E-01	2.17E-01	5.02E-03
	22	0.00E+00	6.10E-01	2.05E-02	2.50E-01	1.57E-01	6.79E-04
	23	2.82E-02	2.01E-01	3.84E-02	6.86E-01	1.42E-01	5.46E-03
	24	3.41E-02	1.41E+00	1.85E-01	1.79E-01	1.03E-01	5.91E-03
	25	0.00E+00	1.24E+00	1.32E-01	1.24E+00	1.06E-01	7.27E-03
	26	0.00E+00	8.28E-01	9.66E-02	1.09E+00	7.99E-02	9.71E-03
	27	0.00E+00	1.05E+00	5.91E-02	1.05E+00	1.17E-01	2.11E-03
	28	0.00E+00	1.23E+00	9.61E-02	1.67E+00	1.69E-01	7.07E-03
	29	0.00E+00	8.23E-01	1.49E-01	5.64E+00	1.81E-01	6.29E-03
	30	0.00E+00	4.94E-01	3.11E-02	2.67E+00	1.06E-01	6.41E-03

Table A-8: Concentrations (ppm) of dry deposition samples for May 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR MAY 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	9.97E-03	8.76E-01	1.80E-01	2.72E+00	1.27E-01	1.17E-02
	2	0.00E+00	2.80E-01	1.36E-01	1.56E+00	3.06E-01	2.90E-03
	3	2.52E-02	4.40E-01	1.95E-01	2.20E+00	3.98E-01	5.26E-03
	4	0.00E+00	9.49E-01	1.61E-01	1.54E+00	3.65E-01	7.83E-03
RAIN	***5***	***4.66E-04***	***8.40E-02***	***5.71E-03***	***6.52E-02***	***5.18E-03***	***6.29E-04***
	6	1.61E-02	1.90E+00	5.70E+00	1.12E+02	1.26E+00	0.00E+00
	8	3.94E-03	6.51E-01	2.40E-01	2.26E+00	3.04E-01	5.84E-03
	9	1.30E-03	9.24E-01	2.76E-01	1.70E+00	8.93E-02	4.48E-03
	10	7.65E-03	6.82E-01	9.72E-01	9.73E+01	5.45E-01	0.00E+00
	11	4.28E-03	4.27E-01	1.45E-01	1.88E+00	5.19E-01	6.11E-03
	12	0.00E+00	1.05E+00	7.68E-01	7.88E+00	3.73E-01	1.17E-02
RAIN	***13***	***1.50E-03***	***6.45E-02***	***3.11E-03***	***1.54E-01***	***7.25E-03***	***1.97E-03***
	14	2.42E-03	4.96E-01	2.30E-01	1.40E+00	4.97E-01	8.06E-03
	15	6.74E-03	8.76E-01	2.44E-01	3.90E+00	3.50E-01	1.00E-02
	16	3.66E-03	1.17E-01	1.22E-01	3.26E+00	3.52E-01	8.74E-03
	18	0.00E+00	8.37E-01	2.77E-01	2.50E+00	3.10E-01	1.04E-02
	19	3.91E-02	3.66E-01	1.21E-01	2.66E+00	5.18E-01	7.25E-03
	20	9.59E-03	1.10E+00	3.45E-01	4.36E+00	5.63E-01	2.18E-02
	21	1.27E-02	4.48E-01	1.75E-01	2.62E+00	4.65E-01	8.09E-03
	23	0.00E+00	4.29E-01	3.00E-01	1.43E+00	3.01E-01	9.37E-03
RAIN	***24***	***8.77E-03***	***3.23E-02***	***5.18E-03***	***5.65E-02***	***2.74E-03***	***2.08E-03***
	25	7.19E-02	1.69E-01	1.69E-01	2.72E+00	2.43E-01	7.18E-03
	26	9.82E-02	4.30E-01	2.08E-01	8.28E-01	6.21E-01	9.74E-03
	27	2.78E-02	5.32E-01	1.72E-01	1.33E-01	1.79E-01	9.67E-03
	28	6.09E-02	4.94E-01	5.23E-01	1.59E+01	3.20E-01	1.38E-01
	29	4.37E-02	5.48E-01	1.80E-01	1.72E+00	2.35E-01	5.07E-03
	30	7.49E-02	3.13E-01	4.02E-01	6.88E+00	2.38E-01	1.14E-02
RAIN	***31***	***2.15E-03***	***2.60E-02***	***2.42E-03***	***2.66E-02***	***2.15E-03***	***2.42E-02***

Table A-10: Concentrations(ppm) of dry deposition samples for June 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR JUNE 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
RAIN	***1***	***1.53E-03***	***2.40E-01***	***5.06E-03***	***2.08E-02***	***6.15E-03***	***8.27E-04***
	2	3.42E-02	8.40E-01	1.34E-01	8.28E-01	2.99E-01	0.00E+00
	3	5.64E-03	0.00E+00	3.68E-01	2.35E+00	0.00E+00	0.00E+00
	4	6.12E-03	3.03E+00	1.31E-01	1.21E+00	6.01E+00	0.00E+00
	5	2.73E-02	1.99E+00	4.57E-03	7.65E-01	1.26E+00	0.00E+00
	6	6.71E-02	1.08E+00	4.24E-01	2.06E+00	1.35E+00	2.70E-02
RAIN	***7***	***7.61E-03***	***2.55E-02***	***3.22E-03***	***3.78E-01***	***4.62E-03***	***9.37E-04***
RAIN	***8***	**3.09E-03**	**1.29E-02**	**1.37E-02**	**8.99E-02**	**2.51E-03**	**2.01E-03**
	9	1.99E-01	1.32E+00	1.10E-01	7.19E-02	7.40E-01	0.00E+00
	10	8.41E-02	9.51E-01	1.02E-01	5.36E+00	1.23E+00	4.48E-03
	11	8.61E-02	2.85E+00	3.19E-01	2.80E+00	1.04E+00	9.58E-03
RAIN	***12***	***1.35E-03***	***5.44E-03***	***3.52E-03***	***8.16E-02***	***2.24E-03***	***1.00E-03***
	13	1.38E-02	7.91E-01	1.30E-01	3.70E-01	1.30E-01	0.00E+00
RAIN	***14***	***2.45E-02***	***7.90E-03***	***1.51E-03***	***2.10E-02***	***1.58E-03***	***1.38E-03***
RAIN	***16***	***5.96E-04***	***6.99E-02***	***3.09E-03***	***5.75E-02***	***1.74E-04***	***1.19E-03***
RAIN	***17***	***1.02E-02***	***7.14E-03***	***1.73E-03***	***4.58E-02***	***1.02E-02***	***5.28E-04***
RAIN	***18***	***9.75E-04***	***1.94E-02***	***3.60E-03***	***6.76E-02***	***3.24E-03***	***6.94E-04***
	19	6.69E-03	9.12E-01	1.31E-01	2.10E-01	2.20E-01	0.00E+00
	20	5.12E-02	4.81E+00	2.54E-01	1.60E+00	6.77E-02	0.00E+00
	21	6.85E-02	5.50E+00	2.11E-01	1.50E+00	1.06E+00	5.55E-03
	22	3.38E-03	8.63E-01	1.69E-01	2.96E+00	5.71E-01	0.00E+00
RAIN	***23***	***6.14E-03***	***3.40E-02***	***3.59E-03***	***4.23E-01***	***8.57E-03***	***1.78E-03***
	24	3.75E-02	1.54E+00	1.90E-01	1.08E+00	2.76E-01	0.00E+00
	26	3.03E-01	1.38E+00	1.55E-01	1.56E+00	6.64E-01	0.00E+00
	27	2.76E-02	1.51E+00	1.42E-01	1.16E+00	6.90E-01	0.00E+00
	28	1.11E-02	1.12E+00	1.43E-01	8.85E-01	1.05E+00	9.16E-03
	29	2.69E-04	1.29E+00	8.50E-02	9.37E-01	4.55E-01	1.20E-02
	30	2.04E-02	1.21E+00	8.26E-02	3.72E+00	1.44E+00	3.11E-04

Table A-11: Concentrations(ppm) of dry deposition control samples for June 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR JUNE 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	4.63E-02	6.03E-01	1.27E-01	8.40E-01	8.17E-01	4.85E-03
	2	8.22E-03	2.92E+00	5.44E-02	4.30E-01	3.43E-01	0.00E+00
	3	1.08E-01	1.19E+00	1.90E-01	1.34E+00	3.05E-01	1.08E-02
	4	0.00E+00	2.51E+00	8.73E-02	0.00E+00	3.51E-01	8.30E-03
	5	6.57E-02	2.20E+00	9.43E-02	2.58E+00	4.21E-01	3.44E-03
	6	1.67E-02	2.59E+00	6.05E-01	5.48E+00	7.50E-01	0.00E+00
	7	4.27E-02	2.16E+00	2.10E-01	2.17E+00	5.13E-01	0.00E+00
	9	1.07E-02	9.24E-01	1.01E-01	1.04E+00	4.60E-01	7.42E-03
	10	4.19E-02	2.23E+00	1.10E-01	3.26E+00	1.95E+00	1.18E-03
	11	7.32E-04	1.42E+00	2.10E-01	6.81E+00	1.49E+00	5.69E-03
	12	2.89E-02	2.69E-01	1.29E-01	1.43E+00	1.59E+00	1.91E-03
	13	2.24E-02	6.59E-03	2.03E-01	2.85E+00	4.15E+00	6.59E-03
	14	4.12E-02	6.73E-01	2.59E-01	4.26E+00	0.00E+00	2.24E-03
	16	4.59E-02	2.55E+00	7.75E-01	4.22E+00	7.00E-01	1.68E-04
	17	2.00E-02	1.42E+00	5.68E-02	3.20E-01	2.88E-01	0.00E+00
	18	3.09E-02	1.81E+00	1.44E-01	3.67E-01	1.05E+00	0.00E+00
	19	8.06E-02	1.14E+00	1.09E+00	1.17E+00	4.56E-01	2.59E-03
	20	7.61E-03	1.05E+00	8.08E-02	6.59E-01	5.60E-01	0.00E+00
	21	2.00E-02	2.18E+00	7.76E-02	6.75E-01	1.72E-01	0.00E+00
	22	5.65E-04	1.45E+00	5.18E-02	3.38E-01	8.79E-02	0.00E+00
	23	1.92E-02	1.88E+00	2.70E-01	4.78E+00	3.99E-01	0.00E+00
	24	2.42E-03	2.06E+00	1.13E-01	7.03E-01	2.78E-01	0.00E+00
	25	5.17E-03	2.25E+00	5.35E-02	1.48E+00	8.18E-01	4.22E-03
	26	7.15E-03	2.30E+00	3.99E-02	9.85E-01	3.30E-01	0.00E+00
	27	1.48E-03	2.17E+00	6.65E-02	1.46E+00	3.10E-01	0.00E+00
	28	3.82E-02	1.73E+00	1.23E-01	6.81E-01	6.00E-02	0.00E+00
	29	2.57E-03	2.80E+00	1.60E-01	1.38E+00	4.35E-01	0.00E+00
	30	2.86E-03	3.04E+00	6.18E-02	5.59E-01	2.02E-01	0.00E+00

Table A-13: Concentrations(ppm) of dry deposition control samples for July 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR JULY 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	2	6.12E-03	2.30E-01	3.52E-01	7.71E-01	0.00E+00	0.00E+00
	3	1.46E-02	4.05E-01	4.05E-01	2.14E+00	0.00E+00	0.00E+00
	5	1.04E-01	4.86E-01	6.63E-02	7.86E-01	3.01E-01	0.00E+00
	6	1.27E-02	5.03E-01	1.18E-01	2.71E-01	0.00E+00	0.00E+00
	7	1.88E-02	5.40E-01	1.75E-01	1.17E-01	0.00E+00	0.00E+00
	8	1.74E-02	1.43E-01	7.85E-02	1.79E-01	0.00E+00	0.00E+00
	9	1.79E-02	4.08E-01	8.24E-02	2.93E-01	2.60E-01	0.00E+00
	10	1.36E-02	7.93E-01	5.14E-02	1.01E+00	0.00E+00	0.00E+00
	12	2.56E-02	9.44E-01	1.09E-01	4.27E-01	0.00E+00	0.00E+00
	13	6.50E-02	6.65E-01	2.47E-01	1.78E-01	0.00E+00	0.00E+00
	14	9.16E-02	2.86E-01	1.00E-01	5.90E-01	0.00E+00	0.00E+00
	15	7.37E-02	1.68E-01	1.22E-01	4.11E-02	0.00E+00	0.00E+00
	16	4.44E-02	1.64E-01	1.67E-01	8.30E-02	2.50E-02	0.00E+00
	17	1.05E-02	6.80E-01	7.01E-02	2.37E-01	0.00E+00	0.00E+00
	18	1.73E-02	6.51E-01	1.40E-01	2.07E+00	2.39E-01	0.00E+00
	19	2.06E-03	1.97E-01	9.79E-02	2.50E-01	0.00E+00	0.00E+00
	20	5.85E-02	8.70E-01	2.33E-01	4.86E-01	0.00E+00	0.00E+00
	21	1.96E-02	3.40E-01	1.09E-01	4.48E-01	0.00E+00	0.00E+00
	22	4.20E-03	1.37E-01	1.40E-01	7.60E-01	8.80E-02	0.00E+00
	23	6.16E-03	4.20E-01	6.56E-02	6.25E-01	0.00E+00	0.00E+00
	25	2.18E-02	2.54E-01	8.69E-02	4.51E-01	0.00E+00	0.00E+00
	26	1.90E-01	3.33E-01	3.13E-01	9.87E-01	0.00E+00	0.00E+00
	27	8.56E-02	4.85E-01	1.50E-01	3.17E-01	4.22E-01	0.00E+00
	28	8.63E-02	7.70E-01	1.61E-01	8.27E-01	0.00E+00	0.00E+00
	29	2.42E-02	1.62E-01	3.14E-01	3.43E-01	0.00E+00	0.00E+00
	30	1.43E-02	2.18E-01	1.56E-01	2.28E+00	7.07E-02	0.00E+00
	31	1.72E-02	2.00E-01	1.23E-02	3.89E-01	0.00E+00	0.00E+00

Table A-14: Concentration (ppm) of dry deposition samples for August 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR AUGUST 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
RAIN	***2***	***0.00E+00***	***2.53E-02***	***1.16E-03***	***3.75E-02***	***1.63E-03***	***0.00E+00***
	3	1.06E-03	1.08E-01	7.10E-02	4.21E-01	9.25E-02	0.00E+00
	4	0.00E+00	2.84E-01	1.44E-01	3.18E-01	2.21E-02	0.00E+00
	5	1.31E-02	4.65E-01	2.19E-01	8.34E+00	3.80E-01	1.02E-02
RAIN	***6***	***6.28E-03***	***1.14E-01***	***4.96E-03***	***9.70E-02***	***1.65E-04***	***0.00E+00***
	7	1.68E-03	2.46E-01	1.01E-01	8.86E-01	1.68E-01	0.00E+00
	8	0.00E+00	3.60E-01	1.12E-01	8.29E-01	2.75E-01	0.00E+00
	9	0.00E+00	4.40E-01	4.36E-01	7.72E+00	9.61E-02	2.10E-02
RAIN	***10***	***1.25E-03***	***2.90E-02***	***1.24E-03***	***3.59E-02***	***1.18E-02***	***0.00E+00***
	11	3.15E-03	4.20E-01	1.07E-01	2.44E+00	2.22E-01	2.02E-03
RAIN	***12***	***2.34E-04***	***1.77E-02***	***1.85E-03***	***8.12E-02***	***3.56E-03***	***2.84E-03***
RAIN	***13***	***4.78E-04***	***8.51E-03***	***1.31E-03***	***1.19E-02***	***2.52E-04***	***1.01E-03***
	14	0.00E+00	3.37E-01	1.24E-01	6.29E-01	7.04E-03	0.00E+00
	15	0.00E+00	1.21E+00	3.27E-02	2.73E+01	0.00E+00	0.00E+00
RAIN	***16***	***3.62E-03***	***4.42E-02***	***3.61E-03***	***1.47E-01***	***5.49E-02***	***0.00E+00***
RAIN	***17***	***3.05E-03***	***2.63E-02***	***1.01E-03***	***2.64E-02***	***3.79E-03***	***4.62E-04***
	19	0.00E+00	3.53E-01	1.77E-01	8.20E-01	7.20E-02	0.00E+00
	20	0.00E+00	2.55E-01	1.74E-01	1.62E+00	5.44E-02	0.00E+00
	21	0.00E+00	4.27E-01	2.73E-01	9.02E-01	1.20E-01	0.00E+00
	22	0.00E+00	4.67E-01	2.33E-01	8.59E-01	1.88E-01	0.00E+00
	23	0.00E+00	4.57E-01	3.60E-01	2.50E+00	6.09E-02	9.32E-03
RAIN	***24***	***2.05E-03***	***1.99E-02***	***1.89E-03***	***7.66E-02***	***2.99E-03***	***3.56E-04***
	25	6.93E-03	5.85E-01	1.49E-01	1.18E+00	4.33E-01	0.00E+00
RAIN	***26***	***6.96E-04***	***5.65E-03***	***1.04E-03***	***4.49E-02***	***2.00E-03***	***2.00E-03***
RAIN	***27***	***4.92E-04***	***6.96E-03***	***7.36E-04***	***1.56E-02***	***5.27E-04***	***1.05E-03***
	28	0.00E+00	2.81E-01	2.70E-01	1.70E+00	9.03E-02	8.74E-03
	29	7.41E-03	3.51E-01	1.05E-01	6.69E-01	3.39E-01	4.20E-03
	30	0.00E+00	2.22E-01	2.65E-01	3.53E+00	3.39E-01	0.00E+00
	31	0.00E+00	1.08E-01	1.01E-01	8.10E-01	3.07E-02	0.00E+00

Table A-15: Concentrations(ppm) of dry deposition control samples for August 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR AUGUST 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	2	4.41E-03	7.51E-02	6.82E-02	5.01E-01	7.78E-02	0.00E+00
	3	0.00E+00	1.86E-01	2.27E-02	7.66E-01	5.95E-02	0.00E+00
	4	0.00E+00	2.02E-01	2.02E-01	4.50E-01	8.67E-02	0.00E+00
	5	0.00E+00	4.38E-01	2.93E-02	6.42E-01	1.21E-01	0.00E+00
	6	2.35E-02	7.00E-02	5.69E-02	9.06E-01	4.86E-02	0.00E+00
	7	0.00E+00	8.50E-03	3.09E-02	5.64E-01	6.91E-02	0.00E+00
	8	8.32E-03	1.85E-01	1.69E-01	1.32E+00	1.46E-01	0.00E+00
	9	0.00E+00	3.90E-01	1.95E-01	3.97E+00	2.53E-03	0.00E+00
	10	0.00E+00	4.12E-01	3.33E-01	7.70E+00	1.66E-01	0.00E+00
	11	0.00E+00	1.94E-01	2.19E-02	7.24E-01	1.98E-01	0.00E+00
	12	0.00E+00	8.67E-02	3.12E-02	1.35E+00	4.63E-02	0.00E+00
	13	0.00E+00	1.63E-01	3.84E-02	1.60E-01	4.26E-02	0.00E+00
	14	0.00E+00	1.45E-01	2.15E-02	2.04E-01	4.70E-02	0.00E+00
	15	0.00E+00	1.77E+00	1.40E-02	1.11E+01	3.96E-01	1.57E-02
	16	1.04E-02	5.10E-01	1.78E-02	1.54E+00	5.14E-01	1.00E-02
	17	2.68E-02	3.69E-01	2.70E-02	4.60E-01	1.63E-02	0.00E+00
	19	0.00E+00	9.20E-02	4.55E-02	5.79E-01	4.17E-03	0.00E+00
	20	0.00E+00	4.10E-02	1.91E-02	2.50E-01	1.49E-02	0.00E+00
	21	0.00E+00	8.44E-02	1.60E-02	1.92E-01	2.47E-02	0.00E+00
	22	0.00E+00	1.26E-01	7.19E-03	2.20E-01	3.43E-02	0.00E+00
	23	0.00E+00	1.26E-01	7.26E-02	9.80E-01	5.16E-02	0.00E+00
	24	0.00E+00	2.38E-01	2.60E-01	3.36E+00	4.91E-01	0.00E+00
	25	0.00E+00	2.65E-01	2.23E-02	5.80E-01	4.76E-02	0.00E+00
	26	0.00E+00	5.07E-01	3.40E-01	2.94E+00	4.63E-01	0.00E+00
	27	0.00E+00	1.55E-01	7.44E-02	1.11E+00	4.39E-02	0.00E+00
	28	0.00E+00	3.50E-02	2.03E-02	1.78E-01	2.59E-02	0.00E+00
	29	0.00E+00	1.59E+00	1.72E-01	1.54E+00	1.92E-01	0.00E+00
	30	0.00E+00	2.00E-01	1.21E-01	1.95E+00	9.78E-02	0.00E+00
	31	0.00E+00	1.90E-01	1.34E-01	1.09E+00	5.36E-02	0.00E+00

Table A-16: Concentration (ppm) of dry deposition samples for September 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR SEPTEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	4.10E-02	0.00E+00	1.97E-01	1.87E+00	0.00E+00	0.00E+00
RAIN	***2***	***1.17E-03***	***1.67E-02***	***4.00E-03***	***5.10E-02***	***5.60E-03***	***1.27E-03***
	3	0.00E+00	0.00E+00	1.59E-01	9.70E-02	0.00E+00	0.00E+00
RAIN	***4***	***1.02E-03***	***1.56E-02***	***2.83E-03***	***8.71E-02***	***7.73E-03***	***0.00E+00***
RAIN	***5***	***3.15E-03***	***1.22E-02***	***5.19E-03***	***2.73E-01***	***1.01E-02***	***1.77E-03***
RAIN	***6***	***8.65E-04***	***4.26E-03***	***3.37E-03***	***2.46E-01***	***4.58E-03***	***2.31E-03***
RAIN	***7***	***0.00E+00***	***5.40E-03***	***4.29E-04***	***4.21E-02***	***4.20E-03***	***6.11E-05***
RAIN	***8***	***5.30E-04***	***7.15E-03***	***4.11E-03***	***4.08E-02***	***4.62E-04***	***9.28E-04***
RAIN	***9***	***0.00E+00***	***5.12E-03***	***4.50E-03***	***8.30E-02***	***5.17E-03***	***4.07E-04***
	10	0.00E+00	0.00E+00	5.71E-02	1.67E+00	0.00E+00	0.00E+00
	11	0.00E+00	0.00E+00	8.79E-02	5.43E-01	0.00E+00	0.00E+00
RAIN	***12***	***0.00E+00***	***1.42E-02***	***1.46E-03***	***2.46E-01***	***1.06E-03***	***2.88E-03***
RAIN	***13***	***0.00E+00***	***4.61E-03***	***1.53E-04***	***5.13E-02***	***1.93E-03***	***1.21E-03***
	14	0.00E+00	0.00E+00	4.62E-03	2.30E-01	0.00E+00	0.00E+00
	15	0.00E+00	0.00E+00	1.04E-01	4.12E-01	0.00E+00	0.00E+00
	16	2.14E-02	0.00E+00	2.10E-01	4.17E+00	0.00E+00	0.00E+00
RAIN	***17***	***0.00E+00***	***9.61E-03***	***1.04E-03***	***3.73E-02***	***2.32E-03***	***1.86E-03***
RAIN	***18***	***2.70E-04***	***1.12E-02***	***2.25E-03***	***3.45E-02***	***1.29E-04***	***3.20E-04***
	20	0.00E+00	0.00E+00	1.36E-01	1.59E+00	0.00E+00	0.00E+00
RAIN	***21***	***4.00E-04***	***2.20E-03***	***5.22E-04***	***1.03E-02***	***1.87E-03***	***1.00E-03***
	22	0.00E+00	0.00E+00	4.29E-02	2.57E-01	0.00E+00	0.00E+00
	23	0.00E+00	0.00E+00	2.45E-01	6.39E+00	0.00E+00	0.00E+00
RAIN	***24***	***5.84E-04***	***1.70E-02***	***7.26E-03***	***1.78E-01***	***1.60E-02***	***2.15E-03***
RAIN	***25***	***0.00E+00***	***9.16E-03***	***6.43E-04***	***5.27E-03***	***1.09E-03***	***1.16E-03***
RAIN	***26***	***0.00E+00***	***1.47E-02***	***3.55E-03***	***1.47E-01***	***2.25E-03***	***2.06E-03***
	27	0.00E+00	0.00E+00	2.38E-01	7.29E-01	0.00E+00	0.00E+00
	28	0.00E+00	0.00E+00	1.48E-02	8.21E-01	0.00E+00	0.00E+00
	29	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	30	0.00E+00	0.00E+00	2.88E-01	2.94E+00	0.00E+00	0.00E+00

Table A-17: Concentrations(ppm) of dry deposition control samples for September 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR SEPTEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	9.48E-02	3.46E-02	3.05E-01	0.00E+00	3.26E-02
	3	0.00E+00	0.00E+00	2.75E-01	1.46E-01	0.00E+00	0.00E+00
	4	0.00E+00	3.51E-01	1.79E-01	2.15E+00	1.76E-01	0.00E+00
	5	0.00E+00	0.00E+00	6.38E-02	1.57E+00	0.00E+00	0.00E+00
	6	0.00E+00	0.00E+00	7.74E-02	9.23E-01	0.00E+00	0.00E+00
	7	0.00E+00	6.10E-02	1.33E-01	2.32E+00	1.33E-01	0.00E+00
	8	0.00E+00	0.00E+00	4.96E-02	0.00E+00	0.00E+00	0.00E+00
	9	0.00E+00	0.00E+00	3.34E-02	5.30E-01	0.00E+00	0.00E+00
	10	0.00E+00	5.29E-02	4.88E-02	3.56E-02	6.00E-02	0.00E+00
	11	0.00E+00	0.00E+00	3.26E-02	2.41E-01	0.00E+00	0.00E+00
	12	0.00E+00	0.00E+00	4.80E-02	3.16E+00	0.00E+00	0.00E+00
	13	0.00E+00	0.00E+00	6.20E-02	4.21E+00	0.00E+00	0.00E+00
	14	0.00E+00	0.00E+00	3.11E-02	0.00E+00	0.00E+00	0.00E+00
	15	0.00E+00	0.00E+00	2.91E-02	1.74E-02	0.00E+00	0.00E+00
	16	0.00E+00	0.00E+00	2.61E-02	2.13E-01	0.00E+00	0.00E+00
	17	0.00E+00	0.00E+00	1.04E-01	1.83E+00	0.00E+00	0.00E+00
	18	0.00E+00	0.00E+00	2.68E-02	6.20E-01	0.00E+00	0.00E+00
	19	0.00E+00	0.00E+00	1.09E-01	0.00E+00	0.00E+00	0.00E+00
	20	2.98E-03	0.00E+00	1.53E-01	1.63E-01	0.00E+00	0.00E+00
	21	0.00E+00	0.00E+00	1.30E-02	2.28E-01	0.00E+00	0.00E+00
	22	0.00E+00	0.00E+00	1.37E-02	3.73E-01	0.00E+00	0.00E+00
	23	0.00E+00	0.00E+00	1.70E-01	2.76E-01	0.00E+00	0.00E+00
	24	0.00E+00	0.00E+00	3.69E-01	4.64E+00	0.00E+00	0.00E+00
	25	0.00E+00	0.00E+00	2.47E-01	7.44E-01	0.00E+00	0.00E+00
	26	0.00E+00	0.00E+00	1.55E-01	1.12E+00	0.00E+00	0.00E+00
	27	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	28	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	29	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	30	0.00E+00	0.00E+00	0.00E+00	7.77E-02	0.00E+00	0.00E+00

Table A-19: Concentrations(ppm) of dry deposition control samples for October 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR OCTOBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	2.13E-01	8.32E-02	7.63E-01	0.00E+00	0.00E+00
	2	0.00E+00	3.34E-01	6.32E-02	2.23E-01	0.00E+00	0.00E+00
	3	0.00E+00	1.67E-01	5.81E-02	7.10E-01	0.00E+00	0.00E+00
	5	0.00E+00	0.00E+00	2.46E-02	3.68E-01	0.00E+00	0.00E+00
	6	5.27E-02	1.72E-01	1.21E-01	4.35E-01	0.00E+00	0.00E+00
	7	7.55E-02	1.35E-01	1.02E-01	3.29E-01	9.66E-02	0.00E+00
	8	2.84E-02	2.20E-01	8.09E-02	3.00E-01	1.34E-01	0.00E+00
	10	0.00E+00	1.96E-01	7.15E-02	1.58E+00	0.00E+00	0.00E+00
	11	1.34E-02	3.09E-01	4.21E-02	3.02E+00	7.43E-02	0.00E+00
	12	0.00E+00	7.12E-02	6.25E-01	4.11E+00	9.81E-02	0.00E+00
	13	1.26E-02	1.83E-01	3.91E-02	5.28E-01	2.49E-02	0.00E+00
	14	0.00E+00	2.26E-01	5.03E-02	1.62E+00	5.09E-02	0.00E+00
	15	0.00E+00	2.54E-01	8.47E-02	3.16E-01	7.48E-03	0.00E+00
	16	0.00E+00	2.93E-01	4.25E-02	2.59E+00	4.50E-02	0.00E+00
	17	0.00E+00	2.30E-01	7.12E-02	2.79E-01	8.21E-02	0.00E+00
	18	0.00E+00	1.67E-01	8.86E-02	1.84E+00	3.02E-02	0.00E+00
	19	1.02E-02	2.95E-01	1.84E-01	1.68E+00	0.00E+00	0.00E+00
	20	2.56E-02	1.89E-01	4.31E-02	2.11E-01	1.36E-01	0.00E+00
	21	2.16E-02	1.37E-01	1.82E-01	1.59E-01	2.19E-02	0.00E+00
	22	0.00E+00	2.04E-01	5.17E-02	4.36E-01	7.68E-03	0.00E+00
	24	0.00E+00	1.83E-01	7.61E-01	4.50E-01	8.37E-02	0.00E+00
	25	0.00E+00	6.17E-02	4.64E-01	4.76E-01	7.51E-02	0.00E+00
	26	0.00E+00	1.09E-01	7.16E-01	1.74E+00	5.35E-04	0.00E+00
	27	0.00E+00	1.63E-01	1.24E-01	6.31E-01	5.57E-02	0.00E+00
	28	0.00E+00	1.45E-01	5.92E-02	3.61E-01	0.00E+00	0.00E+00
	29	0.00E+00	1.22E-01	3.79E-02	3.57E-01	0.00E+00	0.00E+00
	30	0.00E+00	3.30E-01	4.23E-02	5.12E-01	1.67E-01	0.00E+00
	31	0.00E+00	1.90E-01	2.29E-01	1.24E+00	4.58E-02	0.00E+00

Table A-20: Concentrations(ppm) of dry deposition samples for November 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR NOVEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	2.22E-02	1.04E+00	1.60E+00	1.98E+00	0.00E+00	0.00E+00
	4	2.92E-02	2.51E-01	4.41E-01	3.78E+00	5.95E-01	0.00E+00
RAIN	***7***	***4.22E-04***	***1.09E-02***	***3.41E-03***	***4.13E-01***	***2.64E-02***	***5.50E-03***
RAIN	***8***	***2.47E-04***	***2.62E-02***	***1.71E-03***	***4.47E-02***	***4.51E-03***	***6.74E-04***
RAIN	***9***	***2.94E-04***	***9.09E-03***	***2.34E-03***	***1.79E-02***	***8.53E-04***	***0.00E+00***
RAIN	***10***	***0.00E+00***	***1.75E-02***	***6.00E-03***	***1.01E-01***	***4.54E-03***	***2.26E-04***
	11	1.44E-02	5.80E-02	2.57E-01	5.84E-02	5.84E-02	0.00E+00
	15	3.81E-03	2.00E-01	5.41E-01	1.74E-02	1.74E-02	0.00E+00
RAIN	***19***	***0.00E+00***	***4.21E-03***	***1.69E-04***	***1.85E-02***	***1.90E-03***	***1.27E-03***
RAIN	***21***	***6.31E-04***	***3.15E-03***	***1.37E-05***	***3.25E-03***	***1.53E-04***	***1.21E-03***
RAIN	***29***	***4.56E-04***	***1.24E-02***	***7.97E-03***	***1.21E-01***	***7.54E-03***	***3.14E-03***

Table A-21: Concentrations(ppm) of dry deposition control samples for November 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR NOVEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	1.65E+00	8.50E-01	1.46E-01	0.00E+00	0.00E+00
	4	0.00E+00	5.97E-02	4.41E-02	2.68E-01	7.88E-02	0.00E+00
	7	0.00E+00	6.46E-02	1.43E-01	5.90E-01	1.11E-01	3.79E-03
	8	0.00E+00	1.98E-01	1.06E-01	3.56E-01	1.27E-01	1.15E-02
	9	1.78E-01	2.01E-01	3.57E-01	1.48E+00	1.30E-01	1.95E-03
	10	0.00E+00	3.60E-01	4.63E-01	1.17E+00	2.22E-01	0.00E+00
	11	0.00E+00	5.91E-02	1.65E-01	1.22E+00	8.46E-02	0.00E+00
	15	0.00E+00	5.42E-02	1.13E-01	2.46E-01	1.71E-02	0.00E+00
	19	0.00E+00	2.61E-01	2.61E-01	7.89E-01	3.39E-01	0.00E+00
	21	0.00E+00	1.37E-01	1.25E-01	2.47E-01	4.49E-02	4.51E-03
	29	0.00E+00	5.58E-01	5.58E-01	2.02E+00	7.22E-01	0.00E+00

Table A-22: Concentrations(ppm) of dry deposition samples for December 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR DECEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	2.69E-01	2.20E-01	1.36E+00	2.86E-01	0.00E+00
RAIN	***2***	***0.00E+00***	***5.38E-03***	***1.43E-02***	***3.41E-02***	***9.29E-04***	***5.41E-04***
	3	0.00E+00	1.30E-01	1.05E-01	1.30E+00	8.33E-02	0.00E+00
	4	7.69E-02	7.55E-01	1.37E-01	3.92E-01	3.88E-02	0.00E+00
	5	3.46E-02	4.66E-02	4.17E-02	2.68E-01	1.24E-02	0.00E+00
	6	0.00E+00	1.42E-01	1.39E-01	8.61E-01	3.80E-02	0.00E+00
	7	0.00E+00	2.26E-01	2.48E-01	1.84E+00	5.02E-02	0.00E+00
	8	0.00E+00	2.49E-01	1.25E-01	1.30E+00	4.20E-02	0.00E+00
	9	3.71E-03	6.97E-02	6.94E-02	6.02E-01	2.81E-02	0.00E+00
	10	9.79E-02	2.31E-01	2.82E-01	3.58E+00	3.84E-01	0.00E+00
RAIN	***11***	***0.00E+00***	***1.61E-02***	***2.53E-03***	***3.57E-02***	***4.33E-03***	***0.00E+00***
	13	2.63E-01	2.29E-01	1.65E-01	9.97E-01	4.94E-02	0.00E+00
RAIN	***17***	***1.40E-03***	***5.90E-03***	***7.30E-04***	***2.03E-02***	***9.43E-04***	***2.19E-03***
RAIN	***18***	***0.00E+00***	***2.69E-03***	***6.18E-04***	***1.35E-02***	***0.00E+00***	***0.00E+00***
	20	1.77E-02	6.88E-02	8.81E-02	5.72E-01	3.91E-02	0.00E+00
	21	6.66E-02	4.90E-01	2.23E-01	1.96E+00	9.60E-02	0.00E+00
	27	7.15E-01	4.00E-01	2.80E-01	1.47E+00	5.17E-02	0.00E+00
	28	1.30E-01	9.29E-02	3.34E-02	4.57E-01	9.29E-03	0.00E+00

Table A-23: Concentrations(ppm) of dry deposition control samples for December 1996

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR DECEMBER 1996							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	1	0.00E+00	4.88E-02	1.53E-02	3.14E-01	1.71E-02	0.00E+00
	2	2.56E-02	7.11E-01	2.28E-01	1.27E+00	4.10E-01	1.59E-02
	3	0.00E+00	1.29E-01	2.81E-02	1.92E-01	4.45E-03	0.00E+00
	4	0.00E+00	3.06E-01	5.42E-02	2.58E-01	3.63E-02	0.00E+00
	5	0.00E+00	2.58E-02	1.86E-02	2.60E-01	1.34E-04	0.00E+00
	6	0.00E+00	2.25E-02	1.99E-02	2.66E-01	4.72E-03	0.00E+00
	7	0.00E+00	2.03E-02	2.67E-02	9.54E-02	2.01E-02	0.00E+00
	8	0.00E+00	1.40E-01	2.23E-02	2.07E-01	8.60E-03	0.00E+00
	9	0.00E+00	1.08E-01	5.55E-02	1.87E-01	9.52E-03	0.00E+00
	10	0.00E+00	1.11E-01	1.81E-02	1.75E-01	1.34E-02	0.00E+00
	11	3.89E-02	2.07E-01	3.25E-01	7.28E+00	2.75E-01	0.00E+00
	13	7.84E-03	2.35E-01	5.06E-02	4.13E-01	1.95E-02	0.00E+00
	17	4.00E-01	4.46E-01	2.43E-01	1.94E+00	5.76E-02	0.00E+00
	18	2.90E-02	1.44E-01	7.34E-02	4.66E-01	1.49E-02	0.00E+00
	20	0.00E+00	1.32E-01	2.21E-02	1.28E-01	1.17E-02	0.00E+00
	21	0.00E+00	4.70E-01	2.05E-02	3.89E-01	1.67E-02	0.00E+00
	27	0.00E+00	1.32E-01	1.70E-02	2.10E-01	8.00E-03	0.00E+00
	28	0.00E+00	4.99E-02	8.93E-03	4.70E-01	7.21E-03	0.00E+00

Table A-24: Concentration (ppm) of dry deposition samples for January 1997

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR JANUARY 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
RAIN	**2**	**0.00E+00**	**3.37E-02**	**6.61E-04**	**5.06E-03**	**-1.77E-03**	**2.19E-04**
	3	2.99E-01	3.92E-01	2.95E+03	1.16E+00	1.02E-01	0.00E+00
	6	6.40E-01	1.40E-01	8.84E-02	5.02E-01	1.09E-01	0.00E+00
RAIN	***5***	***9.68E-04***	***5.05E-02***	***4.49E-03***	***4.06E-02***	***4.96E-03***	***7.23E-04***
RAIN	**11**	**0.00E+00**	**3.06E-02**	**8.30E-03**	**1.26E-02**	**1.54E-03**	**0.00E+00**
	12	7.62E-02	2.28E-01	3.99E-01	8.70E-01	1.76E-01	0.00E+00
	15	6.23E-01	1.74E-02	1.25E-01	5.60E-01	1.66E-03	0.00E+00
	17	8.39E-02	8.22E-01	1.22E+00	1.22E+00	5.37E-02	8.08E-03
	18	1.29E-01	1.33E-01	1.81E-01	3.61E-01	1.14E-01	0.00E+00
	21	1.24E-01	3.32E-01	4.04E-01	1.54E+00	1.14E-01	0.00E+00
	24	3.20E-01	2.30E-01	5.30E-01	6.20E-01	2.54E-01	0.00E+00
	27	1.34E-01	2.56E-01	3.88E-01	1.41E+00	8.50E-03	0.00E+00
RAIN	***31***	***3.06E-02***	***4.35E-02***	***2.17E-03***	***1.57E-01***	***1.83E-02***	***1.61E-03***

Table A-25: Concentrations(ppm) of dry deposition control samples for January 1997

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR JANUARY 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	2	2.60E-01	2.19E-01	0.254	1.01E+00	1.24E-01	6.65E-03
	3	0.00E+00	2.54E-01	0.1256	1.78E-01	2.04E-02	0.00E+00
	6	0.00E+00	6.68E-02	0.04771	1.15E-01	3.00E-02	0.00E+00
	8	1.47E-01	4.29E-02	0.1078	4.82E-01	5.58E-02	0.00E+00
	11	1.70E-01	4.62E-01	0.8715	2.05E+00	3.46E-01	0.00E+00
	12	0.00E+00	4.30E-02	0.05414	7.17E-02	2.50E-02	0.00E+00
	15	0.00E+00	8.91E-02	0.02381	1.04E-01	3.87E-02	0.00E+00
	17	0.00E+00	3.22E-02	2.54E-01	1.02E-01	3.93E-03	0.00E+00
	18	0.00E+00	4.44E-02	1.26E-01	3.52E-02	0.00E+00	0.00E+00
	21	0.00E+00	3.24E-02	4.77E-02	5.32E-01	5.35E-03	0.00E+00
	24	0.00E+00	7.43E-02	1.08E-01	2.21E-01	7.67E-03	0.00E+00
	27	0.00E+00	6.58E-02	8.72E-01	1.82E-01	2.88E-03	0.00E+00
	31	0.00E+00	3.71E-01	5.41E-02	2.12E+00	1.74E-01	0.00E+00

Table A-26: Concentration (ppm) of dry deposition samples for February 1997

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR FEBRUARY 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
RAIN	***1***	***4.06E-02***	***2.31E-02***	***5.96E-03***	***2.95E-02***	***1.03E-03***	***0.00E+00***
	10	0.00E+00	1.57E-01	3.80E-01	1.35E+00	6.91E-02	0.00E+00
	11	0.00E+00	1.58E-01	4.11E-01	5.16E-01	5.54E-02	0.00E+00
	12	0.00E+00	5.00E-02	1.31E-01	1.64E-01	5.04E-03	0.00E+00
	13	0.00E+00	1.00E-01	3.28E-01	7.41E-01	1.52E-02	0.00E+00
	14	0.00E+00	1.78E-01	4.22E-01	7.28E-01	4.64E-02	0.00E+00
	17	0.00E+00	1.56E-01	5.58E-01	1.96E+00	5.75E-02	1.36E-03
	18	0.00E+00	2.89E-01	2.86E-01	8.78E-01	3.07E-02	0.00E+00
	19	0.00E+00	1.42E-01	2.33E-01	7.54E-01	6.94E-03	0.00E+00
	20	0.00E+00	3.10E-01	3.50E-01	1.15E+00	2.66E-02	0.00E+00
	21	0.00E+00	2.69E-01	1.84E-01	6.43E-01	0.00E+00	0.00E+00
RAIN	***23***	***0.00E+00***	***7.88E-03***	***1.23E-03***	***5.10E-02***	***1.59E-03***	***0.00E+00***
	24	0.00E+00	1.10E-01	0.00E+00	7.64E-01	2.07E-02	0.00E+00
	25	0.00E+00	2.35E-01	5.16E-01	4.86E+00	1.20E-01	0.00E+00
	26	0.00E+00	2.96E-01	7.11E-01	2.18E+00	5.34E-02	0.00E+00

Table A-27: Concentrations(ppm) of dry deposition control samples for February 1997

CONCENTRATIONS(PPM) OF DRY DEPOSITION CONTROL FOR FEBRUARY 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	10	0.00E+00	1.54E-01	1.44E-01	8.20E-01	2.99E-02	0.00E+00
	11	0.00E+00	9.24E-02	1.60E-01	8.45E-01	3.46E-02	0.00E+00
	12	0.00E+00	4.05E-02	6.01E-02	3.51E-01	2.64E-02	0.00E+00
	13	0.00E+00	1.54E-01	1.80E-01	9.21E-01	0.00E+00	0.00E+00
	14	0.00E+00	1.86E-01	1.92E-01	8.47E-01	4.63E-02	1.32E-02
	15	0.00E+00	1.60E-01	8.28E-02	3.46E-01	3.75E-02	0.00E+00
	17	0.00E+00	2.58E-01	2.36E-01	1.20E+00	7.34E-02	6.70E-03
	18	0.00E+00	9.60E-02	9.39E-02	6.84E-01	1.99E-02	0.00E+00
	19	0.00E+00	1.14E-01	9.58E-02	4.11E-01	2.53E-02	0.00E+00
	20	0.00E+00	1.82E-01	1.49E-01	1.73E+00	2.74E-02	0.00E+00
	21	0.00E+00	8.02E-02	6.30E-02	3.36E-01	2.81E-02	0.00E+00
	23	0.00E+00	1.13E-01	1.12E-01	4.57E-01	3.76E-02	0.00E+00
	24	0.00E+00	1.20E-01	2.11E-01	6.37E-01	6.58E-02	0.00E+00
	25	0.00E+00	5.81E-02	2.72E-01	2.17E+00	6.52E-02	4.94E-03
	26	0.00E+00	2.91E-01	1.33E-01	1.39E+00	4.25E-02	2.20E-02

Table A-28: Concentrations(ppm) of dry deposition samples for March 1997

CONCENTRATIONS(PPM) OF DRY DEPOSITION FOR MARCH 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	2	0.00E+00	2.50E-01	8.74E-01	3.86E+00	3.82E-01	0.00E+00
	3	0.00E+00	3.43E-01	7.98E-01	1.79E+00	2.26E-01	0.00E+00
	4	0.00E+00	4.21E-01	6.34E-01	2.41E+00	1.79E-01	0.00E+00
	5	3.06E-02	2.27E-01	1.73E-01	3.51E-01	5.74E-02	0.00E+00
	6	0.00E+00	3.91E-01	3.58E-01	1.65E+00	0.00E+00	0.00E+00
	7	0.00E+00	7.75E-01	1.91E-01	2.23E+00	2.59E-01	0.00E+00
	8	0.00E+00	4.64E-01	1.80E-01	1.18E+00	0.00E+00	0.00E+00
	9	0.00E+00	3.80E-01	5.67E-02	1.22E+00	1.63E-01	0.00E+00
RAIN	***10***	***0.00E+00***	***4.50E-03***	***2.49E-03***	***2.49E-03***	***4.44E-03***	***1.46E-03***
	11	0.00E+00	1.68E-01	1.18E-01	1.05E+00	3.40E-01	0.00E+00
	12	0.00E+00	2.78E-01	4.33E-01	2.92E+01	1.98E-02	0.00E+00
	14	0.00E+00	2.80E-01	1.93E-01	6.05E-01	1.77E-01	0.00E+00
	17	0.00E+00	3.30E-01	6.50E-01	1.26E+00	9.48E-03	0.00E+00
	18	0.00E+00	3.12E-01	8.10E-02	4.92E-01	1.02E-01	0.00E+00
	19	0.00E+00	3.39E-01	2.92E-01	2.23E+00	7.56E-03	0.00E+00
	20	0.00E+00	4.06E-01	1.49E-01	2.16E+00	0.00E+00	0.00E+00
	23	0.00E+00	4.12E-01	2.42E-01	3.12E+00	0.00E+00	0.00E+00
	24	0.00E+00	2.52E-01	1.14E-01	5.87E-01	1.27E-02	0.00E+00
	25	0.00E+00	3.96E-01	2.39E-01	2.81E+00	1.03E-01	0.00E+00
	26	0.00E+00	4.60E-01	3.09E-01	2.60E+00	0.00E+00	0.00E+00
	27	0.00E+00	1.06E-01	1.32E-01	7.05E-01	2.49E-01	0.00E+00
	30	0.00E+00	2.13E-01	2.09E-01	4.42E-01	3.57E-01	0.00E+00

Table A-29: *Concentrations(ppm) of dry deposition control samples for March 1997*

CONCENTRATION(PPM) OF DRY DEPOSITION CONTROL FOR MARCH 1997							
	DATE	Cd	Cu	Pb	Zn	Ni	Co
	2	0.00E+00	4.99E-01	6.79E+00	5.20E+00	5.77E-01	0.00E+00
	3	0.00E+00	1.53E-01	1.91E-01	1.30E+00	3.68E+00	0.00E+00
	4	0.00E+00	7.57E-02	1.37E-01	1.06E+00	2.11E-01	0.00E+00
	5	0.00E+00	1.23E-01	1.72E-01	6.09E-01	2.86E-01	0.00E+00
	6	0.00E+00	3.27E-01	1.42E-01	1.11E+00	2.62E-01	0.00E+00
	7	0.00E+00	2.66E-01	1.70E-01	3.67E+00	7.16E-01	0.00E+00
	8	0.00E+00	4.20E-01	1.13E-01	8.16E-01	1.60E-01	0.00E+00
	9	0.00E+00	2.40E-01	6.87E-02	8.61E-01	7.45E-01	0.00E+00
	10	0.00E+00	2.94E-01	9.20E-01	5.25E+00	2.42E-01	0.00E+00
	11	0.00E+00	1.13E-01	1.97E-01	1.67E+00	6.59E-02	0.00E+00
	12	0.00E+00	1.69E-01	2.15E-01	4.10E+00	2.79E+00	0.00E+00
	14	0.00E+00	5.33E-02	7.18E-02	1.11E+00	1.10E-01	0.00E+00
	17	0.00E+00	1.25E-01	2.72E-01	3.25E+00	1.24E-01	0.00E+00
	18	0.00E+00	3.35E-02	9.20E-02	5.65E-01	1.06E-01	0.00E+00
	19	0.00E+00	1.01E-01	1.99E-01	1.16E+00	2.72E-01	0.00E+00
	20	0.00E+00	5.17E-02	2.00E-01	1.27E+00	2.37E-02	0.00E+00
	23	0.00E+00	2.74E-01	1.96E-01	1.10E+00	4.85E-01	0.00E+00
	24	0.00E+00	5.02E-02	1.14E-01	1.02E+00	3.82E-02	0.00E+00
	25	0.00E+00	8.23E-02	1.93E-01	3.72E+00	1.19E-01	0.00E+00
	26	0.00E+00	2.82E-01	3.54E-01	1.55E+00	4.23E-02	0.00E+00
	27	0.00E+00	1.36E-01	9.94E-02	6.42E-01	1.41E-01	0.00E+00
	30	0.00E+00	2.15E-01	1.72E-01	5.85E-01	1.38E-01	0.00E+00