AN ENVIRONMENTAL STUDY TO EXAMINE THE DISTRIBUTION OF SELECTED AIRBORNE METALS IN THE GREATER CHATSWORTH AREA

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by Suendharan Govender

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Supervisor

Professor A.E.Pillay

Co-supervisor

Mr B.Bisnath

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PREFACE

The work described in this thesis was carried out by the author in the Department of Chemistry, Faculty of Science, M.L.Sultan Technikon, from 1996 to 1999 under the supervision of Professor A.E.Pillay and Mr B.Bisnath.

These studies represent original work by the author and have not been submitted in any form to another Tertiary Institution. Where use is made of the work of others, it has been duly acknowledged in the text.

ABSTRACT

The purpose of this study was to determine the distribution of selected metals in the atmosphere of the greater Chatsworth area. Six primary schools in the area were selected for the investigation. Two high volume air samplers were placed at one of the sites from 7h00 to 15h00 on school days. The filter assembly on which air particulates were collected was placed at a height of 1.45 m's above the ground. The vacuum pumps were preset to start and switch off at the selected times. Sampling was done for seven days from February to June and again for seven days from July to November at each of the six sites.

The filters were collected daily, stored in a desiccator for transportation to the Technikon. The filters were dried in an oven, cooled and stored in a desiccator for analysis. Approximately fourteen samples were analysed for each site for each of the two periods. The filters were digested in 1 M HNO_3 in a microwave digestor. The sample solution was made up to 50 mL with 1 M HNO_3. Standards were prepared using Spectrosol 1000 ppm standards except for cadmium which was prepared from solid CdO.

The samples and standards were analysed using the graphite furnace atomic absorption spectrometer. The samples were subjected to analysis for each of the five elements namely Cd Pb, Cr, Ni and Cu. The concentrations of each of the metals in the filter were determined using a standard calibration curve for the specific metal. The concentration of the metal in the atmosphere was determined for each cubic metre of air sampled.

The concentrations of the metals in the atmosphere were used to assess the air quality and distribution of metal pollutants in the greater Chatsworth area. The levels found for Pb ranged from 0.03 to 0.83 $\mu g/m^3$, for Cd from 0.6 to 25 ng/m^3, for Cr from 0.02 to 1 $\mu g/m^3$, for Ni from 5 to 54 ng/m^3 and for Cu from 7 to 233 ng/m^3. Wind direction showed a clear influence on pollutant level. Emission from vehicles was not conclusive.

DEDICATION

To my dear wife, my two daughters and son, for their patience, understanding and encouragement during the years spent on this research and to my late brother, Sathie Govender, who gave me the opportunity to pursue tertiary education in spite of the difficulties of the time and the lack of financial resources.

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LIST OF ABBREVIATIONS

AA = Atomic Absorption

ac = alternating current

ASV = Anodic Stripping Voltammetry

BAL = British Anti-Lewisite

CW = Crestview Primary School

dc = direct current

DE = Deport Road Primary School

EDL = Electrode-less Discharge Lamps

EDTA = Ethylene diamine tetra-acetic acid

EL = Elora Primary School

EPA = Environmental Protection Agency

ETAAS = Electrothermal Atomic Absorption Spectroscopy

EV = Evergreen Primary School

EX = Excelsior Primary School

GFAAS = Graphite Furnace Atomic Absorption Spectroscopy

GTA = Graphite Tube Atomiser

HPLC = High Performance Liquid Chromatography

IC = Ion Chromatography

ICP = Inductively Coupled Plasma

ICP-AES = Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-MS = Inductively Coupled Plasma Mass Spectroscopy

IQ = Intelligence Quotient

LO = Lotus Primary School

LPM = Litres Per Minute

NAA = Neutron Activation Analysis

NCOH = National Centre for Occupational Health

ppb = parts per billion

ppm = parts per million

RSD = Relative Standard Deviation

TCDD = Tetrachlorodibenzo-β-dioxin

TLV = Threshold Limit Value

WHO = World Health Organisation

XRF = X-Ray Fluorescence Spectroscopy

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CHAPTER 1

1.1 Introduction and Review

The primary aims of this research were:

- to provide a data base of metal pollution levels in the atmosphere of Chatsworth.
- to identify possible sources of metal pollutants.

1.1.1 Objectives

The main objectives of this investigation were to:

- collect particulate material in the atmosphere of primary schools in the greater Chatsworth area.
- develop a suitable digestion procedure for the samples.
- determine the concentrations of selected metals in the collected samples by graphite furnace atomic absorption spectrophotometry .
- compare the levels of the metals with levels in other urban areas nationally and internationally.
- make recommendations based on the results obtained to the local health and environmental authorities.

1.1.2 Significance of this study

From the relevant literature it is known that children, particularly those under the age of seven are most affected by low levels of lead poisoning. A number of studies (Rutter and Jones, 1983; Baird, 1995) have found small but significant neuropsychological impairment in young children due to environmental lead absorbed either before or after birth. About 90% of the lead in the atmosphere comes from the combustion of leaded petrol (Harrison and Laxen, 1981). The inhaled lead enters the blood stream and, when it finally reaches a maximum, the excess lead then enters the soft tissues, particularly the brain (Baird, 1995). The toxicity of lead is proportional to the amount in the soft tissues, due to its affinity for the metal, rather than that in the blood or bone. In particular, lead appears to have a deleterious effect on children's behaviour, attentiveness and possibly even on their IQ's and other educational abnormalities (Baird, 1995). Chatsworth, being a densely populated area, has a large number of primary schools with pre-primary or bridging module classes. Furthermore, these schools are situated close to the main roads and the children are exposed to high levels of exhaust emissions from cars, minibuses and other forms of petrol driven transportation. It was as a result of this concern, that an investigation of the levels of lead, in the vicinity of the schools, was undertaken.

The study was extended to other selected metals that are generally considered toxic, namely, Cr, Ni, Cu and Cd (Alloway and Ayres, 1993).

1.2 Air Pollution

A widely used definition of pollution is "the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenities or interference with legitimate uses of the environment" (Alloway and Ayres, 1993). The transport of atmospheric pollutants depends on the height they reach in the atmosphere, their particle size and climatic factors.

Air pollutants tend to be transported by wind and mixed with the surrounding air until their concentration is relatively uniform. Dispersion in the horizontal plane is generally restricted and occurs more rapidly than vertical mixing. The extent to which air pollutants become diluted is governed by factors determining the degree of turbulence such as incoming solar radiation, wind speed, cloud cover and land topography (Fifield and Haines, 1996). Metals such as Pb, Cd, Cr, Ni and Cu are commonly associated with pollution and toxicity. Since these metals occur naturally in ores, their presence is insufficient evidence of pollution, the relative concentration is therefore more important. The determination of the concentration of these metals require appropriate sample collection, storage and analysis.

1.3 History of Air Pollution

The principal industries associated with the production of air pollutants in the centuries preceding the Industrial Revolution were metallurgy, ceramics as well as those producing animal products. In the bronze and iron-ages, villages were exposed to dust and fumes from many sources. Native copper and gold were forged, and clay was baked and glazed to form pottery and bricks.

The predominant air pollution problem of the nineteenth century was smoke and ash from the burning of coal or oil in the boiler furnaces of power plants, locomotives, marine vessels and in home heating. Great Britain took the lead in addressing the problem and the first Public Health Act was introduced in 1848. Air pollution from the emerging chemical industries was covered by a separate act. As the nineteenth century drew to a close, air pollution, especially in mill towns all over the world, had risen to a peak and there was considerable damage to vegetation (Stern et al, 1984).

In the early part of the nineteenth century, as cities and factories grew in size, the severity of air pollution increased with no significant changes in legislation. By the year 1925 the rapid increase in the number of automobiles added to the problems of air pollution.

During the period 1925-1950 there were many large air pollution problems throughout the world and consequently air pollution surveys and research got underway. While major technological changes were underway to replace pollutant producers with ones that are less problematic, there was still no significant legislation on air pollution. From about 1950 to the present there were several major air pollution disasters resulting in major health problems and the death of hundreds of people. In this regard only three incidents will be mentioned.

1.3.1 Cadmium Poisoning in the Jintsu Valley in the Toyama Prefecture in Japan

A serious case of Cd poisoning occurred in the Jintsu Valley where Zn mining had caused widespread Zn and Cd (zinc ores contain relatively high concentrations of cadmium) contamination of the alluvial soils, most of which were used for paddy rice production. The rice grown in these contaminated paddies is the staple diet of the people in this valley. After the second world war, it was found that more than 200 elderly women had developed kidney damage and skeletal deformities. This condition was known as 'itai-itai' disease which literally means 'ouch-ouch' due to the pain caused by the deformed bones.

The rice which they consumed contained ten times more Cd than that locally legislated (Alloway and Ayres, 1993).

1.3.2 Mercury Poisoning in Iraq and Japan

A serious case of chemical poisoning occurred in 1971/2 in Iraq. A consignment of Hg-treated seed exported to Iraq for growing was mistakenly milled into flour and used for making bread. By the end of 1972, 6530 people had been admitted to hospital suffering from Hg poisoning and 459 of these patients died. In another incident several people of the Minimata Bay area were severely affected by methyl mercury poisoning after eating fish that was contaminated. The source of the mercury was the Minimata Chemical Company which discharged its Hg-containing liquid wastes into the bay (Alloway and Ayres, 1993).

1.3.3 Lead Poisoning in Britain

Historically famous episodes of Pb poisoning from direct contamination of alcoholic beverages have been attributed to Pb cooling coils in rum stills (West Indies Dry Gripes), Pb linings and joints in cider presses (Devonshire Colic) and Pb compounds used for cleaning and preserving wine (Poitou Colic). Illegal whisky production in some areas is still a cause of Pb poisoning. It was found that "moonshine" whisky contained more than 1 mg of Pb per litre. There is some evidence that Pb is the cause of sterility, spontaneous abortion and neonatal malformation among female consumers (Engel et al, 1971). A public outcry at the deaths of several employees at a lead factory in 1882 forced the Government to set regulations limiting such Pb emissions.

1.4 Some Sources of Air Pollution

This section is restricted to discussing sources of metal pollutants and, in particular, the five metals mentioned under 1.2 in the introduction.

1.4.1 Lead

Most of the Pb found in the atmosphere, results from the combustion of leaded petrol. Several reports (Harrison and Laxen, 1981) indicate that automobile traffic contributes about 90% of the total atmospheric lead emissions. Lead has been added to petrol since the early 1920's. Tetra-methyl and tetra-ethyl lead additives prevent engine “knocking”. The atoms of Pb liberated by the combustion of the tetraalkyl compounds must be removed before they can form metallic deposits and damage the vehicle’s engine. Small quantities of ethylene dibromide or dichloride is added to convert the Pb into a volatile form. The addition of the Pb scavengers (ethylene dibromide or dichloride) results in the emission of volatile lead halides such as $PbBr_2$, PbBrCl, etc. into the atmosphere. Subsequently, under the influence of sunlight, these compounds form PbO. The transformation of tetra alkyl lead to inorganic lead is summarized as follows:

$$PbR_4 \rightarrow [Pb] \rightarrow Pb\,Br\,C\ell \rightarrow PbO$$

where R = methyl or ethyl groups.

The lead oxide exists in particulate form as an aerosol in the atmosphere for hours or days, and consequently, not all of it is deposited in the immediate vicinity of the roadway. Thus fine particulate PbO can easily find its way to the classrooms and eventually into the blood stream of young children.

Other sources of lead emission include mining, smelting, refining and manufacturing of Pb containing compounds which contribute to the levels in the atmosphere. However, Chatsworth itself has no major industries, which can contribute significantly to lead emissions, but is surrounded by industries which can significantly affect the level of particulates in the area of study.

It is worth noting that for the European Community, the maximum permissible lead concentration, in ambient air, is 2 $\mu g/m^3$ (Fifield and Haines, 1996). The national air quality standard for Pb in the US is 1.5 $\mu g/m^3$ (Merian, 1991).

1.4.2 Cadmium

Cadmium has been emitted in minor amounts into the environment but in increasingly greater quantities from post world war II in the form of dusts, aerosols and solids from point sources such as incinerators (Nriagu, 1980). Cadmium emissions into the atmosphere are primarily attributed to the following sources:

- non-ferrous metal production and processing
- fossil fuels and waste incineration
- iron and steel production
- battery manufacturing/ recycling.

The World Health Organisation has recommended a long-term exposure level not exceeding 10$\mu g/m^3$. In the USA the National Institute of Occupational Safety and Health recommended in 1983 the reduction of the 40 $\mu g/m^3$ standard for cadmium emission (Merian, 1991)

1.4.3 Chromium

The metal industry uses most of the chromium produced. During the production of alloys, small particles of chromium can escape into the atmosphere as dust. Chromium containing liquids or aerosols can escape into the environment especially in the galvanizing industry. Large amounts of chromium can escape into the atmosphere from effluents of the textile, pigment, catalyst and other chromium compound manufacturing industries. Leather dust also contributes significantly to the chromium content of the atmosphere. The incineration of chromium containing wastes (e.g. audio and video tapes, treated poles, printing industry wastes etc.) can cause the metal to escape into the air in the form of flash or volatile chromium compounds (e.g. chromyl chloride).

In the USA the threshold limit value (TLV) of Cr(VI) in the atmosphere is fixed as 0.1 mg/m^3 (Merian, 1991).

1.4.4 Nickel

Nickel enters the atmosphere from natural sources (e.g. volcanic emissions and wind blown dusts produced by weathering of rocks and soils), from combustion of fossil fuels by stationary and mobile power sources, from the emissions of nickel mining and refining operations, from metal consumption in industrial processes and from incineration of wastes. Recent studies have demonstrated the presence of nickel carbonyl in cigarette smoke (Grandjean, 1984).

In several countries the atmospheric limit for occupational exposure to nickel is $1mg/m^3$ (Grandjean, 1986).

1.4.5 Copper

Copper enters the atmosphere primarily through mining, smelting and refining operations. Copper metal is used in piping, roofing, kitchenware, pharmaceutical equipment and as a pigment. It is also used as an alloy with various other metals. Copper compounds are used as algaecides, as fungicides, in electroplating, as a component of paint, in solvents for cellulose, in electronic devices etc. It is possible that these may end up as wastes and incineration can lead to the presence of copper in the atmosphere. Copper compounds can catalyse many reactions and can also activate the formation of toxic chlorinated dioxins. In the Federal Republic of Germany the maximum allowed concentrations at the workplace are 0.1 $\mu g/m^3$ for copper fume and 1 $\mu g/m^3$ for copper dust (MAK, 1987).

1.5 Effects of Air Pollution

1.5.1 On Human Health

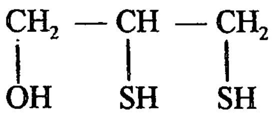
Biochemically, the mechanism of the toxic action of metal cations arises from the strong affinity of these ions for sulphur. Thus "sulphydryl" groups, -SH, which occur commonly in the enzymes that control the speed of critical metabolic reactions in the human body, readily attach themselves to an ingested heavy metal cation or molecules that contain the metals (Baird, 1995). The resultant metal-sulphur bonding affects the entire enzyme, thus preventing it from performing its normal functions. Thus human health is adversely affected and sometimes with fatal consequences. The reaction of heavy metal cations, M^{2+}, with the sulphydryl groups is analogous to the reaction of the cation with the simple inorganic compound H_2S as illustrated below:

$$M^{2+} + H_2S \Rightarrow MS\downarrow + 2H^+$$

In the case of an enzyme with an organic chain indicated by R, the reaction would be as follows:

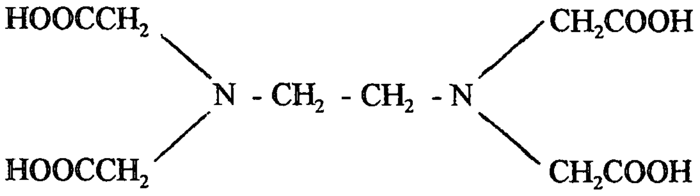
$$2R-S-H \quad + \quad M^{2+} \Rightarrow \quad R-S-M-S-R \quad + \quad 2H^{+}$$

A common medicinal treatment for acute heavy metal poisoning is the administration of a compound that binds the metal even more strongly than does the enzyme. The metal-compound combination is then solubilized and excreted from the body. Two common compounds used for the treatment of heavy metal poisoning is BAL (British Anti-Lewisite) and EDTA (ethylenediaminetetraacetic acid). Their structures are illustrated below:



$$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ OH & & SH & & SH \end{array}$$

BAL



EDTA

In the case of BAL the metal is trapped between the two SH groups. EDTA is effective in chelating almost all +2 and +3 charged ions. It is usually administered as the calcium salt so as to prevent depletion of calcium in the body.

1.5.2 On Atmospheric Conditions

The large concentration of particulates in atmosphere over large cities and industrial areas affect visibility, solar radiation etc. Smoke and fumes tend to increase the atmospheric turbidity reducing visibility and the quantum of solar radiation reaching the earth's surface.

Particulates absorb and reflect incident solar radiation and thus cause about 20% decrease in solar flux in large cities compared to cleaner rural areas. Solid particulates participate in cloud formation. Pollution and water vapour emission in urban air tend to increase cloud cover by 10% resulting in more wet days, more mist, fog and smog relative to rural areas. These processes combine to increase the deposit of large sized particulates on the ground. This leads to erosion and corrosion of buildings, materials, metals and damage to plants (De, 1990).

1.6 Factors that influence the distribution of Air Pollutants

There are several factors that influence the distribution of pollutants in the atmosphere. These include temperature, humidity, wind speed and direction, pressure, rain, topography etc.

In the case of temporal variation in the level of pollutants, particularly lead, many investigators have shown that the concentrations are higher during the winter months than in summer months (Albertyn, 1994; Von Schirnding, 1988). Particularly high concentrations of lead were associated with temperature inversions in the study done by Y.E.R Von Schirnding (D.Phil thesis, 1988) in Cape Town.

The author attempted to relate weather conditions to metal pollutant level but no meaningful correlation could be drawn from the limited data acquired. This would have been possible if there were sufficient samplers for sample collection at the different schools throughout the year. The correlation between pollutant level and meteorological factors is discussed in chapters 4 and 5.

According to Alloway and Ayres (Alloway and Ayres, 1993), under high humidity, smaller particles may sometimes cluster and form larger particles which are deposited more readily in the immediate vicinity. Rain on the other hand results in a washing-out of pollutants and hence, lowering the pollutant level in the atmosphere (Alloway and Ayres, 1993). Hills and valleys, together with large buildings can form a canyon-like topography through which the wind is forced and hence carries away much of the pollutants. Air pollutant concentrations, from point sources, are probably more sensitive to wind direction than any other parameter. Wind speed generally increases with height but other factors such as, atmospheric stability, surface roughness etc. also affect the speed. One of the effects of wind speed, is to dilute continuously released pollutants at the point of emission. Figure 1.1 shows the effect of wind speed on pollutant dispersion, i.e. the greater the wind speed, the smaller the pollutant concentration at a particular sampling point (Stern et al, 1984).

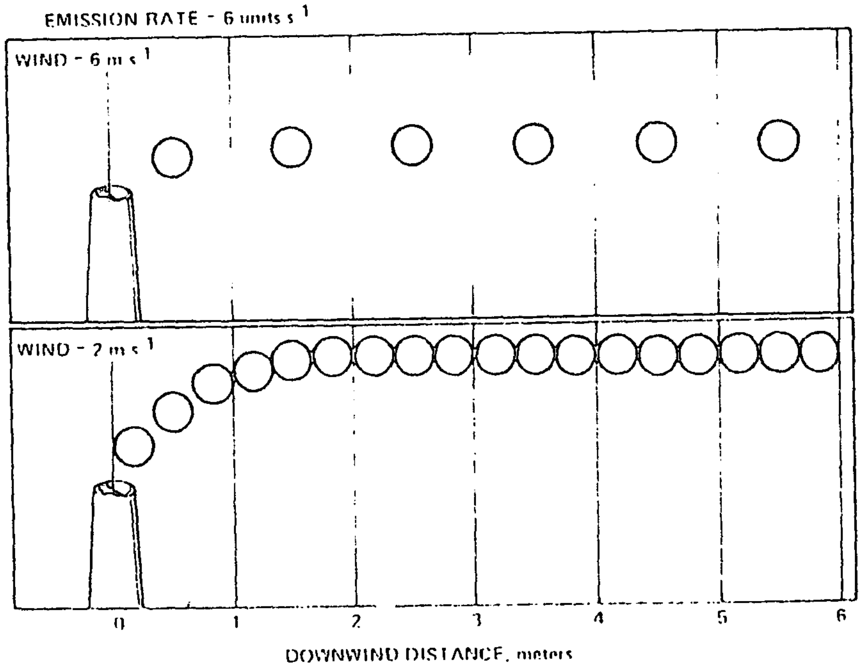


Figure 1.1: Dilution by wind speed.

1.7 Sampling and Analysis of Air Pollutants

1.7.1 Sampling and Sampling Systems

The principal requirement of a sampling technique is to obtain a sample that is representative of the atmosphere at a particular place and time, and which can be evaluated as a mass or volume concentration. The sampling technique should not alter the chemical or physical characteristics of the sample.

The major components of most sampling systems are:

- an inlet manifold
- an air mover
- a collection medium
- a flow measurement device.

The inlet manifold transports material from the ambient atmosphere to the collection medium. The inlet manifold is made out of glass, teflon, stainless steel or other inert material. It also protects the rest of the components from exposure to rain and other weather conditions.

The air mover is an ac or dc pump which is used to create a vacuum or lower pressure at the point of collection.

The collection medium may be a liquid or solid sorbent for dissolving gases, or a filter surface for collecting particulates or a chamber to contain an aliquot of air for analysis.

The flow device measures the volume of air drawn through the collection medium. Examples of flow devices are mass flow meters, rotameters and critical orifices.

Sampling systems may not necessarily have all four components; it depends on the type of sample being collected. Regardless of the configuration or number of components, several characteristics are important for all ambient air sampling systems. These are: collection efficiency, sample stability, recovery, minimal interference and an understanding of the mechanism of collection. Collection efficiency drops drastically when solid or liquid sorbents become saturated. Sample stability becomes increasingly important as the time between sampling and analysis increases. Effects of temperature, trace contaminants and chemical reactions can cause the collected species to be lost from the collection medium (Stern, et al, 1984).

Particulates are sampled for many reasons. They are, inter alia:

- to determine whether there are hazardous concentrations of pollutants in the atmosphere or if ambient air standards have been exceeded.
- to determine the effectiveness of control programs in reducing ambient concentrations of pollutants.
- to determine the emission levels from a source.
- to determine the effectiveness of devices to control emission levels.
- to determine sources contributing to pollution at a receptor (Lodge Ed, 1991).

1.7.2 Analysing Systems

Metals and metallic compounds exist in the atmosphere in three distinct physical forms viz.

solid particulate matter, liquid droplets (mists) and vapours. Airborne particulate matter is by far the most common form of metallic air pollutant (Lee and von Lehmden, 1973 ; Ure and Davidson, 1995).

The three major characteristics of particulates are total mass concentration, size distribution and chemical composition. Total mass concentration has been used as a measurable quantity for air quality standards to protect human health from effects caused by the inhalation of suspended particulates. Size distribution of particulates is very important in understanding the transport and removal of particles in the atmosphere and their deposition behaviour in the human respiratory system. Their chemical composition may determine the type of effect caused by particulate matter on humans, vegetation and materials. The chemical composition of particulate pollutants is determined in two forms viz.: a specific element or specific compounds or ions. Knowledge of their chemical composition is useful in determining the sources of airborne particulates and in understanding the fate of these particulates in the atmosphere.

Although some methods of analysis of particulate matter require no pretreatment of the collected samples prior to analysis, for most analytical methods it is necessary to destroy the organic matter associated with the sample and to render the sample soluble (Harrison and Perry, 1986).

1.8 Analytical methods requiring no pretreatment of a sample.

1.8.1 X-ray Fluorescence Analysis (XRF)

XRF is convenient for elemental analysis for several reasons:

- It requires little or no sample preparation;
- It is fast;
- It can determine total metal concentration and
- It is essentially a non-destructive technique.

The XRF technique is applicable to every element from Na onwards in the periodic table, for both qualitative and quantitative analysis. However the latter require exacting standardization procedures and a computer is essential for the interpretation of data. Difficulties experienced with XRF include the influence of particle size, specific sample characteristics, the overlap of the X-ray emission spectra of many elements and the effects of interfering elements. With wavelength dispersive XRF instruments, detection limits of 5-20 ng/cm^2 for deposits on Millipore filters have been reported (Dzubay and Rickel, 1978).

1.8.2 Neutron Activation Analysis (NAA)

In studies of the origin and fate of trace elements, it is advantageous to be able to analyse samples for a wide spectrum of elements with a high sensitivity and accuracy. This condition is best satisfied with NAA since it is one of the most sensitive, selective and reliable multi-element analytical techniques available. However, the technique has been limited by the expense and sophistication of the equipment and the availability of people with the special expertise needed to perform the analyses. Although the technique is considered to be interference-free, the possibility of errors due to interferences arise when experimental conditions are not properly adjusted or neutron flux is not characterized well enough. Another disadvantage is that the turnaround times for the analysis of long-lived isotopes are around 2-3 weeks because of the delay for the decay of short-lived isotopes. A further disadvantage is that several environmentally important elements such as Si, Ni, Pb, and other lighter elements are impossible to observe, because of inadequate sensitivity, interferences or high blanks (Altshuller, 1972).

1.9 Analytical methods requiring pretreatment of a sample.

1.9.1 Inductively Coupled Plasma(ICP-AES)

Although inductively coupled plasma (ICP) emission technique has only become commercially available since the mid-1970's, it has become widely accepted for the analysis of most metals because of its simplicity of use, wide linear dynamic range, speed and accuracy of analysis. Furthermore freedom from chemical interferences is a distinct advantage. Simultaneous ICP is capable of determining thirty or more elements from a single sample. The limitations of ICP are the high cost of argon gas, high sample throughput and the high capital cost of the equipment. ICP also suffers from spectral interferences and their presence can reduce the accuracy and precision of trace element analysis. The sensitivity of ICP-AES for most metallic elements is in the range 0.01 - 100 ppm (Barnes, 1980). However, much greater sensitivity can be achieved with ICP-MS which has the advantage of extremely low detection limits, wide linear range and an uncomplicated spectra. The instrumental detection limits for more than 60 elements including carbide forming elements and lanthanides, are between 0.03 and 0.3 ppb. A major limitation however is the extremely high cost of the equipment (Lajunen, 1992).

1.9.2 Polarographic Techniques

Polarographic techniques have long been applied to the analysis of metals. The technique, however, is unlikely to be the preferred technique for air pollution analysis because of its sensitivity to other electrolysable components in the matrix of the sample (West, 1968).

1.9.3 Anodic Stripping Voltammetry (ASV)

ASV is a sensitive and precise electro-analytical technique for the detection of metals in trace concentrations in environmental samples. The method has the advantage of pre-concentration to increase sensitivity and also of selectivity due to deposition of the metal at a known, constant potential. The method requires dissolution of a sample but allows for repeated re-analysis of the same sample. Furthermore it provides both quantitative and qualitative information. The main types of interference are inter-metallic compound formation and overlapping stripping peaks. The cause of the latter is the similarity in oxidation potentials which may lead to interferences in the determination of specific elements. The method has been applied by Colovos et al to determine Pb, Cd, Cu and Zn in Millipore filters (Colovos et al, 1973).

1.9.4 Chromatographic Techniques

In recent years several investigators have used ion chromatography (IC) and high-performance liquid chromatography (HPLC) as an analytical tool for the determination of trace metals (Steenkamp and Coetzee, 1994). Its greatest potential lies in the simultaneous determination of metal species present in the sample. However the process involves extracting the metals with an organic chelating agent and consequently the time of analysis is increased. It is likely that chromatographic techniques will become increasingly popular with advances made in IC and HPLC technology.

1.9.5 Analysis by Atomic Absorption Spectroscopy

Atomic absorption falls into two categories viz. flame atomic absorption and non-flame atomic absorption. Generally, flame absorption is not recommended due to poor detection limits and variable matrix effects. Non-flame absorption analysis, however, has become more popular in the past ten years because of its extremely low detection limits and small volumes of samples needed for analysis.

Atomic absorption has rapidly become the most widely used analytical technique for quantitative trace metal analysis. Atomic absorption is a solution-based technique, with only very limited applications for the direct analyses of solids and gases. The technique is discussed in greater detail, under experimental, in chapter 2 since this was the preferred method of sample analysis.

CHAPTER 2

2.1 Sample Origin and Collection

Six sites in the greater Chatsworth area were selected for the collection of airborne particulate material. All the sites selected were primary schools. These schools were selected mainly because of their proximity to the main traffic routes. Other factors, such as willingness by staff to assist in the research, the source of electricity, safety of equipment etc. also had to be considered. Figure 2.1 details the sites where sampling was done.

Preliminary work was done at each of the six schools from September to November of 1995. This entailed setting up the sampler in the designated area and ensuring that the set-up did not pose any danger to the pupils of the school. Only when permission was granted by the Department of Education (Appendix A) did meaningful sampling begin. During the preliminary stage sampling was done, using a sampler borrowed from NCOH in Johannesburg. This sampler, shown in Plate 1, had some limitations:

- It had a maximum height of 50cm which was too low for proper particulate collection.
- The sampler had a fixed flow rate of 20 litres per minute (LPM).
- It had no automatic timing device and hence required to be switched on and off manually at the appropriate times.

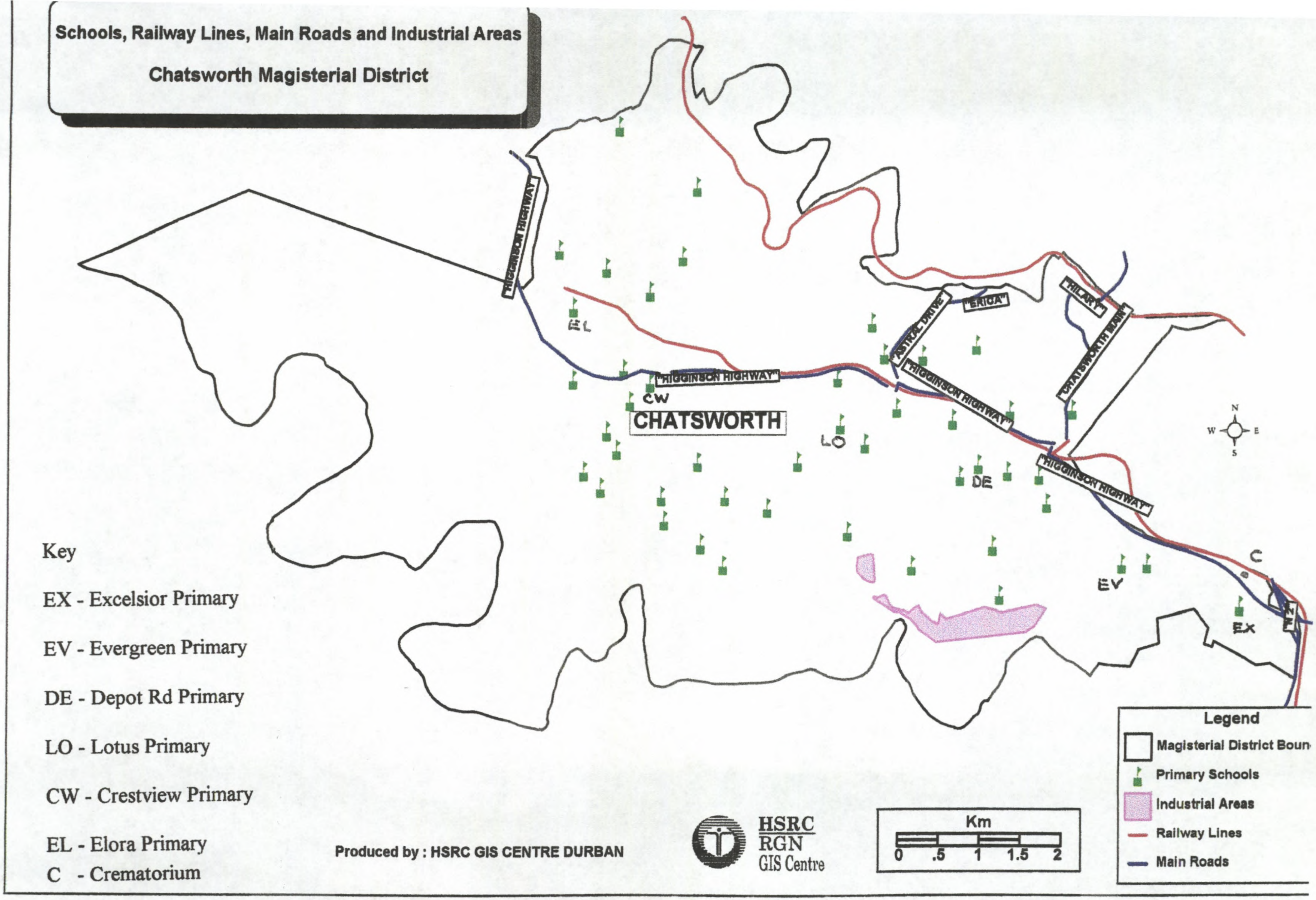


Figure 2.1: Location of schools where air samplers were placed in the study area.

In spite of its limitations, the sampler served a useful purpose in providing samples which were used to establish experimental conditions for the digestion and analysis of future samples.

In January 1996 two sophisticated Gilian Envirocon high volume samplers were used. All results shown are from samples collected by these two instruments (Plate 2). An additional feature of the new instrument is its ability to maintain the flow rate as the filter becomes loaded with particulates.

The samplers were set up on the school premises at 06h30 on each weekday morning. The samplers were programmed to automatically start at 07h00 and to stop at 15h00. Sampling was done only during school hours. No sampling was done after 15h00 on weekdays, on weekends and during school holidays. This was due to the lack of security for the equipment during these times.

At the end of the 8-hour period of sampling, the caretakers simply replaced the cover of the filter holders, to prevent any contamination and put the apparatus away in a well-secured room. The next morning the filter holders were removed and replaced with new ones. The apparatus was set up at the usual place and sampling repeated. At each school, sampling was done for approximately two weeks. For example, sampling at Excelsior Primary School was done from the 28 February to the 8 March 1996 and again from the 29 July to the 5 August 1996. On some days sampling had to be aborted due to rain, power failures, caretaker and teacher strikes etc. The dates when sampling was done at each of the schools is given in Appendix B.

Particulates were collected on 37 mm mixed cellulose-ester membrane filters with 0.8 μm pore sizes. Prior to sampling, these filters were dried in an oven at 70°C for one hour and cooled in a desiccator. The pre-weighed, cooled filters were placed with backing filters (Plate 3) into polyethylene filter holders (Plate 4). The samples collected on the morning of each day were put into a desiccator and transported to the technikon. The sample filters were dried in an oven at 70°C for one hour, cooled and re-weighed. The weighed filters and their backings were put into labelled petri dishes (Plate 5). These petri dishes were stored in a desiccator for analyses at a later date.

2.2 Cleaning Procedure

All glass and plastic equipment used for preparing standards and samples was cleaned by soaking in 50% HNO_3 for 24 hours. This was followed by thorough rinsing with de-ionized water and air dried in a clean air unit. Prior to use all equipment was rinsed with the appropriate solution.

2.3 Standard and Sample Preparation

Prior to analysing a set of samples from a school for a specific metal, standards of that metal were freshly prepared and analysed. During the course of the preliminary work on instrumental optimization, it was found that much higher sensitivities were obtained

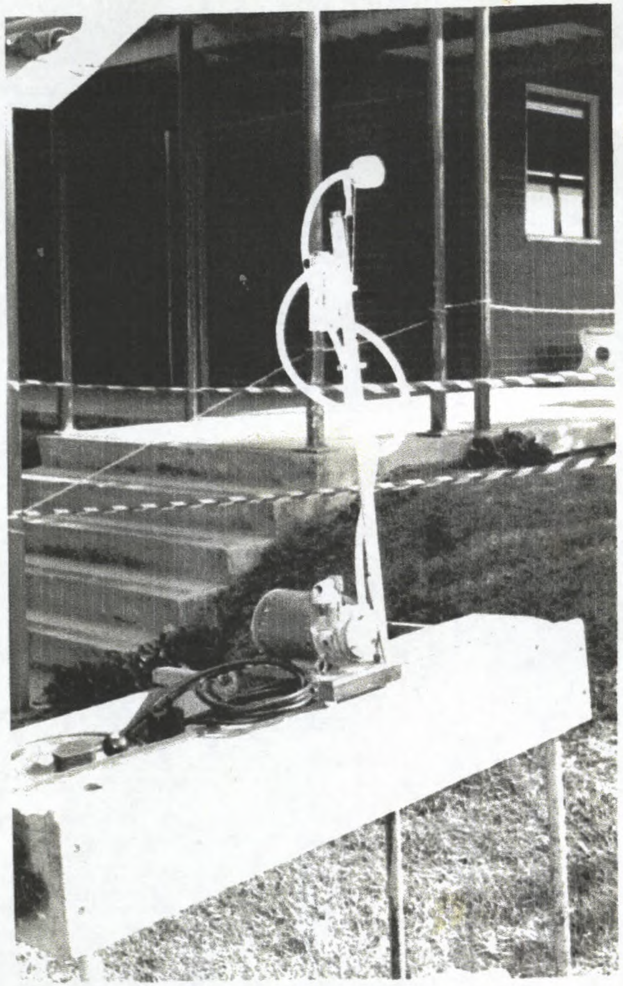


Plate 1: The sampler borrowed from NCOH

Plate 2: The Gilian Envirocon 2 High Volume Sampler

when a new graphite tube was used, compared to a previously 'fired' graphite tube for the same sets of standards. Table 2.1 shows the sensitivity to be approximately two times greater for a new tube than for a previously 'fired' tube. The graphite tube was used for approximately 200-300 'firings' although the Varian manual indicates approximately 500 'firings'. After about 200 'firings' the pyrolytic coating of a graphite tube is severely eroded and loosely bound carbon particles affect the absorbance values considerably, making it more difficult to obtain reproducible absorbance values. Although linearity was maintained, the sensitivity was low. As a result of the high cost factor the same graphite tube was used for the analysis of at least two metals. However, graphite tube usage did not exceed 200 'firings'. Since absorbance values depended on the condition of the tube as seen in Figure 2.2, sample values had to be determined relative to standards used on that tube and thereby eliminating errors caused by tubes of different conditions.

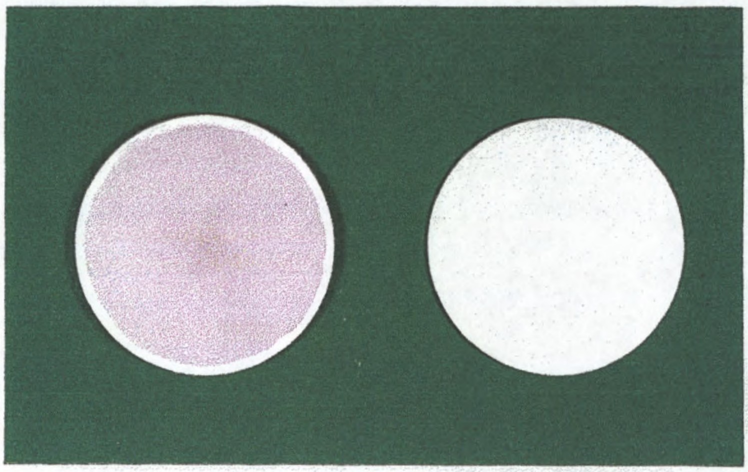


Plate 3: Filter and pre-filter

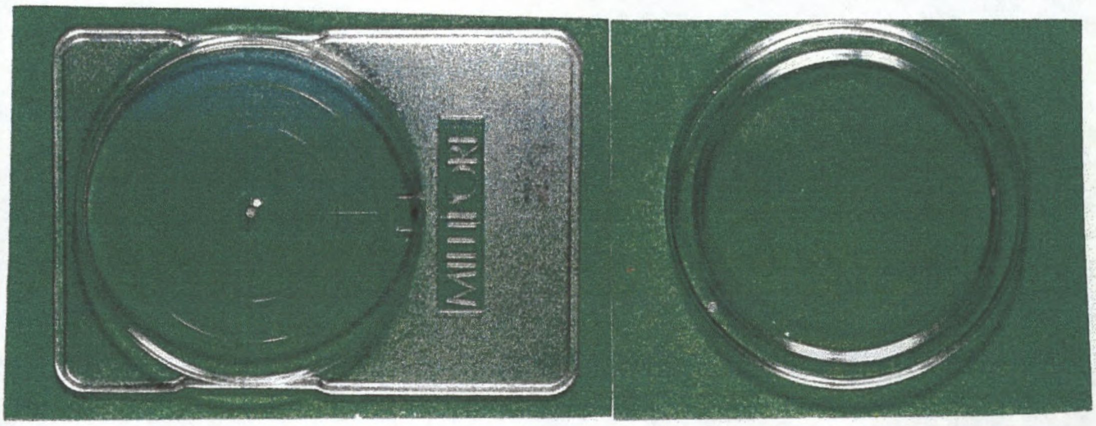


Plate 4: Petri dish with cover.

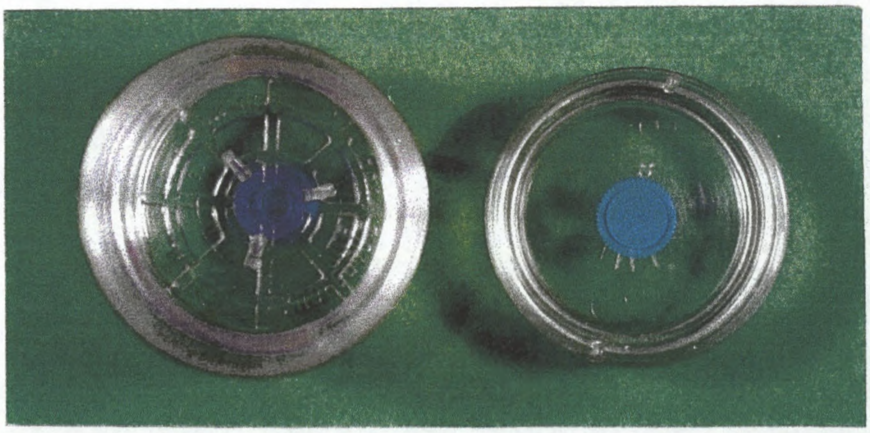


Plate 5: Filter holder and protective cover

Table 2.1: Effect of tube condition on absorbance values

Concentration	Absorbance Values	
[Pb] ppm	'Fired' Tube	New Tube
0.00	0.000	0.000
0.04	0.114	0.245
0.08	0.202	0.462
0.12	0.307	0.641
0.16	0.357	0.803
0.20	0.436	0.936
0.30	0.621	1.273

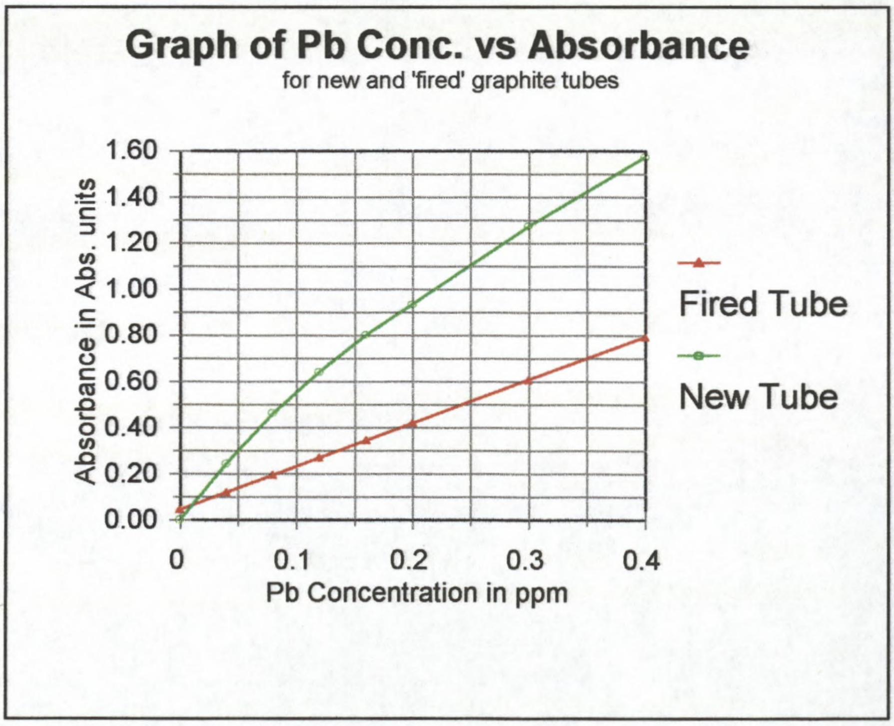


Figure 2.2: Relationship between tube condition and measured absorbance

2.3.1 Standard Preparation

All standards were prepared from Univar 1000 ppm stock solutions guaranteed to within 0.5% of the nominal value with the exception of cadmium which was prepared from 99.5% pure CdO (AR grade, Aldrich Chemical Company) on the day of the analysis. A 1000 ppm cadmium oxide solution was prepared by dissolving approximately 0.1 gram of the solid in 1M HNO_3 and making it up to mark with the same solvent in a 100 mL volumetric flask. For lead, chromium, nickel and copper the standards prepared ranged from 5 ppb to 25 ppb. In the case of cadmium the standards prepared ranged from 0.5 ppb to 2.5 ppb. These standards were freshly prepared in 100 mL "A" grade volumetric flasks using serial dilution. All standards were made up to mark using freshly prepared 1M HNO_3 from 70% HNO_3 (AR grade, Riedel-deHaën).

2.3.2 Sample Preparation

The method adopted for the preparation of air filter samples was a modified version of that used by Vladimir Chernyakhovskiy (Chernyakhovskiy et al, 1994). Only "A" grade glassware was used for the preparation of samples. All apparati such as pipettes, beakers, teflon vessels, volumetric flasks etc. were cleaned by soaking them in 50% nitric acid for 48 hours and thereafter rinsing them with deionized water. The apparati were first rinsed with 1M HNO_3, before being used for the preparation of samples.

The sample filters and blank filters were weighed and then carefully transferred with tweezers into teflon microwave vessels. Thereafter 2 mL of 70% HNO_3 (AR grade, Riedel-deHaën) was added to each vessel. The vessels were sealed and put into the rotor of a microwave digestion unit. A microwave heating programme was used to completely digest the samples.

2.4 Microwave Digestion Programme:

The Milestone MLS 1200 mega high performance microwave digestion unit was used to digest all samples. The instrument has the capability to set the temperature and pressure in the vessels but this feature was not used in the procedure adopted because the need for this information was irrelevant to the study. The purpose of using the microwave digestor was to rapidly dissolve the sample. A suitable programme for digesting filters containing dust particulates collected over three 8-hour periods was determined experimentally. The filter which was exposed to three 8-hours of particulate collection was digested according to the instructions given in the manual for the dissolution of particulates. These conditions did not digest the sample fully. The digestion procedure was repeated for a new sample using different power and time settings. Only when the sample was fully digested was the programme accepted as being more than adequate for the dissolution of any 8-hour sample collected during the period of sampling. The aim was to obtain a digestion programme which would ensure that the sample is completely digested. This final dissolution programme is shown in Table 2.2.

After 15 minutes of digestion the system was allowed to vent for 10 minutes to allow for any noxious fumes to escape into the fume hood. On completion, the rotor with the vessels was removed and allowed to cool for about an hour. The sample and blank solutions were quantitatively transferred to 50 mL volumetric flasks. Thereafter 1M

HNO_3 was used for topping up of the flasks. Blank filters were treated in exactly the same way. For the Ni and Cd determinations exactly 20mL of the sample and blank solutions were reduced to about 1mL by gentle heating on a hot plate and then quantitatively transferred to a 5 mL volumetric flask and brought to mark using the prepared 1M HNO_3. Blanks, standards and samples were all analysed using the Varian AA 1275 model atomic absorption spectrophotometer with the graphite tube atomiser (GTA-95) attachment.

Samples, in which the absorbance values were above that of the linear range of the standards, were diluted to give values within the desired range.

Table 2.2: Microwave digestion programme for blank filters and samples.

STEP NO.	TIME (min)	POWER (watts)	PURPOSE
1	2.00	300	to start the smooth oxidation of organic matter
2	2.00	0	to allow the reaction to proceed without the addition of energy so as to avoid potentially dangerous runaway temperatures and pressures
3	3.00	400	to complete the "soft" oxidation of organic matter
4	4.00	600	to complete both the digestion and oxidation of organic particulate matter. Since digestion is a function of particle size, adequate digestion time is allowed to cater for the different particle sizes trapped onto the filter paper. Furthermore the power applied is increased gradually to avoid loss of material as a result of huge changes in power.
5	4.00	800	

CHAPTER 3

Instrumentation and Data Reduction

3.1 Background

3.1.1 Atomic Absorption

The basic concepts of atomic absorption spectrometry were published first by Walsh (Walsh, 1955) in 1955. At about the same time Alkemade and Milatz (Alkemade and Milatz, 1955) designed an atomic absorption spectrometer in which flames were employed as an atomizer. The commercial manufacture of atomic absorption instruments however did not start until ten years later. Since then, the development of atomic absorption spectrometry has been almost explosive and atomic absorption instruments rank among the most extensively used instruments for trace metal analysis. The use of nitrous oxide as an oxidant and electro-thermal atomization have both significantly extended the use of atomic absorption spectrometry. These techniques aided in increasing the measurement of a number of elements at very low concentrations. The large number of published papers in atomic absorption spectrometry is an indication of its popularity (Fox, 1985; Sneddon, 1983)

The wide popularity of atomic absorption spectrometry can be attributed to its simplicity and relative ease of use. In addition the high sensitivity of graphite furnace atomic absorption spectrometry is very important in many applications. The use of hollow cathode lamps or electrode-less discharge lamps provides extremely narrow radiation lines. Thus spectral interferences are minimized and wavelength selection is made easy.

However, only one to four elements can be determined simultaneously. Multi-element analysis, with GFAAS, can become extremely time-consuming especially if there are a large number of elements to analyse. Furthermore, the graphite furnace determination requires the optimization of instrumental conditions for each element in order to obtain satisfactory results.

3.1.2 Advantages of Atomic Absorption

The technique can be applied to about 44 metals. Atomic absorption is essentially a solution-based technique, with only very limited application for direct analysis of solids and gases. The advantages of atomic absorption are specificity, speed, and ease of use. Detection limits are typically in the ppm to ppb range. A vast amount of published atomic absorption methodology is now available, covering a wide range of applications (De Jonghe and Adams, 1982; Byrne, 1983). In comparison to flame atomic absorption, graphite furnace atomic absorption provides about 50 to 500 times greater improvement in sensitivity depending on the metal analyte.

3.2 Graphite Furnace Atomic Absorption Spectrometry

Graphite furnace atomic absorption spectrometry is also known by other acronyms such as ETAAS. As in the case of FAAS, this technique is based on the fact that free atoms will absorb light at frequencies or wavelengths characteristic of the element of interest. Within certain limits, the amount of light absorbed can be linearly correlated to the concentration of the analyte present. Free ground state atoms of most elements can be produced from aqueous samples by the application of high temperatures. Figure 3.1 illustrates a schematic representation of a graphite furnace atomic absorption spectrophotometer.

3.2.1 Light Source

Each element that is to be analysed requires a lamp in which the cathode is made of that particular element. The lamps generally have a finite life and should be replaced after 2-3 years of daily use. The life span of a hollow cathode tube depends on the operating lamp current. Most manufacturers generally provide a recommended operating lamp current. During the course of finding the optimal conditions for analysis of the samples, a set of standards were analysed to determine the most suitable lamp current for the analysis of each of the five metals. It was found experimentally, that high lamp current does not necessarily give better sensitivity as shown in Figure 3.2. Although not shown graphically, a current of 3 mA gave significantly poorer sensitivity, reproducibility and linearity and consequently was not included in Table 3.1. As a result of this kind of investigation, lamp currents that gave the best sensitivity were used for the analysis of both standards and samples. In the case of Ni for example, a lamp current of 4 mA was used.

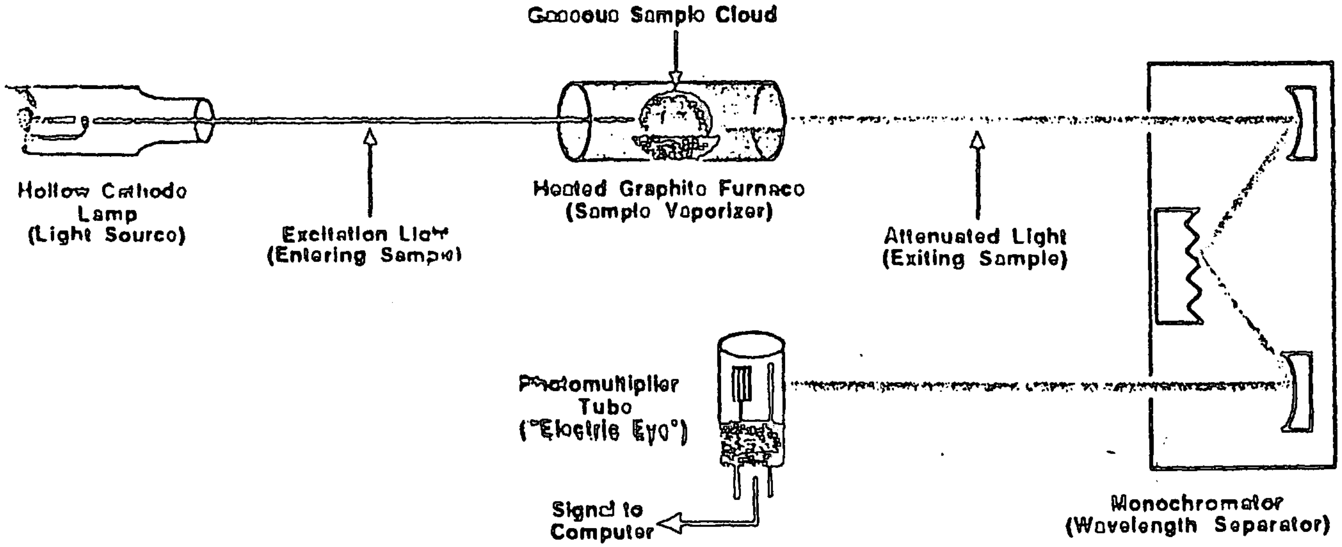


Figure 3.1: A schematic diagram of a Graphite Furnace AA spectrophotometer

Table 3.1: Relationship between Lamp Current and Absorption Values for Ni

Current	4 mA	10 mA	20 mA
[Ni] ppm	Abs	Abs	Abs
0.000	0.000	0.000	0.000
0.005	0.043	0.027	0.015
0.010	0.087	0.053	0.032
0.015	0.128	0.076	0.049
0.020	0.167	0.104	0.067
0.025	0.206	0.128	0.082

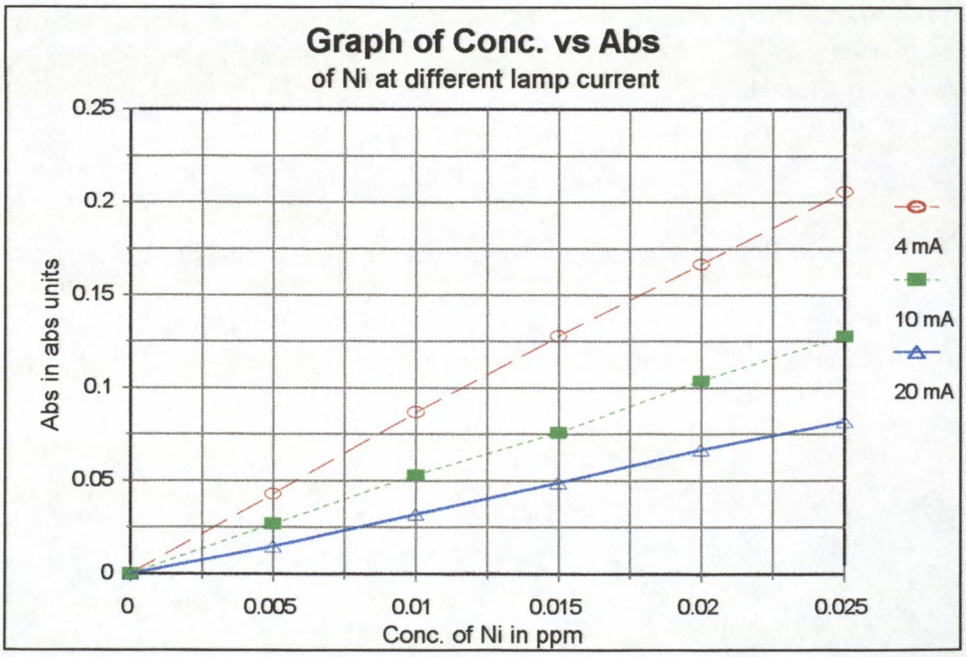


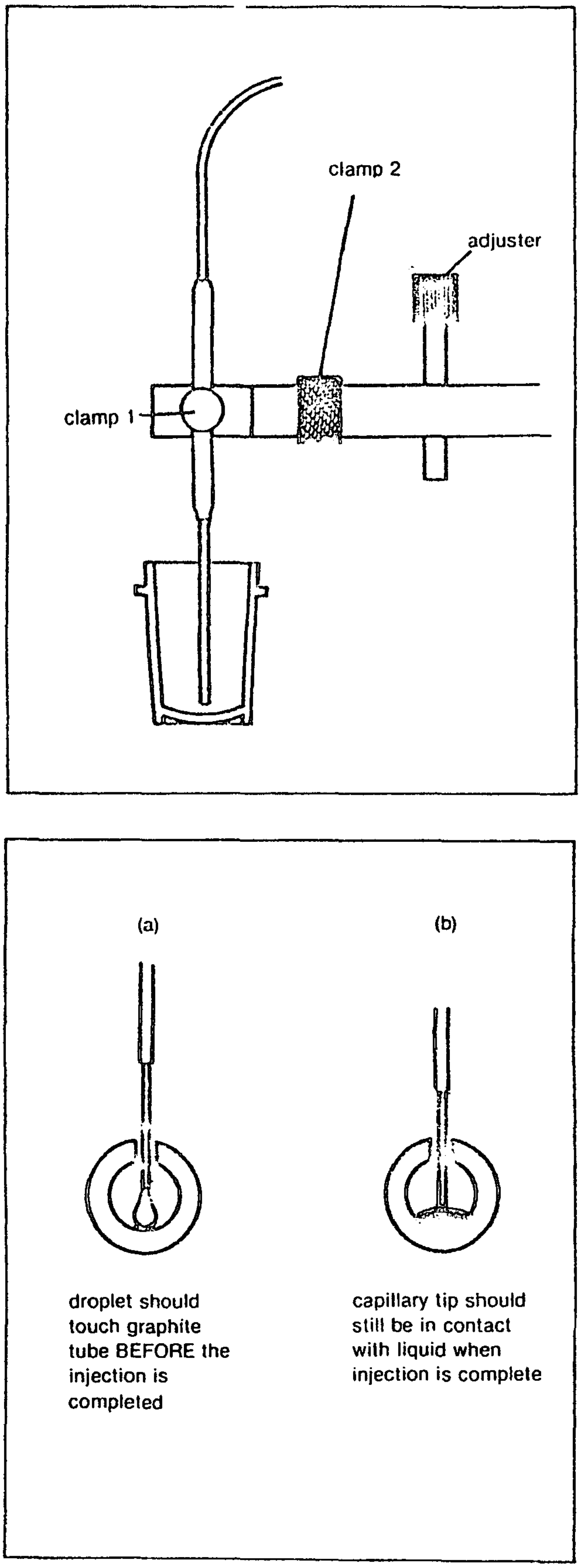
Figure 3.2: Effect of Lamp Current on Absorbance Values

3.2.2 Sampler Considerations

The automatic sample dispenser must be adjusted so that the pipette does not dispense the sample outside of the tube or to the edges. The height adjustment of the pipette is also critical since it must not be allowed to touch the inner base of the tube nor must it be too high above the inner base. The reason for this is to avoid damage to the pipette and to prevent splashing of the analyte within the tube. The correct height of the pipette is shown in the Figure 3.3. Incorrect height adjustment of the pipette usually produces very high or very low blank readings and a small adjustment of the pipette or furnace height gave the desired blank reading. The presence of air bubbles in the syringe also gave rise to inconsistent absorbance values.

3.2.3 Sample Atomization

In GFAAS a small sample or aliquot between 5 µL to 70 µL is pipetted into the graphite tube. The temperature of the tube is then increased in a controlled manner to dry, ash and atomize the sample, and finally to clean the tube of residual material for the next run. Most of the sample matrix is removed during the ashing period. Atomization temperatures up to 3000 °C can be achieved, thus enabling measurement of most refractory elements. The residence time of sample atoms, in the graphite tube, is very much longer than that in flame applications. This longer residence time in the optical path accounts for the dramatically improved sensitivity of the graphite furnace technique. Furthermore, the nebulizer efficiency in flame AAS is 10% where as in GFAAS a discrete volume of sample is atomized. The sensitivity achieved by the graphite furnace atomic



droplet should touch graphite tube BEFORE the injection is completed

capillary tip should still be in contact with liquid when injection is complete

Figure 3.3: Correct height of delivery pipette in graphite tube

absorption is only surpassed by, for example neutron activation and inductively coupled plasma-mass spectroscopy techniques. It is preferable to use one graphite tube for each element in order to prevent contamination from other elements. However, the cost of the tubes does not make this a viable proposition. The cost of the tubes can be considerable if several elements from a large number of samples are to be determined. The tubes generally have a useful life of about 200-300 firings depending on the nature of the matrix (Rothery, 1982). In addition, a single furnace determination takes approximately 2 minutes and if analysis is done in triplicate, the analysis time can be considerable.

3.2.4 Principle of the Method

The light source emits a narrow line spectrum of the analyte element. In addition to the more commonly used hollow cathode lamps, electrode-less discharge lamps are used for several of the more volatile elements, e.g. cesium. The graphite furnace produces the atomic vapour which absorbs the specific wavelength of light emitted by the source. The monochromator isolates the wavelength of interest of the specific analyte. The combination of the narrow emission line from a specific source and the isolation of a particular wavelength is what allows the determination of a selected element in the presence of others. The wavelength of light, isolated by the monochromator, is directed to a photo-multiplier tube. The resultant signal is then amplified and processed by the associated electronics. A signal is produced that is directly proportional to the amount of light absorbed by the sample in accordance with the Beer-Lambert law, i.e.

$$A = \varepsilon \, b \, C$$

where A = absorbance
b = path length
C = concentration
ε = molar absorptivity

The signal from the detector is sent to a readout device such as a printer or computer. The concentration of the sample is obtained from calibration graphs of known standards. With atomic absorption, calibration curves must be constructed for each element that is being determined. Hence suitably prepared reference standards and blanks are necessary for calibration. In GFAAS the most common interferences are from inter-element interferences and background absorption. The latter are generally overcome by using automatic background correction.

In GFAAS, the process of atomization takes place in several discrete, sequential steps which are:

- Injection (injection of the sample into the graphite tube);
- Drying (drying the sample into solid particles);
- Ashing or thermal pretreatment (process of removing volatile matrix constituents to reduce matrix interference and background absorption);
- Atomization (thermal breakdown of solid particles) producing ground state neutral atoms;
- Measurement (interaction of analyte atoms with radiation from the hollow cathode lamp);
- Tube clean (process of removing refractory constituents, if any, of the sample matrix).

Each temperature step in the furnace programme must be optimised. Each step requires different temperatures, times and ramp-rates depending on the analyte and the sample matrix. Other instrumental parameters, that effect precision and sensitivity, are bandpass (slit-width), wavelength and lamp current. Hence these must also be optimized.

3.3 Instrumental Parameters

The data for this study was obtained using the Varian 1275 Atomic Absorption Spectrophotometer fitted with a graphite tube atomiser. The instrument was also fitted with an automatic sampler capable of handling 100 different samples for analysis. Nitrogen was used as a purge gas. Although the operating manual that was supplied with the instrument provided recommended operating procedures for the analysis of specific metals, these conditions were used as a guide to determine the optimum conditions for the analysis of a specific metal. The parameters shown in Table 3.2 were obtained after considerable experimentation with standards.

There are however, three different types of thermal behaviour of the analyte and matrix. These are (i) the decomposition of the matrix takes place at a lower temperature than the atomization of the analyte; (ii) the decomposition of the matrix takes place at a higher temperature than the atomization of the analyte; (iii) the decomposition of both matrix and analyte occurs simultaneously. The first case is the most common. HNO_3 being the matrix in the standards and samples was easily removed before atomization to ensure interference free analysis. Hence the instrument was optimised using only standards.

Table 3.2: Operating conditions used for the analysis of each of the five metals.

Element	Pb	Cd	Cr	Ni	Cu
Wavelength (nm)	283.3	228.8	357.9	232.0	324.8
Slit width (nm)	0.5	0.2	0.2	0.2	0.5
Lamp current (mA)	5	4	7	4	4
Standard conc. (ppm)	0.025	0.0025	0.025	0.025	0.025
Furnace parameters	*	#	#	#	#
Sampler parameters	*	#	#	#	#

* As an example the parameters for Pb are shown in Tables 3.3 and 3.4.

These parameters are shown separately for each element in appendix C.

LEAD DETERMINATION

Operating Conditions:

Wavelength	:	283.3nm
Slit Width	:	0.5nm
Pb std conc.	:	0.025ppm
Blank	:	1M HNO_3
Lamp current	:	5 mA
Signal measurement	:	Peak Area
Background correction	:	Off

Table 3.3: The graphite furnace parameters for Pb determined experimentally

Step no	Temperature °C	time(s)	gas flow	gas type	read command
1	75	5.0	3.0	nitrogen	
2	90	60.0	3.0	nitrogen	
3	600	20.0	3.0	nitrogen	
4	600	5.0	0	nitrogen	
5	2000	4.0	0	nitrogen	read
6	2000	2.0	0	nitrogen	read
7	2700	3.0	3.0	nitrogen	

Table 3.4 Sampler parameters for standards and samples

samples and standards			blank volume (µL)
type	location	volume (µL)	
blank	-	-	20
std 1	51	4	16
std2	51	8	12
std3	51	12	8
std4	51	16	4
std5	51	20	0
samples	-	20	0

last sample no. = 16
no of replicates = 3
reslope rate = 0
first sample no. = 1

multiple injections = 1
last dry phase step = 2
injection temperature = amb

3.4 INTERFERENCES IN GFAAS

Interferences in GFAAS may be classified as follows:

- Physical interferences;
- Stable compound formation;
- Volatile compound formation;
- Vapour phase interferences

The last three interferences are collectively called chemical interferences.

3.4.1 Physical Interferences

Physical interference effects may be due to changes in sample introduction, background signals and memory effects. The spreading of the sample solution inside the tube can be minimized by the use of ridged tubes and peak area measurement. Background absorption and scattering effects are the most serious interferences in GF AAS. In addition continuum emission from the glowing graphite tube may distort the baseline and affect the photo-multiplier response. This effect, however, can be detected by doing an air blank run. Memory effects are due to incomplete atomization, condensation of the matrix and analyte or ineffective tube-cleaning steps. These can be overcome by using higher atomization and tube-cleaning temperatures, a L'vov platform or longer times for these stages.

L'vov and his co-workers proposed that the sample should be introduced onto a 'platform' rather than onto the tube wall. This would enable the sample to be atomized in an environment in which the temperature is not changing and hence lesser chemical interferences. The latest graphite furnace design is a transversely heated graphite furnace with an integrated L'vov platform. The tube and platform are machined from one piece of graphite. The new design provides a uniform temperature profile over the entire tube length. This enables the tube ends to reach the same temperature as the tube centre. The formation of free atoms is optimum, and recombination of atoms to molecules, the loss of atoms and condensation at the cooler ends are effectively avoided.

3.4.2 Chemical Interferences

In the case of stable compound formation, atomization is either completely or partly prevented by the formation of analyte compounds that remain unatomized at the normal atomization temperature. In the case of volatile compound formation the analyte is wholly or partly lost from the graphite tube before atomization temperature has been reached. These interferences can be minimised by matrix modification and by the use of pyrolytic graphite tubes.

Matrix modification is a procedure for reducing or eliminating volatilization and vapour-phase interferences. In this technique a reagent, usually an inorganic salt, is added to both the sample and reference solution in excess. The reagent causes the interfering substance either to become more volatile or to be converted to a less volatile form. In both cases matrix modification serves to make the volatilities sufficiently different to permit easier separation during thermal pretreatment. In the first case the interfering substance is removed before atomization whilst in the second case, more thermally stable substances are formed. The latter enables the use of higher pretreatment and atomization temperatures (Lajunen, 1992). It must be noted that the same filter sample is being analysed for five different metals and that any changes in the matrix of one will impact on the analysis of the other metals. Therefore this study did not make use of matrix modifiers.

3.4.3 Background Correction and Inter-Element Interferences

Prior to the analysis of samples, blank determinations were made to ensure that the blanks themselves had very little or no analyte concentration. Non-specific absorption is due to background absorption and scattering effects. In the graphite furnace, light scatter is caused by mist and smoke due to the recombination of sample matrices at the cooler ends of the tube or from carbon particles released from the tube walls. This is particularly true of samples containing alkali or alkaline-earth halides. The amount of radiation absorbed or scattered must be measured and subtracted from the total measured absorbance in order to obtain net value for the analyte atoms only. The analysis of air-filter samples showed no interference due to smoke or mist with and without the use of the deuterium background correction, i.e. the absorbance values showed no difference. Consequently, deuterium background correction was not applied. As far as inter-element interferences were concerned, the wavelengths of the selected elements were reasonably far apart but there could still have been interferences from elements that were not analysed, e.g. Co in the determination of nickel.

3.5 Calibration Functions and Unknown Concentrations

All the data were analysed using Corel Quattro Pro. version 6.0 for Windows 95. The computer was used to obtain a calibration graph from standards and to determine the RSD and other parameters for the samples. This information was then used to calculate the concentration of the analyte in the sample taking into consideration the dilution or pre-concentration factor. The volume of air sampled was put into the equation so that the concentration of the analyte in the atmosphere was given directly in $\mu g/m^3$ of air.

3.6 Some Problems of Air Analysis

The difficulty with atmospheric analysis is the large variation in the amount and type of particulate material collected on any specific day. On some days the filters showed very high concentration of a particular analyte. This necessitated dilution of the sample in order to ensure that the absorbance values fell within the linear range of the standards. On other occasions the filters showed extremely low levels of a particular analyte. This meant that the sample had to be pre-concentrated before a reasonable absorbance value could be obtained. This was done by taking a known volume of the sample and reducing it to 5 mL by careful evaporation on a hot plate. Thus the analysis time was often much longer than expected. In addition the levels of the metal pollutants were so low that attempts to determine them by ICP and Polarographic techniques failed. In the case of ICP-AES it was difficult to obtain a peak above the noise level for the very low concentration found in the samples. The information in Appendix D-1 clearly shows the peaks to be noisy. Poor sensitivity of the instrument for low concentrations of the analyte made it unsuitable for the analysis of the air filter samples. Differential Pulse Polarography using a dropping mercury electrode was used to analyse Pb standards. Concentrations in the range 10 to 100 ppm, which is shown in Appendix D-2, were easily detected but this was far above the limits found in the air samples. The instrument was not sensitive for the very low concentrations found in the air filter samples and thus no further attempts were made to use polarography.

3.7 Calibration and Analysis of Samples

The instrumental conditions were optimised for standard solutions of the metal to be analysed. The standards were prepared by serial dilution using double deionised water. Linearity of the calibration curves for the standards were checked on the computer before the test samples were analysed. Only when a linear graph was obtained for the standards, were the samples run under the conditions that applied on that particular day. Each standard and sample was analysed three times at two minute intervals. The average absorbance values, of the three separate determinations, were used to calculate the concentration of the test sample. It should be noted that the auto-sampler was set up to perform a rinse step after every determination, thus minimising contamination. Furthermore, the instrument was so programmed that atomization was followed by a tube cleaning step. This was to remove any residue remaining in the graphite tube. This is shown as step 7 under furnace parameters on page 43.

3.8 Typical calculations

3.8.1 Steps for a typical calculation

The steps involved in the calculation of Pb concentration in a sample are given below. The same procedure was adopted for all samples.

Step 1

This step entails obtaining a direct linear relationship between the absorbance and concentration of the prepared standards. Table 3.5 illustrates typical values obtained from an actual run (Appendix E). Note that the instrument records the blank readings and automatically sets its absorbance value to zero.

Table 3.5 Concentration versus Absorbance for Pb standard

[Pb] in ppm	absorbance
0.0000	0.0000
0.0050	0.0440
0.0100	0.0860
0.0150	0.1230
0.0200	0.1590
0.0250	0.1970

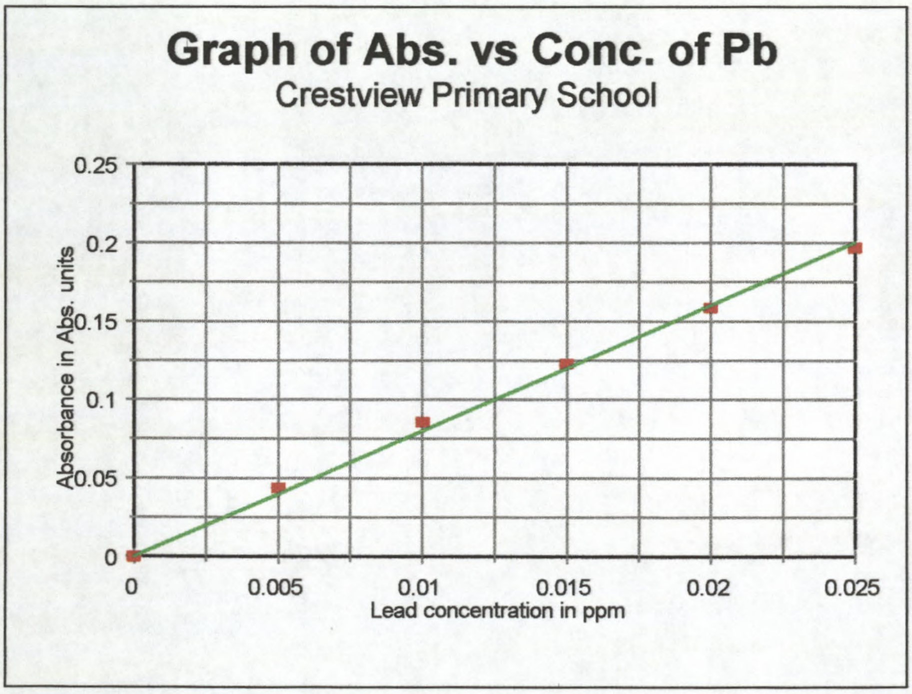


Figure 3.4 Calibration curve of Absorbance versus Concentration of Pb standards

Step 2

In order to verify the direct linear relationship between the absorbance and the concentration a graph of absorbance versus concentration of the standards was plotted as shown in Figure 3.4.

Step3

A regression analysis was done, on the values shown in Table 3.5, in order to obtain the best fit as shown in Table 3.6. The line in the graph indicates the fitted values while the points represent the actual values obtained. The concentration of the sample was computed directly from the graph, upon insertion of the sample absorbance values.

Since the graph is a linear one, the relationship that applies is:

$$y = mx + c$$

$$\text{i.e.} \quad A = mC$$

$$\text{Where} \quad c = 0$$

$$y = A \text{ (absorbance) and}$$

$$x = C \text{ (concentration)}$$

from the graph

$$\text{slope} \quad m = 8{,}0 \pm 0.1$$

Hence

$$A = 8{,}0C \pm 0.004$$

This equation was used to calculate the concentration of the analyte in the sample.

Table 3.6: Computer generated regression data of experimental values.

TYPICAL EXPERIMENTAL VALUES		COMPUTER GENERATED DATA		
concentration (ppm)	absorbance	fitted	regression output	
0.000	0.000	0.000	Constant	0
0.005	0.044	0.040	Std Er of Y Est.	0.004
0.010	0.086	0.080	R Squared	0.997
0.015	0.123	0.120	No. of observations	6
0.020	0.159	0.160	Degrees of Freedom	5
0.025	0.197	0.201	X coefficient(s)	8.02
			Std Err of Coef.	0.101

Table 3.7: Results from a typical analysis

Run No.		Abs. Values		Sample No.	Sampling Date
15	A	0.006	A		
MEAN	A	0.006	A	BLANK 1M HNO_3	
				SAMPLES	
16	A	0.047	A		
16	A	0.044	A		
16	A	0.045	A		
MEAN	A	0.045	A	CR 13	31/10/96
17	A	0.043	A		
17	A	0.045	A		
17	A	0.046	A		
MEAN	A	0.045	A	CR 14	31/10/96
18	A	0.098	A		
18	A	0.096	A		
18	A	0.096	A		
MEAN	A	0.097	A	CR 15	1/11/96
19	A	0.048	A		
19	A	0.051	A		
19	A	0.047	A		
MEAN	A	0.049	A	CR 16	1/11/96
20	A	0.187	A		
20	A	0.188	A		
20	A	0.190	A		
MEAN	A	0.188	A	CR 17	4/11/96
21	A	0.198	A		
21	A	0.200	A		
21	A	0.192	A		
MEAN	A	0.197	A	CR 18	4/11/96

Step 4

Calculation of sample concentrations from sample absorbances

Consider the typical data shown in Table 3.7:

The average absorbance for sample labelled CR13 is 0.045 ± 0.002. The relative standard deviation calculated was 3.4%. The concentration of Pb is calculated by substitution of the average absorbance in the equation:

$$
\begin{aligned}
A &= 8{,}0\ C \\
\text{i.e. } 0.045 &= 8{,}0\ C \\
C &= 0{,}045/\ 8{,}0 \\
&= 5{,}6 \times 10^{-3}\ \mu g/\ mL
\end{aligned}
$$

Since the dilution factor was 200 for this set of samples, the mass of the analyte is obtained as follows:

$$
\begin{aligned}
\text{Mass} &= C \times \text{volume} \\
&= 5{,}6 \times 10^{-3}\ \mu g/\ mL \times 200mL \\
&= 1{,}1\ \mu g
\end{aligned}
$$

This value corresponds to the highlighted value given in Table 3.8

Table 3.8: The calculated mass of Pb in the atmosphere for samples collected at Crestview.

Sample	Absorbance	Concentrations	Dil. factor	Date	Mass µg	Vol Air	µg/m3
CR13	0.045	0.0056	200	31.10.96	1.1	9600	0.12
CR14	0.045	0.0056	200	31.10.96	1.1	9600	0.12
CR15	0.097	0.0121	200	01.11.96	2.4	9600	0.25 #
CR16	0.049	0.0061	200	01.11.96	1.2	9600	0.12 #
CR17	0.188	0.0234	200	04.11.96	4.7	9600	0.49
CR18	0.197	0.0246	200	04.11.96	4.9	9600	0.51
CR19	0.070	0.0087	200	05.11.96	1.7	9600	0.18
CR20	0.070	0.0087	200	05.11.96	1.7	9600	0.18
CR21	0.151	0.0188	200	07.11.96	3.8	9600	0.39
CR22	0.148	0.0184	200	07.11.96	3.7	9600	0.38
CR23	0.107	0.0133	200	08.11.96	2.7	9600	0.28
CR24	0.105	0.0131	200	08.11.96	2.6	9600	0.27

rejected due to the large difference in values

Step 5

Calculation of the volume of air sampled.

The volume of air was calculated using the pump suction rate and the time interval over which the pump was operated. The flow control had a specification of 5% of set point.

pump suction rate = 20 litres per minute

time interval = 8 hours = 480 minutes

∴ volume of air = 20 L/min x 480 min

= 9600 litres

= 9,6 m^3

Hence

$$\text{Pb conc. in the atmosphere} = \frac{\text{mass on filter paper}}{\text{volume of air taken}}$$

$$= \frac{1{,}1\,\mu g}{9{,}6 m^3}$$

$$= 0{,}12\ \mu g/m^3$$

This is the value shown in the top last column of Table 3.8. This procedure was used to obtain the mass per cubic metre for all 5 metals analysed.

3.8.2 Reproducibility Study

In analysing for the metals in the samples, the analysis of standards was repeated seven times. This is shown in Table 3.9. An examination of absorbance values obtained for each of the standards shows an acceptable degree of reliability as evidenced by the figures in Table 3.9 which illustrates the results for the analysis of Pb standards at different times in the year. It must be remembered that it is not possible to get identical conditions because of factors such as graphite tube condition, lamp condition, room temperature conditions etc. However, since we are determining sample values relative to the standards, it is not essential for the conditions to be exactly identical. This is clearly shown by the results tabulated below. Data for other elements are provided in Appendix F.

Table 3.9: Absorbance values for different standard concentrations of Pb (in ppm) at different times of the year.

Std.Pb Conc. in ppm	0.005	0.01	0.015	0.02	0.025
Date	Absorbance Values for standards given above				
12-Oct-97	0.045	0.087	0.121	0.153	0.186
25-Sep-97	0.048	0.083	0.121	0.156	0.194
04-Sep-97	0.042	0.083	0.125	0.163	0.201
23-Aug-97	0.044	0.086	0.125	0.163	0.204
15-Aug-97	0.042	0.089	0.121	0.157	0.193
07-Jul-97	0.043	0.082	0.121	0.157	0.193
27-Apr-97	0.042	0.081	0.123	0.157	0.193
Std. Deviation	**0.002**	**0.003**	**0.002**	**0.003**	**0.005**

3.8.3 Stability Studies

A study was made to determine the shelf-life of standards. Standards of Pb, Ni and Cu were freshly prepared and absorbance readings taken. The freshly prepared standards were divided and kept in a glass volumetric flask ("A"grade) and in a plastic volumetric flask. In order to ensure that the conditions were kept as similar as possible, a separate tube was used for each element. These standards were analysed a month later and the results are shown in Table 3.10.

The results show that the absorbance values are clearly higher for Pb and Ni which indicates possible leaching from the container. In the case of Cu the decrease in absorbance values indicates adsorption by the walls of the container. From these results it is clear that prepared standard solutions should not be stored and used for the analysis of samples at a later date. Consequently all standards were freshly prepared on the day of the analysis.

3.8.4 Recovery Studies

- Six (6) filters were spiked with 1000 μL of a 1 ppm Pb solution using a 1000 μL pipette. This translates to 1 μg of Pb on each filter. This amount falls within the range of the samples as shown in Table 3.8 and can therefore be applied to the actual study.
- They were treated exactly like samples i.e. dried and stored for a month.
- The six spiked samples were digested and made up to 25 mL.
- Pb standards were run (Table 3.11) and the concentration of the spiked samples were determined as shown in Table 3.12.

- The average recovery was 113.3% (Table 3.13) which is acceptable at these concentration levels.
- A possible reason for the high levels could be that the pipette was dispensing slightly more than the 1000 μL of the one ppm solution on to the filter since it has an error of ± 10 μL.

Table 3.10: Variation in absorbance values of old and new standards for different metals

Element	Conc. ppm	Absorbance Reading of New Standards	Absorbance Reading of Old Standards	
			Plastic	Glass
Pb	0.05	0.297	0.348	0.338
	0.10	0.572	0.656	0.635
Ni	0.05	0.460	0.588	0.584
	0.10	0.888	1.000	0.984
Cu	0.05	0.829	0.696	0.654
	0.10	1.282	1.251	1.128

Table 3.11: Variation of absorbance with Pb concentration together with regression data.

Concentration	Absorbance	Fitted	Regression Output	
0.0000	0.000	0.000	Constant	0
0.0400	0.245	0.022	Std. Err. of Y est	0.022
0.0800	0.462	0.442	R Squared	0.993
0.1200	0.641	0.663	No. of Observations	4
			Degrees of Freedom	3
			X Coefficient(s)	5.52
			Std Err. of Coef	0.147

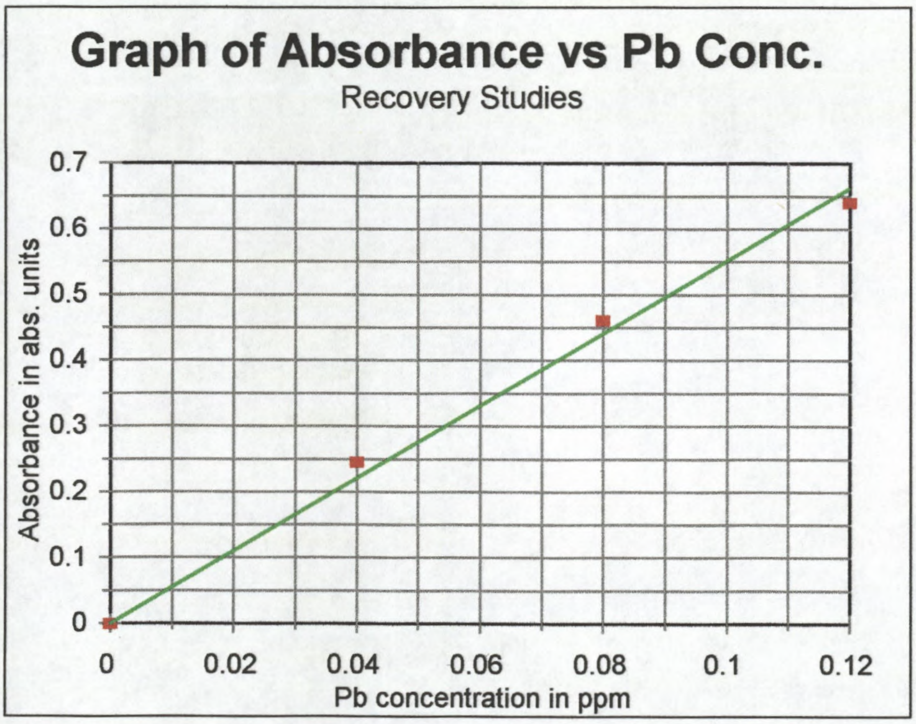


Figure3.5: Linear fit graph of Absorbance against Pb concentration.

Table 3.12: Calculated concentration of Pb in spiked samples

Sample	Absorbance	Concentration
S1	0.242	0.0461
S2	0.235	0.0447
S3	0.238	0.0453
S4	0.245	0.0466
S5	0.236	0.0449
S6	0.234	0.0445

3.8.5 Calculation of % Recovery

This was done to determine the accuracy of the method used for the analyses of samples.

Table 3.13: Recovery of Pb from spiked 0.8 μm millipore filters

Sample	Actual Pb mass μg	Calc. mass (μg)	% Recovery
1	1.0	1.15	115
2	1.0	1.12	112
3	1.0	1.13	113
4	1.0	1.17	117
5	1.0	1.12	112
6	1.0	1.11	111
MEAN			113

As discussed previously, the high recovery may be attributed to the accuracy of the dispensing device. The relative standard deviation for the recovery is 2% and hence the calculated masses vary only slightly with those given in Table 3.13.

CHAPTER 4

THE ANALYSIS OF CADMIUM AND LEAD

This chapter describes and discusses the results of the environmental study of lead and cadmium in the Chatsworth area. The concentration levels of the two metals found in the area are discussed in relation to the various meteorological factors that effect their distribution. The variation of metal concentration with the months of the year and days of the week were also investigated and discussed. The data required to generate the figures that appear in this chapter are given in Appendix G-1 and G-2.

4.1 LEAD ANALYSIS

4.1.1 Toxicity and Speciation

The toxicity of Pb depends very much on the chemical form of the element, i.e. upon its speciation. Lead does not generally become an environmental problem until it dissolves to yield the ionic form Pb(II) which readily replaces Fe (in haemoglobin) and Ca (in bones) (Fifield and Haines, 1996). The inorganic form of Pb(IV) is generally regarded as being non-toxic. However the tetravalent organic lead (PbR_4) where R is the organic chain, is readily absorbed through the skin from where it enters the liver and is converted to PbR_3^+ ions, a neurotoxin, which can easily cross the blood-brain barrier. At very high exposures tetra alkyl lead can be fatal (Baird, 1995).

Speciation of Pb and other metals have been studied fairly extensively (Harrison, 1986; Pacyna et al., 1991). Emissions from vehicle exhausts have dominated the lead input to the atmosphere, emitting both PbO and Pb (Pacyna et al., 1991). Lesser amounts of aerosol-phase lead halides such as $PbCl_2$, PbClBr, $PbBr_2$, etc. has also been identified in the atmosphere by several workers (Harrison, 1986; Pacyna et al., 1991). However, the predominant inorganic aerosol-phase lead species identified, has been $PbSO_4.(NH_4)_2SO_4$ by XRD (Harrison, 1986; Sturges et al., 1989).

4.1.2 Variation of Pb Concentration with Sampling Sites

At each site, sampling was done during two different periods, from February to June 1996 and again from July to November1996, on a rotational basis for each of the six sites. The days when sampling was done at each site are tabulated below.

Table 4.1: Sites and the dates when sampling was done

SITE	DATES OF SAMPLING AT EACH SITE IN 1996 (d/m)
Excelsior	28/02; 29/02; 01/03; 05/03; 06/03; 07/03; 08/03
	29/07; 30/07; 31/07; 01/08; 02/08; 05/08
Evergreen	11/03; 12/03; 14/03; 15/03; 18/03; 19/03; 20/03; 22/03
	06/08; 07/08; 08/08; 13/08; 15/08; 16/08
Depot Road	28/03; 10/04; 12/04
	19/08; 20/08; 21/08; 26/08; 27/08; 29/08
Lotus	15/04; 16/04; 17/04; 18/04; 22/04; 23/04
	09/09; 10/09; 11/09; 13/09; 16/09; 17/09
Crestview	15/05; 16/05; 17/05; 20/05; 21/05; 22/05
	31/10; 01/11; 04/11; 05/11; 07/11; 08/11
Elora	10/06; 11/06; 13/06; 14/06; 18/06; 20/06
	19/11; 20/11; 21/11; 22/11; 25/11; 29/11

The minimum and maximum concentration of Pb for each site was plotted for each period as shown in Figure 4.1. It can be seen that the differences in Pb concentration among the sites range from almost zero to just over 0.8 $\mu g/m^3$. Furthermore the concentrations also vary with the period of sampling for the same site, e.g. in EL the range from February to June is from 0.13 - 0.42 $\mu g/m^3$ and from July to November it is 0.04 - 0.12 $\mu g/m^3$. The total concentration, i.e. from February to November of 1996, for each site was obtained and the mean value found. These values are indicated in Table 4.2. The data is represented in the form of a pie chart in Figure 4.2 which shows that high concentrations of Pb were recorded for sites EV, LO and CW. Site EV is closest to the main road and vehicle emissions may have contributed to this high value. Both LO and CW are situated on hilltops and it is likely that industrial emissions may have contributed significantly to the levels in these schools. The annual mean Pb concentration for the entire study area, i.e. for all sites, is 0.24 $\mu g/m^3$ while that for each site is reflected in the Table 4.2.

4.1.3 <u>Variation of Pb Concentration with Sampling Dates at each site</u>

Figure 4.2 shows that in general the Pb concentrations were lower for those sites situated in a valley with the exception of site EV. It is a known fact that topography does play a role in the distribution of pollutants. Valleys usually produce a venturi effect, dispersing most of the pollutants. A narrow valley has the effect of forcing the wind through it with a higher velocity resulting in greater dispersion of the pollutants. The concentration of Pb in the atmosphere for each day that sampling was done at a particular site is illustrated in Figure 4.3. It must be noted that the sampling was planned to be done on seven

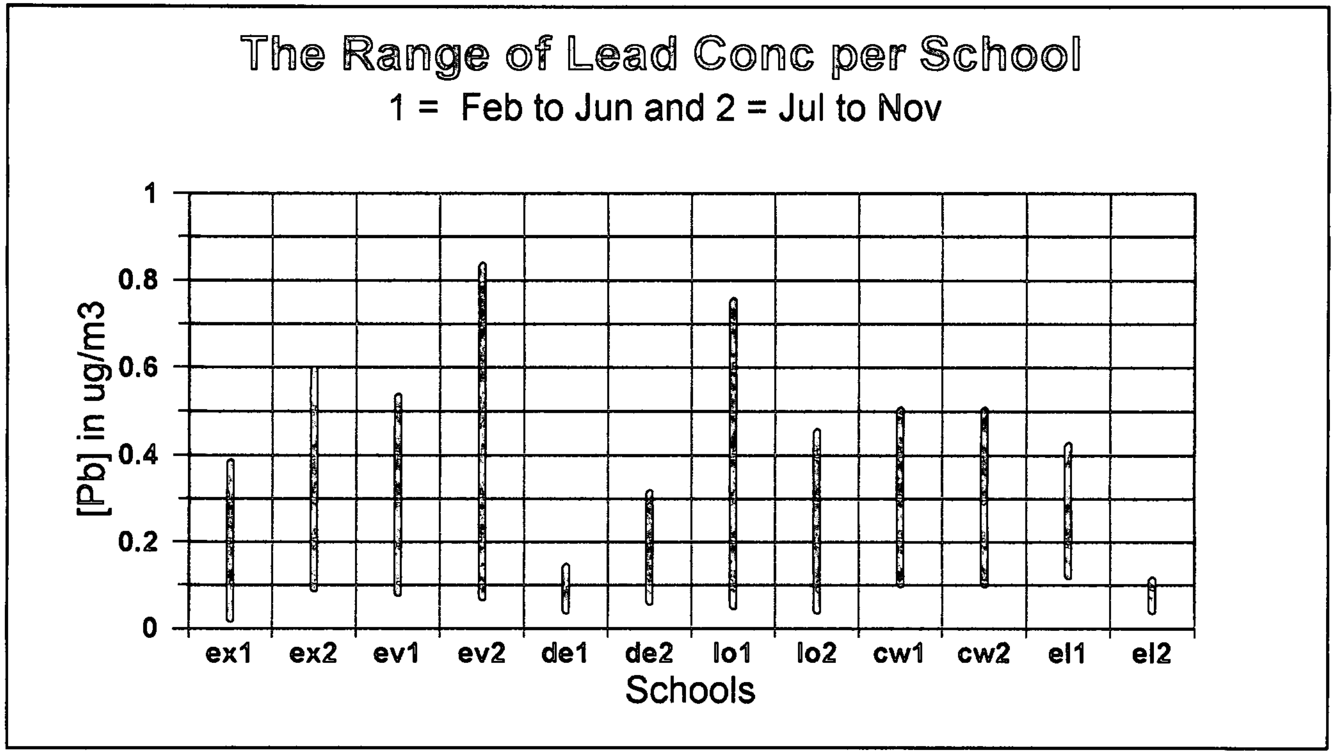


Figure 4.1: The range of Pb concentration for each site for the period February to June and July to November 1996

Table 4.2: Mean lead concentrations for each site in Chatsworth

SITE	MEAN [Pb] in μg/m^3	RSD %
EX	0.19	84
EV	0.33	62
DE	0.14	70
LO	0.29	72
CW	0.30	42
EL	0.16	64

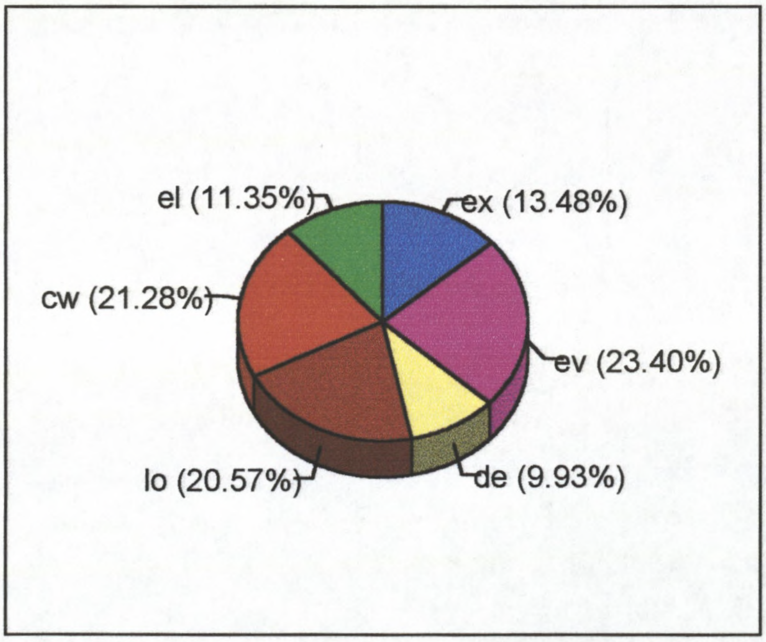
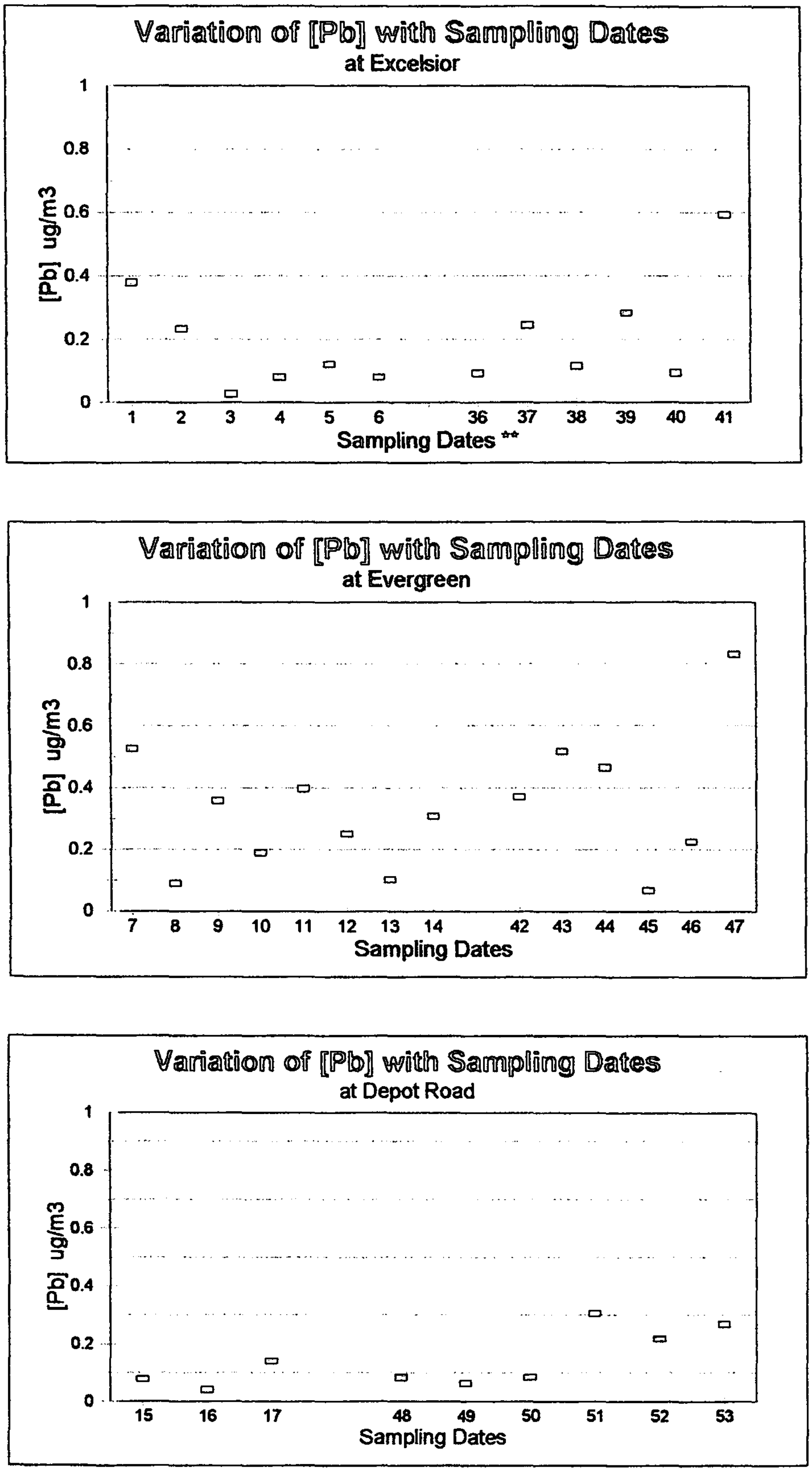


Figure 4.2: The percentage of Pb concentration for each of the six sites

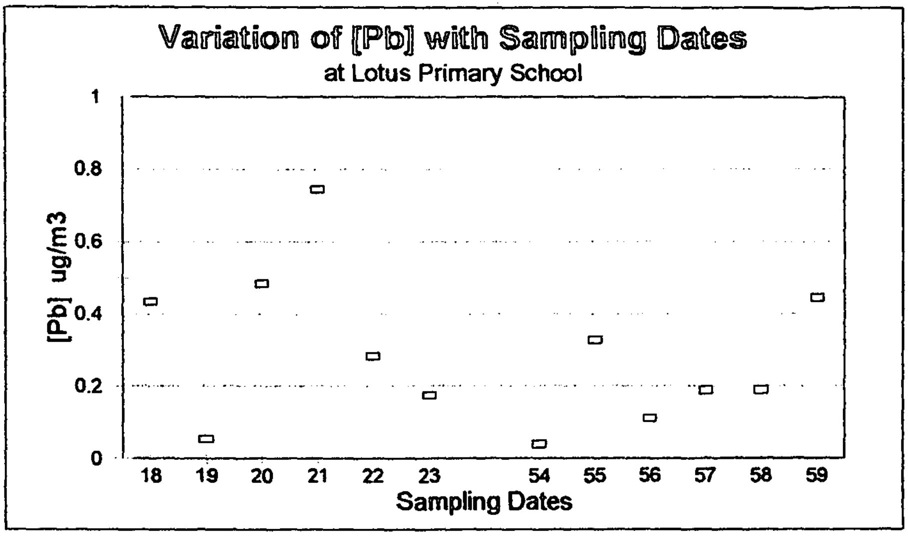
consecutive school days at each site but due to rain, staff strikes, power failure, tampering by students etc. this was not always possible. In a study of this nature, values typically regarded as 'outliers' cannot be disregarded because of the dynamic nature of the atmosphere and factors that contribute to the changing pollutant levels. In studies done by others very high levels of metal pollutants have been indicated (Kim and Fergusson, 1994; Sweet and Vermette, 1993). In this study, therefore, the average value includes 'outliers' and is clearly reflected in Figure 4.3. As an example from Figure 4.3 the mean concentration of lead at Excelsior is 0.19 $\mu g/m^3$ even though on five days during the sampling period the concentration exceeded 0.20 with values as high as 0.6 being recorded on the last day of sampling at that site. Such variations are typical of all sites as reflected in the graphs for each site.

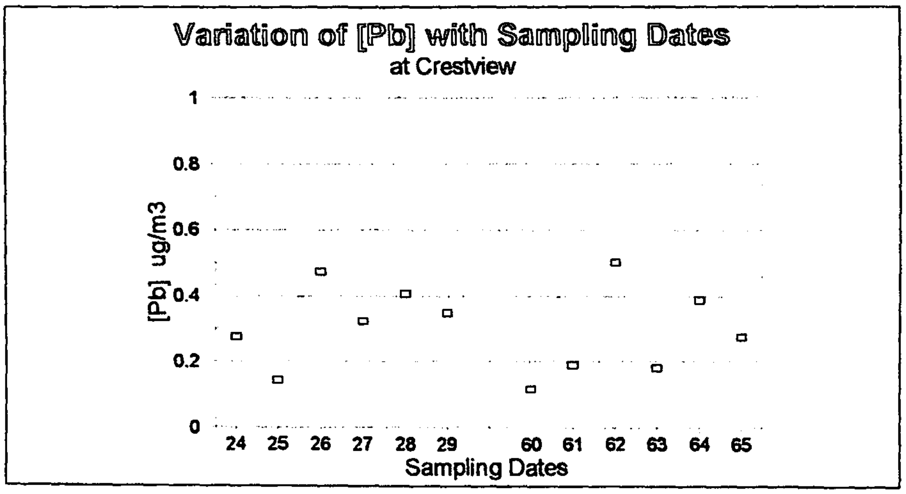
It is clear from the above data that there is no general trend at any of the sites. This can be attributed to the fact that the concentration of Pb in the atmosphere is influenced largely by motor vehicle emissions. By its very nature, vehicle emissions will vary from day to day in any given area. The number, type and age of vehicles in a particular area will further influence the variation in Pb concentration at each site. In all cases, the Pb concentration does not exceed 1 $\mu g/m^3$ which is below the United States EPA standard of 1.5 $\mu g/m^3$ based on a 24-hour three-month average.



** The exact dates is given in Appendix G-3

Figure 4.3: The Pb concentrations in air at each site on a daily basis





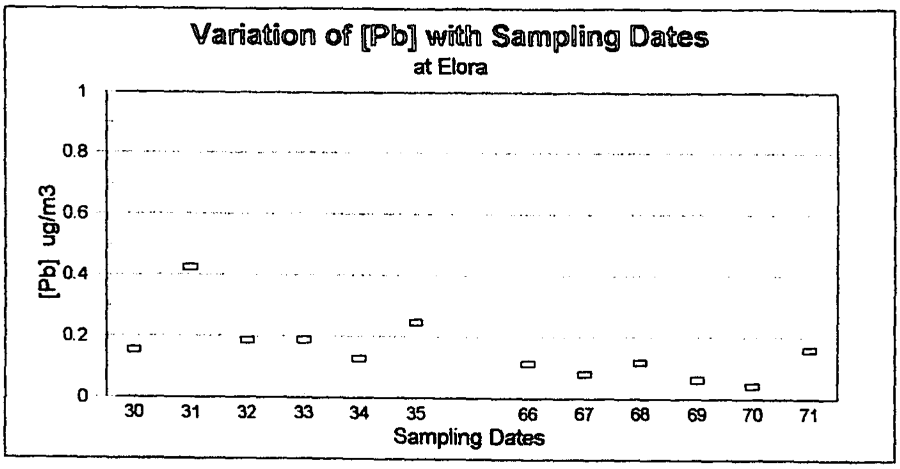


Figure 4.3 contd.: The Pb concentrations in air at each site on a daily basis.

4.1.4 Variations in Pb Concentration with Days of the Week

The report by El-Shobokshy concerning the variation of Pb levels with days of the week in Riyadh showed that Pb levels were high on Saturday, when industrial activity begins and low on Fridays, due to industrial shut down (El-Shobokshy, 1984). An attempt was made to see if a similar trend existed in Chatsworth. However, since data for some days was missing from each of the sites (for reasons given previously), it was not possible to use average values for each day. Hence, only those sites for which there was data for a complete week, i.e. for five consecutive weekdays is reflected in Figure 4.4. The use of the term 'consecutive weekdays' does not imply that the week starts on a Monday and finishes on a Friday. In some cases data was only available from the Thursday of one week to the Wednesday of the following week. Since the data is only for one week no trends can be reported. It is interesting to note that for sites EL and EX the daily patterns are very similar. All four sites show a drop in Pb concentrations on a Wednesday. In this study insufficient data was taken to make any comparison with that done by El-Shobokshy.

4.1.5 Variations in Pb Concentrations (for all sites) on a Monthly Basis

According to the work done by von Schirnding at Woodstock in the Cape, the atmospheric concentration of Pb falls to a minimum during the summer months and rises to a maximum during the winter months (Von Schirnding, 1988). This trend, however was not the case in Chatsworth as reflected by Figure 4.5. The highest mean Pb concentrations were recorded in the months of February, April, May and August. In

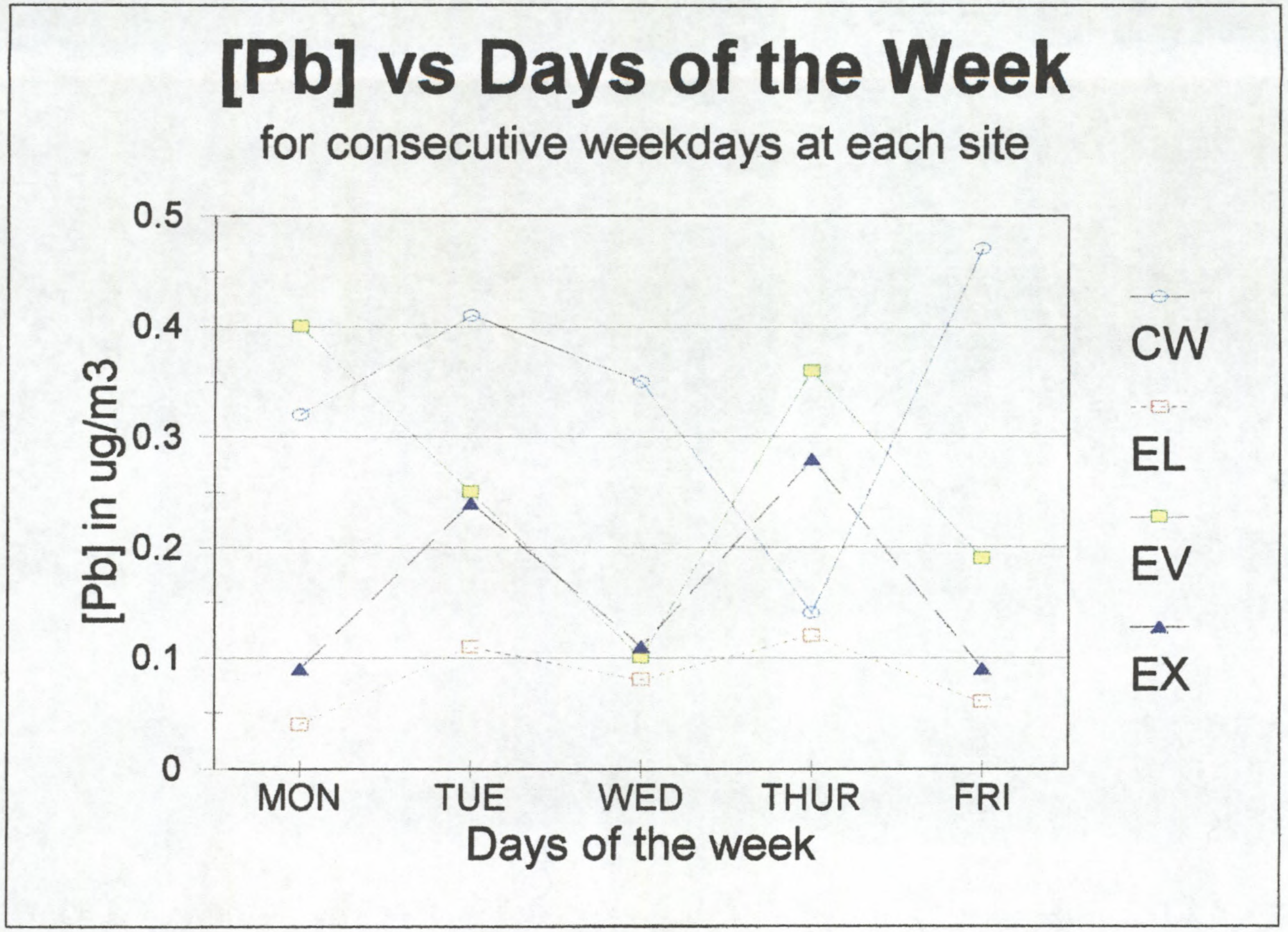


Figure 4.4: Pb concentration in the atmosphere at four schools in Chatsworth on five consecutive weekdays.

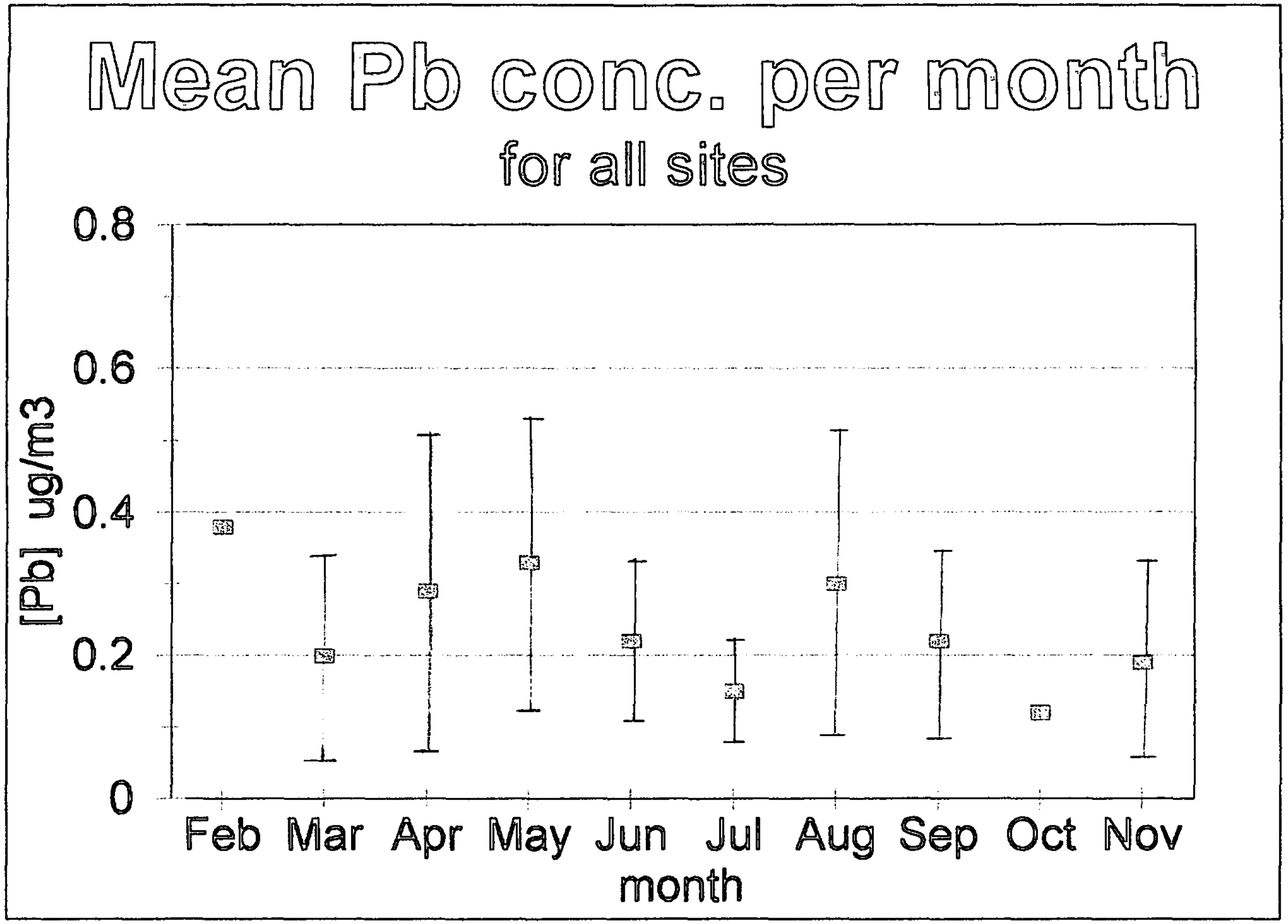


Figure 4.5: The average Pb concentrations in the atmosphere of Chatsworth for each month from February to November 1996.

addition the error bars reflect the large variation from the average value used in Figure 4.5. An examination of the temperatures (Appendix H) recorded for these months, indicate very cold conditions which seem to have influenced the high Pb concentrations in these months. The cold weather tends to reduce dispersion since lower temperatures tend to reduce the movement of particles and this could account for the high levels found in these months even though February is regarded as a summer month. According to the study done by von Schirnding the monthly variation in Pb concentration in Woodstock varied from about 0.5 to 1.8 μg/m^3 with low values being recorded in the summer months. The work done by C.Albertyn (Albertyn, 1994) shows the concentration of Pb in the city of Durban to range from about 0.35 to 0.96 μg/ m^3 for the 1993/1994 period. The data obtained indicates that the atmosphere of Chatsworth has a much lower concentration of Pb pollutant in 1996 than was the case of Woodstock or central Durban in previous years. However one needs to ensure that the atmosphere of Chatsworth does not become highly polluted as a result of unchecked human activity by regular monitoring of pollutant levels.

4.1.6 Annual Variation of Pb Concentration (all sites together)

Considering all sites collectively, the daily Pb concentrations from February to November 1996 is illustrated in Figure 4.6. Wide variations from the annual mean of 0.24 μg/m^3 is clearly evident. However the annual variation shows that for most part of the year the concentration of Pb in the atmosphere is well below 0.6 μg/m^3 but on two days the concentration was exceeded. These high values may be attributed to emissions from the

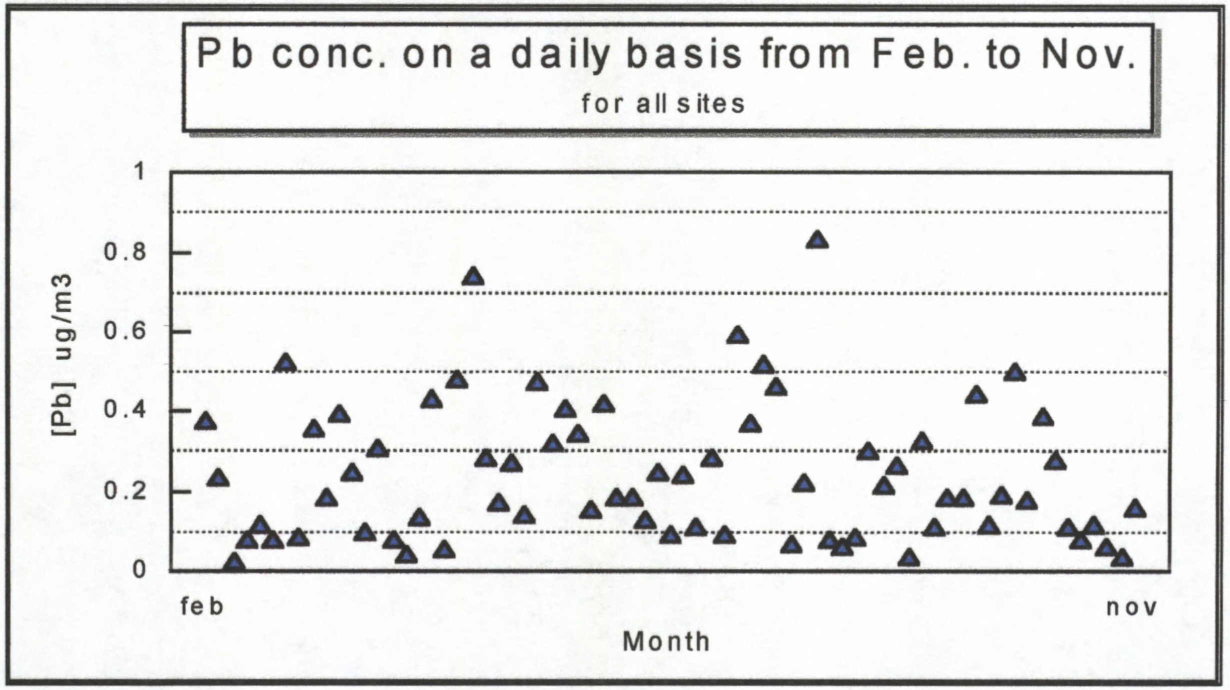


Figure 4.6: Pb concentration for each sampling day in Chatsworth the ten month period from February to November 1996.

industrial sector surrounding Chatsworth since there are known lead industries in the Mobeni and Congella areas. Non-ferrous industries are also found in the Prospecton area which is to the South East of Chatsworth.

The recent introduction of unleaded petrol in South Africa and hopefully the improvement in the economy will enable the community to purchase cars that use unleaded petrol, it is hoped that the concentration of Pb in the atmosphere of Chatsworth will decrease to even lower values.

4.1.7 Variations in Pb Concentration with Meteorological factors

Weather data was obtained from the meteorological office at Durban International Airport. This data (appendix H) was used to determine if any relationship existed between the data and the measured Pb concentration. Rainfall data supplied by the weather bureau was not used since no sampling was done on rainy days. Table 4.3 gives mean values (based on the 8-hour sample collection period) of those weather condition used for the analysis at each site.

From the tabulated data no direct correlation can be deduced between the lead concentrations at a site and a specific weather condition. However in the case of wind direction there seems to be some relationship between the Pb concentration and the direction from which the wind is blowing. This is clearly shown in Table 4.4 by looking at the highlighted figures.

Table 4.3: Mean Lead Concentration as a Function of Weather Data for the Different Sites

Site	Pb Concentration µg/m³	Temperature °C	Humidity %	Wind Velocity km/h
Crestview	0.30	23	73	16
Depot Rd	0.14	20	61	19
Elora	0.16	23	64	15
Evergreen	0.33	22	63	16
Excelsior	0.19	21	68	16
Lotus	0.29	23	70	17

Table 4.4: Sample data of the influence of wind direction on Pb concentration levels for the period February to June

Site	Sampling Month	[Pb] in µg/m³	Wind Vel. in km/h	Wind Direction
EX	March	**0.38**	9	**NE**
		0.02	23	SW
LO	April	**0.75**	9	**NE**
		0.05	29	SW
CR	May	**0.50**	9	**NE**
		0.10	10	SE
EL	June	**0.42**	14	**N**
		0.12	18	SW

1.7.1 Variation of Pb concentration with Temperature, Humidity and Wind Speed.

The daily concentration of Pb was plotted as a function of the three variables viz. temperature, humidity and wind speed. This is shown by means of scatter graphs for each of the variables in Figure 4.7. The trend lines indicate that there is no correlation between Pb concentration and temperature but that there is a slight negative correlation between Pb concentration and both humidity and wind velocity. This is in agreement with that found by Kim and Fergusson (Kim and Fergusson, 1994), i.e. metal concentrations in the air showed strong negative correlations with mean wind speeds. They also found that the this observation did not apply to all sites. Although El-Shobokshy had a weather station fixed to his sampler he made no conclusions regarding the effect of meteorological factors other than wind direction.

4.1.7.2 Variation of Pb Concentration with Wind Speed and Direction

The meteorological data from the weather bureau was used to obtain the wind rose plot shown in Figure 4.8. A wind rose is used to depict graphically the dominant transport direction of the winds for an area. The wind rose plot usually gives the percentage of time the wind blows in a particular direction and the speeds associated with the wind. The wind rose plot shown in Figure 4.8 is a simplified version indicating the average wind speed in a particular direction. From the wind rose shown in Figure 4.8. it can be seen that both wind speeds and directions play a significant role in the level of atmospheric lead. This data was obtained by averaging the Pb concentrations measured when the wind was blowing in a specific direction for the period February to November. Figure 4.8 indicates that more than 90% of the lead pollutant is associated with winds coming from the North and very little from the South West direction.

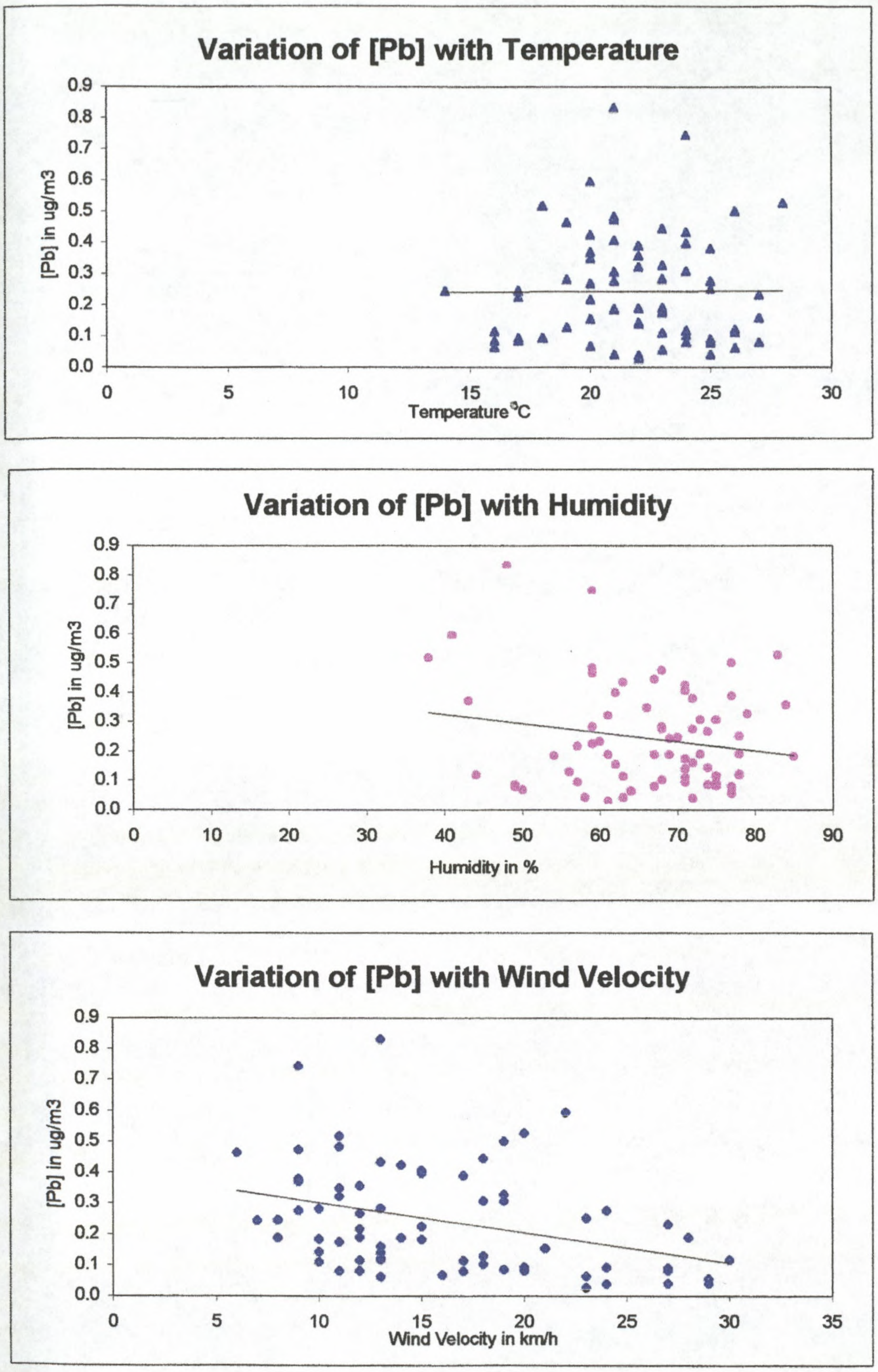


Figure 4.7: Variation of selected meteorological data with Pb concentration in the atmosphere of Chatsworth for the period of sampling from February to November 1996.

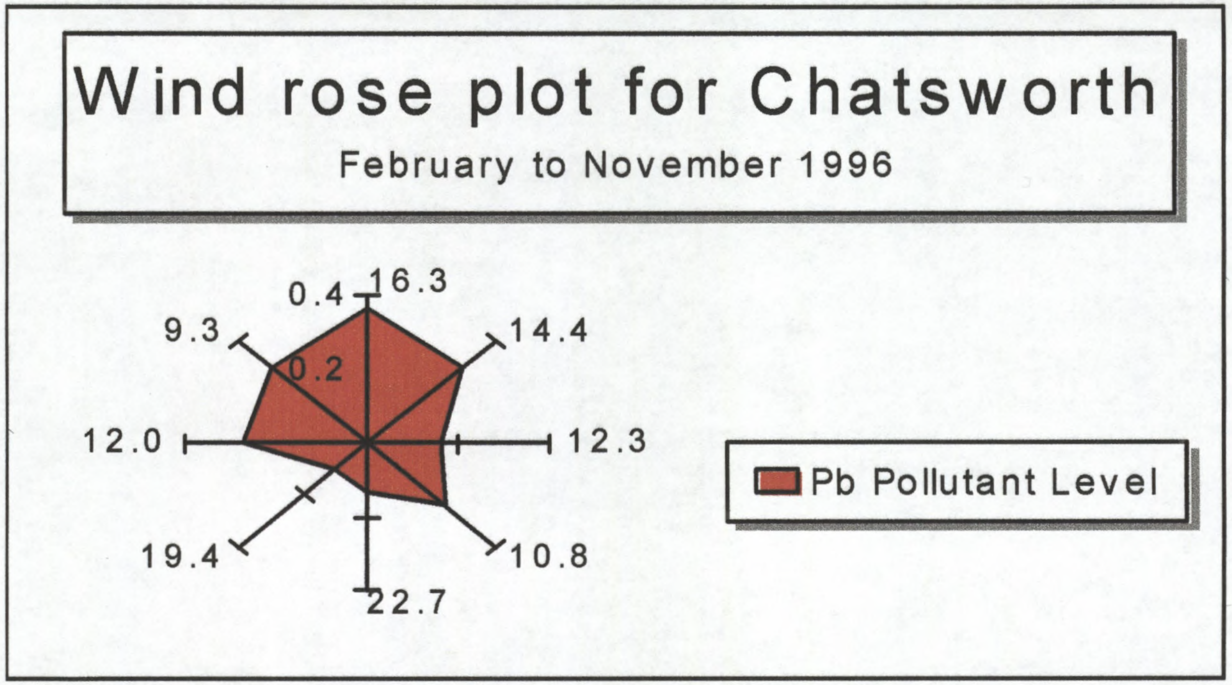


Figure 4.8: Contribution of Pb pollutant levels in the atmosphere of Chatsworth from different directions. Mean wind speeds in km/h are indicated along the axes. The scale of pollutant level is from 0 to 0.4 μg/m^3.

This points to the two major industrial areas viz. Congella and Mobeni which are to the North East and East of Chatsworth. Higher wind speeds reduce the level of pollutants as indicated in Figure 4.8. The strong winds from the south and south-west (19-23 km/h) could be responsible for the low level of Pb pollutant detected when the wind was blowing from this direction. The levels of Pb concentration in the atmosphere of Chatsworth may also be attributed to vehicle emissions from the busy industrial areas and freeways and highways adjacent to Chatsworth. However consideration should be given to the fact that there are little or no industries to the south of Chatsworth that can be considered to be Pb polluters apart from a smelting plant.

4.2 CADMIUM ANALYSIS

4.2.1 Toxicity and Speciation

Cadmium is acutely toxic. The lethal dose to humans is about 1 gram (Baird, 1995). Humans are protected from chronic exposure to low levels of cadmium by the sulphur-rich protein metallothionein. Metallothionein can complex almost all ingested Cd(II), and the complex is then eliminated in the urine. The danger, to humans, is when the amount of cadmium exceeds the capacity of the metallothionien to complex it. Cadmium is an accumulative poison that is found in the liver and kidneys, where it leads to kidney dysfunction (Baird, 1995). High concentrations of inhaled Cd aerosols can cause emphysema and related acute lung conditions.

Cadmium liberated during combustion processes, has been shown to occur in elemental and oxide forms (Ure and Davidson, 1995). Most cadmium is produced as a by-product of zinc smelting since these two metals usually occur together. Consequently, some atmospheric contamination by cadmium often occurs in areas surrounding zinc, lead and copper smelters. Coal burning is known to produce CdO emissions into the atmosphere (Baird, 1995). The incineration of waste materials containing cadmium is also an important source of cadmium in the air. Coal and waste material combustion is extensively used as a source of energy in the informal settlements. Emissions from refuse incineration occur predominantly as $CdCl_2$ (Ure and Davidson, 1995). The incineration of nickel-cadmium batteries releases metallic cadmium (Cd^0) which tends to condense onto small particles in the incinerator smoke stream (Baird, 1995).

4.2.2 Variation of Cd Concentration with Sampling Sites

As in the case of lead, both the range and percentage of Cd were determined for each of the sites for the same period. This data is reflected in Figure 4.9. Once again, it can be seen that there are considerable variations in Cd concentrations between sites. However, the concentration of Cd is extremely low, with values ranging from about 0.7 ng/m^3 at one site to about 25 ng/m^3 at another site. Excelsior Primary and Depot Road Primary Schools seem to show levels that are about 5 times greater than the mean value, particularly during the period of March to June. In spite of this apparent 'high' concentration at these two sites, these levels are far below the levels found in urban and peri-urban areas in other countries (see Table 4.6). Figure 4.9 shows that considerable differences occur at the same site for different periods of the year e.g. in Excelsior, the range for February to June is about 7 - 18 ng/m^3,whereas that for July to November is about 2 - 3 ng/m^3. The annual mean Cd concentration for the study area, i.e. the whole of Chatsworth is 4 ng/m^3, while that for each site is shown in Table 4.5 with the corresponding pie chart given in Figure 4.10. From the figure it is evident that high levels of Cd were recorded at Excelsior, Depot Road and Evergreen schools. These three schools are closer to the Mobeni industrial area than the other three schools. Furthermore the level of Cd in the atmosphere tends to decrease as one moves further away from the east. The trend indicates that Cd emissions are coming from the east with the source being somewhere in the Mobeni industrial area. It is important to note that there is a crematorium in Mobeni which could be a source of Cd and other metal emissions.

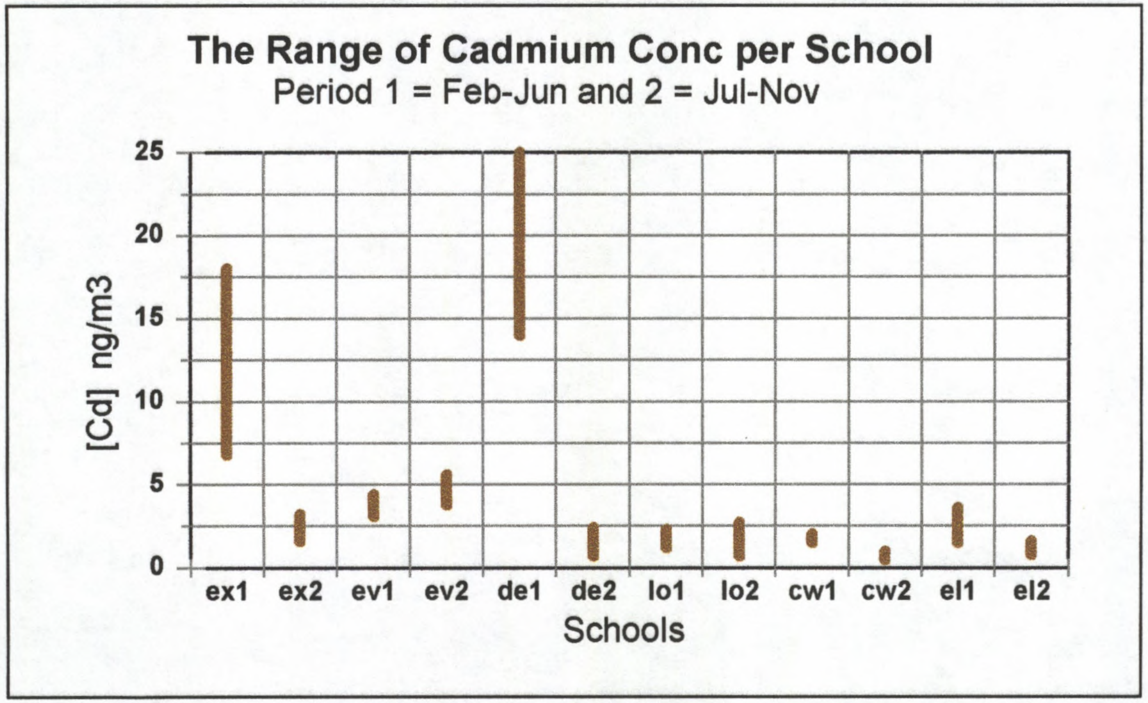


Figure 4.9: The range of Cd concentration for each site for the period February to June 1996 and July to November 1996.

Table 4.5: Mean cadmium concentration for each site in Chatsworth

SITE	MEAN [Cd] in ng/m^3	RSD (%)
EX	7.8	87
EV	4.5	37
DE	7.0	122
LO	1.7	35
CW	1.2	41
EL	1.7	45

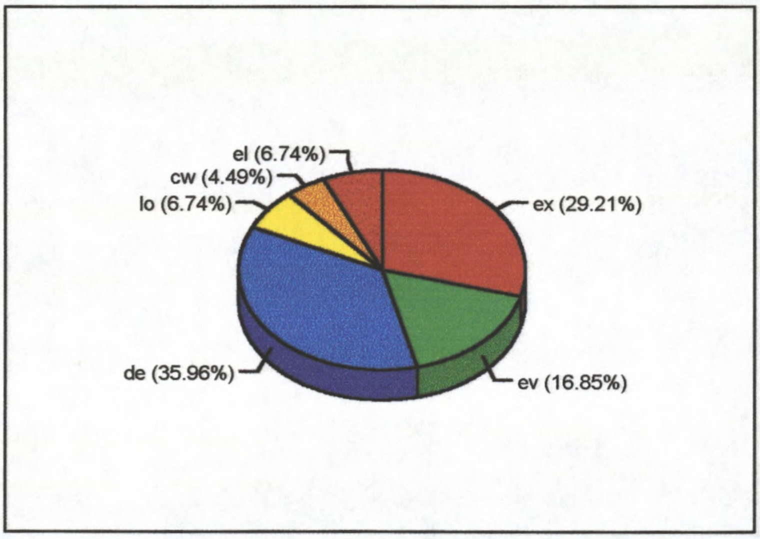


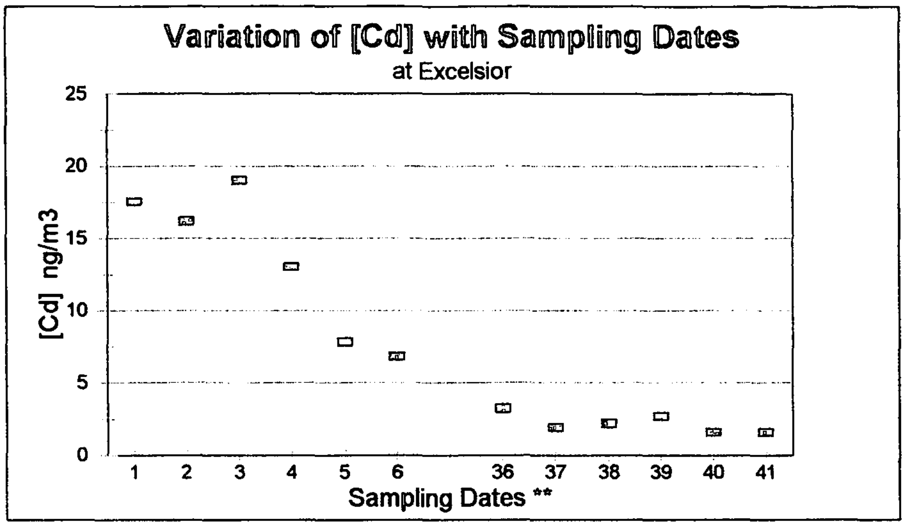
Figure 4.10: The percentage of Cd concentration for each of the six sites.

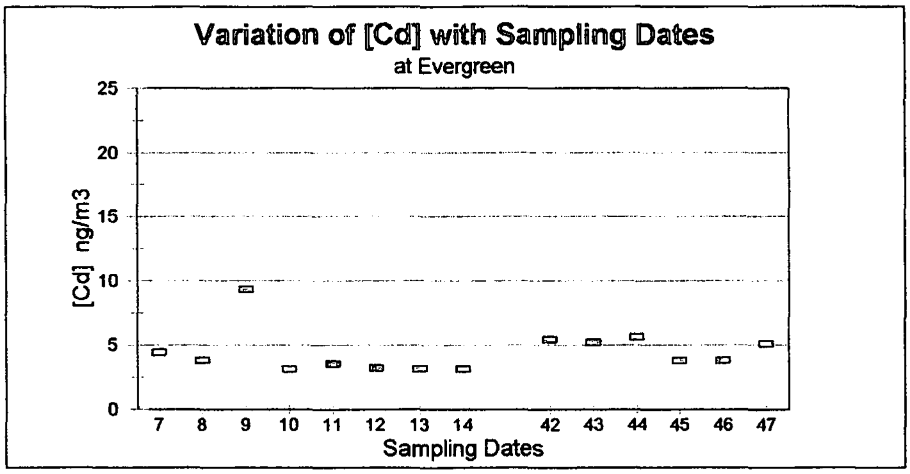
4.2.3 Variation of Cd Concentration with Sampling Dates at each site

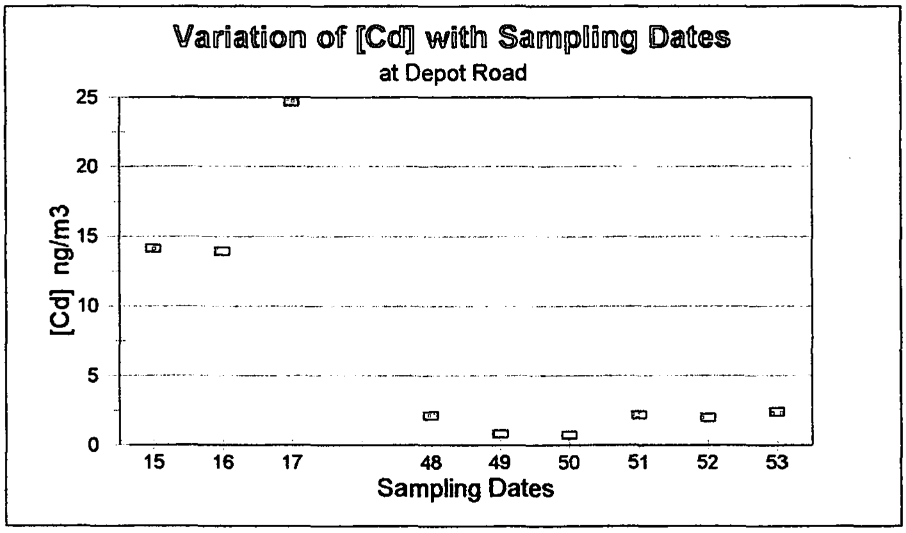
The Cd concentration determined per sampling day at each site is reflected in Figure 4.11. The exact date when sampling was done is indicated in Appendix B. The mean value given in Table 4.4 gives no indication of the large variations obtained for each day that sampling was done. This variation is shown in the graphical representation for each site in Figure 4.11. At each site EV, EL and EX the variation is more than two times the mean value whilst in the case of DE, the variation is more than three times the mean. Clearly the use of mean values as a recommended standard of metal concentration cannot be avoided due to the large variations in concentration levels of various pollutants in the atmosphere. However there is a need to standardize the mean value since some countries use a three-month average while others use the annual average as recommended permissible levels in ambient air.

4.2.4 Variations of Cd Concentration with Days of the Week

From the plot of Cd concentration against days of the week (Figure 4.12), it can be seen that the Cd concentrations are more or less constant for each site with the exception of site EV. The 'outlier' is clearly evident for this site. Whether this is characteristic or not of the site can only be determined by regular monitoring. However, all sites do show a slight increase in Cd concentration on Thursdays. This apparent trend can only be verified if sampling is done over several weeks. The 'trend' shown over the one week period can therefore not be used conclusively and future research may shed some understanding of the trend.

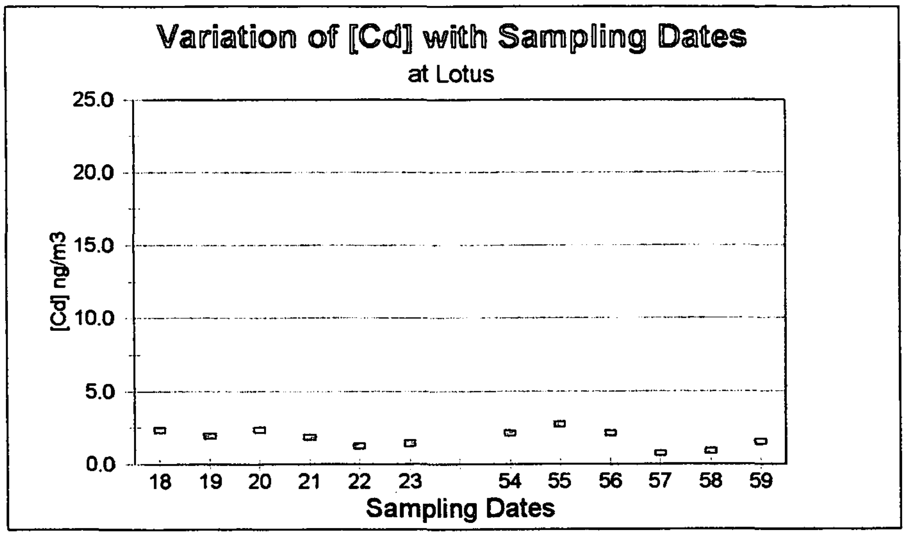


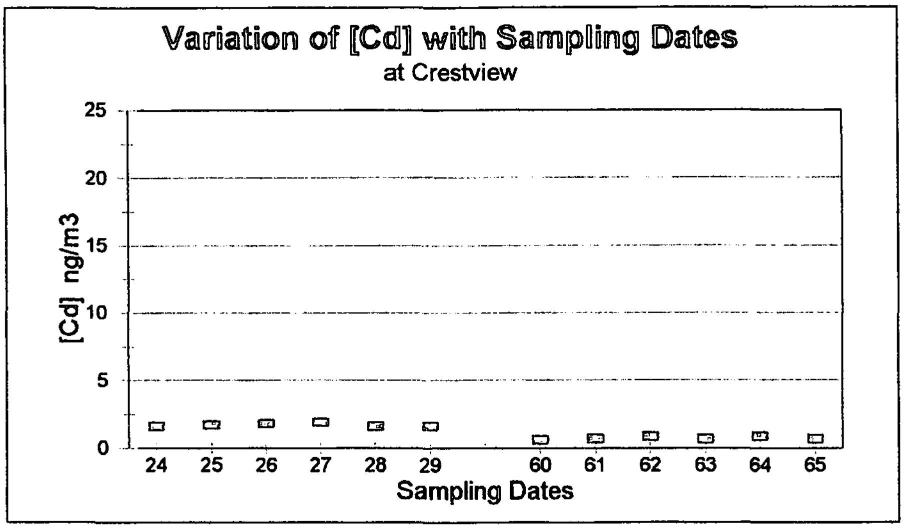




** The exact dates is given in Appendix G-3

Figure 4.11: Variation in Cd concentration at each site on the days when sampling was done.





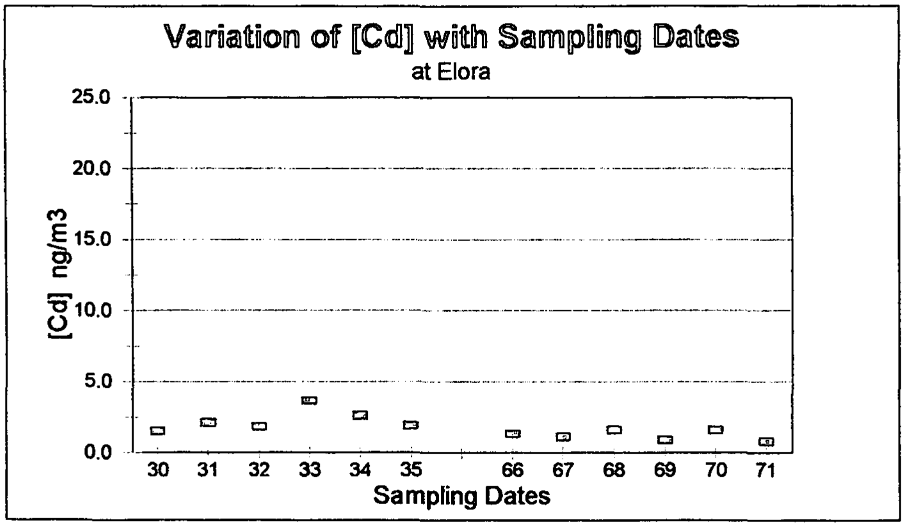


Figure 4.11 contd: Variation in Cd concentration at each site on the days when sampling was done.

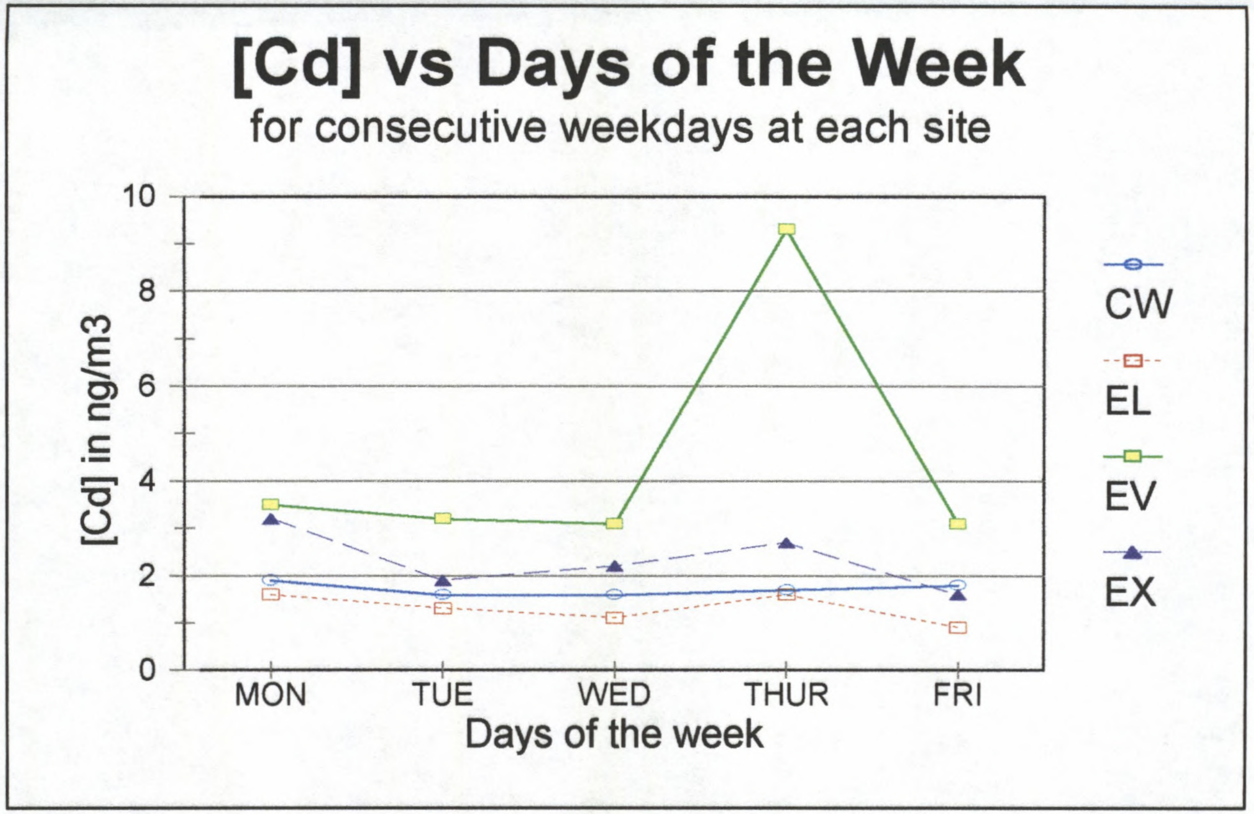


Figure 4.12: Cd concentration in the atmosphere at four schools in Chatsworth on five consecutive weekdays.

4.2.5 Variations in Cd Concentrations (for all sites)on a Monthly Basis

Figure 4.13 indicates that there is a drop in the Cd concentration from the beginning of 1996 to the end of the same year. Whilst the high concentrations of Cd in the first three months are attributed to industrial emissions, the Cd levels for the rest of the months may be attributed to natural sources as well as combustion of waste materials containing cadmium. The graph indicates very high concentrations of Cd in the atmosphere of the Chatsworth area at the beginning of 1996. It is possible that emissions may have resulted from the start-up of industrial activity, just after the summer recess . The emission most likely became diluted as the months passed and hence the gradual decrease from February to November or steps may have been taken by the industry to limit the amount of emission taking place.

4.2.6 Annual Variation of Cd Concentration (All sites together)

Although the annual mean is obtained over a longer period, the value gives no indication of the large variations that occur on a daily basis as shown in Figure 4.14. The annual mean value of approximately 4 ng/m^3 is exceeded by almost six times on a particular day in Chatsworth. Figure 4.14 shows that high concentrations of Cd in the atmosphere were recorded in the first few months of the year. This indicates that there must have been significant release of Cd into the atmosphere from a source situated close to Chatsworth. Electroplating industries in these areas could also be considered to be a source of cadmium emission.

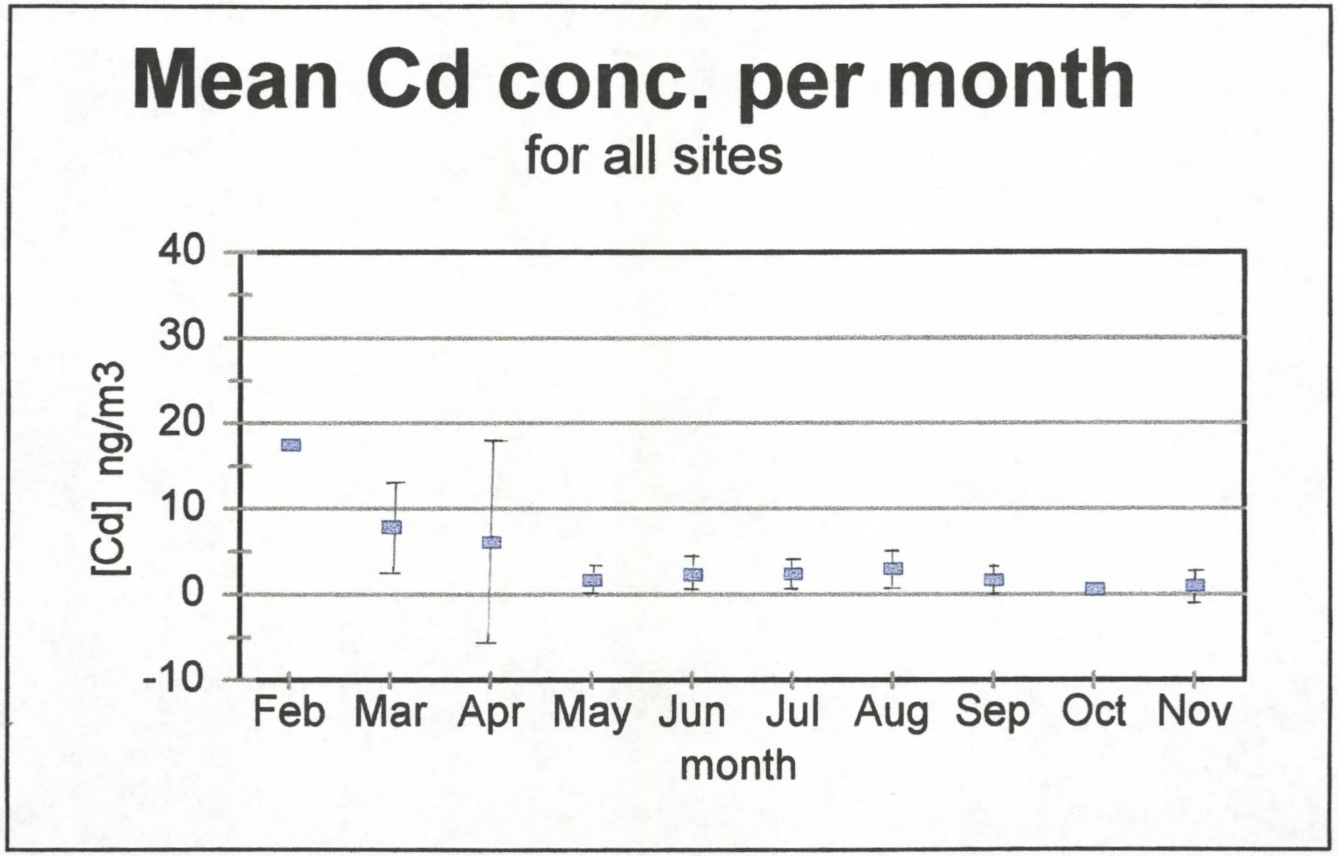


Figure 4.13: Average Cd concentrations in the atmosphere of Chatsworth for each month from February to November 1996.

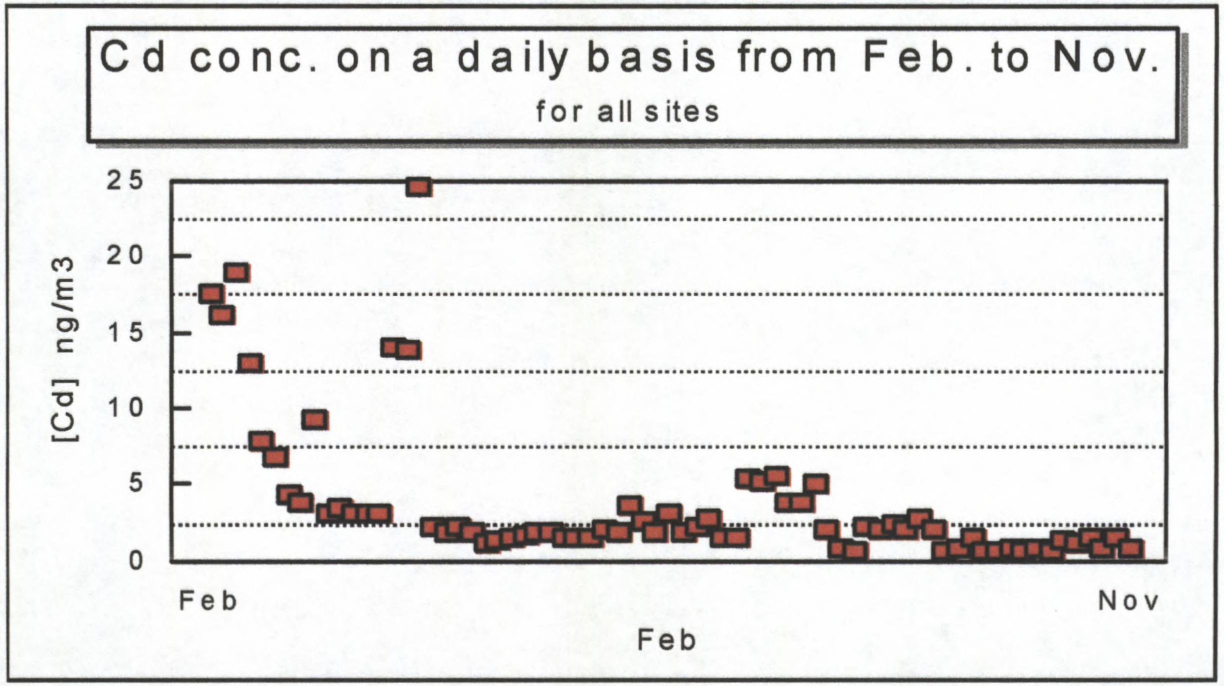


Figure 4.14: Cd concentration for each sampling day in Chatsworth for the ten month period from February to November 1996.

4.2.7 Variations in Cd Concentrations with Meteorological factors

4.2.7.1 Variation of Cd Concentration with Temperature, Humidity and Wind Speed

The variation of Cd concentration with meteorological factors is illustrated in Figure 4.15. No clear correlation between the mean Cd concentration at a site and a specific weather condition can be made from the data. However the lowest Cd concentration was obtained when the wind velocity was at the maximum and some sort of correlation may exist between wind direction and wind speed with Cd concentration.

4.2.7.2 Variation of Cd Concentration with Wind Speed and Direction

Figure 4.16 indicates that the Cd pollutant comes from all directions but the major portion of the pollutant comes from the east. This points to Cd pollutant coming from the Isipingo / Prospecton and Mobeni /Jacobs/Durban industrial areas, all of which, are to the east of Chatsworth. The industrial areas of Pinetown and New Germany, which are to the west of Chatsworth, also contribute to the levels of Cd pollution in Chatsworth. The possible sources of Cd in the atmosphere of the greater Chatsworth area can be attributed to the production of non-ferrous metals, electroplating battery manufacture and waste incineration. In addition there are a number of electroplating industries in the industrial area of Mobeni, Durban, Pinetown and Silverglen. Furthermore, a non-ferrous metal extrusion factory is located at Isipingo, which is only a few kilometres from Chatsworth. Waste incineration of Ni - Cd batteries, plastics, alloys, glasses, enamels and phosphors also contribute to the amount of Cd in the atmosphere. Natural sources include sea sprays, verge-grass incineration by the local authority and residential fires.

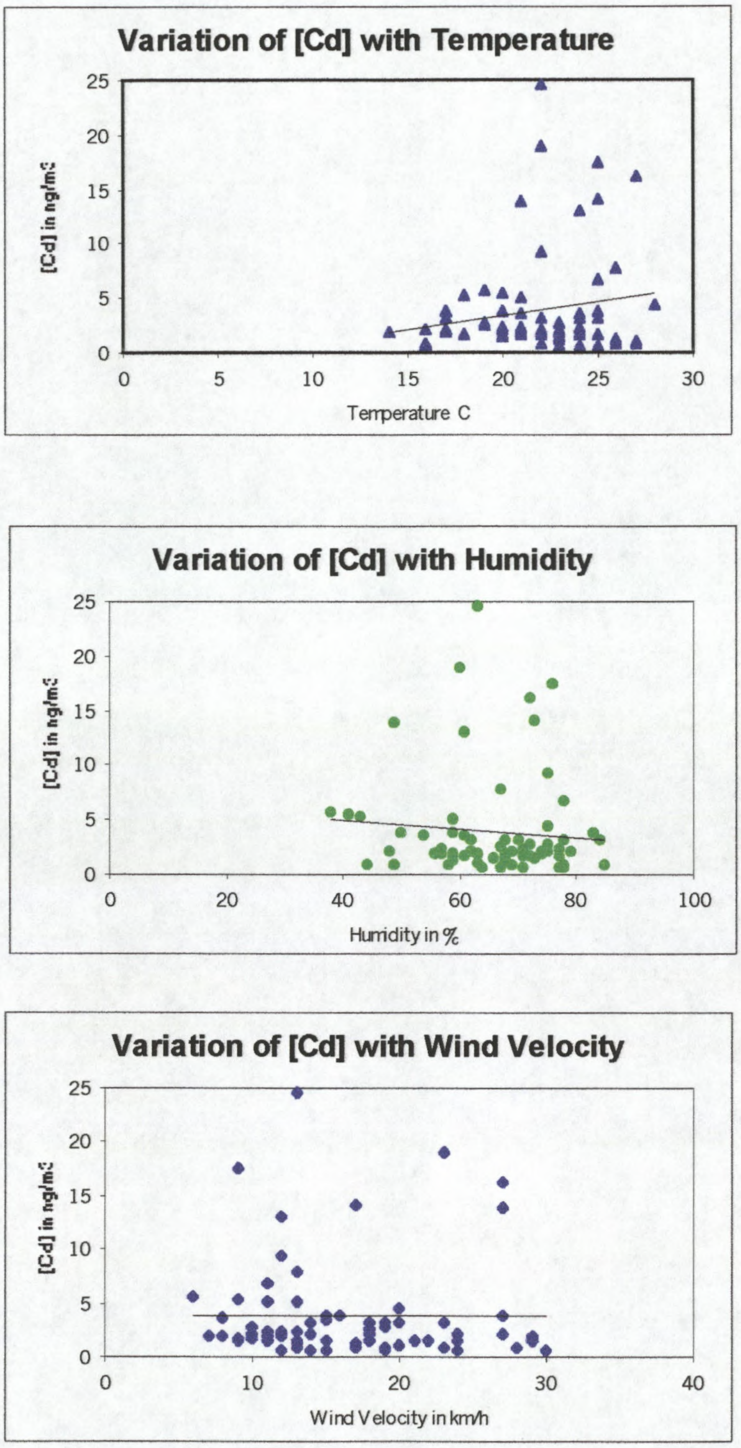


Figure 4.15: Variation of selected meteorological data with Cd Concentration in the Chatsworth area

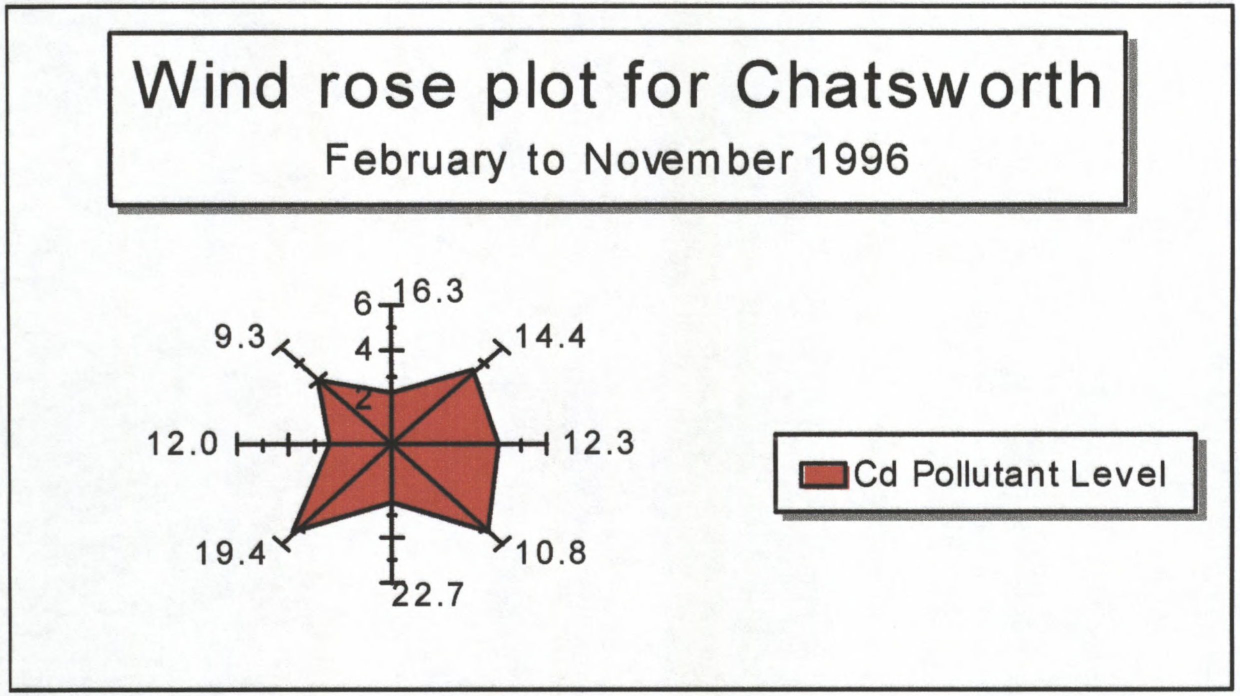


Figure 4.16: Contribution of Cd pollutant levels in the atmosphere of Chatsworth from different directions The values along the axes indicate the average wind speed in km per hour. The scale of pollutant level is from 0 to 6 ng/m^3.

4.3 Comparison of Pb and Cd concentration in the atmosphere with other areas.

A large number of data are available concerning atmospheric concentrations of trace elements associated with particulate matter. Comprehensive surveys have been compiled by Schroeder et al. (1987) and by Wiersma and Davidson (1986). Lowest concentrations of trace elements have been found in the Antarctic (Cunningham and Zoller, 1981) and very low levels in the maritime atmosphere over the pacific ocean (Gordon et al., 1978; Duce et al., 1983; Parrington and Zoller, 1984). Table 4.6. gives a comparison of the Pb and Cd ranges for remote, rural and urban areas. Based on the above classification Chatsworth can be regarded as a rural area with regards to metal pollution levels.

However, for a more realistic picture there is a need to compare the concentration of these metals in the urban areas of South Africa with that of the peri-urban area of Chatsworth. The work done by the National Nuclear Research Institute at Pelindaba in 1977/8 and by Albertyn in 1993/4 gives some indication of the concentrations of Pb and Cd in the various cities of South Africa as shown in Table 4.7. It is important to note that the mean value for both Pb and Cd concentrations in the atmosphere of Chatsworth is significantly lower than the values given in Table 4.7 indicating that the area is relatively unpolluted. This is possibly due to the greater care shown by industries in recent years towards minimising emissions into the environment.

Table 4.6: Comparison of Ranges of Pb and Cd Associated with Particulate Matter in the Atmosphere of various areas (Schroeder et al., 1987) with that of Chatsworth.

Location	Cd (ng/m^3)	Pb (μg/m^3)
Remote	0.003-1.1	0.000007 - 0.064
Rural	0.4-1000	0.002 - 1.700
Urban Area in:		
Canada	2-103	0.353 - 3.416
USA	0.2-7000	0.030 - 96.270
Europe	0.4-260	0.010 - 9.000
Other	0.6-177	0.0013 - 11.020
Chatsworth	0.5-25	0.020 - 0.830

Table 4.7: Comparison of the ranges of Pb and Cd in the atmosphere of various cities in the Republic of South Africa.(1977/8 data from document PEL 274 by the National Nuclear Research Institute at Pelindaba; 1993/4 data from a report by C.H.Albertyn to the Department of National Health and Population Development)

	1977/8		1993/4	
City	[Pb] μg/m^3	[Cd] ng/m^3	[Pb] μg/m^3	[Cd] ng/m^3
Richards Bay	0.017	9.8	-	-
Durban	0.710	4.4	0.51	-
Pretoria	1.260	55	0.84	-
Johannesburg	0.910	6.4	0.50	-
Cape Town	2.500	1.9	1.21	-

CHAPTER 5

THE ANALYSIS OF CHROMIUM, NICKEL AND COPPER

This chapter discusses the results of the analysis of each of the three metals. Their concentrations in the atmosphere are discussed in relation to:

- the different sites where sampling was done
- the effect of different days of the week
- the effect of different months of the year and
- the effect of meteorological factors

on the distribution and concentration levels of these three metals in the atmosphere of the greater Chatsworth area.

5.1 CHROMIUM ANALYSIS

5.1.1 Toxicity and Speciation

Chromium can exist in a trivalent and in a hexavalent form. The toxicity of Cr(VI) has been established but little is known of the toxicity of Cr(III). An oral dose of 0,5-1,0 grams of Cr(VI) is fatal to man. Absorption through the skin is also dangerous resulting in diarrhoea, bleeding from the stomach and intestine and serious liver and kidney damage. It has been known for a long time that workers, exposed to chromate dust for extended periods, suffer perforated nose walls and ulcers can also develop. Studies have also indicated that Cr(VI) may be responsible for eczema (Langard and Norseth, 1986). Furthermore, Cr is carcinogenic, causing cancer of the respiratory organs in those workers exposed to Cr-containing dusts (Alloway and Ayres, 1993).

There has been considerable activity in the development of methodology for the determination and speciation of chromium in biological and environmental samples. Such studies (Menendez-Alonso et al., 1999; Cox et al., 1985) have been prompted by the knowledge that Cr(VI) compounds are relatively toxic whereas Cr(III) is an essential trace element required for glucose, lipid and protein metabolism (Cox and McLeod, 1986). Cr (VI) is also a potent carcinogenic agent for the respiratory tract, requiring continuous monitoring of occupational air e.g. risk assessment related to welding. It is a known fact that private welding operations are being carried out from homes as well as along the streets of Chatsworth. The two chromium species are difficult to determine accurately because of interconversion and contamination during sampling, storage and processing. Cr(III) is mainly of natural origin whereas Cr(VI) arises from human activities, particularly from industries where Cr(VI) compounds have many applications (metallurgy, pigments, plating etc.). This results in levels in the atmosphere often being high.

5.1.2 Variation of Cr concentration with Sampling Sites

The maximum and minimum concentrations of Cr measured at each site for the two periods is illustrated in Figure 5.1. From this figure it can be seen that the Cr concentration was very low for the period July to November at all sites. The high levels of Cr in the atmosphere may be ascribed to the startup of both formal and informal industrial activity. It is possible that the

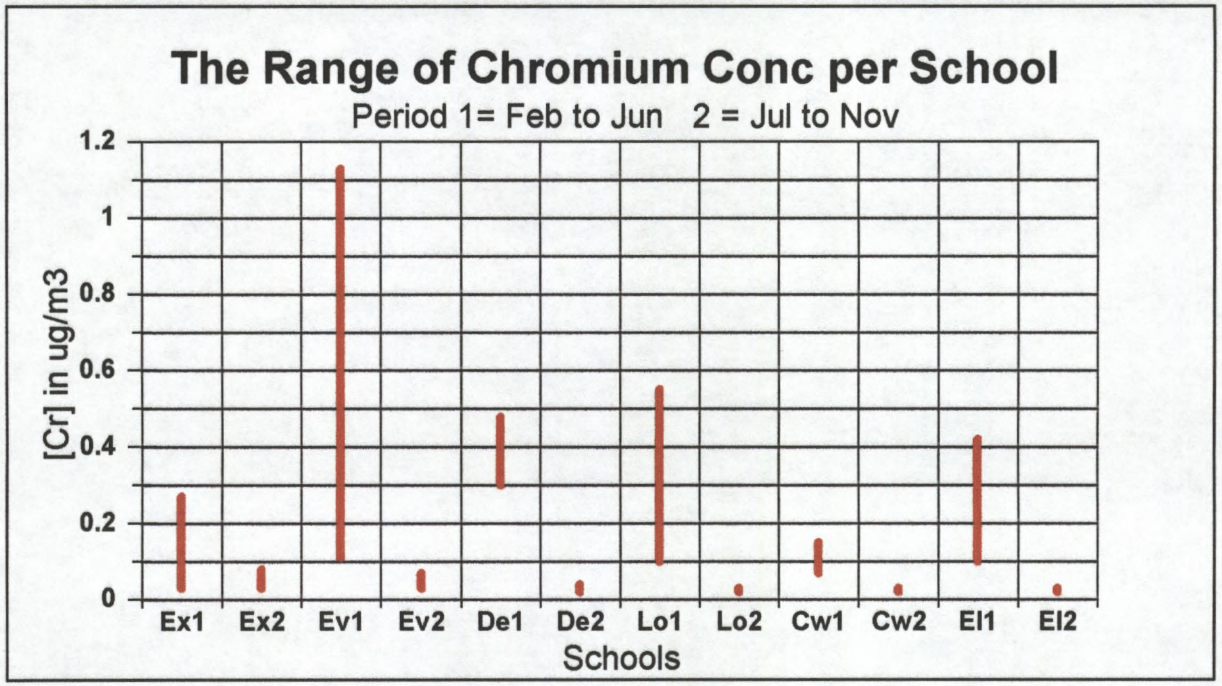


Figure 5.1 The range of Cr concentration for each site for the period February to June and July to November of 1996

emissions slowly became diluted, by atmospheric factors such as wind and rain, as the months progressed. This could account for the very reduced concentrations in latter half of the year. One possible source of chromium emission is a chrome chemical plant at Mobeni. To support the inference, sampling should be done near the industry at the beginning of the year and again towards the end of the year to measure atmospheric concentrations of chromium being emitted by the industry. Other sources of chromium are the many electroplating industries in and around Chatsworth.

Figure 5.2 shows that Evergreen Primary School had the highest concentration of chromium compared to all other sites. Figure 5.2 shows that site EV has almost 5 times the amount measured at site CW. With the relaxation in the establishment of home industries, a large number of such industries have mushroomed in the Chatsworth area. Included among these industries are roadside welding operations carried out for the benefit of motorists with leaking exhausts and other car problems. It is possible that welding operations adjacent to the school may have lead to the high levels of chromium found in the samples.

5.1.3 Variation of Cr concentration with Sampling Dates at each site

Figure 5.3 shows the concentrations of Cr for each day of the sampling period at each of the sites. It is clear that high concentrations of Cr were recorded during the first sampling period at each site. Only at Evergreen Primary was the concentration of Cr in excess of 1 $\mu g/m^3$, where the mean value of 0.29 $\mu g/m^3$ shown in Table 5.1 is significantly lower than the maximum value as indicated in Figure 5.3. The annual mean Cr concentration is 0.15 $\mu g/m^3$

Table 5.1: Mean chromium concentrations for each site in Chatsworth

SCHOOL	Mean [Cr] in µg/m^3	RSD %
EX	0.1	95
EV	0.29	143
DE	0.14	125
LO	0.18	115
CW	0.06	77
EL	0.12	110

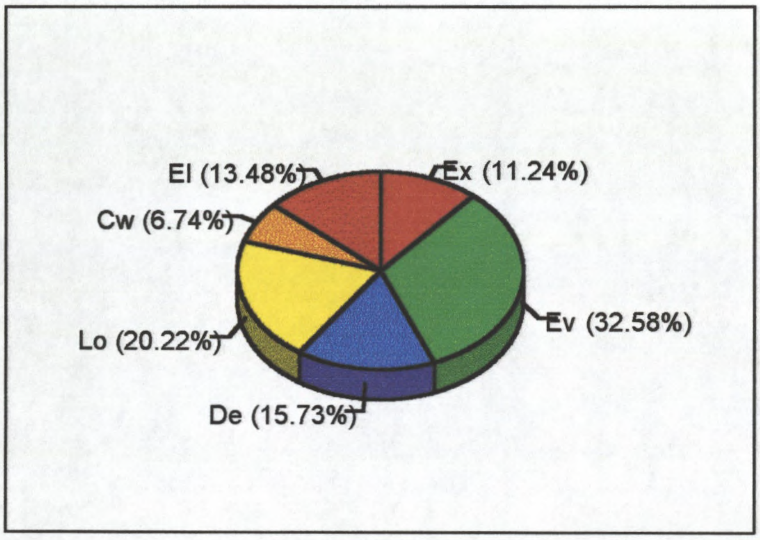
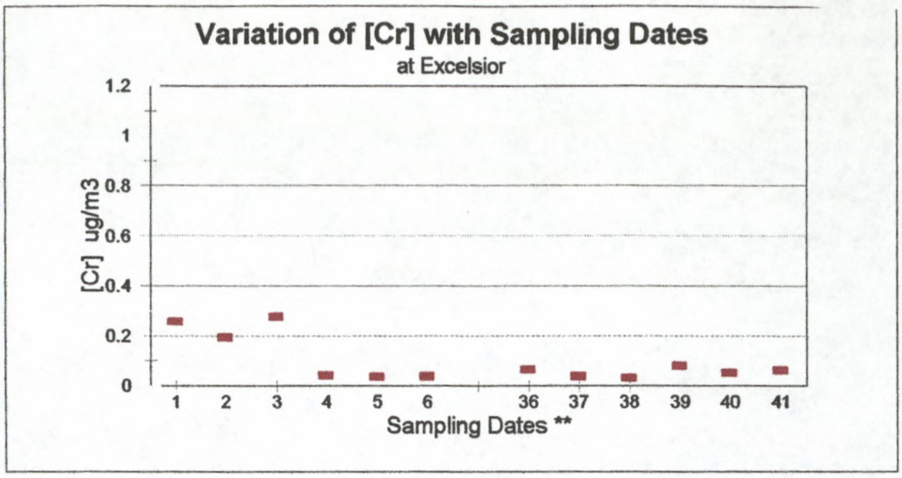
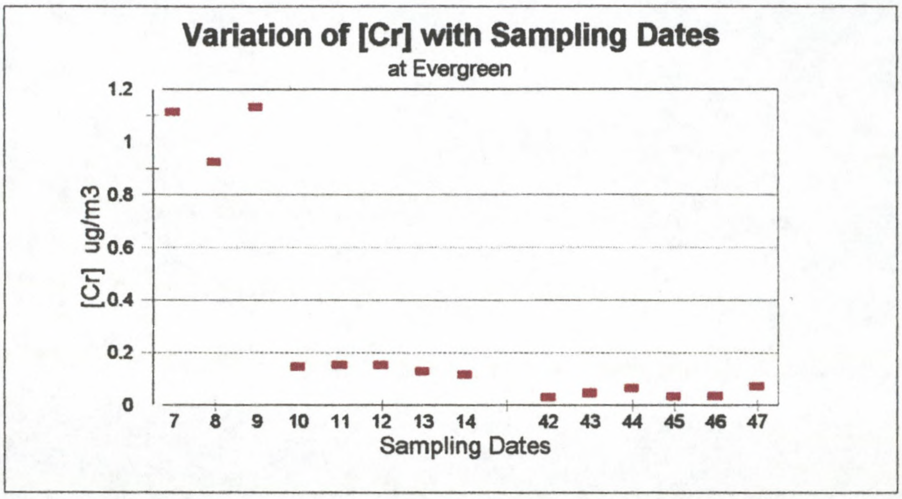
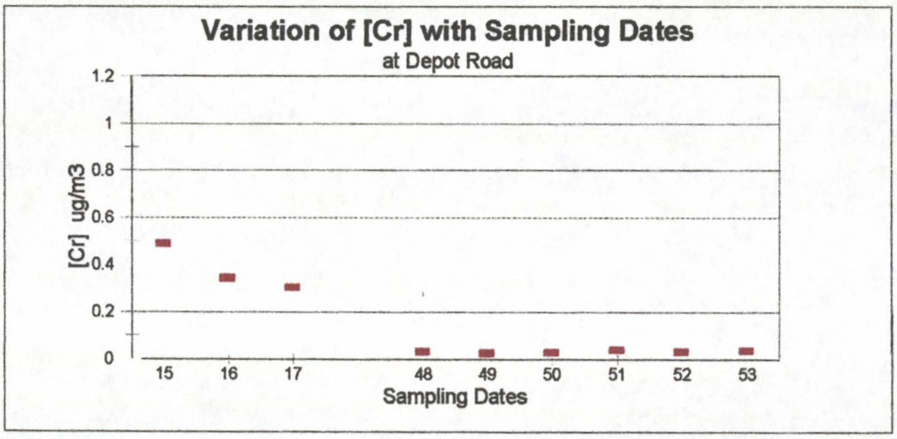


Figure 5.2: The percentage of Cr concentration for each of the six sites.

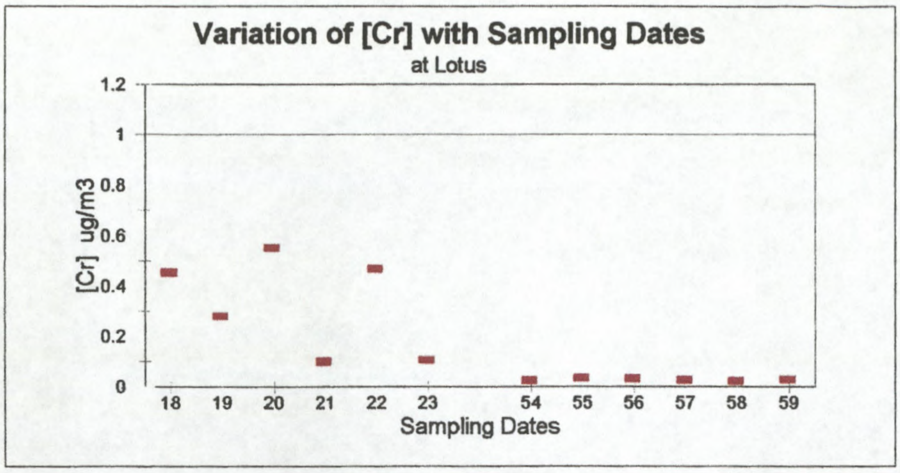


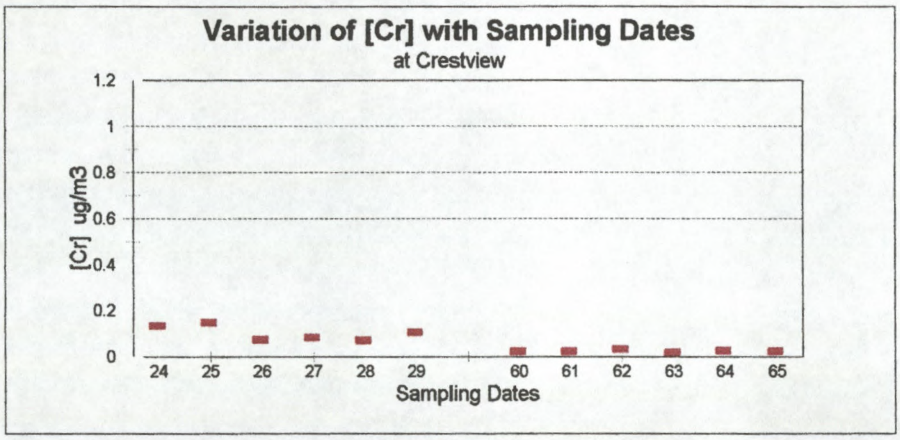




** The exact dates is given in Appendix G-3

Figure 5.3: Variation of Cr concentrations with sampling dates at each site.





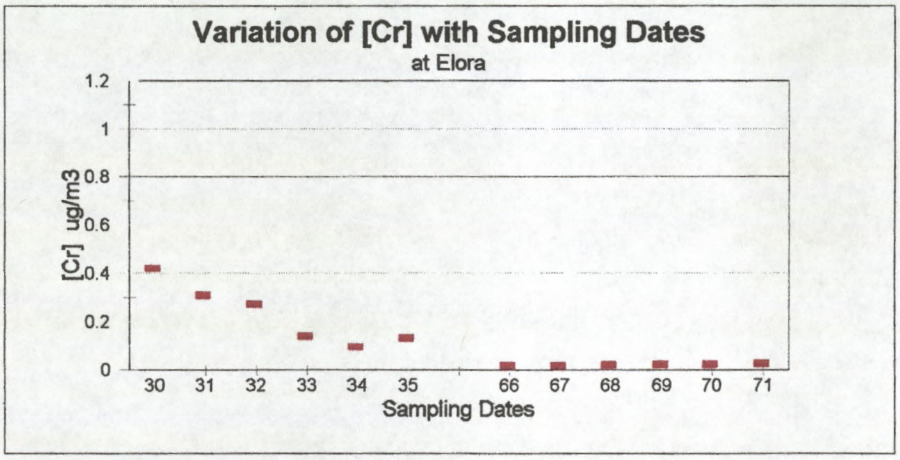


Figure 5.3 contd.: Variation of Cr concentrations with sampling dates at each site.

Only at site CW is the value well below the annual mean for most parts of the year. Crestview is situated at the highest altitude of the six sites and is extremely windy for most parts of the year. This factor could have contributed to lowering the Cr concentrations at this site. Each of the graphs clearly show that the Cr concentrations were high for the period February to June at each site. During the period July to November the Cr concentrations were extremely low. This again points to the possibility of industrial emissions at the beginning of the year. Dispersion of the Cr particulates by rain and wind may be responsible for low levels recorded during the latter half of the year.

5.1.4 Variations in Cr Concentration with Days of the Week

Figure 5.4 shows no general trend with regard to Cr concentration with days of the week but its pattern is very similar to that obtained for Cd. This points to the fact that factors affecting the emission and dispersion of cadmium also affect the emission and dispersion of Cr. It may be that there is a common emission source for both pollutants. The burning of waste by residents could also contribute to the daily variation. The levels for Cr is reasonably constant with the exception of site EV and no trend can be observed from this limited data.

5.1.5 Variation in Cr Concentrations on a Monthly Basis (for all sites)

The average monthly concentrations of Cr in the atmosphere of Chatsworth (Figure 5.5) further support the view that the high concentrations may be due to industrial emission in the first few months of the year. The emissions are diluted by atmospheric factors as the months progress, resulting in lower concentrations towards the end of the year. It is crucial that

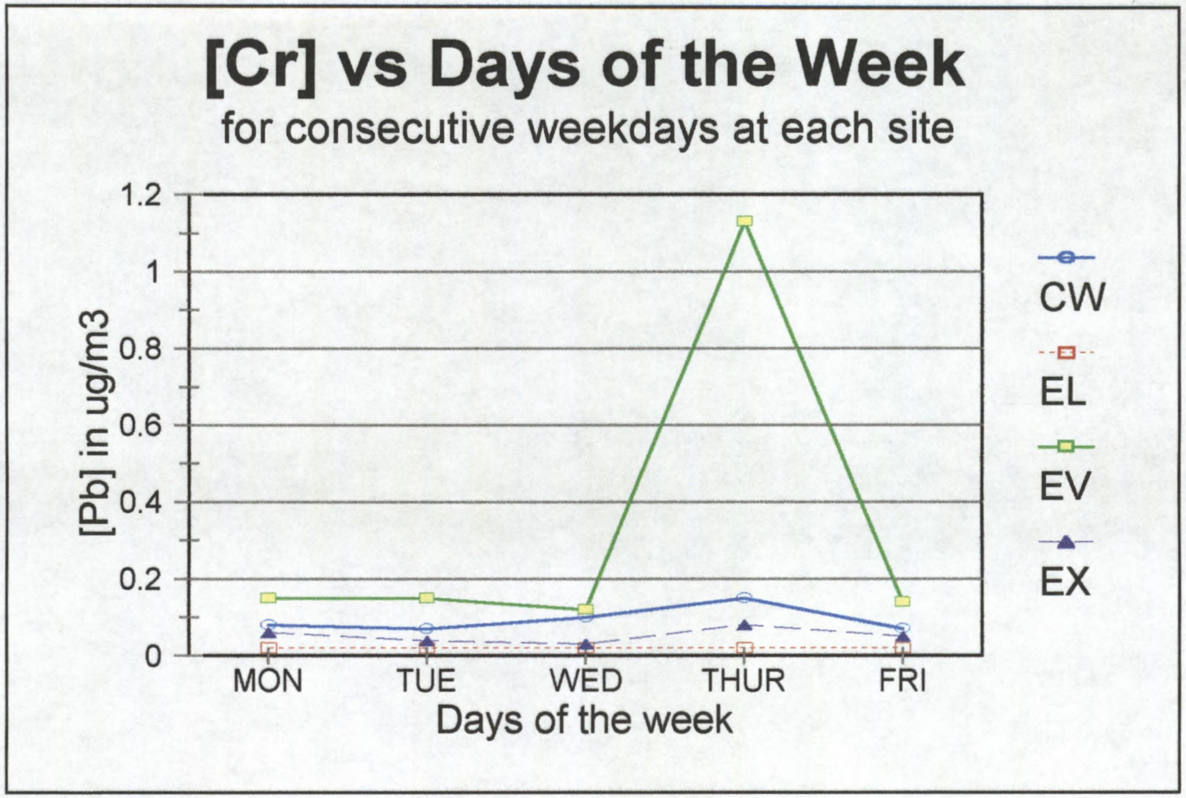


Figure 5.4 : Cr concentration in the atmosphere at four schools in Chatsworth on five consecutive weekdays.

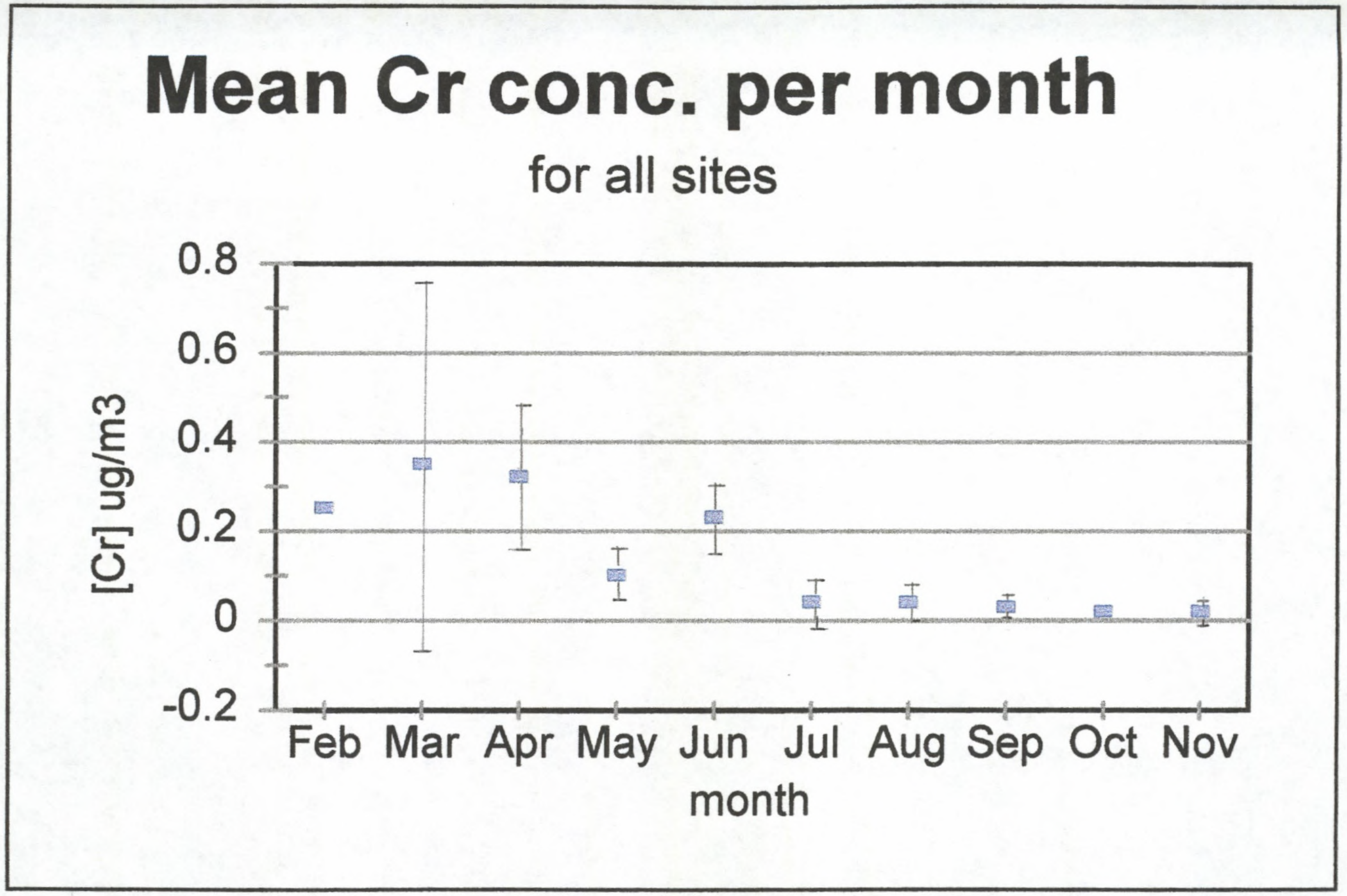


Figure 5.5: Average Cr concentrations in the atmosphere of Chatsworth for each month from February to November 1996.

monitoring of Cr emissions is done from the beginning of the year, i.e. if a survey was carried out only for the latter half of the year, the result would have indicated a very low average value.

5.1.6 Annual Variation of Cr Concentration (all sites together)

Figure 5.6 shows that with the exception of the 3 days on which high Cr concentration were recorded, the levels are well below 0.6 μg/m^3 for all sites. Also, the Cr concentrations were high only for the first half of the year. The combustion of Cr containing materials such as magnetic tapes, plastics etc. by residents of Chatsworth could also contribute to the high levels at the beginning of the year. Another factor that can also be considered is the positions of the schools, i.e. their position in relation to valleys and hill tops. Site CW is situated on a hilltop and the windy conditions usually experienced there could account for the low chromium concentration. In addition, chromium in the atmosphere could also come from recycling factories around Prospecton which is to the South East of Chatsworth. It is also possible that Chromium in the atmosphere can arise when small particles of chromium escape as dust during the production of metal alloys. Such factories exist in the Mobeni-Jacobs industrial area which is to the East of Chatsworth. The possibility of chromium escaping into the atmosphere from solutions and aerosols is of serious concern since a large number of electroplating and galvanizing industries have mushroomed around the residential area of Chatsworth. Such industries are now found in the Silverglen industrial sector in Chatsworth, Pinetown and New Germany which are to the West of Chatsworth and Clairwood and Durban Central which are to the North East of Chatsworth. Hence large once-off emissions from

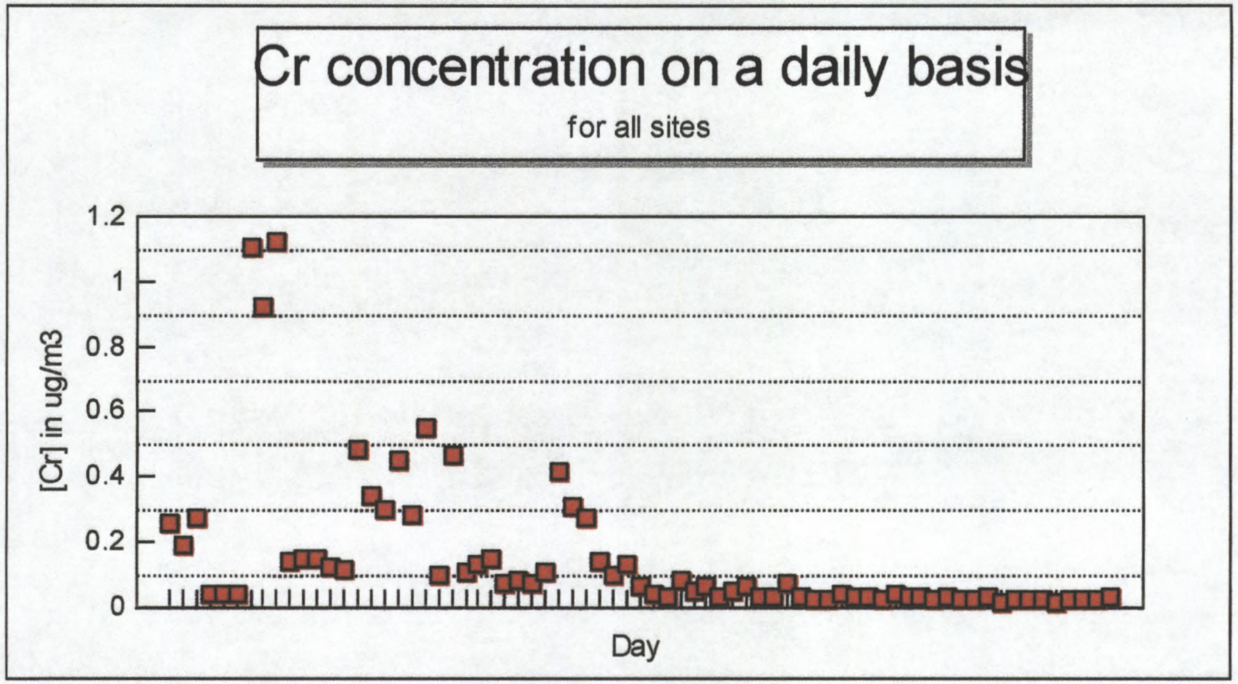


Figure 5.6: Cr concentration for each sampling day in Chatsworth for the ten-month period from February to November 1996.

these industries are a possibility. Other possible sources of chromium emission into the atmosphere are from the burning of audio, video and data storage devices and dyed materials. Chromium is also used in wood impregnation and eventual combustion of the timber adds to the level of Cr in the atmosphere. Several other industries use Cr or Chromium compounds such as the paint, printing oil, match and firework industries.

5.1.7 Variations in Cr Concentration with Meteorological factors

Meteorological variables such as temperature, humidity, wind velocity and direction were measured and their influence on the chromium concentration in the atmosphere was investigated. These relationships are illustrated in Figures 5.7 and 5.8.

5.1.7.1 Variation of Cr Concentration with Temperature, Humidity, and Wind Speed

Figure 5.7 illustrates the relationship between the Cr concentration and the variables temperature, humidity and wind velocity. Temperature, and humidity show a positive correlation with Cr concentration. Wind velocity shows no correlation with Cr concentration.

5.1.7.2 Variation of Cr Concentration with Wind Speed and Direction

From the wind rose diagram in Figure 5.8 it can be seen that much of the chromium pollution comes from the North and North East as well as from the South East and South West areas. This supports the suggested sources of Cr mentioned in 5.1.6

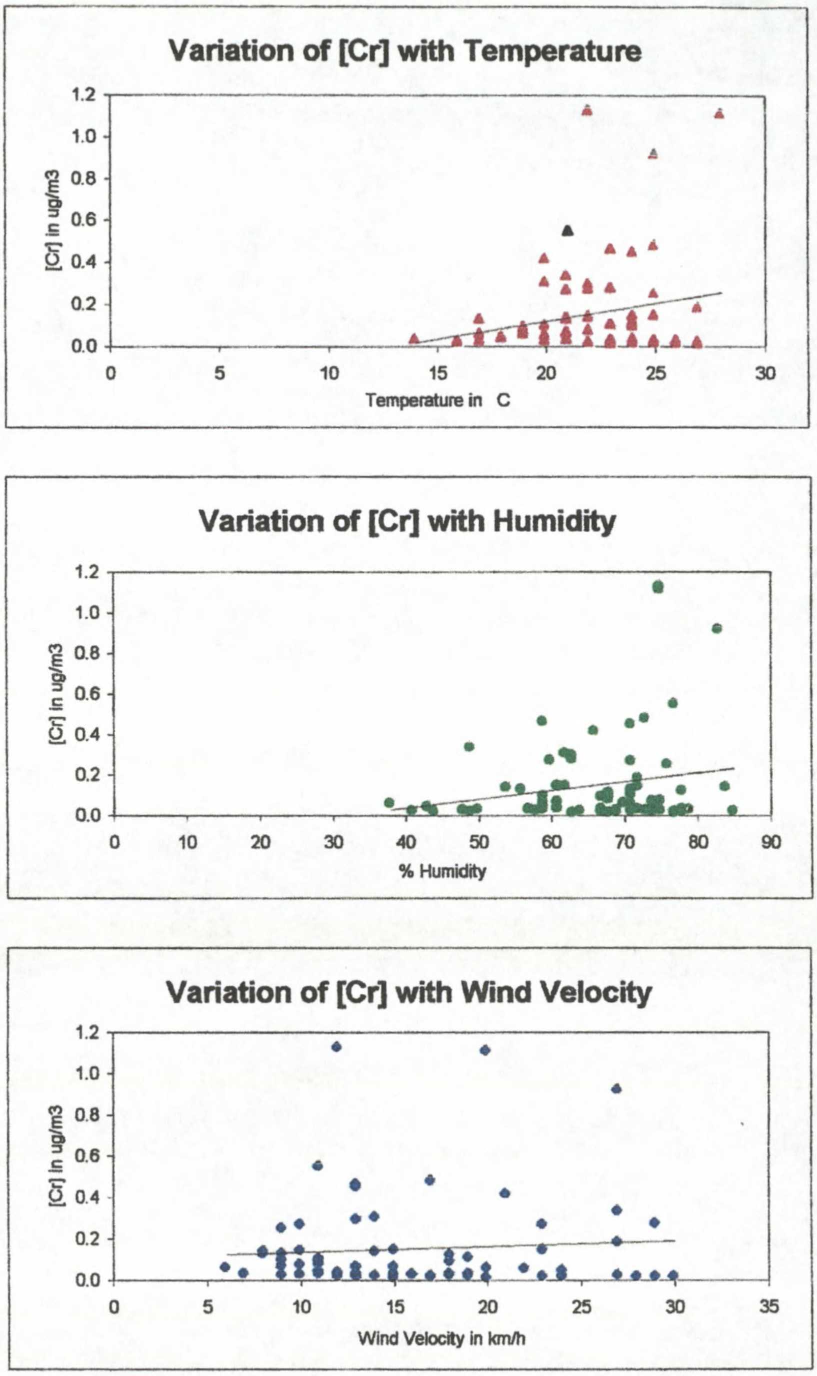


Figure5.7: Variation of selected meteorological data with Cr concentrations in the Chatsworth area.

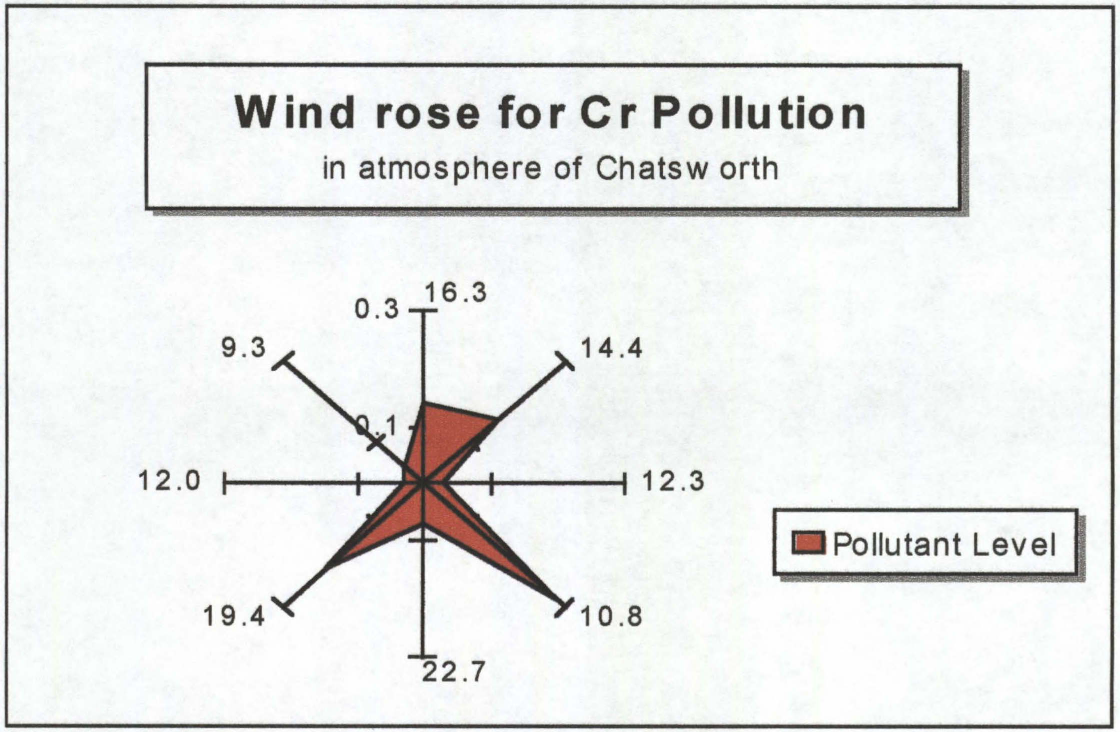


Figure 5.8 Contribution of Cr pollutant level in the atmosphere of Chatsworth from different directions

5.2 NICKEL ANALYSIS

5.2.1 Toxicity and Speciation

Although nickel has oxidation states ranging from (I) to (IV), the most prevalent oxidation state is (II). Human exposure to inorganic, water-soluble nickel compounds usually occurs via inhalation of dusts or fumes from industrial operations. Certain compounds of nickel eg. nickel subsulphide (αNi_3S_2) have been shown to be potent carcinogens. On account of its lipid solubility and volatility, nickel carbonyl ($Ni(CO)_4$) is an extremely toxic vapour which is readily absorbed upon inhalation. Nickel carbonyl poisoning leads to respiratory failure, cerebral edema and haemorrhage (NAS, 1975). $Ni(CO)_4$ is also carcinogenic.

There is very limited information with regard to nickel speciation, particularly in the atmosphere. Much of the literature on nickel speciation relates to water and soil. Nickel is widely distributed in the environment in two oxidation states. The most prevalent oxidation states of nickel are (0) as in the nickel metal and its alloys and (II) in its soluble and insoluble compounds. The most toxic form of nickel is $Ni(CO)_4$ which is formed in processes that use nickel catalysts (FDA, 1993). Respiratory tract cancers among workers in nickel refineries have been associated with inhalation of nickel sulphides and oxides. Nickel carbonyl has been shown to be present in the atmosphere near a busy traffic intersection, in town gas and in trace quantities in cigarette smoke (Merian, 1991). A variety of insoluble nickel compounds such as $Ni(OH)_2$ are known to have been inhaled by glass blowers and welders. Water soluble nickel salts have also been known to affect workers in electroplating and electrolytic industries as a result of inhaling the nickel vapours.

5.2.2 Variation of Ni Concentration with Sampling Sites

Figure 5.9 illustrates the range of Ni concentrations at each of the six schools for the two periods of sampling. Notably high concentrations of Ni are observed at Excelsior and Evergreen Primary Schools. The fact that these high concentrations are observed at different periods would suggest localized emission. The likely source of Ni, at Evergreen, is the welding operations adjacent to the school. This could account for the high levels measured at the school. The source of Ni, at Excelsior, could be from the crematorium, which is situated close to the school.

Figure 5.10 shows that the mean for Ni concentration for all sites is between 10 and 20% of the total. The pie chart shows that all sites have an approximately even percentage of Ni in the atmosphere.

5.2.3 Variation of Ni Concentration with Sampling Dates at each site

Figure 5.11 gives an even better picture of the Ni concentration than the mean values given in the Table 5.2. The wide variation from the mean value is clearly visible from the graph for each site. In the case of Ni, high and low concentrations occur in both periods. No general trend can be observed from Figure 5.11.

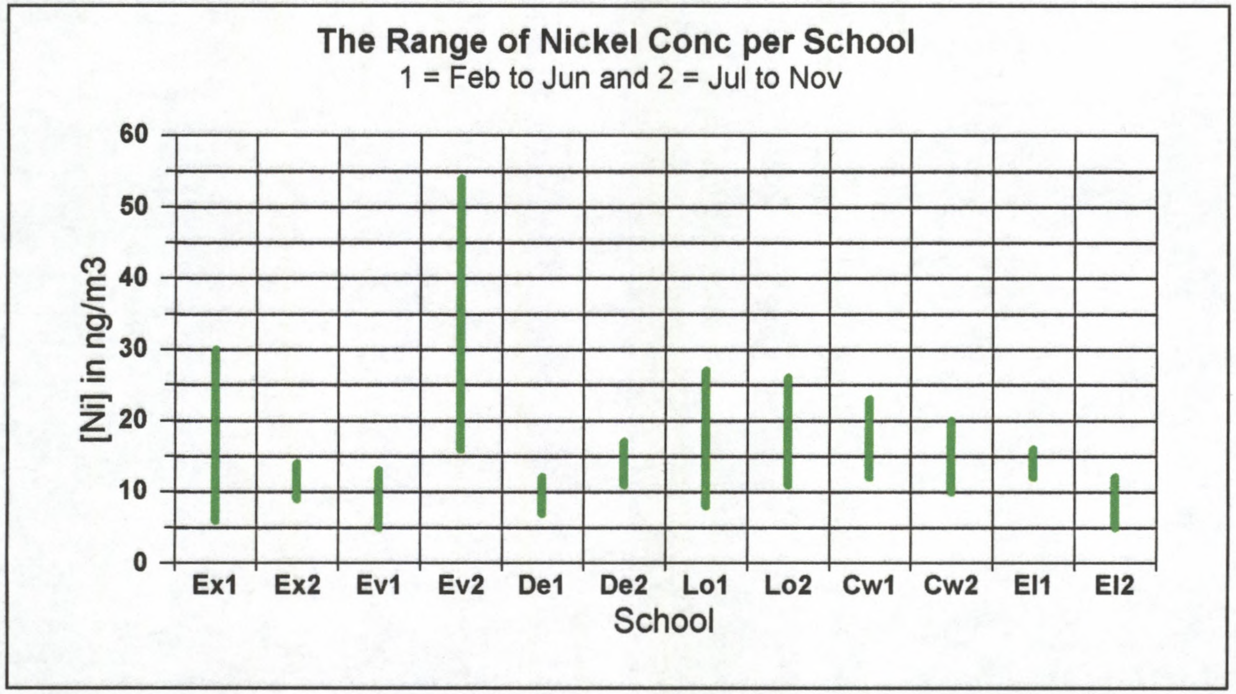


Figure 5.9: The range of Nickel concentration for each site for the period February to June 1996 and July to November 1996

Table 5.2: Mean nickel concentrations for each site in Chatsworth

SCHOOL	MEAN [Ni] in µg/m^3	RSD %
EX	15	49
EV	17	76
DE	12	28
LO	18	36
CW	16	27
EL	11	31

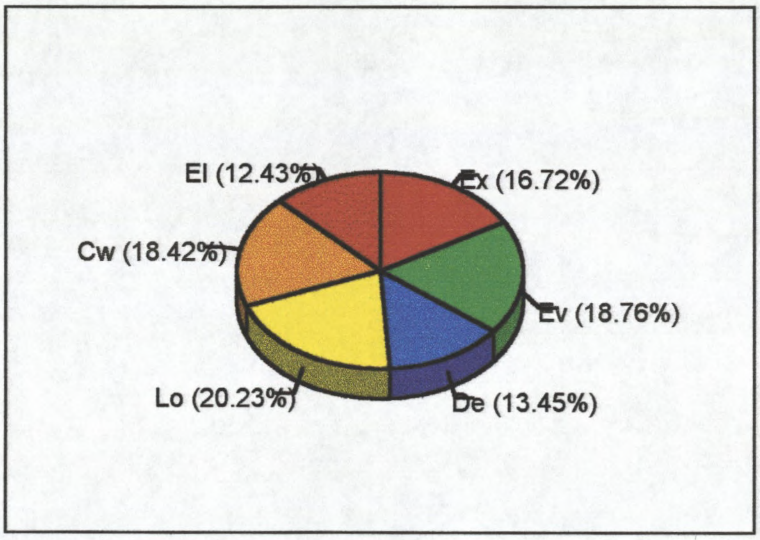
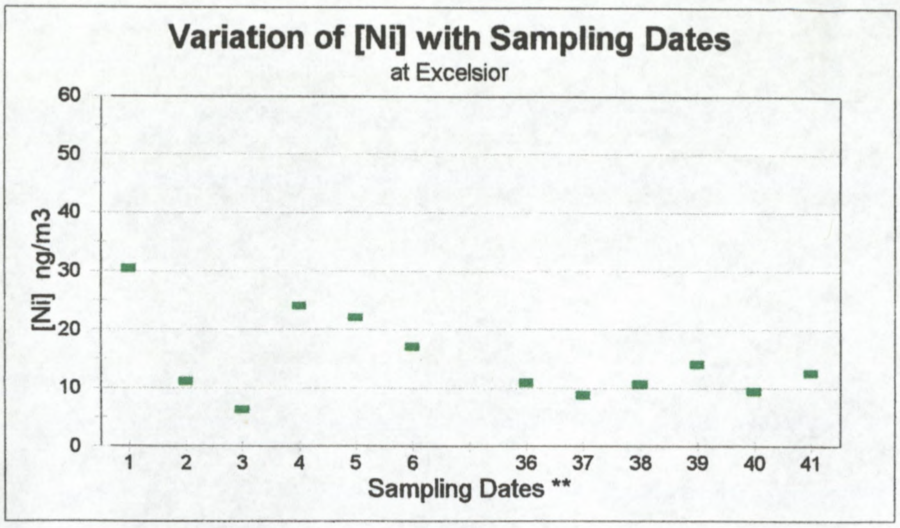
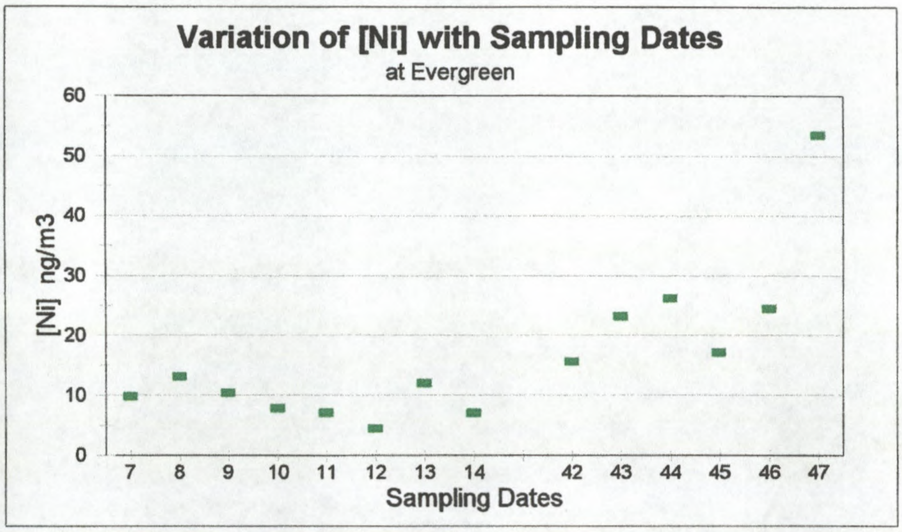
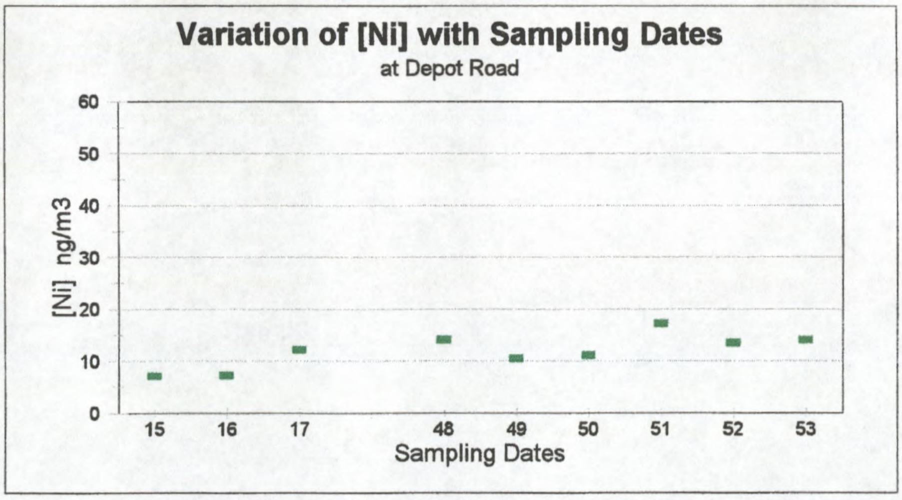


Figure 5.10: The percentage of Ni concentration for each of the six sites.

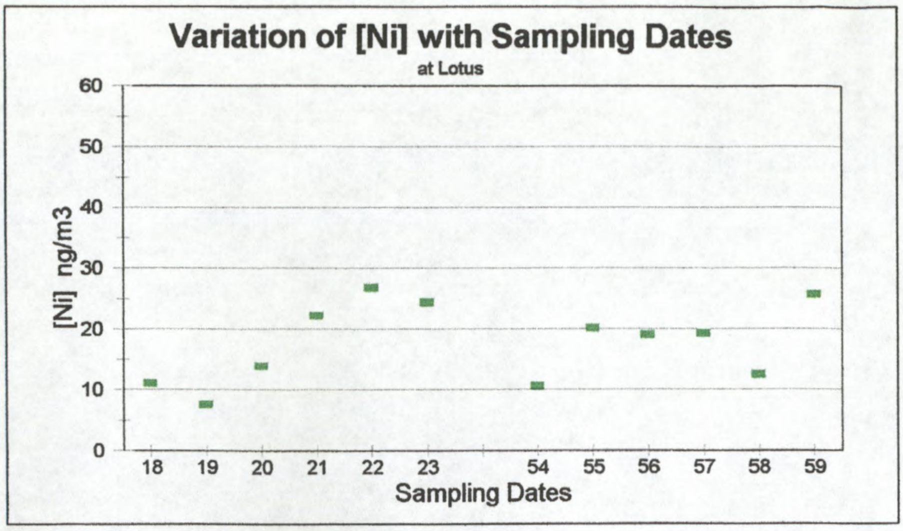


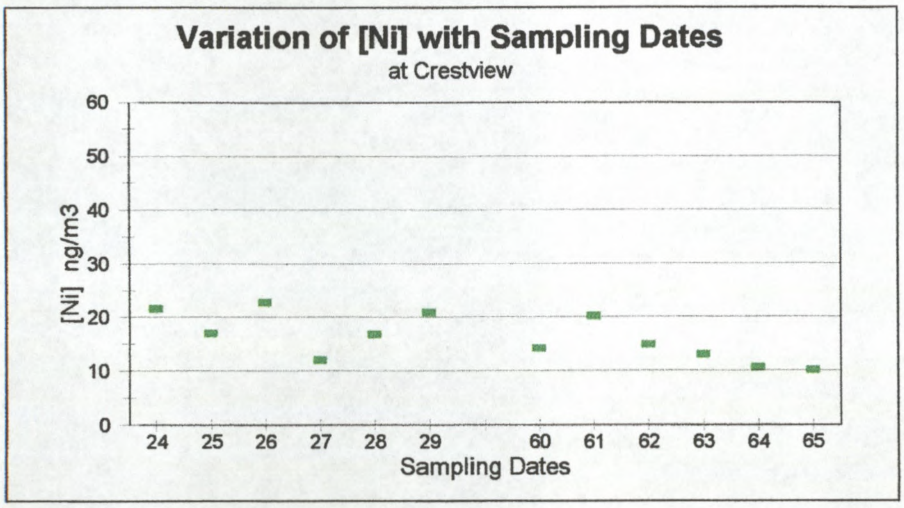




** The exact dates is given in Appendix G-3

Figure 5.11: Variation in Ni concentration with sampling dates at each site.





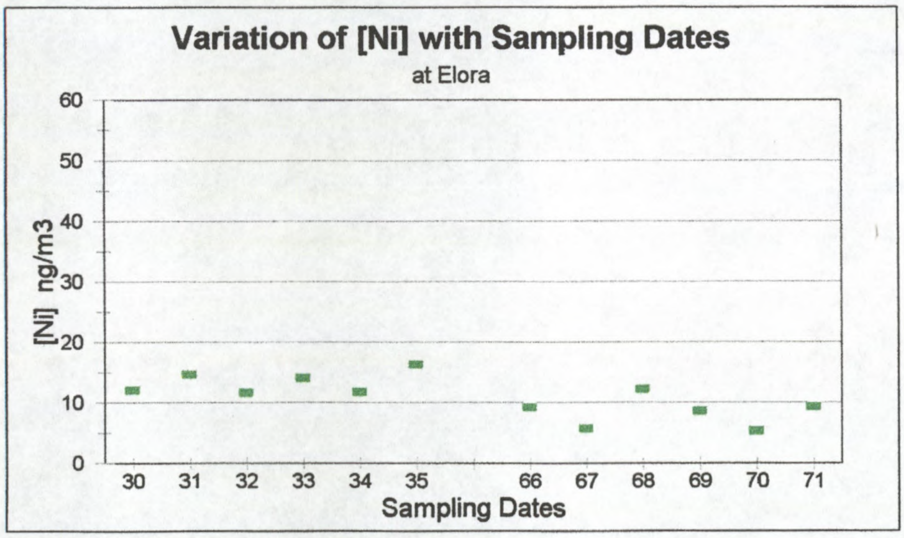


Figure 5.11 contd.: Variation in Ni concentration with sampling dates at each site.

5.2.4 Variation in Ni Concentration with Days of the Week

The pattern observed for nickel in Figure 5.12 is very different from the other metals discussed previously. In most cases there was a similarity in the patterns observed between some sites. In this case all sites show completely different trends. Thus there is no clear trend between nickel concentration and days of the week. This seems to suggest that nickel concentration in the atmosphere of Chatsworth is site specific.

5.2.5 Variations in Ni Concentration on a Monthly Basis (for all sites)

Analysis of the monthly Ni concentration in Chatsworth (Figure 5.13) shows that emissions are high in the month of February, i.e. 30 ng/m^3 whilst the values for the other months are in the region of the annual mean of 15 ng/m^3.

5.2.6 Annual Variation of Ni Concentration (all sites)

The daily concentration of Ni for the year is illustrated in Figure 5.14. With the exception of only one day the Ni concentration is less than 30 ng/m^3. Furthermore, there seems to be a trend for the Ni concentration to periodically fluctuate between the maximum and minimum values. On examination of the weather data no conclusions could be drawn regarding this fluctuation. The graph clearly indicates a periodic fluctuation between minimum and maximum values as seen by the solid line in the figure.

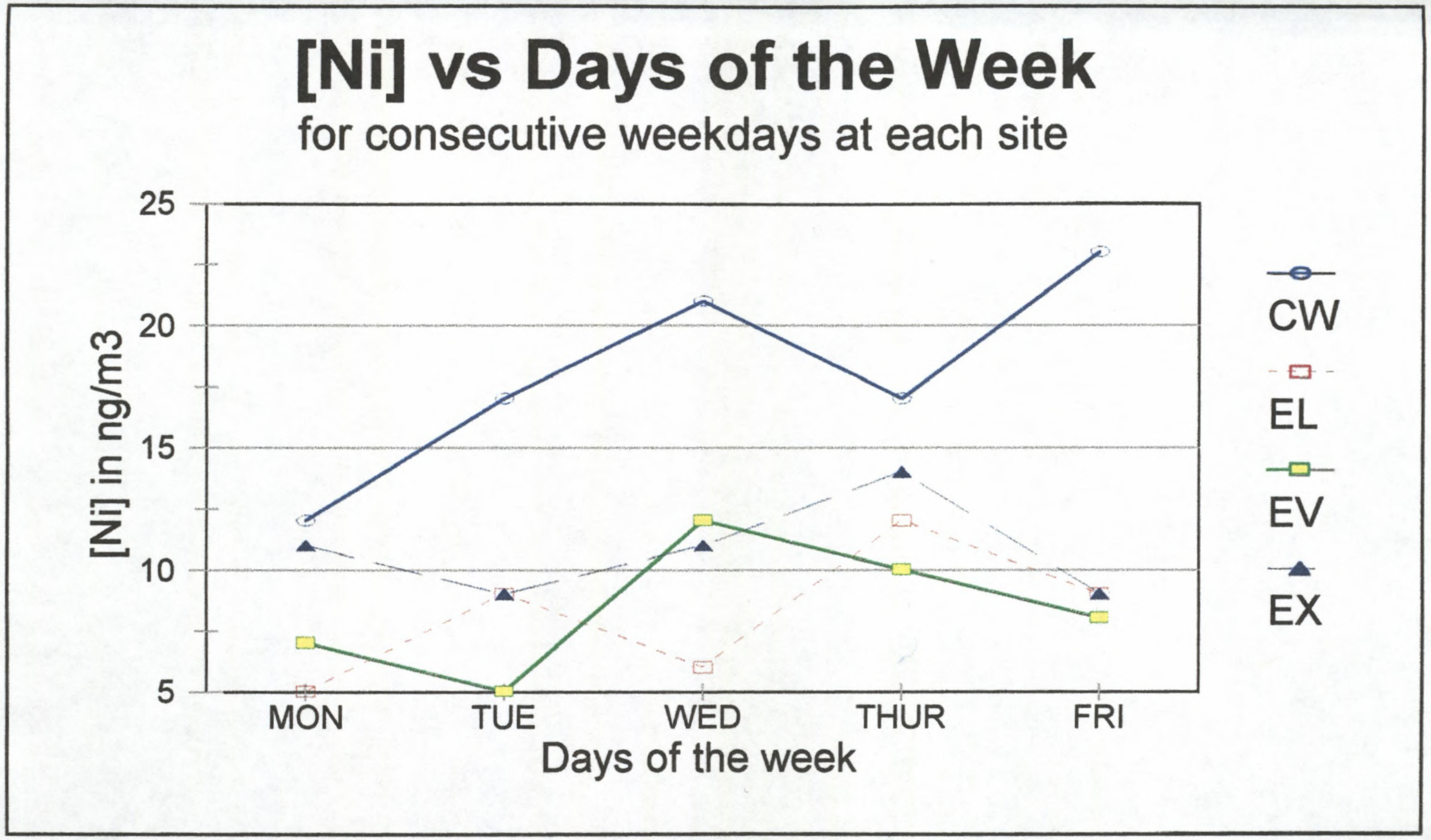


Figure 5.12: Ni concentration in the atmosphere at four schools in Chatsworth on five consecutive weekdays.

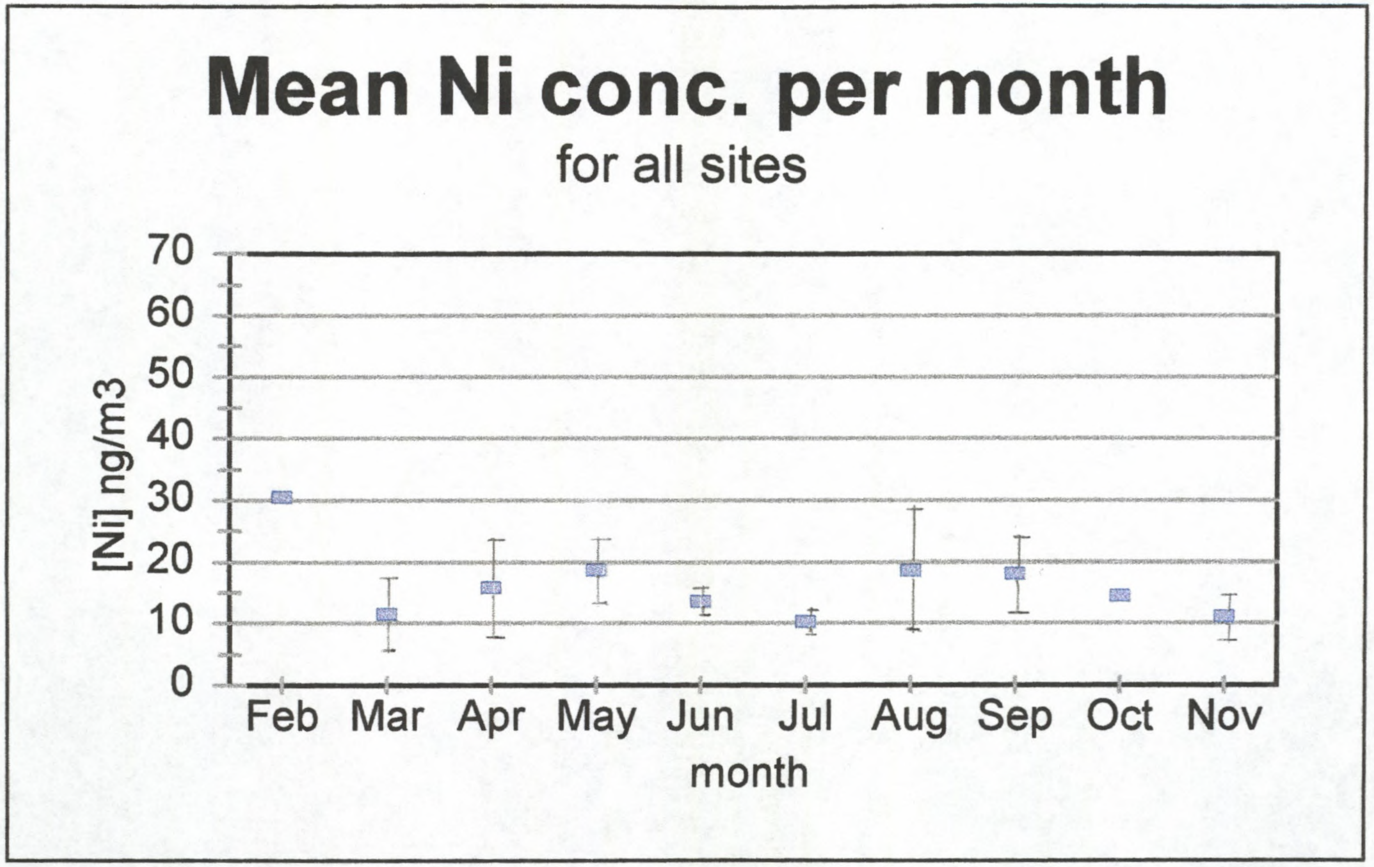


Figure 5.13: Average Ni concentrations in the atmosphere of Chatsworth for each month from February to November 1996.

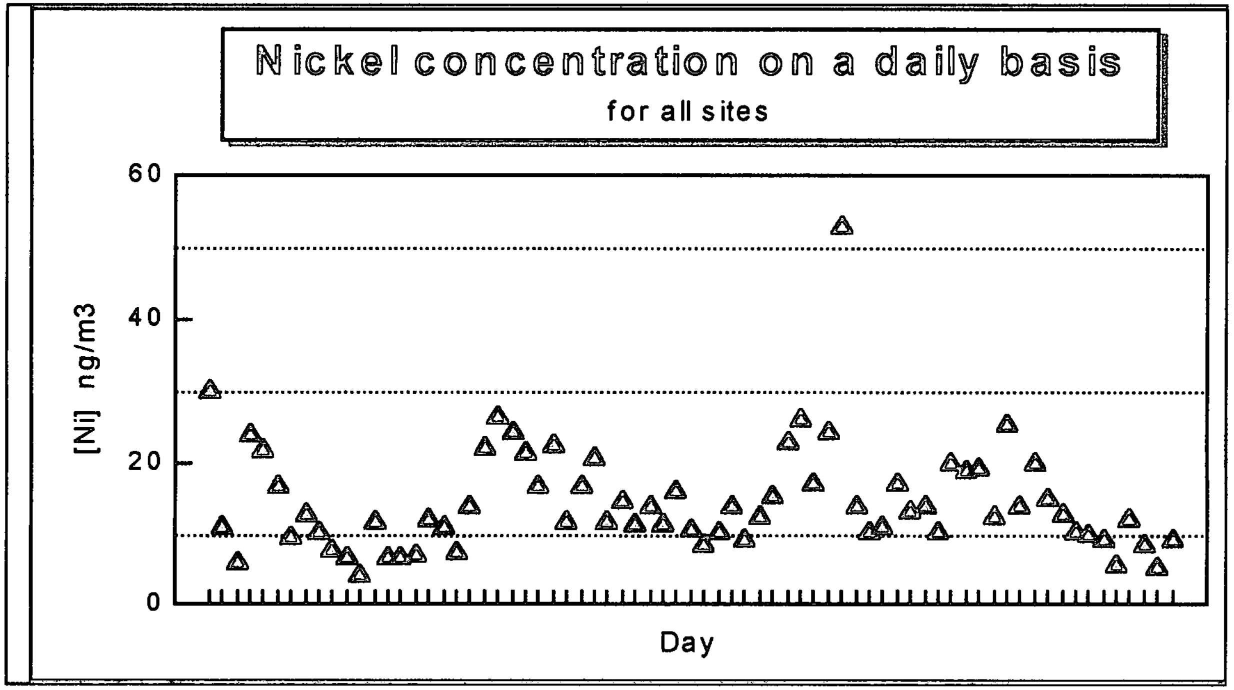


Figure 5.14: Ni concentration for each sampling day in Chatsworth for the ten-month period from February to November 1996

5.2.7 Variation of Concentration with Meteorological factors

5.2.7.1 Variation of Ni Concentration with Temperature, Humidity and Wind Speed

An attempt was made to correlate weather data with the levels of Ni concentration for each month. This is illustrated in Figure 5.15. An inspection of the trend lines reveal that there is a slight negative correlation between the nickel concentration and each of the weather data. The negative correlation with wind velocity is slightly more pronounced. This is in agreement with the work done by Kim and Fergusson (Kim and Fergusson, 1994).

5.2.7.2 Variation of Ni Concentration with Wind Speed Direction

The wind rose in Figure 5.16 shows that Ni reaches Chatsworth from all directions, with no one direction contributing significantly more. This would indicate electroplating operations which are found all around Chatsworth.

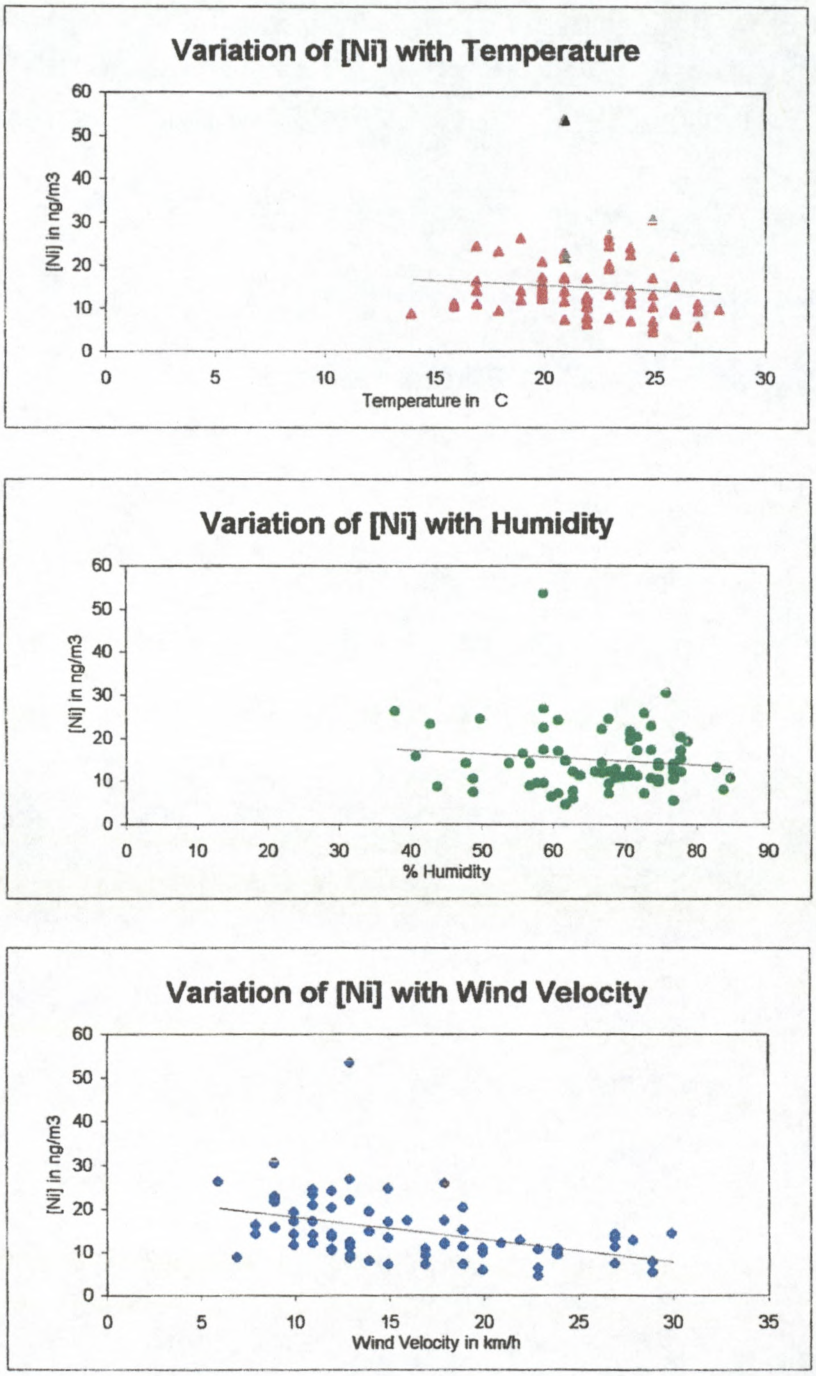


Figure 5.15: Variation of Ni concentration with selected meteorological data in the Chatsworth area.

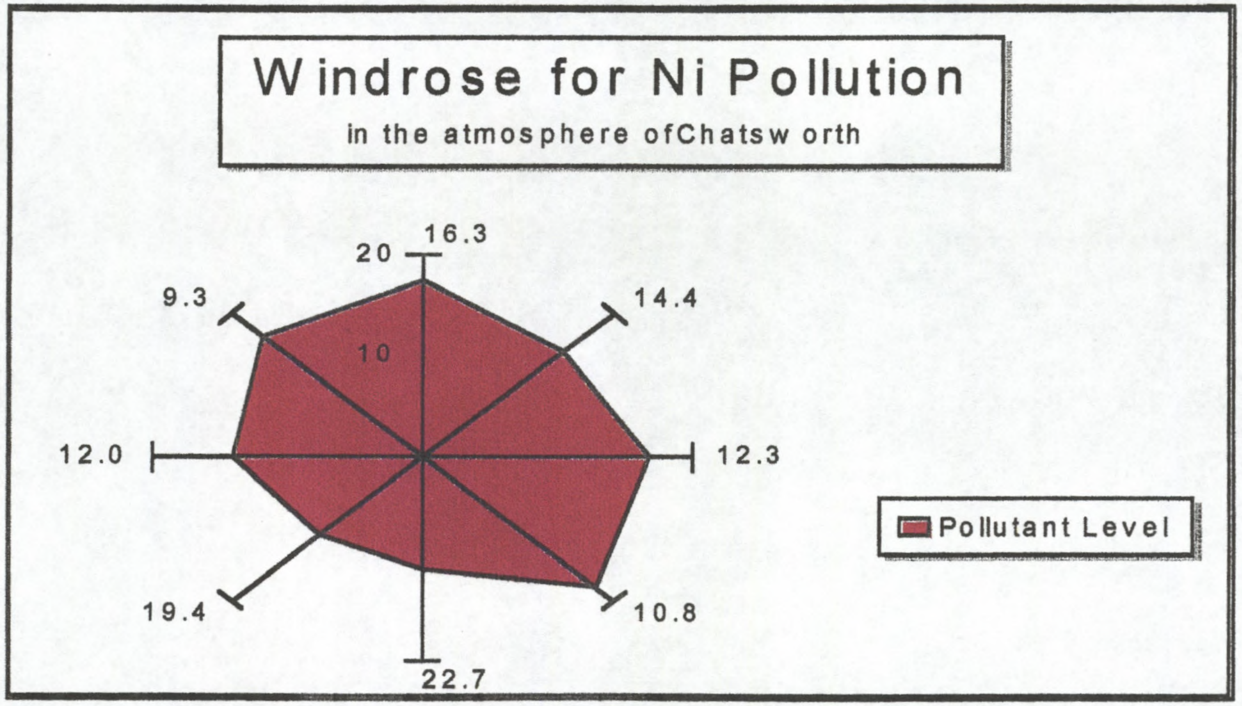


Figure 5.16: Contribution of Ni pollutant levels in the atmosphere of Chatsworth from different directions.

5.3 COPPER ANALYSIS

5.3.1 Toxicity and Speciation

Cu(I) and Cu(II) are the more common oxidation states of copper. However, Cu(I) is unstable in aqueous media and disproportionates to form Cu(II) and copper metal. Copper is one of several metals that are essential to life. Although copper is remarkably non-toxic, the inhalation of dusts, fumes and mists of copper salts can cause congestion of the nasal and mucous membranes and, occasionally, perforation of the nasal septum.

Most of the work on copper speciation is related to water with little emphasis placed on species present in the atmosphere. Atmospheric emissions of copper however, is the main route of entry into water and soil. Approximately 75% of the copper in the atmosphere comes from anthropogenic sources with the remaining 25% coming from natural sources. A variety of copper salts and volatilized metallic copper can exist in the atmosphere as a result of activities such as agriculture where solutions of $CuSO_4$ are used to prevent the growth of mildew. The largest single emission source is attributed to the production of non-ferrous metals. The two main oxidation states of copper are Cu(I) and Cu(II). Copper is most toxic in the free ion state. However, various processes in the environment tend to sequester the copper making it less toxic to living organisms (Lauren, 1986).

5.3.2 Variation of Cu Concentration with Sampling Sites

Figure 5.17 illustrates the range of copper concentration for each of the six sites for the periods from February to June and from July to November. Relative to other sites very high concentrations of Cu were recorded in the second period at Excelsior Primary School.This abnormally high value can be attributed to some localised activity. However the school is close to the crematorium and the Higginson Highway which may also be a source of copper emission. Industrial emission seems to be an unlikely source since the high value was recorded only at one site. Another possible source is the combustion of copper containing waste materials by residents. With the exception of this site, all other sites indicate concentrations of less then 75 ng/m^3. Furthermore the particulate Cu concentration is fairly evenly distributed.

Figure 5.18 shows the percentage of Cu at each site in relation to the total for Chatsworth. Four of the sites have values close to that of the annual mean of 41 ng/m^3 with the exceptions being sites EX and EL. Elora is also in a valley and is the farthest site from the crematorium and Higginson Highway. This could account for the low concentration at this site.

5.3.3 Variation of Cu Concentration with Sampling Dates at each Site

Figure 5.19 shows the variation in copper concentration on a daily basis at each of the sites. The patterns observed for each site are different and hence no trend can be seen. The copper

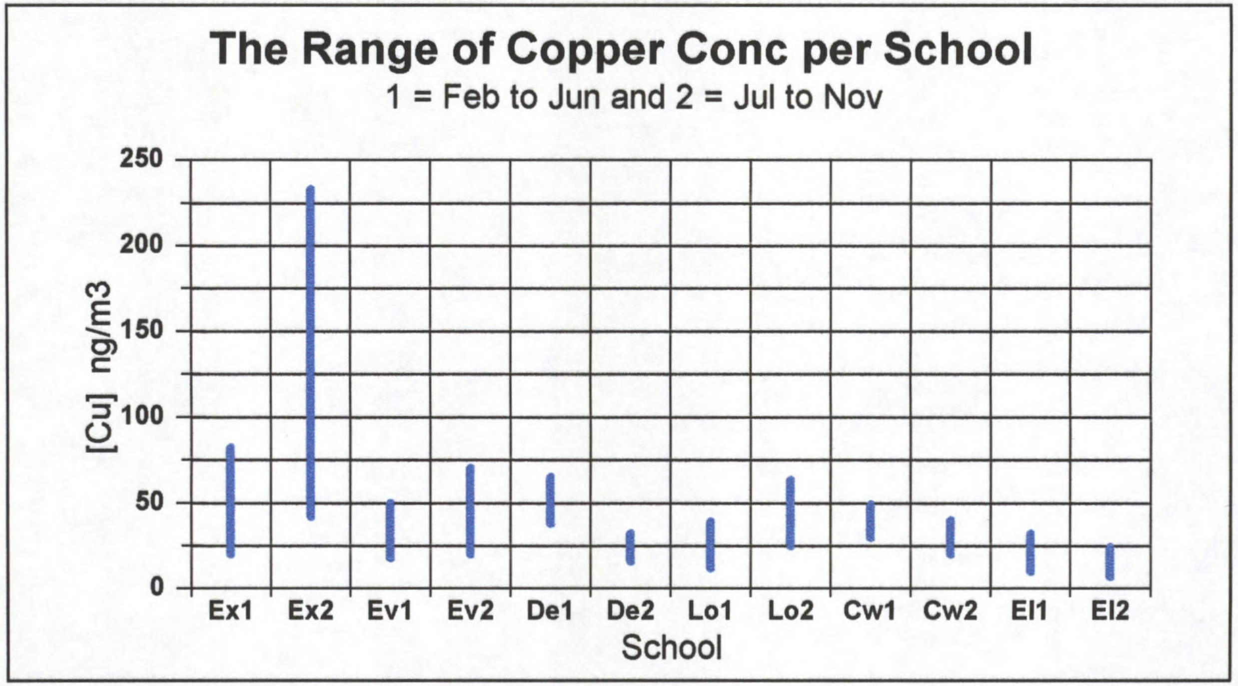


Figure 5.17: The range of Copper concentration for each site for the period February to June1996 and July to November 1996.

Table 5.3: Mean copper concentrations for each site in Chatsworth

SITE	MEAN [Cu] in ng/m^3	RSD %
EX	81	83
EV	34	43
DE	38	48
LO	33	40
CW	38	38
EL	19	46

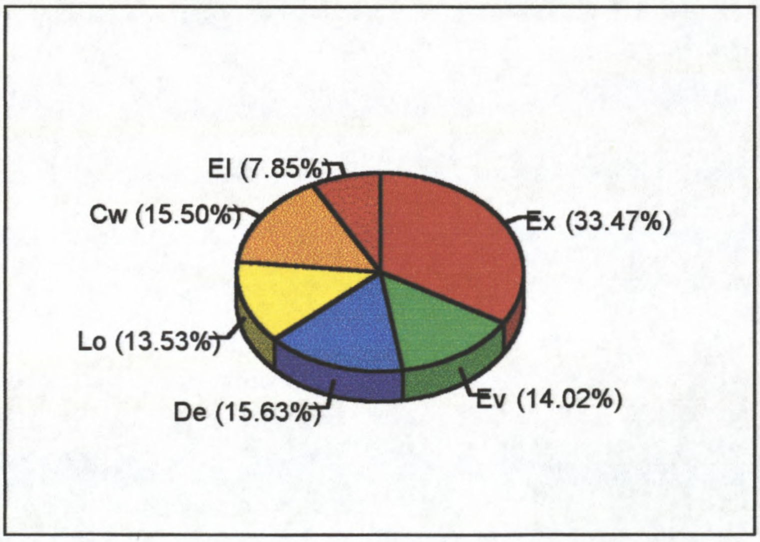
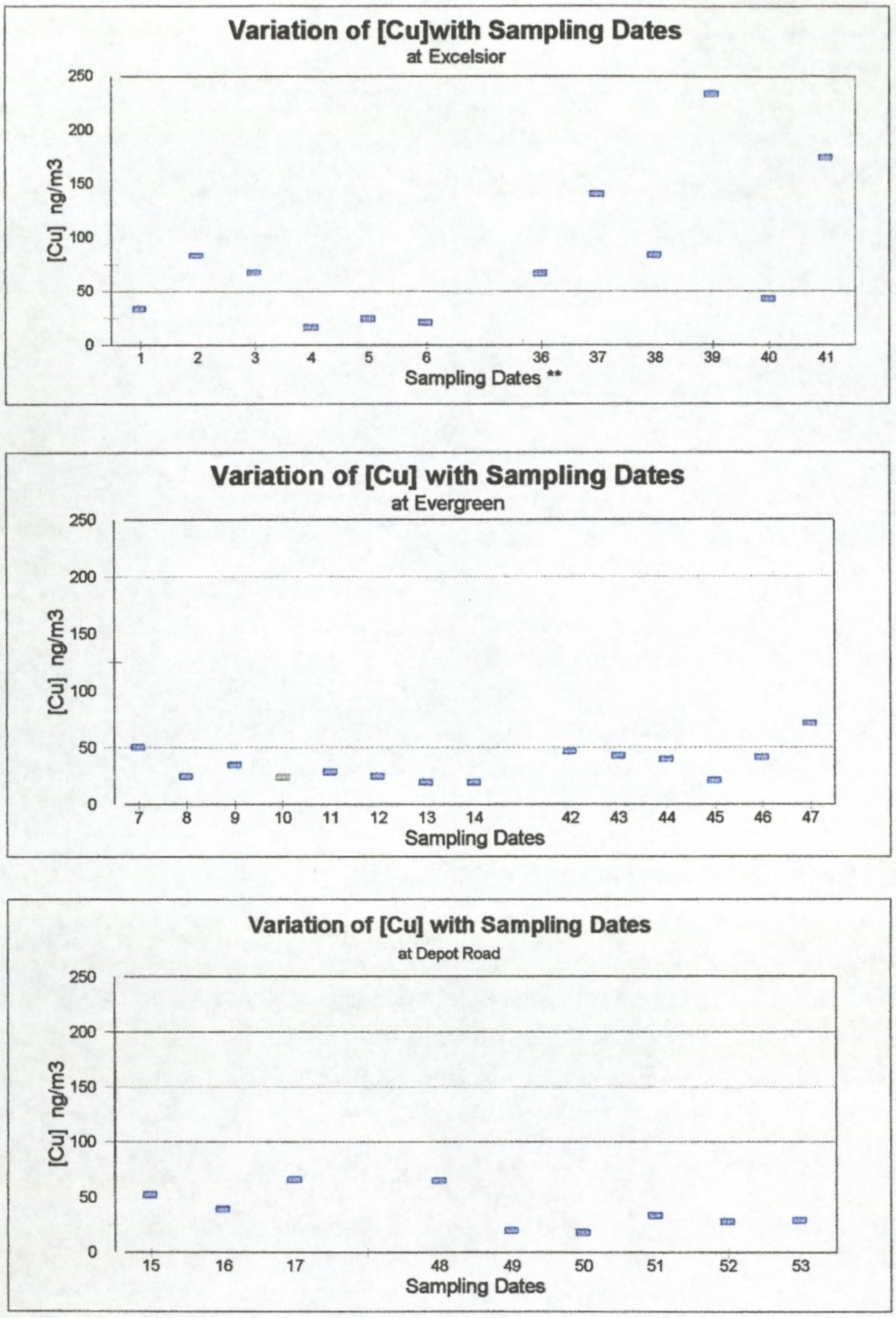
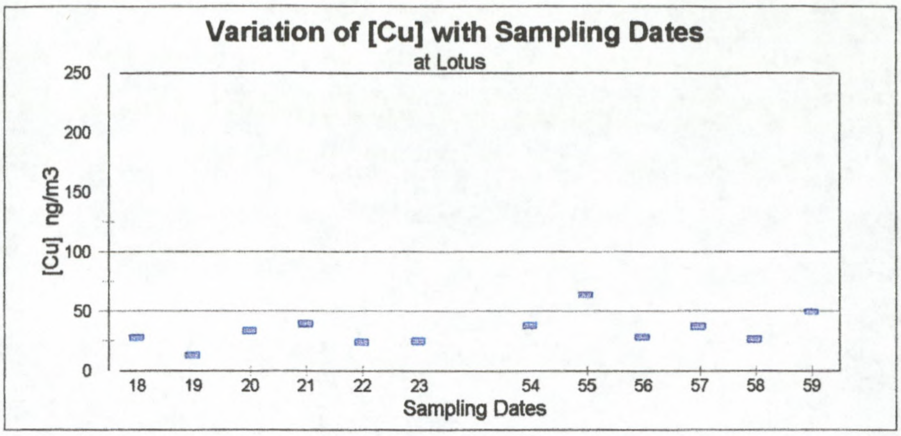


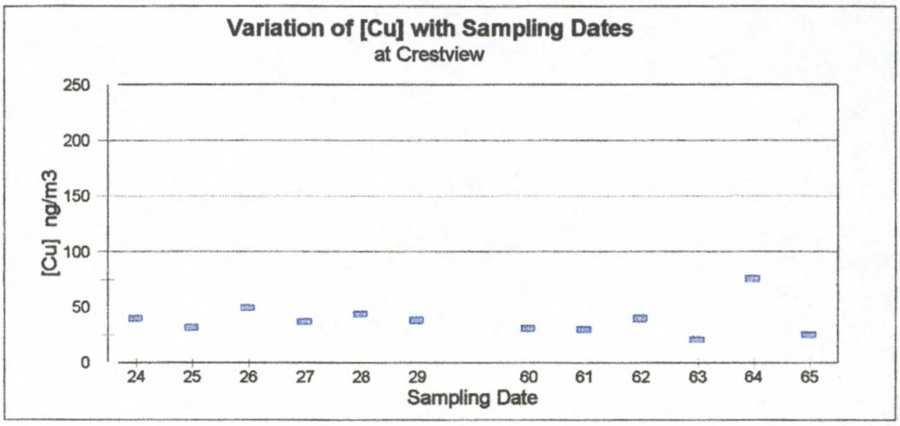
Figure 5.18: The percentage of Cu concentration for each of the six sites.



** The exact dates is given in Appendix G-3

Figure 5.19: Variation in Cu concentration with sampling dates at each site.





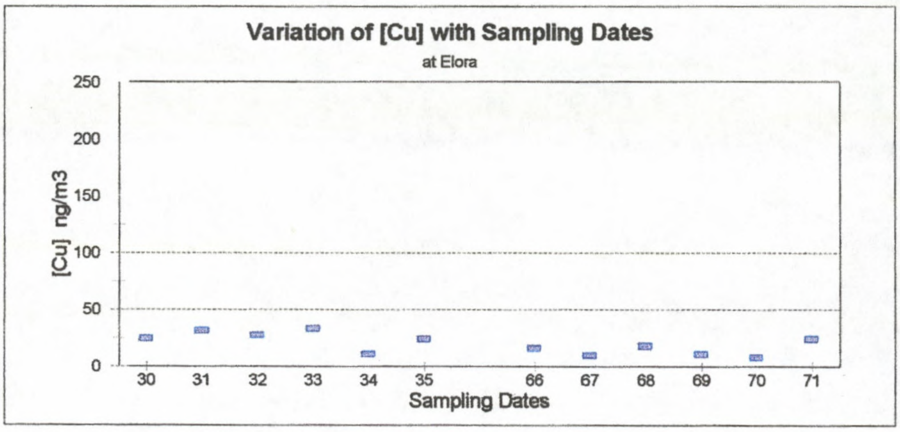


Figure 5.19 contd.: Variation of Cu concentration with sampling dates at each site.

level fluctuates daily at each of the sites. The unexpectedly high values obtained at site EX is clearly depicted in Figure 5.19. This site is closest to the crematorium and industrial areas to the east of Chatsworth and has the highest level of Cu while Elora is farthest and has the lowest level of Cu. Thus the possible source of Cu may be the crematorium and/or the industrial areas. Analysis of emissions from the crematorium (www. 1997) would aid in the identification/elimination of this source.

5.3.4 Variations of Cu Concentrations with Days of the Week

The copper value for each consecutive weekday is shown in Figure 5.20. For most of the sites the values are fairly constant, ranging from about 0 - 50 ng/m^3 with the exception of site EX. This is suggestive of background copper levels in the atmosphere rather than industrial emission. It is also possible that since 2-3 cremations taken place daily at the crematorium, there is a constant level of copper emissions from this source which may account for the higher levels found at site EX.

5.3.5 Variations in Cu Concentrations on a Monthly Basis (for all sites)

Figure 5.21 shows that high levels of copper were recorded in July and August. This may be attributed to household combustion during the colder months. Timber and other materials containing copper is probably incinerated by the locals which may have contributed to the high levels during these two months.

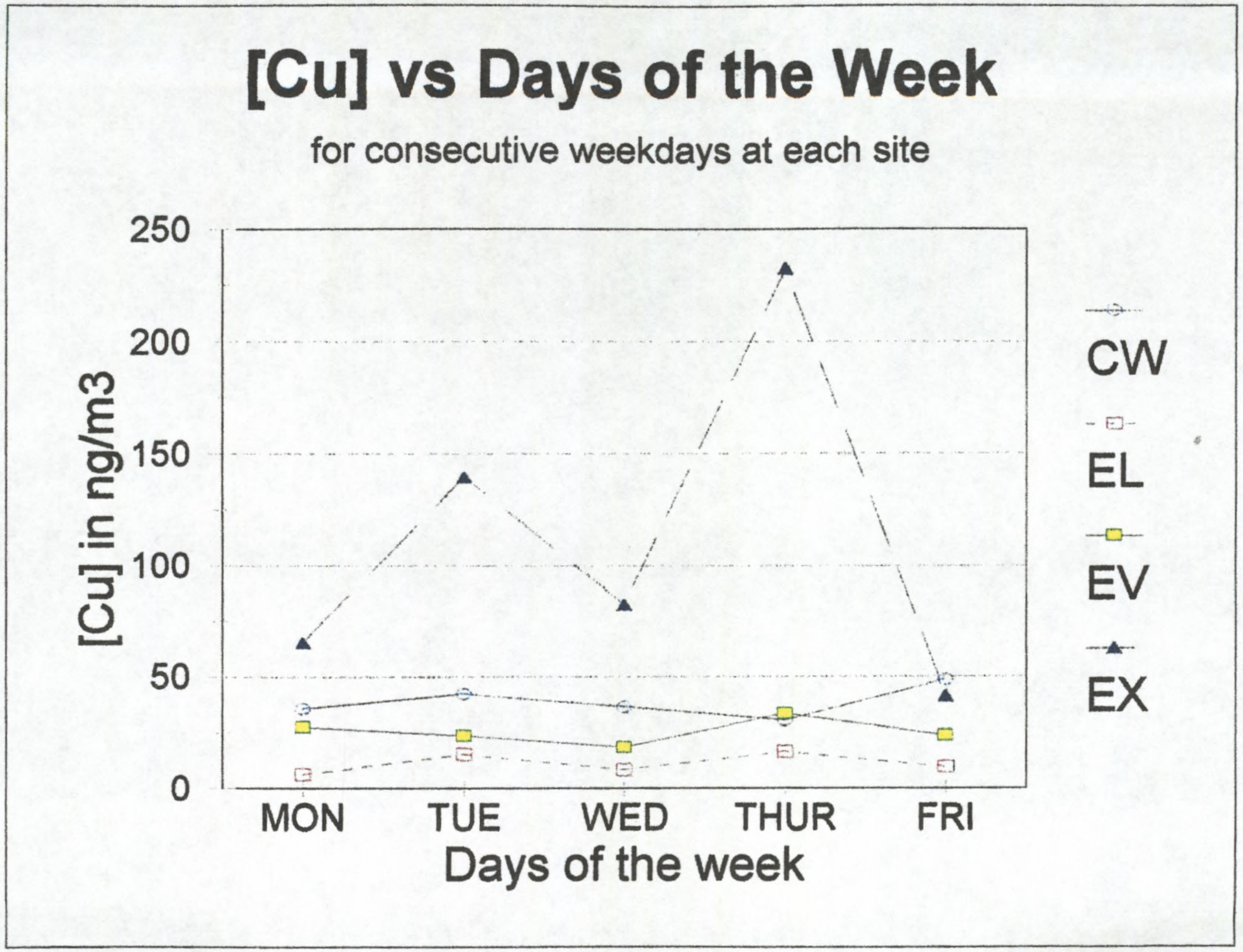


Figure 5.20: Cu concentration in the atmosphere at four schools in Chatsworth on five consecutive weekdays.

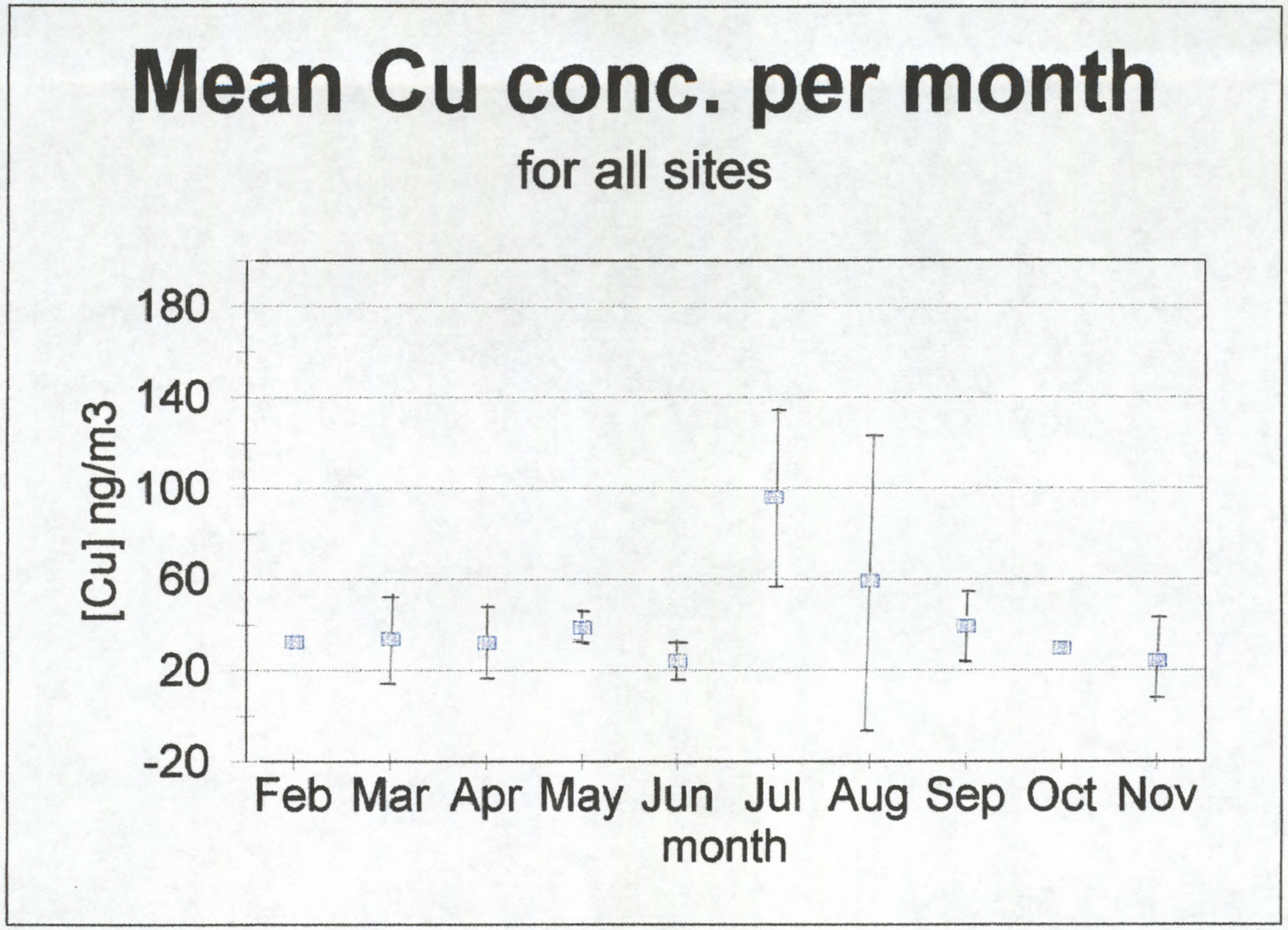


Figure 5.21: Average Cu concentrations in the atmosphere of Chatsworth for each month from February to November 1996.

5.3.6 Annual Variation of Cu Concentration (all sites together)

Figure 5.22 shows that with the exception of 3 days in the year, the levels of copper concentration were generally below 100 ng/m^3. This suggests that the high value may have been due to a sudden emission either by an industry or local incineration. As these three values were found at only one site, it is likely to be due to the incineration at the crematorium. The annual mean copper concentration is 41 ng/m^3 and the value could be lower if the three high values were removed from the calculation of the mean. This value is however relatively low in comparison with places in other parts of the world (discussed under 5.4).

5.3.7 Variation in Cu Concentration with Meteorological factors

5.3.7.1 Variation of Cu Concentration with Temperature, Humidity, and Wind Speed

Figure 5.23 shows scatter graphs of copper concentrations in relation to the mean meteorological factors for that day. The trend lines clearly show that for temperature there is a strong negative correlation with Cu concentration. Humidity and wind velocity show no correlation with copper concentration.

5.3.7.2 A Variation of Cu Concentration with Wind Speed and Direction

The wind rose pattern in Figure 5.24 shows that Cu as an atmospheric pollutant comes from all directions. This leads us to believe that industrial emissions play a minor role in the levels of copper in the atmosphere. Furthermore wind velocity had little effect on the level of Cu in the atmosphere.

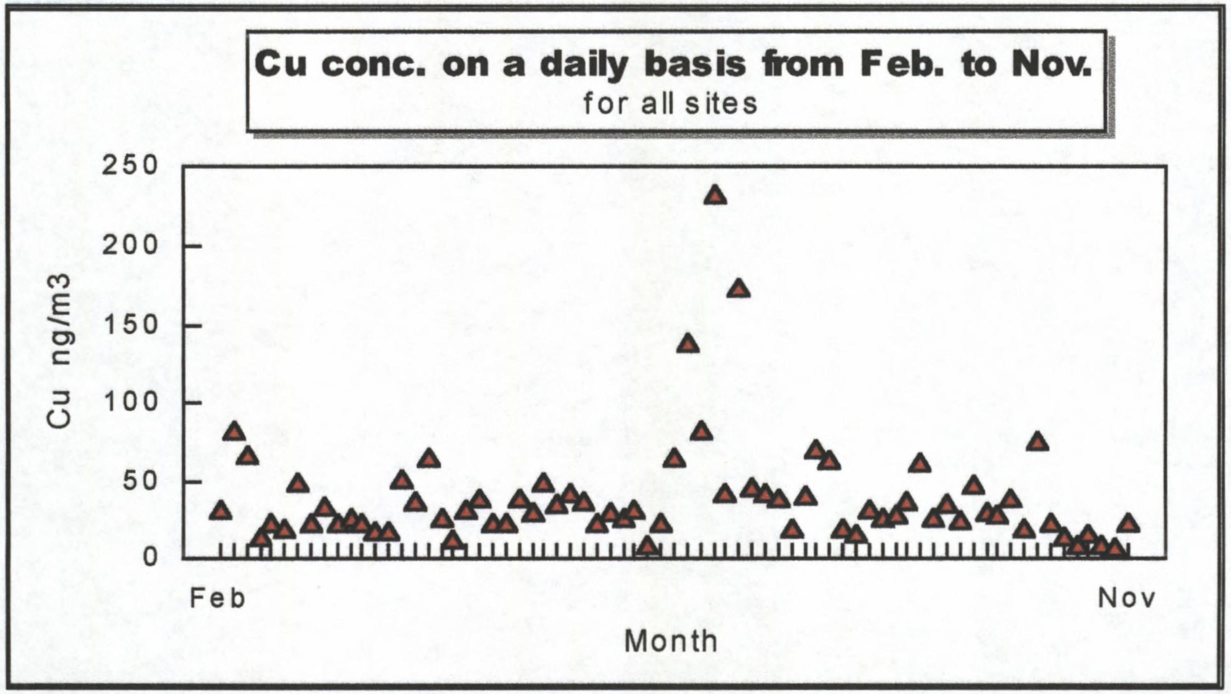


Figure 5.22: Cu concentration for each sampling day in Chatsworth for the ten month period from February to November1996.

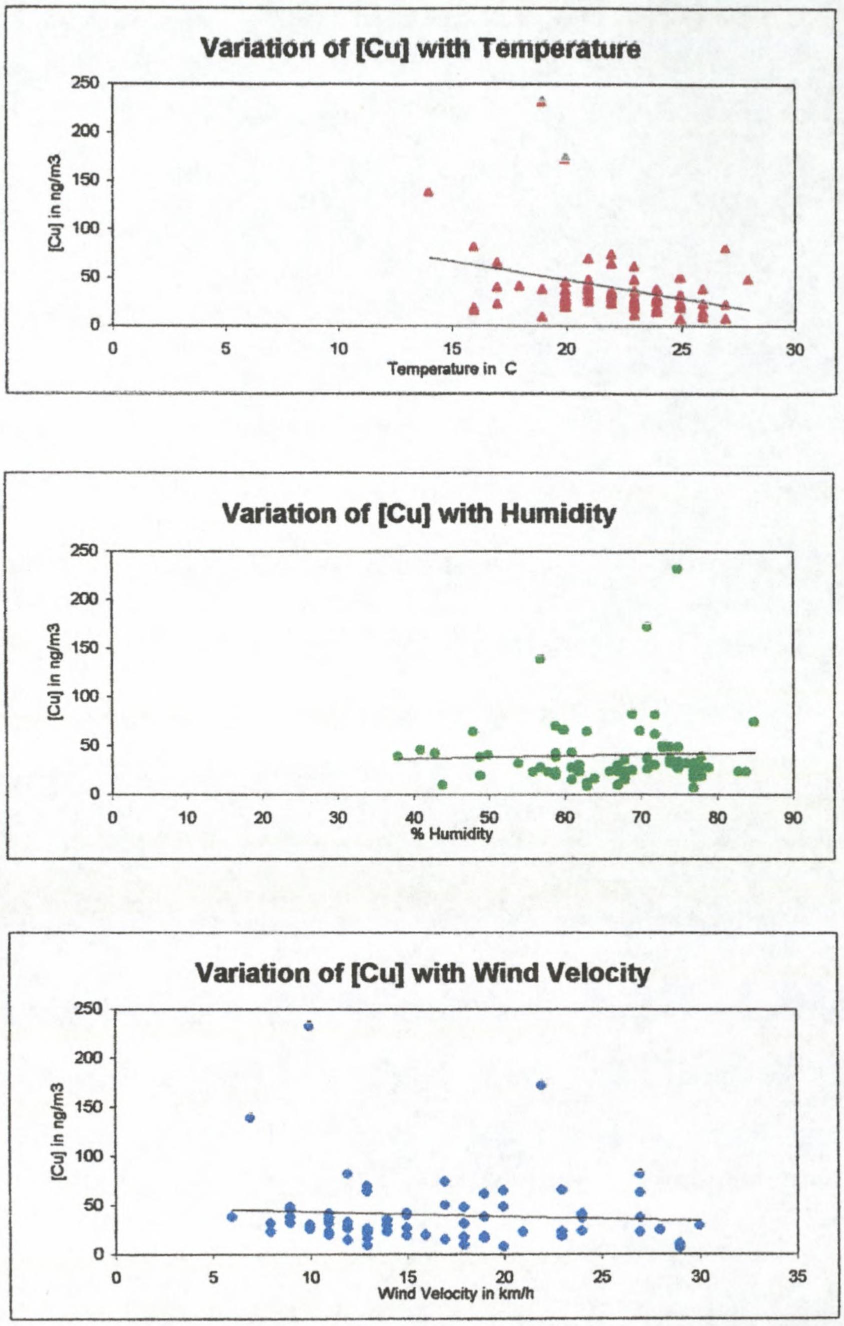


Figure 5.23: Variation of selected meteorological data with Cu concentration in the Chatsworth area.

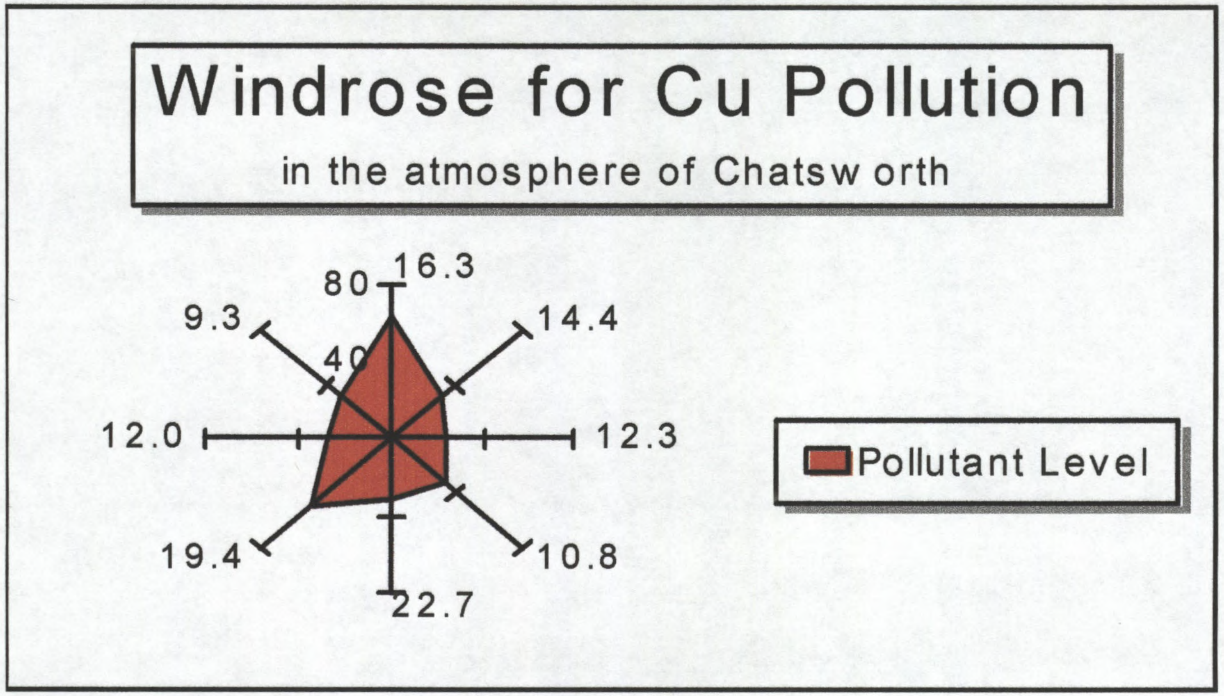


Figure 5.24: Contribution of Cu pollutant level in the atmosphere of Chatsworth from different directions.

5.4 Comparison of Cr, Ni and Cu concentration in the atmosphere with other areas.

Table 5.4 gives a comparison of the Cr, Ni and Cu ranges for remote, rural and urban areas according to Schroeder and others (1987). These values are compared with the values found in Chatsworth.

An inspection of the above table shows that Chatsworth has an abnormally high level of chromium although for most period of the year the value was considerably lower. In the case of copper and nickel the values are closer to that of a rural area which is in keeping with that obtained for lead and cadmium. A more realistic comparison would be to compare the mean values of these metals in the atmosphere of various cities in South Africa with that in Chatsworth. The work done by the National Nuclear Research Institute at Pelindaba in 1977/8 and by Albertyn in 1993/4 gives some indication of the concentrations of Cr, Ni and Cu in the various cities of South Africa as shown in Table 5.5. Although no data is available for the 1993/4 period, it is known that the towns have become more industrialised and consequently the levels of these metals in the atmosphere would have increased tremendously. The mean values for Chatsworth for the metals Cr, Ni and Cu are 150, 15 and 41 ng/m^3 respectively. Comparison of the values obtained with that given for the 1977/8 would be misleading since approximately 22 years have elapsed since the publication of these results.

Table 5.4: Comparison of Ranges of Cr, Ni and Cu Associated with Particulate Matter in the Atmosphere in various areas (Schroeder et al., 1987) with that in Chatsworth.

Location	Cr (ng/m^3)	Ni (ng/m^3)	Cu (ng/m^3)
Remote	0.005 - 11.2	0.01 - 30	0.029 - 12
Rural	1.1 - 44	0.6 - 78	3 - 280
Urban Area in:			
Canada	4 - 26	4 - 371	17 - 500
USA	2.2 - 124	1 - 328	3 - 5140
Europe	3.7 - 227	0.3 - 1400	13 - 2760
Other	traces - 277	2.3 - 158	2.0 - 6810
Chatsworth	20 - 1130	4.5 - 53.5	7.3 - 232.7

Table 5.5: Comparison of the ranges of Cr, Ni and Cu in the atmosphere of various cities in the Republic of South Africa in ng/m^3.

	1977/8			1993/4		
City	Cr	Ni	Cu	Cr	Ni	Cu
Richards Bay	4.4	8.7	5.4	-	-	-
Durban	34.0	8.6	18.0	-	-	-
Pretoria	32.0	9.9	35.0	-	-	-
Johannesburg	27.0	7.4	45.0	-	-	-
Cape Town	6.9	11.9	43.0	-	-	-

CHAPTER 6

General Conclusions and Recommendations

The main objectives of this research were: -

- to set a basis from which future air pollution studies in Chatsworth can be undertaken. The study has provided a considerable amount of data, including those considered to be ‘outliers’ for other researchers to either support or reject the findings.

- to identify possible sources of metal pollutants. The results obtained indicate that wind direction, local home industries and incineration at the crematorium influences the air quality of Chatsworth. The industrial areas and freeways adjacent to Chatsworth also make their contribution to the level metal pollutants in this area in particular the relatively high concentration of Pb compared to that of Cu, Ni and Cd.

The concentration of airborne lead over Chatsworth should decrease as a result of the reduction in the lead content of petrol and through the use of unleaded petrol. At present it is not possible to compare the present airborne lead concentration in Chatsworth with that of previous years as there are no published data of research having been done in the area. It is hoped that this study will assist other research workers and the Durban Metropolitan Environmental Officers. Furthermore it is hoped that the information will become part of a data base of the air quality of different locations in Durban. Although the level of lead is not as high as that in cities such as Riyadh, there are times when the concentration exceeds the normal range. If these sudden high concentrations are to occur frequently, then such pollution can have an adverse effect on the health of the children in the area. Discussion with Dr. Nriagu, a visiting environmentalist from the University of Michigan in the U.S., revealed that there were high levels of atmospheric Pb at the Cato Manor informal settlement. Thus, it would be interesting to compare the Pb in the blood of children from the six sites to that found in the atmosphere of these sites. It is recommended that school planners try to locate schools away from main roads and highways to ensure that the health of our children is protected. Furthermore residential areas should as far as possible be away from industrial centres.

In general the cadmium, nickel and copper concentration in the atmosphere of Chatsworth are low, being in the ng/m^3 range. Likely sources of these metals are home industries, incineration of wastes and local electroplating industries.

The influx of informal settlements in and around Chatsworth also impacts negatively on the air quality of this area. This is because of the combustion of wood, coal and other materials for cooking and heating in these areas may contribute significantly to the concentration of various metals in the atmosphere.

In addition to wood and coal contributing to the levels of Cd in the atmosphere, other materials such as nickel/cadmium batteries, anti-corrosive coatings of metals, pigments and stabilizers for plastics may also contribute to the increased levels in the atmosphere when used as a source of heat. This is a common occurrence in many informal settlements. Cd has the potential to cause cancer and the WHO has recommended that the daily intake should not exceed 1 μg per kg of body weight. For this reason, limits have been set on a national basis for Cd levels in air, water, food and agricultural soils. It is hoped that South Africa will soon set its own threshold limit value for cadmium metal contamination of the atmosphere.

Like cadmium, nickel concentration in the atmosphere of Chatsworth is also relatively low. Sources of nickel include among others smelting, electroplating, welding and painting operations. Humans are exposed to nickel compounds via inhalation of fumes and dust. Such absorption may lead to chronic respiratory diseases such as asthma and bronchitis. In the USA the range of nickel concentration varies from 17-25 ug/cm^3 for urban areas. In comparison the nickel concentration in Chatsworth is approximately 15 ug/m^3 which is relatively low for an urban area. Continuous monitoring is essential to ensure that the level does not steadily increase as a result of incineration and industrial emission.

Although copper is essentially non-toxic in trace quantities, the inhalation of dusts, fumes and mists of copper salts can cause congestion of nasal and mucous membrane and perforation of the nasal septum. A documented case of copper poisoning was that of several children in India who died of extremely high concentration of hepatic copper (Merian, 1991). In the USA the approximate concentration of copper in the atmosphere is between 10-500 ng/m^3. The annual mean value of a copper in the atmosphere of Chatsworth is 41 ng/m^3 which is well below the maximum value shown in figure 5.17. However further investigation is necessary at site EX because of the high concentration found there in the period of July to November. Children from this school should be checked for the level of copper in the blood in order to ensure that there are no long term effects on the health of these children.

Of major concern is the level of chromium in the atmosphere of Chatsworth found in the present study which is tenfold greater than that indicated by the National Nuclear Research Institute at Pelindaba carried out in 1977/8 for the industrial area of Congella, which is to the North East of Chatsworth. Hexavalent chromium is known to cause skin inflamation or eczema in humans and after a long latent period, they produce lung cancer. The probable source of the high chromium concentration in the atmosphere of Chatsworth may be due to industrial emission from the Mobeni/Jacobs area, incineration of chromium containing compounds or the local galvanizing and electroplating industry. The source or sources need to be identified and measures taken to limit the emissions to acceptable values. In addition the species of metal, particularly chromium, present in the atmosphere needs to be identified. Again there is a need for the establishment of a data base and the setting of threshold limit values.

From the research done, there seems to be some indication that the establishment of a crematorium at Mobeni may be affecting the air quality of the atmosphere of Chatsworth. Health authorities need to evaluate the air quality at the crematorium to determine its effect on the overall air quality of Chatsworth.

There is a need to develop a model to determine the influence of meteorological factors on the distribution of metal pollutants in the atmosphere. Such a model should enable more accurate prediction of possible pollutant concentration and sources.

A further recommendation would be to determine the influence of informal businesses on the air quality of this area.

A possible future research should be to investigate the metal levels over weekends and during the summer and winter holidays in the Chatsworth area so as to determine possible trends and correlation with the data acquired in this research.

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www.sdapcd.co.san-diego.ca.us/emission/inciner/inciner.htm

APPENDIX A

EC 1

PROVINCE OF KWAZULU-NATAL | **ISIFUNDAZWE SAKWAZULU - NATAL** | **PROVINSIE KWAZULU-NATAL**

DEPARTMENT OF EDUCATION AND CULTURE | **UMNYANGO WEMFUNDO NAMASIKO** | **DEPARTEMENT VAN ONDERWYS EN KULTUUR**

ADDRESS: / IKHELI: / ADRES: TRURO HOUSE, 17 VICTORIA EMBANKMENT, ESPLANADE, DURBAN
PRIVATE BAG: / ISIKHWAMA SEPOSI: / PRIVAATSAK: X54323, DURBAN, 4000
TELEPHONE: / UCINGO: / TELEFOON: (031) 3506911
FAX: (031) 374261

ENQUIRIES: / IMIBUZO: / NAVRAE: Research: D P Maharaj
REFERENCE: / INKOMBA: / VERWYSING: A 10/29/2/50
DATE: / USUKU: / DATUM: 06 June 1995

Mr S Govender
c/o Chemistry Department
M L Sultan Technikon
P.O. Box 1334
Durban
4000

Dear Sir

REQUEST FOR PERMISSION TO CONDUCT RESEARCH AT 30 SCHOOLS IN THE CHATSWORTH AREA

Your letter dated 1995-05-18 and the meeting with the Department officials on 1995-06-02 have reference

1. Permission is hereby granted to you to conduct your research at the 30 schools in the Chatsworth area provided that:

1.1 prior arrangements are made with the Principals concerned;

1.2 the necessary precautions with regard to the safety of pupils as enunciated by the Chief Inspector of Works (electrical) be implemented;

1.3 the area around the equipment be cordoned off;

1.4 the research is conducted on a voluntary basis;

1.5 the equipment which is to be set up at the first school be inspected by the chief inspector of works as well as official(s) of the Department to ensure that all safety measures are adhered to; and

1.6 a sum of R10.00 per school be paid for electricity as recommended by Mr Kotze, the Chief Inspector of Works.

2. Kindly produce a copy of this letter when visiting the schools.

3. The Department wishes you every success in your research and looks forward to receiving a copy of the findings.

EXECUTIVE DIRECTOR

9507.research.lp

2

EC 1

PROVINCE OF KWAZULU-NATAL	ISIFUNDAZWE SAKWAZULU - NATAL	PROVINSIE KWAZULU-NATAL
DEPARTMENT OF EDUCATION AND CULTURE	UMNYANGO WEMFUNDO NAMASIKO	DEPARTEMENT VAN ONDERWYS EN KULTUUR

ADDRESS: *IKHELI:* *ADRES:*	*TRURO HOUSE* *17 VICTORIA* *EMBANKMENT* *ESPLANADE* *DURBAN*	*PRIVATE BAG:* *ISIKHWAMA SEPOSI:* *PRIVAATSAK:*	*X54323* *DURBAN* *4000*	*TELEPHONE:* *UCINGO:* *TELEFOON:* *FAX:*	*(031) 3606911* *(031) 374261*
ENQUIRIES: *IMIBUZO:* *NAVRAE:*	D P Maharaj	*REFERENCE:* *INKOMBA:* *VERWYSING:*	A 10/29/2/50	*DATE:* *USUKU:* *DATUM:*	1995 -08- 17

Mr S Govender
% Chemistry Department
M L Sultan Technikon
P.O. Box 1334
DURBAN
4000

Dear Sir

REQUEST FOR PERMISSION TO CONDUCT RESEARCH AT 30 SCHOOLS IN THE CHATSWORTH AREA

The Department's letter dated 06 June 1995 and your fax dated 03 August 1995 have reference

1. The arrangement of the equipment and the safety measures adopted by you at the Evergreen Primary School on Wednesday, 16 August 2995 are acceptable to both the officials of Education Planning and the Works Section of the Department.

2. You are kindly requested to adopt similar measures at the other schools in the sample.

3. As decided at the in-loco inspection, please inform Mr A Rangila (Inspector of Works - Electrical) in advance of your visits to the other sample schools.

Yours faithfully

EXECUTIVE DIRECTOR (ACTING)

chemistry/rn

APPENDIX B

APPENDIX B

ate	Pb ug/m3	Cd ng/m3	Cr ug/m3	Ni ng/m3	Cu ng/m3	Temp oC	Humid %	Vel km/h	Direc from	Day
29/02	0.38	17.5	0.25	30.4	32.7	25	76	9	NE	thu
1/03	0.23	16.2	0.19	11.1	82.1	27	72	27	NE	fri
5/03	0.03	19	0.27	6.3	66.3	22	60	23	SW	tue
6/03	0.08	13	0.04	24.1	15.3	24	61	12	E	wed
7/03	0.12	7.8	0.03	22.1	23.9	26	67	13	NE	thu
8/03	0.08	6.8	0.03	17.1	20.3	25	78	11	SE	fri
1/03	0.53	4.4	1.11	9.8	49.3	28	75	20	N	mon
2/03	0.09	3.8	0.92	13.1	23.9	25	83	27	SW	tue
4/03	0.36	9.3	1.13	10.4	33.7	22	75	12	SE	thu
5/03	0.19	3.1	0.14	7.9	23.9	22	84	14	NE	fri
8/03	0.40	3.5	0.15	7.1	27.6	24	61	15	NE	mon
9/03	0.25	3.2	0.15	4.5	23.6	25	62	23	NE	tue
0/03	0.10	3.1	0.12	12.1	18.5	24	78	18	SW	wed
2/03	0.31	3.1	0.11	7.1	18.8	24	68	19	NE	fri
8/03	0.08	14.1	0.48	7.1	51.3	25	73	17	S	thu
0/04	0.04	13.9	0.34	7.3	38.2	21	49	27	SW	wed
2/04	0.14	24.6	0.30	12.2	65.1	22	63	13	S	fri
5/04	0.43	2.3	0.45	11.1	26.8	24	71	13	NE	mon
6/04	0.05	1.9	0.28	7.7	12.1	23	63	29	SW	tue
7/04	0.48	2.3	0.55	14.0	32.6	21	77	11	NE	wed
8/04	0.74	1.8	0.10	22.3	38.6	24	59	9	NE	thu
2/04	0.28	1.2	0.47	26.8	22.9	23	59	13	SE	mon
3/04	0.17	1.4	0.11	24.4	23.8	23	68	11	SE	tue
5/05	0.27	1.6	0.13	21.6	38.7	21	71	9	SE	wed
6/05	0.14	1.7	0.15	17.1	30.6	22	72	10	SE	thu
7/05	0.47	1.8	0.07	22.8	48.9	21	74	9	NE	fri
0/05	0.32	1.9	0.08	12.1	36.1	22	68	11	N	mon
1/05	0.41	1.6	0.07	16.9	42.9	21	61	15	N	tue
2/05	0.35	1.6	0.10	20.9	37.4	20	71	11	N	wed
0/06	0.15	1.5	0.42	12.1	23.9	20	66	21	N	mon
1/06	0.42	2.1	0.31	14.7	30.5	20	62	14	N	tue
3/06	0.18	1.8	0.27	11.6	26.6	21	71	10	NE	thu
4/06	0.19	3.6	0.14	14.1	32.1	21	54	8	N	fri
8/06	0.13	2.6	0.10	11.8	10.2	19	67	18	SW	tue
0/06	0.25	1.9	0.13	16.3	23.4	17	56	8	N	thu
9/07	0.09	3.2	0.06	10.9	65.9	17	70	20	SW	mon
0/07	0.24	1.9	0.04	8.8	139.5	14	57	7	SW	tue
1/07	0.11	2.2	0.03	10.7	82.9	16	69	12	SW	wed
1/08	0.28	2.7	0.08	14.1	232.7	19	75	10	N	thu
2/08	0.09	1.6	0.05	9.4	42.3	18	59	24	S	fri
5/08	0.59	1.6	0.06	12.6	173.3	20	71	22	N	mon
6/08	0.37	5.4	0.03	15.7	45.8	20	41	9	NW	tue
7/08	0.52	5.2	0.04	23.2	42.2	18	43	11	SE	wed
3/08	0.46	5.6	0.06	26.2	38.9	19	38	6	NW	thu
3/08	0.07	3.8	0.03	17.2	20.1	20	59	16	SW	tue
5/08	0.22	3.8	0.03	24.5	40.6	17	50	15	NE	thu
6/08	0.83	5.1	0.07	53.5	70.4	21	59	13	N	fri
9/08	0.08	2.1	0.03	14.1	64.0	17	48	27	S	mon
0/08	0.06	0.8	0.02	10.5	19.3	16	49	23	S	tue
1/08	0.08	0.7	0.02	11.2	16.9	16	64	19	S	wed
6/08	0.31	2.2	0.04	17.2	32.3	21	74	18	S	mon
7/08	0.22	2	0.03	13.5	26.9	20	75	12	E	tue
9/08	0.27	2.4	0.03	14.1	28.1	20	57	12	W	thu
9/09	0.04	2.1	0.02	10.7	37.2	22	74	24	S	mon
0/09	0.33	2.7	0.03	20.3	62.5	23	72	19	N	tue
1/09	0.11	2.1	0.03	19.2	27.6	23	79	10	SE	wed
3/09	0.19	0.7	0.03	19.4	36.5	23	71	14	NE	fri
6/09	0.19	0.9	0.02	12.7	25.5	22	69	28	N	mon
7/09	0.44	1.5	0.03	25.8	48.6	23	73	18	N	tue
/10	0.12	0.6	0.02	14.3	30.1	24	67	30	S	thu
/11	0.19	0.7	0.02	20.3	29.1	23	78	12	E	fri
/11	0.50	0.9	0.03	15.1	39.1	26	78	19	S	mon
/11	0.18	0.7	0.02	13.2	19.6	23	77	15	SW	tue

7/11	0.39	0.9	0.02	10.7	75.2	22	85	17	N	thu
8/11	0.28	0.7	0.02	10.3	24.3	25	77	24	N	fri
9/11	0.11	1.3	0.02	9.3	15.5	26	68	17	NE	tue
0/11	0.08	1.1	0.02	5.8	8.8	27	63	20	S	wed
1/11	0.12	1.6	0.02	12.3	17.2	24	77	13	NE	thu
2/11	0.06	0.9	0.02	8.7	9.9	26	44	13	NW	fri
5/11	0.04	1.6	0.02	5.4	7.3	25	77	29	S	mon
9/11	0.16	0.8	0.03	9.4	23.5	27	58	13	E	fri
nn Av.	**0.24**	**3.9**	**0.15**	**14.9**	**40.5**	**22**	**66**	**16**		

APPENDIX C

C 1

```
01      A     -.008 A
01      A     -.009 A
MEAN    A     -.007 A
```

Air Blank

```
   AA-1275/1475

STANDARD 1         0.
STANDARD 2         0.
STANDARD 3         0.
INT TIME          1.0
EXPN FACTOR       1.0
L1 CURRENT         4.
L2 CURRENT         4.
ABS
BC OFF
PEAK AREA
```

13 October 1997

Copper Determination

Instrument : AA2

Wavelength : 324,8 nm

slit width : 0,5 nm

standard : 0,025 ppm Cu

Peak Sensitivity : ± 80 %

```
FURNACE OPERATING PARAMETERS.


---------------------------------------------------------------
|STEP|TEMPERATURE|  TIME   |  GAS   |  GAS   |  READ  |
| NO.|    "C.    |  SEC.   |  FLOW  |  TYPE  |COMMAND|
---------------------------------------------------------------
|  1 |     75    |    25   |   3.0 |NORMAL|        |
|  2 |     90    |    40   |   3.0 |NORMAL|        |
|  3 |    500    |    10   |   3.0 |NORMAL|        |
|  4 |    500    |   2.0   |    .0 |NORMAL|        |
|  5 |   2300    |   2.0   |    .0 |NORMAL|   *    |
|  6 |   2300    |   1.0   |    .0 |NORMAL|   *    |
|  7 |   2700    |   2.0   |   3.0 |NORMAL|        |
|  8 |           |         |       |NORMAL|        |
|  9 |           |         |       |      |        |
| 10 |           |         |       |      |        |
---------------------------------------------------------------

SAMPLER PARAMETERS                 NORMAL CALIBRATION

  -----------------------------------------------------------
  |   SAMPLES AND STANDARDS    | BLANK    |MODIFIER|
  |   TYPE   |LOCATION| VOLUME | VOLUME   | VOLUME |
  -----------------------------------------------------------
  | BLANK   |   --   |   --   |    20    |        |
  |   STD 1 |   51   |    4   |    16    |        |
  |   STD 2 |   51   |    8   |    12    |        |
  |   STD 3 |   51   |   12   |     8    |        |
  |   STD 4 |   51   |   16   |     4    |        |
  |   STD 5 |   51   |   20   |     0    |        |
  | SAMPLES|   --   |   20   |     0    |        |
  -----------------------------------------------------------

LAST SAMPLE NO.    =    35  MULTIPLE INJECTIONS =   1
NO. OF REPLICATES=    3  LAST DRY PHASE STEP =   2
RESLOPE RATE       =        INJECTION TEMP.      =AMB
FIRST SAMPLE NO.  =    1
```

Samples - undiluted 50 mL

x Factor 50 for all.

```
01      A     0.020 A
02      A     -.004 A
02      A     -.003 A
MEAN    A     0.004 A
```

Blank 1M HNO_3

```
03      A     0.048 A
03      A     0.048 A
03      A     0.048 A
MEAN    A     0.048 A
```

EL 15

19/11/96

C2

14 October 1997
Chromium Determination
Instrument : AA2
Wavelength : 357,9 nm
slit width : 0,2 nm
standard : 0,025 ppm Cr-
Peak Intensity : -80 %

```
   AA-1275/1475

STANDARD 1        0.
STANDARD 2        0.
STANDARD 3        0.
INT TIME        1.0
EXPN FACTOR     1.0
L1 CURRENT        0.
L2 CURRENT        7.
ABS
BC OFF
PEAK AREA

FURNACE OPERATING PARAMETERS.

-------------------------------------------------------------
|STEP|TEMPERATURE| TIME    | GAS   | GAS    | READ   |
| NO.|      "C.  | SEC.    | FLOW  | TYPE   |COMMAND|
-------------------------------------------------------------
|  1 |       75  |  5.0    |  3.0  |NORMAL|         |
|  2 |       90  |   60    |  3.0  |NORMAL|         |
|  3 |      800  |   10    |  3.0  |NORMAL|         |
|  4 |      800  |  4.0    |   .0  |NORMAL|         |
|  5 |     2700  |  1.5    |   .0  |NORMAL|    *    |
|  6 |     2700  |  3.2    |   .0  |NORMAL|    *    |
|  7 |     2700  |  2.0    |  3.0  |NORMAL|         |
|  8 |           |         |       |NORMAL|         |
|  9 |           |         |       |      |         |
| 10 |           |         |       |      |         |
-------------------------------------------------------------

SAMPLER PARAMETERS              NORMAL CALIBRATION

 ----------------------------------------------------------
 |  SAMPLES AND STANDARDS      | BLANK   |MODIFIER|
 |  TYPE   |LOCATION| VOLUME   | VOLUME  | VOLUME  |
 ----------------------------------------------------------
 | BLANK   |   --   |   --     |   20    |         |
 |  STD 1  |   51   |    4     |   16    |         |
 |  STD 2  |   51   |    8     |   12    |         |
 |  STD 3  |   51   |   12     |    8    |         |
 |  STD 4  |   51   |          |         |         |
 |  STD 5  |   51   |          |         |         |
 | SAMPLES|   --   |   20     |    0    |         |
 ----------------------------------------------------------
LAST SAMPLE NO.   =   35   MULTIPLE INJECTIONS =   1
NO. OF REPLICATES=     3   LAST DRY PHASE STEP =   2
RESLOPE RATE      =        INJECTION TEMP.     =AMB
FIRST SAMPLE NO.  =    1
```

C3

```
MEAN   A   0.197 A

STD 5 A    0.197 A
```

0,0025 ppm Cd.

```
   AA-1275/1475

STANDARD 1        0.
STANDARD 2        0.
STANDARD 3        0.
INT TIME         1.0
EXPN FACTOR      1.0
L1 CURRENT        0.
L2 CURRENT        4.
ABS
BC OFF
PEAK AREA
```

15 October 1998
Cadmium Determination
Instrument: AA2
Wavelength: 228,8 nm
Slit width: 0,2 nm
Standard: 0,0025 ppm Cd
Peak Intensity: ± 76%

```
FURNACE OPERATING PARAMETERS.

------------------------------------------------------------
|STEP|TEMPERATURE| TIME   | GAS   | GAS    | READ   |
| NO.|     "C.   | SEC.   | FLOW  | TYPE   |COMMAND|
------------------------------------------------------------
|  1 |     75    |  5.0   |  3.0  |NORMAL|          |
|  2 |     90    |   60   |  3.0  |NORMAL|          |
|  3 |    175    |  8.0   |  3.0  |NORMAL|          |
|  4 |    175    |  2.0   |   .0  |NORMAL|          |
|  5 |   1400    |  1.7   |   .0  |NORMAL|    *     |
|  6 |   1400    |  1.5   |   .0  |NORMAL|    *     |
|  7 |   2000    |  2.0   |  3.0  |NORMAL|          |
|  8 |           |        |       |NORMAL|          |
|  9 |           |        |       |      |          |
| 10 |           |        |       |      |          |
------------------------------------------------------------

SAMPLER PARAMETERS                NORMAL CALIBRATION

 ----------------------------------------------------------
 |  SAMPLES AND STANDARDS       | BLANK   |MODIFIER|
 |  TYPE   |LOCATION| VOLUME    | VOLUME  | VOLUME |
 ----------------------------------------------------------
 | BLANK   |   --   |    --     |   20    |        |
 |  STD 1  |   51   |     4     |   16    |        |
 |  STD 2  |   51   |     8     |   12    |        |
 |  STD 3  |   51   |    12     |    8    |        |
 |  STD 4  |   51   |    16     |    4    |        |
 |  STD 5  |   51   |    20     |    0    |        |
 | SAMPLES|   --   |    20     |    0    |        |
 ----------------------------------------------------------
LAST SAMPLE NO.    =   35   MULTIPLE INJECTIONS =   1
NO. OF REPLICATES=    3   LAST DRY PHASE STEP  =   2
RESLOPE RATE       =        INJECTION TEMP.      =AMB
FIRST SAMPLE NO.  =    1


01     A    0.008 A
01     A    0.003 A
01     A    0.001 A
MEAN   A    0.004 A
```

SAMPLES - CONC to 12,5mL
x Factor 12,5 for ALL

```
02     A    0.003 A
02     A    0.005 A
02     A    0.003 A
MEAN   A    0.003 A
```

BLANK 1M HNO_3

C4

17 October 1997
Ni Determination
Instrument : AA2
Wavelength : 232,0nm
Slit width : 0,2nm
Standard : 0,025ppm Ni
Peak Sensitivity : ±76%

```
AA-1275/1475

STANDARD 1       0.
STANDARD 2       0.
STANDARD 3       0.
INT TIME       1.0
EXPN FACTOR    1.0
L1 CURRENT       0.
L2 CURRENT       4.
ABS
BC OFF
PEAK AREA

FURNACE OPERATING PARAMETERS.

-------------------------------------------------------------
|STEP|TEMPERATURE| TIME  |  GAS  |  GAS   |  READ  |
| NO.|     "C.   | SEC.  |  FLOW |  TYPE  |COMMAND|
-------------------------------------------------------------
|  1 |     75    |  5.0  |  3.0  |NORMAL|        |
|  2 |     90    |   60  |  3.0  |NORMAL|        |
|  3 |    800    |   12  |  3.0  |NORMAL|        |
|  4 |    800    |  3.0  |   .0  |NORMAL|        |
|  5 |   2700    |  1.5  |   .0  |NORMAL|   *    |
|  6 |   2700    |  2.0  |   .0  |NORMAL|   *    |
|  7 |   2700    |  2.0  |  3.0  |NORMAL|        |
|  8 |           |       |       |NORMAL|        |
|  9 |           |       |       |      |        |
| 10 |           |       |       |      |        |
-------------------------------------------------------------

SAMPLER PARAMETERS              NORMAL CALIBRATION

 ---------------------------------------------------------
 |  SAMPLES AND STANDARDS      | BLANK   |MODIFIER|
 |  TYPE   |LOCATION| VOLUME  | VOLUME  | VOLUME |
 ---------------------------------------------------------
 | BLANK   |   --   |   --    |   20    |        |
 |  STD 1  |   51   |    4    |   16    |        |
 |  STD 2  |   51   |    8    |   12    |        |
 |  STD 3  |   51   |   12    |    8    |        |
 |  STD 4  |   51   |   16    |    4    |        |
 |  STD 5  |   51   |   20    |    0    |        |
 | SAMPLES |   --   |   20    |    0    |        |
 ---------------------------------------------------------
LAST SAMPLE NO.   =  35  MULTIPLE INJECTIONS =  1
NO. OF REPLICATES=    3  LAST DRY PHASE STEP =  2
RESLOPE RATE      =      INJECTION TEMP.     =AMB
FIRST SAMPLE NO.  =   1
```

SAMPLES - conc to 12,5 mL
x factor 12,5 for all

```
01      A    0.010 A

01      A    0.002 A
01      A    -.000 A
MEAN    A    0.000 A
```

BLANK 1M HNO_3

```
02      A    0.063 A
02      A    0.065 A
02      A    0.061 A
MEAN    A    0.063 A
```

EL 15   19/11/96

```
03      A    0.059 A
03      A    0.056 A
```

APPENDIX D

J.1-1

ICP Analysis for Samples from 21/8/95 — 30/8/95

-kin Elmer Plasma 40 Emission Spectrometer

```
400 Analysis   Ver.  4.10   Thu 10/19/95 - 15:12:01
-----------------------------------------------------------------------------
 File Name: pb              Replicates:2                Read Delay: 30
s: soya                                                 Data File: soya
-----------------------------------------------------------------------------
```

STANDARDS

```
NK                           REPLICATE  #1        1514 10/19/95
          Pb        EM     6849

NK                           REPLICATE  #2
          Pb        EM     7212

          Pb        AV     7030.5   SD     256.7   CV      3.7 CONC    0.0000
NDARD  #1                    REPLICATE  #1        1515 10/19/95
          Pb        EM    11283

NDARD  #1                    REPLICATE  #2
          Pb        EM    11256

          Pb        AV    11269.5   SD      19.1   CV      0.2 CONC    0.4000
NDARD  #2                    REPLICATE  #1        1516 10/19/95
          Pb        EM    13641

NDARD  #2                    REPLICATE  #2
          Pb        EM    13979

          Pb        AV    13810.0   SD     239.0   CV      1.7 CONC    0.6000
NDARD  #3                    REPLICATE  #1        1518 10/19/95
          Pb        EM    15819

NDARD  #3                    REPLICATE  #2
          Pb        EM    15436

          Pb        AV    15627.5   SD     270.8   CV      1.7 CONC    0.8000
NDARD  #4                    REPLICATE  #1        1519 10/19/95
          Pb        EM    17011

NDARD  #4                    REPLICATE  #2
          Pb        EM    17981

          Pb        AV    17496.0   SD     685.9   CV      3.9 CONC    1.0000

          Pb      CC      0.9987  SLOPE   10576.081   INT 7124.0947
```

```
1PLE    #1  EV           REPLICATE   #1 D1.2   1520 10/19/95
          Pb  21/8      0.2724                           get 'intensity val
                                                         for samples'
1PLE    #1               REPLICATE   #2
          Pb            0.2494

          Pb        AV  0.2609  SD   0.0162  CV     6.23

1PLE    #2  EX           REPLICATE   #1        1522 10/19/95
          Pb  29/8      0.3149

1PLE    #2               REPLICATE   #2
          Pb            0.3430              peak-noisy

          Pb        AV  0.3290  SD   0.0199  CV     6.04

1PLE    #3               REPLICATE   #1        1523 10/19/95
          Pb            0.1529              peak-noisy

1PLE    #3               REPLICATE   #2
          Pb            0.2944              peak-noisy

          Pb        AV  0.2237  SD   0.1001  CV    44.75

 PLE    #4               REPLICATE   #1        1524 10/19/95
          Pb            0.1528

1PLE    #4               REPLICATE   #2
          Pb            0.5894              peak-noisy

          Pb        AV  0.3711  SD   0.3088  CV    83.20

1PLE    #5  EV           REPLICATE   #1        1526 10/19/95
          Pb  24/8      0.1657              peak-noisy

1PLE    #5               REPLICATE   #2
          Pb            0.1760              peak-noisy

          Pb        AV  0.1709  SD   0.0073  CV     4.26

1PLE    #6  Ex           REPLICATE   #1        1527 10/19/95
          Pb  30/8      0.6347

 PLE    #6               REPLICATE   #2
          Pb            0.6669

          Pb        AV  0.6508  SD   0.0227  CV     3.49

1PLE    #7  EV           REPLICATE   #1        1529 10/19/95
          Pb  25/8      0.2308

 PLE    #7               REPLICATE   #2
          Pb            0.2142

          Pb        AV  0.2225  SD   0.0118  CV     5.29

 PLE    #8  EX           REPLICATE   #1        1530 10/19/95
          Pb  28/8      0.2006              peak-noisy

 PLE    #8               REPLICATE   #2
          Pb            0.1870              peak-noisy

          Pb        AV  0.1938  SD   0.0096  CV     4.97
```

1b Standard 100 ppm
Polarographs.

Condition. Pulse (P)
U.st. 0
ΔU 1,5
mV 20
mm/t 0,5
t drop 0,6
fk 25
A/mm $2{,}5 \times 10^{-8}$
Φ = 0
Ic comp 0
UDp 1,80

Blank (100ppm Pb (-1,2)
(new bottle)

KCl needs to
be filtered – smoother base line.

Blank (100ppm Pb)(-1,4)

GREEN 1 m KCl (-1,8)
RED 1 m HNO_3 (-1,2
B

APPENDIX E

```
        A    -.003 A          STANDARDS
        A    -.004 A
        A    -.002 A
MEAN    A    -.003 A

ZERO    A    0.000 A     BLANK 1M HNO3

        A    0.044 A
        A    0.044 A
        A    0.045 A
MEAN    A    0.044 A

STD 1   A    0.044 A     0,005 ppm Pb

        A    0.084 A
        A    0.086 A
        A    0.088 A
MEAN    A    0.086 A

STD 2   A    0.086 A     0,010 ppm Pb

        A    0.121 A
        A    0.124 A
        A    0.124 A
MEAN    A    0.123 A

STD 3   A    0.123 A     0,015 ppm Pb

        A    0.158 A
        A    0.159 A
        A    0.161 A
MEAN    A    0.159 A

STD 4   A    0.159 A     0.020 ppm Pb

        A    0.196 A
        A    0.197 A
        A    0.198 A
MEAN    A    0.197 A

STD 5   A    0.197 A     0,025 ppm Pb

01      A    0.012 A
```

E-2

x FACTOR 200 for ALL.

```
15      A    0.005  A
15      A    0.006  A
MEAN    A    0.006  A     BLANK 1M HNO3

16      A    0.047  A
16      A    0.044  A
16      A    0.045  A
MEAN    A    0.045  A     CR 13        31/10/96

17      A    0.043  A
17      A    0.045  A
17      A    0.046  A
MEAN    A    0.045  A     CR 14        31/10/96

18      A    0.098  A
18      A    0.096  A
18      A    0.096  A
MEAN    A    0.097  A     CR 15        1/11/96

19      A    0.048  A
19      A    0.051  A
19      A    0.047  A
MEAN    A    0.049  A     CR 16        1/11/96

20      A    0.187  A
20      A    0.188  A
20      A    0.190  A
MEAN    A    0.188  A     CR 17        4/11/96

21      A    0.198  A
21      A    0.200  A
21      A    0.192  A
MEAN    A    0.197  A     CR 18        4/11/96

22      A    0.069  A
22      A    0.071  A
22      A    0.070  A
MEAN    A    0.070  A     CR 19        5/11/96

23      A    0.070  A
23      A    0.069  A
23      A    0.070  A
MEAN    A    0.070  A     CR 20        5/11/96

24      A    0.150  A
24      A    0.150  A
24      A    0.152  A
MEAN    A    0.151  A     CR 21        7/11/96

25      A    0.149  A
25      A    0.149  A
25      A    0.146  A
MEAN    A    0.148  A     CR 22        7/11/96

26      A    0.108  A
26      A    0.107  A
26      A    0.108  A
MEAN    A    0.107  A     CR 23        8/11/96

27      A    0.104  A
27      A    0.103  A
27      A    0.108  A
MEAN    A    0.105  A     CR 24        8/11/96
```

APPENDIX F

APPENDIX F

Absorbance values for different standard concentrations of Cr and Cd (in ppm) at different times of the year.

Std.Cr Conc. in ppm	0.005	0.01	0.015		
Date	Absorbance Values for standards given above				
29-11-97	0.14	0.28	0.41		
08-10-97	0.15	0.29	0.44		
27-09-97	0.14	0.27	0.39		
17-09-97	0.16	0.30	0.45		
10-09-97	0.18	0.33	0.48		
29-08-97	0.16	0.30	0.44		
17-08-97	0.16	0.31	0.46		
Std. Deviation	**0.01**	**0.02**	**0.03**		

Std.Cd Conc. in ppm	0.0005	0.0010	0.0015	0.0020	0.0025
Date	Absorbance Values for standards given above				
15-10-97	0.05	0.09	0.13	0.16	0.20
6-10-97	0.04	0.08	0.12	0.15	0.19
2-10-97	0.04	0.08	0.12	0.16	0.19
21-09-97	0.04	0.08	0.11	0.15	0.18
9-09-97	0.05	0.09	0.13	0.17	0.20
26-08-97	0.06	0.10	0.15	0.19	0.23
9-07-97	0.05	0.09	0.13	0.17	0.27
Std. Deviation	**0.01**	**0.01**	**0.01**	**0.02**	**0.03**

APPENDIX F

Absorbance values for different standard concentrations of Ni and Cu (in ppm) at different times of the year.

Std.Ni Conc. in ppm	0.005	0.010	0.015	0.020	0.025
Date	Absorbance Values for standards given above				
17-10-97	0.04	0.08	0.13	0.17	0.21
7-10-97	0.04	0.08	0.12	0.16	0.20
1-10-97	0.04	0.07	0.10	0.14	0.17
20-09-97	0.04	0.08	0.13	0.16	0.20
8-09-97	0.04	0.08	0.12	0.16	0.19
25-08-97	0.05	0.10	0.15	0.19	0.25
10-07-97	0.04	0.09	0.14	0.19	0.24
Std. Deviation	**0.00**	**0.00**	**0.02**	**0.02**	**0.03**

Std.Cu Conc. in ppm	0.005	0.010	0.015	0.020	0.025
Date	Absorbance Values for standards given above				
13-10-97	0.08	0.14	0.21	0.28	0.35
6-10-97	0.08	0.16	0.24	0.31	0.38
26-09-97	0.08	0.16	0.23	0.30	0.38
16-09-97	0.08	0.15	0.22	0.29	0.36
5-09-97	0.08	0.15	0.22	0.29	0.35
24-08-97	0.09	0.17	0.24	0.31	0.40
8-07-97	0.09	0.17	0.24	0.32	0.40
Std. Deviation	**0.00**	**0.01**	**0.01**	**0.02**	**0.02**

APPENDIX G

Pb concentration

School	Min	Max
Ex1	0.02	0.38
Ex2	0.09	0.59
Ev1	0.08	0.53
Ev2	0.07	0.83
De1	0.04	0.14
De2	0.06	0.31
Lo1	0.05	0.75
Lo2	0.04	0.45
Cw1	0.10	0.50
Cw2	0.10	0.50
El1	0.12	0.42
El2	0.04	0.11

Cd concentration

School	min	max
Ex1	6.8	18
Ex2	1.6	3.2
Ev1	3.1	4.4
Ev2	3.8	5.6
De1	14	25
De2	0.7	2.4
Lo1	1.2	2.3
Lo2	0.7	2.7
Cw1	1.5	2.0
Cw2	0.5	1.0
El1	1.5	3.6
El2	0.8	1.6

Cr concentration

School	min	max
Ex1	6	30
Ex2	9	14
Ev1	5	13
Ev2	16	54
De1	7	12
De2	11	17
Lo1	8	27
Lo2	11	26
Cw1	12	23
Cw2	10	20
El1	12	16
El2	5	12

Cr concentration

school	min	max
Ex1	0.03	0.27
Ex2	0.03	0.08
Ev1	0.11	1.13
Ev2	0.03	0.07
De1	0.30	0.48
De2	0.02	0.04
Lo1	0.10	0.55
Lo2	0.02	0.03
Cw1	0.07	0.15
Cw2	0.02	0.03
El1	0.10	0.42
El2	0.02	0.03

Cu concentration

School	min	max
Ex1	20	82
Ex2	42	233
Ev1	18	50
Ev2	20	70
De1	38	65
De2	16	32
Lo1	12	39
Lo2	25	63
Cw1	30	49
Cw2	20	40
El1	10	32
El2	7	24

DATA FOR PIE-CHARTS FOR ALL FIVE METALS

School	Mean [Cd]
Ex	7.8
Ev	4.5
De	9.6
Lo	1.8
Cw	1.2
El	1.8

School	Mean [Pb]
Ex	0.19
Ev	0.33
De	0.14
Lo	0.29
Cw	0.30
El	0.16

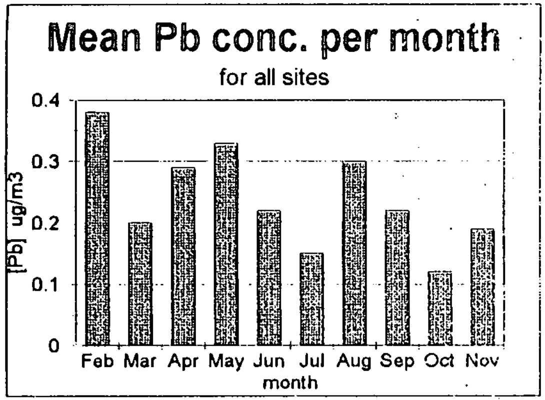
School	Mean [Cu]
Ex	81.4
Ev	34.1
De	38.0
Lo	32.9
Cw	37.7
El	19.1

School	Mean [Cr]
Ex	0.10
Ev	0.29
De	0.14
Lo	0.18
Cw	0.06
El	0.12

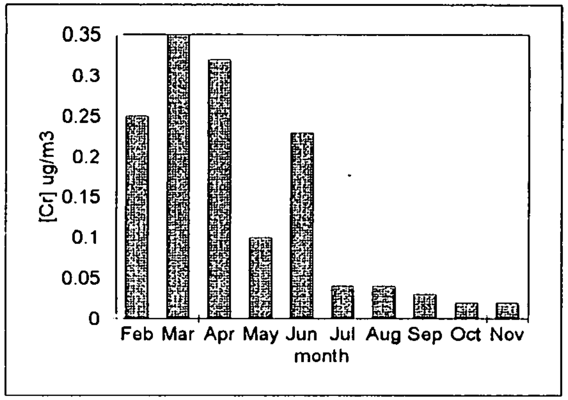
School	Mean [Ni]
Ex	14.3
Ev	16.6
De	11.9
Lo	17.9
Cw	16.3
El	11.0

TOTAL METAL CONCENTRATION PER MONTH ALL SITES

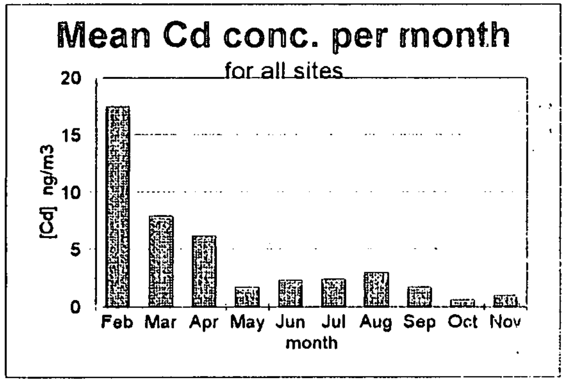
Month	[Pb] ug/m^3
Feb	0.38
Mar	0.20
Apr	0.29
May	0.33
Jun	0.22
Jul	0.15
Aug	0.30
Sep	0.22
Oct	0.12
Nov	0.19



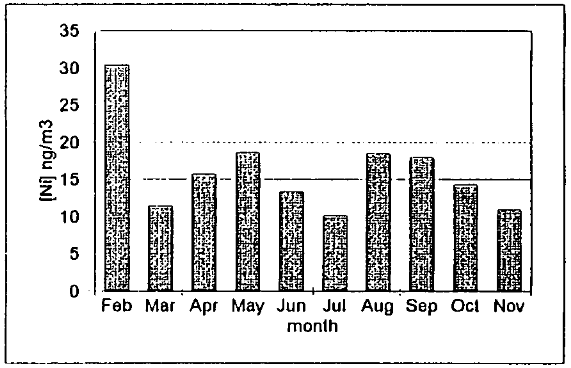
Month	[Cr] ug/m^3
Feb	0.25
Mar	0.35
Apr	0.32
May	0.10
Jun	0.23
Jul	0.04
Aug	0.04
Sep	0.03
Oct	0.02
Nov	0.02



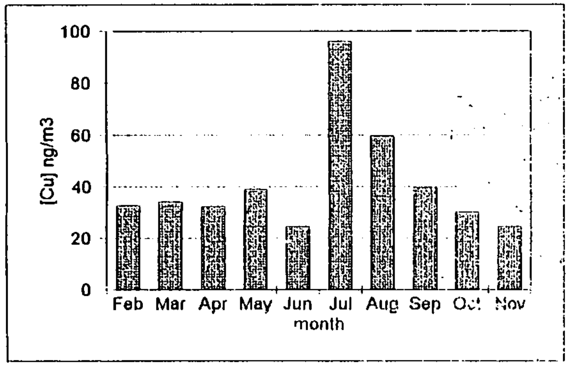
Month	[Cd] ng/m^3
Feb	17.5
Mar	7.9
Apr	6.2
May	1.7
Jun	2.3
Jul	2.4
Aug	3.0
Sep	1.7
Oct	0.6
Nov	1.0



Month	[Ni] ng/m^3
Feb	30.4
Mar	11.4
Apr	15.7
May	18.6
Jun	13.4
Jul	10.1
Aug	18.5
Sep	18.0
Oct	14.3
Nov	11.0



Month	[Cu] ng/m^3
Feb	32.7
Mar	34.2
Apr	32.5
May	39.1
Jun	24.5
Jul	96.1
Aug	59.6
Sep	39.7
Oct	30.1
Nov	24.5



APPENDIX G-3

SAMPLING DATE	EXACT DATE	SCHOOL
1	29-02-96	Excelsior (EX)
2	01-03-96	|
3	05-03-96	|
4	06-03-96	|
5	07-03-96	|
6	08-03-96	↓
7	11-03-96	Evergreen (EV)
8	12-03-96	|
9	14-03-96	|
10	15-03-96	|
11	18-03-96	|
12	19-03-96	|
13	20-03-96	|
14	22-03-96	↓
15	28-03-96	Depot Road (DE)
16	10-04-96	|
17	12-04-96	↓
18	15-04-96	Lotus (LO)
19	16-04-96	|
20	17-04-96	|
21	18-04-96	|
22	22-04-96	|
23	23-04-96	↓
24	15-05-96	Crestview (CW)
25	16-05-96	|
26	17-05-96	|
27	20-05-96	:

G 3 - contd

28	21-05-96	│
29	22-05-96	↓
30	10-06-96	Elora (EL)
31	11-06-96	│
32	13-06-96	│
33	14-06-96	│
34	18-06-96	│
35	20-06-96	↓
36	29-07-96	Excelsior (EX)
37	30-07-96	│
38	31-07-96	│
39	01-08-96	│
40	02-08-96	│
41	05-08-96	↓
42	06-08-96	Evergreen (EV)
43	07-08-96	│
44	08-08-96	│
45	13-08-96	│
46	15-08-96	│
47	16-08-96	↓
48	19-08-96	Depot Road (DE)
49	20-08-96	│
50	21-08-96	│
51	26-08-96	│
52	27-08-96	│
53	29-08-96	↓
54	09-09-96	Lotus (LO)
55	10-09-96	│
56	11-09-96	│
57	13-09-96	│

G 3 - contd

58	16-09-06	↓
59	17-09-96	↓
60	31-10-96	Crestview (CW)
61	01-11-96	↓
62	04-11-96	↓
63	05-11-96	↓
64	07-11-96	↓
65	08-11-96	↓
66	19-11-96	Elora (EL)
67	20-11-96	↓
68	21-11-96	↓
69	22-11-96	↓
70	25-11-96	↓
71	29-11-96	↓

APPENDIX H

H1-1

TEMPERATURE DATA

TE										Mean
2/96	21.6	23	24.1	25.5	25.2	25.8	26.8	26.6	27.2	25.09
				MARCH						
01/03/96	23.9	25.5	26.4	27.7	27.9	27.9	27.9	28.2	27.6	27.00
05/03/96	18.7	20.8	21.9	21.6	22.8	23.9	23.6	24.1	24.4	22.42
06/03/96	18.6	21.6	23.9	24.5	24	24.4	25.1	24.9	24.7	23.52
07/03/96	19.7	22.2	25.1	26.6	27	28.2	28.1	28.6	27.5	25.89
3/96	22.3	23.7	25.4	25.6	25	25.9	25.9	26.1	26	25.10
3/96	23.3	23.8	26.5	28.5	28.6	29.3	29.2	29.4	29.2	27.53
3/96	22.5	24.2	25.4	26.5	26.6	25.9	26	25.6	23.9	25.18
03/96	18.7	20.7	21.9	22.8	23.2	22.5	22.6	20.9	21.5	21.64
03/96	19.3	20.6	23.1	22.2	22.2	22.9	22.6	23.3	22.9	22.12
03/96	18.8	21.8	24.3	25	25.6	26	26.1	26.5	25.5	24.40
03/96	19.6	21.6	24.2	24.9	26.2	26.6	26.8	27.3	26.9	24.90
03/96	21.4	22.4	23.3	24	24.8	24.7	24	23.7	23.4	23.52
03/96	19.6	22.3	23.5	24.7	25.5	25.4	26	25.5	25.1	24.18
03/96	22.5	22.6	23	24.4	25.2	26.3	25.7	25.8	25.3	24.53
				APRIL						
4/96	17.1	18.8	20.5	21.5	20.9	20.9	22.4	21.5	21.8	20.60
4/96	15.9	18.7	21.4	23.1	23.5	23.5	22.9	22.8	22.6	21.60
04/96	19.3	21.6	23.4	24.6	25.8	26.4	26.1	26.3	26	24.39
04/96	22.1	23.2	23.8	23.3	23.1	23.4	22.9	23.8	22.9	23.17
04/96	17.6	18.8	20	21.6	22	23.6	23.6	22.2	22.1	21.28
04/96	17.6	19.8	23.5	25.9	26.7	25.8	25.9	28	26.8	24.44
04/96	15.4	19	22.9	24.3	24.6	24.8	24.7	24.4	24	22.68
04/96	16.6	19.4	22.9	24	24.7	25.2	25	24.2	24.2	22.91
				MAY						
05/96	14.2	17.2	20.6	22.2	22.5	22.7	22.7	23.3	22.9	20.92
05/96	12.6	17.7	21.5	23.6	24	24.4	23.8	23.8	23.3	21,63
05/96	13.4	17.3	19.7	23	23.8	24.4	24.4	23.6	22.9	21.39
05/96	11.9	16.2	20.6	23.4	24.8	25.9	24.9	24.5	23.5	21.74
05/96	13.9	17	19.5	22.8	24	24.7	24.9	23.3	23.1	21.47
05/96	14.6	17.1	18.3	19.9	20.9	22.6	21.7	22.2	21.7	19.89
				JUNE						
10/06/96	11.2	15.7	18.9	21	22.3	22.8	23.5	23	22.5	20.10
11/06/96	9.5	13.8	17.2	20.2	22.8	23.8	23.6	23.7	22.8	19.71
6/96	13.5	15	19.8	22.4	22.5	23	23.7	23.5	23.1	20.72
6/96	11.6	11.8	17	20.4	25.1	26.5	27.4	26.7	25.5	21.33
6/96	7.6	11.8	17.7	22	22	22	22	21.5	21.4	18.67
6/96	6.6	11	15.3	18.3	20.2	21.7	21	21.7	21	17.42
				JULY						
7/96	13.9	15.8	17.7	17.9	17.6	17.7	17.5	17.9	17.9	17.10
7/96	13.2	13.3	14	14.3	14.8	14.9	14.8	15.2	15.2	14.41
7/96	10.3	12.5	13.6	15.2	17.7	18.1	18.8	19.1	18.9	16.02

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AUGUST

1/08/96	16	16.5	16.5	19.1	20.1	19.9	20.6	20.4	19.7	18.76
2/08/96	16.5	17	17.4	18.4	18.6	18.6	18.9	19.2	18.5	18.12
5/08/96	15.5	15.6	16.2	18.3	20.9	22	22.3	23.1	23.3	19.69
06/08/96	13.3	15.2	18.1	20.6	22.3	23	23.2	22.1	21.5	19.92
7/08/96	11.2	14	17.7	20.4	20.8	20.5	20.7	20.6	20.5	18.49
08/08/96	10.3	14.7	18.5	21.7	22.6	22.4	22	21.7	21	19.43
8/96	15.2	18	19.5	21.7	22.1	22.2	21.8	22	21.5	20.44
8/96	11.8	14.3	15.3	18.1	19.1	19.3	18.8	19.1	19	17.20
8/96	8.7	12.7	18.6	22	25.2	26.3	25	24.1	23.6	20.69
8/96	14.1	15	15.7	16.5	17.3	18.4	19.6	18.5	17.1	16.91
8/96	12.4	13.5	14.6	16.5	17	17.8	17.7	17.4	16.6	15.94
8/96	10	12.8	15	16.1	17	17.4	17.2	16.8	17.2	15.50
8/96	16.7	18	20.8	23.3	21.3	21.3	22.1	21.4	21	20.66
8/96	15.8	17	19.6	21.7	21.7	21.2	20.6	20.8	21.6	20.00
8/96	13.9	16.6	19.9	20.8	22.4	21.5	21.5	21.4	21.2	19.91

SEPT

09/09/96	18.5	20.6	22.2	23.5	24	23.3	23.2	22.7	22.5	22.28
0/09/96	18.6	21.6	23.6	24.6	24.4	24.3	24.6	24.3	24.3	23.37
1/09/96	20.4	21.9	23.1	24	23.8	23.9	23.7	22.6	22.8	22.91
9/96	19.4	21.9	23.6	24.7	24.8	24.6	24.8	23.7	23.6	23.46
9/96	17	18.5	20.6	22.3	22.6	23	23	23.8	23.9	21.63
9/96	19.7	21.5	22.5	21.7	23.8	23.8	22.9	24.4	24	22.70

OCT

0/96	22.3	23.8	23.6	23.5	24.2	24.6	24.9	24.7	23.8	23.93

NOV

1/11/96	20.8	22.8	23.9	23.5	23.9	23.8	23.9	23.8	23.7	23.34
4/11/96	23.7	25.9	27.7	28.7	28.3	27.7	25.2	25.5	23.8	26.28
5/11/96	21.5	22.5	23.3	23.2	24.1	22.7	22.4	22.6	23.4	22.86
7/11/96	19.3	20.2	20.8	21.6	22.3	22	23.3	23.4	23.2	21.79
08/11/96	22.6	22.8	23.8	24.6	25.8	27.2	27.3	26.5	26.4	25.22
1/96	22	24.4	25.5	26.3	26	27.3	28	27.3	27.4	26.02
1/96	24	28	29.3	29.8	31.1	26.8	26.5	26.4	24.6	27.39
1/96	21.8	22.1	23.3	22.9	26.1	24.9	23.8	22.7	24.5	23.57
1/96	21.6	24.3	25.3	27.3	29.3	26.1	27	26	26.6	25.94
1/96	23.6	24.4	24.5	25.4	25.5	25.3	24.8	24.8	24.5	24.76
1/96	22.7	25.4	26.3	27.5	27.8	28.5	28.9	28.9	28.9	27.21

MEAN

E HUMIDITY DATA

I(2 - 1

2/96	91	82	77	74	77	76	71	70	65	75.89

MARCH

03/96	89	78	78	65	66	67	68	66	67	71.56
03/96	74	66	61	62	54	55	55	55	54	59.56
03/96	77	63	56	54	56	59	61	61	63	61.11
03/96	90	77	65	58	60	60	65	62	67	67.11
03/96	87	82	74	73	77	77	77	79	79	78.33
03/96	91	91	79	71	72	71	69	65	69	75.33
03/96	91	92	87	83	83	83	79	74	71	82.56
3/96	87	75	63	65	65	76	77	86	82	75.11
3/96	94	85	79	86	87	84	84	78	78	83.89
3/96	94	84	65	56	53	52	43	48	50	60.56
3/96	79	71	61	61	60	59	56	52	57	61.78
3/96	90	82	79	74	72	73	75	77	78	77.78
3/96	84	72	67	67	66	64	64	62	67	68.11
3/96	82	83	80	76	63	63	68	67	74	72.89

APRIL

04/96	53	48	43	45	48	47	48	55	56	49.22
04/96	84	69	59	52	53	55	68	64	63	63.00
4/96	89	80	71	69	65	63	70	65	68	71.11
4/96	73	68	66	66	64	54	54	55	63	62.56
4/96	86	83	79	71	72	73	72	78	78	76.89
4/96	83	71	61	50	57	57	58	47	50	59.33
4/96	74	63	54	57	56	56	56	55	59	58.89
4/96	88	80	63	62	61	58	62	66	68	67.56

MAY

5/96	92	81	69	60	62	65	70	68	70	70.78
5/96	98	89	71	65	61	61	66	69	72	72.44
5/96	94	91	81	67	66	63	60	71	74	74.11
5/96	98	95	69	56	54	48	60	61	67	67.56
5/96	84	70	63	56	51	48	48	62	63	60.56
5/96	90	83	77	69	65	57	63	65	70	71.00

JUNE

6/96	94	86	69	58	54	55	57	57	62	65.78
6/96	95	86	71	57	49	38	47	52	60	61.67
/96	98	98	86	66	65	61	50	55	61	71.11
/96	89	90	68	60	35	36	25	37	43	53.67
/96	100	95	61	32	56	54	65	69	67	66.56
/96	94	85	64	50	41	40	45	43	46	56.44

H 2-2

JULY

7/96	86	80	66	64	67	69	65	70	66	70.33
7/96	65	66	53	60	51	50	55	56	57	57.00
7/96	88	82	77	69	55	58	58	64	72	69.22

AUGUST

08/96	84	80	80	70	67	71	70	73	76	74.56
08/96	72	68	65	59	56	55	48	52	52	58.56
08/96	85	86	83	75	65	62	62	60	57	70.56
08/96	53	40	35	38	35	30	39	48	47	40.56
08/96	66	59	48	37	29	32	34	39	39	42.56
08/96	71	50	39	22	26	26	29	37	43	38.11
8/96	69	74	60	60	53	51	54	58	50	58.78
8/96	61	53	46	42	40	48	52	57	55	50.44
8/96	97	87	56	48	44	43	51	50	55	59.00
8/96	58	51	46	41	39	42	44	48	64	48.11
8/96	55	49	45	42	47	49	46	51	60	49.33
8/96	74	70	61	56	55	59	67	72	62	64.00
8/96	91	86	72	66	73	69	64	70	76	74.11
8/96	84	76	70	66	71	73	77	77	78	74.67
8/96	72	63	56	52	45	55	56	56	61	57.33

SEPT

9/96	89	76	69	66	68	71	74	77	80	74.44
9/96	90	78	66	63	65	69	73	72	75	72.33
9/96	89	82	77	74	74	76	77	81	82	79.11
9/96	95	83	67	62	59	64	67	74	72	71.44
9/96	83	76	67	64	66	65	67	64	65	68.56
9/96	76	70	66	75	72	73	79	71	71	72.56

OCT

0/96	75	67	75	67	64	59	61	63	69	66.67

NOV

1/96	84	77	75	75	77	77	79	80	80	78.22
1/96	88	79	73	70	75	74	81	80	85	78.33
1/96	79	75	75	77	67	76	79	81	81	76.67
1/96	93	91	85	83	82	82	82	80	84	84.67
1/96	88	87	82	80	76	73	71	69	71	77.44
/96	84	73	75	62	63	62	64	64	65	68.00
/96	65	44	45	48	45	75	79	79	84	62.67
/96	80	79	75	78	67	75	78	87	77	77.33
/96	49	32	32	31	23	55	56	62	53	43.67
/96	86	79	77	75	74	75	77	75	76	77.11
/96	80	64	60	59	58	54	50	47	51	58.11

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TE			WIND SPEED		m/s					AVERAGE
2/96	1.80	2	2	2	2.2	2.4	3	3.6	4.2	2.58
			MARCH							
03/96	2.30	3.8	6.4	8.5	9.8	9.3	9.5	9.6	9.5	7.63
03/96	4.4	4.7	6.6	6.4	6.6	6.4	7.4	7.6	6.7	6.31
03/96	1.7	3.3	2.7	1.7	3.5	4.3	4.6	4.2	3.9	3.32
03/96	1.9	2.5	2.9	3.4	4.3	4.4	4.9	4.3	4.5	3.68
03/96	1.9	2.7	2.00	2.3	3.6	3.3	3.6	4.2	4	3.07
03/96	3.8	3.7	3.1	2.9	4.1	5.9	7.1	9.7	10	5.59
03/96	2.1	3.1	3.5	4.1	5.7	8.6	11.2	13.7	15.3	7.48
3/96	1.5	1.6	1.6	2.3	3.3	3.7	4.8	6.3	6.1	3.47
3/96	1.6	1.6	1.6	3.3	3.4	4.9	5.9	6.6	7	3.99
3/96	1.8	1.8	2	3.2	4.2	4.9	6.3	6.3	6.7	4.13
3/96	3.1	4.7	4.2	5	6.2	8.2	8.4	9	9.3	6.46
3/96	2.6	2.6	3.5	4.6	5.4	6.7	6.9	6.5	6.5	5.03
3/96	2	2.4	4.7	6.3	6.1	5.9	6.4	6.3	6.7	5.20
3/96	4.7	5.4	4.8	4.9	4.4	4.5	5.1	4.8	4.9	4.83
			APRIL							
04/96	5.4	6	7.7	8.2	7.9	7.9	7.8	8.1	7.8	7.42
04/96	1.8	1.8	1.9	1.9	3.7	5.1	5.9	5.1	4.1	3.48
4/96	2.3	2.4	3	3.4	3.2	2.9	4.6	5.3	5.8	3.66
4/96	7	6.3	7	8.9	9	9.4	8.8	7.5	9.8	8.19
4/96	2.5	2.1	2.4	1.5	2	3.1	4.1	4.5	5.5	3.08
4/96	2	2.3	1.7	1.6	1.8	2.3	3.2	3.5	4.1	2.50
4/96	1.9	2	2.2	2.6	3.7	4.3	5.1	5.2	4.5	3.50
4/96	1.6	0	1.7	2.3	3.8	4.3	5.3	4.9	4.8	3.19
			MAY							
5/96	1.7	1.6	1.7	1.5	2.8	3.2	2.9	3.2	3.5	2.46
5/96	1.9	1.5	1.7	2.6	2.6	3.4	3.8	3.6	3.6	2.74
5/96	1.9	1.7	1.8	1.8	2	3.7	4.3	3.6	2.9	2.63
5/96	1.6	2	2	1.6	3.3	3.2	3.9	4.7	4.9	3.02
5/96	2	2.5	1.7	2.7	4.9	6.6	5.8	5.5	5.3	4.11
5/96	1.7	1.8	1.7	1.7	1.8	3.4	4.7	5	5.3	3.01
			JUNE							
06/96	2.5	3	4.3	5.6	7.6	7.2	7.3	7.3	7.3	5.79
06/96	1.9	1.8	1.9	2.3	3.8	5.2	6.4	6	6	3.92
6/96	1.5	1.6	1.8	1.6	2.2	2.8	4	4.7	4.2	2.71
6/96	2.1	1.6	1.8	1.8	2	1.9	3.1	3.4	3.5	2.36
6/96	1.7	1.9	2	4.1	7.4	7.4	6.9	6.6	6.6	4.96
6/96	2.1	1.8	2.2	2	1.9	2.4	3.1	2.7	2.7	2.32
			JULY							
7/96	0	2.6	3.3	5.9	6.6	5.8	8	9.2	8.8	5.58
7/96	1.7	1.9	1.6	1.6	2.3	1.9	2.1	2.2	1.8	1.90
7/96	1.8	1.9	1.9	2.5	3.4	3.5	3.3	5.3	6.2	3.31

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AUGUST

8/96	1.8	2.3	2.6	2.4	1.7	2.4	3.4	3.9	3.6	2.68
8/96	6.8	6.8	6.8	6.2	6.9	6.8	6.8	6.6	5.9	6.62
8/96	6.5	5.3	5.3	6	6.5	6.5	6.5	6.1	6	6.08
8/96	2.3	2	1.9	1.9	1.5	2	4.1	3.1	4.4	2.58
8/96	2.5	1.7	1.9	1.8	2.9	4	3.8	4.4	3.5	2.94
8/96	1.5	1.8	1.7	1.5	1.7	0	3.4	4.3	4.4	2.26
/96	2.8	3.2	4.5	5.8	5.7	4.7	4.2	4.2	5.3	4.49
/96	2.4	2.9	2.2	1.9	2.9	4.1	5.6	6.9	7.8	4.08
/96	1.8	1.8	2.1	3.1	3.1	3.6	4.5	5.4	6.3	3.52
/96	4.5	4.3	6.3	8	9.4	7.7	8	9	11.4	7.62
/96	3.2	3.7	5.4	5.3	7.3	8.5	8.6	8.4	8.3	6.52
/96	2.2	2.2	4.4	5.2	5.5	6.6	6.5	7.2	7	5.20
/96	4.5	6.1	3.6	2.3	4.1	6.7	6.9	5.7	5.2	5.01
/96	2.2	2.1	2.2	2.2	3.3	5.8	4.9	4	4	3.41
/96	1.9	2.3	2.3	2.3	2.1	2.8	4.3	5.5	5.3	3.20

SEPT

9/96	3.8	4.3	6.7	7.1	7.8	8.6	7.9	7.6	6.6	6.71
9/96	1.9	1.6	2.2	4	6.3	7.3	8.1	8.3	8.2	5.32
9/96	1.9	2	1.9	1.7	2.9	4.4	4.5	3.7	2.8	2.87
/96	1.8	2.4	2.8	3.6	4.9	5.9	5.3	5.1	4.1	3.99
/96	6	6.1	6.9	7.1	8.1	8.7	8.4	9.5	9.5	7.81
/96	6.1	4.9	5.2	4.4	6.2	5.1	4.9	3.1	4.2	4.90

OCT

/96	3.3	6.6	8.8	11.4	9.9	9.9	9.7	8.6	7.2	8.38

NOV

1/96	1.6	1.5	2.5	3	3	4.2	4.1	4.7	5.1	3.30
1/96	3.7	3.7	2.6	3.1	3	3.7	9.9	10	8.6	5.37
1/96	4.2	5.9	5.6	4.6	3.5	2.8	3	4	3	4.07
1/96	1.6	2.1	2.2	2.7	4	5.4	5.8	8.6	9.4	4.64
1/96	10.8	10.6	4.8	3.6	8.3	7.1	3.2	6	5.7	6.68
1/96	2	2.3	2.6	4.2	6.2	6.1	5.9	6.2	6.3	4.64
1/96	2.7	2.6	1.7	2.4	3.2	9	9.5	9.5	8.2	5.42
1/96	2.2	2.1	1.8	2.5	4.1	5.5	4.3	4.5	6	3.67
1/96	2.4	3	2.9	2.5	3.6	4.6	5.2	5.3	4	3.72
1/96	6.4	8.6	8.3	8.4	7.5	8.3	8.4	8.7	8.2	8.09
1/96	1.7	1.6	2.6	3.4	4.6	5.2	5.2	4.9	4.4	3.73