# CMB7 RECEPTOR MODELLING OF AIRBORNE PARTICULATE MATTER IN THE VAAL TRIANGLE

A thesis submitted by

VISVANATHAN SUBBA REDDY

in partial fulfillment of the requirements for the degree of

Master of Science

in

ENVIRONMENTAL GEOCHEMISTRY

in the Faculty of Science of the

UNIVERSITY OF CAPE TOWN

SUPERVISORS: PROFESSOR JP WILLIS
PROFESSOR HA ANNEGARN

January 1995

# SYNOPSIS

The primary aim of the Vaal Air Monitoring (VAM) programme was to do a one year source apportionment study of airborne particulate matter in the Vaal Triangle. The VAM programme was undertaken by Mintek, in South Africa. Three receptor sites were set up, one each in the Central Business District (CBD) of Vereeniging, Vanderbijlpark and Sasolburg. For this thesis, CMB7 receptor modelling was performed on fifteen samples from the VAM study representing the pre-, mid-, and post-winter periods. Five samples from each receptor site were modelled following the United States Environmental Protection Agency (US-EPA) $PM_{10}$ protocol. $PM_{10}$ size selected particulates were collected on 47 mm Teflon and quartz fibre filter substrates over one week sampling periods.

Thirty three chemical species were analysed for use in the Chemical Mass Balance receptor model. Teflon filters were used for inorganic elemental analysis. Inorganic elements were determined by energy dispersive X-Ray Fluorescence (EDXRFS), inductively coupled plasma mass spectrometry (ICP-MS) and Atomic Absorption Spectrometry (AAS). The quartz fibre filters were used for the determination of water soluble ions and carbon by Ion Chromatography (IC), and Thermal Optical Reflectance (TOR) respectively. Elemental and ion analyses were done at Mintek. Carbon analyses by TOR were done at the Desert Research Institute (DRI) in Reno Nevada, USA. Generally sample preparation and analysis of filter substrates followed DRI guidelines Where required, in-house methods developed at Mintek were successfully applied.

Suitable data processing, validation and management procedures were set up. In most cases DRI methods were applied and supplemented with procedures that were developed at Mintek.

Highest gravimetric sample loadings were recorded during June and July. The high loadings corresponded with high carbon concentrations. CMB7 receptor modelling was successfully performed on fourteen samples. Soil dust and arc furnace emissions were identified as major sources of $PM_{10}$ particulate matter during the study period. Contributions from domestic coalfire emissions peaked during winter. Increased contributions from power stations during the late winter period indicated a weakening of the inversion layer that was present

throughout the winter months. A definite seasonal influence on source contributions was observed.

Using the CMB7 performance measures, source types missing from the existing data base were identified. These included sources of low temperature carbon, bromine calcium and zinc. One week sampling periods only give an average of the sources contributing to the receptor site and daily variations are not observed. Twenty four hour sampling periods will probably highlight these variations and this should be considered in future receptor modelling studies in South Africa.

This study has shown that CMB7 receptor modelling can be successfully applied in South Africa and it should be used for air quality planning and management purposes.

# STATEMENT OF WORK UNDERTAKEN BY THE AUTHOR

This thesis represents part of the Vaal Air Monitoring (VAM) project being undertaken by Mintek. The author works at Mintek and is a co-investigator on the project.

This thesis focuses on the winter phase of the project which spanned the months of end-April 1994 to end-August 1994. The author's contribution to this thesis includes the following aspects:-

- Calibration of the Energy Dispersive X-Ray Fluorescence (EDXRF) instrument under the supervision of Mr. Basil Eddy.
- EDXRF, ICP-MS, and AAS analysis of samples collected from 94/06/10 to 94/09/02.
- EDXRF analysis of the source samples.
- Processing and validation of data for CMB7 model input.
- Setting up of the CMB7 data base with assistance from Dr. Frank Divita of the Desert Research Institute in Reno, Nevada, USA.
- CMB7 modelling and source sensitivity testing.
- Interpretation and discussion of modelling results.

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES



# LIST OF APPENDICES

# CHAPTER 1

# 1. INTRODUCTION

## 1.1 BACKGROUND TO STUDY

Air quality is increasingly becoming a major public concern in the nineties. This has been especially true for South Africa where the haze in the ambient atmosphere of the major industrialized areas such as the Vaal Triangle is the focus of numerous studies. Since 1989 the Department of National Health (DoH), together with other researchers, have conducted studies which firstly investigate the health effects of poor ambient air quality on human health and secondly, identify and quantify sources of airborne particulate matter in the Vaal Triangle.

The Vaal Air Monitoring (VAM) study can be considered to be a culmination of the work done over the past five years in the Vaal Triangle. In 1991 a pilot study in source apportionment of atmospheric was undertaken by researchers from Mintek, University of Witwatersrand (Wits), Atomic Energy Corporation (AEC) and the University of Potchefstroom (de Villiers and Engelbrecht, 1991). The key objectives of the pilot study were to establish standard operating procedures for sampling, chemical analyses and data processing. The most important conclusion from this study was that source data was lacking and a source inventory was required in order to do receptor modelling. In 1992 Mintek, sponsored by the DoH, chemically characterised (fingerprinted) nineteen major sources of air pollution in the Vaal Triangle (Engelbrecht *et al.,* 1993). This project initiated the establishment of a chemical source library of air pollutants both in the Vaal Triangle and at a national level. Since then, during 1993 Mintek has chemically characterised sixteen other sources that were considered unique to the Eastern Transvaal Highveld (Engelbrecht *et al.,* 1994).

Besides the work done at Mintek other researchers have worked on various aspects of air pollution in the Vaal Triangle. A study on the health effects of air pollution on children in the Vaal Triangle was conducted by Terblanche *et al.* (1991). Source apportionment studies undertaken by Tegen *et al.* (1992), Muller (1992) and Annegarn *et al.* (1992) have

been conducted in the Vaal Triangle since the pilot study. These studies have also shown the need to chemically characterise sources of pollution in the Vaal Triangle.

The VAM study is considered to be the beginning of a long term air monitoring network, initially at a regional level and ultimately at a national level. This study follows on preliminary in-house source apportionment work done by Mintek using the Chemical Mass Balance version 7 (CMB7) receptor model (Watson *et al.,* 1990). The results from the Mintek's preliminary work and Muller (1992) demonstrated that receptor modelling could be used as a source apportionment tool for better air quality management in the Vaal Triangle.

The VAM project extended over a one year monitoring period from the beginning of May 1994 to the end of April 1995 and is the most comprehensive source apportionment study undertaken in South Africa. Three receptor sites (sampling stations), one each in Vereeniging, Vanderbijlpark and Sasolburg, were set up. Samples were collected over periods of one week. One week sampling periods were used because of financial constraints and resources. Also the primary aim of the VAM study was to obtain an idea of the seasonal variation of air pollution over a one year period in the Vaal Triangle. Sample sets from every alternate week spanning this period were chemically analysed and subsequently modelled using the CMB7 model.

This thesis will use the chemical data from the VAM study to investigate and improve the following important aspects of the VAM study:

i) Identify and set up procedures for the validation of chemical data before entry into the chemical data base for CMB7 modelling.

ii) Evaluate the suitability of the CMB7 model as a source apportionment tool for an area such as the Vaal Triangle, which has a variety of industrial, biomass burning and natural sources of particulate matter, using samples representative of the pre-, mid-, and post-winter months. This investigation will focus on the period from the end of April to the end of August.

iii) Perform receptor modelling using the CMB7 model for the above-mentioned period.

iv) Use the CMB7 performance measures to identify major source types which may be missing from the existing source inventory set up by Engelbrecht *et al.* (1994).

## 1.2 LITERATURE REVIEW

### 1.2.1 Introduction

The management of ambient air quality involves the identification of sources of airborne particulate matter, the quantitative estimation of source emission rates and their chemical composition, an understanding of the dispersion of the pollutants from a source to downwind locations and a knowledge of the physical and chemical transformations that can occur while the pollutants are airborne (Hopke, 1991). Since scientists cannot effectively deal with all the variables that need to be considered, given the different scales between experimental observation and reality (Watson, 1984), it is necessary to model the atmosphere using mathematical formulae in an attempt to simulate reality (Benarie, 1987; Hopke, 1991).

Air pollution control authorities, can use validated models to develop air pollution control strategies. It is becoming increasingly necessary to assist air quality managers with the identification of sources and the apportionment of observed pollutant concentrations to contributing sources. Such models include the class of receptor models, which focus on properties of the atmosphere at ambient locations or receptor sites (Hopke, 1991). Limitations of earlier methods based on dispersion models only, together with the increased use of receptor models for regulatory purposes, have contributed to the interest and evolution of receptor models (Gordon, 1988).

### 1.2.2 Receptor Models

Receptor models start with the measurement of specific chemical profiles and physical variables of airborne particulate matter at both the source and at the receptor site in order to identify the presence of and quantify source contributions to a receptor concentrations (Watson *et al.,* 1989).

All receptor models are based on the following mass conservation expression (Henry *et al.,* 1984),

$$C_i = \sum_{j=1}^{p} a_{ij} S_j \quad \text{----------(1.1)}$$

where:

$S_j$ = Estimate of the contribution of source $j$ to the receptor.

$C_i$ = The concentration of property $i$ measured at the receptor.

$a_{ij}$ = The fractional concentration of property $i$ in the emissions from source $j$ perceived at the receptor.

$p$ = The total number of independent contributing sources.

Receptor models and their applications are comprehensively dealt with by Gordon (1980), Watson (1984), Watson *et al.* (1989), and Hopke (1991).

There are several different types of receptor models namely chemical mass balance (CMB), multivariate (MVA), multiple linear regression, enrichment factor time series and spatial models. CMB and MVA receptor models and derivatives thereof are the most widely used receptor models (Gordon 1988).

### 1.2.3 CMB Modelling

The concept of a chemical mass balance model was independently suggested by Winchester and Nifong (1971), Miller *et al.* (1972), and Hidy and Friedlander (1972). In these initial models specific elements were associated with particular source types to develop a mass balance model for airborne particles (Hopke, 1991). CMB modelling as it is known today was first adopted by Friedlander in 1973, when more chemical species than sources were used in a least squares fit to provide estimates of the mass contribution of numerous sources to a receptor site. Subsequently CMB receptor models have evolved to meet the requirements of practical applications and changing legislation, which have demanded greater accuracy. CMB has been applied to many studies by Wang and Larson (1993), Thurston and Lioy (1987), Wang and Hopke (1987), Watson *et al.,* (1984), White and Macias (1991) and numerous other workers. There are several review papers in the literature on receptor modelling but the most comprehensive and up to date review of receptor modelling is given by Hopke (1991).

The CMB model consists of a least squares solution to a set of linear sum of products of source profile species and source contributions. The source profile species (i.e. the

fractional amount of the species in the emissions from each source type) and the receptor concentrations together with the appropriate uncertainty estimates serve as input data to the CMB model. The output consists of the contribution from each source to each chemical species, the total contributions from each source to receptor sample and the uncertainties of these values. Input data uncertainties are used to weight the importance of input data values in the solution and the uncertainties of the source contribution estimates (Watson *et al.,* 1990; Henry *et al.,* 1984).

Solutions to the CMB equation (equation 1.1) consists of a tracer solution, a linear programming solution, an ordinary weighted least squares solution, a ridge regression least squares solution and an effective variance least squares solution (Watson *et al.,* 1990). Most workers prefer to use some form of weighted or effective variance least squares solution. In 1984 the Quail Roost II study compared results obtained from the above-mentioned methods on a simulated data set (Currie *et al.,* 1984; Dzubay *et al.,* 1984). Comparison of the results with the original simulated source contributions showed that the source contribution estimates were consistent with the actual contributions to within a factor of 2. However no single method was preferred from this exercise. Since then Watson *et al.* (1984), Wang and Hopke (1989), and Wang and Larson (1993) have proposed refinements to the least squares CMB solution.

According to Watson *et al.* (1990) the following assumptions are required for the principles of the CMB equation to work:

i) Compositions of source emissions must be constant over the period when source and receptor samples are collected.

ii) Chemical species do not react with each other, i.e. they add linearly.

iii) All sources with a potential to contribute to the receptor site of interest have been identified and their emissions characterised.

iv) The source contributions are linearly independent of each other.

v) The number of source or source categories are less than or equal to the number chemical species being modelled.

vi) Measurement uncertainties are random, uncorrelated and normally distributed.

These assumptions are fairly restrictive and all of them will not be complied with in practice. Fortunately the CMB model can accommodate deviations, but this increases the stated uncertainties of the source contribution estimates (Watson *et al.*, 1991). The assumptions have been rigorously tested, modified and refined on various occasions by Watson (1979), Dzubay *et al.* (1988) and Henry *et al.* (1992). The least squares solution is a widely used method for solving the CMB equation. There are two least squares solutions that can be applied. The two methods which are discussed in detail by Hopke (1985), Henry *et al.* (1984) and Watson *et al.* (1984) will be discussed further in the following sections.

1.2.3.1 The weighted least-squares (WLS) solution

The weighted least squares solution is a derivative of equation 1.1.

$$\chi^2 = \sum_{i=1}^{n} \frac{(C_i - \sum_{j=1}^{p} a_{ij} S_j)^2}{\sigma_{C_i}^2} \quad \text{---------- (1.2)}$$

where:

$\chi^2$ = The sum of the differences between the measured values of $C_i$ and those calculated from equation (1.1) weighted by $\sigma_{C_i}^2$.

$\sigma_{C_i}^2$ = the uncertainty in the $C_i$ measurement.

n = the total number of chemical species *i*.

The approach is to minimise the value of $\chi^2$. A $\chi^2$ value of $\leq 1$ indicates a good fit.

The following characteristics make the WLS solution workable (Henry *et al.*, 1984):

i) Theoretically it yields the most likely solution to the CMB equation, provided that the model assumptions are met.

ii) All the chemical species are used and not only so-called tracer species.

iii) WLS is capable of analytically estimating the uncertainty of the source contributions.

1.2.3.2 The effective variance least-squares (EVLS) solution.

The weighted least squares solution is incomplete because $C_i$ is not the only measured variable. Watson (1979), modified equation 1.2 to give the following solution:

$$x^2 = \sum_{i=1}^{n} \frac{(C_i - \sum_{j=1}^{p} a_{ij} S_j)^2}{\sigma_{C_i}^2 + \sum_{j=1}^{p} \sigma_{a_{ij}}^2 S_j^2} \quad \text{---------- (1.3)}$$

where:

$\sigma_{a_{ij}}^2$ = the uncertainty in the $a_{ij}$ measurement.

The EVLS solution has the following characteristics (Watson *et al.*, 1990):

i) It provides realistic estimates of the uncertainties of the source contributions.

ii) Greater influence is given to chemical species with higher precisions in both the source and receptor measurements than to species with lower precisions.

### 1.2.4 Chemical Analysis

Airborne particulate matter collected on filter substrates is varied and usually present in low concentrations (Stuckenberg, 1993). Therefore, chemical analysis techniques used for the determination of airborne particulate matter on filter substrates must have high sensitivities, low detection limits and must have multi-elemental capabilities.

X-Ray fluorescence spectrometry (XRFS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GFAAS), ion chromatography (IC), thermal optical reflectance (TOR) and electrochemical methods can be used for the analysis of airborne particulate matter on filter substrates. Detailed descriptions of these analytical techniques are given by Potts (1987) and Stuckenberg (1993). Chow *et al.* (1989), Stuckenberg (1993), Hopke (1985), and Dzubay and Stevens (1991) describe the use of these techniques for the analysis of airborne particulate matter on filter substrates.

Engelbrecht *et al.*, (1993), used wavelength dispersive XRFS to determine Si, P, S, Cl and Br; ICP-AES to determine Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb; AAS to determine Na and K; IC to determine $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$; and TOR for the determination of low temperature and high temperature organic and elemental carbon. Chow *et al.* (1989) used AAS and energy dispersive XRFS (EDXRFS) for the determination of the above mentioned inorganic elements. The methods and procedures used for carbon analysis are described by Chow *et al.* (1993).

### 1.2.5 Data validation

Validation of data before input into a database is a very important aspect of any study, since the results obtained may be used for decision making, planning and regulatory purposes. Data validation procedures should be able to identify deviations from assumptions and procedures, contaminated samples, and samples that have been improperly collected before being submitted for chemical analysis. The chemical data, furthermore, requires validation. Chow *et al.* (1989) list data validation procedures. These guidelines were used to validate sampling procedures and chemical data from air pollution projects that were undertaken by the Desert Research Institute (DRI) in Reno, Nevada. These procedures follow United States Environmental Protection Agency (US EPA) guidelines. Chow *et al.* (1994) present a comprehensive evaluation of aerosol measurements from the 1987 Southern California Air Quality Study (SCAQS). The aims of the VAM study are similar to those of the SCAQ study.

Chow *et al.* (1989 and 1994) suggest that data validation should include the following important aspects:

i) Proper records should be kept of all data collected in an accessible database. The records should include all field and laboratory measurements.

ii) Constant monitoring of sampling and analytical instruments should be conducted.

iii) The sum of chemically determined concentrations should be $\leq$ the total gravimetric mass.

iv) The sum of all major species (oxides included) should exceed 75% of the measured mass.

v) Analyses of the same element by different analytical methods should yield compatible results.

vi) Analyses of different species of an element by different methods should yield compatible results e.g. the concentration of S determined by XRFS should be ≥ than S in $SO_4^{2-}$ determined by IC.

### 1.2.4 Conclusions

Receptor models have evolved considerably since first being applied in 1967. The constant changes and improvements were enforced by needs for a model that could accurately identify and apportion sources of pollution impacting on receptor sites, This is because the results are used by air quality managers, town planners, industrialists and government officials in their decision making.

Chemical mass balance receptor models are more frequently being used for source apportionment studies as source measurements are improved and more sources are characterised. Advances in modelling software have also helped to improve the results obtained from the various available CMB models.

Data validation procedures are very important, especially in source apportionment studies. They become even more important if the results are to be used for regulatory purposes.

# CHAPTER 2

# 2. STUDY AREA AND SAMPLE COLLECTION

## 2.1 DESCRIPTION OF STUDY AREA

This source apportionment study focuses on the highly industrialised area of the Vaal Triangle (Fig 2.1). The Vaal Triangle is situated in the Highveld region of South Africa in the provinces of Gauteng (previously PWV) and Orange Free State. The area is considered to be the industrial heartland of Southern Africa, hosting a wide variety of industries. Industrial types range from primary metallurgical industries, coal-fired power generation utilities, chemical manufacturing plants, secondary steel processing industries, fuel processing plants and coal mining operations. Together with the intensive industrial activity, agriculture is the other major activity in the area. There is also the added contribution of domestic coalfire emissions to the degradation of the ambient air quality. The contribution of the latter is further enhanced during the long cold Highveld winters since coal is the primary form of domestic fuel in the townships around the Vaal Triangle. The Vaal Triangle is also subject to strong temperature inversions during winter.

Van Nierop (1994), drafted a source inventory of the Vaal Triangle was established. In Table 2.1 the results for the $PM_{10}$ source inventory are summarised.

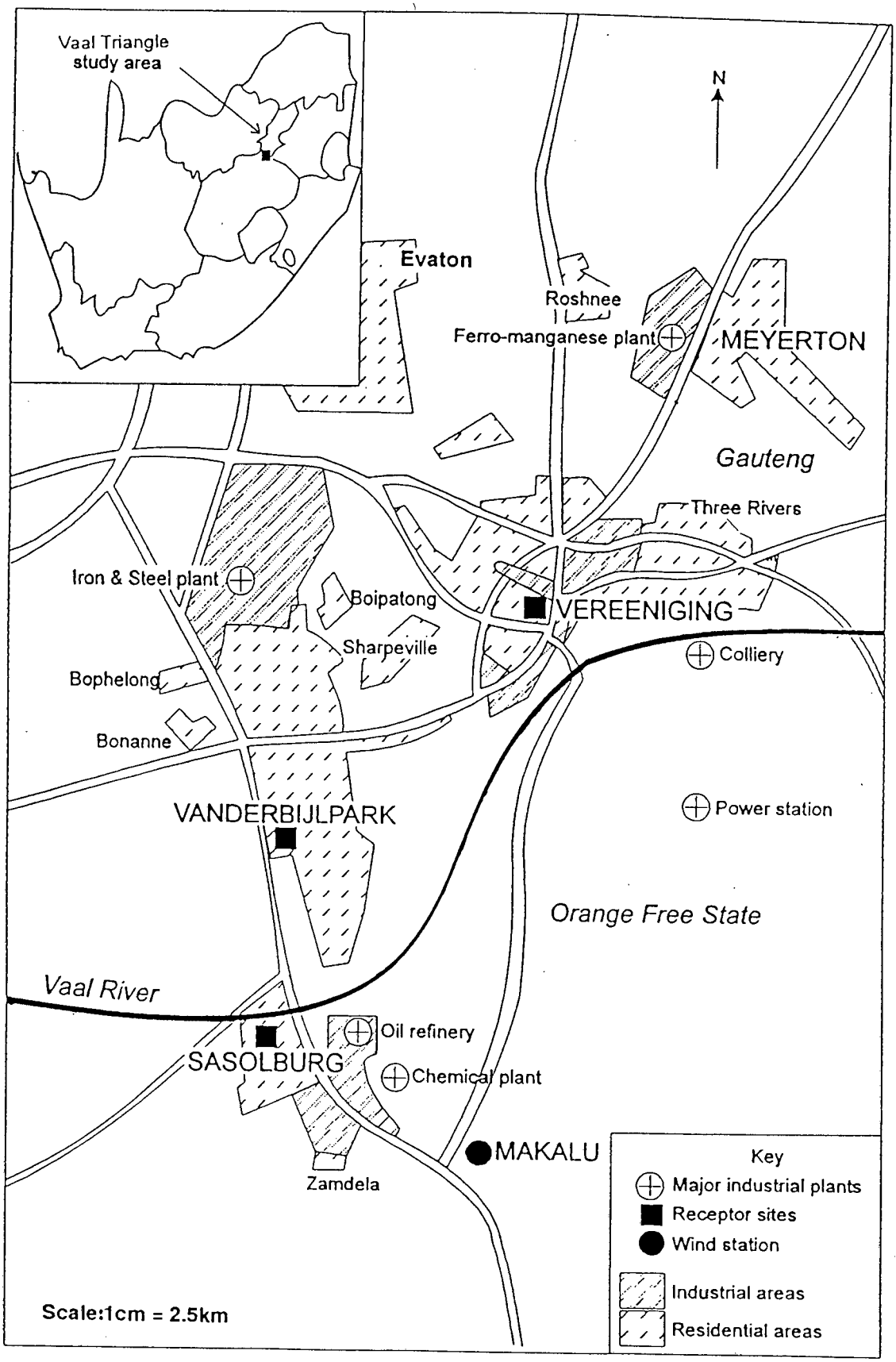



Figure 2.1: Locality map of the study area

**Table 2.1:** Vaal Triangle $PM_{10}$ emissions for point sources (after Van Nierop, 1994).

| Source Type | Emissions (tons/annum) | Percent of total emissions |
|---|---|---|
| **Point Sources** | | |
| Primary Iron and Steel | 7178 | 13 |
| Open Cast Coal Mining | 4968 | 9 |
| Secondary Iron and Steel | 5078 | 9 |
| Power Generation | 5781 | 10 |
| Fertiliser Manufacture | 3654 | 7 |
| Chemical Manufacture | 2207 | 4 |
| Brick and Tile Manufacture | 1904 | 3 |
| Other Industries | 3104 | 6 |
| Total for Point Sources | 33874 | 61 |
| **Area Sources** | | |
| Domestic Coal Combustion | 872 | 2 |
| Domestic Combustion - other fuels | 387 | 1 |
| Industrial Coal Combustion | 1801 | 3 |
| Industrial Combustion - other fuels | 165 | <1 |
| Veld (bush )Fires | 759 | 1 |
| Agricultural Activities | 683 | 1 |
| Heavy Construction | 97 | <1 |
| Paved Roads - fugitive dust | 9908 | 18 |
| Unpaved Roads - fugitive dust | 6467 | 12 |
| Automobile (Exhaust, Brake, Tire Wear) | 837 | 1 |
| Total for Area Sources | 21976 | 39 |
| Total for all sources | 55850 | 100 |

## 2.2. DESCRIPTION OF SAMPLING SITES

Three sites were chosen as receptor sites, one each in the central business districts of Vereeniging, Vanderbijlpark and Sasolburg (Fig. 2.1). All sites can be classified as commercial area urban sites. At Vereeniging the sampler is situated on the roof of a single-storey building at the Civic Centre. The Vanderbijlpark sampler is located on the first floor roof of the Steelpark building in the town centre. The Sasolburg ambient sampler is located on the first floor roof of the Sasolburg public library.

All three sites are situated at a minimum height of one storey above ground level. US EPA siting criteria require that samplers be placed at least two meters above ground level and preferably higher. This minimises the effect of resuspended dust at ground level. The choice of sites was also constrained by security reasons as well as accessibility to an uninterrupted power source.

## 2.3. $PM_{10}$ SAMPLING METHOD

### 2.3.1 Introduction

Sampling methods of airborne particulate matter are constrained by the reasons for which the samples are collected. The VAM project was undertaken to perform source apportionment of airborne particulate matter over a one year period, using the US EPA approved CMB7 receptor model. To achieve these goals there were two major constraints on the sampling procedure used. Firstly, the filter substrates had to stand up to handling during sampling and weighing, and be compatible with the various chemical analytical methods. Secondly, a size selective inlet was used, following the US National Ambient Air Quality Standard (NAAQS) for $PM_{10}$. $PM_{10}$ refers to particulate matter with an aerodynamic diameter $\leq 10\ \mu m$ (US-EPA handbook, 1994).

The $PM_{10}$ inlet standard was used because the South African air pollution control authorities, under the auspices of the Department of Health (DoH), are considering adopting US EPA standards and guidelines with regard to most air pollution regulations. The NAAQS allows $PM_{10}$ concentrations in an air quality maintenance area to reach an annual arithmetic average of 50 $\mu g/m^3$ and a maximum 24-hour average of 150 $\mu g/ m^3$, not to be exceeded more than once per year on a three year moving average (US-EPA handbook, 1994).

For the above-mentioned reasons sampling systems suited to the collection of $PM_{10}$ samples on filter substrates were required. Commercially available systems were not entirely adequate for this sampling program. However, commercially available and approved size-selective inlets, sampling manifolds, filter holders, flow controllers and pumps can be assembled in systems that are suited to the needs for a specific sampling campaign. Mintek designed and built its own ambient sampling system using commercially available components. However some of the components such as enclosures and connectors were designed at Mintek (Engelbrecht *et al.*, 1993; Engelbrecht *et al.*, 1994).

### 2.3.2 Description of the $PM_{10}$ sampling inlet

A $PM_{10}$ size-selective sampling inlet is used to remove particles which exceed an aerodynamic diameter of 10μm from the air stream that will pass through to the sample collection filters. Such inlets are characterised by sampling effectiveness curves which show the fraction of spherical particles of unit density passing through the inlet to the filter surface (Fig. 2.2). The sampling effectiveness is characterised by a 50% cut-point ($d_{50}$), the diameter at which half of the particles in the ambient air pass through the inlet to be collected on the filter (US-EPA handbook, 1994). The 50% cut-off size varies with flow rate through the inlet, hence it is necessary to control sample flow rate accurately. Low volume samplers and inlets have been developed operating at a selected flow rate in the 10 to 20 l/min range. Development of modern analytical techniques have enabled the small mass of particulate matter collected by low volume samplers to be analysed with adequate sensitivity for a whole range of species.

A low volume Rupprecht and Patashnick $PM_{10}$ size selective inlet with a flow-rate of 16.7 l/min was used for this project. Various sampling inlets have been designed to operate on the principles of direct impaction, virtual impaction, cyclonic flow or elutriation. The Rupprecht and Patashnick model operates on the direct impactor principle. In this type of inlet, the inlet's dimensions are selected to allow particles which exceed the desired cut-point to strike the impaction surface, and those that are less than the cut-off point to follow the airstream which passes the impaction plate through to the filter surfaces.

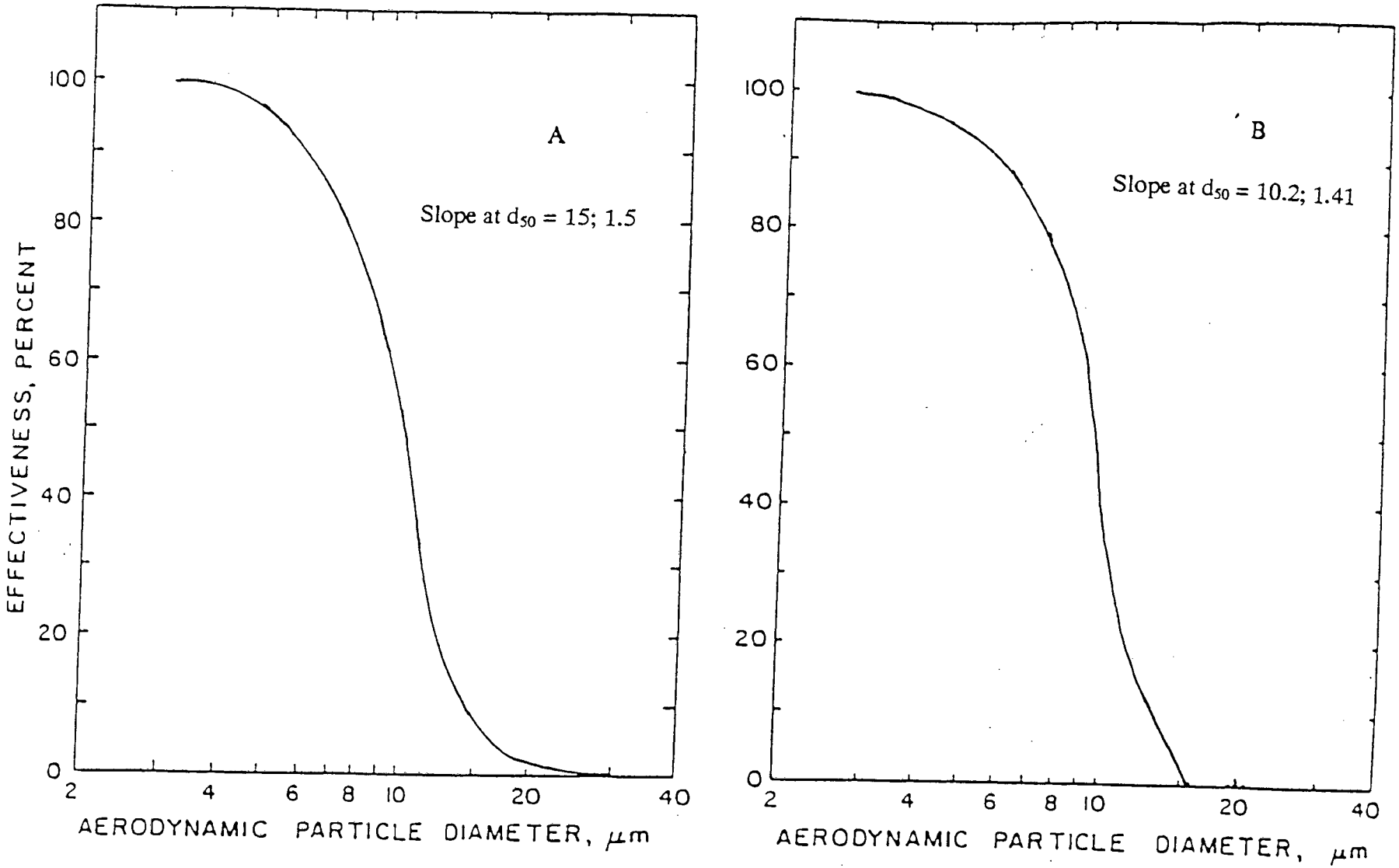



**Figure 2.2:** Comparison of sampling effectiveness curves for a Sierra Anderson 321A high volume inlet (A) and a Sierra Anderson 246B low volume inlet (B) (US EPA Handbook, 1994).

### 2.3.3 Description of the ambient air sampling system

All three sites had identical sampling systems. The $PM_{10}$ size selective inlet is connected to four filter holder inlets by a stainless steel manifold. The manifold branches are similar to each other, so that equivalent amounts of air pass through each of the filter holders. A low to medium rate flow control system was used to control the air flow through the system.

The control system consists of an assembly of commercially available components that are mounted in a stainless steel enclosure that is positioned below the sample holders. The flow control system consists of the following:-

- Four Sierra side-track mass flow controllers
- One Sierra Flo-box controller for mass flow controllers
- One 25 l/min Gast graphite rotary vane pump

A mass flow controller is connected to the outlet of each filter holder. The flow rates were set on the Flo-box at 4.18 l/min for the $PM_{10}$ size-selective inlet. A total volume of 16.7 l/min is drawn through the size selective inlet. A by-pass inlet valve was used to make up the total volume of air drawn by the vacuum pump (Fig. 2.3).

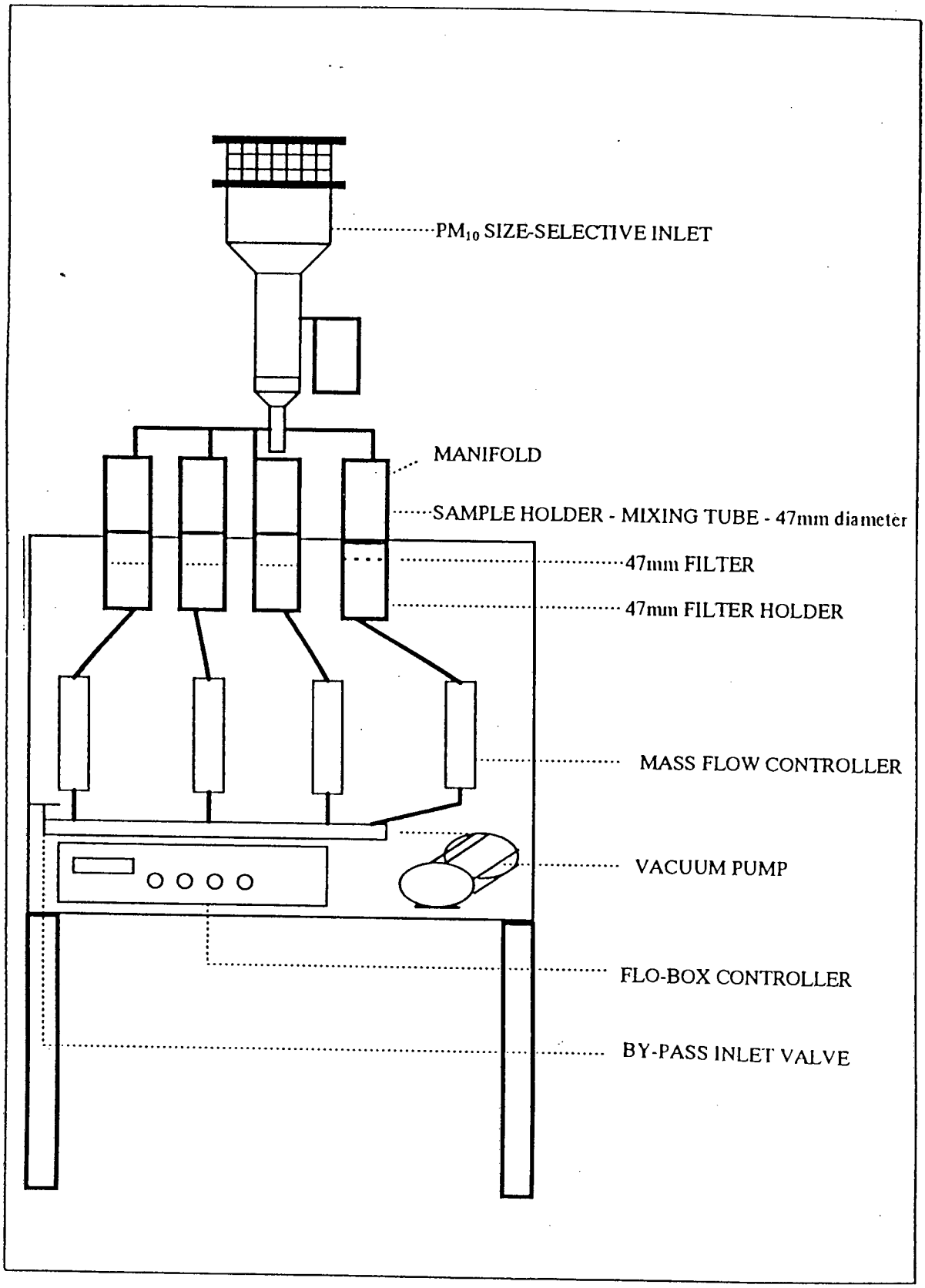



**Figure 2.3:** A schematic diagram of the ambient air sampling system.

## 2.4 FILTER SUBSTRATES

### 2.4.1 Technical specifications of filter substrates

Although there are various types of filter substrates available, only two types were used as prescribed by the Desert Research Institute (DRI) protocol. The filter substrates are Teflon and quartz fibre (Table 2.2). The Teflon filters were used for the analysis of the inorganic elements by EDXRFS, ICP-MS and AAS while the quartz fibre filters were used for the analysis of water soluble ions and the carbon species.

**Table 2.2:** Technical specifications of filters used.

| Filter Type | Filter-size | Pore-size | Manufacturer | Catalogue Number | Description |
|---|---|---|---|---|---|
| Teflon | 47mm | 2μm | Gelman Sciences Inc., Ann Arbor, MI, 48106, USA. | R2PJ047 | PTFE Membrane, W/PMP RNG |
| Quartz Fibre | 47mm | 2μm | Pallflex Products Corp., Putnam, Conn, USA | 2500QAT-UP | Fibre |

### 2.4.2 Preparation of filter substrates for sampling and chemical analysis

All the filter preparation and mass determinations were done in a dust-free room. Dust-free conditions were maintained by sealing the windows, using an airtight door and fitting all inlet vents with filters. An air-conditioner fed filtered air into the room to maintain the air temperature at $22 \pm 2^{\circ}C$. The room was used for conditioning of filters as well as for weighing purposes.

All filters were handled with tweezers on anti-static mats and in some cases anti-static bracelets were used to prevent charge build-up during weighing.

The quartz fibre filters were pre-fired at 900°C for three hours. Pre-firing was done to burn off volatiles. The filters were then cooled to room temperature in a vacuum dessicator before they were sealed in petri-slide dishes. Hereafter the filters were refrigerated until required for sampling. When required each filter was given an identity number The sample filters were placed in a steel sample cabinet, together with three similar blank reference

filters, for conditioning at least 12 hours before weighing. All the petri-slide dishes were partially covered during conditioning. Three quartz fibre and three Teflon blank filters were used per batch of filters. Each batch of comprised six quartz fibre filters and six Teflon filters. A five decimal place Mettler AE 240 balance was used. The balance was housed in a dust-free cabinet on a heavy slate table. The balance was acclimatized to the room conditions by opening the glass sides at least 30 minutes before it was calibrated daily using an internal standard. Thereafter the filters were weighed. The weighing procedure used is described by Engelbrecht *et al.* (1993). The conditioning and weighing procedures were repeated after sampling. After weighing the filters were stored in their respective petri-slide dishes and sealed in plastic bags which were stored in a freezer until they were submitted for chemical analysis.

Both the quartz fibre and Teflon filter masses recorded in the data-base. The masses for a set of four filters are tabulated in Table 2.3. In all cases the masses recorded for the quartz fibre filters exceeded the mass of the Teflon filters by an average of about 6%.

**Table 2.3:** Masses for a set of filters collected at Vanderbijlpark during the week 94/05/06 to 95/05/13.

| Filter No. | Mass |
|---|---|
| VAM 029T | 3942 |
| VAM 030T | 3878 |
| VAM 031T | 4079 |
| VAM 032T | 4193 |

# CHAPTER 3

# 3. CHEMICAL ANALYSIS OF AIRBORNE PARTICULATE MATTER ON FILTER SUBSTRATES

## 3.1 INTRODUCTION

The chemical analyses of the filter substrates were conducted using procedures and guidelines prescribed by the US-EPA (Chow & Richards, 1989). There were a few deviations from the procedures prescribed by these guidelines. These were mainly due to the lack of commercially available standards for X-Ray fluorescence (XRF) analysis. The other was the use of inductively coupled plasma mass spectrometry (ICP-MS) for the analyses of trace elements. All the methods are described for the sake of completeness. The author was actively involved in the XRF, ICP-MS and atomic absorption analysis.

## 3.2 ANALYTICAL METHODS

### 3.2.1 Introduction

Inorganic elemental and ion analyses were conducted at Mintek and the carbon analyses were conducted at the Desert Research Institute (DRI) in Reno Nevada, USA. The individual techniques will be discussed below.

### 3.2.2 Inorganic Elemental Analysis

Energy dispersive X-Ray fluorescence spectrometry (EDXRFS), ICP-MS and flame atomic absorption spectrometry (AAS) were used for the analyses of the inorganic elements. The elements analysed for and the respective techniques used are tabulated in Table 3.1.

**Table 3.1:** List of the elements and ionic species analysed for and the respective techniques used.

| Element | Technique |
|---|---|
| Na, Mg | AAS |
| Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Sr, Mo, Ba, Pb | EDXRFS |
| V, Co, Ge, Y, Zr, Ag, Cd, Sn, Sb, Te, Cs, Hg, Tl, Bi, U | ICP - MS |
| $CL^-$, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$ | Ion chromatography |

3.2.2.1 Energy Dispersive X-Ray Fluorescence Analysis

XRFS is suited to the analysis of atmospheric aerosols on filter substrates for a number of reasons. The most important are its non-destructive nature, the uncomplicated characteristic X-ray spectrum of each element, the wide range of elements that can be determined, the minimal sample preparation required and the high sensitivity of the technique (Stuckenberg, 1993; Quisefit *et al.,* 1994).

The main difficulties lie in the initial calibration, the maintenance of analytical quality between sets of analyses and the recalibration after an instrument modification. Although some commercial reference standards are available, data for all the elements of interest are lacking. Hence it is necessary to prepare standard filters with known amounts of elements. The filters should have no heterogeneity and matrix effects that will compromise analytical quality (Quisefit *et al.,* 1994). In addition to these problems self-absorption of X-rays, matrix and mineralogical effects can be significant in the case of filter substrates that are thin and are loaded with fine particulate matter (Dzubay & Nelson, 1975; Stuckenberg, 1993).

The XRF analyses were performed on a Spectro X-LAB energy dispersive (EDXRFS) analyser using a water cooled 45kV, 3.5kW rhodium tube, four secondary targets and a Si(Li) detector. The primary X-rays bombard the secondary targets to generate monochromatic X-rays which are polarised and used for the analysis of the filter substrates. Figure 3.1 gives a schematic illustration of the instrument. Potts (1987) gives a detailed description of the use of EDXRFS as an analytical tool.

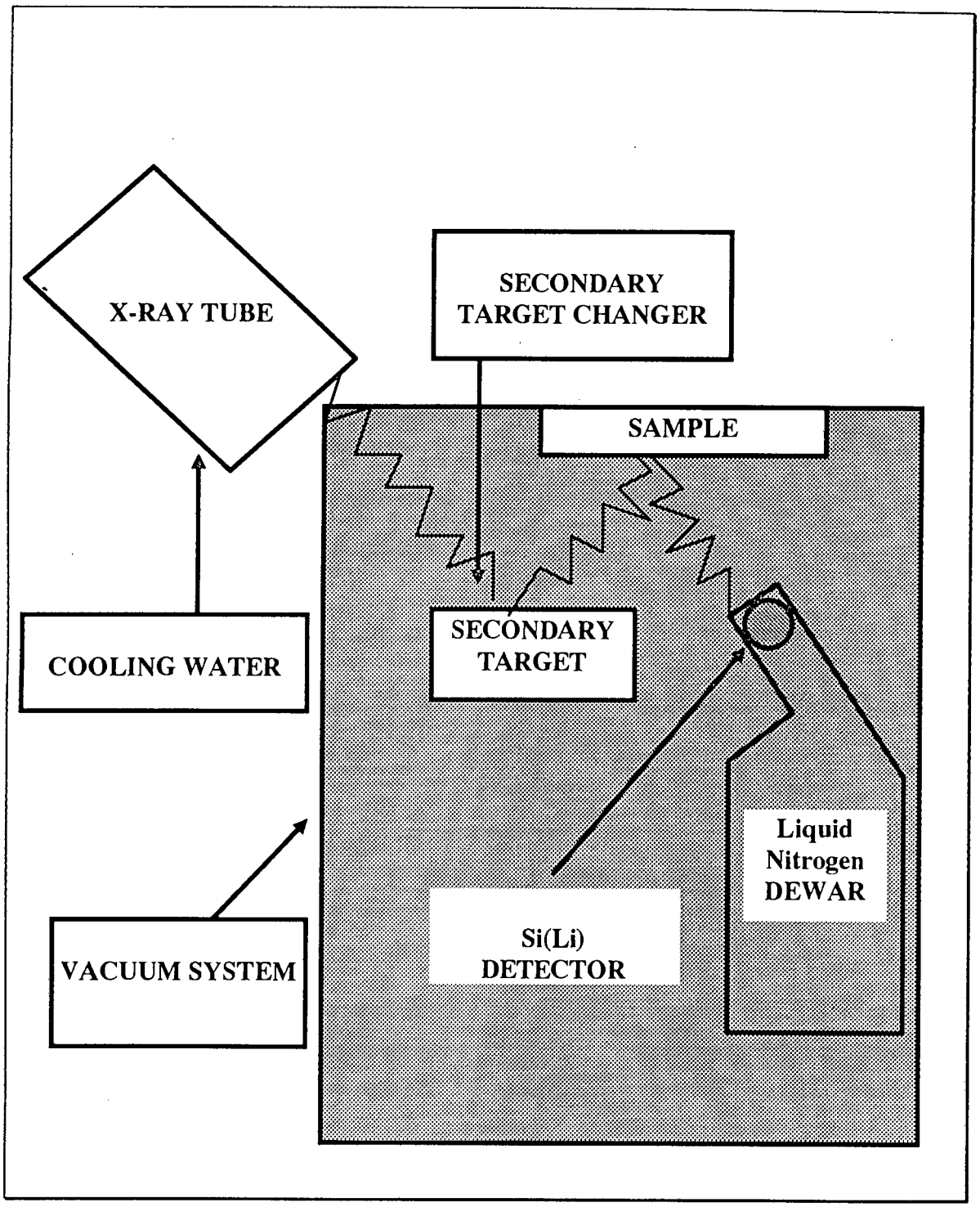



**Figure 3.1:** Schematic of an energy dispersive XRF spectrometer.

The X-Lab instrument uses four secondary targets as sources of excitation. The range of elements determined using each target is listed in Table 3.2. Each sample was counted for 1000s per target.

**Table 3.2:** Elements analysed for and the respective targets used.

| Target and radiation type | Elements by atomic number |
|---|---|
| Pd (K) | 26-42, 70-92 |
| Sm (K) | 42-56 |
| Co (K) | 19-25 |
| Cd (L) | 11-17 |

The analysis of the Teflon filters by XRF does not require any form of sample preparation. After the filters were gravimetrically analysed they were loaded into specially designed sample holders which were placed in a twelve position carousel. The carousel was placed in a vacuum chamber for analysis.

A single batch of analyses comprised a maximum of ten samples plus two reference monitors. The reference monitors were filter samples of an urban particulate standard (NIST, SRM-1648) and the Polish flyash standard CTA-FF-1. Reference monitors served a dual purpose. Firstly they were used to monitor the stability of the instrument and secondly to alert the analyst to any problems that may have affected the analyses during a single analytical run.

Although the instrument was pre-calibrated at the factory, it had to be recalibrated for the analysis of filter samples. A batch of eighteen filters from the VAM project, together with resuspended $PM_{10}$. urban particulate dust and the alternate week ambient filter samples from the VAM sampling campaign, were used to obtain calibration references. These samples were used as calibration standards because it enabled one to closely match the samples and standards and account for matrix and particle size effects that may be present if commercial standards were used. This also meant that no further corrections on the data were required. These reference filters were initially analysed by EDXRFS and the unprocessed spectra stored for processing at a later stage when the instrument was calibrated. The fact that peak intensity spectra of all elements can be stored and reprocessed later is a valuable feature of EDXRFS systems.

All the filters from the VAM project were analysed by ICP-MS and the resuspended urban particulate filters were analysed by ICP-AES. The results obtained from both ICP methods were initially used to calibrate the EDXRFS instrument and later on to check the results obtained from XRF analysis. Once the instrument was calibrated, software that came with the instrument was used to determine the elemental concentrations on the filters. All background corrections, peak overlap and matrix corrections were executed on-line by software that was supplied with the instrument. Mineralogical effects and particle size effects were, however, not corrected for by the software. This problem was overcome by using resuspended $PM_{10}$ filter samples as reference standard (Stuckenberg, 1993). In addition to these resuspended reference standards, ambient $PM_{10}$ samples from the VAM project were used to obtain calibration data.

3.2.2.2 ICP-MS Analysis

ICP-MS is not a widely used technique for the analysis of airborne particulate matter on filter substrates. During an investigation by Stuckenberg (1993) into the suitability of the ICP-MS technique for the analysis of filter samples it was concluded that ICP-MS analysis was suited for the analyses of a limited number of elements. Background and isobaric effects are important factors that must considered when analysing filter samples.

ICP-MS was used both as a calibration tool for elements that were analysed for by EDXRFS, and for the analysis of trace elements. The samples were analysed by a VG PLASMAQUAD 2+ ICP mass spectrometer (Fig 3.2).

ICP-MS requires the samples to be in solution. The matter on the Teflon filters was dissolved by nitric acid in closed high pressure 25 ml Teflon vessels. A 1,5 ml volume of 'specpure' nitric acid (Merck) was added to the dissolution vessel and heated at 100% power for five minutes in a 650 W National commercial microwave oven. Before opening, the vessels were cooled in an ice bath for a minimum of 30 minutes. This step was carried out to ensure that no volatiles were lost. The condensed solution was washed off the vessel walls using doubly distilled water. The solutions were heated for a further five minutes at 100% power, cooled in ice for 30 minutes and transferred to 25 ml plastic volumetric flasks which contained 2,5 ml of a solution containing internal standards scandium, indium and rhenium. Each these elements had a concentration of 1$\mu$g/ml. The

samples were made up to 25 ml with doubly distilled water. Two blank filters were also subjected to the same dissolution treatment.

**Table 3.2:** Minimum detection limits for elements analysed by EDXRFS

| Element | Minimum Detectable Limit ($ng/cm^2$) | Element | Minimum Detectable Limit ($ng/cm^2$) |
|---|---|---|---|
| Na | 6 ppm -AAS | Fe | 205 |
| Mg | 8 ppm - AAS | Ni | 3.73 |
| Al | 126.9 | Cu | 5.6 |
| Si | 227.6 | Zn | 3.7 |
| P | 78.4 | Ga | 1.9 |
| S | 37.3 | As | 9.3 |
| Cl | 82.1 | Se | 9.3 |
| K | 11.2 | Br | 3.7 |
| Ca | 7.5 | Mo | $2.2 \times 10^{-8}$ |
| Ti | 103.6 | Pb | 5.6 |
| V | 52.2 | | |
| Cr | 3.7 | | |
| Mn | 0.6 | | |

Minimum Detectable Limit (MDL) is defined as three times the standard deviation of the blank filter for EDXRFS and AAS (US EPA Handbook, 1994).

Typical radiation area for 47 mm ringed Teflon-membrane filters is 8.04 $cm^2$ for the Spectro X-LAB energy dispersive analyser.

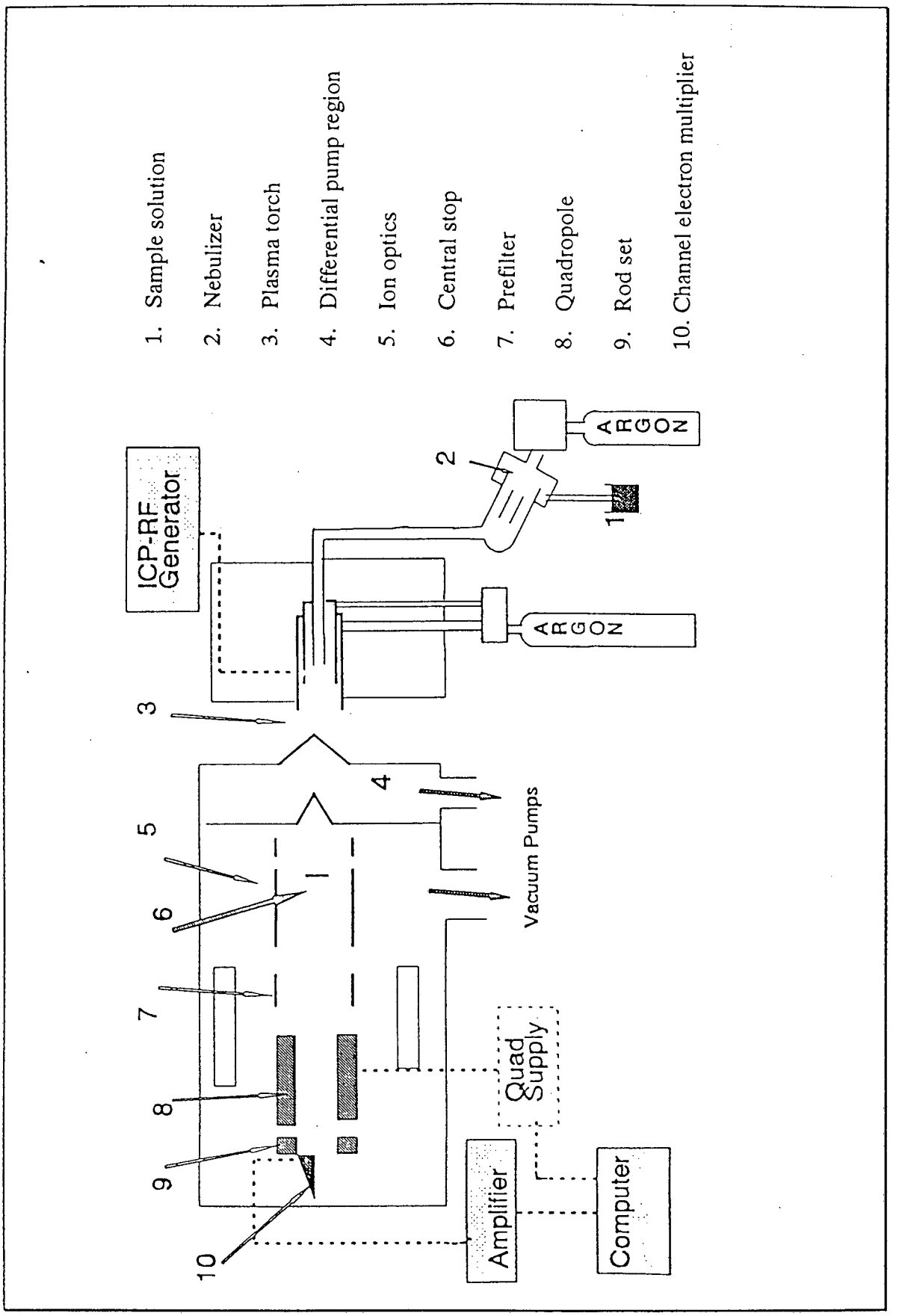



**Figure 3.2:** A schematic diagram of the ICP-MS instrument.

Nitric acid was used because polyatomic interference from hydrofluoric, hydrochloric and boric acids may have prevented the determination of several analytes. There was also the risk that unneutralized hydrofluoric acid could damage delicate instrumental glassware (Stuckenberg, 1993). The elements analysed for by ICP-MS are tabulated in Table 3.1.

3.2.2.3 ICP-AES Analysis

The samples for ICP-AES were prepared by a dissolution method similar to the method used for ICP-MS analysis. The only difference being that *aqua regia* and hydrofluoric acid were used for the dissolution instead of nitric acid. The dissolution involved the addition of 3ml *aqua regia* and 0.5ml of hydrofluoric acid to a microwave high pressure Teflon vessel containing the Teflon sample filter. The vessels were sealed and heated in a 650W National commercial microwave at 100% power for 2 minutes. The vessels were cooled for at least 30 minutes before they were opened. 5ml of 2.5% boric acid in 6.25% HCl was added to each of the vessels which were sealed and heated for a further 4 minutes at high power in the microwave oven. The solutions were transferred from the Teflon vessels to 25ml volumetric flasks, containing 1.25ml of a 0.2 g/l scandium internal standard, and made up to 25ml using doubly distilled water. The procedure ensured proper dissolution of Al, Si, K, Ca, Cr, Fe, Cu and Zn which may not have been adequately dissolved by nitric acid dissolution alone and therefore were not accurately determined by ICP-MS. A SPECTROFLAME ICP-AES instrument was used to analyse the solutions.

The resuspended urban particulate and the CTA-FF1 Polish fly-ash standard filter samples were analysed by ICP-AES. These filters were analysed for the following elements: Al, Si, K, Ca, Cr, Fe, Cu and Zn. The results obtained from these analyses were used to calibrate the Spectro X-Lab for the above-mentioned elements.

3.2.2.4 Atomic Absorption Analysis (AAS)

Although AAS can analyse for a wide range of elements, it is not often used because it is a single element technique. For this project only Na and Mg were routinely analysed for by AAS. Eighteen samples were also analysed by AAS to verify results obtained for Pb determinations by ICP-MS.

The same solutions that were prepared for ICP-MS were also used for the analysis of Na, Mg and Pb by AAS. For Na and Mg the solutions were diluted before analysis. The

solutions were measured on a Varian AA-1275 series atomic absorption spectrometer. Lanthanum was used as the ionisation suppression agent. The final concentration of lanthanum was 1%. Standard stock solutions were used to obtain the calibration graphs for the three elements. The instrumental conditions are tabulated in Table 3.3.

**Table 3.4:** Instrumental conditions for the analysis of Na, Mg and Pb

| Element | Wavelength | Lamp Current | Slit Width |
|---|---|---|---|
| Na | 589 nm | 5 mA | 0.5 nm |
| Mg | 285.2 nm | 1 mA | 0.2 nm |
| Pb | 217 nm | 5 mA | 1.0 nm |

### 3.2.3 Ion Chromatography Analysis

The ion analyses were conducted on the quartz fibre filters at Mintek's ion chromatography laboratory. Water soluble $Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $NH_4^+$ were determined (Table 3.1). Samples were prepared for analysis using the method proposed by Chow and Richards (1989). One half of the 47mm quartz fibre filter was placed in a 10ml aliquot of de-ionised distilled water. The sample bottle was capped and placed in an ultrasonic bath for 30 minutes, shaken for another 30 minutes and then aged overnight to ensure complete extraction. The extracts containing the water soluble ions were filtered before injection into the ion chromatograph.

Anions were determined with a Dionex 2010i instrument using suppressed ion chromatography according to the method prescribed by Cameron and Pohlandt (1987). The chromatographic system consists of a pump, an anion-exchange resin with a hollow-fibre suppresser device (AFS-1) and a conductimetric detector. The anions were separated on pellicular anion-exchange resin with a solution of sodium carbonate (2.8 mM) and sodium bicarbonate (2.3 mM) as the eluant. A 'fast run' anion-guard column (AG-3) and a 'fast run' anion-separator column (AS-3) were used. An eluant flow rate of 2 ml/min was used. The sample loop was 50 $\mu$l (Cameron and Pohlandt, 1987).

For the determination of ammonium the analysing system consisted of a Constametric metering pump, a Dionex cation exchange column (model no. 030831), a sample loop of 100 $\mu$l and a Wesscan conductivity detector (model 213) capable of suppressing the conductance of the eluant electronically. A 0.005 M nitric acid solution containing

0.1 ml/L of methanol was used for the eluant. The eluant flow rate was 0.5 ml/min (Barnes, 1985).

### 3.2.4 Thermal Optical Reflectance (TOR) Carbon Analysis

3.4.4.1 Introduction

There are no laboratories in South Africa that offer appropriate facilities for the analysis of organic and elemental carbon on aerosol filters. Carbon analyses were performed by the Desert Research Institute (DRI) in Reno, Nevada, USA. The second half of the quartz fibre filters were submitted for carbon analyses. Seven different carbon species were analysed for, four being organic carbon species (OC) and three elemental carbon (EC) species. The seven species listed in Table 3.4 are differentiated on the basis of temperature. The different species have been found to be useful in differentiating between sources that have similar inorganic elemental compositions (Fig 3.3).

**Table 3.5:** Temperature ranges (OTC phases) and temperatures (ETC phases) for the seven carbon species (Chow *et al.*, 1993).

| Carbon Species | Temperature Range |
|---|---|
| O1TC | 25°C - 120°C |
| O2TC | 120°C - 250°C |
| O3TC | 250°C - 450°C |
| O4TC | 450°C - 550°C |
| E1TC | 550°C |
| E2TC | 700°C |
| E3TC | 800°C |

3.4.4.2 Method of Analysis

The thermal optical reflectance (TOR) method for organic and elemental carbon analysis is described in detail by Chow *et al.* (1993). The principle of the TOR method used by the DRI is described as follows. A 0.5 $cm^2$ punch of the quartz fibre filter is inserted into a sealed combustion chamber. During the combustion process the emitted carbon compounds are converted first to carbon dioxide by a $MnO_2$ oxidation catalyst , and then to methane by a nickel catalyst in a firebrick matrix. The sample is heated in stages to

550°C in a helium atmosphere. At this temperature a 2% oxygen/helium atmosphere mixture is introduced. A correction is made for pyrolysis, whereafter the temperature is raised to 800°C in the presence of the oxygen/helium atmosphere. The methane concentration is quantified by a calibrated flame ionisation detector. Simultaneously the optical reflectance off the filter is measured by a helium/neon laser (Chow & Richards, 1989).

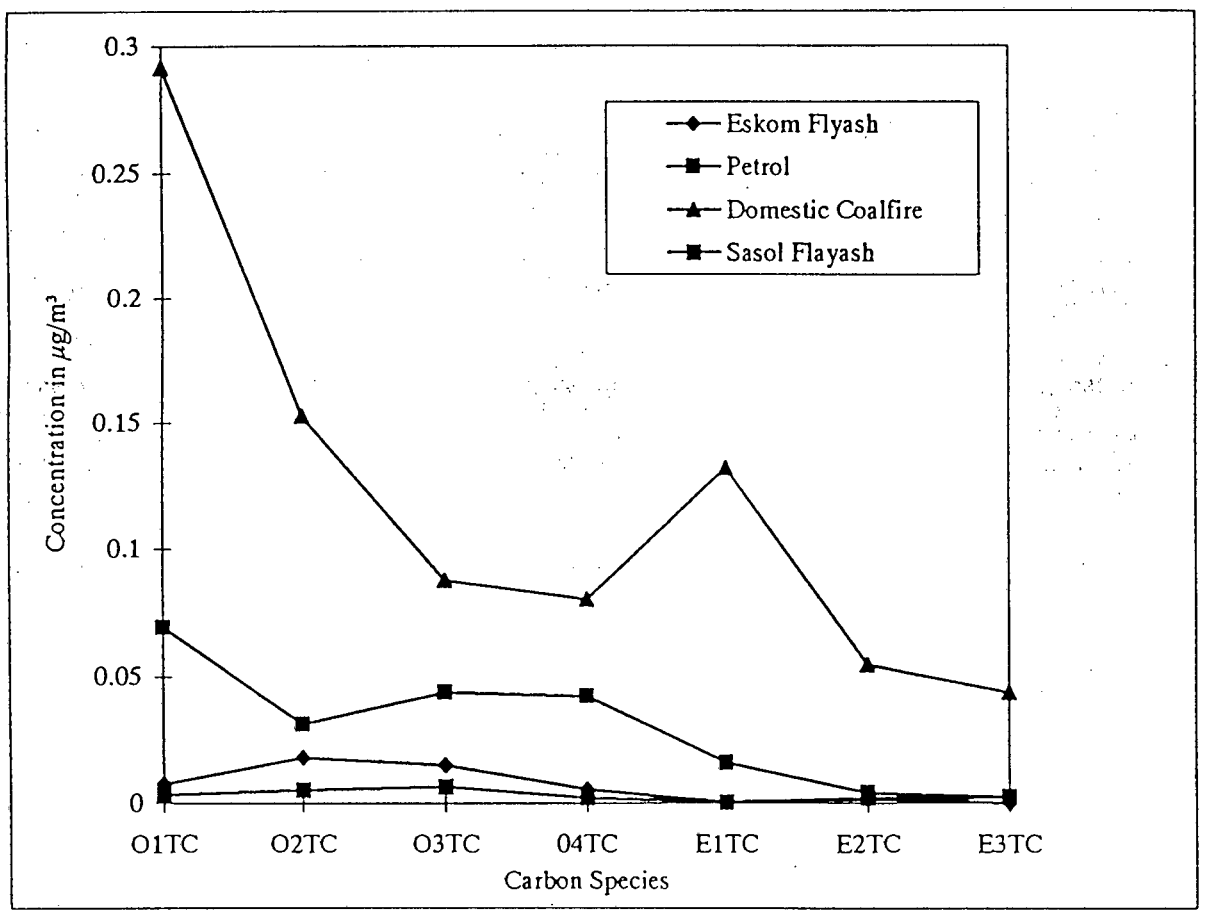



**Figure 3.3:** An illustration of the different carbon species concentrations in some selected fossil fuel burning profiles after pyrolysis corrections

# CHAPTER 4

# 4. DATA PROCESSING, MANAGEMENT AND VALIDATION FOR CMB7 MODEL INPUT

## 4.1 INTRODUCTION

Data validation and auditing procedures are important aspects of any scientific investigation. However it becomes even more important when results from an investigation are used by air quality managers, townplanners, industrialists and government officials. Important decisions involving very large amounts of money may be based on the results obtained. Therefore rigorous procedures had to be set up before data were entered into the data base that would eventually be used for the VAM study.

## 4.2 DATA PROCESSING

Data processing involves a variety of tasks that were performed during the VAM study. Data from the field, sample preparation laboratories and chemical analyses needs to be integrated prior to input into an ambient measurement data base. According to the DRI, procedures and values must be accepted, corrected, flagged as suspect, or removed from the database after they have been evaluated against validation criteria. Data processing consisted of five general tasks (Chow and Richards, 1989). These tasks include the following :

- Recording of the relevant information in a systematic way in logbooks or logsheets.
- Input of the data into computer-accessible files.
- Merging of the data from various files pertaining to an individual sample or sampling period.
- Conversion of data into a desired format. In the case of ambient data, the data are required to be expressed in $\mu g/m^3$ for input into the modelling program.
- Validation of the data by accepted procedures to ensure the validity of the data.

## 4.3 LEVELS OF DATA VALIDATION

### 4.3.1. Introduction

Data validation can be regarded as the most important part of data processing, since it identifies deviations from measurement assumptions and procedures. This helps ensure the validity of the data that will be entered into the database. Chow and Richards (1989) defined four levels of data validation, each level being a progression from the previous level. All levels may not be strictly adhered to, but adherence depends on what the final data will be used for. In the case of the VAM project, the final data set will be used for source apportionment purposes. In view of the implications the results from the source apportionment study will have for policy-makers, industrialists, townplanners and health authorities, strict data validation procedures were followed at all levels.

Three levels of data validation of were applied for the this study and are defined in the following sections.

### 4.3.2 Level 1 data validation

Validation of samples occurred in the field as well as in the laboratory. At the end of each sampling week the mass flow controller readings were recorded. If the total reading of the four mass flow controllers had dropped significantly below 16.7 l/min the batch of filters were flagged as suspect. This was necessary because the $PM_{10}$ inlet is calibrated at 16.7 l/min. Also, if by visual inspection the filters were torn they were flagged as suspect. Any stoppages or failure of the equipment was monitored with a timer device which recorded the total number of hours that the sampler had been running during the week..

In the laboratory, field observations were verified during the gravimetric analysis. Sometimes a filter was observed to have a significantly lower or higher loading than other filters in the set. This observation was cross-checked with the mass-flow controller readings. If a low filter mass corresponded with a low flow reading then the filter was accepted, and vice-versa. However, if the total volume of air passing through the inlet was not 16.7 l/min then that set of four filters was not submitted for chemical analysis. The observations were noted on the gravimetric weighing sheet (Engelbrecht *et al.*, 1993) and flagged when the gravimetric data were captured on the database.

A weekly comparison of the filter loadings obtained from the three sites was also done at this level. A 'normal' pattern was observed after a few weeks of sampling, i.e. filter loadings were consistently highest at Vereeniging and lowest at Sasolburg.

### 4.3.3 Level 2 data validation

Level 2 data validation took place after data from the various methods of analysis had been assembled in a single database. This stage of validation applied consistency tests based on known physical relationships between variables in the assembled data sets. This was a routine check that is recommended by the DRI (Chow and Richards, 1989; Chow *et al.*, 1994).

The following tests were conducted:-

i) The sum of all chemical species in a particulate matter sample should be less than or equal to the gravimetric mass of that sample.

ii) The sum of all major species including oxides should exceed 75% of the measured mass.

iii) The analysis of the same species by different methods should yield compatible results. For example Pb determined by EDXRFS should be similar to the Pb determined by ICP-MS. Samples were re-analysed if they did not meet these criteria.

### 4.3.4 Level 3 data validation

This level of validation was part of the interpretation process. If a measurement was found to be inconsistent with physical expectations and if the difference was not due to measurement error, then the value was assumed to be a valid result of an environmental event. These events could be attributed to spatial and temporal controls on the observed sampling sites.

## 4.4 QUALITY CONTROL OF CHEMICAL DATA

### 4.4.1 EDXRFS data quality control

XRF data quality was checked by two procedures. One of the procedures used reference monitors during analysis. The monitors used and their role as a data quality control tool were discussed in chapter 3, section 3.2.2.1. The other check method of quality control was comparison of XRF results with results from ICP-MS and AAS. The filters were first analysed by XRF and then dissolved and analysed for the same suite of elements by ICP-MS and by AAS. Table 4.1 compares data obtained from XRF, ICP-MS and AAS for Pb.

**Table 4.1:** Comparison of data obtained by EDXRFS, ICP-MS and AAS for Pb.

| Filter No. | EDXRFS | ICP-MS | AAS |
|---|---|---|---|
| 1 | 18.9 | 7.6 | 22.5 |
| 2 | 20.8 | 9.0 | 25.8 |
| 3 | 15.5 | 6.3 | 17.2 |
| 4 | 16.6 | 6.3 | 17.0 |
| 5 | 13.4 | 5.6 | 13.6 |
| 6 | 12.7 | 5.0 | 14.0 |
| 7 | 13.6 | 5.5 | 14.5 |
| 8 | 14.5 | 6.1 | 17.2 |
| 9 | 9.3 | 3.5 | 9.0 |
| 10 | 9.2 | 3.9 | 9.8 |
| 11 | 7.0 | 2.7 | 5.5 |
| 12 | 7.1 | 2.8 | 5.1 |
| 13 | 32.5 | 15.4 | 38.2 |
| 14 | 36.9 | 17.2 | 47.1 |
| 15 | 35.3 | 14.9 | 41.5 |
| 16 | 36.6 | 14.7 | 39.3 |
| 17 | 17.0 | 7.4 | 19.1 |
| 18 | 16.2 | 7.4 | 19.5 |

The value of such a comparison cannot be underestimated. The ICP-MS and XRF measurements for Pb did not correlate very well. Initially it was thought that the nitric acid

dissolution was inadequate and therefore did not dissolve all the Pb present on the filters, since the XRF Pb values were higher than the ICP-MS data (Fig 4.1). As a check on the efficiency of the acid dissolution of Pb, the solutions that were analysed for Pb by ICP-MS were re-analysed by AAS. The AAS results correlated very well with the XRF data (Fig 4.2), and it was concluded that the acid dissolution was adequate and that ICP-MS had underestimated the Pb content in the solution. As a level 2 validation check the solutions were re-analysed by ICP-MS and higher Pb values were obtained (Fig 4.3). The ICP-MS analyses were repeated using new calibration standards. Besides changing the calibration standards no other satisfactory reason for this discrepancy was found.

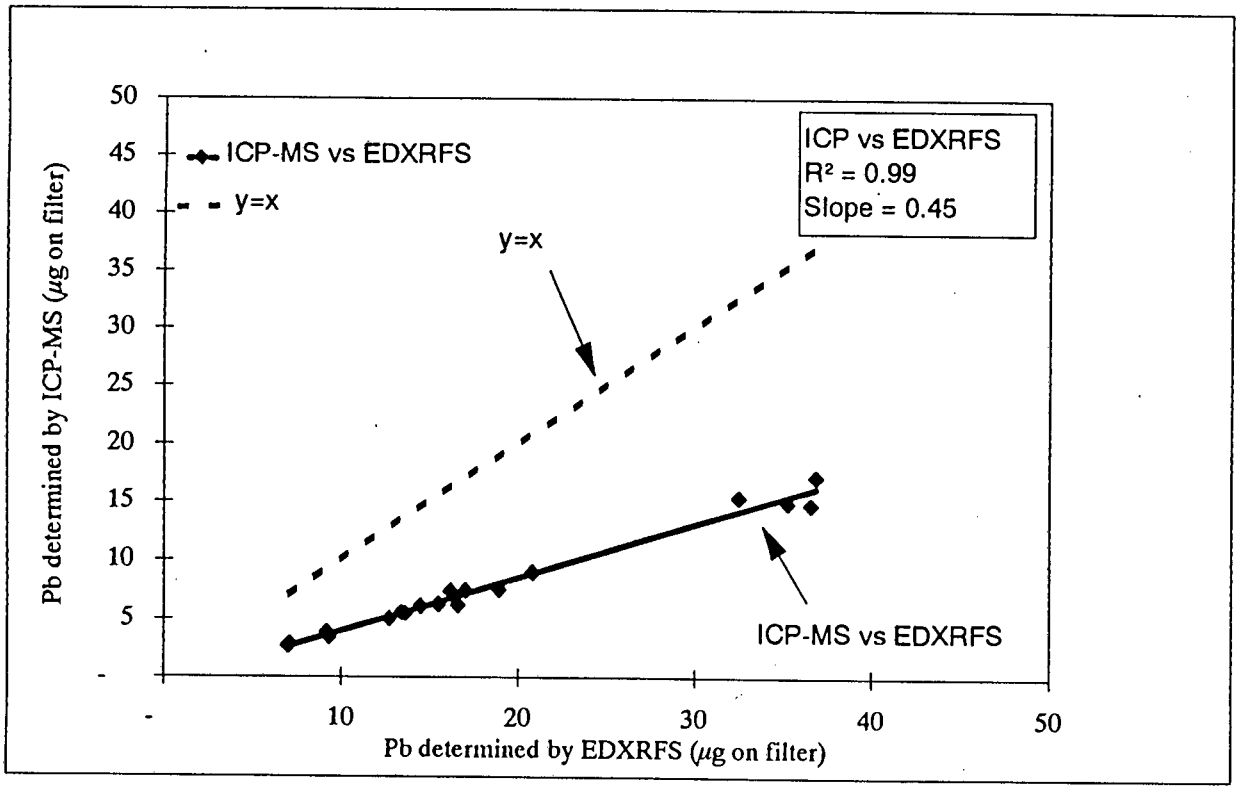



**Figure 4.1:** Comparison of Pb determinations by XRF and ICP-MS for the same set of samples.

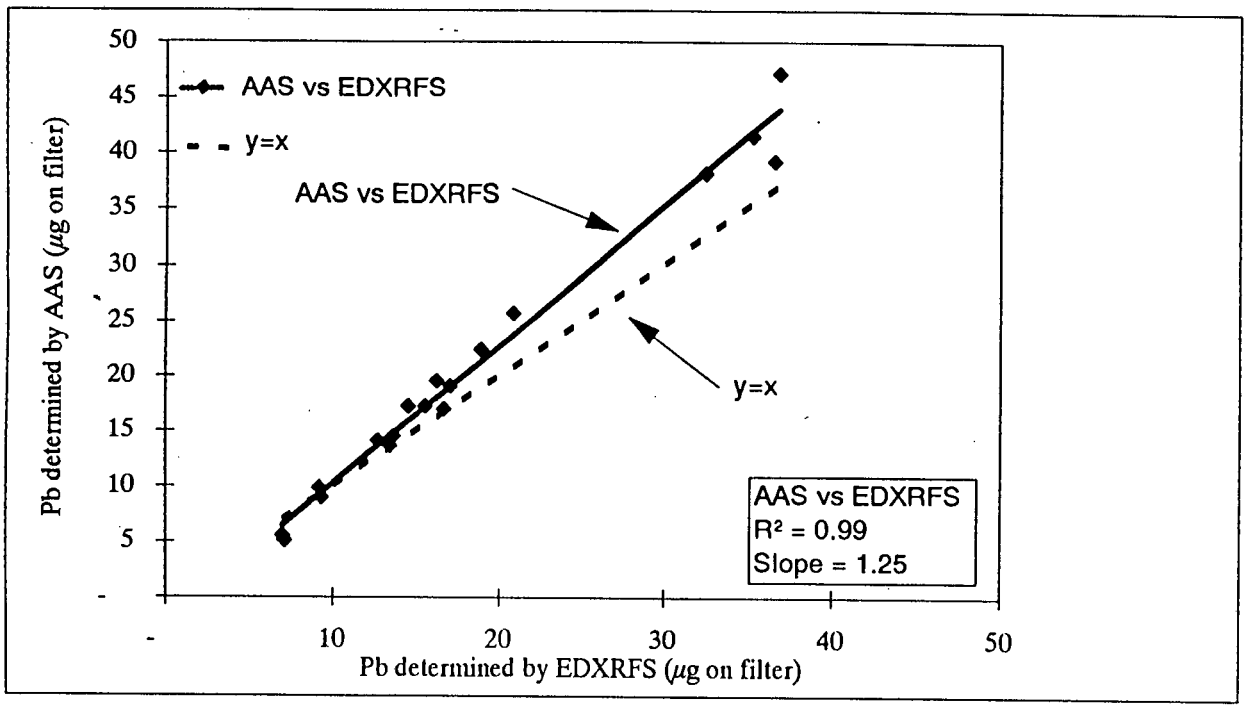



**Figure 4.2:** Comparison of Pb determinations by XRF and AAS for the same set of samples.

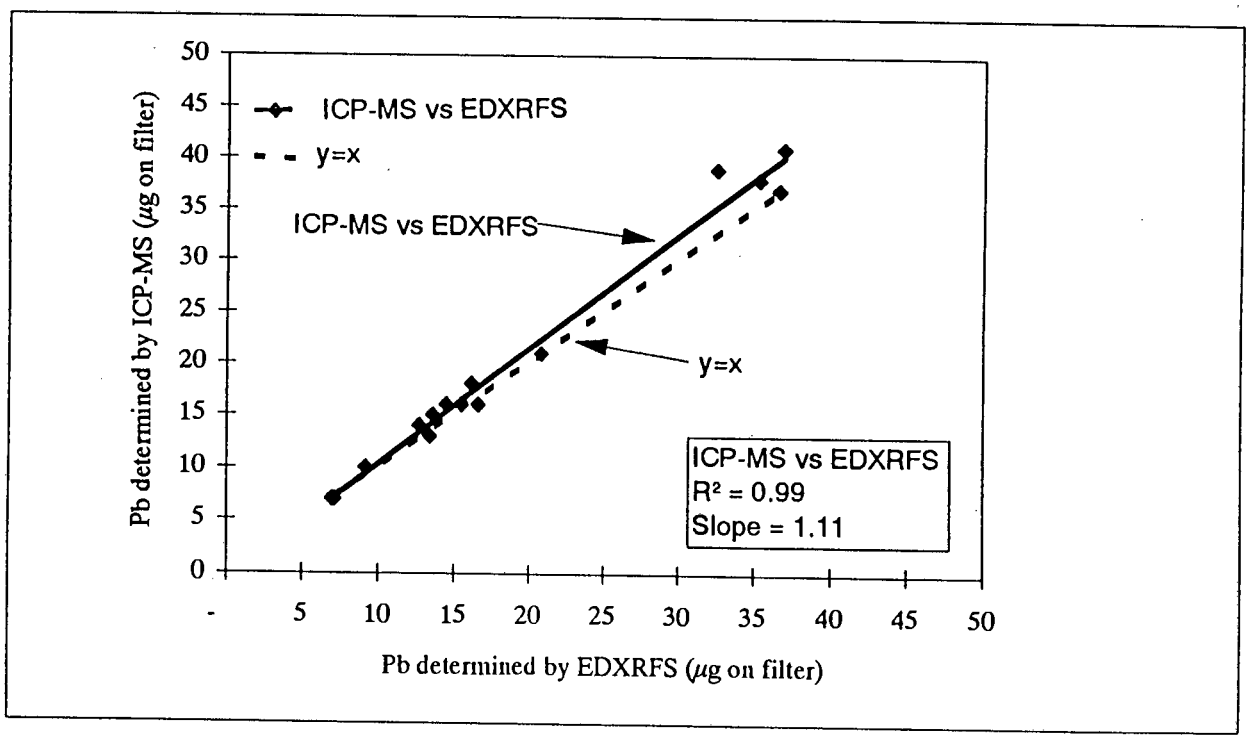



**Figure 4.3:** Comparison of Pb determinations by XRF and the repeated ICP-MS analysis for the same set of samples.

### 4.4.2 ICP-MS data quality control

ICP-MS data were validated by the use of internal standards and control samples.

Sc, In and Re were used as internal standards and the concentration of these elements in the final solution to be measured was 100ppb ($\mu$g/L). As internal standards the elements were used to monitor the stability of the instrument during analysis and also as an indication of the repeatability (precision) of the analysis.

The elements were used as internal standards because they are not present in the samples and their peaks do not overlap with the elements being analysed. The elements are also suitably analysed for by ICP-MS. If the results from the analyses yielded values that differed from the expected concentrations of the internal standards there could have been some problem during the analyses. The instrument and the raw data could then be inspected for any problems that might have caused the erroneous results. Control samples contained known concentrations of the suite of elements being analysed for. They were mainly used for elements which had strong spectral interference, and were normally used as a check on the accuracy and precision of the analysis. Once again, if the results obtained differed from the expected concentrations then the raw data, both raw counts and spectra, were checked for any interferences. An example of data validation in this manner is demonstrated in the case of Pb (section 4.4.1).

As for the Pb data (see section 4.4.1), vanadium determinations were also flagged as suspect because they did not compare very well with the XRF results. Repeat analysis of the solutions for V by ICP-MS yielded the same results as the initial analysis. The control samples returned the expected the values. Using this information a closer inspection of the XRF data was carried out. Re-examination of the XRF data revealed that the XRF calibration graph for V was very poor due to the concentration of V in the calibration samples being close to the detection limit where the precision of analysis is very poor. Therefore the ICP-MS results for V were used.

# CHAPTER 5

# 5. CMB7 MODELLING

## 5.1 INTRODUCTION

The Chemical Mass Balance version 7 model (CMB7) is a receptor models (Watson *et al.*, 1990). This model estimates the contributions of different sources of pollution to ambient pollutant concentrations, by using the chemical concentrations measured in source and receptor samples. There is an increased need for air quality managers from industry, health authorities and townplanners to apportion sources of pollution to observed pollution levels at any receptor site. Therefore receptor models are increasingly being used as an air quality management tool. CMB7 is a US-EPA approved software package that is used for receptor modelling and has been widely applied in many source apportionment studies in the United States. Hopke (1991) reviews in detail the various types of receptor models that are used for air quality management.

## 5.2 THE CMB7 RECEPTOR MODEL

### 5.2.1 Capabilities of the CMB7 Model

The CMB7 model can be used for gaseous species as well as airborne particulate matter. The model quantifies contributions from chemically distinct source-types. Further resolution of a particular source type into individual emitters is not always possible. This resolution depends on the number and types of chemical species that are modelled and the chemical composition of the individual sources. Sources having very similar source compositions cannot be resolved from each other.

A maximum of four different particle size fractions can be modelled separately where source and ambient data are available. This feature allows the user to differentiate between sources by using both chemical and particle characteristics (Watson *et al.*, 1990).

The model can calculate source contributions for each individual sample. This allows for each sample to define a distinct sampling period. A sampling period can be 1-hour, 12-hour, 24-hour or week long periods. This depends on the aim of the study. This is a useful feature because it allows modelling and identification of individual samples which

could be seasonal variations, variations in wind directions and any unusual event that may have resulted in high pollution levels being recorded. These features therefore make the model an attractive air quality management tool. In contrast multivariate techniques require 40 samples or more for modelling.

### 5.2.2 Model Background

Detailed descriptions on the principles as well as how the CMB7 model works are discussed by Watson *et al.* (1990), Hopke (1985) and Hopke (1991). The CMB7 model uses an effective variance least squares estimation method (equation 5.1) to obtain a solution to equation 5.2.

$$x^2 = \sum_{i=1}^{n} \frac{(C_i - \sum_{j=1}^{p} a_{ij} S_j)^2}{\sigma_{C_i}^2 + \sum_{j=1}^{p} \sigma_{a_{ij}}^2 S_j^2} \quad \text{-------- (5.1)}$$

$$C_i = \sum_{j=1}^{p} a_{ij} S_j \quad \text{---------- (5.2)}$$

where:

$C_i$ = The concentration of property *i* measured at the receptor.

$a_{ij}$ = The fractional concentration of property *i* in the emissions from the source *j* as perceived at the receptor.

p = Total number of independent contributing sources.

$x^2$ = The sum of the differences between the measured values of $C_i$ and those calculated from equation (1.1) weighted by $\sigma_{C_i}^2$.

$\sigma_{C_i}^2$ = the uncertainty in the $C_i$ measurement.

n = the total number of chemical species *I*.

$\sigma^2_{a_{ij}}$ = the uncertainty in the $a_{ij}$ measurement.

$Sj$ = the total mass contribution of source $j$ to the receptor.

The solution to equation 5.2 is unique when the number of species is equal to or greater than the number of sources.

### 5.2.3 Input data requirements

The input data file consists of two data files, namely a source data file and an ambient data file. As part of the input data the model requires the uncertainty/precision estimates of both the source and receptor measurements. The input data uncertainties are used to estimate the result in realistic uncertainties associated with the source contribution estimates calculated by the model.

The source data files should contain chemical measurements and associated uncertainty estimates for the sources that are likely to contribute to the receptor sample being collected. Additional information should include a description of the source-type, i.e. name with a code, size fraction and the names of all the chemical species that have been analysed. Elemental concentrations for the source samples are expressed as a fraction of the total filter loading (source fingerprints).

The ambient data file should also include the chemical data and uncertainty estimate of each measurement. Data entries for each receptor sample have a heading which includes, an identity number sampling site, sampling date, sample duration, size fraction, total measured mass concentration and, in the case of 24-hour samples, the start hour. Chemical concentrations are entered in micrograms per cubic metre ($\mu g/m^3$).

### 5.2.4 Model Output

CMB7 modelling output consists of the calculated source contributions (pie chart), the species composition of the sample (bar chart displays of fit of elements) and the mathematical output. The mathematical output consists of two parts (Fig. 5.1). The first part displays the source contribution estimates, which is the main CMB7 output.

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VER02          DATE: 04/29/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .91     PERCENT MASS       71.8
     CHI SQUARE       10.93               DF         21

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      2.8675       .2480     11.5613
1006    PETROL        1.4299       .0873     16.3840
1012    ISCORCF1      6.3505       .7479      8.4916
1017    SOIL1        12.0413       .9101     13.2312
1019    AMSUL         6.4088      1.0018      6.3975
1027    COMCOALT      1.2038       .2424      4.9656
1032    COMARC        5.5728       .4539     12.2774
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      50.0+-      5.0

SPECIES CONCENTRATIONS -  SITE: VER02          DATE: 04/29/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .91     PERCENT MASS       71.8
     CHI SQUARE       10.93               DF         21

SPECIES--I---MEAS----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  49.99390+-  4.99940  35.87460+-  1.22407    .72+-  .08   -2.7
C2  NA    *    .45170+-   .03780 *********+-141.56060  *****+-*****   -1.0
C3  MG    *    .31680+-   .00320    .36901+-   .02197   1.16+-  .07    2.4
C4  AL    *   1.50120+-   .09780   1.43534+-   .06790    .96+-  .08    -.6
C5  SI    *   3.54390+-   .19050   3.25438+-   .13442    .92+-  .06   -1.2
C6  P      -99.00000+--99.00000 *********+-283.88410    .00+-  .00    -.6
C7  S      -99.00000+--99.00000 *********+-283.88410    .00+-  .00    -.6
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00   -1.9
C9  K     *   1.24630+-   .06260   1.15693+-   .03692    .93+-  .06   -1.2
C10 CA        .06560+-   .00330    .66065+-   .02935  10.07+-  .68   20.1
C11 TI    *   .01750+-   .00090    .01940+-   .00092   1.11+-  .08    1.5
C12 V     *   .00240+-   .00010 *********+-317.22170  *****+-*****   -1.3
C13 CR        .00500+-   .00030 *********+-283.88410  *****+-*****   -1.0
C14 MN    *   .44380+-   .02170 *********+-141.56060  *****+-*****   -1.0
C15 FE    *  2.39580+-   .11810   2.50125+-   .08437   1.04+-  .06     .7
C16 NI    *   .00750+-   .00050    .00723+-   .00036    .96+-  .08    -.4
C17 CU    *   .02620+-   .00160    .02811+-   .00181   1.07+-  .10     .8
C18 ZN    *   .50190+-   .02510    .31364+-   .01308    .62+-  .04   -6.7
C19 GA    *   .00500+-   .00030 *********+-*********  *****+-*****   -1.5
C20 AS    *   .00870+-   .00050 *********+-639.89900  *****+-*****   -1.2
C21 SE    *   .00750+-   .00060 *********+-*********  *****+-*****   -1.4
C22 BR    *  1.06510+-   .05390    .56068+-   .05239    .53+-  .06   -6.7
C23 SR        .00620+-   .00040 *********+-628.70250  *****+-*****   -1.0
C24 MO        .01250+-   .00070 *********+-628.70250  *****+-*****   -1.0
C25 BA        .02370+-   .00150 *********+-714.21310  *****+-*****   -1.6
C26 PB    *   .56050+-   .02840    .68667+-   .02928   1.23+-  .08    3.1
C27 NH4+  *  1.27190+-   .12720 *********+-*********  *****+-*****   -1.9
C28 NO3-  *   .83080+-   .08310 *********+-883.31080  *****+-*****   -1.7
C29 SO4=  *  5.56500+-   .55650   5.56525+-   .46879   1.00+-  .13     .0
C30 CL-   *   .96530+-   .09650   1.02248+-   .08688   1.06+-  .14     .4
C31 O1TC  *  1.37960+-   .27590    .43566+-   .05952    .32+-  .08   -3.3
C32 O2TC  *  3.02250+-   .60450    .97829+-   .11832    .32+-  .08   -3.3
C33 O3TC  *  10.55610+-  2.11120  1.16596+-   .13143    .11+-  .03   -4.4
C34 O4TC  *  7.06860+-   1.41370   .83249+-   .09497    .12+-  .03   -4.4
C35 E1TC  *  7.15130+-   1.43030  1.95434+-   .31412    .27+-  .07   -3.5
C36 E2TC  *   .71960+-   .14390    .74264+-   .08889   1.03+-  .24     .1
C37 E3TC  *   .05200+-   .01040    .18689+-   .02313   3.59+-  .85    5.3
```

Figure 5.1: An examples of a source contribution and a species concentration display.

The first two lines of this display are headers which identify the source contribution estimates, sampling site, date, duration, starting hour and size fraction. Lines 3 and 4 display the performance measures which are the R-square, percentage mass and degrees of freedom. The first four lines are followed by the source contribution table. The first column of the table gives the source code, corresponding to its source name in the second column. The next three columns display the source contribution estimates, standard error and the T-statistic. The source contribution table is followed by the uncertainty/similarity clusters table. This table displays collinearity amongst source profiles being modelled.

The second part of the mathematical model output is a species concentration display. The first four lines of this display is the same as first four lines of the source contribution display and is followed by a table of fitting species. The first column gives a code corresponding to the species in the second column. The column marked I indicates which species are used as fitting species. A fitting species is marked with an asterisk. The next two columns are the measured and calculated species concentrations and their corresponding uncertainties. A value of -99 indicates that a species was not determined. The last two columns display the Ratio C/M and Ratio R/U which are important diagnostic statistics. These ratios will be discussed in the following sections

### 5.2.5 CMB7 Performance Measures

As with all models, the model performance needs to be assessed. Watson *et al.* (1990) give a detailed account of the CMB7 performance measures. A summary of the most important performance measures is presented in this section. All performance measures are presented with the output data that are discussed in section 5.2.4.

#### 5.2.5.1 Source Contribution Estimate

The source contribution estimate (SCE) display presents the contribution in $\mu g/m^3$ of each contributing source to the receptor sample being modelled e.g. 1003 Iscorsp1 with a SCE of 2.8675 $\mu g/m^3$ in Figure 5.1. The sum of the SCE approximates the total mass concentration of the filter that has been accounted for. A negative SCE is not physically meaningful. When the absolute value of the SCE is less than its standard error then the source contribution is below the detection limit. In Fig. 5.1 all SCE's are greater than the standard errors. Therefore for this example the source contributions are above the detection limit and the result is acceptable. Standard errors are a single standard deviation

and they reflect the precision of the ambient data, source profiles and colinearities amongst source profiles.

The T-statistic is the ratio of the source contribution to the standard error. T-statistic values less than 2 indicate that the SCE is at or below the detection limit. A low T-statistic also indicates that several source contributions are caused by collinearities among profiles.

5.2.5.2 Goodness of fit measures

These performance measures include the reduced chi-square, the degrees of freedom, R-square, mass percent and the similarity or uncertainty cluster display.

Chi-square ($\chi^2$) values are the weighted sum of squares of the differences between the calculated and measured fitting species concentrations. A $\chi^2$ value less than 2 indicates that the modelling result is a good fit. Values between 2 and 4 are acceptable but values greater than 4 indicate that one or more species concentrations are not well explained by the source contribution estimates.

The degrees of freedom are equal to the number of fitting species minus the number of fitting sources.

The R square ($R^2$) value is the fraction of the variance in the measured concentrations data which is explained by the variance in the calculated species concentrations. It is determined by a linear regression of measured versus model-calculated species values for the fitting species. $R^2$ values range from 0 to 1. The closer the value is to 1, the better does the SCE explain the measured concentrations at the receptor site. $R^2$ values less than 0.8 mean that the SCE is not well explained and the fit should be rejected.

The percent mass indicates the sum of model calculated SCE to the measured mass concentration. Ideally this value should equal 100% but values ranging from 80 to 120% are acceptable.

Similarity clusters are caused by source profiles that are chemically very similar or by high uncertainties in the individual source profiles which the model cannot separate. A source identified in the similarity cluster display usually has a high standard error and this can be verified in the SCE display (Fig. 5.2). The sum of the source contributions and the standard error of the sum are also shown in the similarity cluster display. Sources that appear in the similarity cluster display should either be removed or species that contribute

to the similarity should be identified and removed or additional unique species should be modelled.

UNCERTAINTY/SIMILARITY CLUSTERS CMB7 33889 SUM OF CLUSTER SOURCES

| | | | | | |
|---|---|---|---|---|---|
| 1012 | 1032 | 1035 | | 31.150+- | 1.275 |
| 1003 | 1035 | | | 6.676+- | 1.096 |
| 1003 | 1012 | 1032 | 1035 | 37.206+- | 1.338 |

**Figure 5.2:** An example of a similarity/uncertainty display.

In the above example the Iscor coking furnace (1012), composite arc furnace (1032) and the composite soil source (1035) form clusters because they are collinear.

5.2.5.3 Additional diagnostics

The diagnostics that offer clues on how to improve the performance measures are found in the species concentration display (Fig 5.1), the source contribution matrix and the transpose sensitivity matrix (Fig 5.3).

In the species concentration display R/U ratio is displayed. The R/U ratio specifies the number of uncertainty intervals by which the calculated and measured concentrations differ for each species (the residual). When the absolute value of the R/U ratio is greater than 2 then the residual is significant e.g. Zn in Fig. 5.1. If the R/U value is positive, then one or more source profiles are contributing too much to that species and a negative value means that there is insufficient contribution to that species and a source may be missing. The highest R/U values are the cause of high $\chi^2$ values. The source contribution matrix (Fig. 5.3) shows the fractional contribution of the fitting sources to the chemical species being modelled. The major source contributors to each species can be determined from this matrix. This display is used to verify and look for sources that influence R/U ratios.

Source contribution display

INDIVIDUAL RATIO = CALC SPECIES(PER SOURCE) / MEAS SPECIES(ALL SOURCES)

| SPECIES | MARIN | UDUST | AUTPB | SOURCE CODE RDOIL | KRAFT | ALPRO | STEEL | FERMN |
|---|---|---|---|---|---|---|---|---|
| TOT | .155 | .120 | .126 | .138 | .059 | .133 | .108 | .148 |
| F | .000 | .000 | .000 | .007 | .000 | .720 | .000 | .039 |
| NA | .715 | .017 | .000 | .056 | .086 | .063 | .016 | .053 |
| MG | 1.383 | .290 | .000 | .000 | .069 | .690 | 1.311 | .000 |
| AL | .000 | .182 | .024 | .013 | .003 | .614 | .012 | .016 |
| SI | .000 | .708 | .027 | .035 | .002 | .012 | .144 | .039 |
| S | .139 | .012 | .014 | .499 | .186 | .050 | .058 | .068 |
| CL | .833 | .000 | .051 | .000 | .014 | .024 | .027 | .008 |
| K | .106 | .060 | .004 | .019 | .043 | .014 | .049 | .760 |
| CA | .097 | .131 | .071 | .098 | .000 | .020 | .302 | .087 |
| TI | .000 | .740 | .000 | .147 | .003 | .051 | .209 | .066 |
| V | .000 | .006 | .000 | 1.023 | .000 | .018 | .014 | .008 |
| CR | .000 | .014 | .000 | .017 | .042 | .000 | .578 | .016 |
| MN | .000 | .004 | .000 | .002 | .000 | .000 | .252 | .687 |
| FE | .000 | .127 | .047 | .073 | .012 | .011 | .613 | .055 |
| NI | .000 | .001 | .002 | .775 | .008 | .026 | .079 | .000 |
| CU | .000 | .065 | .167 | .189 | .022 | .106 | .552 | .097 |
| ZN | .000 | .047 | .157. | .197 | .014 | .007 | .463 | .306 |
| BR | .059 | .005 | 1.203 | .003 | .015 | .009 | .000 | .045 |
| PB | .000 | .014 | .797 | .005 | .000 | .001 | .026 | .002 |
| OC | .000 | .150 | .669 | .103 | .011 | .055 | .000 | .142 |

MPIN display

| SPECIES | MARIN | UDUST | AUTPB | SOURCE CODE RDOIL | KRAFT | ALPRO | STEEL | FERMN |
|---|---|---|---|---|---|---|---|---|
| NA | .99 | .01 | -.03 | -.09 | .14 | .01 | -.06 | .01 |
| MG | .21 | -.05 | -.04 | -.04 | -.07 | .13 | .18 | -.08 |
| AL | -.17 | -.03 | -.10 | -.11 | -.05 | 1.00 | -.14 | .01 |
| SI | -.02 | 1.00 | -.05 | -.05 | .04 | -.14 | -.19 | .02 |
| CL | 1.00 | -.02 | .04 | .12 | -.36 | -.04 | .01 | -.02 |
| K | -.04 | .05 | -.03 | -.05 | .11 | -.01 | -.22 | .46 |
| CA | .28 | .02 | .03 | .12 | -.19 | -.03 | .39 | -.06 |
| TI | .00 | .49 | -.07 | .08 | -.03 | -.02 | -.07 | .02 |
| V | .23 | -.04 | -.06 | 1.00 | -.40 | -.04 | -.19 | .04 |
| CR | -.10 | -.07 | -.03 | -.12 | .13 | -.02 | .33 | -.12 |
| MN | -.02 | -.07 | -.10 | -.04 | -.07 | -.03 | -.05 | 1.00 |
| FE | -.08 | -.12 | -.05 | -.14 | .07 | -.06 | 1.00 | -.31 |
| NI | .17 | -.06 | -.06 | .87 | -.32 | -.02 | -.09 | -.00 |
| CU | -.12 | -.19 | .09 | .02 | .05 | .17 | .67 | -.18 |
| ZN | -.02 | -.09 | .07 | .09 | -.02 | -.05 | .31 | .10 |
| BR | .01 | -.02 | .55 | -.05 | .03 | -.04 | -.07 | -.01 |
| PB | .00 | -.04 | 1.00 | -.06 | .00 | -.07 | -.08 | -.05 |
| OC | -.04 | .09 | .61 | .04 | .01 | .02 | -.22 | .11 |
| EC | -.01 | -.03 | .16 | .17 | -.07 | .20 | -.16 | .09 |
| SO4 | -.66 | .01 | -.04 | .04 | 1.00 | -.04 | -.16 | -.01 |
| NO3 | -.00 | .01 | .03 | .06 | -.04 | .04 | -.19 | .35 |

**Figure 5.3:** Examples of source contribution and MPIN displays

The transpose sensitivity matrix (Fig. 5.3) is the transpose of the normalized modified pseudo-inverse matrix (MPIN). This matrix indicates the degree of influence each fitting species concentration has on the contribution and the standard error of the corresponding source category. MPIN is normalized such that it takes on values from -1 to 1. Species with absolute MPIN values of 1 to 0.5 are influential fitting species. Species with a MPIN absolute value of less than 0.5 are considered non-influential.

## 5.3 MODELLING PROCEDURE

The CMB7 modelling procedure is very iterative and detailed examples are presented by Watson *et al.,* (1990). This section will summarise the modelling procedure used. The CMB7 model is menu driven and all commands are invoked by choosing the desired action from a menu. A modelling session is usually started by following a sequence of commands. When the model is started it first asks for the name of the file that contains the input data files. At the next prompt an output data file needs to be named or the default output file name (cmbout) can be used. CMB7 provides its own extensions for the output data files. The user is then prompted to select a sample or a subset of samples to be modelled. For this project only one sample was modelled at a time.

The contributing sources and species to be modelled were selected from the fitting sources and fitting species menus. For the first source contribution calculation the default sources and species were used. The default sources used were representative of the following possible contributors:-

- Domestic coalfire
- Geological dust
- Power station flyash
- Leaded petrol vehicle
- Arc furnace
- Secondary ammonium sulphate

Na, Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Se, Br, Pb, $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, $Cl^-$ and all seven carbon species were used as the default chemical species. There were some

samples for which some of the default chemical species were not determined and these species were excluded before source contributions were calculated.

The source contributions were calculated by invoking the 'calculate source contribution' command. Thereafter the CMB7 performance measures were inspected so as to evaluate the 'goodness of fit' and improve the fit in to order satisfy the chi-square, R square, mass percentage, standard error and T-statistic requirements (see 5.2.5).

Sources for which negative contributions were estimated were excluded since negative source contributions are physically meaningless. However, only a single species being modelled may result in a negative source contribution. This information was obtained from the source contribution matrix (Fig 5.3).

R/U ratios from the species concentration display are important indicators of missing or collinear sources. Information derived from the R/U ratio, uncertainty/similarity cluster display and the MPIN matrix gave an indication of sources and species that needed to be included or removed from the model calculation in order to eliminate collinearity. Addition of fitting species to the model calculation often reduced collinearity amongst sources and therefore a T-statistic value of >2 was obtained. If too many species were removed from the calculation the 'goodness of fit' measures sometimes improved but collinearity increased and unacceptable low T-statistic values (<2) were calculated. Only species with an absolute MPIN value of <0.5 were removed from the calculation since a MPIN value of <0.5 means that the species is non-influential.

When a reasonable fit was obtained the results were subjected to sensitivity tests as described by Watson *et al.* (1994). Sensitivity tests were done because sometimes more that one combination of profiles satisfied the recommended performance measures. From the sensitivity tests the combination of profiles that gave the best performance measures were chosen as the final answer.

# CHAPTER 6

# 6. CHEMICAL AND CMB7 MODELING RESULTS

## 6.1 INTRODUCTION

The results from the chemical analysis (Chapter 3) and the CMB7 modelling (Chapter 5) are presented and discussed in this chapter. Chemical data to be used as input data for the VAM project were obtained from two sources. The source chemical data were obtained from the data files of the Vaal Air Characterisation Study (Engelbrecht *et al.,* 1993) as well as the Eastern Transvaal Highveld Study (Engelbrecht *et al.,* 1994) and the ambient data set was obtained from the present VAM study. The sources were recently re-analysed on the Spectro X-Lab EDXRFS instrument to include the following additional inorganic species, Se, As, Ga, Sr and Mo. The profiles were further extended to include 7 carbon species.

This chapter represents the major original contribution of the author to the overall VAM project.

## 6.2 CHEMICAL DATA

### 6.2.1 Source chemical data

A total of thirty five source profiles were used for modelling the VAM ambient data. Twenty two profiles can be classed as primary sources (Tables 6.1), eight as combined source-type profiles (Table 6.2) and five as secondary sources (Table 6.3). Primary sources are classified as sources that emit particulate matter directly into the air. Secondary source profiles consist of 'pure' compounds. These compounds are normally salts of $NH_4^+$, $SO_4^{2-}$, and $NO_3^-$ that are formed through gas to particle transformation in the atmosphere and cannot be entirely accounted for by primary sources.

The primary source profiles are further combined into profiles that correspond to a composite of many similar sources. The latter source profile therefore represent a source-type and are more representative of receptor measurements (Watson *et al.,* 1994). Four source-types were identified and several combinations of the original profiles types were

generated. The four source-types identified were power station flyash, arc furnace dust, soil dust and domestic coalfire emissions (Table 6.2).

**Table 6.1:** A description of the primary source profiles used for modelling purposes.

| Source Name | Description |
|---|---|
| ISCORBO1 | Iscor Vanderbijlpark - basic oxygen furnace - resuspended sample |
| ESKOMLE1 | Eskom's Lethabo power station flyash - stack sample |
| ISCORSP1 | Iscor, Vanderbijlpark - sinter plant - resuspended sample |
| ISCORAF1 | Iscor, Vanderbijlpark - arc furnace - duct sample |
| ISCORDR1 | Iscor, Vanderbijlpark - direct reduction plant - stack sample |
| PETROL | Leaded petrol vehicle - exhaust emission |
| DIESEL | Heavy diesel motor vehicle - exhaust emission |
| COALFIR1 | Domestic coalfire combustion - Brazier emission |
| GRASS1 | Grass fire emission |
| SAMFSM1 | Samancor, Meyerton - ferrosilicon manganese plant - duct sample |
| ISCORCF1 | Iscor, Vanderbijlpark - Coking furnace - resuspended sample |
| SAMFM1 | Samancor, Meyerton - ferromanganese plant - resuspended sample |
| SAMFS1 | Samancor, Meyerton - ferrosilicon plant - duct sample |
| NATREF | Natref, Sasolburg - Oil/gas boiler - duct sample |
| USCOAF | Usco, Vereeniging - Arc furnace - resuspended sample |
| SASOLPS1 | Sasol I, Sasolburg - power station flyash - resuspended sample |
| SOIL 1 | Sasolburg - Geological dust - local resuspended sample |
| ESKOMKR | Eskom's Kriel power station flyash - resuspended sample. |
| ESKOMMA | Eskom's Matla power station flyash - stack sample. |
| COALFIRH | Domestic coalfire combustion - high smoke coalstove emission |
| COALFIRL | Domestic coalfire combustion - low smoke coalstove emission |
| SOILETH | Kriel - Geological dust - local resuspended sample |

**Table 6.2:** Composite source-type profiles used for modelling purposes.

| Source Name | Description* |
|---|---|
| COMPSFAT | Composite power station flyash profile of all power staion profiles, $PM_{10}$ and $PM_{2.5}$ fractions of ESKOMLE1, SASOLPS1, ESKOMKR1 and ESKOMMA1. |
| COMPSFA | Composite power station flyash profile of all power station profiles, $PM_{10}$ fraction of ESKOMLE1, SASOLPS1, ESKOMKR1 and ESKOMMA1. |
| COMCOALT | Composite coal fire profile of all coalfire profiles, $PM_{10}$ and $PM_{2.5}$ fractions of COALFIR1, COALFIRH and COALFIRL. |
| COMCOAL | Composite coalfire profile of all coalfire profiles, $PM_{10}$ fraction of COALFIR1, COALFIRH and COALFIRL. |
| COMARCT | Composite arc furnace profile of all arc furnace profiles, $PM_{10}$ and $PM_{2.5}$ fractions of ISCORAF1, SAMFM1 and USCOAF. |
| COMARC | Composite arc furnace profile of all arc furnace profiles, $PM_{10}$ fraction of ISCORAF1, SAMFM1 and USCOAF. |
| COMSOILT | Composite geological dust profiles of geological dust profiles, $PM_{10}$ and $PM_{2.5}$ fraction of SOIL1 and SOILETH. |
| COMSOIL | Composite geological dust profiles of geological dust profiles, $PM_{10}$ fraction of SOIL1 and SOILETH. |

* All composite profiles were obtained by calculating the arithmetic means of the source profiles used.

* The composite soil profiles are composite profiles of local soils. These soils were resuspended in the laboratory.

**Table 6.3:** Secondary source profiles used for modelling purposes.

| Source Name | Description |
|---|---|
| NaNO3 | Secondary sodium nitrate |
| AMSUL | Secondary ammonium sulphate |
| AMNIT | Secondary ammonium nitrate |
| AMBISUL | Secondary ammonium bisulphate |
| SECSULPH | Secondary sulphate |

All the primary source profiles were described in detail by Engelbrecht *et al.* (1993; 1994). This included descriptions of the sampling site, sampling method, sampling times and chemical composition. However, the chemical composition of the source profiles used for this project differed from the original profiles. The original profiles were supplemented by the addition of data for As, Se, Sr, Mo and Ba to the database. The carbon species were originally reported as low temperature and high temperature derivatives of elemental and organic carbon, but for this work the carbon fraction was divided into seven carbon species (see chapter 3). Therefore a total of 36 chemical variables could be modelled. Only chemical data of the source profiles that were identified as contributing sources are tabulated in Appendix B. A value of -99 in the data tables means that the species was not determined.

### 6.2.2 Description of the ambient samples modelled

The methods used to obtain ambient data were described in chapters 2, 3 and 4. Although the duration of the VAM project spans one year from the beginning of May 1994 to the end of April 1995 only a selection of samples were used for this thesis.

The samples modelled were chosen to represent the pre-, mid- and post-winter situations. Only a single sampling week each was chosen to represent the pre- and post-winter samples. Four sampling weeks were chosen to represent the mid-winter samples. The mid-winter samples were chosen to represent a week with an average gravimetric loading and a

week with a high gravimetric loading. Three other samples, one from each receptor site were selected to represent the highest gravimetric loading that was recorded at each receptor site during the sampling period. Descriptions of the samples modelled are given in Table 6.4. Figure 6.1 graphically displays the gravimetric loading of the winter samples from the last week of April to the end of August.

Gravimetric loadings recorded at the Vereeniging receptor exceeded the US-EPA the 24-hour standard of 150 $\mu g/m^3$ was exceeded during sampling weeks 7 (225.1 $\mu g/m^3$)and 12 (155.6 $\mu g/m^3$) implying that the 24-hour average concentrations in Vereeniging exceeded this standard on one or more days during these weeks.. Similarly, for the Vanderbijlpark receptor site the 24 hour standard was exceeded only during sampling week 5 (164.5 $\mu g/m^3$). Generally the lowest gravimetric loadings were recorded at the Sasolburg receptor site, with exceptions being sampling weeks 9, 17 and 18. The highest gravimetric loadings for the Sasolburg receptor site were recorded during sampling weeks 3 (99.2 $\mu g/m^3$) and 13 (99.4 $\mu g/m^3$).

### 6.2.3 Ambient chemical data

6.2.3.1 Introduction

A requirement of the CMB7 model is that source and ambient input data files must have the same chemical species. Although elemental S, Cl and P were not determined on the ambient samples they were included in the ambient data files and a value of -99 was used to indicate that they were not determined. However, $SO_4^{2-}$, and $Cl^-$ were determined by ion chromatography. As most of the S and Cl was expected to be present as water soluble ions this is not regarded as a major limitation on the validity of the results. P was however not determined in any form. The ambient chemical data set used is tabulated in Table 6.5. The ambient data and the error (uncertainty) calculated for each measurement is presented in the species concentration display in Appendix A. The profiles of the ambient samples modelled are presented in Appendix C.

**Table 6.4:** List of samples modelled and the total gravimetric concentration of the species analysed.

| Sampling week | Sampling date | Season | Vereeniging ($\mu g/m^3$) | Vanderbijlpark ($\mu g/m^3$) | Sasolburg ($\mu g/m^3$) |
|---|---|---|---|---|---|
| Week 02 | 04/29/94-05/06/94 | Pre-winter | 69.5 | 67.7 | 46.9 |
| Week 07 | 06/03-94-06/10/94 | Mid winter (high) | 225.1 | Not analysed | Not analysed |
| Week 08 | 06/10/94-06/17/94 | Mid-winter (low) | 93.3 | 71.8 | 71.7 |
| Week 12 | 07/08/94-07/15/94 | Mid-winter (average) | 155.7 | 112.1 | 87.8 |
| Week 13 | 07/15/94-07/22/94 | Mid-winter (high) | Not analysed | 134.6 | 99.4 |
| Week 19 | 08/26/94-09/02/94 | Post-winter | 88.0 | 75.5 | 59.3 |

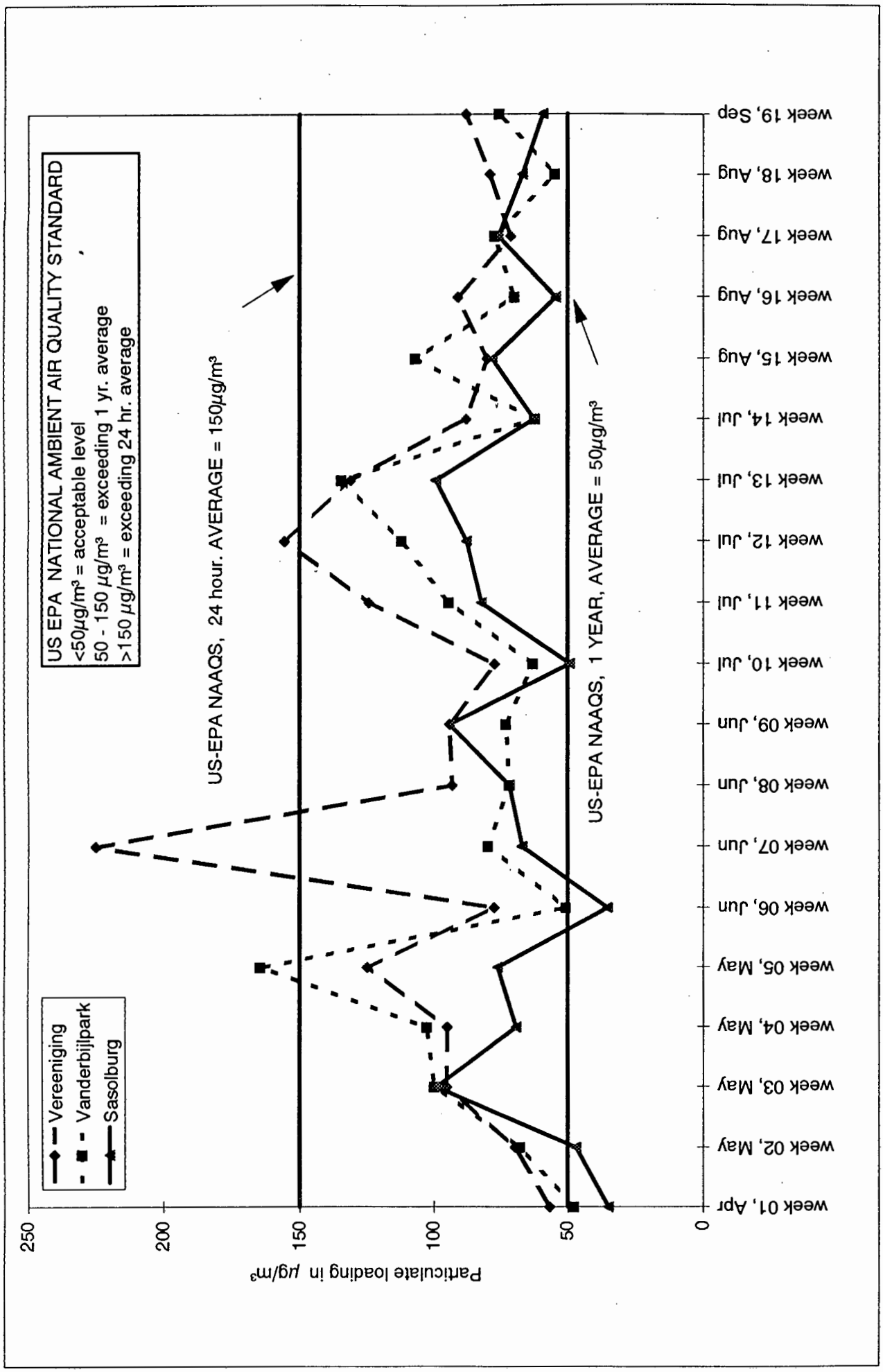



**Figure 6.1:** A plot of the weekly gravimetric data for all three receptor sites.

6.2.3.2 Calculation of error (uncertainty)

Sampling and analysis errors were considered to be the major sources of errors to be used as input for the ambient data. The equations used for the sampling and analytical errors are presented in equations 6.1 and 6.2.

$$\textbf{Relative sampling error} = \frac{\textbf{standard deviation}}{\textbf{mean}} \textbf{x100\%} \quad \text{---- (6.1)}$$

Where:

1. The mean is the mean loading mass on four filters that were sampled simultaneously with the ambient sampler.
2. The standard deviation is the standard deviaton of the loading mass of the four filters.

The counting error was considered to represent the analytical error.

$$\textbf{Relative counting error} = \frac{\sqrt{N}}{N} \textbf{x100 \%} \quad \text{--------- (6.2)}$$

Where:

N is the total number of counts collected at the peak position (Jenkins and De Vries, 1974).

$$\text{Total error} = \sqrt{(\text{relative sampling error})^2 + (\text{relative counting error})^2} \quad \text{- (6.3)}$$

Equation 6.2 was used only for the elements that were analysed by EDXRFS and ICP-MS. For the chemical species analysed by AAS and ion chromatography the uncertainty value used was 10% of the measured concentration. Although the uncertainties for these species should have been calculated estimation of the uncertainty followed the approach used by the DRI to estimate uncertainties for species whose uncertainties were not calculated. An uncertainty of 20% of the measured concentration was used as the uncertainty for the carbon species (Chow *et al.*, 1994b).

**Table 6.5:** Ambient chemical data of receptor samples.

| | VER02 04/29/94 | VAN02 04/29/94 | SAS02 04/29/94 | VER07 06/03/94 | VER08 06/10/94 | VAN08 06/10/94 | SAS08 06/10/94 |
|---|---|---|---|---|---|---|---|
| Na | 0.04 | 0.03 | 0.01 | 1.27 | 0.07 | 0.05 | 0.10 |
| Mg | 0.00 | 0.24 | 0.02 | 2.09 | 0.66 | 0.70 | 0.61 |
| Al | 1.50 | 1.63 | 0.00 | 4.85 | 1.68 | 1.79 | 1.77 |
| Si | 3.54 | 3.38 | 2.85 | 1.47 | 4.53 | 3.95 | 3.57 |
| P | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| S | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cl | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| K | 1.25 | 1.44 | 1.08 | 2.65 | 2.05 | 1.73 | 1.73 |
| Ca | 0.07 | 0.29 | 0.00 | 3.83 | 1.18 | 1.06 | 0.95 |
| Ti | 0.02 | 0.02 | 0.02 | 0.07 | 0.03 | 0.03 | 0.02 |
| V | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 | 0.01 |
| Cr | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 |
| Mn | 0.44 | 0.46 | 0.37 | 1.01 | 0.45 | 0.36 | 0.34 |
| Fe | 2.40 | 3.15 | 1.88 | 8.02 | 3.32 | 2.63 | 2.37 |
| Ni | 0.01 | 0.03 | 0.01 | 0.03 | 0.03 | 0.01 | 0.01 |
| Cu | 0.03 | 0.03 | 0.02 | 0.05 | 0.03 | 0.02 | 0.01 |
| Zn | 0.50 | 0.50 | 0.89 | 0.65 | 0.71 | 0.36 | 0.65 |
| Ga | 0.00 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 | 0.00 |
| As | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Se | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Br | 1.07 | 1.04 | 0.46 | 0.00 | 0.81 | 0.44 | 0.23 |
| Sr | 0.01 | 0.01 | 0.01 | 0.03 | 0.01 | 0.01 | 0.01 |
| Mo | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Ba | 0.02 | 0.02 | 0.00 | 0.04 | 0.03 | 0.02 | 0.02 |
| Pb | 0.56 | 0.64 | 0.33 | 0.71 | 0.56 | 0.41 | 0.35 |
| NH4+ | 1.27 | 1.65 | 1.65 | 0.00 | 0.55 | 0.81 | 2.32 |
| NO3- | 0.83 | 0.67 | 0.19 | 0.50 | 2.67 | 1.97 | 3.58 |
| SO4= | 5.57 | 5.83 | 2.55 | 7.28 | 5.36 | 5.75 | 7.35 |
| Cl- | 0.97 | 1.05 | 0.57 | 0.05 | 0.05 | 0.03 | 0.14 |
| O1TC | 1.38 | 0.99 | 0.84 | 1.39 | 2.51 | 1.83 | 0.48 |
| O2TC | 3.02 | 3.42 | 1.78 | 7.08 | 5.43 | 3.68 | 3.27 |
| O3TC | 10.56 | 10.34 | 6.06 | 12.83 | 8.26 | 7.22 | 5.46 |
| O4TC | 7.07 | 8.33 | 3.94 | 11.67 | 8.53 | 8.31 | 6.08 |
| E1TC | 7.15 | 7.09 | 4.13 | 27.48 | 16.06 | 9.41 | 5.89 |
| E2TC | 0.72 | 0.67 | 0.69 | 2.90 | 0.85 | 0.43 | 0.60 |
| E3TC | 0.05 | 0.07 | 0.04 | 0.59 | 0.21 | 0.21 | 0.13 |
| TOT. | 50.03 | 52.78 | 30.39 | 98.61 | 66.62 | 53.22 | 47.99 |

**Table 6.5 (continued):** Ambient chemical data of receptor samples.

| | VER12 07/08/94 | VAN12 07/08/94 | SAS12 07/08/94 | VAN13 07/15/94 | SAS13 07/15/94 | VER19 08/26/94 | VAN19 08/26/94 | SAS19 08/26/94 |
|---|---|---|---|---|---|---|---|---|
| Na | 0.56 | 0.91 | 0.71 | 0.70 | 0.57 | 0.79 | 0.94 | 0.65 |
| Mg | 0.74 | 0.57 | 0.87 | 0.71 | 0.68 | 0.60 | 0.63 | 0.38 |
| Al | 3.35 | 2.06 | 1.97 | 2.47 | 2.04 | 3.01 | 1.82 | 1.85 |
| Si | 5.81 | 4.96 | 4.63 | 5.31 | 5.11 | 5.92 | 4.66 | 5.07 |
| P | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| S | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cl | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| K | 2.46 | 1.62 | 1.62 | 2.33 | 2.00 | 1.75 | 1.88 | 1.40 |
| Ca | 1.95 | 1.34 | 1.31 | 1.71 | 1.40 | 1.49 | 1.54 | 1.14 |
| Ti | 0.04 | 0.03 | 0.03 | 0.03 | 0.03 | 0.04 | 0.03 | 0.02 |
| V | 0.01 | 0.00 | 0.00 | 0.02 | 0.02 | 0.02 | 0.02 | 0.01 |
| Cr | 0.04 | 0.02 | 0.02 | 0.03 | 0.01 | 0.01 | 0.01 | 0.00 |
| Mn | 0.64 | 0.61 | 0.46 | 0.90 | 0.66 | 0.38 | 0.32 | 0.18 |
| Fe | 5.39 | 3.80 | 3.28 | 5.56 | 3.45 | 4.07 | 2.94 | 1.67 |
| Ni | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Cu | 0.04 | 0.03 | 0.02 | 0.04 | 0.03 | 0.05 | 0.03 | 0.01 |
| Zn | 0.99 | 0.68 | 0.60 | 1.20 | 1.43 | 0.75 | 0.57 | 0.29 |
| Ga | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 |
| As | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Se | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 |
| Br | 1.56 | 1.25 | 0.23 | 0.40 | 0.30 | 0.53 | 0.36 | 0.17 |
| Sr | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Mo | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.02 | 0.00 | 0.00 |
| Ba | 0.05 | 0.03 | 0.02 | 0.03 | 0.01 | 0.03 | 0.02 | 0.01 |
| Pb | 1.06 | 0.92 | 0.41 | 0.85 | 0.43 | 0.71 | 0.42 | 0.19 |
| NH4+ | 2.93 | 4.11 | 3.34 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| NO3- | 5.06 | 4.37 | 8.10 | 0.49 | 0.49 | 1.22 | 3.15 | 5.56 |
| SO4= | 8.21 | 8.40 | 7.94 | 6.35 | 5.64 | 5.33 | 10.06 | 7.55 |
| Cl- | 0.04 | 0.04 | 0.03 | 0.12 | 0.15 | 3.67 | 1.36 | 0.80 |
| O1TC | 3.57 | 4.47 | 1.30 | 4.43 | 0.87 | 0.24 | 0.29 | 0.17 |
| O2TC | 8.16 | 5.87 | 2.98 | 7.58 | 2.70 | 3.15 | 2.92 | 1.77 |
| O3TC | 16.23 | 15.18 | 9.53 | 15.89 | 6.27 | 9.88 | 8.50 | 4.30 |
| O4TC | 13.48 | 14.14 | 8.14 | 16.15 | 1.52 | 8.21 | 5.85 | 2.38 |
| E1TC | 30.99 | 15.76 | 9.54 | 27.51 | 20.32 | 10.74 | 8.64 | 8.80 |
| E2TC | 0.94 | 0.62 | 0.59 | 1.53 | 0.72 | 0.65 | 0.58 | 0.55 |
| E3TC | 0.17 | 0.11 | 0.09 | 0.26 | 0.13 | 0.15 | 0.13 | 0.06 |
| TOT | 114.00 | 91.05 | 67.08 | 102.66 | 56.46 | 63.44 | 57.69 | 45.04 |

### 6.2.4 Discussion of ambient chemical data

The sum of the measured chemical species parallel the increase in gravimetric concentrations recorded during winter, and lower concentrations in the pre- and post-winter periods. Comparisons between the gravimetric concentrations and the total sum of chemical species are presented in Table 6.6.

**Table 6.6:** A comparison between the gravimetric and the total sum of chemical species.

| Sample Name | Gravimetric concentration ($\mu g/m^3$) | Total sum of chemical species ($\mu g/m^3$) | Ratio Chemical:Gravimetric C:G |
|---|---|---|---|
| VER02 | 69.6 | 50.0 | 0.72 |
| VAN02 | 67.7 | 52.8 | 0.79 |
| SAS02 | 46.9 | 30.4 | 0.65 |
| VER07 | 225.1 | 98.6 | 0.44 |
| VER08 | 93.3 | 66.6 | 0.71 |
| VAN08 | 71.8 | 53.2 | 0.74 |
| SAS08 | 71.8 | 47.9 | 0.67 |
| VER12 | 155.7 | 114.0 | 0.73 |
| VAN12 | 112.1 | 91.1 | 0.81 |
| SAS12 | 87.8 | 67.1 | 0.76 |
| VAN13 | 134.6 | 102.7 | 0.76 |
| SAS13 | 99.3 | 56.5 | 0.57 |
| VER19 | 88.0 | 63.4 | 0.72 |
| VAN19 | 75.5 | 57.7 | 0.76 |
| SAS19 | 59.3 | 45.0 | 0.75 |

*Week 02 - (04/29/94 -05/06/94)*

Samples from all three sites show a similar trend with low concentrations of inorganic elements and high concentrations for the carbon species. The major species (>1$\mu g/m^3$) in all three profiles were Al, Si, K, Fe, Br, $NH_4^+$, $SO_4^{2-}$, O1TC, O2TC, O3TC, O4TC and E1TC.

*Week 07 - (06/03/94 - 06/10/94)*

Only the sample from the Vereeniging receptor site was analysed for this week because it was the sample with the highest measured gravimetric loadings for the winter period (Fig 6.1). Na, Mg, Al, Si, K, Ca, Mn, Fe, $SO_4^{2-}$, O1TC, O2TC, O3TC, O4TC, E1TC and E2TC were the major elements that were measured for this sample. The concentrations of the above-mentioned major elements in this sample were relatively higher than the concentrations for the same elements in the pre-winter samples. The sample loadings on these filters were boosted by the higher carbon concentrations. The E1TC (elemental carbon species- 550°C - 580°C) species had a concentration of 27.48 $\mu g/m^3$ which was 28% of the total measured elemental concentration. The Si to Al ratio for this sample is <1 for this week. This is an unusual ratio and is not consistent with the Si/Al ratio of the other samples whose Si/Al ratios were always >1. Only an unusual event which resulted in the emission of an abnormally high amount of Al can explain this observation (Level 3 data validation). This result was subject to the validation procedures described in chapter 4. The ratio of the measured species concentration to the gravimetric concentration is less than 0.5 (Table 6.6). Therefore this result may be regarded as suspect and all analyses performed on this sample should be re-checked. No adequate explanation for the low chemical to gravimetric ratio (C/G) of 0.44 was found.

*Week 08 - (06/10/94 - 06/17/94)*

For this week samples from all three sites were analysed. All three sites showed a similar trend for the elemental concentrations. The species concentration measured at all three sites were considerably lower than those measured for week 7. Nevertheless the carbon species were the major contributors. The major elements in all three samples were Al, Si, K, Ca, Fe, $NO_3^-$, $SO_4^{2-}$, O1TC, O2TC, O3TC, O4TC and E1TC.

*Week 12 - (07/08/94 -07/15/94)*

Samples from all three sites were analysed for this week. Elemental concentrations were higher than those measured during week 10. Once again the high sample loadings were attributed mainly to substantially high contributions from carbon emitting sources. The major elements in these samples were Al, Si, K, Ca, Fe, Br (Vereeniging and Vanderbijlpark only), Pb (Vereeniging only), $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, O1TC, O2TC, O3TC, O4TC and E1TC. The Vereeniging profile differed from the profiles of the other two sites

especially with respect to the E1TC carbon species. The Vereeniging sample had an E1TC concentration twice and three times those measured at the Vanderbijlpark and Sasolburg site respectively. Once again the carbon species contributed the bulk of the measured gravimetric concentration.

*Week 13 - (07/15/94 - 07/22/94)*

Only samples from the Vanderbijlpark and Sasolburg sites were chemically analysed because of the high sample loadings on the filters for this week at these sites (Fig 6.1). The elemental concentrations differed at both sites, especially with respect to the carbon species. Substantially higher concentrations of O2TC, O3TC, O4TC and E1TC were measured at the Vanderbijlpark site. Other major elements in both samples were Al, Si, K, Ca, Fe, and Cu. Once again the high gravimetric concentrations were attributed to high contributions from carbon emitting sources.

*Week 19 - (08/26/94 - 09/02/94)*

The samples from this week were representative of the post-winter situation. The sample loadings on the filters were slightly higher than the loadings on filters collected in April and the first week of May. All three sites had a similar distribution of species. The carbon species accounted for a large amount of the measured mass concentration. Major species at all sites were Al, Si, K, Ca, Fe, $Cl^-$ (Vereeniging and Vanderbijlpark only) $NO_3^-$, $SO4_2^-$, O2TC, O3TC, O4TC, and E1TC.

## 6.3 RESULTS OF CMB7 MODELLING

### 6.3.1 Introduction

A summary of the modelling output is presented in Tables 6.7, 6.8 and 6.9. Pie-charts that supplement these tables are presented in Appendix D. CMB7 output data are presented in Appendix A. Tables 6.7 to 6.9 include the source contribution estimates (SCE), standard error, T-statistic, chi square, r-square and degrees of freedom that were calculated for each sample. These are important source performance measures which were used to evaluate the validity of the calculated source contribution estimate.

None of the samples modelled satisfied the recommended chi-squared value of $\leq 4$ and some of the fits did not fulfill the 80% mass percent requirement. The reasons for this

**Table 6.7:** CMB7 modelling results for Vereeniging.

| Source | VER02 SCE ±Std Err* | T-Stat | VER07** SCE ±Std Err | T-Stat | VER08 SCE ±Std Err | T-Stat | VER12 SCE ±Std Err | T-Stat | VER19 SCE ±Std Err | T-Stat |
|---|---|---|---|---|---|---|---|---|---|---|
| Iscor Sinter plant | 2.9 ± 0.2 | 11.6 | 6.1 ± 0.7 | 8.9 | 5.0 ± 0.5 | 10.3 | 4.1 ± 0.6 | 6.6 | 4.5 ± 0.4 | 10.5 |
| Petrol Vehicle | 1.4 ± 0.1 | 16.4 | 1.1 ± 0.1 | 10.8 | 1.2 ± 0.1 | 15.1 | 2.4 ± 0.2 | 15.2 | 1.3 ± 0.1 | 14.6 |
| Iscor Coking furnace | 6.4 ± 0.7 | 8.5 | 11.9 ± 1.9 | 6.3 | 3.9 ± 0.8 | 4.8 | 3.4 ± 1.4 | 6.0 | 10.8 ± 1.4 | 7.7 |
| Soil | 12.0 ± 0.9 | 13.2 | | | 15.5 ± 1.0 | 15.1 | 23.4 ± 1.7 | 13.9 | | |
| Secondary ammonium sulphate | 6.4 ± 1.0 | 6.4 | | | 5.7 ± 0.9 | 6.1 | | | | |
| Secondary sulphate | | | 5.6 ± 0.9 | 6.1 | | | 6.2 ± 1.0 | 6.0 | 3.9 ± 0.7 | 5.9 |
| Composite flyash | | | | | | | | | 3.8 ± 1.9 | 2.0 |
| Composite domestic coal | | | | | | | 29.6 ± 3.9 | 7.6 | | |
| Composite domestic coal (total) | 1.2 ± 0.2 | 5.0 | 33.1 ± 0.9 | 9.3 | 8.8 ± 0.9 | 9.7 | | | 0.5 ± 0.2 | 2.1 |
| Composite arc furnace | 5.6 ± 0.5 | 12.3 | 18.7 ± 3.6 | 14.4 | 12.3 ± 0.8 | 16.2 | 18.6 ± 1.2 | 15.7 | 11.9 ± 0.9 | 13.0 |
| Composite soil | | | 0.6 ± 0.8 | 0.8 | | | | | 14.5 ± 2.3 | 6.1 |
| Chi-Square | 10.93 | | 28.2 | | 6.94 | | 6.99 | | 7.71 | |
| R-square | 0.91 | | 0.8 | | 0.94 | | 0.95 | | 0.94 | |
| Percentage mass | 71.8 | | 78.2 | | 78.8 | | 81.3 | | 80.8 | |
| Measured mass | 50.0 | | 98.6 | | 66.6 | | 114.0 | | 63.4 | |
| Degrees of freedom | 21 | | 19 | | 18 | | 19 | | 19 | |

*SCE = source contribution estimate in $\mu g/m^3$.
** VER07 Included for completeness as best fit obtained although this fit was not acceptable.

**Table 6.8:** CMB7 modelling results for Vanderbijlpark.

| Source | VAN02 SCE ±Std Err* | T-Stat | VAN08 SCE ±Std Err | T-Stat | VAN12 SCE ±Std Err | T-Stat | VAN13 SCE ±Std Err | T-Stat | VAN19 SCE ±Std Err | T-Stat |
|---|---|---|---|---|---|---|---|---|---|---|
| Iscor Sinter plant | 3.2 ± 0.2 | 11.4 | 4.1 ± 0.4 | 10.0 | | | 4.2 ± 0.6 | 7.4 | 4.7 ± 0.4 | 12.5 |
| Petrol Vehicle | 1.5 ± 0.1 | 16.1 | 0.8 ± 0.1 | 14.7 | 2.2 ± 0.1 | 16.2 | 1.1 ± 0.1 | 12.9 | 0.7 ± 0.1 | 13.8 |
| Iscor Coking furnace | 5.1 ± 0.8 | 6.2 | 1.4 ± 0.5 | 2.7 | 5.0 ± 0.9 | 5.6 | 5.6 ± 1.2 | 4.8 | 3.8 ± 0.8 | 4.8 |
| Soil | 12.0 ± 0.9 | 13.0 | 19.0 ± 1.0 | 18.9 | 18.5 ± 1.2 | 15.4 | 19.0 ± 1.4 | 13.8 | | |
| Secondary ammonium sulphate | 6.7 ± 1.0 | 6.4 | 6.7 ± 1.0 | 6.4 | 9.5 ± 1.5 | 6.3 | | | | |
| Secondary sulphate | | | | | | | 4.6 ± 0.8 | 5.8 | 9.0 ± 1.4 | 6.6 |
| Composite flyash | | | | | | | | | 8.8 ± 1.5 | 5.8 |
| Composite domestic coal | | | 4.3 ± 1.0 | 4.4 | 26.6 ± 2.9 | 9.1 | 24.2 ± 3.3 | 7.3 | | |
| Composite domestic coal (total) | 5.5 ± 0.6 | 8.3 | | | | | | | 1.0 ± 0.2 | 4.5 |
| Composite arc furnace | 8.7 ± 0.6 | 13.1 | | | 13.8 ± 0.8 | 16.8 | 22.2 ± 1.2 | 18.2 | 11.5 ± 0.7 | 16.8 |
| Composite arc furnace (total) | | | 8.6 ± 0.5 | 16.4 | | | | | | |
| Composite soil | | | | | | | | | 4.7 ± 1.8 | 2.6 |
| Chi-Square | 9.3 | | 9.4 | | 8.2 | | 6.6 | | 7.8 | |
| R-square | 0.92 | | 0.92 | | 0.94 | | 0.95 | | 0.94 | |
| Percentage mass | 81.1 | | 84.1 | | 83.0 | | 78.8 | | 76.6 | |
| Measured mass | 67.7 | | 71.8 | | 112.1 | | 134.6 | | 75.5 | |
| Degrees of freedom | 21 | | 21 | | 20 | | 19 | | 19 | |

*SCE = source contribution estimate in $\mu g/m^3$.

**Table 6.9:** CMB7 modelling results for Sasolburg.

| Source | SAS02 SCE ±Std Err* | T-Stat | SAS08 SCE ±Std Err | T-Stat | SAS12 SCE ±Std Err | T-Stat | SAS13 SCE ±Std Err | T-Stat | SAS19 SCE ±Std Err | T-Stat |
|---|---|---|---|---|---|---|---|---|---|---|
| Iscor Sinter plant | 2.3 ± 0.2 | 11.6 | | | 3.4 ± 0.4 | 9.0 | 5.3 ± 0.5 | 10.7 | 3.0 ± 0.3 | 11.8 |
| Petrol Vehicle | 0.8 ± 0.1 | 15.5 | 0.5 ± 0.04 | 13.7 | 0.5 ± 0.04 | 12.3 | 0.7 ± 0.1 | 13.2 | 0.3 ± 0.02 | 12.6 |
| Iscor Coking furnace | 4.2 ± 0.6 | 7.6 | | | 1.5 ± 0.6 | 2.7 | 2.9 ± 0.8 | 3.6 | 1.9 ± 0.4 | 4.3 |
| Soil | 10.6 ± 0.6 | 17.3 | | | 20.2 ± 1.1 | 17.9 | 12.3 ± 2.0 | 6.1 | 8.7 ± 1.6 | 5.5 |
| Secondary ammonium sulphate | 2.5 ± 0.4 | 5.8 | 8.9 ± 1.35 | 6.6 | 9.4 ± 1.1 | 6.5 | | | | |
| Secondary ammonium nitrate | | | 4.5 ± 0.6 | 7.0 | | | | | | |
| Secondary sulphate | | | | | | | 4.4 ± 0.7 | 6.1 | 6.6 ± 1.0 | 6.6 |
| Composite flyash | | | 11.0 ± 0.7 | 15.3 | | | 6.6 ± 1.3 | 5.0 | 9.1 ± 1.1 | 8.6 |
| Composite domestic coal (total) | 1.1 ± 0.2 | 5.5 | | | 1.6 ± 0.3 | 5.4 | 2.7 ± 0.8 | 3.4 | 0.5 ± 0.2 | 3.5 |
| Composite arc furnace | 4.4 ± 0.5 | 9.4 | 12.6 ± 0.5 | 23.5 | 12.9 ± 0.7 | 18.0 | 10.63 ±0.9 | 11.7 | 4.8 ± 0.4 | 12.2 |
| Chi-Square | 9.68 | | 8.81 | | 8.77 | | 6.22 | | 10.99 | |
| Percentage mass | 0.93 | | 0.91 | | 0.93 | | 0.95 | | 0.93 | |
| Percent mass | 84.9 | | 78.4 | | 74.0 | | 80.2 | | 77.8 | |
| Measured mass | 30.4 | | 47.9 | | 67.1 | | 56.5 | | 45.0 | |
| Degrees of freedom | 18 | | 22 | | 22 | | 17 | | 17 | |

*SCE = source contribution estimate in $\mu g/m^3$.

percentage of >70% and a chi-square of <11 were accepted as a successful result for the purposes of this thesis. The rationale for these limits and reasons for non-attainment will be discussed in the following sections.

Wind roses representative of the surface wind conditions during each sampling week are presented in Figure 6.2. The wind data used were obtained from Eskom's Makalu air monitoring station which is situated approximately 3 km south east of Sasolburg (Fig 2.1).

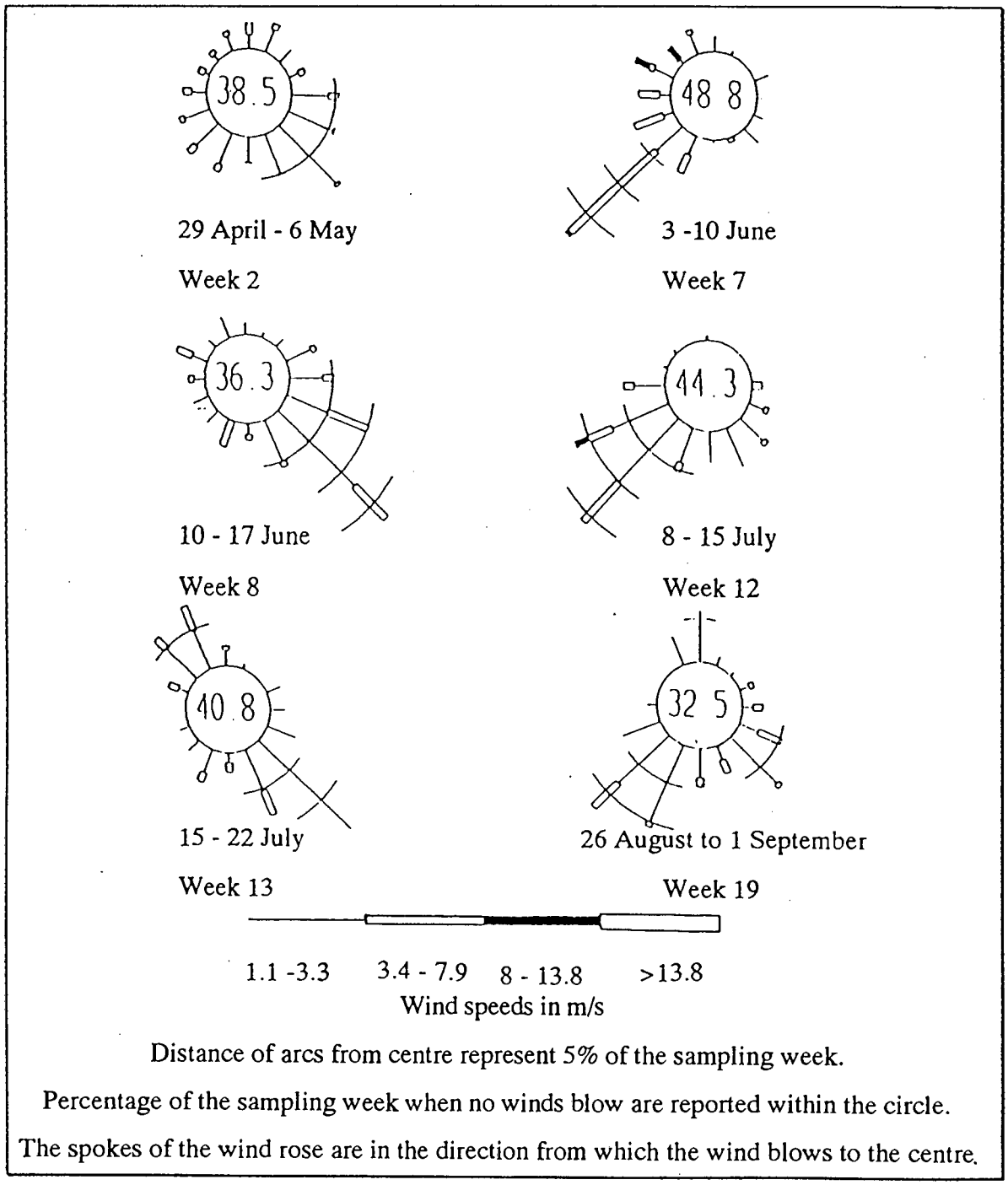



**Figure 6.2:** Weekly wind roses

### 6.3.2 Week 02 (04/29/94 - 05/06/94)

No single wind direction dominated the prevailing winds for this week (Fig 6.2). Calm periods (no wind) were observed for 38% of the sampling week. The prevailing winds that were recorded during the week rarely exceeded 3.3 m/s but did reach a maximum of 7.9 m/s. Winds blowing from the southeast at a speed not exceeding 3.3 m/s prevailed for approximately 10 % of the week.

6.3.2.1 Vereeniging receptor site (VER 02-Appendix A, Table A1; Appendix D, Fig. D1)

Soil dust was the largest known contributor for this week and accounted for 24% of the total particulate matter collected. The coking furnace, composite arc furnace and secondary ammonium sulphate sources accounted for 13%, 11% and 13% of the contributions respectively. Domestic coalfire, motor vehicle and sinter plant emissions were minor contributors to the particulate matter collected.

Due to the lack of winds no specific arc furnace was identified as a contributor to this receptor site and the composite arc furnace profile best explained the receptor measurements. This profile probably was more representative because of the mixing and ageing of accumulated particulate matter in a static atmosphere. The low contribution from domestic coal fire emissions were attributed to the fact that this sample was collected before winter.

For this sample the chi-square calculated was 10.93 and the mass percentage was less than the recommended value of 80% (71.8%). These values can be attributed to missing sources. From the species concentration display (Appendix A), negative R/U ratios were calculated for five of the carbon species, suggesting that a high carbon emitting source was missing from the source library. Ca was not modelled because one of the sources was contributing too much of Ca to the fit which resulted in a high chi-square value. Using the criteria discussed in section 5.2.5.3 and Fig. 5.3 the soil profile was identified as the high Ca source. The high negative R/U ratio (-6.7) for Br suggests that a Br source was missing and that motor vehicle emissions are possibly not the only source of Br since the model calculates a positive R/U ratio for Pb. Therefore missing sources can explain the high chi-square and the low mass percent.

6.3.2.2 Vanderbijlpark receptor site (VAN 02 - Appendix A, Table A2; Appendix D, Fig D2)

The source contributions calculated for this receptor sample were similar to those calculated for the Vereeniging site with two exceptions, namely, the domestic coalfire contribution increased is 10% and the arc furnace emission is 16%. Once again the composite arc furnace profile was used as a fitting source. The closer proximity of this site to the townships and Iscor possibly explains the increased contributions from these sources.

Only the chi-square did not satisfy the recommended value of <4 for this fit. The R/U ratios displayed characteristics that were similar to those observed for the Vereeniging sample and the same explanation is probably true for this sample.

6.3.2.3 Sasolburg receptor site (SAS 02 - Appendix A, Table A3; Appendix D, Fig D3)

Source contributions for this site displayed a similar pattern to the Vereeniging and Vanderbijlpark sites, except for the soil contribution, even though the total measured mass concentration for this sample was approximately 50% of the mass concentration measured at the other two sites. Contribution from the soil source was approximately 10% higher than the contributions at Vereeniging and Vanderbijlpark. Contribution from the ammonium sulphate source was much lower than that calculated for the other two sites.

Only the chi-square of did not satisfy the recommended value of <4. The R/U ratios calculated displayed characteristics similar to those observed at the other two sites. Zn and Mn were not modelled in this calculation because they had high negative R/U ratios especially for Zn. Even though the composite arc furnace profile was modelled, the negative R/U ratio for Zn suggests that another Zn source may be influencing this site and this source may be missing from the chemical source inventory.

### 6.3.3 Week 07 (06/03/94 - 06/10/94)

Calm windless conditions were experienced for approximately 50% of the week. For approximately 15% of the week a 3.4 to 7.9 m/s south-westerly wind prevailed. The rest of the time there was no prevailing wind of any significance (Fig. 6.2).

6.3.3.1 Vereeniging receptor site (VER 07 - Appendix A, Table A4; Appendix D, Fig D4)

The sample from the Vereeniging site was the only one modelled because the highest gravimetric loading for this site was recorded during this week.

The calculated source contribution calculations for this sample resulted in a very poor fit. None of the recommended model performance measures were satisfied. The best result obtained is listed in Table 6.6. However this result was not acceptable. Too many sources were identified as appearing in the similarity/uncertainty display, suggesting a strong colinearity amongst contributing sources. Removal of certain species does reduce collinearity. However this did not result in a satisfactory solution because species diagnostic of certain sources were excluded and this resulted in improbable solutions and too many of the model performance measures were not being satisfied.

### 6.3.4 Week 08 (06/10/94 - 06/17/94)

Calm air conditions were recorded for 36.3% of the week. Winds from the southeast prevailed for approximately 40% of the week. Southeasterly winds with speeds between 3. and 7.9 m/s prevailed for approximately 5% of the time.

6.3.4.1 Vereeniging receptor site (VER 08 - Appendix A, Table A5; Appendix D, Fig D5)

Soil dust (23%), composite arc furnace (18%), and domestic coalfire (13%) sources were identified as the major contributors to this site for this week. Other contributors included secondary ammonium sulphate (9%), Iscor's sinter plant (8%), Iscor's coking furnace (6%) and petrol vehicle (2%) sources. The prevailing winds did not influence the contribution of the point sources on the receptor site.

The mass percent of 78.8% and a chi-square of 6.94 were slightly worse than the recommended values. Nevertheless this fit was accepted because all other performance measures were satisfied within reasonable limits. The $Cl^-$ ion was not modelled for this sample because the fitting sources were contributing too much of $Cl^-$ to the calculated receptor concentration. This could also mean that too little $Cl^-$ is being measured at the receptor site suggesting that all the chlorine present in the sample may not be present as the soluble chloride ion. The R/U ratios of the low temperature carbon species, Zn and Br were significantly negative and therefore suggest that sources contributing to these species were missing from the source data base.

6.3.4.2 Vanderbijlpark receptor site (VAN 08 - Appendix A, Table A6; Appendix D, Fig D6)

Major contributors at this site were soil dust (35%), composite arc furnace (16%), and secondary ammonium sulphate (12%) sources. Minor contributions from domestic coalfire (8%), Iscor's sinter plant (8%), Iscor's coking furnace (3%) and motor vehicle (2%) sources were calculated. The sources contributing to this site were the same as those that contributed to the Vereeniging site.

For this sample only the chi-square did not satisfy the recommended value of <4. All other performance measures were satisfactory and this source contribution model was accepted as being a reasonable solution. The high chi-square was attributed to missing sources which resulted in negative R/U ratios being calculated for some species. $Cl^-$ was not modelled for the same reasons as was the case for the Vereeniging sample. A R/U ratio of -6.7 meant that a Ca contributing source was missing.

6.3.4.3 Sasolburg receptor site (SAS08 - Appendix A, Table A7; Appendix D, Fig D7)

Source contributions for this site differed significantly from those calculated for the other two sites. The composite arc furnace (26%), domestic coalfire (23%) and secondary ammonium sulphate (19%) sources were the major contributors to this site. Secondary ammonium nitrate (9%) and petrol vehicle emissions (1%) were minor contributors to this site for this week.

A mass percent of 78.4% and a chi-square 8.81 were calculated but these results were accepted because R/U ratios of the major species were negative, which were caused by missing sources. K was not modelled for this sample because of a high negative R/U ratio. This is possibly due to the fact the sinter plant was not a contributing source for this sample. Although the sinter plant is recognised as a K emitting source, the model did not use the sinter plant as a fitting source. The trends observed for the low temperature carbon species, Pb and Br are similar to those observed for these species at other sites for this week. A high number of fitting species have negative R/U ratios, suggesting that there are quite a few missing sources.

### 6.3.5 Week 12 (07/08/94 - 07/15/94)

Calm conditions prevailed for 44.3% of this week. Winds blowing from the south-west prevailed for approximately 30% of the week. Wind speeds as high as 3.4 to 13.8 m/s from the south-west prevailed for approximately 5% of the week.

6.3.5.1 Vereeniging receptor site (VER 12 - Appendix A, Table A8; Appendix D, Fig D8)

Domestic coalfire emissions (26%), soil dust (21%), and the composite arc furnace emissions (16%) were identified as the major contributing sources to this site for the week. Minor sources include secondary sulphate (5%), Iscor's sinter plant (4%), petrol vehicles (2%) and Iscor's coking furnace (3%). The high contribution from domestic coalfire emissions was not unexpected because this sample was collected in mid-winter, the period during which domestic coalfire emissions reach their highest levels. In addition to this, calm windless conditions prevailed for 44.3% of the week, when the build-up of airborne particulate matter increases. High contributions from sources within Iscor can also be attributed to the fact that the receptor site was also downwind of Iscor. High contributions from soil dust can attributed to the prevailing winds which caused the resuspension of soil dust.

A chi-square of 6.99 was the only performance measure that did not satisfy the recommended value (<4) and this was attributed to missing sources which resulted in negative R/U ratios for the low temperature carbon species, Br, and Ca. $Cl^-$, E2TC and E3TC carbon species were not modelled because of their high positive R/U ratios which suggested that some of the sources used were contributing too much of these species to the receptor site.

6.3.5.2 Vanderbijlpark receptor site (VER12 - Appendix A, Table A9; Appendix D, Fig D9)

The source contributions calculated for this sample were similar to the result obtained for the Vereeniging site. Domestic coalfire (30%), soil dust (20%), arc furnace (15%) and secondary ammonium sulphate (10%) sources were the major contributors of particulate matter to this site during this week. The coking furnace (6%) and petrol vehicle (2%) emissions were minor contributors to this sample. High domestic coalfire emissions are expected because of the close proximity of this site to the townships of Bophelong,

Bonanne and Sharpeville and the long period of calm windless conditions that prevailed during this week.

All the source performance measures were satisfied except for the chi-square. Once again this value was attributed to missing low temperature carbon and K sources. The sinter plant profile was not used as a contributing source for this sample and therefore a negative R/U value was calculated for K. This is an indication that an unknown K source was contributing to this site. This could be a wood burning source which are known to have high concentrations of K (Engelbrecht *et al.,* 1994) (cf. Table 2.1).

6.3.5.3 Sasolburg receptor site (SAS12 - Appendix A, Table A10; Appendix D, Fig D10)

The source contributions for this sample differed significantly from the contributions estimated for the other two sites during this week. Soil dust (31%), arc furnace (19%) and secondary ammonium sulphate (14%) sources were identified as the major contributors for this sample. Minor contributions were from Iscor's sinter plant (5%), Iscor's coking furnace (2%) and motor vehicle (1%) emissions. The lower contribution from domestic coalfire emissions was not unexpected since Sasolburg is situated upwind of the large townships which are likely sources. A peculiar observation was the high contributions from industrial sources situated downwind of the receptor site. However calm conditions prevailed for 44.3% of the week, and this receptor site was upwind of the major sources of domestic coalfire emissions. South-westerly winds prevailed for approximately 30% of the week. The high contribution attributed to soil dust can be explained by the presence of open agricultural lands upwind of the receptor site.

### 6.3.6 Week 13 (07/15/94 - 07/22/94)

Only samples from the Vanderbijlpark and Sasolburg sites were modelled for this week because the highest sample loadings for these sites for the entire sampling period were recorded during this week. Calm periods prevailed for 40.8% of the time. Winds from the north-west prevailed for about 15% of the week and southeasterly winds were recorded for approximately 25% of the week. Wind speeds rarely exceeded 3.3 $ms^{-1}$ for significant periods (≤10%) from any specific direction (Fig 6.2).

6.3.6.1 Vanderbijlpark receptor site (VAN13 - Appendix A, Table A11; Appendix D, Fig D11)

The major sources of contribution for this week were domestic coalfire (24%), arc furnace (22%) and soil dust (19%). Minor contributions were from Iscor's coking furnace (5%), secondary sulphate (4%), Iscor's sinter plant (4%) and petrol vehicle (1%) sources. Increased domestic coalfire emissions were due to an increase in coal burning over the winter months. The high total emission from Iscor was once again attributed to the close proximity of this receptor site to Iscor's Vanderbijlpark works, and the static air conditions recorded for a considerable period during this week.

Besides the mass percentage (78.8%) and chi-square (6.6) all other performance measures were adequately satisfied. Therefore this result was accepted as a reasonable source contribution estimate. $Cl^-$ and the carbon species E3TC were the two major species not modelled for this sample.

6.3.6.2 Sasolburg receptor site (SAS13 - Appendix A, Table A12; Appendix D, Fig D12)

Soil dust (22%), arc furnace (19%) and composite power station flyash (12%) are the major contributors to this site. Minor contributors include Iscor's coking furnace (5%), secondary sulphate (8%), Iscor's sinter plant (9%) and petrol vehicle (1%) sources. The composite power station flyash profile was the only new source type contributing to this site when compared to previous weeks. There is no obvious explanation for the increased flyash contribution. However one possibility is that the filtering systems at the power stations were not operating optimally during this week and therefore a higher amount of flyash was emitted into the atmosphere Another possibility is that Sasol's power station which is close to the receptor site may be influencing this site since its stack is not as high as the Eskom stack. This may also explain the absence of flyash at Vanderbijlpark.

The chi-square of 6.22 did not fulfill the recommended performance measure. However all other performance measures were adequately satisfied. $Cl^-$ and Zn were the only two major elements that were not modelled. $Cl^-$ had a high positive R/U ratio suggesting that the $Cl^-$ measured at the receptor site was lower than the contributions calculated for the fitting sources. For Zn a negative R/U ratio suggests that a high Zn source was missing from the source inventory.

### 6.3.7 Week 19 (08/26/94 - 09/02/94)

The samples from this week were modelled to represent the post-winter situation when the strong inversion layer was not present to restrict particulate matter to the lower parts of the air basin.

Windless conditions were recorded for 32.5% of the week. Although no single wind direction dominated during the week, southeasterly winds were recorded for 15% of the time and southwesterly winds were recorded for 25% of the time. Winds speeds rarely exceeded 3.3ms$^{-1}$. Therefore the prevailing winds did not have a strong influence on the dispersion of particulate matter.

#### 6.3.7.1 Vereeniging receptor site (VER19 - Appendix A, Table A13; Appendix D, Fig D13)

The major contributors to this sample were soil dust (23%), the composite arc furnace (19%) and Iscor's coking furnace (17%). Minor contributors were Iscor's sinter plant (7%), secondary sulphate (6%), composite power station flyash (6%), petrol vehicle (1%), and domestic coalfire (1%) sources. The domestic coalfire contribution had decreased considerably when compared to the mid-winter contributions. Two reasons can explain this observation. Firstly, coal burning had decreased with the end of winter and secondly the inversion layer had weakened. Hence there was no restriction of particulate matter to the lower parts of the atmosphere. The power station flyash contribution was detected for the first time at this site and was also an indication of a weakening in the influence of the inversion layer.

With the exception of the chi-square all other performance measures satisfied the recommended values. The high chi-square value was attributed to a missing low temperature carbon source because the low temperature carbon sources had high negative R/U ratios. The $Cl^-$ ion was modelled.

#### 6.3.7.2 Vanderbijlpark receptor site (VAN19 - Appendix A, Table A14; Appendix D, Fig D14)

Major contributors to this site were the arc furnace (20%), secondary sulphate (16%) and the composite power station flyash (15%) sources. Minor contributions came from soil dust (8%), Iscor's coking furnace (7%), domestic coalfire (2%) and petrol vehicle (1%)

sources. The source contributions for this sample followed the trend observed for the source contributions calculated for the Vereeniging site with the only exception being the lower soil dust contribution.

The chi-square and mass percentage did not satisfy the recommended performance measure values. The other measures were satisfactory and therefore this result was accepted. The high chi-square value was as a result of a missing low temperature carbon source.

6.3.7.3 Sasolburg receptor site

The major contributors to this site were the composite power station flyash (20%), soil dust (19%) secondary sulphate (15%) and arc furnace (11%) sources. Minor contributions were from Iscor's sinter plant (7%), Iscor's coking furnace (4%), domestic coalfire (1%) and petrol vehicle (1%) emissions. For this week the power station flyash contribution was the highest calculated from this source for all the sites and all samples. The secondary sulphate source contribution was higher than the contribution calculated for the Vereeniging site but the similar to that calculated for the Vanderbijlpark site. Iscor's sinter plant contribution to this site.

The chi-square and mass percentage calculated for this source were higher and lower than the recommended values respectively. However these values are acceptable because most of the fitting species have negative R/U ratios especially the low temperature carbon and Zn. These negative values suggest sources contributing these species were missing from the source inventory.

# CHAPTER 7

# 7. DISCUSSION AND CONCLUSIONS

## 7.1. DATA COLLECTION

### 7.1.1 Sample collection strategy

Sampling procedures using the NAAQ $PM_{10}$ standard guidelines were successfully implemented. Therefore, all data collected from this study can be compared with studies that have adhered to the NAAQ $PM_{10}$ standard. Sampling equipment which was designed and manufactured at Mintek was found to be adequate for the sampling purposes of the VAM project.

### 7.1.2 Chemical analysis

EDXRFS was successfully used to obtain chemical data for 19 inorganic elements. The 19 elements are Al, Si, K, Ca, Ti, Cr, Mn, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Mo, Ba and Pb. The non-destructive nature, minimum sample preparation and the ability to analyse most of the elements used for receptor modelling makes EDXRFS a suitable analytical method for receptor modelling studies. Elements such as Na, Mg, P, S and Cl can be determined by the Spectro X-Lab EDXRFS instrument but suitable calibration data must be obtained.

Although S and Cl were not determined by EDXRFS, ions of these elements viz. $SO_4^{2-}$ and $Cl^-$ were determined by ion chromatography. Ion chromatography was also used to determine $NH_4^+$ and $NO_3^-$. The determination of ions by ion chromatography was successful and the methods used were compatible with those recommended by the DRI.

Na and Mg were successfully determined by AAS and V was suitably analysed by ICP-MS. However, these techniques require time consuming sample preparation and the contamination of samples, especially with Na, is likely. A few trace elements, the most important being Cd and Hg from an environmental point of view, were not determined by EDXRFS because they were below the detection limit. However, these elements can be determined by ICP-MS if they are required for receptor modelling.

The carbon analyses obtained were satisfactory and the identification of seven carbon species proved useful for modelling purposes.

## 7.2. DATA VALIDATION

The methods used for data validation were successful as they ensured that poor and incorrect data were detected and could be excluded from the database. Systematic recording of information proved to be useful, especially when anomalous data were detected since detection of the sources of problems was made easier and corrections made. The levels of data validation defined also ensured that rigorous checks on data were possible throughout the data accumulation process.

The availability and use of more than one analytical technique to cross-check and verify the results obtained by another method was shown to be a useful tool for data validation purposes.

## 7.3 MODELLING RESULTS

### 7.3.1 Model performance

Fourteen of the fifteen samples modelled were satisfactorily modelled. These fourteen samples had chi-square values of <11. Fourteen of the fifteen samples modelled had calculated mass percentages of >70% and seven of the fourteen samples had calculated mass percentages of >80%. Fourteen of the fifteen samples modelled had R-square ($R^2$) values of >0.9. Only the Vereeniging sample collected during week seven was not satisfactorily modelled. Results for samples which had a chi-square of <11, a calculated mass percent of >70% and $R^2$ >0.9 were accepted as satisfactory source contribution estimates.

The high chi-square and low mass percent values were as a result of missing sources. Sources identified to supplement the existing source inventory were:

- A low temperature combustion process to account for the high negative R/U ratios that have been calculated for the low temperature carbon species. A possible source is the contribution from diesel vehicle emissions which have high concentrations of low temperature carbon. However, the CMB7 model is rejecting the existing diesel vehicle source profile as a fitting source suggesting that this profile is not representative of

diesel emissions in the Vaal Triangle. The S and $SO_4^{2-}$ content in this profile is significantly lower than the S and $SO_4^{2-}$ content of the US-EPA diesel profiles (Core *et al.,* 1984). This is expected since local fuels have a high synthetic fuel content. A chemical profile representative of urban road-dust could be a major contributing source. This profile should include dust from tyre rubber, brake-linings and urban dust. Another possible low temperature carbon source is a wood burning profile unique to the Vaal Triangle.

- An additional high Zn source to account for the high Zn concentrations is required, since the Zn from arc furnace emissions does not account for all the Zn measured at the receptor sites. This observation confirms the existence of other Zn sources which are know to exist in the Vaal Triangle (Annegarn *et al.,* 1992; de Villiers and Engelbrecht, 1991).

- An additional source for Br is required since motor vehicle emissions do not account for all the Br measured at the receptor sites.

- An additional source for Ca must be characterised because whenever Ca was used as a fitting species, high negative R/U values were calculated. High Ca contributing sources were also identified by de Villers and Engelbrecht (1991) and Mühlenbruch-Tegen *et al.* (1992).

The model is overestimating the amount of $Cl^-$ that the fitting sources are contributing to the receptor sites for the winter samples only. This discrepancy could be due to the fact that only soluble chlorine was determined and total chlorine must be determined on the receptor and source samples. As a result, $Cl^-$ was excluded as a fitting species especially for the mid-winter samples.

Na was found to be a problem species for the modelling program. In some cases the model reports a negative calculated value which is physically impossible. However excluding or including Na as a fitting species does not affect the source contribution estimates.

Although a few sources were found to be missing from the source inventory, the CMB7 model succeeded in calculating source contributions for the samples modelled. The results can be improved by characterising those sources that are not available in the present database. Compositing profiles improves the results but more research following the

guidelines of Chow *et al.* (1994) is required. Chow *et al.* (1994) recommend that mixing similar source profiles to obtain the best source-type improve the model fits. In this study composite profiles provided better fits because each sample was collected over a week and weekly samples represent an average of daily events and similar sources will not be easily identified.

### 7.3.2 Contributing sources

The thirteen different sources identified as contributors to the three sites are listed in Table 7.1.

Compositing similar primary source measurements to represent a source-type explained receptor measurements better than when individual sources were modelled. Very similar sources usually resulted in high collinearity of profiles and therefore poor modelling fits were obtained. The composite source types are also identified in Table 7.1. The absence of strong winds during the sampling period allowed for the buildup of airborne particulate matter in the air basin and therefore similar sources had become indistinct thereby resulting in composite profiles better explaining receptor measurements.

The arc furnaces source type has been identified as a major contributor to airborne particulate matter in the Vaal Triangle. Contributions range from a minimum of 11% to a maximum of 26%.

Soil dust is the other major source of airborne particulate matter with contributions ranging from a minimum of 0% to a maximum of 35%.

Domestic coalfire emissions peak in mid-winter at 30 %.

Minor contributors at all sites were Iscor's sinter and coking plants, secondary ammonium sulphate and secondary sulphate.

Petrol motor vehicle emissions make a very small contribution to observed receptor measurements.

**Table 7.1:** List of contributing sources

| Primary source | Composite source | Secondary source |
|---|---|---|
| Iscor's sinter plant | Composite flyash | Secondary ammonium sulphate |
| Iscor's coking furnace | Composite domestic coalfire | Secondary sulphate |
| Petrol vehicle | Composite domestic coalfire (total) | Secondary ammonium nitrate |
| Soil | Composite soil dust | |
| | Composite arc furnace | |
| | Composite arc furnace (total) | |

### 7.3.3 Effects of seasonal change on source contributions

Seasonal effects strongly influence total contributions of only some source types. Most notable is the variation in the contribution from domestic coalfire emissions. Contribution from this source peaked in June and July when ambient temperatures were at their lowest. Contributions during April and May and at the end of August are <10% compared to the mid-winter high of 35%.

The composite power station flyash source type also seems to be affected by the change in season. Flyash contributions increase towards the end of winter especially in the samples collected at the end of August. This observation may be as a result of a weakening in the inversion layer as temperature increases during August. This allows the flyash which is emitted by tall stacks above the inversion layer, to impact on the receptor sites.

The absence of strong winds during the sampling period was probably a reason for source contribution estimates at all three sites being very similar for most of the samples.

# CHAPTER 8

# 8. RECOMMENDATIONS FOR FUTURE WORK

## 8.1 CMB7 MODELLING

1. The source inventory needs to be supplemented with new chemical data for diesel vehicle emissions because none of the samples modelled had a diesel source contribution estimate. When compared to the US EPA diesel profile S and $SO_4^{2-}$ were present in significantly lower concentrations in the local profile.

2. An urban road dust source needs to be characterised because it was identified as a missing source from the CMB7 result. Van Nierop (1994) also identifies road dust source to be a major source of airborne particulate matter in the Vaal Triangle.

3. Additional sources for Br, Ca and Zn need to characterised since contributions from these source types were clearly missing form the present source inventory. Arc furnaces are considered to be a major source of Zn in the Vaal Triangle. Representative arc furnace source data must be obtained because arc furnace emissions are dependent on the input raw materials which is variable. This results emissions from arc furnaces being variable.

4. Compositing similar source profiles have improved the modelling results. However research is required with respect to obtaining composite profile that are truly representative of sources in the Vaal Triangle.

5. The data used for this study should be used for multivariate statistical modelling (MVA) and the modelling results compared with that of CMB7. This will be useful to identify sources that are missing from the present source inventory. Also MVA can be used to generate these source profiles.

6. CMB7 modelling can be complimented by individual particle scanning electron microscopy (SEM) based analyses in order to obtain. Preliminary work at Mintek has shown that SEM based analyses can be used to confirm CMB7 modelling results by use of tracer particles that are diagnostic of the various processes (e.g. Zn rich particles that are representative of electric arc furnaces).

# CHAPTER 8

# 8. RECOMMENDATIONS FOR FUTURE WORK

## 8.1 CMB7 MODELLING

1. The source inventory needs to be supplemented with new chemical data for diesel vehicle emissions because none of the samples modelled had a diesel source contribution estimate. When compared to the US EPA diesel profile S and $SO_4^{2-}$ were present in significantly lower concentrations in the local profile.

2. An urban road dust source needs to be characterised because it was identified as a missing source from the CMB7 result. Van Nierop (1994) also identifies road dust source to be a major source of airborne particulate matter in the Vaal Triangle.

3. Additional sources for Br, Ca and Zn need to characterised since contributions from these source types were clearly missing form the present source inventory. Arc furnaces are considered to be a major source of Zn in the Vaal Triangle. Representative arc furnace source data must be obtained because arc furnace emissions are dependent on the input raw materials which is variable. This results emissions from arc furnaces being variable.

4. Compositing similar source profiles have improved the modelling results. However research is required with respect to obtaining composite profile that are truly representative of sources in the Vaal Triangle.

5. The data used for this study should be used for multivariate statistical modelling (MVA) and the modelling results compared with that of CMB7. This will be useful to identify sources that are missing from the present source inventory. Also MVA can be used to generate these source profiles.

6. CMB7 modelling should be complimented by individual particle scanning electron microscopy (SEM) based analyses. Preliminary work at Mintek has shown that SEM based analyses can be used to confirm CMB7 modelling results by use of tracer particles that are diagnostic of the various processes (e.g. Zn rich particles that are representative of electric arc furnaces).

## 8.2 GENERAL

1. In any future study closer attention needs to be given to the role of climatological and topographical effects on the dispersion of particulate matter in the Vaal Triangle and they should be integrated with CMB modelling results. The climatological and topographical effects are known to influence the dispersion of airborne particulate in the Vaal Triangle (de Villiers and Engelbrecht, 1991).

2. Receptor modelling of $PM_{2.5}$ particulate matter should be considered in future, because the high contributions from soil dust for the PM10 fraction dominates the source contributions. Soil dust could be regarded as part of the natural background contribution. Also $PM_{2.5}$ dust has a greater impact on human health.

3. Future studies should concentrate on 24-hour sampling periods so that polluting events can be accurately identified because one week sampling only gives an average source contribution estimate for the week. This immediately masks individual pollution events as well as the influence of prevailing winds on the dispersion of airborne particulate matter.

# 9. ACKNOWLEDGMENTS

This study was undertaken in the Mineralogy and Process Chemistry Division at Mintek and I would therefore like to thank the following staff members for their help and support:

Dr. JPR de Villiers for giving me the opportunity to attend the Environmental Geochemistry MSc course at UCT.

Dr. Johann Engelbrecht for his technical supervision during the study.

Mr. Leon Swanepoel for sample collection.

Mrs. Jeanne Mostert for filter preparation and weighing.

Mr. Basil Eddy for his supervision during the calibration of the EDXRFS instrument.

Members of staff of Mintek's Analytical Science Division for allowing me to use the ICP-MS and AAS instruments and also for their assistance during analysis.

Dr. Frank Divita of the Desert Research Institute in Reno, Nevada, USA for the carbon analyses and for assisting me with formatting the data base for CMB7 modelling.

I would also like to thank the following organisations and individuals for their contributions:

Mintek for financial support during the course of this year.

The Department of National Health and Population Development for permission to use the data from the VAM project.

Eskom for permission to use the data from the VAM project as well as for supplying me with wind data.

The Desert Research Institute in Reno, Nevada, USA for their co-operation and guidance since the inception of source apportionment studies in South Africa in 1990.

Professors JP Willis of the University of Cape Town and HA Annegarn of the University of Witwatersrand for their supervision and advice during the study.

Finally I would like to thank all my family and friends for their support during my studies.

# 10. REFERENCES


Annegarn HJ, Müller C, Lipworth AD, Frewin MA, Tucker OD and Zucchiatti (1991) Source profiles from ambient monitoring sites - time-sequence sampling and wind trajectory analysis. *Proceedings of the 1992 NACA - Air pollution and the environment conference,* 14-15 November 1991.

Barnes DE (1985) The determination of selected alkali metals and ammonium by single-column ion chromatography. *Mintek Report.,* **No. M215.**

Benarie MM. (1987) The limits of air pollution modelling. *Atmospheric Environment* **21** No. 1, p. 1-5.

Cameron A and Pohlandt C, (1987) The simultaneous determination of common anions by ion chromatography. *Mintek Report.,* **No. M222D.**

Chow JC and Richards WL. (1989) Monitoring and analysis for aerosols and visibility. *Technical proposal for San Joaquin Valley Air Quality Study (SJVAQS) / Atmospheric Utility Signatures - Predictions and Experiment.,* **Part F.**

Chow JC, Watson JG, Pritchett LC, Pierson WR, Frazier CA and Purcell RG. (1993) The DRI thermal/optical reflectance carbon analysis system: Description, Evaluation and Applications in U.S. air qualities studies. *Atmospheric Environment,* **27B** No 8, p 1185-1201.

Chow JC, Watson JG, Lu Z, Fujita EM, Lowenthal DH and Lawson DR. (1994) Chemical Mass Balance Source Apportionment of $PM_{10}$ during the Southern California Air Quality Study. *Aerosol Science and Technology,* **21**, p 1-36.

Chow JC, Fujita EM, Watson JG, Lu Z, Lawson DR and Ashbaugh LL. (1994b) Evaluation of filter-based measurements during the 1987 Southern California Air Quality Study. *Environmental Monitoring and Assessment,* **30**, p49-80.

Commission of Trace Analysis of the committee for Analytical Chemistry of the Polish Academy of Sciences. *Certificate for the Polish certified reference material fine flyash CTA-FF1,* Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, 03-195 Warszawa, Poland

Cooper JA and Watson JG. (1980) Receptor orientated methods of air particulate source apportionment. *Journal of Air Pollution Control Association,* **30** No 10, p. 1116-1125.

Core JE, Shah JJ and Cooper JA. (1984) Receptor model source composition library. *US EPA Office of Air Quality Planning and Standards report,* **EPA-450/4-85-002.**

Currie LA, Gerlach RW, Lewis CW, Balfour WD, Cooper JA, Dattner SL, De Cesar RT, Gordon GE, Heisler SL, Hopke PK, Shah JJ, Thurston GD and Williamson HJ. (1984) Interlaboratory comparison of Source Apportionment Procedures: Results for simulated data sets. *Atmospheric Environment.* **18** No 8, p. 1517-1537.

De Villiers JPR and Engelbrecht JP (1991) Pilot study in source apportionment of atmospheric particulates in the Vaal Triangle. *Mintek Communication.,* **C1664M.**

Dzubay TG and Nelson RO (1975) Self Absorption Corrections for X-Ray Fluorescence Analysis of Aerosols, *in Advances in X-Ray Analysis,* Pickles L, Barrett CS, Newkirk JB and Ruud C., Editors. Plenum Press. p 619-631.

Dzubay TG and Stevens RK (1991) Sampling and analysis methods for ambient PM-10 aerosol, *in Receptor modelling for air quality management,* Hopke PK, Ed, Elsevier Science Publishers B.V., Amsterdam. p. 11-44.

Dzubay TG, Stevens SK, Gordon GE, Olmez I, Sheffield AE and Courtney WJ (1988) A composite receptor model applied to Philadelphia aerosol. *Environmental Science and Technology* **22** No 1 p. 46-52.

Dzubay TG, Stevens RK, Balfour WD, Williamson HJ, Cooper JA, Core JE, De Cesar RT, Crutcher ER, Dattner SL, Davis BL, Hiesler SL, Shah JJ, Hopke PK and Johnson DL. (1984) Interlaboratory comparison of Receptor Model Results for Houston Aerosol. *Atmospheric Environment* **18** No 8, p. 1555-1566.

Ehrman SH, Pratsinis SE and Young JR. (1992) Receptor modelling of the fine aerosol at a residential Los Angeles site. *Atmospheric Environment* **26B** No. 4, p. 473-481.

Engelbrecht JP, Reddy VS, Swanepoel L, Mostert JC, Stuckenberg B, de Beer H and Jones-Watson EA (1993) The establishment of chemical source profiles, and their application to the apportionment of aerosols in the Vaal Triangle. *Mintek Communication.,* **C2023M.**

Engelbrecht JP, Reddy VS, Swanepoel L, Mostert JC, Stuckenberg B and de Beer H (1994) The establishment of chemical and other emissions on the Eastern Transvaal Highveld. *Mintek Communication.,* **C2129M**

Gordon GE. (1980) Receptor Models. *Environmental Science and Technology* **14** No 14, p. 792-800.

Gordon GE. (1988) Receptor Models, A critical review. *Environmental Science and Technology* **22** No 10, p. 1132-1142.

Hopke PK (1985) Sampling and Analytical Methodologies in *Receptor modelling in environmental chemistry.* John Wiley and Sons, New York p. 7-38.

Hopke PK (1991) An Introduction to receptor modelling, in *Receptor modelling for air quality management.* Hopke PK, ed., Elsevier Science Publishers B.V., Amsterdam. p. 1-10.

Henry RC, Lewis CW, Hopke PK and Williamson HJ. (1984) Review of receptor model fundamentals. *Atmospheric Environment* **18** No 8, p. 1507-1515.

Henry RC. (1992) Dealing with near collinearity in CMB receptor models. *Atmospheric Environment* **26A** No. 6, p. 933-948.

Jenkins R and de Vries JL (1970) *Worked Examples in X-Ray Analysis.* Macmillan Press Limited. Thetford, Norfolk.

Mühlenbruch-Tegen A, Annegarn HJ, MA Kneen and Chow JC (1993) Chemical Mass Balance modelling in the Vaal Triangle. *Proceedings of the NACA National Conference - Vaal Triangle,* 8-10 November 1992.

Müller CM (1992) Source apportionment of airborne particulate matter in the Vaal Triangle. *Unpublished MSc thesis.* University of Witwatersrand.

National Bureau Of Standards. Standard Reference Material 1648 - Urban Particulate Matter. *Certificate of Analysis,* US Department of Commerce.

Potts PJ. (1987) *A Handbook of Silicate Rock Analysis.* Blackie. London.

Quiesefit JP, de Chateaubourg P, Garivait S and Steiner E (1994) Quantitative Analyses of Aerosol Filters by Wavelength-Dispersive X-Ray spectrometry from Bulk Reference Samples. *X-Ray Spectrometry* **23** p59-64.

Stuckenberg BL (1993) X-Ray fluorescence and inductively coupled plasma mass spectrometry analysis of airborne particulate matter on filter substrates. *Unpublished MSc thesis.* Faculty of Natural Sciences of the University of Pretoria.

Tegen AM, Annegarn HJ, Chow JC, and Müller C (1992) Final report on to Vaal Air Characterisation Study. *AER Document* **VACS 92 MOD.1**.

Terblanche AP, Opperman L and Nel CME (1991) Vaal Triangle air pollution health study: Design and preliminary results. *Proceedings of the 1992 NACA - Air pollution and the environment conference,* 14-15 November 1991.

Thurston GD and Lioy PJ. (1987) Receptor modelling and aerosol transport. *Atmospheric Environment* **21** No. 3, p. 687-698.

US Environmental Protection Agency. (1994) Guidelines for PM10 sampling and analysis applicable to receptor modelling. *US EPA Office of Air Quality Planning and Standards report,* **EPA-452/R-94-009.**

Van Nierop PG and Annegarn HJ (1994) Results of the 1992 Vaal Triangle source inventory. *Proceedings of the 1994 NACA Clean Air Conference,* 24-25 November 1994.

Wang D and Hopke PK. (1989) The use of constrained least squares to solve the chemical mass balance problem. *Atmospheric Environment* **23** No 10, p. 2143-2150.

Wang S and Larson T. (1993) Ambient error weighted partial least-squares regression: A new receptor model. *Analytica Chimica Acta* **272**, p. 333-337.

Watson JG. (1979) Chemical element balance receptor model methodology for assessing the sources of fine and total particulate matter. *PhD Dissertation,* Oregon graduate centre, Beaverton, OR.

Watson JG, Cooper JG and Huntzicker JJ. (1984) The effective variance weighting for least squares calculations applied to the mass balance receptor model. *Atmospheric Environment.,* **18** No 7, p. 1347-1355.

Watson JG. (1984) Overview of Receptor Model Principles. *Air Pollution Control Association Journal* **34** No 6, p. 619-623.

Watson JG, Chow JC and Mathai CV. (1989) Receptor Models in Air Resources Management: A Summary of the APCA International Specialty Conferences. *Air Pollution Control Association Journal* **39** No 4, p 419-426.

Watson JG, Robinson NF, Chow JC, Henry RC, Kim B, Nguyen QT, Meyer EL and Pace TG. (1990) CMB7 Users Manual. *EPA Receptor Model Technical Series* **3** p. A1-A15.

Watson JG, Chow JC, and Pace TG. (1991) Chemical Mass Balance, *Receptor Modelling for air quality management,* Hopke PK, Ed, Elsevier Science Publishers B.V., Amsterdam. p 83-116.

White WH and Macias ES. (1991) Chemical Mass Balancing with ill-defined sources: Regional apportionment in the California desert. *Atmospheric Environment* **25 A** No. 8, p 1547-1557.

# APPENDIX A

# CMB7 OUTPUT FILES

# Table A1: VER02 CMB7 Output

SOURCE CONTRIBUTION ESTIMATES - SITE: VER02 DATE: 04/29/94
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .91 PERCENT MASS 71.8
CHI SQUARE 10.93 DF 21

| SOURCE * | TYPE | SCE(UG/M3) | STD ERR | TSTAT |
|---|---|---|---|---|
| 1003 | ISCORSP1 | 2.8675 | .2480 | 11.5613 |
| 1006 | PETROL | 1.4299 | .0873 | 16.3840 |
| 1012 | ISCORCF1 | 6.3505 | .7479 | 8.4916 |
| 1017 | SOIL1 | 12.0413 | .9101 | 13.2312 |
| 1019 | AMSUL | 6.4088 | 1.0018 | 6.3975 |
| 1027 | COMCOALT | 1.2038 | .2424 | 4.9656 |
| 1032 | COMARC | 5.5728 | .4539 | 12.2774 |

MEASURED CONCENTRATION FOR SIZE: COARS
50.0+- 5.0

UNCERTAINTY/SIMILARITY CLUSTERS CMB7 33889 SUM OF CLUSTER SOURCES

SPECIES CONCENTRATIONS - SITE: VER02 DATE: 04/29/94 CMB7 33889
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .91 PERCENT MASS 71.8
CHI SQUARE 10.93 DF 21

| SPECIES | I | MEAS | | CALC | | RATIO C/M | | RATIO R/U |
|---|---|---|---|---|---|---|---|---|
| C1 TOT | T | 49.99390+- | 4.99940 | 35.87460+- | 1.22407 | .72+- | .08 | -2.7 |
| C2 NA | * | .45170+- | .03780 | *********+- | 141.56060 | *****+- | ***** | -1.0 |
| C3 MG | * | .31680+- | .00320 | .36901+- | .02197 | 1.16+- | .07 | 2.4 |
| C4 AL | * | 1.50120+- | .09780 | 1.43534+- | .06790 | .96+- | .08 | -.6 |
| C5 SI | * | 3.54390+- | .19050 | 3.25438+- | .13442 | .92+- | .06 | -1.2 |
| C6 P | | -99.00000+- | -99.00000 | *********+- | 283.88410 | .00+- | .00 | -.6 |
| C7 S | | -99.00000+- | -99.00000 | *********+- | 283.88410 | .00+- | .00 | -.6 |
| C8 CL | | -99.00000+- | -99.00000 | *********+- | ********* | .00+- | .00 | -1.9 |
| C9 K | * | 1.24630+- | .06260 | 1.15693+- | .03692 | .93+- | .06 | -1.2 |
| C10 CA | | .06560+- | .00330 | .66065+- | .02935 | 10.07+- | .68 | 20.1 |
| C11 TI | * | .01750+- | .00090 | .01940+- | .00092 | 1.11+- | .08 | 1.5 |
| C12 V | * | .00240+- | .00010 | *********+- | 317.22170 | *****+- | ***** | -1.3 |
| C13 CR | | .00500+- | .00030 | *********+- | 283.88410 | *****+- | ***** | -1.0 |
| C14 MN | * | .44380+- | .02170 | *********+- | 141.56060 | *****+- | ***** | -1.0 |
| C15 FE | * | 2.39580+- | .11810 | 2.50125+- | .08437 | 1.04+- | .06 | .7 |
| C16 NI | * | .00750+- | .00050 | .00723+- | .00036 | .96+- | .08 | -.4 |
| C17 CU | * | .02620+- | .00160 | .02811+- | .00181 | 1.07+- | .10 | .8 |
| C18 ZN | * | .50190+- | .02510 | .31364+- | .01308 | .62+- | .04 | -6.7 |
| C19 GA | * | .00500+- | .00030 | *********+- | ********* | *****+- | ***** | -1.5 |
| C20 AS | * | .00870+- | .00050 | *********+- | 639.89900 | *****+- | ***** | -1.2 |
| C21 SE | * | .00750+- | .00060 | *********+- | ********* | *****+- | ***** | -1.4 |
| C22 BR | * | 1.06510+- | .05390 | .56068+- | .05239 | .53+- | .06 | -6.7 |
| C23 SR | | .00620+- | .00040 | *********+- | 628.70250 | *****+- | ***** | -1.0 |
| C24 MO | | .01250+- | .00070 | *********+- | 628.70250 | *****+- | ***** | -1.0 |
| C25 BA | | .02370+- | .00150 | *********+- | 714.21310 | *****+- | ***** | -1.6 |
| C26 PB | * | .56050+- | .02840 | .68667+- | .02928 | 1.23+- | .08 | 3.1 |
| C27 NH4+ | * | 1.27190+- | .12720 | *********+- | ********* | *****+- | ***** | -1.9 |
| C28 NO3- | * | .83080+- | .08310 | *********+- | 883.31080 | *****+- | ***** | -1.7 |
| C29 SO4= | * | 5.56500+- | .55650 | 5.56525+- | .46879 | 1.00+- | .13 | .0 |
| C30 CL- | * | .96530+- | .09650 | 1.02248+- | .08688 | 1.06+- | .14 | .4 |
| C31 O1TC | * | 1.37960+- | .27590 | .43566+- | .05952 | .32+- | .08 | -3.3 |
| C32 O2TC | * | 3.02250+- | .60450 | .97829+- | .11832 | .32+- | .08 | -3.3 |
| C33 O3TC | * | 10.55610+- | 2.11120 | 1.16596+- | .13143 | .11+- | .03 | -4.4 |
| C34 O4TC | * | 7.06860+- | 1.41370 | .83249+- | .09497 | .12+- | .03 | -4.4 |
| C35 E1TC | * | 7.15130+- | 1.43030 | 1.95434+- | .31412 | .27+- | .07 | -3.5 |
| C36 E2TC | * | .71960+- | .14390 | .74264+- | .08889 | 1.03+- | .24 | .1 |
| C37 E3TC | * | .05200+- | .01040 | .18689+- | .02313 | 3.59+- | .85 | 5.3 |

## Table A2: VAN02 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VAN02        DATE: 04/29/94
SAMPLE DURATION        7D      START HOUR        0         SIZE:    COARS
       R SQUARE        .92     PERCENT MASS      81.1
     CHI SQUARE       9.28               DF        21

   SOURCE
      * TYPE      SCE(UG/M3)     STD ERR       TSTAT
 ---------------------------------------------
 1003    ISCORSP1      3.2425       .2838     11.4263
 1006    PETROL        1.5390       .0958     16.0677
 1012    ISCORCF1      5.1390       .8268      6.2158
 1017    SOIL1        12.0422       .9296     12.9539
 1019    AMSUL         6.6586     1.0457      6.3679
 1027    COMCOALT      5.4984       .6628      8.2962
 1032    COMARC        8.6854       .6635     13.0908
 ---------------------------------------------
 MEASURED CONCENTRATION FOR SIZE: COARS
       52.8+-     5.3

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
 SPECIES CONCENTRATIONS -  SITE: VAN02        DATE: 04/29/94    CMB7 33889
 SAMPLE DURATION        7D      START HOUR        0         SIZE:    COARS
       R SQUARE        .92     PERCENT MASS      81.1
     CHI SQUARE       9.28               DF        21

 SPECIES--I---MEAS-----------------CALC-----------RATIO C/M----RATIO R/U
 C1 TOT    T  52.78390+-  5.27840  42.80506+-  1.36757    .81+-  .09   -1.8
 C2  NA    *    .55540+-   .02720 *********+-152.36150  *****+-*****   -1.0
 C3  MG    *    .43010+-   .23780    .47797+-   .03200   1.11+-  .62     .2
 C4  AL    *   1.63450+-   .10740   1.43144+-   .06678    .88+-  .07   -1.6
 C5  SI    *   3.38150+-   .18420   3.32104+-   .13212    .98+-  .07    -.3
 C6  P      -99.00000+--99.00000 *********+-321.00490    .00+-  .00    -.7
 C7  S      -99.00000+--99.00000 *********+-321.00490    .00+-  .00    -.7
 C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00   -2.1
 C9  K     *   1.44440+-   .07260   1.36792+-   .04200    .95+-  .06    -.9
 C10 CA        .28630+-   .01420    .80976+-   .03030   2.83+-  .18   15.6
 C11 TI    *    .01830+-   .00100    .02263+-   .00090   1.24+-  .08    3.2
 C12 V     *    .00050+-   .00010 *********+-355.32820  *****+-*****   -1.3
 C13 CR         .00570+-   .00030 *********+-321.00490  *****+-*****   -1.0
 C14 MN    *    .45840+-   .02240 *********+-152.36150  *****+-*****   -1.0
 C15 FE    *   3.15260+-   .15500   3.10773+-   .10633    .99+-  .06    -.2
 C16 NI    *    .02860+-   .00170    .01830+-   .00139    .64+-  .06   -4.7
 C17 CU    *    .03310+-   .00200    .02860+-   .00152    .86+-  .07   -1.8
 C18 ZN    *    .49900+-   .02510    .43344+-   .01740    .87+-  .06   -2.1
 C19 GA    *    .00570+-   .00040 *********+-*********  *****+-*****   -1.5
 C20 AS    *    .00980+-   .00050 *********+-745.07860  *****+-*****   -1.4
 C21 SE    *    .00700+-   .00060 *********+-*********  *****+-*****   -1.6
 C22 BR    *   1.03830+-   .05260    .61508+-   .05645    .59+-  .06   -5.5
 C23 SR         .00850+-   .00050 *********+-508.75720  *****+-*****   -1.0
 C24 MO         .01710+-   .00090 *********+-508.75720  *****+-*****   -1.0
 C25 BA         .02250+-   .00150 *********+-825.46970  *****+-*****   -1.8
 C26 PB    *    .64020+-   .03250    .76084+-   .03161   1.19+-  .08    2.7
 C27 NH4+  *   1.64740+-   .16470 *********+-*********  *****+-*****   -1.9
 C28 NO3-  *    .66820+-   .06680 *********+-*********  *****+-*****   -1.6
 C29 SO4=  *   5.82900+-   .58290   5.82925+-   .48689   1.00+-  .13     .0
 C30 CL-   *   1.04950+-   .10500   1.26107+-   .09915   1.20+-  .15    1.5
 C31 O1TC  *    .98710+-   .19740   1.25546+-   .24783   1.27+-  .36     .8
 C32 O2TC  *   3.41520+-   .68300   1.79649+-   .23547    .53+-  .13   -2.2
 C33 O3TC  *  10.34110+-  2.06820   1.89084+-   .22285    .18+-  .04   -4.1
 C34 O4TC  *   8.33010+-  1.66600   1.25100+-   .14492    .15+-  .03   -4.2
 C35 E1TC  *   7.09000+-  1.41800   2.38009+-   .30877    .34+-  .08   -3.2
 C36 E2TC  *    .66910+-   .13380   1.05111+-   .11237   1.57+-  .36    2.2
 C37 E3TC  *    .06570+-   .01310    .36355+-   .04555   5.53+- 1.30    6.3
```

## Table A3: SAS02 CMB7 Output

SOURCE CONTRIBUTION ESTIMATES - SITE: SAS02 DATE: 04/29/94
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .93 PERCENT MASS 84.9
CHI SQUARE 9.68 DF 18

| SOURCE * | TYPE | SCE(UG/M3) | STD ERR | TSTAT |
|---|---|---|---|---|
| 1003 | ISCORSP1 | 2.2961 | .1974 | 11.6331 |
| 1006 | PETROL | .7599 | .0491 | 15.4840 |
| 1012 | ISCORCF1 | 4.1701 | .5518 | 7.5576 |
| 1017 | SOIL1 | 10.5761 | .6109 | 17.3134 |
| 1019 | AMSUL | 2.5391 | .4373 | 5.8064 |
| 1027 | COMCOALT | 1.0696 | .1949 | 5.4885 |
| 1032 | COMARC | 4.3855 | .4675 | 9.3806 |

MEASURED CONCENTRATION FOR SIZE: COARS
30.4+- 3.0

UNCERTAINTY/SIMILARITY CLUSTERS CMB7 33889 SUM OF CLUSTER SOURCES

SPECIES CONCENTRATIONS - SITE: SAS02 DATE: 04/29/94 CMB7 33889
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .93 PERCENT MASS 84.9
CHI SQUARE 9.68 DF 18

| SPECIES | I | MEAS | CALC | RATIO C/M | RATIO R/U |
|---|---|---|---|---|---|
| C1 TOT | T | 30.38940+- 3.03890 | 25.79644+- .67876 | .85+- .09 | -1.5 |
| C2 NA | | .27390+- .01340 | -74.61041+- 75.23464 | *****+-***** | -1.0 |
| C3 MG | * | .42740+- .02130 | .29092+- .01741 | .68+- .05 | -5.0 |
| C4 AL | * | 1.08380+- .02130 | 1.19711+- .05785 | 1.10+- .06 | 1.8 |
| C5 SI | * | 2.85060+- .15810 | 2.71039+- .11395 | .95+- .07 | -.7 |
| C6 P | | -99.00000+--99.00000 | *********+-227.31530 | .00+- .00 | -.5 |
| C7 S | | -99.00000+--99.00000 | *********+-227.31530 | .00+- .00 | -.5 |
| C8 CL | | -99.00000+--99.00000 | *********+********* | .00+- .00 | -1.8 |
| C9 K | * | 1.07760+- .05490 | .92395+- .02942 | .86+- .05 | -2.5 |
| C10 CA | | -99.00000< .00010 | .49619< .02035 | .00< .00 | 4888.2 |
| C11 TI | * | .01740+- .00100 | .01493+- .00064 | .86+- .06 | -2.1 |
| C12 V | * | .00040+- .00010 | *********+-239.44210 | *****+-***** | -1.3 |
| C13 CR | | .00290+- .00020 | *********+-227.31530 | *****+-***** | -1.0 |
| C14 MN | | .36930+- .01820 | -74.57099+- 75.23464 | *****+-***** | -1.0 |
| C15 FE | * | 1.88300+- .09370 | 1.97451+- .06475 | 1.05+- .06 | .8 |
| C16 NI | * | .00580+- .00040 | .00583+- .00030 | 1.01+- .09 | .1 |
| C17 CU | * | .01710+- .00110 | .01991+- .00120 | 1.16+- .10 | 1.7 |
| C18 ZN | | .89230+- .04410 | .23701+- .00968 | .27+- .02 | -14.5 |
| C19 GA | * | .00290+- .00020 | *********+********* | *****+-***** | -1.5 |
| C20 AS | * | .00710+- .00040 | *********+-426.19880 | *****+-***** | -1.2 |
| C21 SE | * | .00580+- .00050 | *********+********* | *****+-***** | -1.4 |
| C22 BR | * | .46130+- .02440 | .30767+- .02788 | .67+- .07 | -4.1 |
| C23 SR | | .00580+- .00040 | *********+-412.83500 | *****+-***** | -1.0 |
| C24 MO | | .01450+- .00100 | *********+-412.83500 | *****+-***** | -1.0 |
| C25 BA | | -99.00000< .00010 | *********< 488.85370 | .00< .00 | -1.5 |
| C26 PB | * | .33220+- .01740 | .38634+- .01564 | 1.16+- .08 | 2.3 |
| C27 NH4+ | * | 1.64580+- .16460 | *********+********* | *****+-***** | -1.8 |
| C28 NO3- | * | .18980+- .01900 | *********+-640.78580 | *****+-***** | -1.7 |
| C29 SO4= | * | 2.54650+- .25460 | 2.54656+- .18899 | 1.00+- .12 | .0 |
| C30 CL- | * | .57200+- .05720 | .81597+- .06956 | 1.43+- .19 | 2.7 |
| C31 O1TC | * | .83560+- .16710 | .34385+- .05083 | .41+- .10 | -2.8 |
| C32 O2TC | * | 1.78190+- .35640 | .81302+- .10275 | .46+- .11 | -2.6 |
| C33 O3TC | * | 6.06150+- 1.21230 | .94454+- .11184 | .16+- .04 | -4.2 |
| C34 O4TC | * | 3.94350+- .78870 | .61833+- .06817 | .16+- .04 | -4.2 |
| C35 E1TC | * | 4.13180+- .82640 | 1.36165+- .20817 | .33+- .08 | -3.3 |
| C36 E2TC | * | .69200+- .13840 | .54936+- .06170 | .79+- .18 | -.9 |
| C37 E3TC | * | .04350+- .00870 | .14979+- .01846 | 3.44+- .81 | 5.2 |

# Table A4: VER07 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VER07          DATE: 06/03/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .78     PERCENT MASS        78.2
     CHI SQUARE       28.21               DF          19

  SOURCE
     * TYPE       SCE(UG/M3)     STD ERR       TSTAT
-------------------------------------------------
1003   ISCORSP1       6.0562       .6833      8.8626
1006   PETROL         1.1286       .1045     10.8027
1012   ISCORCF1      11.8679      1.8973      6.2552
1022   SECSULP        5.6448       .9283      6.0808
1027   COMCOALT      33.1325      3.5655      9.2926
1032   COMARC        18.6620      1.3004     14.3512
1035   COMSOIL        .6197       .8045       .7703
-------------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      98.6+-      9.9
UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------
1012   1032   1035                                  31.150+-      1.275
1003   1035                                          6.676+-      1.096
1003   1012   1032   1035                          37.206+-      1.338
-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VER07          DATE: 06/03/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .78     PERCENT MASS        78.2
     CHI SQUARE       28.21               DF          19

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  98.60830+-  9.86080  77.11172+-  3.20626    .78+-  .08    -2.1
C2  NA    *   1.26880+-   .12690 *********+-111.73650  *****+-88.48    -1.0
C3  MG    *   2.08650+-   .20870    .87345+-   .06676    .42+-  .05    -5.5
C4  AL    *   4.84660+-   .27750    .84930+-   .05092    .18+-  .01   -14.2
C5  SI    *   1.47340+-   .07450   2.17930+-   .10995   1.48+-  .11     5.3
C6  P      -99.00000+--99.00000 *********+-599.56120    .00+-  .00     -.8
C7  S      -99.00000+--99.00000 *********+-599.56120    .00+-  .00     -.8
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.7
C9  K     *   2.65150+-   .13080   2.62704+-   .09129    .99+-  .06     -.2
C10 CA    *   3.82780+-   .18510   1.76507+-   .07300    .46+-  .03   -10.4
C11 TI    *    .07080+-   .00350    .05159+-   .00309    .73+-  .06    -4.1
C12 V     *    .01940+-   .00100 *********+-609.88410  *****+-*****    -1.2
C13 CR         .01440+-   .00070 *********+-599.56120  *****+-*****    -1.0
C14 MN    *   1.00780+-   .04880 *********+-111.73640  *****+-*****    -1.0
C15 FE    *   8.01560+-   .38820   5.17170+-   .21664    .65+-  .04    -6.4
C16 NI         .02640+-   .00160    .08896+-   .00829   3.37+-  .37     7.4
C17 CU    *    .05400+-   .00320    .06532+-   .00359   1.21+-  .10     2.4
C18 ZN    *    .64800+-   .03240    .99145+-   .03945   1.53+-  .10     6.7
C19 GA    *    .00600+-   .00040 *********+-*********  *****+-*****    -1.4
C20 AS    *    .01080+-   .00060 *********+-*********  *****+-*****    -1.3
C21 SE    *    .01080+-   .00090 *********+-*********  *****+-*****    -1.3
C22 BR     -99.00000<     .00010    .51759<    .04209     .00<   .00   364.2
C23 SR         .02880+-   .00160 *********+-*********  *****+-*****    -1.0
C24 MO         .01440+-   .00080 *********+-*********  *****+-*****    -1.0
C25 BA    *    .03610+-   .00180 *********+-*********  *****+-*****    -1.5
C26 PB    *    .70780+-   .03600    .69643+-   .02457    .98+-  .06     -.3
C27 NH4+   -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.6
C28 NO3-  *    .49920+-   .04990 *********+-*********  *****+-*****    -1.6
C29 SO4=  *   7.27590+-   .72760   7.27590+-   .57197   1.00+-  .13      .0
C30 CL-        .04990+-   .00500   2.85136+-   .19882  57.14+- 6.98    14.1
C31 O1TC  *   1.38970+-   .27790   6.42998+-  1.48513   4.63+- 1.41     3.3
C32 O2TC  *   7.08190+-  1.41640   6.74548+-  1.26033    .95+-  .26     -.2
C33 O3TC  *  12.83230+-  2.56650   6.38842+-  1.12417    .50+-  .13    -2.3
C34 O4TC  *  11.67480+-  2.33500   4.60508+-   .75195    .39+-  .10    -2.9
C35 E1TC  *  27.48350+-  5.49670   8.43198+-  1.21372    .31+-  .08    -3.4
C36 E2TC  *   2.90470+-   .58090   3.59686+-   .50432   1.24+-  .30      .9
C37 E3TC  *    .59060+-   .11810   1.31862+-   .19874   2.23+-  .56     3.1
```

# Table A5: VER08 CMB7 Output

SOURCE CONTRIBUTION ESTIMATES - SITE: VER08 DATE: 06/10/94
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .94 PERCENT MASS 78.8
CHI SQUARE 6.94 DF 22

| SOURCE * | TYPE | SCE(UG/M3) | STD ERR | TSTAT |
|---|---|---|---|---|
| 1003 | ISCORSP1 | 5.0083 | .4867 | 10.2900 |
| 1006 | PETROL | 1.2097 | .0800 | 15.1298 |
| 1012 | ISCORCF1 | 3.9999 | .8405 | 4.7588 |
| 1017 | SOIL1 | 15.4826 | 1.0240 | 15.1201 |
| 1019 | AMSUL | 5.7418 | .9397 | 6.1100 |
| 1027 | COMCOALT | 8.7618 | .9020 | 9.7135 |
| 1032 | COMARC | 12.2676 | .7551 | 16.2462 |

MEASURED CONCENTRATION FOR SIZE: COARS
66.6+- 6.7

UNCERTAINTY/SIMILARITY CLUSTERS CMB7 33889 SUM OF CLUSTER SOURCES

SPECIES CONCENTRATIONS - SITE: VER08 DATE: 06/10/94 CMB7 33889
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .94 PERCENT MASS 78.8
CHI SQUARE 6.94 DF 22

| SPECIES | I | MEAS | CALC | RATIO C/M | RATIO R/U |
|---|---|---|---|---|---|
| C1 TOT | T | 66.62200+- 6.66220 | 52.47161+- 1.45646 | .79+- .08 | -2.1 |
| C2 NA | * | .70570+- .07060 | *********+-119.75570 | *****+-***** | -1.0 |
| C3 MG | * | .66370+- .06640 | .64642+- .04486 | .97+- .12 | -.2 |
| C4 AL | * | 1.68070+- .09620 | 1.76370+- .08365 | 1.05+- .08 | .7 |
| C5 SI | * | 4.52800+- .22880 | 4.11541+- .16488 | .91+- .06 | -1.5 |
| C6 P | | -99.00000+--99.00000 | *********+-495.82090 | .00+- .00 | -.8 |
| C7 S | | -99.00000+--99.00000 | *********+-495.82090 | .00+- .00 | -.8 |
| C8 CL | | -99.00000+--99.00000 | *********+********* | .00+- .00 | -2.0 |
| C9 K | * | 2.04750+- .10100 | 1.96581+- .06305 | .96+- .06 | -.7 |
| C10 CA | * | 1.17630+- .05770 | 1.00878+- .03525 | .86+- .05 | -2.5 |
| C11 TI | * | .02850+- .00140 | .02751+- .00102 | .97+- .06 | -.6 |
| C12 V | * | .00700+- .00050 | *********+-510.07820 | *****+-***** | -1.2 |
| C13 CR | | .01000+- .00050 | *********+-495.82090 | *****+-***** | -1.0 |
| C14 MN | * | .45360+- .02200 | *********+-119.75570 | *****+-***** | -1.0 |
| C15 FE | * | 3.31870+- .16070 | 4.05402+- .14153 | 1.22+- .07 | 3.4 |
| C16 NI | * | .02720+- .00170 | .02717+- .00220 | 1.00+- .10 | -.0 |
| C17 CU | * | .02990+- .00180 | .03203+- .00133 | 1.07+- .08 | 1.0 |
| C18 ZN | * | .70720+- .03530 | .57088+- .02338 | .81+- .05 | -3.2 |
| C19 GA | * | .00570+- .00040 | *********+********* | *****+-***** | -1.5 |
| C20 AS | * | .01140+- .00060 | *********+-953.52790 | *****+-***** | -1.3 |
| C21 SE | * | .00990+- .00080 | *********+********* | *****+-***** | -1.5 |
| C22 BR | * | .81160+- .04140 | .51455+- .04459 | .63+- .06 | -4.9 |
| C23 SR | | .00560+- .00030 | *********+-395.98860 | *****+-***** | -1.0 |
| C24 MO | | .01420+- .00080 | *********+-395.98860 | *****+-***** | -1.0 |
| C25 BA | * | .03130+- .00150 | *********+********* | *****+-***** | -1.7 |
| C26 PB | * | .56500+- .02870 | .66072+- .02523 | 1.17+- .07 | 2.5 |
| C27 NH4+ | * | .55180+- .05520 | *********+********* | *****+-***** | -1.8 |
| C28 NO3- | * | 2.67060+- .26710 | *********+********* | *****+-***** | -1.5 |
| C29 SO4= | * | 5.35970+- .53600 | 5.35985+- .42221 | 1.00+- .13 | .0 |
| C30 CL- | | .05140+- .00510 | 1.90759+- .15304 | 37.11+- 4.74 | 12.1 |
| C31 O1TC | * | 2.50960+- .50190 | 1.87253+- .39353 | .75+- .22 | -1.0 |
| C32 O2TC | * | 5.42930+- 1.08590 | 2.56453+- .36034 | .47+- .12 | -2.5 |
| C33 O3TC | * | 8.25630+- 1.65130 | 2.60916+- .33344 | .32+- .08 | -3.4 |
| C34 O4TC | * | 8.53350+- 1.70670 | 1.60579+- .20801 | .19+- .04 | -4.0 |
| C35 E1TC | * | 16.06170+- 3.21230 | 2.69422+- .34540 | .17+- .04 | -4.1 |
| C36 E2TC | * | .85100+- .17020 | 1.33413+- .15021 | 1.57+- .36 | 2.1 |
| C37 E3TC | * | .21390+- .04280 | .52722+- .06806 | 2.46+- .59 | 3.9 |

# Table A6: VAN08 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VAN08          DATE: 06/10/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .92     PERCENT MASS        84.1
     CHI SQUARE        9.43               DF          21

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      4.0762       .4073     10.0090
1006    PETROL         .8030       .0546     14.7009
1012    ISCORCF1      1.3920       .5149      2.7036
1017    SOIL1        19.0396      1.0071     18.9060
1019    AMSUL         6.5742      1.0332      6.3630
1028    COMCOAL       4.2500       .9767      4.3515
1032    COMARC        8.6258       .5270     16.3688
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      53.2+-      5.3

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VAN08          DATE: 06/10/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .92     PERCENT MASS        84.1
     CHI SQUARE        9.43               DF          21

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  53.21900+-  5.32190  44.76075+-  1.56795    .84+-  .09   -1.5
C2  NA    *    .48570+-   .04860 -78.33817+- 79.49750  *****+-*****   -1.0
C3  MG    *    .69540+-   .06950    .50031+-   .03311    .72+-  .09   -2.5
C4  AL    *   1.78510+-   .11280   1.92707+-   .10024   1.08+-  .09     .9
C5  SI    *   3.95270+-   .21010   4.41395+-   .19628   1.12+-  .08    1.6
C6  P      -99.00000+--99.00000 *********+-403.54360    .00+-  .00    -.7
C7  S      -99.00000+--99.00000 *********+-403.54360    .00+-  .00    -.7
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00   -1.7
C9  K     *   1.72880+-   .08610   1.59235+-   .05142    .92+-  .05   -1.4
C10 CA    *   1.06130+-   .05200    .67964+-   .02297    .64+-  .04   -6.7
C11 TI    *    .02550+-   .00130    .01897+-   .00064    .74+-  .05   -4.5
C12 V     *    .00780+-   .00040 *********+-588.38760  *****+-*****   -1.5
C13 CR         .01020+-   .00050 *********+-582.99240  *****+-*****   -1.4
C14 MN    *    .35800+-   .01760 *********+-428.19680  *****+-*****   -1.2
C15 FE    *   2.63480+-   .12990   3.25686+-   .10901   1.24+-  .07    3.7
C16 NI         .00890+-   .00060    .00473+-   .00023    .53+-  .04   -6.5
C17 CU    *    .01660+-   .00100    .01911+-   .00064   1.15+-  .08    2.1
C18 ZN    *    .36190+-   .01810    .37284+-   .01602   1.03+-  .07     .5
C19 GA    *    .00380+-   .00030 *********+-*********  *****+-*****   -1.3
C20 AS    *    .00770+-   .00070 *********+-442.74710  *****+-*****   -1.3
C21 SE    *    .01020+-   .00080 *********+-*********  *****+-*****   -1.3
C22 BR    *    .44340+-   .02270    .34797+-   .02963    .78+-  .08   -2.6
C23 SR         .00770+-   .00050 *********+-137.81280  *****+-*****   -1.0
C24 MO         .01280+-   .00080 *********+-137.81280  *****+-*****   -1.0
C25 BA    *    .02170+-   .00100 *********+-604.31140  *****+-*****   -1.7
C26 PB    *    .40940+-   .02110    .45042+-   .01684   1.10+-  .07    1.5
C27 NH4+  *    .80740+-   .08070 *********+-*********  *****+-*****   -1.8
C28 NO3-  *   1.96670+-   .19670 *********+-954.49950  *****+-*****   -1.5
C29 SO4=  *   5.75280+-   .57530   5.75297+-   .48203   1.00+-  .13     .0
C30 CL-        .02910+-   .00290   1.41642+-   .12347  48.67+- 6.44   11.2
C31 O1TC  *   1.82750+-   .36550    .98309+-   .09293    .54+-  .12   -2.2
C32 O2TC  *   3.68140+-   .73630   1.77202+-   .23240    .48+-  .12   -2.5
C33 O3TC  *   7.21790+-  1.44360   1.71653+-   .21668    .24+-  .06   -3.8
C34 O4TC  *   8.31370+-  1.66270    .93084+-   .11018    .11+-  .03   -4.4
C35 E1TC  *   9.41440+-  1.88290   1.38902+-   .16954    .15+-  .03   -4.2
C36 E2TC  *    .43350+-   .08670    .79638+-   .08474   1.84+-  .42    3.0
C37 E3TC  *    .21080+-   .04220    .33553+-   .04187   1.59+-  .38    2.1
```

# Table A7: SAS08 CMB7 Output

SOURCE CONTRIBUTION ESTIMATES - SITE: SAS08 DATE: 06/10/94
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .91 PERCENT MASS 78.4
CHI SQUARE 8.81 DF 22

| SOURCE * | TYPE | SCE(UG/M3) | STD ERR | TSTAT |
|---|---|---|---|---|
| 1006 | PETROL | .5460 | .0399 | 13.6722 |
| 1019 | AMSUL | 8.8959 | 1.3503 | 6.5883 |
| 1020 | AMNIT | 4.5489 | .6485 | 7.0143 |
| 1024 | COMPSFA | 11.0401 | .7221 | 15.2898 |
| 1031 | COMARCT | 12.5980 | .5358 | 23.5112 |

MEASURED CONCENTRATION FOR SIZE: COARS
48.0+- 4.8

UNCERTAINTY/SIMILARITY CLUSTERS CMB7 33889 SUM OF CLUSTER SOURCES

SPECIES CONCENTRATIONS - SITE: SAS08 DATE: 06/10/94 CMB7 33889
SAMPLE DURATION 7D START HOUR 0 SIZE: COARS
R SQUARE .91 PERCENT MASS 78.4
CHI SQUARE 8.81 DF 22

| SPECIES | I | MEAS | CALC | RATIO C/M | RATIO R/U |
|---|---|---|---|---|---|
| C1 TOT | T | 47.99060+- 4.79910 | 37.62890+- 1.63866 | .78+- .09 | -2.0 |
| C2 NA | * | .99600+- .09960 | -53.44462+- 54.05151 | *****+-54.53 | -1.0 |
| C3 MG | * | .61450+- .06150 | .55509+- .04188 | .90+- .11 | -.8 |
| C4 AL | * | 1.77250+- .11330 | 2.02339+- .13826 | 1.14+- .11 | 1.4 |
| C5 SI | * | 3.56680+- .19030 | 2.69843+- .15473 | .76+- .06 | -3.5 |
| C6 P | | -99.00000+--99.00000 | .12723+- .01146 | .00+- .00 | 1.0 |
| C7 S | | -99.00000+--99.00000 | .27565+- .01972 | .00+- .00 | 1.0 |
| C8 CL | | -99.00000+--99.00000 | *********+********* | .00+- .00 | -1.4 |
| C9 K | | 1.72970+- .08630 | .54287+- .02244 | .31+- .02 | -13.3 |
| C10 CA | * | .94730+- .04660 | 1.10466+- .05283 | 1.17+- .08 | 2.2 |
| C11 TI | | .02160+- .00110 | .07563+- .00524 | 3.50+- .30 | 10.1 |
| C12 V | * | .00810+- .00040 | -54.04660+- 54.05149 | *****+-***** | -1.0 |
| C13 CR | | .00810+- .00040 | .01533+- .00091 | 1.89+- .15 | 7.2 |
| C14 MN | * | .34450+- .01700 | -52.26495+- 54.05156 | *****+-***** | -1.0 |
| C15 FE | * | 2.36590+- .11690 | 2.99219+- .13521 | 1.26+- .08 | 3.5 |
| C16 NI | | .00810+- .00060 | .00389+- .00019 | .48+- .04 | -6.7 |
| C17 CU | * | .01350+- .00090 | .01093+- .00077 | .81+- .08 | -2.2 |
| C18 ZN | * | .64580+- .03290 | .52204+- .02482 | .81+- .06 | -3.0 |
| C19 GA | * | .00270+- .00020 | .00307+- .00020 | 1.14+- .11 | 1.3 |
| C20 AS | * | .00810+- .00080 | .00465+- .00020 | .57+- .06 | -4.2 |
| C21 SE | * | .00810+- .00070 | .00560+- .00030 | .69+- .07 | -3.3 |
| C22 BR | * | .23240+- .01210 | .25948+- .02081 | 1.12+- .11 | 1.1 |
| C23 SR | | .00810+- .00050 | .02296+- .00146 | 2.83+- .25 | 9.6 |
| C24 MO | | .01350+- .00080 | .00592+- .00029 | .44+- .03 | -8.9 |
| C25 BA | * | .01890+- .00090 | -54.00862+- 54.05149 | *****+-***** | -1.0 |
| C26 PB | * | .35270+- .01830 | .35310+- .01250 | 1.00+- .06 | .0 |
| C27 NH4+ | * | 2.31910+- .23190 | *********+********* | *****+-***** | -1.0 |
| C28 NO3- | * | 3.58200+- .35820 | 3.58206+- .35256 | 1.00+- .14 | .0 |
| C29 SO4= | * | 7.35050+- .73510 | 7.35080+- .64981 | 1.00+- .13 | .0 |
| C30 CL- | * | .14000+- .01400 | .15940+- .01229 | 1.14+- .14 | 1.0 |
| C31 O1TC | * | .47580+- .09520 | .15151+- .02999 | .32+- .09 | -3.2 |
| C32 O2TC | * | 3.27200+- .65440 | .23871+- .03172 | .07+- .02 | -4.6 |
| C33 O3TC | * | 5.45620+- 1.09120 | .37870+- .05041 | .07+- .02 | -4.6 |
| C34 O4TC | * | 6.07920+- 1.21580 | .13485+- .01678 | .02+- .01 | -4.9 |
| C35 E1TC | * | 5.89090+- 1.17820 | .16621+- .02890 | .03+- .01 | -4.9 |
| C36 E2TC | * | .60400+- .12080 | .39553+- .06779 | .65+- .17 | -1.5 |
| C37 E3TC | * | .12960+- .02590 | .25821+- .04180 | 1.99+- .51 | 2.6 |

# Table A8: VER12 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VER12          DATE: 07/08/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .95     PERCENT MASS        81.3
     CHI SQUARE        6.99               DF          18

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-------------------------------------------
1003    ISCORSP1      4.0751       .6149      6.6278
1006    PETROL        2.4402       .1608     15.1780
1012    ISCORCF1      8.3655      1.4066      5.9473
1017    SOIL1        23.4384      1.6888     13.8787
1022    SECSULP       6.1838      1.0346      5.9771
1028    COMCOAL      29.5836      3.9022      7.5813
1032    COMARC       18.6136      1.1826     15.7396
-------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
     114.0+-    11.4

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------


-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VER12          DATE: 07/08/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .95     PERCENT MASS        81.3
     CHI SQUARE        6.99               DF          18

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T 113.99810+- 11.39980  92.70018+-  3.73674    .81+-  .09    -1.8
C2  NA    *    .56040+-   .05600 *********+-241.58350  *****+-*****    -1.0
C3  MG    *    .73690+-   .07370    .94601+-   .06741   1.28+-  .16     2.1
C4  AL    *   3.34710+-   .21820   2.72340+-   .12846    .81+-  .07    -2.5
C5  SI    *   5.81470+-   .31200   6.43396+-   .25414   1.11+-  .07     1.5
C6  P      -99.00000+--99.00000 *********+-403.43350    .00+-  .00     -.7
C7  S      -99.00000+--99.00000 *********+-403.43350    .00+-  .00     -.7
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.0
C9  K     *   2.46330+-   .12280   2.37191+-   .07001    .96+-  .06     -.6
C10 CA    *   1.94930+-   .09520   1.59985+-   .05794    .82+-  .05    -3.1
C11 TI    *    .04140+-   .00220    .04307+-   .00161   1.04+-  .07      .6
C12 V     *    .00920+-   .00050 *********+-*********  *****+-*****    -1.2
C13 CR    *    .03660+-   .00190 *********+-*********  *****+-*****    -1.1
C14 MN    *    .63930+-   .03160 *********+-*********  *****+-*****    -1.1
C15 FE    *   5.38630+-   .26750   6.28912+-   .21895   1.17+-  .07     2.6
C16 NI    *    .01540+-   .00120    .01095+-   .00046    .71+-  .06    -3.5
C17 CU    *    .04280+-   .00300    .04937+-   .00250   1.15+-  .10     1.7
C18 ZN    *    .98520+-   .05040    .87748+-   .03601    .89+-  .06    -1.7
C19 GA         .00920+-   .00080 *********+-*********  *****+-*****    -1.4
C20 AS    *    .01540+-   .00090 *********+-*********  *****+-*****    -1.2
C21 SE    *    .01370+-   .00130 *********+-*********  *****+-*****    -1.6
C22 BR    *   1.56050+-   .08660   1.00383+-   .08968    .64+-  .07    -4.5
C23 SR         .01060+-   .00070 *********+-828.17970  *****+-*****    -1.0
C24 MO         .01850+-   .00100 *********+-828.17970  *****+-*****    -1.0
C25 BA         .04890+-   .00300 *********+-*********  *****+-*****    -1.4
C26 PB    *   1.06120+-   .05780   1.24872+-   .05039   1.18+-  .08     2.4
C27 NH4+       2.93050+-   .29300 *********+-*********  *****+-*****    -2.0
C28 NO3-  *    5.06090+-   .50610 *********+-*********  *****+-*****    -1.5
C29 SO4=  *    8.20930+-   .82090   8.20930+-   .62696  1.00+-  .13      .0
C30 CL-        .04210+-   .00420   1.78994+-   .12722 42.52+- 5.21    13.7
C31 O1TC  *   3.57440+-   .71490   5.88354+-   .62347   1.65+-  .37     2.4
C32 O2TC  *   8.16340+-  1.63270   7.06956+-  1.14365    .87+-  .22     -.5
C33 O3TC  *  16.22880+-  3.24580   5.84508+-   .84619    .36+-  .09    -3.1
C34 O4TC  *  13.48000+-  2.69600   4.20663+-   .63318    .31+-  .08    -3.3
C35 E1TC  *  30.98770+-  6.19750   7.69339+-  1.11498    .25+-  .06    -3.7
C36 E2TC       .94190+-   .18840   3.40060+-   .46085   3.61+-  .87     4.9
C37 E3TC       .17370+-   .03470   1.29190+-   .18594   7.44+- 1.83     5.9
```

# Table A9: VAN12 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VAN12          DATE: 07/08/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .94     PERCENT MASS        83.0
     CHI SQUARE        8.18               DF          20

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1006    PETROL        2.1612       .1337     16.1640
1012    ISCORCF1      5.0355       .8961      5.6192
1017    SOIL1        18.4793      1.2037     15.3518
1019  * AMSUL         9.4927      1.4999      6.3290
1028    COMCOAL      26.5721      2.9263      9.0805
1032    COMARC       13.8059       .8228     16.7801
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      91.1+-      9.1

UNCERTAINTY/SIMILARITY CLUSTERS     CMB7 33889      SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VAN12          DATE: 07/08/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:    COARS
       R SQUARE         .94     PERCENT MASS        83.0
     CHI SQUARE        8.18               DF          20

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  91.05170+-  9.10520  75.54665+-  3.06503    .83+-  .09   -1.6
C2  NA    *    .91220+-   .09120 *********+-213.96190  *****+-*****   -1.0
C3  MG    *    .57260+-   .05730    .65285+-   .04983   1.14+-  .14    1.1
C4  AL    *   2.06470+-   .12550   2.03608+-   .09975    .99+-  .08    -.2
C5  SI    *   4.95610+-   .25790   4.87414+-   .19690    .98+-  .06    -.3
C6  P      -99.00000+--99.00000    .21119+-   .01691    .00+-  .00    1.0
C7  S      -99.00000+--99.00000    .39746+-   .02243    .00+-  .00    1.0
C8  CL     -99.00000+--99.00000 *********+*********    .00+-  .00   -1.8
C9  K     *   1.61800+-   .08040   1.09282+-   .04332    .68+-  .04   -5.8
C10 CA    *   1.33640+-   .06540   1.15516+-   .04089    .86+-  .05   -2.3
C11 TI    *    .02700+-   .00140    .03239+-   .00121   1.20+-  .08    2.9
C12 V     *    .00460+-   .00020 *********+********* *****+-*****   -1.1
C13 CR         .02310+-   .00110 *********+********* *****+-*****   -1.0
C14 MN    *    .60600+-   .02960 *********+********* *****+-*****   -1.1
C15 FE    *   3.80040+-   .18590   4.61046+-   .16126   1.21+-  .07    3.3
C16 NI    *    .01160+-   .00080    .00845+-   .00038    .73+-  .06   -3.5
C17 CU    *    .02950+-   .00180    .02858+-   .00154    .97+-  .08    -.4
C18 ZN    *    .68440+-   .03400    .64216+-   .02636    .94+-  .06   -1.0
C19 GA         .00640+-   .00040 *********+********* *****+-*****   -1.2
C20 AS    *    .01280+-   .00070 *********+********* *****+-*****   -1.2
C21 SE    *    .01160+-   .00090 *********+********* *****+-*****   -1.5
C22 BR    *   1.24840+-   .06270    .86962+-   .07933    .70+-  .07   -3.7
C23 SR         .00770+-   .00050 *********+-498.51310 *****+-*****   -1.0
C24 MO         .01540+-   .00090 *********+-498.51310 *****+-*****   -1.0
C25 BA         .03210+-   .00210 *********+********* *****+-*****   -1.2
C26 PB    *    .92330+-   .04660   1.06913+-   .04445   1.16+-  .08    2.3
C27 NH4+  *   4.11170+-   .41120 *********+********* *****+-*****   -1.9
C28 NO3-  *   4.36600+-   .43660 *********+********* *****+-*****   -1.3
C29 SO4=  *   8.39800+-   .83980   8.39824+-   .69449   1.00+-  .13     .0
C30 CL-        .04270+-   .00430    .45279+-   .02731  10.60+- 1.24   14.8
C31 O1TC  *   4.46940+-   .89390   5.24960+-   .55982   1.17+-  .27     .7
C32 O2TC  *   5.87050+-  1.17410   6.15377+-  1.02309   1.05+-  .27     .2
C33 O3TC  *  15.17700+-  3.03540   4.96202+-   .75253    .33+-  .08   -3.3
C34 O4TC  *  14.14220+-  2.82840   3.54630+-   .56321    .25+-  .06   -3.7
C35 E1TC  *  15.75510+-  3.15100   6.24466+-   .96325    .40+-  .10   -2.9
C36 E2TC  *    .61920+-   .12380   2.79466+-   .40489   4.51+- 1.11    5.1
C37 E3TC       .10780+-   .02160   1.09175+-   .16303  10.13+- 2.53    6.0
```

# Table A10: SAS12 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: SAS12          DATE: 07/08/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .93     PERCENT MASS        74.0
     CHI SQUARE        8.77               DF          22

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      3.4362       .3827      8.9795
1006    PETROL         .5327       .0433     12.2921
1012    ISCORCF1      1.5314       .5625      2.7223
1017    SOIL1        20.2462      1.1309     17.9020
1019    AMSUL         9.3841      1.4437      6.4999
1027    COMCOALT      1.6150       .3005      5.3750
1032    COMARC       12.8663       .7131     18.0421
-----------------------------------------------

MEASURED CONCENTRATION FOR SIZE: COARS
      67.1+-     6.7

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: SAS12          DATE: 07/08/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .93     PERCENT MASS        74.0
     CHI SQUARE        8.77               DF          22

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  67.08010+-  6.70800  49.61185+-  1.73942    .74+-  .08    -2.5
C2  NA    *    .71160+-   .07120 -51.63058+- 52.73367  *****+-74.46    -1.0
C3  MG    *    .86650+-   .08670    .64550+-   .04710    .74+-  .09    -2.2
C4  AL    *   1.96970+-   .12440   2.07663+-   .10702   1.05+-  .09      .7
C5  SI    *   4.63070+-   .24370   4.84929+-   .21010   1.05+-  .07      .7
C6  P      -99.00000+--99.00000 *********+-340.18870    .00+-  .00     -.7
C7  S      -99.00000+--99.00000 *********+-340.18870    .00+-  .00     -.7
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.6
C9  K     *   1.61770+-   .08100   1.51997+-   .04622    .94+-  .06    -1.0
C10 CA    *   1.31350+-   .06430    .89880+-   .03267    .68+-  .04    -5.8
C11 TI    *    .02610+-   .00140    .02163+-   .00071    .83+-  .05    -2.9
C12 V     *    .00470+-   .00030 *********+-344.25160  *****+-*****    -1.1
C13 CR         .01610+-   .00080 *********+-340.18870  *****+-*****    -1.0
C14 MN    *    .45810+-   .02230 -50.82760+- 52.73371  *****+-*****    -1.0
C15 FE    *   3.27760+-   .16080   4.26354+-   .15019   1.30+-  .08     4.5
C16 NI    *    .00870+-   .00060    .00922+-   .00048   1.06+-  .09      .7
C17 CU    *    .01860+-   .00120    .02112+-   .00075   1.14+-  .08     1.8
C18 ZN    *    .59710+-   .02980    .53837+-   .02379    .90+-  .06    -1.5
C19 GA    *    .00500+-   .00030 *********+-*********  *****+-*****    -1.2
C20 AS    *    .00750+-   .00040 *********+-220.33300  *****+-*****    -1.4
C21 SE    *    .01240+-   .00100 *********+-*********  *****+-*****    -1.1
C22 BR    *    .22730+-   .01150    .26593+-   .02028   1.17+-  .11     1.7
C23 SR         .00750+-   .00050 *********+-151.60600  *****+-*****    -1.0
C24 MO         .01490+-   .00080 *********+-151.60600  *****+-*****    -1.0
C25 BA    *    .02480+-   .00160 *********+-408.72460  *****+-*****    -1.7
C26 PB    *    .41220+-   .02070    .37147+-   .01222    .90+-  .05    -1.7
C27 NH4+  *   3.33600+-   .33360 *********+-*********  *****+-*****    -1.6
C28 NO3-  *   8.10180+-   .81020 *********+-*********  *****+-*****    -1.3
C29 SO4=  *   7.93710+-   .79370   7.93737+-   .68599   1.00+-  .13      .0
C30 CL-        .03240+-   .00320   1.27245+-   .10477  39.27+- 5.05    11.8
C31 O1TC  *   1.29660+-   .25930    .49295+-   .07684    .38+-  .10    -3.0
C32 O2TC  *   2.98240+-   .59650   1.34295+-   .18845    .45+-  .11    -2.6
C33 O3TC  *   9.53040+-  1.90610   1.49644+-   .20248    .16+-  .04    -4.2
C34 O4TC  *   8.13840+-  1.62770    .69672+-   .07819    .09+-  .02    -4.6
C35 E1TC  *   9.53540+-  1.90710    .98685+-   .10404    .10+-  .02    -4.5
C36 E2TC  *    .58700+-   .11740    .71909+-   .07863   1.23+-  .28      .9
C37 E3TC  *    .08610+-   .01720    .34012+-   .05052   3.95+-  .98     4.8
```

# Table A11: VAN13 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VAN13          DATE: 07/15/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .95     PERCENT MASS        78.8
     CHI SQUARE        6.60               DF          19

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      4.2114       .5690      7.4012
1006    PETROL        1.1472       .0887     12.9341
1012    ISCORCF1      5.6208      1.1713      4.7988
1017    SOIL1        19.0340      1.3787     13.8054
1022    SECSULP       4.5530       .7885      5.7741
1028    COMCOAL      24.1866      3.3265      7.2710
1032    COMARC       22.1801      1.2167     18.2294
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
     102.7+-    10.3

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-----------------------------------------------------------------------


-----------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VAN13          DATE: 07/15/94    CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .95     PERCENT MASS        78.8
     CHI SQUARE        6.60               DF          19

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T 102.66020+- 10.26600  80.93306+-  3.14909    .79+-  .08    -2.0
C2  NA    *    .69850+-   .06990 *********+-113.56990  *****+-*****    -1.0
C3  MG    *    .71080+-   .07110   1.01958+-   .07895   1.43+-  .18     2.9
C4  AL    *   2.47010+-   .15270   2.25480+-   .10481    .91+-  .07    -1.2
C5  SI    *   5.31150+-   .27670   5.46763+-   .20850   1.03+-  .07      .5
C6  P      -99.00000+--99.00000 *********+-416.92600    .00+-  .00     -.7
C7  S      -99.00000+--99.00000 *********+-416.92600    .00+-  .00     -.7
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.0
C9  K     *   2.33170+-   .11540   2.28257+-   .06697    .98+-  .06     -.4
C10 CA    *   1.70810+-   .08340   1.60233+-   .05913    .94+-  .06    -1.0
C11 TI    *    .03370+-   .00170    .03651+-   .00126   1.08+-  .07     1.3
C12 V     *    .02170+-   .00110 *********+-*********  *****+-*****    -1.2
C13 CR    *    .02740+-   .00140 *********+-*********  *****+-*****    -1.2
C14 MN    *    .89790+-   .04350 *********+-*********  *****+-*****    -1.0
C15 FE    *   5.56150+-   .27100   6.58421+-   .24555   1.18+-  .07     2.8
C16 NI    *    .01370+-   .00090    .00960+-   .00040    .70+-  .05    -4.2
C17 CU    *    .04240+-   .00250    .04320+-   .00186   1.02+-  .07      .3
C18 ZN    *   1.19710+-   .05890    .96561+-   .04152    .81+-  .05    -3.2
C19 GA        .00750+-   .00050 *********+-*********  *****+-*****    -1.4
C20 AS    *    .01250+-   .00070 *********+-*********  *****+-*****    -1.2
C21 SE    *    .01620+-   .00120 *********+-*********  *****+-*****    -1.6
C22 BR    *    .39890+-   .02040    .54120+-   .04306   1.36+-  .13     3.0
C23 SR        .00870+-   .00050 *********+-556.45940  *****+-*****    -1.0
C24 MO        .01350+-   .00080 *********+-556.45940  *****+-*****    -1.0
C25 BA        .02650+-   .00140 *********+-*********  *****+-*****    -1.4
C26 PB    *    .84790+-   .04280    .71771+-   .02517    .85+-  .05    -2.6
C27 NH4+   -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.0
C28 NO3-  *    .48740+-   .04870 *********+-*********  *****+-*****    -1.4
C29 SO4=  *   6.34950+-   .63500   6.34950+-   .46510   1.00+-  .12      .0
C30 CL-       .12250+-   .01230   1.79241+-   .13096  14.63+- 1.82    12.7
C31 O1TC  *   4.42520+-   .88500   4.75799+-   .50924   1.08+-  .24      .3
C32 O2TC  *   7.58420+-  1.51680   5.77595+-   .93495    .76+-  .20    -1.0
C33 O3TC  *  15.88910+-  3.17780   4.77814+-   .69171    .30+-  .07    -3.4
C34 O4TC  *  16.15090+-  3.23020   3.35597+-   .51520    .21+-  .05    -3.9
C35 E1TC  *  27.51190+-  5.50240   6.04359+-   .89193    .22+-  .05    -3.9
C36 E2TC  *   1.52520+-   .30500   2.87322+-   .38189   1.88+-  .45     2.8
C37 E3TC      .25620+-   .05120   1.18311+-   .16390   4.62+- 1.12     5.4
```

# Table A12: SAS13 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: SAS13        DATE: 07/15/94
SAMPLE DURATION        7D      START HOUR        0          SIZE:    COARS
       R SQUARE       .95    PERCENT MASS      80.2
     CHI SQUARE      6.22              DF        17

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR      TSTAT
-------------------------------------------
1003   ISCORSP1      5.3182       .4960    10.7215
1006   PETROL         .6719       .0510    13.1801
1012   ISCORCF1      2.8555       .7879     3.6243
1017   SOIL1        12.2743      2.0197     6.0773
1022   SECSULP       4.4231       .7208     6.1363
1024   COMPSFA       6.6082      1.3216     5.0003
1027   COMCOALT      2.7443       .8162     3.3624
1032   COMARC       10.6326       .9066    11.7281
-------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      56.8+-     5.7

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889     SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
 SPECIES CONCENTRATIONS -  SITE: SAS13        DATE: 07/15/94    CMB7 33889
SAMPLE DURATION        7D      START HOUR        0          SIZE:    COARS
       R SQUARE       .95    PERCENT MASS      80.2
     CHI SQUARE      6.22              DF        17

SPECIES--I---MEAS----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  56.75130+-  5.67510  45.52805+-  1.46381    .80+-  .08    -1.9
C2  NA    *    .57480+-   .05750 -65.07555+- 66.51498  *****+-*****    -1.0
C3  MG    *    .67620+-   .06760    .66306+-   .04036    .98+-  .11     -.2
C4  AL    *   2.03850+-   .12870   2.53834+-   .10574   1.25+-  .09     3.0
C5  SI    *   5.11350+-   .26810   4.51463+-   .15876    .88+-  .06    -1.9
C6  P      -99.00000+--99.00000 *********+-526.49800    .00+-  .00     -.8
C7  S      -99.00000+--99.00000 *********+-526.49800    .00+-  .00     -.8
C8  CL     -99.00000+--99.00000 *********+*********     .00+-  .00    -2.1
C9  K     *   2.00390+-   .09950   1.93165+-   .06443    .96+-  .06     -.6
C10 CA    *   1.40020+-   .06850   1.15253+-   .04000    .82+-  .05    -3.1
C11 TI        .02580+-   .00130    .05806+-   .00316   2.25+-  .17     9.4
C12 V     *    .02290+-   .00120 *********+-530.68300  *****+-*****    -1.1
C13 CR        .01100+-   .00060 *********+-526.49800  *****+-*****    -1.0
C14 MN    *    .66350+-   .03230 -64.93884+- 66.51496  *****+-*****    -1.0
C15 FE    *   3.45140+-   .16950   3.52290+-   .12101   1.02+-  .06      .3
C16 NI        .01100+-   .00080    .01191+-   .00071   1.08+-  .10      .9
C17 CU    *    .02580+-   .00160    .02706+-   .00103   1.05+-  .08      .7
C18 ZN       1.42610+-   .06980    .47093+-   .01994    .33+-  .02    13.2
C19 GA    *    .00490+-   .00040 *********+*********  *****+-*****    -1.5
C20 AS    *    .00740+-   .00040 *********+-392.08770  *****+-*****    -1.4
C21 SE    *    .01230+-   .00100 *********+*********  *****+-*****    -1.4
C22 BR    *    .29590+-   .01570    .30908+-   .02502   1.04+-  .10      .4
C23 SR        .00860+-   .00050 *********+-282.69870  *****+-*****    -1.0
C24 MO        .00700+-   .00040 *********+-282.69870  *****+-*****    -1.0
C25 BA    *    .01450+-   .00080 *********+-659.81610  *****+-*****    -1.7
C26 PB    *    .43020+-   .02230    .41644+-   .01446    .97+-  .06     -.5
C27 NH4+   -99.00000+--99.00000 *********+*********     .00+-  .00    -1.8
C28 NO3-  *    .49110+-   .04910 *********+*********  *****+-*****    -1.5
C29 SO4=  *   5.64470+-   .56450   5.64470+-   .44631   1.00+-  .13      .0
C30 CL-       .14610+-   .01460   1.85397+-   .16103  12.69+- 1.68    10.6
C31 O1TC  *    .87450+-   .17490    .72673+-   .12549    .83+-  .22     -.7
C32 O2TC  *   2.69770+-   .53950   1.30510+-   .15177    .48+-  .11    -2.5
C33 O3TC  *   6.26970+-  1.25390   1.46839+-   .15443    .23+-  .05    -3.8
C34 O4TC  *   1.51780+-   .30360    .81179+-   .08246    .53+-  .12    -2.2
C35 E1TC  *  20.32110+-  4.06420   1.39684+-   .16848    .07+-  .02    -4.7
C36 E2TC  *    .72350+-   .14470    .79782+-   .07802   1.10+-  .25      .5
C37 E3TC  *    .12690+-   .02540    .34946+-   .04409   2.75+-  .65     4.4
```

# Table A13: VER19 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VER19          DATE: 08/26/94
SAMPLE DURATION          7D      START HOUR          0          SIZE:     COARS
       R SQUARE         .94    PERCENT MASS       80.8
     CHI SQUARE        7.71              DF         19

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      4.5052       .4309     10.4544
1006    PETROL        1.2728       .0869     14.6407
1012    ISCORCF1     10.8413      1.4153      7.6603
1022    SECSULP       3.9269       .6697      5.8637
1024    COMPSFA       3.8272      1.8817      2.0339
1027    COMCOALT       .5182       .2466      2.1010
1032    COMARC       11.8852       .9136     13.0088
1035    COMSOIL      14.4986      2.3645      6.1319
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      63.4+-      6.3

UNCERTAINTY/SIMILARITY CLUSTERS    CMB7 33889      SUM OF CLUSTER SOURCES
-------------------------------------------------------------------------

-------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VER19          DATE: 08/26/94    CMB7 33889
SAMPLE DURATION          7D      START HOUR          0          SIZE:     COARS
       R SQUARE         .94    PERCENT MASS       80.8
     CHI SQUARE        7.71              DF         19

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  63.44020+-  6.34400  51.27538+-  1.44729    .81+-  .08    -1.9
C2  NA    *    .78900+-   .07890 *********+-126.00880  *****+-*****    -1.0
C3  MG    *    .60440+-   .06040    .69589+-   .04392   1.15+-  .14     1.2
C4  AL    *   3.01210+-   .18430   3.03399+-   .16283   1.01+-  .08      .1
C5  SI    *   5.91850+-   .30830   5.54569+-   .28084    .94+-  .07     -.9
C6  P      -99.00000+--99.00000 *********+-446.01280    .00+-  .00     -.8
C7  S      -99.00000+--99.00000 *********+-446.01280    .00+-  .00     -.8
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.7
C9  K     *   1.74680+-   .08770   1.89079+-   .06096   1.08+-  .06     1.3
C10 CA    *   1.48820+-   .07290   1.44477+-   .05680    .97+-  .06     -.5
C11 TI        .03620+-   .00190    .06991+-   .00337   1.93+-  .14     8.7
C12 V     *   .02330+-   .00130 *********+-463.47130  *****+-*****    -1.2
C13 CR        .00750+-   .00040 *********+-446.01280  *****+-*****    -1.0
C14 MN    *   .38280+-   .01880 *********+-126.00880  *****+-*****    -1.0
C15 FE    *  4.07200+-   .20020   4.43852+-   .16300   1.09+-  .07     1.4
C16 NI    *   .01060+-   .00080    .00811+-   .00032    .77+-  .07    -2.9
C17 CU    *   .04540+-   .00270    .04829+-   .00310   1.06+-  .09      .7
C18 ZN    *   .74840+-   .03740    .61359+-   .02586    .82+-  .05    -3.0
C19 GA    *   .00620+-   .00040 *********+-*********  *****+-*****    -1.6
C20 AS    *   .01230+-   .00070 *********+-*********  *****+-*****    -1.0
C21 SE    *   .01230+-   .00100 *********+-*********  *****+-*****    -1.4
C22 BR    *   .53430+-   .02790    .53656+-   .04687   1.00+-  .10      .0
C23 SR        .01060+-   .00070 *********+-*********  *****+-*****    -1.0
C24 MO        .01730+-   .00110 *********+-*********  *****+-*****    -1.0
C25 BA        .02700+-   .00140 *********+-*********  *****+-*****    -1.4
C26 PB    *   .70780+-   .03620    .69064+-   .02651    .98+-  .06     -.4
C27 NH4+   -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.9
C28 NO3-  *   1.21770+-   .12180 *********+-*********  *****+-*****    -1.6
C29 SO4=  *   5.32900+-   .53290   5.32900+-   .39959   1.00+-  .12      .0
C30 CL-   *   3.66920+-   .36690   1.61587+-   .13671    .44+-  .06    -5.2
C31 O1TC  *   .23830+-   .04770    .40338+-   .03995   1.69+-  .38     2.7
C32 O2TC  *   3.14920+-   .62980    .95388+-   .10473    .30+-  .07    -3.4
C33 O3TC  *   9.87640+-  1.97530   1.42602+-   .08893    .14+-  .03    -4.3
C34 O4TC  *   8.20680+-  1.64140   1.14654+-   .14905    .14+-  .03    -4.3
C35 E1TC  *  10.74140+-  2.14830   2.99673+-   .53123    .28+-  .07    -3.5
C36 E2TC  *   .65210+-   .13040   1.16410+-   .15058   1.79+-  .43     2.6
C37 E3TC  *   .14680+-   .02940    .30689+-   .04592   2.09+-  .52     2.9
```

# Table A14: VAN19 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: VAN19          DATE: 08/26/94
SAMPLE DURATION          7D      START HOUR          0          SIZE:    COARS
       R SQUARE         .94    PERCENT MASS       76.6
     CHI SQUARE        7.79              DF         19

  SOURCE
     * TYPE      SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------
1003    ISCORSP1      4.6767       .3754     12.4586
1006    PETROL         .7249       .0527     13.7567
1012    ISCORCF1      3.7753       .7945      4.7518
1022 *  SECSULP       8.9686      1.3500      6.6435
1024    COMPSFA       8.7755      1.5236      5.7599
1027    COMCOALT      1.0357       .2319      4.4663
1032    COMARC       11.5072       .6849     16.8025
1035    COMSOIL       4.7445      1.8187      2.6088
-----------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      57.7+-     5.8

UNCERTAINTY/SIMILARITY CLUSTERS     CMB7 33889      SUM OF CLUSTER SOURCES
-----------------------------------------------------------------------

-----------------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: VAN19          DATE: 08/26/94     CMB7 33889
SAMPLE DURATION          7D      START HOUR          0          SIZE:    COARS
       R SQUARE         .94    PERCENT MASS       76.6
     CHI SQUARE        7.79              DF         19

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  57.68580+-  5.76860  44.20830+-  1.62199    .77+-  .08    -2.2
C2  NA    *    .93540+-   .09350 -70.45541+- 71.76398  *****+-77.09    -1.0
C3  MG    *    .62930+-   .06290    .66653+-   .04336   1.06+-  .13      .5
C4  AL    *   1.81610+-   .11670   2.41367+-   .12138   1.33+-  .11     3.5
C5  SI    *   4.66090+-   .24720   3.64542+-   .15300    .78+-  .05    -3.5
C6  P       -99.00000+--99.00000 *********+-462.98890    .00+-  .00     -.8
C7  S       -99.00000+--99.00000 *********+-462.98890    .00+-  .00     -.8
C8  CL      -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.2
C9  K     *   1.88140+-   .09370   1.70220+-   .05740    .90+-  .05    -1.6
C10 CA    *   1.53580+-   .07500   1.28783+-   .04899    .84+-  .05    -2.8
C11 TI        .02510+-   .00130    .07243+-   .00424   2.89+-  .23    10.7
C12 V     *    .02290+-   .00120 *********+-468.51760  *****+-*****    -1.1
C13 CR        .00530+-   .00030 *********+-462.98890  *****+-*****    -1.0
C14 MN    *   .31790+-   .01570 -70.07127+- 71.76399  *****+-*****    -1.0
C15 FE    *  2.93970+-   .14500   3.33161+-   .12739   1.13+-  .07     2.0
C16 NI    *    .00790+-   .00060    .00731+-   .00032    .93+-  .08     -.9
C17 CU    *    .02650+-   .00170    .02839+-   .00123   1.07+-  .08      .9
C18 ZN    *    .56980+-   .02860    .50338+-   .02172    .88+-  .06    -1.8
C19 GA    *    .00260+-   .00020 *********+-758.07470  *****+-*****    -1.7
C20 AS    *    .00790+-   .00040 *********+-387.56260  *****+-*****    -1.2
C21 SE    *    .00790+-   .00070 *********+-608.95880  *****+-*****    -1.6
C22 BR    *    .35790+-   .01880    .32834+-   .02699    .92+-  .09     -.9
C23 SR        .00790+-   .00050 *********+-373.75450  *****+-*****    -1.0
C24 MO        .00490+-   .00030 *********+-373.75450  *****+-*****    -1.0
C25 BA        .01720+-   .00090 *********+-608.04070  *****+-*****    -1.7
C26 PB    *    .42380+-   .02200    .43563+-   .01557   1.03+-  .06      .4
C27 NH4+    -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.8
C28 NO3-  *   3.15360+-   .31540 *********+-********* *****+-*****    -1.5
C29 SO4=  *  10.05920+-  1.00590  10.05920+-   .89874   1.00+-  .13      .0
C30 CL-   *   1.36240+-   .13620   1.62653+-   .14171   1.19+-  .16     1.3
C31 O1TC  *    .28870+-   .05770    .39574+-   .05348   1.37+-  .33     1.4
C32 O2TC  *   2.91780+-   .58360    .64108+-   .05822    .22+-  .05    -3.9
C33 O3TC  *   8.49860+-  1.69970    .87958+-   .06044    .10+-  .02    -4.5
C34 O4TC  *   5.85230+-  1.17050    .57704+-   .05778    .10+-  .02    -4.5
C35 E1TC  *   8.64010+-  1.72800   1.26462+-   .18894    .15+-  .04    -4.2
C36 E2TC  *    .58070+-   .11610    .69464+-   .07638   1.20+-  .27      .8
C37 E3TC  *    .12810+-   .02560    .30949+-   .04504   2.42+-  .60     3.5
```

# Table A15: SAS19 CMB7 Output

```
SOURCE CONTRIBUTION ESTIMATES -  SITE: SAS19          DATE: 08/26/94
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .93     PERCENT MASS        77.8
     CHI SQUARE       10.99               DF          17

  SOURCE
     * TYPE       SCE(UG/M3)     STD ERR       TSTAT
-----------------------------------------------------
1003    ISCORSP1       3.0299       .2574     11.7692
1006    PETROL          .3063       .0242     12.6433
1012    ISCORCF1       1.9198       .4475      4.2899
1017    SOIL1          8.7248      1.5744      5.5415
1022    SECSULP        6.5868      1.0042      6.5593
1024    COMPSFA        9.1096      1.0588      8.6039
1027    COMCOALT        .5376       .1529      3.5170
1032    COMARC         4.8400       .3959     12.2251
-----------------------------------------------------
MEASURED CONCENTRATION FOR SIZE: COARS
      45.0+-     4.5

UNCERTAINTY/SIMILARITY CLUSTERS     CMB7 33889      SUM OF CLUSTER SOURCES
-----------------------------------------------------------------------

-----------------------------------------------------------------------
SPECIES CONCENTRATIONS -  SITE: SAS19          DATE: 08/26/94     CMB7 33889
SAMPLE DURATION          7D       START HOUR          0          SIZE:     COARS
       R SQUARE         .93     PERCENT MASS        77.8
     CHI SQUARE       10.99               DF          17

SPECIES--I---MEAS-----------------CALC-------------RATIO C/M----RATIO R/U
C1 TOT    T  45.04300+-  4.50430  35.05479+-  1.34771    .78+-  .08    -2.1
C2  NA    *    .65120+-   .06510 -29.49601+- 30.32121  *****+-46.78    -1.0
C3  MG    *    .38190+-   .03820    .43063+-   .02334   1.13+-  .13     1.1
C4  AL    *   1.84910+-   .11900   2.51174+-   .12270   1.36+-  .11     3.9
C5  SI    *   5.07500+-   .26840   3.87762+-   .15422    .76+-  .05    -3.9
C6  P      -99.00000+--99.00000 *********+-299.96470    .00+-  .00     -.6
C7  S      -99.00000+--99.00000 *********+-299.96470    .00+-  .00     -.6
C8  CL     -99.00000+--99.00000 *********+-*********    .00+-  .00    -2.0
C9  K     *   1.40380+-   .07070   1.16960+-   .03775    .83+-  .05    -2.9
C10 CA    *   1.14080+-   .05590    .90153+-   .04116    .79+-  .05    -3.4
C11 TI        .02370+-   .00130    .06520+-   .00430   2.75+-  .24     9.2
C12 V     *   .01320+-   .00070 *********+-301.49330  *****+-*****    -1.1
C13 CR        .00280+-   .00020 *********+-299.96470  *****+-*****    -1.0
C14 MN        .18360+-   .00920 -29.59595+- 30.32119  *****+-*****    -1.0
C15 FE    *   1.66890+-   .08360   1.96563+-   .06101   1.18+-  .07     2.9
C16 NI    *   .00560+-   .00040    .00495+-   .00021    .88+-  .07    -1.4
C17 CU    *   .01390+-   .00090    .01567+-   .00064   1.13+-  .09     1.6
C18 ZN    *   .29080+-   .01500    .22641+-   .00926    .78+-  .05    -3.7
C19 GA     -99.00000+--99.00000 *********+-933.89870    .00+-  .00    -1.3
C20 AS    *   .00560+-   .00030 *********+-197.37170  *****+-*****    -1.2
C21 SE    *   .00830+-   .00070 *********+-886.01400  *****+-*****    -1.2
C22 BR    *   .17360+-   .00970    .14455+-   .01141    .83+-  .08    -1.9
C23 SR        .00560+-   .00040 *********+-190.05980  *****+-*****    -1.0
C24 MO        .00250+-   .00020 *********+-190.05980  *****+-*****    -1.0
C25 BA        .00950+-   .00050 *********+-360.35230  *****+-*****    -1.6
C26 PB    *   .18900+-   .01030    .20445+-   .00670   1.08+-  .07     1.3
C27 NH4+   -99.00000+--99.00000 *********+-*********    .00+-  .00    -1.7
C28 NO3-  *   5.56480+-   .55650 *********+-596.40160  *****+-*****    -1.6
C29 SO4=  *   7.55250+-   .75530   7.55250+-   .66082   1.00+-  .13      .0
C30 CL-   *   .79730+-   .07970   1.04494+-   .09166   1.31+-  .17     2.0
C31 O1TC  *   .17470+-   .03490    .26895+-   .03570   1.54+-  .37     1.9
C32 O2TC  *  1.77000+-   .35400    .67992+-   .08236    .38+-  .09    -3.0
C33 O3TC  *  4.29930+-   .85990    .82763+-   .09204    .19+-  .04    -4.0
C34 O4TC  *  2.37980+-   .47600    .40920+-   .04041    .17+-  .04    -4.1
C35 E1TC  *  8.79530+-  1.75910    .71518+-   .09774    .08+-  .02    -4.6
C36 E2TC  *   .55060+-   .11010    .41319+-   .03927    .75+-  .17    -1.2
C37 E3TC  *   .06050+-   .01210    .17827+-   .02113   2.95+-  .69     4.8
```

# APPENDIX B

# TABLES AND GRAPHS OF SOURCE CHEMICAL DATA

Table B1: Source chemical data used for modelling.

| NAME | SINTER | PETROL | ISCORCF1 | SOIL | COMSOIL | AMSUL | AMNIT | SECSULP | PSFA | COMCOALT | COMARCT | COMARC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na | 0.138 | -99.000 | 0.009 | 0.007 | 0.018 | 0.000 | 0.000 | 0.000 | 0.017 | 0.065 | 0.033 | 0.028 |
| Uncertainty | 0.014 | -99.000 | 0.001 | 0.001 | 0.002 | 0.000 | 0.000 | 0.000 | 0.002 | 0.006 | 0.003 | 0.003 |
| Mg | 0.016 | 0.002 | 0.008 | 0.006 | 0.004 | 0.000 | 0.000 | 0.000 | 0.016 | 0.001 | 0.030 | 0.035 |
| Uncertainty | 0.002 | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 | 0.003 | 0.004 |
| Al | 0.014 | 0.001 | 0.039 | 0.090 | 0.122 | 0.000 | 0.000 | 0.000 | 0.171 | 0.001 | 0.011 | 0.011 |
| Uncertainty | 0.001 | 0.000 | 0.004 | 0.005 | 0.010 | 0.000 | 0.000 | 0.000 | 0.012 | 0.000 | 0.001 | 0.001 |
| Si | 0.013 | 0.012 | 0.082 | 0.200 | 0.228 | 0.000 | 0.000 | 0.000 | 0.186 | 0.003 | 0.050 | 0.048 |
| Uncertainty | 0.001 | 0.001 | 0.008 | 0.010 | 0.018 | 0.000 | 0.000 | 0.000 | 0.014 | 0.000 | 0.003 | 0.003 |
| P | -99.000 | 0.001 | 0.002 | 0.001 | 0.005 | 0.000 | 0.000 | 0.000 | 0.010 | 0.011 | 0.001 | 0.001 |
| Uncertainty | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 |
| S | -99.000 | 0.000 | 0.025 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.014 | 0.005 | 0.009 | 0.009 |
| Uncertainty | -99.000 | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.001 | 0.001 |
| Cl | -99.000 | -99.000 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | -99.000 | -99.000 | -99.000 | -99.000 |
| Uncertainty | -99.000 | -99.000 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | -99.000 | -99.000 | -99.000 | -99.000 |
| K | 0.243 | 0.009 | 0.016 | 0.017 | 0.019 | 0.000 | 0.000 | 0.000 | 0.015 | 0.016 | 0.030 | 0.023 |
| Uncertainty | 0.012 | 0.001 | 0.002 | 0.001 | 0.002 | 0.000 | 0.000 | 0.000 | 0.001 | 0.002 | 0.002 | 0.001 |
| Ca | 0.005 | 0.003 | 0.040 | 0.008 | 0.013 | 0.000 | 0.000 | 0.000 | 0.054 | 0.010 | 0.040 | 0.049 |
| Uncertainty | 0.000 | 0.000 | 0.004 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.004 | 0.001 | 0.002 | 0.002 |
| Ti | 0.000 | 0.000 | 0.001 | 0.001 | 0.002 | 0.000 | 0.000 | 0.000 | 0.006 | 0.001 | 0.001 | 0.000 |
| Uncertainty | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| V | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Uncertainty | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cr | -99.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 |
| Uncertainty | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mn | 0.000 | -99.000 | 0.002 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.142 | 0.146 |
| Uncertainty | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.007 | 0.007 |
| Fe | 0.014 | 0.004 | 0.075 | 0.062 | 0.060 | 0.000 | 0.000 | 0.000 | 0.018 | 0.001 | 0.221 | 0.220 |
| Uncertainty | 0.001 | 0.000 | 0.007 | 0.003 | 0.004 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.011 | 0.011 |
| Ni | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.000 | 0.000 |
| Uncertainty | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cu | 0.002 | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 |
| Uncertainty | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Zn | 0.000 | 0.002 | 0.013 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.001 | 0.004 | 0.041 | 0.038 |
| Uncertainty | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.002 |
| Ga | -99.000 | 0.002 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Uncertainty | -99.000 | 0.000 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| As | 0.000 | 0.004 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 |
| Uncertainty | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 |
| Se | 0.000 | 0.002 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 |
| Uncertainty | 0.000 | 0.000 | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 |
| Br | 0.002 | 0.366 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.005 | 0.004 |
| Uncertainty | 0.000 | 0.037 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Sr | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 | 0.000 | 0.000 |
| Uncertainty | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mo | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Uncertainty | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ba | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | -99.000 | 0.001 | 0.001 |
| Uncertainty | -99.000 | -99.000 | -99.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 | 0.000 | 0.000 |
| Pb | 0.002 | 0.423 | 0.002 | 0.002 | 0.002 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.009 | 0.008 |
| Uncertainty | 0.000 | 0.020 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NH4+ | -99.000 | -99.000 | -99.000 | -99.000 | -99.000 | 0.273 | 0.226 | 0.000 | 0.000 | 0.000 | -99.000 | -99.000 |
| Uncertainty | -99.000 | -99.000 | -99.000 | -99.000 | -99.000 | 0.027 | 0.023 | 0.000 | 0.000 | 0.000 | -99.000 | -99.000 |
| NO3- | -99.000 | 0.007 | -99.000 | 0.004 | 0.003 | 0.000 | 0.775 | 0.000 | 0.002 | 0.003 | 0.002 | -99.000 |
| Uncertainty | -99.000 | 0.001 | -99.000 | 0.000 | 0.000 | 0.000 | 0.078 | 0.000 | 0.000 | 0.000 | 0.000 | -99.000 |
| SO4= | 0.008 | 0.008 | 0.053 | 0.030 | 0.017 | 0.727 | 0.000 | 1.000 | 0.047 | 0.011 | 0.028 | 0.030 |
| Uncertainty | 0.001 | 0.001 | 0.005 | 0.003 | 0.002 | 0.073 | 0.000 | 0.100 | 0.005 | 0.001 | 0.003 | 0.003 |
| Cl- | 0.302 | 0.005 | 0.005 | 0.003 | 0.003 | 0.000 | 0.000 | 0.000 | 0.004 | 0.023 | 0.009 | 0.011 |
| Uncertainty | 0.030 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.001 | 0.001 |
| O1TC | 0.001 | 0.069 | 0.004 | 0.006 | 0.008 | 0.000 | 0.000 | 0.000 | 0.008 | 0.189 | 0.002 | 0.002 |
| Uncertainty | 0.000 | 0.014 | 0.001 | 0.001 | 0.002 | 0.000 | 0.000 | 0.000 | 0.003 | 0.045 | 0.000 | 0.000 |
| O2TC | 0.003 | 0.031 | 0.020 | 0.044 | 0.031 | 0.000 | 0.000 | 0.000 | 0.011 | 0.190 | 0.008 | 0.007 |
| Uncertainty | 0.001 | 0.006 | 0.004 | 0.009 | 0.006 | 0.000 | 0.000 | 0.000 | 0.002 | 0.038 | 0.002 | 0.002 |
| O3TC | 0.011 | 0.044 | 0.037 | 0.048 | 0.044 | 0.000 | 0.000 | 0.000 | 0.017 | 0.169 | 0.014 | 0.011 |
| Uncertainty | 0.002 | 0.009 | 0.007 | 0.010 | 0.001 | 0.000 | 0.000 | 0.000 | 0.003 | 0.034 | 0.003 | 0.002 |
| 04TC | 0.005 | 0.042 | 0.064 | 0.016 | 0.018 | 0.000 | 0.000 | 0.000 | 0.004 | 0.111 | 0.005 | 0.004 |
| Uncertainty | 0.001 | 0.008 | 0.013 | 0.003 | 0.004 | 0.000 | 0.000 | 0.000 | 0.001 | 0.022 | 0.001 | 0.001 |
| E1TC | 0.001 | 0.016 | 0.244 | 0.011 | 0.008 | 0.000 | 0.000 | 0.000 | 0.001 | 0.161 | 0.011 | 0.009 |
| Uncertainty | 0.000 | 0.003 | 0.049 | 0.002 | 0.002 | 0.000 | 0.000 | 0.000 | 0.000 | 0.032 | 0.002 | 0.002 |
| E2TC | 0.002 | 0.004 | 0.063 | 0.009 | 0.008 | 0.000 | 0.000 | 0.000 | 0.005 | 0.071 | 0.027 | 0.025 |
| Uncertainty | 0.000 | 0.000 | 0.013 | 0.002 | 0.002 | 0.000 | 0.000 | 0.000 | 0.001 | 0.014 | 0.005 | 0.005 |
| E3TC | 0.000 | 0.003 | 0.003 | 0.002 | 0.001 | 0.000 | 0.000 | 0.000 | 0.005 | 0.028 | 0.016 | 0.019 |
| Uncertainty | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.006 | 0.003 | 0.004 |

**Figure B1: Sinter Plant - Iscor (resuspended - coarse fraction only)**

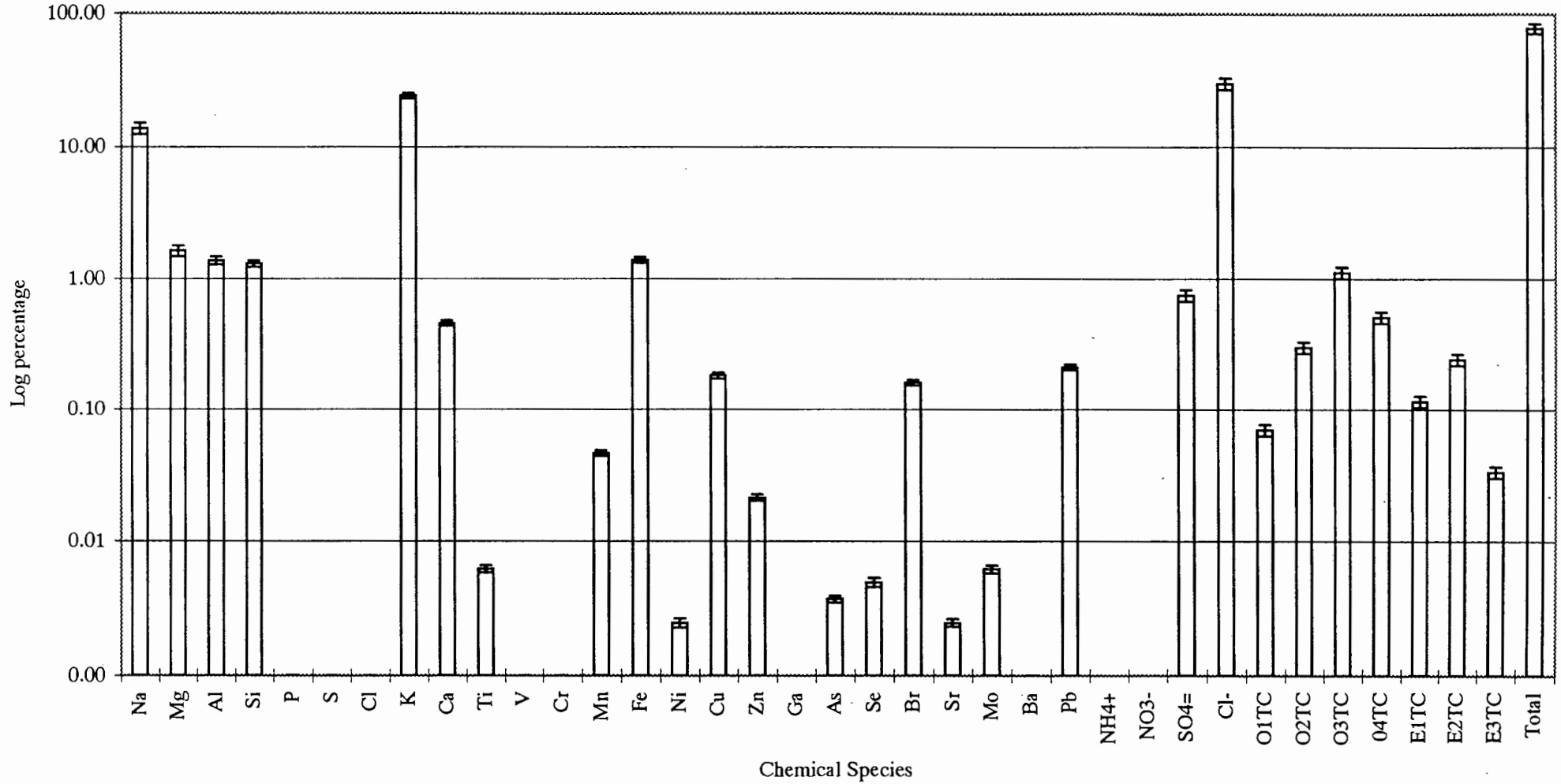


**Figure B2: Leaded petrol - Light motor vehicle emission (environmental sample - coarse fraction only)**

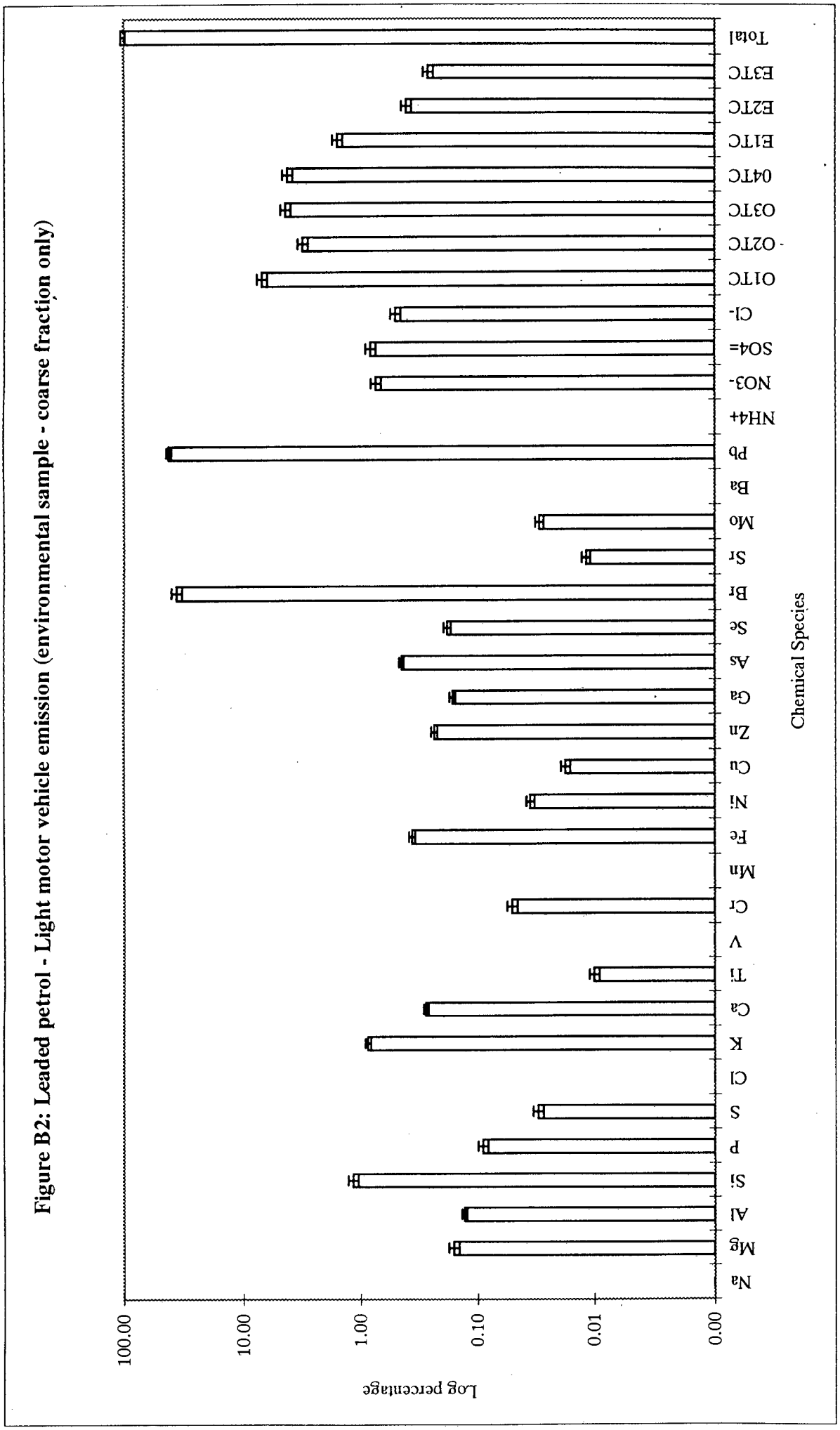
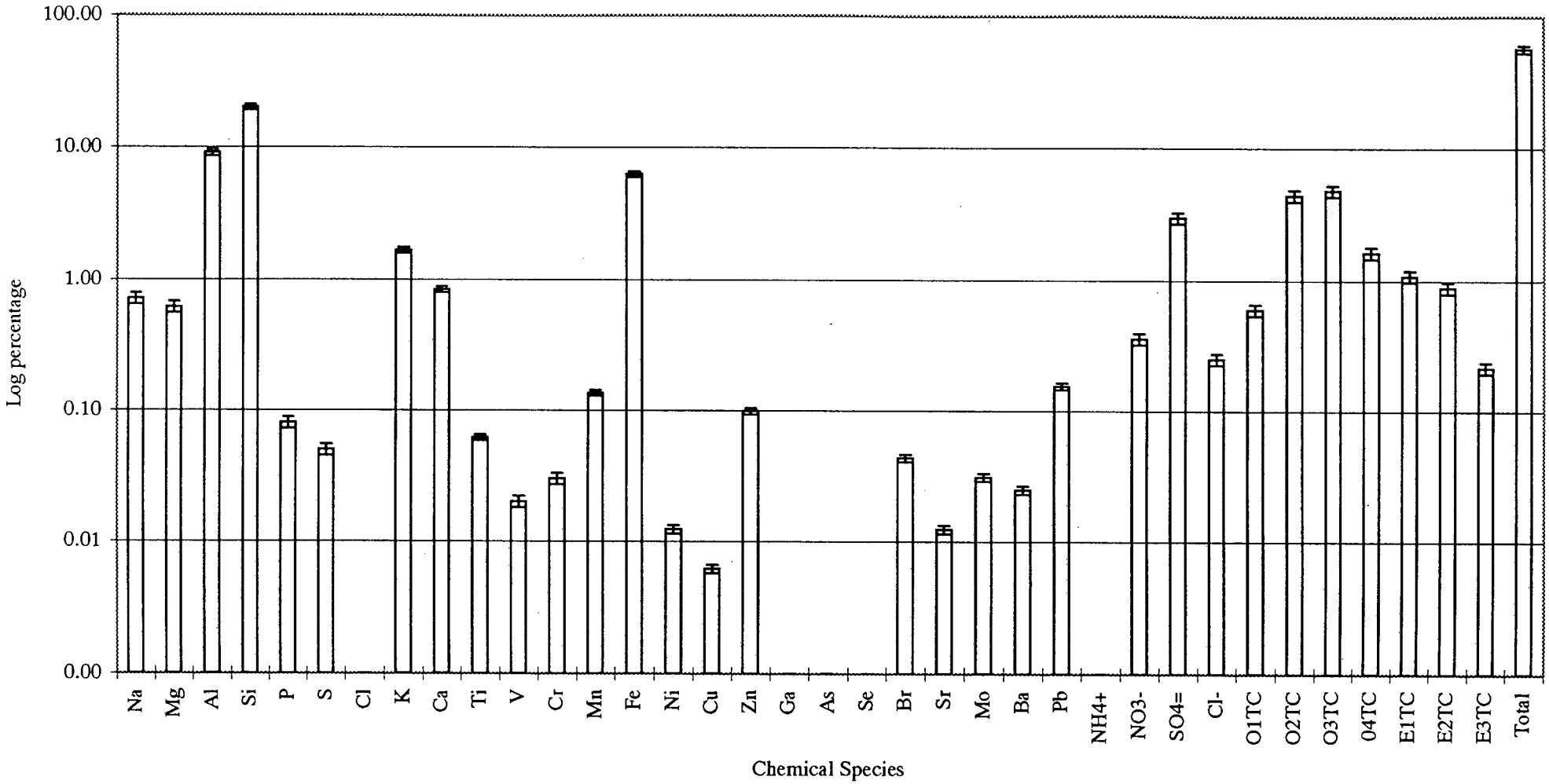


**Figure B3: Soil - Environmental source (resuspended - coarse fraction only)**



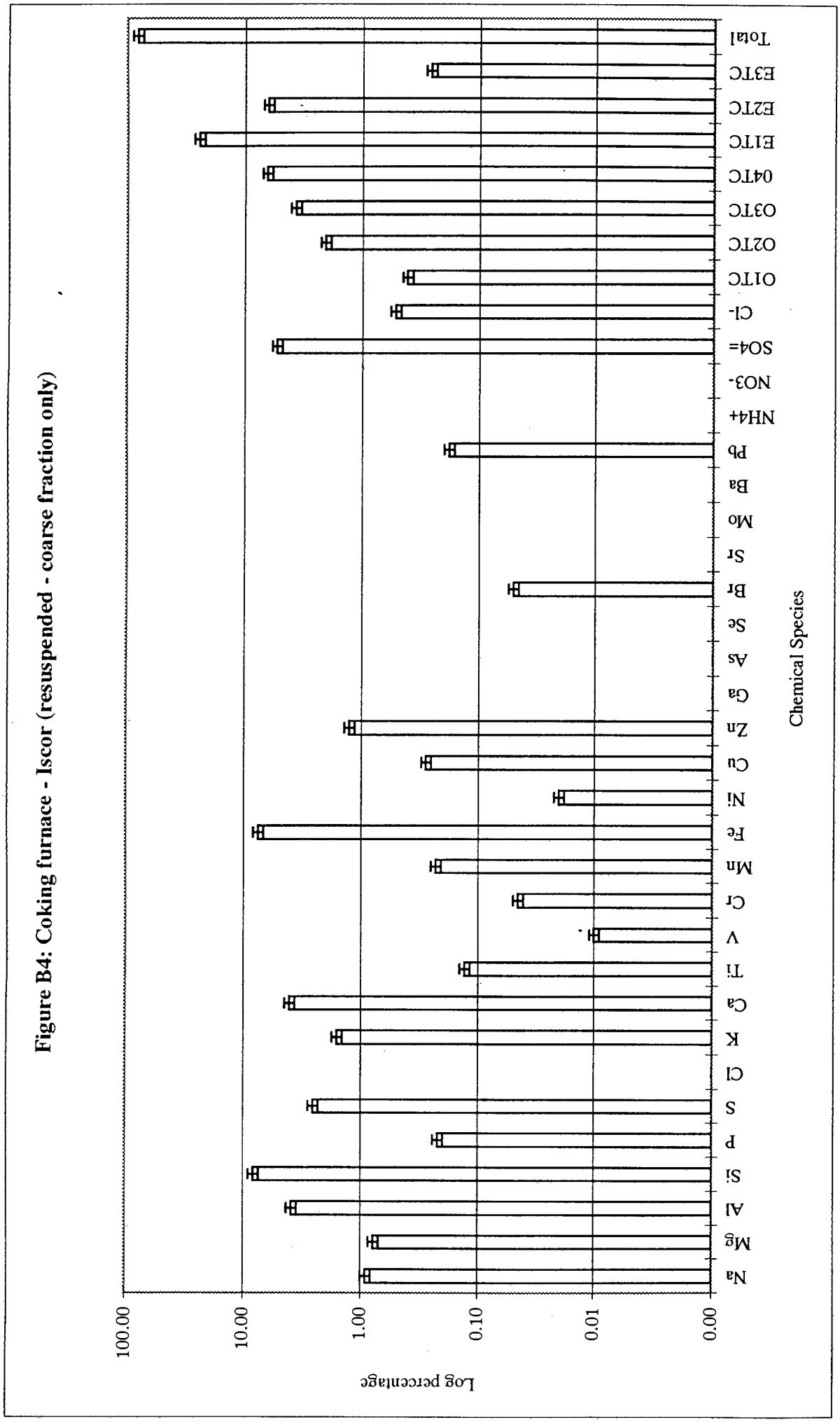


Figure B4: Coking furnace - Iscor (resuspended - coarse fraction only)
Log percentage
100.00
10.00
1.00
0.10
0.01
0.00
Chemical Species
Na
Mg
Al
Si
P
S
Cl
K
Ca
Ti
V
Cr
Mn
Fe
Ni
Cu
Zn
Ga
As
Se
Br
Sr
Mo
Ba
Pb
NH4+
NO3-
SO4=
Cl-
01TC
02TC
03TC
04TC
E1TC
E2TC
E3TC
Total

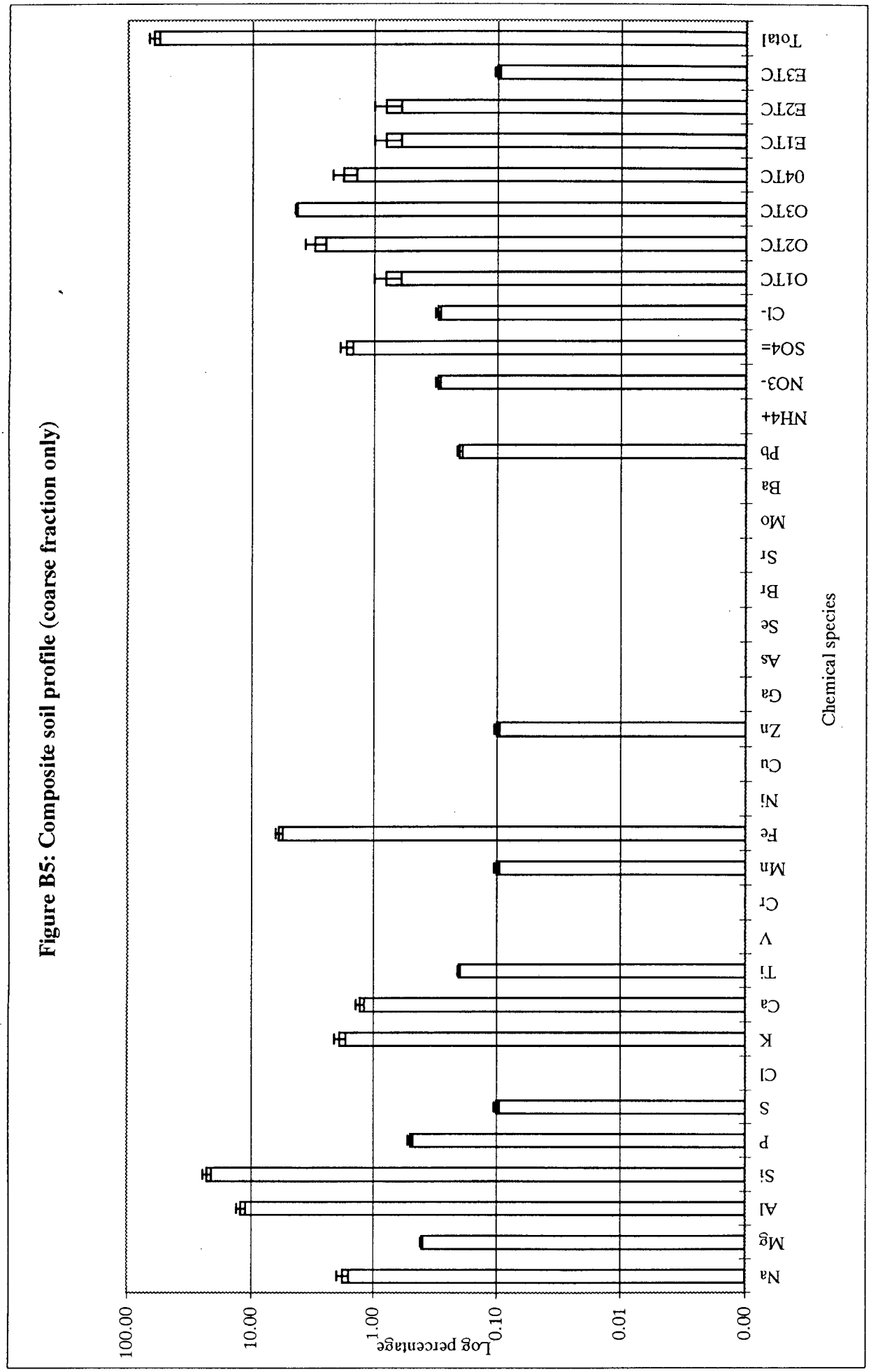


Figure B5: Composite soil profile (coarse fraction only)
100.00
10.00
1.00
0.10
0.01
0.00
Log percentage
Na
Mg
Al
Si
P
S
Cl
K
Ca
Ti
V
Cr
Mn
Fe
Ni
Cu
Zn
Ga
As
Se
Br
Sr
Mo
Ba
Pb
NH4+
NO3-
SO4=
Cl-
01TC
02TC
03TC
04TC
E1TC
E2TC
E3TC
Total
Chemical species

**Figure B6: Secondary ammonium sulphate**

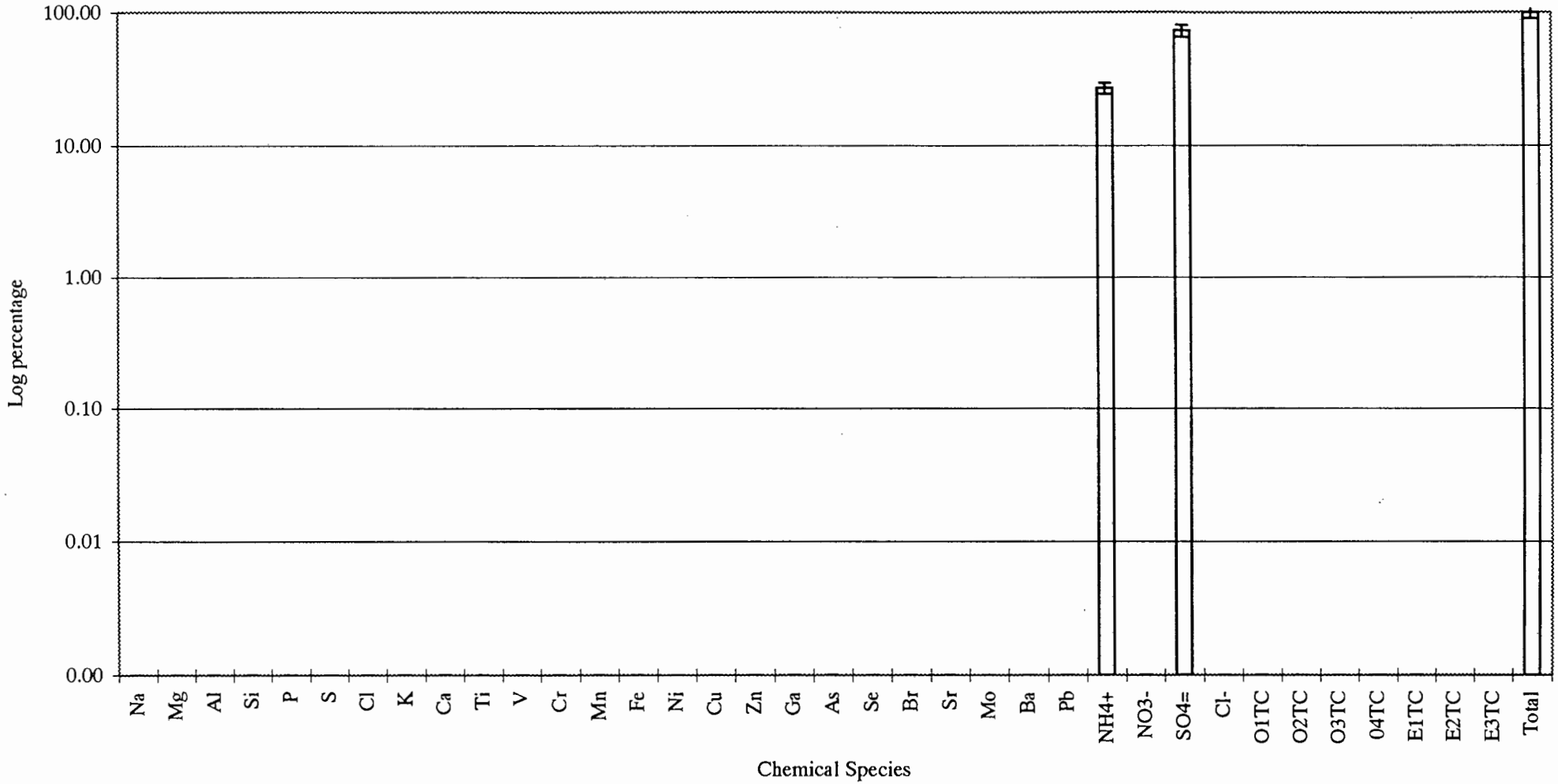


**Figure B7: Secondary ammonium nitrate**

**Figure B8: Secondary sulphate**

**Figure B9: Composite power station flyash (coarse fraction only)**

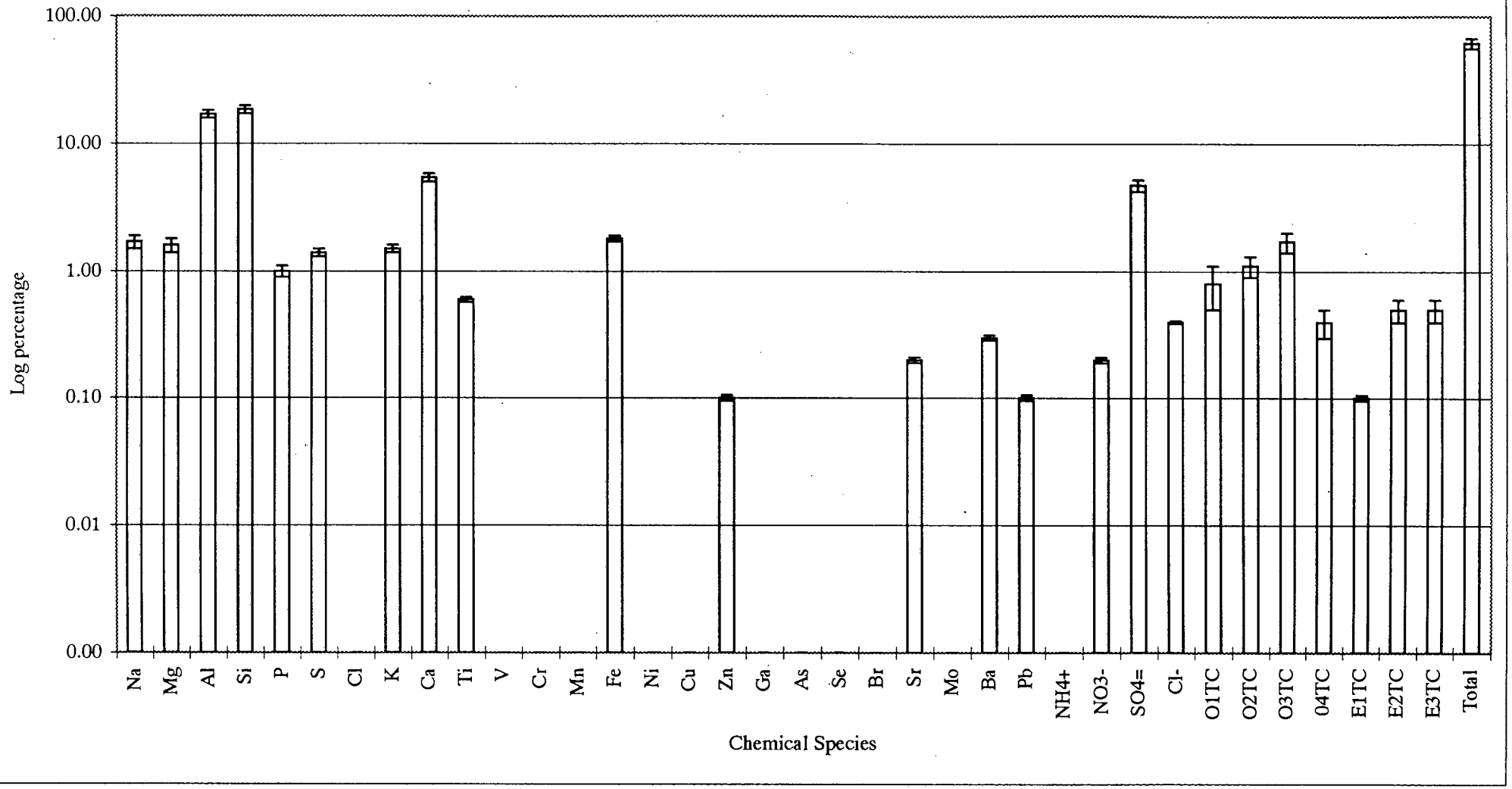
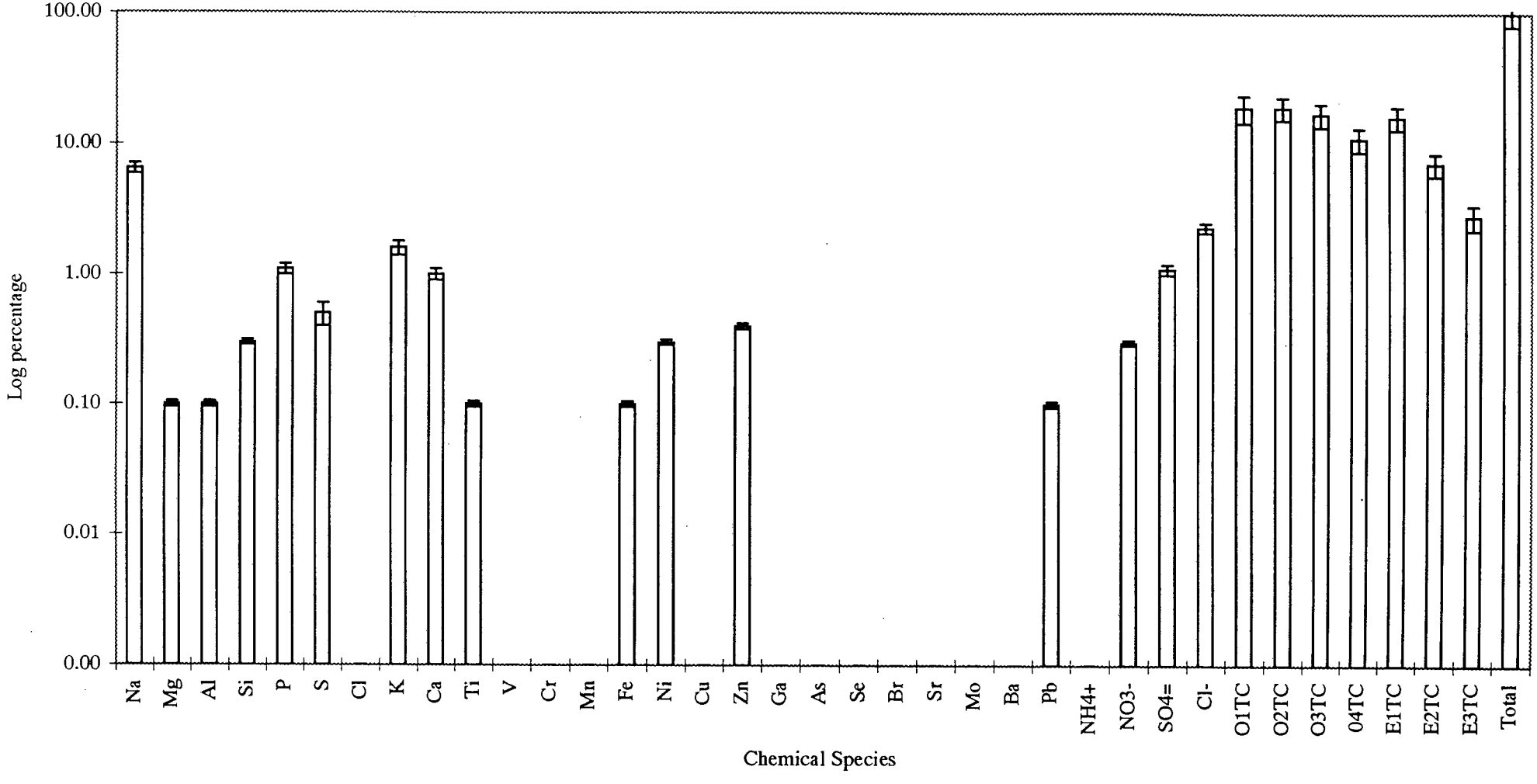


**Figure B10: Composite domestic coal burning profile (coarse and fine fractions)**



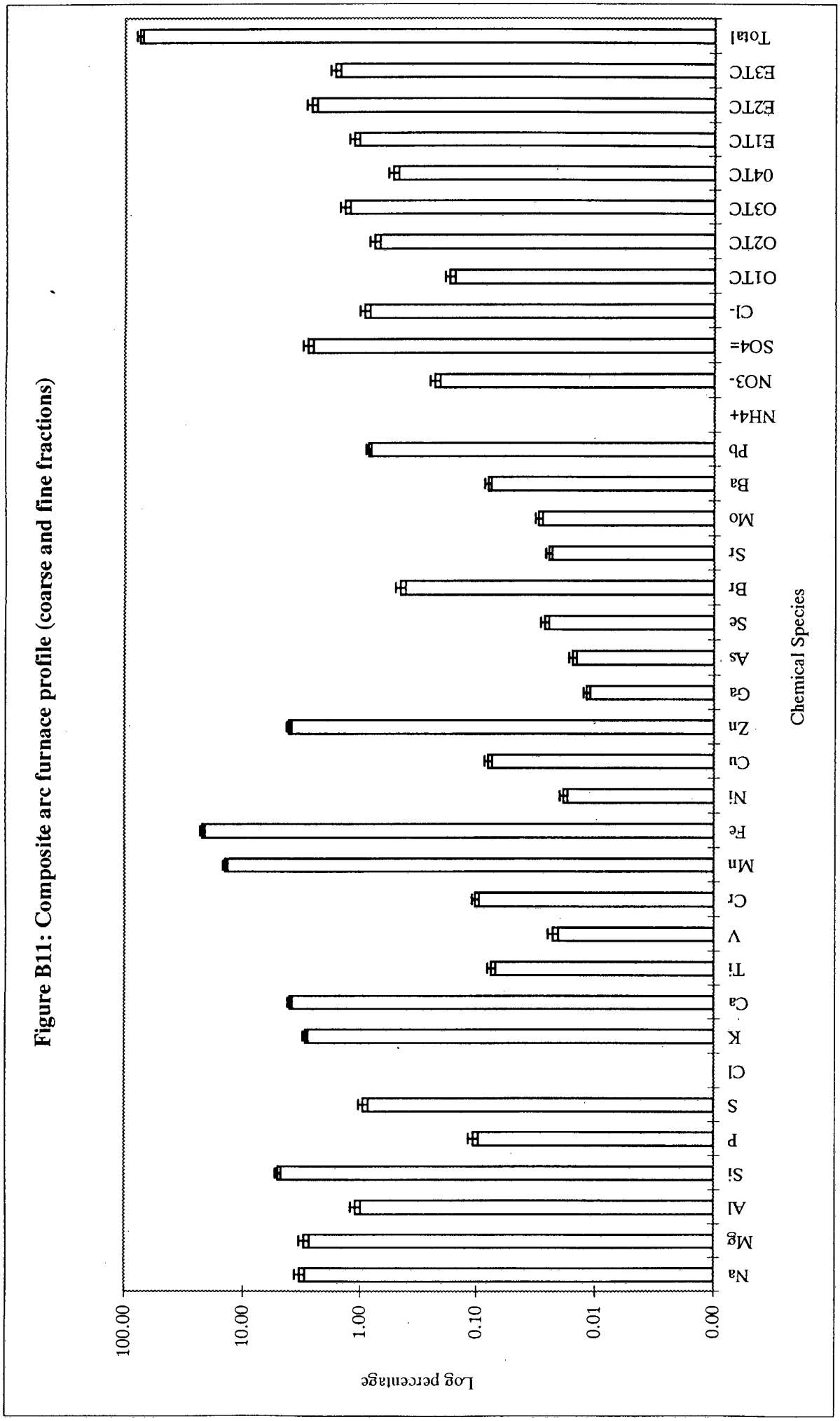



**Figure B11: Composite arc furnace profile (coarse and fine fractions)**

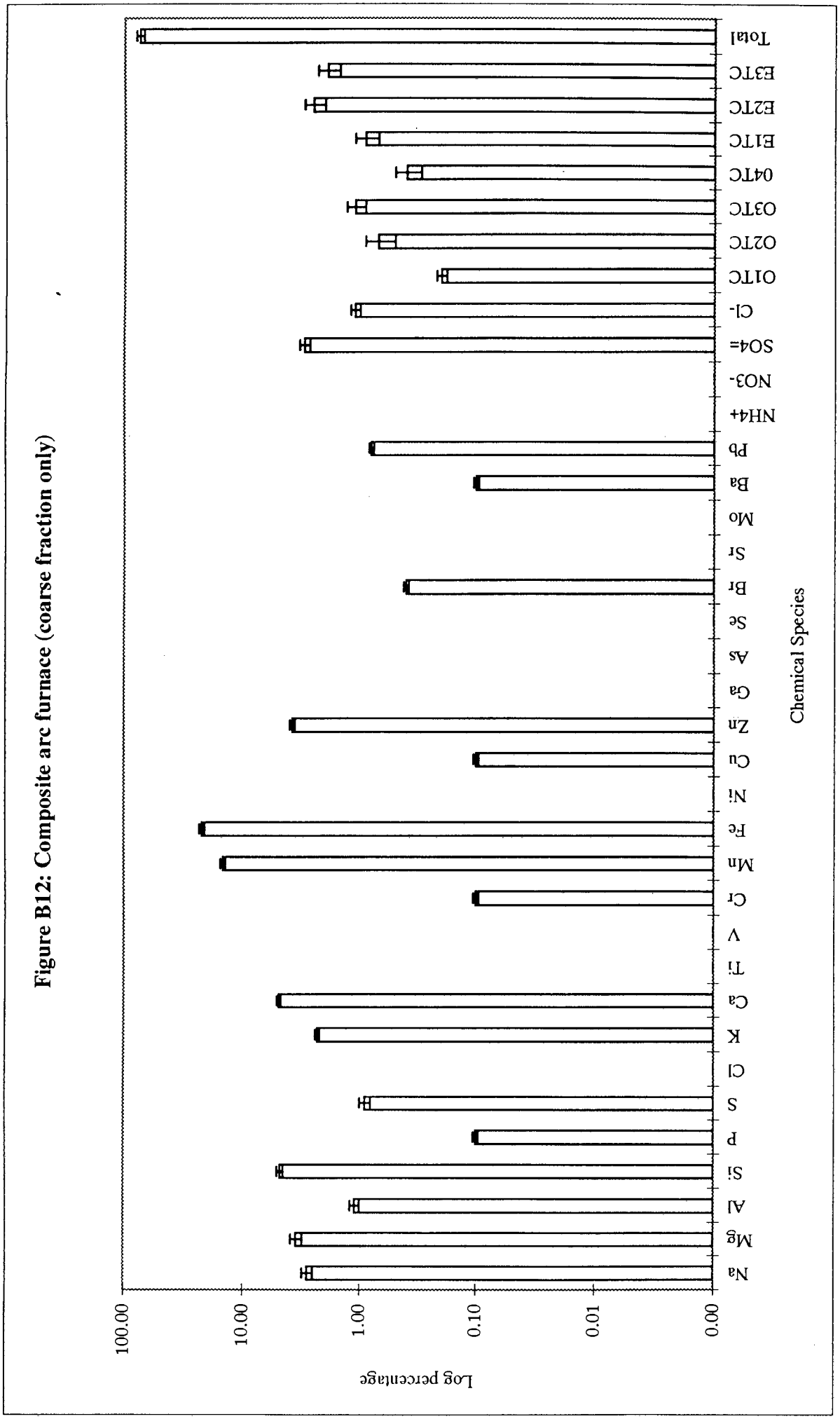



**Figure B12: Composite arc furnace (coarse fraction only)**

# APPENDIX C

# SPECIES CONCENTRATION PLOTS

**Figure C1: SPECIES CONCENTRATION: Vereeniging, 29 April 1994 (VER 02)**

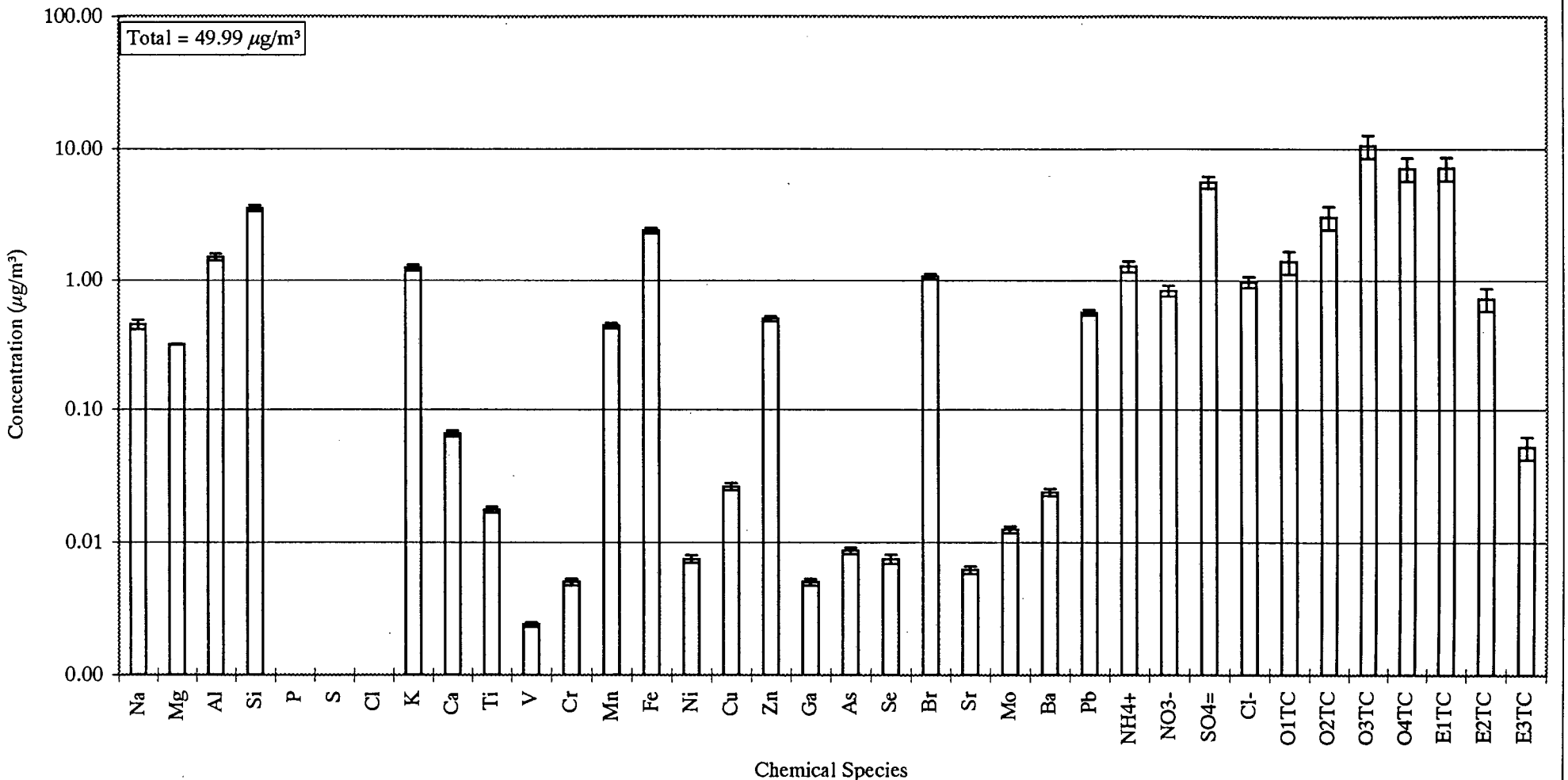


**Fig C2: SPECIES CONCENTRATION: Vanderbijlpark, 29 April 1994 (VAN 02)**

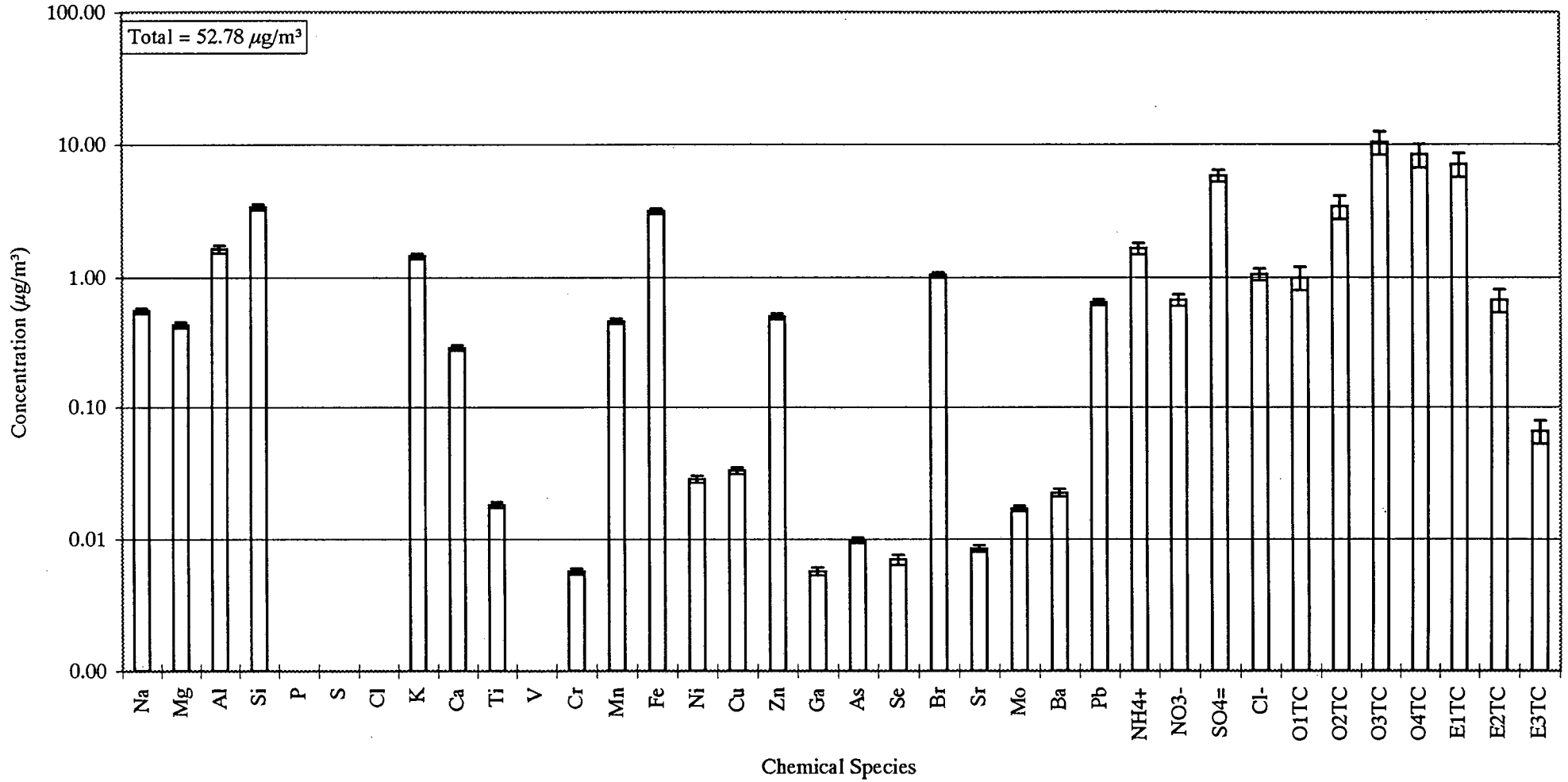


**Figure C3: SPECIES CONCENTRATION: Sasolburg, 29 April 1994 (SAS 02)**

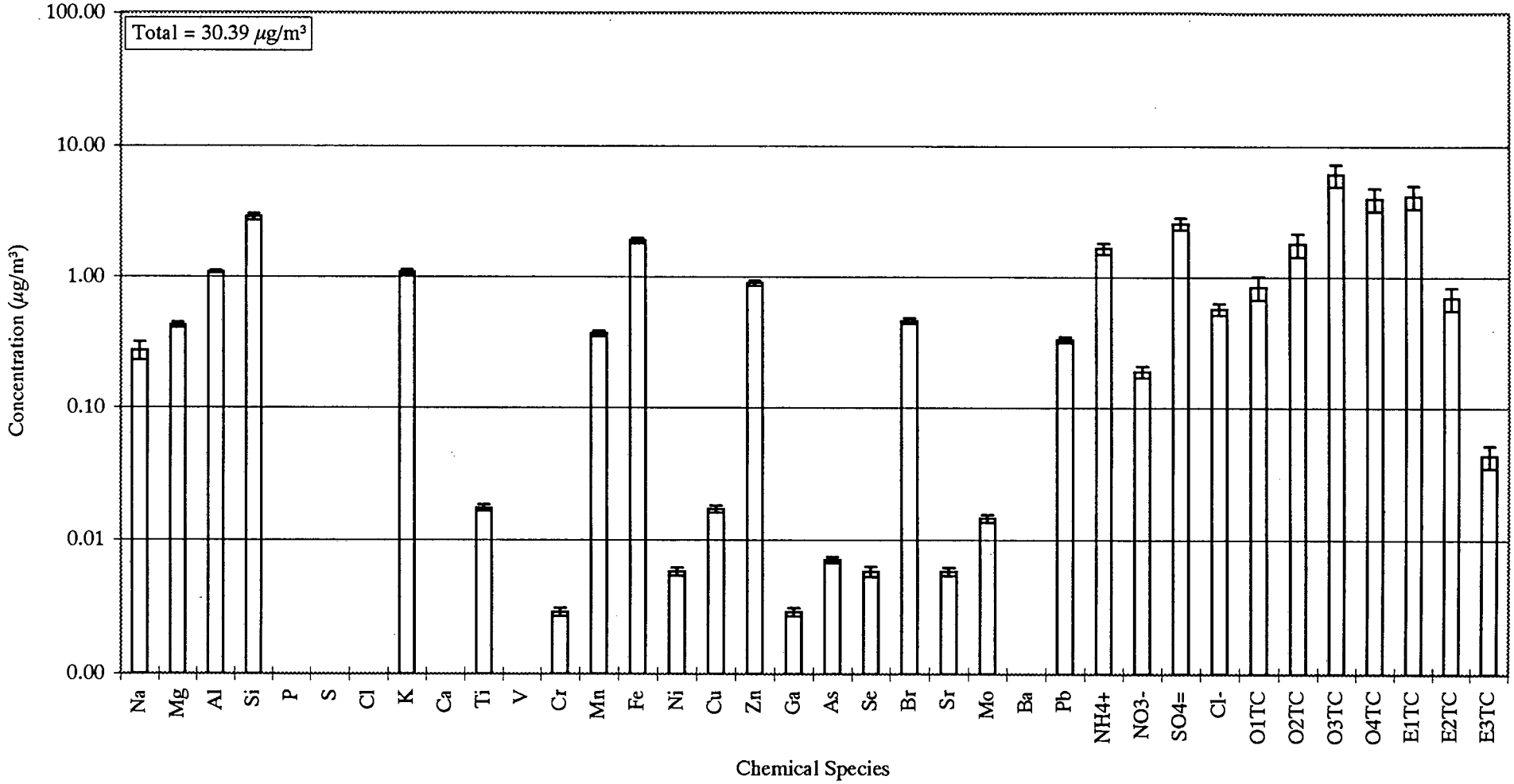


**Figure C4: Species Concentration: Vereeniging, 3 June 1994 (VER 07)**

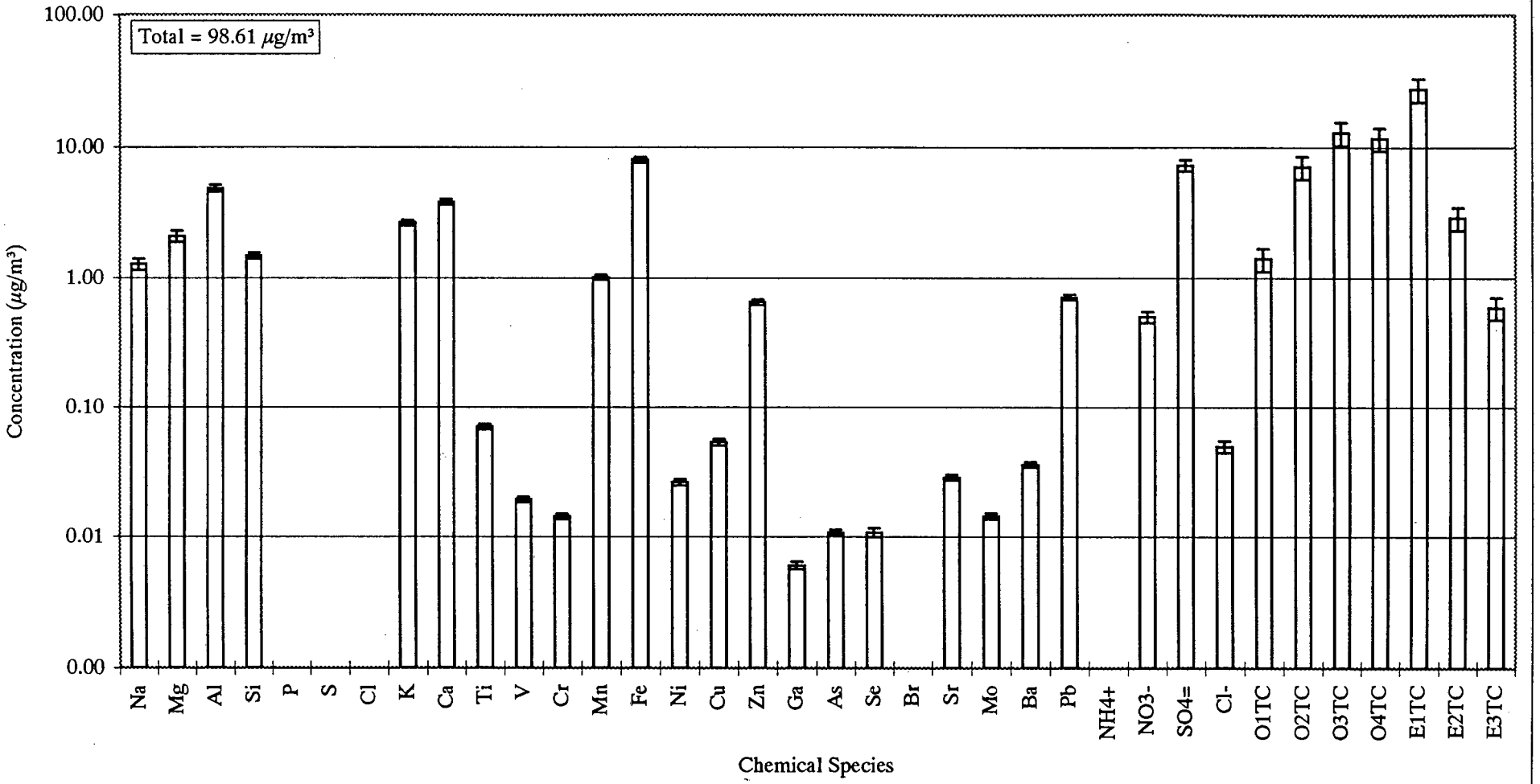


**Figure C5: SPECIES CONCENTRATION: Vereeniging, 10 June 1994 (VER 08)**

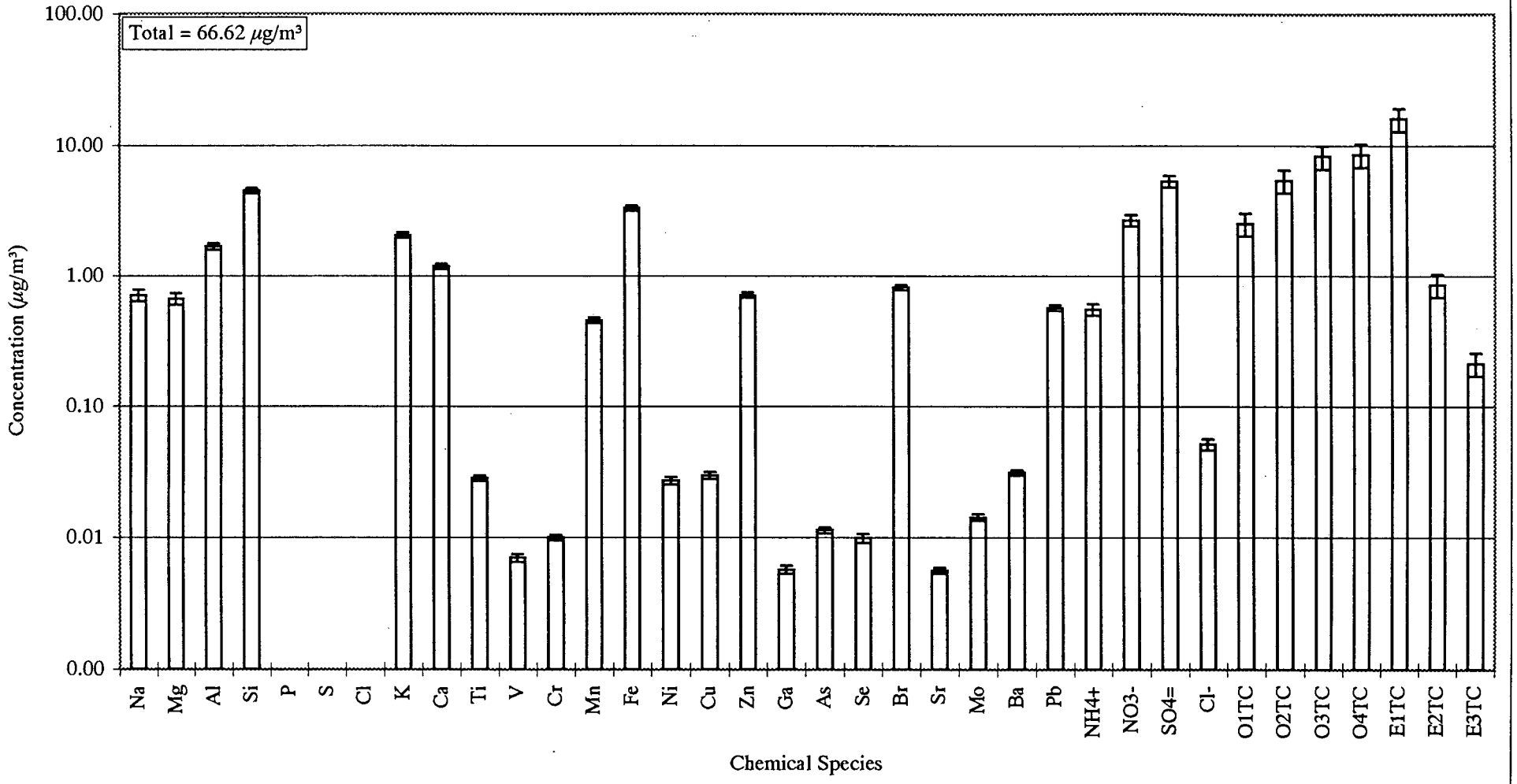


**Figure C6: SPECIES CONCENTRATION: Vanderbijlpark, 10 June 1994 (VAN 08)**

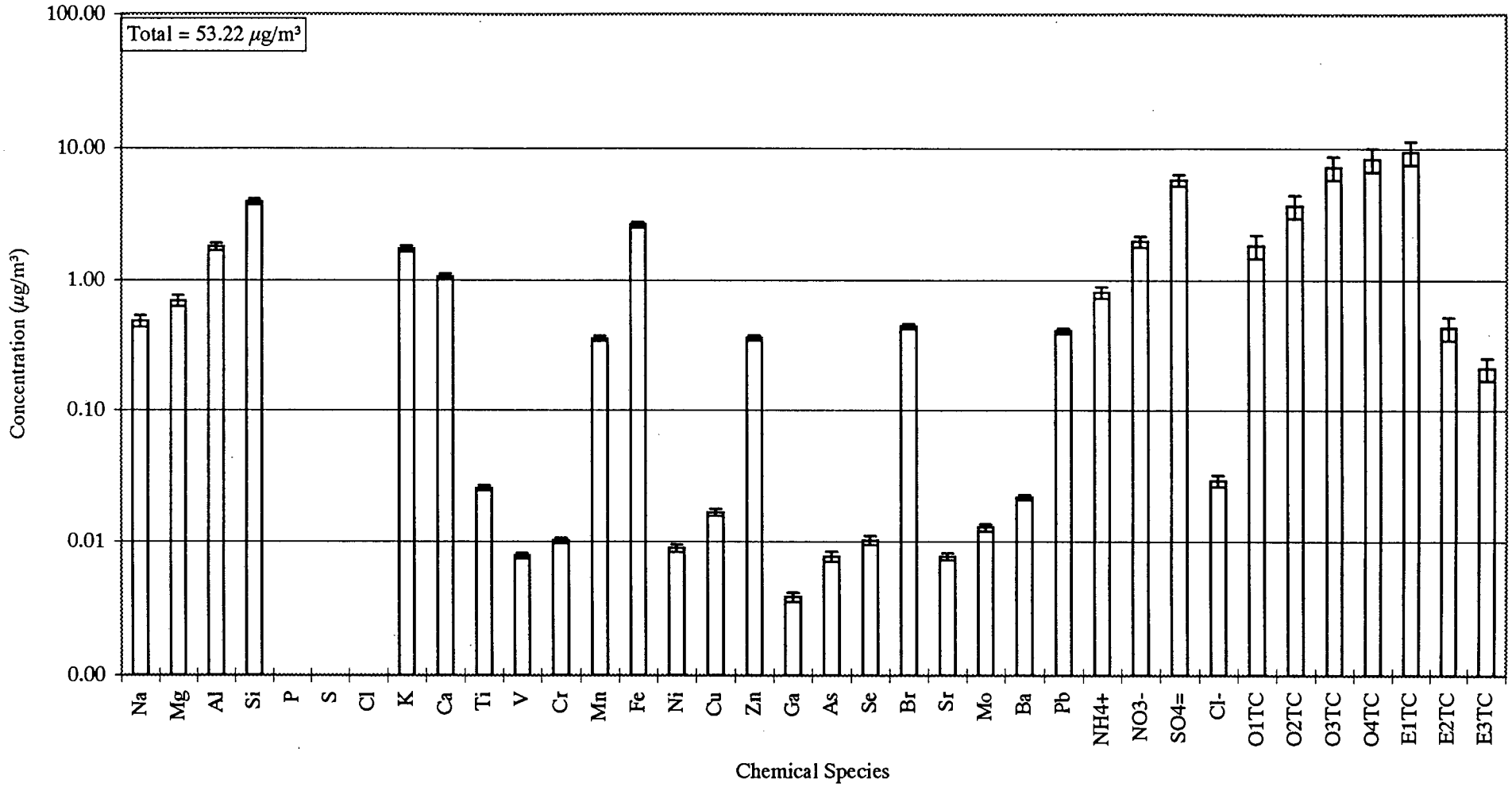


**Figure C7: SPECIES CONCENTRATION: Sasolburg, 10 June 1994 (SAS 08)**

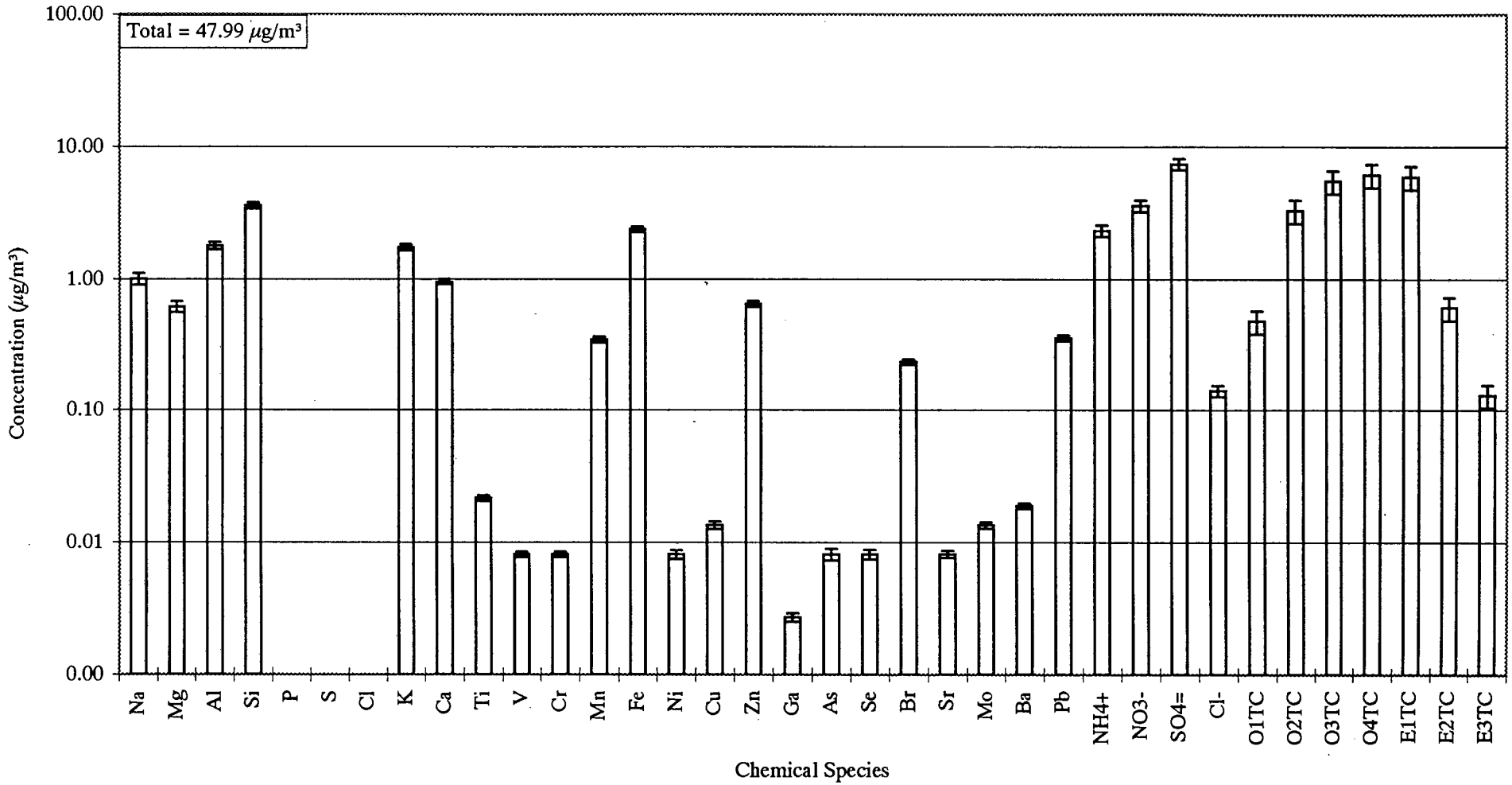


**Figure C8: SPECIES CONCENTRATION: Vereeniging, 8 July 1994 (VER 12)**

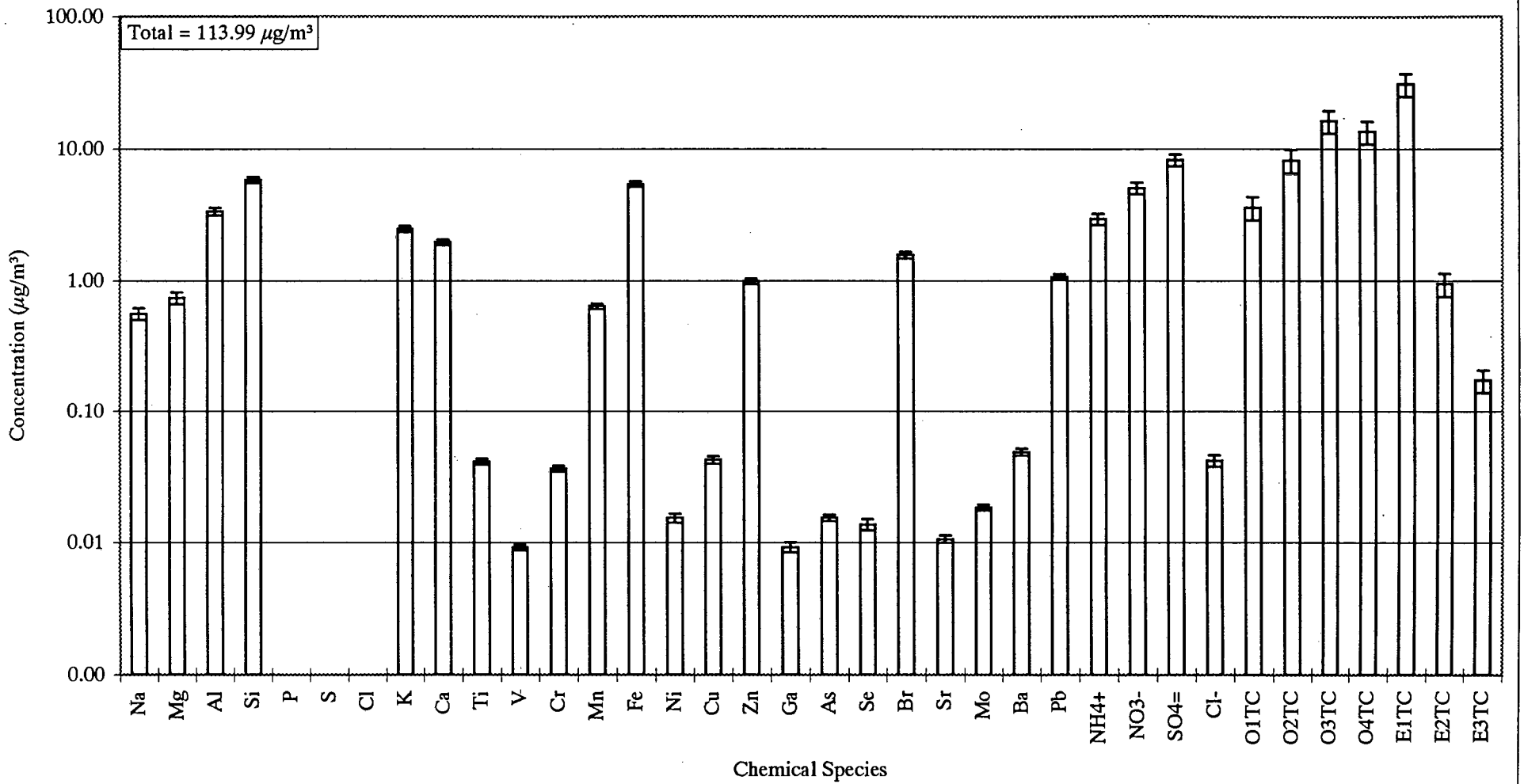


**Figure C9: SPECIES CONCENTRATION: Vanderbijlpark, 8 July 1994 (VAN 12)**

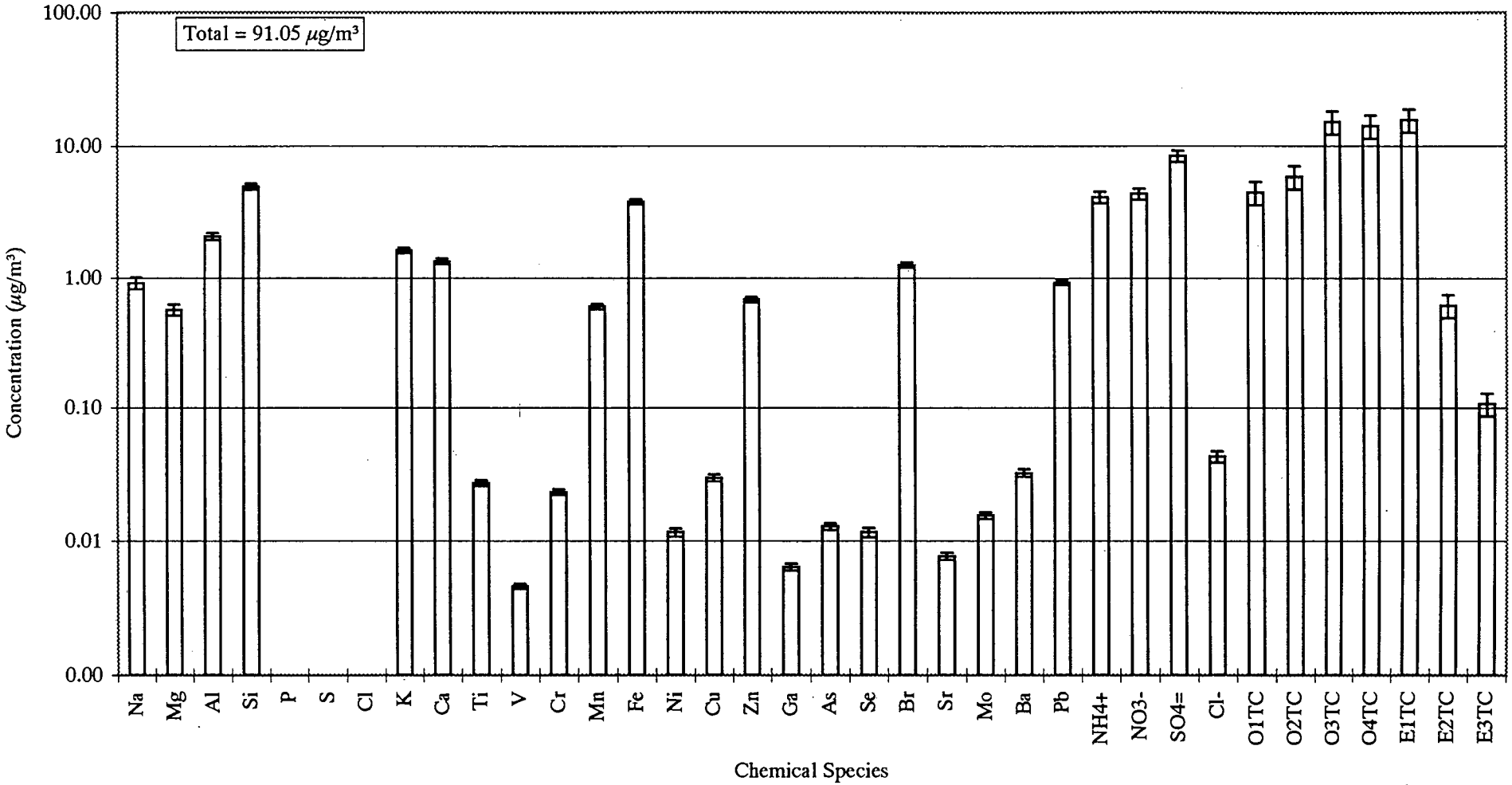


**Figure C10: SPECIES CONCENTRATION: Sasolburg, 8 July 1994 (SAS12)**

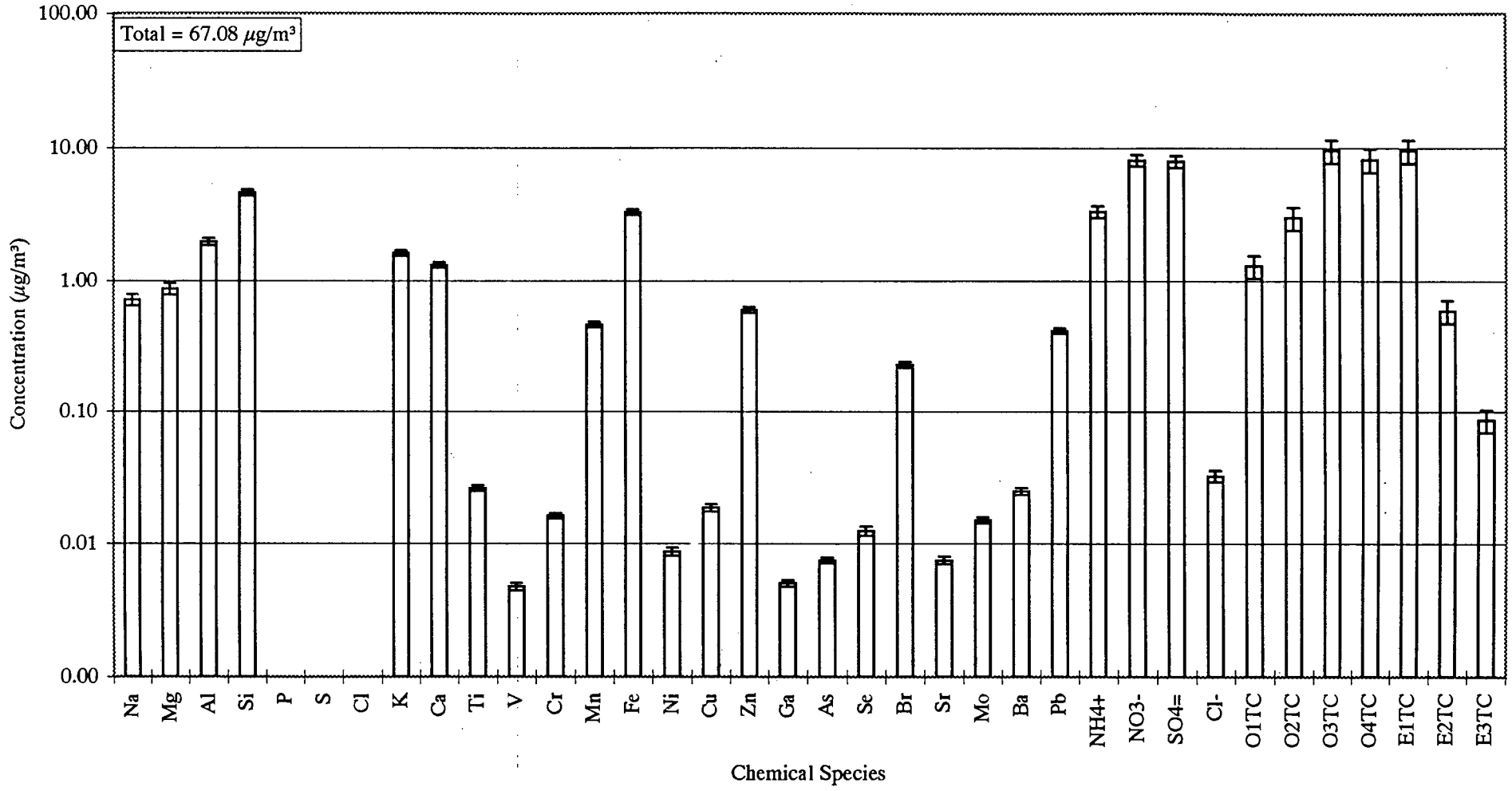


**Figure C11: SPECIES CONCENTRATION: Vanderbijlpark, 15 July 1994 (VAN 13)**

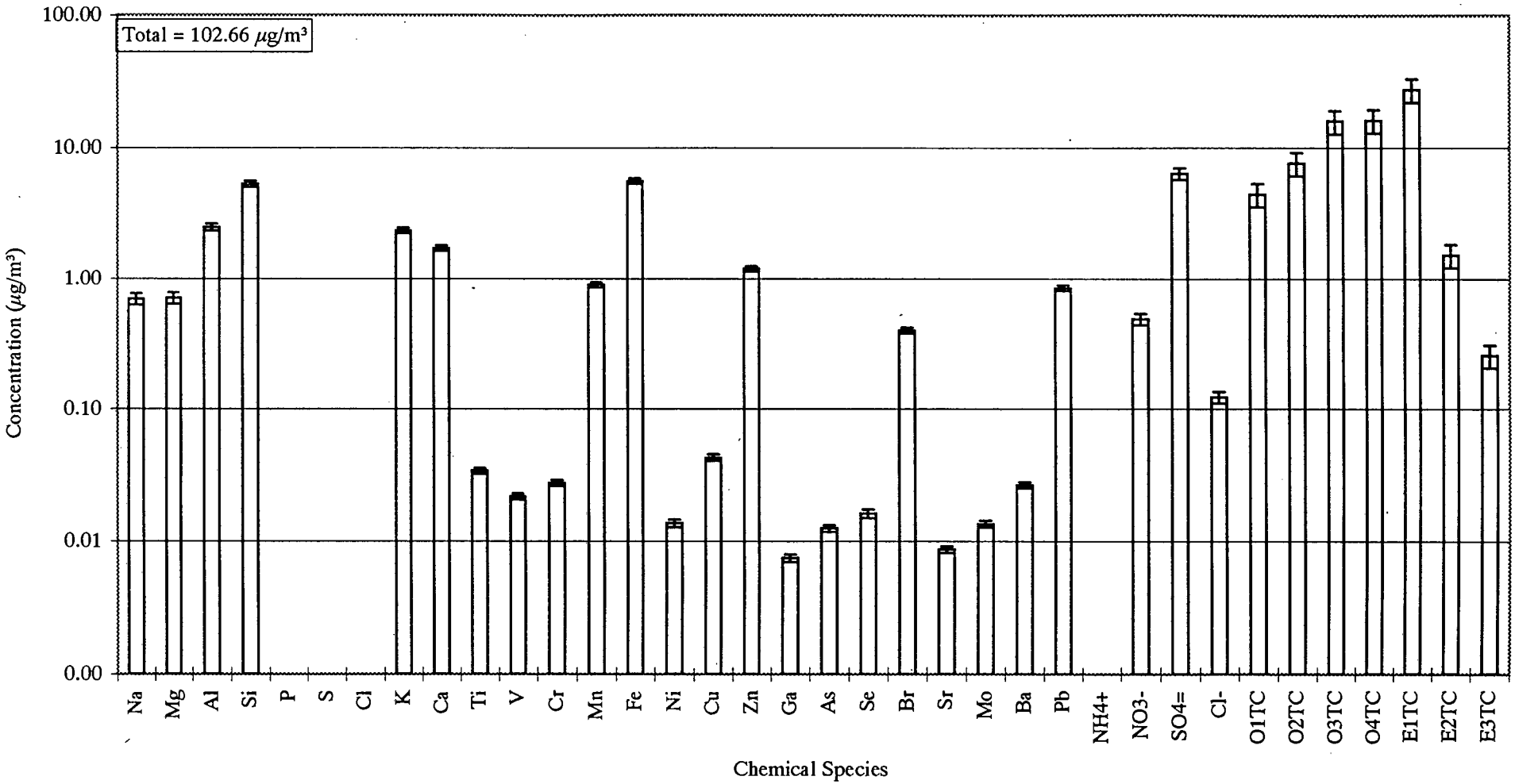


**Figure C12: SPECIES CONCENTRATION: Sasolburg, 15 July 19994 (SAS 13)**

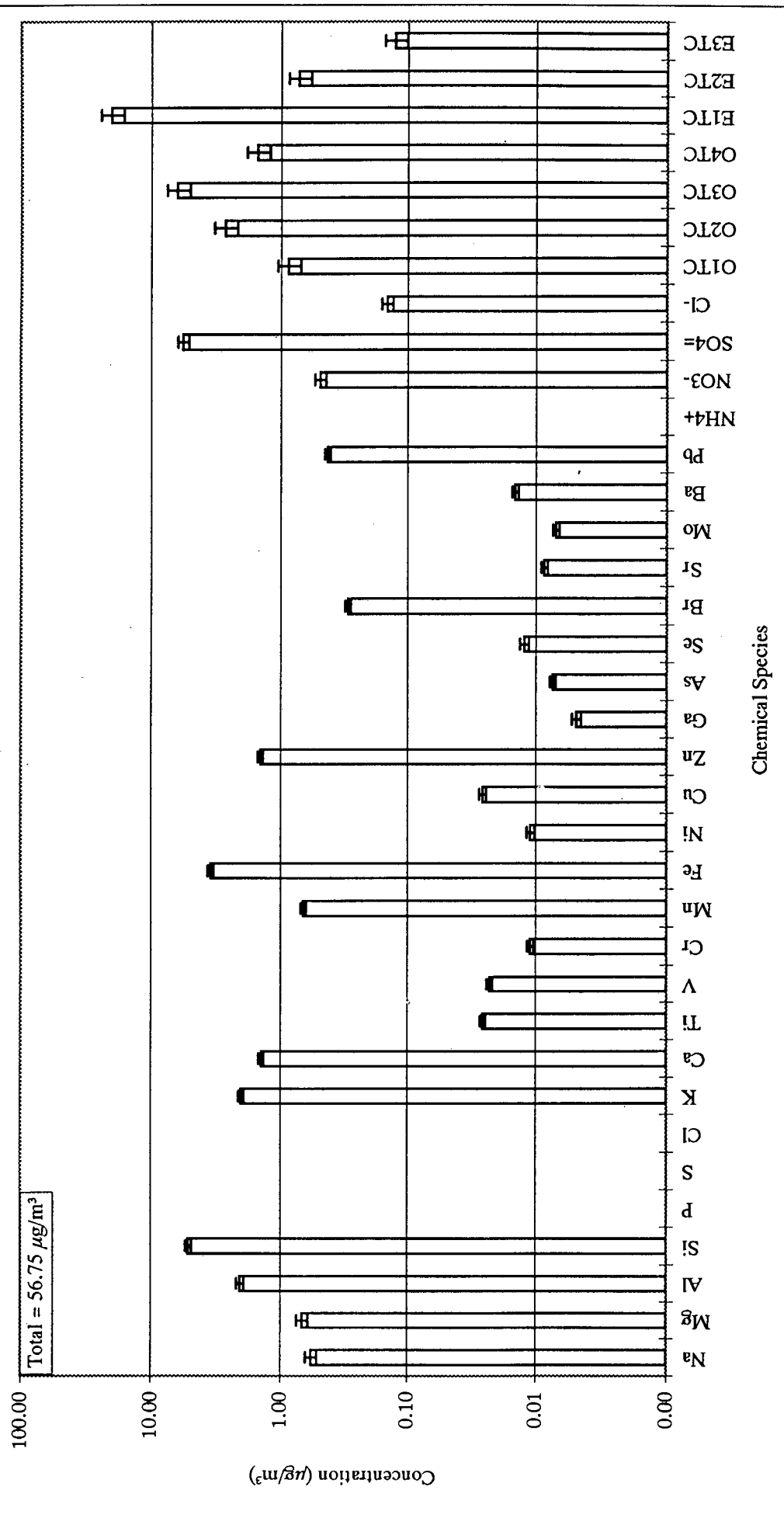


**Figure C13: SPECIES CONCENTRATION: Vereeniging, 26 August 1994 (VER 19)**

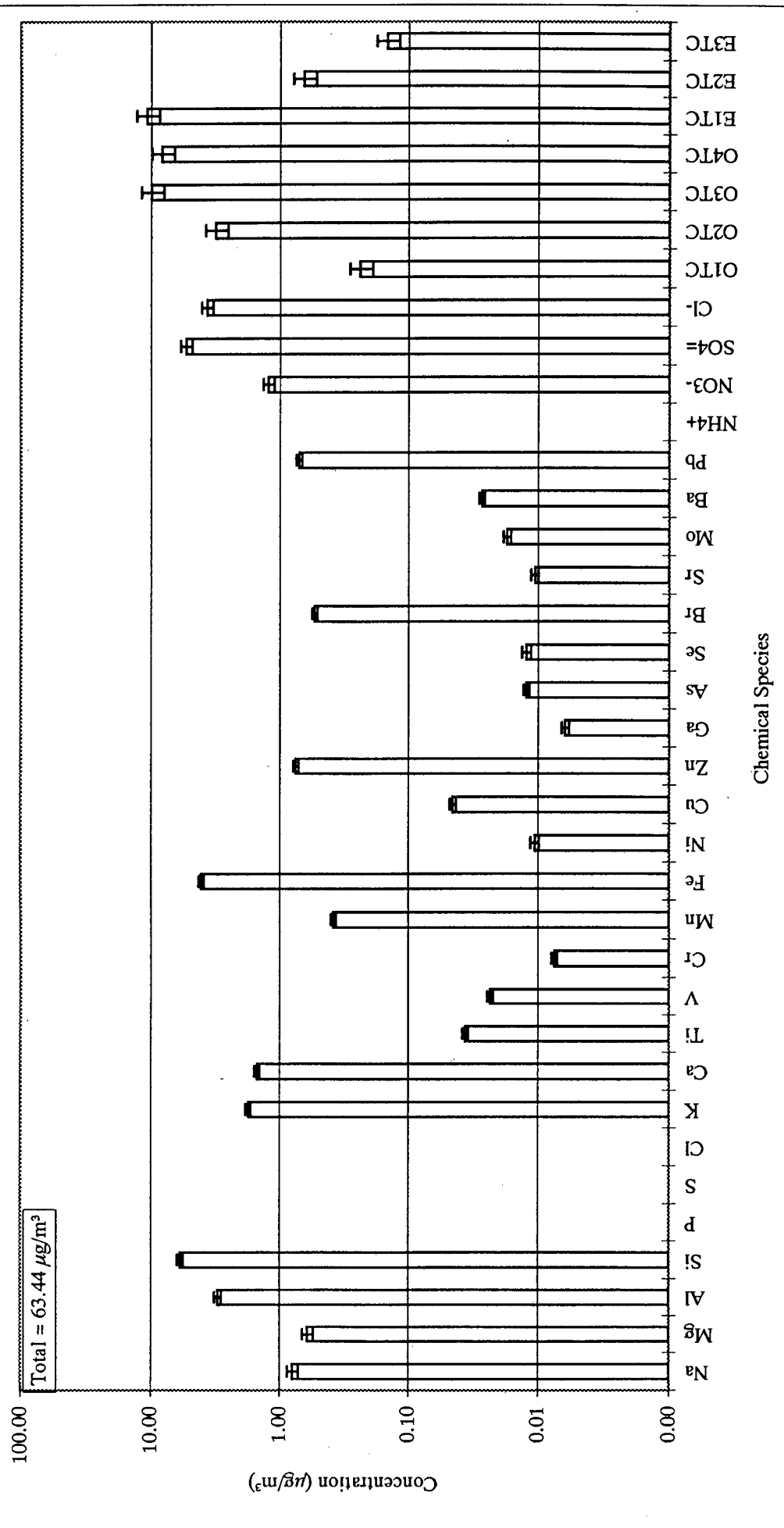


**Figure C14 : SPECIES CONCENTRATION: Vanderbijlpark, 26 August 1994 (VAN 19)**

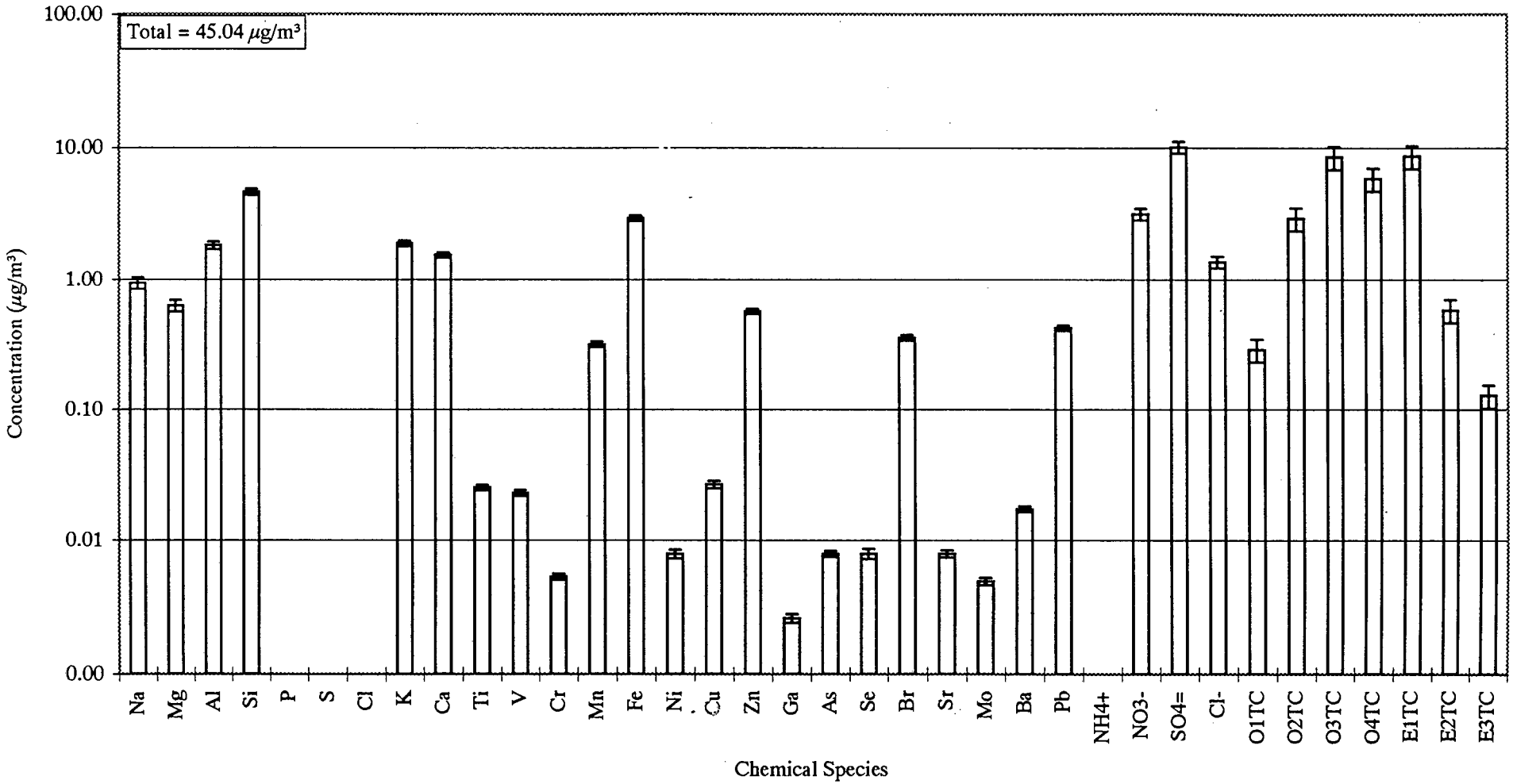
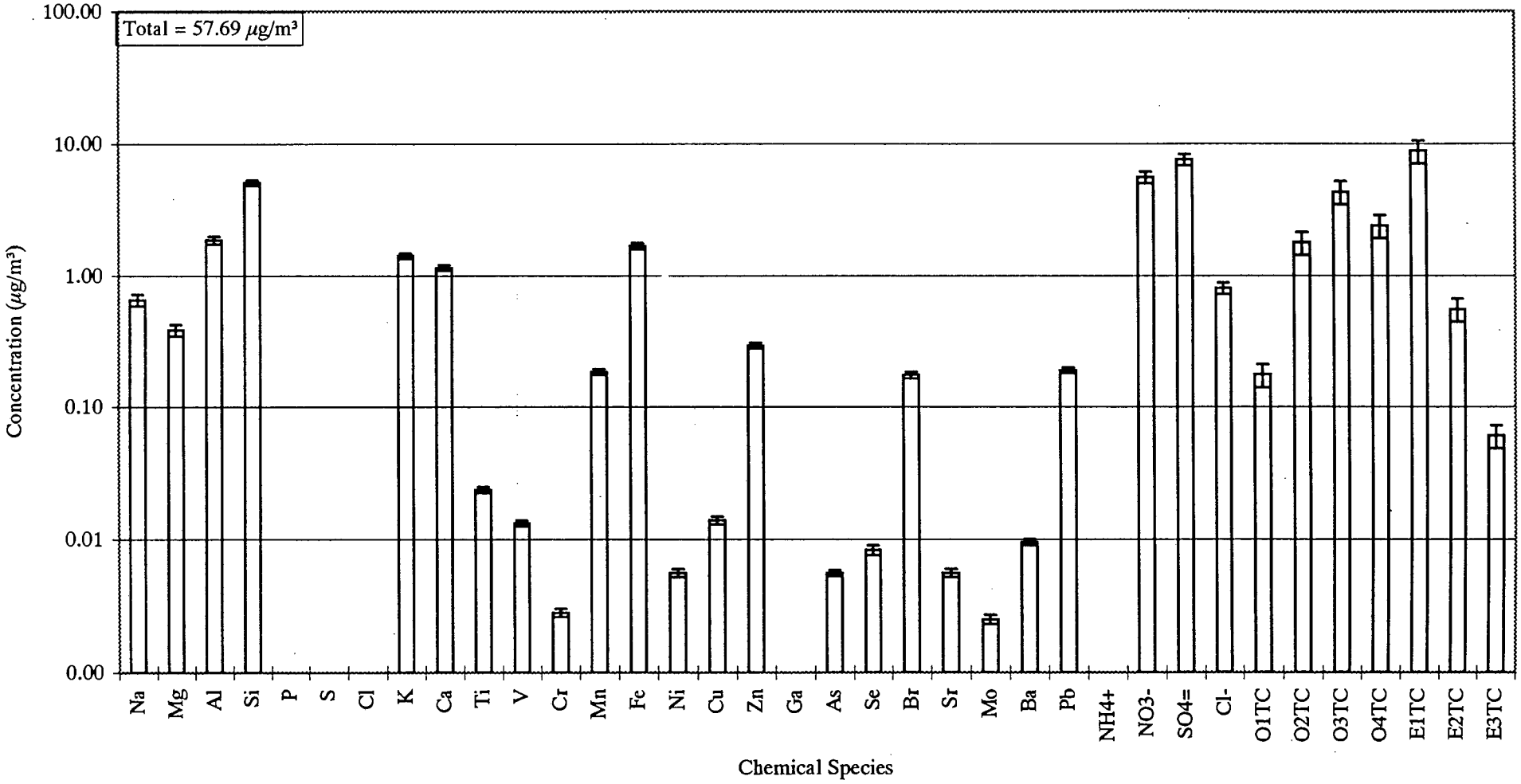


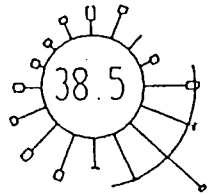
**Figure C15: SPECIES CONCENTRATION: Sasolburg, 26 August 1994 (SAS19)**



# APPENDIX D

## CMB7 SOURCE CONTRIBUTION PIE GRAPHS

**Figure D1: Vereeniging - Week 02 (04/29/94 - 05/06/94) Duration: 7 days Size: Coarse**



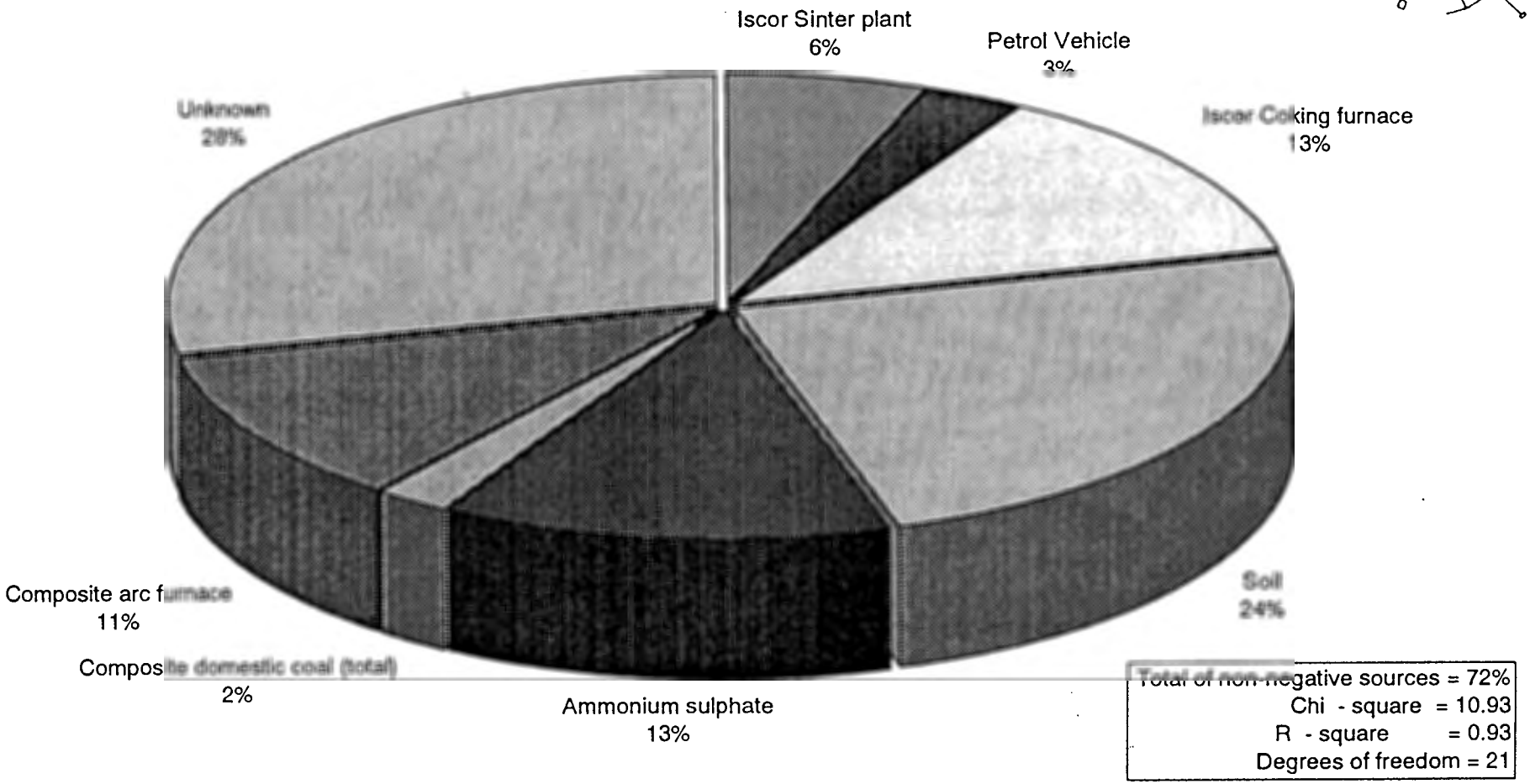
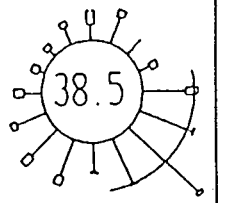
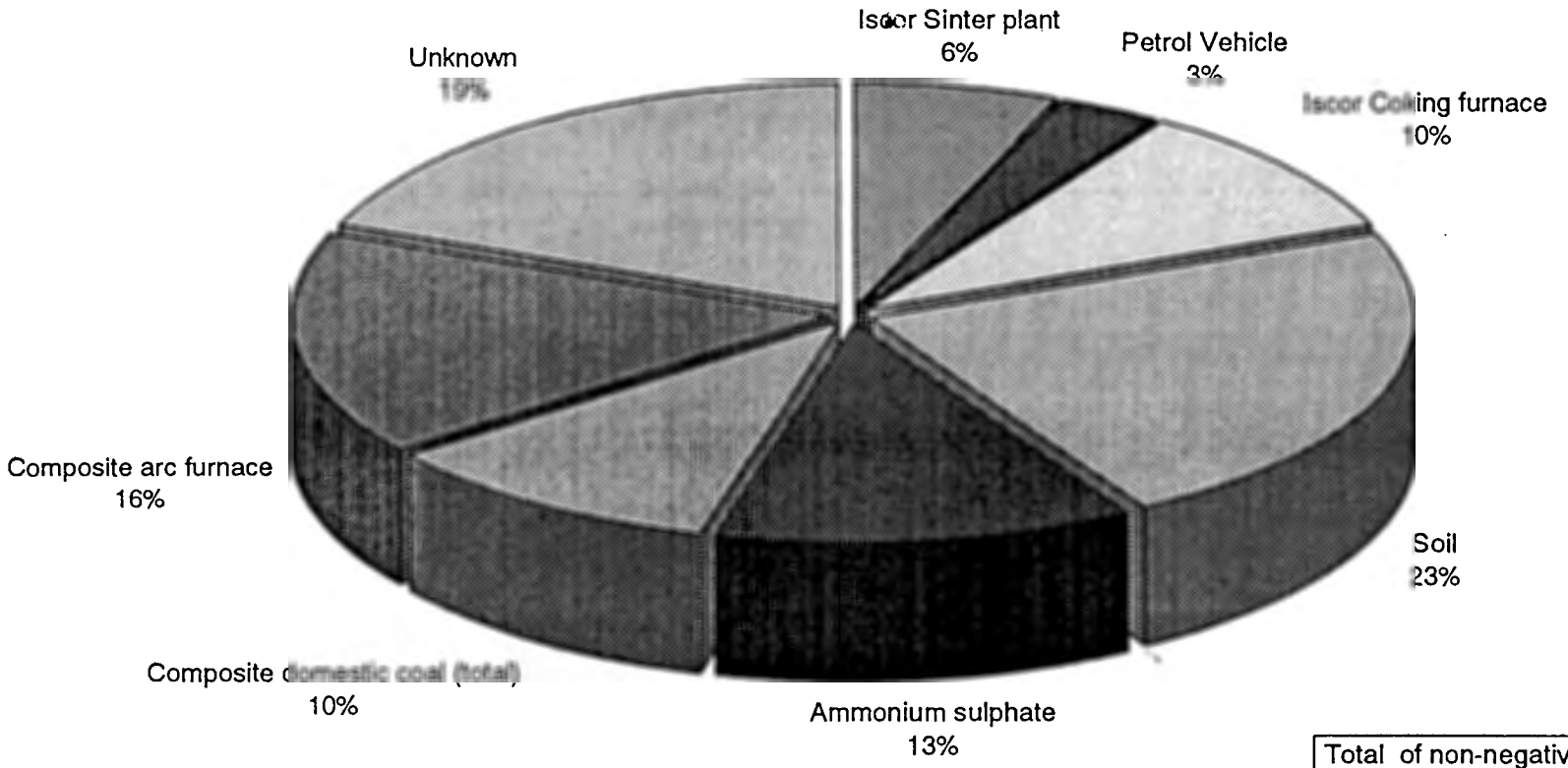



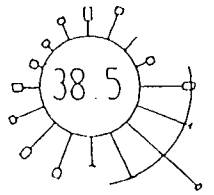
**Figure D2: Vanderbijlpark - Week 02 (04/29/94 - 05/06/94) Duration: 7 days Size: Coarse**

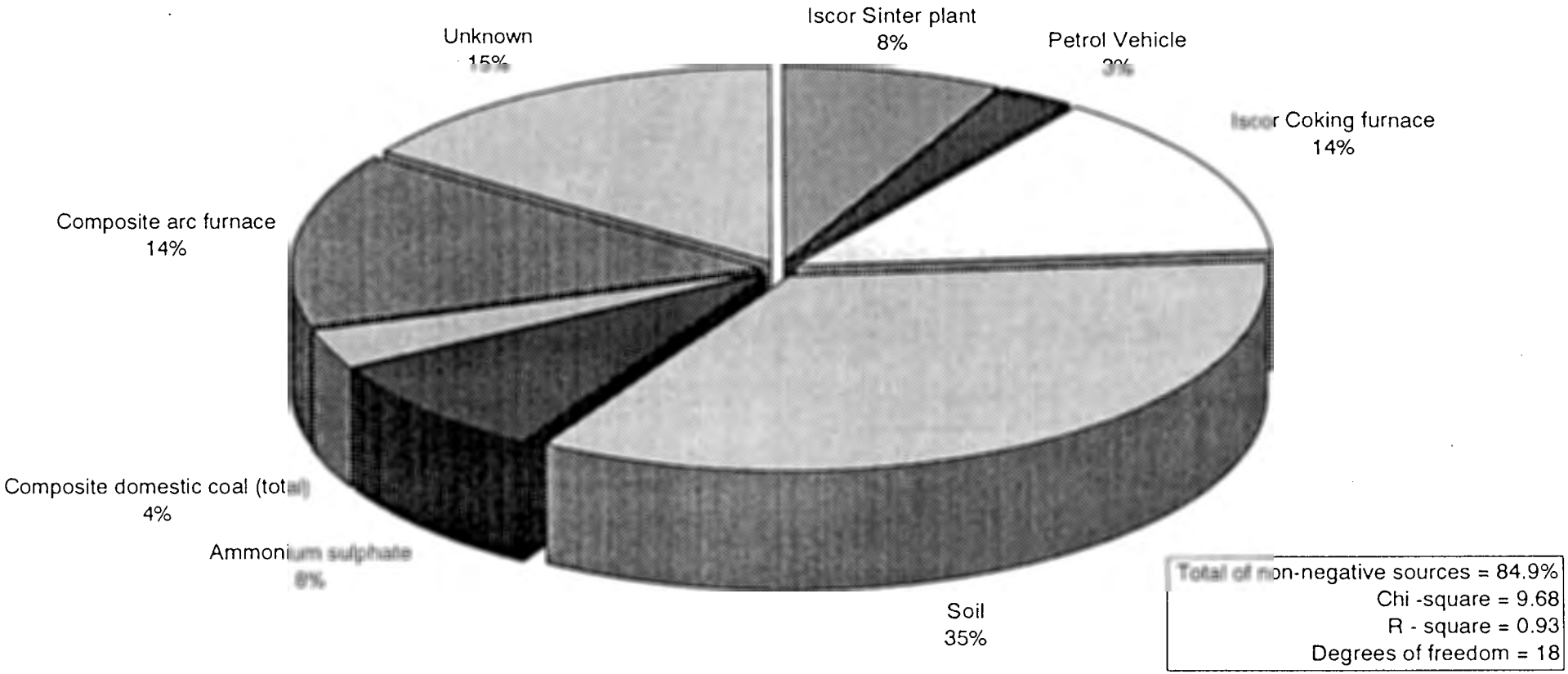


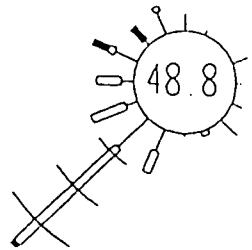

| |
|---|
| Total of non-negative sources = 81.1% |
| Chi - square = 9.3 |
| R- sqaure = 0.92 |
| Degrees of reedom = 21 |

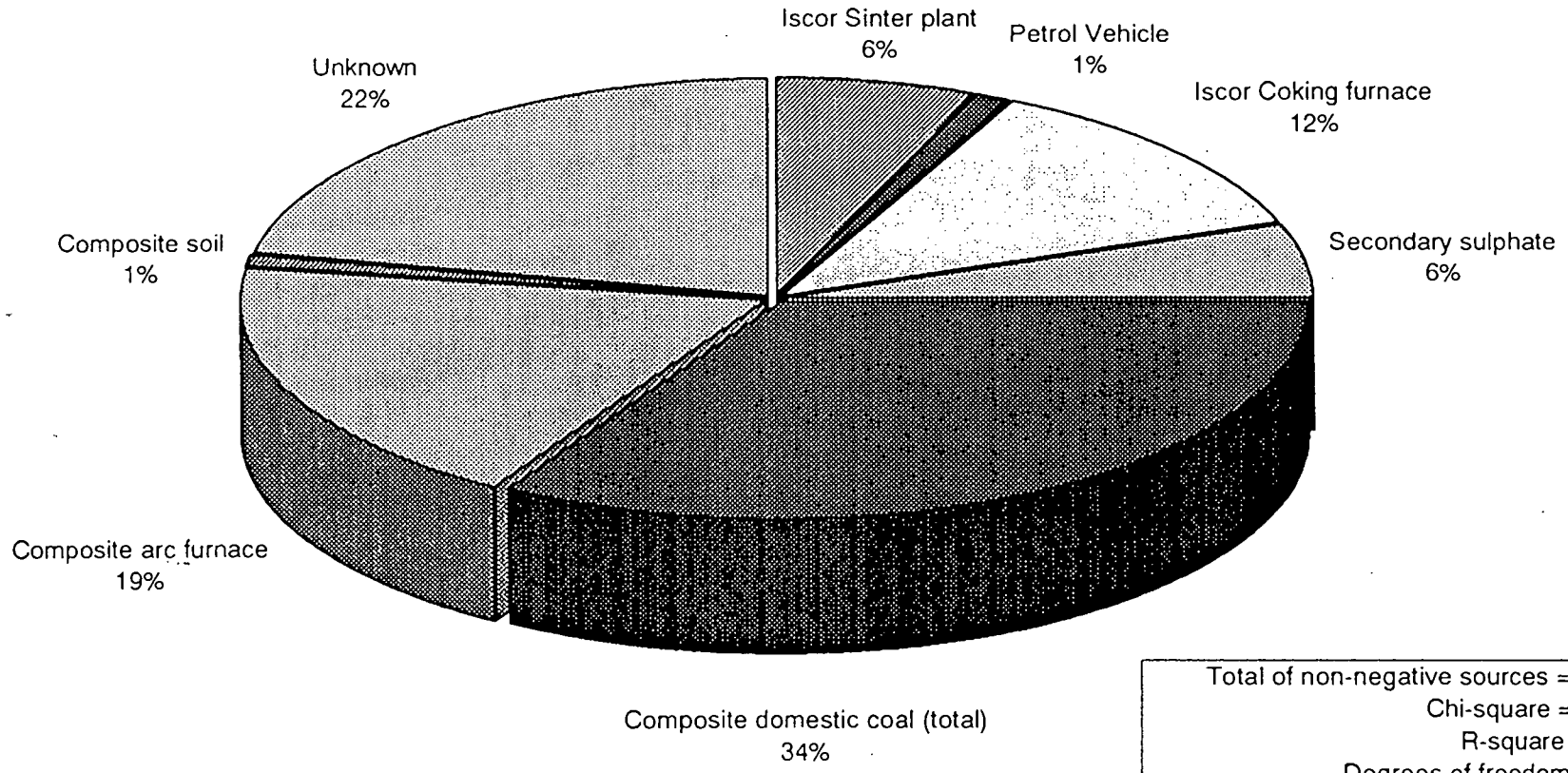
Figure D3: Sasolburg - Week 02 (04/29/94 - 05/06/94) Duration: 7 days Size: Coarse



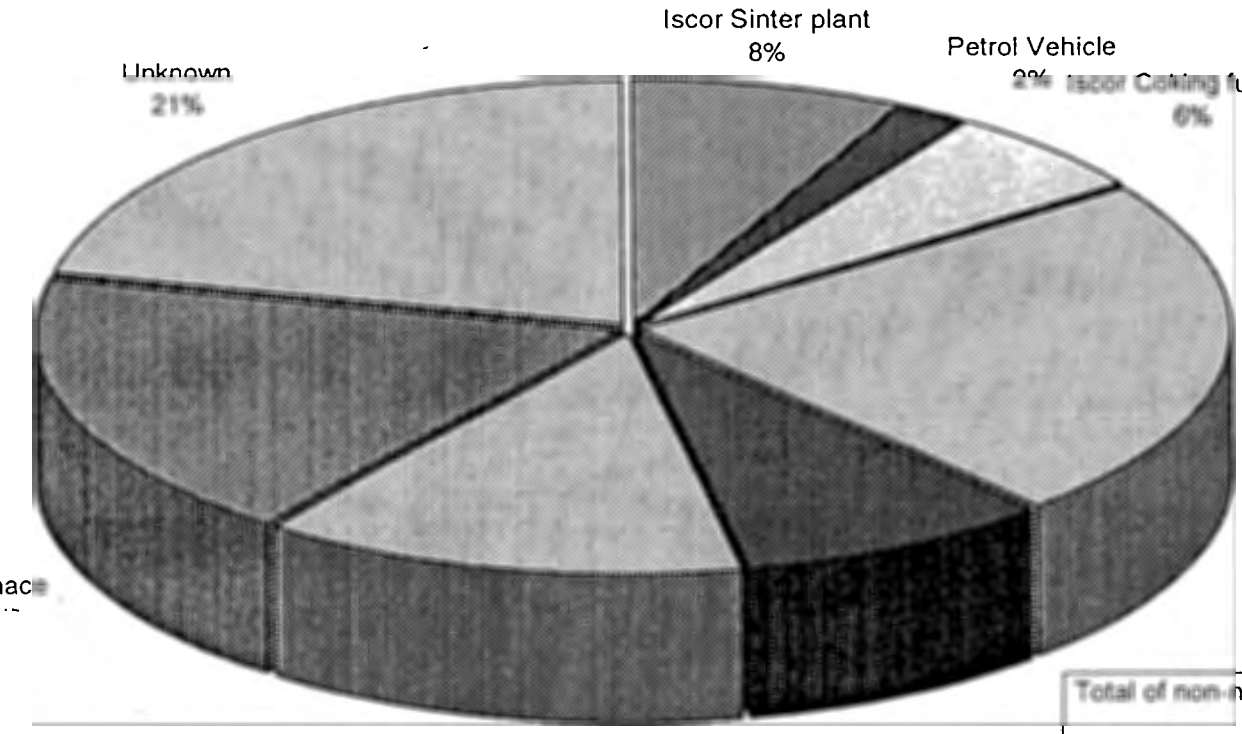
## Figure D4: Vereeniging - Week 07 (06/03/94 - 06/10/94) Duration: 7 days Size: Coarse



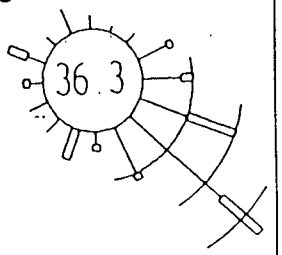



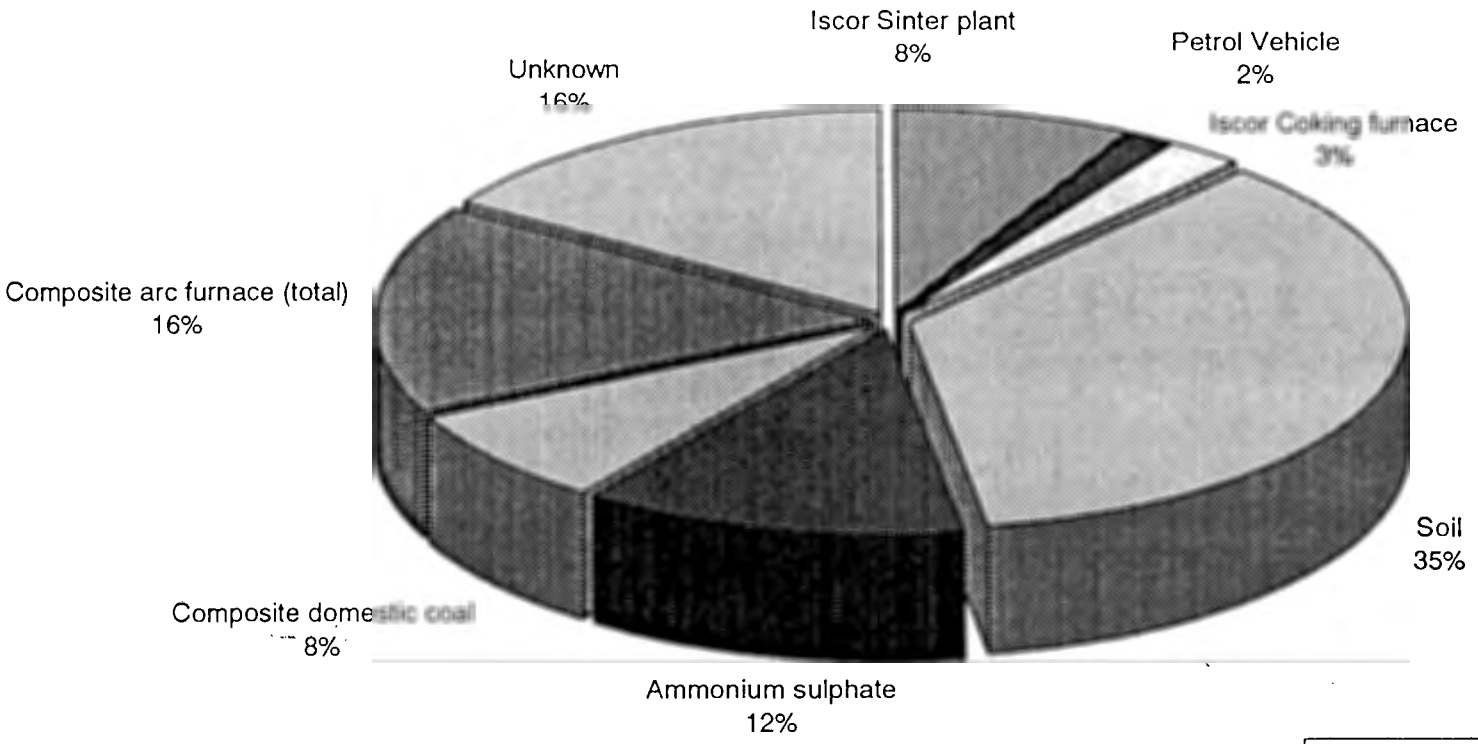

Total of non-negative sources = 78%
Chi-square = 28.2
R-square = 0.8
Degrees of freedom = 19

Figure D5: Vereeniging - Week 08 (06/10/94 - 06/17/94) Duration: 7 days Size: Coarse



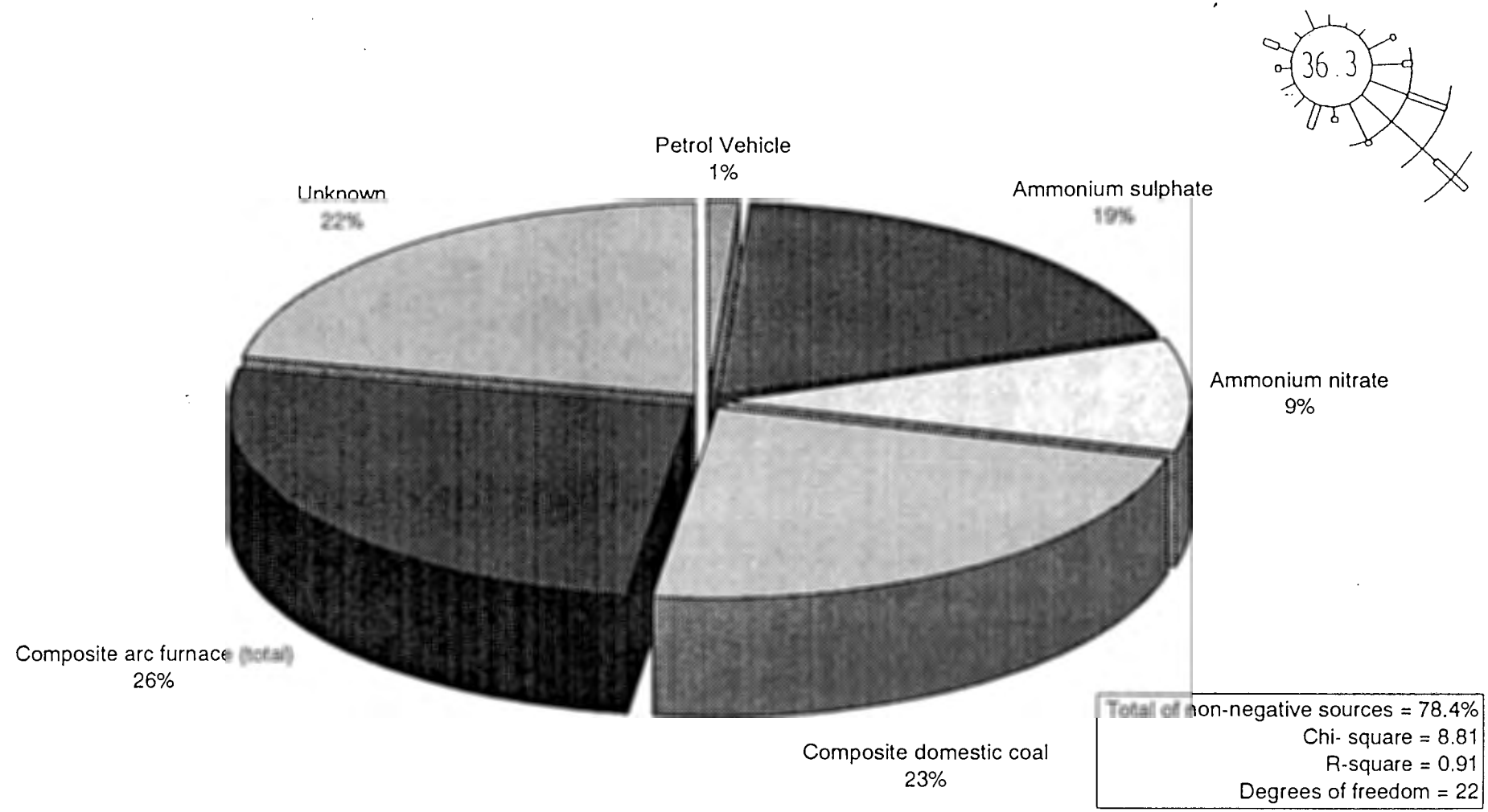
## Figure D6: Vanderbijlpark - Week 08 (06/10/94 - 06/17/94) Duration: 7 days Size: Coarse



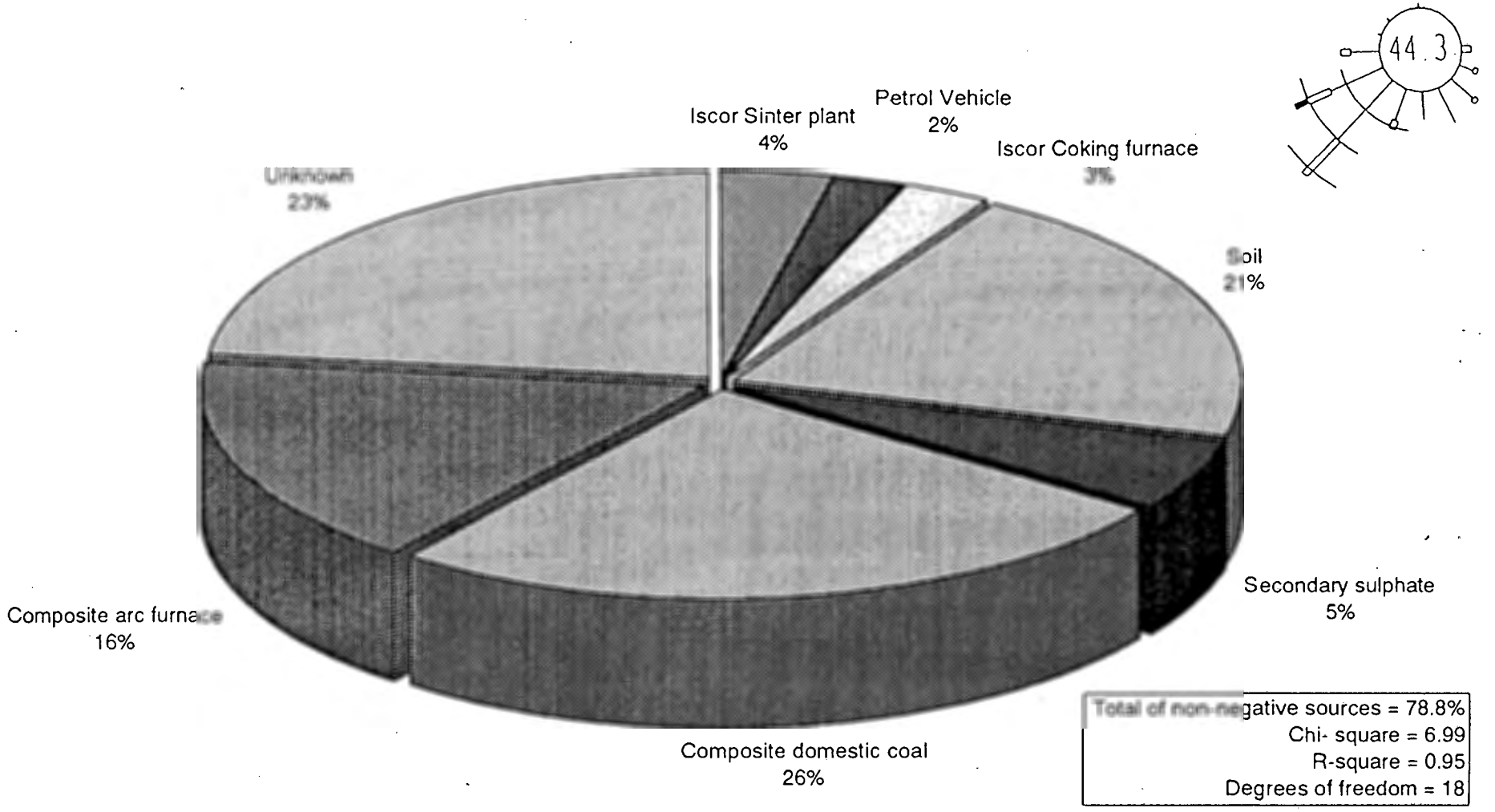




| |
|---|
| Total of non-negative sources = 84.1% |
| Chi-square = 9.4 |
| R-square = 0.92 |
| Degrees of freedom = 21 |

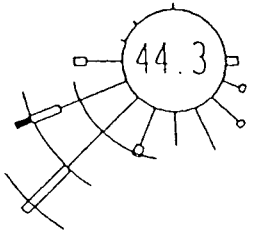
**Figure D7: Sasolburg - Week 08 (06/10/94 - 06/17/94) Duration: 7days Size: Coarse**

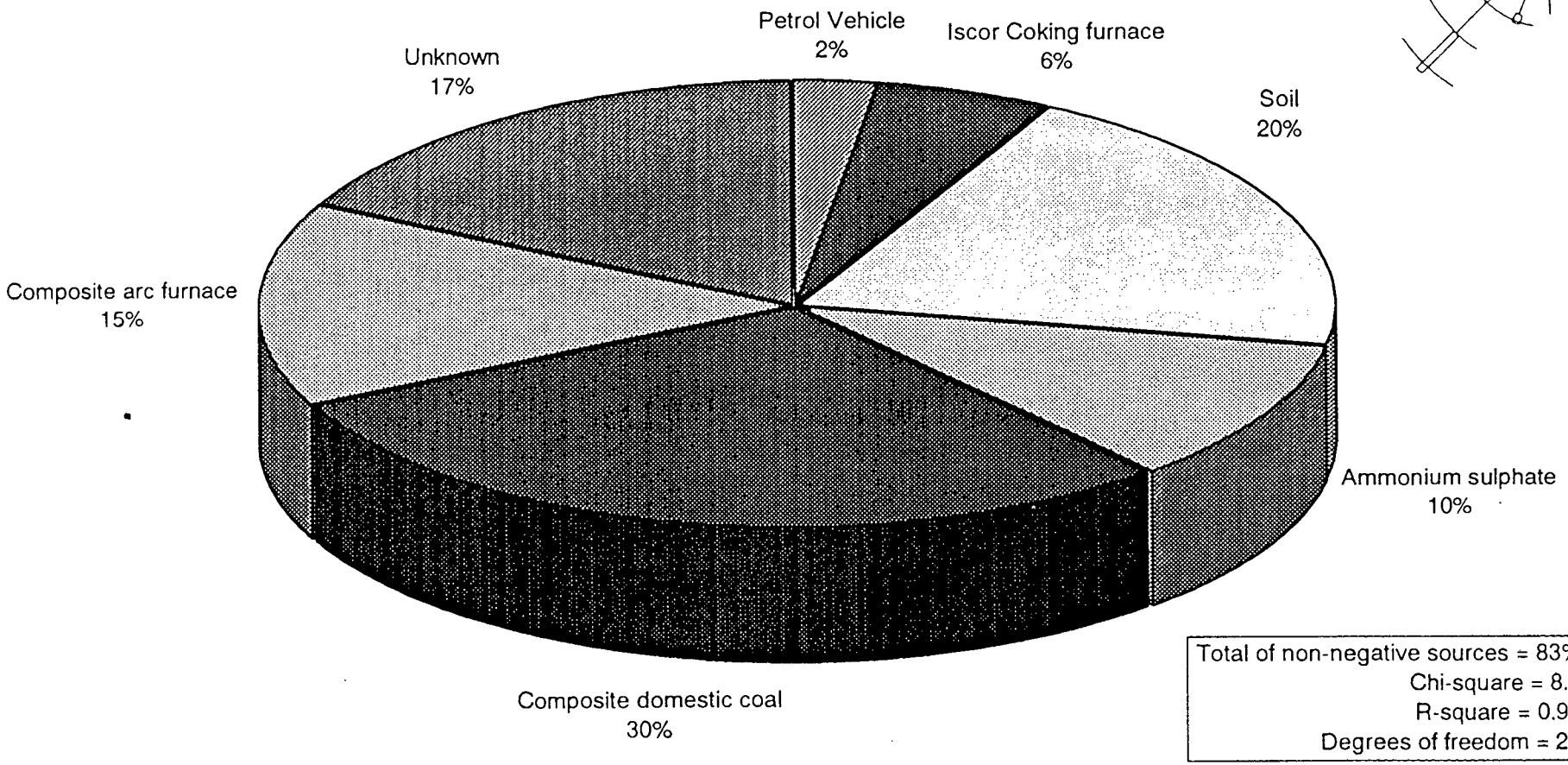


## Figure D8: Vereeniging - Week 12 (07/08/94 - 07/15/94) Duration: 7 days Size: Coarse



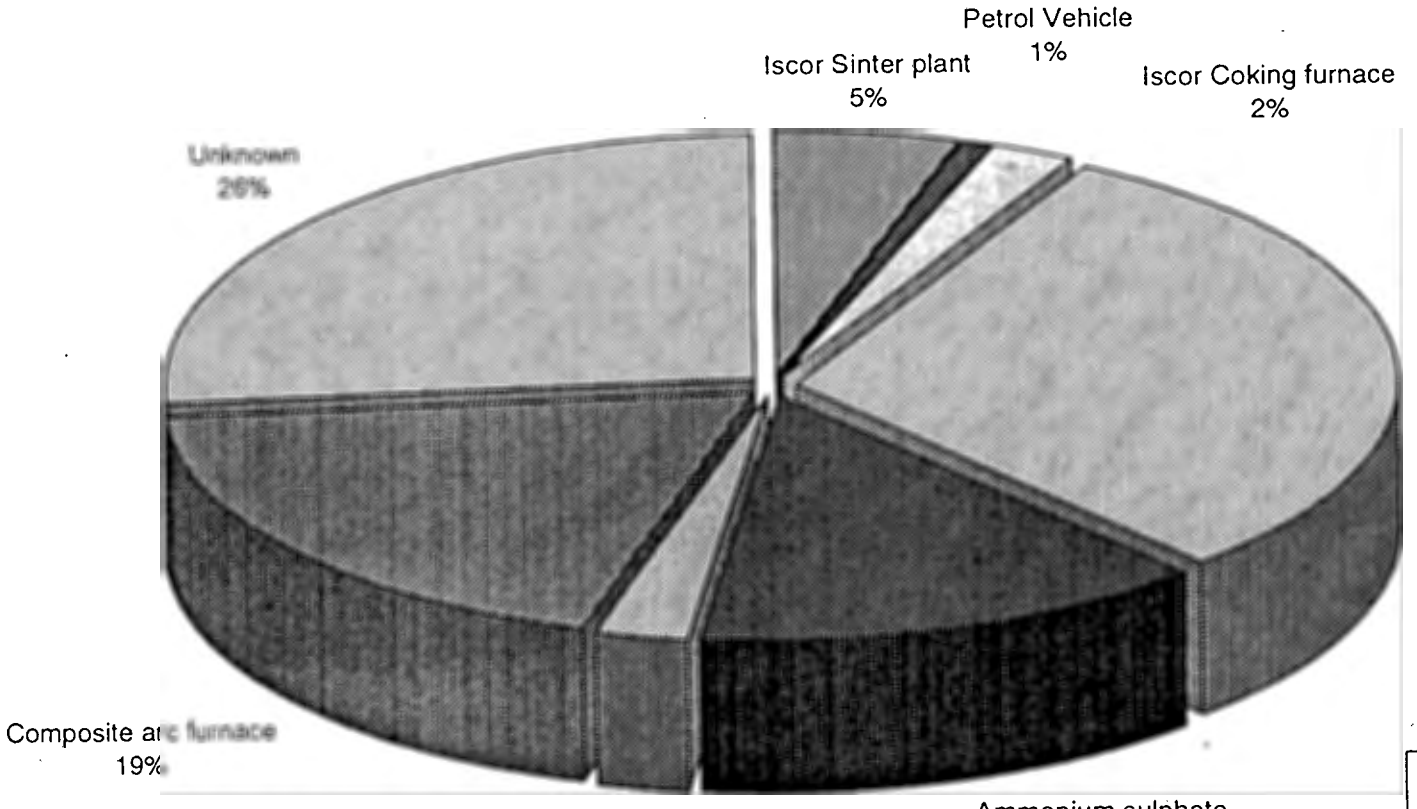
## Figure D9: Vanderbijlpark - Week 12 (07/08/94 - 07/15/94) Duration: 7 days Size: Coarse




Total of non-negative sources = 83%
Chi-square = 8.2
R-square = 0.94
Degrees of freedom = 20

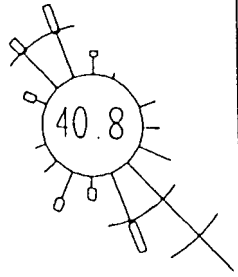
## Figure D10: Sasolburg - Week 12 (07/08/94 - 07/15/94) Duration: 7days Size: Coarse




Total of non-negative sources = 74%
Chi-square = 8.77
R-square = 0.93
Degrees of freedom = 22

D10

Figure D11: Vanderbijlpark - Week 13 (07/15/94 - 07/22/94) Duration: 7 days Size: Coarse



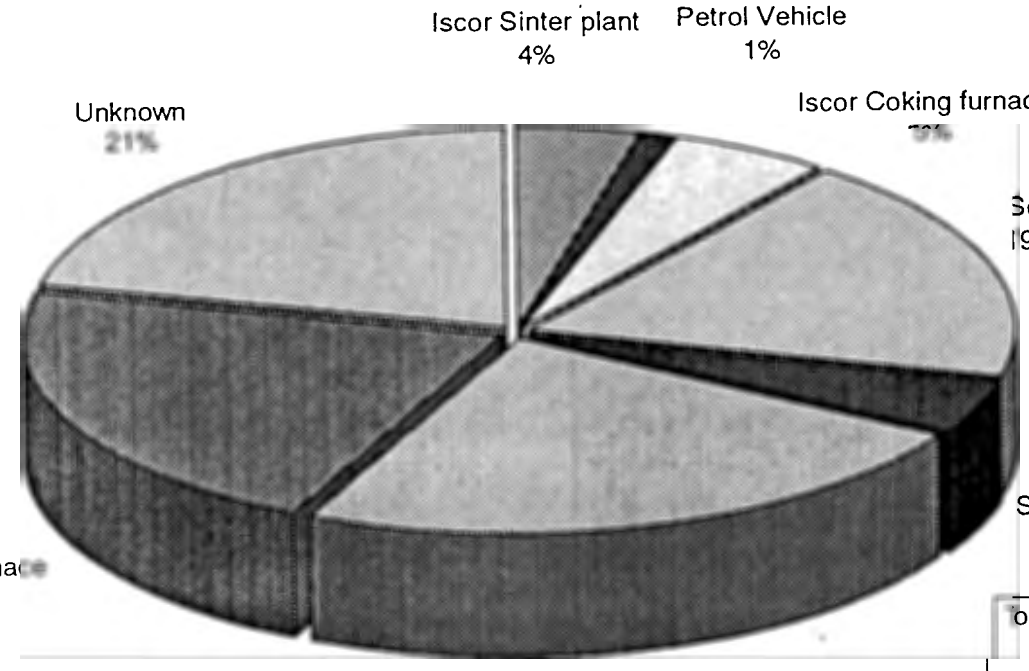
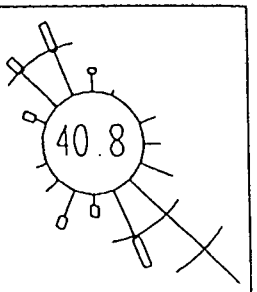
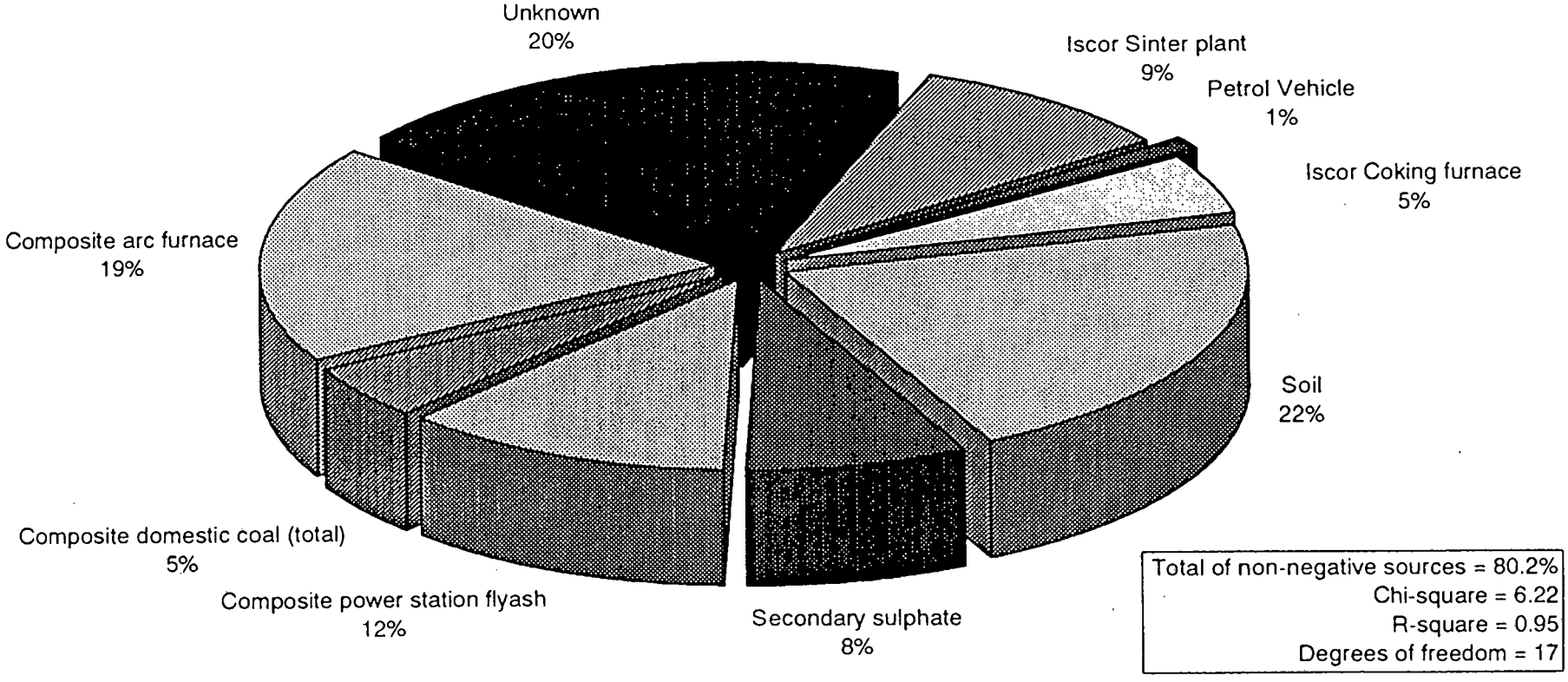
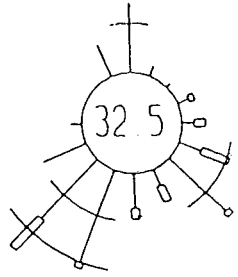



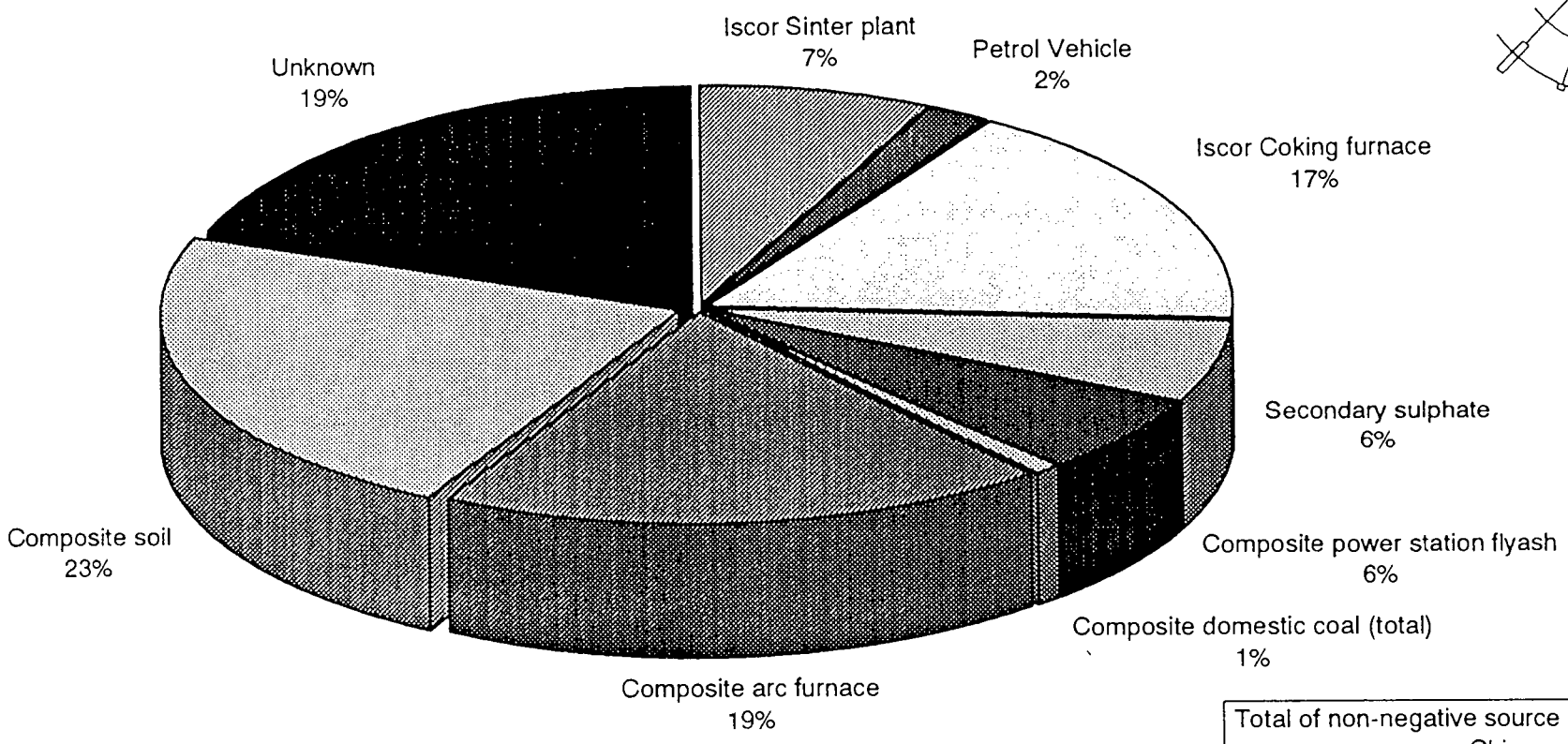
Figure D12: Sasolburg - Week 13 (07/15/94 - 07/22/94) Duration: 7 days Size: Coarse



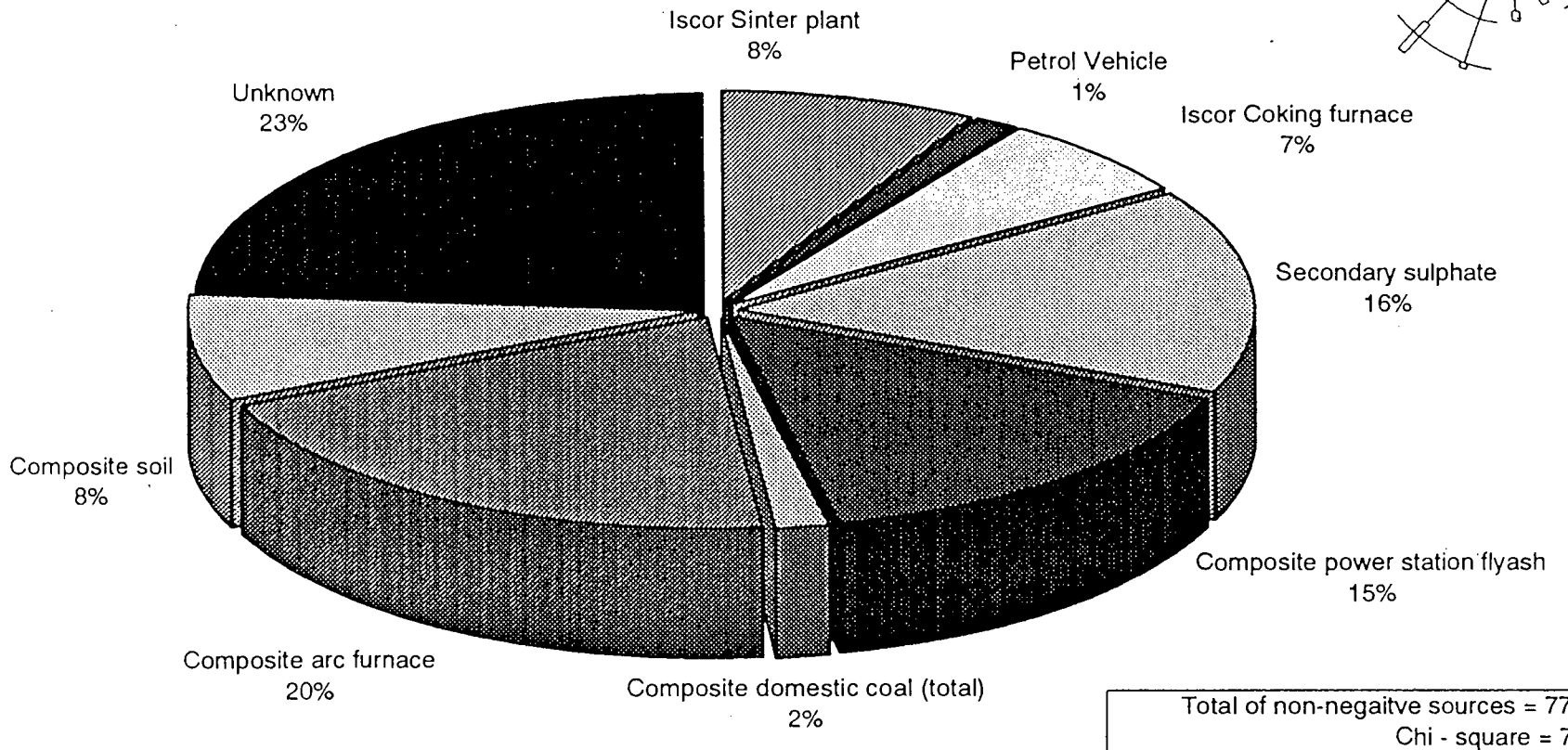
## Figure D13: Vereeniging - Week 19 (08/26/94 - 09/02/94) Duration: 7 days Size: Coarse



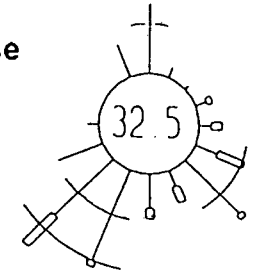

Total of non-negative source = 80.8%
Chisquare = 7.71
R - square = 0.94
Degressof freedom = 19

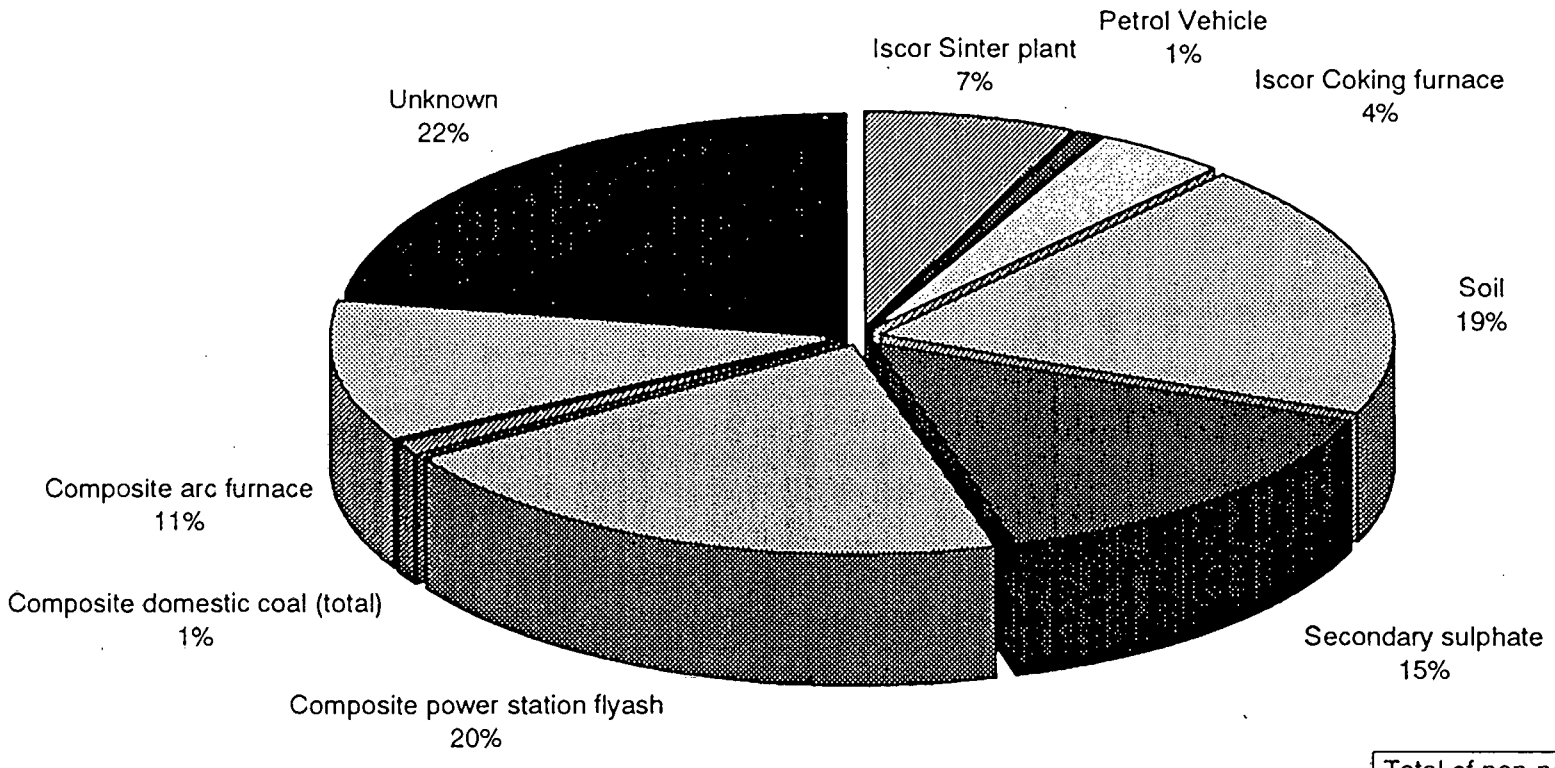
## Figure D14: Vanderbijlpark - Week 19 (08/26/94 - 09/02/94) Duration: 7 days Size: Coarse




Total of non-negaitve sources = 77%
Chi - square = 7.8
R-square = 0.94
Degrees of freedom = 19

## Figure D15: Sasolburg - Week 19 (08/26/94 - 09/02/94) Duration: 7 days Size: Coarse




Total of non-negative sources = 77.8%
Chi-square = 10.99
R-square = 0.93
Degrees of freedom = 17