CHEMICAL ELEMENT BALANCE RECEPTOR MODEL METHODOLOGY FOR ASSESSING THE SOURCES OF FINE AND TOTAL SUSPENDED PARTICULATE MATTER IN PORTLAND, OREGON

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DEDICATION

This work is dedicated to my parents, John and Jane Watson, and to my wife, Linda Ann Houghton, who have given me so much.

J.G.W.

ACKNOWLEDGEMENTS

Though only the author's name appears on the title page, this work cannot be considered his alone; it is only proper that those who made significant contributions receive their due recognition, in addition to the profound gratitude of the author for making this work possible. Each one of these individuals went the extra mile to make this project what it is, and if the hours of unpaid overtime, donated services and unreimbursed expenses were totaled, the pricetag of the Portland Aerosol Characterization Study would surely be double what it was. Major contributions to specific sections of this report will be noted.

Jim Huntzicker initiated discussions with the DEQ in 1975 and helped to prepare the first scope of work. Peter Mueller, Steve Heisler and Steve Cohen provided the framework of the study and first suggested the meteorological regime stratified sampling schedule of section 4.2, the windflow pattern averaging of section 3.4 and the inclusion of secondary aerosol species in the chemical element balance as single constituent source types in section 6.2.

Overall direction of the project was in the hands of Neil Berg of EPA, as project manager. John Kowalczyk and John Core of DEQ worked closely with Neil in this regard.

John Cooper of the Oregon Graduate Center managed the analytical and data interpretation portions of the project and his influence is pervasive in this report. Dr. Cooper's treatment of this author as

a full partner in the aerosol study rather than as a subordinate is greatly appreciated. The learning experience which resulted is rare in most university settings.

Dennis Duncan and his fine field crew devised field sampling standard operating procedures presented in section 4.7.5 and the sampler calibration and maintenance of section 4.4. In all weather for 94 days they traveled the 130 mile circuit necessary to service the samplers.

Source sampling, as described in section 4.5, was devised and accomplished by Spence Erikson and Bill Hartford with help from Pat Hanrahan. This task carried them to many dangerous places at odd hours. Each source sample chemical composition in section 3.1 was personally inspected and validated by John Cooper, a task which required over a hundred hours of effort because some of the filters were damaged and others had non-typical elemental compositions which required special correction techniques.

In the laboratory at OGC, Jeff Weiderholt, Barbara Nelson, Colleen Browder, John Dean, Jim Mohan, Cliff Frazier, Bob Cary, Helen Cooper, and Barbara Eby kept the analytical processes operating 24 hours a day, seven days a week for the four months required to analyze all of the samples. John Rau, Jitu Shah and Rick Johnson put in unpaid efforts in this task. Cliff Frazier designed the filter loading, handling and storage standard operating procedures in sections 4.7.1, 4.7.2, and 4.7.3 while Sybil Jarrett, Bob Cary and the author produced the weighing procedures of sections 4.7.2 and 4.7.3.

Bob Cary and Gail Moak perfected the ion chromatography described in section 4.7.9 and Rick Johnson and Jim Huntzicker devised the unique carbon analyzer of section 4.7.10.

Dan Freeman of DEQ compiled all of the meteorological measurements noted in section 4.6 and classified the intensive analysis sampling sequences into the flow patterns he defined in section 3.4. Neil Berg and John Kowalczyk defined and classified the sampled days into the meteorological regimes in section 4.2 and Jitu Shah worked with the author in calculating the averages of this section.

Neutron activation analysis was done under the auspices of the Reactor Sharing Program at the Nuclear Radiation Center of Washington State University under the sponsorship of that center and the Energy Research and Development Administration. Most of the computer time was donated by the Oregon Graduate Center.

Cliff Frazier and Dave Torkelson handled most of the data management and quality assurance tasks and wrote a number of the computer programs.

All figures in this report were produced by Barbara Ryall and typing was accomplished by Marcia Freed, Jeannie Youngbar, Angeline McClurg, and Dorothy Malek. Dorothy deserves particular recognition for the extra hours and patience she put into the equations of chapters two and three.

Gail Massey, John Cooper and Jim Huntzicker read the manuscript and offered many helpful suggestions. Jim went through every

derivation and pointed out errors that would have been embarrassing had they not been corrected.

The author's thinking in chapter two was greatly influenced by the work of S. K. Friedlander and Ron Henry. Dave Torkelson ran the simulations of section 3.3. Jitu Shah provided a tremendous service in a time of need by performing about 50% of the chemical element balances described in section 6.2.

As a final acknowledgement, the author thanks his wife, Lynn Houghton, and friends for tolerating him during the time in which this document was produced.

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ABSTRACT

The chemical element balance receptor model is explored as a method of determining the major contributors to the fine and total suspended particulate in Portland, Oregon.

Its major weaknesses in previous applications are evaluated and an attempt is made to rectify them. Aerosol source chemical compositions from original source tests are reported, evaluated and compared with results from other source tests. A new least squares fitting procedure which incorporates errors in the source compositions as well as the errors in the ambient chemical concentrations is derived. The validity of this "effective variance" least squares calculation method is verified in a series of simulation studies comparing it to the ordinary weighted least squares calculations used in previous element balance studies. These simulations show that the effective variance least squares fit is superior in all respects. A method for identifying specific sources within a source type grouping by averaging source contributions within distinct surface windflow patterns is proposed.

To test these refinements in the chemical element balance, filter samples of Portland's fine (<2 μm) and total suspended particulate were taken at six locations, two background, one industrial, one urban, one urban/industrial and one residential. Ninety-four days were sampled between July, 1977 and April, 1978. Three or six sequential lo-vol filter samples and one hi-vol sample of fine and total suspended particulate were taken at each site. Each day sampled was classified into

a meteorological regime based on surface windflow direction and speed. A 32 day subset of samples was selected to represent each regime in rough proportion to its frequency of occurrence throughout the year. 1300+ lo-vol filters were subjected to x-ray fluorescence, instrumental neutron activation and ion chromatographic analysis for NO_3^-, SO_4^{-2}, F^-, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, Se, As, Cd, and Ba. Volatilizable and non-volatilizable carbon concentrations were quantified on hi-vol filters. The data set was validated by interlaboratory and intermethod comparisons.

Aerosol source contributions to each specimen were calculated using the effective variance least squares fit implemented by an interactive computer program, *CALCEB. This routine allows the operator to call up any set of data and to attempt fits with various sources and concentrations.

The chemical element balance receptor model was found to be successful in estimating major source impacts for control strategy purposes. An average of 40-48% of the total suspended particulate loading in the Portland airshed can be ascribed to geological material, presumably the result of vehicular resuspension. 7-13% of the total suspended particulate is attributed to vegetative burning (i.e. fireplace, woodstove, slash or field), but this figure is somewhat suspect because of the uncertainties in the chemical composition of emissions from this source type. The average contributions show 1-9% of the TSP coming from automobile exhaust and 2-7% due to the intrusion of marine background aerosol. Industrial point sources average less than

1% in their contributions; it is probable that these are upper limits. 8-14% of the total suspended particulate is due to volatilizable carbon, 3-7% is due to sulfate and 3-7% is due to nitrate which cannot be accounted for by the primary source types and could be due to secondary formation. Ninety percent of the total suspended particulate is accounted for by the balances, on the average.

The chemical element balance is compared to other receptor models and a program of future research in the areas of source characterization, receptor model development, and ambient aerosol study procedures is presented.

CHAPTER ONE: INTRODUCTION

Anthropogenic particulate pollution of the air is a fact of life today, just as it has been for thousands of years. It came into being when Man lit his first fire, and as he discovered new ways to apply the conversion of fuel into energy, energy into sustenance and leisure, and sustenance and leisure into more men, his particulate emissions increased. Under certain conditions, the presence of these foreign species has been deemed intolerable; thus, the first royal proclamation prohibiting the use of coal in London was issued in the thirteenth century (Halliday, 1961), though with sporadic, if any, enforcement.

From then until recently the philosophy of air pollution control focused on setting standards for emissions (Halliday, 1961; de Nevers, 1977). Much research was commissioned on fuel preparation and combustion techniques, backyard burning was banned, industries were required to install scrubbers, and utilities switched from coal to low sulfur oil and natural gas. Black smoke belching from stacks, at least in the developed countries, disappeared, the mass of emissions was measurably reduced and air quality improvement in many areas was noticeable.

With the advent of the U. S. Clean Air Act in 1970, the focus switched. While not abandoning emission standards, the philosophy changed to the establishment of ambient air quality standards, maximum concentrations to which the general population can be exposed without damage to life or property. The U. S. primary standard for total suspended particulate (TSP) is 260 $\mu g/m^3$ in a 24 hour sample not to be exceeded more than once per year or an annual geometric mean less than 75 $\mu g/m^3$ and was determined by assessing the effects of various dosage rates through clinical, epidemiological, toxicological and laboratory studies (U. S. Dept. of Health Education and Welfare, 1969).

Under this philosophy, even emitters meeting the emission standards might be shut down, further controlled or prevented from expanding if it could be shown that their discharges contributed a substantial fraction of the ambient concentration in excess of the standard.

Presently much attention is being directed to fine suspended particulate (FSP) matter, that portion of the TSP in a size range less than 2 μm in aerodynamic diameter (Friedlander, 1973b). Particles in the .1 to 1 μm size range are most effective in scattering light and are responsible for much of the haze which characterizes polluted areas. These particles defy the impaction and interception removal mechanisms of the human body's upper air passages because of their small size, yet they are too massive to be eliminated by Brownian diffusion to the walls of those passages. The result is penetration deep into the lungs where they may cause damage. Particles of this size contain a greater proportion of toxic substances than the larger particles. Arsenic, lead, cadmium, sulfate and organic carcinogens have all been measured in urban areas. Furthermore, it has been shown that most particles in this mode are the result of anthropogenic emissions (Willeke and Whitby, 1975), mainly combustion, which might be controlled, thus foregoing visibility degradation and possible health effects. Such controls are costly, however, and will not be made on a specific emissions source unless a significant amount of the fine particulate in ambient air can be directly attributed to that source.

Many urban areas in the world today exceed the U. S. federal primary standard, and even residents of those that don't violate that standard express concern about visibility reduction and toxic substances. Leaders in these cities need to know: (1) which chemical substances are in the fine and total fractions of the atmospheric particulate to assess visibility and health effects and their relationship to the federal primary standard, and (2) the extent to which local anthropogenic sources impact mass loadings and how this affects the 24 hour and annual particulate concentrations in relation to the standard for the design and implementation of a control strategy.

Emissions inventories and source oriented atmospheric dispersion models have been used in the past to supply this knowledge. Much uncertainty is associated with these models, however, and corroborating evidence of source impacts on ambient concentrations has been sought.

Receptor oriented models have been proposed and tested in limited situations for this purpose, but their large-scale deployment and the extent of their validity have not been adequatly validated.

The Portland Air Quality Maintenance Area (AQMA) has continually exceeded the federal primary standard for particulate on a 24 hour and on an annual basis. In 1972, Oregon adopted its Clean Air Act Implementation Plan, as required by federal law, which set emissions standards for industrial sources and limited open burning. In 1974, Oregon's Environmental Quality Commission (EQC) set interim standards limiting additional new particulate emissions to the Portland airshed to 425 tons/year. The consequences of this limitation to the economic growth of the region are significant, and its enforcement in light of expanding residential area sources is difficult.

The EQC recognized the dearth of knowledge upon which this plan was based and the Oregon State Department of Environmental Quality (DEQ) was given a mandate to improve the data base sufficiently to assess source emissions impact on ambient air quality. With such solid evidence, a case could be made for the control of major contributors to TSP loadings violating the federal standard and an understanding of the fine particulate contributors could be gained. Since 1974, the DEQ has upgraded its monitoring facilities, refined the airshed emissions inventory (Seton, et.al., 1976), developed and applied an airshed disperson model (Fabrick and Sklarew, 1975) and commissioned the Portland Aerosol Characterization Study (PACS) application of Friedlander's (1973a) chemical element balance (CEB) receptor model as part of an overal data base improvement project.

The PACS progam was developed jointly by DEQ, the Oregon Graduate Center (OGC) and Environmental Research and Technology, Inc. (Mueller et al., 1977) and was refined substantially in progress by DEQ and OGC personnel. The final reports for the PACS and the data base improvement project will be available in early 1979. This document does not attempt to answer the detailed questions they deal with.

The overall purpose of this report is to develop the concept of receptor models in general, to evaluate and apply one, the chemical element balance, to the task of assessing source impacts on the fine and total suspended particulate, and to relate these impacts to federal primary standard violations in the Portland, Oregon AQMA.

The PACS, for this purpose, should not be considered the end product, but rather as a means of exploring the medium scale application of the chemical element balance receptor model. Thus, emphasis is not on the results, but on the process of obtaining those results. Experimental design and standard operating procedures, data management and validation, and receptor model conceptualization, applications and limitations are examined within the context of the PACS. The interdependence of these components is established, and the beginnings of a standard methodology for aerosol characterization projects can be discerned.

This chapter serves to put the subsequent work into historical perspective, to point out what is to come, and to summarize the specific original contributions of this work.

Chapter Two defines a receptor model and demonstrates the relationship to a source model. Five receptor models are identified in the literature: the chemical element balance, enrichment factor, time series correlation, multivariate and spatial. Their requirements, capabilities, limitations, and similarities are discussed in a general way and future areas of research are suggested.

In Chapter Three, one of these receptor models, the chemical element balance, is explored in greater detail. Its limitations--lack of source chemical compositions, inadequate inclusion of uncertainty, and inadequate validation--are reiterated and an attempt is made to rectify them. A refined interpretation by averaging source impact results within specific windflow patterns is proposed. This is the first presentation of a systematic methodology to explore receptor models.

The PACS experimental design and standard operating procedures are presented in Chapter Four. Criteria for site, filter media, sampler and meteorological regime selection are laid out and the extent to which the PACS meets these criteria is stated. Each standard operating procedure for filter preparation, handling, and storage, field sampling, weighing, x-ray fluorescence, instrumental neutron activation, ion chromatography and carbon analysis is briefly summarized. Interlaboratory and intermethod comparisons are presented to validate the data.

Management of over fifty measurements from five standard operating procedures on close to 2000 individual filters and the association of these measurements with sampling sites, periods and meteorological conditions is not a task to be performed manually. Tha PACS interactive mini-computer based data management and quality assurance system is outlined in Chapter Five.

Chapter Six contains an explanation of the application of the chemical element balance to the PACS chemical compositions, the averaged source impacts and a discussion of the implications of and reservations about these results.

Finally, in Chapter Seven, the results of this work are summarized, conclusions are drawn and areas where further research and development are needed are suggested.

Specific orginal or unique features of this work include:

1. the explication and inter-relation of receptor models.
2. the most thorough review to date of primary aerosol source chemical compositons and their uncertainties, with many additional measurements of the fine and coarse particulate fractions from emitters never before sampled.
3. a new approach to least squares fitting of the chemical element balance parameters which takes into account uncertainties in the source compositions as well as uncertainties in the ambient concentrations.
4. a sensitivity test of this procedure, and more important, a methodology for performing such tests on all receptor models.
5. averaging of source contributions within windflow patterns for the identification of specific upwind sources.
6. a method of selecting days for intensive analysis that will represent the yearly mean with greater precision than a random sample.
7. an interactive, medium-scale data management system for implementation on a mini-computer without specialized personnel.
8. the widest application to date of the chemical element balance receptor model for the assessment of source impacts on the fine and total suspended particulate in an urban airshed.

This is the first time that a receptor model has been verified and applied to a large set of ambient chemical concentration data in two size ranges. The major original contribution of this dissertation is in beginning to systematize the understanding and application of receptor models in this way on a routine basis. Such an undertaking is enormous and involves an integration of data acquisition, data management and data interpretation tasks. No single study, let alone a moderate one (with financing an order of magnitude less than that of the Regional Air Pollution Study in St. Louis or the Aerosol Characterization Experiment in California) such as the PACS can claim to be conclusive. Nevertheless, the work presented here represents a major step in the synthesis and application of previous research and should provide some guidelines for future studies, freeing more resources for new explorations.

The conclusions drawn here are neither the ultimate nor the definitive ones. Many questions remain that need to be investigated. This document's value may be that it poses some of these questions, and to a greater extent than before, answers them.

CHAPTER TWO: INTRODUCTION TO RECEPTOR MODELS

The relationship between particulate emissions and ambient concentrations measured at a receptor site distant from the pollution source is a complicated one; though a rough proportionality exists, other variables, primarily meteorological, intervene to make the direct correlation between source emissions and ambient concentrations a poor one. Each of these variables is random in nature, will vary with space and time, and may combine with other variables in a non-linear manner. Thus, any estimation of source impact on ambient loadings is approximate at best. The conceptualization of this admittedly complex and intractable "real-life" situation is a comparatively simple "model" based on physical principles which can be used to determine the average contribution of specific sources to particulate loadings.

One can begin at either end of the system: The emission rates of a set of sources can be compiled, the appropriate transport parameters measured and incorporated into a source oriented model which will predict ambient concentrations at specified sampling sites and times.

On the other hand, one can start with the ambient concentration as measured at a receptor site by a representative sampling technique, determine some properties of this sample which are unique to specific sources or source types and assign the origin of that fraction of the sample possessing a property to its appropriate source. These two models, source oriented and receptor oriented, are represented schematically in Figure 2.0 and though it will be shown that they are theoretically equivalent, their practical application is quite different.

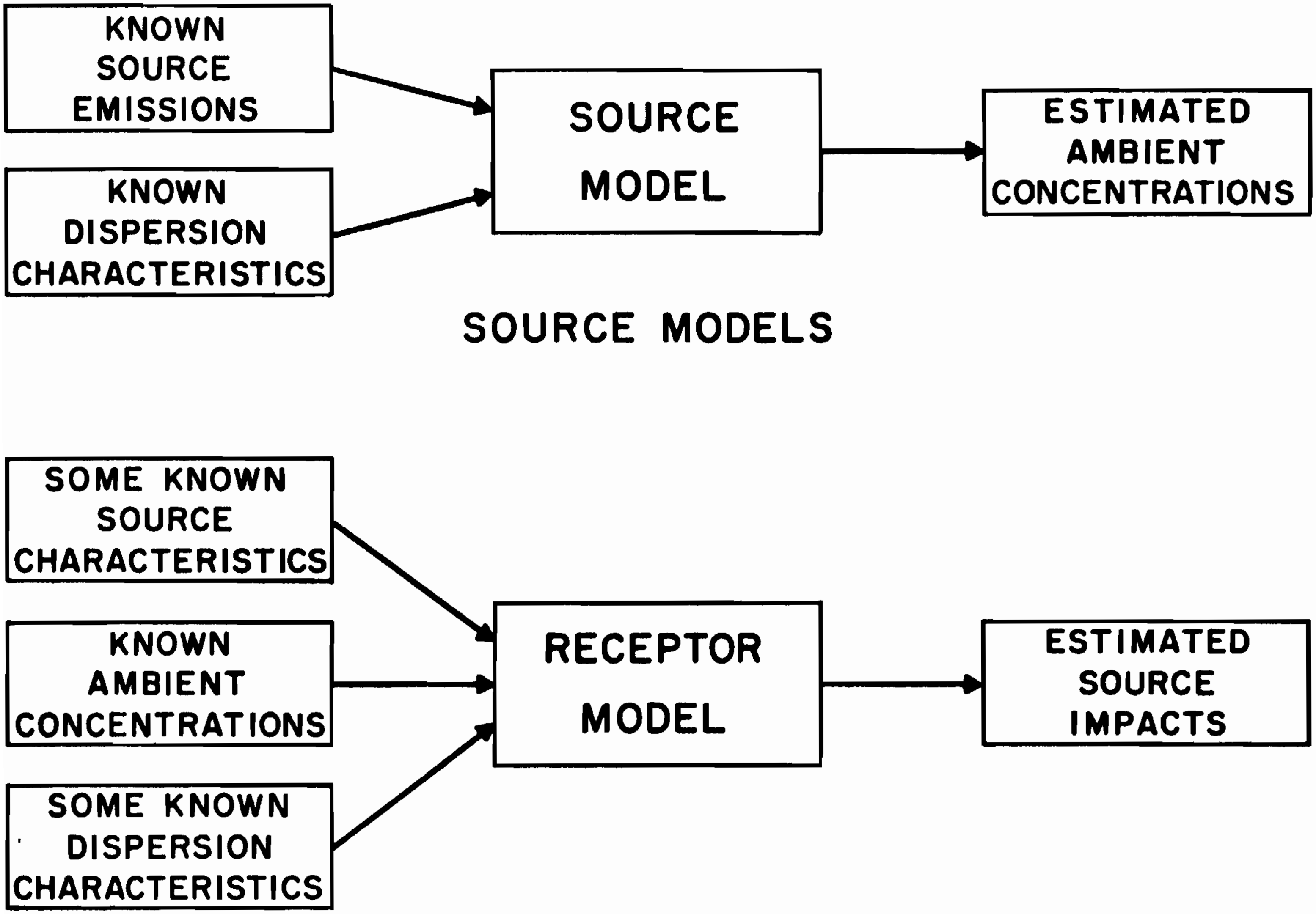


Figure 2.0. RECEPTOR MODELS

The foundation for the formulation and application of source-oriented models is well laid, the classic reference being Pasquill (1974). Though often used, no unified account of receptor models, their relationship to source models and their application presently exists. Obrusník, et al. (1976), Neustadter, et al. (1976) and Henry (1977a) have presented the best summaries to date. This chapter extends Henry's work and represents an attempt to generalize the present knowledge of receptor oriented models in which elemental composition is the property relating source to receptor.

First, each receptor model will be justified on the basis of a simple, yet physically significant source model. Second, a brief review of the applications to date is made. Third, the strengths and weaknesses of each model are enumerated. Finally, additional areas of investigation into the use and development of the models are described.

Five chemical element receptor oriented model types present themselves in the literature as separate entities; Table 2.0 summarizes the major works in which they appear. The models are:

1. Chemical Element Balance (CEB): Knowledge of the percentage elemental composition of the ambient particulate and the source particulate allows a mass balance to be formed for each species measured. The contribution of each source to the atmospheric loading is estimated.

2. Enrichment Factor (EF): The ratios of atmospheric concentrations of elements to a reference element are compared to the same ratios in geological or marine material. Differences are explained in terms of anthropogenic sources.

3. Time Series Correlation (TSC): Ambient elemental concentrations are measured as a function of time. Those that show the same fluctuations are associated

Table 2.0 Examples in the Literature of Receptor Model Applications based on Aerosol Chemical Composition

CHEMICAL ELEMENT BALANCE

Hidy & Friedlander	(1970)	Hidy, et al.	(1974)
Winchester & Nifong	(1969, 1971)	Hammerle and Pierson	(1975)
Miller, et al.	(1972)	Gartrell & Friedlander	(1975)
Kneip, et al.	(1972)	Gatz	(1975)
Friedlander	(1973a)	Henry	(1977a)
Heisler, et al.	(1973)	Kowalczyk, et al.	(1978)
		Gordon	(1979)

ENRICHMENT FACTOR

Rahn	(1971)	Struempler	(1975)
Hoffman & Duce	(1972)	Mroz & Zoller	(1975)
Tsunagai, et al.	(1972)	Duce, et al.	(1975)
Bogen	(1973)	Obrúsnik, et al.	(1976)
Gordon, et al.	(1973)	Paciga & Jervis	(1976)
Zoller, et al.	(1973)	King, et al.	(1976)
Wesolowski, et al.	(1973)	O'Donnell, et al.	(1976)
Bressan, et al.	(1973)	Neustadter, et al.	(1976)
Heindryckx & Dams	(1974)	Moyers, et al.	(1977)
Zoller, et al.	(1974a&b)	Lawson & Winchester	(1978)
Hidy, et al.	(1974)	Buat-Ménard & Arnold	(1978)

TIME SERIES CORRELATION

Rahn	(1971)	Struempler	(1975)
Wesolowski, et.al.	(1973)	Hammerle & Pierson	(1975)
Giaque, et al.	(1974)	Neustadter, et al.	(1976)
Wedberg, et al.	(1974)	Pilotte, et al.	(1976)
Johansson, et al.	(1974)	Moyers, et al.	(1977)
Winchester, et al.	(1974 a&b)	Tiao & Hilmer	(1978)
Rahn, et al.	(1974)	O'Conner, et al.	(1978)
		Pilotte, et al.	(1978)
		Courtney, et al.	(1978)

MULTIVARIATE MODELS

Blifford & Meeker	(1967)	Kleinman	(1977)
Prinz & Stratmann	(1968)	Henry	(1977a,1977b)
Laamanen & Partanen	(1971)	Gaarenstroom	(1977)
Hammerle & Pierson	(1975)	Gatz	(1978)
Neustadter, et al.	(1976)	Dattner	(1978)
Hopke, et al.	(1976)	Gordon	(1979)

SPATIAL MODELS

Blifford & Meeker	(1967)	Gatz	(1975)
Dams, et al.	(1971)	Scott Environmental Technology	(1975)
Crozat, et al.	(1973)	Neustadter, et al.	(1976)
John, et al.	(1973)	O'Donnell, et al.	(1976)
Hendryckx & Dams	(1974)	Obrúsnik, et al.	(1976)
		Laird & Miksad	(1978)

with a common source. Linear regression of one elemental concentration with another provides information about their concentration ratios in source type emissions.

4. Multivariate: An application of factor analysis or cluster analysis to a correlation matrix formed from a series of chemically characterized samples yields certain "natural functions" which are identified as sources.

5. Spatial Models: Elemental concentrations at a number of sites within an airshed are combined with the above models and wind direction data to zero in on specific source locations.

The first four models will be discussed in some detail while only possibilities for the spatial models will be alluded to.

2.1 THE PHYSICAL BASIS FOR RECEPTOR MODELS

A receptor oriented model must always be a representation of reality and not just a series of equations. The relationship between a source model and a receptor model is simple and is presented here.

In general, the aerosol mass concentration at a receptor during sampling period k of length T_k due to a source j with constant emission rate E_{jk} is

$$S_{jk} = D_{jk}E_{jk} \qquad 2.1.1$$

where

$$D_{jk} = \int_0^{T_k} d(\vec{u}(t),\ \sigma(t),\ \vec{x}_j)dt \qquad 2.1.2$$

is a dispersion factor depending on wind velocity, $\vec{u}$, atmospheric stability, $\sigma(t)$, and the location of source j with respect to the receptor, $\vec{x}_j$, $\vec{u}$ and σ, and possibly even $\vec{x}_j$ in the case of a mobile source, will vary with time, so the instantaneous dispersion factor, d, must be integrated over the sampling period. When $\vec{u}\cdot\vec{x}_j \not\leq -1$, the source of emissions E_{jk} is not in an upwind quadrant with respect to the receptor and $d \rightarrow 0$.

Various forms for d have been proposed (Pasquill, 1974, Benarie, 1976, Seinfeld, 1975), some including provisions for chemical reactions, removal and specialized topography. None are completely adequate to describe the complicated, random nature of dispersion in the atmosphere. The advantage of receptor models is that an exact knowledge of D_{jk} is unnecessary.

If a number of sources, p, exists and there is no interaction between their aerosols to cause mass removal, the total aerosol mass measured at the receptor, C_k, will be a linear sum of the contributions from the individual sources

$$C_k = \sum_{j=1}^{p} D_{jk} = \sum_{j=1}^{p} S_{jk} \qquad 2.1.3$$

Similarly, the concentration of elemental component i, C_{ik} will be

$$C_{ik} = \sum_{j=1}^{p} a_{ij} S_{jk} = \sum_{j=1}^{p} a_{ij} D_{jk} E_{jk}, \; i = 1,n \qquad 2.1.4$$

where a_{ij} is the fraction of source contribution S_j composed of element i.

In the source model each S_{jk} is known from eqs. 2.1.1 and 2.1.2, the a_{ij} are determined by chemical analyses of representative samples from source j, and C_{ik} is calculated from eq. 2.1.4.

The receptor model starts with the measurements of C_{ik}, uses some knowledge about the chemical composition of the sources and attempts to quantify S_{jk}, or at least to make a statement about its variability or significance as a contributor to the total mass concentration, C_k.

2.2 THE CHEMICAL ELEMENT BALANCE

Eq. 2.1.4 looks similar to Friedlander's (1973a) chemical element balance (CEB) which has been used in Pasadena (Miller, et al., 1972), Chicago (Gatz, 1975), Fresno, Pomona, San Jose, Riverside (Gartrell and Friedlander, 1975), New York (Kneip et al., 1972), Portland (Henry, 1977a) and Washington D.C. (Kowalczyk, et al., 1978) to assess source contributions. The chemical element balance equation for each of n elemental concentrations measured at a receptor during a period k is

$$C_{ik} = \sum_{j=1}^{p} a_{ij} S_{jk}, \quad i = 1,n \qquad 2.2.1$$

Equations 2.2.1 are not the same as eqs. 2.1.4 because, as will become evident, they cannot distinguish between individual emitters of aerosols whose chemical composition is similar. These must be considered as a "source type." If eq. 2.1.1 is thought of being composed of an "equivalent" dispersion factor and an "equivalent" emission rate for source type j, then eqs. 2.2.1 and 2.1.4 will be identical. Eq. 2.1.1 will be treated in this sense here.

If the C_{ik} and the a_{ij} at the receptor for all p of the source types suspected of affecting the receptor are known, and $p \leq n$, a set of simultaneous equations exists from which the source type contributions, S_{jk}, may be calculated.

In practice, researchers have acquired concentrations of many trace elements on air filters by multi-element chemical analysis techniques and have sought source type emissions compositions from the literature or actual measurements.

Three methods have been applied to the solution of eqs. 2.2.1: tracer element, linear least squares fitting, and linear programming.

The tracer element method assumes that each source type possesses a unique chemical component, or "tracer," which is not common to any other source type. Thus, eqs. 2.2.1 reduce to

$$S_{jk} = \frac{C_{t_j}}{a_{t_j j}} \qquad 2.2.2$$

where $i = t_j$ is the tracer element for source j. This approach was originally suggested by Hidy, et al. (1970) and has been applied by Kneip, et al. (1972), Miller, et al. (1972), Gatz (1975), Hammerle, et al (1976), and Hidy, et al. (1974). It works well if the tracer elements meet the following criteria:

1. $a_{t_j j}$ perceived at the receptor is well known and invariant.
2. t_j is a major component of source j.
3. C_{t_j} can be measured accurately and precisely in the ambient sample.
4. The concentration of element t_j at the receptor comes only from source type j.

The propagated uncertainty of S_{jk}, $\sigma_{S_{jk}}$, assuming independent measurement errors of C_{ik}, $\sigma_{C_{ik}}$, and a_{ij}, $\sigma_{a_{ij}}$, is (Bevington, 1969).

$$\sigma_{S_{jk}} = \frac{C_{t_j}}{a_{t_j j}} \sqrt{\frac{\sigma^2_{C_{t_j k}}}{C^2_{t_j k}} + \frac{\sigma^2_{a_{t_j j}}}{a^2_{t_j j}}} \qquad 2.2.3$$

When the tracer element t_g for source S_{gk} is also present in another source, S_{hk}, which has a unique tracer, t_h, then the contribution to the ambient loading S_{hk} can be estimated from eq. 2.2.2

$$S_{hk} = \frac{C_{t_h k}}{a_{t_h h}} \qquad 2.2.4$$

the contribution to $C_{t_g k}$ due to S_{hk} can be subtracted, and eq. 2.2.2 can be applied to the remainder

$$S_{gk} = \frac{1}{a_{t_g g}} \left[C_{t_g k} - \frac{a_{t_g h}}{a_{t_h h}} C_{t_h k} \right] \qquad 2.2.5$$

This argument can be extended to any number of sources whose contributions can be determined by independent tracers. In general

$$S_{gk} = \frac{1}{a_{t_g g}} \left[C_{t_g k} - \sum_{j \neq g} \frac{a_{t_g j}}{a_{t_j j}} C_{t_j k} \right] \qquad 2.2.6$$

Uncertainties associated with the C_{ik} and a_{ij} will accumulate in eq. 2.2.6 to the extent that the value obtained for S_{jk} will be meaningless if the tracer element chosen overlaps with many other sources.

A problem arises when the same tracer is used to characterize more than one source. Gatz used Al as the unique component for both coal burning and soil dust (making both of these of the same source type from a receptor model point of view). He could estimate the maximum contribution of each one by assuming the other to be nonexistent and he could make a "reasonable" assumption that half of the measured Al was due to soil and the other half due to coal, but he could not definitely resolve them.

The linear least squares solution of eqs. 2.2.1 does not require an element unique to each source type. The looser restriction of a set of a_{ij} for source j which is linearly independent of the a_{ij} sets of the other sources is imposed. This includes the unique element case as a subset. If n=p then n linearly independent equations can be solved for n source contributions. When p<n, as is usually the case, the S_{jk} are overdetermined and a different set will be calculated for each subset of p equations selected. A reasonable approach justified on the basis of maximum likelihood (Mathews and Walker, 1965; see section 3.2 of this document) is to choose the set of S_{jk} which minimizes the weighted sum of the squares of the differences between the measured concentrations and those obtained from eqs 2.2.1

$$\chi^2 = \sum_i \frac{\left(C_{ik} - \sum_{j=1}^{p} a_{ij} S_{jk}\right)^2}{\sigma_{C_{ik}}^2} \qquad 2.2.7$$

The weighting by $\frac{1}{\sigma_{C_{ik}}^2}$ is consistent with the theory of maximum likelihood and gives greater emphasis to those elements measured with higher precision.

Taking the derivative of χ^2 with respect to each S_{jk} and setting the results equal to zero yields the following solution

$$\vec{S}_k = \underset{\sim}{X}_k^{-1} \vec{P}_k \qquad 2.2.8$$

where $\vec{S}_k$ is a pxi column vector whose jth element is S_{jk}, $\vec{P}_k$ is a pxi column vector whose jth element is

$$\left(\vec{P}_k\right)_j = \sum_{i=1}^{n} \frac{C_{ik} a_{ij}}{\sigma_{C_{ik}}^2} \qquad 2.2.9$$

and $\underset{\sim}{X}_k$ is a pxp matrix with elements

$$\left(\underset{\sim}{X}_k\right)_{\ell m} = \sum_{i=1}^{n} \frac{a_{i\ell} a_{im}}{\sigma_{C_{ik}}^2} \qquad 2.2.10$$

The uncertainty in the determination of the S_{jk} when the C_{ik} are known absolutely is (see section 3.2)

$$\sigma_{S_{jk}} = \left[\underset{\sim}{X}_k^{-1} \right]_{jj}^{1/2} \qquad 2.2.11$$

It is important to note that these errors are correlated with each other to the extent indicated by the off diagonal elements of $\underset{\sim}{X}_k^{-1}$ and they cannot be propagated in further calculations as if they were independent errors.

Least squares fitting of the chemical element balance equations was first introduced by Friedlander (1973a) and has since been used by Kowalczyk, et al. (1978) for chemical element balance applications.

Though measurements for numerous elements are available in both ambient and source samples, there are restrictions that must be placed on those chosen for inclusion in the sum of the squares of eq. 4.2.6. These are:

1. All important sources of the element i must be included. If one is missing, the other source contributions will be overestimated to fill in the gap in the sum of the squares.
2. The fraction of element i from the aerosol emissions of source j measured at the source must be known and cannot change by the time it reaches the receptor. This is a problem for volatile elements such as the halogens. Pre-suspended source material, such as salt from seawater, bulk soil dust and incinerator fly ash does not

necessarily have the same composition as the suspended matter for which it is a precursor.

3. The elemental concentration at the receptor must be above the minimum detectable limits of the analysis technique. An upper limit can be placed on source contributions when concentrations are below minimum detectable limits. When one element in a source cannot be detected and another can, Gartrell suggests using the minimum detectable concentration divided by 2 as the best estimate of the unknown concentration. Kushner (1976) offers some support for this estimate, but its use requires further investigation.

Gartrell fitted five sources with seven elements and Kowalczyk used six sources with eight elements, though they had ambient measurements for 16 and 27 elements respectively. They chose their fitting elements on the basis of the above criteria and included the common tracers of V for fuel oil, Na for sea salt, Pb for automobile exhaust and Al for soil dust plus a few extras. Kowalczyk attributed most of the zinc to refuse incinerators without the inclusion of other zinc sources which, though their gross emissions are small, are highly enriched in Zn (Huntzicker, et al. 1975) and therefore possible major sources of that element. The effect described in criterion 1 occurs. Kowalczyk demonstrated the advantage of the least squares over the tracer method in resolving the coal and soil components by the inclusion of As and Mn which are present in soil and coal aerosol in different proportions.

When the calculated S_{jk} are substituted into eqs. 2.2.1, the resulting C_{ik} compare well with the measured values for the elements included in the fit, as is expected, but not so well for those not included. In fact, deviations of several hundred percent, well outside the uncertainties that would be expected on the basis of eq. 2.2.11, are common.

A linear programming method applied to eqs. 2.2.1 was proposed, then abandoned, in a material balance of gaseous hydrocarbons by Mayrsohn and Crabtree (1976). Henry (1977a) first applied it to the chemical element balance equations. He observes that the following constraints must be met by the source contributions

$$0 \leq S_{jk} \leq C_k, \; j = 1,p \qquad 2.2.12$$

$$C_{ik} + 3\sigma_{C_{ik}} \leq \sum_{j=1}^{p} a_{ij} S_{jk}, \; i = 1,n \qquad 2.2.13$$

$$0 \leq \sum_{j=1}^{p} S_{jk} \leq C_k \qquad 2.2.14$$

Given the C_{ik}, $\sigma_{C_{ik}}$, and a_{ij}, the object of the linear programming is to maximize the sum of the source contributions,

$$\text{MAX}\left(\sum_{j=1}^{p} S_{jk}\right) \qquad 2.2.15$$

subject to these constraints. Algorithms for this process are somewhat complicated (Hadley, 1962) but are well documented and widely available.

Henry (1977a) asserts that this approach is superior to the previous two because (1) it allows the possibility that a source of a particular element i has not been included and (2) it estimates source contributions when the number of sources is greater than the number of elements measured. These assertions probably won't hold up under closer examination. Leaving out a source would cause overestimation of the remaining sources because of 2.2.15. Though assertion (2) is mathematically correct, it is not clear that the results obtained would be physically significant.

Propagation of experimental error to the source contributions is not clear in this instance. One possibility is to perturb each C_{ik} by a Gaussian distributed random number times its standard deviation and use these values to calculate a set of S_j. Performing this procedure five to ten times would yield five to ten values for a single S_j from which an average and standard deviation could be computed.

There are three main limitations of the chemical element balance and its associated calculation techniques:

1. Information about the number and composition of sources affecting the receptor at the time of measurement is inadequate. Usually sources are included because their chemical compositions are available and no assessment of sources for which no chemical compositions exist is made. Source compositions of one location at one time are applied to the source type as a whole as if they were exact. For certain elements in certain sources these can vary by over 100% because of different source operating conditions, fractionation in the atmosphere, and analytical uncertainty of the measurements. At the very least this variability should be estimated.

2. Neither the linear least squares nor the linear programming contains a provision for consideration of the uncertainty in the a_{ij}. a_{ij} with higher uncertainty should receive less weight in the fitting and that uncertainty should be propagated to the S_j.

3. The linear least squares and linear programming procedures need to be better understood. The effects of large experimental uncertainties, the exclusion of important sources, concentrations below minimum detectable limits, similar but unequal source compositions and the violation of basic assumptions on the calculated source contributions need to be assessed.

The chemical element balance is, however, the only receptor model which allows quantification of source contributions and as will be seen, it is basic to all other receptor models.

2.3 ENRICHMENT FACTOR

The elemental character of the sources of ambient aerosol may not be known or may be available qualitatively rather than quantitatively. This is often the case in a region which has just been designated on Air Quality Maintenance Area (AQMA) and where an initial estimation of possible impacts is desired or in a so-called "pristine" or "background" location where the ambient loadings may result from an unknown local source or long range transport.

For this type of study the enrichment factor model coupled with a rudimentary knowledge of elemental "tracer" characteristics of common sources is useful.

It is assumed that the "natural background" composition is known and that it contains one unique tracer element unique to it and it alone. The enrichment factor for element i is then defined as

$$E_{ik} = \frac{\dfrac{C_{ik}}{C_{tk}}}{\dfrac{a_{ib}}{a_{tb}}} \qquad 2.3.1$$

where t refers to the tracer of background, b. This element must satisfy the criteria outlined for the CEB tracer method.

The uniqueness of tracer t combined with eq. 2.2.1 requires that

$$C_{tk} = a_{tb}S_{bk} \qquad 2.3.2$$

so combining eq. 2.3.2 and eq. 2.2.1 with eq. 2.3.1 yields

$$E_{ik} = 1 + \frac{\sum\limits_{j\neq b} a_{ij} S_{jk}}{a_{ib} S_{bk}} \qquad 2.3.3$$

If no sources of element i other than background exist, $E_{ik} = 1$. $E_{ik} > 1$ indicates that the added term in eq. 2.3.3 is not equal to 0 and that other sources of element i have an impact on the receptor location. An examination of known source compositions will offer some guidance in narrowing down the field of possible contributors, though the existence of some unknown unique source should never be discounted.

Normally, the a_{ib} "natural background" values are chosen as those of average crustal rock, found in the geochemical literature (Mason, 1966, Vinogradov, 1959, Wedepohl, 1968; Taylor, 1964) or the salt content of bulk seawater (Vinogradov, 1959; Riley and Chester, 1971).

Tracer elements including Al, Fe, Sc, Si and Mn have been used with the crustal rock background while Na is the invariable choice for sea salt enrichment.

Even in urban areas, Al, Mn, Sc, La, Sm, Ce, Ti, Th, Si and Rb do not generally experience significant enrichment over crustal material and Na and Mg are not generally enriched over sea salt. Ca, Fe, Cr, and Co exhibit variable enrichments while Cu, Zn, As, Se, Br, In, Sb, Cl, I, Ag, Cd, V, Ni, Tl, Sn, Hg, Pb, W, Cs, Ga, and Bi show substantial enrichments in a number of cities.

The enrichment factor receptor model cannot quantify the contribution of a specific source type without recourse to the chemical element balance, but its use can offer insight into the definition of those sources which do and do not affect the receptor without a knowledge of their chemical composition. For example, King, et al. (1976) noticed a high Sb enrichment at one site in Cleveland, Ohio. Further investigation revealed the existence of a nearby chemical plant producing Sb compounds. The enrichment factor model in this case pointed to an ambient aerosol source which had not been previously considered. Elements with equal enrichments might originate in the same source type, adding one more piece of information that could aid in the identification of unknown sources. In the case of assessing contributions to background aerosol in remote locations with no local sources, the enrichment factor model has been used to estimate which source types experience long range transport from urban areas; approximately 50% of the applications listed in Table 2.0 are in this regard.

Choices of aerosol precursor material compositions as background representatives must be made with caution. Significant fractionation between certain elemental ratios in these substances and their ambient aerosol exists (see section 3.1) which may lead to spurious conclusions. Published values may not fully characterize the local background aerosol. King, et al. (1976) and O'Donnell, et al. (1976) chose suburban and rural aerosol measurements, respectively, in the areas of interest and determined the urban enrichments with respect to these. This normalization is advantageous from a control strategy point of view as it shows which elemental concentrations are within the airshed and therefore subject to local control.

The choice of the tracer must also be made carefully. Though Al, Si, and Na are naturals, anthropogenic sources of these elements do exist, and before one of them is chosen as a tracer it should be ascertained that no local sources of it within the airshed exist. Enrichments less than one for many of the "natural" crustal elements would lead one to suspect an additional source of the tracer.

No provision for the propagation of uncertainty on the enrichment factors has been made to date. For large enrichments, greater than 50, this is surely unnecessary, but for those between 1 and 50 some estimate must be made so that the enrichment may be interpreted as real or not. Crustal elemental abundance estimates, while consistent for major elements such as Al and Si, can differ by an order of magnitude for minor constituents. The Se/Al ratio of Vinogradov (1959) used by Heindryckx and Dams (1974) is 1.37×10^{-7} whereas the same ratio obtained from Wedepohl (1968) by Gordon, et al. (1973) is 1.1×10^{-6}. Many other elements exhibit similar variability depending on where they were measured. This uncertainty alone may account for many high enrichment factors unexplainable by other sources. By summing independent errors of eq. 2.3.1 in quadrature, the enrichment factor uncertainty is

$$\frac{\sigma_{E_{ik}}}{E_{ik}} = \sqrt{\frac{\sigma^2_{C_{ik}}}{C^2_{ik}} + \frac{\sigma^2_{C_{tk}}}{C^2_{tk}} + \frac{\sigma^2_{a_{ib}}}{a^2_{ib}} + \frac{\sigma^2_{a_{tb}}}{a^2_{tb}}} \qquad 2.3.4$$

The major limitations of the enrichment factor model are that it cannot quantify source impacts and it is very dependent on the background composition chosen.

2.4 TIME SERIES CORRELATION

To this point the impact of sources on an individual sample taken at a receptor has been discussed. Air monitoring programs normally collect many consecutive samples at a particular location, thus offering the opportunity to examine the variation of elemental concentrations with time. These variations are compared with each other and those which correlate in time are then attributed to a common source or cause. Thus the designation time series correlation.

Both a graphical and a statistical approach to time series correlation have been made. The statistical technique will be discussed first because it lays the foundation for interpreting the graphical representation. Cahill, et al. (1977) present a less rigorous but instructive summary of the statistical approach.

Suppose m samples of the aerosol at a receptor have been taken consecutively over a period of time and that each has been characterized for n different elements. The correlation between the concentration of element u and element v is defined as

$$r_{C_u C_v} = \frac{1}{m} \sum_{k=1}^{m} C^s_{uk} C^s_{vk} \quad . \qquad 2.4.1$$

where the "standardized form" of C_{ik} is

$$C^s_{ik} = \frac{C_{ik} - \overline{C}_i}{V_{C_i}^{1/2}} \qquad 2.4.2$$

with the mean

$$\overline{C}_i = \frac{1}{m} \sum_{k=1}^{m} C_{ik} \qquad 2.4.3$$

and variance

$$V_{C_i} = \frac{1}{m} \sum_{k=1}^{m} (C_{ik} - \overline{C}_i)^2 \qquad 2.4.4$$

The m in the denominator of these expressions becomes m-1 when one desires an unbiased estimator (Meyer, 1975).

In the common formulation of this receptor model, the C_{ik} are known, but the a_{ij} and the number of source types, p, are unknown precluding the use of a chemical element balance.

Elemental pairs u and v for which

$$.80 \leq r_{C_u C_v} \leq 1.0 \qquad 2.4.5$$

are assumed to originate in a common source. If $r_{C_u C_v}$ of one element u with several other elements, v, satisfy criterion 2.4.5, then they are all attributed to the same source type. Usually a rudimentary qualitative knowledge of source compositions is enough to identify the source. In the absence of this knowledge, a source with this composition is sought.

Correlations of less than ∿ .80 can indicate more than one source for either or both of the elemental concentrations being compared. Sometimes a statistical significance test is applied to appraise the probability of obtaining a value for $r_{C_v C_u}$ assuming perfectly random variations of C_v and C_u. If the probability is high (>1-5%) the correlation is rejected as insignificant and the correlated elemental concentrations are assumed to originate in different source types, in a source whose contribution to the receptor doesn't vary, or in many different sources. Most of these tests are strictly valid only if the C_{ik}

are normally distributed, an assumption that has never been verified. Negative correlations are hard to interpret but are almost always insignificant.

The validity of these conclusions must be tested against the physical formulation of this receptor model. By incorporating eqs. 2.2.1 into eqs. 2.4.3, 2.4.4 and 2.4.2 they become

$$\overline{C}_i = \frac{1}{m}\sum_{k=1}^{m}\sum_{j=1}^{p} a_{ij}S_{jk} = \sum_{j=1}^{p} a_{ij}\left[\frac{1}{m}\sum_{k=1}^{m} S_{jk}\right] = \sum_{j=1}^{p} a_{ij}\overline{S}_j \qquad 2.4.6$$

$$V_{C_i} = \frac{1}{m}\sum_{k=1}^{m}\left[\sum_{j=1}^{p} a_{ij}S_{jk} - \sum_{j=1}^{p} a_{ij}\overline{S}_j\right]^2 = \sum_{j=1}^{p}\sum_{\ell=1}^{p} a_{ij}a_{i\ell}V_{S_j}^{\frac{1}{2}}V_{S_\ell}^{\frac{1}{2}}r_{S_jS_\ell} \qquad 2.4.7$$

$$C^s_{ik} = \frac{\sum_j a_{ij}\left(S_{jk}-\overline{S}_j\right)}{V_{C_i}^{\frac{1}{2}}} = \sum_{j=1}^{p}\frac{a_{ij}V_{S_j}^{\frac{1}{2}}}{V_{C_i}^{\frac{1}{2}}}S^s_{jk} \qquad 2.4.8$$

where S^s_{jk} is the standardized form of S_{jk}, after eq. 2.4.2.

When eq. 2.4.7 is combined with eq. 2.4.1

$$r_{C_uC_v} = \frac{1}{m}\sum_{k=1}^{m}\left[\sum_{j=1}^{p}\frac{a_{uj}V_{S_j}^{\frac{1}{2}}}{V_{C_u}^{\frac{1}{2}}}S^s_{jk}\right]\left[\sum_{\ell=1}^{p}\frac{a_{v\ell}V_{S_\ell}^{\frac{1}{2}}}{V_{C_v}^{\frac{1}{2}}}S^s_{\ell k}\right] \qquad 2.4.9$$

$$r_{C_uC_v} = \frac{\sum\limits_{j=1}^{p}\sum\limits_{\ell=1}^{p} a_{uj}a_{v\ell}V_{S_j}^{\frac{1}{2}}V_{S_\ell}^{\frac{1}{2}}r_{S_jS_\ell}}{\left[\sum\limits_{j=1}^{p}\sum\limits_{\ell=1}^{p} a_{uj}a_{u\ell}V_{S_j}^{\frac{1}{2}}V_{S_\ell}^{\frac{1}{2}}r_{S_jS_\ell}\right]^{\frac{1}{2}}\left[\sum\limits_{j=1}^{p}\sum\limits_{\ell=1}^{p} a_{vj}a_{v\ell}V_{S_j}^{\frac{1}{2}}V_{S_\ell}^{\frac{1}{2}}r_{S_jS_\ell}\right]^{\frac{1}{2}}} \qquad 2.4.10$$

Eq. 2.4.10 now relates the correlation coefficient of elemental concentrations at the receptor to the properties of the source types. Using this equation in its source model mode (i.e. with a knowledge of source and dispersion properties, but no knowledge of the receptor concentrations) any hypotheses advanced about $r_{C_uC_v}$ may be tested.

First consider the validity of this assertion: Condition 2.4.5 implies elements u and v originate uniquely in a common source type, g.

Assume they do, then

$$a_{uj} = a_{ug}\delta_{jg} \qquad 2.4.11$$

$$a_{v\ell} = a_{vg}\delta_{\ell g}$$

where δ is a Kronecker delta. Eq. 2.4.10 then reduces to

$$r_{C_uC_v} = \frac{a_{ug}a_{vg}V^{\frac{1}{2}}_{S_g}V^{\frac{1}{2}}_{S_g}}{a_{ug}a_{vg}V_{S_g}}\, r_{S_gS_g} = r_{S_gS_g} = 1 \qquad 2.4.12$$

Random errors in the determination of the C_{ik} have not been considered. If they are reasonably small compared to the temporal variation of C_v and C_u, $r_{C_uC_v}$ under the assumption that u and v originate only in source g will be less than, but close to, unity. Thus, the range of values for $r_{C_vC_u}$ in condition 2.4.5 (The lower cutoff of .80 is arbitrary).

Now suppose that element u is unique to source g and element v is unique to source h.

$$a_{uj} = a_{ug}\delta_{jg}, \quad h \neq g \qquad 2.4.13$$

$$a_{v\ell} = a_{vh}\delta_{\ell h}$$

and eq. 2.4.10 becomes

$$r_{C_u C_v} = \frac{a_{ug} V_{S_g}^{\frac{1}{2}} \, a_{vh} V_{S_h}^{\frac{1}{2}}}{\left(a_{ug}^2 V_{S_g}\right)^{\frac{1}{2}} \left(a_{vh}^2 V_{S_h}\right)^{\frac{1}{2}}} = r_{S_g S_h} \qquad 2.4.14$$

This shows that though a correlation coefficient meeting criterion 2.4.5 will result if u and v come from only one source and measurement errors are small, the converse, that 2.4.5 implies u and v are unique to one source, is not necessarily true. More information concerning $r_{S_g S_h}$ is required.

In general, the correlation between any variable X and another variable Y on which m paired measurements have been made is (Meyer, 1975).

$$r_{XY} = \frac{\overline{XY} - \overline{X}\,\overline{Y}}{V_X^{\frac{1}{2}} V_Y^{\frac{1}{2}}} \qquad 2.4.15$$

where

$$\overline{XY} = \frac{1}{m} \sum_{k=1}^{m} X_k Y_k \qquad 2.4.16$$

Mean: $$\overline{X} = \frac{1}{m} \sum_{k=1}^{m} X_k, \quad \overline{Y} = \frac{1}{m} \sum_{k=1}^{m} Y_K \qquad 2.4.17$$

Mean square: $$\overline{X^2} = \frac{1}{m} \sum_{k=1}^{m} X_k^2, \quad \overline{Y^2} = \frac{1}{m} \sum_{k=1}^{m} Y_k^2 \qquad 2.4.18$$

Variance: $$V_X = \overline{X^2} - \overline{X}^2, \quad V_Y = \overline{Y^2} - \overline{Y}^2 \qquad 2.4.19$$

Coefficient of variation: $$CV_X = \frac{V_X^{\frac{1}{2}}}{\overline{X}}, \quad CV_Y = \frac{V_Y^{\frac{1}{2}}}{\overline{Y}} \qquad 2.4.20$$

Solving eq. 2.4.15 for XY gives

$$\overline{XY} = \overline{X}\,\overline{Y} + r_{XY} V_X^{\frac{1}{2}} V_Y^{\frac{1}{2}} = \overline{X}\,\overline{Y} \left(1 + CV_X CV_Y r_{XY}\right) \qquad 2.4.21$$

and if there is no correlation between X and Y, or if the variance of X or Y is very small,

$$CV_XCV_Yr_{XY} << 1 \Rightarrow \overline{XY} = \overline{X}\;\overline{Y} \qquad 2.4.22$$

Eqs. 2.4.1, 2.4.2, 2.4.3 and 2.4.4 are consistent with these relationships. Eqs. 2.4.15-2.4.21 will be used in the examination of $r_{S_jS_h}$. By definition 2.4.15 and substitution of eq. 2.2.1

$$r_{S_gS_h} = \frac{\overline{S_gS_h}-\overline{S_g}\;\overline{S_h}}{V_{S_g}^{\frac{1}{2}}\;V_{S_h}^{\frac{1}{2}}} = \frac{\overline{D_gE_gD_hE_h}-\overline{D_gE_g}\;\overline{D_hE_h}}{V_{S_g}^{\frac{1}{2}}\;\;V_{S_h}^{\frac{1}{2}}} \qquad 2.4.23$$

On repeated invocation of eq. 2.4.21

$$r_{S_gS_h} = \left(V_{S_g}V_{S_h}\right)^{-\frac{1}{2}}\left[\overline{D_gD_h}\;\;\overline{E_gE_h}\left(1+CV_{(D_gD_h)}CV_{(E_gE_h)}r_{(D_gD_h)(E_gE_h)}\right) - \overline{D_gE_g}\;\;\overline{D_hE_h}\right] \qquad 2.4.24$$

$$\begin{aligned} r_{S_gS_h} = \left(V_{S_g}V_{S_h}\right)^{-\frac{1}{2}}\overline{D}_g\overline{D}_h\overline{E}_g\overline{E}_h&\Big[\left(1 + CV_{D_g}CV_{D_h}r_{D_gD_h}\right)\left(1 + CV_{E_g}CV_{E_h}r_{E_gE_h}\right) \\ &\times\left(1 + CV_{(D_gD_h)}CV_{(E_gE_h)}r_{(D_gD_h)(E_gE_h)}\right)^{-}\left(1 + CV_{D_g}CV_{E_g}r_{E_gD_g}\right) \\ &\times\left(1 + CV_{D_h}CV_{E_h}r_{D_hE_h}\right)\Big] \end{aligned} \qquad 2.4.25$$

Some "reasonable assumptions" for an urban airshed will simplify eq. 2.4.25:

Assumption 1: Different source type emission rates are not highly correlated with each other.

$$r_{E_gE_h} = \delta_{gh} \qquad 2.4.26$$

Assumption 2: Source type emission rates are uncorrelated with dispersion factors.

$$r_{D_gE_h} = 0 \qquad 2.4.27$$

Assumption 3: The products of dispersion factors and products of emission rates are uncorrelated.

$$r_{\left(E_g E_h\right)\left(D_g D_h\right)} = 0 \qquad 2.4.28$$

Under these assumptions, V_{S_j} becomes

$$V_{S_j} = \overline{D_j^2}\;\overline{E_j^2} - \bar{D}_j^2\,\bar{E}_j^2 = \left(\overline{D_j^2} - \bar{D}_j^2\right)\left(\overline{E_j^2} - \bar{E}_j^2\right) + \bar{D}_j^2\left(\overline{E_j^2} - \bar{E}_j^2\right) + \bar{E}_j^2\left(\overline{D_j^2} - \bar{D}_j^2\right) \qquad 2.4.29$$

$$CV_{S_j}^{\;2} = CV_{D_j}^{\;2}\, CV_{E_j}^{\;2}\left(1 + CV_{E_j}^{\;-2} + CV_{D_j}^{\;-2}\right) \qquad 2.4.30$$

$r_{S_g S_h}$ simplifies to

$$r_{S_g S_h} = \frac{\bar{D}_g \bar{E}_g \bar{D}_h \bar{E}_h}{V_{S_g}^{\;½}\, V_{S_h}^{\;½}}\left(CV_{D_g}\, CV_{D_h}\, r_{D_g D_h}\right) \qquad 2.4.31$$

and from eqs. 2.4.14, 2.4.30 and 2.4.31

$$r_{C_u C_v} = r_{S_g S_h} = r_{D_g D_h}\left[\left(1 + CV_{E_g}^{\;2} + \frac{CV_{E_g}^{\;2}}{CV_{D_g}^{\;2}}\right)\left(1 + CV_{E_h}^{2} + \frac{CV_{E_h}^{\;2}}{CV_{D_h}^{\;2}}\right)\right]^{½} \qquad 2.4.32$$

$$g \neq h$$

Now suppose that $r_{D_g D_h}$ is negative. This will be the case when $\overline{XY} \leq \bar{X}\,\bar{Y}$ in eq. 2.4.15 and corresponds to the physical situation of source type g being in an upwind sector different from that of source type h: a large value for D_g automatically implies a small value for D_h and vice versa. In this case, a negative correlation between two ambient elemental concentrations is not insignificant, but indicative of the directionality of the source with respect to the receptor.

If both source types are located in the same upwind sector, the dispersion they experience will be very nearly the same and

$r_{D_g D_h} \simeq 1$. This makes eq. 2.4.32

$$r_{C_u C_v} = r_{S_g S_h} = \left[\left(1+CV_{E_g}^2 + \frac{CV_{E_g}^2}{CV_{D_g}^2}\right)\left(1+CV_{E_h}^2 + \frac{CV_{E_h}^2}{CV_{D_h}^2}\right)\right]^{\frac{1}{2}} \qquad 2.4.33$$

which, depending on the variability of emission rates, could very well meet criterion 2.4.5 even though the source types from which u and v come are distinct.

Of course, many situations, even ones violating assumptions 1-3, which were invoked for illustrative purposes, can be proposed and their effects on the correlation of one elemental concentration with another examined. The development here is probably over-restrictive, and most of those elemental concentrations with high correlations, Pb-Br, Na-Cl, Al-Si-Mn-Ti, V-Ni, surely do come from common source types, an assertion borne out by the extensive knowledge of the chemical composition of major aerosol sources. The point is that the effects of the dispersion factor on correlations should always be considered; it may explain anomolous correlations for which no common source is to be found and account for at least a portion of the correlation of elements coming from the same source.

Interpretation of $r_{C_u C_v}$ in terms of the time series correlation receptor model, eq. 2.4.10, would be much simplified if the source type variations could be uncoupled, that is, if

$$r_{S_g S_h} = 0 \qquad 2.4.34$$

Henry (1977a) and Kleinman (1977) suggest that this is possible, at least to some extent, because of the similarity of the dispersion factors to which all sources are exposed at a given time. They impose the condition that

$$D_{jk} = D_k, \; j = 1, p \tag{2.4.35}$$

from which it follows that

$$r_{D_g D_h} = 1 \tag{2.4.36}$$

and

$$S_{jk} = D_k E_{jk} \tag{2.4.37}$$

(This condition seems reasonable for sources upwind of the receptor or widely distributed area sources, but not for sources located in different upwind sectors. As noted before, a large D_{gk} implies a D_{hk} near zero in this case. A not too elegant way out of this dilemma is to assign the directionality to E_{jk} rather than to D_{jk}, saying that as far as the receptor is concerned, the emissions from source type j into the air mass sampled are zero. A source model formulation compatible with this situation needs to be developed and the implications for the receptor model explored. A more restrictive, but more rigorous, application would be to consider only widely dispersed source types or to stratify samples by wind direction.)

Substitution of eq. 2.4.37 into 2.1.1 gives

$$\mathcal{C}_{ik} = \frac{Cik}{D_k} = \sum_{j=1}^{p} a_{ij} E_{jk} \tag{2.4.38}$$

When these dispersion normalized concentrations, $\mathcal{C}_{ik}$, are correlated with each other

$$r_{\mathcal{C}_u \mathcal{C}_v} = \frac{\sum_{j=1}^{p} \sum_{\ell=1}^{p} a_{uj} a_{v\ell} V_{E_j}^{\frac{1}{2}} V_{E_\ell}^{\frac{1}{2}} r_{E_j E_\ell}}{\left[\sum_{j=1}^{p} \sum_{\ell=1}^{p} a_{uj} a_{u\ell} V_{E_j}^{\frac{1}{2}} V_{E_\ell}^{\frac{1}{2}} r_{E_j E_\ell}\right]^{\frac{1}{2}} \left[\sum_{j=1}^{p} \sum_{\ell=1}^{p} a_{vj} a_{v\ell} V_{E_j}^{\frac{1}{2}} V_{E_\ell}^{\frac{1}{2}} r_{E_j E_\ell}\right]^{\frac{1}{2}}} \tag{2.4.39}$$

and if assumption 1 in eq. 2.4.26 holds (and it won't when source types g and h are unique and separated with respect to windflow) then

$$r_{\mathcal{C}_u\mathcal{C}_v} = \frac{\sum_j a_{uj} a_{vj} V_{E_j}}{\left(\sum_j a_{uj}^2 V_{E_j}\right)^{1/2} \left(\sum_j a_{vj}^2 V_{E_j}\right)^{1/2}} \qquad 2.4.40$$

The difficulty with this normalization is that the greatest virtue of the receptor model, that D_k need not be known, is negated.

Kleinman, et al. (1973, 1976, 1977) have proposed and used a simple box model type dispersion factor, after Leahey (1972), of the inverse average windspeed u_k times mixing depth, z_k

$$D_k = \frac{1}{u_k z_k} \qquad 2.4.41$$

for application to samples taken in New York over several years. They recognize the value of such normalization and show that normalized concentrations for specific species (residual oil combustion is their prime example) track yearly emission cycles better than non-normalized concentrations, lending credence to eq. 2.4.35.

Henry (1977a, 1977b), however, factors out the dispersion factor without having to know its value by realizing that eq. 2.4.37 combined with 2.1.3 means that the total particulate loading

$$C_k = D_k \sum_{j=1}^{p} E_{jk} = D_k E_k \qquad 2.4.42$$

and that dividing both sides of eq. 2.1.4 by both sides of eq. 2.4.42 gives

$$\mathcal{C}_{ik} = \frac{C_{ik}}{C_k} = \sum_{j=1}^{p} a_{ij} \frac{E_{jk}}{E_k} = \sum_{j=1}^{p} a_{ij} \mathcal{S}_{jk} \qquad 2.4.43$$

where the script $\mathcal{C}_{ik}$ and $\mathcal{S}_{jk}$ no longer represent the absolute ambient concentrations and source contributions, but are the fractional, or percent concentrations and contributions, respectively.

Eq. 2.1.3 becomes

$$\sum_{j=1}^{p} S_{jk} = 1 \qquad 2.4.44$$

which, when placed in standardized form after eq. 2.4.2, yields

$$\sum_{j=1}^{p} S^{s}_{jk} = 0 \qquad 2.4.45$$

Multiplying eq. 2.4.45 by itself and summing over k

$$\frac{1}{m}\sum_{k=1}^{m}\left[\sum_{j=1}^{p} S^{s}_{jk}\right]\left[\sum_{\ell=1}^{p} S^{s}_{\ell k}\right] = \sum_{j=1}^{p}\sum_{\ell=1}^{p}\left[\frac{1}{m}\sum_{k=1}^{m} S^{s}_{jk}\, S^{s}_{\ell k}\right] = \sum_{j=1}^{p}\sum_{\ell=1}^{p} r_{S_j S_\ell} = 0$$

2.4.46

and since the correlation of any standardized variable with itself is equal to unity

$$\sum_{j=1}^{p}\sum_{\ell=j+1}^{p} r_{S_j S_\ell} = -\frac{p}{2} \qquad 2\text{-}4\text{-}47$$

Henry's normalization can be expected to introduce a negative correlation between source contributions (and in some cases positive correlations as well) even though the emission rates, assumption 1, remain independent. This is particularly evident when two major sources dominate; p=2 and $r_{S_1 S_2} = -1$. This makes sense, for as one source increases its fraction, the fact that all fractions must add up to one automatically reduces the other. If several source types exist and none dominates the mass loading, then the correlations are negligible; in Henry's application his ambient data show this to be the case.

Henry goes on to show that this simple normalization can be of great service in the interpretation of correlations between ambient elemental concentrations. He estimates on the basis of his observations that in eq. 2.4.32

$$CV_{E_g} \simeq CV_{E_h} \simeq CV_{D_g} \simeq CV_{D_h} \simeq .2 \qquad 2.4.48$$

which, with 2.4.33, reduces 2.4.32 to

$$r_{C_u C_v} = r_{S_g S_h} \simeq \frac{1}{(2+(.2)^2)} = .49,\ g \neq h \qquad 2.4.49$$

Thus, in the absence of any origin in a common source, one should expect correlations coefficients between the absolute concentrations of elemental constituents to be approximately .5. A little thought and this is obvious. Under low windspeed, stable conditions, the total ambient concentration rises, and all of its constituents rise as well. Under high speed unstable circumstances, the total mass loading drops and its components decrease commensurately. It is only natural that significant correlations should exist, irrespective of source type origins.

This is borne out by an experiment Henry performed on ambient data. Table 4.4.1 contains in its lower left half the correlations between the absolute concentrations of 12 elements measured in 14 twenty-four hour air pollution samples taken in Portland, Oregon; in most cases they are greater than or equal to .5.

The upper right half of this table presents the correlations of the fractional concentrations, C_i. Notice that the usual source emissions related correlations stand out, though reduced somewhat from their un-normalized counterparts, and that most of the other correlations

Table 2.4.1 Elemental Correlations of Absolute & Fractional Concentrations[a] (Henry, 1977b)

Correlations of Fractional Concentrations

	Mass	Al	Si	Cl	K	Ca	Fe	V	Cr	Mn	Ni	Zn	Pb	
Mass														Mass
Al	.850		.820	-.313	.761	.476	.434	.434	.355	.340	.552	.155	-.057	Al
Si	.904	.969		.120	.680	.574	.495	.471	.517	.391	.505	.230	.147	Si
Cl	-.622	-.408	-.371		-.266	.219	.083	.044	.015	-.048	-.191	.328	.726	Cl
K	.906	.944	.941	-.593		.426	.371	.096	.389	.536	.436	.041	-.072	K
Ca	.840	.870	.892	-.495	.890		.871	-.117	.194	.580	.223	.712	.436	Ca
Fe	.769	.810	.832	-.460	.818	.948		-.035	.345	.801	.342	.849	.160	Fe
V	.696	.743	.779	-.070	.647	.511	.482		.221	-.127	.305	-.072	-.066	V
Cr	.717	.714	.792	-.102	.707	.707	.749	.612		.568	.704	.275	-.281	Cr
Mn	.718	.747	.764	-.512	.794	.845	.938	.415	.767		.456	.670	-.153	Mn
Ni	.739	.794	.837	-.164	.767	.708	.708	.696	.865	.711		.338	-.139	Ni
Zn	.437	.508	.520	-.174	.469	.680	.831	.253	.648	.821	.598		.384	Zn
Pb	.463	.570	.546	.147	.564	.549	.381	.371	.257	.448	.448	.262		Pb
	Mass	Al	Si	Cl	K	Ca	Fe	V	Cr	Mn	Ni	Zn	Pb	

Correlations of Absolute Concentrations

[a] 14 ~24 hr. samples taken in Portland, Oregon, September, 1975.

have been markedly lowered.

The values in Table 2.4.1 also demonstrate that the basic assumptions made in forming this receptor model must always be kept in mind and violations actively sought and evaluated. Cl exhibits a negative correlation with most other elements because the assumptions in 2.4.35 and 2.4.36 are violated. Henry concludes that high Cl concentrations are associated with clean air masses moving in from the oceans which promulgate low receptor concentrations from local emitters making $r_{D_g D_h}$, and consequently $r_{S_g S_h}$, negative. Because the dispersion parameters are not equal, the normalization of eq. 2.4.33 does not uncouple the dispersion and eq. 2.4.40 is no longer valid. Henry emphasizes that background aerosol will not experience the same dispersion as that locally generated, and it should be subtracted out, when possible.

The graphical representation of time series correlation, while not as rigorous as the statistical approach just described, is much easier to interpret and preserves the temporal relationships of the ambient concentrations for comparison with source emissions cycles, wind direction changes or other parameters.

Figure 2.4.1 is a time series correlation plot of 18 four hour ambient concentrations of five variables taken over a three day period at the Central Air Monitoring Station in downtown Portland. This plot is similar to those appearing in Winchester, et al. (1974), Giaque, et al. (1974), Kleinman (1977), Wesolowski, et al. (1973), and Pilotte, et al. (1976, 1978). All five plots show a similar trend, and the uninitiated might conclude that Al, Si, Pb and Br are all emitted by the same source.

Figure 2.4.2 presents plots of the same data normalized to TSP as suggested by Henry in eq. 2.4.43. Now the similarity of Al-Si and Pb-Br is in marked contrast to that between these two groups.

The best graphical presentation of elemental time series is a linear plot of standardized, fractional concentrations, C_{ik}^{s} obtained from eq. 2.4.2. Figure 2.4.3 presents the data of the previous figures in this way; deviations from the mean value over the entire sampling sequence are noticeable and all deviations are related to a common scale. Al and Si can easily be attributed to one source, one of a geological nature, while Pb and Br are clearly related to a separate source, auto exhaust. Close examination of the Pb and Br plots shows cyclic increases during period five, which spans the evening rush hour between 4 and 8 p.m.

Correlation coefficients for these time series are presented in Table 2.4.2. All correlations of absolute concentrations are high, as predicted by Henry. Correlations of the fractional concentrations are not only reduced, but actually are significantly negative as foreseen by eq. 2.4.47. This implies that soil and auto exhaust are not only two contributors to the total suspended particulate at the place and times considered, but are two major contributors. Henry's normalization seems to hold great potential for distinguishing sources from time series correlation and, in certain situations, quantifying their impacts.

Time series correlation brings another dimension, time, into the picture and allows relationships between variables to be drawn on

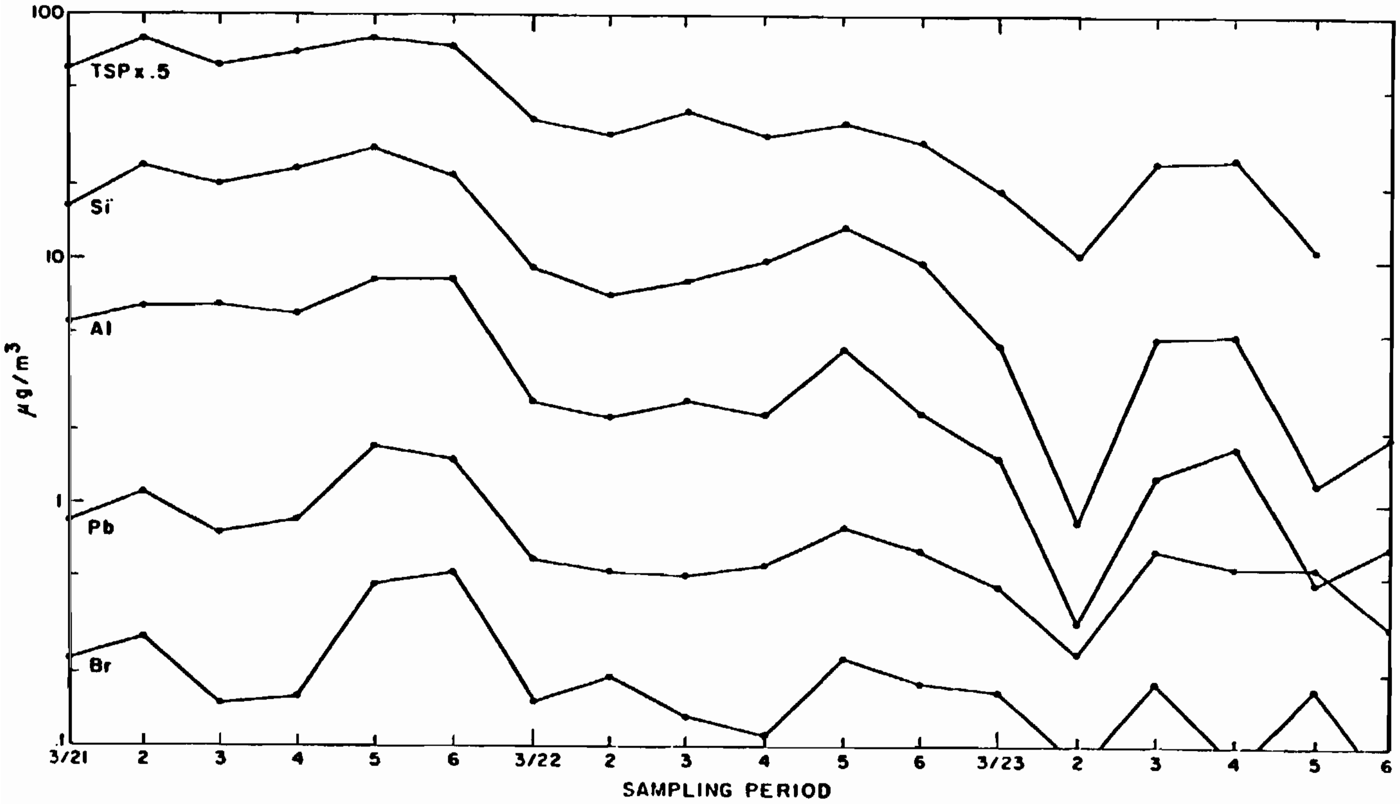


Figure 2.4.1. Time series of absolute concentrations. Eighteen consecutive four hour aerosol samples from Portland's Central Air Monitoring Station beginning at 12:01 a.m. on 3/21/78 compose the series.

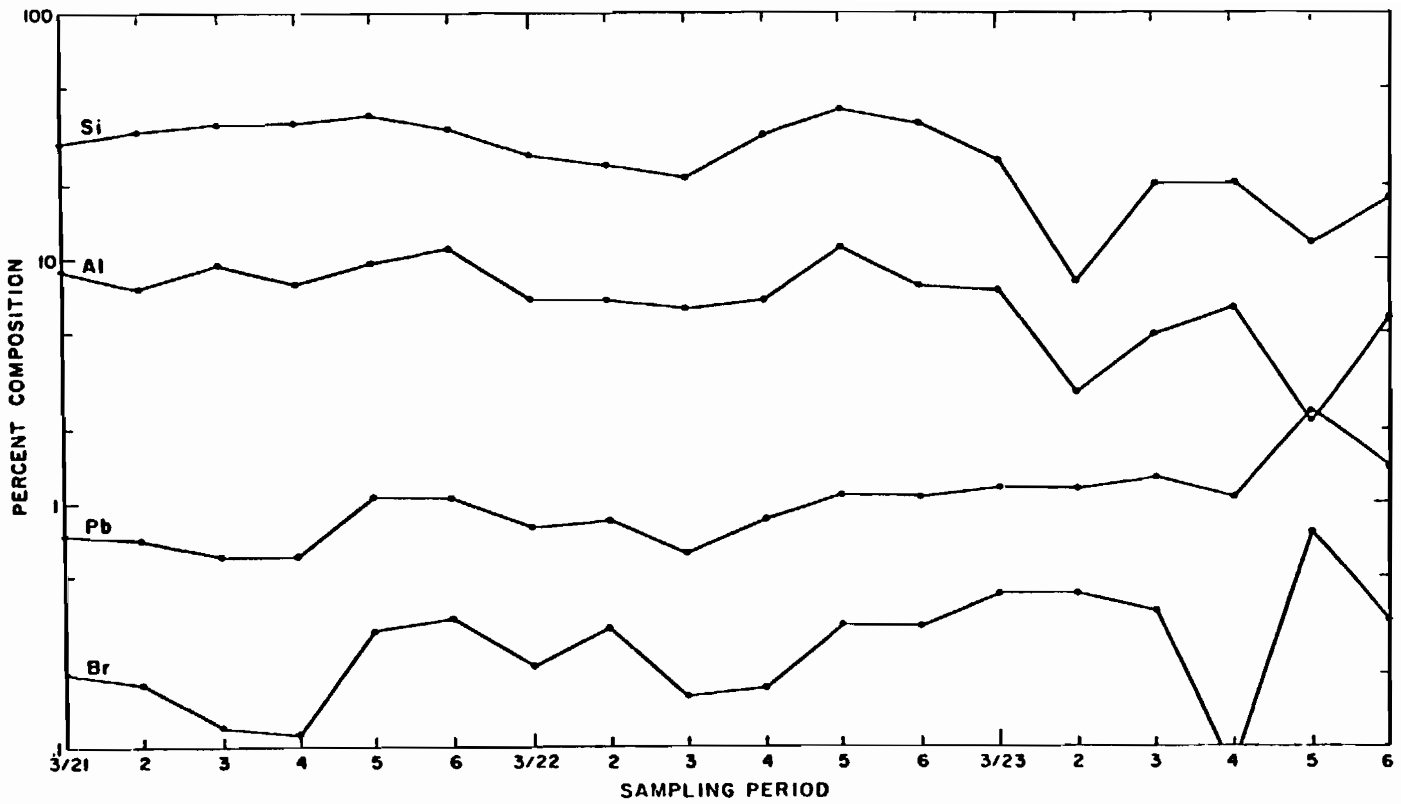


Figure 2.4.2. Time series of fractional concentrations. Eighteen consecutive four hour aerosol samples from Portland's Central Air Monitoring Station beginning at 12:01 a.m. on 3/21/78 compose the series.

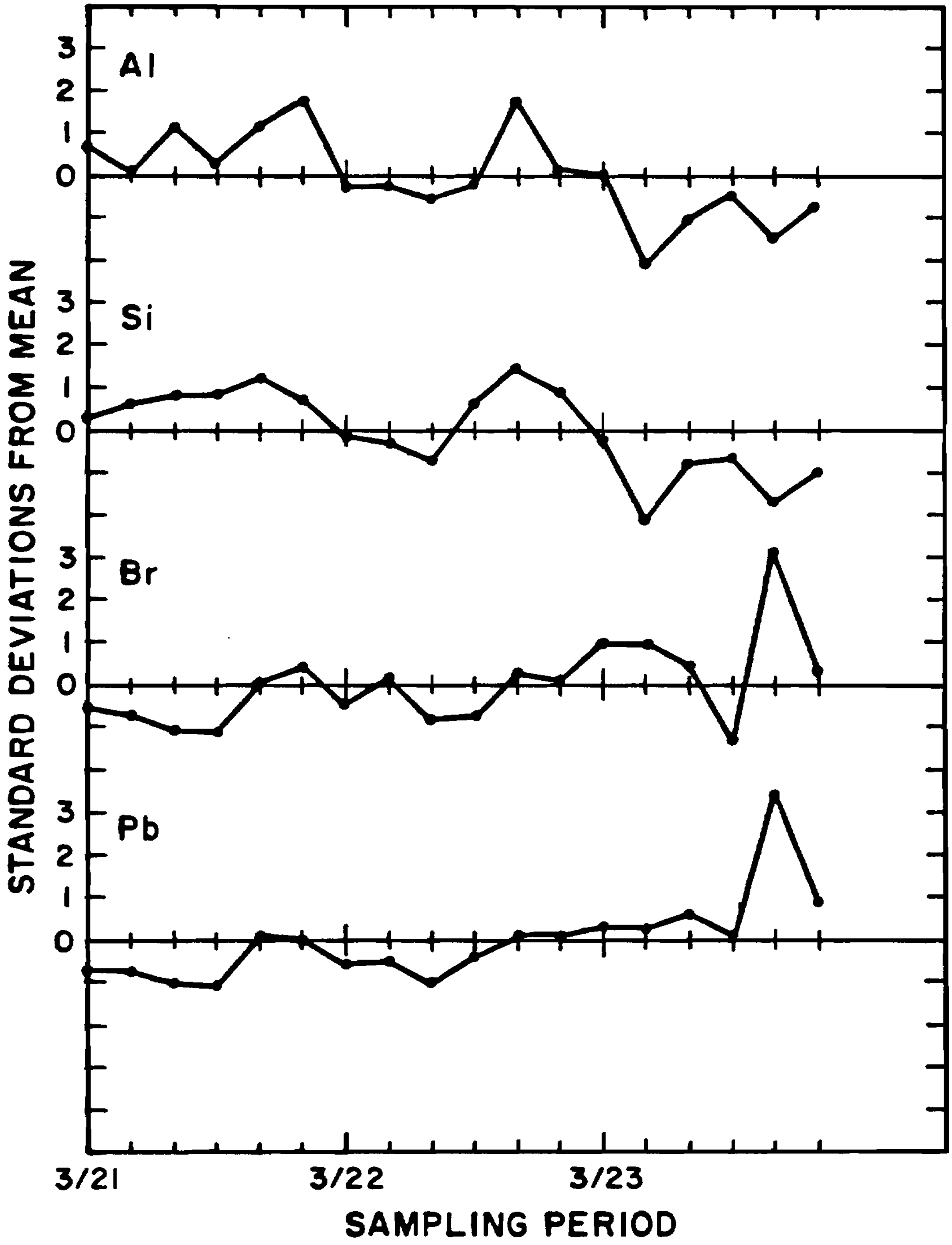


Figure 2.4.3. Time series of fractional concentrations in standardized form. Eighteen consecutive four hour aerosol samples from Portland's Central Air Monitoring Station beginning at 12:01 on 3/21/78 compose the series.

Table 2.4.2 Elemental Correlations of Absolute and Fractional Concentrations: Example from PACS data[a]

Correlation of Fractional Concentrations

	Mass	Al	Si	Br	Pb	
Mass		----	----	----	----	Mass
Al	.964		.895	-.360	-.417	Al
Si	.980	.974		-.504	-.536	Si
Br	.691	.788	.710		.893	Br
Pb	.853	.907	.876	.922		Pb
	Mass	Al	Si	Br	Pb	

Correlation of Absolute Concentrations.

[a] 18 consecutive 4 hour samples taken at CAMS, 3/21/78 - 3/23/78.

the basis of their variations along this dimension. The cause of this relationship, however, must be inferred from the known physical situation joining source and receptor in which both dispersion and emissions may vary. Under certain circumstances these two variables can be separated.

A high time series correlation between elements known to come from a common source can confirm its influence at a receptor and a negative correlation strongly suggests that the source types are separate. The inference of an unknown source type on the basis of observed elemental correlations that do not occur in recognized sources should be made with great care. Compliance with the basic assumptions of the time series model should be examined. Other explanations should be explored before instituting a search for a recondite source of the indicated composition.

Only cases in which elemental concentrations are dominated by unique and variable source types have been considered so far. The time series correlation receptor model, eq. 2.4.10, needs greater study in its source mode to assess the implications at the receptor of various a_{ij} and CV_{S_j}. Correlations not close to ±1 or 0 may contain information of value. The effects of random errors and the underlying distributions of the C_{ik} and C_{ik} on the correlations merits extensive investigation.

The model deals only with variability, not with absolutes; to quantify the contribution of a source type on the basis of elemental concentrations resort must be made to the chemical element balance.

Combining time series correlation with another receptor model shows promise. Wesolowski, et al. (1973) did this with a variation of the enrichment factor model in an attempt to isolate the source of excess lead in the atmosphere of a small rural community. They plotted the Br/Pb ratios from two-hour averages taken over a period of days. The resulting line varied little about the average value for automobile exhaust, but for a brief time when the ratio decreased four-fold, a time which was later found to correspond to the operating schedule of a lead smelter several miles away.

An examination of the time series fluctuations of results from the chemical element balance would be of great interest. Basic assumptions (1-3) of the time series model and the normalizations of Kleinman and Henry could be tested by actual examination of source contribution correlations. The results of the CEB would be confirmed, at least qualitatively, by relating them to known emission and dispersion changes.

Long term time series, properly normalized, can indicate trends and the intervention caused by specific actions such as control measures. Kleinman (1977) presents an example of such an application. The work of Box and Jenkins (1976) merits careful study and application in this regard.

The major importance of the time series model, however, may be as the input to the fourth type of receptor model. In the next section the elemental correlation coefficients will be the starting point for another type of receptor model, the multivariate model.

2.5 MULTIVARIATE MODELS

"Multivariate" is a possible misnomer for this specific class of model as, strictly speaking, all receptor models are multivariate problems as a result of the many, random observables employed. The designation is used, however, as a temporary classification for the use of so-called multivariate methods, specifically factor/principal components analysis (Harman, 1976; Rummel, 1970), cluster analysis (Everitt, 1974), canonical correlation analysis (Hotelling, 1936), least squares fitting/linear regression (Cooley and Lohnes, 1971) and possibly other techniques to assess the suspended particulate on the basis of chemical composition. The major emphasis will be given to orthogonal factor techniques as these require the most elucidation at present. Linear regression techniques are well summarized and exemplified by Pierson and Brachaczek (1976), Kleinman (1977), Hammerle and Pierson (1975) and Neustadter, et al. (1976).

Though the first efforts to apply factor analysis or principal components analysis (which will be treated as essentially the same here, much to the chagrin of social scientists who are vehement in their distinction of the two) to air pollution date (Blifford and Meeker, 1967) are a decade old, and though their use has expanded since then, only Henry (1977a, 1977b) has tried to relate a factor receptor model to a source model. The attempt will be made to expand and generalize somewhat on this beginning with the realization that much more exploration is required than can be developed here.

Our thinking must shift, now, from the individual scaler quantities treated in the previous sections to a multi-dimensional hyperspace. The change is not easy for those of us firmly established in a three coordinate world, but with some effort (and recourse to simple sketches for special cases in 3-d of which Kleinman (1977) offers some splendid examples) we will find our outlooks expanding into new dimensions. Equations will be written in matrix, vector, and individual component form where possible to accommodate the reader whose mathematical background has accustomed him to a specific notation. Table 2.5.1 defines symbols and relates them to each other.

Eq. 2.4.43 can be expressed

$$\underset{\sim}{C}^s = \underset{\sim}{\alpha}\, \underset{\sim}{S}^s, \quad \overrightarrow{C_i^s} = \sum_{j=1}^{p} \alpha_{ij} \overrightarrow{S_j^s}, \quad C_{ik} = \sum_{j=1}^{p} \alpha_{ij} S_{jk}^s \qquad 2.5.1$$

The components of $\underset{\sim}{C}^s$ are measured at the receptor and are known; $\underset{\sim}{\alpha}$, $\underset{\sim}{S}^s$ and p are unknown. The factor model purports to determine them.

$\overrightarrow{C_i^s}$ is specified by m components, one measurement of element i's standardized concentration for each specimen in the time series. It can be thought of as an actual geometric vector in m-space, a "specimen space" of m orthogonal axes. One component, C_{ik}^s, equals the projection of $\overrightarrow{C_i^s}$ onto coordinate axis k. Figure 2.4.3 graphically illustrates exemplar values for the components of four of these time series vectors. Each component is a relative deviation from the mean, so $\overrightarrow{C_i^s}$ mapped in m-space is a record of the variation in the concentration of element i over all m specimens.

This means that if two vectors, $\overrightarrow{C_u^s}$ and $\overrightarrow{C_v^s}$, point in nearly the same direction, the variation of elemental concentrations u and v is

Table 2.5.1 Meanings and Relationships of Symbols

Matrix		Dimensions		Vectors		Matrix Element
Name	Symbol	Columns	Rows	Column Vector	Row Vector	
Standardized percent concentration matrix	$\underset{\sim}{C}^s$	m specimens	n elements	$\vec{C}^s_k$	$\vec{C}^s_i$ $\vec{C}^s_u$ $\vec{C}^s_v$	$C^s_{ik} = \frac{C_{ik}-\bar{C}_i}{V^{1/2}_{C_i}}$ Standardized percentage concentration of element i in kth specimen
Standardized percent source contribution matrix	S^s	m specimens	p sources	$\vec{S}^s_k$	$\vec{S}^s_i$ $\vec{S}^s_g$ $\vec{S}^s_h$	$S^s_{jk} = \frac{S_{jk}-\bar{S}_j}{V^{1/2}_{S_j}}$ Standardized fractional contribution of source j to specimen i
Modified source composition matrix	$\underset{\sim}{\alpha}$	p sources	n elements	$\vec{\alpha}_j$	$\vec{\alpha}_i$ $\vec{\alpha}_u$ α_v	$\alpha_{ij} = \frac{a_{ij}V^{1/2}_{S_j}}{V^{1/2}_{C_i}}$ Fraction of S^s_{jk} contributed to C^s_{ik}
Symmetric concentration correlation matrix	$\underset{\sim}{R}_C$	n elements	n elements	$\vec{R}_{C_i}$	$\vec{R}_{C_i}$	$r_{C_uC_v} = \frac{1}{m}\sum_{k=1}^{m} C^s_{uk}C^s_{vk}$ Correlation of element v with element u

Matrix		Dimensions		Vectors		Matrix Element
Name	Symbol	Columns	Rows	Column Vector	Row Vector	
Matrix of basis vectors for reduced coordinate system	$\underset{\sim}{G}$	m specimens	$p \le n$ vectors	$\overrightarrow{G}_k$	$\overrightarrow{G}_j$	G_{jk} Coordinate of G_j on kth axis m space
Orthogonal matrix of eigenvectors of R_C	$\underset{\sim}{\beta}$	$p \le n$ eigenvectors	n elements	$\overrightarrow{\beta}_j$	$\overrightarrow{\beta}_i$	β_{ij} Projection of C^s_i onto G_j
Diagonal matrix of eigenvalves of R_C	$\underset{\sim}{\lambda}$	$p \le n$ eigenvalves	$p \le n$ eigenvalves	$\overrightarrow{\lambda}_j$	$\overrightarrow{\lambda}_j$	$\lambda_{ij} = \lambda_j \delta_{ij}$ eigenvalue of $\overrightarrow{\beta}_j$
Symmetric, orthogonal correlation matrix of S and G	R_{SG} R_{GS}	p sources	p sources	$\overrightarrow{R}_{S_jG}$	$\overrightarrow{R}_{S_jG}$	$r_{S_jG_h} = \frac{1}{m}\sum_{k=1}^{m} S^s_{jk} G_{hk}$ projection of S^s_j onto G_h
Matrix of errors in $\underset{\sim}{C}^s$	$\underset{\sim}{\varepsilon}$	m specimens	n elements	$\overrightarrow{\varepsilon}_k$	$\overrightarrow{\varepsilon}_i$	$\varepsilon_{ik} = C^s_{ik} - \Sigma_j \alpha_{ij} S^s_{jk}$ error in C^s_{ik}

nearly the same. The angle between the vectors, Θ_{uv}, measures the extent of their homo-directionality and is obtained from their scalar product

$$\cos \Theta_{uv} = \frac{\overrightarrow{C^s_u}\,\overrightarrow{C^s_u}^T}{\| C^s_u \| \, \| C^s_v \|} = \frac{\overrightarrow{C_u}^s \overrightarrow{C_v}^{s\,T}}{m} = \frac{1}{m} \sum_{k=1}^{m} C^s_{uk} C^s_{vk} = {}^r C_u C_u \qquad 2.5.2$$

$$R_{\underset{\sim}{C}} = \frac{\underset{\sim}{C}^s \underset{\sim}{C}^{sT}}{m} \qquad 2.5.3$$

where the squared length of $\overrightarrow{C_i}^s$ is obtained from eq. 2.4.3

$$\| \overrightarrow{C_i}^s \|^2 = \sum_{k=1}^{m} C^{s\,2}_{ik} = \sum_{k=1}^{m} \frac{\left(C_{ik} - \overline{C}_i \right)^2}{V_{C_i}} = m \qquad 2.5.4$$

and the superscript T denotes a transpose.

Thus the length of $\overrightarrow{C_i}^s$ is $\sqrt{m}$ and the cosine of the angle between two time series vectors is equal to the correlation coefficient of their time series; a correlation of 1 or -1 implies an angle between vectors of 0 or π, respectively, while a zero correlation corresponds to an angle of $\frac{\pi}{2}$. Time series vectors of uncorrelated variables are orthogonal to each other.

Coordinates on the axes in m space are only one way of specifying the vectors $\overrightarrow{C_i}^s$. Any coordinate system which preserves the geometric relationships between these vectors is just as good, and in fact preferable if the number of dimensions can be reduced. Eq. 2.5.1 states that the $\overrightarrow{C_i}^s$ can be represented as a linear sum of p vectors, and if $p < m$ and $p < n$, which is often the case for aerosol source types, then a relatively uncomplicated set of vectors in p-space, a "source space," should be sufficient to describe the observed standardized concentrations and their correlations. The approach of the factor models is to choose a set of orthogonal basis vectors, $\vec{G}_j$, on which the sum of the squared projections of the $\vec{C}_i^{\,s}$, these projections being denoted by β_{ij}, is maximized. These $\vec{G}_j$ vectors define the new "source space."

A set of p vectors in m-space, $\vec{G}_j$, is selected such that these vectors account for the $\vec{C}_i^{\,s}$

$$\underset{\sim}{C}^s = \underset{\sim}{\beta}\,\underset{\sim}{G}, \qquad \vec{C}_i^{\,s} = \sum_{j=1}^{p}\beta_{ij}\vec{G}_j, \qquad C^s_{ik} = \sum_{j=1}^{p}\beta_{ij}G_{jk} \qquad 2.5.5$$

and are orthogonal to each other with length m.

$$\underset{\sim}{R}_G = \frac{\underset{\sim}{G}\,\underset{\sim}{G}^T}{m} = I, \qquad \frac{\vec{G}_g\vec{G}_h^{\,T}}{m} = \delta_{gh}, \qquad \frac{1}{m}\sum_{k=1}^{m}G_{gk}G_{hk} = \delta_{gh} \qquad 2.5.6$$

Eq. 2.5.5 implies that

$$\underset{\sim}{G} = \underset{\sim}{\gamma}\,\underset{\sim}{C}^s \qquad \vec{G}_j = \sum_{i=1}^{n}\gamma_{ji}\vec{C}_i^{\,s} \qquad G_{ik} = \sum_{i=1}^{n}\gamma_{ji}C^s_{ik} \qquad 2.5.7$$

such that

$$\gamma = (\beta^T\beta)^{-1}\beta^T \qquad 2.5.8$$

and combining eq. 2.5.7 with 2.5.6 yields

$$\underset{\sim}{\gamma}\,\frac{\underset{\sim}{C}^s\underset{\sim}{C}^{sT}}{m}\,\underset{\sim}{\gamma}^T = \underset{\sim}{\gamma}\underset{\sim}{R}_C\underset{\sim}{\gamma}^T = I \qquad \sum_u\sum_v\gamma_{gu}\gamma_{hv}r_{C_uC_v} = \delta_{gh} \qquad 2.5.9$$

The projection of C_i^s on G_j is

$$\beta_{ij} = \|\vec{C}_i^{\,s}\|\cos\theta_{jk} = \sqrt{m}\,r_{C_iG_j} = \frac{1}{\sqrt{m}}\vec{C}_i^{\,s}\vec{G}_j^{\,T} = \sqrt{m}\sum_{k=1}^{m}\gamma_{ji}r_{C_uC_v}$$

$$\vec{\beta}_j = \frac{1}{m}\,\underset{\sim}{C}^s\,\vec{G}_j^{\,T} = \sqrt{m}\,\underset{\sim}{R}_c\gamma_j^{\,T} \qquad 2.5.10$$

$$\underset{\sim}{\beta} = \frac{1}{\sqrt{m}}\,\underset{\sim}{C}^s\underset{\sim}{G}^T = \frac{1}{\sqrt{m}}\,\underset{\sim}{C}^s\,\underset{\sim}{C}^{sT}\,\underset{\sim}{\gamma}^T = \sqrt{m}\,\underset{\sim}{R}_C\underset{\sim}{\gamma}^T$$

and the sum of the squares of these projections on $\vec{G}_j$ with the help of eq. 2.5.7 is

$$\underset{\sim}{\beta}^{T}\underset{\sim}{\beta} = m\,\underset{\sim}{\gamma}\,\underset{\sim}{R}_{C}{}^{2}\,\underset{\sim}{\gamma}^{T} \qquad 2.5.11$$

$$\vec{\beta}_{j}{}^{T}\vec{\beta}_{j} = \sum_{i=1}^{n}\beta^{2}_{ij}{}^{2} = m\sum_{u=1}^{n}\sum_{v=1}^{n}\sum_{w=1}^{n}\gamma_{ju}\gamma_{jw}r_{C_uC_v}r_{C_vC_w}$$

Maximizing this sum is equivalent to maximizing $\underset{\sim}{\gamma}\underset{\sim}{R}_{C}^{2}\underset{\sim}{\gamma}^{T}$ (since m is a constant) subject to the constraint of eq. 2.5.9, a simple task handled by the use of LaGrange multipliers (Boas, 1966). The objective function is

$$\underset{\sim}{\chi} = \frac{\underset{\sim}{\beta}^{T}\underset{\sim}{\beta}}{m} = \underset{\sim}{\gamma}\underset{\sim}{R}_{C}{}^{2}\underset{\sim}{\gamma}^{T} - \underset{\sim}{\lambda}\left(\underset{\sim}{\gamma}\underset{\sim}{R}^{T}_{C}\underset{\sim}{\gamma}-1\right) \qquad 2.5.12$$

$$\chi_{jj} = \frac{\vec{\beta}_{j}{}^{T}\vec{\beta}_{j}}{m} = \sum_{uvw}\sum\sum\gamma_{ju}\gamma_{jw}r_{C_uC_v}r_{C_vC_w} - \lambda_{j}\left(\sum_{uv}\sum\gamma_{ju}\gamma_{jw}r_{C_uC_w}-1\right)$$

where λ_j are arbitrary multipliers. The derivatives with respect to γ_{ju} are taken and set equal to 0, as is normal in extremum problems, leaving

$$\underset{\sim}{R}_{C}{}^{2}\underset{\sim}{\gamma}^{T}-\underset{\sim}{\lambda}\underset{\sim}{R}_{C}\underset{\sim}{\gamma}^{T} = \left(\underset{\sim}{R}_{C}-\underset{\sim}{\lambda}\right)\underset{\sim}{R}_{C}\underset{\sim}{\gamma}^{T} = 0 \qquad 2.5.13$$

or with eq. 2.5.10

$$\underset{\sim}{R}_{C}\underset{\sim}{\beta} = \underset{\sim}{\lambda}\underset{\sim}{\beta} \qquad \underset{\sim}{R}_{C}\vec{\beta}_{j} = \lambda_{j}\vec{\beta}_{j} \qquad \sum_{i}\beta_{ij}\vec{R}_{C_i} = \lambda_{j}\beta_{ij} \qquad 2.5.14$$

The set of vectors $\vec{G}_j$ should be chosen such that the projections of the $\vec{C}_i$s on them are eigenvectors of the correlation matrix of the $\vec{C}_i$s. Procedures for obtaining these vectors are well known (Carnahan, et al., 1969) but tedious and can only be practically performed by a computer. This operation will yield n eigenvalues, λ_j, but if the $\vec{C}_i$s can be spanned by p<n vectors, as eq. 2.5.1 asserts, then n-p of these values will equal 0.

To prove this, note first that eq. 2.5.13 premultiplied by $\underset{\sim}{\gamma}$ and with eq. 2.5.9 is

$$\underset{\sim}{\gamma}\,\underset{\sim}{R}_C{}^2\underset{\sim}{\gamma}^T = \underset{\sim}{\lambda}\underset{\sim}{\gamma}\underset{\sim}{R}_C\underset{\sim}{\gamma}^T = \underset{\sim}{\lambda}\ , \qquad \vec{\gamma}_j\underset{\sim}{R}_C{}^2\vec{\gamma}_j{}^T = \lambda_j\vec{\gamma}_j\underset{\sim}{R}_C\vec{\gamma}_j{}^T \qquad 2.5.15$$

which when combined with eq. 2.5.11 tells us

$$\frac{\underset{\sim}{\beta}^T\underset{\sim}{\beta}}{m} = \underset{\sim}{\lambda}, \qquad \frac{\vec{\beta}_j{}^T\vec{\beta}_j}{m} = \lambda_j, \qquad \frac{1}{m}\sum_{i=1}^{n}\beta_{ij}{}^2 = \lambda_j \qquad 2.5.16$$

Eq. 2.5.13 can be rewritten

$$\underset{\sim}{R}_C\left(\underset{\sim}{R}_C\underset{\sim}{\gamma}^T - \underset{\sim}{\lambda}\underset{\sim}{\gamma}^T\right) = 0\ , \qquad \underset{\sim}{R}_C\left(\underset{\sim}{R}_C\vec{\gamma}_j{}^T - \lambda_j\vec{\gamma}^T\right) = 0 \qquad 2.5.17$$

which will be true only if

$$\underset{\sim}{R}_C\underset{\sim}{\gamma}^T = \underset{\sim}{\lambda}\underset{\sim}{\gamma}^T, \qquad \underset{\sim}{R}_C\vec{\gamma}_j{}^T = \lambda_j\vec{\gamma}_j{}^T \qquad 2.5.18$$

proving $\vec{\gamma}_j{}^T$ to be eigenvectors of $\underset{\sim}{R}_C$ as well and, with eq. 2.5.10, that

$$\underset{\sim}{\beta} = \sqrt{m}\ \underset{\sim}{\lambda}\underset{\sim}{\gamma}^T\ , \qquad \vec{\beta}_j = \sqrt{m}\ \lambda_j\vec{\gamma}_j{}^T \qquad 2.5.19$$

which says that $\vec{\beta}_j$ and $\vec{\gamma}_j{}^T$ are essentially the same vector, just scaled to different lengths. That these eigenvectors are orthogonal to each other follows from the symmetric nature of $\underset{\sim}{R}_C$

$$\begin{aligned} \vec{\beta}_g{}^T\underset{\sim}{R}_C\vec{\beta}_h &= \lambda_h\vec{\beta}_g{}^T\vec{\beta}_h\ , & \sum_{u}\sum_{v}\beta_{uh}\,\beta_{uh}r_{C_uC_v} &= \lambda_h\sum_{i}\beta_{ig}\beta_{ih} \\ \vec{\beta}_h{}^T\underset{\sim}{R}_C\vec{\beta}_g &= \lambda_g\vec{\beta}_h{}^T\vec{\beta}_g, & \sum_{u}\sum_{v}\beta_{ug}\,\beta_{vh}r_{C_vC_u} &= r_g\sum_{i}\beta_{ih}\beta_{ig} \end{aligned} \qquad 2.5.20$$

$$\begin{gathered} \lambda_h\vec{\beta}_g{}^T\vec{\beta}_h = \lambda_g\vec{\beta}_h{}^T\vec{\beta}_g \\ \Longrightarrow \\ \lambda_h\sum_{i}\beta_{ig}\beta_{ih} = \lambda_g\sum_{i}\beta_{ih}\beta_{ig} \end{gathered} \qquad 2.5.21$$

In general, $\lambda_h \neq \lambda_g$ so the only way eq. 2.5.21 can be true in all cases is if

$$\vec{\beta}_g^{\,T}\vec{\beta}_h = 0,\ g \neq h,\ \sum_i \beta_{ig}\beta_{ih} = 0 \qquad 2.5.22$$

$$\Rightarrow\ \vec{\gamma}_g\vec{\gamma}_h^{\,T} = 0,\ g \neq h,\ \sum_i \gamma_{gi}\gamma_{hi} = 0 \qquad 2.5.23$$

The squared magnitude of an eigenvector is

$$\underset{\sim}{\beta}^T\underset{\sim}{\beta} = m\underset{\sim}{\lambda}^2\underset{\sim}{\gamma}\underset{\sim}{\gamma}^T,\quad \|\vec{\beta}_j\|^2 = \vec{\beta}_j^{\,T}\vec{\beta}_j = m\lambda_j^2\vec{\gamma}_j\vec{\gamma}_j^{\,T}$$

$$\underset{\sim}{\beta}^T\underset{\sim}{\beta} = \underset{\sim}{\lambda}\underset{\sim}{\gamma}\underset{\sim}{R}_C\underset{\sim}{\lambda}^T,\quad \|\vec{\beta}_j\|^2 = m\lambda_j\vec{\gamma}_j\underset{\sim}{R}_C\vec{\lambda}^T$$

$$\underset{\sim}{\beta}^T\underset{\sim}{\beta} = m\lambda\ ,\qquad \|\vec{\beta}_j\|^2 = \vec{\beta}_j^{\,T}\vec{\beta}_j = m\lambda_j \qquad 2.5.24$$

proportional to its corresponding eigenvalue and since the squared projections must add up to the sum of $\|\vec{C}_i^{\,s}\|^2$

$$\sum_{j=1}^{p} \lambda_j = n \qquad 2.5.25$$

If the λ_j are placed in order of decreasing magnitude.

$$\lambda_j = 0 \qquad \text{for} \qquad j > p \qquad 2.5.26$$

since the magnitudes of the $\vec{C}_i^{\,s}$ will have been accounted for by the first p eigenvalues.

The geometric relationships between these vectors, their correlation coefficients, are

$$\underset{\sim}{R}_C = \frac{\underset{\sim}{\beta}\underset{\sim}{G}\underset{\sim}{G}^T\underset{\sim}{\beta}^T}{m} = \underset{\sim}{\beta}\underset{\sim}{\beta}^T = m\underset{\sim}{\gamma}^T\underset{\sim}{\lambda}^2\underset{\sim}{\gamma}$$

$$r_{C_uC_v} = \sum_{j=1}^{p}\beta_{uj}\beta_{vj} = m\sum_j \lambda_j^2\ \gamma_{ju}\gamma_{uv} \qquad 2.5.27$$

Thus, finding the eigenvalues and the eigenvectors of the time series correlation matrix provides the minimum number of vectors, p, necessary to explain the $\vec{C}_i^s$ by simply counting the number of non-zero eigenvalues, and the reduced hyperspace is defined through the eigenvectors.

A brief recap is in order: We suspect, on the basis of our source model formulation, that the observed times series of n standardized concentrations can be explained as linear sums of the times series of p standardized source contributions (eq. 2.5.1). We see that these can be expressed as vectors in an m-dimensional "specimen space" but that a p dimensional "source space" is really all that is required. We reason that such a space is defined by p orthogonal vectors, $\vec{G}_j$, in the m space. The way these $\vec{G}_j$ are determined is by maximizing the squared projections of the $\vec{C}_j$ are determined is by maximizing the squared projections of the $\vec{C}_i^s$ on them and it is found that this condition is met when the projections of the $\vec{C}_i^s$ on each $\vec{G}_j$ are components of the eigenvectors of the elemental concentrations' correlation matrix, $\underset{\sim}{R}_C$. The number of such vectors is equal to the number of non-zero eigenvalues and the axes of the new coordinate system run along the $\vec{G}_j$, their positions being known in the reference m-space via $\underset{\sim}{G}$ and $\underset{\sim}{C}^s$.

The question now is "Why deal with the $\vec{G}_j$ and not with the $\vec{S}_j^s$ directly? Are they not the same thing?" The answer is "No, they are not." The p $\vec{G}_j$, as will be recalled, define the vector space in which the maximum amount of the variability of the $\vec{C}_i^s$ can be explained without resort to other dimensions. This space can be defined by an infinite number of basis vectors besides the $\vec{G}_j$, though each one of these will be a linear combination, or a rotation of the $\vec{G}_j$.

Consequently,

$$\underset{\sim}{S}^{s} = \underset{\sim}{R}_{SG}\underset{\sim}{G} \; , \; \vec{S}_j^{\,s} = \sum_{h=1}^{p} r_{S_g G_h} \vec{G}_h \; , \; S^{s}_{jk} = \sum_{h=1}^{p} r_{S_g G_h} G_{hk} \qquad 2.5.28$$

where R_{SG} is the symmetric correlation matrix of $\underset{\sim}{S}^{s}$ and $\underset{\sim}{G}$

$$\underset{\sim}{R}_{SG} = \frac{S^{s}G^{T}}{m} = \frac{GS^{s^{T}}}{m} \; , \quad r_{S_j G_h} = \cos\Theta_{jh} \frac{\vec{S}_j^{\,s}\, \vec{G}_h^{\,T}}{m} \qquad 2.5.29$$

$$r_{S_j G_h} = \frac{1}{m} \sum_{k=1}^{m} S^{s}{}_{jk} G_{hk}$$

If the S_j^s are uncorrelated with each other,

$$\underset{\sim}{R}_{S} = \frac{\underset{\sim}{S}^{s}\underset{\sim}{S}^{s^{T}}}{m} = \underset{\sim}{I} = \underset{\sim}{R}_{SG} \frac{\underset{\sim}{G}\underset{\sim}{G}^{T}}{m} \underset{\sim}{R}_{SG}{}^{T} = \underset{\sim}{R}_{SG}\underset{\sim}{R}_{SG}{}^{T} = \underset{\sim}{R}_{SG}{}^{2} \qquad 2.5.30$$

proving that $\underset{\sim}{R}_{SG}$ is an orthogonal transformation of the $\vec{G}_j$ into the $\vec{S}_j^{\,s}$.

The projections of the $\vec{C}_i^{\,s}$ onto the $\vec{S}_j^{\,s}$ are found since

$$\underset{\sim}{C}^{s} = \underset{\sim}{\alpha}\underset{\sim}{S}^{s} = \underset{\sim}{\beta}\underset{\sim}{G} \qquad 2.5.31$$

and post multiplying by $\underset{\sim}{S}^{sT}$ and dividing by m

$$\underset{\sim}{\alpha} \frac{\underset{\sim}{S}^{s}\underset{\sim}{S}^{s^{T}}}{m} = \underset{\sim}{\alpha} = \underset{\sim}{\beta} \frac{\underset{\sim}{G}\underset{\sim}{S}^{s^{T}}}{m} \underset{\sim}{\beta}\, \underset{\sim}{R}_{SG} \; , \quad \vec{\alpha}_j = \underset{\sim}{\beta}\vec{R}_{S_j G} \qquad 2.5.32$$

$$\alpha_{ij} = \sum_{h=1}^{p} r_{S_j G_h} \beta_{ih}$$

The key to obtaining $\underset{\sim}{\alpha}$ and $\underset{\sim}{S}^{s}$ lies in $\underset{\sim}{R}_{SG}$. Without additional conditions a variety of these orthogonal transformations exists.

A "target rotation" has been employed by Kleinman (1977) and Henry (1977a) which is similar to the tracer element application of the chemical element balance. If each source, j, contains a unique tracer element, t_j, then

$$\alpha_{t_j j} = \frac{a_{t_j j} V_{S_j}^{\frac{1}{2}}}{\left(\sum_{\ell} a^2_{t_j j} V_{S_j}\right)^{\frac{1}{2}}} = 1 \qquad 2.5.33$$

which says that $\vec{S}^s_j$ should be aligned with $\vec{C}^s_{t_j}$

$$\underset{\sim}{R}_{SG} = \underset{\sim}{\beta}_t$$

$$\vec{R}_{S_j G} = \vec{R}_{C_{t_j} G} = \frac{\vec{C}^s_{t_j} \underset{\sim}{G}^T}{m} = \vec{\beta}_{t_j} \frac{\underset{\sim}{G}\underset{\sim}{G}^T}{m} = \vec{\beta}_{t_j} \qquad 2.5.34$$

where $\underset{\sim}{\beta}_t$ is a pxp matrix composed of the projections of the i tracer elements of the $\vec{G}_j$.

When tracers are unknown the so-called varimax method (Kaiser, 1958) has been used. The reasoning is that certain $\vec{C}_i{}^s$ vectors originating from the same source $\vec{S}_j{}^s$ will cluster together, pointing in nearly the same direction. This is identical to the time series correlation criteria outlined in section 2.4; elemental concentrations with high correlations originate in a common source. The objective of a varimax transformation is to choose $\underset{\sim}{R}_{SG}$ such that the $\vec{S}^s_j$ line up as well as possible with these clumps of quasi-unidirectional vectors; the idea is to maximize the projections of the $\vec{S}^s_j$ within a bundle on a particular $\vec{C}^s_i$ while minimizing those projections from $\vec{C}^s_i$ associated with another bundle.

A mathematical condition which satisfies this criterion is the maximization of the variance of the variances of the squared projections on the $\overline{S}_j{}^s$.

$$\chi = \sum_{j=1}^{p} \frac{1}{n} \sum_{i=1}^{n} \left(\alpha_{ij}{}^2 - \overline{\alpha_j{}^2}\right)^2 \qquad 2.5.35$$

where

$$\overline{\alpha_j^{\ 2}} = \frac{1}{n} \sum_{i=1}^{n} \alpha_{ij}^{\ 2} \qquad 2.5.36$$

This is accomplished effectively (Harman, 1976) for p>2 only by a computer program which tries various transformations iteratively until χ reaches its maximum. Blifford and Meeker (1967), Gaarenstroom, et al. (1977), Gatz (1978), Hopke, et al. (1976), and Prinz and Strattman (1968) used this method.

Henry refines the tracer transformation by supplying quantitative estimates of the α_{ij}. He claims that the best selection for $\vec{R}_{S_jG}$ is that which minimizes

$$\chi_j = \frac{1}{n} \sum_{i=1}^{n} \left(\frac{\alpha_{ij} V_{C_i}^{\ \frac{1}{2}}}{a_{ij}} - \overline{\frac{\alpha_{ij} V_{C_i}^{\ \frac{1}{2}}}{a_{ij}}} \right)^2 \qquad 2.5.37$$

where

$$\overline{\frac{\alpha_{ij} V_{C_i}^{\ \frac{1}{2}}}{a_{ij}}} = \frac{1}{n} \sum_{i=1}^{n} \frac{\alpha_{ij} V_{C_i}^{\ \frac{1}{2}}}{a_{ij}} \qquad 2.5.38$$

From Table 2.5.1 it can be seen that eq. 2.5.37 minimizes the variances of the $V_{S_j}^{\ \frac{1}{2}}$ as determined by each a_{ij}.

No comparison of these transformations as applied to the same data set exists.

In reality, the determination of these "principal components" which fully describe the $\vec{C}_i^{\ s}$ and their correlations is not so simple. The source-oriented model in eq. 2.5.1 must be put into its receptor oriented mode by the addition of an error term

$$\underset{\sim}{C}^s = \underset{\sim}{\alpha}\underset{\sim}{S}^s + \underset{\sim}{\varepsilon}, \quad \vec{C}_i^{\ s} = \vec{\alpha}_i \underset{\sim}{S}^s + \vec{\varepsilon}_i, \quad C_{ik}^{\ s} = \sum_{j=1}^{p} \alpha_{ij} S_{jk}^{\ s} + \varepsilon_{ik} \qquad 2.5.39$$

$$\underset{\sim}{C}^s = \underset{\sim}{\beta}\underset{\sim}{G}+\underset{\sim}{\varepsilon}, \quad \vec{C}_i^s = \vec{\beta}_i\underset{\sim}{G}+\vec{\varepsilon}_i, \quad C_{ik}^s = \sum_{j=1}^{p} \beta_{ij}G_{jk}+\varepsilon_{ik} \qquad 2.5.40$$

where these errors are assumed uncorrelated with each other

$$\frac{\underset{\sim}{\varepsilon}\underset{\sim}{\varepsilon}^T}{m} = \underset{\sim}{U}, \quad \frac{\vec{\varepsilon}_u\vec{\varepsilon}_v^{\,T}}{m} = U_u\delta_{uv}, \quad r_{\varepsilon_u\varepsilon_v} = \frac{1}{m}\sum_{k=1}^{m} \varepsilon_{uk}\varepsilon_{vk} = U_u\delta_{uv} \qquad 2.5.41$$

and with the vectors in "source space"

$$\frac{\vec{S}_j^{\,s}\,\vec{\varepsilon}^{\,T}}{m} = 0 , \qquad \frac{1}{m}\sum_{k=1}^{m} S_{jk}^{s}\varepsilon_{ik} = 0 \qquad 2.5.42$$

$$\frac{\vec{G}_j\vec{\varepsilon}^{\,T}}{m} = 0 , \qquad \frac{1}{m}\sum_{k=1}^{m} G_{jk}\varepsilon_{ik} = 0 \qquad 2.5.43$$

These errors arise from random experimental uncertainties, disagreement between the model and reality, and sources contributing measurable quantities of only one element. With their inclusion it is no longer true that a p<n space exists in which the $\vec{C}_i^{\,s}$ and their correlations are completely described.

The correlation matrix becomes

$$\underset{\sim}{R}_C = \frac{\underset{\sim}{C}^s\underset{\sim}{C}^{s^T}}{m} = \frac{1}{m}\left(\underset{\sim}{\beta}\underset{\sim}{G}+\underset{\sim}{\varepsilon}\right)\left(\underset{\sim}{\beta}\underset{\sim}{G}+\underset{\sim}{\varepsilon}\right)^T = \underset{\sim}{\beta}\underset{\sim}{\beta}^T+\underset{\sim}{\varepsilon}\underset{\sim}{\varepsilon}^T = \underset{\sim}{\beta}\underset{\sim}{\beta}^T+\underset{\sim}{U} \qquad 2.5.44$$

A "reduced correlation matrix,"

$$\underset{\sim}{R}_C^* = \left(\underset{\sim}{R}_C-\underset{\sim}{U}\right) = \underset{\sim}{\beta}\underset{\sim}{\beta}^T \qquad 2.5.45$$

is one in which the unit diagonals have been replaced by $1-U_i$. Replacing $\underset{\sim}{R}_C$ by $\underset{\sim}{R}_C^*$ in eq. 2.5.14 will then reduce the number of non-zero eigenvectors to p and specify the eigenvectors $\vec{\beta}_j$. The error terms, $\underset{\sim}{\varepsilon}$ in eq. 2.5.39, will then be found by the difference

$$\underset{\sim}{\varepsilon} = \underset{\sim}{C}^s - \underset{\sim}{\beta}\underset{\sim}{G} \qquad 2.5.46$$

This is circular reasoning, however. $\underset{\sim}{U}$ is defined by $\underset{\sim}{C}$, but in order to specify $\underset{\sim}{C}$, $\underset{\sim}{U}$ must be known and subtracted from $\underset{\sim}{R}_C$. Some estimate of $\underset{\sim}{U}$ is necessary; this estimation has caused great consternation in the theory of factor analysis and its application to receptor modeling is no exception.

Henry (1977a, 1977b) sets U_i equal to the standardized form of the squared uncertainty of the measurements C_{ik}. Hopke, et al. (1976) chose the squared multiple correlation of each variable, but in a subsequent work (1977) they leave the diagonals of the correlation matrix equal to one as do Blifford and Meeker (1967). Gatz (1978), after trying several estimates including the assumption that $\underset{\sim}{U} = \underset{\sim}{0}$, found that little difference was made in the results obtained. The area remains controversial, however.

The major consequence of mis-specifying $\underset{\sim}{U}$, aside from the possible introduction of negative eigenvalues, is that the p-dimensional "source space" is not completely defined. It is left up to the researcher to select just how many dimensions this space must have. A reasonable choice is to reject $\vec{G}_j$ on which the projections of the $\vec{C}_i^{\,s}$ are small; eq. 2.5.20 says that those with the smallest eigenvalues should be eliminated. Duewar, et al. (1976) summarize the choice criteria commonly in use and actually test their efficacy on randomly perturbed data with some potentially helpful, but inconclusive results for air pollution applications.

Usually, the vectors corresponding to the p largest eigenvalues such that

$$\frac{\sum_{j=1}^{p} \lambda_j}{\sum_{j=1}^{n} \lambda_j} = \frac{1}{n} \sum_{j=1}^{p} \lambda_j > .80 \qquad 2.5.47$$

are chosen because these account for more than 80% of the common variance of all the $\vec{C}_i^{\,s}$ since the total variance

$$\text{Total Variance} = \sum_{i=1}^{n} \left[\frac{1}{m} \sum_{k=1}^{m} C_{ik}^{s^2} \right] = n \qquad 2.5.48$$

is just the denominator of condition 2.5.47. The remaining n-p vectors are ignored as being part of the error term.

After the number of vectors, p, is chosen, the $\vec{G}_j$ are transformed into the $\vec{S}_j^{\,s}$ by one of the methods described. The elemental concentration vector projected into this space is

$$\vec{C}_i^{\,s^*} = \vec{C}_i^{\,s} - \vec{\varepsilon}_i = \sum_{j=1}^{p} \beta_{ij} \vec{G}_j \qquad 2.5.49$$

and the projections of $\vec{C}_i^{\,s^*}$ onto the new $\vec{S}_j^{\,s}$ are those used in the transformation criteria.

The $\vec{S}_j^{\,s}$ are associated with actual source types through the relative dependence of certain elemental concentration variations, $\vec{C}_i^{\,s}$, on them. Obviously if a tracer transformation is incorporated to determine the $\vec{S}_j^{\,s}$ then the source types and their tracers must be known beforehand. This knowledge is really only an educated guess in practice, and can result from trials in which different elements are chosen as tracers. If other elements which are known to be present in the same source type emissions have substantial projections of their time series vectors, $\vec{C}_i^{\,s}$, on the resulting $\vec{S}_j^{\,s}$ then the transformation is considered adequate and $\vec{S}_j^{\,s}$ is identified as that source type.

Most researchers have preferred the varimax rotation, ostensibly because of its greater objectivity and because a priori source composition is unnecessary. Elemental concentration vectors which are highly correlated with a resulting $\vec{S}_j^{\,s}$ are associated with the same source type and a real source with those characteristics is sought.

Table 2.5.2 summarizes the source type interpretations drawn from a number of factor analyses of urban aerosol chemical compositions. Some of these contain spatial as well as time series variation, but this does not detract from the illustrative purpose of this comparison. The interpretation is somewhat hampered in several of these examples because some members of certain elemental concentration combinations which are related to source types, i.e. Pb-Br/auto exhaust, Na-Cl/sea salt, Al-Si-Fe-Mn-Ti/geological material, V-Ni/residual oil combustion, were not quantified in the samples.

The interpretations are many times obvious, as is Hopke, et al.'s (1976) geological material, other times ambiguous, as Blifford and Meeker's (1968) steel making whose elemental loadings are suspiciously similar to those of geological material, or are simply unknown, presumably due to a source emitting the indicated combination of elements which lurks nearby awaiting discovery.

A critical evaluation of factor analysis applications to ambient aerosol chemical composition is yet to be performed. The benchmark until now has been the extent to which the elemental correlation matrix, $\underset{\sim}{R}_{C}$, is reproduced by the "factor loadings," the α_{ij}. If one is interested in a "good" factor analysis, this is a fine criterion, but reproducing the

Table 2.5.2 Interpretatations Given to Factors with Various Elemental Correlations

	FACTOR NUMBER											
	1		2		3		4		5		6	
Study	Elemental Correlation	Interpretation	Elem. Corr.	Interp.	Elem. Corr.	Interp.	Elem. Corr.	Interp.	Elem. Corr.	Interp.	Elem Corr.	Interp.
Blifford & Meeker (1967)	Fe,Mn,Ti	Steel making	Pb,C,NO_3^-	Auto exhaust	TSP,SO_4^{-2}	Coal combustion	Ni,Pb	Gasoline Production	Zn,Sn	Plating	Cr	Plating
Hopke et.al. (1976)	Al,Fe,Se,Th	Crustal dust	Na,Cl	Sea salt	V	Residual oil combustion	Br	Auto exhaust	Mn,Se	?	Zn,Sb	Municipal Incinerator
Gaarenstroom et.al.(1977)	Na,K,Fe, Zn,Mg,Rb, Sr,Al,Ti, Si,Li,Mn, Cr,TSP	Soil	SO_4^{-2},NH_4^+, Cu	Background	Zn,K,Ca, Fe,Mg	Common Analysis Aliquot	Cd,Ni, NO_3^-,Zn	Combustion	Pb, NO_3^-	Auto exhaust	Cr,Ni, Cu	?
Kleinman (1977)	Cu, Cd,Zn	Incineration	Mn,Cr,Fe	Soil	V	Fuel oil	Pb	Auto exhaust	SO_4^{-2}	Secondary Aerosols		
Henry (1977a,1977b)	Mn,Fe,Zn	Metallurgical	Al,Si,K	Street dust	Cr,Ni Al,Si	Plating	Zn,Ca Fe	Zinc				
Gatz (1978)	Al,Si,Ti,K	Soil or Coal	Br,Si,Pb	Auto exhaust	Zn,Pb,Br	?	Ca	Cement	Mn,Fe	Steel mill		
Dattner (1978)	Al,Cu,K, Si,Ti,V TSP	Soil	Pb,Br	Auto exhaust	Ca,Mn,Sr, Zn,V,Zr, TSP.	Soil	Cu	Pump motor	Cl	?	S	?
Lesmanen & Partamen (1971) Turku	Ti,V,Sn, Ni,Cr,Mn,Pb,	Industrial sources	Ca,Cl,$SO_4^=$	Ore processing	V,Cu,Pb	Specific industry?						

correlation matrix is not the same as identifying sources and it is not clear that factor analysis does a better job of this than the simpler time series correlation.

The claim is made that the factor analysis discerns the source-receptor relationship of elements resulting from a linear combination of sources, but the infinite number of $\vec{S}_j$s that could be chosen does not support this. The assumption that several elements are dominant in only specific source types is the basis of each transformation of the eigenvectors; any elemental concentration vector which is truly a linear combination of contributions from several sources only clouds the issue. Even the supposedly source-composition-independent varimax method looks for "bundles" of $\vec{C}_i$s, a process which could be performed to some extent by examining groups of elements with high interelement correlations or another geometric clustering criteria. The vector rotation criteria does not seem adequate.

The second claim is that, at the very least, the factor analysis specifies how many source types are responsible for the variation. But, this too, is a murky area which is obscured by unknown random error. Malinowski (1977a) shows that some of this error is actually contained in the derived $\vec{G}_j$ and β_{ij} while another portion of it surfaces in the eigenvectors corresponding to the n-p eigenvalues which are dropped. He reiterates the problem of determining which eigenvectors are associated with this error and suggests some new approaches (Malinowski, 1977b) which have yet to be applied to air pollution data. His examination of factor analysis in other fields shows that some estimates of p are unwarranted. Both

Malinowski (1977b) and Preisendorfer and Barnett (1977) have factor analyzed simulated data matrices generated from purely random numbers and both find the normal decreasing trend of eigenvalues typical of that obtained from analyses on real data matrices (all eigenvalues should equal one for the correlations of these matrices). Preisendorfer and Barnett's work indicates this effect is due primarily to the small number of specimens on which measurements have been made; the correlation coefficients are only estimates of what they would be if the entire population of possible specimens comprised the sample. Thus, correlations which in reality are zero are represented by non-zero values. Duewer, et al. (1976) calculated the range of eigenvalues from correlation matrices of simulated measurements randomly perturbed by 1% of their respective magnitudes; the lowest eigenvalues increased by orders of magnitude. It would be interesting to test the effect with the 10% perturbations typical of analytical uncertainties. The criteria presently in use to determine the number of basic source types via factor analysis are limited by this lack of knowledge concerning the effects of uncertainty.

Related to this is the effect of deviations from the linear orthogonal factor model. As pointed out in section 2.4, condition 2.5.30 will definitely not be met if the absolute concentrations, C_{ik}, are used to form the correlation matrix. Other variability is introduced which does not correspond to that of a source type. In fact, Henry (1977c) shows that under some very conservative assumptions for an urban airshed the eigenvector explaining the largest portion of the variation in the $\vec{C}_i$s (the one with the largest eigenvalue) will correlate most strongly with the dispersion factor variation, $\vec{D}$, in eq. 2.1.1. Even Henry's normalization may not be adequate to satisfy eq. 2.5.30 under certain conditions (see eq. 2.4.47). The robustness of the factor model under the onslaught of irregularities has yet to be assessed.

The underlying distributions of the C_{ik} and C_{ik} and the cases of truncated and censored data sets can have an effect, one which has never been evaluated. Dattner (1978) has expressed these concerns about statistical effects and is apparently investigating them.

The interpretation of "factors," $\vec{G}_j$, as sources, $\vec{S}_j^{\,s}$, is in a primitive stage and is by no means independent of source composition knowledge, a line which is commonly espoused, since all "factors" are assigned to sources based on their correlations with the observed chemical concentrations. The orthogonality requirement of eq. 2.5.30 does fix the location of the pth $\vec{S}_p^{\,s}$ after the other p-1 $\vec{S}_j^{\,s}$ have been determined, but the doubt in p, as already discussed, nullifies this advantage. As already mentioned the adherence to 2.5.30 is often in doubt. The major sources found in Table 2.5.2 would be identifiable merely by inspecting the chemical composition of the sample, and the amount of speculation and explanation required to justify the minor ones is worthy of a trial lawyer or politician.

Matalas and Reiher (1967) speculate that one of the reasons factor analysis becomes popular is because it is often thought to be different from what it is. It would seem from the previous discussion that we really don't know what it is in terms of air pollution; it tells us that autos, soil, sea, salt and residual oil affect our air quality, albeit like time series correlation it cannot quantify that effect. But so what? We knew that anyway. What about the receptor perceived composition of those sources and their quantitative impact? What about other sources? Here, the lone factor model fails, or at least must be considered somewhat dubious, until its properties have been explored and documented.

This is not to say that previous researchers are wrong; the truth is that we don't know what the factor model is for aerosol chemical composition. The answers to the questions raised in this chapter concerning uncertainty, the number of factors, meeting model specifications, and eigenvector transformation, do not exist, but in order for the factor models to gain credibility they must be assessed. Tests on simulated and real aerosol data similar to those performed by Matalas and Reiher (1967), Wallis (1965), Rozett and Petersen (1975), Malinowski (1977a, 1977b) and Duewer, et. al (1976) should be carried out. The work of Henry (1977a, 1977b, 1977c) in relating the factor receptor model to the source model is of utmost importance and must be extended. This work inherently establishes the connection between this model and the other receptor models.

The factor models may indeed be able to break down ambient concentrations into source components, but on the other hand they may be just a more complicated and obfuscating way of expressing something that can be deduced by simpler methods. The resolution of this dichotomy is a prime area for research.

2.6 SPATIAL MODELS

The time series receptor models have concentrated on variations of the receptor-perceived emission rates, the E_{jk} in eq. 2.1.1 over time. To do this it was necessary to reduce the effect of the dispersion factor, D_{jk}, variation on the variability of the ambient elemental concentrations.

In spatial models the measured concentrations from a number of receptors of known geographical relationship at the same time are available. Thus, the source emissions, E_{jk}, are the same, but the dispersion factors will vary.

A greater knowledge of the dispersion factor must be incorporated into these models and the formulation from a simple source model is not as straightforward as that of the previous single site models. This section will merely summarize applications made to date in anticipation of a more rigorous source-formulated spatial receptor model which can serve as a basis for advancing hypotheses concerning what should be observed at a receptor.

Four types of spatial models are reported: spatial isopleths, spatial correlation, cluster analysis and pollution/wind rose.

Spatial Isopleths: Dams, et al. (1971) plotted lines of constant concentration for Cu, Fe, and K obtained from 25 simultaneous hi-vol samplers located throughout northern Indiana. Fe and Cu plots peaked in certain areas where metallurgical industries were located while K concentrations varied little over the region. The obvious conclusion was that the industries were a source (though possibly indirect through settling and reentrainment) of Cu and Fe.

Similar spatial isopleths can be combined with other receptor models, as did Gatz (1975) with the chemical element balance. He plotted isopleths of the calculated source type contributions from measurements at 22 locations in the Chicago area. The steel mill contribution did not peak where the location of these mills suggested it should, thereby casting some doubt on that source assessment, doubt which would not exist at a single receptor.

He also explored the possibility of pinpointing the location of unknown emitters of certain elements by subtracting the fraction of the elemental concentration attributable to the calculated source contributions and plotting isopleths of this difference. One such plot he presents as an example seems to locate an unknown source of cobalt.

Spatial Correlation: The development of this model would be entirely analogous to time series correlation with the looser restriction that the variation due to the dispersion factor would not have to be removed. John, et al. (1973) provide an excellent example. They find the usual correlations of elements in geological material. One caveat they advance concerning spatial models is of value; when considering all sites in their sample the Na-Cl correlation, usually indicative of sea salt, is low, but is high for the coastal sites and inland sites separately. Apparently the Na/Cl ratio changes from one set of sites to the other (see section 3.1.10). Aerosol chemical fractionation over the area comprising the spatial model can have grave consequences for this, and presumably all spatial models.

Cluster Analysis: A number of grouping techniques can be used to group elemental correlations which can then be identified with a source type, or to group individual receptors which have similar elemental concentration patterns. Two dimensional mapping procedures are used to facilitate visual interpretation of these clusters. Neustadter, et al. (1976), however, observe that these diagrams sometimes distort the actual relationships.

Hopke, et al. (1976) have combined factor analysis to assess sources with this type of cluster analysis to classify receptors. They attempt to substantiate the conclusions of their factor analysis by comparing the factor compositions of specimens within each cluster.

Pollution/Wind Rose: Both Scott Environmental Technology (1975) and Neustadter, et al. (1976) have suggested including the directionality of the dispersion factor in the receptor model. Elemental concentration measurements are stratified by prevailing wind direction and averaged within these categories. These averages are then plotted as polar "pollution roses." The speculation is that elemental concentrations originating in specific sources will exhibit a higher average concentration when the source is upwind of the receptor. Roses from a number of receptors would pinpoint the source through triangulation. This model depends on constant wind directions and emission rates while the samples are being taken, deviations from which are probably common in practical situations.

The scrutiny to which the models in previous sections were subjected should also be applied to the spatial receptor models when an adequate source model is formulated in receptor model terminology.

2.7 THE FUTURE OF RECEPTOR MODELS

The receptor models described in this chapter rely on characteristic chemical compositions of certain sources and their variation with respect to time and space to assess the impact of those sources at a receptor. They have been applied to ambient aerosol chemical composition data in a number of locations, though those applications seem to have been made as an afterthought; many authors emphasize how much better their results would be if their experiments had been designed with the model in mind. It does not appear that any aerosol study has been undertaken with the specific intent of rigorous receptor modeling.

It may be premature to undertake such a study until the formulation and application of receptor models are better understood. The source model shows that the measurements at a receptor are linear combinations of many individual sources, but receptor models always predict a few, basic source types. The source contributions deduced from receptor modeling tell us what could reproduce the ambient observations, but not necessarily what actually does. When one considers the many factors which contribute to observed ambient concentrations, aerosol growth, sedimentation, gas to particle conversion, fractionation of chemical composition, which have not been included in the models questions arise concerning what they are really telling us. Certain assumptions are made in each model about the source compositions and the statistical distributions underlying the measurements which may not be met in actuality. It may not be possible to include everything in the models, but a prerequisite for using them should be to define all basic assumptions and to evaluate the effects of deviations from them. This has not been done.

Receptor models need to be put on a firm foundation through development from a source model which would generate simulated ambient concentrations incorporating typical uncertainties and reasonable deviations from basic assumptions. The receptor model would then be applied to this simulated data set and the deviation of the predicted source contributions from those specified for the source model would be evaluated as a function of the perturbed assumptions.

In many ways the models can be improved by introducing parameters other than chemical composition. Gartrell and Friedlander (1975) and Heisler, et al. (1973) have made inroads in the inclusion of particle size relationships between source and receptor and Tiao and Hilmer (1978) demonstrate a specific case in which emission rates and dispersion factor variations are incorporated into a model. Combining receptor models holds great promise, but since they are all related to a common source model one should not rest satisfied with consistent results. A hybridization or iterative procedure in conjunction with the source model should also be examined in detail.

The models should be tested in a number of configurations and combinations on the same set of complete ambient and source elemental data. Anomalies and inconsistencies should be sought and attempts to explain them in the source model mode made.

To a very small extent this chapter has begun to do these things, though in terms of a review rather than as original work. Its purpose has been didactic and exploratory rather than exhaustive. The amount of research required is immense, but not so tantamount as the efforts being made to characterize ambient particulate and its sources nor as great as that which has been invested in source dispersion modeling. Receptor model use could be as routine tomorrow as the use of source models is today if they become as well explored and documented. They could do much to make use of the expensive measurements being made in many cities of particulate chemical composition to relate the ambient concentrations to sources.

In the following chapter a step of this research will be taken starting with some of the unknown features of the most basic receptor model, the chemical element balance.

CHAPTER THREE: REFINEMENTS IN THE CHEMICAL ELEMENT BALANCE

Each of the receptor models described in the previous chapter could be traced to Friedlander's chemical element balance which in turn results directly from a physically significant, mass conservative dispersion model. It is fitting, then, that any attempt to refine the application of receptor models begins with this one. The primary original contribution of this work will be in this regard.

The major shortcomings of the chemical element balance as applied in the studies to date are the following.

1. All major sources of the ambient aerosol have not been identified and characterized at the time ambient concentrations are taken. Literature values for source composition, possibly having limited relevance to the actual aerosol chemical makeup, have been used and no assessment of uncharacterized sources has been made (with the possible exception of the emission inventory scaling adjustment employed by Gartrell and Friedlander, 1975).

2. No estimate of the uncertainties in the source composition matrix elements has been made, nor has a method been devised to incorporate them in and propagate them through the least squares fitting procedure for estimating source contributions.

3. No study has been made, nor does the methodology to perform one exist, of the effects of deviations from the basic assumptions of the chemical element balance and the fitting procedure on the calculated source contributions.

This study attempts to meet these objections, if not in total, at least in part, and more importantly, it outlines a methodology that can be incorporated and improved upon in subsequent work. In this chapter we will:

1. Present source composition data obtained from each major emitter in the Portland airshed, compare them with other data when they exist and estimate their variability.

2. Derive and justify a weighted least squares fitting procedure which weights variables according to the precision in both the ambient concentrations and the source composition coefficients and places a reasonable confidence interval around the calculated source contributions.

3. State the basic assumptions of the chemical element balance and the solution method, outline a method for assessing the effect of not meeting them and evaluate the consequences of logical deviations from those assumptions.

4. Propose the averaging of chemical element balance results within surface windflow pattern groupings for the further distinction of individual aerosol sources and as a verification of the predicted source type contributions.

3.1 SOURCE COMPOSITIONS AND THEIR UNCERTAINTIES

Estimated annual anthropogenic emissions to the fine and total suspended particulate in the Portland Airshed in 1977-78 are presented in Tables 3.1.1a&b. This list has been developed over a period of years on a geographical basis using standard EPA emission factors of proportionality between an input variable (i.e. traffic count, gallons of fuel consumed, etc.) and the quantity of emissions (EPA, 1973). Though a small number of sources accounts for most of the total yearly emissions, and indeed probably does constitute the major anthropogenic contribution to ambient loadings, the other sources cannot be summarily neglected. Actual points of emission vary widely and the relative impact of a source at a receptor will depend on the distance between them. Some sources are

Table 3.1.1a-Fine Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL[c] in PORTLAND	COMMENTS
1.Geological	495.4	100. %	5.74%	
a.Agricultural Tilling	64.	12.9%	0.74%	
b.Rock Crusher [a]	26.6	5.4%	0.31%	
c.Asphalt Production [a]	39.8	8.0%	0.46%	
d.Street Dust [a]	365.	73.7%	4.23%	
2.Transportation	1938.	100. %	22.48%	
a.Auto-leaded[a,b] Gas	1372.	70.8%	15.91%	
b.Auto-non-[a,b] leaded	50.	2.6%	0.58%	
c.Diesel Truck [a,b]	205.	10.6%	2.38%	
d.Diesel Train [a]	124.	6.4%	1.44%	
e.Misc.(Ships, air, tires, brakes	187.	9.6%	2.17%	

[a] Tested in PACS

[b] Literature values for chemical composition exist.

[c] Total emissions are 8622.8 Tons/Year

Table 3.1.1a-Fine Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
3.Fossil Fuel	780.8	100. %	9.05%	
a.Residual Oil[a,b]	342.7	43.9%	3.97%	
b.Distillate Oil[a]	271.4	34.7%	3.15%	
c.Coal[b]	10.6	1.4%	0.12%	
d.Natural Gas[a]	156.1	20.0%	1.81%	
4.Vegetative Burning	394.7	100. %	4.58%	
a.Forest Fires	1.7	0.4%	0.02%	Tons/Yr Projected from DEQ Report 1976
b.Slash Burns[a]	14.	3.6%	0.16%	
c.Orchard Pruning Burns[a]	---	---	---	No Data
d.Fireplace[a]	---	---	---	"
e.Wood Stove[a]	---	---	---	"
f.Domestic Burning[a]	370.	93.7%	4.29%	
g.Field Burning[a,b]	9.0	2.3%	0.10%	

Table 3.1.1a-Fine Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
5.Forest Products Industry	2197.2	100. %	25.48%	
a.Kraft Recovery[a] Boiler	353.0	16.1%	4.09%	
b.Smelt Tank	14.1	0.6%	0.16%	
c.Incinerator	13.0	0.6%	0.15%	
d.Wood Processing	26.0	1.2%	0.30%	
e.Veneer Dryer	44.9	2.1%	0.52%	
f.Lime Recovery Kiln	122.4	5.6%	1.42%	
g.Sulfite Recovery Boiler[a]	290.9	13.2%	3.37%	
h.Hog Fuel Boiler[a]	1206.8	54.9%	14.00%	Ton/Yr was previously 1910.7
i.Paper Sludge Boiler	126.1	5.7%	1.46%	

Table 3.1.1a-Fine Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
6.Vegetative	270.7	100. %	3.14%	
a.Flour Processing[a]	8.4	3.1%	0.10%	
b.Grain Elevators[a]	241.7	89.3%	2.80%	
c.Animal Feed Processing	20.6	7.6%	0.24%	
d.Pollen	---	---	---	No Data
7.Aluminum Industry	1022.8	100.%	11.86%	
a.Aluminum Processing Stack[a]	502.1	49.1%	5.82%	
b.Aluminum Processing Roof Vent[a]	429.4	42.0%	4.98%	
c.Aluminum Handling[a]	91.3	8.9%	1.06%	

Table 3.1.1a-Fine Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
8. Iron Industry	211.1	100. %	2.54%	
a. Steel elec. Arc Furnace[a]	176.5	83.6%	2.05%	
b. Union Carbide Furnace[a]	34.6	16.4%	0.40%	
9. Miscellaneous	1312.1	100. %	15.22%	
a. Carborundum Process[a]	758.0	57.8%	8.79%	
b. Glass Furnace[a]	88.4	6.7%	1.03%	
c. Small Pt. Sources (car shredder)[a]	368.	28.0%	4.27%	
d. Pacific Carbide Furnace[a]	1.8	0.14%	0.02%	
e. Cement Kiln	79.1	6.0%	0.92%	
f. Limestone Kiln	0.3	0.02%	0.003%	
g. N.L. Industries	2.4	0.18%	0.028%	
h. Galvanizing	---	---	---	No Data
i. Sewage sludge Burning	11.5	0.9%	0.13%	
j. Chemical	1.2	.09%	0.014%	
k. Manufacturing Industry	---	---	---	No Data
l. Incinerators	1.4	0.11%	0.016%	

Table 3.1.1b–Total Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL[c] in PORTLAND	COMMENTS
1. Geological	4411.5	100. %	26.08	
a. Agricultural Tilling	645.	14.6%	3.81%	
b. Rock[a] Crusher	66.5	1.5%	0.39%	
c. Asphalt[a] Production	46.0	1.1%	0.27%	
d. Street[a,b] Dust	3654.	82.8%	21.60%	
2. Transportation	3688.	100. %	21.80%	
a. Auto-[a,b] leaded Gas	1829.	49.6%	10.81%	
b. Auto-[a] non-leaded	67.	1.8%	0.40%	
c. Diesel[a,b] truck	273.	7.4%	1.61%	
d. Diesel[a] train	131.	3.6%	0.77%	
e. Misc. (Tires,[b] Brakes, ships, air)	1388.	37.6%	8.21%	

[a] Tested in PACS

[b] Literature values for chemical composition exist.

[c] Total emissions are 16913.6 Tons/Year

Table 3.1.1b–Total Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
3.Fossil Fuel	814.6	100. %	4.82%	
a.Residual Oil [a,b]	359.8	44.2%	2.13%	
b.Distillate Oil [a]	285.9	35.1%	1.69%	
c.Coal [b]	11.8	1.4%	0.07%	
d.Natural Gas [a]	157.1	19.3%	0.93%	
4.Vegetative Burning	428.	100. %	2.89%	
a.Forest Fires	2.0	0.4%	0.01%	Ton/Yr projected from DEQ Report 1976
b.Slash Burns [a]	15.	3.1%	0.09%	
c.Orchard Pruning Burns [a]	--	--	--	No Data
d.Fireplace [a]	--	--	--	"
e.Wood Stove [a]	--	--	--	"
f.Domestic Burning [a]	461.	94.4%	2.73%	
g.Field Burning [a,b]	10.	2.1%	0.06%	

Table 3.1.1b-Total Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
5.Forest Product Industry	3225.3	100. %	19.07%	
a.Kraft recovery boiler[a]	356.6	11.1%	2.11%	
b.Smelt tank	15.6	0.5%	0.09%	
c.Incinerator	13.0	0.4%	0.08%	
d.Wood Processing	213.3	6.6%	1.26%	
e.Veneer Dryer	44.9	1.4%	0.27%	
f.Lime Recovery Kiln	144.	4.5%	0.85%	
g.Sulfite recovery boiler[a]	293.8	9.1%	1.74%	
h.Hog fuel[a]	2011.4	62.3%	11.89%	
i.Paper sludge boiler	132.7	4.1%	0.78%	

Table 3.1.1b-Total Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
6.Vegetative	567.6	100. %	3.36%	
a.Flour Processing[a]	10.9	1.9%	0.06%	
b.Grain elevators[a]	532.	93.7%	3.15%	
c.Animal feed Processing	24.7	4.4%	0.15%	
d.Pollen	---	---	---	No Data
7.Aluminum Industry	1650.2	100. %	9.75%	
a.Aluminum Processing Stack[a]	776.1	47.0%	4.59%	
b.Aluminum Processing roof vent[a]	766.7	46.5%	4.53%	
c.Aluminum Handling[a]	107.4	6.5%	0.63%	

Table 3.1.1b-Total Particulate Emission Rates in Portland Airshed

SOURCE TYPE	TONS/YR (1977-1978)	% of MAJOR SOURCE TYPE	% of TOTAL in PORTLAND	COMMENTS
8.Iron Industry	260.7	100. %	1.54%	
a.Steel Elec. arc Furnace[a]	220.	84.4%	1.30%	
b.Union carbide Furnace[a]	40.7	15.6%	0.24%	
9.Miscellaneous	1807.7	100. %	10.69%	
a.Carborundum Process[a]	848.4	46.9%	5.02%	
b.Glass Furnace[a]	97.8	5.4%	0.58%	
c.Small Pt.Sources (Car Shredder included)[a]	737.	40.8%	4.36%	
d.Pacific carbide Furnace	2.6	0.14	0.02%	
e.Cement Kiln	102.8	5.7%	0.61%	
f.Limestone Kiln	0.6	0.03%	0.004%	
g.N.L. Industries	2.7	0.15%	0.02%	
h.Galvanizing	---	---	---	No Data
i.Sewage sludge burning	12.8	0.7%	0.08%	
j.Chemical	1.5	0.08%	0.01%	
k.Manufacturing Industry	---	---	---	No Data
l.Incinerator	1.5	0.08%	0.01%	

episodic or cyclic in nature and may have a great impact on specific samples even though their annual emissions are low. Removal mechanisms, such as rainout, washout and sedimentation, will attenuate emissions, particularly those composed of larger particles. Sources not listed may affect the ambient loadings at the receptor, particularly unknown local sources whose area-wide input may be small. Finally, the emission estimates in Tables 3.1.1a&b are approximate, at best. Corroborating evidence, such as that from this study, is needed to verify them.

As noted in the previous chapter, receptor models, as opposed to source models, can assess the impact of sources without a quantitative source inventory; however, such an inventory used qualitatively to identify candidates for characterization and inclusion in the fitting should be a pre-requisite for employing the chemical element balance.

Though the source composition matrix, $\underset{\sim}{A}$ (see section 2.2), is the most important component of the chemical element balance receptor model, the priority of its determination has been low in previous studies. The PACS improved on this somewhat in its attempt to identify probable sources on the basis of an emissions inventory, review extensively and summarize elemental concentrations from the literature, and to chemically characterize a number of sources identified as potential contributors to the ambient aerosol. For the resources expended the accomplishment is remarkable: results from 356 filter samples of 37 source types are reported and summarized. Still, the primary dedication of manpower was toward ambient sampling and analysis with few hours remaining for the formalization of source chemical characterization standard operating procedures or a detailed examination of the results obtained. Table 4.5.2 contains many blank spaces, particularly as regards raw materials and source operating parameters. This information undoubtedly resides in the minds of many who participated in the source characterization program and it is hoped that this presentation will stimulate the filling in of those blanks for the PACS Final Report. Concentrations and averages for major components (>1%) in the tables of sections 3.1.1 to 3.1.10 have been double checked, but minor constituents (<1%) have only been evaluated once due to lack of time. Subjective decisions have been made that might be more objective upon greater reflection. Future users of this section should keep this in mind and use the information presented here as a guide rather than as the definitive reference.

Ideally, a source test program should begin with a thorough study of the source type, its modes of operation and emission controls. Major emission points should be clearly identified at representative members of the source type and samples should be taken. The sampler should provide for some type of dilution and aging of hot emissions to approximate the actual contribution of the emissions to the atmosphere just after they leave the source. Artifact formation of NO_3 and SO_4 should be assessed and eliminated. Each source type operating mode should be sampled several times to assess its variability within and between modes. All important parameters concerning the sampler (temperature, nozzle size, flows, filter IDs, sampling times, deviation from standard operating procedures) and the source (source name, process, exact location of probe, control equipment, raw material, unusual circumstances) should be recorded in a standard format.

The source samples should be subjected to special chemical analyses with the objective of characterizing them as much as possible. Longer than usual counting times for x-ray fluorescence and instrumental neutron activation analysis and special interference correction procedures should be considered. The carbonaceous fraction should be broken down into many components as it is a dominant fraction of most combustion processes. Unique chemical components of source types and operating modes should be sought and their variability assessed.

Finally, a test of chemical composition as a fingerprint of the source type should be carried out by ambient sampling in a region known to be dominated by the source as did Mroz (1976) in his characterization of an oil fired power plant. When ambient samples are taken the source operating mode should be recorded and the corresponding source composition compared to the ambient sample to detect signs of atmospheric chemical fractionation.

All of this should be done before the first ambient sample is taken with spot checks of the source types during ambient sampling to assure that process changes are not affecting emissions compositions. Hypotheses should be advanced concerning the effect of certain sources on certain ambient elemental concentrations at certain sites and the sampling frequency should be such that variations in the source operating cycle can be detected. Greater emphasis should be given to the determination of those chemical species in the ambient sample that are truly unique to specific source types.

The PACS source characterizations do not meet all of these ideals in all cases, but they are of value nonetheless. First and foremost, they are estimates of source compositions and variabilities that were not available before. As such, they fill a gap in the qualitative knowledge of source compositions. This is important because it indicates those sources which cannot be explicitly included in a chemical element balance, at least for the species quantified, because they lack a unique fingerprint. Finally, they provide a best estimate for the composition of sources that can be included in the balance and an indication of the variability of those estimates.

Sections 3.1.1 to 3.1.10 are keyed to Tables 3.1.1a&b and contain the results from PACS measurements, a discussion of the validity of those results, their outstanding features, literature references to measurements on similar sources and a comparison with those other measurements. Average percent compositions of several samples of the same source type and the resulting standard deviations are presented where applicable.

The following information will be helpful in understanding the tabular format. A blank space means that no value was available or that minimum detectable limits have not been defined; many of these spaces will be filled in for the final report and a distinction made. No uncertainties are reported on individual measurements as the variability between samples of the same source type is usually much more significant. The uncertainty reported for the average concentrations is the standard deviation of the average value or the analytical uncertainty, whichever is larger. Carbon values straddling the two carbon columns (VC stands for volatilizable carbon and NVC stands for nonvolatilizable carbon) represent total carbon (VC+NVC). Some elemental concentrations were not available as percentages. A ≡ preceding a value indicates that this value has been arbitrarily set for comparison purposes; the values of other elemental concentrations maintain their reported ratios to this value. PACS results can be referenced to source and sampling information in Table 4.5.2 through the IDs. The chemical constituents reported in these tables are those quantified for PACS; where other species were found in x-ray spectra they are noted in the discussion but not necessarily reported. Many literature sources report values for elements not included here. The final column of many tables contains the fraction of the emissions found in the fine or course particle modes.

The data will be formed into a chemical element balance source type composition matrix in section 3.1.12.

3.1.1 GEOLOGICAL MATERIAL

This category contains soil-related particles placed into the air by man's activities.

a. Agricultural Tilling: No samples were taken of this source. Its composition is assumed similar to the continental background.

b. Rock Crusher (Tables 3.1.1.1a&b): Gravel precursor material is selected by manufacturers to contain little clay, thereby decreasing the Al/Si ratio when compared to normal soil. Otherwise characteristic elemental ratios are similar to other geological materials.

c. Asphalt production (Table 3.1.1.2a&b): Exhaust occurs before the gravel is mixed with the tar and the composition is very similar to the crushed rock. More carbon might be expected in the mixed asphalt.

d. Street Dust (Tables 3.1.1.3a&b): Extensive literature values

Table 3.1.1.1a Rock Crushers, Fine Particulate Composition

												Percent												
ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0266			.35	<.05	<.01	2.27	1.42	8.59	28.64	.046	<.01	1.48	2.74	.580	.016	.016	.083	4.16	.0041	.012	.0093	.0012	<.005	36.2
Z0251			.174	<.05	<.01	2.16	1.486	7.89	30.04	.087	<.01	1.643	3.114	.607	.0126	.0171	.0843	5.2	.0044	.0063	.009	.0091	<.007	62.5
Z0289			.39	<.05	<.01	1.59	1.23	7.99	30.98	.084	<.01	1.313	3.519	.501	.0128	.0146	.0739	4.294	.0037	.017	.015	<.005	<.005	42.8
Z0255			.731	<.05	<.01	1.765	1.574	7.824	30.08	.048	<.01	1.416	3.687	.55	.0168	.0180	.0821	4.70	.0034	.0236	.0076	<.005	.0157	46.4
Avg.			.41			1.95	1.43	8.07	29.94	.066		1.46	3.27	.56	.0146	.0164	.081	4.59	.0039	.053	.0102	.0038	.0061	47.0
Std±			.23	.05	.01	.32	.146	.35	.97	.022	.01	.74	.42	.045	.0022	.00147	.0047	.47	.00044	.078	.0033	.0036	.0065	11.2

Table 3.1.1.1b Rock Crushers, Coarse Particulate Composition

												Percent												
ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0241			<.1	<.05	<.01	.695	.52	7.02	34.00	.059	<.01	1.09	2.67	.45	.0095	.0146	.070	4.24	.0051	.0042	.0070	<.01	.0055	63.8
Z0258			<.1	<.05	<.01	1.075	.755	9.47	31.21	.062	<.01	.93	3.014	.576	.017	.0086	.086	3.83	.0039	.0086	.0051		.0016	53.6
Z0244			<.1	<.05	<.01	1.59	1.12	7.48	32.92		<.01	.81	2.48	.44	.0092	.0100	.707	3.31	.0020	.0067		<.005	<.005	57.2
Avg.						1.12	.80	7.99	32.71	.061		.94	2.72	.49	.012	.011	.29	3.79	.0037	.0065	.0061		.0032	58.2
Std±			.1	.05	.01	.45	.30	1.30	1.41	.0021	.01	.14	.27	.076	.0044	.0031	.36	.47	.0016	.0022	.0013	.01	.0020	5.2

Table 3.1.1.2a Asphalt Production, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0315			<.1	<.1	<.01	1.58	1.637	9.11	27.01	.418	<.01	1.18	2.98	1.14	.019		.356	7.37			.018		<.01	97.6
Z0321	2.71	1.16	<.1	<.05	<.01	1.41	1.91	8.66	26.11	.12	<.01	1.11	2.57	.84	.024	.032	.121	6.73	.0069	.014	.0146		<.01	98.3
Z0215	1.26	.517	<.1	<.05	<.01	1.466	1.502	8.22	28.26	.12	<.01	1.13	3.017	.613	.019		.1226	7.03		.0156	.013	.008	<.006	81.9
Avg.	1.99	.84				1.49	1.68	8.66	27.13	.22		1.14	2.86	.86	.021	.032	.20	7.04	.0069	.0148	.0152	.008		92.6
Std±	1.03	.45	.1	.1	.01	.087	.21	.45	1.08	.17	.01	.036	.25	.26	.0029	.0032	.14	.32	.00069	.0011	.0026	.0008	.01	9.3

Table 3.1.1.2b Asphalt Production, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0305	<5	<1	<.1	<.1	<.01	.709	.62	6.15	26.59		<.01	.65	2.63	.37			.089	4.16			.73			2.4
Z0304	<5	<1	<.1	<.1	<.01	3.53	2.33	5.29	20.6		<.01	.46	1.88	1.77	.058	.115	.36	3.64	.011	.248			<.02	4.8
Z0187	5.05	1.12	<.1	1.0	<.01	1.16	1.03	7.72	26.76		<.01	.59	2.46	.27	.011		.084	4.06		.097	.114	.02		18.1
Avg.	5.0	1.04		.37		1.80	1.33	6.39	24.65			.57	2.32	.80	.035	.115	.18	3.95	.011	.17	.42	.02		8.4
Std±	1	.21	.1	.55	.01	1.52	.89	1.23	3.51		.01	.097	.39	.84	.033	.0115	.16	.28	.0011	.11	.44	.002	.02	8.5

Table 3.1.1.3a Street Dust, Fine Particulate Composition

	Percent																						
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Z0423	15	2.7	<.1	.56	<.01	1.11	1.18	6.82	23.1	.33	<.01	1.07	2.18	.59	.022	.063	.126	6.35	.013	.036	.12	.025	.24
Z0427	8.6	.61	<.1	.76	<.01	1.47	1.24	9.27	23.4	.25	<.01	1.08	2.67	.78	.030	.040	.127	5.82	.006	.032	.084	.012	.35
Z0440	7.6	2.3	<.1	<.05	<.01	1.57	1.68	12.5	21.2	.34	<.01	.97	2.02	.68	.024	.024	.140	6.23	.0071	.013	.068	.019	.34
Z0473	16.0	1.8	<.1	<.35	<.01	.83	1.08	6.76	21.6	.57	<.01	.98	2.88	.51	.017	.054	.099	5.58	.011	.039	.15	.022	.58
Avg.	11.8	1.85		.42		1.25	1.30	8.84	22.33	.37		1.03	2.44	.64	.023	.045	.123	6.00	.0093	.030	.11	.020	.37
Std±	4.3	.91	.1	.31	.01	.34	.27	2.71	1.09	.14	.01	.058	.40	.12	.0054	.017	.017	.6	.0033	.012	.037	.0056	.15
Z0474 Composite	16.6	1.4	.42	.62	.054	1.07	1.17	8.40	20.6	.43	1.21	1.05	2.39	.67	.023	.040	.137	6.92	.012	.032	.11	.022	.47

Table 3.1.1.3b Street Dust, Total Particulate Composition

	Percent																						
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Z0901	3.2	1.6	.01	.088	.02	1.60	1.54	6.78	28.9	<.02	<.02		2.9	.82	.025		.121	6.2				<.005	
Z0902	2.6	1.4	.025	.027	.002	1.76	1.74	6.34	28.8	<.02	<.02		3.1	1.27	.033		.092	5.65				<.005	
Z0903	3.3	1.7	.011	.026	.002	1.85	1.53	7.22	27.8	<.02	<.02		2.8	.93	.023		.096	5.62				<.005	
Z0904	5.0	2.5	.035	.12	.007	1.77	1.73	5.52	27.3	<.02	<.02		3.3	1.12	.032		.100	5.74				.023	
Z0905	2.6		.020	.11	.007	1.76	1.42	7.11	29.1	<.02	<.02		2.8	.91	.022		.102	5.43				.010	
Avg.	3.34	1.55	.020	.074	.008	1.75	1.59	6.59	28.4				3.0	1.01	.027		.10	5.73				.0081	
Std±	.98	.78	.010	.045	.007	.091	.14	.69	.79	.02	.02		.22	.18	.0051		.011	.29				.0089	
Z0911 Composite	2.5	2.4	.013	.79	.005	1.82	1.73	6.6	27.2	<.02	<.02	(2.0)	2.8	.91	.024	(.01)	.112	5.89	<.01	(.2)	<.005	.030	(.51)
Hopke (1977)						.53						.94	2.67			.021	.035	6.24	.024		.032	.008	.179
Rahn (1976a)						.44	4.2	1.8			0.11			.14	.0041	.014	.056	4.8	.0084	.021	.11	.026	
Henry (1977a)								7.54	19.9			.78	1.59	.645			.131	5.62			.03		.279

of chemical composition (Hopke, et al., 1977, Rahn, et al., 1976a, Henry, 1977a) exist only for the total fraction of street dust which probably emphasizes the coarse particulate. PACS values for Zn, Cu, and Ni were not measured on the coarse fraction because of interference from the tungsten carbide grinder which pulverized the sample. Rahn (1976a) shows greater Mg, Cl, and Cu but less Al in his samples. Greater Cl could be due to salting of the streets in Chicago. Other discrepancies could be due to differences between the geology of the various areas.

Fine particulate obtained from resuspension studies exhibits the increased Al/Si ratio when compared with the ratio in the total particulate as noted by Rahn (1976b).

The composite mixture of all dusts sampled is very similar to the average of dusts from a variety of streets showing that street dust compsotion across the city of Portland appears to be uniform.

Several samples showed traces of Zr and further studies should attempt to quantify this element. Pb, Zn, and Ca in all cases are enriched with respect to soil and continental background (see section 3.1.10).

3.1.2 TRANSPORTATION

Emissions from the powerplants of mobile sources are the major concerns, though aerosol due to abrasion, such as tire and brake wear, is also included. Resuspended road dust, through transportation related, is treated as a geological source because of its similar chemical composition.

a. Leaded Auto Exhaust (Tables 3.1.2.1a-c): The PACS values are

Table 3.1.2.1a Leaded Auto Exhaust, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
20245	49	5.9	.125	.43	<.01	<.01	<.1	.034	.10	.62	.63	<.012	.022	<.005	<.0005	<.001	<.001	.47	<.005	.0035	.028	.64	2.0	97.6
20243	7.9	3.0	.04	.04	<.01	<.01	<.1	.051	.05	.42	.34	<.012	.026	<.001	<.0005	<.001	<.007	.027	<.005	.0040	.014	.65	2.0	96.6
Avg.	28	4.5	.083	.24				.043	.075	.52	.49		.025	.0015			.0006	.25		.0038	.021	.65	2.0	97.1
Stdt	24	2.1	.06	.28	.01	.01	.1	.012	.035	.14	.20	.012	.0028	.0014	.0005	.001	.00014	.31	<.005	.0004	.01	.07	.2	.7

Table 3.1.2.1b Leaded Auto Exhaust, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
20252	63	5	1.2	1.1	<.01	.05	<.5	.25	.16	.79	.8	<.05	.15	<.1	<.0005	<.001	.006	.32	<.01	.012	.044	.42	14.8	2.4

Table 3.1.2.1c Leaded Auto Emissions, Total Particulate Composition

											Percent												
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Kowalczyk etal.[a,b] (1978)											2		1.0					1.0			.3	7.6	≅20
Miller etal.[b] (1972)											6.8							.4			.14	7.9	40
Hirschler etal. (1957,1964)																							56-70
McKee & McMahan[d] (1960)																							~44
Mueller etal.[d] (1967,1970)																							40
Ninoyama etal. (1970)																							~35
Moran etal.[d] (1971)																							~38
Moran etal.[d] (1972)																							~50
TerHaar & Bayard[d] (1971)																							~25
TerHaar etal.[d] (1972)																							13-25
Sampson & Springer[d] (1973)																							~35
Ganley & Springer[d] (1974)																							46
Wilson etal.[d] (1973)																							12-20
Pierson & Bracjeczek[a] (1976)																							>20
Ondov etal[a] (1979)							<2.2	<1.1			2.0		1.08	<.84	<.03	<.07	<.14	1.0	.012	.1	.28	7.6	≅20
Larsen[a] (1966)																							>20
Cahill[e] (1978)							2.4				3.4		2.4					4.0		<.2	.6	7.4	≅20
Lininger etal.[e] (1966)																						.25±.16	≅1
Jernigan etal.[e] (1971)																						.22±.04	≅1
Pillay & Thomas[e] (1971)																						.31	≅1
Moyers etal.[e] (1972)																						.23±.05	≅1
Bowman etal.[e] (1974)																						.28±.02	≅1
Martens etal.[e] (1973)																						.25±.05	≅1
Dzubay & Stevens[e] (1975)																						.25±.03	≅1
Hammerle & Pierson[e] (1975)																						.34±.05	≅1
Paciga etal[e] (1975)																						.32±.05	≅1
PACS[e,f] (1978)																						.25	≅1

[a] Results of tunnel study, includes all motor vehicles

[b] Cites literature

[c] Original measurement

[d] As cited by Pierson (1976)

[e] Ambient Br/Pb ratios in areas known to have a high auto exhaust contribution

[f] Average of many PACS ambient measurements

not in good agreement with other researcher's measurements, the most incriminating feature being the extremely low percentage of lead. These results cannot be considered of use.

Automotive exhaust particulates have been studied extensively both in the laboratory and in the field but the results of these measurements do not appear to be consistent and do not include trace element information. This state of uncertainty exists primarily because of the tremendous number of variables which need to be defined and the fact that these variables have been constantly changing over the years with decreasing lead content of fuel and improvements in exhaust emissions control systems.

Table 3.1.2.1c summarizes the results of dynamometer, tunnel and ambient measurements. The wide range of values for the percent lead composition is obvious, but the tunnel value of Pierson and Brachaczek (1976) is felt to best represent general automotive traffic. They note that the extent to which the Pb content is greater than 20% is related to the extent to which other sources contribute to the Pb measured in the tunnel. If it is assumed that lead from automotive sources contributed over 90% of the lead, then their results would suggest a value between 20 and 22%.

The bromine to lead ratio of automotive exhaust and ambient air particulates have been studied extensively, some findings being included in Table 3.1.2.1c. It is generally accepted that fresh automotive exhaust from the combustion of leaded gasoline has a Br/Pb ratio very similar to that in the fuel, i.e. .39; however, this ratio decreases rapidly with aging (Robbins and Snitz, 1972; Boyer and Laitinen, 1974; Moyers, et al., 1972; Martens, et al., 1973; Lininger, et al., 1966). Laboratory measurements of the Br/Pb ratio change with respect to time are inconclusive, but ambient measurements near roadways in many diverse areas suggest that it reaches an equilibrium value near .25. Several results are presented in Table 3.1.2.1c.

Only two references report values for constituents other than C, Cl, Br, and Pb (Cahill, 1978; Ondov, 1979). Cahill's data was obtained by subtracting upwind from downwind aerosol measurements in a freeway study. Ondov attributed the difference between the outflux and influx of aerosol at a tunnel to motor vehicle emissions. Both of these measurements will include diesel trucks, unleaded autos and tire and brake wear as well as the exhaust from leaded autos in their net compositions. Other substances quantified by these researchers, specifically Ca, Fe, Cu, and Zn, are in qualitative agreement with the PACS source tests.

Though large particles have been found in auto exhaust (Ter Haar and Bayard, 1971; Habibi, 1973) those that remain airborne are usually small which is consistent with the PACS measurements.

b. Unleaded Auto Exhaust (Tables 3.1.2.2a-c): PACS samples were obtained from a car which previously used leaded gas. Therefore, these results cannot be considered representative. Ter Haar, et al (1972) show a neglible concentration of trace elements in unleaded auto exhaust and emission rates a factor of four less than those of leaded autos.

c. Diesel Truck (Tables 3.1.2.3a-c): Carbon is the main component of this source type with the nonvolatilizable fraction being dominant in the fine particulate mode. Low measured concentrations of other elements are consistent with previous studies (Frey and Corn, 1967).

Table 3.1.2.2a Unleaded Auto Exhaust, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0317			.30	.12	<.01	<.01	.17	.054	.42	2.1	.83	.027	.14	<.005	<.0006	<.0008	.0097	.085	.011	.013	.97	3.3	9.0	83
Z0312	50	1.8	.93	.24	<.01	<.01	<.5	.18	.60	2.5	1.8	1.8	.20	<.2	<.0006	<.0008	.020	.14	.018	.035	.08	5.5	14.2	89
Avg.	50	1.8	.63	.18				.12	.51	2.3	1.32	.044	.17				.015	.11	.015	.024	.08	4.4	11.6	86
Std±	.5	.2	.45	.09	.01	.01	.01	.06	.13	.28	.69	.023	.04	.2	.0006	.0008	.007	.04	.005	.016	.01	1.6	4	5

Table 3.1.2.2b Unleaded Auto Exhaust, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0318			1.2	.56	<.01	<.05	<1.	.31	.66	.84	.67	.24	.77	.08		.090		.067	<.01	.040	<.005	.40	.79	17.1
Z0275	21.5	5.8	2.1	<.1	<.01	<.01	<1.	1.1	.65		1.1	<.05	.18			.027		1.2	<.01	.047	<.005	.20	.61	10.6
Avg.	21.5	5.8	1.7	.31				.71	.66	.84	.89	.13	.48	.08		.059		.63		.044		.30	.70	13.9
Std±	3	.6	.64	.36	.01	.05	<1.	.56	.07	.09	.30	.15	.42	.01		.045		.8	.01	.005	<.005	.14	.13	4.6

Table 3.1.2.3a Diesel Truck Exhaust, Fine Particulate Composition

	Percent																							
FILTER ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0195			.u	3.1	<.5	.57	<1	.13	.1	.50	1.0	<.01	.34	<.2	.004	<.02	.013	.40	<.005	.091	.072	.035	<.05	86.3
Z0201	32	64	.42	.77	<.5	.12	<1	.084	.1	.23	.96	<.01	.31	<.1	<.01	<.001	.0051	.72	<.01	.085	.054	.013	<.05	92.5
Z0212			<.5	.99	<.5	.53	<2	.86	.2	<.02	1.9	<.01	1.0	<.2	<.01	<.001	.013	.37	<.02	.16	.19	.032	.16	37.9
Z0196	33	72	1.6	11.8	<.5	.25	<2	.27	.27	3.7	2.9	<.01	1.7	.006	.028	<.03	.077	3.8	<.005	2.6	.62	.043	.17	75.1
Avg.	32.5	68	.72	4.2		.37		.34	.17	1.12	1.69		.84		.010		.027	1.32		.73	.23	.031	.095	73.0
Std±	30	5.66	.61	5.2	.5	.22	2	.36	.08	1.73	.92	.01	.66	.2	.012	.03	.033	1.66	.02	1.24	.26	.013	.081	24.5

Table 3.1.2.3b Diesel Truck Exhaust, Coarse Particulate Compositions

	Percent																							
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	%Mass
Z0204	51	31	<1	3.7	<.5	(1.6)			1.2		(3.1)	<.012		<1			<.02	4.6			.15	<.1		5.8
Z0198			<.5	<.3	<.5	.17	<1	.15	<.1		.35	<.012	.47	<.2	<.004	<.01	.007	.062	<.005	.087	<.01	<.04	<.05	62.1
Z0211	37	16	1.4	.86	<.5	.38	<2	.88	<.1	<.01	1.7	<.012	.79	<.2	<.01	<.01	.01	.55	<.02	.13	.068	.04	<.1	24.9
Avg.	41	23.5	.72	1.6		.72		1.5	.43		1.7		1.7				.0090	1.74		.30	.074	.030		30.9
Std±	9.9	10.6	.60	1.9	.5	.77	2	1.7	.66	.01	1.4	.012	2.1	.2	.01	.01	.0017	2.49	.02	.32	.073	.017	.1	28.6

Table 3.1.2.3c Diesel Exhaust, Total Particulate Compositions

	% Composition																					
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Frey & Corn (1967)	55-60							.05-.10	.5-.7				.03 .02-.05	.001		.001		.1-.35	.05-.1	.0005	.1-.25		

Table 3.1.2.4a Diesel Train, Fine Particulate Composition

	Percent																							
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0342	65.3	21.4	1.3	2.2	<.1	.042	<.4	.26	.22	<.1	.55	.037	.68	.019	.001	.011	.0046	<.01	.0152	.013	<.01	<.005	.10	97.9
Z0329			3.6	1.8	<.1	.052	<.5	.17	1.74		.92		.57	<.001	<.0005	<.001	<.005	.36	.016	<.001	<.01	<.005	<.005	87.7
Avg.	65.3	21.4	2.5	2.0		.047	.225	.22	.98		.74	.037	.63	.0098	.00063	.005	.0058	.18	.016	.0067			.051	92.8
Std±	6.53	2.14	1.6	.28	<.1	.0071	.035	.064	1.07	<.1	.26	.0037	.078	.013	.00053	.005	.0074	.25	.00057	.0088	<.01	<.005	.069	7.2

Table 3.1.2.4b Diesel Train, Coarse Particulate Composition

	Percent																							
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0343			2.3	4.0	<.1	.16	<2	24.2	14.4		1.1	<.012	.29	<.2	<.001		.004	<.01	<.05	.030	<.1	.037		2.1
Z0337	23	14	4.2	2.3	<.1	<.5	<4	<3	<12	<4	<6	<2	<4.5	<.2	<.00005	<1	<.06	<.4	<.005		<.005	<.02		12.3
Avg.	23	14	3.3	3.2		.21		12.9	10.2		2.0		1.27				.017			.030		.023		7.2
Std±	2.3	1.4	1.3	1.2	.1	.064	2	16.0	5.94	4	1.3	2	1.39	.2	.001	1	.018	.4	.05	.003	.1	.019		7.2

d. Diesel Train (Tables 3.1.1.4a&b): These emissions are similar to those from trucks except that the volatilizable and nonvolatilizable carbon ratios are reversed and the S/SO4 contribution is less.

e. Misc. (Ships, air, tires, brakes): Some literature values exist (Dannis, 1974; Pierson and Brachaczek, 1974a&b, 1975, 1976; Mamuro, et al., 1973; Fordyce and Sheibley, 1975) but the contribution of these sources was not deemed well enough characterized nor of sufficient magnitude to merit a review.

3.1.3 STATIONARY FOSSIL FUEL COMBUSTION

Though some of these fuels are derived from the same sources as the fuels used in transportation, their refinement and combustion causes their aerosol composition to differ.

a. Residual Oil Combustion (Tables 3.1.3.1a-c): PACS measurements for fine particulate are in close agreement with those of Mroz (1976) normalized to V, with the exception of Na. Henry, et al. (1978) and Dietz, et al. (1978) show large magnesium and low nickel contributions. The precursor oils of their samples were also high in Mg and low in Ni and the emissions from their combustion reflects this. V and Ni are the outstanding elements with fair amounts of Na, Ca and Fe present. SO_4^{-2} composes a major fraction of these emissions and independent tests (Nader, 1978; Himolya and Cheney, 1978; Henry, et al. 1978; Dietz, et al., 1978) confirm that this isn't just an artifact due to SO_2 conversion on a moist sampling filter. The chemical composition of the coarse fraction is much less consistent owing to the relatively small amount of mass collected; the mass emissions of small particles are ten times those of the coarse.

Table 3.1.3.1a Residual Oil Combustion, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0287	7.6	3.6	.74	42.2	.085	2.63	<1	.30	.42	12.3	<.1	.16	1.31	.068	3.75		.067	2.15	6.21	.061	.258	.0073	.066	89.0
Z0277	2.4	.51	.39	49.2	<.1	3.07	<3	.33	.46	14.5	<.1	.18	1.34	.060	4.09	.038	.038	2.27	6.54	.069	.270	.0048	.0064	82.5
Z0301	2.7	7.3	.82	61.6	.11	2.80	<1	.88	1.49	17.3	<.1	.38	1.31	.111	2.69	.041	.046	2.86	3.75	.077	.70	<.01	.17	93.2
Z0260	20.5	1.4	.67	57.7	<.1	7.0	<2	.79	1.47	15.1	<.1	.41	1.42	.13	2.64	.048	.053	3.06	3.66	.080	.62	<.01	.17	93.7
Z0265	3.8	6.0	.23	49.7	.026	4.0	<3	.60	1.17	11.5	<.1	.24	2.44	.14	4.42	.061	.050	3.25	5.46	.059	.33	.061	.094	97.6
Z0235	4.7	3.4	.23	51.4	.049	3.4	<2	.55	1.20	11.7	<.1	.24	2.49	.16	3.79	.067	.043	3.29	5.51	.050	.33	<.01	.094	96.1
Z0191	3.0	.58																						90.5
Z0214	11.0	2.2	1.5	25.1	<.1	1.86	<3	.29	.51	10.6	.33	.34	.76	.081	2.67	.027	.027	3.90	6.41	.126	.27	<.01	.173	86.9
Avg.	7.0	3.1	.65	48.1	.052	3.5		.53	.96	13.3		.28	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	.013	.11	91.2
Stdt	6.2	2.5	.44	11.9	.019	1.7	3	.24	.48	2.4	.1	.10	.64	.038	.75	.015	.013	.61	1.21	.025	.18	.021	.064	5.0
Mroz (1976)						10.2		.089					1.8		≡3.44	.055	.018	1.52			.14			

Table 3.1.3.1b Residual Oil Combustion, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0216	.22	19.4	<2	9.5	<.2	.43	<10	1.36	2.41	2.97	.50	.011	5.94	.168	2.97	.090	.019	1.44	2.08	.050	.0072	<.01		11.0
Z0276	5.4	16.7	<1.5	10.8	<.2	.65	<3	1.60	3.12	3.73	.37	.121	7.36	.21	4.13	.091	.034	1.82	2.65	.099	.029	<.01	<.01	17.5
Z0271			<2	9.97	<.2	2.11	<3	1.39	6.20	2.63	1.2	<.1	2.90	.195	1.19	.065	.031	2.40	1.03	.126	.115	<.01		6.8
Z0249	9.2	<2	<1.5	5.86	<.2	.93	<2	1.46	3.38	1.47	.50	<.1	1.57	.115	0.70	.039	.021	1.35	.58	.024	.059	<.01	<.04	6.3
Z0261	6.6	10.6	<1.5	10.5	<.2	1.38	<5	2.78	6.04	3.2	.77	<.1	4.49	.200	2.63	.046	.046	1.97	2.32	.127	.075	<.01	<.01	2.4
Z0286	95	<5	<1.5	3.06	<.2	.56	<1	1.24	4.97	.91	.83	<.1	1.78	.074	0.65	.036	.021	.80	.62	.111	.017	<.01	<.01	3.9
Z0206	<2	37.0																						9.5
Z0202	5.5	10.3	<1.5	1.33	<.2	.24	<2	.47	.24	.018	.98		.85	.015	.308	.010	.014	.48	.47	.067	.011	<.01	<.05	13.1
Avg.	17.6	13.9		7.3		.90		1.47	3.7	2.1	.74		3.56	.14	1.79	.054	.027	1.47	1.39	.086	.050			8.8
Stdt	34.3	12.2	2	3.9	.2	.65	2	.68	2.1	1.4	.30	.1	2.45	.074	1.45	.030	.011	.69	.93	.040	.051	.01	.05	5.0
Mroz (1976)						1.76		0.7					1.81		≡1.8	.026	.024	1.41			.29			

Table 3.1.3.1c Residual Oil Combustion, Total

											Percent												
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Gartrell etal. (1972)[a]	58.1			17.5		.67	.12	.8	.28				.14		1.7		.02	2.16		.008			.09
Gartrell etal. (1972)[a]	18.1			25.0		2.22	.42	7.9	.45		.5		.28		3.2		.02	2.59		.2	.05		.18
Gartrell etal. (1972)[a,b]						5	.06	.8	1			.2	1.3		7		.06	6		.2	.02		.07
Winchester & Nifong (1971)						1.5	.3	5.0				.10	.4	.03	2.5	.12	.03	2.5	6.0	.16	.05		.18
Kowalczyk etal. (1978)[a]						1.6	.51	.0054			1.6	.057	1.05	.0033	≡3.0	.0078	.013	.36	.51	.11	.21	.007	.051
Homolya & Cheney (1978)				~30																			
Henry etal. (1978)[c] #1	12.4		.005	36.9		3.91	18.4	1.25	.31		.05	.13	1.0	.05	2.27	.01	.02	.61	1.66	.05	.004	.001	
Henry etal. (1978)[c] #2	69.0		.013	12.0		.30	3.41	.05	.2		.02	.1	.31	.03	6.68	.05	.02	.40	.85	.01	.004	.0003	
Henry etal. (1978)[c] #4	21.5		.02	41.2		.50	5.94	.4	.2		.02	.10	.1	.04	10.2	.1	.02	.41	1.29	.02	.02	.0025	
Henry etal. (1978)[c] #5	1.5		.02	57.6		2.02	2.60	.01	.05		.05	.10	.2	.04	12.85	.05	.05	.48	2.28	.04	.04	.0025	
Henry etal. (1978)[c] #6	14.5		<.01	49.2		.2	2.4	1.42	.22		.06	.12	.32	.07	1.10	.045	.03	.40	.35	.04	.02	.0002	
Dietz etal. (1978)[d] 31-0	11			15.7		1.2	4.7						.51		≡3.0			2.4	.43				
Dietz etal. (1978)[d] 34-0	5.5			15.7		1.4	3.7						.55		≡3.0			1.8	.40				
Dietz etal. (1978)[d] 36-0	6.2			13.8		1.2	3.6						.12		≡3.0			.67	.66				
Dietz etal. (1978)[d] 37-F	6.1			8.5		1.1	3.5						.20		≡3.0			.54	.49				

[a] Literature values

[b] Fly ash residue left in furnace or boiler

[c] Collected from stack in fine mesh Teflon bag. Values are probably more representative of coarse particle fraction
Precursor fuels were at high mg content

[d] Soluble plus insoluble fractions

Table 3.1.3.2a Distillate Oil Furnace, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
20279	22	1.6	1.1	9.8	<.2	.28	<1	.18	<.1	5.8	.59	<.04	.20	<.3	.20	<.02	.0076	.084	<.01	.22	.034	.019	.016	80.2
20119			<1	6.0	<.2	.058	<1	<.1	.14	3.2	.34		.14	<.4	<.001	<.01	.006	<.01	<.01	.067	<.01	<.01	<.04	71.5
20043			.69	24	<.2	.14	<.5	.18	.89	7.5	.59	.034	.14	.015	.0013	<.01	.006	.079		.16	.038	<.01	.35	
20063			<1	15	<.2	.71	<1	.33	.08	6.0	.80	<.05	.13	<.1	.002	<.01	.013	.078	<.01	.23	.056	.010	.57	
20186			<3	2.3	<.2	.33	<2	.55	.37	11	2.7	<.01	1.1	<.3	.0034	.1	.024	.18	<.03	.19	.032	.10	1.16	31.3
20189	14	34	<3	22	<.2	.39	<2	.57	<.2	8.1	1.9	<.01	1.3	<.3	<.002	<.05	.03	.31	<.03	.15	<.02	.07	1.1	
Avg.	18	17.8	1.0	13.2		.32		.31	.27	6.93	1.2	.018	.50		.005		.014	.12	.0090	.17	.029	.026	.54	61.0
Stdt	5.66	22.9	.5	8.7	.2	.23	2	.21	.32	2.62	.9	.013	.55	.4	.081	.05	.010	.11	.0055	.059	.019	.028	.51	26.1

Table 3.1.3.2b Distillate Oil Furnace, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
20203	10	7.8	<1.5	<.5	<.5	.17	<1	.14	<.005	<.01	.62	<.012	.46	<.2	.001	<.1	.011	.16	<.02	.075	.027	<.01	<.05	68.7
20190			<2	<3	<.5	<.2		.40	<.005	<.01	1.5	<.012	1.0									<.01	<.01	
20253	5	<2	<2	1.4	<.5	.26	<1	1.4	.36	<.01	2.0	<.012	.16	<.2	<.01	<.02	<.01	.43	<.01	.13	<.005	.022	<.08	26.4
20096	16	4.1	<2	<1	<.5	.24	<3	<.2	.81	<.01	1.2	<.012	.32	<.2	<.001		<.01	<.03	<.02	.055	<.005	<.01	<.01	28.5
20040	<2	13	<2		<.5			1.28			3.0	<.012								.14	<.005	<.01		
20087	16	12	<2		<.5			.20			1.2	<.012	.56	<.3	<.002		.033	<.1		.10	<.005	<.01	<.1	
Avg.	9.6	7.6				.69		.59	.29		1.6		.50				.013	.23		.11				41.2
Stdt	6.7	5.1	2	3	.5	1.1	3	.59	.38	.01	.82	.012	.32	.3	.01	.1	.02	.21	.02	.043	.005	.01	1	23.8

Table 3.1.3a Natural Gas Combustion, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
20250			2.3	5.2	<.2	1.84	1.08	.14	.12	.45	2.3	.33	.54	.018	.046		.044	.21	.082	.022	.25	.013		80

Table 3.1.3b Natural Gas Combustion, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
20256			<1	<1	<1	<.1	<1.5	.30	.35		2.2	<3	.45	<.2	.018		.017	.043	.042	.117		.028		19.8

b. Distillate Oil Combustion (Tables 3.1.3.2a&b): The fuel is similar in composition to diesel fuel and the basic composition of emissions from this source is similar to that from trains and trucks with a very low and variable trace element content. The volatilizable/nonvolatilizable carbon ratio is in contrast to that of the truck. The SO_4^{-2} and Pb portions for the fine particulate are higher in these emissions than they are in those from the diesel fueled mobile sources.

c. Coal: Emissions from coal fired power plants have received a great deal of scrutiny in recent years (Gordon, et al., 1974; Zoller, et al., 1974a; Bennet and Knapp, 1978; Block and Dams, 1976; Nadkarni, 1975; Hulett, et al., 1976). Little coal burning takes place in the Portland airshed so this source is not considered in detail here.

d. Natural Gas Combustion (Tables 3.1.3.3a&b): The figures in these tables cannot be considered reliable because the boiler sampled had previously burned residual oil. Elements quantified are similar to those in residual oil suggesting that contamination is significant. The amount of particulate collected on fine and coarse filter samples was very small, even with a long sampling time, confirming the clean burning nature of this fuel.

3.1.4 VEGETATIVE BURNING

All types of burning of recently alive material are included here.

a. Forest Fires: This source was not tested and no chemical element tests have been found. It is not considered important for the days studied.

b. Slash Burns (Tables 3.1.4.1a&b): Chlorine is emphasized over potassium in the fine particulate mode whereas they make equivalent

Table 3.1.4.1a Slash Burn, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0029			4.0	2.9	<.5	.63		.77	1.89		4.47	.60	.57				.015	.27				.036		
Z0049			5.8	1.2	.9	.91		1.37	.10	.21	7.17	.60	.87				.14							
Z0033	75.0	8.12	6.1	1.4	<1	.71		3.02			5.89	.61	1.31				.35					.049		
Z0031	54.1	.60	4.5	1.5	<1	.58		1.31		.64	5.94	.60	.85				.066			.064		.12		
Z0028	49.2	5.42	8.7	2.2	<1	.58		.73	2.29		3.19	.60	1.65				.076	.11		.12		.034		
Z0017	59.4	1.4	6.1	1.8	<1	.50		1.46	.14		6.66	.57	1.16				.21					.10		
Avg.	59.4	3.5	5.1	1.6		.65		1.44	.89	.43	5.55	.60	1.07				.12	.19		.09		.053		99
Std±	9.7	3.2	2.5	.88	<1	.14		.83	1.1	.30	1.47	.013	.38				.12	.11		.04		.044		

Table 3.1.4.1b Slash Burn, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0037			.32	<.1	<.1	.19					1.00	1.48					.011					.023		
Z0032			1.0	<.3	<.2	.16		.18	.48		1.00		.22				.0089	.54		.014				
Z0019	65.4	3.78	1.3	1.1	<.3	.19		.21	17.7	9.29	1.00		.074				.0066							
Z0026	29.4	6.00	2.0	2.4	.55	.15		.33	3.42		.66		.15								.039			
Z0020			.37	<.1	<.2	.091		.22	.13		1.00		.07											
Avg.	47.4	4.9	1.0	.75	.19	.16		.23	5.4		.93		.13				.009							1
Std±	25.4	1.6	.70	1.0	.20	.04		.06	8.3		.15		.07				.002							

Table 3.1.4.2a Fireplace Burn, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0115	49.8	16.6	.10	.06	.42	<.01	<.01	.012	.007	.013	.57	.60	.06	< 001	<.00006	<.001	.002	.002	<.0005	.034	.002	.003	<.004	58.3
Z0094	42.1	9.2	.16	.16	.33	.068	<.01	.037	.041	.061	.65	.45	.049	<.004	<.00006	<.0008	.001	.0025	.0007	.0036	.23	.011	.019	64.7
Avg.	45.9	12.9	.13	.11	.38	.037		.024	.024	.037	.61	.53	.055				.0015	.0023	.00048	.019	.12	.007	.011	61.5
Std±	5.5	5.2	.04	.07	.064	.045	.01	.018	.024	.034	.057	.11	.0071	.004	.00006	.0008	.00071	.00035	.00032	.021	.16	.0057	.012	4.5

Table 3.1.4.2b Fireplace Burn, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0095	39.9	7.25	<1	<.5	<.4	.53		<.1	.22		≡2.0	.08	.45		<.00006	<1	.035	.02	<.001	.06	<.005	.02	<.00	41.7
Z0111	44	12.2	<1	<.5	<.4	.10	<2	.21	.22		≡2.0	<.02	.27	.02	<.00006	<.0008	.01	<.002	<.001	.035	.02	.01	<.06	35.3
Avg.	42.0	9.7				.32	1	.13	.22		2.0	.045	.36	.02		.28	.023	.013		.048	.013	.015	.018	38.5
Std±	2.9	3.5	1	.5	.4	.30	.1	.11	.022		.2	.049	.13	.002	.00006	.32	.018	.011	.001	.018	.011	.0071	.018	4.5

Table 3.1.4.3a Choked Off Woodstove, Fine Particulate Composition

										Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0223	49.1	8.3	<.05	<.04	.19	.043	<.01	.018	<.005	<.01	.09	.083	.038	<.001	<.001	<.001	.0014	.003	<.004	.002	<.01	.0037	<.005	99.6
Z0259			.04	.07	.67	.074	<3		<.005	<.01	.097	.022	.035	<.003	.002	<.001	.023	.004	<.004	.003	<.01	<.001	<.005	99.6
Avg.	49.1	8.3	.033	.055	.43	.060	.75	.018			.094	.053	.037		.0013		.012	.0035		.0025		.0021		99.6
Stdt	4.9	.83	.011	.02	.34	.023	1.06	.0018	.005	.01	.0049	.043	.0021	.003	.0011	.001	.015	.00071	.004	.00071	.01	.0023	.005	99.6

Table 3.1.4.3b Choked Off Woodstove, Coarse Particulate Composition

										Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0298			2.6	<.6	<.6	.12	<2	.18	<.01	<.01	1.6	<.01	.67	<.02	.005	<.02	.03	<.04	<.02	.12	<.01	<.01	<.01	.4
Z0225			<1	<.3	<.3	.61	<2		.19	<.01	.90	<.01	.44	<.02	.013	<.02	<.01	<.01	<.01	.06	<.01	<.01	<.01	.4
Avg.			1.6			.37		.18	.098		1.3		.56		.0090		.018			.090				.4
Stdt			1.5	.6	.6	.35	2	.02	.13	.01	.5	.01	.16	.02	.0057	.02	.018	.04	.02	.042	.01	.01	.01	.04

Table 3.1.4.4a Domestic Burning, Fine Particulate Composition

										Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0335	48	9.6	4.0	3.1	.54	.39	<.009	.49	1.9	<.01	5.1	.83	.50	.030	<.001	<.001	<.01	.070	<.05	.055	.16	.016	4.1	
Z0123	37.8	4.4	.17	2.0	.23	.042		.20	.065	1.1	.70	4.6	.28	<.001	<.001	<.001	.0052	.014	<.05	.009	.067	.014	.059	79.7
Z0122	42.7	3.5	<.07	<.02	.13	.013		<.001		.043	.18	.33	.037	<.001	<.001	<.001	.001	<.005	<.05	<.001	<.001	.002	<.01	67.1
Z0099	37.2	.37	.08	.34	.22	.018	<.009	.006	.012	.12	.20	.64	.12	<.001	<.001	<.001	.002	<.005	<.05	.0021	.004	.0027	<.01	42.9
Z0113	1.4	.50	.11	.68	.26	.015	<.009	.051	.022	.23	.57	1.9	.11	<.001	<.001	.007	.003	<.005	<.05	.002	.018	.006	.017	~30
Avg.	29.8	3.7	.88	1.2	.28	.096		.15	.50	.28	1.35	1.66	.21			.0018	.003	.017		.014	.050	.0080	1.8	54.9
Stdt	17.9	3.7	1.7	1.3	.16	.17	.009	.21	.93	.46	2.11	1.75	.19	.001	.001	.0029	.0018	.030	.05	.023	.067	.0065	2.5	22.6

Table 3.1.4.4b Domestic Burning, Coarse Particulate Composition

										Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0334			<20		2.1	<1	<4		<.1		7.6	<.5	2.4	<.04	<.05	<.05	<.03	<.2	<.2	<.1	<.1	.024	<.1	
Z0121	63.0	1.7	<3	5.2	5.5	.52	<3	.86	.47	.13	9.5	4.8	2.4	<.04	<.05	<.05	.16	.36	<.2	<.05	.15	.027	<.1	20.3
Z0098	50.1	1.2	<9	<5	<3	.71	<5	.39	<.1	<.1	12.9	.98	≡2.4	<.4	<.05	.22	.12	.25	<.2	.43	<.1	<.02	<.1	32.9
Z0117	40.7	.33	<3	<1	<1	.41	<4	.44	.8	<.1	2.6	1.1	≡2.4	<.04	<.05	<.05	.05	.18	<.2	.14	<.1	<.03	<.1	57.1
Z0112	1.7	.14	<2.6	<1	<.7	1.8		<.1	<.1		4.7	3.0	≡2.4	<.04	<.05	.52		.16	<.2	.12	<.1	<.01	<.1	~70
Avg.	38.9	.84			2.1	.79		.44	.28	.77	7.5	2.0	2.4			.16	.086	.21		.15		.016		45.1
Stdt	26.4	.73	5	5	2	.58	4	.33	.34	.046	4	1.9	.24	.04	.05	.22	.066	.099	.2	.16	.1	.0093	.1	22.6

Table 3.1.4.5a Simulated Field Burning, Fine Particulate Composition

ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
	Percent																							
Z0036	37.8	1.00	.24	.65	.18	.18		.014	.066	.57	4.45	1.52	.19			.007	.006	.002		.002		.015	.035	
Z0064			1.14	17.3	.32	.042		.023			5.98	9.64										.048		98.0
Z0089	18.1	23.5	.56	1.94	.25	.86		.41	.18	.80	13.9	5.98	.38									.018		97.3
Z0023	47.8	.20	2.49	6.67	.63			.36	.32	4.51	20.1	12.0	.86			.017								
Z0075	39.5	.15	.75	6.48	.22	.22		.64	.26	1.97	9.20	12.0	.66	.003				.011				.021		98.0
Z0018			.46	1.80	.18			.096	.21	.69	11.4	9.51	.44							.004		.011		97.2
Z0078	.61	.020	.37	2.54	.39	.12		.042			7.34													99.9
Z0092	38.4	.32	.84	2.90	.25	.045		.48	.19	.99	7.04	5.54	.36									.044		99.9
Z0013[b]	91.2	1.8	7.6	2.6	<.5	.32		.78	2.4		3.6	1.5	3.2	.15			.045	.13		.12		<.1		
Z0045[b]	104	8	5.4	2.9	<1	.89		1.69	.31		8.5	1.2	1.3	.07			.09	.074		.09		.15		
Avg.	47.2	4.4	2.0	5.0	.32	.33		.45	.49	1.6	9.9	6.5	.92	.07		.012	.047	.054		.054		.045		98.4
Std±	37.4	8.2	2.5	5.4	.15	.34		.51	.78	1.5	5.1	4.5	.98	.07		.007	042	.060		.060		.045		1.2
Lyons & Tomback (1978)[a] Avg.	50-71.4					1.00	.84	2.0	4.0	.90	6.7	≡6.0	2.1				.18	.24						
Core & Terraglio (1978)[a] Std.						.90	.70	3.2	4.5	.78	7.7	5.0	1.9	.6			.18	.30						

[a] Average of simulated, aircraft and ground based samples

[b] Aircraft-sampled actual field burn, compiled after Table 4.5.2

Table 3.1.4.5b Simulated Field Burning, Coarse Particulate Composition

ID	VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
	Percent																							
Z0042	27.0	12.0	1.3	.83	.86	.50		.41	1.84	.78	4.46	3.18	1.51				.13	.10						
Z0073	21.1	21.9	2.6	4.7	<.54	.58		1.24	2.31	3.37	9.34	8.89	2.88					.038				.083		2.0
Z0084	21.2	26.						1.04	2.14	2.86		11.3	1.95											2.7
Z0074	35.8	.49	3.2	6.4	<1	.85		.64	.58	4.32	11.1	9.84												
Z0061	34.7	.44	5.4	6.0	2.5	.99			1.55	2.63	22.4	12.5	1.71									.13		2.0
Z0091	35.3	.17	4.8		<1	.63		1.07	2.29	2.55		8.42	1.96				.077					.051		2.8
Z0050[b]	89	.65	5.6	<1	<2	<.1		.6			7.5													.1
Z0038[b]	57	2.3	1.9	.93	<.2	.10		1.7	2.0		.74		1.4				.006	.25	.017	.016		<.1		
Avg.	40.1	8.0	3.5	3.2	.8	.53		.96	1.8	2.8	9.3	9.0	1.9				.071	.13				.079		1.9
Std±	22.8	10.6	1.7	2.8	.8	.35		.44	.61	1.2	7.4	3.3	.53				.062	.11				.038		1.1

[b] Aircraft-sampled actual field burn, compiled after Table 4.5.2

Table 3.1.4.5c Field Burning, Total Particulate Composition

ID		VC	NVC	NO$_3$	SO$_4$	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
		Percent																						
Shum & Loveland	Avg.						25		29			17	≡9		4.1	.11	.11	1.1	16		<.09		.23	
(1974)	Std±						8.1		9.4			.8			.16	.05	.02	.3	10				.09	

contributions to the coarse. These two elemental concentrations show the smallest variability. Similarly, Al and Si contributions differ between the two modes with the fine particulate Al/Si ratio being quite different from, in fact the inverse of, that for soil. Carbon is a large contributor to both modes as would be expected in an inefficient combustion process. The coarse fraction is practically nonexistent, thus measurement inconsistencies are expected.

Some doubt exists concerning the quality of sampling and analysis of these filters. They were taken early in the program when flight sampling standard operating procedures were being developed, they had very low mass loadings and were not subjected to PACS standard x-ray analysis as the ORTEC TEFA x-ray spectrometer was not in operation when results were desired. This may be a major cause of variability between samples.

c. Orchard prunings: These are classed with domestic burns because of their similarity.

d. Fireplace burning (Tables 3.1.3.2a&b): The volatilizable carbon contribution is high. Otherwise, these emissions are nondescript.

e. Choked off Woodstove (Tables 3.1.3.3a&b): Unfortunately no carbon data is available. Other constituents are similar to fireplace burns.

f. Domestic Burning (Tables 3.1.3.4a&b): Carbon is, of course, a significant component. Cl and K are present, similar to field burns. Calcium makes a substantial contribution as well.

g. Grass Field Burning (Tables 3.1.3.5a-c): Organic substances condensed inside the sampler upon collection thereby biasing the results; Cl and K are the dominant elements in the fine mode and are accompanied by Si and Ca in the coarse. Shum and Loveland's (1974) measurements seem to contain a much larger soil component, which is reasonable considering they sampled on the ground downwind of the plume. Drafts created by the burn can easily whip up soil particles, but these would soon settle out away from the burn.

3.1.5 FOREST PRODUCTS INDUSTRY

This industry contributes the largest share of industrial emissions to the airshed and contains a variety of distinct sources.

a. Kraft Recovery Boiler (Tables 3.1.5.1a&b): Na in both the fine and coarse particulate modes is the outstanding feature of this source with appreciable Cl, K and Fe present. SO_4^{-2} is high, though the emissions from this source are moist which could engender SO_2 conversion to SO_4^{-2} on the filter. The fine particulate mass emissions are almost an order of magnitude greater than the coarse particulate emissions. Huntzicker, (1978) finds much more Cl than the PACS.

b. Smelt Tank: This was not sampled and is not considered important.

c. Incinerator: This was not sampled and is not considered important.

d. Wood processing: This was not sampled and is not considered important.

e. Veneer Dryer: This was not sampled and is not considered important.

f. Lime Kiln: This was not sampled and is not considered important.

g. Sulfite Recovery Boiler (Tables 3.1.5.2a&b): Independent tests confirm that K is the major component of the fine particulate wherein most of the trace element emissions reside. SO_4^{-2} might suffer from the artifact formation previously mentioned.

Table 3.1.5.1a Kraft Recovery Boiler, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0221	1.8	.38	<.3	38	<.1	12.2	1	.24	.14	11.0	1.5	1.4	<.5	.007	.002	.22	.033	1.12	.13	.011	.084	.17	.02	87.7
Z0213	1.5	<.1	<.3	41	<.1	13.2	<.5	.26	.16	12.4	2.1	1.6	<.2	.004	<.001	.34	.027	1.28	.15	.030	.054	.08	.01	86.9
Avg.	1.7	.22		40		12.7	.63	.25	.15	11.7	1.8	1.5		.006	.001	.28	.03	1.2	.14	.021	.069	.13	.013	87.3
Std±	.21	.23	.3	2.1	.1	.71	.53	.014	.014	1.0	.42	.14	.5	.002	.001	.08	.004	.11	.014	.013	.021	.06	.011	.57
Huntzicker (1978)			1.7	12.6	.4	5.8		.3	.2	3.1	25	.8										.5		
Huntzicker (1978)			.2	51	.06	28		.5			8.9									.001				

Table 3.1.5.1b Kraft Recovery Boiler, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0194	13.5	<1	<.8	12.8	<.2	5.8	<.5	.34	.13	3.7	2.1	.48	.31	<.1	<.001	.36	.044	1.45	.18	.04	<.01	.058	<.02	12.3
Z0232	18.2	3.1	<1.4	10.6	<.5	4.8	<1	.22		3.0	3.8	.32	.42	<.2	<.001	.61	.060	2.23	.26	.07	<.01	.054	<.01	13.1
Avg.	15.8	1.8		11.8		5.3		.28	.13	3.3	2.9	.40	.36			.48	.052	1.84	.22	.06		.056		12.7
Std±	3.3	1.8	1.4	1.5	.5	.71	1	.08		.5	1.2	.11	.07	.2	.001	.18	.011	.35	.05	.02	.01	.003	.02	.57

Table 3.1.5.2 Sulfite Recovery Boiler, Fine Particulate Composition

											Percent												
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Z0148			<.05		<.01	1.8	.36		.29	10.8	.56	23.0	2	.01	<.001	<.001	.054	.066	<.001	.016	.017	<.001	<.01
Huntzicker (1978)			.3	56	.033	2.9	1.1		.5	14.9	.6	37					.070	.036		.017		.005	.032

Table 3.1.5.2b Sulfite Recovery Boiler, Coarse Particulate Composition

											Percent												
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Z0147			<.1	1.4	<.04	.11	.09	.04	.025	.53	<.12	.92	<.05	<.08	<.001	<.01	.0052	.0064		.011	<.01	<.01	<.01

Table 3.1.5.3a Hog Fuel Boiler, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0080			.45	43.6	.10	2.0	<1	.27	1.03	11.2	8.1	32.2	7.4		<.001	.016	.72	1.78	.01	.18	.86	.065	.62	53.0
Z0090			.32	32.2	.14	1.5	<1	.40	.92	8.9	5.5	24.8	8.4	<.06	<.002	.020	.70	1.76	.008	.13	.96	.08	.45	
Z0024			.76	25.7	.20	6.8	<1	<.1	.34	6.4	15	10.1	1.03	<.01	<.001	.009	.12	.24	<.004	.064	.34	.02	.176	92.2
Avg.			.51	33.8	.15	3.4		.24	.76	8.8	9.5	22.4	5.6			.015	.51	1.26	.0067	.12	.73	.055	.42	72.6
Std±			.23	9.06	.05	2.9	1	.18	.37	2.4	4.9	11.2	4.0	.06	.002	.0056	.34	.88	.0042	.058	.34	.031	.22	27.7

Table 3.1.5.3b Hog Fuel Boiler, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0082	7.2	5.3	<.2	1.43	.084	.14	.60	.30	.95	.58	.41	1.52	5.2	.050	.008	.007	.33	1.1	<.005	.02	.035	.002	.023	47.0
Z0081			<.3	1.18	.16	.14	.27	.19	.83	.50	.37	1.33	≡5.2	.050		.006	.29	.98	<.005	.021	.037	<.001	.020	
Z0070	14.9	3.3	.35	1.9	.096	1.8	.50	.36	1.1	.68	1.7	1.1	≡5.2	.19	.003	.009	.25	.68	.005	.027	.044	.0013	.017	7.8
Avg.	11.1	4.3	.20	1.5	.11	.69	.46	.28	.96	.59	.83	1.3	5.2	.097	.0055	.0073	.29	.92		.023	.039	.0013	.020	27.4
Std±	5.4	1.4	.13	.37	.041	.96	.17	.086	.14	.090	.76	.21	.52	.080	.0035	.0015	.04	.22	.005	.0038	.0047	.00075	.0030	27.7

h. Hog Fuel Boiler (Tables 3.1.5.3a&b): The output of this source depends on what is being burned. Cl, K, and Ca are the major emissions for this sample, but the variability is substantial.

i. Paper Sludge Boiler: This was not sampled and is not considered important.

3.1.6 VEGETATIVE SOURCES

No combustion takes place here. This category is concerned only with suspension due to handling of these materials.

a. Flour Processing (Table 3.1.6.1a&b): No significant trace element concentrations are evident.

b. Grain elevators (Tables 3.1.6.2a&b): The elemental ratios are very similar to those of geological material and these concentrations are probably due to the presence of dirt in the grain.

c. Animal Feed Processing: Capar, et al. (1978) present elemental measurements on the raw feed. These are similar to those obtained from the grain elevator.

d. Pollen: This was not sampled and is not considered important.

3.1.7 ALUMINUM INDUSTRY

This is the second largest industrial emitter.

a. Aluminum Processing Stack (Tables 3.1.7.1a&b): Al, of course, is dominant with respectable contributions from F, Na, and Mg.

b. Aluminum Processing Roof Vent (Tables 3.1.7.2a&b): There is no appreciable difference between these emissions and those from the stack.

c. Alumina Handling (Tables 3.1.7.3a&b): This substance contains

Table 3.1.6.1a Flour Processing, Fine Particulate Composition

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
	Percent																							
Z0164	25.3	.28	<.6	12.6	<.2	.10	<1	.20	<.1	<.1	.34	<.03	.24	<.05	<.01	<.01	<.01	.03	<.01	.05	<.01	<.01	<.05	88.8

Table 3.1.6.1b Flour Processing, Coarse Particulate Fraction

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
	Percent																							
Z0165	11.8	.23	<1	.83	.2	.06	<2	.05	<.1	<.1	.61	<.1	.18	.05	<.01	<.01	.01	.018	<.01	.027	<.01	.007	<.01	11.2

Table 3.1.6.2a Grain Elevator, Fine Particulate

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
	Percent																							
Z0180	35.4	1.1	<.3	.35	<.1	.072	<.5	1.1	4.4	.15	.3	1.6	.75	.053	<.001	<.0008	.032	.75	<.001	.02	.018	.006	<.004	16.3
Z0168	20.2	<1	<.3	.59	<.1	.13	.34	1.2	4.3	.14	.35	1.6	.77	.044	.001	<.0008	.032	.80	<.001	.026	.0079	.008	<.004	21.3
Avg.	27.8	.80		.47		.10	.30	1.2	4.35	.145	.33	1.6	.76	.049	.00075		.032	.78		.023	.013	.007		18.8
Std±	10.7	.42	.3	.17	.1	.04	.064	.071	.071	.0071	.035	.16	.014	.0064	.00035	.0008	.0032	.035	.001	.0042	.0071	.001	.004	3.5

Table 3.1.6.2b Grain Elevator, Coarse Particulate

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
	Percent																							
Z0170	30.4	<1	<.1	.04	<.03	.10	<.5	1.1	6.6	.21	.15	2.0	.67	.050	<.001	<.001	.026	.78	<.001	<.01	.016	.002	<.005	83.7
Z0169	20.9	1.4	<.1	.12	.026	.13	.33	1.25	6.5	.22	.18	1.9	.68	.059	.001	<.001	.029	.81	<.001	<.01	.014	.002	<.005	78.7
Avg.	25.7	.95		.08	.021	.115	.29	1.18	6.55	.215	.17	1.95	.675	.055	.00075		.028	.80			.015	.002		81.2
Std±	6.7	.64	.1	.057	.008	.021	.057	.106	.071	.0071	.021	.071	.0071	.0064	.00035	.001	.0021	.021	.001	.01	.0014	.0002	.005	3.5

Table 3.1.7.1a Aluminum Processing Stack, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0346	8.4	1.8	<1	4.2	4.0	2.2	<1.5	17.4	.73		2.3	.15	.30	.07	.023	<.01	<.01	.114	.096	.038	<.005	.007	<.014	44.4
Z0182	2.4	3.5	<.4	.52	8.5	5.3	3.7	32.5	.15	1.5	.88	.26	.36	.025	.092	<.01	.02	.64	.26	.052	.018	<.01	.025	67.2
Z0185	.9	1.6	.52	8.4	3.6	4.8	3.9	29.9	.12	1.2	.80	.24	.33	.024	.078	<.01	.0081	.59	.22	.042	.024	.10	<.005	60.8
Avg.	3.9	2.3	.41	4.4	6.0	4.1	2.8	26.7	.34	1.4	1.33	.22	.33	.040	.064		.011	.45	.19	.044	.015	.037	.012	56.1
Stdt	3.9	1.0	.18	3.9	2.3	1.7	1.8	8.1	.34	.21	.84	.06	.03	.026	.036	.01	.008	.29	.085	.007	.011	.053	.010	10.2
Huntzicker (1978)				9.6	2.4	4.7		7.2	0.8		15.8	2.7	3.4	.1	.1			.1		.1	.8			
Huntzicker (1978)				3.5	0.8	1.7	.2	1.1			6.5	0.4	.6		.04			.065		.032	.2			
Avg.				6.6	1.6	3.2	.2	4.1	.8		11.1	1.6	2.0	0.1	.07			.08		.07	.5			

Table 3.1.7.1b Aluminum Processing Stack, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0338	<2	<2	<2	.90	2.3	1.7	3.3	36.5	.19	<.3	1.3	<.1	.43	<.2	.028	<.01	<.02	.21	.28	.085	<.01	.35	<.01	55.6
Z0209	<2	3.3	<2	2.9	6.0	2.6	2.2	30.7	<.1	<.01	1.0	<.1	1.1	<.2	.04	<.01	<.01	.47	.19	.17	<.02	<.02	<.1	32.8
Z0184	<1	<1	<1.7	1.2	4.3	2.8	2.7	26.8	<.1	<.01	1.2	<.1	.91	.028	.05	.037	<.02	.47	.16	.15	.013	<.01	<.01	39.2
Avg.		1.6		1.7	4.2	2.4	2.7	31.3	.097		1.2		.81	.076	.040	.016		.38	.21	.14	.009	.12		42.5
Stdt	2	1.5	2	1.1	1.9	.6	.55	4.9	.080	.3	.15	.1	.34	.041	.011	.018	.02	.15	.063	.04	.004	.20	.1	11.8

Table 3.1.7.2a Aluminum Processing Roof Vent, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0171	5.0	<1	<2	5.3	<.6	5.5	<2	25.8	.76	1.5	5.2	2.6	1.2	.047	.078	.02	<.02	.71	.15	.19	<.001	<.005	<.1	61.8

Table 3.1.7.2b Aluminum Processing Roof Vent, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0208	12	5.8	<.4	.53	.53	.66	1.2	14.1	.13	<.01	.42	<.05	.29	.078	.018	<.001	<.01	.17	.033	.040	<.01	<.01	.03	38.2

Table 3.1.7.3a Alumina Handling, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0236			.44	.50	.094	.33	.12	31.8	.27		.33	.087	.60	.019	.003	<.03	.057	.41	.028	.02	.015	<.02	<.03	79.6
Z0256			.73	.36	.14	.15	<.3	40.3	.18	.061	.39	.048	.35	.011	.0019	.018	.04	.21	.0086	.02	.0089	<.001	<.05	85.3
Avg.			.59	.43	.12	.24	.135	36.1	.23	.061	.36	.068	.48	.015	.0025	.0165	.049	.31	.018	.020	.012			82.5
Stdt			.21	.099	.033	.13	.021	6.0	.064	.0061	.042	.028	.18	.0057	.00078	.021	.012	.14	.014	.0020	.0043	.001	.05	4

Table 3.1.7.3b Alumina Handling, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0264			<2	1.2	<.5	.20	<1	1.17	.24	<.01	1.2	<.012	.19	.021	<.004		.096	.067		.096		<.01		20.4
Z0220			<1.2	.84	<.4	.10	<1	3.4	.17	<.01	.5	<.012	.36	<.01	<.002		.012	<.01		.056		.03		14.7
Avg.				1.0		1.5		2.29	.21		.85		.28	.013	.0015		.054	.036		.076		.02		17.6
Stdt			2	.25	.5	.7	1	1.58	.049	.01	.5	.012	.12	.011	.00071		.059	.044		.028		.014		4

plenty of Al.

3.1.8 IRON INDUSTRY

While total emissions may not be great, they will be rich in certain trace elements and source compositions are necessary to attain a mass balance of those elements.

a. Steel Electric Arc Furnace (Tales 3.1.8.1a-c): As expected, Fe is the major component followed by Mn and Cr. Al, Ca and Zn make significant contributions in both size modes. These results are consistent with those of other researchers. Coarse particulate composition was difficult to quantify as mass emissions in this mode are a factor of ten less than those of the fine particulate.

b. Ferromanganese Furnace (Tables 3.1.8.2a&b): The fine particulate composition is quite distinct from the coarse with respect to major components. K, Mn, and Fe stand out in the fine but not in the coarse. The Mn/Fe ratio is the key to distinguishing between this source and the electric arc furnace. Both elements contribute substantial portions of the total emissions, but their roles are reversed in the arc furnace with respect to this source.

3.1.9 MISCELLANEOUS POINT SOURCES

Many single, small emitters exist within the airshed.

a. Carborundum Process (Tables 3.1.9.1a&b): This process includes several steps in which the emissions vary, thus the wide variability exhibited by the concentrations of carbon, Al, Si, SO_4^{-2}, and K. Some sort of a weighted average, weighted by the fraction of time during which a

Table 3.1.8.1a   Steel Electric Arc Furnace, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0172			<1.4	3.4	<.47	1.6	7	.76	5.1	1.9	2.4	.97	6.6	.20		2.0	8.8	31.4	.68	.30	1.2	<.1	.78	92.2
Z0181			<.4	1.5	<.12	.92	6	.53	4.8	2.0	1.3	.87	5.8	.20	.063	2.2	8.6	32.5	.73	.26	1.2	<.1	.73	90.6
Avg.				2.5		1.26	6.5	.65	5.0	1.95	1.85	.92	6.2	.20	.063	2.1	8.7	31.95	.71	.28	1.2		.76	91.4
Std±			1.4	1.3	.5	.48	.71	.16	.21	.071	.78	.071	.57	.020	.0063	.14	.9	3	.035	.028	.12	.1	.035	1.1

Table 3.1.8.1b   Steel Electric Arc Furnace,Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0175			<3	1.3	<1	1.4	<4	<1	6.6	<1	3.8	.56	6.9	.11	.058	2.1	9.5	30.8	.62	.43	1.2	<.1	.64	9.4

Table 3.1.8.1c   Steel & Iron Industry, Total Particulate Composition

												Percent												
ID		VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Jacko[a] (1977)	Avg.																		43	.07	.16	18.7		4.2
	Std±																		13	.02	.05	5.5		1.2
Jacko[b] (1977)	Avg.																		9.0	.37	.20	18		2.6
	Std±																		1.9	.08	.04	4		.006
Gatz (1975)								1.6	2.4					5.4				2.4	38.7		1.6	1.8		
Lee[c] et al. (1975)																.04	1.5	8.2	59	.05	.21			1.1
Lee[d] et al. (1975)																	1.3	3.5						2.5

[a] Jacko and Neuendorf (1977), Open hearth furnaces, no controls

[b] Jacko and Neuendorf (1977), Open hearth furnaces, with electrostatic precipitator

[c] No controls, Electric Arc Furnace

[d] Baghouse, Electric Arc Furnace

Table 3.1.8.2a   Ferromanganese Furnace, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	% of total mass
Z0278			7.7	4.4	.23	3.1	<4	.55	.77	1.9	.53	13.2	1.2	.041	.01	.04	16.6	2.0	<.005	.033	.76	<.01	.056	99.4
Z0295	9	1.5	3.7	4.0	.35			.73	1.2	1.4	.3	7.7	1.4	.051	.037	.044	18.0	2.2	<.005	.038	.40	.32	.034	92.4
Avg.	9	1.5	5.7	4.2	.29	3.1		.64	.99	1.7	.42	10.5	1.3	.046	.024	.042	17.3	2.1		.036	.58	.16	.045	95.9
Std±	.9	.15	2.8	.28	.08	.31	4	.13	.30	.35	.16	3.9	.14	.0071	.019	.0028	.99	.14	.005	.0035	.25	.22	.016	4.9

Table 3.1.8.2b   Ferromanganese Furnace, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	% of total mass
Z0294			1.7	.92	.79	.22	<2	.1	.10	<.01	.70	1.4	.62	<.5	<.005	.04	3.0	.4	<.02	.095	.034	<.1	<.05	.6
Z0224	16	3	<1.3	1.3	.34	.45	<1	.25	.48	<.01	1.0	1.0	.51	<.4	.015	<.01	2.5	.36	<.005	.052	.036	<.2	<.05	7.6
Avg.	16	3	1.2	1.1	.57	.34		.18	.29		.85	1.2	.57		.0088	.0225	2.75	.38		.074	.035			4.1
Std±	1.6	.3	.71	.27	.32	.16	2	.11	.27	.01	.21	.28	.078	.5	.0088	.025	.35	.028	.02	.030	.0014	.2	.05	4.9

Table 3.1.9.1a Carborundum Manufacture, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0269	13.7	4.2	4.8	53.7	<.06	.020	.20	.13	.27	14.5	1.8	.21	.024	.0081	.0075	.0078	.0021	.032	<.001	.010	<.001	.024	<.0090	88.7
Z0302			.28	8.0	.024	.24	2.6	.93	9.3	.66	.65	2.5	.26	.0021	.0004	<.004	.084	.020	<.001	.0053	.0037	.0027	<.005	97.5
Z0307	21	115	.32	1.9	.056	.054	.1	.029	.26	3.2	3.8	.096	.032	.002	.0008	<.002	<.001	.021	<.001	.007	.0010	.025	<.005	88.0
Z0311	6.2	46	1.1	.59	<.2	.18	<.4	.32	4.0	.78	.6	.37	.25	.043	.018	.024	.056	1.25	.014	.054	.009	.015	<.005	51.7
Avg.	13.6	55	1.6	16	.05	.12	.78	.35	3.5	4.8	1.7	.79	.14	.014	.007	.009	.035	.33	.004	.019	.004	.017		81.5
Std±	7.4	56	2.1	25	.03	.10	1.2	.40	4.3	6.6	1.5	1.1	.13	.019	.008	.011	.041	.61	.007	.023	.004	.010	.01	20.3

Table 3.1.9.1b Carborundum Manufacture, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0234	<4	22	<1.3	<.5	<.4	.04	.26	.52	.114	<.1	1.1	<.06	.33	<.01	<.0005	.016	.014	.025	.049	.066		.020	<.01	11.3
Z0235			<.5	2.2	<.2	.45	1.3	9.3	34.8	.76	.46	2.4	1.3	.036	.014	<.004	.066	.31	<.001	.028		.018		2.5
Z0306	7.6	10.6	1.4	3.9	<.4	.33	<.1	.56	4.2	.26	1.5	.092	.32	.045	.01	<.002	.018	.22	<.001	.067	<.01	<.01	<.01	12.0
Z0310	4.2	40.4	.97	<.02	<.3	.22	<.4	.81	9.7	.56	.88	.34	.32	.044	.025	<.006	.018	.54	.016	.057	<.01	<.001		48.3
Avg.	4.6	24	.83	1.6		.26		2.8	12	.41	.99	.72	.57	.033	.012	.004	.029	.27	.017	.055		.011		18.5
Std±	2.8	15	.48	1.83	.4	.17	.4	43	15	.31	.43	1.1	.49	.019	.010	.007	.025	.21	.023	.018	.01	.009	.01	20.3

Table 3.1.9.2a Glass Furnace, Fine Particulate Composition

											Percent														
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Se	Fine
Z0272			.86	72	.070	9.2	<.05	.20	.30	12.9	.062	1.56	.3	<.005	.0048	.21	.0016	.020	<.003	.0059	.012	<.005	.42	1.36	96.2
Z0248			.37	58	.038	≡9.2	<1	.18	.20	9.6		1.17		<.005	.0045	.16	.0026	.02	<.01	.0035	.0093	.01	.33	1.1	89.5
Avg.			.62	65	.054	9.2		.19	.25	11.3	.062	1.37	.3		.0047	.19	.0021	.02		.0047	.011	.0063	.38	1.23	92.9
Std±			.35	9.9	.023	.92	1	.014	.071	2.3	.0062	.28	.03	.005	.00021	.035	.00071	.002	.01	.0017	.0019	.0053	.064	.18	4.7

Table 3.1.9.2b Glass Furnace, Coarse Particulate Composition

											Percent														
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Se	Coarse
Z0228			4.6	26	<.3	5.1	<1	.23	.53	6.8	.53	.80	1.35	.10	<.005	.090	.023	.18	<.02	.045	.010	<.05	.13	.27	3.8
Z0299			3.0	45	<.4	8.8	<2		.12	1.6	.77	.92	1.1	.03		.17	.037	.18	<.02	.069		<.05	.13	.59	10.5
Avg.			3.8	35.5		6.95		.23	.33	4.2	.65	.86	1.23	.065		.13	.030	.18		.057	.010		.13	.43	7.2
Std±			1.1	13.4	.4	2.62	2	.023	.29	3.7	.17	.085	.18	.049	.005	.056	.0099	.018	.02	.017	.0010	.05	.013	.23	4.7

Table 3.1.9.3a Car Shredder, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_3	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0177	10	.6	<.3	.27	<.1	.35	<.1	.51	1.0	.53	1.0	.39	.44		<.001	.04	.12	6.45	.036	.09	2.0	.73	.47	94.5
Z0178	5.4	.6	<.3	.30	<.1	<.02	<.2	.42	.73	.41	.35	.14	.52	<.05	<.001	.039	.056	5.07	.026	.11	2.2	.24	.50	92.9
Avg.	7.7	.6		.29		.18		.47	.87	.47	.68	.27	.48			.040	.088	5.76	.031	.10	2.1	.49	.49	93.7
Stdt	3.3	.06	.3	.02	.1	.24	.2	.064	.19	.085	.46	.18	.057	.05	.001	.00071	.045	.98	.0071	.014	.14	.35	.021	1.13

Table 3.1.9.3b Car Shredder, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0176	29	<2	<10	<5	<2			1.6			8.0		6.0			<2		4.5		.78	.95	9.2		5.5
Z0167	33	6.9	<15	<6	<5			2.1			9.4		5.0				.15	2.9		1.2	.78	7.6		7.1
Avg.	31	4.0						1.9			8.7		5.5				.078	3.7		.99	.87	8.4		6.3
Stdt	2.8	4.2	15	6	5			.35			.79		.71			2	.10	1.1	.001	.30	.12	1.1	.005	1.1

Table 4.1.9.4a Carbide Furnace, Fine Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Z0280	8.2	1.4	.74	3.5	<.03	.98	2.6	.65	2.5	1.9	1.0	1.5	32.4	<.02	.0063	<.01	.044	.59	.027	.012	.020	<.01	.011	62.4
Z0230	6.3	1.0	.40	2.9	<.1	.85	2.1	.50	2.4	1.3	1.1	1.0	26.9	<.02	.0056	<.01	.039	.48	.016	.027	.010	<.01	<.01	48.5
Avg.	7.3	1.2	.57	3.2		.92	2.4	.58	2.5	1.6	1.05	1.25	29.7		.0060		.042	.54	.022	.020	.015		.0080	55.5
Stdt	1.3	.28	.24	.42	.1	.092	.35	.11	.071	.42	.071	.35	3.9	.02	.00050	.01	.0035	.078	.0078	.011	.0071	.01	.0042	9.8

Table 4.1.9.4b Carbide Furnace, Coarse Particulate Composition

											Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
Z0229	3.9	2.3	<.5	1.7	<.2	.43	1.0	.95	3.8	.99	.51	.69	31.9	<.02	.0087		.029	.42	.025	.036	<.01	<.01	<.02	37.6
Z0218	5.0	4.9	<.5	<.3	<.2		1.5	.77	1.9	.18	1.4	.27	19.6	<.02		<.01	.043	.23	.017	.042	<.01	<.01	<.01	51.5
Avg.	4.5	3.6		.93		.43	1.25	.86	2.9	.59	.96	.48	25.8		.0087		.036	.33	.021	.039				44.6
Stdt	.78	1.8	.5	1.1	.2	.043	.35	.13	1.3	.57	.63	.30	8.7	.02	.0087	.01	.0099	.13	.0057	.0042	.01	.01	.02	9.8

specific process takes place, would characterize this source better. In the absence of more information concerning the operation of this source, a straight arithmetic average is presented.

b. Glass Furnace (Tables 3.1.9.2a&b): Silicon is not a major component, as might be expected, but sulfur is. Sulfur is used in certain processes to color glass brown. Selenium was also observed in the x-ray spectrum; it is used as a clarifying agent in glass production. The composition of these emissions depends on the products being produced.

c. Small Point Sources (Tables 3.1.9.3a&b): Only the car shredder was sampled as a representative of these sources which may be important contributors on a local basis or of a specific element. Chemical compositions of some other small point sources have been quantified (Zoller, et al., 1978; Lannefors and Akselsson, 1977; Akselsson, et al., 1974; Buchnea and Buchnea, 1974) but are not reviewed here. For the car shredder, Fe and Zn stand out in the fine mode while Al, Ca and Fe are substantially present in the coarse. The coarse mode also contains a high volatilizable carbon component. The precursor material surely affects the composition of the aerosol to a great extent.

d. Carbide Furnace (Table 4.1.9.4a&b): Calcium is the dominant element in these emissions with Mg, Si, S, and Cl contributing respectable amounts.

e. Cement Kiln: No source tests were made, though excess Ca may originate in this source.

f. Limestone Kiln: No tests were made and this source is not considered important.

g. National Lead Industries: A study of the emissions from this plant would have been revealing regarding possible non-auto contributions of Pb.

h. Galvanizing: These operations and other Zn-related sources should definitely have been sampled. Many cities have observed high Zn concentrations but the emissions from these operations has never been assessed as a possible source. Huntzicker and Davidson (1975) felt that these emissions accounted for half of the Zn observed in Los Angles.

i. Sewage Sludge Burning: Shen (1978) presents chemical characterization data. This source is not considered important and is not reviewed here.

j. Chemical: This source is not reviewed here and is considered unimportant.

k. Manufacturing Industry: No one knows why this is here.

l. Incinerators: Municipal inciperator measurements have been obtained by Greenberg, et al. (1976, 1978) and Kleinman (1977). These emissions are not considered important in Portland.

3.1.10 BACKGROUND AEROSOL

Background is that which enters the airshed with the prevalent air mass and cannot be subjected to control. Table 3.1.10.1 shows the average of TSP and FSP measured at the two rural sampling sites to the average of the four urban sites for each season of the PACS year and for the whole year. As a rough approximation, 45% of the urban aerosol loading cannot be affected by local controls of any kind.

Four major components, each of which has some interaction with the others, will affect the overall background entering Portland's AQMA,

Table 3.1.10.1 Urban and Background Averages

Season	Urban Average[a] μg/m³ FSP	Urban Average[a] μg/m³ TSP	Background Average[b] μg/m³ FSP	Background Average[b] μg/m³ TSP
SUMMER	24	64	18	44
AUTUMN	32	83	18	39
WINTER	36	74	11	24
SPRING	38	110	14	38
ANNUAL	33	83	15	36

[a] Arithmetic average of individual arithmetic averages from sites 2, 3, 4 and 5 for all PACS hi-vol samples taken within the season.

[b] Average of measurements from sites 1 and 6.

FSP-Fine Suspended Particulate, mass of particles less than 2 microns in diameter.

TSP-Total Suspended Particulate

(a) tropospheric background, representing the composition of the homogeneous troposphere, (b) continental background, representative of local geological material, (c) marine background, and (d) long range anthropogenic background.

a. Tropospheric background is composed primarily of lithophile elements, some of which are purported to be enriched by anthropogenic contributions, and exhibits a remarkably consistent chemical composition as evidenced by measurements in disparate locations (Adams, et al., 1977; Dams and DeJonge, 1976). Measurements above one or two kilometers over the sea's surface at a number of sites (Blifford and Gillette, 1972; Gillette and Blifford, 1971; Simpson, 1972) show that this background is present over the ocean and probably extends down to the surface.

Many properties of this aerosol have been measured in different parts of the world (Junge, 1972; Bigg, 1977; Flyger, et al., 1976; Hogan, 1975; Charlson, et al., 1978; Cattell, et al., 1978) but only a few of these include extensive chemical analyses (Adams, et al., 1977, Dams and DeJonge, 1976, Reiter, et al., 1976). Table 3.1.10.2 contains these results; their similarity with each other and with continental background/soil is striking which strongly suggests that a well mixed aerosol of primarily geological origin permeates the entire earthly troposphere. Much of the discussion which applies to continental background/soil applies to this aerosol and they shall be treated more or less identically.

b. Continental background is very similar to the trospospheric background but its composition is not as uniform due to its more local origin. This category contains dust and soil which has been entrained by wind and, for the most part, remains in the first kilometer of the atmosphere. Portions of it are surely candidates for the tropospheric background, but it

Table 3.1.10.2a Soil Dust, Fine Particulate Composition

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
											Percent													
Z0482	4.3	.48	<.1	<.05	<.01	.33	1.93	14.7	22.3	.059	<.01	.70	.42	1.00	.033	.039	.32	8.49	.013	.014	.023	<.01	.018	
Z0479	2.3	.13	<.1	<.05	<.01	.50	1.31	11.8	29	.037	<.01	.69	.68	.58	.024	.018	.090	3.75	.0047	.024	.024	<.01	.023	
Z0461	6.8	.56	<.1	<.05	<.01	.60	2.16	12.4	21.7	.099	<.01	1.19	1.01	1.00	.027	.035	.23	8.85	.008	.019	.040	<.01	.035	
Z0494	3.2	1.3	<.1	<.05	<.01	1.32	2.46	10.6	25.5	.050	<.01	1.11	1.26	.76	.025	.035	.22	7.81	.013	.023.	.086	<.01	.052	
Z0490	5.0	.48	<.1	<.05	<.01	.72	.94	8.9	28.5		<.01	1.29	1.27	.48	.015	.027	.128	4.88	.0073	.019	.030	<.01	.0021	
Avg.	4.32	.59				.69	1.76	11.7	25.4	.069		1.0	.93	.76	.025	.031	.20	6.8	.0092	.020	.041		.026	~10
Std±	1.73	.38	.1	.05	.01	.38	.62	2.2	3.4	.027	.01	.28	.37	.24	.006	.008	.091	2.3	.0037	.0040	.026	.01	.0019	
Z0499 Composite	5.5	.26	<.1	<.05	<.01	.53	1.39	11.4	25.9	.056	<.01	1.04	.73	.80	.029	.031	.185	6.91	.008	.018	.030	<.01	.021	

Table 3.1.10.2b Soil Dust, Coarse Particulate Composition

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Coarse
											Percent													
Z0910			.014	.0053	.0022	.44	.68	8.20	29.0		<.01	1.8	.4	.85	.013	<.006	.126	5.49					.050	
Z0909			.0046	.0034	.0023	1.38	1.31	6.8	31.0		<.01	2.3	1.4	.86	.016	<.006	.060	4.02					.036	
Z0908			.014	.0032	.0029	1.41	1.23	7.34	28.5		<.01	2.3	1.3	.93	.016	<.006	.091	4.92					.057	
Z0907			.010	.0024	.0015	1.61	1.52	7.1	29.8		<.01	2.1	2.1	.90	.027	<.006	.090	5.63					.029	
Z0906			.0029	.0042	.0024	1.66	1.30	6.60	30.2		<.01	2.4	1.9	.56	.012	<.006	.057	3.75					.039	
Avg.			.0091	.0037	.0023	1.3	1.2	7.2	29.7			2.2	1.4	.82	.017		.085	4.76					.042	~90
Std±			.0052	.0011	.0005	.50	.31	.62	.98		.01	.24	.67	.15	.006	<.006	.028	.85					.011	
Z0912 Composite	1.41	1.10	.12	.0027	.0020	1.25	1.17	7.30	31.2		<.01	2.2	1.4	.73	.014		.081	4.16					.025	

Table 3.1.10.2c Soil Dust, Continental, Tropospheric Background, Total Particulate Composition

ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
											Percent												
Kowalczyk etal [a,d](1978)						.42	.74	≡8			.026	1.52	.65	.51	.01	.008	.13	5.0	.005	.002	.01	.001	.0015
Miller etal [a](1972)						2.4	.7	6.9	26			2.5	1	.3	.004		.06	2.0	.002	.002	<.01		.006
Miller etal [b](1972)						2.5	1.4	8.2	20			1.5	1.5	.4	.006		.11	3.2	.004	.008	<.01		.02
Gatz[a,d](1975)						.6	.7	5				2	.8	.3	.007	.005	.03	3	.005	.003	.01		.005
Taylor[a,d](1964) Crustal	.02					2.36	2.33	8.23	28.15	.026	.013	2.09	4.15	.57	.0135	.01	.095	5.63	.0073	.0055	.0070	.00025	.00125
Taylor[a,d](1964) Basalt	.01					1.94	4.5	8.76	24.0	.025	.006	.83	6.72	.90	.025	.02	.15	8.56	.015	.010	.010	.00036	.0005
Taylor[a,d](1964) Granite	.03					2.77	.16	7.70	32.3	.027	.02	3.34	1.58	.23	.020	.0004	.04	2.70	.00005	.001	.004	.00013	.0020
Adams etal[e](1977) 12						2.18	.8	≡8		6.5	2.4	2.10	3.2	.35	.02	.062	.062	4.72	.067	.072		.039	.47
Adams etal[e](1977) 13						1.70	1.0	≡8		4	1.86	2.67	1.66	.44	.012	.040	.053	6.14	.038	.044		.030	.25
Dams & DeJonge[e](1976)						3.45	1.57	≡8			1.12	3.13		.38	.045	.056	.024	5.65		.140	1.6	.20	.69
PACS[f] 7/9/77,4-12p.m.			2.3	2.3	.18	3.7	3.3	17.5	69	.38	1.1	1.4	4.2	1.5	.026	.03	.13	6.2		.026	.073	.024	.09
PACS[f] 7/15/77,8-4p.m.			2.2		.10	3.7	2.97	13.2	43.2	1.8	.83	1.14	3.8	1.14	.021	.026	.11	7.5	.009	.027	.038	.014	.093
PACS[f] 7/16/77,4-12p.m.			1.3	2.4	.14	2.43	11.6	2.2	50	.90	1.02	1.15	4.8	1.0	.017	.025	.09	7.8	.006	.087	.047	.023	.093
PACS[g]11/14/77,12-8a.m.			3.75	5.4	<.004	10.9	<.03	1.97	4.9	1.27	15	1.30	1.09	.148	<.0002	.055	.033	.76	<.0004	<.0005	.068	.075	<.002

[a] Soil sample

[b] Resuspended soil sample

[c] Ambient sample

[d] Literature values, reference given is secondary source

[e] Tropospheric background

[f] Sauvie Island Background under high speed north wind

[g] Carus Background under high speed south wind

is distinct in that the variability of its elemental concentrations is larger. Among others, Lannefors, et al. (1977), Corradini, et al. (1977), Ronneau, et al. (1978), and Shani and Hacoun (1976) present several examples.

Many chemical characterizations are reported, though some are frustrating in that they present no data for Si, a major soil component; one cannot help but think that the major purpose of such studies was to make use of a reactor facility rather than to characterize the aerosol.

Tables 3.1.10.2a&b present PACS measurements of resuspended and bulk soil from several parts of the region as well as a summary of some PACS background aerosol measurements under clean air conditions and continental background, both bulk soil and aerosol, measurements from the literature.

Rahn (1976b) has pointed out that bulk soil composition is not the best approximation of the elemental concentrations in ambient aerosols dominated by geological material. He summarizes Al and Si measurements from 26 ambient aerosol studies and finds an average Si/Al ratio of 2.67 with a range from 1.4 to 4.63; he cites literature values for this ratio in bulk soil ranging from 3.41 to 4.65.

The results in Table 3.1.10.2a-c bear this out; the Si/Al ratio for the resuspended dust collected in the fine particulate mode is 2.17 as opposed to 4.13 for the bulk soil analysis.

Rahn asserts that this difference is due to the greater portion of fine particulate clay, in which the Si/Al values range from 1.04 to 2.07, in the aerosol. The larger particles with the higher ratio tend to settle out faster. Thus, ambient fine particle samples should yield lower Si/Al ratios since most clay granules have diameters less than 2 μm.

Other elemental concentrations which appear to differ between the resuspended fine and bulk soil in Tables 3.1.10.2a&b are those of K, Cr, and Mn. The confidence intervals of other elements overlap between the fine resuspended and bulk modes and their concentrations cannot be said to differ.

c. Marine aerosol is a potential contributor to the natural background particulate impacting the Portland AQMA. The physical and chemical aspects of this aerosol are intriguing, but too lengthy for this discussion. Junge (1972) and Bressan, et al. (1973) present excellent reviews, however, of the size distribution and chemical composition of the marine background which are supplemented with more recent studies by Duce, et al. (1975, 1976), Hidy, et al. (1974), Hoffman and Duce (1976), Martens, et al. (1973a), Meinert and Winchester (1977), Winkler (1975) and Zoller, et al. (1974b).

Unfortunately, the variability in sampling, analysis techniques and species quantified, due to the differing objectives and resources of the investigators, makes the comparison of results difficult and the application of literature values for the maritime aerosol elemental composition to quantitative chemical element balance calculations dubious. Miller, et al. (1972) noted this difficulty six years ago and used the salt composition in bulk sea water as the best approximation to the aerosol.

In reality, the marine aerosol composition is more complicated than this and the elemental ratios will not be those of bulk seawater, as a quick comparison of measurements in Table 3.1.10.3 will verify. Four phenomena affect these ratios: (1) mixture with aerosols of continental and anthropogenic origin, (2) ion fractionation during particle formation, (3) high enrichment in the oceanic microlayer, and (4) modification of particles in the atmosphere. A brief review of the seminal studies in each

Table 3.1.10.3. Marine Background, Total Particulate Composition

										Percent													
ID	VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Miller et al.[a,b](1972)	.0035	-.0087	$3x10^{-5}$ -.002	7.68		30.61	3.69	.00046 -.0055	$1.4x10^{-4}$ -.0094		55	1.1	1.16		$9x10^{-7}$		$2.5x10^{-6}$ $-2.5x10^{-5}$	.00005 -.0005			$1.4x10^{-5}$ $-4x10^{5}$	.19	$1.2x10^{-5}$ $-1.4x10^{-4}$
Chesselet[b](1972)						≡30					54		1.1										
Hoffman & Duce[a,b](1972)						≡30	3.57					1.11	1.14										
Hoffman & Duce[b](1972)						≡30	3.69					1.12	1.17										
Hoffman & Duce[b](1972)						≡30		$1.5x10^{-5}$							$6x10^{-6}$		$3x10^{-7}$			$6x10^{-6}$			$1.5x10^{-6}$
Wilkness & Bressan[a,b](1972)					$3.7x10^{-3}$	≡30					54	1.07											
Barker & Zeitlan[b](1972) Microlayer						≡30	3.57					1.12	1.16					.16		.032	.11		
Barker & Zeitlan[b](1972) 6m deep						≡30	3.66					1.07	1.15					.038		.010	.04		
Barker & Zeitlan[b](1972) 20m deep						≡30	3.69					1.11	1.16										
Gillette & Blifford[c](1971) .015km high						≡30																	
Gillette & Blifford[c](1971) 1.8km high						≡30			38.0	.63	120	27	10.2	4.8									
Gillette & Blifford[c](1971) 3.7km high						≡30			45.0	30.0	188	23	15	7.5									
Gillette & Blifford[c](1971) 6.1km high						≡30			180.0	150.0	660	180	120	30									
Tsunogai et al.[c](1972)						≡30	4.32				135	2.43	3.96										
Tsunogai et al.[c](1972)						≡30	4.68				29.4	2.67	3.63										
Hidy et al.[d](1974)SN-3	1.9	1.9	2.3	11.4		5.9		2.8	3.3		25.3	.5	2.7	.03		<.01	<.01	.36	<.06	<.06		.23	<.36
Hidy et al.[d](1974)SN-22	1.2		.40	10.2		5.0		<1.5	3.7		27.4	.8	2.7	.08		<.03	<.01	1.24		2.5	.16	.24	<.16
Adams et al.[a,d](1977)Norway						≡30	4.9	2.9	9.8		20.2	3.3	3.1	.21	.115	.045	.17	3.5		.16	.59	.32	.38
Sadasivan[c](1978)						≡30				18.3												.19	
Sadasivan[c](1978)						≡30				43.8												.16	
Sadasivan[c](1978)						≡30				46.5												.13	
Sadasivan[c](1978)						≡30				48.3												.13	
Hidy et al[e](1974)SN-1	4.2	3.7	6.9	18.1		2.0		3.9	6.7		3.3	.35	3.5	.10		<.02	.02	1.8		.4	.3	.2	<.5
Hidy et al.[e](1974)SN-8	1.3		5.9	21.2		3.1		1.4	5.5		2.6	1.3	1.1	.11		.02	.06	1.7		.66	.63	.24	.96
Hidy et al.[e](1974)SN-12	1.7		5.3	10.9		2.2		1.6	2.0		1.7	.57	.21	.15		.021	.063	1.82		.25	.72	.15	1.6
Hidy et al.[e](1974)SN-14	1.9		8.0	9.1		2.1		2.0	3.3		2.3	.45	1.1	.26		<.02	.09	3.6		.06	.38	.16	.44
Hidy et al.[e](1974)SN-19	2.8		6.8	19.2		1.8		.23	7.1		1.0	2.1	2.2	.11		.028	.057	1.1		.28	.11	.20	.63
Hidy et al.[e](1974)SN-20	2.5		2.9	14.3		1.2		1.03	6.8		.30	.76	1.2	.09		.02	.05	1.0		.20	.10	.18	.55
PACS[f] 7/9/77, 4-12p.m.			2.3	2.3	.18	3.7	3.3	17.5	69	.38	1.1	1.4	4.2	1.5	.026	.03	.13	6.2		.026	.073	.024	.09
PACS[f] 7/15/77,8-4p.m.			2.2		.10	3.7	2.97	13.2	43.2	1.8	.83	1.14	3.8	1.14	.021	.026	.11	7.5	.009	.027	.038	.014	.093
PACS[f] 7/16/77, 4-12p.m.			1.3	2.4	.14	2.43	11.6	2.2	50	.90	1.02	1.15	4.8	1.0	.017	.025	.09	7.8	.006	.087	.047	.023	.093
PACS[g] 11/14/77, 12-8 a.m.			3.75	5.4	<.004	10.9	<.03	1.97	4.9	1.27	15.0	1.30	1.09	.148	<.0002	.055	.033	.76	<.0004	<.0005	.068	.075	<.002

[a] Literature values, cited source is secondary reference

[b] Bulk seawater

[c] Sea based Aerosol Measurement

[d] Land based coastal Aerosol Measurement with previous air mass trajectory over ocean

[e] Land based coastal Aerosol Measurement, Aged aerosol

[f] Sauvie Island Background site under high speed north wind conditions

[g] Carus Background site under high speed south wind conditions

of these areas is enlightening.

(1) "Non-marine" sources - The most ubiquitous contributor to this class is the pervasive tropospheric background.

Within the first two kilometers the aerosol loadings can be affected by "local" continental aerosol. Toba (1965) has discerned dust from the Sahara in the mid-Atlantic and Duce, et al. (1976) observe the same in Bermuda. Table 3.1.10.3 shows a much greater influence of soil derived elements such as Al, Ti, Fe and Si in coastal sampling situations than on the open sea even though the figures presented are limited to air masses whose recent history does not place them over land. Even the remote mid-sea sites exhibit this enrichment, however.

Chow, et al. (1969) observed detectable concentrations of lead, a notorious anthropogenic pollutant, which did not decrease with distance from the U.S., during a cruise in the mid-Pacific; their results are hard to compare with others because they made no simultaneous measurements of other parameters.

The spectre of volcanoes always comes to fore in the discussion of background aerosols; the forces involved can project particles high into the troposphere, even into the stratosphere, and residence times are long. Recent elemental studies (Buat-Ménard and Arnold, 1978; Mroz and Zoller, 1975) prove these emissions to be highly enriched in many elements common to crustal weathering residue and sea spray. The actual effect of these is speculative given that no major eruptions have occurred recently and it is probably safe to assume that any remaining aerosol from previous blasts has incorporated itself into the tropospheric background. Another speculative source of calcium enrichment is the wearing of coral reefs by wave action (Hoffman and Duce, 1972a) which may be a consideration if samples are taken near such a reef.

One approach is to separate the true marine component from the geological by normalizing all values to a unique, abundant crustal element, say Al or Si, and using average crustal ratios (Mason, 1966) to this component to assess its contribution which can then be subtracted from the total. Chesselet, et al. (1972) applied this method and their results appear in Table 3.1.10.3. Not surprisingly, the remaining elements are ionic in nature. The drawback of this correction is that soil compositions vary widely with geography and any given set of ratios are not necessarily those of the soil present. Neither does this method remove the non-soil/non-sea contributors.

Another method separates the sample into a soluble and a non-soluble fraction, the prior assumed to be truly of oceanic origin and the latter of continental incipience. Naturally, any soluble components of geological material will be associated with the sea and vice versa.

One can argue that a distinction is not really necessary...that the non-sea originated constituents of aerosol over the ocean are distinct from the local continental background and should justifiably be included in the "marine background." Green (1972) suggests that the term "marine aerosol" be reserved for those particles which are sampled in mid-oceanic regions under controlled conditions.

Though the difficulties of definition and quantification remain, it is clear that non-sea sources can result in substantial elemental enrichment and variation in the marine background.

(2) Ion Fractionation during particle formation-MacIntyre (1970)

reviews previous studies on the injection of ionic components into the air. The primary mechanism is the bursting of bubbles at the surface and the subsequent projection of small drops which are caught, dehydrated and mixed by the wind. Complicated thermodynamic and electrical properties associated with droplet formation preferentially concentrate certain ionic species over others. MacIntyre summarizes laboratory simulations and field experiments demonstrating enrichments of Ca^{+},Mg^{+},K^{+},SO_4^{-2},Br^{-}, and PO_4^{-2} in aerosols and finds the enrichment probability increases with higher ionic potential. Chesselet, et al. (1972) in later experiments found that organic surfactants promoted the enrichment of K^{+}. The actual enrichment over the contents of bulk seawater is highly variable and seems to be associated with the electrical charge character of the ocean's surface. Though MacIntyre speculates that this mechanism may be a major cause of enrichment, it seems to have received little study since his work.

(3) High enrichment in the oceanic microlayer - The droplets propelled by the bursting bubble form at the ocean-air interface and this transition layer which separates these phases does not exhibit the same elemental content as bulk seawater. The studies of Barker and Zeitlen (1972, see Table 3.1.10.3) show enrichments over bulk seawater (Na is the normalization element) by factors of 2 to 5 for Sr, Cu, Fe and Zn in the microlayer, and Piotrowicz, et al. (1972) found Al, Cu, Fe, Mn, Pb, and V enriched in the first 150 μm of ocean surface in the North Atlantic, near New York and off Rhode Island Sound. Piotrowicz, et al. (1972) speculate that the majority of this enrichment may be contained in the first micron of the sea-air interface, a conjecture that, if borne out, would increase the actual enrichments he reports by 150 times. Once again, the microlayer

enrichments are highly variable due to sea state, presence or absence of apparent slicks, biological activity, local pollution sources, and uneven settling of past aerosols. The quantitative transfer of this surface layer to aerosol particles is yet to be elucidated, but if MacIntyre's (1970) observation that most of the droplet mass comes from the first micron of the sea's surface is true, then elemental enrichments could be quite substantial in the aerosol, even for elements of negligible concentration in the bulk seawater.

(4) Modification of Particles in the Atmosphere - Interaction between the particulate and gas phases is well documented among certain elements in the urban aerosol (Friedlander, 1977) and the same processes studied there take place over the ocean. Miyake and Tsunogai (1963) showed that I^- can be photochemically converted to I_2 in seawater and released to the atmosphere where Duce, et al. (1967) contend that it diffuses to the surface of aerosol particles. Moyers and Duce (1972) detail possible exchanges of Br between the solid and gaseous phases. A reactive route for the conversion of NaCl to HCl in the presence of NO_2 has been proposed by Robbins, et al. (1959) and supported by Martens, et al. (1973b) in comparisons between polluted and unpolluted atmospheres. Junge (1963) proposes oxidation of SO_2 aand NO_2 as significant sources of sulfate and nitrate. The apparent loss of Cl with respect to Na is evident from PACS background measurements representative of air masses from the ocean presented in Table 3.1.10.3. The Na/Cl ratio is close to unity in these cases.

d. Long Range Anthropogenic Background - Anthropogenic aerosol can travel far as evidenced by lead measurements over the ocean (Chow, 1969). It is entirely possible that a portion of the elemental concentrations measured in the Portland airshed comes from polluters outside the region. Forest products industries northwest of Portland along the Columbia River can make a substantial contribution of their characteristic emissions to air masses headed toward the AQMA. Grass field and slash burning supply a tremendous burden to the air coming from the north or south when those activities are allowed. Chemical element balances performed at background measurement locations must consider these sources as well as the geological and marine sources of strictly natural origin.

3.1.11 SECONDARY AEROSOL

The aerosol considered to this point has been that which exits from its source as particles, or condenses into particles immediately upon cooling a short time in the atmosphere; this is known as primary aerosol. Additional particulate matter is contributed to the fine particle mode by the transformation of SO_2, NO and NO_2, NH_3, hydrocarbons and other trace gases into a solid phase, usually species such as SO_4^{-2}, NO_3^-, NH_4^+ and volatilizable carbon, respectively. The transformations are complex (Friedlander, 1977) and are functions of gas concentrations, primary particulate sizes and chemical compositions, relative humidity, temperature and insolation. Needless to say the processes involved are not completely understood.

Such secondary aerosol has been implicated in Los Angeles (Hidy, 1970, 1975) in particular as a major contributor to TSP and a cause of substantial visibility reduction; its importance in Portland has yet to be assessed.

Since SO_4^{-2}, NO_3^- and volatilizable organic carbon, the secondary species quantified in the PACS, are contained in many of the primary emission compositions presented in the previous sections, no unique fingerprint exists to set them apart. The secondary aerosol contribution to the concentrations of these species must be estimated from the difference between the ambient loadings and that accounted for by the primary source types.

3.1.12. THE CHEMICAL ELEMENT BALANCE SOURCE MATRIX AND ITS UNCERTAINTIES FOR PORTLAND

As specified in Chapter 2, the number of sources, p, to be included in the chemical element balance and their chemical compositions as perceived at the receptor, the a_{ij}, must be known *a priori*. The underlined portion of the previous statement is most important for it is clear that certain fractionation effects can occur which will cause the elemental ratios at the receptor to be different from those determined from source precursor material and even from samples of source aerosol emissions.

For certain source compositions not enough is known about possible metamorphoses after leaving the emitter. In such cases the average elemental concentration ascertained from a few samples must be used. For other sources, more information concerning chemical composition and its changes has been accumulated. This knowledge can be synthesized to form a best estimate of the receptor perceived source composition.

In either case, an estimate should be made of the uncertainty associated with each a_{ij}. Several factors compose this uncertainty. The analytical error which accompanies any measurement, usually in the range of 10-30%, will always be present and should be reported if no other estimate is available. The larger variability in the receptor perceived source type composition will be caused by differences between individual emitters within the source types. Their processes, precursor materials and control equipment will not be the same, thus affecting their emissions compositions. Even emissions from a single source will change as its operating cycle progresses. The true composition perceived at the receptor will be a weighted average of many emissions characterizations, the weighting depending on source receptor spatial separations, pollutant transport and the source operating parameters. Obviously an exact knowledge of the weights is impossible and if they were known the receptor model would be superfluous. The extremes can be assessed by various source tests, however, and included in the uncertainty of the source composition.

Finally there is the uncertainty introduced by chemical fractionation after emissions have left the source. Sedimentation and volatility have been cited as examples. Source compositions should be modified to reflect likely modifications of this type and appropriate uncertainty estimates should be assigned.

No formula yet exists for assigning errors to the source compositions so the approach must be somewhat subjective. When only one sample is available at the very least its analytical error should be reported. With several samples from the same source type, the best estimate has to be the standard deviation of the individual measurements or the analytical uncertainty, whichever is larger (or they could be summed in quadrature). When atmospheric fractionation has been established, relative errors must be assigned to each component somewhat arbitrarily to reflect the confidence in each.

In selecting members of the chemical element balance source concentration matrix all potential contributors should be identified and all data pertaining to their chemical composition assembled. Sources which are known to have emitted nothing during the sampling period may be eliminated from consideration. Sources with similar compositions must be combined into representative source types and sources whose chemical compositions are non-descript cannot be included. This is not to say that these sources are unimportant contributors to the suspended particulate; they simply cannot be assessed by the chemical element balance unless other characteristics, perhaps a breakdown of their carbon compositions, are known. Other methods such as emission inventory scaling to contributions from sources included in the balance must be used to assess their impact.

For those source types remaining a best estimate of each chemical composition and its uncertainty must be made in the manner prescribed. This procedure will now be applied to the PACS source test data.

Table 3.1.12.1 contains the results of the winnowing process which reduces the number of source types for possible inclusion in the balance to sixteen. Where specific sources have been combined into a source type the composition of the best characterized or most likely source is chosen. The averages and standard deviations of PACS measurements are used to estimate source type compositions and their uncertainties except in the case of leaded auto exhaust and marine background which will be discussed shortly. Tables 3.1.12.2a&b present the source matrix candidates, their chemical compositions and uncertainties in the fine and coarse particulate modes.

When less than 10% of the total particulate was collected in the coarse mode the compositions of the fine particulate are reported; the

Table 3.1.12.1 Sources Included in and Excluded From the Chemical Element Balance

Eliminated due to lack of emissions during PACS intensive chemical analysis days.

3c. Coal combustion
4a. Forest Fires
7c. Alumina Handling
9i. Sludge Burning

Eliminated because emissions do not appear significant even though they do exist.

5b. Forest Products Smelt Tank
5c. Forest Products Incinerator
5e. Forest Products Veneer Dryer
5d. Forest Products Wood Processing
6c. Animal Food Processing
9j. Chemical
9k. Manufacturing
9l. Incinerators

Eliminated because chemical composition data is inadequate.

2e. Misc. Transportation (Ships, air, tires, brakes)
5f. Forest Products Lime Recovery Kiln
5i. Paper Sludge Boiler
6d. Pollen
9c. Small Point Sources
9e. Cement Kiln
9f. Limestone Kiln
9g. National Lead Industries
9h. Galvanizing

Eliminated because source chemical composition is non-descript for constituents quantified.

2b. Unleaded Auto Exhaust
2c. Diesel Trucks
2d. Diesel Trains
3b. Distillate Oil Combustion
3d. Natural Gas Combustion
6a. Flour Processing
6b. Grain Elevators

Table 3.1.12.1 (continued)

Combined into One Source Type (Underlined source indicates source composition chosen to be representative of that source type on the basis of its high emission rate in Table 3.1.1)

- Continental Background
  - Soil
  - Continental Background
  - Tropospheric Background
  - 1a. Agricultural Tilling

- Urban Dust
  - 1d. Street Dust
  - 1b. Rock Crusher
  - 1d. Asphalt Production

- Wood Burn
  - 4b. Slash Burn
  - 4c. Orchard Pruning
  - 4d. Fireplace
  - 4e. Woodstove
  - 4f. Domestic Burn

- Aluminum Industry
  - 5a. Aluminum Processing Stack
  - 5b. Aluminum Processing Roof Vent

Specific Source Types for inclusion in the Chemical Element Balance

- Continental Background (at background sites)
- Urban Dust (at urban sites)
- Marine Background
- 2a. Leaded Auto Exhaust
- 3a. Residual Oil Combustion
- Wood Burning
- 4g. Grass Field Burning
- 5a. Kraft Recovery Boiler
- 5g. Sulfite Recovery Boiler
- 5h. Hog Fuel Boiler
- Aluminum Industry
- 8a. Electric Arc Furnace
- 8b. Ferromanganese Furnace
- 9a. Carborundum Process
- 9b. Glass Furnace
- 9d. Carbide Furnace

Table 3.1.12.2a Chemical Element Balance Source Composition Matrix, Fine Particulate Composition

			Percent																							Percent
	Mnemonic		VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Fine
Marine	MARINF	Avg.	0.0	0.0	0.0	10	0.0	40	4.8	0.0	0.0	3.3	40	1.4	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.2	0.0	
		Std±				4		4	.9			1.3	10	.2	.2									.05		
Continental Dust	CDUSTF	Avg.	4.32	.59	0.0	0.0	0.0	.69	1.76	11.7	25.4	.07	0.0	1.0	.93	.76	.025	.03	.20	6.8	.0092	.02	.041	0.0	.006	
		Std±	1.7	.38	.1	.05	.01	.38	.62	2.2	3.4	.03	.01	.28	.37	.24	.006	.008	.09	2.3	.004	.004	.026	.01	.002	
Urban Dust	UDUSTF	Avg.	11.8	1.85	0.0	.42	0.0	1.25	1.30	8.84	22.3	.37	0.0	1.03	2.44	.64	.023	.045	.123	6.0	.0093	.030	.11	.020	.37	~10
		Std±	4.3	.91	.1	.31	.01	.34	.27	2.71	1.1	.15	.01	.06	.40	.12	.005	.017	.017	.6	.0033	.012	.037	.0056	.15	
Leaded Auto Exhaust	AUTPBF	Avg.	50	3.8	.91	1.3	0.0	0.0		1.1	.82	.4	3.0	.072	1.25	0.0	0.0	0.0	0.0	2.1	.018	.073	.35	5.0	20	~80
		Std±	10	1.4	.30	.4	.01	.05	.5	.5	.3	.13	1.0	.029	.5	.1	.005	.01	.016	.8	.008	.03	.13	1.7	3	
Residual Oil Combustion	RDOILF	Avg.	7.0	3.1	.65	48.1	.053	3.5	0.0	.53	.96	13.3	0.0	.28	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	.013	.11	90
		Std±	6.2	2.5	.44	11.9	.019	1.7	3	.24	.48	2.4	.1	.10	.64	.038	.75	.015	.013	.61	1.21	.025	.18	.021	.064	
Vegetative Burn 1	VBRN1F	Avg.	59	3.5	5.1	1.6	0.0	.65	0.0	1.44	.89	.43	5.55	.60	1.07	0.0	0.0	0.0	.12	.19	0.0	.09	0.0	.053	0.0	~99
		Std±	10	3.2	2.5	.88	1	.14		.83	1.1	.3	1.47	.013	.38				.12	.11		.04		.044		
Vegetative Burn 2	VBRN2F	Avg.	47	4.4	2.0	5.0	.32	.33	0.0	.45	.49	1.6	9.9	6.5	.92	.07	0.0	.012	.047	.054	0.0	.054	0.0	.045	0.0	~99
		Std±	37	8.2	2.5	5.4	.15	.34	1	.51	.78	1.5	5.1	4.5	.98	.07		.007	.042	.060		.060		.045		
Kraft Recovery Boiler	KRAFTF	Avg.	1.7	.22	0.0	40	0.0	12.7	.63	.25	.15	11.7	1.8	1.5	0.0	.006	.001	.28	.03	1.2	.13	.021	.069	.13	.013	87
		Std±	.21	.23	.3	2.1	.1	.71	.53	.014	.016	1.0	.42	.14	.5	.002	.001	.08	.004	.11	.014	.013	.021	.06	.011	
Sulfite Recovery Boiler	SULFTF	Avg.	0.0	0.0	.3	56	0.0	2.5	.73	0.0	.40	12	.58	30	2	.01	0.0	0.0	.054	.066	0.0	.016	.017	0.0	0.0	~90
		Std±						.8	.52		.15	2	.1	10	.2	.001	.001	.001	.070	.036	.001	.017	.002	.005	.03	
Hog Fuel Boiler	HOGFUF	Avg.	0.0	0.0	.51	33.8	.15	3.4	0.0	.24	.76	8.8	9.5	22.4	5.6	0.0	0.0	.015	.51	1.26	.0067	.12	.73	.055	.42	73
		Std±			.23	9	.05	2.9	1.0	.18	.37	2.4	4.9	11.2	4.0	.06	.002	.006	.34	.88	.0042	.06	.34	.03	.22	
Aluminum Processing	ALPROF	Avg.	3.9	2.3	.41	4.4	6.0	4.1	2.8	27	.34	1.4	1.33	.22	.33	.04	.064	0.0	.011	.45	.19	.044	.015	.C37	.012	56
		Std±	3.9	1.0	.18	3.9	2.3	1.7	1.8	8	.34	.2	.84	.06	.03	.03	.036	.01	.008	.29	.085	.007	.011	.054	.010	
Steel Electric Arc	STEELF	Avg.	0.0	0.0	0.0	2.5	0.0	1.26	6.5	.65	5.0	1.9	1.85	.92	6.2	.20	.06	2.1	8.7	32	.7	.28	1.2	0.0	.76	92
		Std±			1.4	1.3	.5	.48	.71	.16	.21	.0	.78	.07	.57	.02	.01	1.4	.9	3	.07	.03	.12	.1	.07	
Ferromanganese	FERMNF	Avg.	9	1.5	5.7	4.2	.29	3.1	0.0	.64	.99	1.7	.42	10.5	1.3	.046	.024	.042	17.3	2.1	0.0	.036	.58	.16	.045	92
		Std±	.9	.15	2.8	.4	.08	.3	4	.13	.30	.35	.16	3.9	.14	.007	.019	.0028	.99	1.4	.005	.004	.25	.22	.016	
Carborundum	CARBOF	Avg.	13.6	55	1.6	16	.05	.12	.78	.35	3.5	4.8	1.7	.79	.14	.014	.007	.009	.035	.33	.004	.019	.004	.017	0.0	82
		Std±	7.4	56	2.1	25	.03	.10	1.2	.40	4.3	6.6	1.5	1.1	.13	.019	.008	.011	.041	.61	.007	.023	.004	.010	.01	
Glass Furnace	GLASSF	Avg.	0.0	0.0	.62	65	.054	9.2	0.0	.19	.25	11.3	.06	1.37	.3	0.0	.0047	.19	.0021	.02	0.0	.0047	.011	.0063	.38	93
		Std±			.35	9.9	.023	1.0	1	.014	.07	2.3	.006	.28	.03	.005	.0002	.035	.0007	.002	.01	.0017	.0019	.0053	.06	
Carbide Furnace	CARBFF	Avg.	7.3	1.2	.57	3.2	0.0	.92	2.4	.58	2.5	1.6	1.05	1.25	30	0.0	.006	0.0	.042	.54	.022	.020	.015	0.0	.008	55
		Std±	1.3	.28	.24	.42	.1	.10	.35	.11	.07	.42	.07	.35	4	.02	.0005	.01	.0035	.08	.008	.011	.007	.01	.004	

Table 3.1.12.2b Chemical Element Balance Source Composition Matrix, Coarse Particulate Composition

	Mnemonic		VC	NVC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Percent Coarse
			Percent																							
Marine	MARINC	Avg.	0.0	0.0	0.0	10	0.0	40	4.8	0.0	0.0	3.3	40	1.4	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.2	0.0	
		Std±				4		4	.9			1.3	10	.2	.2									.05		
Continental Dust	CDUSTC	Avg.	4.32[a]	.59[a]	.009	.004	.0023	1.3	1.2	7.2	29.7	0.0	0.0	2.2	1.4	.82	.017	.01	.085	4.76	.009[a]	.02[a]	.041[a]	0.0	.042	
		Std±	1.73	.38	.005	.001	.0005	.50	.31	1.7	1.5		.01	.24	.67	.15	.006	.006	.028	.85	.004	.004	.026	.01	.011	
Urban Dust	UDUSTC	Avg.	3.34	1.55	.02	.074	.008	1.75	1.54	6.6	28	0.0	0.0	1.03	3.0	1.01	.027	.045	.10	5.73	.004	.03	.11	.008	.37	~90
		Std±	.98	.78	.01	.045	.007	.091	.14	.7	1.5	.02	.02	.058	.22	.18	.005	.017	.011	.29	.003	.012	.037	.009	.15	
Leaded Auto Exhaust[a]	AUTPBC	Avg.	50	3.8	.91	1.3	0.0	0.0	0.0	1.1	.82	.4	3.0	.072	1.25	0.0	0.0	0.0	0.0	2.1	.018	.073	.35	5.0	2.0	~20
		Std±	10	1.4	.30	.4	.01	.05	.5	.5	.3	.13	1.0	.029	.5	.1	.005	.01	.016	.8	.008	.03	.13	1.7	3	
Residual Oil Combustion[a]	RDOILC	Avg.	7.0	3.1	.65	48.1	.052	3.5	0.0	.53	.96	13.3	0.0	.28	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	.013	.11	10
		Std±	6.2	2.5	.44	11.9	.019	1.7	3	.24	.48	2.4	.1	.10	.64	.038	.75	.015	.013	.61	1.21	.025	.18	.021	.07	
Vegetative Burn 1[a]	VBRN1C	Avg.	59	3.5	5.1	1.6	0.0	.65	0.0	1.44	.89	.43	5.55	.60	1.07	0.0	0.0	0.0	.12	.19	0.0	.09	0.0	.053	0.0	~1
		Std±	10	3.2	2.5	.88	<1	.14		.83	1.1	.36	1.47	.013	.38				.12	.11		.04		.044		
Vegetative Burn 2[a]	VBRN2C	Avg.	47	4.4	2.0	5.0	.32	.33	0.0	.45	.49	1.6	9.9	6.5	.92	.07	0.0	.012	.047	.054	0.0	.054	0.0	.045	0.0	~1
		Std±	37	8.2	2.5	5.4	.15	.34	1	.51	.78	1.5	5.1	4.5	.98	.07		.007	.042	.060		.060		.045		
Kraft Recovery Boiler	KRAFTC	Avg.	15.8	1.8	0.0	11.8	0.0	5.3	0.0	.28	.13	3.3	2.9	.40	.36	0.0	0.0	.48	.052	1.84	.22	.06	0.0	.056	0.0	13
		Std±	5.3	1.8	1.4	1.5	.5	.71	1	.09		.5	1.2	.11	.07	.2	.001	.18	.011	.55	.05	.02	.01	.003	.02	
Sulfite Recovery Boiler[a]	SULFTC	Avg.	0.0	0.0	.3	56	0.0	2.5	.73	0.0	.40	12	.58	30	2	.01	0.0	0.0	.054	.066	0.0	.016	.017	0.0	0.0	~10
		Std±			.1	6		.8	.52		.15	2	.1	10	.2	.001	.001	.001	.070	.036	.001	.017	.002	.005	.03	
Hog Fuel Boiler	HOGFUC	Avg.	11.1	4.3	.2	1.5	.11	.69	.46	.28	.96	.59	.83	1.3	5.2	.097	.0055	.0073	.29	.92	0.0	.023	.039	.0013	.020	~20
		Std±	5.4	1.4	.13	.37	.041	.96	.17	.09	.14	.06	.76	.21	.52	.08	.0035	.0015	.04	.22	.005	.0038	.0047	.00075	.003	
Aluminum Processing	ALPROC	Avg.	0.0	1.6	0.0	1.7	4.2	2.4	2.7	31.3	.097	0.0	1.2	0.0	.81	.076	.040	.016	0.0	.38	.21	.14	.009	.12	0.0	42
		Std±	2	1.5	2	1.1	1.9	.6	.55	4.9	.08	.3	.15	.1	.34	.041	.011	.018	.02	.15	.06	.04	.004	.20	.1	
Steel Electric Arc[a]	STEELC	Avg.	0.0	0.0	0.0	2.5	0.0	1.26	6.5	.65	5.0	1.95	1.85	.92	6.2	.20	.06	2.1	8.7	32	.7	.28	1.2	0.0	.76	8
		Std±			1.4	1.3	.5	.48	.71	.16	.21	.07	.78	.07	.52	.02	.01	1.4	.9	3	.07	.03	.12	.1	.07	
Ferromanganese[a]	FERMNC	Avg.	9	1.5	5.7	4.2	.29	3.1	0.0	.64	.99	1.7	.42	10.5	1.3	.046	.024	.042	17.3	2.1	0.0	.036	.58	.16	.045	8
		Std±	.9	.15	2.8	.4	.08	.3	4	.13	.30	.35	.16	3.9	.14	.007	.019	.0028	.99	1.4	.005	.004	.25	.22	.016	
Carborundum	CARBOC	Avg.	4.6	24	.83	1.6	0.0	.26	0.0	2.8	12	.41	.99	.72	.57	.033	.012	.004	.029	.27	.017	.055	0.0	.011	0.0	19
		Std±	2.3	15	.48	1.83	.4	.17	.4	4.3	15	.31	.43	1.1	.49	.019	.010	.007	.025	.21	.023	.018	.01	.009	.01	
Glass Furnace[a]	GLASSC	Avg.	0.0	0.0	.62	65	.054	9.2	0.0	.19	.25	11.3	.06	1.37	.3	0.0	.0047	.19	.0031	.02	0.0	.0047	.011	.0063	.38	7
		Std±			.35	9.9	.023	1.0	1	.014	.07	2.3	.006	.28	.03	.005	.0002	.035	.0007	.002	.01	.0017	.0019	.0053	.06	
Carbide Furnace	CARBFC	Avg.	4.5	3.6	0.0	.93	0.0	.43	1.25	.86	2.9	.54	.96	.48	25.8	0.0	.009	0.0	.036	.33	.021	.04	0.0	0.0	0.0	45
		Std±	.78	1.8	.5	1.1	.2	.05	.35	.13	1.3	.57	.63	.30	8.7	.02	.0009	.01	.01	.13	.006	.004	.01	.01	.02	

[a] Same as fine particulate

coarse mass collected in these cases was of the order of 100 μg and subject to large uncertainties (see section 4.7.2) and many of the chemical constituents measured were near their minimum detectable limits. Therefore percent compositions in these cases are not reliable.

The Al/Si fractionation is evident in the continental dust and urban dust fine particulate modes. Rahn (1976b) also observes fractionation in the total particulate mode; he attributes the lower Al/Si ratio for coarse particles to adhesion of small clay granules to the larger soil particles. PACS background Al/Si ratios for the total particulate samples are for the most part lower and more variable than the Al/Si ratio chosen for coarse continental dust in Table 3.1.12.2b, but in the absence of further investigation into these fractionation effects the PACS bulk soil measurements for urban dust and continental dust have been chosen as best estimates with percentage compositions from the resuspended sample substituted for those elements on which no data was obtained.

Only the actual sea salt portion of the marine background will be considered to obtain differentiation from the continental background, thus only SO_4^{-2}, Na, Mg, Cl, K, Ca and Br, those elements present in bulk seawater, need be quantified. The aged aerosol measurements of Hidy, et al. (1974) and PACS background sites show that the loss of Cl is substantial making the Cl/Na ratio of the sea aerosol typically quantified in the Portland area close to unity. Bromine probably experiences a similar effect, but its low contribution to the total sea salt mass makes its accurate determination less important. The sea salt composition presented in Tables 3.1.12.2a&b as marine background is obtained by assuming a Cl/Na ratio of one and that all constituents aside from Cl retain their basic bulk sea water ratios to Na. This approximation is fairly consistent with marine aerosol measurements presented in Table 3.1.10.3 after geological components have been subtracted. Since the sum of all components must be close to 100%, the figures in Tables 3.1.12.2a&b result. Uncertainties are chosen subjectively, but realistically; the Cl fraction could easily vary by ±30% of its value as an examination of ambient measurements in Table 3.1.10.3 shows. Other uncertainties are evaluated accordingly. For lack of further information the same composition is chosen for both fine and coarse marine background.

There is not a general consensus of how to precisely estimate the contribution of leaded auto exhaust despite its nearly unique tracer element, Pb. Pierson (1976) has noted that his reported value of >20% was representative of the conditions in 1971 and that two subsequent measurements in 1973 and 1974 of the mg of Pb emitted per mile decreased from 1971 in direct proportion to the average Pb/gallon concentration in gasoline. Although this does not necessarily imply a corresponding decrease in the percent Pb concentration in auto emissions it does suggest a sensitivity to the changing controls and regulations. Two trends suggest that Pierson's 20% value or a somewhat lower value is the one to use in contrast to the higher values presented in Table 3.1.2.1c, the decreasing lead content of gasoline and the increasing number of cars using lead free gasoline. Thus, a value of 20 ± 3% is used to represent the concentration of lead in automotive exhaust particulates as measured at a receptor site. Note that Pierson's value concerns all motor vehicles, not just lead burning autos, so that while this figure applies strictly to leaded auto exhaust it probably also includes the impact of all motor vehicles as their emissions should behave in the same manner. Br and Cl are volatile in nature and cannot be expected to retain the ratios to Pb measured in fresh auto exhaust. Table 3.1.2.1c shows an average Br/Pb ratio in ambient air of approximately .25, and since there are no significant sources of Pb common to all of the areas in which this ratio occurs it must be assumed typical of aged auto exhaust, with a larger uncertainty to reflect its less precise quantification. Minor components, including Cl, have been estimated very subjectively from Tables 3.1.2a-c and uncertainties have been assigned to reflect the confidence in these values.

Vegetative burning chemical compositions are included in the source matrix with great trepidation. The variability of all species is tremendous and the quality of the samples is somewhat dubious. True, samples from a chimney and woodstove are available, but these are very nondescript chemically when compared to the slash and simulated field burn samples and their small number can in no way reflect the variability which surely exists between different units. Averages of slash burn aircraft samples and field burn specimens were chosen because they represent extremes, the wood burn with much more chlorine than potassium and the grass burn with nearly equal quantities of each. This researcher does not believe that a distinction can be made between these two types of burn at this time, thus the designations Vegetative Burn 1 and Vegetative Burn 2 in Tables 2.1.12.2a&b. These source types should be considered equivalent, representing slash, grassfield, fireplace, woodstove, orchard prunings and domestic burning, contrary to the implied grouping of Table 3.1.12.1 which suggests distinctive chemical characters for wood and grass combustion.

3.2 LEAST SQUARES FITTING WITH ERRORS IN THE SOURCE COMPOSITIONS

The assumptions of the least squares fitting scheme are the following:

1. The correct form of the equations is known, in this case

$$\overline{C}_i = \sum_{j=1}^{p} \overline{a}_{ij} S_j, \quad i = 1,n, \quad \vec{\overline{C}} = \underset{\sim}{A}\vec{S} \qquad 3.2.1$$

   where the overbar indicates that the quantity is the true value, i.e., the value obtained in the absence of error. (Refer to Table 3.2.1 for the meaning of symbols. Equations are presented in matrix form and in individual component form where appropriate to accommodate readers of different mathematical backgrounds.)

2. The errors in measurement of $\overline{C}_i$ and $\overline{a}_{ij}$ are are uncorrelated and normally distributed with standard deviations of σ_{C_i} and $\sigma_{a_{ij}}$ respectively.
3. The measurements C_i and a_{ij} are representative samples of the population and contain no outliers.

A fourth assumption has been made commonly in the past: that the source composition coefficients are known exactly. Even a cursory examination of the source composition coefficients in the previous section verifies that the uncertainty in these values may be the major contributor to error in the predicted source contributions.

Only Hammerle and Pierson (1975) in the aerosol literature have considered the effect of errors in all observables on fitting parameters to an assumed function. They used the method described by Acton (1966), however, which is based on the assumption of equal standard deviations for all measurements, or homoscedasticity, a prerequisite rarely met by the majority of measurements. Least squares fitting when all observables contain error is a common problem in environmental work; an ancillary service of this discussion should be to inform the environmental research community

Table 3.2.1 Meanings of Symbols

C_i = The measured ambient concentration of element i

$\vec{C}$ = $(C_1 \ldots\ldots C_n)^T$, a column vector whose ith component is C_i

a_{ij} = The fraction of source j composed of element i, the source composition coefficient

$\vec{A}_j$ = $(a_{ij} \ldots\ldots a_{nj})^T$

$\underset{\sim}{A}$ = An nxp matrix whose jth column is $\vec{A}_j$; the source composition matrix

n = Number of ambient elemental concentrations used in the fit

p = Number of sources used in the fit

σ_{C_i} = Standard deviation of the C_i measurement

$\sigma_{a_{ij}}$ = Standard deviation of the a_{ij} measurement

$\underset{\sim}{V}_C$ = Diagonal matrix of variances of $\vec{C}$, $(\underset{\sim}{V}_C)_{ii} = \sigma^2_{C_i}$

$\underset{\sim}{V}_{A_j}$ = Diagonal matrix of variances of $\vec{A}_j$, $(\underset{\sim}{V}_{Aj})_{ii} = \sigma^2_{a_{ij}}$

S_j = Source contribution of source j

$\vec{S}$ = $(S_1 \ldots\ldots S_p)^T$

$\bar{\vec{C}}$, $\bar{\underset{\sim}{A}}$, $\bar{a}_{ij}$, $\bar{\vec{A}}_j$, $\bar{C}_{ij}$ = The overbar designates the true values of the observable

$\vec{C}^{k,k+1}$ etc. = The k or k+1 superscript designates the kth or (k+1)st estimate of a value

λ_i = Lagrange Multiplier

$\vec{\lambda}$ = $(\lambda_1 \ldots\ldots \lambda_n)^T$

that methods do exist to handle it (Deming, 1943; York, 1966; Hust and McCarty, 1967; Britt and Luecke, 1973; Barker and Diana, 1974; MacDonald, 1974, 1975; Luecke and Britt, 1975).

An analysis of the general case in approximate form was first proposed by Deming (1943) with an exact formulation for an arbitrary function being presented by Britt and Luecke (1973). The following derivation parallels Britt and Luecke's analysis.

By assumption 2, the probabilities of observing particular values between C_i and C_i+dC_i and a_{ij} and $a_{ij}+da_{ij}$ are

$$P(C_i)dC_i = \frac{1}{\sqrt{2\pi}\sigma_{C_i}} \exp\left\{-\frac{1}{2}\frac{(C_i-\bar{C}_i)^2}{\sigma_{C_i}}\right\}dC_i, \quad i=1,n \qquad 3.2.2$$

$$P(a_{ij})da_{ij} = \frac{1}{\sqrt{2\pi}\sigma_{a_{ij}}} \exp\left\{-\frac{1}{2}\frac{(a_{ij}-\bar{a}_{ij})^2}{\sigma a_{ij}^2}\right\} da_{ij}, \quad \begin{matrix} i=1,n \\ j=1,p \end{matrix} \qquad 3.2.3$$

Also by assumption 2, these probabilities are independent of each other, so the probability of observing a set of values between $C_1 \ldots . C_n$, $a_{11} \ldots$ $\ldots . a_{np}$ and $C_1 + dC_1 \ldots . C_n + dC_n$, $a_{11} + da_{11} \ldots a_{np} + da_{np}$ is the product of all the probabilities in eqs. 3.2.2 and 3.2.3

$$P(C_1 \ldots C_n, a_{11} \ldots . a_{np})dC_1 \ldots dC_n da_{11} \ldots .. da_{np} =$$

$$\frac{1}{(2\pi)^{\frac{n(1+p)}{2}}\sigma_{C_1} \ldots . \sigma_{a_{np}}} \exp\left\{-\frac{1}{2}\left(\sum_{i=1}^{n}\frac{(C_i-\bar{C}_i)^2}{\sigma^2_{C_i}} + \sum_{i=1}^{n}\sum_{j=1}^{p}\frac{(a_{ij}-a_{ij})}{\sigma^2_{a_{ij}}}\right)\right\} d_{C_1} \ldots . da_{np} \qquad 3.2.4$$

The unknown $\bar{C}_i$ and $\bar{a}_{ij}$, subject to the constraint of eq. 3.2.1, should be chosen to maximize the probability of obtaining the observed values. This is the case when

$$\chi^2 = \left[\sum_{i=1}^{n} \frac{(C_i-\overline{C}_i)^2}{\sigma^2_{C_i}} + \sum_{i=1}^{n} \sum_{j=1}^{p} \frac{(a_{ij}-\overline{a}_{ij})^2}{\sigma^2_{a_{ij}}} \right] \qquad 3.2.5$$

is a minimum.

To include the constraints, Eqs. 3.2.1 times arbitrarily chosen LaGrange Multipliers, λ_i, (Boas, 1966) can be added to the right side of eq. 3.2.5 without affecting the value of χ^2 (since 0 is being added).

$$\chi^2 = \left[\sum_{i=1}^{n} \frac{(C_i-\overline{C}_i)^2}{\sigma^2_{C_i}} + \sum_{j=1}^{p} \frac{(a_{ij}-\overline{a}_{ij})}{\sigma^2_{a_{ij}}} + \lambda_i \left(\overline{C}_i - \sum_{j=1}^{p} \overline{a}_{ij} S_j \right) \right] \qquad 3.2.6$$

The extremum value of χ^2 will occur when its derivatives with respect to the unknowns $\overline{C}_i$, $\overline{a}_{ij}$, λ_i, and S_j equal 0.

$$\frac{\partial\chi^2}{\partial\overline{C}_i} = \frac{C_i-\overline{C}_i}{\sigma^2_{C_i}} - \lambda_i = 0, \; i=1,n: \quad \underset{\sim}{V}_C^{-1} (\vec{C}-\vec{\overline{C}}) - \vec{\lambda} = \vec{0} \qquad 3.2.7$$

$$\frac{\partial\chi^2}{\partial\overline{a}_{ij}} = \frac{a_{ij}-\overline{a}_{ij}}{\sigma^2_{a_{ij}}} + \lambda_i S_j = 0, \; \begin{matrix} i=1,n \\ j=1,p \end{matrix}: \quad \underset{\sim}{V}_{A_j}^{-1}\left(\vec{A}_j-\vec{\overline{A}}_j\right) + S_j\vec{\lambda} = \vec{0} \qquad 3.2.8$$

$$\frac{\partial\chi^2}{\partial\lambda_i} = \overline{C}_i - \sum_{j=1}^{p} \overline{a}_{ij} S_j = 0, \; i=1,n: \quad \vec{\overline{C}} - \underset{\sim}{\overline{A}}\vec{S} = 0 \qquad 3.2.9$$

$$\frac{\partial\chi^2}{\partial S_q} = \sum_{i=1}^{n} \overline{a}_{iq}\lambda_i, \; q=1,p: \quad \underset{\sim}{\overline{A}}^T \vec{\lambda} = \vec{0} \qquad 3.2.10$$

Since the S_j are of primary importance, eqs. 3.2.7, 3.2.8, 3.2.9 and 3.2.10 can be manipulated, as did York (1966) in the two variable case, to eliminate the $\overline{a}_{ij}$ $\overline{C}_i$, and λ_i. This leaves p complicated equations, each cubic in a particular S_q with coefficients depending on the remaining S_j and mildly on S_q itself, thus requiring an interative solution.

An alternative approach (Britt and Luecke, 1973), which is still interative but computationally less complex, is to estimate values for the unknowns which satisfy eqs. 3.2.7 - 3.2.10 and calculate new estimates in terms of the old. The (k+1)th estimate of eq. 3.2.9's unknowns are found by a first order Taylor expansion about the previous, the kth, estimates.

$$\begin{aligned}&\vec{\bar{C}}^{k+1} - \bar{\underset{\sim}{A}}^{k+1}\vec{\bar{S}}^{k+1} \simeq \vec{\bar{C}}^{k} - \bar{\underset{\sim}{A}}^{k}\vec{\bar{S}}^{k} + \left(\vec{\bar{C}}^{k+1} - \vec{\bar{C}}^{k}\right)\\ &- \left(\bar{\underset{\sim}{A}}^{k+1} - \bar{\underset{\sim}{A}}^{k}\right)S^{k} - \bar{\underset{\sim}{A}}^{k}\left(\vec{\bar{S}}^{k+1} - \vec{\bar{S}}^{k}\right) = \vec{\emptyset}\end{aligned} \qquad 3.2.11$$

Obviously, once the first estimates are made, subsequent estimates can serve as inputs to the next iteration, a process that can be continued until a specified convergence (assuming the process does converge) is achieved. The choice of the initial estimate will be dealt with shortly.

Eqs. 3.2.7 and 3.2.8 are premultiplied by $\underset{\sim}{V}_{C_i}$ and $\underset{\sim}{V}_{A_j}$ respectively and $\vec{C}-\vec{\bar{C}}$ and $\vec{A}_j-\vec{\bar{A}}_j$ are replaced by the estimates $\left(\vec{C}-\vec{\bar{C}}^{k}\right) + \left(\vec{\bar{C}}^{k}-\vec{\bar{C}}^{k+1}\right)$ and $\left(\vec{A}_j-\vec{\bar{A}}_j^{\,k}\right)+\left(\vec{\bar{A}}_j^{\,k}-\vec{\bar{A}}_j^{\,k+1}\right)$. The results are substituted into eq. 3.2.11 to give

$$\vec{\bar{C}}^{k} - \bar{A}^{k}\vec{\bar{S}}^{k} \qquad 3.2.12a$$

$$+ \left(\vec{C}-\vec{\bar{C}}^{k}\right) \qquad 3.2.12b$$

$$- \left(\underset{\sim}{A}-\bar{\underset{\sim}{A}}^{k}\right)\vec{\bar{S}}^{k} \qquad 3.3.12c$$

$$- \bar{\underset{\sim}{A}}^{k}\left(\vec{\bar{S}}^{k+1}-\vec{\bar{S}}^{k}\right) \qquad 3.2.12d$$

$$- \left[\underset{\sim}{V}_C+\sum_{j=1}^{p}\underset{\sim}{V}_{A_j}\left(S_j^{\,k}\right)^2\right]\vec{\lambda} \qquad 3.2.12e$$

$$= \vec{\emptyset}$$

The matrix multiplier of $\vec{\lambda}$ in term 3.2.12e can be identified as what Barker and Diana (1974) term "the effective variance" of $\vec{C}$.

$$\underset{\sim}{V}_e^{\,k} = \underset{\sim}{V}_C + \sum_{j=1}^{p} \underset{\sim}{V}_{A_j} \left(S_j^{\,k}\right)^2 \qquad 3.2.13$$

Examination of a single element of this diagonal matrix

$$V_{e_{ii}}^{\,k} = \sigma_{C_i}^{2} + \sum_{j=1}^{p} \sigma_{a_{ij}}^{2} \left(S_j^{\,k}\right)^2 \qquad 3.2.14$$

shows each effective variance to be that which would be obtained by standard propagation of independent errors (Bevington, 1969) for the difference between the measured and calculated values of C_i, $C_i - \sum_{j=1}^{p} a_{ij} S_j^k$.

Substituting eq. 3.2.13 into eq. 3.2.12, premultiplying by $\underset{\sim}{\bar{A}}^{kT} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1}$ invoking eq. 3.2.10 and solving for $\vec{S}^{k+1}$ leaves

$$\vec{S}^{k+1} = \vec{S}^{k} + \left(\underset{\sim}{\bar{A}}^{kT} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1} \underset{\sim}{\bar{A}}^{k}\right)^{-1} \underset{\sim}{\bar{A}}^{kT} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1} \left[\vec{C} - \underset{\sim}{A}\vec{S}^{k}\right] \qquad 3.2.15$$

On the basis of this new estimation of $\vec{S}^k$, a new approximation of $V_e^{\,k}$ can be obtained from eq. 3.2.13 and a refined reckoning of $\bar{A}^k$ from a combination of eqs. 3.2.12, 3.2.15 and 3.2.8

$$\vec{\bar{A}}_j^{\,k+1} = \vec{A}_j + S_j^{\,k} \underset{\sim}{V}_{A_j} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1} \left[\underset{\sim}{I} - \underset{\sim}{\bar{A}}^{k} \left(\underset{\sim}{\bar{A}}^{kT} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1} \underset{\sim}{A}^{k}\right)^{-1} \underset{\sim}{\bar{A}}^{kT} \left(\underset{\sim}{V}_e^{\,k}\right)^{-1}\right] \left[\bar{C} - \underset{\sim}{A}\vec{S}^{k}\right] \qquad 3.2.16$$

for fresh input into eq. 3.2.15.

When

$$\frac{S_j^{\,k+1} - S_j^{\,k}}{S_j^{\,k}} < .01,\ j=1,p \qquad 3.2.17$$

for all S_j, the iteration process can be terminated with the confidence that additional passes will not improve values by more than 1%.

An important aspect of least squares fitting is the relationship between the errors of the calculated parameters and those of the observables. Certainly the source contributions, S_j, obtained from a fitting of the element balance equations can be no more precise than the measured concentrations in the atmosphere and in the sources, but the values obtained by Gartrell and Friedlander (1975) and Kowalczyk, et al. (1978) give that impression by making no provision for the propagation of uncertainties in the source characterization.

We assume that the final estimates, $\vec{\bar{\bar{C}}}^k$, $\vec{S}^k$, and $\bar{\underset{\sim}{A}}^k$, are close enough to the true values, $\vec{\bar{\bar{C}}}$, $\vec{S}$, and $\bar{\underset{\sim}{A}}$, that the Taylor series explansion of eq. 3.2.1 about the estimates is valid. Eq. 3.2.15 can then be used to obtain the difference between the true and estimated values of $\vec{S}$ and, with eq. 3.2.1, its relationship to the deviations of $\vec{\bar{\bar{C}}}$ and $\bar{\underset{\sim}{A}}$ from their true values. An estimate of the variance is the average of the sum of the squares of these deviations which would be obtained from many experiments which produces (Britt and Luecke, 1973)

$$\underset{\sim}{V}_S = \left[\bar{\underset{\sim}{A}}^{kT}\left(\underset{\sim}{V}_e^{\,k}\right)^{-1}\bar{\underset{\sim}{A}}^k\right]^{-1} \qquad 3.2.18$$

$\underset{\sim}{V}_S$ is not a diagonal matrix, indicating that the errors in the S_j are correlated with each other, a fact that must be remembered when they are propagated in other calculations. The square root of jjth diagonal element will provide the standard deviation estimate of the corresponding S_j.

A simplification offers an insight into the workings of the fitting procedure. First, assume that the estimated true values $\bar{\underset{\sim}{A}}^k$ are close enough to the measured values $\underset{\sim}{A}$ to be replaced by them.

$$\bar{\underset{\sim}{A}}^k = \underset{\sim}{A} \qquad 3.2.19$$

Eq. 3.2.15 then reduces to

$$\vec{S}^{k+1} = \left(\underset{\sim}{A}^T\left(\underset{\sim}{V}_e^{\,k}\right)^{-1}\underset{\sim}{A}\right)^{-1}\underset{\sim}{A}^T\left(\underset{\sim}{V}_e^{\,k}\right)^{-1}\vec{C} \qquad 3.2.20$$

which is in exactly the form of the normal least squares fitting problem

(Clifford, 1973, Mathews and Walker, 1965) with the exception that the *weighting* is now by the *inverse of the effective variances* as given by eq. 3.2.13 rather than solely by the inverse of the ambient concentration variances. If the error in the source compositions were nonexistent, $\bar{\underset{\sim}{A}}^k$ would equal $\underset{\sim}{A}$ identically, each effective variance would equal that of the corresponding ambient measurement, and eq. 3.2.19 would be exactly that used by Gartrell and Friedlander and Kowalczyk and Gordon. Barker and Diana (1974), Britt and Luecke (1973) and Powell and MacDonald (1972) show that eq. 3.2.19 used iteratively with eq. 3.2.13 gives an estimate of the parameters very close to those obtained from the more refined procedure of eqs. 3.2.5, 3.2.6 and 3.2.3. Such an estimate, termed "the effective variance fit" by Barker and Diana (1974), may be adequate for most applications.

It is now possible to outline an algorithm for implementation on a digital computer. Though conceivably any initial values for $\vec{S}^k$ and $\bar{\underset{\sim}{A}}^k$ could be chosen, it is wise to choose ones which are in the right neighborhood to facilitate a quick convergence. A bootstrap procedure suggests itself in which as a first cut

$$\bar{\underset{\sim}{A}}^0 = \underset{\sim}{A} \qquad 3.2.21$$

$$\vec{S}^0 = 0 \qquad 3.2.22$$

The first pass through eq. 3.2.13 and eq. 3.2.15 will produce $\vec{S}^1$ equal to that obtained by the normal least squares fitting with errors considered only in $\vec{C}_i$. Eqs. 3.2.16, 3.2.13 and 3.2.15 can then be used in turn until the convergence criterion of eq. 3.2.17 is met. An algorithm for the simpler effective variance technique would start with eq. 3.2.22 and would apply eqs. 3.2.13 and 3.2.20 successively until condition 3.2.17

is satisfied.

Britt and Luecke note that absolute convergence to a specific value is not guaranteed, though the convergence attained may be sufficient for practical purposes. Thus, the algorithm should contain a provision to alert the operator to convergence problems after a preset number of passes, allow him to step through several iterations, viewing the calculated parameters, and to decide whether the convergence available is suitable to his ends. Runs that do not settle down to unique values within a specified range must be dealt with case by case by changing the inputs on a physical basis.

The mathematical justification of a least squares fitting and error propagation scheme has been presented and an algorithm for applying it formulated. It is not yet clear how this fitting procedure compares with the traditional least squares approach nor how sensitive it is to deviations from its basic assumptions. These questions will be explored in the next section.

3.3 THE SENSITIVITY OF THE LEAST SQUARES CHEMICAL ELEMENT BALANCE TO TYPICAL MODEL MIS-SPECIFICATIONS

If the physical basis for a receptor model is correct, the assumptions of the solution procedure are met and the measurements of the observables are precise, then one can rest assured that the source influences implied by the model are realistic. In reality we know that none of the conditions is met in its entirety yet we apply these models to ambient data and accept the results without giving a thought to the effects of deviations from basic assumptions on our final results. Certainly some of those results appear reasonable, and the models may be robust enough to tolerate substantial aberration.

The application of more than one receptor model might lend credence to the results obtained from each if they are consistent, but as was shown in the previous chapter, since all models are based on the same physical source model, such consistency should be expected.

The effects of model mis-specifications cannot be assessed by the application of a receptor model to actual ambient data because the source impacts are unknown _a priori_; any values obtained have no standard against which to be compared. Furthermore, the matrix operations required for the least squares chemical element balance and factor analysis obscure direct relationships between inputs and outputs due to the interaction of the observables.

A standard can be defined, however. A simulated set of observables can be generated on the basis of an elementary source model and "experimental" uncertainty can be introduced by Monte Carlo perturbations. The source model can be as complicated as necessary to supply any desired deviation.

As discussed in Chapter 2 this general procedure can and should be applied to all receptor models. Many unmet conditions for many models can be postulated, however, too many to be examined in this document. The work here will confine itself to formulating an adequate source model to test a limited number of assumptions of the chemical element balance with least squares fitting.

The basic assumptions of the least squares version of the chemical element balance receptor model are the following:

1. The concentration of any species quantified at a receptor is a linear sum of the source contributions of that species.
2. All significant sources of each species included in the least squares fit are known.
3. The fractional composition of each source type measured at the receptor is known.
4. The variability of the source compositions is known.
5. Errors in the source type compositions are Gaussian distributed.
6. Errors in the source type compositions are uncorrelated with each other and with the errors in the ambient concentration measurements.
7. The uncertainties of the ambient measurements are known.
8. Errors in the ambient measurements are Gaussian distributed.
9. Errors in the ambient measurements are uncorrelated with each other and with the source composition errors.

A basic violation is inherent in the combination of assumptions three and four; if the source compositions are known, how can they contain error? The ordinary weighted least squares (OWLS) method deletes assumptions four through six. The Britt and Luecke and the effective variance methods would modify assumption three to read "the average values of the fractional source compositions are known."

In this work assumptions 1, 5, 6, 8 and 9 will not be questioned. Deviations from these are possible and could be significant; eventually the effects of these deviations should be evaluated. At the present time, however, it is felt that the greatest scrutiny should be given to deviations from assumptions 2, 3, 4 and 7.

The source model used to generate the simulated ambient data is a simple one, very similar to the chemical element balance receptor model of eq. 2.2.1, and follows directly from assumptions 1, 5, 6, 8, and 9.

$$C_i = \sum_{j=1}^{p'} \left(a'_{ij} + \varepsilon_{ij}\sigma'_{a_{ij}}\right) S'_j + \varepsilon_i \sigma'_{C_i}, \quad i=1,n \qquad 3.3.1$$

where ε_{ij} and ε_i are random numbers selected from a normal distribution with a mean of zero and a standard deviation equal to one. The symbols carry the same meanings as they did in the previous section (see Table 3.2.1) with the prime designating their source model rather than receptor model roles. The values of these primed parameters are not necessarily the same as their unprimed counterparts. In this way a set of C_i, with <u>a priori</u> known source contributions, is generated. Some or all of these C_i can be combined with any a_{ij}, p, σ_{C_i}, and $\sigma_{a_{ij}}$ in eq. 3.2.1 and the extent to which the known S_j' falls within the calculated $S_j \pm \sigma_{S_j}$ can be assessed.

An infinite number of such tests can be devised, so it is necessary to pose some important questions and select a subset of tests which will resolve them. The questions to be answered here are:

1. What is the effect on the S_j of mis-specification of the a_{ij} due to their uncertainties? (testing assumption 3).
2. Under what circumstances do the OWLS and effective variance fitting methods best estimate the S_j and σ_{S_j}?
3. What is the effect on the S_j and σ_{S_j} of mis-specification of $\sigma_{a_{ij}}$ and σ_{C_j}? (testing assumptions 4 and 7)
4. How does the selection of elemental concentrations to be included in the fit affect the S_j and σ_{S_j}?
5. Can two sources with similar contributions and similar compositions be resolved? At what values of uncertainties σ_{C_i} and $\sigma_{a_{ij}}$ does this resolution break down?

6. What is the effect on the S_j of under-specifying the number of source types in the least squares fit, $p<p'$? (testing assumption 2).

7. What is the effect on the S_j of over-specifying the number of source types in the least squares fit, $p>p'$? (testing assumption 2).

The chemical element balance source model was implemented by the computer program *CONGEN which used a standard algorithm based on the central limit theorem (Meyer, 1976) to create a list of zero mean, unit variance Gaussian-distributed random numbers from which ε_{ij} and ε_i were chosen sequentially. Any values for S_j', a_{ij}', σ_{C_i}', $\sigma_{a_{ij}}'$ and p' could be placed in appropriate files accessed by this program.

Ten sets of ambient concentrations, C_i, each with the same S_j', a_{ij}', σ_{C_i}', $\sigma_{a_{ij}}'$, and p', but with different values for ε_{ij} and ε_i, were produced from eq. 3.3.1 each time *CONGEN was run. The receptor model with assumed a_{ij}, σ_{C_i}, $\sigma_{a_{ij}}$, and p, which could be identical to or different from their primed source model counterparts, was then applied individually to each of these data sets. The purpose of this was to obtain an average S_j and the corresponding standard deviation. The same list of random numbers was used to generate each group of ten simulated ambient concentrations.

When the Britt and Luecke least squares fitting scheme incorporating eqs. 3.2.15, 3.2.16 and 3.2.13 was applied to these simulated data, convergence of the $\bar{a}_{ij}^{k+1}$ in eq. 3.2.16 could not be obtained. In one example, $\bar{a}_{V,RDOIL}$ increased by about 5% with each iteration while $\bar{a}_{Ni,RDOIL}$ decreased by about the same amount until their respectively large and small values caused computer overflows and non-invertable matrices. While the convergence properties of the Britt and Luecke algorithm in this application merit further investigation, the goals of the aerosol study were considered to be better served by a comparison of the traditional ordinary weighted least squares fit and the "effective variance" approximation to Britt and Luecke's exact formulation.

The computer program *CALCEB1 accessed the simulated data sets as well as the a_{ij} and $\sigma_{a_{ij}}$ and performed both the ordinary weighted least squares and the effective variance calculations of the source contributions. The number of chemical concentrations, n, and the number of sources, p, included in the fit could be chosen by operator interaction with the program. The output of *CALCEB1 consisted of the calculated source contributions and their uncertainties, the simulated ambient chemical concentrations and their uncertainties, the chemical concentrations calculated from eq. 2.2.1 based on the source contributions, and the ratios of the calculated to actual concentrations. This information was obtained for each of the ten data sets. The average and standard deviation of each source contribution over all ten sets was also calculated and reported.

Twenty-five trials involving different S_j', a_{ij}', σ_{C_i}', $\sigma_{a_{ij}}'$, p', a_{ij}, $\sigma_{C_{ij}}$, $\sigma_{a_{ij}}$, and p were made to obtain some answers to questions one through seven. The trials and the questions they were intended to investigate are reported in Table 3.3.1 and a summary of the results appears in Table 3.3.2.

Four modes of the chemical element balance were applied to the ten simulated data sets in each trial: the ordinary weighted least squares and effective variance methods with eight chemical concentrations included in the fit (the tracers Na, Cl, Al, Si, V, Ni, Br and Pb were chosen) and

Table 3.3.1 Description of Simulated Ambient Concentrations Tests of the Chemical Element Balance Receptor Model

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
1	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =5% of a'_{ij} σ'_{C_i} =5% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =5% of a_{ij} σ_{C_i} =5% of C_i	1,2,4	
2	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =10% of a'_{ij} σ'_{C_i} =10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =10% of a_{ij} σ_{C_i} =10% of C_i	1,2,4	
3	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =20% of a'_{ij} σ'_{C_i} =20% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =20% of a_{ij} σ_{C_i} =20% of C_i	1,2,4	
4	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =20% of a'_{ij} σ'_{C_i} =10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =20% of a_{ij} σ_{C_i} =10% of C_i	1,2,4	

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
5	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =20% of a'_{ij} σ'_{C_i} =20% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =10% of a_{ij} σ_{C_i} =10% of C_i	1,2,3,4	
6	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =30% of $a'_{\mathrm{Cl,MARIN}}$ =30% of $a'_{\mathrm{Br,\ AUTPB}}$ =25% of $a'_{\mathrm{K,UDUST}}$ =25% of $a'_{\mathrm{Fe,UDUST}}$ =25% of $a'_{\mathrm{Ca,UDUST}}$ $\sigma'_{a_{ij}}$ =10% of a'_{ij} for all others σ'_{C_i} =10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =10% of a_{ij} σ_{C_i} =10% of C_i	1,2,3,4	

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
7	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =30% of $a'_{Cl,MARIN}$ =30% of $a'_{Br,AUTPB}$ =25% of $a'_{K,UDUST}$ =25% of $a'_{Fe,UDUST}$ =25% of $a'_{Ca,UDUST}$ $\sigma'_{a_{ij}}$ =10% of all others σ'_{C_i}=10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}=\sigma'_{a_{ij}}$ σ_{C_i}=10% of C_i	1,2,3,4	
8	$p'=5$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =5% of a'_{ij} σ'_{C_i}=5% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =5% of a_{ij} σ_{C_i}=5% of C_i	1,2,4,5	When n=8, five sets showed negative contributions from UDUST or CDUST in both OWLS and eff. var.
9	$p'=5$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =10% of a'_{ij} σ'_{C_i}=10% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =10% of a_{ij} σ_{C_i} =10% of C_i	1,2,4,5	When n=8, seven sets showed negative contributions from UDUST or CDUST in both OWLS and eff. var.

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
10	$p'=5$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =20% of a'_{ij} σ'_{C_i}=20% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =10% of a_{ij} σ_{C_i}=10% of C_i	1,2,4,5	When n=8, nine sets (all but set 8) showed negative contributions from UDUST or CDUST in both OWLS and eff. var. None of the effective variance fits satisfied condition 3.2.17 after ten iterations.
11	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=from Table	1,2,4	Unusual ratios, calculated/ambient, data set 8. 1. n=8, OWLS F:.44,Cr:3.0,Pb:.45 2. n=8, eff.var. F:.47,Cr:3.1,Br:3.3 3. n=23, OWLS F:.35,Cr:2.1 4. n=23,eff.var. Cr:3.3
12	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,7	When n=8, eight sets showed substantial negative contributions from KRAFT in both OWLS and eff. var. When n=23, five sets showed a negative contribution, but it was always less than the predicted uncertainty. Ratios 1. SO_4:-1.0,Mg:2.4,S:-1.9,K:-.4,Cr:-31 Mn:.25 2. SO_4:-.9,Mg:2.3,S:-1.8,K:-.4,Cr:-30, Mn:.25,Br:2.2 3. All between .5 & 2.0 4. All between .5 & 2.0

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
13	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i} =10% of C_i	$p=6$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i} =10% of C_i	1,2,4,7	Most KRAFT and ALPRO contributions less than uncertainties though negative in many cases. <u>Ratios</u> for data set 8 1. SO_4:-1.0,Mg:2.4,S:-1.9,K:-.4,Cr:-30, Mn:.25,Cu:.46,Pb:.48 2. SO_4:-.8,F:-.8,Mg:2.3,S:-1.7,K:-.3, Cr:-29,Mn:.26,Br:2.2 3. All ratios between .5 and 2.0 4. All ratios between .5 and 2.0
14	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i} =10% of C_i	$p=7$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,7	When n=8 most data sets showed negative values for KRAFT and FERMN. The effective variance source contributions failed to converge within ten iterations in one data set: <u>Ratios</u> 1. VC:-1.5,NVC:-1.7,NO_3:-104,F:-46, Mg:3.7,S:-.1,K:-68,Ca:-22,Ti:-.4, Cr:-9,Mn:-1492,Fe:-2.2,Cu:-2.8, Zn:-14 2. NO_3:-14,SO_4:-.5,F:-8,Mg:2.5,S:-1.4, K:-11,Cr:-25,Mn:-226,Fe:.25,Cu:.26, Br:2.2 3. S:.49,Pb:.49 4. Br:2.1

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
15	$p'=4$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=8$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,7	Many negative values for ALPRO, FERMN & STEEL when n=8. Ratios 1. Large negative ratios for all species except tracers for which ratios are identically one. 2. " " 3. Cl:.47,Pb:.49 4. Br:2.1
16	$p'=6$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,6	Ratios 1. NVC:2.4,F:.02,Al:.35,Cr:.24,Zn:2.03 2. NVC:2.4,F:.02,Al:.34,Cr:.23,Zn:2.02 3. F:.02,Al:.27,Cr:.19 4. NVC:2.3,F:.02,Al:.31,Cr:.23
17	$p'=6$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,6	Ratios 1. NVC:2.4,F:.02,Al:.35,Cr:.28,Zn:2.04 2. NVC:2.4,F:.02,Al:.34,Cr:.35,Zn:2.05 3. F:.01,Al:.27 4. NVC:2.06,F:.02,Al:.3
18	$p'=6$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=6$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4	When n=8, the KRAFT contribution was negative in two out of 10 cases. Ratios 1. NVC:2.9,F:2.4,Cr:.02 2. NVC:2.9,F:2.4,Cr:0.0 3. All ratios between .5 and 2.0 4. NVC:2.3

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
19	$p'=6$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=7$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,7	Two trials in effective variance fit did not converge when n=8. The KRAFT contribution was negative in 8 cases and the FERMN contribution was negative in five Ratios 1. NVC:2.8,NO_3:.07,F:2.4,K:-.2,Cr:.05, Mn:-30 2. NVC:2.5,NO_3:-1.7,F:2.3,K:-2.1, Cr:.07, Mn:-92 3. All ratios between .5 and 2.0 4. NVC:2.3
20	$p'=6$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=8$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,7	When n=8 there were many negative contributions from KRAFT, FERMN and STEEL Ratios 1. Tracer ratios identically equal to one, most others outside of .5 to 2.0 limits 2. " " 3. NO_3:.49 4. NVC:2.3
21	$p'=8$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=4$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4,6	Ratios 1. NO_3:.25,F:.01,Mg:2.1,Al:.32,K:.25, Cr:.04,Mn:.01,Fe:.32,Cu:.46,Zn:.43 2. NO_3:.29,F:.01,Mg:2.1,Al:.32,K:.25, Cr:.04,Mn:.01,Fe:.33,Zn:.47 3. NO_3:.32,F:.01,Al:.31,K:.20,Ca:.48, Cr:.04,Mn:.01,Fe:.34 4. NO_3:.43,F:.01,Mg:2.5,Al:.37,K:.3, V:2.1,Cr:.06,Mn:.01,Fe:.43

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
22	$p' = 8$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i} =10% of C_i	$p=5$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i} =10% of C_i	1,2,4,6	Ratios 1. NO_3:.25,F:.01,Mg:2.1,Al:.32,K:.30, Ca:.48,Cr:.1,Mn:.01,Fe:.34,Cu:.49, Zn:.45 2. NO_3:.29,F:.01,Al:.32,K:.32,Mn:.01, Fe:.35 3. NO_3:.29,F:.01,Al:.31,K:.31,Ca:.44, Cr:.17,Mn:.01,Fe:.36 4. NO_3:.34,F:.01,Mg:2.1,Al:.38,K:.41, Cr:.22,Mn:.01,Fe:.42
23	p'=8 a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i} =10% of C_i	$p=6$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i} =10% of C_i	1,2,4,6	Ratios 1. NO_3:.33,Mg:2.8,K:.25,Ca:.47,Cr:.05, Mn:.01,Fe:3,Zn:.43 2. NO_3:.36,Mg:2.7,K:.27,Cr:.07,Mn:.01, Fe:.32,Zn:.47 3. NO_3:.35,Cl:.37,K:.28,Ca:.40,Cr:.16, Mn:.01,Fe:.34 4. NO_3:.20,K:.37,Mn:.01,Fe:.32,Zn:.49
24	p'=8 a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i} =10% of C_i	$p=7$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i} =10% of C_i	1,2,4,6	Many negative values for FERMN and KRAFT when n=8. Values did not converge for one data set with effective variance. Ratios 1. Nearly all ratios aside from the 2. tracers are too large or too small 3. Cl:.39,Ca:.46,Cr:.15,Fe:.36 4. Mg:2.6,Cr:.17,Fe:.42

Table 3.3.1 Continued

Trial	Source Model Parameters	Receptor Model Parameters	Questions being investigated	Observations
25	$p'=8$ a'_{ij}=from Table 3.1.12.2a $\sigma'_{a_{ij}}$ =from Table 3.1.12.2a σ'_{C_i}=10% of C_i	$p=8$ a_{ij}=from Table 3.1.12.2a $\sigma_{a_{ij}}$ =from Table 3.1.12.2a σ_{C_i}=10% of C_i	1,2,4	When n=8, many negative values for KRAFT, FERMN, and STEEL Ratios 1. Ratios are out of bounds for most 2. species not included in the fit 3. Ratios are all within .5-2.0. 4. " "

Table 3.3.2 Source Contributions Resulting from the Application of the Chemical Element Balance Receptor Model to Simulated Ambient Concentrations

Trial	Source Types	True source contribution S_j', $\mu g/m^3$	Average[a] Receptor Model Source Contributions, $\mu g/m^3$				"Best Results"[b] Receptor Model Source Contributions, $\mu g/m^3$			
			n=8 Fitting concentrations[c]		n=23 Fitting concentrations[d]		n=8 Fitting concentrations		n=23 Fitting concentrations	
			OWLS[e]	Effective Variance[f]	OWLS	Effective Variance	OWLS	Eff.Var.	OWLS	Eff.Var.
1	MARINF	20	19.4± .9	19.4± .9	19.3± .6	19.3± .6	19.3± .8	19.4±1.0	19.3± .6	19.2± .9
	UDUSTF	35	33.7±1.4	33.8±1.4	34.9±1.2	35.0±1.2	32.5±1.3	32.5±1.7	34.1± .8	33.8±1.0
	AUTPBF	30	30.2±1.7	30.3±1.6	29.6± .9	29.7± .9	29.6±1.1	30.1±1.5	29.5± .8	30.7±1.1
	RDOILF	15	14.8± .5	14.9± .5	15.0± .4	15.0± .4	14.7± .5	14.8± .8	15.3± .4	14.8± .5
	Total	100	98±2	98±2	99±2	99±2	96±2	97±3	98±1	99±2
2	MARINF	20	18.5±1.9	18.7±1.8	18.2±1.2	18.4±1.1	17.9±1.5	18.5±2.0	17.8±1.2	18.4±1.6
	UDUSTF	35	32.2±3.0	32.4±2.8	34.3±2.4	34.6±2.4	29.9±2.4	29.9±3.2	32.6±1.5	33.0±2.1
	AUTPBF	30	29.8±3.7	30.5±3.5	28.7±2.0	29.1±1.8	27.6±2.1	29.1±3.0	28.1±1.5	28.7±2.0
	RDOILF	15	14.5±1.0	14.6±1.0	14.8± .8	15.0± .7	14.3±1.0	14.5±1.5	15.5± .7	15.7±1.0
	Total	100	95±5	96±5	96±3	97±3	90±4	92±5	94±3	96±3
3	MARINF	20	15.9±4.1	16.6±3.8	15.3±2.6	15.9±2.2	13.7±2.4	15.3±3.5	13.8±2.0	15.2±2.8
	UDUSTF	35	28.6±6.6	29.2±6.1	31.5±5.4	32.9±4.9	24.1±3.9	24.5±5.3	27.9±2.7	29.1±3.8
	AUTPBF	30	27.7±8.4	29.6±8.0	25.4±4.8	27.0±3.8	21.3±3.4	25.0±5.4	24.0±2.6	26.2±3.8
	RDOILF	15	13.4±2.3	13.9±2.0	13.6±1.7	14.5±1.6	12.9±1.9	13.6±2.8	15.0±1.4	15.9±2.1
	Total	100	86±12	89±11	86±8	90±7	72±6	78±9	81±4	86±6

[a] Average and standard deviation of S_j obtained from ten independent simulated ambient concentration data sets.

[b] Results from one of the ten sets of source contributions, set 8.

[c] Concentrations of Na, Al, Si, Cl, V, Ni, Br and Pb were included in the least squares fit.

[d] Concentrations of VC(volatilizable carbon), NVC(non-volatilization carbon), NO_3^-, $SO_4^=$, F^-, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb were included in the fit.

[e] Ordinary weighted least squares fit after eqs. 2.2.8 - 2.2.11.

[f] Effective Variance least squares fit after eqs. 3.2.12, 3.2.20 and 3.2.18.

Table 3.3.2 Continued

Trial	Source Types	True S_j μg/m³	Averages, μg/m³ n=8 OWLS	Averages, μg/m³ n=8 Eff.Var.	Averages, μg/m³ n=23 OWLS	Averages, μg/m³ n=23 Eff.Var.	"Best Results", μg/m³ n=8 OWLS	"Best Results", μg/m³ n=8 Eff.Var.	"Best Results", μg/m³ n=23 OWLS	"Best Results", μg/m³ n=23 Eff.Var.
4	MARINF	20	18.0±3.5	18.7±3.3	17.3±1.9	18.0±1.6	16.9±1.4	19.6±3.2	17.1±1.2	19.5±2.6
	UDUSTF	35	29.5±6.4	30.7±5.4	32.3±4.8	34.0±3.6	30.5±2.4	30.2±4.9	29.8±1.4	31.5±3.0
	AUTPBF	30	28.9±6.2	31.5±4.9	28.0±3.5	29.7±2.3	24.5±1.9	31.2±5.0	26.5±1.4	29.4±3.0
	RDOILF	15	13.6±1.9	14.2±1.7	13.8±1.6	14.7±1.4	14.1±1.0	14.9±2.4	15.4± .7	16.1±1.6
	Total	100	90±8	95±8	91±6	96±5	86±4	96±8	89±2	97±5
5	MARINF	20	15.9±4.1	16.6±3.8	15.3±2.6	16.0±2.2	13.7±1.2	15.3±1.7	13.8±1.0	15.2±1.4
	UDUSTF	35	28.6±6.6	29.2±6.1	31.6±5.4	32.9±4.9	24.1±1.9	24.5±2.6	27.9±1.4	29.1±1.9
	AUTPBF	30	27.7±8.4	29.6±8.0	25.4±4.8	27.0±3.8	21.3±1.7	25.0±2.7	24.0±1.3	26.2±1.9
	RDOILF	15	13.4±2.3	13.9±2.1	13.6±1.8	14.5±1.6	12.9±1.0	13.6±1.4	15.0± .7	15.9±1.0
	Total	100	86±12	89±11	86±8	90±7	72±3	78±5	81±2	86±3
6	MARINF	20	18.3±2.8	18.8±3.2	17.6±1.4	18.0±1.5	18.7±1.6	20.6±2.3	18.4±1.3	19.9±1.8
	UDUSTF	35	32.4±3.1	32.6±2.9	34.1±2.8	34.4±2.8	30.5±2.3	30.4±3.2	33.2±1.5	33.2±2.1
	AUTPBF	30	27.5±6.8	28.7±6.1	27.0±4.0	28.1±3.0	20.3±1.6	23.1±2.5	23.2±1.3	25.9±1.9
	RDOILF	15	14.5±1.0	14.6±1.0	14.9± .9	15.1± .8	14.3±1.0	14.5±1.5	15.8± .7	15.9±1.0
	Total	100	93±8	95±8	94±5	96±4	84±3	89±5	91±2	95±4
7	MARINF	20	18.3±2.8	17.7±2.4	17.6±1.4	17.6±1.2	18.7±1.6	17.5±2.3	18.4±1.3	17.7±1.8
	UDUSTF	35	32.4±3.1	32.3±2.9	34.1±2.8	34.8±2.6	30.5±2.3	29.5±3.2	33.2±1.5	32.3±2.1
	AUTPBF	30	27.5±6.8	32.0±5.0	27.0±4.0	29.1±2.0	20.3±1.6	34.9±4.7	23.2±1.3	29.7±2.3
	RDOILF	15	14.5±1.0	14.7±1.0	14.9± .9	15.0± .7	14.3±1.0	14.5±1.5	15.8± .7	15.6±1.0
	Total	100	93±8	97±6	94±5	97±4	84±3	96±6	91±2	95±4
8	MARINF	20	20.2± .7	20.2± .7	20.1± .7	20.1± .7	20.3± .9	20.3±1.1	19.7± .7	19.7±1.0
	UDUSTF	35	29.7±40	31.1±39	33.3±3.6	33.3±3.5	54.8±36	57.9±45	39.2±3.6	39.2±4.4
	AUTPBF	30	30.4±1.4	30.5±1.3	30.4±1.0	30.4±1.0	27.7±1.1	27.8±1.5	28.7± .8	28.7±1.1
	RDOILF	15	15.2± .7	15.2± .65	14.9± .5	14.9± .5	14.6± .5	14.6± .8	14.3± .3	14.3± .5
	CDUSTF	35	38.1±33	37.0±32	35.2±3.6	35.3±3.5	23.4±29	20.8±37	32.9±5.1	32.9±4.2
	Total	135	133±50	134±50	133±5	134±5	140±46	141±58	135±6	135±5

Table 3.3.2 Continued

			Averages, μg/m³				"Best Results", μg/m³			
			n=8		n=23		n=8		n=23	
Trial	Source Types	True S'_j μg/m³	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.
9	MARINF	20	20.2±1.5	20.3±1.4	19.9±1.4	20.0±1.4	20.7±1.7	20.7±2.3	19.2±1.5	19.1±1.9
	UDUSTF	35	22.4±81	26.8±81	31.6±7.2	31.6±6.9	67.8±75	71.9±97	42.6±7.2	42.8±8.8
	AUTPBF	30	30.5±2.9	30.8±2.7	30.4±2.1	30.7±2.0	25.0±2.1	25.4±2.8	26.9±1.5	27.5±2.1
	RDOILF	15	15.4±1.3	15.4±1.3	14.7±1.0	14.8±1.0	14.1±1.0	14.1±1.4	13.4± .6	13.5± .9
	CDUSTF	35	42.6 67	39.2±67	34.4±7.4	35.0±7.2	17.1±60	13.7±79	31.4±6.9	31.3±8.4
	Total	135	131±84	133±84	131±10	132±10	145±96	146±125	133±10	134±13
10	MARINF	20	Not calcu-lated	Not calcu-lated	18.9±3.2	19.4±3.0	21.6±3.5	21.6±4.8	17.6±2.9	17.7±3.7
	UDUSTF	35			28.8±15.4	28.4±14.5	78.5±162	81.0±210	47.5±14	48.9±17.3
	AUTPBF	30			29.0±4.8	30.4±4.2	19.1±3.8	20.3±5.0	22.2±2.6	23.9±3.7
	RDOILF	15			13.7±2.2	14.1±2.1	12.9±1.9	12.9±2.6	11.1±1.1	11.5±1.6
	CDUSTF	35			29.8±16.2	32.1±15.4	16.6±130	14.8±170	29.5±13.6	28.6±16.7
	Total	135			120±22	124±21	149±208	151±270	128±20	131±25
11	MARINF	10	9.3±1.3	9.1±1.14	8.2±1.6	9.0± .7	9.5± .8	9.1±1.2	8.0± .5	9.6±1.1
	UDUSTF	10	9.7±1.1	9.5± .9	9.8±2.0	9.9± .9	8.6± .7	8.6±1.0	5.3± .5	9.4± .9
	AUTPBF	10	9.1±2.7	10.9±1.9	8.9±1.9	10.4±1.1	6.9± .5	12.4±2.0	8.2± .4	11.1±1.5
	RDOILF	10	8.9±1.4	9.4±1.2	8.2±1.9	10.0±1.3	9.2± .7	9.9±1.7	7.3± .4	10.4±1.1
	Total	40	37±3	39±2	35±3	39±2	34±1	40±3	29±1	41±2
12	MARINF	10	11.6±3.8	11.4±3.7	8.1±1.5	9.1± .8	17.9±1.9	17.7±5.0	7.5± .5	10.3±1.2
	UDUSTF	10	9.9±1.2	9.6± .9	10.2± .9	9.9± .9	9.2± .7	8.9±1.0	9.8± .5	9.7± .9
	AUTPBF	10	9.2±2.6	10.9±1.9	8.6±1.9	10.4±1.1	6.8± .5	12.3±2.1	6.8± .4	10.9±1.5
	RDOILF	10	9.0±1.4	9.6±1.2	8.7±2.3	10.1±1.5	9.9± .7	10.5±1.8	11.5± .5	11.5±1.4
	KRAFTF	0	-9.6±12.8	-9.0±12.4	0.0±1.3	-0.2±1.0	-33.3±6.7	-32.6±19	-2.5± .2	-2.0±1.1
	Total	40	30±14	33±13	36±4	39±2	11±7	17±20	33±1	40±3
13	MARINF	10	11.7±3.9	11.5±3.7	8.1±1.5	9.1± .8	17.9±1.9	17.6±5.4	7.4± .5	10.3±1.2
	UDUSTF	10	9.6± .9	9.5± .9	10.1±1.0	9.9± .8	9.3±1.0	9.0±1.1	9.7± .5	9.8± .9
	AUTPBF	10	9.2±2.6	10.9±1.9	8.6±2.0	10.4±1.1	6.8± .5	12.3±2.1	7.0± .4	10.1±1.5
	RDOILF	10	9.0±1.4	9.6±1.2	9.1±2.2	10.1±1.6	9.9± .7	10.5±1.8	11.0± .5	11.1±1.4
	KRAFTF	0	-10.0±13	-9.4±13	-0.1±1.1	-.2± .9	-33.2±67	-31.9±19	-2.4± .15	-1.8±1.1
	ALPROF	0	.3± .7	0.3± .7	0.0± .05	0.0± .05	-0.1± .5	-0.2±1.1	0.1± .02	.1± .1
	Total	40	30± 14	32± 14	36±2	39±2	11±7	17±20	33±1	40±3

Table 3.3.2 Continued

Trial	Source Types	True S_j' $\mu g/m^3$	Averages, $\mu g/m^3$				"Best Results", $\mu g/m^3$			
			n=8		n=23		n=8		n=23	
			OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.
14	MARINF	10	Not calculated	Not calculated	8.1±1.5	9.1± .8	17.4±1.9	17.2±5.4	7.5± .5	10.3±1.2
	UDUSTF	10			10.0± .9	9.7± .8	18.0±2.6	10.3±9.1	9.3± .5	9.2± .9
	AUTPBF	10			8.6±2.0	10.5±1.1	11.5±1.4	13.5±2.5	7.0± .4	11.1±1.5
	RDOILF	10			9.0±2.2	10.0±1.6	9.4± .7	10.4±1.9	10.9± .5	10.8±1.4
	KRAFTF	0			-0.1±1.1	-.1± .9	17.7±16	-23.1±52	-2.3± .2	-1.8±1.0
	ALPROF	0			0.0± .04	0.0± .04	1.3± .6	-0.1±2.3	.1± .02	0.1± .1
	FERMNF	0			0.0± .02	0.0± .03	-206± 57	-31.3±207	0.04±.01	.04±.02
	Total	40			36±4	39±3	-131±60	-3±214	32±1	40±3
15	MARINF	10	Not calculated	Not calculated	8.2±1.7	9.0±1.0	20.1±2.0	20.1±8.9	7.0± .5	9.6±1.3
	UDUSTF	10			10.0± .9	9.7± .8	47.7±6.7	47.7±75	9.6± .6	9.3± .9
	AUTPBF	10			8.6±2.0	10.5±1.1	17.9±1.9	17.9±7.3	6.9± .4	11.3±1.5
	RDOILF	10			9.0±1.7	10.0±1.7	16.8±1.7	16.8±11	10.0± .6	10.4±1.4
	KRAFTF	0			.3±1.8	.04±1.3	81.8±20	81.7±257	.5± .9	-.4±1.8
	ALPROF	0			.01±.04	0.0± .05	-0.9± .8	-0.9±6.7	.1± .01	.1± .1
	FERMNF	0			.04±.1	.03±.1	-482±81	-482±1106	.2± .06	.2± .1
	STEELF	0			-.05±.3	-.03±.15	-83±17	-83±135	-.4± .1	-.2± .3
	Total	40			36±4	39±2	-381±85	-382±1146	34±1	40±3
16	MARINF	10	11.9±1.8	12.9±1.2	12.4±2.6	13.9±1.5	11.9± .9	11.8±1.6	13.8± .8	12.6±1.5
	UDUSTF	10	12.7±1.8	12.1±1.5	11.6±1.5	11.8±1.3	13.8±1.2	13.2±1.4	10.9± .7	12.2±1.1
	AUTPBF	10	9.8±2.2	10.0±1.9	9.5±1.9	9.7±1.4	12.3± .9	12.3±2.0	7.5± .6	10.1±1.4
	RDOILF	10	9.3±1.3	9.6±1.4	10.9±1.6	14.9±1.8	10.6± .8	10.7± .8	8.7± .5	11.7±1.3
	KRAFTF	10								
	ALPROF	10								
	Total	60	44±4	45±3	44±4	50±3	49±2	48±3	41±1	47±3
17	MARINF	10	10.3±2.4	9.9±2.1	10.4±2.4	10.5±1.4	11.7±1.5	11.3±3.6	11.8± .9	10.3±1.4
	UDUSTF	10	12.6±1.7	12.0±1.5	10.7±1.4	11.2±1.2	13.8±1.2	13.2±1.4	10.6± .7	11.6±1.0
	AUTPBF	10	9.7±2.2	10.0±1.9	9.7±1.9	10.4±1.5	12.3± .9	12.3±2.0	8.1± .6	10.4±1.4
	RDOILF	10	9.1±1.4	9.4±1.4	9.0±1.5	9.8±1.7	10.5± .8	10.6±1.8	6.5± .6	8.4±1.3
	KRAFTF	10	11.5±9.3	12.5±8.8	10.6±2.1	10.6±2.5	.7±7	1.9±13	7.3±1.1	7.2±1.8
	ALPROF	10								
	Total	60	53±10	54±10	51±4	53±4	49±7	49±14	44±2	48±3

Table 3.3.2 Continued

			Averages, µg/m³				"Best Results", µg/m³			
			n=8		n=23		n=8		n=23	
Trial	Source Types	True S'_j µg/m³	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	EFf.Var.
18	MARINF	10	10.4±2.4	10.4±2.4	9.1±2.8	9.7±1.4	11.8±1.5	11.8±3.8	11.4± .9	9.7±1.4
	UDUSTF	10	10.5±1.3	10.5±1.4	9.6±1.3	10.0±1.2	11.4±1.3	11.5±1.4	10.0± .7	10.5±1.0
	AUTPBF	10	9.7±2.2	9.8±1.8	9.2±1.9	9.9±1.4	12.3± .9	12.0±1.9	7.5± .6	10.0±1.3
	RDOILF	10	9.0±1.4	9.3±1.4	8.5±1.5	9.1±1.6	10.4± .8	10.5±1.8	6.0± .6	7.8±1.2
	KRAFTF	10	7.6±9.5	7.3±9.6	10.8±2.1	10.6±2.4	-3.2±6.7	-3.5±13.8	7.5±1.1	7.2±1.8
	ALPROF	10	9.8±2.0	9.8±2.0	8.2±2.7	9.8±2.4	10.6±1.6	10.7±3.7	4.5± .4	7.2±1.9
	Total	60	57±10	57±10	55±5	59±4	53±7	53±15	47±2	53±4
19	MARINF	10	Not calcu-lated	Not calcu-lated	9.1±2.8	9.7±1.4	11.8±1.5	11.8±3.8	11.4± .9	9.7±1.4
	UDUSTF	10			9.6±1.5	10.1±1.2	11.6±2.9	11.9±7.2	9.6± .7	10.5±1.1
	AUTPBF	10			9.2±1.8	9.9±1.4	12.3±1.2	12.1±2.2	7.6± .6	10.0±1.3
	RDOILF	10			8.5±1.5	9.1±1.4	10.4± .8	10.5±1.8	6.0± .6	7.8±1.2
	KRAFTF	10			10.8±2.1	10.6±2.4	-2.3±17	-1.0±42	7.4±1.1	7.3±1.8
	ALPROF	10			8.2±2.7	9.8±2.4	10.7±1.6	10.7±3.9	4.5± .4	7.2±1.9
	FERMNF	0			0.0± .02	0.0± .02	-3.6±63	-11±165	.02±.01	0.0± .02
	Total	60			55±5	59±4	51±65	45±170	47±2	52±4
20	MARINF	10	Not calcu-lated	Not calcu-lated	9.1±2.9	9.6±1.5	11.1±1.7	11.1±4.0	12.1± .9	10.1±1.5
	UDUSTF	10			9.7±1.5	10.2±1.3	5.1±7.4	5.1±19.7	8.7± .8	10.2±1.2
	AUTPBF	10			9.2±1.8	9.9±1.4	11.2±1.7	11.2±3.1	7.7± .6	9.9±1.4
	RDOILF	10			8.5±1.4	9.1±1.5	9.2±1.5	9.2±3.6	6.5± .6	7.9±1.2
	KRAFTF	10			11.4±3.5	10.7±2.7	-17.0±23	-17.0±62	5.5±1.2	6.5±1.9
	ALPROF	10			8.2±2.7	9.8±2.4	11.1±1.7	11.1±3.9	4.5± .4	7.3±1.9
	FERMNF	0			.1± .2	0.0± .1	60±91	60±263	-.3± .1	-.1± .2
	STEELF	0			-.1± .5	-.1± .3	17±18	17±43	.7± .2	.3± .3
	Total	60			56±5	59±4	107±96	108±275	45±2	52±4

Table 3.3.2 Continued

Trial	Source Types	True S_j' µg/m³	Averages, µg/m³ n=8 OWLS	Averages, µg/m³ n=8 Eff.Var.	Averages, µg/m³ n=23 OWLS	Averages, µg/m³ n=23 Eff.Var.	"Best Results", µg/m³ n=8 OWLS	"Best Results", µg/m³ n=8 Eff.Var.	"Best Results", µg/m³ n=23 OWLS	"Best Results", µg/m³ n=23 Eff.Var.
21	MARINF	10	12.5±2.0	14.3±1.3	13.9±2.9	16.9±1.7	14.8±1.1	15.3±2.0	9.4± .7	17.7±2.2
	UDUSTF	10	15.7±1.5	14.7±1.4	15.7±2.4	17.0±1.7	15.1±1.3	14.4±1.5	13.8± .9	16.5±1.5
	AUTPBF	10	10.3±2.0	11.0±1.5	10.9±1.9	13.0±1.7	9.1± .7	11.4±1.9	10.9± .6	13.6±1.9
	RDOILF	10	11.0±1.5	11.7±1.4	13.9±2.1	23.2±3.2	12.0± .9	12.4±2.1	16.1± .7	22.7±2.4
	KRAFTF	10								
	ALPROF	10								
	FERMNF	10								
	STEELF	10								
	Total	80	49±4	52±3	54±5	70±4	51±2	53±4	50±2	71±4
22	MARINF	10	10.3±2.5	9.9±2.3	11.4±2.8	11.9±2.4	13.7±1.7	12.8±4.1	7.1± .8	11.7±2.0
	UDUSTF	10	15.5±1.5	14.6±1.4	16.1±2.8	17.4±1.9	15.0±1.3	14.4±1.5	14.0± .9	16.8±1.4
	AUTPBF	10	10.2±2.1	11.0±1.5	10.8±2.0	14.2±1.9	9.1± .7	11.5±1.9	10.8± .6	15.2±1.9
	RDOILF	10	10.1±1.5	11.4±1.4	11.3±1.6	12.1±3.0	11.9± .9	12.2±2.1	13.1± .8	12.0±2.0
	KRAFTF	10	17.2±8.0	18.4±7.3	15.9±7.3	19.1±8.1	6.7±8.2	10.4±15.3	14.6±2.0	19.8±3.6
	ALPROF	10								
	FERMNF	10								
	STEELF	10								
	Total	80	64±9	66±8	66±9	75±9	57±9	61±16	60±3	76±5
23	MARINF	10	10.3±2.5	10.2±2.5	10.5±3.1	10.9±2.0	13.7±1.7	13.4±4.3	3.7± .9	11.0±2.0
	UDUSTF	10	12.8±1.2	12.8±1.2	14.3±2.9	15.8±2.0	12.5±1.4	12.4±1.5	12.1± .9	15.1±1.4
	AUTPBF	10	10.1±2.1	10.8±1.4	10.5±2.0	13.6±1.7	9.1± .7	11.3±1.9	10.6± .6	14.4±1.9
	RDOILF	10	10.6±1.5	11.2±1.4	10.8±1.7	11.3±2.3	11.8± .9	12.1±2.1	12.8± .8	11.4±1.9
	KRAFTF	10	13.1±8.4	13.5±8.2	15.5±7.1	18.6±7.8	1.9±8.3	3.6±16	14.3±2.0	18.8±3.5
	ALPROF	10	10.3±3.4	10.3±3.4	9.3±4.0	11.7±5.3	12.6±1.8	12.6±4.4	10.0±1.0	13.2±3.3
	FERMNF	10								
	STEELF	10								
	Total	80	67±10	69±10	71±10	82±10	62±9	65±17	64±3	84±6

Table 3.3.2 Continued

Trial	Source Types	True S'_j μg/m³	Averages, μg/m³				"Best Results", μg/m³			
			n=8		n=23		n=8		n=23	
			OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS	Eff.Var.
24	MARINF	10	Not calcu-lated	Not calcu-lated	10.2±2.8	9.7±1.6	13.2±1.7	13.2±4.4	4.1± .9	10.6±1.9
	UDUSTF	10			13.0±2.7	14.0±2.0	21.0±2.8	21.7±12.3	11.1± .9	13.0±1.4
	AUTPBF	10			9.2±1.9	10.9±1.2	12.8±1.3	12.7±2.4	9.3± .6	11.1±1.9
	RDOILF	10			10.2±1.6	10.8±2.0	12.2± .9	12.2±2.2	12.0±..8	12.8±3.5
	KRAFTF	10			12.5±6.5	14.0±6.9	53.1±17	56.4±67	11.6±2.0	12.3±3.1
	ALPROF	10			8.6±3.9	9.3±4.3	14.0±1.8	14.1±5.6	9.3±1.0	12.3±
	FERMNF	10			11.7±1.9	15.2±1.5	-204±58	-218±275	11.9± .8	17.3±1.8
	STEELF	10								
	Total	80			75±9	84±9	-78±60	-88±284	69±	88±
25	MARINF	10	Not calcu-lated	Not calcu-lated	9.7±3.2	10.6±1.5	13.0±1.9	13.0±5.1	2.0±1.0	11.8±2.0
	UDUSTF	10			10.0±3.2	10.0±1.3	19.6±7.3	19.6±35	9.7±1.0	9.4±1.4
	AUTPBF	10			9.2±1.7	10.1±1.1	12.5±1.7	12.5±4.1	9.3± .6	10.3±1.5
	RDOILF	10			10.0±1.5	10.4±1.2	11.9±1.5	11.9±5.6	11.8± .8	11.5±2.0
	KRAFTF	10			9.2±4.9	8.9±4.0	50.4±21.2	50.4±114	11.1±2.0	6.1±3.6
	ALPROF	10			8.7±3.9	9.8±2.9	14.1±1.9	14.1±5.5	8.3±1.1	11.8±3.0
	FERMNF	10			10.4±2.0	10.5±1.7	-192±80	-192±487	11.6± .8	12.4±1.8
	STEELF	10			7.4±3.8	9.2±1.5	4.2±20	4.2±68	3.3± .7	8.9±1.4
	Total	80			75±9	79±3	-67±86	-67±86	67±3	82±6

with 23 chemical concentrations included (volatilizable carbon (VC), non-volatilizable carbon (NVC), NO_3^-, SO_4^{-2}, F^-, Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, and Pb--these are the species quantified by the PACS.) Thus, questions 1,2 and 4 were investigated in all trials.

Trials 1-7 were directed toward the investigation of question three. In these tests a basic source set consisting of fine particulate contributions from marine background, urban dust, leaded auto exhaust and residual oil combustion was chosen as the most general one since these sources are present in many urban areas, have some relatively unique and well-quantified tracer elements (Na and Cl for marine, Al and Si for urban dust, Pb and Br for auto exhaust and V and Ni for residual oil combustion), and have some minor chemical constituents in common (K and Mg in marine and urban dust, Cr in urban dust and residual oil, Zn in auto and residual oil, Fe in urban dust, auto exhaust and residual oil combustion). The true source model contributions, the S_j', were chosen as 20,35,30 and 15 $\mu g/m^3$ for marine background, urban dust, auto exhaust, and residual oil combustion, respectively. These values are high for an urban area but are convenient for illustrative purposes because their sum is 100 $\mu g/m^3$. Their ratios to each other are possible in certain urban situations and were selected to be within a factor of three so that no subset of source types would dominate the simulated ambient concentrations, the C_i.

Trials 8-10 were intended to study question 5, the resolution of two source types of similar composition. A 35 $\mu g/m^3$ contribution of continental background dust was added to the source model; its source composition was added to the receptor model.

In trials 11-25 an attempt was made to resolve questions six and seven. *CONGEN was run with four, six and eight source model source contributions of 10 $\mu g/m^3$ apiece. The receptor model with the number of source types ranging from four to eight was applied to each of these data sets.

In all trials the source compositions, a_{ij}' and a_{ij}, were selected from Table 3.1.12.2a and the mnemonics in Table 3.3.2 correspond to the source types listed in Table 3.1.12.2a. Uncertainties in these coefficients, $\sigma'_{a_{ij}}$ and $\sigma_{a_{ij}}$, were selected as fixed percentages of a_{ij}' and a_{ij} in trials 1-10 and were set equal to the standard deviations in Table 3.1.12.2a for trials 11-25. Standard deviations of ambient concentrations, σ'_{C_i} and σ_{C_i}, were always chosen as fixed percentages of those concentrations.

The detailed output of these twenty-five trials comprises a volume of computer output four inches thick. Fortunately, the salient features can be compactly summarized in the form of Table 3.3.2.

The third column of this table contains the standard against which the calculated source contributions should be compared. These are the S_j' used in the source model, and they would be obtained exactly from the receptor model if assumptions 1-9 were met and all uncertainties were equal to zero.

Columns four through eight contain the averages and standard deviations of the source contributions obtained from the ten simulated data sets contained within each trial. Columns 9 through 13 contain the results from the application of the four receptor model modes to one of the ten simulated data sets within each trial. Set eight was chosen because, of the ten, its results appeared to most closely approximate the average values. Since the same list of random numbers in the same order was used in all runs of *CONGEN, the changes in the results in this data set from trial to trial are comparable.

Also included with each trial is the total mass loading predicted by each mode of the receptor model obtained by summing the individual source contributions. The standard deviation associated with this value equals the square root of the sum of the squares of the standard deviations of the individual source contributions. This procedure is not strictly valid in the "best results" cases because the source contribution uncertainties are not independent of each other (see section 3.2).

The following points of comparison are important:

1. The ratios of the average and best results source contributions to the true source contributions: The receptor model mode for which these ratios most closely approximate unity is the most accurate for the conditions of that trial.

2. The standard deviations of the source contribution averages: If these represent large proportions of the averages then the values obtained between individual data sets must have been highly variable. The receptor model mode for which these standard deviations are the smallest is the most precise for the conditions of the trial.

3. The extent to which the uncertainty of a single application of the receptor model accounts for the actual uncertainty of the source contribution: Comparing the standard deviations reported in the best results columns with those of the corresponding receptor model mode average columns shows whether or not the actual variability is well estimated by receptor model analysis of a single data set.

4. Inconsistencies in calculated source contributions or the ratios of calculated to ambient concentrations (ambient refers to the simulated concentrations, calculated refers to those obtained from summing individual source contributions to a chemical species based on the receptor model prediction): Many negative or extreme values for source contributions suggest receptor model inadequacy. Calculated to ambient concentration ratios significantly different from unity reflect the same thing.

As an example, consider the results of trial 3. This is a good illustration because the uncertainties of 20% applied to all observables (a_{ij}, a_{ij}', and C_i) are close to those to be expected in actual field study data; in certain cases they are probably conservative.

Figures 3.3.1a-f show the variability of one of the source type contributions, that of urban dust, for the ten data sets of trial 3 obtained for six different receptor model modes. The application of the tracer method, eq. 2.2.2, using Si and Al in Figures 3.3.1a and 3.3.1b respectively, exhibits a major limitation of this method when uncertainties exist; different magnitudes of the source contributions are obtained from the same data sets. In set six the Si tracer predicts 18 $\mu g/m^3$ while the Al tracer yields 42 $\mu g/m^3$, a factor of two difference. This is an extreme case, but perfectly possible when uncertainties of 20% exist. This type of discrepancy argues for the use of more than one tracer for each source type, and this research has been conducted in that vein.

The dotted lines in Figure 3.3.1a-f represent the averages of all ten source contributions and the bar labeled (b) at the beginning of each graph measures one positive and negative standard deviation of the ten values on both sides of this average. The bar labeled (a) represents the positive and negative standard deviation predicted by the receptor model, results from eq. 2.2.3 for the tracer method, from eq. 2.2.11 for the ordinary weighted least squares (OWLS) method, and from eq. 3.2.17 for the effective variance method.

From these figures it is evident that as the number of concentrations included in the fit increases, the variability in the source contributions decreases and that the effective variance estimates of the standard

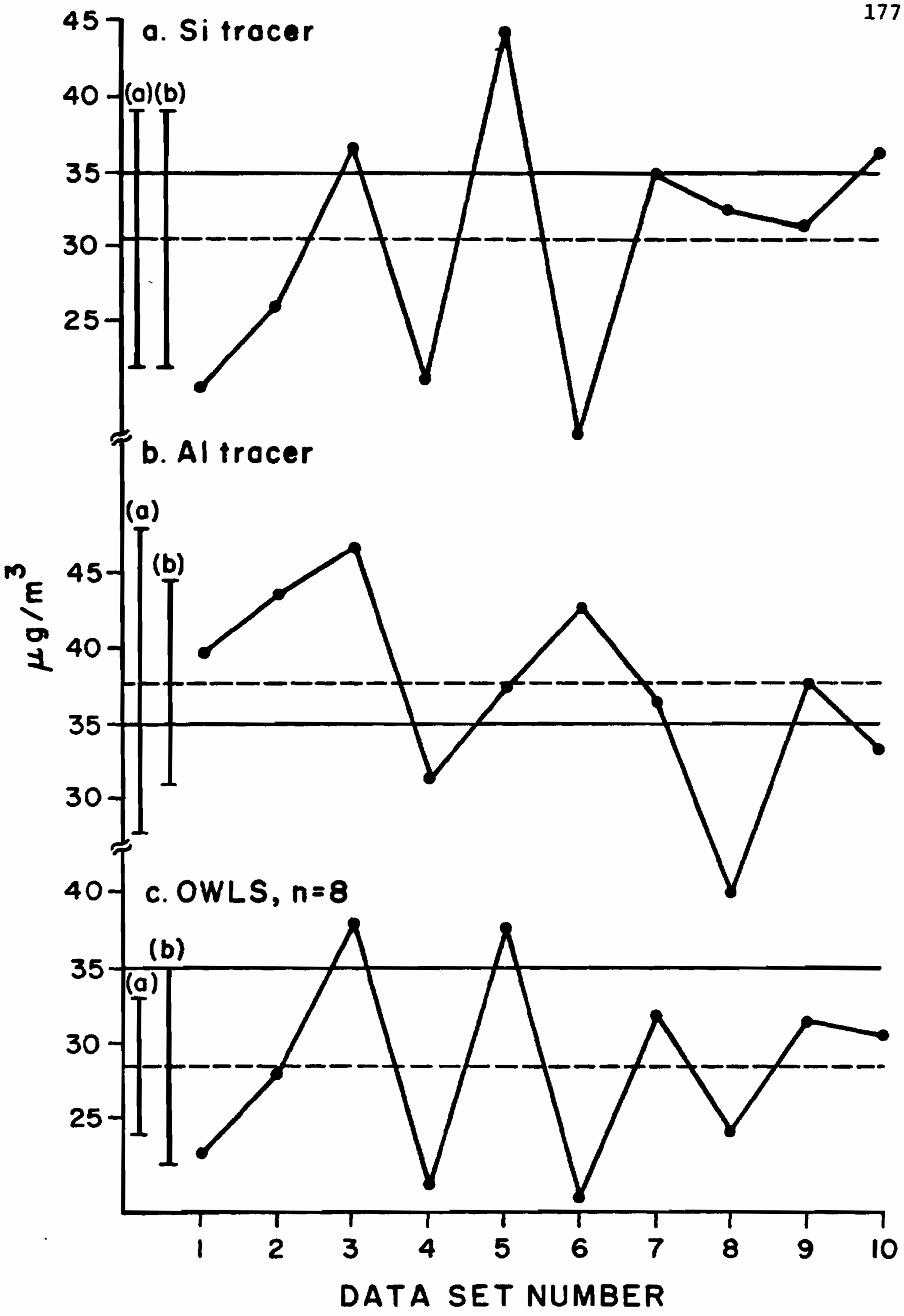


Figure 3.3.1. Variation of urban dust contribution for all data sets of trial 3. The uncertainty of each observable is 20%.

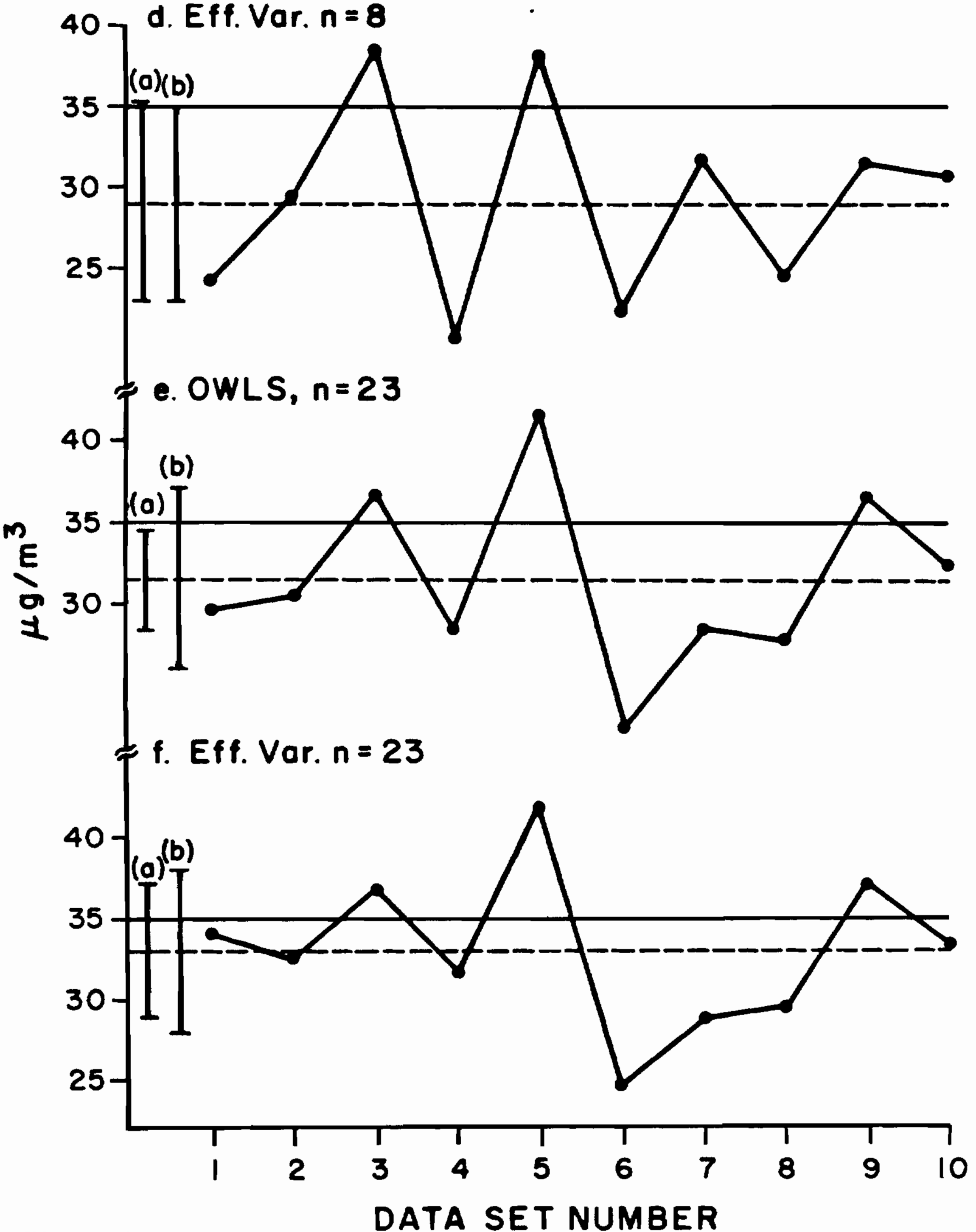


Figure 3.3.1. (continued) The solid line represents the true source contribution while the dotted line indicates the average of the ten data sets. Bar (b) is equal in length to two standard deviations of the ten data set values. Bar (a) is equal in length to two standard deviations as calculated by the receptor model applied to data set 8.

deviation is a better approximation than the estimate of the ordinary weighted least squares.

Drawings such as these could be made for all source contributions calculated by all receptor model modes from all data sets of every trial; certainly such an encyclopedia is unnecessary if the information in Table 3.3.2 can be mentally visualized.

Additional information from the ratios of calculated to measured concentrations for data set eight of trial three is summarized in Table 3.3.3. These ratios have been used in previous applications of the chemical element balance receptor models as a verification of the presence of the predicted sources. Ratios of unity are desired. Ratios much less than one suggest a missing source of that chemical species while ratios greater than one point to a source which doesn't belong (all of this assumes that the source chemical compositions are known fairly well). In trial 3, even with all sources accounted for, Table 3.3.3 shows that these ratios can easily vary from .5 to 2.0 solely due to uncertainties in the ambient measurements and source compositions of 20%. When the unique tracer method is used, the discrepancies are even higher. Ratios obtained from ambient data by Kowalczyk, et al. (1978) are also presented for comparison. With the possible exceptions of Cl and Cr these ratios derived from an ordinary weighted least squares (which was really a unique tracer method for all sources except geological material and coal combustion) are comparable to those of the unique tracer application to data set 8 of trial 3. In these trials, instances in which ratios did not fall reasonably within the .5 to 2.0 range are noted in the observations portion of Table 3.3.1.

Table 3.3.3 Ratios[a] of Calculated and Measured Concentrations

Species	Concentrations in fit $n=8^b$		Concentrations in fit $n=23^c$		Concentrations in fit $n=4^d$	Ratios from Kowalczyk et al.(1978)
	OWLS	Eff.Var.	OWLS	Eff.Var.	OWLS & Eff.Var.	
VC	.71	.77	.77	.83	.77	
NVC	.83	.91	1.0	.91	.71	
NO_3^-	.84	.93	.93	1.0	.63	
SO_4^{-2}	.63	.67	.70	.76	.83	
F	.53	.56	.63	.68	.76	
Na	1.2	1.3	1.23	1.4	1.0	1.0[e]
Mg	1.1	1.2	1.13	1.2	1.2	.48
Al	1.2	1.2	1.3	1.4	1.0	1.15[e]
Si	.76	.77	.92	.92	.59	
S	.96	1.0	.98	.96	.77	
Cl	.53	.59	.53	.59	.50	6.2
K	.50	.54	.56	.59	.43	.67
Ca	.80	.80	.84	.90	.89	.36
Ti	.83	.83	.92	1.0	.63	1.0
V	.71	.71	.83	.92	1.0	1.0[e]
Cr	1.1	1.1	1.3	1.3	1.0	.27
Mn	.48	.50	.56	.59	.38	.83[e]
Fe	.67	.70	.77	.84	.77	1.06[e]
Ni	1.2	1.2	1.4	1.4	1.6	.40
Cu	.83	.93	.92	1.0	.71	.53
Zn	.93	1.0	.93	.89	.63	1.0[e]
Br	1.2	1.4	1.4	1.5	2.7	2.6
Pb	.43	.53	.50	.57	1.0	1.01[e]

[a] This ratio is $\sum_{j=1}^{p} a_{ij}S_j/C_i$ for calculated source contributions, S_j, and simulated ambient concentrations from Trial 3, data set 8.

[b] Na, Al, Si, Cl, V, Ni, Br and Pb were included in the fit.

[c] All 23 concentrations were included in the fit.

[d] Na, Al, V and Pb were included in the fit.

[e] Fitting element of Kowalczyk, et al.(1978).

Some discussion of the information in Table 3.3.2 will guide the reader to the more important conclusions that can be drawn from it.

In trials one to three the uncertainties of the observables were systematically increased from 5% to 10% to 20%. The true source contributions are reproduced reasonably well in all receptor model applications to these trials with the best precision and accuracy obtained from the effective variance with twenty-three fitting elements. Actual standard deviations of the source contributions are well estimated by single applications of both the ordinary weighted least squares and effective variance methods when uncertainties are small, but with errors of the order of 20% the effective variance does a much better job. The superiority of the effective variance method in this regard is even more pronounced in trial four where the deviations in the source compositions are greater than those in the ambient concentrations.

The effect of mis-specifying the uncertainties in the receptor model is treated in trial 5. The simulated data sets are identical to those of trial 3, but the uncertainties in the receptor model applications are halved. The calculated source contributions are exactly the same as those of trial 3, indicating that as far as the fit is concerned it is the relative uncertainty which is important rather than the absolute uncertainty. The calculated source standard deviations are exactly one half their values in trial 3 and underestimate the standard deviations associated with the averages.

An example in which the receptor model uncertainties do not retain their true proportions to each other is presented in trial 6. Not only do the calculated uncertainties for urban dust and auto exhaust underestimate the actual uncertainties, even for the effective variance fits, but source contribution estimates for auto exhaust are underestimated in the best results case, due primarily to the large deviation in the Br concentration.

In trial seven the true source composition uncertainties are incorporated into the receptor model modes and applied to the same simulated data sets treated in trial 6. The ordinary weighted least squares results of both trials are identical, as expected since the source composition uncertainties play no role in this fit. The effective variance trials not only better estimate the standard deviations of the ten values, they also better estimate the auto exhaust source contribution. The standard deviation in this trial shows the variation of auto exhaust contributions calculated from the effective variance to be much less than that obtained from the ordinary weighted least squares. The reason is obvious when one examines the weighting of the differences between measured and calculated source contributions.

For the ordinary weighted least squares fit, eq. 2.2.7 is minimized

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)^2}{\sigma_{C_i}^2} \qquad 3.3.2$$

For the effective variance least squares

$$\chi^2 = \sum_{i=1}^{n} \frac{\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)^2}{\sigma_{C_i}^2 + \sum_{j=1}^{p} \sigma_{a_{ij}}^2 S_j^2} \qquad 3.3.3$$

the minimization of which would yield eq. 3.2.20. A large uncertainty in the amount of chemical species i due to source j gives that constituent less influence in the effective variance fit, as it should. In the ordinary weighted least squares fit, however, that species receives no such special weighting and can play just as major a role in the fit as the constituent whose presence in a source type is well quantified.

In the best results situation of trial 7 for eight fitting elements, the ambient Br/Pb ratio is .11, substantially below the .25 value in Table 3.1.12.2a. The ordinary weighted least squares mode gives Br and Pb approximately equal weight in the fit, and their calculated to ambient ratios are 1.22 and .53, respectively. The calculated source contribution is 68% of its true value and its uncertainty is substantially underestimated.

The ambient Br/Pb ratio is identical for the effective variance application. The Br and Pb calculated to ambient ratios are 2.05 and .89, however, indicating that the lead, because of greater precision of its determination in the auto exhaust source, is playing a more important role in the fit. The effective variance prediction of the auto exhaust contribution is within 16% of its true value, and its calculated uncertainty reflects this; it is nearly identical to the standard deviation of the average.

One might argue that the ordinary weighted least squares fit would work fine if those chemical components for which large source composition uncertainties exist were eliminated completely from the fit. This has been the justification for excluding Br in other element balance applications and opting for the unique tracer approach, in this case Pb. If Figure 3.3.1 is not convincing enough, let it suffice to say that the Pb tracer approach applied to data set 8 of trial 7 would yield a source contribution of 39.7 ± 5.6 $\mu g/m^3$, a value of no more accuracy than the ordinary weighted least squares estimate in this instance. The less precisely quantified species play important supporting roles, but they are not the stars. This is exactly the way the effective variance treats them. The more species included in the fit, the more chance exists for random variations to cancel each other out. This is not true in trial 7 alone, but can be seen in the comparison of the 8 species fits to the 23 species fits in all 25 trials.

If chemical species i is quantified precisely in one source but imprecisely in another, the effective variance fit offers the additional advantage of automatically giving it more weight when only the precise source is present and less weight when the imprecise source contribution reaches significant levels. Thus, one does not need to decide a priori which species to include and which to eliminate on the basis of their uncertainties.

All of these features of the effective variance technique are predicated on a reasonable assessment of the $\sigma_{a_{ij}}$. In trial 6 the Br uncertainty in auto exhaust was underestimated and the effective variance fit was little better than the ordinary weighted least squares application.

Trials 8-10 show conclusively that the separation of two source types whose compositions are very similar is nearly impossible in the presence of reasonable uncertainties. The Al and Si tracers for urban dust and continental dust are completely inadequate even when errors are as low as 5% and even though their Si/Al ratios in Table 3.1.12.2a are 2.52 and 2.17, respectively. Though urban dust is slightly enriched in Br and Pb over continental dust, the small contributions of these species from these sources are overwhelmed by the contributions from auto exhaust.

When all 23 species are included in the fit, the receptor model predictions are more accurate, presumably due to substantial differences between urban and continental dust in VC, NVC, SO_4, Na, and Ca (in an actual ambient situation other sources of these elements would negate their effect on the fit). Yet even in this mode, when uncertainties approach 20% the variability of the source contributions of urban and continental dust become unacceptably large.

Because both urban and continental dust contain most other species, at least to some degree, when one of them is overestimated, as urban dust is, the differences in the numerators of eqs. 3.3.2 and 3.3.3 to be filled in by the other source types are smaller, and their contributions are underestimated; these trials clearly show this. Neither the effective variance nor the ordinary weighted least squares seems capable of resolving source types whose compositions are similar, though with more fitting species the similarity becomes less of a problem. Two such sources should be combined into one source type or included one at a time in the least squares fit.

Probably the most important question about the chemical element balance concerns the number of sources to include in the fit and how to tell if they are the right ones, too many or too few. Trials 11-25 attempted to simulate actual ambient situations by using the real, measured variabilities in the source compositions and by over and under estimating the number and types of sources involved. More calculated to ambient concentration ratios outside of the .5 to 2.0 range are reported in these trials; this is due to the larger $\sigma_{a_{ij}}$ and to the mis-specification of sources.

A new parameter is useful in assessing the goodness of the fits. The reduced chi square, χ^2_{n-p}, is defined as

$$\chi^2_{n-p} = \frac{\chi^2}{n-p} = \frac{1}{n-p} \sum_{j=1}^{n} \frac{\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)^2}{\sigma^2_{C_i}} \qquad 3.3.4$$

for the ordinary weighted least squares fit and

$$\chi^2_{n-p} = \frac{\chi^2}{n-p} = \frac{1}{n-p} \sum_{j=1}^{n} \frac{\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)^2}{\sigma^2_{C_i} + \sum_{j=1}^{p} a_{ij}^2 S_j^2} \qquad 3.3.5$$

for the effective variance fits.

If more sources contribute than are included in the fit, some of the squared differences $\left(C_i - \sum_{j=1}^{p} a_{ij} S_j\right)^2$ will be larger than they would be if all sources had been included. The same holds true when a source type which in reality makes no contribution is included in a fit and that fit overestimates its true contribution.

Of course, unless all of the observables are known exactly, χ^2_{n-p} will rarely be equal to zero. Its probability distribution when only random deviations are present is well characterized (Meyer, 1975; Beyer, 1968), however, and a statement about the probability of obtaining a certain value of χ^2_{n-p} if the only causes of the differences $C_i - \Sigma a_{ij} S_j$ are random errors can be made.

Ten values for χ^2_{n-p} were calculated for each receptor model mode of each trial from eq. 3.3.4 or 3.3.5. The ranges of values, the maximum and minimum χ^2_{n-p}, for each mode of each trial are presented in Table 3.3.4. The number of degrees of freedom is an indicator of the extent to which the constraints exceed the parameters being calculated, n-p, and it dictates which member of the family of reduced chi square distributions is appropriate. The 1% χ^2_{n-p} is the value that χ^2_{n-p} would exceed 1% of the time if it were calculated for many data sets within a trial

Table 3.3.4 Ranges of Reduced Chi-Square for Least Squares Fits to Simulated Data

	n=8				n=23			
Trial	n-p Degrees of Freedom	χ^2_{n-p} OWLS	χ^2_{n-p} Eff.Var.	1%[a] χ^2_{n-p}	n-p Degrees of Freedom	χ^2_{n-p} OWLS	χ^2_{n-p} Eff.Var.	1%[a] χ^2_{n-p}
1	4	1.2-6.3	.64-3.3	3.3	19	1.5-2.7	.83-1.6	1.9
2	4	1.2-6.0	.63-3.4	3.3	19	1.4-2.6	.87-1.5	1.9
3	4	1.2-5.0	.70-3.3	3.3	19	1.5-2.4	.86-1.5	1.9
4	4	2.6-13.4	.65-3.4	3.3	19	3.0-6.0	.85-1.6	1.9
5	4	4.8-20.3	2.7-13.3	3.3	19	5.5-9.4	3.4-6.0	1.9
6	4	.38-13.3	.20-8.4	3.3	19	1.9-5.8	1.1-3.2	1.9
7	4	.38-13.3	.18-2.3	3.3	19	1.9-5.8	.73-1.4	1.9
8	3	7.1-14.4	4.4-11.5	3.8	18	2.5-4.5	1.8-3.4	1.9
9	3	1.7-5.5	1.0-4.8	3.8	18	1.2-3.1	.80-2.0	1.9
10	3	.25-3.9	.12-2.1	3.8	18	1.0-2.6	.62-1.8	1.9
11	4	.62-15.3	.11-2.8	3.3	19	4.9-23.4	.66-4.7	1.9
12	3	.75-15.6	.13-3.1	3.8	18	5.0-11.9	.47-1.6	1.9
13	2	.85-20.2	.14-4.6	4.6	17	3.4-11.8	.47-1.7	2.0
14	1	.007-25.0	0.0-2.4	6.6	16	3.3-12.1	.44-1.6	2.0
15	0				15	3.3-12.8	.43-1.8	2.0
16	4	11.7-20.4	4.8-10.9	3.3	19	13.5-21.3	7.9-10.4	1.9
17	3	12.9-27.2	5.5-14.3	3.8	18	9.7-14.7	6.7-8.3	1.9
18	2	.82-11.2	.077-1.73	4.6	17	2.1-14.2	.45-2.0	2.0
19	1	.015-16.7	.001-3.3	6.6	16	2.3-15.0	.48-2.1	2.0
20	0				15	2.4-15.0	.50-4.0	2.0
21	4	7.8-20.9	2.4-9.7	3.3	19	31.5-38.8	18.2-23.3	1.9
22	3	9.5-23.9	3.0-12.7	3.8	18	28.8-35.1	15.6-22.4	1.9
23	2	.11-12.7	.02-2.7	4.6	17	22.3-30.5	13.7-16.5	2.0
24	1	.002-18.8	0.0-2.6	6.6	16	10.5-19.1	3.4-7.7	2.0
25	0				15	2.0-18.5	.36-1.4	2.0

[a] From Beyer (1968). If the value of the sum of the squares is just due to normally distributed random deviations, there is only a 1% probability that χ^2_{n-p} exceeds this number.

(many more than the ten sets analyzed here) and the only cause of deviations was random error. Thus, in the cases where the range of χ^2_{n-p} exceeds 1% χ^2_{n-p}, there is probably a mis-specification in the receptor model: either the uncertainties $\sigma_{a_{ij}}$ and σ_{C_i} have been underestimated or the source set included in the fit is not the real one.

The χ^2_{n-p} ranges for the ordinary weighted least squares mode show that χ^2_{n-p} calculated from eq. 3.3.4 is a worthless measure of the agreement between the receptor model and reality. The actual uncertainty in the denominator is always underestimated because the deviations in the source compositions are neglected. The range of χ^2_{n-p} in every trial exceeds the 1% χ^2_{n-p}.

In the effective variance mode, however, χ^2_{n-p} seems to be a good indicator of the absence of certain source types. In trials 16 and 17 and trials 21-24 the calculated χ^2_{n-p} far exceed the highest value one would expect if only random error were in play; when the actual source set is used or exceeded in trials 18-20 and trial 25, the entire range of χ^2_{n-p} falls below the maximum 1% χ^2_{n-p}, consistent with the hypothesis that deviations are just due to random error and not to the absence of a source contribution.

The value of χ^2_{n-p} is very sensitive to the estimates of the uncertainties used in the receptor model. In trials 5 and 6 the uncertainties were underestimated and the upper end of the χ^2_{n-p} range exceeds the 1% χ^2_{n-p} even though the source model and receptor model source sets are identical. Because the squares of σ_{C_i} and $\sigma_{a_{ij}}$ enter eq. 3.3.5 mis-specification of them can have a large effect. In trial 5 all uncertainties were underestimated by a factor of 2, yet the limits of χ^2_{n-p} are four times the range of trial 3 in which the uncertainties were correctly specified.

Overestimation of the uncertainties would cause χ^2_{n-p} to take on a range of smaller values, a span which might fall under the 1% χ^2_{n-p} even with a mis-specified source set. The 1% χ^2_{n-p} is only valid when errors are random and normally distributed. Obviously, even when using the effective variance fitting method, the χ^2_{n-p} is of little value in determining the right source set if assumptions 4-9 are not met.

But χ^2_{n-p} is not the only indicator of appropriate source set selection. The ratios of calculated to ambient concentrations,

$$R = \sum_{j=1}^{p} a_{ij} S_j \;/\; C_i \qquad 3.3.6$$

also can point to other sources to be included. Though these ratios vary due to typical random error, as Table 3.3.3 shows, it is improbable that many of them should be outside the range .5 to 2.0 unless a source or sources were left out of the fit. Table 3.3.1 contains ratios for the four chemical element balance receptor model modes applied to data set 8 of trials 11-25 which exceeded these limits. Even when the receptor model source set is correct in trials 11, 18, and 25 uncertainties associated with the source compositions cause some ratios to be exceedingly large or small, particularly when only eight concentrations are included in the fit. The number and magnitude of these discrepancies increases when the source set is underestimated as in trials 16 and 17 and trials 21-24.

As more sources which belong are added to the receptor model in trials 21-25, the gaps separating ambient from calculated concentrations are filled in until a complete source set is confirmed by no out-of-bounds ratios in trial 25. This series of trials offers some insight into the selection of sources that should be added to the fit. In trial 22, F and Mn are the most grossly underestimated concentrations. Running a finger down the F column of Table 3.1.12.2a shows aluminum production to be the only significant fluoride source. Running the finger horizontally to the right shows that if this source type is really the fluoride contributor then it will provide a substantial amount of aluminum as well. Sure enough, the calculated Al concentration underestimates the measured. Adding ALPRO as a source in trial 23 eliminates both Al and F from the list of violators. A similar procedure can be applied to Fe and Mn to add the ferromanganese source in trial 24 and the steel electric arc furnace in trial 25.

This procedure will not catch every source, however. The out-of-bounds ratios of trial 21 are the same as those of trial 22, and the discrepancies for SO_4, Na, and Cl which should suggest a kraft mill source are not present. Instead the excess concentrations are apportioned to the four sources which are included, particularly to the marine component; this experiences substantial reduction when the kraft mill source is added to the fit in trial 22.

The final method of assessing source set completeness is to over-specify the sources in the fit and to assess which calculated source contributions are less than their uncertainties. Trials 15-11 (working backwards) explore this possibility. These tests show that the number of fitting chemical species should be significantly larger than the total number of sources through a comparison of the 8 and 23 species fits, and should contain some species prominent and relatively unique to members of the source set. A single application of the effective variance, with its larger and more accurate estimate of the source contribution uncertainty, makes this elimination more palatable, as in the case of ALPROF in trial 13 where the ordinary weighted least squares contribution is five times its uncertainty. Elimination of the zero contribution sources from the fit improves the precision, as a comparison of the standard deviations from column 7 of Table 3.3.2 in trials 15 and 11 shows; all sources not included in the fit are then assumed to make no contribution to the ambient concentrations.

With these observations several tentative answers to questions 1-7 and the inherent implications concerning the robustness of assumptions 2, 3, 4, and 7 can be proffered:

1. The error in S_j due to mis-specification of a_{ij} is in direct proportion to the magnitude (percentage) of that mis-specification if only species i is used to characterize source j. If, however, the mis-specifications are random, their average magnitudes can be estimated, and several species i are used to quantify source j, then the random errors will cancel each other somewhat and a weighted least squares approximation to S_j will have greater precision and accuracy.
2. Ordinary weighted and the effective variance least squares fitting techniques yield similar results when all uncertainties are small or when the uncertainties in the ambient concentration measurements are larger than those of the source compositions. When the latter become dominant, and particularly when they are unequal (percentage) the effective variance is to be preferred in estimating S_j and σ_{S_j}.
3. The quantification errors, σ_{C_i} and $\sigma_{a_{ij}}$, must have relative accuracy to adequately estimate S_j and absolute accuracy to estimate σ_{S_j}. A factor of two might be the maximum deviation to be tolerated; a more precise range should be defined after further study.
4. More chemical species included in a least squares

calculation of source contributions increases the accuracy of those calculations if all of the sources of those species are also included. The effective variance method gives each species a weight in the fit related to the precision of its quantification both in sources and in the ambient air.

5. In the presence of likely uncertainties, sources such as urban dust and continental background dust cannot be adequately resolved by least squares fitting, even though their compositions are not identical. Several nearly unique ratios must exist for good separation.

6. Excluding source types from a least squares fit has little effect on the calculated source contributions if chemical concentrations prominent in the missing sources are also excluded. If some fitting species are common to those sources which are included then their contributions will be overestimated. When uncertainties are well estimated, the calculated χ^2_{n-p} will not meet the 1% χ^2_{n-p} test, indicating that source types should be added, and calculated to measured concentration ratios will often exceed the range of .5 to 2.0.

7. Sources included in the fit which in reality make no contribution will not affect the true source contributions if their chemical compositions are distinct and the concentrations of chemical species which are relatively unique to each source are included in the fit. This over-specification decreases the precision of the true source contribution estimates.

These tests are limited, of course, and further trials involving actual, calculated source contributions determined by the PACS chemical element balances as the S_j' should be carried out in the future. It would be interesting to create several sets of simulated data, some violating assumptions and others not, and to distribute these to various researchers for resolution via their own chemical element balance techniques. The source contribution results obtained could be compared with each other and against the true values; the effect of more subjective decisions such as which chemical species and which source types to include in the fit might airshed can be different from, even the opposite of, that on the ground.

Still, the evidence of a high point source impact under "upwind" conditions and low impact under "downwind" circumstances would add credence to the whole chemical element balance procedure. Specific emitters within a source type might be distinguished, or at least the field of choice narrowed, by examining the directionality of windflows and the spatial relationship between source and receptor.

It is well documented that Portland's airshed experiences a small number of well defined, though non-rectilinear, flow patterns (Mathews, 1971, Cohen, 1977). In the PACS, wind direction and speed were measured at 13 stations scattered throughout the airshed, vector averaged on an 8-hourly basis to correspond to each lo-vol filter sample taken, and plotted on a map of the region for each sampling period of the 32 intensive analysis days (see section 4.6). The 96 periods were classified by a meteorologist (Freemen, 1978) on the basis of these maps as being members of nine basic flow patterns.

Wind data from the Federal Building (site 8) were used as the main criteria, due to its central location within the sampled area. Eight hour periods with no consistent pattern were placed in special categories so as not to contaminate those with consistency. Areas far from downtown (Troutdale, station 4, and Carus, station 7) showed variation within groups, especially under southerly and easterly flows.

Table 3.4.1 lists the flow patterns, their characteristics, the number of 8-hour periods characterized by each and the meteorologist's evaluation of likely source impacts within each pattern.

Figures 3.4.1-3.4.6 contain maps typical of those used in the flow

Table 3.4.1 Surface Windflow Pattern Characteristics

Surface Flow Pattern Group	Basic Flow Description	Classification Criteria	Number of 8 hr.periods in group	Likely Source Impacts
1	Northerly, highspeed	$270^\circ<\theta<360^\circ, 0<0<45^\circ$ velocity ≥ 3.4m/sec. at Airport and Federal Building	5	Sources north of sampling sites. Best background characteristics for Sauvie Island for north wind conditions.
2	Northerly, moderate speed	$270^\circ<\theta<360^\circ, 0<0<45^\circ$ $1.9<$Velocity ≤ 3.4m/sec. at Fed.Bldg.and/or Airport	18	Sources north of sampling sites
3	Northerly, light speed	$270^\circ<\theta<360^\circ$ $.9<V\leq 1.9$ at Fed.Bldg.and/or Airport	8	Borderline in exactitude. Samples may show impacts from sources from upwind <u>or</u> downwind due to effects of fumigation.
4	Southwesterly, high speed	$185^\circ<\theta<270^\circ$ $V\geq 3.4$m/sec. at Fed.Bldg.and/or Airport	9	Best representation of background at Carus under southerly flow conditions. This is the highest speed group.
5	Southwest to westerly, moderate speed	$185^\circ<\theta<270^\circ$ $.9\leq V\leq 3.4$m/sec Fed.Bldg.and/or Airport	14	Sources south of sites
6	Easterly to southerly	$90^\circ<\theta<185^\circ$ $.9\leq V\leq 3.4$m/sec. Fed.Bldg.and/or Airport	17	Sources southeast and east of sites.
7	Erratic or calm	Wind stability factors $<.6$ or $V<.9$m/sec. at Fed.Bldg.	13	Local sources

Table 3.4.1 (Continued)

Surface Flow Pattern Group	Basic Flow Description	Classification Criteria	Number of 8 hr. periods in group	Likely Source Impacts
8	Indefinite with northerly trend	$270° < \theta < 360°$, $0 < 0 < 45$ $V \leq .9$m/sec. at Fed.Bldg.	8	Possibly sources north of site.
9	Unknown for reasons of insufficient data			

Table 3.4.2 Point Source Map Key and operation schedules

Code #	Company & Sources	Intensive analysis days when source not in operation
1	Publishers Paper-Or. City	unknown
	Forest Products Industry/Fossil Fuel	
	5g - Sulfite recov. boiler	
	3a - Resid.oil	
	3d - Nat.gas	
	5i - sludge boiler	
2	Crown Z-West Linn	unknown
	Forest Products/Fossil Fuel	
	3a - Resid,oil	
	3d - Nat. gas	
	5h - hog fuel	
3	Durham Sewage Treatment	unknown
	Miscellaneous/Fossil Fuel	
	9i - sludge incin.	
	3b - dist oil	
4	Oregon Portland Cement	
	Miscellaneous/Fossil Fuel	
	3a - Resid.oil	1-24,26,27
	9e - cement kiln	1-24,26,27
5	H. L. Cobb Crushed Rock	unknown
	Geological	
	1b - Rock crusher	
6	Western Foundry-Tigard	unknown
	Iron Industry	
	8a - Arc furnace	
7	Milwaukie Plywood	unknown
	Forest Products	
	5e - veneer dryer	
	5d - processing	
	5h - hog fuel	
8	Publishers Paper-Portland	unknown
	Forest Products/Fossil Fuel	
	5e - veneer dryer	
	5d - processing	
	5h - hog fuel	
	3d - Nat.gas	

Table 3.4.2 (continued)

Code #	Company & Sources						
9	Cascade Construction						
	Geological/Fossil Fuel						
	1c - Asphalt Production	7-16	11-12	12-11	1-21	3-18	4-15
	3b - dist oil	7-16	11-12	12-11	1-21	3-18	4-15
	3d - Nat gas	7-16	11-12	12-11	1-21	3-18	4-15
10	Ross Is. Sand & Gravel	unknown					
	Geological						
	1b - Rock crusher						
11	Mayflower Farms	unknown					
	Vegetative/Fossil Fuel						
	6a - flour processing						
	6b - grain elevator						
	3d - Nat. gas						
	3a - Resid. oil						
12	Dreyfuss Corp.	unknown					
	Vegetative						
	6b - grain elevator						
13	Barker Manufacturing	unknown					
	Forest Products/Fossil Fuel						
	3a - Resid. oil						
	5h - hog fuel						
(A)14	Alber's Milling	unknown					
	Vegetative/Fossil Fuel						
	6a - flour milling						
	6b - grain elevator						
	3a - Resid. oil						
	3d - Nat gas						
(A)15	Centennial Mills	unknown					
	Vegetative/Fossil Fuel						
	6a - flour milling						
	6b - grain elevator						
	3a - Resid. oil						
(A)16	Triangle Milling	unknown					
	Vegetative/Fossil Fuel						
	6a - flour milling						
	3a - Resid oil						
(A)17	Willamette Hi-Grade	unknown					
	Geological						
	1b - Rock crusher						

Table 3.4.2 (continued)

Code #	Company & Sources						
(A)18	K. F. Jacobsen						
	Geological/Fossil Fuel						
	1c - Asphalt Prod.	7-16	11-12	12-11	1-21	3-18	4-15
	3d - Nat.gas	7-16	11-12	12-11	1-21	3-18	4-15
	3b - dist.oil	7-16	11-12	12-11	1-21	3-18	4-15
19	Esco Corp.						
	Iron Industry						
	8a - Elec Arc furn	7-9,16	11-12	12-11	1-21	3-18	4-15
20	Hercule Inc.	unknown					
	Fossil Fuel						
	3a - resid.oil						
21	Trumbull Asphalt						
	Geological/Fossil Fuel						
	1c - Asphalt Prod.	7-16	11-12	12-11	1-21	3-18	4-15
	3a - Resid.oil	7-16	11-12	12-11	1-21	3-18	4-15
22	Reynolds Aluminum						
	Aluminum Industry/Fossil Fuel						
	7a - stack						
	7b - Roof vent						
	3d - Nat.gas						
23	Owens Illinois						
	Miscellaneous						
	9b - Glass furnace	10-13,17					
24	Ash Grove Lime						
	Miscellaneous/Fossil Fuel						
	3d - Nat. gas						
	3b - dist. oil						
	9f - limestone kiln						
25	Western Farmers Assn.	unknown					
	Vegetative/Fossil Fuel						
	6b - grain elevator						
	3d - Nat. gas						
(B) 26	Chevron Asphalt						
	Geological/Fossil Fuel						
	1c - Asphalt Prod.	7-16	11-12	12-11	1-21	3-18	4-15
	3a - Resid.oil	7-16	11-12	12-11	1-21	3-18	4-15
	3d - Nat.gas	7-16	11-12	12-11	1-21	3-18	4-15

Table 3.4.2 (continued)

Code #	Company & Sources						
(B) 27	Oregon Steel Mills	unknown					
	Iron Industry/Fossil Fuel						
	8a - elect. Arc furn.						
	3a - Resid. oil						
	3d - Nat gas						
(B) 28	NL Industries						
	Miscellaneous						
	9g - NL (National Lead Industries	7-9(ox only),16	11-12	12-11	1-21		4-15
(B) 29	Pioneer Flintcote Co.	unknown					
	Geological/Fossil Fuel						
	1c - Asphalt Prod.						
	3a - Resid.oil						
(B) 30	Bird & Son	unknown					
	Fossil Fuel						
	3a - Resid oil						
	3b - dist. oil						
	3d - Nat. gas						
31	Crown Z - Sulfite	unknown					
	Forest Products/Fossil Fuel						
	5g - sulfite recovery						
	5c - Nat. gas incinerator						
32	Crown Z - KRAFT	unknown					
	Forest Products/Fossil Fuel						
	5a - Kraft recovery boil						
	5f - lime kiln						
	5b - smelt tank						
	5h - hog fuel						
	3a - Resid oil						
	3d - Nat. gas						
	5c - incinerator						
33	Nicolai Door Mfg.	unknown					
	Forest Products/Fossil Fuel						
	5d - processing						
	5h - hog fuel						
	3a - Resid.oil						
34	Brand S Corp.	unknown					
	Forest Products						
	5d - processing						
	5h - hog fuel						

Table 3.4.2 (continued)

Code #	Company & Sources	
35	Rich Mfg. Iron Industry 8a - Elec. Arc furn.	unknown
36	Pacific Carbide Miscellaneous 9d - Pacific Carb furn. 9f - limestone kiln	Normally 1 furnace 3/16 (off 20 hrs, on 4), 17 (on 12, off 12), 18 (off 12, on 12) 4-13,15 (2 furnaces)
37	Linnton Plywood Forest Products/Fossil Fuel 5e - veneer dryer 5d - processing 3a - Resid. oil 3d - Nat. gas	unknown
38	Terminal Flour Mills Vegetative 6a - flour milling 6b - grain elevator	unknown
39	Terminal 4 Aluminum Industry 7c - alumina handling	not in use any PACS day
40	Cargill Grain Vegetative 6b - grain elevator	unknown
41	Union Carbide Iron Industry/Fossil Fuel 8b - Ferromanganese Furnace 3b - dist oil	unknown
42	Oregon Steel Mills Iron Industry/Fossil Fuel 8a - Elec. Arc furn. 3b - Nat. gas	unknown
43	Midrex Iron Industries/Geological 8a - Elec. Arc 1b - Rock crusher	unknown
44	Boise Cascade Forest Products/Fossil Fuel 5h - hog fuel 3a - Resid. oil	

Table 3.4.2(continued)

Code #	Company & Sources	
45	United Grain Vegetative 6b - grain elevator	unknown
46	Fort Vancouver Plywood Forest Products /Fossil Fuel 5h - hog fuel 5e - veneer dryer 5d - wood processing 3a - Resid. oil	unknown
47	Carborundum Miscellaneous 9a - carborundum process	unknown
48	Cook Industries Vegetative 6b - grain elevator	unknown
49	Alcoa Aluminum Aluminum Industry/Fossil Fuel 7a - stack 7b - roof vent 7c - alumina handling 3b - dist. oil 3d - Nat. gas	unknown
50	Acme Construction Geological 1b - Rock crusher 1c - Asphalt production	 7-16 11-12 12-11 1-21 3-18 4-15 7-16 11-12 12-11 1-21 3-18 4-15

SURFACE FLOW PATTERN

GROUP 1

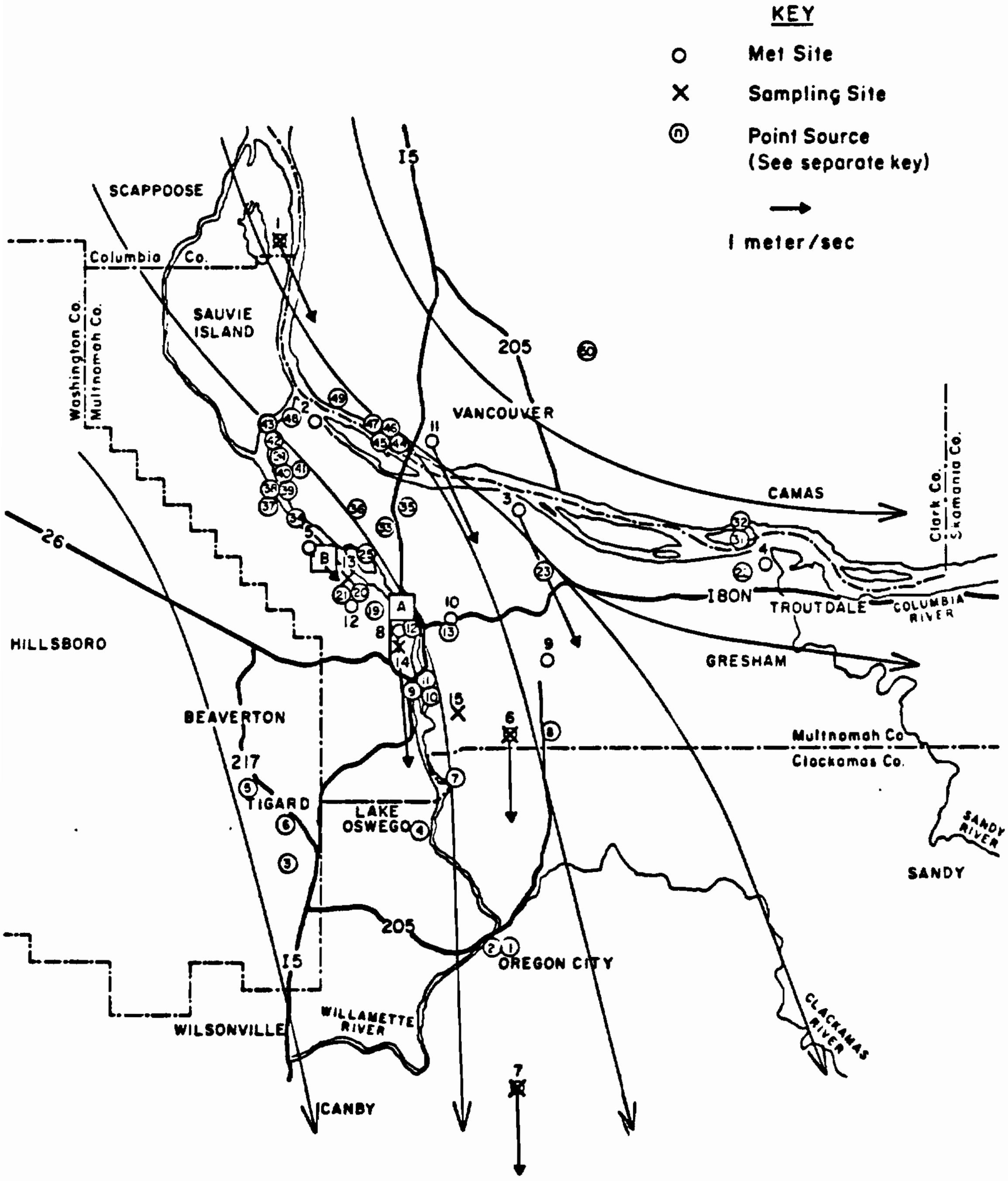


Figure 3.4.1

SURFACE FLOW PATTERN

GROUP 2

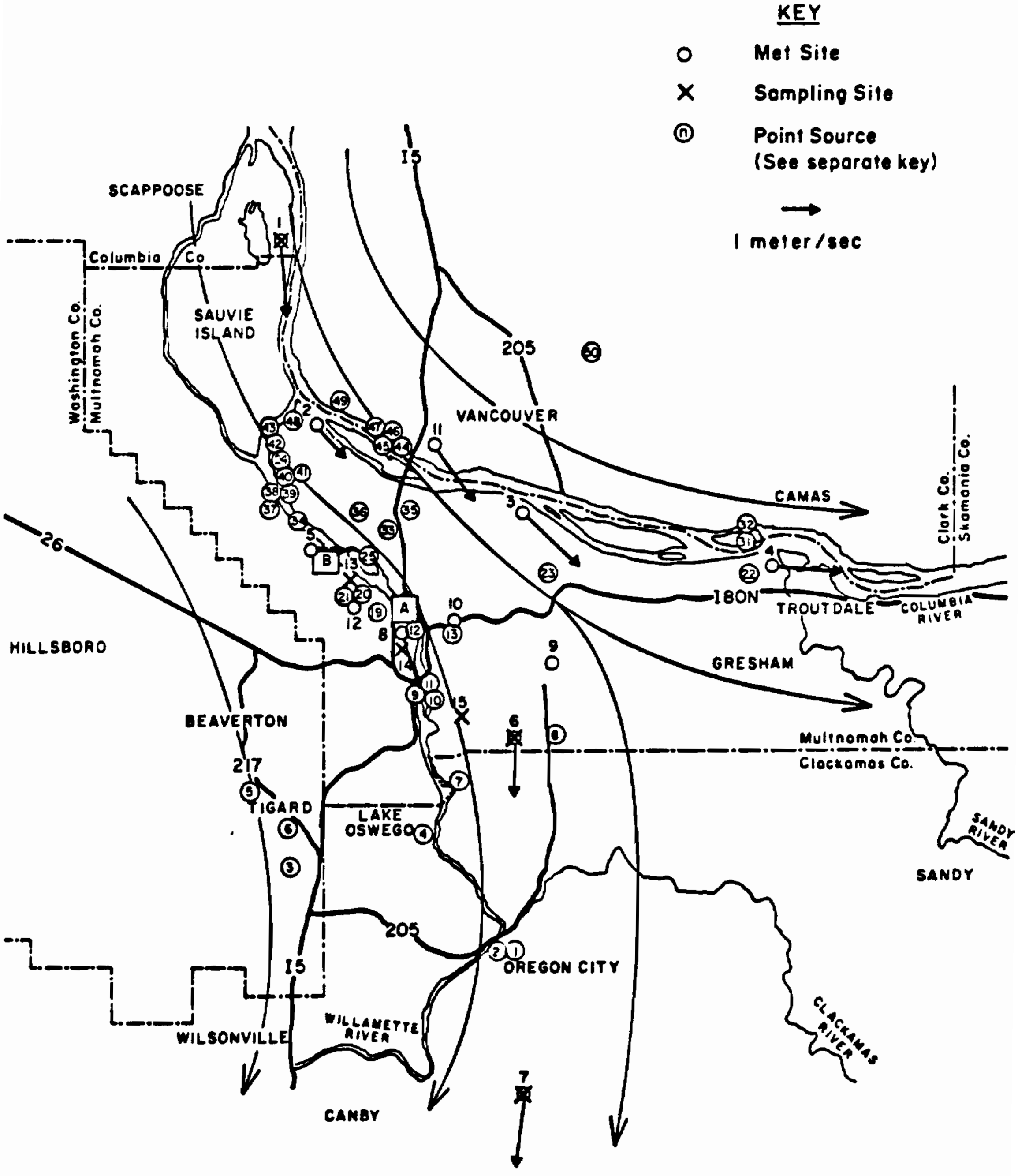


Figure 3.4.2

SURFACE FLOW PATTERN

GROUP 3

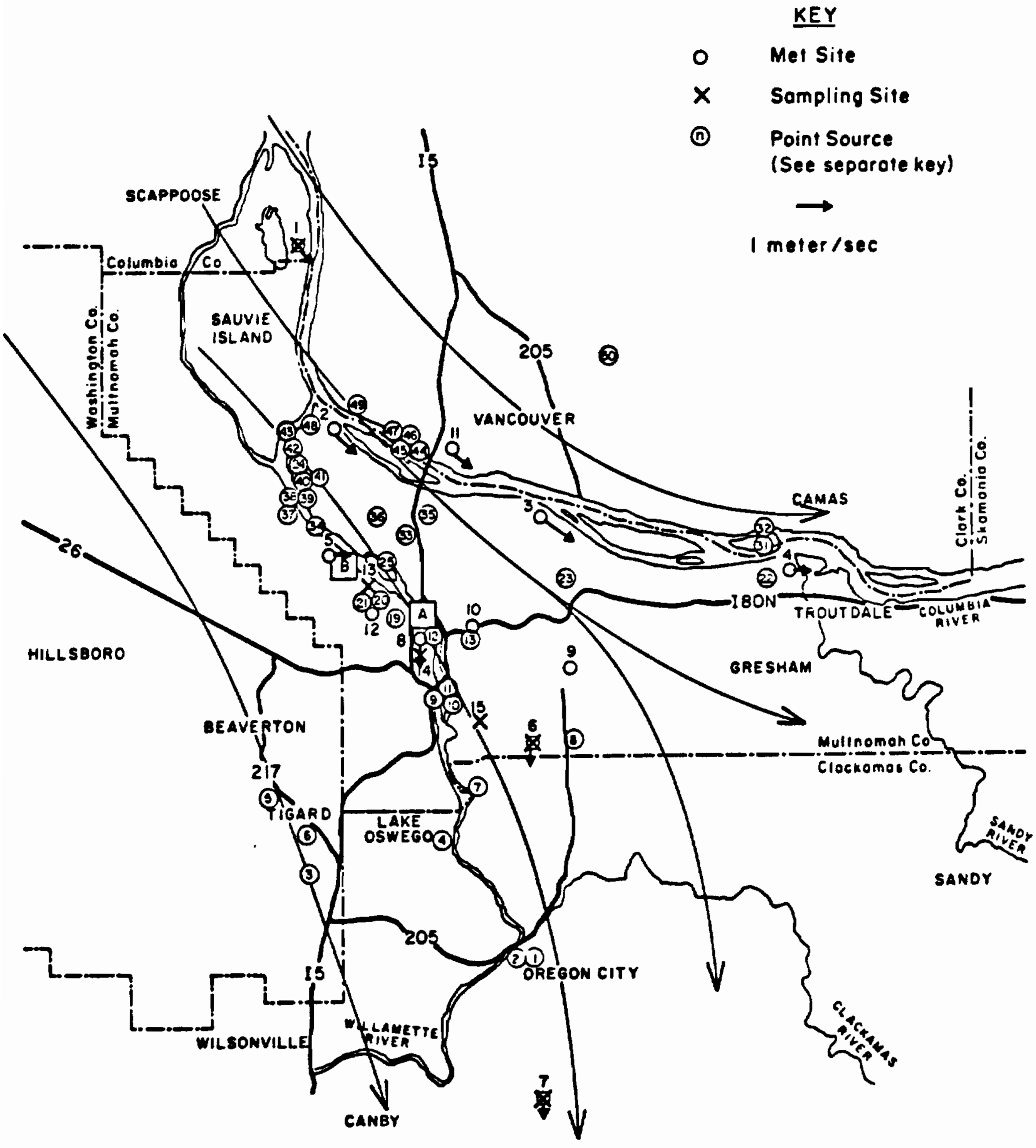


Figure 3.4.3

SURFACE FLOW PATTERN

GROUP 4

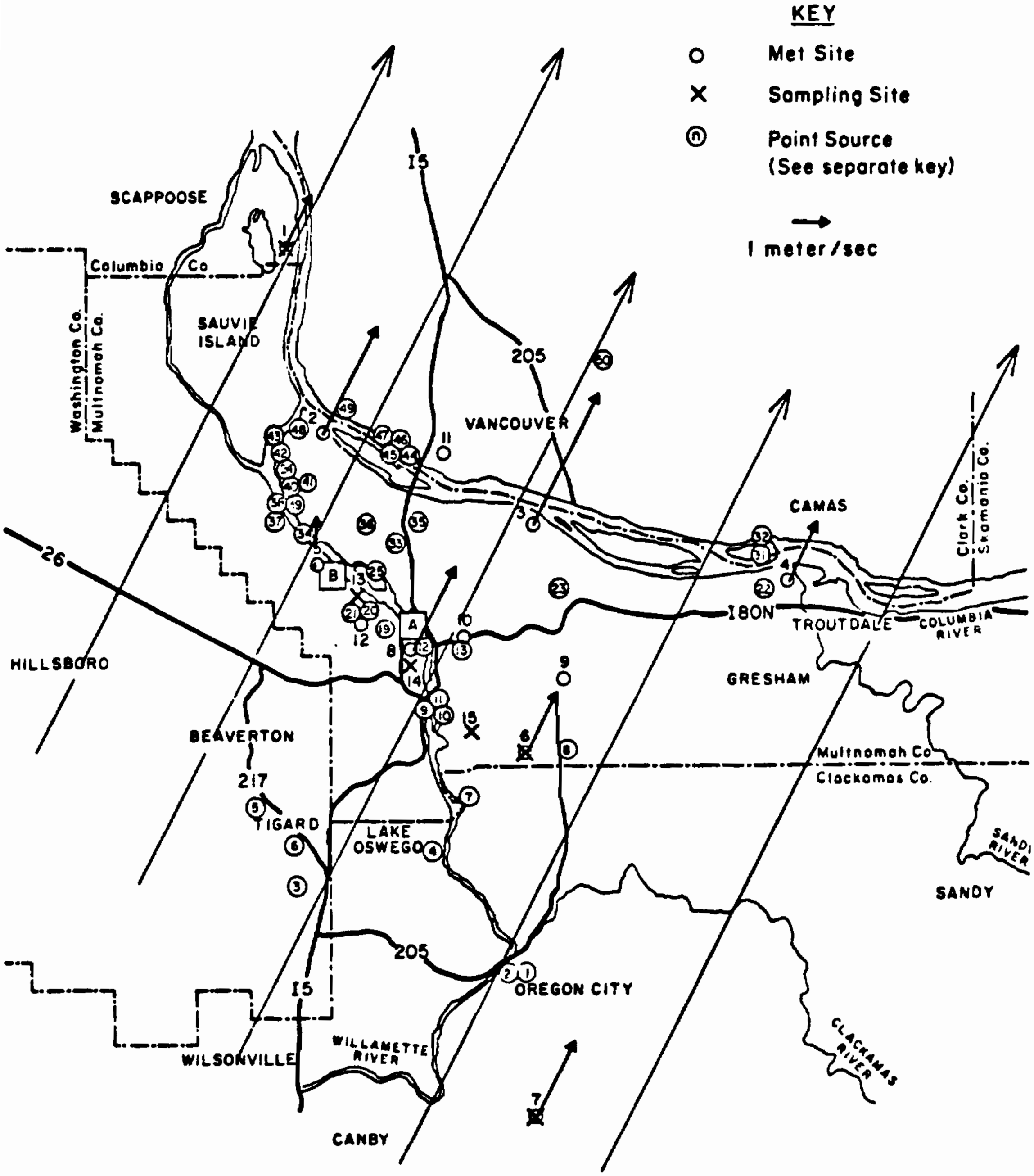


Figure 3.4.4

SURFACE FLOW PATTERN

GROUP 5

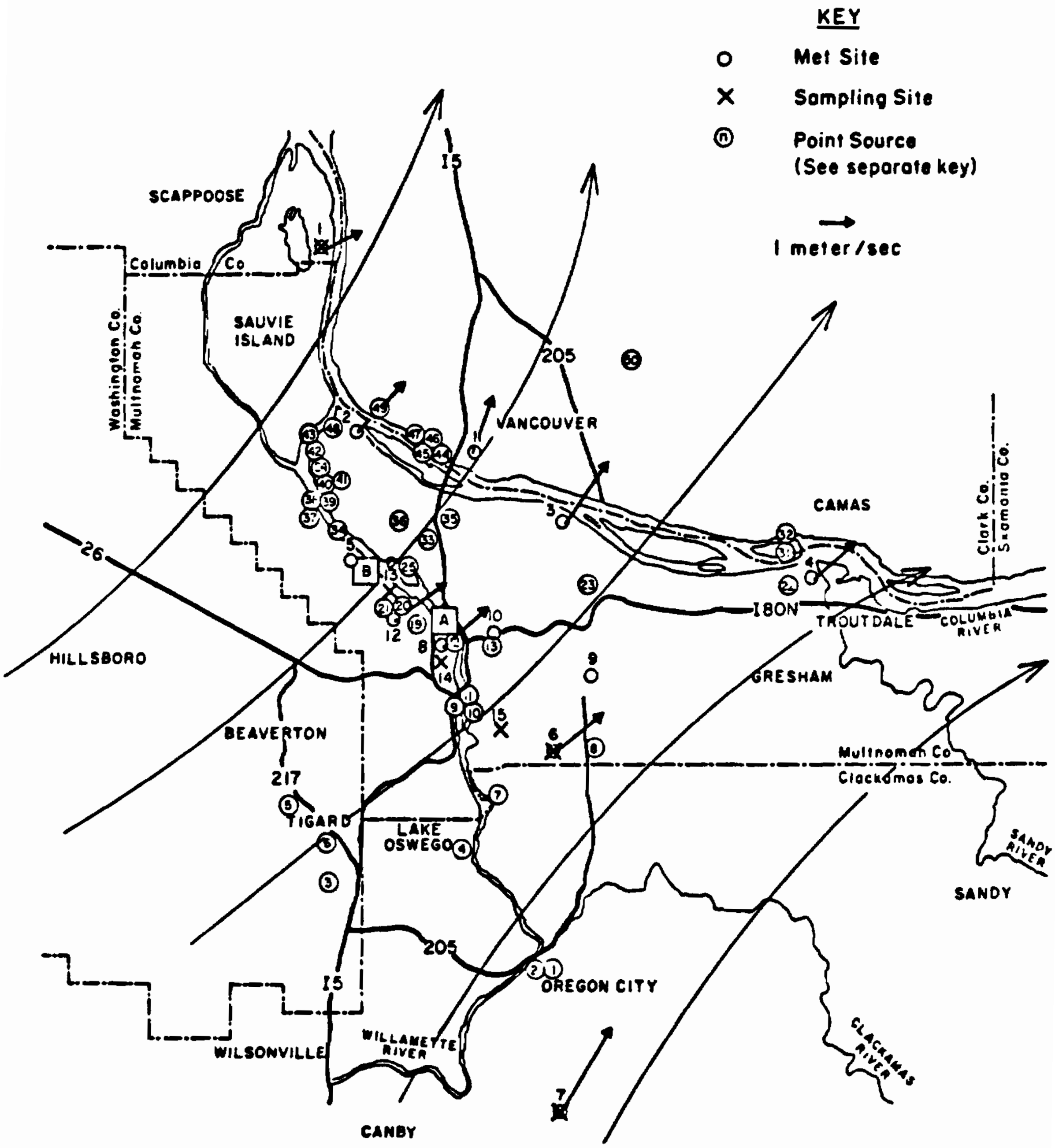


Figure 3.4.5

SURFACE FLOW PATTERN

GROUP 6

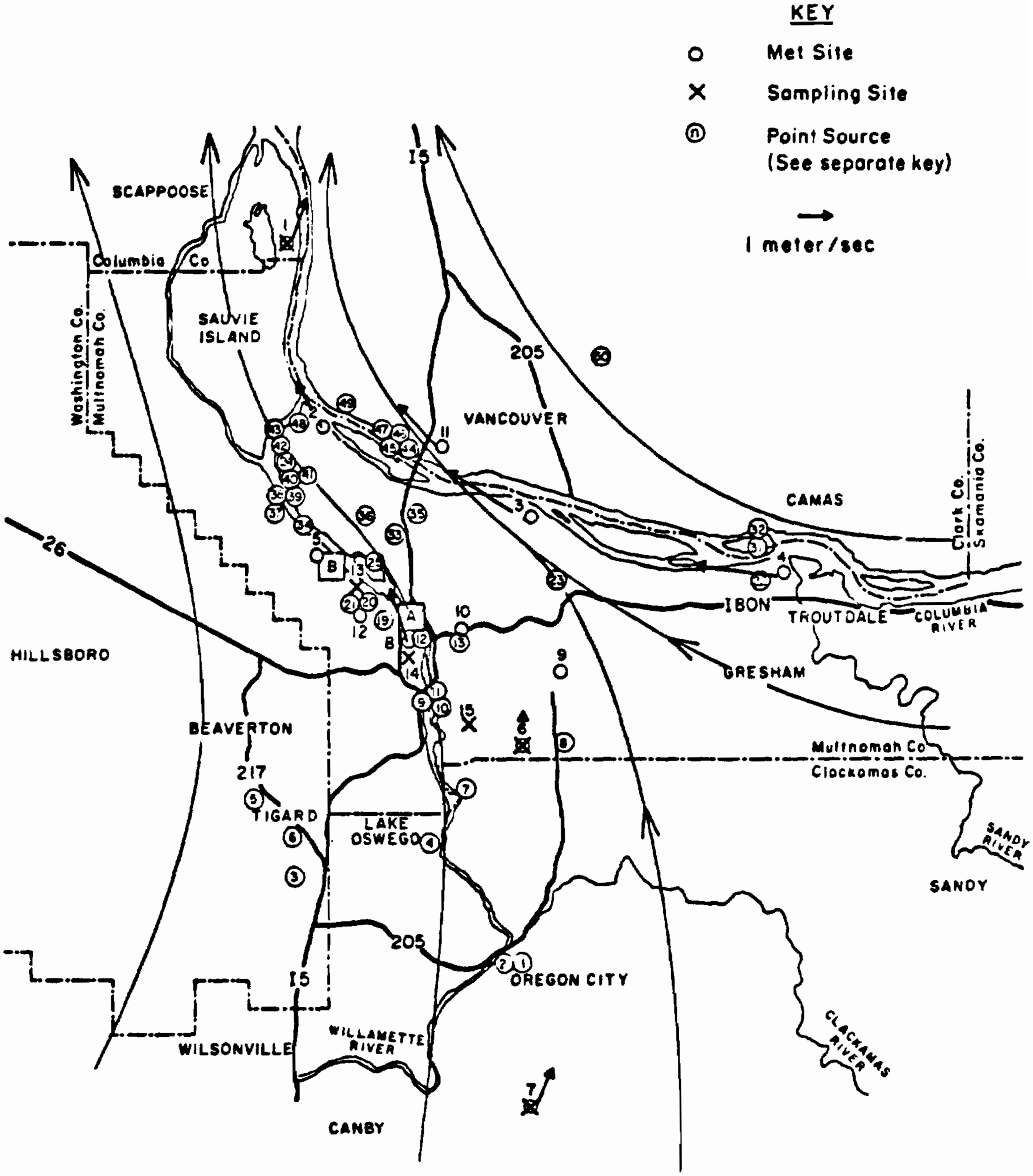


Figure 3.4.6

Table 3.4.3 Windflow Pattern Group Identification for Intensive Analysis Sampling Periods.

Summer, 1977

Date	Flow Pattern Group Number Period[a] 1	Period[a] 2	Period[a] 3
7/9/77	9	9	1
7/15/77	2	1	1
7/16/77	2	2	1
8/17/77	2	1	9
8/18/77	7	5	2
8/22/77	2	3	8
8/23/77	7	2	2

Autumn, 1977

Date	Flow Pattern Group Number Period 1	Period 2	Period 3
9/13/77	2	7	2
9/15/77	5	5	2
10/13/77	3	2	2
10/17/77	2	2	2
10/21/77	6	6	9
11/12/77	5	6	6
11/14/77	4	5	6
11/15/77	4	4	5
11/17/77	7	5	5

Winter, 1977-78

Date	Flow Pattern Group Number Period 1	Period 2	Period 3
12/11/77	4	4	4
1/21/78	6	4	5
1/24/78	6	6	6
1/26/78	8	7	3
1/27/78	3	7	3
2/16/78	8	6	6
2/17/78	6	6	6
2/23/78	6	8	7

Spring, 1978

Date	Flow Pattern Group Number Period 1	Period 2	Period 3
3/16/78	3	7	8
3/17/78	8	7	3
3/18/78	8	2	7
3/21/78	8	2	7
3/22/78	6	5	5
3/23/78	6	4	4
4/13/78	7	5	5
4/15/78	7	5	3

[a] Period 1: Midnight - 8 a.m.
Period 2: 8 a.m. - 4 p.m.
Period 3: 4 p.m. - midnight

pattern classification. PACS sites, meteorological stations and major point sources, keyed by number in Table 3.4.2, are labeled and demonstrate the spatial relationship between sources and receptors. Wind vectors point in the direction of 8-hour vector averaged windflow with length corresponding to vector average windspeed. Members of these six flow pattern groups were specifically chosen from periods with persistent wind directions. All others were relegated to groups 7, 8, or 9. Typical streamlines of air mass movement are superimposed on each map. The classification for each sampling period by season appears in Table 3.4.3. Table 3.4.2 also contains source operation schedules for major point sources willing to divulge that information. The information contained in Tables 3.4.1 to 3.4.3 can be used in conjunction with the chemical element balance in two ways.

One difficulty of the chemical element balance concerns the selection of source types to include in the balance. The windflow grouping and operating schedules could be used on an _a priori_ bases to eliminate certain sources because of their obvious lack of interaction with the air mass being sampled at the receptor. It must be remembered, however, that these periods are classified on the basis of surface wind pattern only, disregarding upper level airflows, mixing heights and hence, variations in vertical transfer. A grouping according to patterns containing these variables might make this approach feasible, but one solely based on surface wind is probably inadequate. It is reasonable to omit from consideration source types not in operation during the PACS intensive analysis days, but _a priori_ exclusion of those with a variable schedule may not be as effective a verification of the chemical element balance as the second application of windflow pattern grouping.

The windflow groupings can be used a postiori to test the predicted source contributions against the physical transport situation. The ambient data should be fit for each period and site with as many sources as possible; the reasonableness of the impacts obtained should be assessed by examining the source operating schedule and the windflow relationship between source and receptor.

The latter approach will be attempted here in order to judge whether or not such surface windflow grouping carries any potential for specific source identification. The source contributions determined for each sampling period and site will be averaged within each flow pattern grouping. Significant source type contribution averages which exhibit a large difference between groups can be examined with reference to Figures 3.4.1-3.4.6 and Table 3.4.2 to identify a specific emitter. Individual samples taken during periods when certain important sources were not in operation can be compared to similar specimens taken when they were operating to confirm that the chemical element balance is really assessing that source.

In a very crude form, what is being proposed here is a hybridization of source dispersion modeling and receptor modeling. The receptor model breaks the ambient TSP up into fractions due to specific source types. The source modeling scheme is then simplified from a huge model containing all particulate emitters, with the cumulative errors in emission rates and dispersion factors for each one, to a model containing only the specific emitters within a source type, and whose result is to be compared with the fractional source type contribution. Only those source types which the receptor model deems important (assuming it accounts for the observed mass loading) need be included in the source model. The source model applied to individual emitters within a source type under the dispersion conditions at the time the receptor sample was taken would indicate which ones were the major components of the source type contribution.

The surface windflow pattern averaging suggested here is primitive, but it considers the most important variable in the source models, wind direction, and should be able to distinguish upwind and downwind emitters of similar character and confirm the impact where only one emitter exists. The inclusion of emission rates, source receptor distance and vertical stability and windspeed might be able to weight the receptor impact of several upwind sources within a source type.

The source-receptor hybridization holds much promise and merits further investigation.

This chapter has refined the chemical element balance receptor model through a thorough assessment of likely source types and their compositions, the derivation of a weighted least squares calculating procedure which incorporates all uncertainties, a simulation study of deviations from basic assumptions and the effect of different application modes, and the possibility of source/receptor model hybridization through windflow pattern averaging of chemical element balance results. The results, however, of this receptor modeling can be only as valid as the data it acts upon. A brief digression in Chapters 4 and 5 is now in order to assure the reader that the aerosol data collected are representative of the Portland airshed and that their integrity has been maintained.

CHAPTER FOUR: EXPERIMENTAL METHODS

The objective of the experimental phase of the PACS project was to obtain representative samples of the Portland aerosol and major sources in both the fine and total particulate modes, to determine their chemical composition, and to record dispersion related meteorological data to be used as inputs to the chemical element balance receptor model stratified by meteorological regimes. This section will describe the experimental design, field and source sampling, analytical/laboratory, quality control and quality assurance aspects of the data acquisition program.

4.1 SITE SELECTION

It is doubtful that the fine spatial structure of suspended particulate concentrations can ever be measured with complete accuracy; in the absence of practical remote sensing techniques such a measurement would require a closely spaced grid of samplers throughout the area of interest, a network far in excess of the practical and financial constraints on most sampling designs. It is possible, to a certain extent, to pick locations which will be representative of typical situations and to extrapolate the results obtained from these measurements to similar circumstances. Solomon, et al. (1977) verified this in the university town of Champaign, Illinois, where they placed 17 ground level hi-vol samplers in residential, university, city commercial, suburban commercial and rural areas. Analysis of the variance performed on the Pb concentrations obtained from stations within groupings showed no statistically significant differences between those concentrations with the exception of those in the university grouping. A statistically significant difference in Pb levels did exist between the groupings indicating that representative values for an area must be classified according to land use.

Stalker, et al. (1962) have made an extensive study of the number of stations necessary to achieve a representation of the true geographical mean in Nashville, Tennesee. They located 123 SO_2 monitors throughout the city and statistically compared the mean values obtained from subsets of stations to those yielded by the entire network. They found that 32 stations were required to estimate the mean allowing a 31% difference between the sample mean and the true mean at the 95% confidence level (i.e., there is a 95% probability that the true mean is within the sample mean ± 31%). They emphasize the importance of representing urban and suburban areas when obtaining rough estimates of means with smaller networks. A factor of three decrease in mean SO_2 concentration was observed between the urban center and a site three miles from it during the high SO_2 winter period.

The PACS was limited to six sites; an additional constraint was the desire to estimate the impact of specific industrial point sources as well as more diffuse area sources dealt with in the cited studies (Pb is widely associated with auto exhaust and SO_2 with fossil fuel burning). A pilot study with closely spaced hi-vol samplers and a statistical comparison of means similar to the Nashville study would be

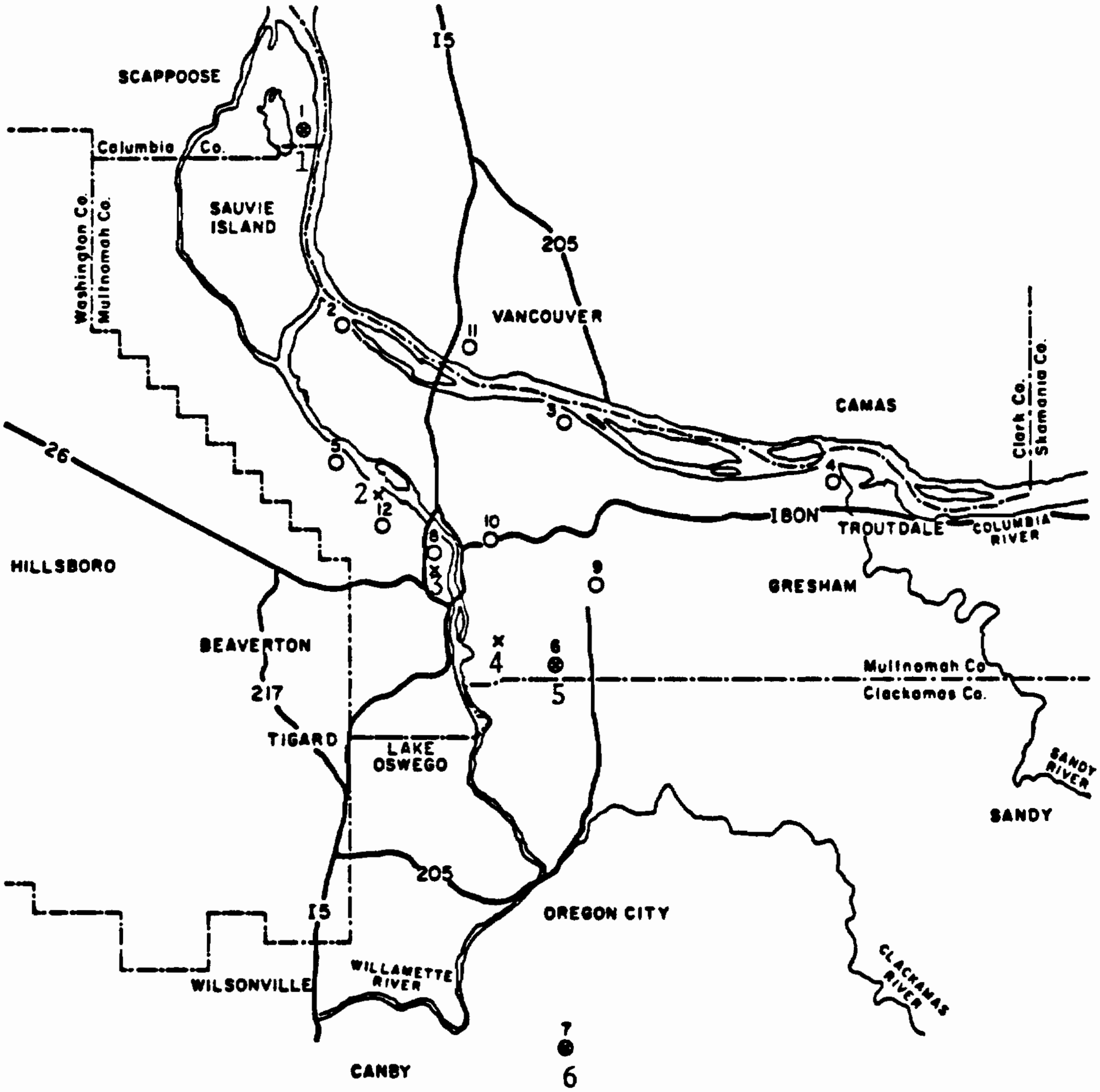


Figure 4.1.1. PACS sampling sites (x with large number) and meteorological stations (o with small number) in the Portland Airshed.

Table 4.1.1, Description of PACS Sampling Sites

PACS Site Code	Location	Description	Deviations from Criteria	Consequences of Deviations
1	Sauvie Island	Northern background station. ~5 m above ground on top of trailer on agricultural land	Favorite fishing spot within 1 mile of sampler	Possible local dust from traffic.
2	Industrial Air Products (IAP)	Industrial area. ~8m above ground on IAP roof in Guild's Lake Industrial Area.		
3	Central Air Monitoring Station (CAMS)	Urban area. ~3 m above ground on roof of building in downtown Portland.	Sampler too high above ground.	Possible discrimination against large particles.
4	Pacific Motor Trucking (PMT)	Urban/industrial area. ~8m above ground on roof of PMT building.	Much truck and rail traffic in immediate vicinity	Possible overweighting of local sources in sample.
5	Flavel Park	Residential Area. ~5m above ground on top of trailer in public park.	Site lacked security. Occasional dirt clods thrown at samples.	Some samples lost, possible contamination on others
6	Carus	Southern background station. ~5m above ground on top of trailer on agricultural land.		

helpful in deciding the confidence limits which should be placed on any geographical mean obtained from these sites. Until such limits are known, means obtained from each site should be considered as "representative" of the site type and any geographical means should be interpreted as "rough estimates."

The sampling sites were located within the airshed as illustrated in Figure 3.1.1. Sites 1 and 6 represent upwind and downwind (prevailing winds) background areas, useful in determining the flow of pollutants into and out of the region. Site 2 sampled an industrial area, site 3 the urban core, site 4 an urban/industrial area, and site 5 a residential section of the airshed. Thus, though more sites would improve the estimate of the geographical mean, each important land use element in the airshed has been represented and typical values can be obtained.

Specific site selection criteria have been delineated by the EPA (1975) and include the following points:

1. Availability: A site capable of supporting and powering the sampling equipment must exist and permission must be obtained to use it.
2. Accessibility: The sampling crew must be able to service the equipment without undue danger or hardship.
3. Security: Equipment should be accessible only to the designated personnel and secured from theft, tampering and vandalism.
4. Potential effect of surroundings: No sources of aerosols, such as chimneys, should be within 100 feet of the sampler (Duncan, 1978). Structures such as trees or tall buildings may encourage or inhibit the flow of aerosols around the samplers. These structures can have a profound effect on surface wind measurements. As a rule of thumb, the sampling site should be located away from structures at a distance greater than three times the height of the tallest structure.

5. Probe location: The sample intake should be placed 3 to 15 meters above ground level to avoid large re-entrained particles near the ground, but still represent the concentrations at ground level, and 1 to 2 meters above the platform surface to mitigate against re-entrainment from it. It should be at a distance greater than two meters from the nearest vertical structure.

Table 4.1.1 lists the sampling sites, a description of them, deviations from the specific site criteria and the possible consequences of these deviations. The elevation of the urban site 3 at the Central Air Monitoring Station is of major concern. A study of variations of TSP measured by hi-vol samplers with height showed that the TSP at sampler level is 65% of the value obtained at 5 m (Duncan, 1978). No data is available for the fine particle mode, though the attenuation with height is expected to be less due to the lower settling velocity of these particles. Examination of PACS results (see section 6.1) indicates that this is not a problem.

4.2 METEOROLOGICAL REGIME FREQUENCY STRATIFICATION

The primary federal standard for total suspended particulate (TSP) is 75 $\mu g/m^3$ annual geometric mean; an AQMA is considered in violation of this standard if its annual geometric mean estimated from samples taken throughout the year exceeds this value. Ideally, 24 hour specimens would be taken each day of the year from which the true mean would be calculated; however, practical constraints do not permit this so in the past a subset of 61 hi-vol specimens per year taken every sixth day has been used to estimate the true mean of Portland TSP. Using a similar method, Akland (1972) estimated the true geometric mean in Buffalo, New York to within 4 to 8% for six years from a sample of 26 daily TSP values (a nearly complete daily TSP data set existed from which the true mean was calculated). Yet another study in Nashville, Tennessee, (Stalker and Dickerson, 1962a) underestimated the annual mean by 14%. Hunt (1972) has developed formulas to assign confidence levels around an estimate of the mean so that there is a 95% probability that the true mean lies within those limits for log-normally distributed TSP values. For an annual geometric standard deviation typical of Portland these confidence regions are approximately ± 15% for a three day per month sampling schedule and ± 12% for a four day per month schedule. These confidence limits rise to approximately ± 35% and ± 28%, respectively, for seasonal means.

The objective of the PACS is to determine the impact of specific source types on the annual geometric mean by intensive analysis of a selected sample of daily specimens. It is important to select these specimens from days which will be truly representative of each season and the entire year. The confidence limits indicated by Hunt are based on random samples from a log-normal distribution. These limits could be reduced by properly stratifying the sample into sub-samples or "regimes", within which TSP values are relatively homogeneous, but between which the TSP varies significantly.

A straightforward analytical method of choosing regimes for stratification does not exist (Zeldin and Meisel, 1977); however, in many cases it has been established that the variability of TSP from day to day is primarily a function of the weather, so classifications based

Table 4.2.1 ERT Synoptic Regime Classification, Composite Frequency of Occurrence, 1974-75 Regime Geometric Means and Geometric Standard Deviations

Regime	Characteristics	N_i/N[a]	N_i[b]	n_i	$\overline{TSP_i}$	σ_{TSP_i}
A	High pressure ridge at surface and 500 mb	.17	124	25	78.7	1.54
B	High pressure ridge at surface, low pressure trough at 500 mb	.15	110	16	62.3	1.49
C	Front at surface, ridge or trough at 500 mb	.20	146	27	42.9	1.85
D	Low pressure trough at surface and 500 mb	.16	117	21	65.0	1.60
E	High index flow at 500 mb	.12	82	9	42.8	1.45
F	Low pressure trough at surface, high pressure ridge or low index flow at 500 mb.	.14	102	10	117.2	1.30
G	Closed low pressure center at surface, or low index flow 500 mb with a high pressure ridge or front at surface.	.06	44	4	59.7	1.70

[a] These are the fractional frequencies of occurrence of each regime over the period 1957-1967

[b] The length of the averaging period is 2 years, 1974-1975

Table 4.2.2 B&K Surface Wind Regime Classification, Composite Frequency of Occurrence, 1974-75 Regime Geometric Means and Geometric Standard Deviations

Regime	Characteristics	N_i/N[b]	N_i[c]	n_i	$\overline{TSP_i}$	σ_{TSP_i}
1 & 7	Northerly flow -- moderate to high speed wind at airport[a] NE-NW ≥ 5 mph	.39	285	41	75.8	1.53
5 & 4	Southerly flow -- moderate to high wind at airport	.28	204	38	37.3	1.48
8	Northerly flow -- light wind at airport NE-NW ≤ 4 mph	.11	80	8	92.2	1.27
3	Southerly flow -- light windspeed with Southerly flow at airport. Wind at airport S-SW ≤ 6 mph and at downtown and Rivergate SW-SE > mph	.10	73	4	92.0	1.65
2	Southerly flow -- light speed with Easterly flow at airport, E-SE ≤ 8 mph and at downtown and Rivergate S-SE ≤ 3 mph	.05	51	4	90.8	1.53
9	Easterly flow -- high speed, wind at airport E-SE > 9 mph	.07	37	9	72.2	1.90

[a] Resultant direction, average daily speed

[b] These are fractional frequencies of occurrence of each regime over the period 1973-76

[c] The length of the averaging period is 2 years, 1974-1975

on meteorological parameters have been proposed for the Portland area.

Tables 4.2.1 and 4.2.2 present two such classifications, their frequencies of occurrence over a specified base period, the within regime geometric means and standard deviations and the overall geometric mean and standard deviation. The ERT regime classification was based on a synoptic weather classification performed by Mathews (1971) for a base period of 1957 to 1967. It was considered because it was the only one which existed. Berg and Kowalczyk (1977) subsequently classified TSP by regime based on surface wind, mainly because these are the regimes included in the DEQ's airshed dispersion model.

The objective of sample stratification is to estimate the geometric mean TSP for the sampling period with the smallest geometric standard deviation. The meanings of symbols appear in Table 4.2.3.

Table 4.2.3 Symbols for Regime Stratification

N_i = total number of daily occurrences of regime i (of m regimes total) during the experimental period.

$N = \sum_{i=1}^{m} N_i$ = total number of days in experimental period.

N_i/N = frequency of daily occurrence of regime i during the experimental period.

n_i = number of days sampled of regime i during experimental period.

$n = \sum_{i=1}^{m} n_i$ = total number of days sampled of regime i during experimental period.

m = number of regimes.

TSP_{ij} = 24 hour average TSP collected on jth day of the ith regime.

$\overline{TSP}_i$ = geometric mean of total suspended particulate in regime i.

σ_{TSP_i} = geometric standard deviation of total suspended particulate in regime i.

$\overline{TSP}$ = unstratified geometric mean.

$\sigma_{\overline{TSP}}$ = geometric standard deviation of the unstratified mean.

$\overline{TSP}_s$ = stratified geometric mean.

$\sigma_{\overline{TSP}_s}$ = geometric standard deviation of the stratified mean.

The usual statistic computed is the non-stratified geometric mean of n random samples

$$\ln \overline{TSP} = \frac{1}{n} \sum_{i=1}^{m} \sum_{j=1}^{n_i} \ln TSP_{ij} \qquad 4.2.1$$

with an unbiased geometric standard deviation of the mean

$$\ln^2 \sigma_{\overline{TSP}} = \frac{N-n}{n(N-1)(n-1)} \sum_{i=1}^{m} \sum_{j=1}^{n_i} (\ln TSP_{ij} - \ln \overline{TSP})^2 \qquad 4.2.2$$

(The coefficients remove the bias of this estimate from a finite sample of a finite population. Meyer, 1976).

The regime stratified geometric mean and unbiased geometric geometric deviation of that mean are (Meyer, 1976)

$$\ln \overline{TSP}_s = \sum_{i=1}^{m} \frac{N_i}{N} \ln \overline{TSP}_i \qquad 4.2.3$$

$$\ln^2 \sigma_{TSP_s} = \sum_{i=1}^{m} \left(\frac{N_i}{N}\right)^2 \left[\frac{N_i - n_i}{n_i(N_i-1)}\right] \ln^2 \sigma_{TSP_i} \qquad 4.2.4$$

where $\overline{TSP}_i$ and σ_{TSP_i} are the geometric mean and standard deviation within the ith regime as given by

$$\ln \overline{TSP}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} \ln TSP_{ij} \qquad 4.2.5$$

$$\ln^2 \sigma_{TSP_i} = \frac{1}{n_i - 1} \sum_{j=1}^{n_i} (\ln TSP_{ij} - \ln \overline{TSP}_i)^2 \qquad 4.2.6$$

Both $\overline{TSP}$ and $\overline{TSP}_s$ are valid estimators of the geometric mean over the experimental period (one year for the Federal Primary Standard);

the better estimation is that which possesses the smaller σ for the same number of samples. The calculated values appear in Table 4.2.4. The two sigma, 95% confidence limits are also presented for comparison with Hunt's tables. The skewness of the log-normal distribution is evidenced by the non-symmetric nature of these limits.

Both stratified means exhibit nearly the same geometric standard deviation which is lower than the corresponding uncertainty in the unstratified mean even though the averaging period of two years is quite long.

Selection of one scheme over the other is somewhat subjective in light of their similar precision in predicting the mean. The B&K classification was chosen mainly because the surface flow patterns correspond to those of the computerized airshed model (Fabrick and Sklarew, 1975) and grouping actual measurements into these classifications would facilitate the comparison between simulated and experimental values. The ease of classification on the basis of surface wind data over the difficulty of obtaining and interpreting synoptic scale weather maps and one less category were additional points in favor of the B&K approach. The objective of this study is to relate ambient concentrations to specific sources and since surface wind plays the predominant role in this relationship it is advantageous to have all typical flows represented. Though a sample based on a synoptic classification would probably contain these flows, the B&K scheme is more likely to classify source impact averages with greater precision.

The importance of weighted stratified means to a true

Table 4.2.4 A Comparison of Stratified and Unstratified Geometric Mean TSP

Classification	Two Year Geometric Mean TSP μg/m³	Geometric Standard Deviation of mean μg/m³	95% Confidence Limits in % after Hunt (1972)	
			Low limit	High limit
ERT	63.1	1.041	-7.8%	+8.4
B&K	65.4	1.043	-8.1%	+8.8%
No stratification	60.2	1.051	-9.5%	+10.5%

Table 4.2.5 Regime and Annual Geometric Mean TSP for 4 years in $\mu g/m^3$

Regime i	1973-1976 Composite N_i/N	1973 $\overline{TSP}_i$	$\sigma_{\overline{TSP}_i}$	$n_i/\frac{n_i}{n}$ [a]	1974 $\overline{TSP}_i$	$\sigma_{\overline{TSP}_i}$	$n_i/\frac{n_i}{n}$	1975 $\overline{TSP}_i$	$\sigma_{\overline{TSP}}$	$n_i/\frac{n_i}{n}$	1976 $\overline{TSP}_i$	$\sigma_{\overline{TSP}_i}$	$n_i/\frac{n_i}{n}$
1&7	.39	74.6	1.36	18/.36	89.5	1.58	19/.39	65.9	1.41	22/.38	60.1	1.53	27/.34
8	.11	109.7	1.69	9/.18	103.4	1.15	5/.10	76.2	1.30	3/.05	115.6	1.63	12/.15
2	.05	145.8	1.29	5/.10	92.0	1.68	3/.06	87.0	1.70*	1/.02	74.2	1.70	4/.05
3	.10	69.7	1.18	3/.06	89.3	1.83	3/.06	57.4	1.65	3/.05	88.3	1.78	12/.15
5&4	.28	43.8	1.44	10/.20	39.7	1.44	15/.31	37.5	1.53	23/.40	34.9	1.54	14/.18
9	.07	77.8	1.26	5/.10	93.0	2.0	4/.08	62.5	1.71	6/.10	69.5	1.4	7/.09
Unstratified		$\overline{TSP}$	$\sigma_{\overline{TSP}}$	n	$\overline{TSP}$	$\sigma_{\overline{TSP}}$	n	$\overline{TSP}$	$\sigma_{\overline{TSP}}$	n	$\overline{TSP}$	$\sigma_{\overline{TSP}}$	n
means		76.9	1.067	50	71.1	1.080	49	51.8	1.061	58	64.4	1.060	79
Stratified		$\overline{TSP}_s$	$\sigma_{\overline{TSP}_s}$	n	$\overline{TSP}_s$	$\sigma_{\overline{TSP}_s}$	n	$\overline{TSP}_s$	$\sigma_{\overline{TSP}_s}$	n	$\overline{TSP}_s$	$\sigma_{\overline{TSP}_s}$	n
means		69.9	1.047	50	72.7	1.064	49	57.4	1.068	58	58.9	1.051	79
Unstratified 95% confidence interval		67.5 to 87.5			61.0 to 82.9			46.0 to 58.3			57.3 to 72.4		
Stratified 95% confidence interval		63.8 to 76.6			64.2 to 82.3			50.3 to 65.5			53.3 to 65.		
		* estimate											

[a] $n_i/\frac{n_i}{n}$ = number of days sampled in regime i/fraction of total days sampled

representation of the yearly average is illustrated by comparing the unstratified annual geometric means of Portland TSP for each of four years (See Table 4.2.5). Several features are of interest:

First, in the absence of stratification, the compliance with the Federal standard depends too much on being "lucky" enough to sample on low pollution potential, "clean" days, or "unlucky" to have drawn a large share of high pollution potential, "dirty" days. In 1973, the standard was violated by the unstratified mean, 76.9 $\mu g/m^3$, but easily met by the stratified mean, 69.9 $\mu g/m^3$. Comparing the sample regime occurrence frequency, n_i/n, to that of the four year composite, N_i/N, for this year shows that the "clean" days of regime 5&4 were undersampled and the "dirty" days of regime 8 were oversampled with respect to their composite frequencies, thus the higher estimate. The opposite occurred in 1975 when regime 5&4 specimens composed 40% of the sample and regimes 8 and 2 only 7% as opposed to 28% and 17% respectively for the composite frequencies. Weighted stratified averaging increases the annual mean in this case.

Second, the unstratified geometric mean shows a decreasing trend in TSP from 1973 to 1975 with a significant increase in 1976. The trend is seen differently when comparing the stratified means where a precipitous drop between 1974 and 1975 is detected with TSP levels before and after remaining quite consistent. A statistical test would be required to conclude that the decrease is not random. The 95% confidence intervals of all stratified means overlap, so there is a reasonable chance that the true means did not vary from year to year. These intervals for the unstratified means do not all overlap. Though the change in TSP from one year to the next might be ascribed to emission controls, it is clear that the sampling schedule would be a major factor.

Finally, the standard deviation of the mean, and the corresponding 95% confidence interval, is less for each stratified mean with the exception of that for 1975. The precision of this value is less because only one specimen from regime 2 was obtained and its contribution to the total variance was 30% as opposed to the other years in which regime 2's portion was 5-10%. One additional specimen from regime 2 would have reduced the stratified standard deviation to 1.062.

This last point suggests that there is an optimum allocation of specimens throughout the regimes that will yield the greatest precision. From this point of view the best apportionment of days throughout the regimes is the one which minimizes the geometric standard deviation of the mean. Taking the derivative of eq. 4.2.4 setting it equal to 0 and solving for n_i yields

$$n_i = \frac{nN_i\sqrt{\frac{N_i}{N_i - 1}}\ \ln\sigma_i}{\sum_{\ell} N_\ell\sqrt{\frac{N_\ell}{N_\ell - 1}}\ \ln\sigma_\ell} \qquad 4.2.7$$

which would reduce to

$$\frac{n_i}{n} = \frac{N_i}{N} \qquad 4.2.8$$

if the standard geometric deviations of each regime were identical and $N_\ell >> 1$.

Ensuring the capture of the required number of specimens within each regime required the sampling of a large portion of days (originally 120 were planned) from which to select the 32 day subset for intensive chemical characterization. A ten day sampling period once a month was an arbitrary compromise between minimizing startups, weekend work, technician and instrument fatigue, allowing enough time between sampling periods for instrument calibration and maintenance, and seasonal representation.

Normally, sampling periods started on the Tuesday of each month nearest the tenth to allow Monday for network startup and to reduce the number of weekends within a sampling period to one; provision was built into the sampling scheme to allow for up to seven days slippage to increase the chances of catching rare regime occurrences. The seasonal regime goals were compared to the regimes represented in the first and/or second of the three seasonal sampling periods and periods were shortened, lengthened or delayed accordingly. For example, the summer regime goal included one occurrence of south wind flow. Since no southerly flow occurred in July or in early August, the August period was delayed until the 17th with the commitment to sample the rest of the month if necessary. When the first southerly flow occurred on August 23, the seasonal goals were met and the sampling period was terminated.

A total of 94 daily specimens covering the composite regime occurrence frequencies was obtained from which a selection of days for intensive chemical analysis could be made. Tables 4.2.6 a-d present each sampling day on a seasonal basis, the B&K regime which it

Table 4.2.6a PACS Summer 1977 Sampling Days

Sampling Date	B & K Regime	Special Impact	Urban TSP μg/m³ [a]	Weekend	Rain [b]	Sample Data Completeness [c]	Intensive Analysis	Reason Chosen
7/7/77	1 & 7		83			94		
7/8/77	1 & 7		79			87		
7/9/77	1 & 7	Slash burn	34	Sat.		98	*	Special impact & weekend, complete data
7/10/77	1 & 7		34	Sun.		100		
7/11/77	1 & 7		74			91		
7/12/77	1 & 7		57		brief shower 1400	85		
7/13/77	1 & 7		61			89		
7/14/77	1 & 7		73			96		
7/15/77	1 & 7		65			100	*	Complete data
7/16/77	1 & 7		53	Sat.		100	*	Weekend, complete data
7/17/77	1 & 7		27	Sun.	rain 1500-2100	100		
7/18/77	1 & 7		50			94		
7/19/77	1 & 7		58			93		
8/17/77	1 & 7	Slash/field burning. Hazy all day. Temp. 100+. Strong, persistent low level inversion	155			81	*	Special impact, worst case
8/18/77	1 & 7		86			91	*	Reasonably complete data, though 7/19 would have been just as good
8/19/77	1 & 7		91			93		
8/20/77	1 & 7		72	Sat.	short shower 2300	96		
8/21/77	1 & 7		45	Sun.	showers & drizzle 0100-1000	96		
8/22/77	1 & 7		57			100	*	Complete data
8/23/77	3	Field burning. Strong low inversion	64		rain 0900-2400	100	*	Regime 3 representation
8/24/77	5 & 4		37		rain 0100-0200	100		

[a] Average of 4 urban stations

[b] From NWS Weather Summaries

[c] On each sampling day 42 lovol and 12 hivol filters were sampled. This number is the percentage of 54 filters run which were recovered.

Table 4.2.6b PACS Autumn 1977 Sampling Days

Sampling Date	B & K Regime	Special Impact	Urban TSP μg/m³	Weekend	Rain	Sample Data Completeness	Intensive Analysis	Reason Chosen
9/8/77	1 & 7		87			80		
9/9/77	1 & 7		83			91		
9/10/77	1 & 7		64	Sat.		91		
9/11/77	1 & 7		56	Sun.		89		
9/12/77	1 & 7		107			94		
9/13/77	8	Stable conditions with low M.H. Strong inversion	133			98	*	Regime 8
9/14/77	5 & 4		81		drizzle 0630-0900	94		
9/15/77	5 & 4		73		little rain 1400, 1900, 2400	96 96	*	Regime 5 & 4, rain, data completeness
9/16/77	2		61		rain 0100-0300	67		
9/17/77	2		44	Sat.	widely separated brief showers	83		
10/12/77	2		120		rain/drizzle 1900-2400	83		
10/13/77	1 & 7		93			93	*	Regime 1 & 7, data relatively complete
10/14/77	1 & 7		115			93		
10/15/77	1 & 7		119	Sat.		89		
10/16/77	1 & 7		61	Sun.		85		
10/17/77	8		127			85	*	Regime 8
10/18/77	1 & 7		150			87		
10/19/77	1 & 7		126			80		
10/20/77	1 & 7		117			80		
10/21/77	2	Slash & field burning	104			80	*	Special impact
11/10/77	2		105		rain 0100-0400	100		
11/11/77	4 & 5		80		rain 1500-1700	100		
11/12/77	9		43	Sat.	rain 1700-2400	100	*	Regime 4 & 5, data complete, rain weekend
11/13/77	4 & 5		19	Sun.	intermittent rain showers all day	100		
11/14/77	5 & 4		33		rain & showers 00-2400	100	*	Regime 4 & 5, data complete
11/15/77	5 & 4		45		little rain 00-02	98	*	Regime 4 & 5
11/16/77	1 & 7		60		showers 0100-0700	100		
11/17/77	3		69		showers 13,16 rain/snow 2100-2400	100	*	Regime 3
11/18/77	1 & 7		49		rain/snow 0100-0200 intermittent rain/snow showers after	100		

Table 4.2.6c PACS Winter 1977-78 Sampling Days

Sampling Date	B & K Regime	Special Impact	Urban TSP $\mu g/m^3$	Weekend	Rain	Sample Data Completeness	Intensive Analysis	Reason Chosen
12/9/77	9		55		intermittent snow,ice,rain drizzle	100		
12/10/77	9		43	Sat.	rain 00-09, 17-24	98		
12/11/77	4 & 5		12	Sun.	rain 00-12 showers 1200-2400	100	*	Regime 4 & 5, weekend, rain
12/12/77	4 & 5		23		showers 06-15 rain 16-24	98		
12/13/77	4 & 5		17		rain all day	98		
1/19/78	9		48		intermittent showers. rain 16-24	96		
1/20/78	9		58		drizzle 01-07 rain/drizzle 14-16	100		
1/21/78	4 & 5		24	Sat.	rain 00-06 showers 06-24	98	*	Regime 4 & 5, weekend, rain
1/22/78	2		53	Sun.	showers 1100-1200		100	
1/23/78	8		153			98		
1/24/78	2	Air stagnation advisory	131			100	*	Special impact
1/25/78	2		86		rain 100-1600	100		
1/26/78	8	Air stagnation advisory	118		slight rain 0900	100	*	Special impact
1/27/78	8	Air stagnation advisory	153			98	*	Special impact
2/14/78	9		73		rain 1200-1800	100		
2/15/78	3		64		rain 0200-0600	98		
2/16/78	3		70		rain 10-12 showers 15-21	100	*	Regime 3
2/17/78	9		72		rain 06-07	100	*	Regime 9
2/18/78	2		98	Sat.	rain 0600 showers 17-19	100		
2/19/78	2		62	Sun.		100		
2/20/78	9		78			100		
2/21/78	2		89			100		
2/22/78	2		109			98		
2/23/78	2		150		rain 08-10, 23,24	96	*	Regime 2, rain

Table 4.2.6d <u>PACS Spring 1978 Sampling Days</u>

Sampling Date	B & K Regime	Special Impact	Urban TSP $\mu g/m^3$	Weekend	Rain	Sample Data Completeness	Intensive Analysis	Reason Chosen
3/14/78	2		105			100		
3/15/78	8		133			98		
3/16/78	8		240			100	*	Worst case day
3/17/78	2	Slash burning, haze	240			100	*	Worst case day, special impact
3/18/78	8		133	Sat.		100	*	Regime 8, weekend
3/19/78	8		123	Sun.		96		
3/20/78	1 & 7		185			98		
3/21/78	2		193			100	*	Regime 2
3/22/78	3		148			100	*	Regime 3
3/23/78	4 & 5		32		rain 02-08 showers 15,17-18, 21	100	*	Regime 1 & 5, rain
4/9/78	1 & 7		65	Sun.				
4/10/78	1 & 7		106					
4/11/78	1 & 7		83					
4/12/78	1 & 7		107					
4/13/78	5 & 4		72		showers 10-11,16 rain 17-24		*	Regime 4 & 5
4/14/78	3		55		rain 00-12			
4/15/78	1 & 7	Backyard burning	54	Sat.	rain 15-24		*	Regime 1 & 7, special impact, weekend
4/16/78	4		24	Sun.	rain 01-14			
4/17/78	9		28		rain 07-24			
4/18/78	2		46		rain 01-04 few after showers			

represents, the data completeness (percent of filters in the network that were recovered), and important information about that day (special emission impacts, rain or weekend).

The choice of days for intensive analysis was guided, but not controlled, by the optimization condition of eq. 4.2.7. A comparison of the regime occurrence frequencies for the 32 day subset, for the entire PACS year and the composite year appears in Table 4.2.7. The subset frequencies do not match the yearly frequencies exactly for the following reasons:

1. The sampling year regime frequencies of occurrence were not the same as the composite frequencies. The desire to obtain a stratified mean for both made exact optimization by eq. 4.2.7 impossible.

2. Each important regime in a season had to be represented at least once, and the fact that only 7 to 9 days from each season could be selected meant that the intensive analysis frequencies would always be multiples of .11 to .14 for each season.

3. Rainy days and weekends needed to be represented in rough proportion to their frequencies of occurrence. A refined regime classification scheme should probably include these features.

4. Special impact days on which permits were issued for specific emissions (slash, field and backyard burning) were included for individual comparison with similar days without such impact. Some days on which air stagnation advisories were in effect were also chosen for individual comparison. These features might also be included in a refined classification.

5. Three "worst case" days with heavy TSP loadings were selected for individual assessment.

6. Days with high data completeness were given preference.

The success of this intensive chemical analysis day selection in representing each regime mean and each stratified mean on a seasonal

Table 4.2.7 Composite, PACS Year and Intensive Analysis Day Regime Frequencies of Occurrence by Season for the Entire Year

June 1977 - April 1978

B & K Regime	SUMMER Comp. Freq.	SUMMER PACS Yr. Freq.	SUMMER Intens. An. Freq.	AUTUMN Comp. Freq.	AUTUMN PACS Freq.	AUTUMN Int. An. Freq.	WINTER Comp. Freq.	WINTER PACS Yr.	WINTER Int. An. Freq.	SPRING Comp. Freq.	SPRING PACS Yr.	SPRING Int. An. Freq.	ANNUAL Comp. Freq.	ANNUAL PACS Yr.	ANNUAL Int. An. Freq.
1 & 7	.78	.91	.86	.30	.40	.11	.08	.09	0	.38	.32	.13	.39	.45	.25
8	.04	0	0	.17	.06	.22	.10	.03	.25	.16	.18	.25	.11	.05	.19
4 & 5	.15	.07	0	.23	.28	.33	.42	.18	.25	.32	.22	.25	.28	.20	.22
3	.02	.02	.14	.13	.04	.11	.17	.02	.13	.07	.06	.13	.10	.03	.13
2	0	0	0	.06	.10	.11	.11	.21	.25	.04	.06	.25	.05	.10	.16
9	0	0	0	.11	.11	.11	.13	.46	.13	.04	.16	0	.07	.16	.06

and annual basis is evident in Table 4.2.8 where the means obtained from the 32 specimen subset are compared with those obtained from all 94 days sampled.

The coincidence of the two means in each case is striking with the exception of regime 1&7 and regime 3 for spring, in which the intensive day averages contained only one specimen, and regime 2 for winter and spring, where the days selected were exceptionally "dirty" and therefore of special interest on an individual basis. Only in the case of regime 2 did these special selections affect the similarity of the annual regime means. With this exception, these annual means and their geometric standard deviations are almost exactly represented by the 32 specimen subset.

Two selection mistakes can be observed. One specimen from regime 4&5 for the summer and one from regime 9 for the spring should have been included for intensive chemical analysis. The former regime occurred 15% of the time during the composite summer and the latter's frequency of occurrence was 16% during the PACS year. These are significant fractions and since representatives did exist they should have been used. The lack of a summer regime 4&5 intensive day average resulted in an unfavorable comparison of the composite year stratified means for that season. The effect on the annual mean, however, is negligible.

All other comparisons of sub-sample stratified means and total sample stratified means for both the composite year and the PACS year show close agreement, much better than that exhibited by the

Table 4.2.8 PACS Year Total Suspended Particulate Averages in μg/m^3

Regime	Summer 1977		Autumn 1977		Winter 1977-78		Spring 1978		PACS Year			
	$\overline{TSP_i}^a$	$\overline{TSP_i}^b$	$\overline{TSP_i}^a$	$\overline{TSP_i}^b$	$\overline{TSP_i}^a$	$\overline{TSP_i}^b$	$\overline{TSP_i}^a$	$\overline{TSP_i}^b$	$\overline{TSP_i}^a$	$\overline{\sigma TSP_i}^a$	$\overline{TSP_i}^b$	$\overline{\sigma TSP_i}^b$
1&7	64.1	66.8	86.9	93.0	----	----	92.1	54	72.4	1.55	67.8	1.58
8	----	----	130	130	140	134	151	179	143	1.24	146	1.29
2	----	----	92.3	104	92.3	140	122	215	95.0	1.61	157	1.39
3	64.0	64.0	66.9	69	66.9	70	90.2	148	73.8	1.42	82.2	1.48
4&5	37.0	----	48.7	47.7	18.3	17.0	38.0	48.0	34.0	1.91	35.6	1.89
9	----	----	59.7	43.	59.7	72	28	----	52.9	1.39	55.6	1.44
Unstratified means	$\overline{TSP}^a$ 59.8	$\overline{TSP}^b$ 66.4	$\overline{TSP}^a$ 75.8	$\overline{TSP}^b$ 72.1	$\overline{TSP}^a$ 64.8	$\overline{TSP}^b$ 69.0	$\overline{TSP}^a$ 88.7	$\overline{TSP}^b$ 113.3	$\overline{TSP}^a$ 69.2	$\sigma\overline{TSP}^a$ 1.071	$\overline{TSP}^b$ 78.4	$\sigma\overline{TSP}^b$ 1.130
Composite Year Stratified means	$\overline{TSP_s}^a$ 54.4^c	$\overline{TSP_s}^b$ 66.3^d	$\overline{TSP_s}^a$ 75.8	$\overline{TSP_s}^b$ 75.1	$\overline{TSP_s}^a$ 47.2^e	$\overline{TSP_s}^b$ 49.1^e	$\overline{TSP_s}^a$ 75.6	$\overline{TSP_s}^b$ 74.0^f	$\overline{TSP_s}^a$ 62.6	$\sigma\overline{TSP_s}^a$ 1.057	$\overline{TSP_s}^b$ 64.6	$\sigma\overline{TSP_s}^b$ 1.099
PACS Year Stratified Means	$\overline{TSP_s}^a$ 61.7^c	$\overline{TSP_s}^b$ 66.5^d	$\overline{TSP_s}^a$ 69.2	$\overline{TSP_s}^b$ 69.0	$\overline{TSP_s}^a$ 56.4^e	$\overline{TSP_s}^b$ 55.5^e	$\overline{TSP_s}^a$ 69.6	$\overline{TSP_s}^b$ 73.9^f	$\overline{TSP_s}^a$ 60.3	$\sigma\overline{TSP_s}^a$ 1.047	$\overline{TSP_s}^b$ 62.9	$\sigma\overline{TSP_s}^b$ 1.100

---- No specimens available for this regime.

[a] For all 94 PACS sampling days.

[b] For intensive analysis day samples only

[c] Regime 8 & 1&7 frequencies combined.

[d] Regime 3 & 4&5 combined,
Regime 8 & 1&7 combined.

[e] Regime 8 & 1&7 frequencies combined.

[f] Regime 9 & 4&5 frequencies combined.

unstratified means.

The annual geometric means show once again the value of regime stratification in obtaining a true representation of the year. The difference between means for all 94 specimens and for the 32 day subset is 9.2 $\mu g/m^3$ for the unstratified means, but only 2.0 $\mu g/m^3$ and 2.6 $\mu g/m^3$ for the composite and PACS year stratified means. The smaller geometric standard deviation of these stratified means attests to their greater precision in estimating the true annual geometric mean TSP.

The selection of days for intensive chemical analysis in terms of their impact on the seasonal and annual geometric mean TSP levels has been justified. It has been shown that this 32 day subset will estimate these means with high precision, contains a representative mix of surface wind directions from which the aerosol may come, contains known episodic emissions, weekends and rainy days, and has a high rate of data completeness (average recovery of filters for these days is 96.5%).

4.3 FILTER SELECTION

No instrument for the continuous monitoring of aerosol multielement composition and physical characteristics exists. Time integrated samples must be collected on a substrate amenable to the sampling situation and the analysis techniques employed. Air filtration through appropriate media has long been used for this purpose.

The ideal air filter used for chemical analysis should meet the following criteria:

1. Mechanical stability: The filter cannot deform or break under necessary operating procedures. Ease of handling is also an advantage.

2. Chemical stability: The filter must be stable enough to withstand required variations of temperature and treatment without decomposing or interacting with the aerosol deposit.

3. High particle collection efficiency: All particles in the size range of interest must be removed by the filter from the air passing through it.

4. Low flow resistance: A lower resistance to airflow through the filter increases the volume of air that can be sampled in a given time with a given pump.

5. Good retention without clogging: An acceptable quantity of deposit must adhere to the filter without clogging filter pores to the extent that the flow rate declines.

6. Low and consistent blank values and artifacts: The properties being sought of the aerosol should not be interfered with by the properties of the filter. To the extent that they are, the filter influences should be constant so that they may be subtracted.

7. Cost and availability: The manufacturer must be a dependable supplier of a constant quality product and his cost must be within the limits imposed by the financing of the study.

For routine XRF analysis two additional conditions are imposed.

8. Homogeneous surface deposit: The aerosol must form a homogeneous deposit on the surface of the filter. Distribution of aerosol throughout the filter would require x-ray absorption corrections which are difficult to quantify.

9. Low areal mass density: The scattered primary radiation intensity is directly proportional to the mass per unit area of the filter material. A low mass per unit area assures low background in the x-ray spectra and greater sensitivity for the elements being quantified.

Each filter commercially available meets these criteria to varying degrees; no one filter meets them entirely. In selecting a filter, the field may be narrowed by determining the most important conditions to be met and eliminating those filters that don't comply, then selecting the next most important conditions and eliminating on that basis, etc. The "right" filter type is usually evident. This procedure will now be applied to the selection of the filter types used in the PACS.

Filters for multi-element analysis: Conditions 8 and 9 are of major concern since x-ray fluorescence is a prime analytical tool in this study. This limits the field to membrane filters of which three are commonly available for air sampling. Nuclepore filters did not adequately meet criteria three, four or five and were quickly eliminated. Teflon filters adequately satisfied all criteria except one and four (and six if fluoride is measured). These filters curled or wadded up, particularly after washing (this problem has recently been solved by manufacturing filters attached to a solid plastic ring around the perimeter), making filter holder loading, x-ray analysis and filter cutting difficult. High fluoride blank levels were also observed. The cost of these filters was a factor of four greater than that of the other candidates.

The selection of Millipore 1.2 μm cellulose acetate filters seemed to optimize the congruence between the available and the ideal. These filters have high collection efficiencies for typical aerosol particle sizes. Nominal flow rates of 75 ℓ/min could be maintained for the required sampling periods with the chosen samplers. These filters remained flat after washing and were very easy to cut. The ground concentration levels, after washing in deionized water, are reported as averages of many determinations throughout the project in Table 4.3.1. They were low for the elements quantified. The cost was reasonable and the manufacturer was reliable.

Not all is perfect with these filters. First, they are hygroscopic, which causes their weight to change with relative humidity. This requires all weighing to be done in a constant humidity chamber. Second, and more serious, studies reported subsequent to the selection and utilization of this filter type (Spicer et al., 1978) reveal that artifact NO_3^- forms in the filter and on the aerosol deposit when HNO_3 gas is present at trace levels in the airstream. 550 μg of NO_3^- was detected on a 47 mm cellulose acetate filter when .96 m^3 of particle-free air at 38% relative humidity containing 3 ppm of HNO_3 was drawn through it. Though a saturation level was eventually reached, the studies show that a large portion of the nitrate measured may not be due to the particles collected. It is unfortunate that these studies were not carried out at HNO_3 concentrations typical of ambient air, in the range of 10-100 ppb. The effect in ambient sampling is probably less than that reported by Spicer et al., but may still be significant. Companion studies (Coutant, et al., 1977) involving sulfur bearing air and sulfate show that any similar artifacts for sulfur species are insignificant.

The final limitation of the cellulose acetate in this research effort is with respect to high temperatures in source sampling. The maximum tolerance for these filters is 80° C, well below the 100° C required to prevent the condensation of water vapor in several stacks

Table 4.3.1 Blank levels on Washed 1.2 μm Millipore Filters. Average values and Standard Deviations for batches used in PACS.

Substance	Concentration $\mu g/cm^2$
NO_3^-	.41 ± .34
$SO_4^=$	.13 ± .10
F^-	.09 ± .11
Na	.009 ± .003
Mg	< .046
Al	.02 ± .01
Si	< .027
S	.10 ± .07
Cl	.10 ± .02
Cl^-	.25 ± .10
K	.06 ± .03
Ca	.04 ± .02
Ti	.0025 ± .0027
V	.00003 ± .00003
Cr	< .004
Mn	.00041 ± .00018
Fe	< .011
Ni	< .005
Cu	< .006
Zn	< .005
Se	< .006
As	< .005
Br	.0009 ± .0006
Br^-	< .70
Pb	< .020
Cd	< .050
Ba	< .360

sampled. Adjustments in the standard operating procedure were required.

In future urban aerosol studies, a teflon filter mounted on a plastic annulus would probably be more appropriate. In the studies (Coutant et al., 1977; Spicer, et al., 1978) cited it showed no artifact formation of sulfate or nitrate and Mroz (1976) found it could tolerate stack temperatures of up to 300° C. Experiments with different washing techniques might reveal a method of reducing the fluoride blank level, and the price is sure to come down as the filters become more widely accepted and are produced in volume.

Hi-vol sampling for carbon analysis: The flow resistance of membrane filters makes them unsuitable for high volume sampling. Fiber filters are superior in this respect, but they have high areal mass density, high blank levels, and the aerosol they collect is deposited throughout the filter making them inappropriate for the previous application. Analysis for carbon precludes the use of any carbon containing substrate such as cellulose. Hence, glass fiber and quartz fiber filters remain in the field of choice. Gelman type AE glass fiber filters were chosen for this purpose because of their availability and low carbon blank levels.

4.4 SAMPLERS

The standard hi-vol sampler was used to collect TSP samples and hi-vol sampler with a Sierra Model 235 Cascade Impactor head collected hi-vol fine particles. Only the first four stages of this five stage impactor were used so that 50% cut point of the upper size limit was .95 μm (Sierra Instruments, Inc., 1978). Impaction surfaces were cleaned, then the third stage was covered with Apiezon grease, to prevent re-entrainment of large particles, at the beginning of each sampling period.

Flowrates were measured before and after the exposure of each filter with a rotameter. These readings for each sampler and its rotameter were calibrated against a dry test meter on a periodic basis. A timer was set to start each sampler at midnight and run for 24 hours. A separate clock recorded the actual sampling time. Two sets of samplers were used at each station so that one set could be serviced while the other was running. Normal flowrates were 1100 ℓ/min.

Two ERT sequential lo-vol samplers were also located at each site for the sampling of total and fine particulate matter on the membrane filters. Time intervals were preset on the timing device which controlled solenoid valves between the pump and each sampling port to collect three consecutive eight hour samples each day at all sites with the exception of site 3 at CAMS where six consecutive four hour samples per day were taken.

Flows were related to the pressure drop across the filter as measured by a vacuum gauge by comparison in the laboratory with a dry test meter; the relationship over the region of interest was relatively linear as evidenced by Figure 4.4.1. Flow audits were made with a calibrated rotameter throughout the entire sampling period to verify the initial calibration. Several of these audits are also indicated in Figure 4.4.1. Normal flowrates were approximately 70 ℓ/min.

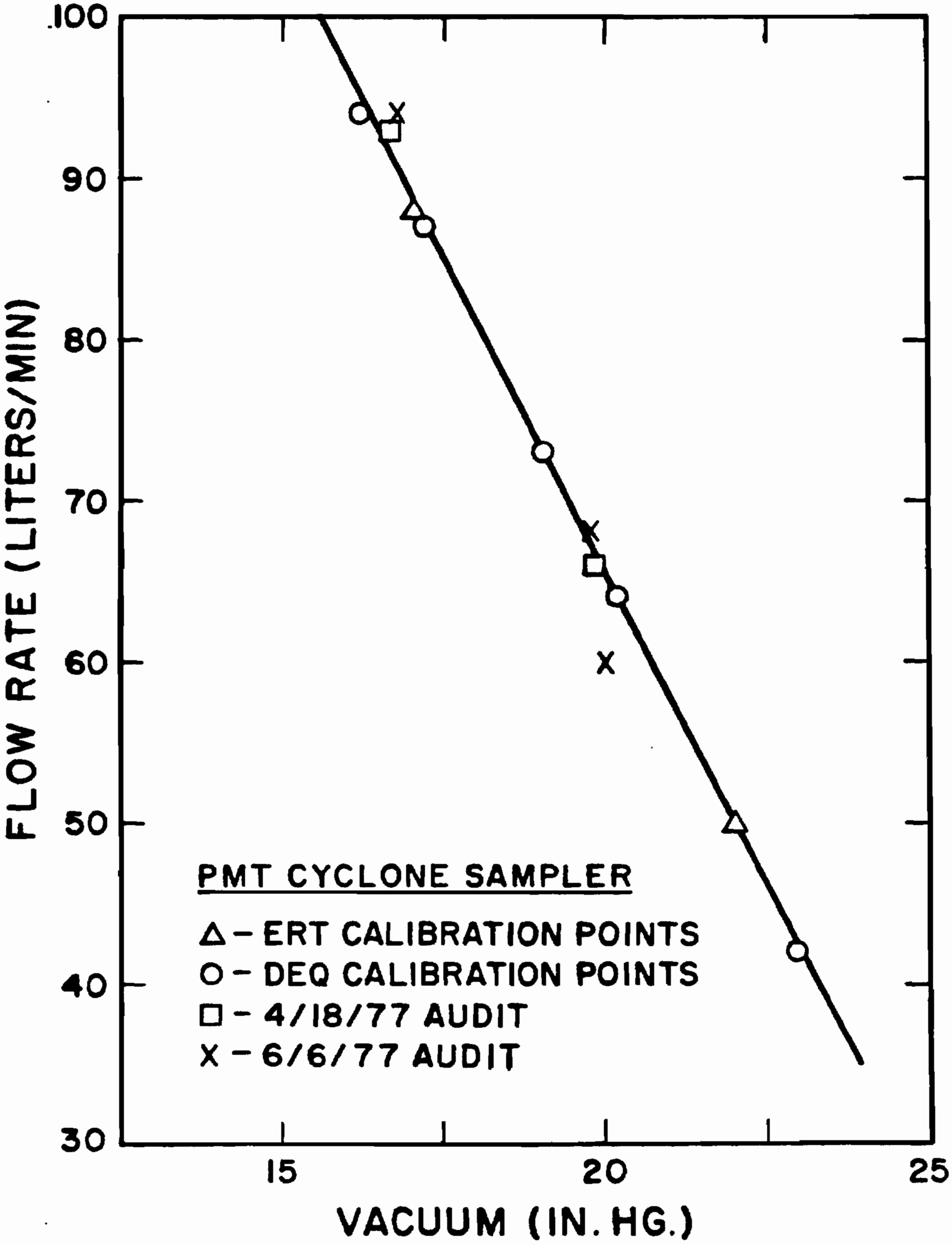


Figure 4.4.1. Typical Flowrate calibration for an ERT sequential sampler.

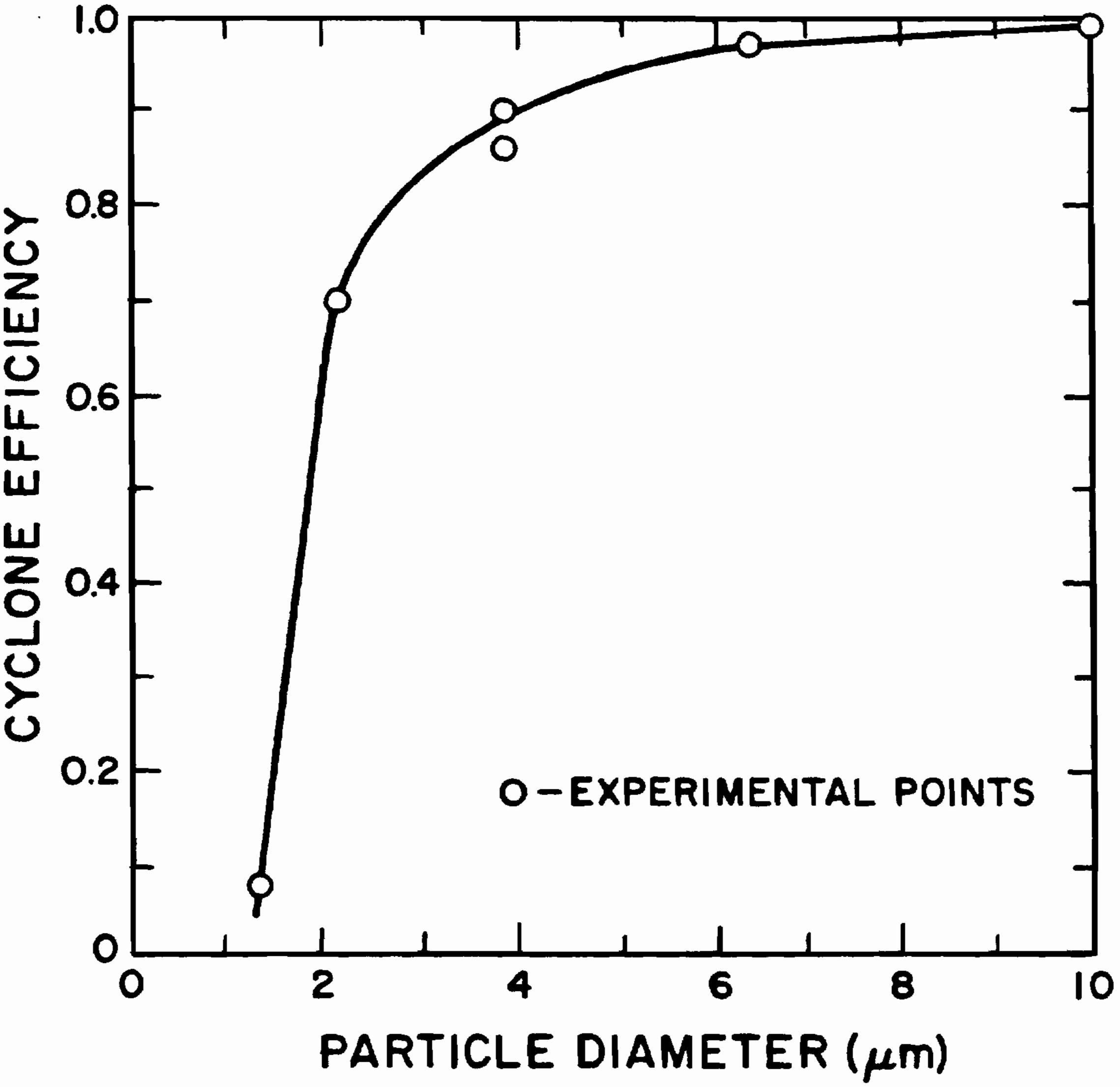


Figure 4.4.2. Collection efficiency of an ERT cyclone at 80 l/min as a function of aerodynamic particle diameter. The test particles were monodisperse, solid $(NH_4)_2SO_4$ produced by a Berglund-Liu vibrating orifice aerosol generator. The 50% efficiency point is 1.9 ± .2 um.

Coarse particles were removed by a cyclone attached to the sampling inlet which eliminated particles greater than 2 μm as verified by a test performed at OGC (See Figure 4.4.2). The inside of the cyclone was cleaned and coated with Apiezon prior to each sampling period.

Initial tests with the total particulate ERT samplers showed that the quantity of mass collected was very similar to that collected by the fine particulate samplers indicating a discrimination against the coarse fraction by the air inlet. An EPA intercomparison (Camp et al., 1978) of this sampler with 27 others (5 hi-vols, the remainder lo-vols) supported this observation. In this intercomparison the ERT sequential sampler total mass measurements were consistently 81% of the mean measurement of all of the samplers. It is to be emphasized that the majority of the samplers to which the ERT sampler was being compared were low volume samplers. The efficiency with respect to high volume samplers alone is much lower, consistent with PACS findings.

Also, filter contamination resulted from dirt accumulation on the inside of the plenum and disintegration of the gasket material at the sampler/plenum interface. The gasket on the cyclone samplers was replaced with neoprene rubber and the plenum and sampling tube were completely removed from the total particulate samplers. Each filter holder was covered with a fallout protector cap fashioned out of PVC to prevent dust from settling on the filter surfaces. The dimensions of this cap were such that the air velocity through the annular opening between the filter holder and the cap would be the same as the velocity of air entering the inlets of a standard hi-vol housing.

Table 4.4.1 Average Collection Efficiencies of ERT Samplers with Respect to Hi-Vol Measurements

Season	Site	Total HiVol μg/m^3	Total ERT % of Total HiVol	Fine ERT % of Total HiVol	Fine HiVol % of HiVol
SUMMER	1	52	83	23	41
	2	65	75	39	44
	3	60	74	30	37
	4	76	75	28	35
	5	56	86	31	34
	6	36	82	41	41
AUTUMN	1	38	89	47	44
	2	88	72	33	37
	3	76	79	32	42
	4	100	81	29	34
	5	66	96	39	40
	6	39	80	45	49
WINTER	1	28	93	49	49
	2	79	78	34	36
	3	69	92	39	43
	4	85	83	31	37
	5	63	93	38	85*
	6	19	79	44	42
SPRING	1	40	79	49	39
	2	102	66	28	38
	3	92	86	26	36
	4	158	84	20	29
	5	87	106	34	38
	6	55	92	34	34
AVERAGE			83	35	39

*Outlier not included in Average

The collection efficiencies relative to hi-vol of these modified samplers are presented in Table 4.4.1 for each site by season for the entire sampling program.

4.5 SOURCE SAMPLING

Source sampling is a difficult task for which a single standard operating procedure is difficult to define. Cooper and Rossano (1971) describe stack sampling for total mass in detail and EPA has established guidelines as its Method V for measuring the mass emission rates from stacks. Source sampling for chemical analysis and non-stack sources is not well established in practice, however, and the requirements of the PACS to dichotomously sample 37 source types identified by the emission inventory as potential contributors to the ambient loading required great skill and ingenuity on the part of the two man sampling crew.

The basic sampling unit consisted of a virtual impactor of Lawrence Berkeley Laboratory design which was fitted with a ball joint fitting for coupling to a sampling probe; the entire unit was located with pump and rotameters in an insulated case whose internal temperature could be varied from ambient to 60° C by means of a thermostat. The probe used for most samples was a standard heated stainless steel three foot probe of 1/2 inch inside diameter with interchangeable buttonhook nozzles of 1/8, 1/4, 3/10, 5/16, 3/8, and 1/2 inch inside diameters: an S type tube accompanied the probe. Figure 4.5.1 illustrates the entire appartus.

The probe is of standard design and merits no further discussion.

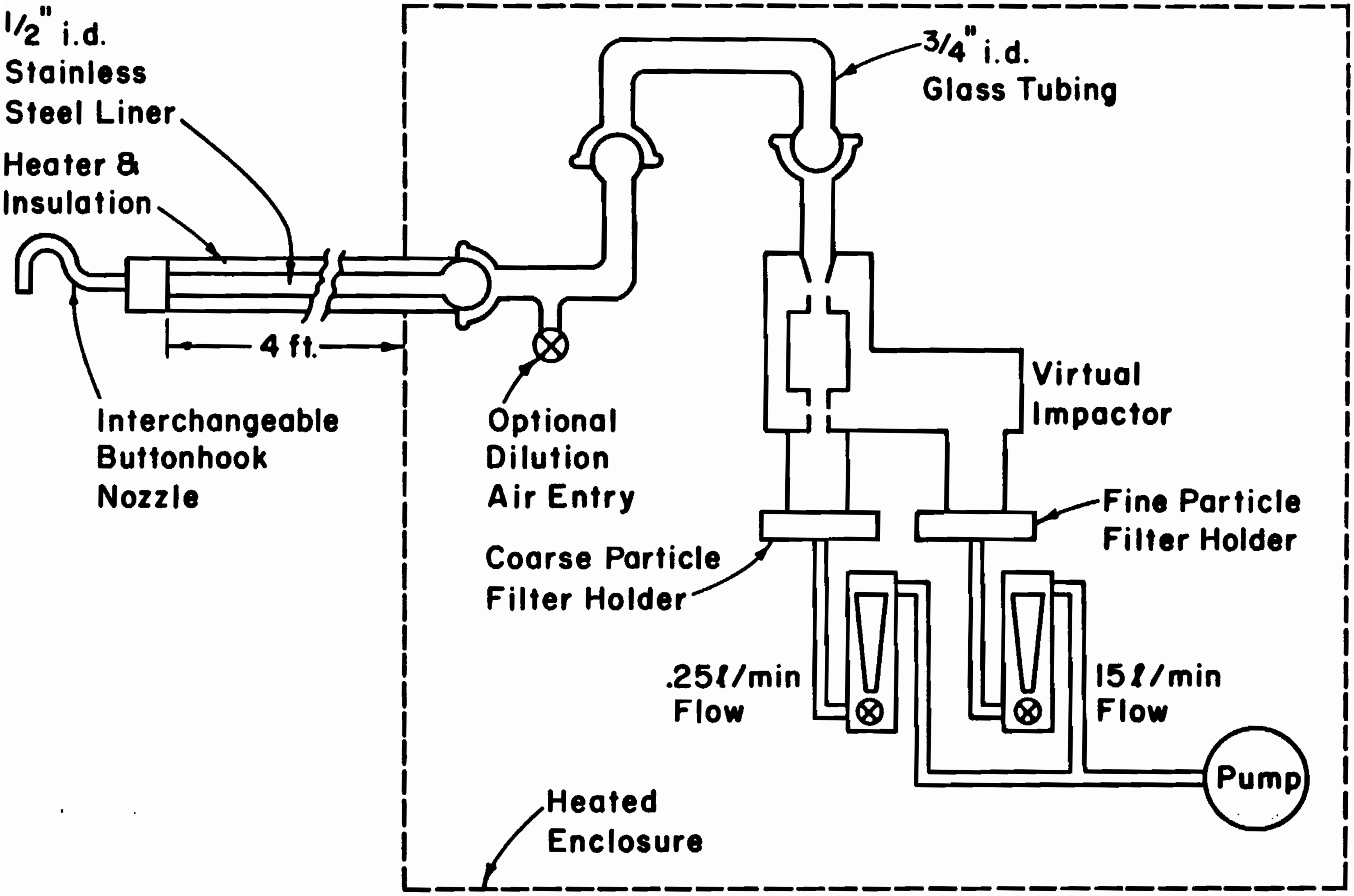


Figure 4.5.1. SOURCE SAMPLING APPARATUS

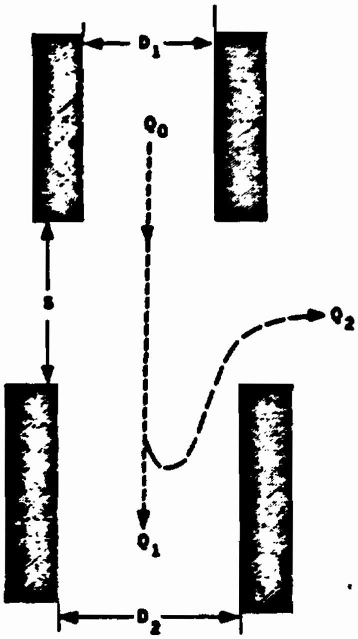


Figure 4.5.2. Virtual Impactor Critical Parameters from Loo, *et al.* (1975).

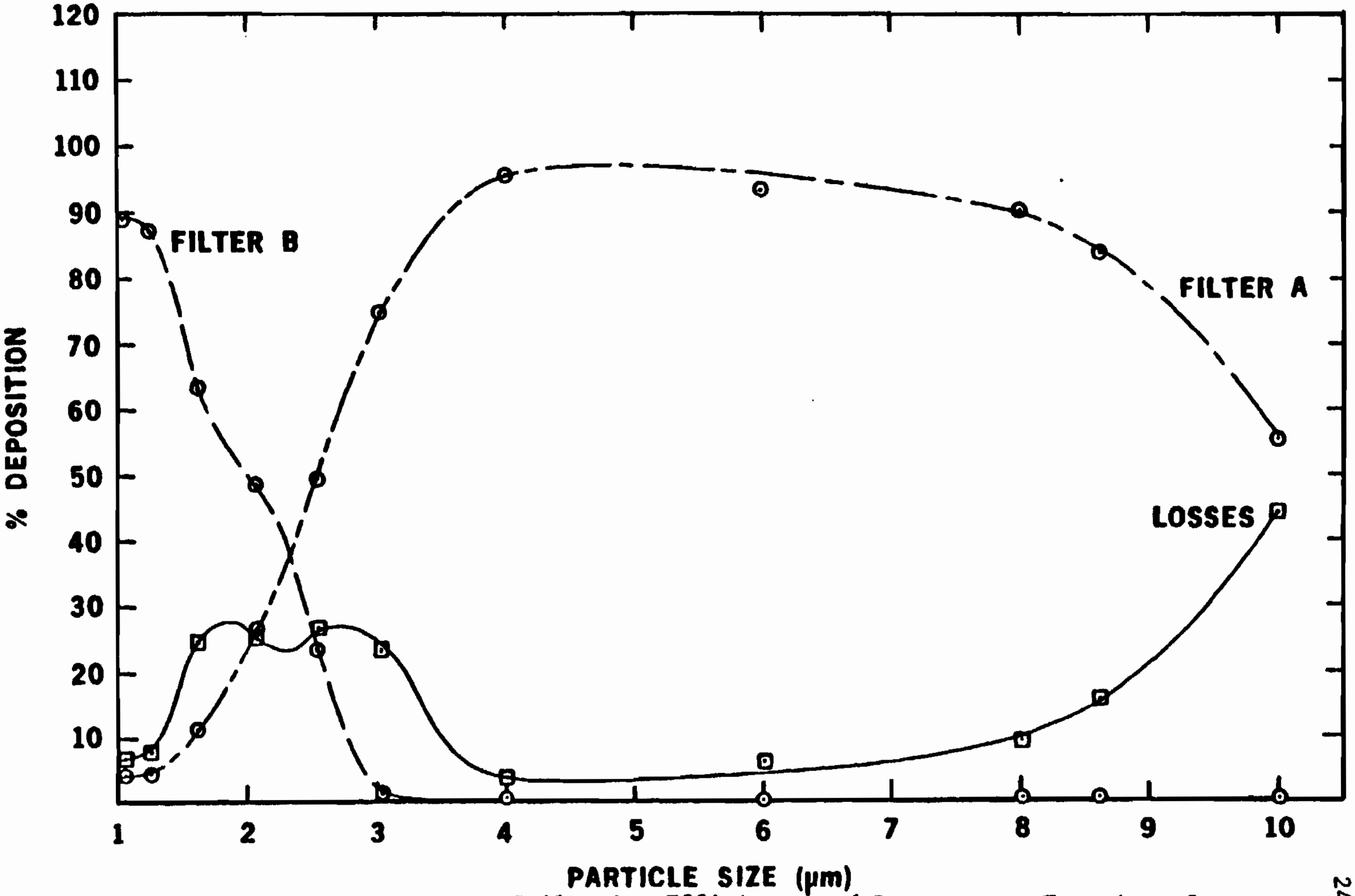


Figure 4.5.3. Virtual Impactor Collection Efficiency and Losses as a Function of Particle Size. Filter B is Fine particulate filter and Filter A is Coarse particulate filter. From Loo and Jaklevic (1974).

The virtual impactor is just leaving the research stage and is being applied to source sampling for the first time in this study and its operation requires some elaboration.

The device was first proposed by Houman and Sherwood (1965) and a design for dichotomous sampling was constructed and tested by O'Conner (1966). A later model for personal air sampling is described by Langmead and O'Conner (1969). The major research for its application to ambient sampling was performed by Loo and Jaklevic (1974) with field tests by Dzubay and Stevens (1975). Further studies by Loo and Jaklevic (1975) have resulted in substantial improvements; the model used in this study was based on their earlier (1974) work and was obtained from the EPA.

Figure 4.5.2 illustrates the principle of operation and the critical parameters of the virtual impactor jet. The total flow Q_o is broken into two components: one, Q_1, continues on a straight trajectory while the other, Q_2, exits through a lateral opening. If $Q_2 >> Q_1$, the streamlines make a right angle turn at the lateral opening. Particles with low inertia follow these lines while high inertia particles are projected straight into the region where they are caught in Q_1. Filters at the airflow exit trap the particles in each region as a homogeneously distributed surface deposit, perfect for XRF analysis in contrast to conventional impactors whose deposits take the form of small piles or lines. The virtual impactor also minimizes crossover between sizes due to re-entrainment and bounce-off. Though some fine particulate does enter the coarse mode because of the flow Q_1, the flow ratio Q_1/Q_2 is typically less than .02 making this contribution insignificant if the aerosol mass is more or less evenly distributed between the fine and coarse particulate modes.

Figure 4.5.3 shows the 50 per cent size cut at 2.5 μm of this type of impactor and the losses as evaluated by Loo and Jaklevic (1974) and verified by electron micrograph sizing of selected samples by DEQ.

As Figure 4.5.1 shows, the flow through each stage was measured by a rotameter calibrated with ambient air at 20° C and atmospheric pressure. To achieve the 2.5 μm cut point flows of 15 ℓ/min through the fine particle filter and .25 ℓ/min through the coarse particle filter were required. The uncertainties on these measurements were estimated to be ± 1 ℓ/min and .01 ℓ/min respectively.

Even if all of the stack gases measured are assumed to have the same composition, aside from trace gases and aerosol, as ambient air, the flow readings of the rotameters used in the configuration of Figure 4.5.1 will be biased because the gas flowing through them is not of the same density as the gas with which they were calibrated since (1) in some cases the temperature is higher and (2) the pressure is not atmospheric due to the pressure drop across the sampler. The effect of this bias on the size cut is easily evaluated. Mercer (1973) shows that the actual flow through a rotameter at a given reading is proportional to the square root of the density of the gas, ρ, and Marple (1975) demonstrates that the 50 percent cut point of an impactor jet, D_{50}, is inversely proportional to the square root of the flow through it. The actual cutpoint under the non-calibration readings of the rotameter is then

$$D_{50} = D_{50c} \sqrt[4]{\rho_c/\rho} \qquad 4.5.1$$

$$D_{50} = D_{50c} \sqrt[4]{\frac{T}{T_c}\,\frac{P_c}{P}} \qquad 4.5.2$$

where the gas densities have been related to pressure, P, and absolute temperature, T, by the ideal gas law and the c subscript refers to the calibration values. A worst case situation occurs when the temperature is 65° C and the pressure is .5 atmosphere. Under these conditions the 50% cut point would increase by 23% to 3.1 μm, a change of minimal consequence in this application.

A pressure gauge should be installed behind the impactor and a thermometer placed in the sampler box so gas density changes can be accounted for and the proper rotameter scale correction made to assure a 15 ℓ/min flow rate. Assumed isokinetic conditions may be in error by as much as 50% due to this bias tending to underestimate the concentration of large particles.

Prior to each sampling the probe and impactor assemblies were brushed, soaked in soap and water and rinsed in acetone; the plastic filter holder was washed with soap and water and dried. Both 37 mm washed and preweighed Millipore and preweighed glass fiber filters were loaded in the field, one right after the other, over clean drain disks into the two parts of the sampler. The probe was placed into the stack, duct, or over the vent or chimney of the source being tested and a stack velocity pressure drop measurement was made with the pitot tube. A nomograph was used to associate a nozzle size with the pressure drop and thus approximate isokinetic sampling; the constant flow required by

Table 4.5.1 Deviations from Isokinetic Sampling

Nozzle Diameter	a Vs,m/sec	b Vn, m/sec	Vs/Vn	c 5 um	c 20 um
1/8"	>15	1.6	>.47	>95%	>60%
1/4"	6.7-15	7.9	.85-1.9	98%-120%	87%-155%
3/10"	5.3-6.7	5.5	.96-1.2	94%-103%	97%-107%
5/16"	4.3-5.3	5.1	.84-1.0	98%-100%	87%-100%
3/8"	2.7-4.3	3.5	.77-1.2	98%-108%	80%-107%
1/2"	<2.7	2.0	<1.35	100%-104%	100%-109%

[a] Stack velocity range for which nozzle was chosen.

[b] Gas velocity through nozzle at a flowrate of 15 l/min.

[c] Collection efficiency estimates from Mercer (1973, p.362) The figures are from measurements at $V_s = 5$ m/sec. and are only meant to provide an order of magnitude approximation errors. For particles less than 5um these errors do not appear to be serious. At low velocities <2.7 m/sec. the error is very small.

the dichotomous sampler to maintain its size cut did not allow stack and nozzle velocities to match exactly. Table 4.5.1 shows the maximum deviation of stack from sampler velocity for each available nozzle. It is possible that the collection of large particles was either enhanced or attenuated as shown.

The probe and sampler were heated at the discretion of the sampling crew up to a maximum of 65° C, a temperature which could not be exceeded lest the cellulose acetate filters melt, to prevent the condensation of water vapor in the sampling train. In two cases, both recovery boilers, this heating was insufficient to prevent condensation and dry dilution air was added at the point illustrated in Figure 4.5.1 to bring the overall concentration of water vapor below the saturation point. The flows were adjusted, checked and rechecked after sampling. The probe was inserted into the center of the stack, duct, vent or chimney and a sample was taken for an amount of time estimated by the field crew to collect 1-5 mg of deposit on each filter. Upon completion of sampling the filters were removed from the samplers, placed in their protective petri dishes and returned to the lab for reweighing.

No traverses were made of the stacks tested, but since emission rates were not the objective of the experiments this was not deemed necessary. If the particulates in the airflow are of uniform composition across the airflow then any sample of them is adequate for chemical characterization. Further tests are needed to verify this assumption.

Slash burns were sampled with Millipore filters by airplane flights through plumes using the unheated dichotomous sampler connected to an external air inlet located upwind of the engines; the filters were treated as in the stack sampling. Isokinetic sampling was attempted by choosing a nozzle on the intake pipe through which the flow would approximate the plane's airspeed. Glass fiber filter samples were taken with a hi-vol sampler connected to another air inlet. A Sierra sampler head was used to obtain a measurement of particles less than 2 μm. The samplers were only in operation when the plane was actually in the plume. Background aerosol mass measurements for comparable sampling times were over a factor of ten lower than the measurements contained within the plume and were not subtracted.

Several simulated grass field burns were created by setting fire to ~20 kg of grass stubble and inserting the probe into the resulting plume. Organic substances were found deposited on the inside of the probe and impactor after sampling, apparently having condensed at the lower temperature of the sampler. The greater cooling in plumes over real burns apparently allows this condensation to occur in the atmosphere prior to sampling. Some sort of plume aging should be designed into future simulated burn sampling.

Street dust samples were collected from freeways and assorted locations near the urban sampling sites by using an enclosed hi-vol sampler containing a glass fiber filter. A vacuum cleaner hose connected this unit to a brush which was pushed over the road surface between the center line and a distance of three feet from the curb for 2-15 minutes, the time required to obtain a .5 to 1.0 inch layer of dust on the filter. Originally a shop-type vacuum cleaner was tested, but the bag was found to be an inefficient collector of small particles. Pure suction without a brush was attempted, but this too discriminated against small particles apparently because of adhesion to the roadway (A sample of these particles was placed in acetone. Subsequent filtration and evaporation of the acetone left an oily residue which could have facilitated adhesion. The brush apparently dislodged them for entrainment in the suction airflow. Such an oil film may be common on roadway particles and might act as an implicit control device to keep the fine portion from being re-entrained.)

Soil dust from various land formations was obtained near the sampling sites and dried in the lab.

Each of these specimens was sieved through a Tyler 200 mesh screen which effectively eliminated granules with a diameter greater than 75 µm, and was placed in a labeled bottle.

Resuspension of the dust for sized collection on filters by the dichotomous sampler was hampered by the dielectric properties of the individual particles, the glass puffing container and the glass sampling probe originally used; many particles adhered to the probe and apparently to each other as evidenced by microscopic examination of the filters which showed no size separation.

The configuration which yielded best results is presented in Figure 4.5.4. A puffer ball resuspended the dust in its sample bottle and projected the aerosol into a disposable cellulose container's 1500 cm^3 "aging" region where it was sampled with the grounded stainless steel stack probe. Micrographs revealed that size separation did take

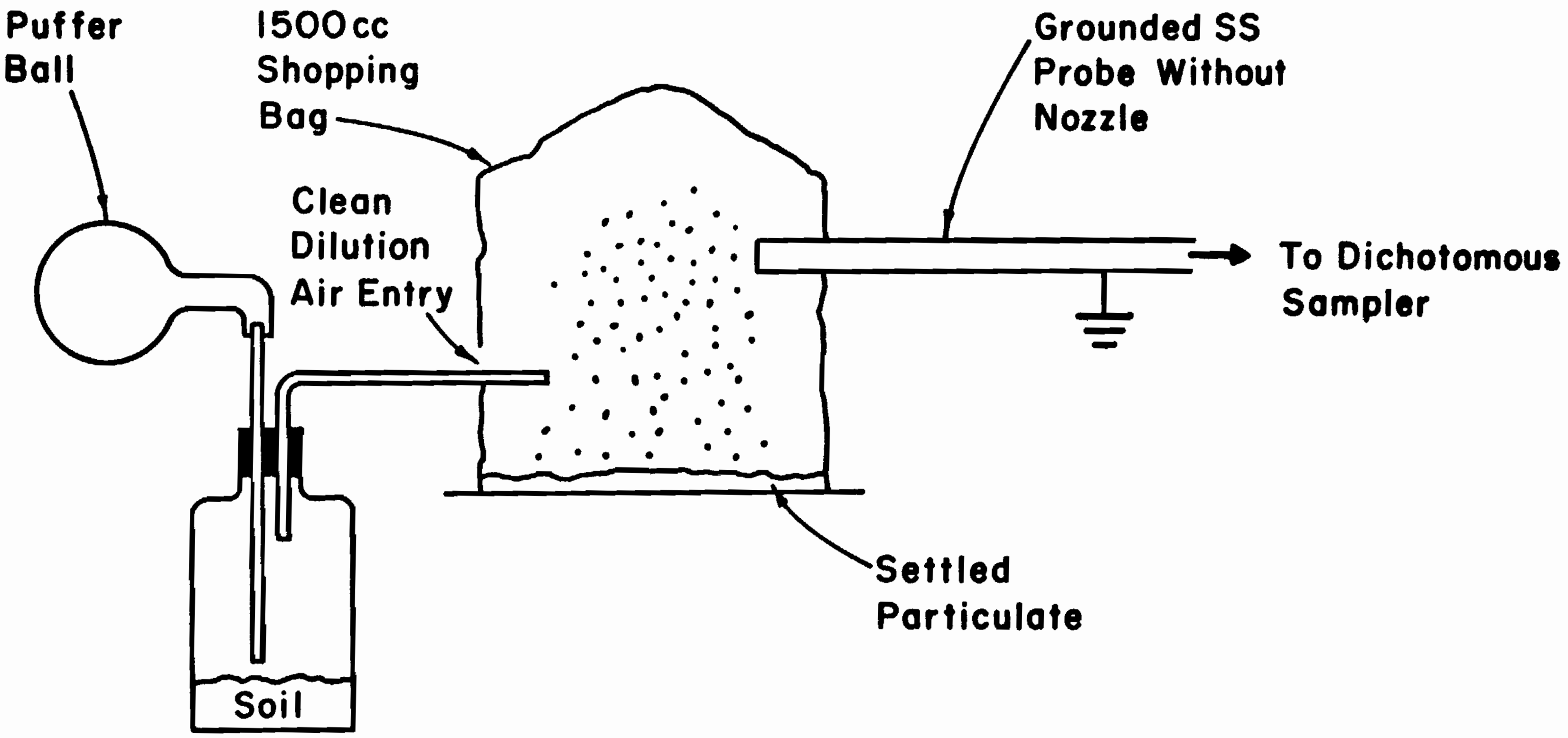


Figure 4.5.4. RESUSPENDED SOIL SAMPLING APPARATUS

Table 4.5.2 Source Tests

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Rock Crusher Ross Island	Z0266 Z0241 ____d ____d		65°C		Leakage from crusher (Simons 4'x3') (Pioneer roll)		Z0241 - Coarse Has some particles flaked off
Rock Crusher Ross Island	Z0251 Z0283 ____d ____d		65°C		Same as above		Z0283 - Coarse Has some unattached deposit
Rock Crusher Western Pacific	Z0255 Z0244 ____d ____d		65°C		No exhaust stack, sampled through holes near rock inlet	Some water spray to control dust	Z0244 - loose deposit
Rock Crusher Western Pacific	Z0289 Z0258 ____d ____d		65°C		"	"	Z0258 - loose deposit
Asphalt Batching Cascade Const.	Z0315 Z0305 Z1094 Z1110		65°C	Natural gas, Gravel	Bag house exhaust where gravel enters	85% Drum Rotation 15% Bag Shaking Hot batch process. Natural gas combustion exhausts through same outlet	
Asphalt Cascade Const.	Z0321 Z0304 Z1149 Z1180		65°C	"	"		

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Asphalt H. K. Jacobsen	Z0215 Z0187 Z1106 Z1105		65°C		Near center of bag house exhaust pipe in average velocity section. Very fast airflow.		Non-uniform deposit
Road dust IAP Winter	Z0423 Z0901 Z1146 ______[d]	b	Ambient		See text	b	See text
Road dust PMR Winter	Z0427 Z0902 Z1186 ______[d]	b	Ambient		"	b	See text
Road dust S.E. Portland Winter	Z0440 Z0903 Z1208 ______[d]	b	Ambient		"	b	See text
Road dust CAMS Spring	Z0473 Z0904 Z1136 ______[d]	b	Ambient		"	b	"
Road dust Freeways Fall	______[d] Z0905 Z1165 ______[d]	b	Ambient		"	b	"
Soil Sauvies Island	Z0490 Z0906 Z1209 ______[d]	b	Ambient		"	b	"

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Soil Liquid Air	Z0494 Z0907 Z1200 ____[d]	b	Ambient		"	b	See text
Soil Flavel Park	Z0461 Z0908 Z1210 ____[d]	b	Ambient		"	b	"
Soil PMT	Z0479 Z0909 Z1201 ____[d]	b	Ambient		"	b	"
Soil Carus	Z0482 Z0910 Z1202 ____[d]	b	Ambient		See text	b	See text
Road dust Composite	Z0474 Z0911 Z1204 ____[d]	b	Ambient		See text	b	See text
Soil Composite	Z0499 Z0912 Z1203[d]	b	Ambient		See text	b	See text
Auto Leaded	Z0245 Z0252 Z1178 Z1181		65°C	1968 Ford 6 cylinder Pickup w/ leaded gas	At exhaust pipe		5 minutes sampling time
Auto Leaded	Z0243 Z0291 Z1143 Z1108		65°C	"	"		Same

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Auto Unleaded	Z0317 Z0318 Z1140 Z1132		65°C	Unleaded gas, but car had previously used leaded	At exhaust pipe	30 seconds idle 2 start stop then 35 mph for total 5 minutes	1973 Dodge Pickup V8
Auto Unleaded	Z0312 Z0275 Z1150 Z1185		65°C	"	"	"	"
Truck Cummins	Z0196 Z0211 Z1098 Z1030		65°C	Diesel fuel	6-8 ft. above exhaust pipe		NTC 350 engine w/125,000 miles just overhauled (80% of Oregon engines)
Truck Cummins	Z0195 Z0205 Z1090 Z1096		65°C	Diesel fuel	"	Dynamometer test 50% idle 50% full H.P. 80% idle 20% full H.P.	NTC 350 w/116,000 miles
Truck Cummins	Z0201 Z0204 Z1103 Z1102		65°C	Diesel fuel	"	C 33% Full 67% idle	NTC 350 w/ 441,000 miles
Truck Cummins	Z0212 Z0198 ______d ______d		65°C	Diesel fuel	"	Unknown	NTC 350/w 200,000 miles
Train Burlington Northern	Z0329 Z0337 Z1119 Z1133		65°C	Diesel fuel	Over stack	3/4 throttle while standing w/simulated load	1/2 throttle ~ 400 H.P. on 1200 H.P. engine
"	Z0342 Z0343 Z1153 Z1163		"	"	"	"	"
Residual oil Rasmussen Apts.	Z0214 Z0202 Z1089 Z1092		65°C	Unspec. residual oil	Over chimney	Twin boilers -single chimney 2 Ray burners	
"	Z0191 Z0206 Z1085 Z1088		"	"	"	"	

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Residual oil V. A. Hospital	Z0260 Z0249 Z1117 Z1109		65°C	Unspec. residual oil	Over chimney		
"	Z0301 Z0271 Z1170 Z1169		"	"	"		
Residual oil Lincoln High	Z0287 Z0216 Z1120 Z1121		65°C	Shell PS 400 residual oil	Over chimney	Ray burner	
"	Z0277 Z0276 Z1114 Z1174		"	Alaskan with high sulfur content	"	"	
Residual oil Boise Cascade	Z0265 Z0261 Z1116 Z1115		65°C				
"	Z0285 Z0286 Z1074 Z1118		65°C				
Distillate oil Castle Manor	Z0186 Z0203 Z1099 Z1086		60°C	Arco distillate oil	Inside horizontal duct		
"	Z0189 Z0190 Z1095 Z1079		60°C	Arco distillate oil	"		

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Distillate oil Hanrahan	Z0043 Z0040 Z1017 Z1003		65°C	Distillate oil	6' from furnace in horizontal duct through damper	Before tune-up, inefficient operation	
"	Z0063 Z0087 Z1021 Z1026		"	"	"	"	
Distillate oil Hartford	Z0119 Z0096 Z1007 Z1004		65°C	"	At chimney		
Distillate oil Hanrahan	Z0279 Z0253 Z1171 Z1123		65°C	"	In duct through damper	After tune-up, efficient operation	
"	Z0290 Z0239 ____d ____d		"	"			
Natural gas boiler Publishers Paper	Z0296 Z0250 ____d ____d		65°C		Boiler exhaust	Fire brick stack. Boiler had previously burned oil	
SLASH Walton 9-22	____d ____d Z1637 Z1638	b	65°C	Broadcast slash	Aircraft	3700'-4000'	See text
"	Z0049 ____d ____d Z1721	b	65°C	"	"		See text

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
SLASH clean ambient air	Z0035 Z0037 ____[d] Z1722	b	65°C	Clean ambient air	Aircraft		See text
SLASH GREEN PETER	Z0033 Z0014 Z1320 Z1322	b	65°C	Broadcast slash	Aircraft		See text
SLASH Newport	Z0031 Z0019 Z1315 Z1316	b	65°C	"	Aircraft		See text
SLASH Cottage Grove	Z0028 Z0026 Z1738 Z1317	b	65°C	"	Aircraft		"
SLASH clean ambient air	Z0029 Z0032 Z1736 Z1737	b		Ambient air	Aircraft		"
"	____[d] ____[d] Z1319 Z1318	b	65°C	"	"		"
SLASH Alsea	Z0034 Z0020 Z1311 Z1310	b	65°C	Broadcast slash	Aircraft		"
SLASH Albany	Z0017 Z0048 Z1427 Z1426	b	65°C	Piled slash	Aircraft		"

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Fireplace Hartford	Z0094 Z0111 Z1331 Z1329		65°C	Cedar, fir, pine, alder	Chimney		After white smoke had dissipated, trash such as newspaper, cartons, etc., were added
Same	Z0115 Z0095 Z1333 Z1332		65°C	"	"		"
Choked off wood stove	Z0259 Z0225 Z1134 Z1159		65°C	Douglas fir			
Same	Z0223 Z0298 Z1175 Z1138		65°C	"			
Domestic Burn	Z0123 Z0121 Z1334 Z1326		65°C	Pine trim			
Domestic Burns Hartford	Z0122 Z0098 Z1328 Z1531		65°C	Orchard trim wet leaves, brush, ivy			
"	Z0099 Z0117 Z1009 Z1010		"	"			
"	Z0113 Z0112 Z1008 Z1007		"	"			

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Domestic Burn Erickson	Z0319 Z0348 Z1139 Z1162			Kitchen trash			
Field Burn Eugene	Z0036 Z0042 Z1428 Z1429	1/2"	65°C	Bentgrass	In plume over burn	Simulated burn. ~20Kg of raw material piled and set afire	Organic condensation in sampler probe
"	______d ______d Z1430 Z1325	1/2"	"	"	"	"	"
"	Z0064 Z0073 Z1433 Z1431	1/2"	65°C	Bluegrass	"	"	"
Field Burn	Z0089 Z0084 Z1435 Z1434	1/2"	65°C	Rye gulf	"	"	"
Field	Z0023 Z0093 Z1437 Z1436	1/2"	65°C	Wheat	"	"	"
Field	Z0075 Z0074 Z1439 Z1438	1/2"	65°C	Fine leaf	"	"	"
Field	Z0018 Z0061 Z1441 Z1440	1/2"	65°C	Orchard grass	"	"	"

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Field	Z0092 Z0091 Z1527 Z1526	1/2"	65°C	Tall Fescue	In plume over burn	Simulated burn. ∿20Kg of raw material piled and set afire	Organic condensation in sampler probe
"	Z0078 Z0079 Z1529 Z1528	1/2"	65°C	"	"	"	"
Kraft Recovery Boiler Boise Cascade	Z0221 Z0194 Z1083 Z1113		65°C		Stack		Z1113 may have got wet Sampled under extremely moist conditions in exhaust gas Dilution air used
"	Z0213 Z0232 Z1122 Z1112		65°C		"		"
Sulfite Recovery Boiler Publishers Paper	Z0148 Z0147 Z1005 Z1006		65°C		Stack		Sampled under extremely moist conditions in exhaust gas Dilution air used.
Hog fuel Publishers Paper	Z0090 Z0081 Z1008 Z1025	1/4"	65°C	Hog fuel Bark dust	Stack 40 ft up, 12 ft top at regular sampling port	Velocity: 2050 FPM at 500°F	Glass fibers were partially lost Cell coarse had large sootlike particles which flaked off
"	Z0080 Z0082 Z1014 Z1001	1/4"	65°C	"	"	"	"
Hog fuel Barker	Z0024 Z0070 Z1011 Z1024	3/8"	65°C	Hog fuel No bark May have had glue	Stack	1325 FPM at 370°F	Non-uniform deposition
Flour Mill Terminal	Z0164 Z0165 Z1012 Z1020		65°C	Dark - Hard winter wheat	Baghouse		May have large artifact Zn & Fe due to polishing of probe and galv. pipe

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Grain elevator Dreyfuss	Z0168 Z0169 Z1018 Z1015		65°C	Soft white wheat	Under tarps where loading takes place	Grain transfer	Uneven deposition
"	Z0180 Z0170 Z1073 Z1078		65°C	"	"	"	
Aluminum reduction Alcoa	Z0346 Z0338 Z1135 Z1176		162°F		In stack 100' from baghouse		
Aluminum reduction Reynolds	Z0185 Z0184 Z1093 Z1077		65°C		Courtyard Scrubber Stack		Z1193 edge contaminated Will affect mass but not carbon
"	Z0182 Z0209 Z1070 Z1091		65°C		"		
Aluminum reduction Reynolds	Z0171 Z0208 Z1009 Z1068		Ambient		Roof vent		Z0208 has water marks
Alumina handling General Ore	Z0236 Z0264 ______d ______d		Ambient				
Same	Z0256 Z0220 ______d ______d		Ambient				

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Steel foundry ESCO	Z0172 Z0207 ____d ____d		Ambient		Baghouse fed by furnace canopy	Sampled when baghouse was being cleaned Partial of 1+ cycle	Z0207 - wet
"	Z0181 Z0175 ____d ____d		Ambient		Same	Same 2 cycles	Z0175 - wet
Ferro-manganese Union Carbide	Z0278 Z0294 Z1151 Z1183				Baghouse door above bags (all exhaust #3) (top exhaust #4)		
"	Z0295 Z0224 Z1182 Z1131				"		
Carborundum Carborundum	Z0311 Z0310 Z1124 Z1184		Ambient	Coke + electric + SiO_2 - sand		Burn cycle	2-3 blowouts/hr
"	Z0307 Z0306 Z1129 Z1130		"				
"	Z0269 Z0234 Z1168 Z1157		"				
Glass furnace Owens	Z0272 Z0228 ____d ____d		65°C		Furnace A		Se & S added to glass to reduce color and produce brown
"	Z0248 Z0299 ____d ____d				"		

Table 4.5.2 Source Tests (continued)

Source Type Location	Filter IDs	Nozzle	Sampler Temp.	Fuel or Raw Material	Probe Location	Source Operating Mode	Sampling Details
Car shredder American Ship	Z0177 Z0176 Z1080 Z1075		65°C	Cars, washing machines, barrels, galv. roofing			Z0177 - fragmented
"	Z0178 Z0167 Z1019 Z1031		65°C	"			
Carbide furnace Pacific Carbide	Z0280 Z0229 Z1154 Z1144		65°C			1/3 of bags in baghouse contained holes	
"	Z0230 Z0218 Z1158 Z1142		65°C			"	

a Order of sample in list corresponds to sample type:
Cellulose Fine
Cellulose Coarse
Glass Fiber Fine
Glass Fiber Coarse
b Not applicable
c Unknown
d Sample not taken or unsuitable

place with this method. The addition of a radioactive charge neutralizer would further refine this procedure.

The coarse particle fraction of the soil samples would not stay on the filter and subsequent chemical analysis could not be performed. Therefore, an analysis of the total dust was made by submitting known quantities of the bulk material to each of the chemical analyses. The only deviation from standard operating procedures was required for XRF. Here, the sample was pulverized in a rotary swing mill with a calcium sterate grinding aid and binder and pressed into a pellet. Similar samples of characterized soils were prepared in the same way as standards. Actual concentrations were then calculated by the method of Cooper, et al. (1976).

Table 4.5.2 presents the source samples taken and specific information concerning individual variations in the sampling technique and the source itself.

4.6 METEOROLOGICAL DATA

Hourly windspeeds, s_i, and directions, θ_i, throughout the airshed were required to classify sampled days into meteorological regimes and to determine basic flow patterns during the sampling period of each filter. Thirteen anemometers and windvanes were located in the positions noted in Figure 4.1.1. Table 4.6.1 lists the locations of each site, the wind equipment in use and a meteorologist's (Freeman, 1978) evaluation of the representativeness of the data from that site.

Eight hour vector windspeeds and directions were calculated for each site and plotted on a map of the airshed by the computer

Table 4.6.1 Windspeed and Direction Sensors Used in the Portland AQMA

Operated By	Site ID	Site Description	Equipment Description	Approx. Data Completeness	Data Evaluation	Avg. Methods - (hourly representation)
DEQ	1 (Sauvie Island)	½ mile North of Game Commission check-out Station. Large bush (15-20') about 50' south	Xonics cup and vane.* Telemetry to central DEQ Data Acquisition System	70%	Fair, seems to show some westerly bias.	wind components (x & y) are integrated hourly averages, re-composed to give speed and direction
DEQ	2 (R.G.)	Rivergate-Port of Portland Term. #6	*	50%	Good. Represents river channeled flow	*
NWS	3 (PDX)	Portland Int. Airport, located by runway, good expos.	Cup anemometer on 20' mast. Wind vane at same level on separate mast.	99%	Good representation of winds near river but only fair correlation with winds downtown	10 minute averages taken 10 minutes before the hour.
Reynolds Metals	4 (T.D.)	Reynolds Metals, Troutdale. Instrument mounted on mast 111' above ground, 30' above top of bldg #30, no obstructions	Bendix-Frieze Acrovane and strip chart recorder	90%	Good. Best representation of Gorge-channeled flow	Hourly averages read from strip chart.
DEQ	5 (S.O.)	Standard Oil of California offices. Poor siting. Affected by very local topography, not area-wide representative.	*	75%	Poor, possibly due to siting. Appears to be biased to westerly directions	*
DEQ	6 (Flavel)	Center of open park area, near south boundary	*	50%	Fair to good. Frequent data losses make evaluation diff.	*
DEQ	7 (Carus)	Edge of road 0.4 mi. west of 213 on Spandler Rd. 0.9 mi.so. of Carus	*	80%	Good. Best representation of flow patterns in southern portion	*
DEQ	8 (F.B.)	Cup and vane approx. 10-15' above roof of Fed. Bldg. Good exposure, no nearby taller buildings	*	80%	Good. Best representation of winds over downtown area	*
ODOT	9 (Clark School)	30' to 40' above ground on Clark School grounds. 1 lg. tree 30' to 40' so. otherwise good exposure	MRI portable weather station Cup and vane with strip chart recorder	0	? no data	Average of 6 - 10 min. averages
OSHD	10 (KATU)	Sensors mounted on mast extending to approx. 20' above roof of KATU studio bldg. 22nd & Sandy (no longer there)	MRI portable weather station Cup & vane w/strip chart recorder	40%	Poor. Shows bias to high windspeeds and southerly directions. Directions are only to nearest 45°	Averages read from strip chart, direction approx. to nearest 45°.
DOE (Wash)	11 (Vancouver)	Near Vancouver military barracks. Park-like area, good exposure	Climet cup and vane mounted on 20' mast. Data telemetered to Olympia. Backup strip chart Scans every 2 min.	80%	Good. Consistent with PDX & Rivergate & represents wind-channeling by Col. Riv. Gorge.	Hourly averages of wind speed and direction taken every 2 minutes

Table 4.6.1 Windspeed and Direction Sensors Used in the Portland AQMA

Operated By	Site ID	Site Description	Equipment Description	Approx. Data Completeness	Data Evaluation	Avg. Methods - (hourly representation)
DEQ	12 KPTV 2	KPTV tower on West Hills' ridge, 450 m. level	*	50%	Fair, not truly representative of surface flow because of some speedup effect by W. Hills. Better for vertical structure	*
DEQ	13 KPTV 3	KPTV tower, 560 m.	*	50%	Good. Gives best representation of upper level flow directions	*

DEQ: Oregon Department of Environmental Quality
NWS: National Weather Service
DOE: Washington Department of Ecology
ODOT: Oregon Department of Transportation
OSHD: Oregon State Highway Division
*: Same for all DEQ stations

program *MTPLT. A persistence factor, P, (Heidorn, 1978) defined as

$$P = \frac{V}{s}$$

$$V = \sqrt{V_x^2 + V_y^2},\ V_x = \frac{1}{8}\sum_{i=1}^{8} s_i\cos\theta_i,\ V_y = \frac{1}{8}\sum_{i=1}^{8} s_i\sin\theta_i \qquad 4.6.1$$

$$s = \frac{1}{8}\sum_{i=1}^{8} s_i$$

where V is the 8 hour vector average speed and s is the 8 hour scalar average speed determined by *MTPLT to aid in the determination of stable flow patterns. A value of P close to unity indicates an uni-directional windflow at that station over the eight hour period while a value near zero implies a highly variable wind direction.

Ninety-six of these plots were produced, one for each sampling period of the 32 intensive analysis days, and each was classified by the meteorologist into one of the flow patterns explained in section 3.4.

4.7 ANALYTICAL METHODS AND STANDARD OPERATING PROCEDURES

Detailed standard operating procedures were developed for each phase of the experimental operation according to the format presented in Table 4.7.1. Table 4.7.2 lists each standard operating procedure (SOP) and its associated number. The importance of a written, continually updated SOP in which each technician has been well grounded cannot be overstated; it is the basis for any quality control and the first step in assuring a uniform treatment of all samples. Each technician possessed copies of the SOPs and received extensive training prior to performing the operation on his own. Quality was controlled

Table 4.7.1 Format of Standard Operating Procedures

1. General Discussion
   a. Analytical Problem
   b. Principle
   c. Interferences
   d. Minimum Detectable Concentration
   e. Precision and Accuracy

2. Apparatus and Instrumentation
   a. Description
   b. Characterization
   c. Maintenance

3. Standards
   a. Preparation
   b. Use
   c. Accuracy

4. Procedure
   a. General Flow Diagram
   b. Daily Start Up
   c. Routine Operation
   d. Daily Shutdown

5. Quantification
   a. Calibration with Standards
   b. Background subtraction
   c. Interference corrections
   d. Uncertainty estimate

6. Quality Control
   a. Possible errors
   b. Steps to prevent them

7. Quality Assurance
   a. Inclusion of QA standards in routine analyses
   b. Rejection and reanalysis criteria
   c. Data flags for deviations from SOP

8. References

Table 4.7.2 PACS Standard Operating Procedures

OGC/PACS SOP Number	
1.	Cellulose Acetate (Lo-vol) Filter Preparation
2.	Weighing of Lo-vol Filter
3.	Lo-vol Filter Loading, Handling and Storage
5.	Energy Dispersive X-ray Fluorescence (XRF) Analysis of Lo-vol Filters
6.	Lo-vol Filter Cutting
7.	Short Irradiation Instrumental Neutron Activation Analysis (INAA) of Lo-vol Filter Sections
8.	Ion Chromatographic Analysis of Lo-vol Filter Sections
9.	Lo-vol Field Sampling with the ERT sequential sampler
10.	Weighing, handling and storage of Glass Fiber (Hi-vol and Sierra) Filters
11.	Hi-vol Field Sampling with the Sierra Impactor Head
12.	Carbon Analysis of Hi-vol Filters

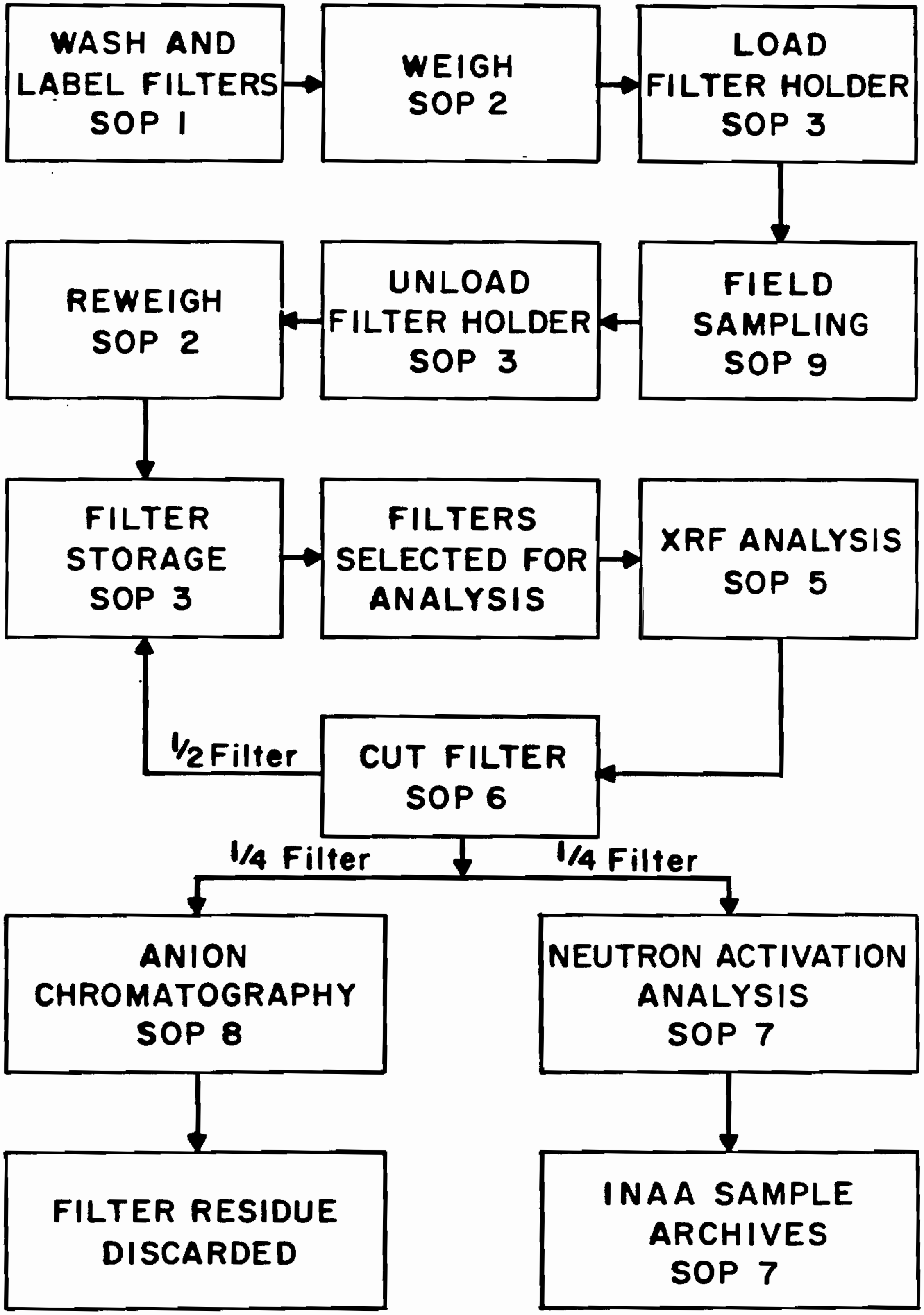


Figure 4.7.1. Flow of tasks performed on Lo-vol filters and corresponding Standard Operating Procedures.

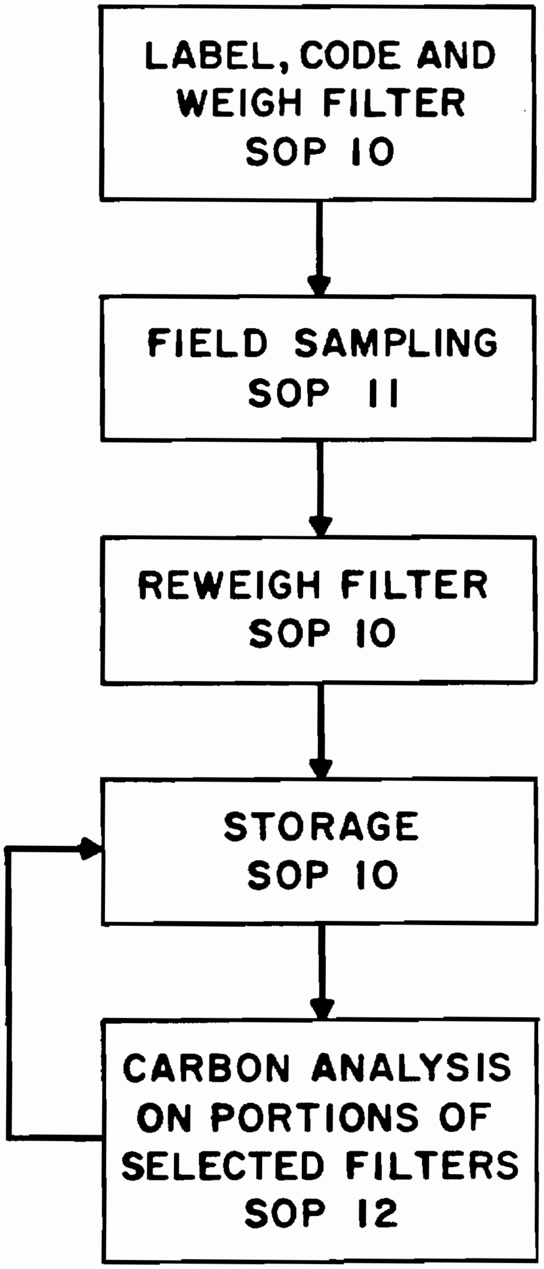


Figure 4.7.2. Flow of tasks performed on Hi-vol filters and corresponding Standard Operating Procedures.

by ultra-clean procedures, random spotchecks of the technicians' procedure by the laboratory supervisor and by assigning codes to common deviations from the procedure and noting these codes on the data sheets. Continuous feedback was solicited from technicians and SOPs were modified according to their suggestions for improving efficiency or quality.

Figures 4.7.1 and 4.7.2 indicate the general flow of tasks for both the lo-vol and hi-vol filters and the corresponding SOP number. A description of each analytical method and its SOP is presented briefly below.

4.7.1 CELLULOSE FILTER PREPARATION

Each filter was soaked in 18 megohm deionized water for 24 to 48 hours to remove soluble ions acquired during the manufacturing process. The filters were then transferred with teflon coated forceps to a previously cleaned polyethylene sheet inside a laminar flow hood and allowed to dry for 45 minutes.

Plastic petri dishes from the Millipore Corporation were cut in the bottom portion (to expose the filter to the prevailing relative humidity during weighing), washed in deionized water and allowed to dry. These were labeled with unique ID codes and one dried filter was transferred to each dish which was then sealed and archived. A visual inspection of each filter took place at this point and defective filters were discarded based on lack of structural integrity or a high degree of surface nonuniformity. Polyethylene gloves were worn throughout the procedure, the resistance of the 18 megohm water was checked daily and selected blank filters were run through the entire analysis program to monitor background concentrations on a continuous basis.

4.7.2 WEIGHING OF CELLULOSE FILTERS

Cellulose acetate filters absorb water as the prevailing relative humidity increases. Therefore, all filters were allowed 48 hours in a box which maintained nearly constant relative humidity with a saturated solution of $NaNO_2$ prior to and during weighing.

Most filters were weighed on a Cahn 25 electrobalance tared at 80 mg with class M weights and with a precision of ±·1 μg. Tare and calibration remained constant within ± 1 μg over the time required to weigh one full set of 41 filters. The standard deviation of repeated weighings of the same filter was on the order of 10 μg. The standard deviation of weighings over a period of time was 20 μg with corrections for changes in the relative humidity (23 μg/percent + change in RH). Filters were divided into sets of 41 with consecutive ID numbers and weighed as a group. Each petri dish was opened, the filter removed with teflon coated or Millipore forceps, exposed to a Po^{210} charge neutralizer and placed on the balance pan. The weigh chamber window was closed and when equilibrium was reached after approximately 30 seconds the mass was recorded.

Four filters from each set were selected as controls and never went out to the field. These were reweighed after each weighing session by a different operator and if the two weight measurements did not agree within 20 μg for all controls, the entire set was reweighed.

All filters were weighed before and after exposure. Relative humidity in the weighbox, tare and calibration readings were recorded before and after the weighing of each set.

Net masses were calculated by the computer program *MSS according to the formula

$$W_n = W_a - W_b - \left(\frac{1}{4} \sum_{j=1}^{4} (C_{aj} - C_{bj}) \right) \qquad 4.7.2.1$$

where

W_n = net weight of the deposit on the filter

W_a = weight after exposure

W_b = weight before exposure

C_{aj} = weight of jth control filter during after exposure weighing

C_{bj} = weight of jth control filter during before exposure weighing

The constant uncertainty associated with this calculation is ±29 μg.

The control filter weight change offset was found to be more accurate than the linear relative humidity correction. It appears that over storage times comparable to those between pre and post exposure weighing the relative humidity of the storage area fluctuates substantially. In coming back into equilibrium in the constant R.H. chamber for the post exposure weighing the filters do not absorb the same amount of water as they did when they were pre-weighed. Blank filters demonstrated this hysterisis and the offsets were nearly constant for control filters from the same weighing set. Examination of blank filters which had been sent out to the field but not exposed showed that these experienced offsets similar to the controls in their weighset. This justified the use of this correction for exposed filters.

4.7.3 WEIGHING, HANDLING AND STORAGE OF GLASS FIBER FILTERS

Gelman Type AE glass fiber filters were stamped with unique ID numbers in the lower right hand corner, placed in foil lined manilla folders to which a data sheet was attached and inserted into individual manilla envelopes.

These were pre-weighed in sets of 41 on a Mettler H20 five place balance with an enlarged weigh chamber and custom pan to accommodate the 8x10 inch filters. The balance was tared, the filter was transferred from its folder to the pan with teflon forceps, the appropriate weight for equilibrium was dialed and that weight was recorded on the data sheet. The filter was then returned to its folder for field exposure. The first, 21st and 41st filters were kept in the lab as controls.

Pre-weighing at constant relative humidity was not required since changes in relative humidity of up to 10% do not result in weight changes of over 30 μg. The reproducibility of immediate re-weighing of the same filter at the same relative humidity is ±90 μg.

Upon return from the field, the filters were stored in a constant humidity chamber (approx. 51%) to allow the water concentration in the deposit to reach common equilibrium, and reweighed. After reinsertion into their folders, the filters were stored in a refrigerator to prevent the volatilization of certain carbon species.

Net mass on the filter is calculated from

$$W_n = W_a - W_b \qquad 4.7.3.1$$

where

W_n = net weight of the deposition on the filter

W_a = weight after exposure

W_b = weight before exposure

Quality was assured by checking balance calibration against standard masses weighed three times before and after each weighing set, re-weighing of the control filters by a separate operator and by monitoring the weight changes of the controls between pre and post weighing. If criteria were not met, the filters were reweighed.

4.7.4 LO-VOL FILTER HANDLING AND STORAGE

Filters for field sampling were loaded into and unloaded from the Nuclepore filter holders under the clean conditions of the laboratory.

Filter holders were disassembled and soaked in tap water prior to each use, then dried. Portions of the holder coming in contact with the filter, locking rings and O rings, were cleansed in deionized water. All loading took place in the laminar flow hood, the filters being handled with clean forceps in gloved hands. A drain disk was placed under each filter in the holder to foster an even deposit on the filter surface by homogenizing the airflow (the construction of Nuclepore filter holders usually causes deposits to accumulate in lines). The holder was labeled with the filter ID, inserted into a polyethylene bag, protected with a hard cover and placed in a specially constructed carrying case, one for each site, which secured the holders rigidly. A spare, loaded holder was included in each case for emergencies.

After sampling, the filter was unloaded and placed in its appropriate petri dish. If the filter had obviously gotten wet, the drain disk was saved for possible ion analysis with the filter; otherwise it was discarded. An evaluation of this problem was not made.

After the post-sampling weighing, exposed filters were stored in their petri dishes inside of cardboard boxes in a locked cabinet. The average storage time between sampling and intensive chemical analysis was two months, though some filters experienced a six month delay.

4.7.5 FIELD SAMPLING

Field sampling and maintenance was performed by DEQ personnel. Loaded sample cases and Sierra filters were picked up in the morning and placed carefully and securely in a van which then made its rounds to the six sampling sites. At each site the pressure readings of the previous day's samples were checked in sequence and recorded on the data sheet. The plenum was then removed from the fine particulate sampler and wiped clean. The fallout caps were removed from the filters to be exchanged and a visual inspection of the filter surface was made to assure that no sample was skipped due to a malfunction of the timing mechanism.

Exposed filters were removed, placed in polyethylene bags, capped and replaced with the fresh filters. Fallout caps were cleaned and replaced and the plenum was relocated on the fine particulate sampler. Initial pressure readings for the new filters were checked and recorded on the appropriate data sheet.

Total volumes sampled by the lo-vol samplers were calculated by the computer program *FIELD from

$$V_L = \left[a \left(\frac{p_1 + p_2}{2} \right) + b \right] t \qquad 4.7.5.1$$

where

V_L = Volume sampled by lo-vol sampler in m^3

a = slope of flowrate/pressure drop calibration curve

b = intercept of calibration curve

p_1 = pressure drop prior to sampling

p_2 = pressure drop after sampling

t = sampling duration

The uncertainty of this volume determination, σ_{V_L} is of the order of 5%.

For hi-vol volumes

$$V_H = \left(\frac{F_1 + F_2}{2} \right) t \qquad 4.7.5.2$$

where

V_H = volume sampled by hi-vol in m^3

F_1 = flowrate prior to sampling

F_2 = flowrate after sampling

t = sampling time

The uncertainty of this volume, σ_{V_H} is also approximately 10%.

4.7.6 X-RAY FLUORESCENCE

Energy-dispersive photon-induced x-ray spectrometry (Giaque et al., 1973; Rhodes, 1973) has been applied to air pollution samples by a large number of researchers (Hammerle, et al, 1975;

Martens, et al., 1973a; Wedberg, et al., 1974; Miller, et al., 1972; Dzubay, et al., 1975; Hidy, et al., 1975; Rancitelli, et al., 1974; Giaque, et al., 1973, 1974, 1975). Its low detection limits for elements of atomic number 13 and up, simultaneous multi-element determination capability, and non-destructive treatment of samples make it an ideal tool for the PACS.

Atoms in the sample are excited from their ground state to higher energy levels by x-radiation from an x-ray tube. These excited atoms emit discrete energy x-rays as they return to their normal ground state energy levels. The energy of these emitted x-rays is characteristic of the emitting element and is used to identify the element while the number of observed x-rays, which is proportional to the number of atoms, is used to quantitatively determine a specific element's concentration through a direct comparison with standards.

An ORTEC TEFA 6110 system with a dual Mo-W anode x-ray tube and .03 mm Mo and Cu foil filters and a 160 eV FWHM Si(Li) detector was used for the analysis. Three different excitation conditions were used for each aerosol sample, each condition being most sensitive for a certain set of elements. Figures 4.7.6.1 a, b and c state these conditions and compare the spectra obtained from a typical air filter under them. Table 4.7.6.1 displays the elements sought under each condition, their typical values and ranges in the urban aerosol (Cooper, 1973a), and on a PACS filter, and the minimum detectable concentration of each defined by

$$MDC_i = 3\sqrt{\frac{B_i C_i}{N_i}} \qquad 4.7.6.1$$

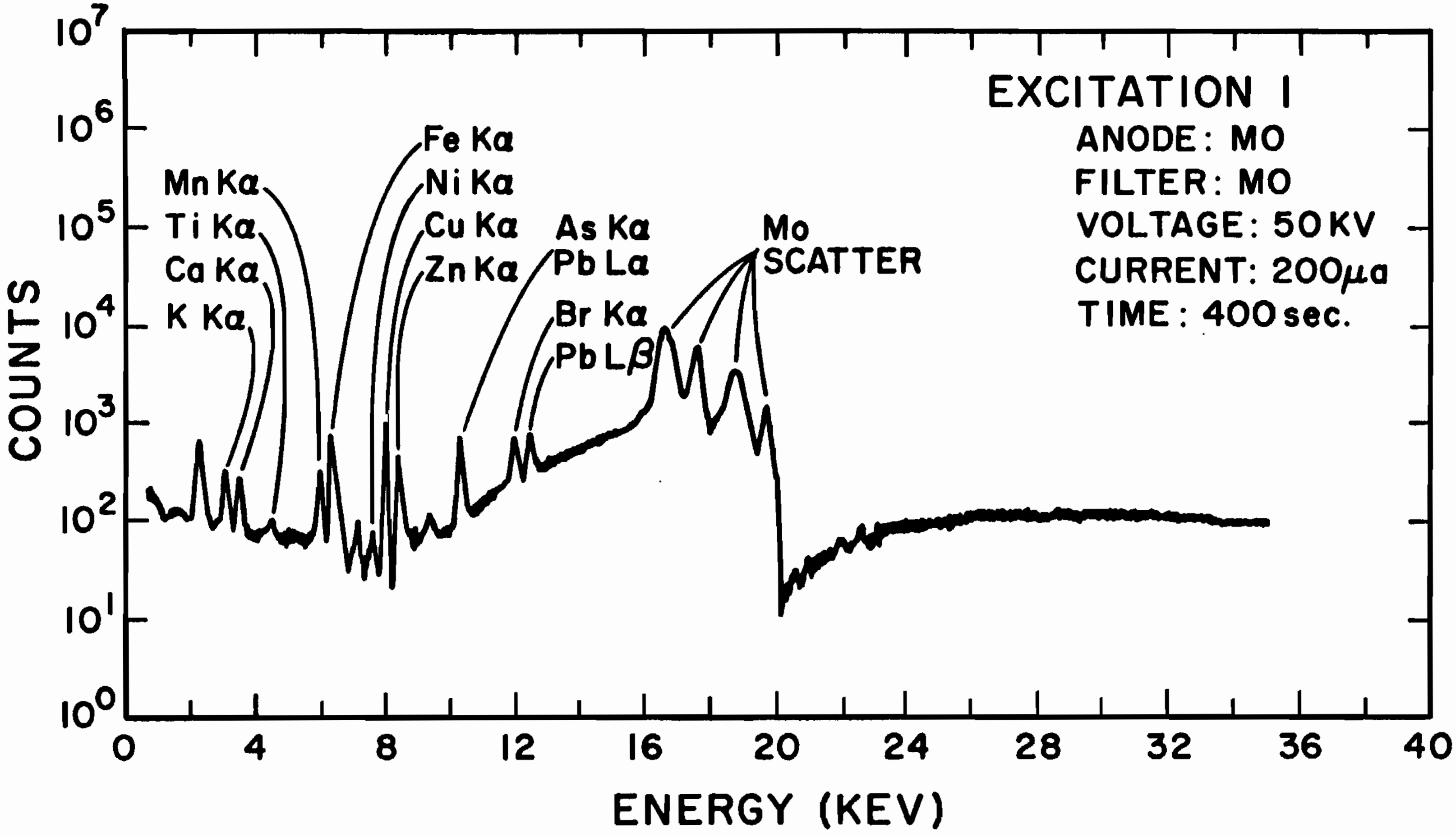


Figure 4.7.6.1a. Typical spectrum and excitation for Condition 1.

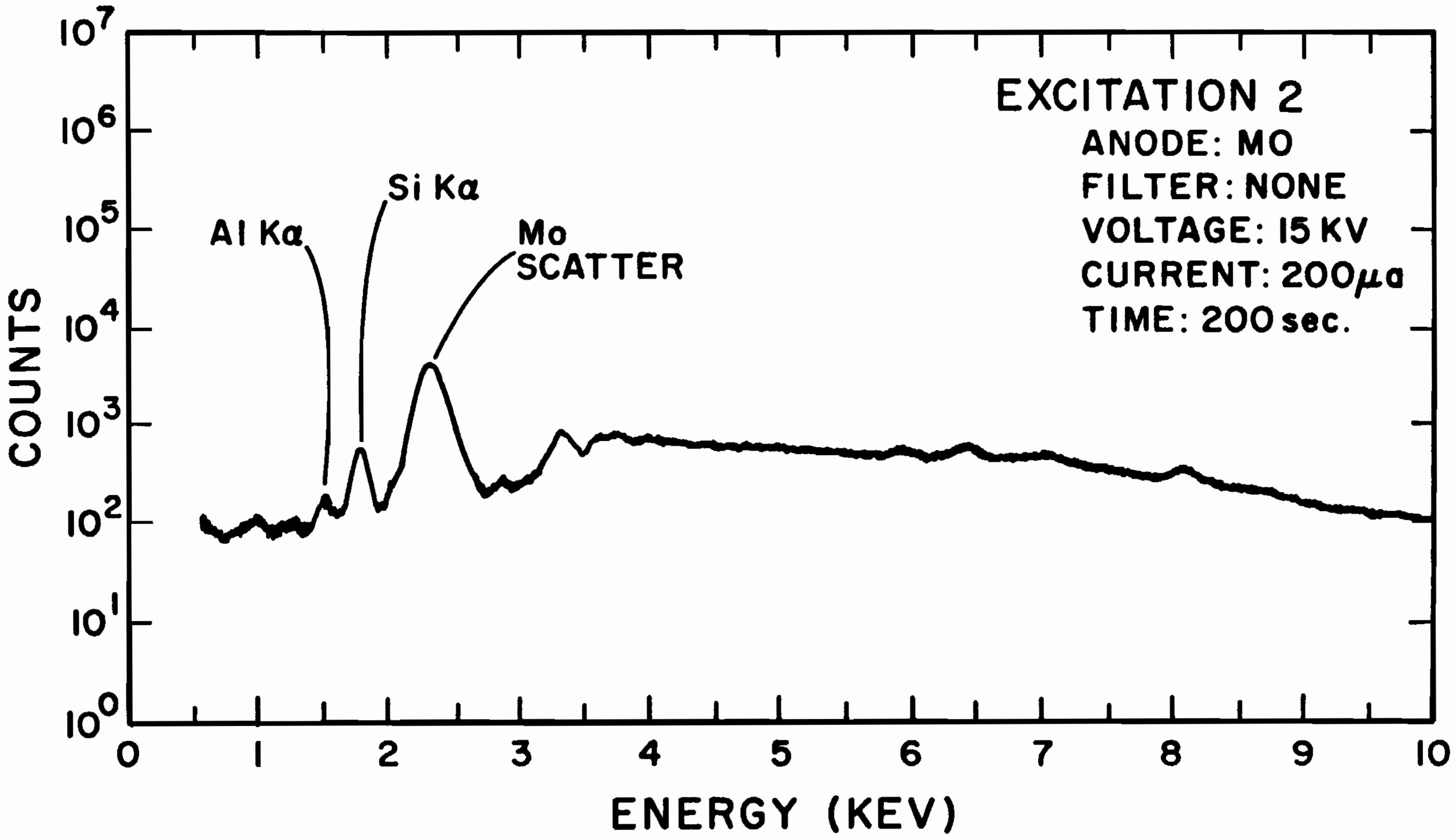


Figure 4.7.6.1b. Typical spectrum and excitation for Condition 2

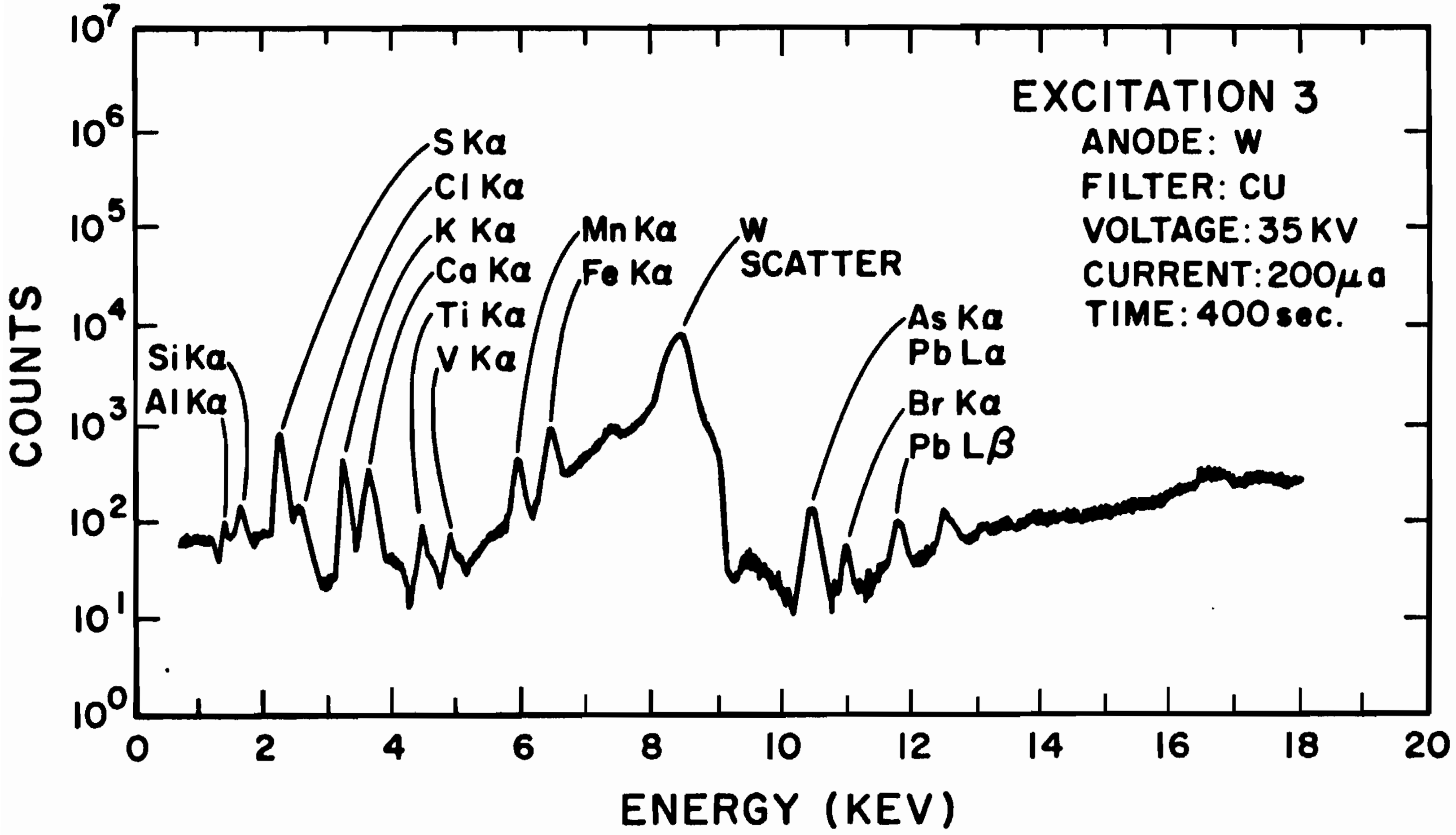


Figure 4.7.6.1c. Typical spectrum and excitation for Condition 3.

Table 4.7.6.1 Elements Quantified by XRF

Element	$\mu g/m^2$ Typical[a]	Range[a]	PACS $\mu g/cm^2$ on filter[b] Typical	Range	Non-interference MD.C., $\mu g/cm^2$ Cond.1	Cond.2	Cond.3	Analyte Line	Corrected for spectral interference from
Al	4.000	.140-10	8.0	.28 -20		.049		Kα	Br Lα
Si	10.0	4.2 -50	20.0	8.4 -100		.038		Kα	
S	5.0	1.4 -15.0	10.0	2.8 -30		.410	.133	Kα	Pb M
Cl	0.50	.070-10	1.0	.14 -20			.089	Kα	S Kα, Pb M
K	2.0	.21 -5	4.0	.42 -10		.046	.031	Kα	
Ca	5.5	.49 -30.0	11.0	.98 -60		.064	.031	Kα	K Kβ
Ti	0.30	.007- 7.0	0.60	.014 -14			.007	Kα	Ba Lβ
V	.050	.0007-3.0	.1	.0014-6			.006	Kα	Ba Lα
Cr	.020	.0017- .30	.40	.0034- .6			.006	Kα	Ti Kβ
Mn	.100	.007- 2.0	.20	.014 -4			.007	Kα	V Kβ
Fe	4.0	.28 -20	8.0	.56 -40	.016		.010	Kα	Cr Kβ
Ni	.032	.0007- .4	.064	.0014- .8	.007			Kα	Mn Kβ
Cu	.30	.014-6	.60	.028 -12	.009			Kα	Ni Kβ
Zn	.60	.014-10	1.2	.028 -20	.007			Kα	Cu Kβ
As	.016	.002- .1	.032	.004 - .2	.007		.011	Kα	Pb Lα
Se	.002	.0001- .01	.004	.0002- .02	.009			Kα	Pb Ln
Br	.140	.0035-1.0	.280	.007 - 2.0	.011		.016	Kα	
Cd	.002	.0003- .05	.004	.0006- .1	.070			Kα	
Ba	.08	.04 - .1	.16	.08 .2	.510			Kα	
Pb	1.20	.10 - 8.0	2.40	.20 -16.0	.030		.044	Lβ	

[a] From Cooper (1973a)

[b] Based on ∿35m^3 drawn through a 47mm filter

where

MDC_i = the minimum detectable concentration of of element i in $\mu g/cm^2$

C_i = known concentration of element i on Millipore filter in $\mu g/cm^2$

N_i = net number of counts measured when element i is analyzed under standard conditions

B_i = number of background counts subtracted from total counts in region of interest i to obtain N_i

Each filter to be analyzed was removed from its petri dish and placed into a numbered holder which had been previously cleaned with a methanol soaked wiper; a clean retainer ring was inserted to hold it in place and the filter ID was recorded opposite the holder number on a data sheet to assure that it would be returned to the proper petri dish after analysis. These operations were performed in a clean laminar flow hood with gloved hands. The specimens were transferred to the TEFA unit in a specially constructed tray enclosed in a carrying case where they were removed and placed in the sample carousel openings whose numbers corresponded to those on the filter holders. The sample chamber was closed and evacuated.

The analysis was controlled by a 16K PDP 11/04 minicomputer with dual floppy disk drives and a UNIBUS interface to the ORTEC multichannel analyzer. A computer program *XRF was written in the ORACL interpretive language for control and data analysis. This routine accepted the filter IDs from the data terminal, informed the user of the appropriate excitation condition, set regions of interest, started analysis, integrated total counts in each region of interest, performed spectral interference and background subtractions, compared the results to standards, printed hard copy, stored elemental compositions and spectra on floppy disk, and advanced the carousel to the next sample. Each excitation condition was set manually by the operator after all filters had been run on the previous condition.

After analysis under condition 3 the sample chamber vacuum was released and the filter holders were transferred in the sample case back to the laminar flow hood where filters were returned to their appropriate petri dishes under clean conditions.

For conventional aerosol deposits on air filters, the number of x-ray photon events from element i measured by the detector, N_i, is proportional to the mass of element i, M_i, times an attenuation factor, A_i, which takes into consideration the absorption of the primary excitation and the characteristic x-rays in the specimen

$$N_i = K_i M_i A_i \qquad 4.7.6.2$$

where K_i is a proportionality constant. An unknown mass, M_i, may be determined by comparison of the number of events measured when it is irradiated to the number of events, N_{is}, obtained from a known mass, M_{is}. If the respective absorption coefficients A_i and A_{is} are known,

$$M_i = \frac{N_i}{N_{is}} \frac{A_{is}}{A_i} M_{is} \qquad 4,7.6.3$$

Standards were prepared on Millipore cellulose acetate filters by the Columbia Scientific Company. Known amounts of aqueous solutions were micropipetted in a homogeneous array of dots over the surface of the filter (Rhodes, 1975,1977) with the exception of the Al-Si standard which was composed of a surface deposit of alumino-silicate particles in the 2 to 10 micron size range.

Measurements performed on both sides of these solution filters yielded the same count rate (within 10%) for each element in the deposit which indicated the solution to be uniformly distributed throughout the thickness of the filter. The absorption factor in this case is (Adams and Van Grieken, 1975; Davis, et al. 1977)

$$A_{is} = \frac{1 - e^{-\mu m}}{\mu m} \qquad 4.7.6.4$$

where

$\mu = \mu_i \sec\theta_1 + \mu_e \sec\theta_2$

θ_2 = angle of incidence (with respect to perpendicular to filter) of the excitation radiation

θ_1 = angle between detector centerline and perpendicular to filter

μ_i = mass absorption coefficient of filter material for radiation from element i

μ_e = mass absorption coefficient of filter material for excitation radiation

m = areal mass density ($\mu g/cm^2$) of filter

Values of this absorption coefficient were calculated based on a mass per unit area measurement of Millipore filters and published mass absorption coefficients for carbon and oxygen, the major components of cellulose acetate. μm was also measured by comparing the count rate obtained from the standard filter alone and with another, blank Millipore filter in front of it (Rhodes, 1975). Table 4.7.6.2 shows that the comparison was favorable. The product $A_{is}M_{is}$ was used as the "surface

Table 4.7.6.2 Filter Absorption Corrections for Uniformly Distributed Deposit in PACS XRF Standards

Analyte	Condition 1		Condition 2		Condition 3	
Line	A_i Calc.	A_i Exp.	A_i[b]Calc.	A_i. Exp.	A_i Calc.	A_i Exp.
S Kα	a	a	.26	a	.42	.42
Cl Kα	a	a	.32	a	.56	.60
K Kα	a	a	.57	.65	.69	.73
Ca Kα	a	a	.67	.71	.79	.76
Ti Kα	a	a	a	a	.85	.86
V Kα	a	a	a	a	.87	.88
Cr Kα	a	a	a	a	.90	.91
Mn Kα	a	a	a	a	.92	.92
Fe Kα	a	.95	a	.93	a	.93
Ni Kα	a	.97	a	a	a	a
Cu Kα	a	.98	a	a	a	a
Se Kα	a	.98	a	a	a	a
As Kα	a	.98	a	a	a	.96
Br Kα	a	1.0	a	a	a	1.0
Pb Lβ	a	1.0	a	a	a	1.0
Cd Kα	a	1.0	a	a	a	a
Ba Kα	a	1.0	a	a	a	a

[a] Not measured or not calculated

[b] Filter assumed to be 43%C, 57%O, 4.3 mg/cm^2, $\theta_1=\theta_2=47^\circ$, mass absorption coefficients from Bertin (1975), primary excitation energy: Absorption edge energy for each element in condition 2, WKα in condition 3.

deposit" value for the concentration on the filter when calibrating.

These values were cross-checked with neutron activation analysis for Br, V, Ti and Cl and with XRF analysis at UC Berkeley by replicate analysis of the same ambient air filters. The precision of the intercomparison was excellent, as will be seen in the interlaboratory comparison section (section 4.8), but a consistent, multiplicative bias of 5 to 15% was observed. This was attributed to uncertainty of the absolute surface deposit corrected values on the standards. These values were multiplied by the factors in Table 4.7.6.3 to obtain the unbiased standard calibration mass densities. In the future, multiple standards for each element spanning the range of concentrations expected should be used in calibration.

Aluminum and silicon are primarily associated with geological material in large (greater than 2 μm) particle sizes. Their low x-ray energies are easily absorbed upon exit from particles in this size range. Several methods for estimating this attenuation have been proposed (Hunter and Rhodes, 1972; Rhodes and Hunter, 1972; Dzubay and Nelson, 1974; Criss, 1976; Wagman, et al., 1978) but they all depend upon _a priori_ knowledge of the particle size and chemical composition. It was first thought that the best way to circumvent this problem would be to use a standard of a composition and size similar to that of the geological deposit, thus making A_{is}/A_i in eq. 4.7.6.3 equal to unity. A consistent bias was exhibited in comparing Al values from INAA and XRF with this standard. INAA experiences no absorption and high sensitivity for Al. The normalization factors for fine and total filters listed in Table

Table 4.7.6.3 Normalization Factors Applied to Calibration Standard Values As A Result of Intercomparisons

Element	Excitation Condition	Normalization Factor [a]	Reason Chosen
Al	2	.8(fine),1.4(total)	INAA comparison
Si	2	.8(fine),1.4(total)	Assumed to react same as Al
S	3	1.17	Ion chromatograph (IC) &Berkeley comparisons consistent
Cl	3	.20	INAA,IC,&Berk. consistent (Not used as a final value)
K	2	.92	Berk. comparison
K	3	.87	Berk. comparison
Ca	2	1.27	Berk. comparison
Ca	3	1.17	Berk. comparison
Ti	3	1.00	Many below MDC, INAA better choice.
V	3	1.00	Many below MDC, INAA better choice.
Cr	3	1.13	Berk. comparison
Mn	3	1.15	Berk.&INAA consistent.
Fe	1	1.10	Berk. comparison
Fe	2	1.07	Berk. comparison
Fe	3	1.14	Berk. comparison
Ni	1	1.08	Berk. comparison
Cu	1	1.13	Berk. comparison
Zn	1	1.15	Berk. comparison
As	1 & 3	1.0	Many below MDC
Se	1	1.0	Many below MDC
Br	1	.87	INAA, Berk. consistent
Br	3	.87	INAA, Berk. consistent
Cd	1	1.0	Below MDC
Ba	1	1.0	Below MDC
Pb	1	1.15	Berk. comparison
Pb	3	1.15	Berk. comparison

[a] after Weisz (1974)

4.7.6.3 are based on intercomparisons with INAA.

An option of the *XRF program allowed the operator to input the known masses on these standard filters during a special calibration run. The relationship between mass and number of photon events detected was then stored on the disk and referenced during the normal runs to convert integrated counts in the regions of interest to mass concentrations.

N_i and N_{is} are the net counts in the spectrum region of interest i which are obtained after subtracting the bremsstrahlung background counts scattered from the primary beam by the filter and any contributions to the region by elements in other regions of the spectrum (Table 4.7.6.1 points out the important interferences).

Many methods for the subtraction of background and elimination of spectral interferences have been proposed (Statham, 1976, 1977; Nielson, 1978; Parkes, et al., 1974; Mencik, et al., 1975; Russ, 1977; Van Espen, 1976). The approach adopted here is similar to that proposed by Bonner, et al. (1973) and Giaque, et al. (1974) and was chosen for its simplicity and accuracy.

An estimation of the background was made by analyzing a blank filter with each run and integrating the counts in each region of interest. The Mo Kα scatter peak count was monitored for all specimens and its ratio with that of the blank was used to normalize the background in each region prior to subtraction.

After background subtraction, spectral interferences were eliminated by determining the fraction of the net counts in region of interest j contributed to region of interest i, F_{ij}, from spectra of non interfering elements. Then, for interfering peaks

$$N_{Ti} = N_{Ai} - \sum_{\substack{j=1 \\ j\neq i}}^{n} F_{ij} N_{Tj} \qquad 4.7.6.5$$

where the A subscript designates the actual number of net counts (after background subtraction) including interferences and the T subscript indicates the true number after interferences have been eliminated. In most cases, only one interfering line is present, as noted in Table 4.7.6.1.

The uncertainty in the calculation is estimated by summing in quadrature the uncertainties in each of the parameters of eq 4.7.6.3.

$$\frac{\sigma_{M_i}}{M_i} = \left(\frac{\sigma_{N_i}{}^2}{N_i{}^2} + \frac{\sigma_{N_{is}}{}^2}{N_{is}{}^2} + \frac{\sigma_{M_{is}}{}^2}{M_{is}{}^2} \right)^{.5} \qquad 4.7.6.6$$

where $\frac{\sigma_{M_{is}}}{M_{is}} = .05$ from manufacturers' specifications and

$$\frac{\sigma_{N_i}}{N_i} = \sqrt{\frac{N_i+2B_i}{N_i{}^2} + \sum_{j\neq i} F_{ij}{}^2 \frac{\sigma_{N_j}{}^2}{N_j{}^2}}$$

where B_i is the background contribution in region i.

Each set of ten filters was accompanied by a multielement quality assurance standard. If the values for this standard as a result of analysis did not check within 5% of their known values on each excitation condition, the system was re-calibrated and the samples rerun.

4.7.7 FILTER CUTTING

The remaining analyses required portions of the filter to represent the whole. It was also desired to retain some of the sample for possible microscopic study and additional analyses. To accomplish this a precision cutting jig was machined from a nylon block. It consisted of a circular recessed area of exactly the filter diameter and a crossed pair of grooves dividing that circle into four sectors of equal shape and area.

The filter was placed in the recess and a clean blade was aligned in one groove and rocked gently until an incision divided the filter in two. The blade was then inserted into the other groove at right angles to the original cut and the filter was quartered. Each quarter was placed in a clean petri dish labeled with the filter ID and its destination, neutron activation, anion chromatography, or archives (two quarters were archived). These dishes were placed in appropriate boxes from which they were drawn for the appropriate analysis. The jig and the blade were wiped with methonal between each sample to prevent cross contamination. The operations were performed with gloved hands in a laminar flow hood.

The precision of obtaining quarter filters with the jig and blade was better than 1 percent as determined by visually comparing the sector areas of cut blank filters. On several source samples, the deposit was not always located in the exact center of the filter. A 25 mm diameter punch was used to remove a completely covered segment from each of these filters; this segment was then quartered using a 25 mm jig. Results of analyses on four quarters of the same filter appear in Table 4.7.7.1 and indicate the degree of inhomogeneity of elemental

Table 4.7.7.1 Analyses of different portions of the same filters

Filter Section Analyzed							Chemical Constituent									
XRF	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Filter #1								μg/cm^2								
Center	4.80	14.0	3.52	8.51	1.45	2.43	.424	.0735	.0440	.130	4.36	.097	.0785	.121	1.35	2.84
1st Quarter	4.82	14.6	2.95	6.95	1.17	2.34	.439	.0734	.0540	.144	4.28	.106	.0580	.109	1.80	2.92
2nd Quarter	5.44	16.9	2.93	8.65	1.58	2.76	.491	.0792	.0389	.153	5.03	.106	.0649	.165	1.78	2.79
3rd Quarter	4.80	14.3	2.70	6.70	1.19	2.39	.448	.0646	.0372	.144	4.07	.079	.0576	.094	1.62	2.52
4th Quarter	5.48	16.8	3.27	8.00	1.51	2.73	.495	.0786	.0336	.147	4.69	.087	.0700	.136	1.80	2.75
Average	5.07	15.3	3.08	7.76	1.38	2.53	.459	.0739	.0415	.143	4.49	.095	.0658	.125	1.67	2.77
% Std. dev.	7.0	9.2	10.4	11.5	13.8	7.7	6.9	7.9	19.0	5.9	8.4	12.5	13.3	21.7	11.7	5.4
Filter #2								μg/cm^2								
Center	3.53	9.23	2.16	5.70	.948	1.16	.268	.0251	.0142	.0573	2.21	.0354	.0480	.0574	1.16	2.71
1st Quarter	3.66	10.4	2.10	5.35	.936	1.24	.308	.0294	.0122	.0541	2.46	.0231	.0498	.0529	1.64	2.73
2nd Quarter	3.70	10.0	1.77	4.98	.806	1.25	.305	.0359	.0056	.0644	2.42	.0182	.0557	.0563	1.59	2.59
3rd Quarter	3.85	10.2	1.86	4.29	.853	1.26	.302	.0293	<.005	.0682	2.45	.0303	.0456	.0501	1.55	2.66
4th Quarter	4.11	10.5	1.69	5.38	.813	1.33	.326	.0192	.0115	.0702	2.41	.0346	.0429	.0671	1.53	2.68
Average	3.77	10.1	1.91	5.14	.871	1.25	.302	.278		.0628	2.39	.032	.0484	.0568	1.50	2.67
% Std. dev.	5.9	5.2	10.2	10.6	7.7	4.9	7.0	22.2		11.1	4.2	4.3	10.0	11.4	12.7	2.1

AIC	F^-	Cl^-	NO_3^-	SO_4^{-2}	AIC	F^-	Cl^-	NO_3^-	SO_4^{-2}
Filter #1		μg			Filter #2		μg		
1st Quarter	88.4	---	152	424	1st Quarter	79.6	139	88.8	225
2nd Quarter	94.8	1210	153	434	2nd Quarter	67.2	80.8	72.8	214
3rd Quarter	87.4	954	148	432	3rd Quarter	85.2	139	80	227
4th Quarter	138	1136	152	422	4th Quarter	88	131	84.8	235
Average	122	131	151	428	Average	80	122	81.6	225
% Std. dev.	19.7	11.9	1.47	1.4	% Std. dev.	11.5	22.9	8.4	3.9

deposits across the filter surface. The average deviation of 7% was added in quadrature to the analytical uncertainty of each section analyzed. All measured concentrations were normalized to the area of the deposit upon entry into the chemical analysis data files.

4.7.8 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Instrumental neutron activation analysis with short irradiations is a valuable supplement to XRF for several reasons. Several elements of importance, specifically Na and Mg, cannot be detected by XRF at their normal concentration levels because of absorption of their low energy x-rays in the thin Be window of the Si (Li) detector. Al experiences much absorption by other elements coexisting with it in large (>2μm) aerosol particles with XRF but faces no absorption with INAA. Other elements, i.e. V and Ti, could benefit from somewhat lower detection limits than are obtainable under the stated XRF excitation conditions. Finally, the reliability of the two methods can be verified <u>on every specimen</u> by a comparison of concentrations of the same element obtained by both methods.

INAA (Zoller and Gordon, 1970; Filby and Shah, 1974; Robertson and Carpenter, 1974) is another sensitive, non-destructive multi-element technique with a proven reputation in aerosol elemental characterization (Bogen, 1973; Obrusník, et al., 1976; Paciga and Jervis, 1976; King, et al., 1976; Gordon, et al., 1973; Neustadter, et al., 1976; Dams, et al., 1971a; Martens, et al., 1973a; Rahn, et al., 1974; Heindryckx and Dams, 1974; Kowalczyk, et al., 1978; John, et al., 1973; Gladney, et al., 1974; Harrison, et al., 1971; Hidy, et al., 1975; Leaderer, et al., 1978;

TABLE 4.7.8.1 Elements Quantified by Instrumental Neutron Activation Analysis

Element	Typical Urban Concentration, Ug/m^3 [a]		MDC PACS[b] Filter, ug/m^3	ug[c]	Target Isotope	Isotopic Abundance (%)	Product Nuclide	Half-Life	Best γ For Measurement (KEV)	Possible Interfering Nuclide In Diode Measurement	Possible Interfering Nuclear Reactions Producing Nuclides Of Interest
Al	3.0	.2-10	.007	.06	^{27}Al	100	^{28}Al	231m	1779	^{151}Nd(1776)	^{28}Si(n,p)^{28}Al ^{31}P(n,a)^{28}Al
Br	.2	.07-1.0	.001	.01	^{79}Br	50.5	^{80}Br	17.6m	617	^{108}Ag(614)	^{80}Kr(n,p)^{80}Br
Cl	.5	.1-10	.029	.24	^{37}Cl	24.5	^{38}Cl	37.3m	1643	None	^{36}Ar(n,p)^{38}Cl ^{41}K(n,a)^{38}Cl
Mg	2.0	.7-7	.095	.8	^{26}Mg	11.2	^{27}Mg	9.45m	844	^{101}Mo(840) ^{151}Nd(841) ^{87}Kr(846) ^{56}Mn(847)	^{27}Al(n,p)^{27}Mg ^{30}Si(n,a)^{27}Mg
									1014	^{101}Mo(1012) ^{151}Nd(1016) ^{125}Sn(1017) ^{188}Re(1018)	
Mn	.10	.010-2.0	.0008	.007	^{55}Mn	100	^{56}Mn	2.58h	847 1811	^{27}Mg(844) None	^{56}Fe(n,p)^{56}Mn ^{59}Co(n,a)^{56}Mn
Na	2.0	.2-10	.014	.12	^{23}Na	100	^{24}Na	15.0h	1369	^{125m}Sn(1369) ^{117}Cd(1373) ^{188}Re(1368)	^{24}Mg(n,p)^{24}Na ^{27}Al(n,a)^{24}Na
Ti	.30	.010-7.0	.014	.12	^{51}Ti	5.3	^{51}Ti	5.79m	320	^{199}Pt(317) ^{151}Nd(320) ^{105}Ru(317) ^{182m}Ta(318)	^{51}V(n,p)^{51}Ti ^{54}Cr(n,a)^{51}Ti
V	.06	.001-2.0	.0002	.002	^{51}V	99.8	^{52}V	3.76m	1434	^{139}Ba(1430)	^{52}Cr(n,p)^{52}V ^{55}Mn(n,a)^{52}V
K	2.0	.3-5.0	.70	6.0	^{41}K	6.91	^{42}K	1.24 hr	1524		

[a] Cooper (1973a)

[b] Approximately 35m^3 sampled and 1/4 of a 47mm filter analyzed.

[c] For typical aerosol composition.
This value is particularly sensitive to Al concentration because of the large spectral background it engenders.

Rancitelli, et al., 1974; Pillay and Thomas, 1971; Dams, et al., 1972). The elements of interest in this application, their typical concentrations and ranges in urban air, their minimum detectable limits under the conditions of this study, and other pertinent data are outlined in Table 4.7.8.1.

The principle of INAA is as follows: When placed in a neutron flux from a nuclear reactor, the elements of a specimen will absorb neutrons and undergo nuclear transmutations forming radioactive elements. The number of radionuclide atoms of each species created is proportional to the number of original atoms present; the radiation emitted by them, in this case gamma radiation, is proportional in intensity to the number of radionuclide atoms and occurs at an energy unique to that radionuclide. A comparison of the specific radioactivity produced from a standard and an unknown is sufficient for a quantitative analysis.

The PACS SOP is consistent with those of the Nuclear Radiation Center at Washington State University (WSU, 1975). Air filter quarters were heat sealed in 15 to 20 cm^2 of polyethylene (Gladwrap was found to have the lowest trace element levels) and placed into clean (soaked in dilute HNO_3 and rinsed with deionized water) 2/5 dram polyvials labeled with the filter identification code. These operations were carried out with gloved hands in a laminar flow hood. Groups of these samples were sent to a technician permanently stationed at the Nuclear Radiation Center at Washington State University in Pullman, Washington where they were associated with pre-weighed Cu flux monitors in a 2 dram vial and ordered in a sample holder. Clean 2/5 dram vials

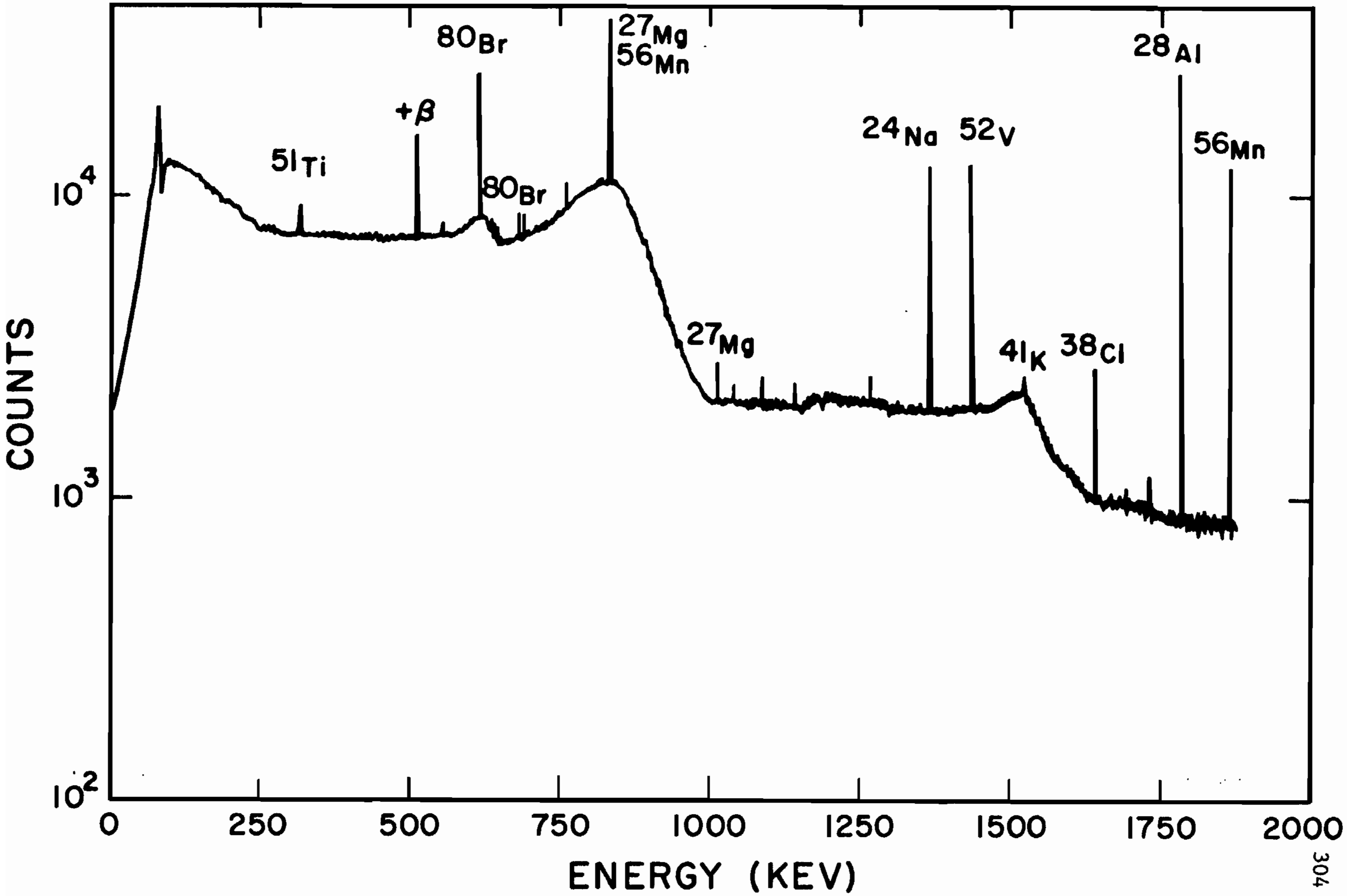


Figure 4.7.8.1. Typical gamma ray spectrum of aerosol sample, short irradiation.

were marked with the specimen identification codes and ordered in a duplicate holder; after irradiation each specimen was transferred to this clean vial for counting. Specimens were loaded into rabbit capsules and injected into the G4 position of WSU's Triga Reactor for five minute irradiations at a thermal neutron flux of 5.3 x 10^{12} neutrons/ cm^2/sec with a cadmium ratio of 4.6.

Upon return to the rabbit room, the time out of the reactor was noted, the Cu flux monitor was placed in temporary storage, and the specimen was transferred from the irradiated vial to the corresponding, un-irradiated counting vial.

This vial was taken to the counting room where it decayed for ten minutes prior to a 200 second counting with a 2 Kev FWHM at 1014 Kev ORTEC 15% Ge(Li) detector and multichannel analyzer system. A typical spectrum appears in Figure 4.7.8.1. A shelf arrangement provided reproducible positioning of the specimens above the detector face and an appropriate shelf was chosen to maintain the overall deadtime at less than 20% to minimize pileup, peak shifts and broadening. In practice, all aerosol samples were counted at the detector face (shelf 1) and standards were counted from four to 12 cm from the face (shelves 3 to 7) depending on their activities. Some source samples were counted on shelf 2.

Counts obtained were normalized to the detector face through multiplication by a factor determined via measurements for each region of interest on each shelf. Figure 4.7.8.2 indicates these factors as a function of energy for each of the shelves. The change in this factor

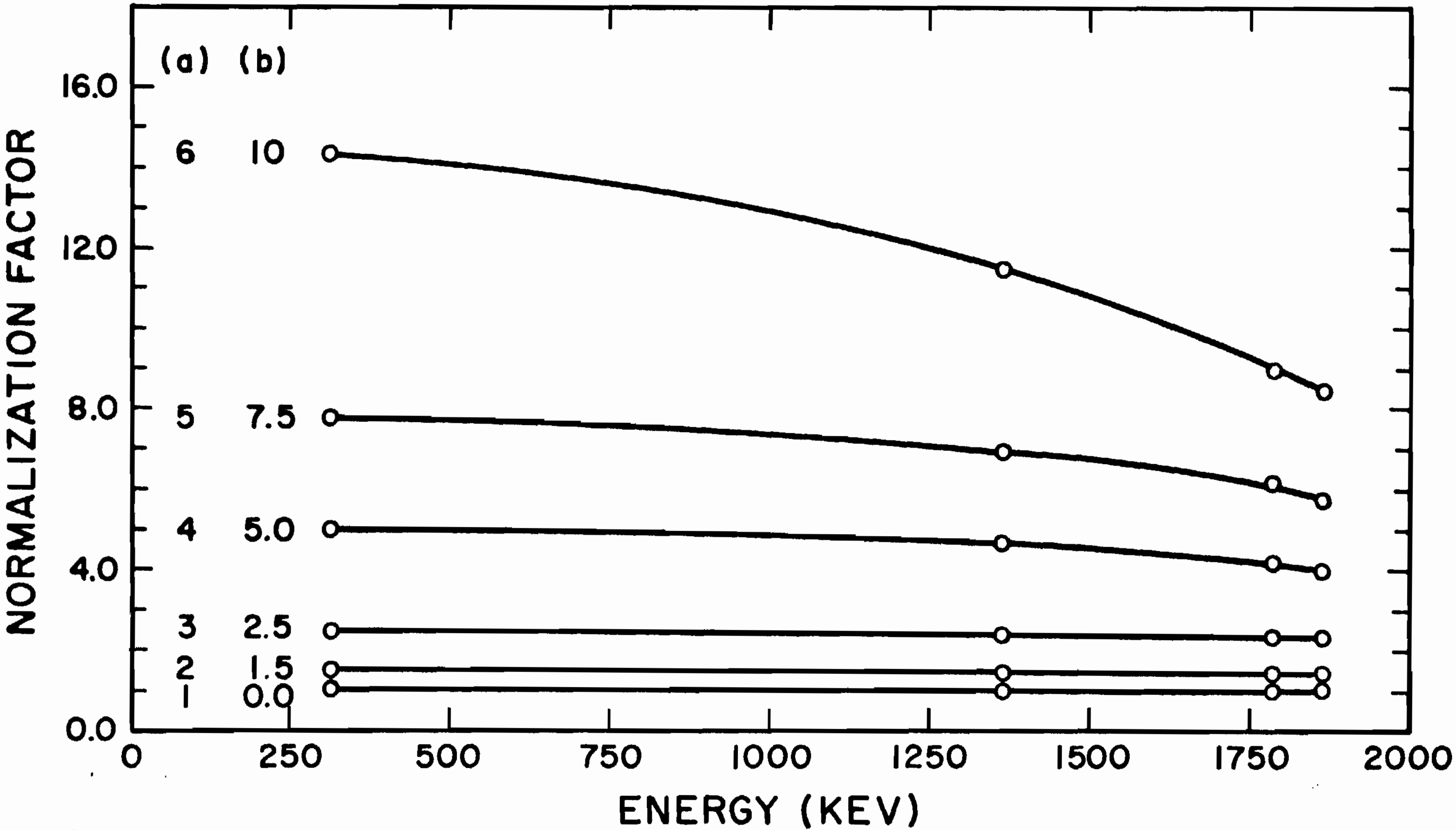


Figure 4.7.8.2. Shelf geometry normalization factors as a function of energy. Column (a) contains the shelf ID number and column (b) contains the approximate distance, in cm. from the detector face.

for a shelf over the spectrum is an outstanding feature and is due to the greater average path length required for high energy photons to create an event in the Ge(Li) crystal.

Count start time and stop time were noted on the data sheet with the specimen identification code, then typed onto paper tape via the teletype. This was followed by automatic punching of region of interest integrals for the energy regions listed in Table 4.7.8.1. Background regions on both sides of each peak were also included.

Copper flux monitors, whose purpose was to normalize the neutron flux irradiating each specimen to that which irradiated the standard, were counted for forty seconds on the day following irradiation and the net integral count was recorded on the data sheet with the count start time opposite the ID code. These ID codes had been associated with the mass of each copper when they were originally prepared. The count was high enough to insure counting errors of less than one percent.

Calibration and quality assurance standards consisted of National Bureau of Standards BCR-1 and ARCHO 5 standard geological reference materials for quantification of Na, Mg, Al, Ti, V, and Mn, and solution deposits of KBr and KCl for quantification of K, Cl and Br.

8-12 mg of the geological standard was weighed on the Mettler 5-place balance and spread uniformly over the surface of a 3x3 cm piece of Whatman 41 filter paper. Solutions were prepared by drying ultra pure reagents at 105° C for three hours, weighing .3-.4 g of KBr and 5.0-6.25 g. of KCl and dissolving each of these in deionized water in clean 25 ml volumetric flasks. 20 μl of each solution was micropipetted onto separate Whatman 41 filter squares.

All weights were recorded on a data sheet with a unique ID coded to the type of standard.

Standards were sealed in polybags and loaded into ID labeled polyvials in the same manner as the ambient filters. One geological, one KCl and one KBr standard preceded each set of 70 specimens (the approximate number that could be run during an eight hour day) for the purpose of calibration. Every fifteenth specimen in the set was a quality assurance standard which could be of any type.

Data sheets and paper tapes were shipped back to OGC by registered mail for computer processing by the program *INAA which calculates the mass concentration of each element in each specimen.

The activity (i.e. the number of radionuclide atoms decaying per unit time), A_i, of element i upon removal from the reactor after t minutes of irradiation is

$$A_i = K_i \emptyset M_i \left(1-e^{-\lambda_i t}\right) \qquad 4.7.8.1$$

where K_i is a proportionality constant, M_i is the mass of the element i in the sample, λ_i is the decay constant of radionuclide i, and $\emptyset$ is the average neutron flux encountered by the sample during irradiation.

After removal from the reactor, the sample is allowed to decay for t_1 minutes, then counted until t_2 minutes. The net number of counts (normalized to a common shelf) detected, N_i, is proportional to the number of radionuclide i atoms decaying in the interval between t_1 and t_2, the original activity, and the fraction of the total counting interval actually processed by the multichannel analyzer,

$$N_i = GA_i\left(e^{-\lambda_i t_1} - e^{-\lambda_i t_2}\right)\left(\frac{t_L}{t_2 - t_1}\right) \qquad 4.7.8.2$$

where G is a proportionality constant determined by the detector efficiency and detector-sample geometry and t_L is the preset "live time" counting period.

Standards which contain a fraction f_i of element i and of measured total mass M_s are irradiated for an equal time and counted between times t_{1s} and t_{2s} after irradiation. Analogous to eq. 4.7.8.2 the net number of counts measured is

$$N_{is} = GK_i\emptyset_s f_i M_s\left(1 - e^{-\lambda_i t}\right)\left(e^{-\lambda_i t_{1s}} - e^{-\lambda_i t_{2s}}\right)\left(\frac{t_{Ls}}{t_{2s}-t_{1s}}\right) \qquad 4.7.8.3$$

where the s subscript indicates quantities unique to the standard.

Dividing eq. 4.7.8.2 by eq. 4.7.8.3 and cancelling like quantities yields

$$\frac{N_i}{N_{is}} = \frac{\emptyset}{\emptyset_s}\frac{M_i}{f_i M_s}\frac{\left(e^{-\lambda_i t_1} - e^{-\lambda_i t_2}\right)}{\left(e^{-\lambda_i t_{1s}} - e^{-\lambda_i t_{2s}}\right)}\frac{\left(\frac{t_L}{t_2 - t_1}\right)}{\left(\frac{t_{Ls}}{t_{2s} - t_{1s}}\right)} \qquad 4.7.8.4$$

The flux ratio, $\emptyset/\emptyset s$, is determined from the copper foil flux monitors of known mass. This ratio is

$$\frac{\emptyset}{\emptyset_s} = \frac{N_c}{N_{cs}}\frac{M_{cs}}{M_c}\frac{e^{-\lambda_c t_{1cs}}}{e^{-\lambda_c t_{1c}}} \qquad 4.7.8.5$$

where the subscript c refers to quantities associated with the flux monitors.

Eq. 4.7.8.4 is solved for M_i and incorporating eq. 4.7.8.5

$$M_i = f_i M_s \frac{N_i}{N_{is}} \frac{N_{cs}}{N_c} \frac{M_c}{M_{cs}} \frac{e^{-\lambda_c t_{1c}}}{e^{-\lambda_c t_{1cs}}} \frac{\left(\frac{t_{Ls}}{t_{2s}-t_{1s}}\right)\left(e^{-\lambda_i t_{1s}}-e^{-\lambda_i t_{2s}}\right)}{\left(\frac{t_L}{t_2-t_1}\right)\left(e^{-\lambda_i t_1}-e^{-\lambda_i t_2}\right)} \qquad 4.7.8.6$$

The relative standard deviation will be determined by adding significant contributions in quadrature

$$\frac{\sigma_{M_i}}{M_i} = \left[\frac{\sigma_{M_c}^{\ 2}}{M_c^{\ 2}} + \frac{\sigma_{M_{cs}}^{\ 2}}{M_{cs}^{\ 2}} + \frac{\sigma_{M_s}^{\ 2}}{M_s^{\ 2}} + \frac{\sigma_{N_i}^{\ 2}}{N_i^{\ 2}} + \frac{\sigma_{N_{is}}^{\ 2}}{N_{is}^{\ 2}} + \frac{\sigma_{N_c}^{\ 2}}{N_c^{\ 2}} + \frac{\sigma_{N_{cs}}^{\ 2}}{N_{cs}^{\ 2}}\right]^{\frac{1}{2}} \qquad 4.7.8.7$$

The relative contribution to the uncertainty of the exponential terms is insignificant for the elements under consideration.

N_i in eq. 4.7.8.6 refers to the net counts due to the decay of element i exclusive of background or peak overlaps from other elements. Numerous techniques for the subtraction of background and the elimination of spectral interferences in γ-ray spectra exist (Connelly and Black, 1970; Covell, 1959; Helmer, et al., 1967; Heath, 1966; Routti and Prussin, 1969; Yule, 1967; Heft and Martin, 1977). The superior resolution of the Ge(Li) detector and the widely spaced γ-ray peaks of short lived elements in ambient aerosols obviates the need for such complicated procedures.

The background counts under each peak were determined by a linear interpolation between background measurements on the high energy and low energy sides of the peak

$$N_i = N_{Ti} - \left(\frac{B_L + B_H}{2}\right) \qquad 4.7.8.8$$

$$\sigma_{N_i} = \sqrt{N_i + \left(\frac{B_L + B_H}{2}\right)} \qquad 4.7.8.9$$

where N_{Ti} equals the total counts in the peak window and B_L and B_H are windows of equal widths on the low and high sides.

The ^{27}Mg 844 Kev line and the ^{56}Mn 847 Kev lines normally interfered with each other, thus quantification of these elements was based on the ^{27}Mg 1014 Kev and ^{56}Mn 1181 Kev peaks. No other spectral interferences were present.

After computer processing, the calculated concentrations, flux monitor ratios, decay times and quality assurance standards were reviewed. Suspicious values for samples were checked and the samples were re-irradiated after a three week cooling period if necessary. If values from the quality assurance standards did not agree to within 20% of those determined from the known composition of those standards, the cause of the discrepancy was sought. If corrections could not be made, specimens associated with the errant standard were rerun.

4.7.9 ION CHROMATOGRAPHY

Of growing interest is the amount of ambient particulate matter due to the conversion of gases to particulates. SO_2, NO_x, and NH_3 are known to undergo complicated and as yet quantitatively unexplained processes (Friedlander, 1977) resulting in compounds containing ionic SO_4^{-2}, NO_3^-, and NH_4^+ which can represent a substantial fraction of the aerosol, particularly in the fine particle mode (Hidy, 1975).

Ion chromatography (IC) offers a unique means of quantifying these ions as well as others in a multi-element mode. Originally, the PACS intended to perform both cation and anion analysis on all samples.

Time and financial constraints limited the project to anion analysis, thus leaving the impact of NH_4^+ for all but a few selected samples in question.

IC was developed by Small et al. (1975) and has been applied to aerosol measurements by Mulik et al. (1976, 1978), Mueller, et al. (1978) and Butler, et al. (1978). Because IC is a new technique, its track record is not as extensive as that of XRF and INAA, but intercomparison with standard methods for determining SO_4^{-2}, NO_3^-, NO_2^-, Cl^- F^-, PO_4^-, Na^+, NH_4^+, and K^+ on NASN air filters (Butler et al. 1978) are quite satisfactory.

The principle of ion chromatography is similar to that of all chromatographic approaches. The sample is extracted in a known amount of solvent to which all soluble species are transferred. This is injected into an eluent flow that passes the sample through a separator column containing a strong base anion exchange resin; this resin separates anions by differences in bonding strengths.

The catch is that the resin performs the function for anions only in the presence of cations, which requires the eluent to be ionic in its own right. Thus, conductimetry, one of the most efficient methods of measuring ionic concentrations, is useless because of the high background caused by the eluent.

The novel approach of ion chromatography is to remove the eluent ions and convert sample ions to their acid forms by passing the flow through a strong acid ion exchange resin. The conductivity cell then detects only the current passed by the ions of each acid separated

Table 4.7.9.1 Ions Quantified By Anion Chromatography

Element	Typical[a] Urban Concentration μg/m^3 Average	Range	Minimum Detectable Concentration μg/m^{3b}	μg
F^-	.05	.02- .6	.011	.1
Cl^-	.5	.01-10.	.023	.2
Br^-	.10	.05- 1.0	.034	.3
NO_3^-	12	8.0 -32.	.057	.5
SO_4^{-2}	15	6.0 -50.	.057	.5

[a] Cooper (1973a)

[b] Assuming 35m^3 sampled and 1/4 filter analyzed

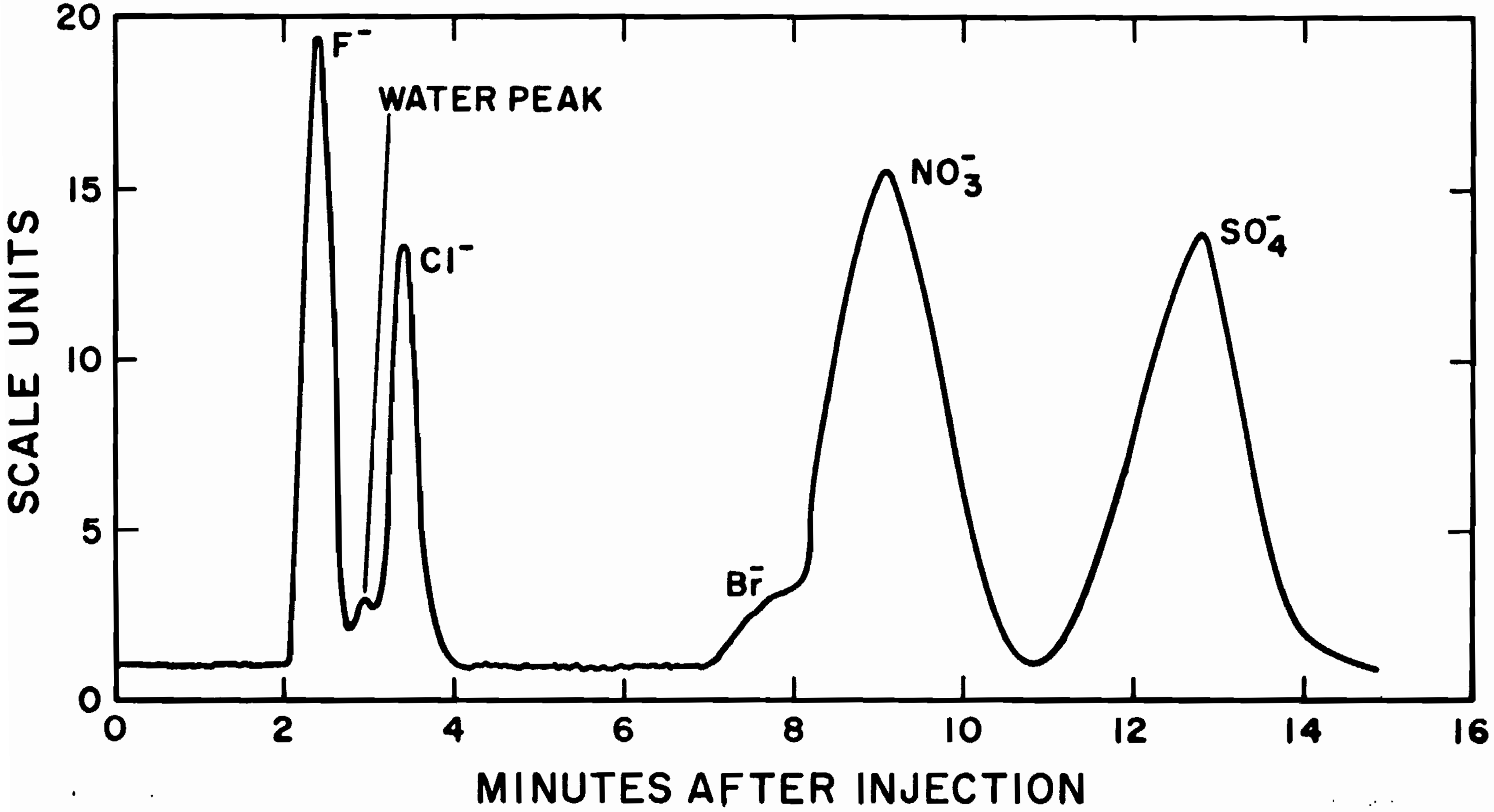


Figure 4.7.9.1. Typical Output of Ion Chromatograph

in time. These currents are proportional to the number of ions present and comparison to the current generated by prepared standards is sufficient to quantify each specimen.

A Dionex Ion Chromatograph with a .1 M $NaHCO_3$-Na_2CO_3 eluent was used. Table 4.7.9.1 presents ions sought by this technique, the typical urban concentrations and ranges under PACS sampling conditions and SOPs, and the minimum detectable concentrations of the system.

Quarter filters were extracted in clean, dry, labeled beakers with 10 ml of .1 M $NaHCO_3$-Na_2CO_3 for sixty minutes. The solution was drawn into a clean 10 ml syringe, then passed through a .45 μm membrane filter, to remove non-soluble matter, into a clean, labeled polyethylene bottle. 2.5 ml of this solution was injected into the sample loop and allowed 30 seconds to pass to the separator column. The sample loop was then removed from the eluent flow and flushed with distilled water.

Typical stripchart output appears in Figure 4.7.9.1 and indicates the separation properties of the ion exchange resin. Two scales were used and the peak heights from the most sensitive one were measured and recorded on the data sheet.

The suppressor column was regenerated approximately every seven hours by passing 1 N H_2SO_4 through it for one hour.

Stock solutions of NaCl, NaF, KBr, KNO_3, and K_2SO_4 were prepared from salts heated for 2-3 hours at 105° C, cooled in a desicator and weighed on an analytical balance to the nearest .1 mg. These were dissolved in measured volumes of eluent in incrementing concentrations to provide standards spanning the range of concentrations of the aerosol

Table 4.7.9.2 Analytical uncertainties of species quantified by Anion Chromatography

ION	Analytical[a] Uncertainty	Blank[b]	Blank Uncertainty, μg
F^-	15%	.39μg	± .48
Cl^-	18%	1.1μg	± .43
Br^-	10%	<3.0μg	
NO_3^-	8%	1.8μg	±1.5
$SO_4^=$	8%	.56μg	± .43

[a] From repeated analyses of the same standards

[b] Blank concentration on 1/4 filter

specimens. Slopes and intercepts of calibration curves were determined by a least squares fitting of a straight line for all calibration curves. These values were incorporated in the computer program *IC and ambient loadings on the section of filter analyzed were calculated from the formula

$$M_i = a_i X_i + b_i - B_i \qquad 4.7.9.1$$

where

M_i = mass of element i
a_i = slope of calibration line
b_i = intercept of calibration line
X_i = peak height in common scale units
B_i = blank value for ion i

The uncertainty of each determination was estimated by repeated measurement of common standards and is presented for each ion in Table 4.7.9.2. This value was added in quadrature to the uncertainty of the blank to obtain the overall uncertainty.

A working standard was run as every eighth specimen as a quality assurance check on calibration and adherance to the standard operating procedure. If the values obtained for these standards did not agree within the uncertainty levels with their known concentrations all of the samples between that standard and the previous standard were rerun.

4.7.10 CARBON ANALYSIS

Carbon in the form of carbonates, organic compounds and elemental carbon as soot has long been an ubiquitous component of ambient aerosols. Its sources are both primary and secondary. In the fine particulate mode it results from combustion processes (Mueller, et al., 1972; Hidy, et al., 1975) and the condensation of organic vapors (Grosjean, 1977). In the coarse particle mode geological material, primarily carbonate, rubber particles, vegetable fibers and biological material are the major contributors. Estimates of the fraction of TSP in Portland attributable to carbon range from 20 to 38 percent.

A novel technique to characterize simultaneously both elemental and organic carbon by their volatilization and oxidation properties has been developed by Johnson and Huntzicker (1978) and has been applied to the ambient and source samples collected on glass fiber filters for the PACS. The minimum detectable concentrations of the technique are defined by the carbon content of the blank filter (MDC=three times the blank uncertainty and are presented in Table 4.7.10.1 where they are compared to ambient and source values expected under PACS SOPs.

Organic and carbonate carbon are volatilized by heating a specimen to 580° C; the volatilized carbon is converted to CO_2. The resultant CO_2 is then mixed with hydrogen and passes through a methanator (Ni on firebrick) where it is reduced to CH_4. A flame ionization detector coupled to an electrometer produces a voltage peak, the area of which is proportional to the number of carbon atoms present; the area of this peak is compared with the signal generated by a known amount of CH_4 injected directly into the FID for quantification.

Table 4.7.10.1 Species Quantified by Carbon Analysis

Species	Typical Urban Concentration μg/m^3[a]	μg/cm^2[b]	Minimum Detectable[c] Limit μg/cm^2	Uncertainty	Blank μg/cm^2	Uncertainty μg/cm^2
Volatile Carbon (VC)	20	70	2.3	10%	5	±.75
Non Volatile Carbon (NVC)	3	10	.75	20%	.5	±.25

[a] PACS data

[b] Assuming 1500m^3 sampled with normal 8"x10" filter

[c] Three times the uncertainty of the blank

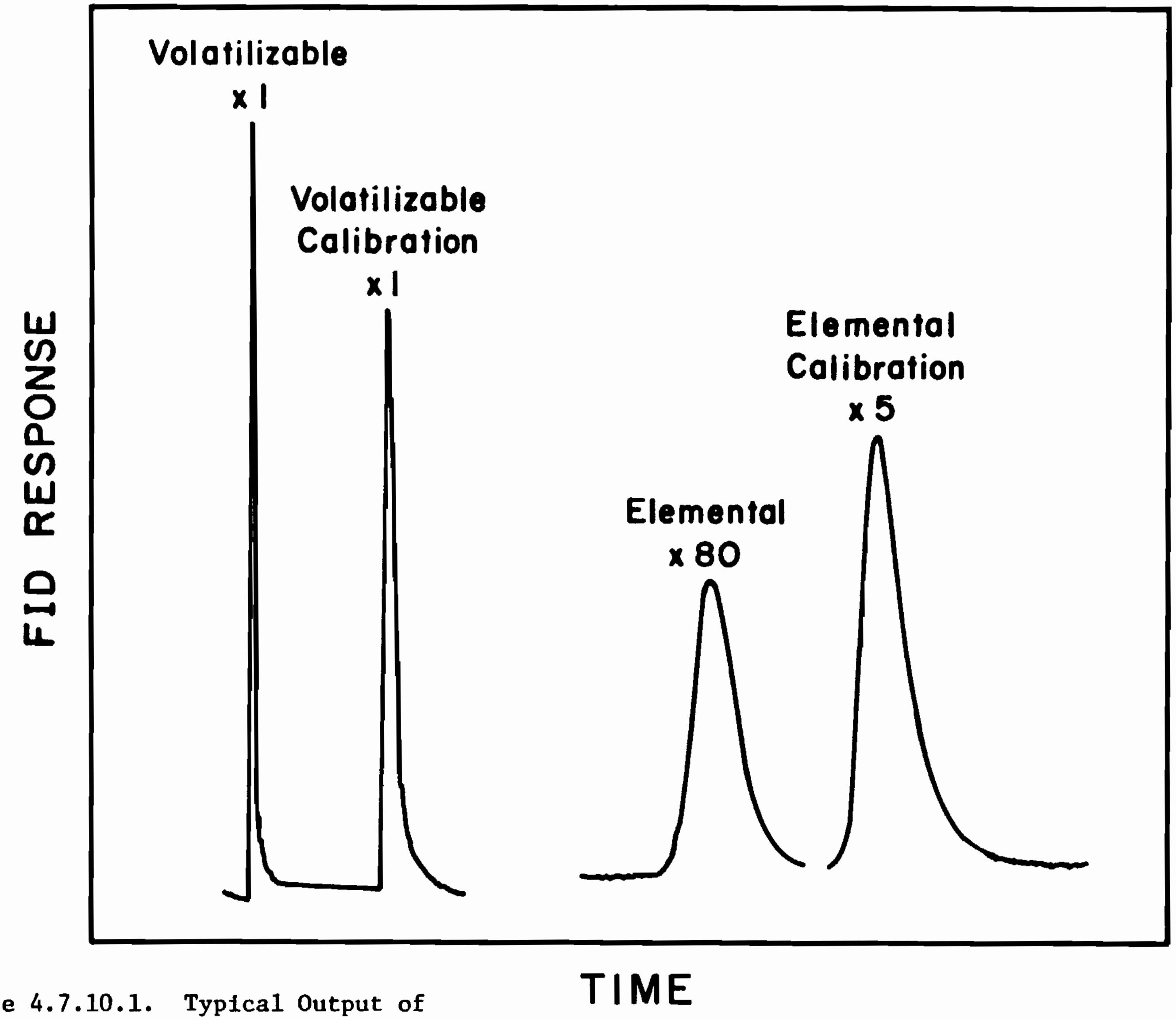


Figure 4.7.10.1. Typical Output of Carbon Analyzer

After the organic fraction has been quantified, the remaining sample is exposed to O_2 at 580° C and the elemental carbon is oxidized to gaseous CO_2. The O_2-CO_2 mixture passes through a spherocarb column which separates the CO_2 for passage to the methanator and quantification via the FID. Typical strip chart responses appear in Figure 4.7.10.1.

The standard operating procedure was conceptually simple but, since this unique instrument was still in its developmental stages, the detailed SOP underwent numerous revisions throughout the measurement program. Four .25 cm^2 circles were punched from each ambient glass fiber filter, or one circle from each source sample (these were more heavily loaded), and placed in a quartz boat which was inserted into the oven under the He atmosphere. Gas flows were controlled manually by a set of multiport zero dead volume valves. Peak areas as reported by an integrator were recorded for calibration and sample runs for volatile and elemental carbon. Calibration was performed every four samples. If calibration peak areas differed from the previous calibration by more than 10% the intervening specimens were re-run. The uncertainty of each measurement was determined by repeated measurements of portions of the same sample. This uncertainty includes the variability of the deposit across the surface of the filter.

The non-volatilizable carbon measurement is in reality an upper limit estimate of the elemental carbon concentration. Non-volatilized organics and organics pyrolized to elemental carbon may make contributions to the values obtained. The volatilizable carbon measurement represents a combination of both the organic and carbonate carbon in the sample.

Concentrations were calculated by the computer program *CARBON using the relationship

$$M_i = \frac{X_i}{X_{is}} M_{is} - B_i$$

where

M_i = mass of carbon type i

X_i = peak area yielded by sample for carbon type i

X_{is} = peak area yielded by standard for carbon type i

M_{is} = mass equivalent of carbon type i in standard

B_i = constant filter blank of carbon type i.

The uncertainty of each determination results from summing the analytical and blank uncertainties in quadrature.

4.8 INTERLABORATORY AND INTERMETHOD COMPARISONS

The true test of any analytical procedure is passed when analyses of the same specimens are performed by other laboratories and by completely independent methods with the same results. Such interlaboratory and intermethod comparisons should be performed on a regular basis and standard operating procedures of one or both of the analyses should be evaluated and improved upon as a result.

Each chemical analysis standard operating procedure used in the PACS was created specifically for the project and is being evaluated for the first time. This section reports on the validation of these procedures. Three interlaboratory comparisons were made on x-ray fluorescence analysis (XRF), two with Lawrence Berkeley Laboratories (LBL) and one with the Environmental Protection Agency/Research Triangle

(EPA). Ion chromatography (IC) and carbon analysis were compared with EPA/Corvallis and the Oregon Department of Environmental Quality (DEQ). Instrumental neutron activation analysis results were continually checked against standard reference materials and in intermethod comparisons with XRF. This latter comparison is of particular importance because it represents an analytical quality assurance check on every filter through the evaluation of different measurements obtained for the same chemical constituents.

The method of comparison is ordinary linear regression modeled after King (1977). This model is strictly appropriate only when the major source of error is in the dependent variable and is constant (homoscedastic) over the entire range of values. Intercomparison measurements normally exhibit errors which are roughly proportional to the value of the measurement and are of equal magnitude in both the independent and dependent variable. Statistical methods for treating this situation do exist (see section 3.2) but have not been fully developed for this application; the timeframe of this study does not permit their development here. The results indicate that King's (1977) linear regression model is a reasonable approximation.

In ordinary linear regression it is important to realize that the slope and intercept obtained depend on which variable is chosen as the independent one. Usually, the home laboratory, X selects its measurements as independent and implicitly assigns all of the data scatter to "the other guy," Y. It is just as fair to calculate a slope and intercept choosing Y as independent. Two relationships between Y and

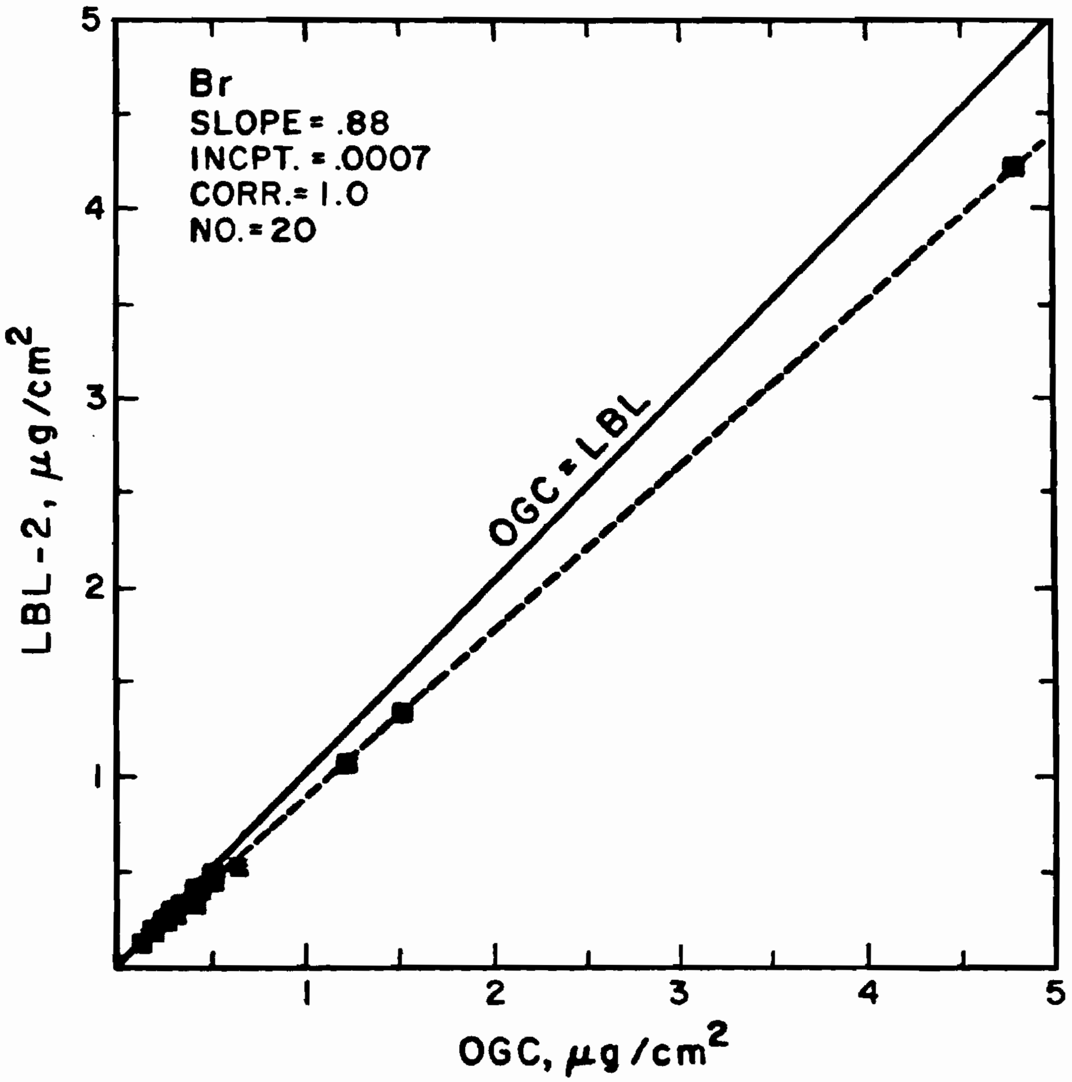


Figure 4.8.1a. X-ray Fluorescence Bromine Intercomparison with Lawrence Berkeley Laboratories. The dotted line is the linear regression line with the OGC value as the independent variable. Solid line is that of an ideal intercomparison.

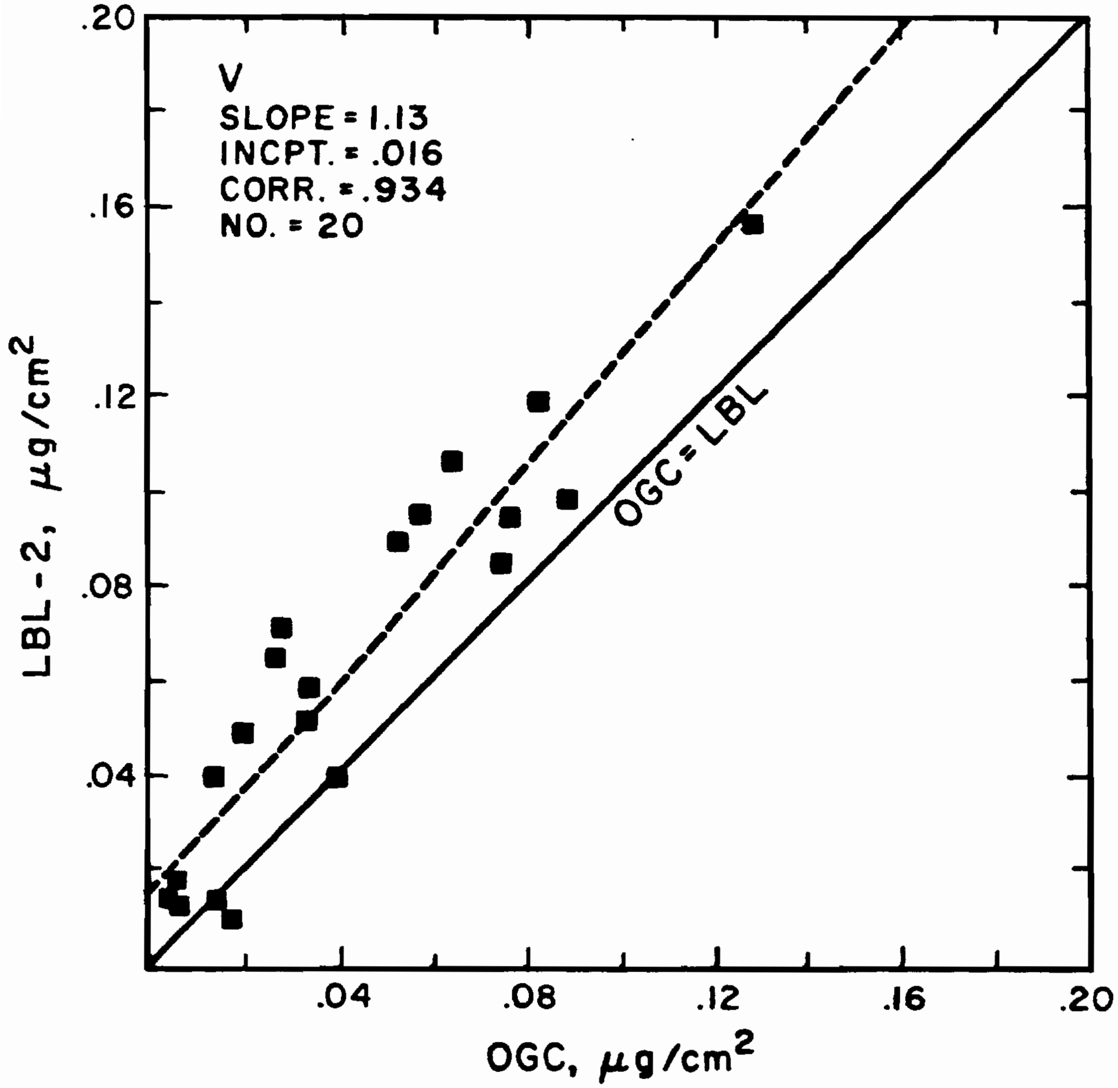


Figure 4.8.1b. X-ray Fluorescence Vanadium Intercomparison with Lawrence Berkeley Laboratories. Dotted line is a linear regression line. Solid line represents a perfect intercomparison.

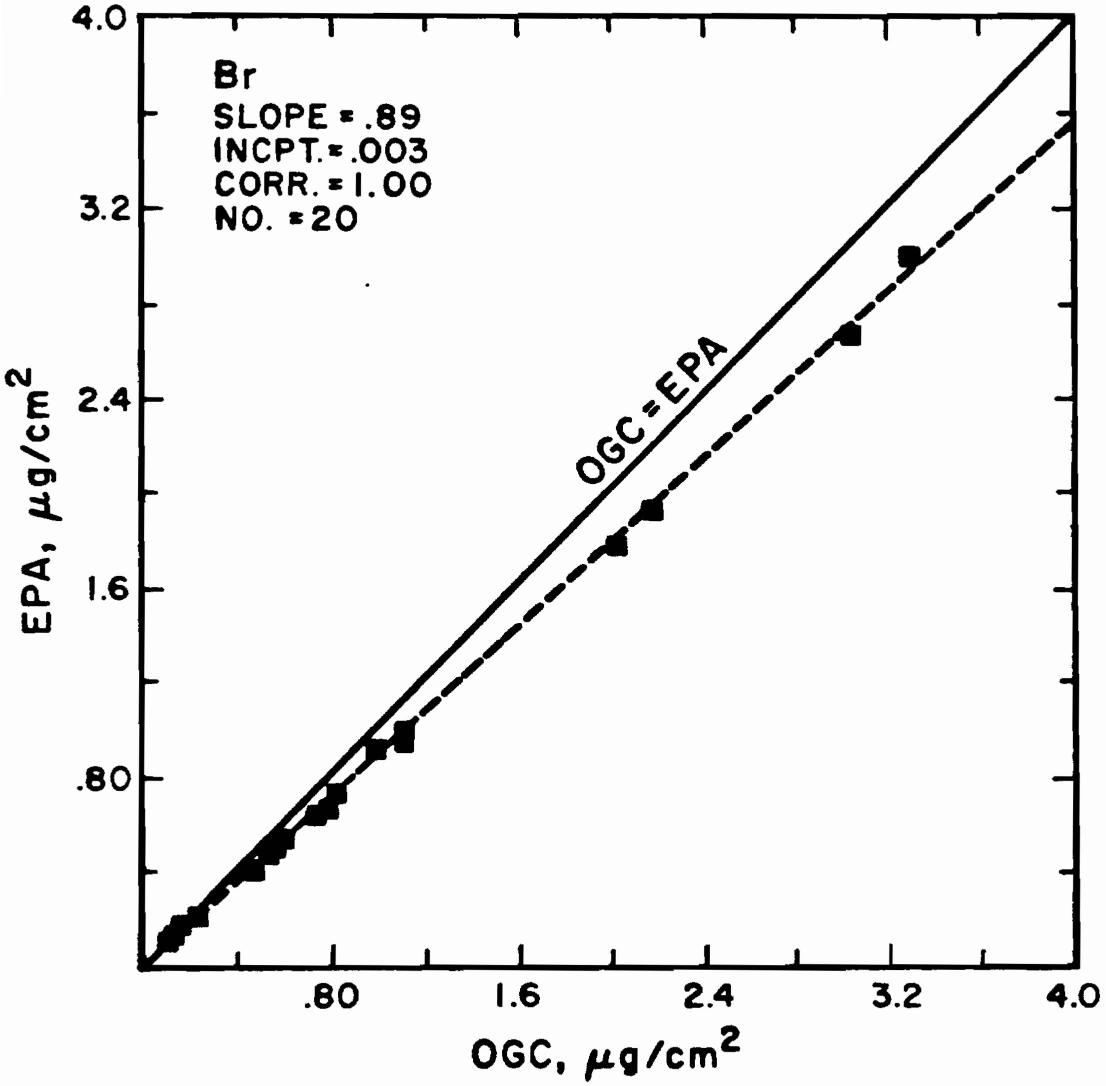


Figure 4.8.2a. X-ray Fluorescence Bromine Intercomparison with Environmental Protection Agency. Dotted line is a linear regression line. Solid line represents a perfect intercomparison.

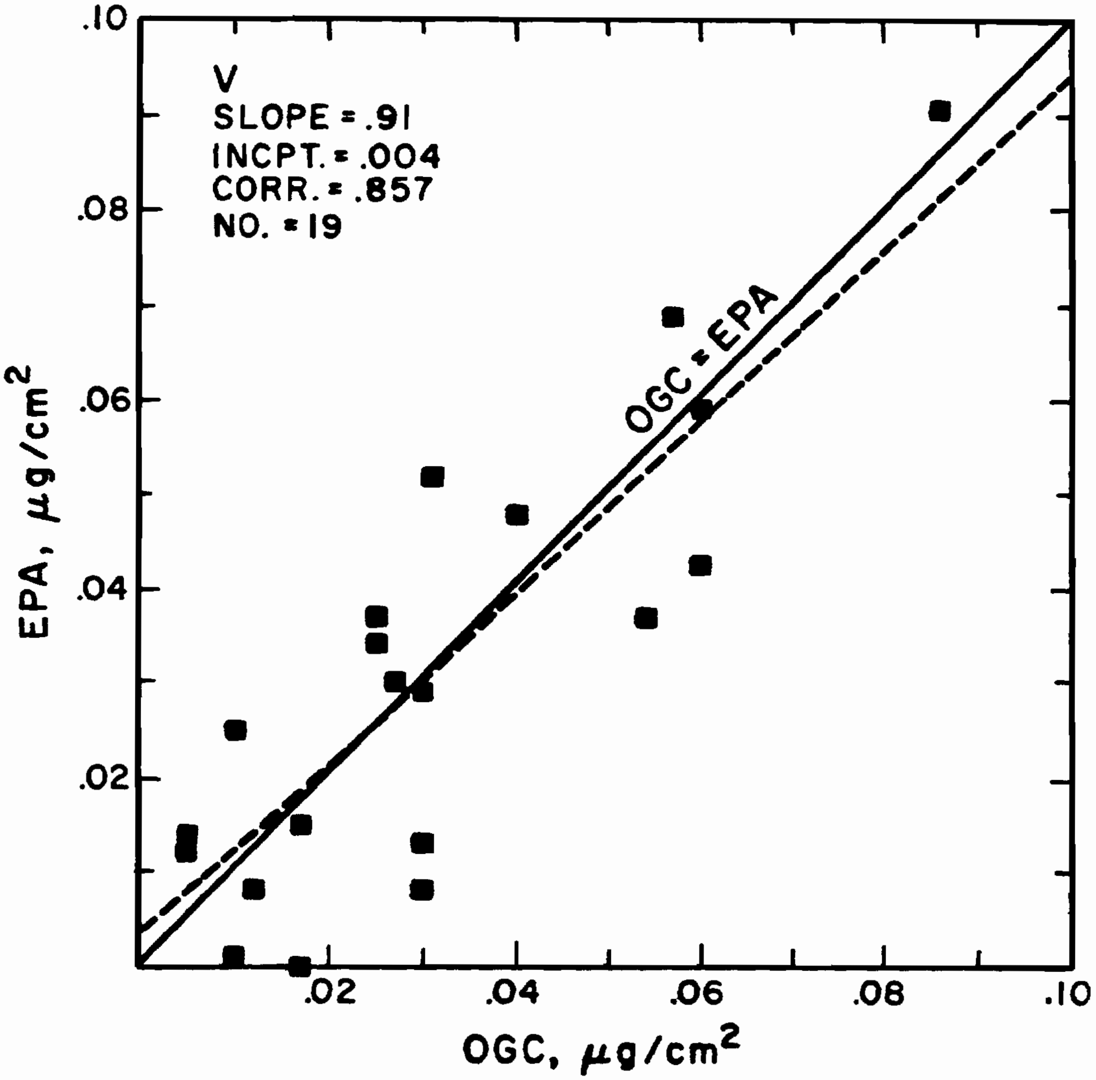


Figure 4.8.2b. X-ray Fluorescence Vanadium Intercomparison with Environmental Protection Agency. Dotted line is a linear regression line. Solid line represents a perfect intercomparison.

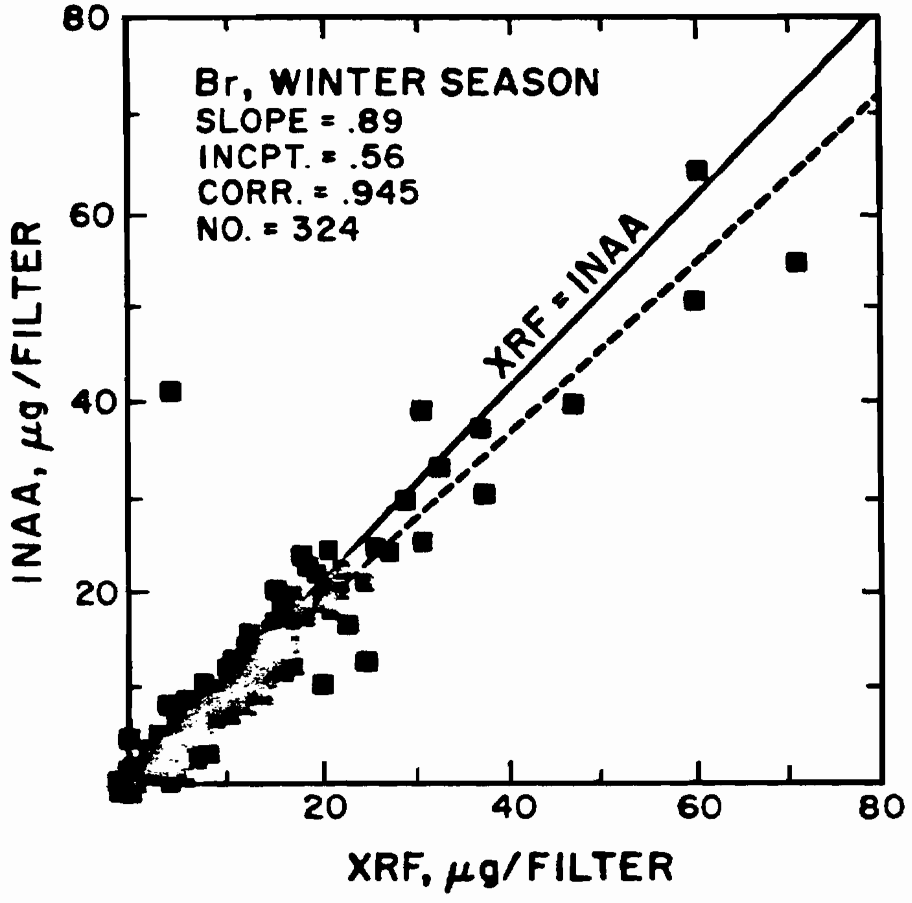


Figure 4.8.3a. Neutron Activation/X-ray Fluorescence Intermethod comparison for PACS Bromine Analyses, Winter Season. Dotted line is a linear regression line. Solid line represents a perfect intercomparison.

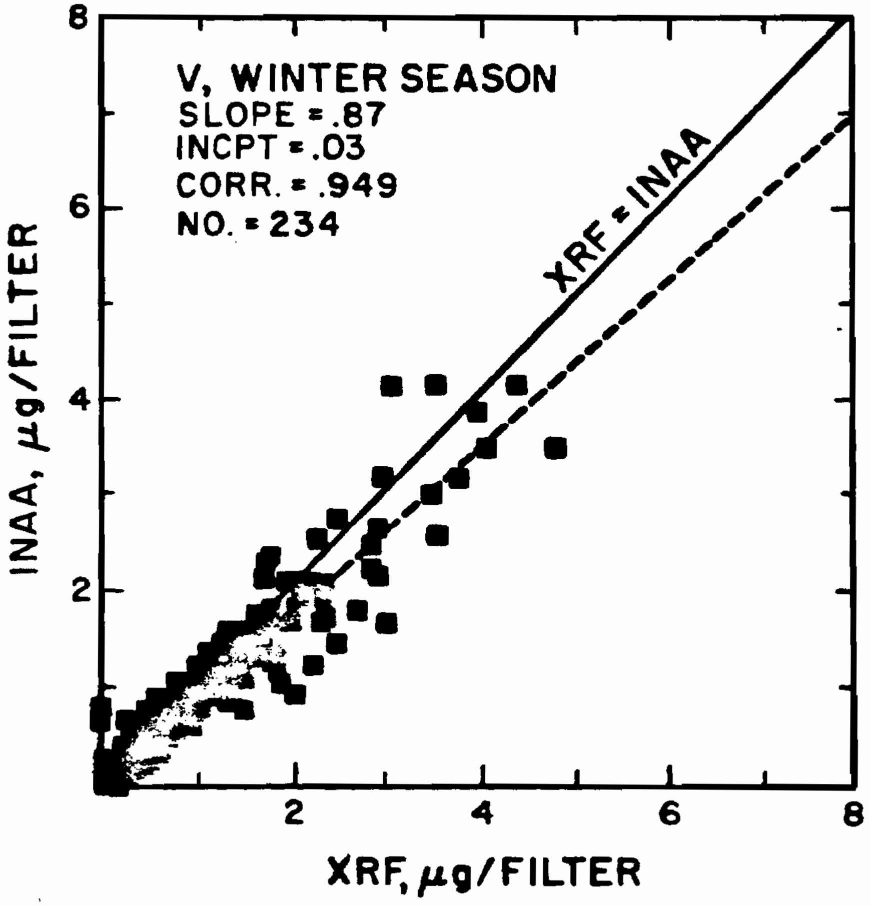


Figure 4.8.3b. Neutron Activation/X-ray Fluorescence Intermethod comparison for PACS Vanadium Analyses, Winter Season. Dotted line is a linear regression line. Solid line represents a perfect intercomparison.

X then exist in the form

$$Y = b_1X + a \qquad 4.8.1$$

$$Y = b_1'X + a' \qquad 4.8.2$$

the former (X independent) with slope $b = b_1$ and the latter (Y independent) with $b = b_1'$ ($b_1' = 1/b_2$ where b_2 is the slope when X and Y are switched in eq. 4.8.1). King (1977) shows that

$$b_1' = \frac{b_1}{r^2} \qquad 4.8.3$$

where r is the correlation coefficient between the two variables. He suggests that a "best estimate" of the slope is

$$b = \sqrt{b_1'b_1} = \frac{b_1}{r} \qquad 4.8.4$$

which is an exact relationship when the standard deviations of the two measurements are equal.

In the ideal intercomparison, $a = 0$, indicating that the blanks have been properly subtracted, $r = 1$, confirming that the precision of both laboratories is excellent (this implies $b = b_1' = b_1$) and $b = 1$, proving that the determinations are in agreement and strongly attesting to the accuracy of the analyses (the accuracy is better validated by intermethod comparisons as inherent biases in the same technique are eliminated).

A scatterplot of paired chemical constituent determinations was made and the slope, intercept and correlation coefficient were calculated. Figures 4.8.1 a & b, 4.8.2 a & b and 4.8.3 a & b are examples of Br, a "best case" and V, a "worst case" intercomparisons.

Bromine is a prominent aerosol element that can be precisely measured by both XRF and INAA. It has a high x-ray energy which experiences no x-ray spectral interferences and little absorption. Br has a high nuclear cross-section. Its product nuclide has a moderate half-life and is without γ-ray interferences from other elements under the conditions of this study. Vanadium is present in many ambient aerosols at concentrations near the XRF detection limit and experiences a strong interference from the Ti Kα line. Since the typical urban Ti concentration is about an order of magnitude greater than the V concentration (Cooper 1973a), since the Ti Kβ exhibits about 10% of the intensity of the Ti Kα, and since XRF sensitivities for V and Ti are comparable, nearly 50% of the counts in the V Kα region of interest can be due to Ti and must be subtracted out. Vanadium has excellent sensitivity when measured by INAA and no spectral interferences, however.

These characteristics are amply illustrated in Figures 4.8.1 - 4.8.3. Figures 4.8.1b and 4.8.2b show that the intercomparison is far from ideal. The intercept in the first case is above the minimum detectable limit, the slopes are not equal to one and there is too much scatter. Contrast these to those of Br in Figures 4.8.1a and 4.8.2a. Here the intercept is well below the minimum detectable limits and the scatter is virtually nonexistent. The bias discussed in section 4.7.6 is evident and will be treated shortly. These results are consistent with the XRF spectral characteristics just mentioned.

When intercomparison results do not agree, the question of "who is right?" arises. The only way to definitely answer this question is to make comparisons with a large number of laboratories by various analytical methods on specimens of known composition. The best estimate of the true values will be the average of the measurements obtained with the elimination of obvious outliers. Such an undertaking is beyond the scope of the PACS and the answer to "who is right?" must be based on the information at hand and the past history and reputations of the intercomparison laboratories. The case of vanadium is an obvious one. Figure 4.8.1b exhibits much less scatter than Figure 4.8.2b, suggesting that the EPA determination, possibly because of inadequate subtraction of the Ti interference, is the one which includes the larger error. Figure 4.8.3b, a scatterplot of OGC INAA and XRF results on over 200 PACS filters, also lends credence to the belief that the OGC values are reliable.

Table 4.8.1 lists b_1, b_1', b and r for each of the XRF intercomparisons. In each case the intercept was at or near the minimum detectable limits and is not included. The precision is indicated by the correlation coefficients which are greater than .98 (meaning that 4% of the variance about the regression line is attributable to experimental uncertainty of both procedures) for all elements with the exception of Al, Cl and V. (S, Ni, Mn, Br and Pb demonstrate less precision in LBL-1 attributable to a difficulty in mounting filters for this first intercomparison). The Al Kα x-ray is subject to absorption and an interference from the Br x-ray; the LBL/OGC comparisons are more precise than the EPA/OGC comparisons, similar to the V case. The low Cl correlation with LBL-1 and LBL-2 does not have an obvious explanation.

The multiplicative bias of the intercomparisons presents a

Table 4.8.1 X-Ray Fluorescence Interlaboratory Comparison

		LBL-1[a]				LBL-2[b]				EPA[c]				
Element	Excitation	b_i^*	b_i'	b	r	b_i^*	b_i'	b	r	b_i^*	b_i'	b	r	bn^d
Al	2	.411	.422	.416	.987	.430	.468	.448	.959	.31	.39	.35	.898	
Si	2	.440	.445	.443	.994	.450	.453	.451	.997	.39	.39	.39	.994	
S	3	1.10	1.15	1.12	.979	1.17	1.19	1.18	.992	.88	.89	.88	.992	1.03
Cl	3	.196	.209	.202	.968	.140	.176	.157	.872	.82	.85	.84	.984	.17
K	3	.700	.710	.705	.993	.860	.861	.861	.999	.83	.84	.83	.994	.72
Ca	3	1.18	1.18	1.18	.998	1.17	1.18	1.18	.995	.71	.72	.72	.994	.84
Ti	3	.960	.979	.970	.990	1.01	1.04	1.02	.987	.88	.91	.90	.985	.90
V	3	1.32	1.45	1.38	.955	1.13	1.30	1.21	.934	.90	1.23	1.05	.857	1.05
Cr	3	1.16	1.17	1.17	.995	1.13	1.13	1.13	.998	.83	.83	.83	.998	.94
Mn	3	1.35	2.82	1.95	.692	1.15	1.16	1.15	.996	.83	.84	.84	.995	.92
Fe	1	1.05	1.05	1.05	.999	1.10	1.10	1.10	.999	.80	.81	.80	.993	.88
Ni	1	1.66	1.91	1.78	.932	1.08	1.09	1.08	.995	.84	.86	.85	.991	.92
Cu	1	1.43	2.15	1.75	.815	1.13	1.15	1.14	.993	.84	.86	.85	.990	.96
Zn	1	1.11	1.12	1.12	.995	1.15	1.15	1.15	1.0	.85	.86	.86	.995	.99
Br	1	.830	.860	.840	.984	.87	.87	.87	1.0	.80	.80	.80	1.0	.70
Pb	1	1.14	1.20	1.17	.974	1.16	1.16	1.16	1.0	.89	.89	.89	1.0	1.02

[a] Lawrence Berkeley Laboratories XRF intercomparison, May, 1978. 40 ambient air samples.
Some of these were not flatly mounted so this intercomparison should be given less weight.
OGC values before LBL Normalizations of Table 4.7.6.2

[b] Lawrence Berkeley Laboratories XRF intercomparison, June, 1978, 20 ambient air samples.
OGC values before LBL Normalizations of Table 4.7.6.2

[c] Environmental Protection Agency XRF intercomparison, Aug., 1978, 20 ambient air samples.
OGC values after LBL Normalizations of Table 4.7.6.2

[d] b for EPA without Normalizations of Table 4.7.6.2

* OGC value is the independent variable

difficulty. A slope of one cannot be expected for Al and Si because of the particle absorption discussed in section 4.7.6. The intercomparison laboratories had no idea of the particle sizes sent to them and therefore had no way to account for that variable. The V and Cl intercomparisons are imprecise so a bias is plausible for those elements. Most other slopes are greater than one for the LBL comparisons and less than one for the EPA comparison. A recent direct comparison of the two laboratories (Camp, et al., 1978) presented in Table 4.8.5 shows results consistent with OGC for S, Br and Pb but inconsistent for Cu, Fe and Zn. These do not represent analyses on the same filters, however.

The intermethod comparisons help to clear the issue somewhat. Comparing the slopes in Table 4.8.4 for Br, Mn, Ti, Cl, and S-SO_4 obtained by OGC XRF, IC, and INAA with slopes for the same elements in Table 4.8.1 shows the same multiplicative bias in the intermethod comparisons and in the LBL-2 interlaboratory comparison. LBL does not use a separate calibration standard for every element (Goulding and Jaklevic, 1973) but interpolates sensitivities between measurements from some elemental standards across certain portions of the spectrum. This is possible because the sensitivity is a smooth and slowly varying function of atomic number away from absorption edges for monochromatic excitation radiation (Bertin, 1975). The significance of this is that if the LBL values for a certain element are correct, the values for elements immediately above or below it in the periodic table should also be correct. This knowledge coupled with the OGC INAA/XRF and IC/XRF intermethod comparisons led to the normalization constants of Table

4.7.6.2 for XRF measurements. More intercomparisons are required to verify the validity of this normalization. There is some consolation in the realization that the largest bias introduced is 17%, somewhat comparable to the overall analytical error in many cases.

Ion Chromatography intercomparison values appear in Table 4.8.2. They are very close to the ideal in all cases and validate that procedure without explanation. No comparison for fluoride was made.

Carbon analysis intercomparison results in Table 4.8.3 indicate a lack of precision in the EPA case. Comparison with DEQ is precise, but exhibits a multiplicative bias. In the absence of other information, the OGC values were accepted as is. More interlaboratory comparisons are required of this analysis.

INAA was continually compared against standard geological reference materials and ionic solution deposits as part of the quality assurance program. Of course, the same materials were used for calibration, so this represents a check on precision, but not on accuracy. A better check consists of the intermethod comparisons with IC and XRF exhibited in Table 4.8.4 for the PACS samples from three separate seasons and from the three seasons combined. The slopes are consistent across the board and for XRF differ from one for the reasons discussed. The disagreement between AIC/INAA Cl could be due to some non-chloride species, though considering the high solubility of Cl, this doesn't seem likely. More investigation is needed. The correlation coefficients are naturally smaller than those for the interlaboratory comparisons at about .93 (meaning that 14% of the variance about the regression

Table 4.8.2 Ion Chromatography Interlaboratory Comparison

Ion	b_1^*	b_1'	b	r
NO_3^-[a]	.97	.97	.97	.999
$SO_4^=$[b]	.94	.94	.94	.999
Cl^-[b]	.92	.93	.93	.994

[a] EPA LASS, Corvallis comparison, May 1978, 15 samples. EPA method was conversion to NO_2 with colormetric determination.

[b] EPA LASS, Corvallis comparison, May 1978, 15 blind samples of NBS reference materials were prepared.

[*] OGC independent variable.

Table 4.8.3. Carbon Analysis Interlaboratory Comparison

	DEQ[a]				EPA[b]			
Constituent	b_1^*	b_1'	b	r	b_1^*	b_1'	b	r
Total Carbon	.83	.85	.84	.990	1.02	1.23	1.12	.907

[a] Department of Environmental Quality, April, 1978. 10 HiVol samples by combustion techniques.

[b] Environmental Protection Agency, April, 1978.

[*] OGC independent variable

Table 4.8.4 OGC Inter Method Comparisons[a] on PACS Ambient Samples for Three Seasons

Constituent	Dependent Variable	Independent Variable	SUMMER b_1	SUMMER b_1'	SUMMER b	SUMMER r	AUTUMN b_1	AUTUMN b_1'	AUTUMN b	AUTUMN r	WINTER b_1	WINTER b_1'	WINTER b	WINTER r	ALL THREE SEASONS b_1	ALL THREE SEASONS b_1'	ALL THREE SEASONS b	ALL THREE SEASONS r
Al(total)	INAA	XRF,2	1.47	1.71	1.58	.928	1.36	1.56	1.46	.934	1.38	1.52	1.45	.954	1.41	1.59	1.50	.941
Al(Fine)	INAA	XRF,2	.80	.90	.85	.942	.72	.79	.76	.953	b				b			
S-SO$_4$	XRF,3	AIC	.27	.29	.28	.968	.26	.33	.31	.932	.25	.28	.27	.941	.25	.27	.26	.957
Cl	INAA	XRF,3	.36	.43	.39	.920	.24	.32	.28	.863	.28	.44	.35	.795	.24	.32	.28	.868
Cl$^-$-Cl	AIC	XRF,3	.26	.31	.28	.918	.27	.32	.32	.853	.20	.24	.22	.917	.26	.35	.30	.861
Cl$^-$-Cl	AIC	INAA	.63	.84	.73	.864	.72	.80	.76	.949	.52	.66	.59	.885	.81	1.37	1.05	.768
Ti	INAA	XRF,3	1.06	1.19	1.12	.943	.85	1.02	.93	.914	.90	1.0	.95	.947	.90	1.06	.98	.920
V	INAA	XRF,3	1.02	1.18	1.10	.928	.84	1.05	.94	.893	.87	.97	.92	.949	.85	.96	.91	.939
Mn	INAA	XRF,3	1.21	1.32	1.26	.959	1.14	1.53	1.32	.863	1.11	1.17	1.14	.975	b			
Br	INAA	XRF,3	.87	1.02	.94	.922	.87	.99	.93	.936	.89	1.0	.94	.945	b			

---

[a] XRF measurements were not normalized by factors in Table 4.7.6.2

[b] No value available

Table 4.8.5 A Comparison of Results from LBL and EPA[a]

	LBL[b]		EPA[b]		LBL[d]	LBL/OGC[e]
Constituent	Ratio to Avg[c]	Ratio to Mass	Ratio to Avg[c]	Ratio to Mass	EPA	EPA/OGC
Mass	.89		.88			
S	1.09	1.22	.94	1.07	1.14	1.14
Si	.65	.73	.63	.72	1.01	
Ca	.56	.63	.56	.64	.98	1.40
Ti	.78	.88	.74	.84	1.05	1.13
Fe	.65	.73	.70	.80	.91	1.25
Cu[f]	1.51	1.70	.95	1.08	1.57	1.19
Zn	1.01	1.13	.88	1.00	.85	1.16
Se	.90	1.01	1.05	1.19	.85	
Br	1.14	1.28	.88	1.00	1.28	1.24
Pb	1.08	1.21	.89	1.01	1.20	1.14

[a] From Camp et al. (1978)

[b] LBL Sampler S and EPA sampler R, fine particulate fraction. These two were chosen because they were located next to each other and the mass they sampled was comparable. Analyses were performed on different filter samples of the same air so some of the difference in ratios could be due to sampling. LBL's sampler has a 2.4μm size cut and EPA's sampler has a 3.5μm size cut.

[c] This is the average over 16 sampling periods of contituent measurement for the particular sampler divided by the average for that period of determinations from 10 samplers.

[d] Quotient of value in column 3 of this table divided by value in column 5.

[e] From column 9 value divided by column 15 value table 4.8.1

[f] Local sources of Cu were present

line is due to experimental error) because analyses were performed on different portions of the same filters and normalized to the total area of deposit (see section 4.7.7), much added handling was involved, and because of the large number of samples involved, more outliers were present. For high values, these affect the correlation coefficient out of proportion to their numbers, confirming the reservation expressed at the beginning of this section. Figures 4.8.3 a&b present typical scatterplots of these intermethod comparisons. Obvious outliers on the graphs were identified, examined and submitted for reanalysis if required (see section 5.5).

The final verdict cannot be delivered on the validity of the PACS data until the intercomparison results presented here are placed in perspective by an examination of larger studies pitting the results of one highly reputed analytical lab against others. It must be realized that the OGC/PACS standard operating procedures, while profitting greatly from the experience of others, were being used for the first time and that all personnel was new, inexperienced and trained on the job. Each set of values for intercomparison was obtained only once by a regular technician with no special care other than that given to normal PACS samples. Contrast this to the laboratories who have long established SOPs and have experienced or supervisory personnel run replicate analyses with special attention for intercomparison purposes.

Camp, et al. (1973, 1975) have carried out such studies. Filter specimens of known composition were sent to many laboratories for analysis. Even within the subset of XRF analyses done, the range of

Table 4.8.6 Intercomparisons of other laboratories[a]

Element	Camp.(1974) Range[b]	Camp(1975) Range
Al	.58-5.0	.87-1.27
S	c	.66-2.65
K	.73-1.25	.78-1.80
V	.68-1.17	.71-1.03
Cr	c	.84-1.01
Mn	.68-1.17	.75-1.0
Fe	.65-1.16	.69-1.11
Cu	.60-1.20	c
Zn	c	.64-1.44
As	.69-1.20	c
Pb	.69-1.09	c
Cd	c	.85-1.09
Au	c	.69-1.22

[a] Camp, et al. (1974, 1975)

[b] Range of ratios of measured to true concentrations of prepared solution deposits on millipore filters given to 12 labs in 1973 (using XRF and other techniques) and 8 labs using XRF in 1975.

[c] Not measured.

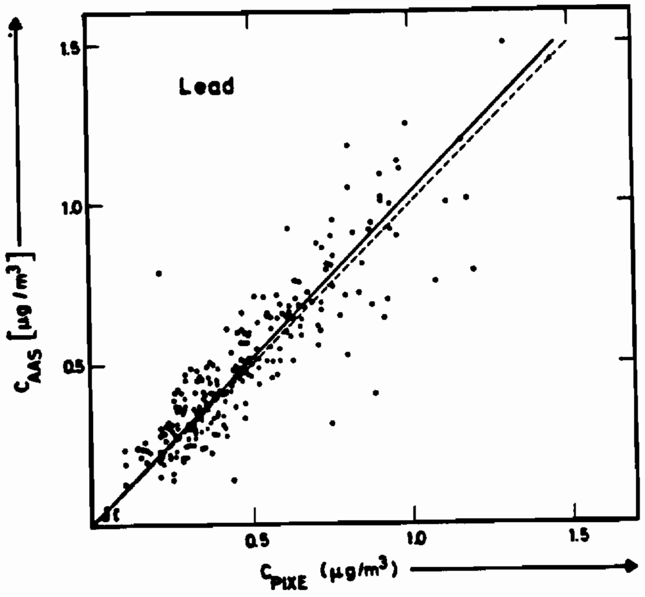


Figure 4.8.4. Elemental concentrations C_{ASS} determined from Atomic Absorption Spectroscopy vs. elemental concentrations C_{PIXE} determined from Proton Induced Xray Emission Spectroscopy for lead. Solid line: most likely straight line calculated from least squares; dashed line has slope of one. From Nottrodt, *et al.* (1978).

ratios to true values was large, as Table 4.8.6 shows. Figure 4.8.4 reproduces an intermethod scatterplot of Pb concentrations on air filters determined by Proton Induced X-ray Emission (PIXE) and Atomic Absorption Spectroscopy (AA) (Nottrodt, et al., 1978). The results of Tables 4.8.1 to 4.8.4 and Figures 4.8.1 to 4.8.3 are more acceptable when measured against these examples.

More intercomparison studies should be carried out in the future, but the evaluation of those performed to date validates the PACS analytical program to a degree at least commensurate with other laboratories.

CHAPTER FIVE: DATA MANAGEMENT

Any large air pollution study will generate hundreds of thousands, possibly millions of individual digits from a variety of sources representing a broad spectrum of information; sample identification, site, date, time, volume sampled, elemental composition--- each of these must be archived and related to the others in such a way that it can be accessed quickly and accurately and manipulated for whatever interpretative purposes may be required. To perform this task, computer based data management must be considered as an integral part of the study.

Every standard operating procedure should include the recording of data in a standard format and in the most efficient, accurate way. Methods must be established to transfer these data into the data bank and to verify that they have been entered correctly. The data storage device must be compatible with the constraints placed on the computer system user, constraints which are particularly tight on a multiple user system, yet allow reasonable access times for entering, editing and reading the data.

The small scale (1-100 samples) data management and quality assurance situation can be handled without the development of computer based procedures because the relatively small number of data items involved can be dealt with more or less individually. Likewise, the large scale data management situation ($>10^4$ samples) is one in which specialized human resources and equipment are brought into play such that the ordinary researcher may treat the system as a "black box." The PACS data management program must be considered "mid-scale" (10^2 to 10^4 samples): too big to deal with each sample individually yet too small to merit the additional expense of a full time data management expert and dedicated devices.

Though such mid-scale projects are handled frequently, the resources used are commonly those of the large scale or the small scale, depending on what the investigative organization is tooled up for. Being tooled up for neither, the PACS chose the creation of an original system to be maintained and operated by non-specialist personnel on existing time-sharing, mini-computer facilities.

This chapter describes the data management program that was devised for the PACS and implemented on the Oregon Graduate Center PRIME 300 computer system. The system has two fixed disks and two removable disks, but its multi-user mode treats all disks as fixed and the common property of all users. Thus, long term storage on disk was not feasible. Data were therefore broken up into blocks, each corresponding to a season, summer, autumn, winter, or fall, of the PACS year and maintained on disk when in use but stored on magnetic tape, and later on floppy disk, when not needed. In this way the PACS storage never exceeded 20% of one disk.

PRIME (1978) supports the MIDAS (Multiple Index Direct Access System) Data Manipulation Language (DML) which consists of subroutines hosted by the FORTRAN language. Haseman and Whinston (1977) and Meadows (1977) detail general procedures and file structures of DMLs which not only locate, add, delete, change, merge and reorder data item values, but also preserve the relationships between those values and make the access of them quick, convenient and compatible with the computer operating system. This would have been an ideal DML to use in the PACS, but it was not adequately documented at the time the PACS system was designed and it is a disk based system which does not allow easy transfer back and forth with magnetic tape, though it would not have been a great task to compose a series of routines for this purpose.

Figures 5.0.1 to 5.0.14 present the data management flow for ambient specimens with specific components described in Tables 5.0.1 to 5.0.3. Source samples, because of their specialized nature and smaller number, were managed individually, though the chemical analyses calculations and merging operations were the same as those of Figures 5.0.5 to 5.0.9.

Six general tasks comprise the PACS data management system:

1. Recording: The relevant information obtained at the time an operation is performed is registered on a data sheet, paper tape of other transfer medium.

2. Input: The data are transferred from the recording medium into computer accessible files.

3. Calculations: Data items are combined in mathematical expression to yield a desired result.

4. Merging: Data from various files pertaining to an individual sample or sampling day are retrieved and related to each other.

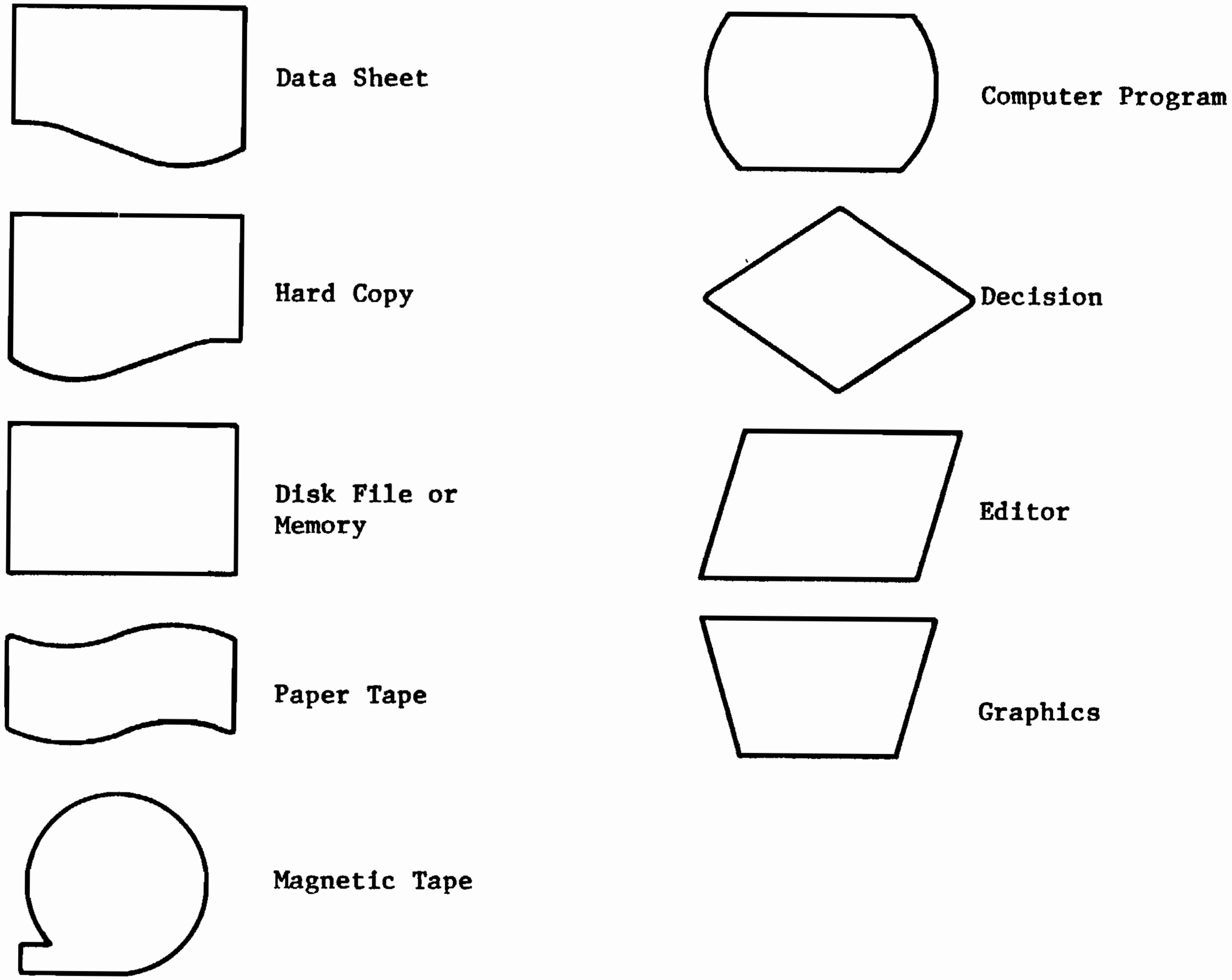
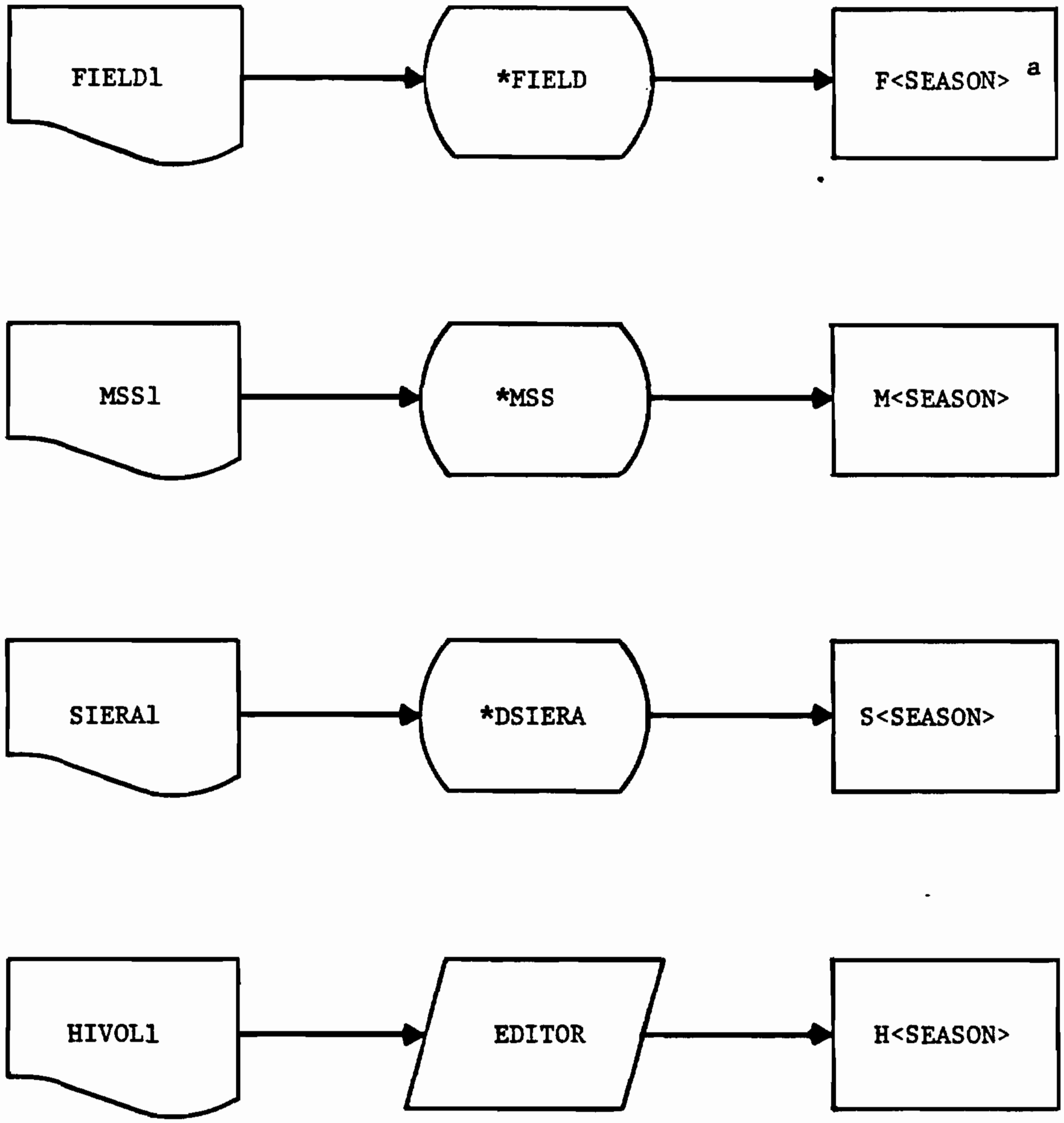
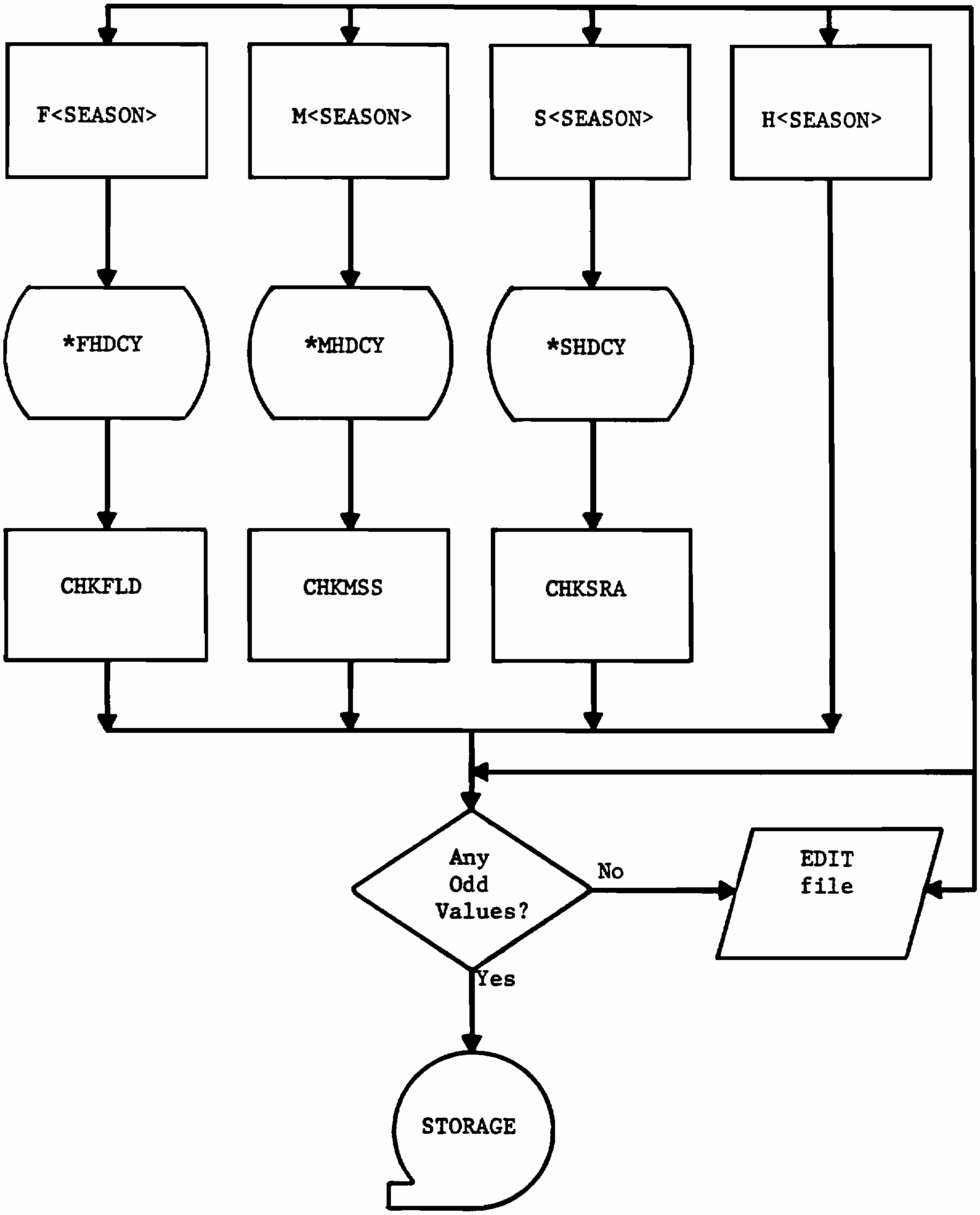


Figure 5.0.1 Data Management Flowchart Symbol Key

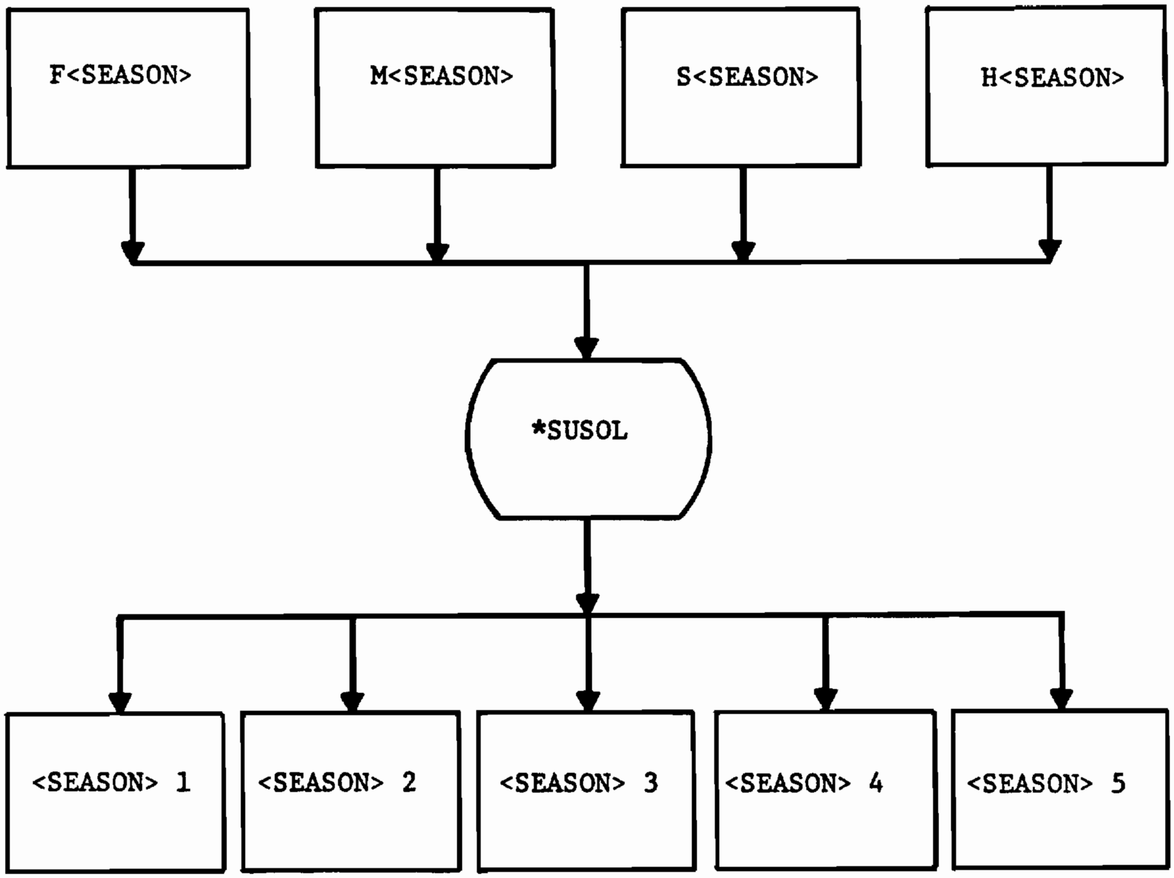


[a] <SEASON> was replaced by SUMMR, AUTMN, WINTR, or SPRNG

Figure 5.0.2 Mass and Field Data Input



5.0.3 Mass and Field Data Quality Assurance



5.0.4 Mass and Field Data Merging and Output

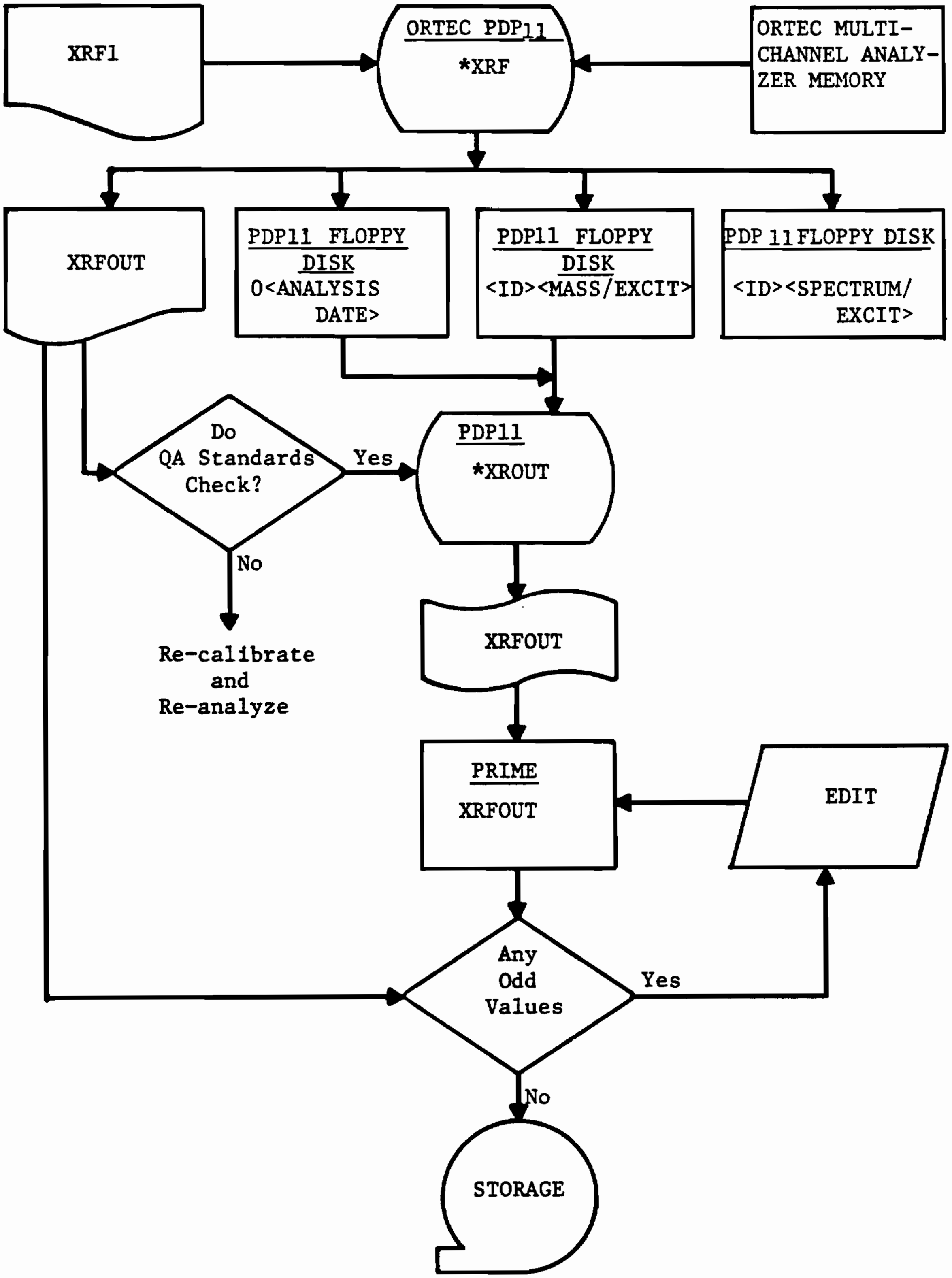


Figure 5.0.5 XRF Data Input, Calculations, Output and Quality Assurance

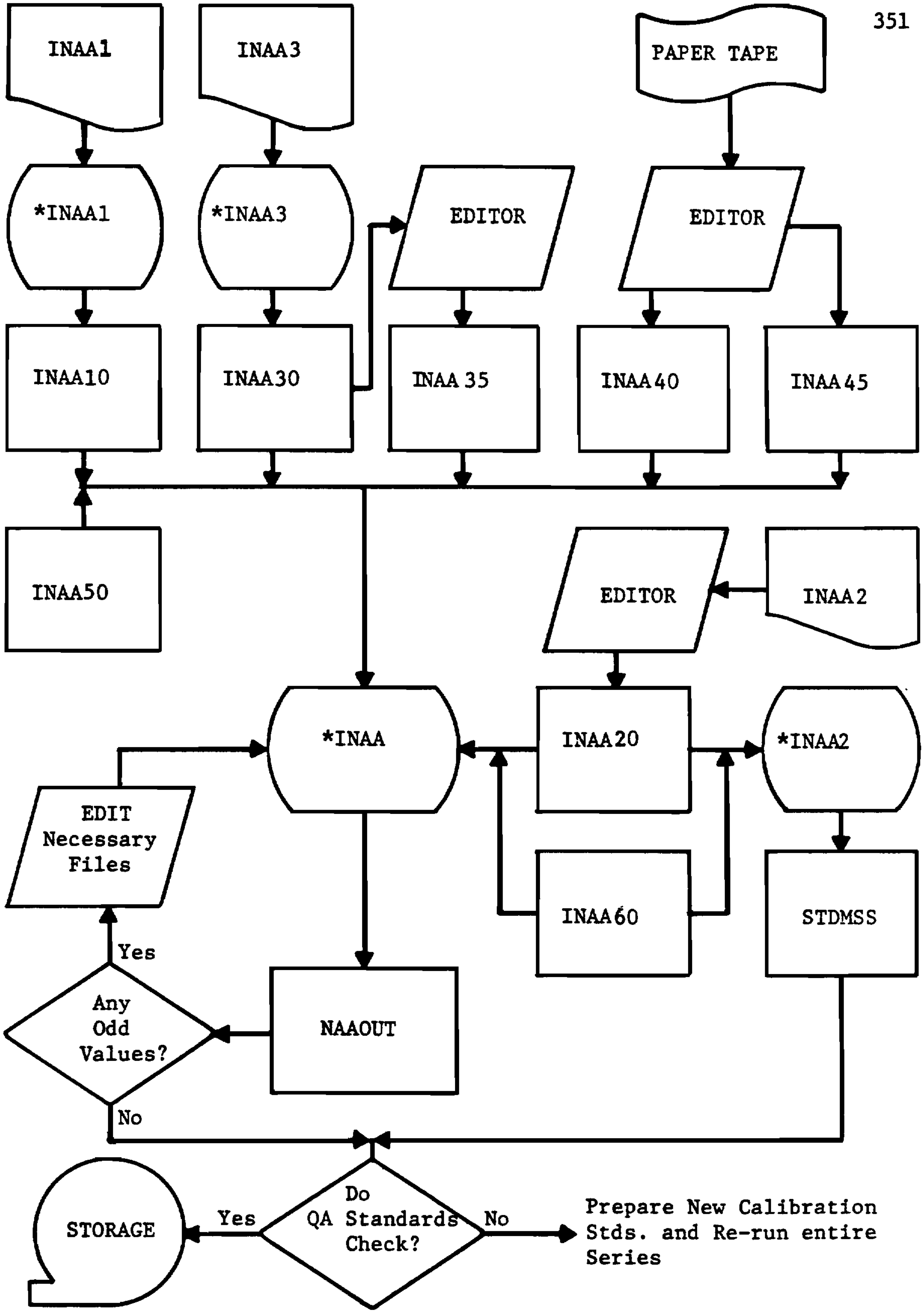


Figure 5.0.6 INAA Data Input, Calculations, Output and Quality Assurance

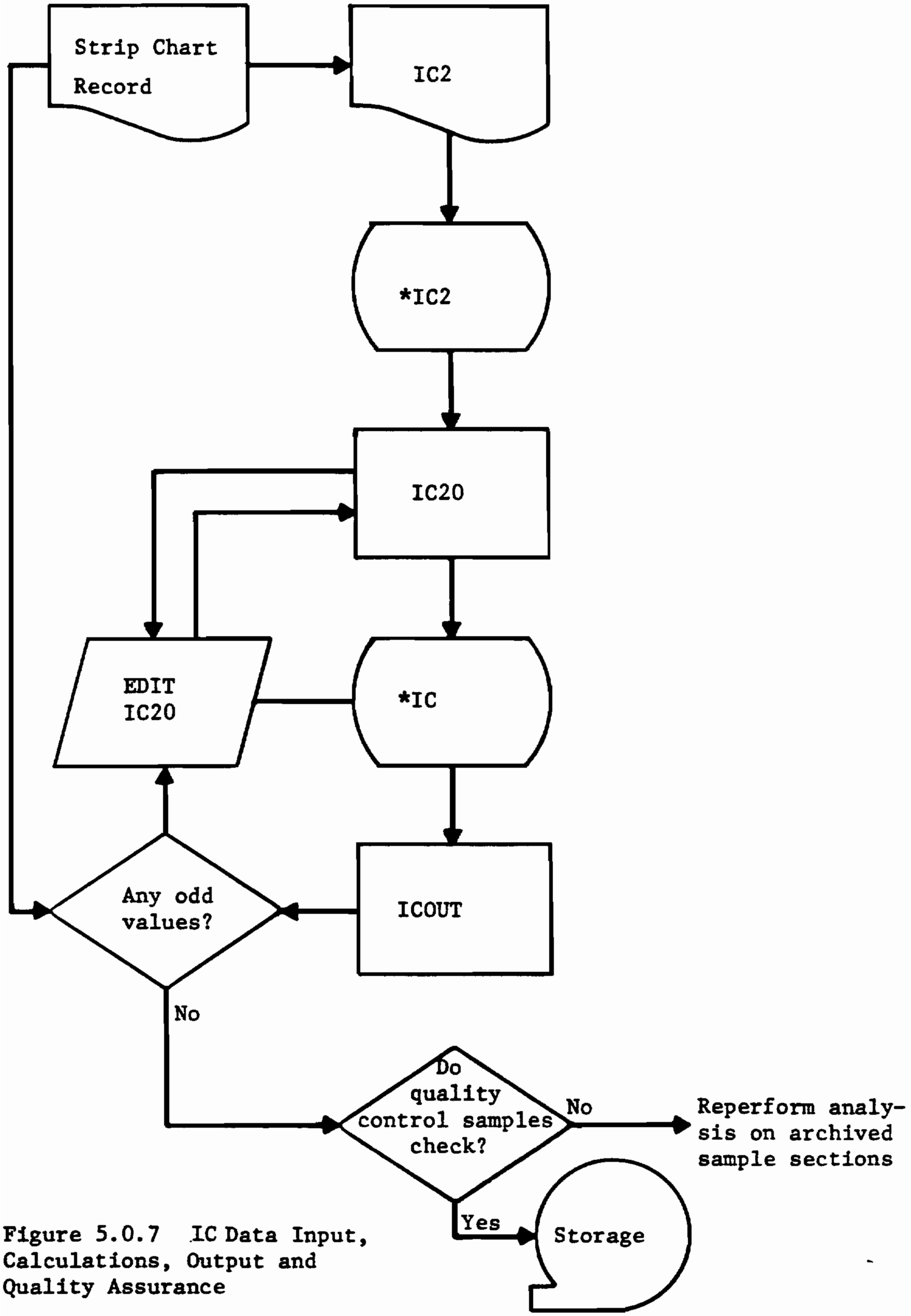


Figure 5.0.7 IC Data Input, Calculations, Output and Quality Assurance

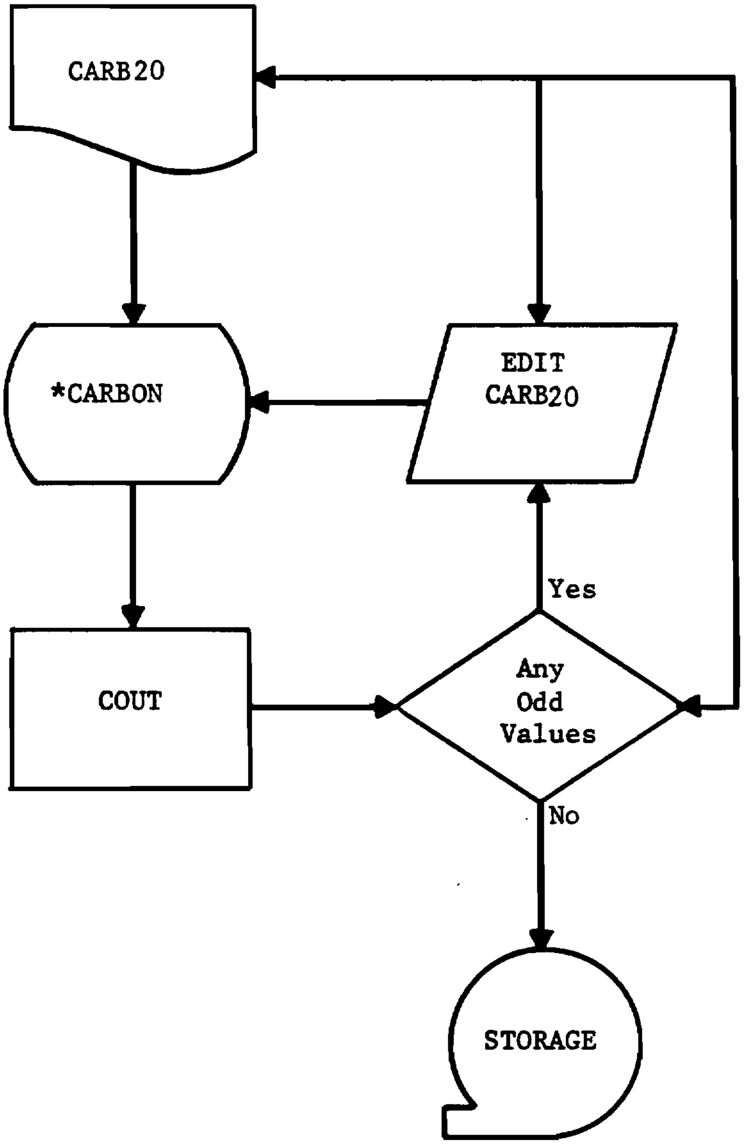


Figure 5.0.8 Carbon Data Input, Calculations, Output and Quality Assurance

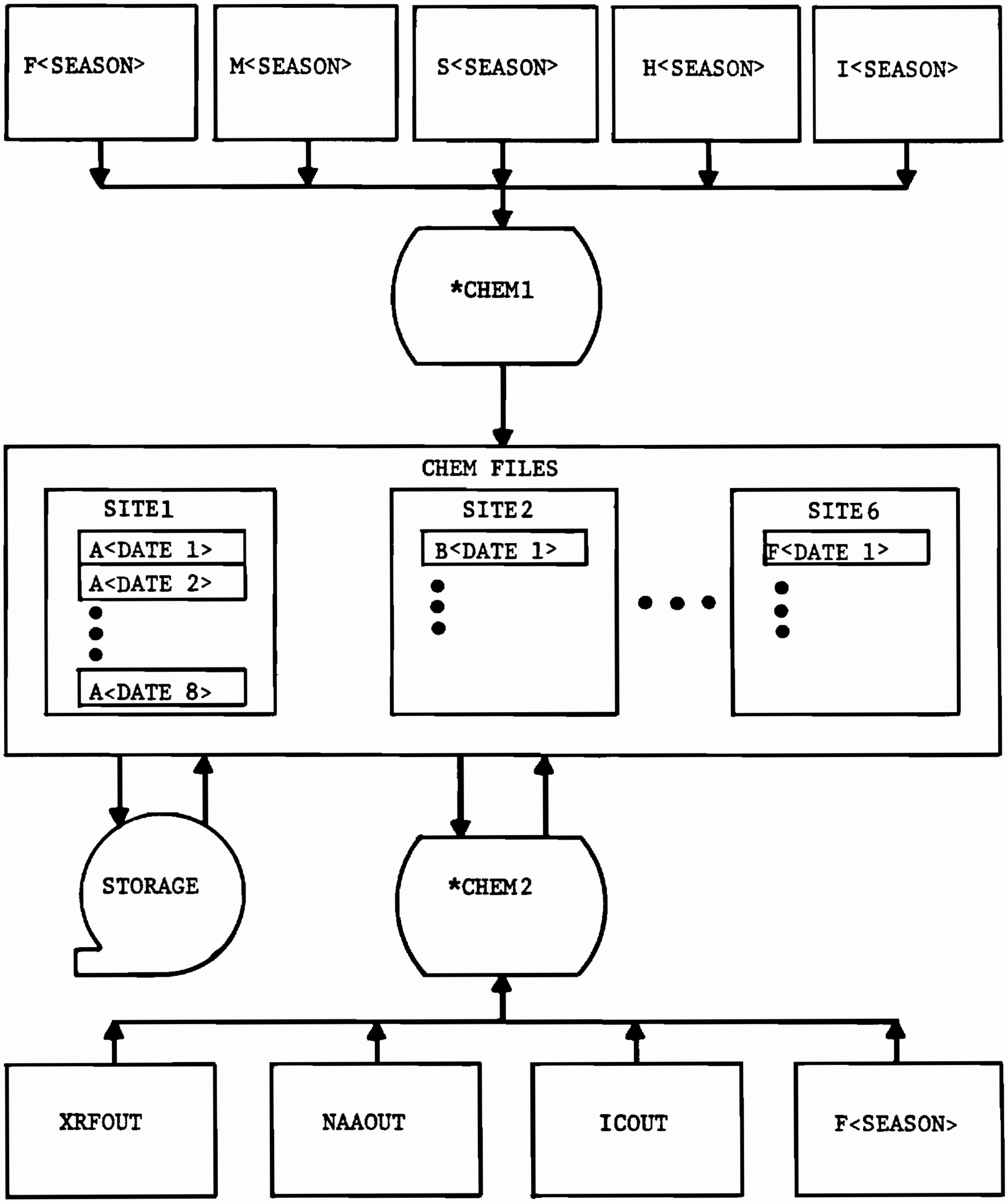


Figure 5.0.9 Chemical Analyses, Mass and Field Data Merging for Selected Days

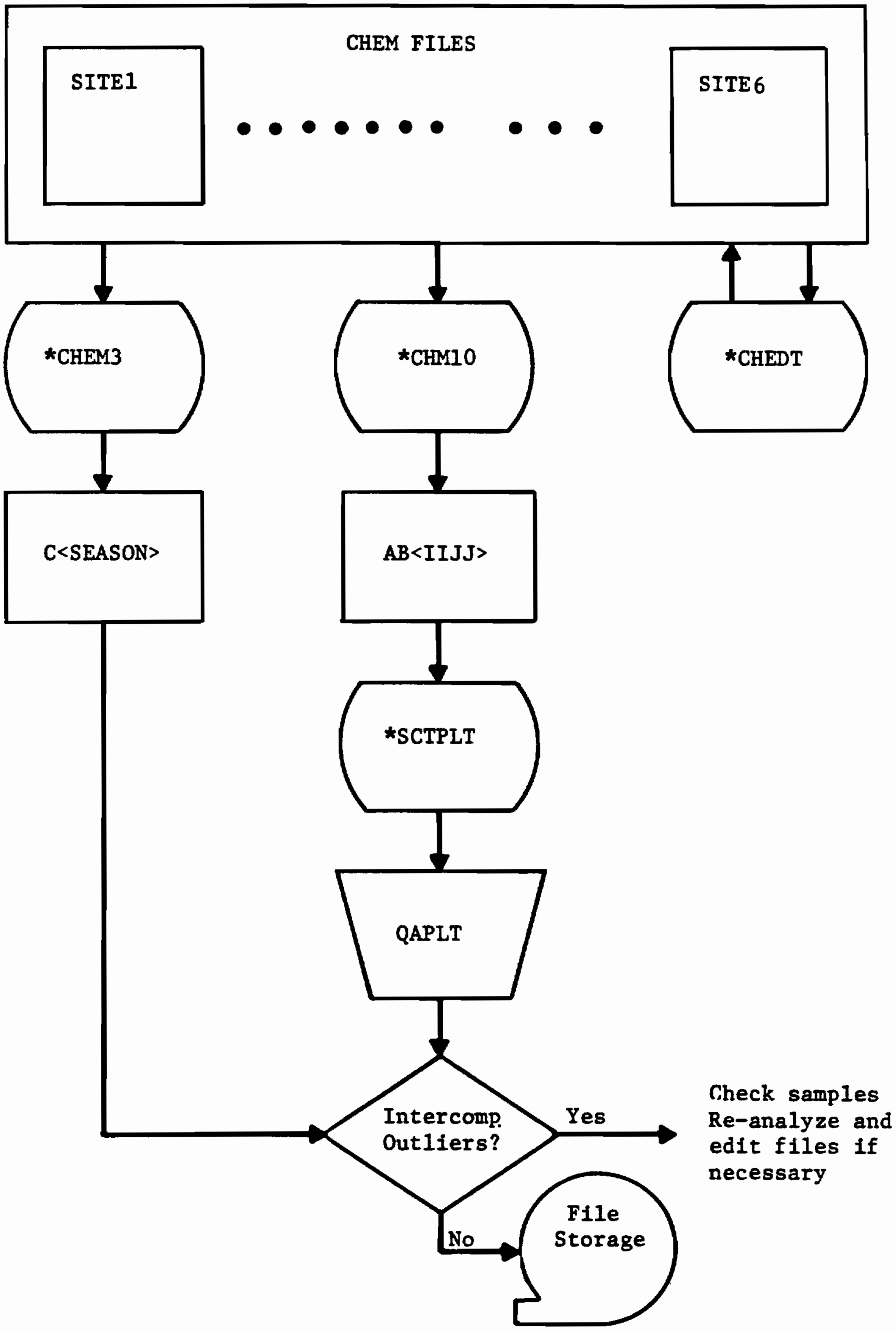


Figure 5.0.10 Chemical Analysis Data Output and Inter Method Quality Assurance

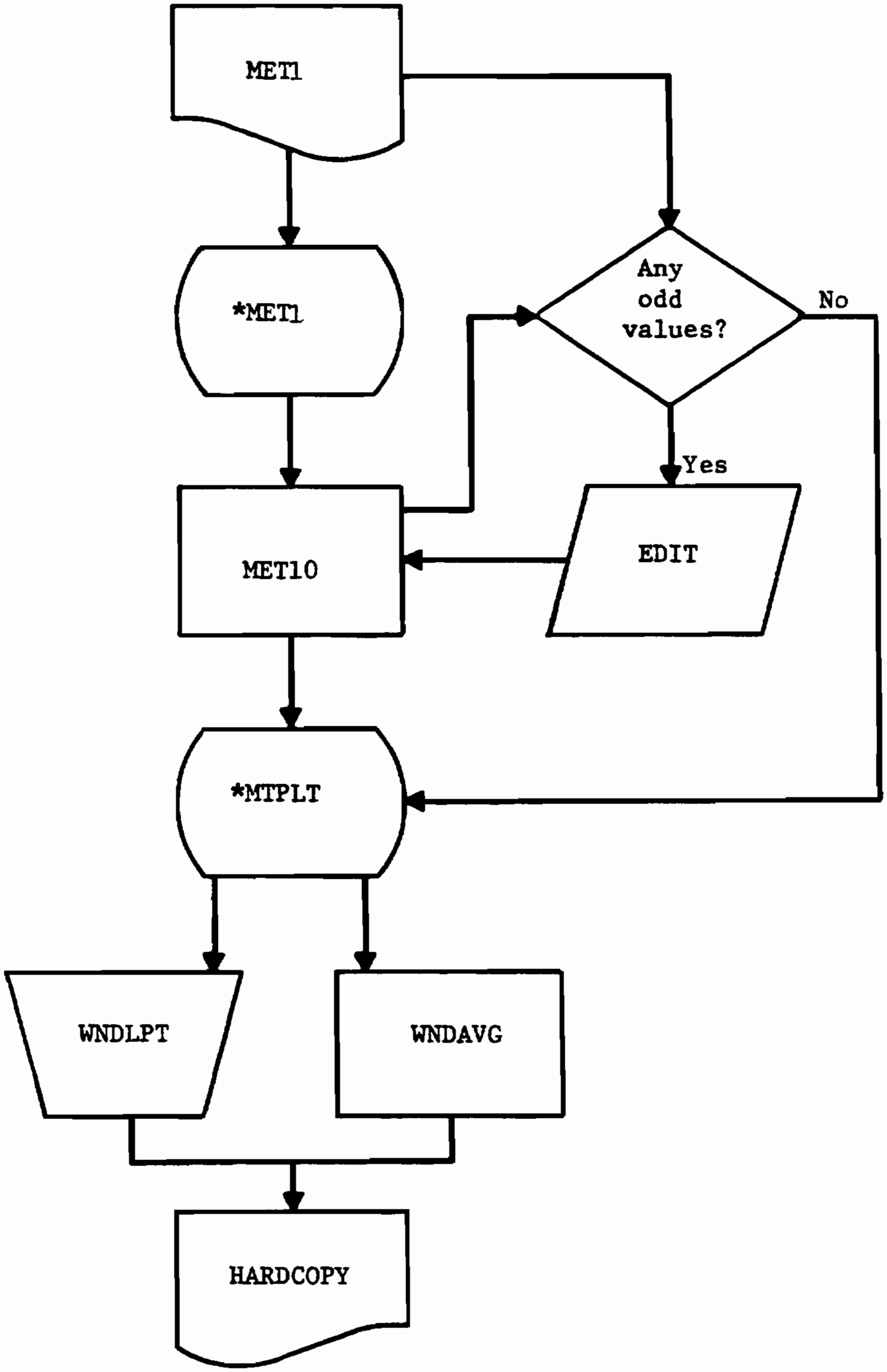
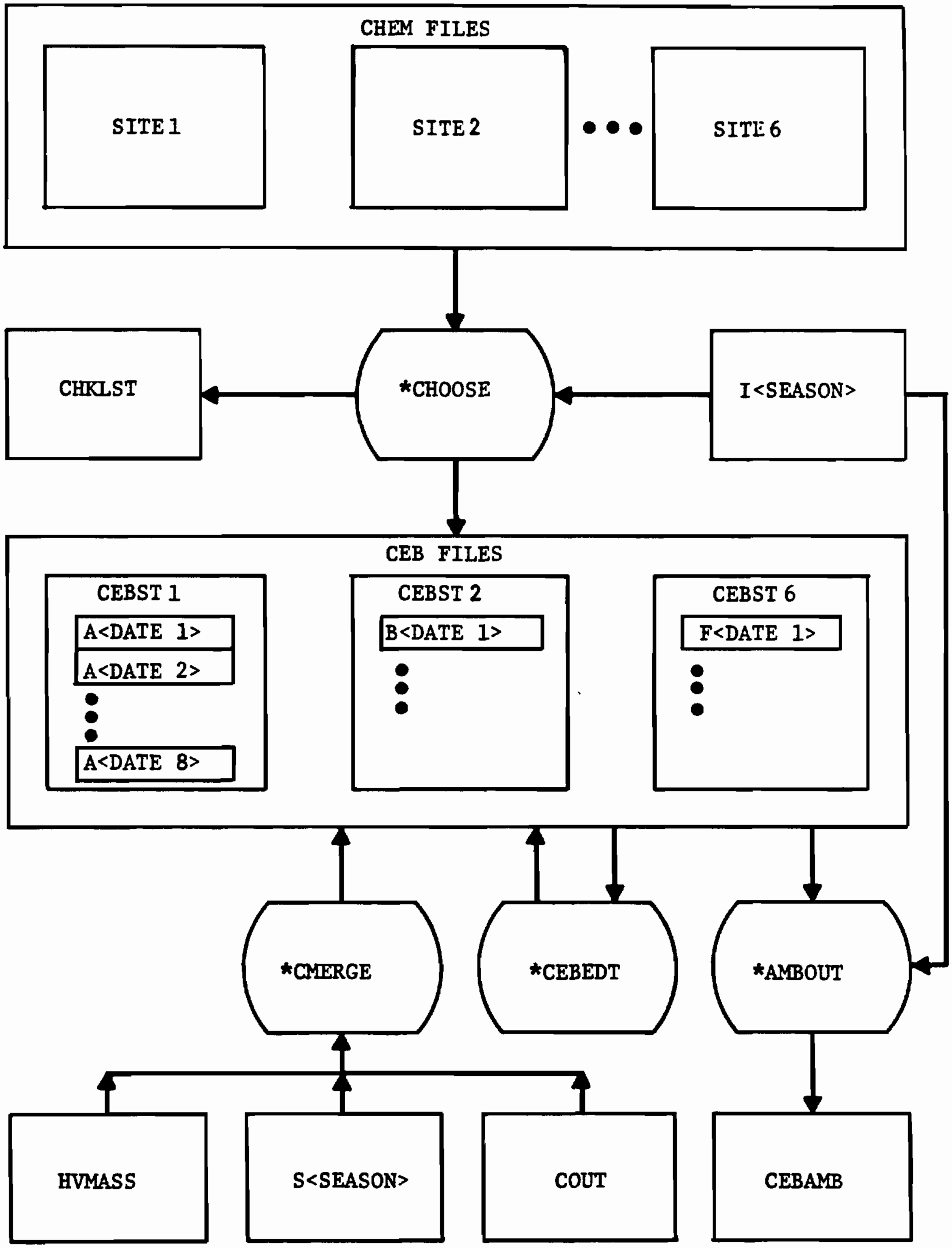


Figure 5.0.11 Surface Wind Data Input, Calculations, Quality Assurance and Output



5.0.12 Final Chemical Analysis Data Selection, Merging, Quality Assurance and Output

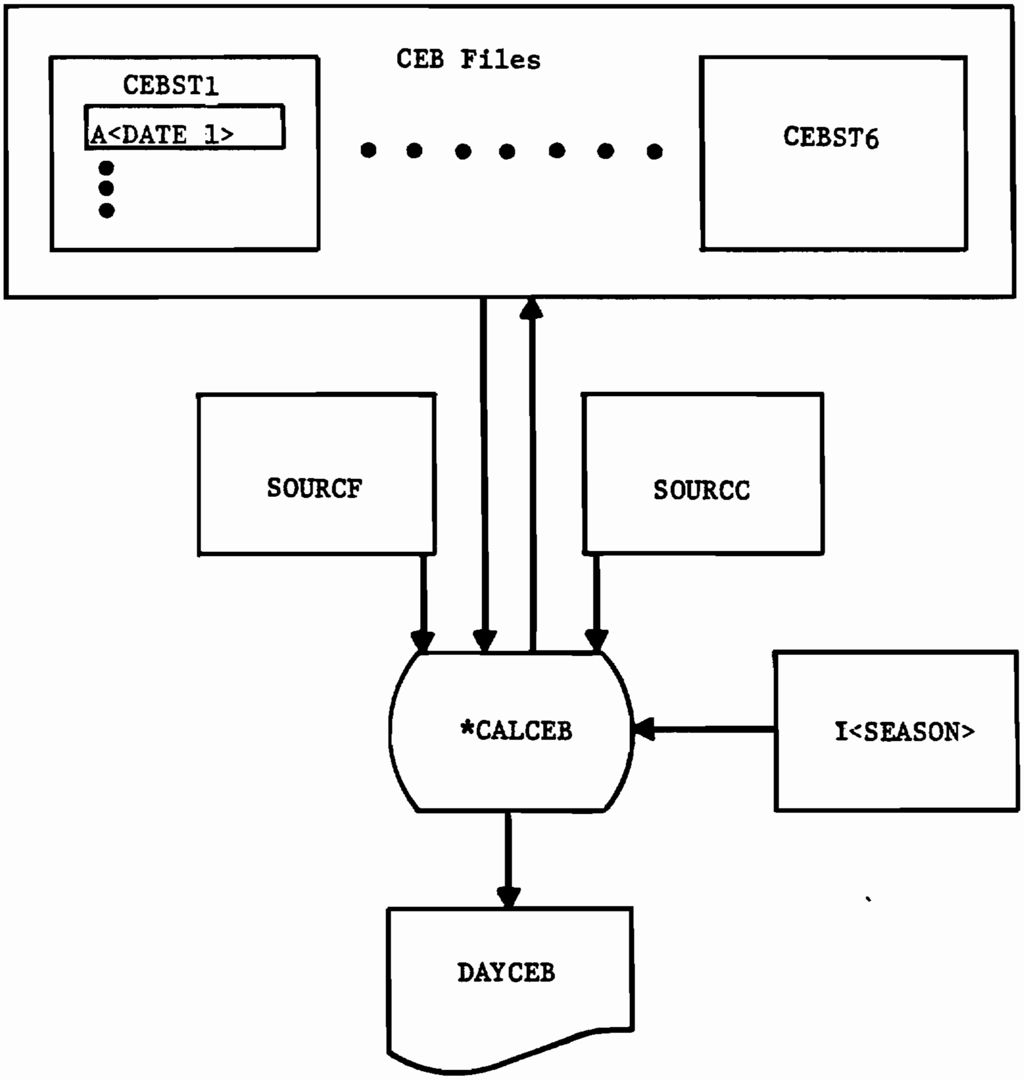


Figure 5.0.13 Daily Chemical Element Balance Calculations and Output

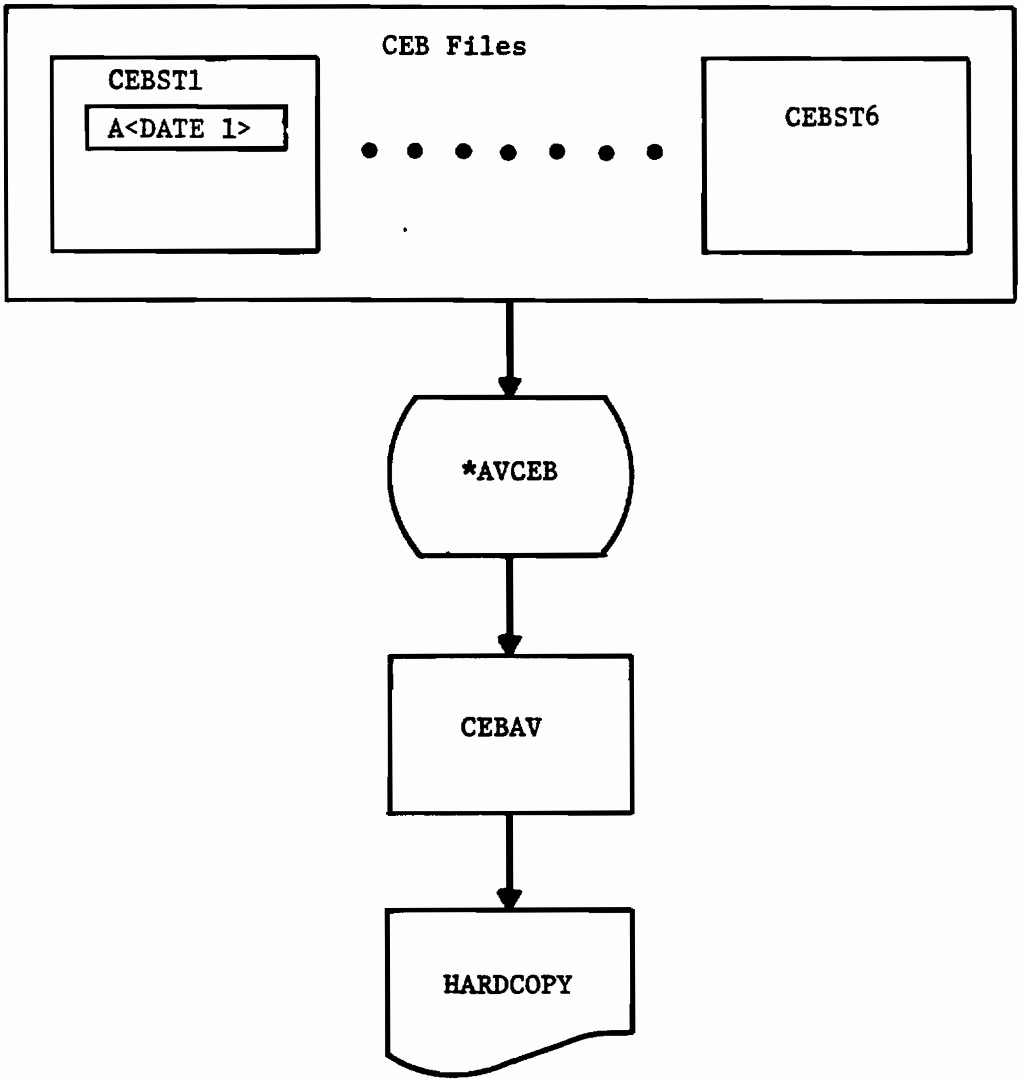


Figure 5.0.14 Calculation of Source Impact Averages

Table 5.0.1 Data Recording and Input Files

Source of Data	Data Sheet	Computer Data File	Data Items
SOP 2. Lo-vol Filter Weighing	MASS1	M<SEASON>[a]	Specimen ID, Pre and post exposure values for: Calibration check, Relative Humidity, Filter weights, Flags, Net mass calculated by MSS in computer file.
SOP 5. XRF Analysis	XRF1	O<Run Time>[b]	Specimen IDs
SOP 7. INAA Analysis	INAA1	INAA10	Cu. flux monitor IDs and Weights
	INAA2	INAA20	IDs & Weights of standards
	INAA3	INAA30	Specimen ID, Flux monitor ID, Reactor out time, Cu count & time.
		INAA35	Same as above for calibration standards.
	INAA4	INAA40	Specimen ID, count start and stop times, Region of interest integrals
	(Paper tape)	INAA45	Same as above for calibration standards.
	INAA5	INAA50	Shelf Normalization Factors
	INAA6	INAA60	Fractional element composition of standards
SOP 8. IC Analysis	IC2	IC20	Specimen ID, Scale, Response
SOP 9. Lo-vol Field Sampling	FIELD1	F<SEASON>[a]	Specimen ID, Sampling Site, & date, Sequence, Flows Before & After Exposure, Flags, Volume sampled in F <SEASON>, Calculated by *FIELD

Table 5.0.1 Data Recording and Input Files (continued)

SOP 10.	Hi-vol Fine (Sierra) Filter Weighing	SIERA1	S<SEASON>[a]	Specimen ID, Wt. before and after exposure, sampling site, date, and duration, Flows before and after exposure, Flags, Net wts. and volume sampled in S<SEASON> calculated by *DSIERA
SOP 11.	Sierra Field sampling			
SOP 12.	CARBON ANALYSIS	CARB2	CARB20	Specimen ID, integrated peak areas for volatile & nonvolatile carbon. Integrated peak areas for corresponding calibration standards. Size of sample analyzed
	HIVOL TOTAL MASS (DEQ)	HIVOL1	H<SEASON>[a] HMASS	TSP concentration and volume sampled, site, date, ID
	SELECTED INTENSIVE ANALYSIS DAYS (DEQ)	INDAY1	I<SEASON>[a]	Dates of sampled days designated for intensive chemical analysis. Regime & flow pattern classifications.
	SURFACE WIND DATA (DEQ)	MET1	MET10	Hourly wind speed and direction, site, date.
	SOURCE COMPOSITION DATA	SOURCF	SOURCF	Fractional fine particle element compositions of sources
		SOURCC	SOURCC	Fractional coarse particle element compositions of sources

[a] <Season> is either Summer, Autumn, Winter or Spring

[b] <Run Time> is MDDHH = Month, Day, Hour of analysis start

Table 5.0.2 OUTPUT FILES

Filename	Purpose	Data Items
CHKFLD	Hardcopy format of ambient field data	Same as F<SEASON>
CHKMSS	Hardcopy format of ambient lo-vol mass data	Same as M<SEASON>
CHKSRA	Hardcopy format of ambient hi-vol fine fraction mass and field data	Same as S<SEASON>
<SEASON> 1	Hardcopy format of suspended particulate data	Lo-vol ID, mass, volume, and flags concentration. Daily averages of lo-vol data. Hi-vol fine fraction mass, volume, concentration and flags. Hi-vol total fraction concentration and flag. All for each site and data.
<SEASON> 2	Same as above-abbreviated version	Same as <SEASON> 1 excluding mass and volume data.
<SEASON> 3	Lovol daily averages by date and site.	Lo-vol daily averages, hi-vol fine fraction, hi-vol total fraction, % of each to hi-vol total fraction.
<SEASON> 4	Area averages by sampling method and date	Area (city site or rural site) averages by date of lo-vol fine, lo-val total, hi-vol fine, hi-vol total, and percentage of each to hi-vol total.
<SEASON> 5	Season average by site	Season average of lo-vol fine, total, hi-vol fine, total, and % of each to hi-vol total by site.
STDMSS	INAA Std. QC	Elemental masses of stds.

Table 5.0.2 OUTPUT FILES
(Cont.)

Filename	Purpose	Data Items
NAAOUT	Elemental concentrations in samples	ID; mass, net counts for each element
ICOUT	Ion concentrations	ID, concentrations, scale, response.
XRFOUT	Elemental concentrations	ID, concentrations, std., counts, net counts.
COUT	Carbon concentrations	Same as CARB20 plus volatile and elemental carbon conc.
SITE 1>A<DATE 1> <DATE 8> SITE 2>B<DATE 1> SITE 6>F<DATE 1>	Contains all chemical, mass, and volume data for that site and date written in binary format	Date, ID, mass, volume, flags, elemental values.
C<SEASON>	Hardcopy format of SITE files	Same as SITE files
AB IIJJ	Intermethod QA	II, JJ data pairs of intermethod comparison, for specified days, fine fraction, total, or both
CEBST1<A(DATE) CEBST2<B(DATE) CEBST6<F(DATE)	CEB FILES Contain "best" chemical data and source contributions, met. regime	Elemental concentration, source contributions, met. flow regime, ID, data, mass, volume, flags
CEBAMB	Hardcopy format of CEBST (DATE) files	Same as CEBST (DATE) files
CHKLST	Contains elements flagged during execution of *CHOOS	ID, Flag, elemental concentrations
WNDAVG	8 hour vector average wind vectors at each station and Persistance factor	Date, Site, Direction, Speed, Persistance factor

Table 5.0.2 OUTPUT FILES
(Cont.)

Filename	Purpose	Data Items
DAYCEB	Individual Element Balance Results	Individual filter Elemental concentrations, Source contributions
CEBAV	Averaged Element Balance Results	Seasonal and yearly averages
QAPLT	Scatter plot of intermethod comparison values.	
WNDPLT	Vector plot of 8 hour average wind vectors	

Table 5.0.3 PACS Computer Programs

Program Name	Major Tasks Performed	Description
*FIELD	INPUT CALCULATION	Creates input data file F<SEASON> from user input of lo-vol field data. Calculates volume of air sampled based on calibration constants from each sampler contained in program.
*FHDCY	QUALITY ASSURANCE	Creates formatted output of lo-vol field data for check against data sheet.
*MSS	INPUT CALCULATION	Creates input data file M<SEASON> from user input of lo-vol mass data and calculates net masses on filters.
*MHDCY	QUALITY ASSURANCE	Creates formatted output of lo-vol mass data for check against data sheet.
*DSIERA	INPUT	Creates input data file S<SEASON> from user input of sierra data sheet.
*SHDCY	QUALITY ASSURANCE	Creates formatted output of sierra data for check against data sheet.
*SUSOL	MERGE CALCULATION OUTPUT	Merges mass and volume data, calculates mass concentrations and prints them.
*XRF	CALCULATION	Calculates $\mu g/cm^3$ of elements on air filters.
*XROUT	OUTPUT	Reads mass concentrations from floppy disk and punches them onto paper tape.
*INAA1	INPUT	Transfers flux monitor data to disk file.
*INAA3	INPUT	Transfers rabbit room and flux monitor data to disk file.

Table 5.0.3 (Continued)

Program Name	Major Tasks Performed	Description
*INAA2	QUALITY ASSURANCE	Calculates and outputs known masses of elements in INAA quality assurance standards.
*INAA	MERGE CALCULATION OUTPUT	Retrieves all necessary information on a sample from disk files, calculates elemental concentration and outputs it in standard format.
*IC2	INPUT	Transfers ion chromatography data to disk file.
*IC	CALCULATION OUTPUT	Calculates masses of anions on air filters. Calibration constants are contained in program.
*CARBON	CALCULATION OUTPUT	Calculates masses of volatile and non volatile carbon.
*CHEM1	MERGE	Merges mass and field data for intensive analysis days and creates file locations for elemental data.
*CHEM2	MERGE	Places elemental concentrations in proper file locations. Normalizes measured values to total area of filter.
*CHEM3	OUTPUT	Produces hardcopy of elemental concentrations.
*CHEDT	QUALITY ASSURANCE	Edits values in intensive analysis files.
*CHM10	QUALITY ASSURANCE	Creates (X,Y) data pairs for inter-method comparisons.
*SCTPLT	QUALITY ASSURANCE	Plots scatter plot of inter-method comparison on terminal graphics.

Table 5.0.3 (Continued)

Program Name	Major Tasks Performed	Description
MET1	INPUT	Transfer meteorological data to disk file.
*METPLT	CALCULATION OUTPUT	Calculate vector averages and stability and plot spatial wind vector display.
*CHOOSE	OUTPUT QUALITY ASSURANCE	Obtains best value for each elemental determination and locates it in its proper position in the chemical element balance files.
*CMERGE	MERGE	Merges carbon data into CEB files.
*CEBEDT	QUALITY ASSURANCE	Editing of CEB files.
*AMBOUT	OUTPUT	Print hardcopy output of best values from chemical analysis.
*CALCEB	CALCULATION	Calculatessource contributions.
*AVCEB	CALCULATION	Calculatesseasonal and annual flow pattern and regime averages of elemental concentrations and source impacts for each site.

5. Quality Assurance: (a) Data item values in computer files and those recorded during the corresponding standard operation are compared and corrections to computer files are made when disagreement is found. (b) Known values for quality assurance standards are compared with those yielded by a standard operating procedure and causes for disagreement are sought. In the event that corrections cannot be made specimens are designated for re-analysis. (c) Replicate measurements of the same parameter are compared and the best value is obtained. (d) Non-standard operating procedures are flagged.

6. Output: Information is arranged into a desired format for input to another task or as a final result.

Table 5.0.3 lists the major tasks performed by each program.

A close study of the tables and figures in this section will explain the relationship of each standard operating procedure and calculation to the overall data management system. A brief discussion of each task as applied to the PACS follows.

5.1 RECORDING

Each standard operating procedure producing measurements was accompanied by one or more data coding sheets on which the relevant information was recorded and associated with a specimen identification code (See Table 5.0.1). The format was exactly that in which it would be entered into the computer file.

The exact reading from the measurement was recorded and, in most cases, no calculations were made to prevent non-traceable arithmetic mistakes. All necessary mathematical operations were performed by computer programs after data input. A comments column allowed the technician to note any non-standard procedures.

With over 2000 filters and many operations on each involved it was essential to keep track of the history of each one. Since all samples went through the same operations it was sufficient to create a logbook in which each ID code was recorded in one column. Adjacent columns were headed with the appropriate SOP titles and contained the date on which that event took place for the filter ID on the same line. Non-standard procedures were also indicated in the column.

5.2 INPUT

A Beehive CRT terminal interfaced to the PRIME was used for keying data into computer disk files. The standard keyboard was augmented by an adding machine keyboard which was more convenient for purely numerical punching. Most data were entered via input programming which prompted the user to input the correct parameter from the appropriate data sheet, checked it for proper format, checked to see if it was within reasonable bounds, and displayed the values entered for the user to check against the data sheet. The user could then choose to enter the values into the file or to correct individual data items in the field. If values were rejected by the format check or data filter the program was automatically routed to a message requesting correction.

The use of a time sharing system and input programming for the entry of handwritten data to a disk file offered several advantages over keypunching IBM cards.

Common mistakes such as typing a lower case L in place of a 1 or misplacing decimal points were caught by the format check and data filters. If a mistake was made in one entry and the operator realized it he could use the rubout feature of the computer to erase, then re-enter it. Any mistake on an IBM card could only be corrected by repunching the entire card. Data was written directly onto disk and no cumbersome cards could be mixed up, lost, or mutilated. Finally, when consecutive data items were numbered consecutively, such as the ID codes in a weigh set, the program supplied these values and the user wasn't required to key them in. These features added up to savings in time, an increase in accuracy and the possibility of employing less trained personnel than that required by traditional keypunching.

Paper tape from the neutron activation analysis and x-ray fluorescence was read directly into input disk files by existing PRIME software.

5.3 CALCULATIONS

Programs involving calculations are listed in Table 5.8.3. The equations involved are presented in sections 4.6, 4.7.2, 4.7.3, 4.7.6, 4.7.8, 4.7.9, 4.7.10 and 3.2 for *MTPLT, *MSS, *FIELD, *XRF, *INAA, *IC, *CARBON, and *CALCEB respectively. All calculations were performed in single precision floating point mode with the exception of those in *CALCEB where double precision mode was used in conjunction with PRIME's mathematical subroutine library because the matrix operations, particularly matrix inversions, were susceptible to round-off error.

The flow diagrams illustrate that merging and output were also major functions of these programs. In fact, though the calculation usually required but a few lines, these routines consisted of over one hundred lines apiece to accommodate the tasks of getting all values necessary for the calculation together and writing the results into a useful format.

5.4 MERGING

The routines involving substantial merging were *SUSOL, *INAA, *CHEM1, and *CHEM2.

Merging was always keyed to specimen ID or a sampling site and date which was supplied by the first file accessed. Subsequent files were then searched sequentially until the key was found. Then the necessary data item values associated with it were retrieved. The samples were arranged in quasi-chronological order (in the approximate temporal order in which they were used for sampling) so the searching algorithm on long files would read forty lines from its present position. If the ID wasn't encountered within this interval, the record pointer was set to the top of the file and a search of the entire file was made (PRIME software did not support backspacing of the pointer without repositioning at the top of the file). If the key was not encountered, the operator was notified at the user terminal and the merge program skipped to the next key. The user recorded all terminal messages in a Data Management notebook, the missing datum was found after the merge was completed and included in a subsequent merge.

The biggest merge in the PACS system was that of uniting the measurements for each sampling site and day. I<SEASON> contained the seasonal intensive chemical analysis days which were associated with fine and total lo-vol filter IDs in F<SEASON>. Hi-vol total and fine filter data were retrieved from H<SEASON> and S<SEASON> respectively.

The CHEM FILES consisted of a set of separate files for each sampling site and date. The file name was a combination of an alphabetic site code and a numeric date code. Files for each site were grouped together in a sub-directory, compatible with PRIME file system software.

Each CHEM FILE consisted of an alphanumeric header record containing all the filter IDs and data flags for the sampling day and site. The sampling sequence and the total or fine designation was implicit in the order.

All measured values and their uncertainties for the sampling date and site were located in a binary array with the specific data item value corresponding to a specific array position. This large array was broken up into smaller arrays containing values for all measurements on a given filter by an EQUIVALENCE statement in each program accessing the array. A subroutine INOUT read or wrote the array when given a specific site and date.

*CHEM1 inserted IDs, masses and volumes sampled into the CHEM FILES. All empty array positions were filled with -1.

*CHEM2 read a filter ID from the chemical analysis output files, found the date and site associated with this ID in the F<SEASON>

file and called up the array from the CHEM FILES for this site and date. The appropriate array locations were filled with data item values from the output file.

After merging the files were printed by *CHEM3. Any remaining -1s indicated missing data which were tracked down and merged. Values from samples that were reanalyzed replaced the previous values in the array.

5.5 QUALITY ASSURANCE

The four quality assurance tasks outlined above were implemented as follows:

a. Even with the extensive screening provided by input programming, errors occurred in the input files. Therefore, the contents of each file were compared number by number with the original output from the measuring device. In the case of ion chromatography and carbon analysis, the original strip charts were reassessed against the values in the computer file. Others were compared to the numbers recorded on the original data sheets. Mistakes were corrected in the computer file using PRIME's text editor.

b. Analysis values for quality assurance standards which were interspersed with the unknown filter samples in the XRFOUT, NAAOUT, and ICOUT files were compared with their known values. Each carbon measurement was associated with a unique calibration so such comparisons for those measurements were unnecessary. Quality Assurance standard comparisons with disagreements greater than the tolerances specified in the standard operating procedures (section 4.7)

Table 5.5.1 Criteria for Choosing Best Values for Elemental Concentrations

Species	Measurement		Final Value Selection
Al	XR2	1.	Average* XF2 and NAA, if $\lvert XF2-NAA \rvert \le 0.4$ (NAA)
	NAA	2.	Otherwise use NAA.
As	XF1		Use XF1
	XF3		
Ba	XF1		Use XF1
Br	XF1	1.	Average XF1 and NAA, if $\lvert XF1-NAA \rvert \le 0.2(XF1+NAA)$
	XF3	2.	Otherwise use NAA
	AIC		
	NAA		
Ca	XF2	1.	Average XF2 and XF3 if $\lvert XF2-XF3 \rvert \le 0.2(XF2+XF3)$
	XF3	2.	Otherwise use XF3
Cd	XF1		XF1
Cl	XF3	1.	Average AlC and NAA if $\lvert AlC-NAA \rvert \le 0.2(AlC+NAA)$
	AIC	2.	Otherwise use NAA
	NAA		
Cr	XF3		XF3
Cu	XF1		XF1
Fe	XF1	1.	Average XF1 and XF3 if $\lvert XF1-XF3 \rvert \le 0.2(XF1+XF3)$
	XF2	2.	Otherwise use method with best MDC
	XF3		
F^-	AIC		AIC
K	XF2		Same as Ca
	XF3		
	NAA		
Mg	NAA		Use NAA (Second value)
	NAA		
Mn	XF3	1.	Average XF3 and NAA if $\lvert XF3-NAA \rvert < 0.2(XF3+NAA)$
	NAA	2.	Otherwise use method with lowest uncertainty.
Na			NAA
	NAA		
Ni	XF1		XF1
NO_3^-	AIC		AIC
Pb	XF1		XF1
	XF3		
S	XF2		XF3
	XF3		
Se	XF1		XF1
Si	XF2		XF2
$SO_4^=$	AIC		AIC
Ti	XF3		Same as Mn
	NAA		
V	XF3		Same as Mn
	NAA		
Zn	XF1		XF1

*Average is used to mean weighted average in this table.

Table 5.5.2 Data Flags

Flags (field and mass data)

B	Blank Sample
T	Sampling time error > 10% nominal sample time
X	No sample
S	Skipped sample
N	Negative net weight
V	Volume estimated
R	Filter ripped
D	Sample dropped
A	Air leak between gasket and sample
W	Sample got wet during exposure
L	Sierra Filter returned from field not folded
G	See logistics data book
M	See mass data sheet
F	See field data sheet
P	Sauvie's Island sample taken at PGE trailer site
*	One or more data points missing from average

Flags (elemental data)

*	Value of As, Ba, Cd, Se above MDC	
M	One comparison method has no data	
>	$\lvert A-B \rvert > 0.2(A+B)$	(For Al, $\lvert XF2-NAA \rvert > 0.4(NAA)$)
>>	$\lvert A-B \rvert > 0.4(A+B)$	$\lvert XF2-NAA \rvert > 0.8(NAA)$
>!	$\lvert A-B \rvert \approx 1.\ (A+B)$	$\lvert XF2-NAA \rvert > 2.\ (NAA)$
!!		$\lvert XF2-NAA \rvert > 4.\ (NAA)$

were investigated. If a cause could not be determined, all specimens between the previous and the next QA standard were submitted for reanalysis. The new values replaced the old values when they became available.

c. The computer program *CHOOSE selected the best, single values for chemical constituent concentrations on which more than one measurement was made. Table 5.5.1 lists the replicate measurements available and the method by which the best value was obtained. When agreement of separate measurements was good (within experimental error), the average was normally taken. If the agreement was not good, the cause was usually due to the proximity to the minimum detectable concentrations (MDC) of one of the analysis methods, and the technique having the lower MDC was preferred.

d. Non-standard operating procedures were recorded in the form of flags listed in Table 5.5.2. Individual chemical constituent flags resulting from disagreements between methods of analysis in quantifying the same species were assigned by *CHOOSE and are also listed. Any anomolies in data interpretation may be cleared up by a measurement impact assessment of the non-standard procedure.

5.6 OUTPUT

Hardcopy output was produced at many stages to inspect and report the results. Formats most appropriate for the task at hand were chosen. Many of the output files also served as input files for other tasks.

The essentials of the PACS data management system have been presented in this chapter. A detailed working knowledge must be gleaned from the source listings of the computer programs and files and has not been attempted here. The purpose has been to demonstrate that the system promoted and maintained the integrity of the data and to report the location and manipulation of specific data items for future reference.

CHAPTER SIX: APPLYING THE CHEMICAL ELEMENT BALANCE

With a refined and better understood chemical element balance receptor model, a representative sample of source chemical compositions, and ambient concentrations it is now possible to devise a receptor model methodology to estimate source contribution magnitudes and to relate them to violations of the ambient standards.

In the first section of this chapter, the stratified and unstratified averages of ambient chemical compositions at selected receptors will be presented and discussed qualitatively to gain an overall view of the Portland aerosol makeup, the accuracy and precision of the measurements and to draw some conclusions concerning which source types might be expected based on the measurements.

In the second section, the chemical element balance receptor model as applied to the PACS data will be presented. The suggestions of section 3.3.3 will be examined and refined within the context of real, rather than simulated, data and a methodology for application to each specimen will be developed and illustrated.

Finally, in section 6.3, annual source contribution averages will be examined to identify sources affecting violation of the ambient standard. The use of PACS data summaries, source summaries, and averages to confirm source impacts will be demonstrated.

It should be emphasized once again that this work is a study of methodology, not of the Portland Aerosol. Conclusions concerning major contributors are drawn for illustrative or exploratory purposes only and neither the entirety of the PACS results (over 1700 individual chemical element balances, over 1600 sets of flow pattern averages, and over 1400 sets of regime and regime stratified averages) nor all of the conclusions to be drawn from them will be presented here.

This chapter will report how those results were achieved, point out the important things to look for and express the author's reservations about them. Those to whom the task of interpretation will fall, the planners desiring to propose an optimal control strategy for Portland, the dispersion modelers who need to calibrate their systems under certain surface flow conditions, and the future receptor modelers who will improve this methodology further, should use this chapter as a reference to understand the PACS data rather than as the final word on it.

6.1 CHEMICAL COMPOSITION OF THE PORTLAND AEROSOL

Chemical analyses for 27 species were performed on over 1300 individual filter samples of the Portland aerosol. Averages and standard deviations of concentrations within each meteorological regime, flow pattern, season, size range and site were calculated. This section explains the formats in which the averages were recorded, evaluates the precision of the measurements, presents annual 24 hour averages for fine and total particulate at each of the sites and examines them for patterns and possible source contributions.

The most useful statistics are the annual 24 hour means for fine and total suspended particulate which are presented for each PACS site in Tables 6.1.1a&b - 6.1.6a&b. There is evidence (Donagi, et al., 1979) that the distribution of aerosol chemical concentrations is more closely approximated by a log-normal distribution than by a Gaussian distribution, similar to the distribution of the total suspended particulate. The Oregon Department of Environmental Quality calculates arithmetic averages from runs of its dispersion model, so this statistic was also calculated. The tables show that the difference between the two means is not great.

As pointed out in section 2.4, the fractional concentration can express information less influenced by atmospheric dispersion, so the geometric and arithmetic means of the percent concentrations were also calculated. Obviously, the distribution of this observable can be neither strictly log-normal nor strictly Gaussian because the range of values is limited to the interval 0-100; a truncated distribution would be required. In the absence of a careful examination of appropriate distributions and their parameters, the geometric and arithmetic means of the percents were calculated.

Many concentration measurements below minimum detectable concentrations (MDC) pose a problem in calculating means. Setting all such values equal to zero will bias the mean low and the standard deviation high because actual concentrations greater than zero, but still less than the detection limit, do exist. When calculating a geometric mean, this alternative is inapplicable because the logarithm of zero is undefined. On the other hand, setting all undetectable concentration values equal to the minimum detectable limit, or deleting them entirely, will bias the mean higher and the standard deviation lower than they actually are.

King, et al. (1976) calculated geometric means of 762 measurements of Sb and Si in Cleveland, Ohio, systematically eliminating the lowest 20 values each time a new mean was calculated. Each of these means obtained from a truncated data set was compared to the true mean as estimated from the entire data set. The mean Si concentration increased by 50% when 38% of the lowest values had been deleted. The Sb mean concentration increased by 50% when only the lowest 15% of the measurements had been eliminated. King, et al. found that the amount of truncation possible to maintain a constant percentage increase of the calculated mean depends heavily on the variability of the data. Silicon concentration measurements showed low variability and the degree of truncation possible to limit the bias to 50% was over twice that of the Sb measurement, which showed high variability.

Kushner (1976) has explored the problem in great detail. He observes that the distribution of values below the minimum detectable concentration is unknown. Nehls and Akland (1973) advocate approximating values below the detection limit by one half the value of the minimum detectable concentration. This would be the best estimate if all values in the 0-MDC range were uniformly distributed. Kushner demonstrates the extent to which this is a good approximation when in actuality the values below the detection limit follow the same log-normal distribution as those above the detection limit. With 50% of the observables in a data set so approximated, calculated geometric means equal 75%, 89%, 96%, 107%, and 119% of the true means (assuming all values follow the log-normal distribution) for geometric standard deviations of 1.28, 1.65, 2.12, 2.72, and 3.49, respectively.

The one half MDC approximation seems to be the best estimate of the undetectable values for inclusion in the means, and these means can probably be considered representative even though as many as one half of the measurements are below minimum detectable concentrations. When the data set is truncated by more than 50%, however, the calculated means should be viewed with caution.

Geometric and arithmetic means of both absolute and percentage concentrations and the corresponding standard deviations were calculated in this manner for Tables 6.1.1a&b-6.1.6a&b. The # IN AVG column records how many specimens were included in the average; this can be less than 32 because of lost data. The # GT MDC column contains the number of measurements which were above minimum detectable concentrations, and when this number is less than one half of the number in the previous column, the mean is more representative of the average detection limit than of the average concentration in the air. The final two columns list the arithmetic average absolute and percentage uncertainties of concentrations above the minimum detectable limits.

A similar format appears in Table 6.1.4d which represents the concentration flow pattern average presentation. Whereas the unstratified annual averages in Tables 6.1.1a&b-6.1.6a&b are functions of the 24 hour average measurements, the means in Table 6.1.4d result from sums of individual sequential samples grouped into one of the surface windflow patterns of Table 3.4.1 by the classification in Table 3.4.3. The format is exactly the same as that of Tables 6.6.1a&b-6.1.6a&b.

Regime stratified means of 24 hour average concentrations were calculated after the formulation of eqs. 4.2.3 and 4.2.4. They are recorded in the format of Table 6.1.4c. The standard errors here are not those of the data set but of the mean itself. The corresponding standard errors for the unstratified means are approximated by dividing their standard deviations (or the logarithms of the standard deviations in the case of the geometric means) by $\sqrt{32}$. Thus, the standard error of the unstratified arithmetic mean total particulate volatilizable carbon concentration at site 4 is 2.09

compared to a standard error of .482 for the corresponding stratified mean.

The stratified means, in almost all cases, are more precise (as evidenced by their smaller standard errors) than the unstratified means. Unstratified annual mean formats contain more information about the analytical data, however, and they are preferred for the purposes of this discussion. In most cases the unstratified means are within 20% of the stratified means, which is not surprising since the 32 intensive analysis days were chosen from regimes in rough proportion to their composite year frequencies of occurrence. The example of the total suspended particulate at site 4 was chosen as a good illustration of the importance of sampling schedule in meeting the ambient Federal Standard. Site 4 is in violation with an annual geometric mean TSP of 81.1 µg/m3. Yet Tables 4.2.6a-d show that the 32 day sample was heavily biased in favor of the dirtier days of regimes 2 and 8. This was intentional, of course, because these days, by themselves, tend to contain violations of the Federal 24 hour standard, but the effect of their inclusion in the annual mean calculation causes a violation to occur. When the bias caused by the over-sampling of these days is removed by stratified averaging, a more representative mean results which is not in violation of the standard.

A brief survey of the analytical data summaries contained in Tables 6.1.1-6.1.6 is useful in evaluating the accuracy and precision of the PACS analytical program, assessing major differences between receptor locations, getting a rough idea of which source types might be making contributions, and in improving analytical techniques in future studies.

Average uncertainties on single air filters are best expressed in the final column of Table 6.1.4d; though these are the averages of only

16 specimens, they represent typical values for the whole analysis program. These uncertainties result from the propagation of errors specified in Chapter Four by standard addition in quadrature. The dominant uncertainty for most neutron activation and x-ray fluorescence values is due to the 7% inhomogeneity error evaluated in section 4.7.7. In some cases the error is lower. This occurs when two determinations of the same constituent (e.g. bromine concentration from XRF and INAA) are averaged as explained in Table 5.5.1; the average has greater precision than either one of the individual measurements. Ion chromatographic uncertainties in NO_3^- and SO_4^{-2} reflect the analytical uncertainties reported in Table 4.7.9.2 as well as the deposit homogeneity error. Fluoride concentrations are dominated by the blank level uncertainty recorded in Table 4.7.9.2. Several concentrations often occur near the minimum detectable limits, as in the cases of Mg, Cr, and Ni. Counting statistics play a substantial role in the uncertainties of these concentrations.

Selenium and Cd were measured near the detectable limit, when they were detectable at all. As and Ba were never found in this set of samples, and rarely in other PACS specimens.

Tables 6.1.1a&b-6.1.6a&b contain average percent uncertainties for each constituent concentration in the 24 hour average, but these are significantly lower, in most cases, than those in Table 6.1.4d. The 24 hour averages were obtained by summing three sequential (or six in the case of site 3) volume measurements and three sequential (or six) mass measurements and propagating their uncertainties. The percent uncertainties of these sums turn out to be smaller than the percent uncertainties of any of the individual samples. Volatilizable carbon and non-volatilizable

Table 6.1.1a Average Concentrations at Sauvie Island, Background Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE CONCENTRATION AVERAGES AT SITE 1
COMPOSITE YEAR   FREQUENCIES

     ***************UG/M3****************** #IN #GT*****************PERCENT**************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------------
 VC     3.397( 2.260)          4.317( 2.680)  31   30* 23.775( 1.665)          25.770( 7.893)  31   30 0.534   13.23  VC
 NVC    0.670( 2.751)          0.910( 0.587)  31   29*  4.693( 2.513)           6.112( 3.810)  31   29 0.217   23.93  NVC
 NO3    1.091( 2.589)          1.526( 1.099)  31   31*  7.634( 1.595)           8.365( 3.310)  31   31 0.111    8.79  NO3
 SO4    1.826( 2.316)          2.453( 1.772)  31   31* 12.783( 1.401)          13.475( 4.355)  31   31 0.163    6.97  SO4
 F      0.031( 2.747)          0.045( 0.034)  31   26*  0.216( 1.914)           0.265( 0.215)  31   26 0.009   23.40  F
 NA     0.249( 2.040)          0.317( 0.224)  31   31*  1.745( 2.058)           2.258( 1.762)  31   31 0.016    5.74  NA
 MG     0.037( 1.823)          0.047( 0.049)  31    6*  0.258( 2.095)           0.350( 0.362)  31    6 0.059   65.14  MG
 AL     0.111( 2.314)          0.160( 0.172)  31   31*  0.774( 1.814)           0.915( 0.551)  31   31 0.009    6.60  AL
 SI     0.176( 3.200)          0.349( 0.500)  31   30*  1.232( 2.407)           1.802( 1.063)  31   30 0.027   13.27  SI
 S      0.580( 2.752)          0.832( 0.598)  31   31*  4.059( 1.658)           4.477( 1.701)  31   31 0.044    6.12  S
 CL     0.380( 1.531)          0.423( 0.186)  31   31*  2.714( 2.105)           3.676( 3.610)  31   31 0.023    5.46  CL
 K      0.117( 2.056)          0.140( 0.101)  31   31*  0.816( 1.400)           0.862( 0.295)  31   31 0.008    6.34  K
 CA     0.065( 2.212)          0.093( 0.104)  31   31*  0.457( 1.858)           0.552( 0.366)  31   31 0.005    7.41  CA
 TI     0.004( 3.583)          0.009( 0.014)  31   20*  0.027( 2.943)           0.047( 0.051)  31   20 0.002   20.60  TI
 V      0.004( 2.755)          0.005( 0.004)  31   30*  0.025( 1.881)           0.030( 0.017)  31   20 0.000    5.10  V
 CR     0.001( 2.170)          0.002( 0.000)  31   15*  0.008( 2.223)           0.012( 0.014)  31    7 0.001   49.71  CR
 MN     0.008( 1.949)          0.010( 0.008)  31   31*  0.057( 1.936)           0.074( 0.072)  31   31 0.001    6.76  MN
 FE     0.058( 2.740)          0.097( 0.120)  31   31*  0.406( 1.988)           0.517( 0.405)  31   31 0.005    6.13  FE
 NI     0.004( 3.530)          0.007( 0.007)  31   25*  0.028( 2.295)           0.037( 0.025)  31   25 0.001   10.06  NI
 CU     0.017( 2.558)          0.025( 0.027)  31   31*  0.116( 1.889)           0.142( 0.098)  31   31 0.002    9.29  CU
 ZN     0.019( 2.520)          0.025( 0.015)  31   30*  0.134( 2.035)           0.159( 0.077)  31   30 0.002    6.80  ZN
 BR     0.030( 2.161)          0.038( 0.024)  31   31*  0.211( 1.770)           0.245( 0.130)  31   31 0.002    5.13  BR
 PB     0.101( 2.531)          0.135( 0.080)  31   30*  0.709( 1.881)           0.817( 0.355)  31   30 0.008    6.56  PB
 SE     0.001( 1.675)          0.001( 0.000)  31    1*  0.007( 2.069)           0.009( 0.008)  31    1 0.003   93.23  SE
 AS     0.003( 1.796)          0.004( 0.003)  31    4*  0.020( 1.653)           0.023( 0.012)  31    4 0.004   44.55  AS
 CD     0.010( 1.279)          0.010( 0.002)  31    0*  0.067( 1.764)           0.080( 0.057)  31    0 0.000    0.00  CD
 BA     0.063( 1.262)          0.065( 0.013)  31    0*  0.443( 1.711)           0.516( 0.329)  31    0 0.000    0.00  BA
 MASS  14.287( 1.817)         16.661( 8.710)  31   31*100.000( 1.002)         100.000( 0.000)  31   31 0.492    3.94  MASS
--------------------------------------------------------------------------------------------------------------------
```

STD: Standard Deviation of data in mean, geometric or arithmetic

\# IN AVG: The number of individual concentrations summed to obtain the average.

\# GT MDC: The number of individual concentrations in the average which were greater than minimum detectable concentrations

Table 6.1.1b Average Concentrations at Sauvie Island, Background Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 1
COMPOSITE YEAR   FREQUENCIES

      •••••••••••••••UG/M3••••••••••••••••••• #IN #GT•••••••••••••••PERCENT•••••••••••••••• #IN #GT ARITH AV UNC
      GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC•GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC  UG/M3    %
----------------------------------------------------------------------------------------------------------------
 VC     5.975( 1.941)            7.374( 5.220)  29  29• 18.882( 1.610)           20.720( 0.563)  29  29 1.061   14.66  VC
 NVC    1.095( 4.059)            1.838( 1.346)  29  27•  3.447( 4.382)            5.808( 4.417)  29  27 0.447   25.19  NVC
 NO3    2.187( 2.165)            2.813( 1.848)  31  31•  7.136( 1.786)            7.991( 3.319)  31  31 0.107    6.79  NO3
 SO4    2.538( 2.078)            3.185( 2.085)  31  31•  8.281( 1.610)            9.160( 4.086)  31  31 0.206    6.54  SO4
 F      0.049( 2.924)            0.074( 0.057)  31  28•  0.160( 1.990)            0.281( 0.152)  31  20 0.011   20.62  F
 NA     0.651( 2.139)            0.859( 0.761)  31  31•  2.126( 2.333)            3.235( 4.039)  31  31 0.040    4.80  NA
 MG     0.163( 2.820)            0.250( 0.214)  31  26•  0.532( 2.281)            0.699( 0.474)  31  26 0.056   31.40  MG
 AL     0.795( 3.137)            1.305( 1.165)  31  31•  2.593( 1.986)            3.184( 1.998)  31  31 0.061    4.83  AL
 SI     2.410( 3.378)            4.180( 3.895)  31  31•  7.863( 2.107)           10.045( 6.917)  31  31 0.213    5.20  SI
 S      0.888( 2.120)            1.085( 0.640)  31  31•  2.610( 1.582)            2.863( 1.210)  31  31 0.052    5.30  S
 CL     0.714( 2.196)            1.064( 1.423)  31  31•  2.331( 3.179)            4.993( 7.982)  31  31 0.051    5.10  CL
 K      0.274( 1.914)            0.330( 0.198)  31  31•  0.893( 1.383)            0.926( 0.282)  31  31 0.017    5.27  K
 CA     0.474( 2.309)            0.635( 0.441)  31  31•  1.546( 1.475)            1.656( 0.614)  31  31 0.031    4.88  CA
 TI     0.052( 4.282)            0.104( 0.112)  31  30•  0.170( 2.547)            0.243( 0.283)  31  30 0.006    0.67  TI
 V      0.007( 2.376)            0.009( 0.006)  31  31•  0.022( 1.799)            0.026( 0.013)  31  30 0.001    7.54  V
 CR     0.003( 2.776)            0.005( 0.004)  31  26•  0.011( 1.885)            0.012( 0.007)  31  10 0.001   25.47  CR
 MN     0.024( 2.214)            0.031( 0.023)  31  31•  0.078( 1.782)            0.098( 0.055)  31  31 0.002    5.77  MN
 FE     0.491( 3.476)            0.893( 0.940)  31  31•  1.681( 2.168)            2.180( 1.604)  31  31 0.045    5.05  FE
 NI     0.007( 2.891)            0.011( 0.009)  31  29•  0.023( 2.271)            0.030( 0.020)  31  25 0.001   15.14  NI
 CU     0.069( 2.644)            0.095( 0.063)  31  31•  0.226( 2.174)            0.289( 0.195)  31  31 0.005    6.30  CU
 ZN     0.031( 1.648)            0.034( 0.016)  31  31•  0.100( 1.576)            0.111( 0.051)  31  31 0.002    5.83  ZN
 BR     0.038( 2.100)            0.048( 0.029)  31  31•  0.125( 2.291)            0.165( 0.115)  31  31 0.002    5.21  BR
 PB     0.140( 2.249)            0.178( 0.102)  31  31•  0.458( 2.155)            0.564( 0.298)  31  31 0.010    6.74  PB
 SE     0.001( 1.608)            0.001( 0.000)  31   1•  0.003( 2.266)            0.004( 0.004)  31   0 0.003   92.12  SE
 AS     0.003( 2.029)            0.005( 0.006)  31   5•  0.010( 2.058)            0.013( 0.010)  31   5 0.003   25.23  AS
 CD     0.010( 1.243)            0.010( 0.002)  31   1•  0.031( 1.849)            0.038( 0.033)  31   1 0.012   99.29  CD
 BA     0.060( 1.271)            0.062( 0.013)  31   0•  0.196( 1.924)            0.243( 0.100)  31   0 0.000    0.00  BA
 MASS  30.649( 1.840)           35.933(19.185)  31  31•100.000( 1.002)          100.000( 0.000)  31  31 0.620    2.13  MASS
----------------------------------------------------------------------------------------------------------------
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ARITH AV UNC: Arithmetic Average of the uncertainties of those concentrations which were above minimum detectable concentrations

UG/M3: Average absolute uncertainty

%: Average relative (percent) uncertainty

Table 6.1.2a Average Concentrations at Industrial Air Products, Industrial Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE CONCENTRATION AVERAGES AT SITE 2
COMPOSITE YEAR   FREQUENCIES

   **************UG/M3***************** #IN #GT****************PERCENT*************** #IN #GT ARITH AV UNC
   GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------
VC     7.383( 2.056)          9.299( 6.202)  32   32* 26.000( 1.491)          20.881(11.933)  32   32 1.130  12.35  VC
NVC    1.175( 2.930)          1.703( 1.165)  32   31*  4.267( 2.683)           5.894( 3.968)  32   31 0.301  24.37  NVC
NO3    1.539( 2.405)          2.190( 1.820)  32   32*  5.588( 1.686)           6.387( 3.498)  32   32 0.155   7.41  NO3
SO4    4.003( 2.429)          5.484( 3.612)  32   32* 14.529( 1.577)          16.007( 7.167)  32   32 0.335   6.40  SO4
F      0.035( 2.718)          0.051( 0.038)  32   28*  0.128( 1.854)           0.151( 0.003)  32   28 0.009  23.96  F
NA     0.687( 2.826)          1.005( 1.073)  32   32*  2.492( 2.592)           3.702( 3.661)  32   32 0.052   5.32  NA
MG     0.055( 1.654)          0.063( 0.039)  32    4*  0.199( 1.975)           0.258( 0.226)  32    4 0.067  45.60  MG
AL     0.201( 2.212)          0.269( 0.289)  32   32*  0.730( 1.781)           0.870( 0.642)  32   32 0.014   5.60  AL
SI     0.381( 2.655)          0.551( 0.436)  32   32*  1.385( 1.985)           1.789( 1.238)  32   32 0.036   6.07  SI
S      1.389( 2.364)          1.800( 1.003)  32   32*  5.043( 1.514)           5.450( 2.147)  32   32 0.091   5.22  S
CL     0.915( 1.789)          1.079( 0.655)  32   32*  3.321( 1.874)           4.186( 3.625)  32   32 0.054   5.06  CL
K      0.204( 2.140)          0.265( 0.193)  32   32*  0.742( 1.472)           0.883( 0.375)  32   32 0.014   5.51  K
CA     0.138( 1.993)          0.170( 0.114)  32   32*  0.500( 1.766)           0.582( 0.320)  32   32 0.009   5.43  CA
TI     0.016( 2.724)          0.025( 0.024)  32   29*  0.059( 2.071)           0.079( 0.070)  32   29 0.002  11.72  TI
V      0.014( 2.003)          0.010( 0.013)  32   32*  0.050( 1.751)           0.050( 0.033)  32   32 0.001   4.62  V
CR     0.033( 2.469)          0.048( 0.047)  32   32*  0.121( 2.076)           0.162( 0.156)  32   32 0.003   7.62  CR
MN     0.068( 2.342)          0.080( 0.057)  32   32*  0.247( 1.626)           0.272( 0.115)  32   32 0.004   4.82  MN
FE     0.458( 2.210)          0.570( 0.351)  32   32*  1.662( 1.690)           1.882( 0.978)  32   32 0.029   4.95  FE
NI     0.025( 2.199)          0.032( 0.021)  32   32*  0.089( 1.969)           0.109( 0.066)  32   32 0.002   6.71  NI
CU     0.032( 2.132)          0.041( 0.031)  32   32*  0.115( 1.590)           0.127( 0.058)  32   32 0.003   6.38  CU
ZN     0.137( 3.177)          0.244( 0.277)  32   32*  0.497( 2.266)           0.696( 0.670)  32   32 0.014   5.74  ZN
BR     0.120( 2.096)          0.151( 0.103)  32   32*  0.434( 2.196)           0.573( 0.420)  32   32 0.007   4.45  BR
PB     0.382( 1.925)          0.459( 0.266)  32   32*  1.380( 1.729)           1.577( 0.734)  32   32 0.023   5.14  PB
SE     0.001( 2.028)          0.003( 0.007)  32    6*  0.005( 2.983)           0.011( 0.023)  32    6 0.002  29.55  SE
AS     0.003( 1.806)          0.004( 0.003)  32    3*  0.012( 1.726)           0.014( 0.009)  32    3 0.004  37.19  AS
CD     0.010( 1.236)          0.018( 0.002)  32    1*  0.036( 1.795)           0.044( 0.033)  32    1 0.010  85.69  CD
BA     0.060( 1.329)          0.062( 0.016)  32    0*  0.219( 1.698)           0.254( 0.160)  32    0 0.000   0.00  BA
MASS  27.549( 1.781)         31.680(14.979)  32   32*100.000( 1.003)         100.000( 0.000)  32   32 0.524   2.12  MASS
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Table 6.1.2b Average Concentrations at Industrial Air Products, Industrial Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 2
COMPOSITE YEAR    FREQUENCIES

     ***************UG/M3****************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC  UG/M3   %
------------------------------------------------------------------------------------------------------------------
 VC   11.287( 2.119)         14.540(10.256)  29  29* 10.407( 1.531)           20.031( 7.569)  29  29 2.065  14.30  VC
 NVC   1.710( 3.466)          2.061( 2.547)  30  30*  2.019( 2.000)            4.018( 2 725)  30  30 0.645  26.06  NVC
 NO3   2.530( 2.405)          3.635( 2.990)  32  32*  4.091( 1.529)            4.485( 2.102)  32  32 0.242   6.72  NO3
 SO4   4.071( 2.360)          6.437( 4.249)  32  32*  7.050( 1.635)            8.863( 4.710)  32  32 0.390   6.34  SO4
 F     0.076( 2.426)          0.103( 0.077)  32  31*  0.123( 1.574)            0.135( 0.059)  32  31 0.013  15.19  F
 NA    1.562( 2.065)          1.949( 1.261)  32  32*  2.510( 2.047)            3.310( 2.904)  32  32 0.009   4.73  NA
 MG    0.450( 2.507)          0.629( 0.470)  32  30*  0.725( 1.613)            0.805( 0.372)  32  30 0.113  21.92  MG
 AL    2.067( 2.750)          2.970( 2.147)  32  32*  3.331( 1.570)            3.646( 1.460)  32  32 0.127   4.40  AL
 SI    6.204( 2.900)          9.157( 6.744)  32  32* 10.000( 1.507)           10.962( 4.532)  32  32 0.435   4.03  SI
 S     1.593( 2.215)          1.993( 1.120)  32  32*  2.560( 1.567)            2.040( 1.373)  32  32 0.099   5.10  S
 CL    1.476( 2.026)          1.084( 1.455)  32  32*  2.379( 2.300)            3.577( 4.221)  32  32 0.091   5.14  CL
 K     0.465( 2.230)          0.599( 0.303)  32  32*  0.750( 1.275)            0.773( 0.211)  32  32 0.029   5.07  K
 CA    1.220( 2.626)          1.725( 1.271)  32  32*  1.966( 1.417)            2.002( 0.728)  32  32 0.000   4.69  CA
 TI    0.199( 3.003)          0.297( 0.222)  32  32*  0.322( 1.731)            0.364( 0.179)  32  32 0.016   6.02  TI
 V     0.026( 2.194)          0.033( 0.021)  32  32*  0.042( 1.502)            0.046( 0.024)  32  32 0.001   4.52  V
 CR    0.081( 1.987)          0.099( 0.067)  32  32*  0.131( 1.750)            0.158( 0.125)  32  32 0.005   5.54  CR
 MN    0.151( 2.390)          0.199( 0.143)  32  32*  0.243( 1.526)            0.266( 0.131)  32  32 0.009   4.53  MN
 FE    3.104( 2.518)          4.250( 2.750)  32  32*  5.132( 1.470)            5.475( 1 932)  32  32 0.199   4.69  FE
 NI    0 040( 2.160)          0.050( 0.029)  32  32*  0 065( 1.829)            0.077( 0.046)  32  32 0.003   5.92  NI
 CU    0.111( 2.157)          0.143( 0.100)  32  32*  0.170( 1.550)            0.196( 0.094)  32  32 0.008   5.30  CU
 ZN    0.233( 3.170)          0.309( 0.370)  32  32*  0.375( 1.096)            0.455( 0.286)  32  32 0.021   5.44  ZN
 BR    0.142( 2.127)          0.101( 0.120)  32  32*  0.229( 2.033)            0.289( 0.201)  32  32 0.000   4.45  BR
 PB    0.540( 2.012)          0.660( 0.304)  32  32*  0.803( 1.619)            0.983( 0.451)  32  32 0.033   5.02  PB
 SE    0.002( 3.344)          0.004( 0.000)  32   0*  0.003( 3.332)            0.007( 0.014)  32   4 0.002  25.07  SE
 AS    0.003( 1.030)          0.004( 0.003)  32   2*  0.006( 1.030)            0.007( 0.005)  32   2 0.007  47.46  AS
 CD    0.013( 1.030)          0.016( 0.012)  32   0*  0.021( 1.904)            0.027( 0.021)  32   0 0.013  41.79  CD
 BA    0.060( 1.333)          0.062( 0.010)  32   0*  0.096( 1.046)            0.117( 0.003)  32   0 0.000   0.00  BA
 MASS 62.044( 1.996)         75.470(43.957)  32  32*100.000( 1.003)          100.000( 0.000)  32  32 0.747   1.23  MASS
------------------------------------------------------------------------------------------------------------------
```

Table 6.1.3a Average Concentrations at Central Air Monitoring, Urban Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE CONCENTRATION AVERAGES AT SITE 3
COMPOSITE YEAR   FREQUENCIES

     ***************UG/M3****************** #IN #GT*****************PERCENT**************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------------
 VC     5.923( 5.616)            9.338( 5.886)  32  31* 22.373( 6.436)           31.787(12.720)  32  31 1.100  11.83  VC
 HVC    0.848( 5.478)            1.546( 1.120)  32  29*  3.282( 5.874)            5.484( 3.345)  32  29 0.362  23.86  HVC
 NO3    1.562( 2.709)            2.392( 2.126)  32  32*  6.243( 1.753)            7.289( 4.262)  32  32 0.136   7.64  NO3
 SO4    2.485( 2.610)            3.584( 2.746)  32  32*  9.933( 1.631)           11.012( 4.687)  32  32 0.177   5.66  SO4
 F      0.034( 2.801)            0.051( 0.048)  32  25*  0.135( 2.079)            0.172( 0.117)  32  25 0.012  20.66  F
 NA     0.282( 2.129)            0.360( 0.239)  32  32*  1.126( 1.948)            1.447( 1.301)  32  32 0.016   5.29  NA
 MG     0.052( 1.522)            0.057( 0.030)  32   7*  0.286( 1.830)            0.249( 0.160)  32   7 0.067  72.19  MG
 AL     0.192( 2.106)            0.256( 0.229)  32  32*  0.769( 1.705)            0.895( 0.593)  32  32 0.011   4.66  AL
 SI     0.282( 3.043)            0.375( 0.369)  32  29*  0.888( 2.582)            1.174( 1.098)  32  29 0.023   8.77  SI
 S      0.772( 4.011)            1.293( 0.945)  32  31*  3.007( 2.536)            3.920( 1.053)  32  31 0.053   7.02  S
 CL     0.044( 1.689)            0.940( 0.443)  32  32*  3.374( 1.663)            3.927( 2.043)  32  32 0.036   4.01  CL
 K      0.150( 2.426)            0.204( 0.146)  32  32*  0.599( 1.598)            0.661( 0.207)  32  32 0.009   6.61  K
 CA     0.119( 2.011)            0.149( 0.105)  32  32*  0.478( 1.719)            0.550( 0.312)  32  32 0.007   6.10  CA
 TI     0 009( 3.034)            0.015( 0 015)  32  25*  0.036( 2.248)            0.049( 0.041)  32  25 0.003  27.66  TI
 V      0.012( 2.466)            0.017( 0.015)  32  32*  0.047( 1.696)            0.052( 0.024)  32  31 0.001   4.05  V
 CR     0.008( 3.528)            0.015( 0.015)  32  28*  0.031( 2.408)            0.044( 0.034)  32  20 0.002  20.85  CR
 MN     0.032( 3.793)            0.060( 0.082)  32  32*  0.128( 2.471)            0.186( 0.162)  32  32 0.003   5.45  MN
 FE     0.196( 3.489)            0.347( 0.342)  32  32*  0.785( 2.278)            1.034( 0 717)  32  32 0.013   4.98  FE
 NI     0.019( 3.070)            0.031( 0.029)  32  32*  0.074( 1.944)            0 090( 0.050)  32  32 0.002  13.46  NI
 CU     0.026( 1.695)            0.029( 0.015)  32  32*  0.102( 1.540)            0.111( 0.040)  32  32 0.002   6.22  CU
 ZN     0.062( 2.342)            0.085( 0.067)  32  32*  0.247( 1.555)            0.269( 0.103)  32  32 0.004   4.76  ZN
 BR     0.236( 2.000)            0.299( 0.221)  32  32*  0.944( 1.686)            1.072( 0.533)  32  32 0.010   3.33  BR
 PB     0.645( 1.847)            0.769( 0.470)  32  32*  2.577( 1.468)            2.761( 1.000)  32  32 0.030   3.07  PB
 SE     0.002( 3.109)            0.008( 0.029)  32   8*  0.009( 3.096)            0.026( 0.003)  32   7 0.005  54.33  SE
 AS     0.004( 1.305)            0.005( 0.001)  32   1*  0.017( 1.536)            0.019( 0.000)  32   1 0.005  70.64  AS
 CD     0.015( 1.205)            0.015( 0.005)  32   2*  0.058( 1.825)            0.069( 0.045)  32   2 0.025  82.00  CD
 BA     0.091( 1.267)            0.093( 0.022)  32   0*  0.363( 1.043)            0.442( 0.319)  32   0 0.000   0.00  BA
 MASS 25.020( 1.799)           29.211(15.769)  32  32*100.000( 1.003)          100.000( 0.000)  32  32 0.667   3.00  MASS
-------------------------------------------------------------------------------------------------------------------
```

Table 6.1.3b Average Concentrations at Central Air Monitoring, Urban Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 3
COMPOSITE YEAR    FREQUENCIES

    ***************UG/M3***************** 0IN 0GT****************PERCENT**************** 0IN 0GT ARITH AV UNC
    GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC  UG/M3   %
----------------------------------------------------------------------------------------------------------------
VC   11.992( 2.117)          15.436(10.801)  29  29* 19.697( 1.418)           20.812( 6.713)  29  29 2.191  14.20  VC
NVC   1.763( 3.280)           2.812( 2.432)  29  28*  2.896( 2.386)            3.698( 2.058)  29  28 0.654  22.77  NVC
NO3   3.141( 2.366)           4.279( 3.074)  32  32*  4.982( 1.552)            5.392( 2.537)  32  32 0.219   5.62  NO3
SO4   3.813( 2.253)           5.041( 3.729)  32  32*  5.951( 1.377)            6.242( 1.938)  32  32 0.249   5.35  SO4
F     0.080( 2.916)           0.119( 0.087)  32  29*  0.126( 2.043)            0.160( 0.140)  32  29 0.014  15.55  F
NA    1.030( 1.956)           1.251( 0.702)  32  32*  1.688( 1.807)            2.073( 2 067)  32  32 0.046   3.01  NA
MG    0.356( 3.414)           0.596( 0.470)  32  25*  0.555( 2.060)            0.673( 0.342)  32  25 0.115  20.53  MG
AL    2.116( 2.909)           3.158( 2.392)  32  32*  3.303( 1.619)            3.624( 1.364)  32  32 0.104   3.43  AL
SI    6.321( 3.023)           9.780( 7.782)  32  32*  9.866( 1.615)           10.780( 3.080)  32  32 0.349   3.71  SI
S     1.445( 2.260)           1.864( 1.212)  32  32*  2.255( 1.310)            2.332( 0.566)  32  32 0.071   4.42  S
CL    1.655( 1.789)           2.080( 1.594)  32  32*  2.583( 2.419)            4.864( 5.093)  32  32 0.077   3.74  CL
K     0.475( 2.184)           0.618( 0.438)  32  32*  0.741( 1.194)            0.753( 0.137)  32  32 0.023   4.02  K
CA    1.393( 2.595)           1.963( 1.471)  32  32*  2.175( 1.481)            2.347( 1.004)  32  32 0.069   3.64  CA
TI    0.170( 3.212)           0.271( 0.226)  32  32*  0.265( 1.712)            0.295( 0.115)  32  32 0.012   6.78  TI
V     0.024( 2.306)           0.035( 0.030)  32  32*  0.030( 1.551)            0.042( 0.019)  32  32 0.001   3.69  V
CR    0.024( 4.151)           0.047( 0.048)  32  30*  0.037( 2.377)            0.049( 0.032)  32  29 0.003   9.99  CR
MN    0.088( 3.599)           0.169( 0.193)  32  32*  0.137( 1.970)            0.169( 0.107)  32  32 0.006   4.03  MN
FE    2.039( 3.191)           3.316( 2.930)  32  32*  3.182( 1.679)            3.543( 1.450)  32  32 0.116   3.60  FE
NI    0.034( 2.801)           0.055( 0.052)  32  32*  0.054( 1.725)            0.061( 0.031)  32  32 0.003   7.16  NI
CU    0.084( 1.819)           0.099( 0.057)  32  32*  0.131( 1.621)            0.149( 0.089)  32  32 0.004   4.16  CU
ZN    0.132( 2.600)           0.197( 0.174)  32  32*  0.206( 1.504)            0.224( 0.102)  32  32 0.000   4.15  ZN
BR    0.335( 1.916)           0.407( 0.256)  32  32*  0.523( 1.033)            0.620( 0.362)  32  32 0.014   3.41  BR
PB    1.056( 1.792)           1.238( 0.713)  32  32*  1.649( 1.559)            1.011( 0.795)  32  32 0.049   3.95  PB
SE    0.003( 3.697)           0.010( 0.033)  32  11*  0.004( 3.793)            0.016( 0.049)  32   0 0.005  40.96  SE
AS    0.005( 1.419)           0.005( 0.002)  32   2*  0.000( 1.643)            0.009( 0.005)  32   0 0.010  77.34  AS
CD    0.015( 1.403)           0.017( 0.012)  32   3*  0.024( 2.104)            0.032( 0.030)  32   3 0.025  64.01  CD
BA    0.094( 1.254)           0.096( 0.022)  32   0*  0.146( 1.993)            0.190( 0.179)  32   0 0.000   0.00  BA
MASS 64.070( 2.009)          79.058(49.116)  32  32*100.000( 1.003)          100.000( 0.000)  32  32 0.040   1.50  MASS
----------------------------------------------------------------------------------------------------------------
```

Table 6.1.4a Average Concentrations at Pacific Motor Trucking, Urban/Industrial Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE CONCENTRATION AVERAGES AT SITE 4
COMPOSITE YEAR   FREQUENCIES

     ••••••••••••••UG/M3••••••••••••••••• #IN #GT••••••••••••••••PERCENT••••••••••••••• #IN #GT ARITH AV UNC
     GEOM MEAN(STD)        ARITH MEAN(STD) AVG MDC•GEOM MEAN(STD)        ARITH MEAN(STD) AVG MDC  UG/M3   %
-----------------------------------------------------------------------------------------------------------
VC     9.865( 2.047)        12.304( 7.466)  32  32* 33.544( 1.541)      36.361(14.434)  31  31 1.307  11.05  VC
NVC    1.943( 2.146)         2.479( 1.759)  32  32*  6.922( 2.207)      10.277(15.430)  32  32 0.519  21.99  NVC
NO3    1.481( 2.609)         2.062( 1.703)  32  32*  4.993( 1.695)       5.789( 3.073)  32  32 0.140   8.01  NO3
SO4    2.304( 2.450)         3.104( 2.303)  32  32*  8.289( 1.620)       9.134( 4.055)  32  32 0.289   6.72  SO4
F      0.047( 2.671)         0.067( 0.050)  32  30*  0.166( 1.926)       0.203( 0.139)  32  30 0.011  24.61  F
NA     0.259( 2.131)         0.330( 0.219)  32  32*  0.923( 2.006)       1.204( 1.154)  32  32 0.017   5.91  NA
MG     0.050( 1.704)         0.059( 0.030)  32   9*  0.177( 1.705)       0.217( 0.200)  32   9 0.065  67.14  MG
AL     0.199( 2.472)         0.290( 0.257)  32  32*  0.700( 1.942)       0.861( 0.523)  32  32 0.016   5.02  AL
SI     0.346( 3.322)         0.595( 0.574)  32  32*  1.232( 2.529)       1.696( 1.104)  32  32 0.040   8.13  SI
S      0.962( 2.380)         1.203( 0.844)  32  32*  3.427( 1.537)       3.716( 1.419)  32  32 0.066   5.35  S
CL     0.606( 1.795)         0.709( 0.395)  32  32*  2.159( 1.903)       2.729( 2.610)  32  32 0.036   5.33  CL
K      0.180( 1.967)         0.221( 0.135)  32  32*  0.641( 1.315)       0.666( 0.204)  32  32 0.012   5.56  K
CA     0.127( 2.217)         0.173( 0.147)  32  32*  0.452( 1.752)       0.529( 0.325)  32  32 0.009   5.54  CA
TI     0.014( 3.824)         0.026( 0.020)  32  29*  0.049( 3.011)       0.072( 0.051)  32  29 0.004  24.34  TI
V      0.008( 2.650)         0.012( 0.010)  32  32*  0.029( 1.757)       0.034( 0.010)  32  31 0.001   5.41  V
CR     0.004( 3.294)         0.006( 0.006)  32  25*  0.013( 2.602)       0.021( 0.033)  32  22 0.001  24.63  CR
MN     0.020( 3.923)         0.056( 0.056)  32  32*  0.101( 2.010)       0.156( 0.136)  32  32 0.003   6.37  MN
FE     0.305( 3.276)         0.516( 0.453)  32  32*  1.087( 2.333)       1.425( 0.897)  32  32 0.027   5.36  FE
NI     0.013( 2.734)         0.019( 0.017)  32  32*  0.045( 1.746)       0.052( 0.020)  32  32 0.001  12.35  NI
CU     0.015( 2.207)         0.019( 0.013)  32  32*  0.053( 1.512)       0.057( 0.023)  32  32 0.001   9.61  CU
ZN     0.047( 2.153)         0.060( 0.039)  32  32*  0.160( 1.453)       0.180( 0.072)  32  32 0.003   5.71  ZN
BR     0.260( 2.008)         0.336( 0.261)  32  32*  0.920( 1.537)       1.015( 0.439)  32  32 0.015   4.35  BR
PB     0.707( 1.955)         0.874( 0.599)  32  32*  2.521( 1.398)       2.662( 0.905)  32  32 0.045   5.03  PB
SE     0.003( 4.119)         0.011( 0.032)  32  13*  0.011( 3.241)       0.029( 0.001)  32  12 0.004  30.11  SE
AS     0.005( 1.716)         0.006( 0.005)  32   3*  0.016( 1.612)       0.019( 0.013)  32   3 0.006  46.40  AS
CD     0.014( 2.151)         0.021( 0.027)  32   6*  0.050( 2.524)       0.079( 0.095)  32   6 0.018  41.62  CD
BA     0.068( 1.300)         0.070( 0.017)  32   0*  0.242( 1.779)       0.287( 0.186)  32   0 0.000   0.00  BA
MASS  28.065( 1.869)        33.386(18.250)  32  32*100.000( 1.003)     100.000( 0.000)  32  32 0.540   2.12  MASS
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Table 6.1.4b Average Concentrations at Pacific Motor Trucking, Urban/Industrial Site

```
FMCS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 4
COMPOSITE YEAR   FREQUENCIES

     ****************UG/M3******************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------------
 VC    14.194( 2.084)          17.937(11.822)  29   29* 10.510( 1.676)         21.086(11.192)  29   29 2.547   14.20  VC
 NVC    2.385( 3.562)           4.880( 6.949)  29   29*  3.111( 2.322)          4.063( 2.549)  29   29 1.096   23.91  NVC
 NO3    2.001( 2.242)           3.742( 2.812)  31   31*  3.453( 1.467)          3.707( 1.438)  31   31 0.242    6.57  NO3
 SO4    3.200( 2.214)           4.175( 2.846)  31   31*  3.954( 1.493)          4.286( 1.072)  31   31 0.261    6.33  SO4
 F      0.116( 2.888)           0.239( 0.523)  31   31*  0.143( 2.135)          0.200( 0.220)  31   31 0.032   15.93  F
 NA     1.127( 2.127)           1.443( 0.972)  31   31*  1.390( 1.560)          1.561( 0.929)  31   31 0.067    4.00  NA
 MG     0.573( 3.359)           1.005( 1.044)  31   29*  0.706( 1.843)          0.815( 0.374)  31   29 0.126   17.42  MG
 AL     3.040( 2.916)           4.791( 4.239)  31   31*  3.748( 1.536)          4.049( 1.419)  31   31 0.200    4.24  AL
 SI     9.263( 3.110)          14.990(13.173)  31   31* 11.420( 1.624)         12.546( 4.645)  31   31 0.700    4.84  SI
 S      1.235( 2.009)           1.506( 0.864)  31   31*  1.523( 1.471)          1.629( 0.598)  31   31 0.075    5.06  S
 CL     1.176( 2.006)           1.554( 1.598)  31   31*  1.450( 2.818)          2.639( 3.033)  31   31 0.099    5.65  CL
 K      0.580( 2.290)           0.794( 0.603)  31   31*  0.724( 1.161)          0.732( 0.107)  31   31 0.030    4.97  K
 CA     1.644( 2.750)           2.515( 2.273)  31   31*  2.027( 1.393)          2.122( 0.574)  31   31 0.114    4.61  CA
 TI     0.250( 3.237)           0.436( 0.426)  31   31*  0.310( 1.601)          0.354( 0.139)  31   31 0.022    5.54  TI
 V      0.019( 2.491)           0.027( 0.020)  31   31*  0.024( 1.515)          0.026( 0.011)  31   30 0.001    6.60  V
 CR     0.021( 3.114)           0.032( 0.026)  31   30*  0.026( 1.812)          0.030( 0.010)  31   30 0.002    0.74  CR
 MN     0.085( 3.149)           0.136( 0.113)  31   31*  0.105( 1.820)          0.123( 0.060)  31   31 0.006    5.01  MN
 FE     2.386( 3.106)           4.625( 4.024)  31   31*  3.558( 1.615)          3.896( 1.395)  31   31 0.215    4.72  FE
 NI     0.023( 2.507)           0.033( 0.026)  31   31*  0.029( 1.705)          0.033( 0.019)  31   31 0.002    7.56  NI
 CU     0.040( 2.861)           0.060( 0.038)  31   31*  0.059( 1.671)          0.060( 0.044)  31   31 0.003    5.01  CU
 ZN     0.105( 2.293)           0.140( 0.099)  31   31*  0.129( 1.469)          0.139( 0.050)  31   31 0.007    5.20  ZN
 BR     0.342( 2.031)           0.436( 0.337)  31   31*  0.421( 1.838)          0.500( 0.300)  31   31 0.019    4.32  BR
 PB     1.073( 1.916)           1.303( 0.043)  31   31*  1.323( 1.616)          1.474( 0.705)  31   31 0.066    5.00  PB
 SE     0.004( 4.010)           0.015( 0.036)  31   17*  0.005( 4.437)          0.017( 0.043)  31   11 0.003   26.06  SE
 AS     0.005( 1.047)           0.006( 0.009)  31    2*  0.006( 2.042)          0.000( 0.011)  31    1 0.006   20.03  AS
 CD     0.024( 2.421)           0.035( 0.030)  31   17*  0.030( 2.240)          0.043( 0.044)  31   17 0.014   31.39  CD
 BA     0.074( 1.400)           0.061( 0.041)  31    3*  0.092( 1.856)          0.112( 0.081)  31    3 0.130   76.14  BA
 MASS  81.113( 2.110)         105.115(70.734)  31   31*100.000( 1.002)        100.020( 0.000)  31   31 0.957    1.10  MASS
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Table 6.1.4c Example of Stratified Means Report Format

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PACS 24 HOUR ANNUAL   STRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 4
COMPOSITE YEAR   FREQUENCIES

    ***************UG/M3*****************         ****************PERCENT****************
    GEOM MEAN            ARITH MEAN             *GEOM MEAN              ARITH MEAN
-------------------------------------------------------------------------------------------------------------
VC    12.299,  1.045         15.658+- 0.482        * 10.354,  1.044         21.293+- 0.923
HVC    1.909,  1.095          3.891+- 0.233        *  2.049,  1.080          3.785+- 0.189
NO3    2.455,  1.039          3.189+- 0.105        *  3.494,  1.024          3.732+- 0.100
SO4    2.889,  1.030          3.682+- 0.100        *  3.997,  1.023          4.384+- 0.099
F      0.099,  1.040          0.165+- 0.011        *  0.141,  1.047          0.181+- 0.010
NA     0.982,  1.053          1.265+- 0.057        *  1.397,  1.032          1.571+- 0.059
MG     0.471,  1.073          0.001+- 0.041        *  0.671,  1.044          0.774+- 0.025
AL     2.519,  1.063          3.955+- 0.104        *  3.504,  1.031          3.899+- 0.101
SI     7.711,  1.066         12.395+- 0.500        * 10.973,  1.035         12.116+- 0.333
S      1.107,  1.035          1.350+- 0.034        *  1.575,  1.021          1.669+- 0.034
CL     1.136,  1.042          1.522+- 0.111        *  1.617,  1.051          2.787+- 0.234
K      0.505,  1.044          0.677+- 0.026        *  0.719,  1.010          0.727+- 0.007
CA     1.375,  1.056          2.076+- 0.093        *  1.957,  1.022          2.048+- 0.036
TI     0.213,  1.060          0.356+- 0.017        *  0.304,  1.037          0.340+- 0.010
V      0.016,  1.055          0.023+- 0.001        *  0.023,  1.030          0.026+- 0.001
CR     0.018,  1.065          0.027+- 0.001        *  0.026,  1.046          0.030+- 0.002
MN     0.072,  1.060          0.117+- 0.005        *  0.102,  1.033          0.121+- 0.004
FE     2.413,  1.063          3.830+- 0.163        *  3.434,  1.032          3.774+- 0.091
NI     0.020,  1.050          0.020+- 0.001        *  0.028,  1.039          0.033+- 0.001
CU     0.043,  1.042          0.053+- 0.002        *  0.061,  1.037          0.071+- 0.003
ZN     0.092,  1.047          0.123+- 0.004        *  0.131,  1.027          0.142+- 0.004
BR     0.306,  1.030          0.387+- 0.012        *  0.435,  1.045          0.519+- 0.023
PB     0.971,  1.035          1.169+- 0.031        *  1.382,  1.035          1.539+- 0.053
SE     0.004,  1.124          0.011+- 0.002        *  0.005,  1.136          0.017+- 0.003
AS     0.004,  1.037          0.002+- 0.001        *  0.006,  1.040          0.004+- 0.001
CD     0.023,  1.075          0.033+- 0.002        *  0.032,  1.000          0.047+- 0.004
BA     0.069,  1.017          0.074+- 0.001        *  0.090,  1.041          0.110+- 0.005
MASS  70.277,  1.039         89.446+- 3.061        *100.000,  1.000        100.000+- 0.000
-------------------------------------------------------------------------------------------------------------
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Table 6.1.4d Example of Flow Pattern Averages Report Format

```
PACS ANNUAL CONCENTRATION AVERAGES FOR TOTAL  PARTICULATE AT SITE 4 IN FLOW PATTERN 6
NUMBER IN FLOW PATTERN:  17


 SPE ****************UG/M3******************** BIN  PCT*****************PERCENT****************** BIN PCT ARITH AV UNC
 CIE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3    %
-----------------------------------------------------------------------------------------------------------------------
 VC    0.000( 0.000)          0.000( 0.000)   0    0*  0.000( 0.000)          0.000( 0.000)   0    0 0.000    0.00  VC
 NVC   0.000( 0.000)          0.000( 0.000)   0    0*  0.000( 0.000)          0.000( 0.000)   0    0 0.000    0.00  NVC
 NO3   2.212( 1.929)          2.700( 1.922)  16   16*  3.453( 1 417)          3.660( 1.326)  16   16 0.297   11.32  NO3
 SO4   2.444( 2.092)          3.169( 2.551)  16   16*  3.014( 1.433)          4.043( 1.407)  16   16 0.340   10.97  SO4
 F     0.074( 1.800)          0.087( 0.049)  16   16*  0.115( 1 697)          0.133( 0.003)  16   16 0.020   26.00  F
 NA    0.719( 2.626)          1.040( 0.817)  16   16*  1.121( 1.675)          1.287( 0.033)  16   16 0.070    7.95  NA
 MG    0.370( 3.619)          0.705( 0.731)  16   12*  0.577( 2.133)          0.731( 0.493)  16   12 0.156   20.93  MG
 AL    1.670( 3.695)          3.226( 3.205)  16   16*  2.610( 2.190)          3.291( 1.907)  16   16 0.222    7.04  AL
 SI    5.410( 3.766)         10.662(10.003)  16   16*  0.456( 2.109)         10.667( 6.259)  16   16 0.014    7.65  SI
 S     1.020( 1.009)          1.243( 0 901)  16   16*  1.591( 1.281)          1.638( 0.413)  16   16 0.103    0.42  S
 CL    1.038( 1.824)          1.287( 1.210)  16   16*  1.620( 2.400)          2.277( 2.170)  16   16 0.090    0.06  CL
 K     0.437( 2.101)          0.576( 0.431)  16   16*  0.601( 1.210)          0.693( 0.132)  16   16 0.046    0.29  K
 CA    0.998( 3.162)          1.711( 1.650)  16   16*  1.550( 1.770)          1.791( 0.902)  16   16 0.126    7.43  CA
 TI    0.147( 3.006)          0.295( 0.300)  16   16*  0.229( 2.275)          0.295( 0.102)  16   16 0.024    0.96  TI
 V     0.017( 1.990)          0.021( 0.014)  16   16*  0.026( 1.715)          0.030( 0.010)  16   16 0.001    7.23  V
 CR    0.016( 2.076)          0.020( 0.013)  16   16*  0.025( 1.692)          0.020( 0.014)  16   16 0.002   13.70  CR
 MN    0.042( 2.550)          0.061( 0.050)  16   16*  0.065( 1.502)          0.070( 0.025)  16   16 0.005    7.05  MN
 FE    1.744( 3.090)          2.955( 2.790)  16   16*  2.721( 1.015)          3.133( 1.494)  16   16 0.220    7.45  FE
 NI    0.025( 1.976)          0.031( 0.022)  16   16*  0.039( 1 829)          0.046( 0 030)  16   16 0.003   11.10  NI
 CU    0.071( 1.432)          0.075( 0.027)  16   16*  0.111( 2.050)          0.142( 0.100)  16   16 0.006    0.61  CU
 ZN    0.091( 1.927)          0.100( 0.062)  16   16*  0.141( 1.576)          0.159( 0.090)  16   16 0.009    0.49  ZN
 BR    0.329( 1.645)          0.364( 0.154)  16   16*  0.513( 1.767)          0.500( 0.301)  16   16 0.025    6.09  BR
 PB    0.909( 1.592)          1.005( 0.449)  16   16*  1.544( 1.600)          1.732( 0.007)  16   16 0.007    0.07  PB
 SE    0.005( 2.309)          0.007( 0.005)  16    6*  0.000( 2.243)          0.010( 0.009)  16    6 0.003   22.47  SE
 AS    0.007( 1.454)          0.007( 0.002)  16    0*  0.011( 2.019)          0.013( 0.006)  16    0 0.000    0.00  AS
 CD    0.030( 2.031)          0.042( 0.049)  16    5*  0.040( 2.313)          0.071( 0.095)  16    5 0.016   22.29  CD
 BA    0.137( 1.220)          0.140( 0.037)  16    0*  0.213( 1.002)          0.250( 0.140)  16    0 0.000    0.00  BA
 MASS 64.079( 1.950)         70.358(50.668)  16   16* 99.999( 1.003)        100.000( 0.000)  16   16 1.375    2.05  MASS
-----------------------------------------------------------------------------------------------------------------------
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Table 6.1.5a Average Concentrations at Flavel Park, Residential Site

PACS 24 HOUR ANNUAL UNSTRATIFIED FINE FARTICULATE CONCENTRATION AVERAGES AT SITE 5
COMPOSITE YEAR FREQUENCIES

	UG/M3 GEOM MEAN(STD)	UG/M3 ARITH MEAN(STD)	#IN AVG	#GT MDC	PERCENT GEOM MEAN(STD)	PERCENT ARITH MEAN(STD)	#IN AVG	#GT MDC	ARITH AV UNC UG/M3	ARITH AV UNC %	
VC	8.573(2.168)	11.213(7.973)	30	30*	37.978(1.548)	41.345(16.118)	30	30	1.309	11.92	VC
NVC	0.734(3.458)	1.131(0.762)	30	27*	3.251(2.685)	4.209(2.044)	30	27	0.275	23.73	NVC
NO3	1.058(2.426)	1.493(1.335)	30	30*	4.649(1.675)	5.385(2.915)	30	30	0.111	8.61	NO3
SO4	1.589(2.541)	2.099(1.437)	30	30*	6.683(1.018)	7.824(4.214)	30	30	0.137	7.25	SO4
F	0.037(2.436)	0.049(0.034)	30	27*	0.162(1.013)	0.189(0.104)	30	27	0.009	23.91	F
NA	0.188(1.944)	0.224(0.178)	30	30*	0.796(2.178)	1.154(1.412)	30	30	0.013	6.46	NA
MG	0.039(1.691)	0.045(0.020)	30	7*	0.174(1.795)	0.206(0.128)	30	7	0.040	63.16	MG
AL	0.179(2.420)	0.246(0.181)	30	30*	0.794(2.042)	1.004(0.715)	30	30	0.013	6.21	AL
SI	0.250(4.033)	0.434(0.351)	30	28*	1.100(3.118)	1.687(1.439)	30	28	0.030	8.63	SI
S	0.545(3.007)	0.805(0.527)	30	30*	2.416(1.983)	2.913(1.570)	30	30	0.042	6.88	S
CL	0.503(1.661)	0.571(0.385)	30	30*	2.220(1.787)	2.747(2.477)	30	30	0.029	5.26	CL
K	0.180(1.990)	0.222(0.144)	30	30*	0.795(1.455)	0.853(0.344)	30	30	0.012	5.49	K
CA	0.093(1.850)	0.111(0.068)	30	30*	0.411(1.633)	0.467(0.200)	30	30	0.006	5.55	CA
TI	0.009(3.769)	0.016(0.014)	30	22*	0.039(3.112)	0.065(0.068)	30	22	0.003	19.10	TI
V	0.004(2.600)	0.006(0.005)	30	30*	0.016(1.649)	0.018(0.009)	30	26	0.000	5.67	V
CR	0.001(2.412)	0.002(0.000)	30	18*	0.006(2.295)	0.009(0.007)	30	11	0.001	39.05	CR
MN	0.007(2.679)	0.010(0.008)	30	29*	0.033(1.800)	0.037(0.017)	30	29	0.001	6.79	MN
FE	0.111(2.847)	0.160(0.116)	30	30*	0.491(2.172)	0.638(0.489)	30	30	0.008	6.66	FE
NI	0.004(3.474)	0.008(0.008)	30	26*	0.019(2.109)	0.025(0.016)	30	22	0.001	25.90	NI
CU	0.022(1.796)	0.025(0.013)	30	30*	0.095(1.553)	0.104(0.044)	30	30	0.002	6.75	CU
ZN	0.028(1.940)	0.034(0.020)	30	30*	0.126(1.433)	0.133(0.046)	30	30	0.002	6.13	ZN
BR	0.149(2.654)	0.229(0.227)	30	30*	0.660(1.678)	0.747(0.378)	30	30	0.011	4.61	BR
PB	0.412(2.437)	0.502(0.489)	30	30*	1.824(1.526)	1.981(0.802)	30	30	0.032	5.44	PB
SE	0.002(2.693)	0.003(0.004)	30	0*	0.008(2.195)	0.011(0.010)	30	6	0.003	41.61	SE
AS	0.003(1.626)	0.003(0.002)	30	0*	0.014(1.680)	0.015(0.007)	30	0	0.000	0.00	AS
CD	0.010(1.320)	0.010(0.003)	30	0*	0.044(1.626)	0.050(0.024)	30	0	0.000	0.00	CD
BA	0.066(1.470)	0.072(0.042)	30	0*	0.292(1.718)	0.340(0.222)	30	0	0.000	0.00	BA
MASS	22.575(1.829)	26.515(14.460)	30	30*	100.000(1.002)	100.000(0.000)	30	30	0.503	2.51	MASS

Table 6.1.5b   Average Concentrations at Flavel Park, Residential Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 5
COMPOSITE YEAR   FREQUENCIES

     ****************UG/M3******************** #IN #GT****************PERCENT***************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC  UG/M3    %
---------------------------------------------------------------------------------------------------------------------
 VC    12.675( 2.054)           16 095(11.090)  31  31* 10.696( 1.594)          20.724( 9.536)  31  31 2.204  14.26  VC
 NVC    1.284( 3.325)            2.031( 1.679)  31  30*  1.894( 2.526)           2.456( 1.413)  31  30 0.475  24.44  NVC
 NO3    2.932( 2.274)            3.956( 3.052)  32  32*  4.561( 1.541)           5.014( 2.349)  32  32 0.250   6.76  NO3
 SO4    2.668( 2.292)            3.470( 2.184)  32  32*  4.150( 1.497)           4.455( 1.566)  32  32 0.210   6.03  SO4
 F      0.087( 2.002)            0.109( 0.072)  32  32*  0.136( 1.550)           0.149( 0.067)  32  32 0.014  16.10  F
 NA     0.926( 2.091)            1.190( 0.933)  32  32*  1.440( 2.101)           2.040( 2.513)  32  32 0.057   4.99  NA
 MG     0.401( 3.030)            0.612( 0.474)  32  20*  0.624( 1.921)           0.745( 0.425)  32  20 0.096  17.79  MG
 AL     2.252( 3.372)            3.696( 3.020)  32  32*  3.503( 1.982)           4.106( 2.134)  32  32 0.165   4.63  AL
 SI     6.522( 3.566)           10.926( 9.119)  32  32* 10.145( 2.030)          12.075( 5.464)  32  32 0.549   5.00  SI
 S      0.977( 2.244)            1.247( 0.728)  32  32*  1.519( 1.424)           1.613( 0.566)  32  32 0.063   5.40  S
 CL     1.102( 2.028)            1.476( 1.562)  32  32*  1.714( 2.733)           3.154( 4.056)  32  32 0.074   5.23  CL
 K      0.520( 2.170)            0.671( 0.458)  32  32*  0.809( 1.237)           0.827( 0.174)  32  32 0.034   5.22  K
 CA     1.020( 2.413)            1.480( 1.061)  32  32*  1.506( 1.367)           1.659( 0.407)  32  32 0.066   4.79  CA
 TI     0.101( 3.500)            0.304( 0.259)  32  32*  0.201( 2.048)           0.340( 0.172)  32  32 0.017   6.29  TI
 V      0.011( 2.504)            0.016( 0.011)  32  32*  0.010( 1.434)           0.019( 0.006)  32  30 0.001   5.06  V
 CR     0.010( 2.421)            0.014( 0.011)  32  32*  0.016( 1.445)           0.017( 0.006)  32  29 0.001  16.09  CR
 MN     0.047( 2.677)            0.060( 0.052)  32  32*  0.073( 1.527)           0.079( 0.020)  32  32 0.003   5.21  MN
 FE     1.541( 3.523)            2.598( 2.264)  32  32*  2.397( 1.996)           2.847( 1.338)  32  32 0.129   4.96  FE
 NI     0.012( 2.942)            0.018( 0.014)  32  30*  0.019( 1.785)           0.021( 0.010)  32  29 0.001  10.35  NI
 CU     0.117( 1.776)            0.132( 0.060)  32  32*  0.101( 2.264)           0.253( 0.220)  32  32 0.007   5.20  CU
 ZN     0.065( 2.070)            0.082( 0.055)  32  32*  0.101( 1.430)           0.107( 0.030)  32  32 0.004   5.62  ZN
 BR     0.251( 2.570)            0.375( 0.342)  32  32*  0.391( 1.728)           0.443( 0.203)  32  32 0.010   4.66  BR
 PB     0.785( 2.447)            1.110( 0.914)  32  32*  1.221( 1.550)           1.325( 0.496)  32  32 0.059   5.34  PB
 SE     0.003( 3.654)            0.007( 0.009)  32  11*  0.004( 2.944)           0.000( 0.000)  32   0 0.003  24.01  SE
 AS     0.004( 1.770)            0.005( 0.002)  32   1*  0.006( 2.057)           0.000( 0.007)  32   1 0.004  40.96  AS
 CD     0.013( 1.609)            0.015( 0.010)  32   4*  0.021( 1.729)           0.024( 0.013)  32   4 0.020  63.41  CD
 BA     0.079( 1.501)            0.087( 0.050)  32   0*  0.124( 2.053)           0.160( 0.132)  32   0 0.000   0.00  BA
 MASS  64.290( 2.035)           80.555(53.996)  32  32*100.000( 1.003)         100.000( 0.000)  32  32 0.958   1.46  MASS
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Table 6.1.6a Average Concentrations at Carus, Background Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE CONCENTRATION AVERAGES AT SITE 6
COMPOSITE YEAR   FREQUENCIES

    *************UG/M3***************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
    GEOM MEAN(STD)         ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)         ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------
VC     3.016( 2.097)          4.040( 3.202)  32  32* 27.727( 1.547)      30.255(12.031)  31  31 0.593  13.92  VC
HVC    0.390( 2.704)          0.561( 0.415)  32  30*  2.790( 2.011)       4.006( 3.065)  31  29 0.146  30.26  HVC
NO3    1.026( 3.126)          1.660( 1.447)  32  32*  7.229( 2.129)       9.203( 6.102)  31  31 0.123  12.11  NO3
SO4    1.001( 3.405)          1.624( 1.146)  32  31*  7.142( 2.276)       0.953( 4.931)  31  30 0.113   0.60  SO4
F      0.020( 2.967)          0.033( 0.030)  32  22*  0.144( 2.079)       0.100( 0.111)  31  21 0.009  32.61  F
NA     0.131( 2.623)          0.200( 0.234)  32  32*  0.909( 2.310)       1.452( 1.670)  31  31 0.012   0.30  NA
MG     0.034( 1.914)          0.040( 0.073)  32   5*  0.254( 1.996)       0.327( 0.270)  31   5 0.043  59.07  MG
AL     0.091( 2.902)          0.192( 0.395)  32  32*  0.670( 2.113)       0.945( 1.056)  31  31 0.010   7.90  AL
SI     0.092( 5.507)          0.335( 0.039)  32  24*  0.679( 3.717)       1.474( 2.316)  31  23 0.026  15.25  SI
S      0.273( 5.065)          0.571( 0.446)  32  30*  1.944( 3.024)       2.904( 1.905)  31  29 0.036  14.46  S
CL     0.324( 1.595)          0.370( 0.322)  32  32*  2.301( 2.429)       3.635( 4.006)  31  31 0.021   5.95  CL
K      0.007( 3.092)          0.164( 0.107)  32  30*  0.624( 2.261)       0.011( 0.612)  31  29 0.011   9.06  K
CA     0.053( 2.255)          0.076( 0.096)  32  31*  0.380( 2.042)       0.497( 0.393)  31  30 0.005   7.27  CA
TI     0.004( 3.690)          0.012( 0.032)  32  15*  0.027( 3.195)       0.059( 0.097)  31  15 0.002  24.47  TI
V      0.001( 3.045)          0.003( 0.003)  32  30*  0.009( 2.703)       0.013( 0.010)  31  15 0.000   9.69  V
CR     0.001( 2.093)          0.001( 0.000)  32  11*  0.007( 1.907)       0.009( 0.005)  31   6 0.001  50.58  CR
MN     0.005( 2.709)          0.007( 0.009)  32  31*  0.033( 1.903)       0.040( 0.029)  31  29 0.001  10.66  MN
FE     0.034( 4.253)          0.106( 0.266)  32  30*  0.249( 2.072)       0.457( 0.710)  31  29 0.006  11.30  FE
NI     0.002( 3.233)          0.003( 0.004)  32  14*  0.011( 2.549)       0.016( 0.015)  31  12 0.001  27.30  NI
CU     0.006( 2.439)          0.000( 0.000)  32  31*  0.041( 2.027)       0.050( 0.027)  31  29 0.001  25.30  CU
ZN     0.012( 2.100)          0.016( 0.009)  32  31*  0.000( 2.097)       0.122( 0.144)  31  30 0.001  10.77  ZN
BR     0.040( 2.060)          0.050( 0.030)  32  32*  0.291( 1.650)       0.333( 0.196)  31  31 0.002   7.16  BR
PB     0.119( 2.247)          0.155( 0.103)  32  32*  0.850( 1.560)       0.944( 0.439)  31  31 0.009   6.90  PB
SE     0.001( 1.770)          0.001( 0.000)  32   0*  0.009( 2.423)       0.013( 0.015)  31   0 0.000   0.00  SE
AS     0.003( 1.405)          0.003( 0.001)  32   2*  0.022( 1.915)       0.027( 0.010)  31   2 0.005  70.65  AS
CD     0.010( 1.396)          0.011( 0.005)  32   1*  0.074( 2.052)       0.097( 0.004)  31   0 0.021  69.61  CD
BA     0.070( 1.595)          0.000( 0.061)  32   1*  0.406( 2.159)       0.663( 0.634)  31   0 0.152  44.45  BA
MASS  12.036( 2.694)         16.174( 9.012)  32  31*100.000( 1.002)     100.000( 0.000)  31  31 0.514   4.53  MASS
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Table 6.1.6b Average Concentrations at Carus, Background Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE CONCENTRATION AVERAGES AT SITE 6
COMPOSITE YEAR    FREQUENCIES

    ***************UG/M3****************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
     GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)         ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------
 VC     5.632( 2.115)          7.153( 4.774)  31  31* 21.700( 1.399)        22.990( 0.700)  31  31 1.032  14.90  VC
 NVC    0.691( 3.350)          1.073( 0.756)  31  29*  2.665( 3.442)         4.573( 4.422)  31  29 0.265  25.01  NVC
 NO3    1.987( 2.905)          2.984( 2.314)  32  32*  7.753( 1.759)         8.899( 4.440)  32  32 0.194   8.33  NO3
 SO4    1.461( 2.622)          2.042( 1.347)  32  32*  5.700( 1.611)         6.293( 2.729)  32  32 0.130   7.64  SO4
 F      0.034( 2.901)          0.051( 0.040)  32  26*  0.131( 1.756)         0.140( 0.064)  32  26 0.009  17.50  F
 NA     0.419( 2.407)          0.650( 0.929)  32  32*  1.636( 2.625)         3.039( 5.463)  32  32 0.032   5.29  NA
 MG     0.133( 3.206)          0.225( 0.201)  32  24*  0.520( 2.077)         0.672( 0.570)  32  24 0.056  20.29  MG
 AL     0.687( 3.689)          1.276( 1.313)  32  32*  2.679( 1.927)         3.210( 1.818)  32  32 0.055   4.01  AL
 SI     1.884( 4.053)          3.629( 3.391)  32  32*  7.353( 2.120)         9.125( 5.031)  32  32 0.176   5.10  SI
 S      0.400( 3.644)          0.649( 0.454)  32  31*  1.559( 2.145)         1.086( 0.942)  32  31 0.035   7.94  S
 CL     0.568( 2.250)          0.930( 1.585)  32  32*  2.216( 3.540)         5.317( 9.421)  32  32 0.046   5.34  CL
 K      0.212( 2.640)          0.313( 0.262)  32  32*  0.827( 1.467)         0.890( 0.391)  32  32 0.016   5.79  K
 CA     0.270( 2.549)          0.404( 0.325)  32  32*  1.007( 1.448)         1.156( 0.394)  32  32 0.019   4.06  CA
 TI     0.046( 4.065)          0.090( 0.085)  32  32*  0.179( 2.164)         0.227( 0.137)  32  32 0.005   8.95  TI
 V      0.003( 3.650)          0.005( 0.004)  32  31*  0.010( 2.177)         0.013( 0.007)  32  19 0.000   9.76  V
 CR     0.002( 3.151)          0.004( 0.003)  32  22*  0.009( 2.177)         0.012( 0.009)  32  20 0.001  21.90  CR
 MN     0.015( 3.642)          0.025( 0.021)  32  31*  0.058( 1.880)         0.067( 0.030)  32  31 0.001   6.72  MN
 FE     0.373( 4.016)          0.716( 0.655)  32  32*  1.455( 2.112)         1.816( 1.043)  32  32 0.034   4.98  FE
 NI     0.002( 3.632)          0.005( 0.006)  32  19*  0.009( 2.401)         0.012( 0.009)  32  12 0.001  21.53  NI
 CU     0.023( 2.630)          0.033( 0.020)  32  32*  0.089( 2.567)         0.133( 0.124)  32  32 0.002   9.19  CU
 ZN     0.020( 1.770)          0.024( 0.013)  32  32*  0.079( 1.822)         0.095( 0.065)  32  32 0.001   6.55  ZN
 BR     0.054( 1.832)          0.063( 0.035)  32  32*  0.211( 1.876)         0.263( 0.200)  32  32 0.003   4.64  BR
 PB     0.162( 2.155)          0.286( 0.130)  32  32*  0.632( 1.557)         0.695( 0.313)  32  32 0.011   5.00  PB
 SE     0.001( 1.071)          0.001( 0.000)  32   1*  0.004( 2.650)         0.007( 0.000)  32   0 0.002  49.98  SE
 AS     0.003( 1.670)          0.003( 0.002)  32   2*  0.011( 2.001)         0.013( 0.009)  32   2 0.005  56.91  AS
 CD     0.009( 1.291)          0.010( 0.003)  32   0*  0.036( 2.204)         0.050( 0.047)  32   0 0.000   0.00  CD
 BA     0.060( 1.445)          0.065( 0.034)  32   0*  0.234( 2.316)         0.337( 0.330)  32   0 0.000   0.00  BA
 MASS  25.627( 2.133)         32.281(19.650)  32  32*100.000( 1.003)       100.000( 0.000)  32  32 0.511   2.41  MASS
-------------------------------------------------------------------------------------------------------------
```

carbon concentration average uncertainties can be evaluated on these 24 hour samples and are consistent with the analytical errors of Table 4.7.10.1 and the hi-vol sampler volume uncertainty stated in section 4.7.5.

The average percent composition of the Portland aerosol appears very similar over the entire region, at least on an annual average basis. The average total suspended particulate is composed of approximately 20% volatilizable carbon, 9-12% silicon, 4-8% sulfate, 4-9% nitrate, 3-5% nonvolatilizable carbon, 2-3% sodium, 3-5% chlorine, 3-4% aluminum, 2-5% iron, .5-2% calcium, and .8-1.8% lead. The average concentrations of other measured components are less than 1%. In the fine particulate mode, the composition is different with approximately 25-40% volatilizable carbon, 8-16% sulfate, 5-9% nitrate, 4-6% nonvolatilizable carbon, 3-4% chlorine, 1-4% sodium, 1-2% silicon, .5-1.5% iron, and .5-2.5% lead with other measured constituents less than 1%. The similarity of the measurements at site 3 to those of the other samplers lessens the concern expressed in section 4.1 about its elevated location.

Though the percent compositions seem somewhat uniform over the region, the urban absolute concentration averages are approximately twice those of the background receptors, confirming a definite anthropogenic source of much of the mass. The background site averages contain specimens both upwind and downwind of the AQMA, so a diluted urban aerosol is probably affecting their percent compositions. A true assessment of the background aerosol averages can be obtained from the regime or flow pattern averages in which the background site was upwind of Portland.

Using the results of section 3.1 in a qualitative manner it is possible to identify certain source types which will generally appear in a chemical element balance. First, the high amounts of Al, Si, Ca, Ti and Fe which occur in the total, but not in the fine averages strongly indicate a geological component at all sites. Similarly, the presence of Na and Cl implicate marine aerosol as a likely contributor, though the amount of Cl exceeds the Cl/Na ratio of one chosen in section 3.1.12. This ratio could be different, or another source of Cl, such as some form of vegetative burning or automobile exhaust, could exist.

The Pb and Br presence and its large average in the downtown area at site 3 implicates auto exhaust. V and Ni concentrations are small, but detectable nonetheless and reach their maximum average concentrations in the industrial area, site 2, where many residual oil boilers exist. Similarly, Cr, Mn and Fe demonstrate higher concentrations at site 2 in both size modes; the steel electric arc and ferromanganese furnaces are closer to this receptor than to any of the others.

Large portions of the aerosol consist of SO_4^{-2}, NO_3^-, and volatilizable carbon, particularly in the fine particulate mode, and the possibility of secondary formation of these species surely exists.

Finally, it should be noted that Se is rarely found in the ambient measurements, and when it is its concentration is close to detection limits. Since this constituent was found in glass furnace emissions, it seems that this source is less likely to be found significant in a chemical element balance.

This appraisal of sources is not meant to be a pre-selection of source types; as the following section will show, all source types which have a unique chemical fingerprint will be included in the master source matrix of the chemical element balance. Rather this examination of the average chemical concentrations in comparison with the source composition matrix provides a rough indication of the directions in which those bal-balances will lead.

The PACS ambient chemical characterization data set seems adequate for input to the chemical element balance receptor model. The variability of each concentration measurement far exceeds the variability due to analytical error in most cases. Selenium, As, Cd and Ba often exhibit values below detection limits. As, Cd and Ba were not detected in appreciable quantities in any of the source tests, so their measurement is probably unnecessary; the Se measurement is of use, even though it is below minimum detectable limits, because of its unique presence in one of the source type emissions. Magnesium concentrations often occurred below minimum detectable limits, but this constituent is not particularly unique to any source type. If its analytical technique could be improved, it would be a worthwhile measurement, but as long as Mn is also present in the sample, neutron activation analysis with short irradiations is not appropriate.

The average percentage uncertainties should be improved for non-volatilizable carbon and fluoride in future studies. The uncertainties of the remaining measurements are probably underestimated on an absolute basis, but should be fairly close on a relative basis as they include most of the possible variation which can take place between the analyses of separate samples. The extensive intermethod comparisons add credence to the quality of the data set.

With these observations about the ambient data set complete, the task turns to the application of the chemical element balance receptor model to it.

6.2 PERFORMING THE CHEMICAL ELEMENT BALANCE

Over 1700 individual chemical element balances were produced by the PACS, primarily by two people working over a period of 2.5 weeks. Each final balance resulted from an average of five trial balances with different combinations of sources and chemical concentrations. This section describes how such a gargantuan task of data management and interpretation was accomplished by so few people in such a short period of time.

The key to the entire system is the interactive computer program *CALCEB. This routine provides a number of functions which can be invoked by the user to perform various complicated tasks with a single command. These tasks, which are presented with their command mnemonics in Table 6.2.1, can be strung together within the *CALCEB routine and the whole set can be executed with a single command. This hierarchy makes normal operations simple enough to train any user, yet still provides flexibility for special cases such as missing or incorrect data.

At present the routine is oriented toward applications of the chemical element balance receptor model, but future generations could easily incorporate enrichment factor, time series correlation and multivariate receptor models as well. The interactive mode is far superior to batch processing in that the researcher can test many variations and obtain nearly instantaneous response. He can develop a "feeling" for his data and make them much more than just a large set of numbers.

Table 6.2.1 Command Summary of the Computer Program *CALCEB

HELP - LISTS THESE COMMANDS
DATE - SETS INTENSIVE ANALYSIS DATE
BSITE - SETS BACKGROUND SITE
USITE - SETS URBAN SITE
BSEQ - SETS BACKGROUND SEQUENCE
USEQ - SETS URBAN SEQUENCE
GBACK - GETS DATA FOR BACKGROUND SITE
GURB - GETS DATA FOR URBAN SITE
BCON - SET BACKGROUND OPERATION CONCENTRATIONS
UCON - SET URBAN OPERATIONS CONCENTRATIONS
BCRS - SET BACKGROUND COARSE CONCENTRATIONS
UCRS - SET URBAN COARSE CONCENTRATIONS
SBACK - SUBTRACT BACKGROUND FROM URBAN
AEL - ADD AN ELEMENT TO THE FIT
DEL - DELETE AN ELEMENT FROM THE FIT
ASOURC - ADD A SOURCE TO THE FIT
DSOURC - DELETE A SOURCE FROM THE FIT
CEB - PERFORM CEB, EFFECTIVE VARIANCE
CEBOWL - PERFORM CEB, OWLS
PINFO - PRINT CURRENT STATUS ON SCREEN
PBACK - PRINT BACKGROUND DATA ON SCREEN
PURB - PRINT URBAN DATA ON SCREEN
WSUM - WRITE SOURCE SUMMARY TO HDCPY
WDATA - WRITE ENTIRE DATA TO HDCPY
WDSK - WRITE URBAN DATA BACK TO DISK
INIT1 - INITIALIZE FITTING ELEMENTS AND SOURCES
SIZE - SET PARTICLE SIZE FRACTION
CALCON - GET CALCULATED CONCENTRATIONS
HELP!!!! - WHEN ALL ELSE FAILS
RESUM - RESUME AUTOFIT
AUTOFIT - PERFORM CEBS AUTOMATICALLY
EXIT - CLOSE FILES AND LEAVE
CEDIT - EDIT CONCENTRATIONS
SEDIT - EDIT SOURCES
FCEDIT - EDIT CONCENTRATION FLAGS
FMEDIT - EDIT METHOD FLAGS
BSOURC - FORM BACKGROUND SOURCE COMPOSITION

An individual specimen is identified by the input to the DATE, USITE/BSITE, SIZE, and USEQ/BSEQ commands. The chemical composition data is retrieved from disk storage by GURB/GBACK, placed in internal operations arrays by the UCON/BCON command, and displayed on the cathode ray terminal by the PURB/PBACK commands. Since source characterizations were carried out on the fine and coarse fractions rather than on the fine and total portions of the aerosol, and because major source contributions differ between these two modes, the contents of the operations array for total concentrations can be replaced with concentrations in the coarse particle mode (by subtraction of fine from total) by the UCRS/BCRS command. All uncertainties are propagated by standard addition in quadrature of uncorrelated errors (Bevington, 1969).

The U and B prefixes of several commands stand for urban and background, respectively, and provide the opportunity to include the uncontrollable upwind "background" contribution to the aerosol in the airshed. A background receptor is selected on the basis of the sampling period's flow pattern classification (see section 3.4) with BSITE and BSEQ, and its concentration values reside in a separate internal array. They can be subtracted from the urban values with the SBACK command and the chemical element balance is performed on this difference. If the background receptor values are truly representative then this should eliminate the portion of the concentrations in the urban area which cannot be controlled.

This was attempted at all sites for several days, and it provided reasonable results in the fine particulate mode. The marine and soil components were reduced substantially while the auto and oil combustion source types experienced only a small diminuation.

In the coarse particulate mode, however, success with this technique was minimal. On several days the background masses of soil-related constituents, which compose the major fraction of the mass in the coarse mode, exceeded the values at the urban sites. It may be that this portion is more locally generated and that measurements taken many miles away cannot be compared with those in the urban area. The use of SBACK was abandoned in the PACS.

Another approach to the inclusion of background aerosol is to insert it into the chemical element balance as a specific source type, its fractional composition being identical to that of the upwind background specimen. BSOURC calculates these fractions and places them in the master source matrix for possible inclusion in the least squares fit. Trials in this mode proved it infeasible because the background aerosol is a linear combination of the other source types to begin with. When these were added to the fit with the background source many matrix inversions could not take place, convergence was difficult to attain, and the results were uninterpretible. The PACS did not pursue this option further.

The background contribution was handled by treating both background receptors (sites 1 and 6) as urban sites and performing chemical element balances on the concentrations measured there with the same source matrix determined for the urban area. Source contributions to the urban specimens were then associated with those of the appropriate upwind background sites and output together in the form of Table 6.2.3. Thus a direct comparison of relative source contribution magnitudes can be easily made for control purposes. This format will be discussed in greater detail shortly.

Table 6.2.2 Example of PACS Data Summary

```
COARSE  PARTICULATE FRACTION

FILTER IDS  FINE: H1980    TOTAL:
DATE: 78 124 SITE: 3 SEQUENCE: 7
UPWIND BACKGROUND SITE: 1 SEQUENCE: 4
SITE 3 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: F/C BACKGROUND: _/_
SITE 1 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: F/C BACKGROUND: _/_
REGIME:  2

EFFECTIVE VARIANCE FITTING.  REDUCED CHI SQUARE:   2.165 DEGREES OF FREEDOM:  9
CODE SOURCE FLG     UG/M3               %
------------------------------------------------------------------------------------------
 3   UDUST   *  54.691+- 1.773   74.580+- 2.679
 4   AUTPB   *   2.829+- 0.572    3.858+- 0.782
 5   RDOIL   *   0.264+- 0.076    0.360+- 0.104
 6   VBRN1   *   3.871+- 1.442    5.278+- 1.968
11   ALPRO   *   1.766+- 0.925    2.408+- 1.262
13   FERMN   *   0.126+- 0.052    0.172+- 0.071
17   NO3     *   1.321+- 0.315    1.801+- 0.431
18   SO4     *   1.364+- 0.532    1.859+- 0.725
19   VC      *   7.567+- 4.546   10.319+- 6.201
------------------------------------------------------------------------------------------
TOTAL:          73.797+- 5.240  100.635+- 7.314

     SPE FIT QA    COARSE SUSPENDED PARTICULATE  ** LESS BACKGROUND   CALCULATED        RATIO
CODE CIE FLG FLG        UG/M3          PERCENT   **      UG/M3          UG/M3
------------------------------------------------------------------------------------------
  1  VC   *          13.122+- 4.345  17.894+- 5.932 **  13.122+- 4.345  13.122+- 1.045  1.000+-0.341  VC
  2  NVC  *           1.660+- 0.072   2.263+- 1.198 **   1.660+- 0.072   1.129+- 0.447  0.680+-0.447  NVC
  3  NO3  *           1.564+- 0.257   2.132+- 0.352 **   1.564+- 0.257   1.564+- 0.160  1.000+-0.196  NO3
  4  SO4  *           1.665+- 0.509   2.270+- 0.695 **   1.665+- 0.509   1.665+- 0.140  1.000+-0.318  SO4
  5  F    *           0.036+- 0.017   0.049+- 0.023 **   0.036+- 0.017   0.079+- 0.051  2.194+-1.765  F
  6  NA   *           0.965+- 0.041   1.316+- 0.059 **   0.965+- 0.041   1.038+- 0.051  1.075+-0.070  NA
  7  MG               0.858+- 0.122   1.168+- 0.167 **   0.858+- 0.122   0.898+- 0.079  1.047+-0.177  MG
  8  AL   *    >      4.790+- 0.163   6.532+- 0.244 **   4.790+- 0.163   4.251+- 0.394  0.887+-0.080  AL
  9  SI   *          14.549+- 0.532  19.840+- 0.780 **  14.549+- 0.532  15.377+- 0.822  1.057+-0.060  SI
 10  S                0.555+- 0.140   0.757+- 0.191 **   0.555+- 0.140   0.519+- 0.049  0.936+-0.252  S
 11  CL   *    >>     0.330+- 0.045   0.450+- 0.061 **   0.330+- 0.045   0.321+- 0.065  0.974+-0.236  CL
 12  K    *           0.535+- 0.027   0.729+- 0.038 **   0.535+- 0.027   0.603+- 0.032  1.126+-0.082  K
 13  CA   *           2.029+- 0.073   2.766+- 0.109 **   2.029+- 0.073   1.738+- 0.122  0.857+-0.068  CA
 14  TI   *           0.400+- 0.016   0.545+- 0.023 **   0.400+- 0.016   0.554+- 0.090  1.385+-0.252  TI
 15  V    *           0.026+- 0.002   0.036+- 0.003 **   0.026+- 0.002   0.025+- 0.003  0.933+-0.145  V
 16  CR               0.026+- 0.002   0.035+- 0.003 **   0.026+- 0.002   0.025+- 0.009  0.981+-0.373  CR
 17  MN   *           0.083+- 0.004   0.113+- 0.006 **   0.083+- 0.004   0.081+- 0.008  0.978+-0.103  MN
 18  FE   *           3.546+- 0.132   4.835+- 0.195 **   3.546+- 0.132   3.218+- 0.160  0.907+-0.056  FE
 19  NI   *           0.022+- 0.003   0.029+- 0.005 **   0.022+- 0.003   0.023+- 0.004  1.002+-0.241  NI
 20  CU               0.052+- 0.004   0.071+- 0.005 **   0.052+- 0.004   0.025+- 0.007  0.472+-0.135  CU
 21  ZN               0.105+- 0.009   0.143+- 0.013 **   0.105+- 0.009   0.072+- 0.021  0.688+-0.206  ZN
 22  BR   *           0.221+- 0.023   0.301+- 0.031 **   0.221+- 0.023   0.150+- 0.049  0.680+-0.230  BR
 23  PB   *           0.620+- 0.066   0.846+- 0.091 **   0.620+- 0.066   0.769+- 0.110  1.239+-0.232  PB
 24  SE        *      0.006+- 0.005   0.009+- 0.006 **
 25  AS                   <   0.016       <   0.022 **
 26  CD                   <   0.041       <   0.055 **
 27  BA                   <   0.257       <   0.350 **
------------------------------------------------------------------------------------------
SITE 3 LOVOL/HIVOL, UG/M3:  FINE  42.6+- 0.6/ 42.1+- 1.5 COARSE  73.3+- 1.1/ 97.9+-15.7 TOTAL 115.9+- 0.9/140.0+-15.7
```

Table 6.2.3 Example of PACS Source Summary

```
         ***SOURCE CONTRIBUTION SUMMARY***
DATE: 78 124 SITE: 3 SEQUENCE: 7
UPWIND BACKGROUND SITE: 1 SEQUENCE: 4
SITE 3 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: F/C BACKGROUND: _/_
SITE 1 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: F/C BACKGROUND: _/_
REGIME:  2

HIVOL FINE AT SITE 1  23.7+- 1.0 UG/M3     HIVOL TOTAL AT SITE 1  55.0+- 6.1 UG/M3
HIVOL FINE AT SITE 3  42.1+- 1.5 UG/M3     HIVOL TOTAL AT SITE 3 140.0+-15.7 UG/M3

SOURCE TYPE                  FINE                              COARSE                               TOTAL
-------------------------------------------------------------------------------------------------------------------------
                    UG/M3           %                 UG/M3           %                 UG/M3           %
BACKGROUND      30.336+- 0.511  71.247+- 1.612    24.281+- 0.806  33.112+- 1.313    54.617+- 0.724  47.120+- 0.731
   PRIMARY
      MARIN      0.463+- 0.056   1.087+- 0.133     0.291+- 0.166   0.396+- 0.226     0.754+- 0.175   0.650+- 0.151
      CDUST      0.972+- 0.130   2.282+- 0.325    11.352+- 0.749  15.480+- 1.049    12.323+- 0.762  10.632+- 0.663
      AUTPB      1.512+- 0.209   3.550+- 0.494     0.620+- 0.149   0.845+- 0.203     2.131+- 0.257   1.839+- 0.222
      RDOIL      0.305+- 0.050   0.716+- 0.117     0.145+- 0.044   0.198+- 0.061     0.450+- 0.067   0.388+- 0.058
      KRAFT      0.000+- 0.000   0.000+- 0.000     1.020+- 1.555   1.060+- 2.120     1.020+- 1.555   0.671+- 1.341
      SULFT      0.614+- 0.193   1.443+- 0.454     0.000+- 0.000   0.000+- 0.000     0.614+- 0.193   0.530+- 0.167
      ALPRO      0.298+- 0.114   0.699+- 0.269     0.651+- 0.396   0.888+- 0.541     0.949+- 0.412   0.810+- 0.356
      STEEL      0.000+- 0.000   0.000+- 0.000     0.239+- 0.056   0.326+- 0.077     0.239+- 0.056   0.206+- 0.048
      FERMN      0.103+- 0.010   0.241+- 0.025     0.000+- 0.000   0.000+- 0.000     0.103+- 0.010   0.089+- 0.009
      CARBF      0.000+- 0.000   0.000+- 0.000     2.904+- 0.504   3.960+- 0.690     2.904+- 0.504   2.505+- 0.435
   SECONDARY
      NO3        1.895+- 0.232   4.451+- 0.549     1.401+- 0.288   1.911+- 0.393     3.297+- 0.370   2.844+- 0.320
      SO4        6.747+- 0.844  15.847+- 1.996     2.091+- 0.835   2.851+- 1.140     8.838+- 1.107   7.625+- 1.026
      VC         5.979+- 0.984  14.042+- 2.322     3.415+- 1.853   4.657+- 2.520     9.394+- 2.090   8.105+- 1.812
      NVC        1.266+- 0.310   2.973+- 0.731     0.639+- 0.565   0.871+- 0.771     1.905+- 0.645   1.643+- 0.556

URBAN           42.579+- 0.644 100.000+- 2.130    73.332+- 1.135 100.000+- 0.164   115.911+- 0.935 100.000+- 0.807
   PRIMARY
      UDUST      0.974+- 0.329   2.287+- 0.773    54.691+- 1.773  74.580+- 2.679    55.664+- 1.803  48.024+- 1.603
      AUTPB      5.305+- 0.712  12.460+- 1.682     2.829+- 0.572   3.858+- 0.782     8.134+- 0.913   7.018+- 0.790
      RDOIL      0.783+- 0.125   1.840+- 0.295     0.264+- 0.076   0.360+- 0.104     1.047+- 0.147   0.903+- 0.127
      VBRNI      7.762+- 2.040  18.229+- 4.790     3.871+- 1.442   5.278+- 1.960    11.632+- 2.498  10.035+- 2.156
      KRAFT      0.684+- 0.194   1.605+- 0.456     0.000+- 0.000   0.000+- 0.000     0.684+- 0.194   0.590+- 0.167
      SULFT      0.340+- 0.124   0.797+- 0.291     0.000+- 0.000   0.000+- 0.000     0.340+- 0.124   0.293+- 0.107
      ALPRO      0.000+- 0.000   0.000+- 0.000     1.766+- 0.925   2.408+- 1.262     1.766+- 0.925   1.523+- 0.798
      FERMN      0.091+- 0.056   0.213+- 0.132     0.126+- 0.052   0.172+- 0.071     0.217+- 0.077   0.187+- 0.066
   SECONDARY
      NO3        2.477+- 0.360   5.817+- 0.850     1.321+- 0.315   1.801+- 0.431     3.798+- 0.479   3.276+- 0.414
      SO4        5.809+- 0.679  13.644+- 1.609     1.364+- 0.532   1.859+- 0.725     7.173+- 0.863   6.188+- 0.746
      VC         7.912+- 2.352  18.581+- 5.530     7.567+- 4.546  10.319+- 6.201    15.479+- 5.110  13.354+- 4.417
      NVC        1.325+- 0.404   3.113+- 1.130     0.000+- 0.000   0.000+- 0.000     1.325+- 0.404   1.143+- 0.410
-------------------------------------------------------------------------------------------------------------------------
CALC. MASS      33.461+- 3.347  78.586+- 7.950    73.797+- 5.240 100.635+- 7.314   107.258+- 6.210  92.535+- 5.416
MASS (LOVOL)    42.579+- 0.644  36.734+- 0.629    73.332+- 1.135  63.266+- 1.104   115.911+- 0.935 100.000+- 1.141
```

Source types to be included in the fit are added and deleted by the ASOURC and DSOURC commands, respectively. Each source type is represented internally by a number code (it appears with the source mnemonic in Table 6.2.2) which is input by the operator to add or delete a source type. Similarly, AEL and DEL add and delete chemical concentrations.

The least squares fit to the chemical element balance equations with any designated combination of sources and concentrations is carried out in the effective variance mode when the CEB command is given; the ordinary weighted least squares fit is executed by CEBOWL.

Calculated concentrations based on the sources determined by the fit and the given source compositions are computed via eq. 3.3.6 by the CALCON segment; uncertainties in the a_{ij} and C_i are propagated by standard addition in quadrature. Measured ambient concentrations, calculated concentrations, the ratio of calculated to measured and all corresponding uncertainties are displayed with the calculated source contributions in a format similar to that of Table 6.2.2 on the data terminal screen by the PURB command. Several trials can be made before a hard copy of the most acceptable fit is reproduced in the format of Table 6.2.2 by the WDATA command. A source contribution summary for fine, coarse and total particulate with that of the corresponding upwind background receptor is written for each sampling sequence in the format of Table 6.2.3 by the WSUM command after chemical element balances have been performed on the fine and coarse fractions of that period. Calculated source contributions are also stored on disk with the ambient concentrations for future manipulations, such as averaging and visibility regression analysis, by WDSK.

The output formats are structured to contain as much information as possible about the source contributions, the ambient concentrations and the least squares fit. Data summary sheets, Table 6.2.2, were produced for each sampling sequence at each receptor and for the 24 hour average concentrations obtained by summing the mass loadings and sampling volumes of all sequential samples taken during a day and calculating the chemical concentrations. Volatilizable and nonvolatilizable carbon concentrations measured on the fine and total 24 hour hi-vol samples were associated with these concentrations and do not appear in the data sets of the sequential specimens. Separate summaries for fine, coarse and total particulate were made, the coarse concentrations being obtained by subtraction of fine from total and the total source contributions resulting from the addition of the fine and coarse portions; all uncertainties have been propagated. Filter identification codes are reported for possible quality assurance purposes. The site numbers correspond to those in Table 4.1.1. Sequence refers to the portion of the day during which the sample was taken (for all sites except site 3 the sequence numbers correspond to the times 1: 0000-0000, 2: 0000-1600, 3: 1600-2400, 4: 0000-2400. For site 3, 1: 0000-0400, 2: 0400-0800, 3: 0800-1200, 4: 1200-1600, 5: 1600-2000, 6: 2000-2400, 7: 0000-2400). The upwind background specimen associated with the data is identified so that it may be referred to if a comparison is desired.

Method flags refer to special situations. The field flags, mass flags and their meanings appear in Table 5.5.2 and are meant to alert the person interpreting the data to deviations in the field sampling or weighing operations which might lead to spurious conclusions. Flags for both the fine and total specimens are presented because both enter into the computation of the coarse particulate concentrations. The size flag refers to the size fraction of the chemical concentrations on which the chemical element balance has been performed; it is always F for the fine particulate concentrations, and it is usually C for the coarse particulate fraction. Sometimes when the fine concentrations were not available, the balance was performed on the total particulate concentrations, and the lower flag indicates this with a T. The background flag records which background concentrations have been subtracted from the urban values prior to performance of the chemical element balance, 1 for site one and 6 for site 6. No background was subtracted from PACS specimens so this flag remains blank in all summaries.

A similar set of flags for the upwind background site is reported and is important when the background subtraction option is used.

The meteorological regime is the 24 hour classification into which the day falls and refers to Table 4.2.2. As noted in section 4.2 these classifications are somewhat subjective. The flow pattern number serves as the basis for choosing the upwind background site and is referenced in Table 3.4.1 and Figures 3.4.1 to 3.4.6. No flow pattern classification exists for the 24 hour concentrations and upwind background sites were assigned on the basis of regime classification, site one for regimes 1&7, 8, and 9 and site 6 for regimes 5&4, 3 and 2.

The type of least squares fit is reported; for all PACS samples the effective variance was used. The χ^2_{n-p} and number of degrees of freedom associated with the fit are consistent with eq. 3.3.5.

Source mnemonics appear in Tables 3.1.12.2a&b and the calculated source contributions, their uncertainties and their percentage of the measured mass loading are listed; all source types which do not appear can be considered to have contributed nothing to the ambient concentrations. These contributions are summed to provide the total calculated mass loading and the fraction of the measured mass accounted for by the calculated source contributions. The uncertainty of this total is the square root of the summed squares of the individual, calculated source contribution uncertainties. As pointed out in sections 2.2 and 3.2, this method of error propagation is not entirely correct because the errors are correlated; however, examination of the off-diagonal elements of matrix 3.2.18 in several cases showed them to be often an order of magnitude less than the diagonal elements, making this approximation a reasonable one.

Chemical species quantified by the PACS for the specimen appear as $\mu g/m^3$ and as percent of the suspended particulate mass in the size range. The code number is the *CALCEB representation of that species. The fit flag column contains an asterisk if that concentration was included in the least squares fit (this flag also appears with the source types). The QA quality assurance flags are defined in Table 5.5.2 and express the degree of confidence that the value should be given.

The concentrations in the LESS BACKGROUND columns have background concentrations subtracted from them if the background method flag is other than blank. Otherwise the ambient concentrations are repeated. Calculated concentrations and the ratios of calculated to measured concentrations appear in the last two columns of the summary. At the bottom the mass loadings in each size mode for the sampling period being treated are compared with the corresponding 24-hour hi-vol mass loadings.

The source summary in Table 6.2.3 abbreviates and combines information from several of the data summaries for a quick assessment of source contributions during a period and a comparison with likely background aerosol contributions. All percentages are taken with respect to the urban mass loading within the size range so that the approximate fraction of the urban loading due to source contributions present at the background site can be estimated. The percentages reported for the measured mass on the bottom line are taken with respect to the total suspended particulate.

Primary source types and their compositions chosen for inclusion in the chemical element balance appear in Tables 3.1.12.2a & b for the fine and coarse particulate modes, respectively. Since SO_4^{-2} and NO_3^-, volatilizable carbon (VC), and non-volatilizable carbon (NVC) concentrations experience contributions from other than these sixteen sources, particularly from secondary aerosol formation in the first three cases, they were included as single constituent source types in the source matrix. This is accomplished by setting all source composition coefficients, a_{ij}, equal to 0 with the exception of the coefficient of the single constituent which is set equal to unity. Any measured SO_4^{-2}, NO_3^-, VC or NVC not accounted for by the other source types is ascribed to one of these single constituent source types, and in the cases of VC, SO_4^{-2}, and NO_3^-, an upper limit on the contribution due to secondary aerosol formation is made. Of course, primary sources not included in the balance could also be contributing to these concentrations, but Tables 3.1.12.2a & b contain most of the major emitters of these species, so, to the extent that the values in these tables are correct, the upper limit is a good approximation of the actual secondary aerosol contribution.

Chemical element balances were performed on each intensive analysis day in consecutive order. Background sites one and six were examined first so that the source contributions to their aerosols would appear on each source summary. These were followed by urban sites two through five. Twenty-four hour average concentrations were balanced first for the fine and coarse size modes and the final source/element fitting combination for each of these modes was retained by *CALCEB for the initial trial of the concentrations measured during sequence one. Reasoning that the most likely source set for the present sample is the one which contributed to the previous sample, each initial balance on a sequential specimen employed the final source/element set of the one before it.

All of this was accomplished by the command AUTOFIT, which, after a site and date are supplied by the operator, weaves its way through the operations listed in Table 6.2.1. AUTOFIT calls the data from disk for both the urban and background sites, sets up the internal arrays, obtains the coarse fraction, initializes the source/species fitting set, runs the chemical element balance, calculates the concentrations and ratios and displays the initial balance results on the screen. The operator then adds and deletes sources and elements and runs additional fits until he achieves one which satisfies him.

The command RESUM advances to the next size fraction or next sequential sample and the process is repeated. Data summaries and source summaries are automatically written at appropriate intervals and the calculated source contributions are written to disk when balances for the entire day have been completed. The operator can exit and spool out the hard copies or he can specify another site and/or date for examination.

The use of *CALCEB is an art and a skill as much as it is a science at the present time. It requires a good knowledge of the source type compositions in Tables 3.1.12.2a & b and how they interact with each other in the fitting procedure. Only working experience with ambient data and trials with different source/concentration combinations can truly convey the power and limitations of this method and illustrate the myriad of special cases. Certainly much research needs to be carried out to objectify what are at present somewhat subjective criteria.

Some feeling for the operation can be communicated, however, by following the reasoning through an element balance on the fine and coarse suspended particulate concentrations of a single sample and by summarizing some of the qualitative observations noted by the author and his colleague in the 1600+ chemical element balances they performed.

The data set chosen for this example is that of the 24-hour average at site 3 on January 24, 1978. This site and date yielded data like many others, making it good for illustrative purposes.

Several criteria for a good fit of source contribution values to ambient measurements can be stated. These are in the vein of section 3.3.

1. The calculated to measured concentration ratios should be close to unity, and at least within the range .5 to 2.0.
2. The calculated mass should approach, but not significantly exceed, the measured mass.
3. The χ^2_{n-p} should be minimized.

Tables 6.2.4a & b present the results of trial fits and the parameters specified in these criteria for the fine particulate concentrations. Tables 6.2.5a & b display the same for the coarse fraction.

It was also suggested in section 3.3 that if all source types and all concentrations were included in the initial balance, then sources which did not belong would automatically eliminate themselves. Fit 1 of Tables 6.2.4a & b for the fine particulate attempts this with most of the source types listed in Table 3.1.12.2a plus the four single constituent source types.

Notice that only sixteen out of a possible twenty source types are included; internal storage capacity of the PRIME 300 computer placed a limit of 16 fitting sources and 21 fitting concentrations on manipulations with *CALCEB. The routine could be restructured to accommodate a larger number, but it did not seem necessary to do so at the time these balances were made. Ambient concentration fits containing both continental dust and urban dust experienced the same difficulties as did the simulated data fits in section 3.3. Vegetative burns 1 and 2 could rarely be included in the same fit and ferromanganese contrib-

Table 6.2.4a Source Contribution Fits to the 24 hr. Average Fine Particulate Concentrations at Site 3 on January 24, 1978

	Concentration, $\mu g/m^3$							
	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6	Fit 7	Fit 8
χ^2_{n-p}	1.297	77.1	50.2	77.1	4.8	1.75	2.44	1.76
n-p	5	9	10	9	7	6	7	6
Source								
MARIN	-2.7±2.1	.64±.08	1.5±.2	.64±.08	.41±.06	.24±.07	-----	-----
UDUST	1.0±.6	2.3±.15	1.9±.17	2.3±.15	1.4±.14	1.1±.3	1.0±.4	.97±.33
AUTPB	5.2±.8	5.9±.7	4.7±.64	5.9±.7	6.6±.8	5.3±.7	5.1±.7	5.3±.7
RDOIL	.77±.13	.88±.14	5.6±.7	.88±.14	.76±.12	.79±.13	.86±.14	.78±.13
VBRN1	-----	-----	-----	-----	-----	6.5±2.0	11.2±2.3	7.8±2.0
VBRN2	15.5±8.9	-----	-----	-----	-----	-----	-----	-----
KRAFT	7.3±6.1	-----	-----	-----	-----	-----	-----	.68±.19
SULFT	10.9±7.5	-----	-----	-----	.45±.15	.37±.13	.34±.13	.34±.12
HOGFU	12.2±5.5	-----	-----	-----	-----	-----	-----	-----
ALPRO	-.03±.4	-----	-----	-----	-----	-----	-----	-----
STEEL	-.754±.6	-----	-----	-----	-----	-----	-----	-----
FERMN	.16±.38	-----	-----	-----	.14±.01	.10±.05	.081±.08	.091±.056
CARBF	-1.6±1.9	-----	-----	-----	-----	-----	-----	-----
NO_3	2.5±.52	2.9±.32	2.9±.3	2.9±.32	2.9±.3	2.5±.3	2.3±.4	2.5±.4
SO_4	5.0±4.2	6.3±.7	-----	-----	6.1±.7	6.1±.7	6.0±.7	5.8±.7
VC	5.2±7.4	12.0±2.1	12.3±2.2	12.0±2.1	11.8±2.2	8.7±2.3	6.0±2.5	7.9±2.3
NVC	.92±1.4	1.5±.4	1.5±.4	1.5±.4	1.5±.4	1.4±.5	1.2±.5	1.3±.5
CALC. MASS	39.9±17.0	32.5±2.4	30.4±2.4	26.2±2.3	32.1±2.4	33.0±3.3	34.1±3.7	33.5±3.3

Table 6.2.4b Calculated to Measured Concentration Ratios for Fits to the 24 hr. Average Fine Particulate at Site 3 on January 24, 1978

Species	QA Flag	Measured Concentration μg/m^3	Ratio, Calculated Concentration to Measured							
			Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6	Fit 7	Fit 8
VC		15.3±1.6	1.0±.4	1.0±.14	1.0±.14	1.0±.14	1.0±.14	1.0±.14	1.0±.14	1.0±.13
NVC		1.8±.4	1.0±.7	1.0±.23	1.0±.24	1.0±.23	1.0±.23	1.0±.25	1.0±.29	1.0±.26
NO_3		2.9±.2	1.0±.2	1.0±.11	1.0±.11	1.0±.11	1.0±.11	1.0±.11	1.0±.13	1.0±.12
SO_4		6.9±.3	1.0±.2	1.0±.10	.43±.10	.084±.017[a]	1.0±.10	1.0±.10	1.0±.10	1.0±.10
F		.09±.01	.73±.3	.005±.007[a]	.03±.01[a]	.005±.007[a]	.009±.008[a]	.008±.7[a]	.007±.1.2[a]	.007±.8[a]
NA		.19±.01	.29±2.0	1.7±.19	4.3±.64	1.7±.19	1.2±.13	1.0±.1	.68±.12	1.0±.1
MG		<.08	-6.5±13[a]	1.6±3.4[a]	2.5±6.8[a]	1.6±3.4[a]	1.1±2.4[a]	.75±1.8[a]	.42±1.3[a]	.52±1.4[a]
AL	>>	.19±.01	1.3±.5	1.5±.4	1.3±.3	1.5±.4	1.1±.27	1.3±.4	1.7±.5	1.4±.4
SI		.39±.02	.87±.34	1.5±.1	1.3±.1	1.5±.1	.98±.08	.89±.19	.98±.32	.87±.23
S		2.6±.1	.99±.2[a]	.89±.09[a]	.32±06[a]	.07±.01[a]	.88±.09[a]	.87±.09	.87±.09	.87±.08
CL	>>	.79±.03	2.3±1.3	.55±.11	.92±.20	.55±.11	.46±.1	.78±.14	.99±.22	.77±.16
K		.19±.01	3.0±10	.21±.02	.32±.04	.21±.02	.94±.24	.97±.2	1.0±.2	.98±.19
CA		.11±.01	1.4±4.5	1.3±.3	1.9±.4	1.3±.3	1.3±.3	1.6±.3	2.0±.4	1.7±.4
TI		.011±.001	1.5±1.3	1.5±.6	1.7±.6	1.5±.6	.94±.7	.72±.52	.71±.50	.67±.52
V		.028±.001	.94±.21	1.1±.2	6.9±1.5	1.1±.2	.94±.2	.97±.21	1.1±.2	.97±.21
CR		.004±.001	2.14±2.9	.34±.20[a]	.81±.36[a]	.34±.2[a]	.24±.18[a]	.21±.15[a]	.21±15[a]	.64±.28[a]
MN		.027±.001	1.05±1.6	.12±.04	.18±.04	.12±.04	1.0±.08	1.0±.3	1.1±.5	1.0±.4
FE		.227±.008	.84±.52	1.3±.2	1.7±.2	1.3±.2	1.1±.2	.94±.20	.96±.20	.96±.20
NI		.043±.002	1.08±.23	1.1±.25	7.0±1.6	1.1±.25	.96±.2	1.0±.2	1.1±.2	1.0±.2
CU		.033±.002	.77±.37	.17±.06[a]	.25±.06[a]	.17±.06[a]	.18±.06[a]	.33±.10[a]	.46±.15[a]	.37±.1[a]
ZN		.106±.004	1.08±.4	.25±.08[a]	.39±.11[a]	.25±.08[a]	.27±.08[a]	.22±.07[a]	.22±.07[a]	.23±.07[a]
BR		.419±.012	.67±.21	.71±.24	.58±.19	.71±.24	.79±.27	.65±.22	.63±.2	.65±.22
PB		.94±.02	1.1±.17	1.2±.2	.98±.15	1.2±.2	1.3±.2	1.1±.2	1.0±.2	1.1±.2
MASS		42.6±.6	.94±.40	.76±.06	.71±.06	.62±.06	.75±.06	.78±.08	.80±.09	.79±.08

[a] Concentration not included in the fit.

QA flag >> refers to Table 5.5.2 and indicates a discrepancy between two determinations of these values which is greater than 20%.

Table 6.2.5a Source Contribution Fits to the 24 Hour Average Coarse Particulate Concentrations at Site 3 on January 24, 1978

	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6
χ^2_{n-p}	4.63	4.21	3.43	2.67	2.50	2.17
n-p	9	10	9	8	9	9
SOURCE						
MARIN	.27±.12	.27±.12	.28±.12	-.18±.20	------	------
UDUST	56.9±1.7	56.9±1.7	55.2±1.8	56.2±1.8	55.7±1.7	54.7±1.8
AUTPB	3.1±.6	3.2±.6	3.2±.6	2.8±.6	2.8±.6	2.8±.6
RDOIL	.30±.08	.30±.08	.31±.08	.31±.08	.31±.08	.26±.08
VBRN1	------	------	------	5.6±2.4	4.3±1.5	3.9±1.4
ALPRO	------	------	------	------	------	1.8±.9
FERMN	------	------	.15±.04	.099±.062	.12±.05	.13±.05
NO^3	1.5±.3	1.5±.3	1.5±.3	1.2±.3	1.3±.3	1.3±.3
SO^4	1.4±.5	1.4±.5	1.4±.5	1.4±.5	1.4±.5	1.4±.5
VC	9.6±4.5	9.6±4.5	9.7±4.5	6.5±4.7	7.3±4.6	7.6±4.5
NVC	.65±.98	------	------	------	------	------
Calc. Mass	73.8±5.0	73.2±4.9	71.7±4.9	74.0±5.6	73.2±5 1	73.8±5.2

Table 6.2.5b Calculated to Measured Concentration Ratios for Fits to the 24 Hour Average Coarse Particulate at Site 3 on January 24, 1978

Specie	QA Flag	Measured Concentration μg/m³	Ratio, Calculated Concentration to Measured					
			Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6
VC		13.1±4.3	1.0±.3	1.0±.34	1.0±.34	1.0±.34	1.0±.34	1.0±.34
NVC		1.7±.9	1.0±.6	.61±.42	.60±.41	.71±.47	.68±.45	.68±.44
NO_3		1.6±.3	1.0±.2	1.0±.2	1.0±.2	1.0±.2	1.0±.2	1.0±.2
SO_4		1.7±.5	1.0±.3	1.0±.3	1.0±.3	1.0±.3	1.0±.3	1.0±.3
F		.036±.017	.13±.13[a]	.13±.13[a]	.14±.13[a]	.14±1.6[a]	.14±1.2[a]	2.2±1.8
NA		.97±.04	1.2±.07	1.2±.07	1.1±.07	1.0±.07	1.1±.07	1.1±.07
MG		.85±.12	1.0±.2[a]	1.0±.2[a]	1.0±.2[a]	1.0±.2[a]	1.0±.2[a]	1.0±.18[a]
AL	>	4.8±.16	.79±.09	.79±.09	.78±.09	.80±.09	.80±.09	.89±.09
SI		14.5±.5	1.1±.07	1.1±.07	1.1±.07	1.1±.07	1.1±.07	1.1±.07
S		.56±.14	.96±.26[a]	.96±.26[a]	.96±.26[a]	.95±.25[a]	.95±.25[a]	.94±.25[a]
CL	>>	.33±.05	.61±.15	.61±.15	.64±.16	.98±.3	.98±.3	.97±.24
K		.54±.03	1.1±.08	1.1±.08	1.1±.08	1.2±.08	1.1±.08	1.1±.08
CA		2.0±.07	.87±.07	.87±.07	.84±.07	.88±.07	.87±.07	.86±.07
TI		.40±.02	1.4±.3	1.4±.3	1.4±.3	1.4±.3	1.4±.3	1.4±.3
V		.026±.002	.98±.16	.98±.16	.97±.16	.98±.16	.98±.16	.93±.15
CR		.026±.002	1.0±.4[a]	1.0±.4[a]	.98±.4[a]	1.0±.4[a]	.99±.38[a]	.98±.37[a]
MN		.083±.004	.69±.08	.69±.08	.99±.09	.97±.12	.97±.11	.98±.10
FE		3.5±.132	.94±.06	.94±.06	.92±.06	.93±.06	.92±.06	.91±.06
NI		.022±.003	1.0±.24	1.0±.24	1.0±.24	1.0±.24	1.0±.25	1.1±.24
CU		.052±.004	.37±.13[a]	.37±.13[a]	.37±.13[a]	.46±.14[a]	.44±.14[a]	.47±.14[a]
ZN		.11±.01	.72±.22[a]	.72±.22[a]	.71±.21[a]	.70±.21[a]	.70±.21[a]	.69±.21[a]
BR		.22±.02	.74±.26	.74±.26	.74±.26	.67±.23	.67±.23	.68±.23
PB		.62±.07	1.4±.3	1.4±.3	1.4±.3	1.2±.2	1.2±.2	1.2±.2
Mass		73.3±1.1	1.00±.07	.98±.07	.98±.07	1.00±.08	1.00±.07	1.01±.05

[a] Concentration not included in the fit.

QA flags are referenced in Table 5.5.2.

utions often interfered with those of the steel electric arc furnace. With the uncertainties present on most source composition values, even dissimilar patterns can interact strongly with each other.

The large uncertainties associated with the carborundum source not only caused its calculated uncertainty to exceed its calculated source contribution, they also increased the uncertainties associated with other source contributions to the point where they could no longer be detected; this was particularly acute for the urban dust contribution. Carborundum was rarely entered as a source type. It was usually not needed because its major components, non-volatilizable carbon and silicon, were well accounted for by the single constituent NVC source and geological material, respectively.

The glass furnace, as mentioned in section 6.1, was not expected to make a substantial contribution because of the low Se content of the aerosol. It was included in a number of fits, but its contribution was usually ridiculously large and it grossly over-estimated the amount of ambient sulfate present.

Therefore, fit 1 was made with all reasonable source types which could be included together; it is not a good fit. Though criteria 2 and 3 are met, the calculated to measured ratios in Table 6.2.4b are not close to unity, even though their propagated uncertainties are large enough to encompass the .5-2.0 interval. The large contributions from the forest products industry seem out of proportion to the more commonly expected urban dust and automobile exhaust. The propagated uncertainties are high.

This type of fit was observed many times when most sources and concentrations were included. Often convergence of the iterative effective variance solution procedure could not be achieved. At other times a matrix inversion was impossible.

Some source types can almost always be expected and have relatively unique compositions; continental/urban dust, automobile exhaust, residual oil combustion, and marine aerosol are among these. The four single constituent source types, VC, NVC, SO_4^{-2}, and NO_3^-, can also be expected as a matter of policy. The results of an initial fit with these source types is presented in fit 2.

All concentrations except those for F, Mg, S, Cr, Cu and Zn were chosen as fitting species for these sources. No significant source of F exists aside from aluminum production, and F was added to the fit only when that source was also included. Magnesium concentrations were so often near or below minimum detectable limits that it made little difference whether they were included or not. The sulfur concentration duplicates the role of SO_4^{-2} making it unnecessary.

Chromium, copper and zinc were continually underestimated, with calculated to measured ratios of about .2 no matter what combination of sources was used. Sources of these species which have not been assessed must be making substantial contributions or the chemical concentrations in the source types which were quantified are incorrect. Copper is widely touted as an emission from the hi-vol sampler motor (King and Toma, 1975), and zinc has been ascribed to plating operations (Huntzicker and Davidson, 1975), surreptitious tire burning (Giaque, et al., 1974) or municipal incinerators (Kowalczyk, et al., 1978). The copper source is plausible, but inexcusable--it would seem a simple task to clean up hi-vol motor exhausts when element concentrations are to be measured.

Unaccounted for zinc has been observed in many areas and the tire burning and refuse incineration sources seem farfetched even in the areas where they have been suggested, let alone in Portland where there is no evidence that these activities are occurring. The consistent calculated Zn deficiency at background as well as urban sites intimates the possibility of geological fractionation similar to that of Al and Si described in section 3.1.10, and a close study of geologically dominated samples might back this up. Copper and zinc were excluded as fitting elements because of possible unknown sources.

Chromium could have been used as a fitting element for the steel electric arc furnace, but its concentration was often close to or below the detection limit and it was excluded from the fits. Its calculated to ambient ratio tipped the scales, however, when there was some question between the electric arc furnace and the ferromanganese furnace.

The results of this combination constitute fit 2 of Tables 6.2.4a & b. Notice that most uncertainties, on both the sources and on the ratios, have been reduced substantially. The urban dust and marine aerosol contributions become more prominent, as might be expected. The reduced chi square is large, however, and the ratios are not close to unity. Only 76% of the measured mass in this fine particulate sample is accounted for.

Before rectifying these deficiencies, it is worthwhile to examine the bahavior of the so-called single constituent source types, NO_3^-, SO_4^{-2}, VC and NVC. Their source contributions and uncertainties certainly changed between fit 1 and fit 2, but the ratios of their fitting concentrations remain equal to one. In fact, in all cases where a single constituent source and its concentration are included in the fit, the calculated to measured ratio is equal to one.

This should come as no surprise. The only constraint on the value of a single constituent source type contribution is that it fill in the difference between that portion of its corresponding concentration which is measured and that portion accounted for by other source types. Whatever that difference is, the single constituent source contribution will fill it exactly.

What is not so obvious is that the inclusion of a single constituent source type implicitly removes any influence of its corresponding chemical concentration from the fit. Fit 3 shows what happens when the sulfate source is removed as a fitting source, but SO_4^{-2} is retained as a fitting concentration. The effect of the SO_4^{-2} fitting concentration is easily seen in the six-fold increase of the residual oil combustion contribution. The remaining source contributions in fit 4, with both the SO_4^{-2} source and concentration lacking, are identical to those of fit 2, however.

An understanding of this effect is important because certain source types which are not thought of as single constituent (i.e. they have more than one a_{ij} not equal to zero) can behave just like the single constituent SO_4^{-2} source in fits 2-4. Several PACS source types listed in Tables 3.1.12.2a & b fall into this category.

The kraft mill, sulfite mill and carbide furnace emissions have significant contributions from Na, K, and Ca, respectively. Sulfate, nitrate, volatilizable carbon and non-volatilizable carbon will not be fitting concentrations if their single constituent sources are also present in the fit. Thus, even though these species constitute major portions of these three source types, they cannot be counted on to have any effect on their least squares calculated source contributions. When the kraft mill is added, any difference between the measured and calculated sodium concentration will be filled in by the kraft mill contribution, removing Na as a tracer for marine aerosol. Similarly, the inclusion of the sulfite mill and carbide furnace effectively remove potassium and calcium as fitting concentrations for other source types.

When one fitting concentration for a source remains, the chemical element balance is really being made in its tracer element mode outlined in section 2.2, and instead of the added verification provided by reasonable calculated to measured ratios for a number of species constituting a source type, one must rely on the value of only one concentration.

This progressive elimination of fitting elements due to single constituent source compositions argues against their inclusion in the initial trial of a chemical element balance. Sources with varied compositions, like urban/continental dust, marine background, residual oil combustion and leaded auto exhaust, should be used to obtain the first source contributions and calculated to measured concentration ratios, as was done in fit 2. Then, ratios which are low can be filled in by the single constituent source types on a case by case basis. The resulting source contributions of these source types should be viewed with great care, however, for they are subject to only one constraint, the difference between the measured and calculated value of each one's single constituent, and whether this difference is caused by analytical error or underestimation by another source contribution, the single constituent source type will fill in that gap. In removing a concentration from the fit, the single constituent source type may cause another source type which was not previously of the single constituent variety to turn into one.

With this caveat in mind, an examination of the concentration ratios of fit 2 (or of fit 4 for that matter) shows the K and Mn concentrations to be underestimated by the eight source types in the fit so far. A glance at Table 3.1.12.2a shows that the sulfite mill and the ferromanganese furnace are likely candidates to fill in the gap. Sure enough, the χ^2_{n-p} in fit 5 drops substantially and the K and Mn ratios are brought into line. Notice also that many other ratios, those for Al, Si, and Ti which were high in fit 5, have come closer to unity in fit 6. The urban dust contribution is no longer being fit to the Mn and K concentrations, its contribution has dropped by a factor of two, and the chemical concentration ratios which it affects most have become more acceptable. The same effect would be achieved if K and Mn were removed from the fit. The marine contribution has also decreased from its value in fit 4, bringing the Cl concentration ratio outside the range of acceptable values.

Now the Cl concentration does have a quality assurance flag on it, which means that there was some discrepancy between the analytical techniques, so it may not be reliable and this low calculated to measured ratio might be disregarded. The approach taken in all PACS element balances, however, was to assume all data to be good and to fit it as well as possible. The flag does not necessarily mean that the particular value reported is wrong, the error may have been with the technique to which it was compared. Vegetative burn 1 is added in fit 6, and this lowers χ^2_{n-p} to a value less than the 1% χ^2_{n-p} of 2.8 for 6 degrees of freedom and brings most of the concentration ratios into a close approximation to unity. The effective elimination of Cl as a fitting concentration for auto exhaust by the addition of the burn can be seen in the substantial reduction of the auto source contribution between fits 6 and 7.

Given the extreme sensitivity of χ^2_{n-p} to the uncertainties in the source compositions and given that at present these uncertainties are only rough estimates, it is probably unwise to place great faith in the 1% χ^2_{n-p} criterion as a goodness of fit measure. Particularly when uncertainties are large, as they are for many species in the vegetative burns, χ^2_{n-p} will frequently attain a low value even though calculated to measured concentration ratios are not close to unity (these ratios will have large propagated uncertainties associated them). Very high values of χ^2_{n-p}, such as those of fits 2-4, can invariably be reduced by the addition of other source types, and the minimum possible value of χ^2_{n-p} is always desirable. It is the validity of the statistical significance test which is in question here.

Fit 6 seems to meet criteria 1-3 rather well. The χ^2_{n-p} is low and the concentration ratios are close to unity. Seventy-eight percent of the mass is accounted for, but given the 8% standard deviation of this value, this is not too unreasonable. In many of the fine particulate specimens on which chemical element balances were run the calculated mass underestimated the measured mass by 20-50%. The possible contributors of this missing mass will be dealt with in section 6.3.

All in all, fit 6 is a good one, but it is not the only good one. Deleting the marine aerosol in fit 7 still offers an acceptably low χ^2_{n-p} and actually raises the calculated mass by a couple of percent. The lower Na concentration ratio is easily accounted for by the addition of the kraft mill in fit 8. Fit 6 and fit 8 meet criteria 1-3 equally well, but one shows the marine influence and the other the kraft mill influence. This underscores the warning of chapter 2: _The receptor model tells what could be the contributors, not necessarily what are the contributors_.

The general policy in the PACS chemical element balances was to eliminate the eight basic source types, urban/continental dust, marine background, residual oil combustion, auto exhaust, VC, NVC, NO_3^-, and SO_4^{-2}, only as a last resort. If a good fit could be obtained with them, another set of source types which might combine to replace them was not sought.

A similar procedure is followed in the balance of the coarse particulate fraction in Tables 6.2.5a & b. The eight initial trial sources in fit 1 account for the measured mass remarkably well. χ^2_{n-p} is low and the ratios are reasonable with Mn, Cl, and Al being on the low side.

The NVC source contribution in fit 1 is less than its uncertainty, so it is eliminated in fit 2. This makes the NVC concentration a fitting concentration, but the effective variance weighting minimizes its influence in the fit, and the remaining source contributions change little between fits 1 and 2. General policy was to eliminate any source type from the fit when its contribution was less than its uncertainty. The ferromanganese furnace is added in fit 3 to rectify the low Mn concentration ratio and the vegetative burn is inserted in fit 4 to bring the Cl ratio into line. This eliminates the marine background contribution and it is removed in fit 5. Finally, in fit 6 the aluminum processing has been included, with its associated fitting concentration, F, to raise the Al ratio. The fitting procedure ends here.

Over 90% of the measured mass was usually accounted for in the chemical element balances of the coarse particulate mainly because the greatest contribution to this size fraction was always continental/urban dust for which a very good chemical characterization exists.

Tables 6.2.2 and 6.2.3 show the coarse particulate data summary and the source summary for this pair of samples.

The interaction of source types and the tremendous advantage conferred by the near uniqueness of certain chemical constituents in certain source types can be evaluated by following the variability of source contributions through the various trial fits in Tables 6.2.4a and 6.2.5a. Leaded auto exhaust and residual oil combustion, both of which have unique constituents, exhibit little variability throughout the fits. The urban dust contribution in the fine particulate mode, where it is a minor component, is affected by the ferromanganese and steel sources. But when it is the dominant source type, as it is in the coarse mode, the other source contributions exert little influence on it. The interaction between vegetative burning and kraft mills with marine aerosol is an important one, and these can be expected to demonstrate substantial variation between fits with different source combinations. Thus, these source type contribtuions should be subject to more skepticism than the continental/urban dust, residual oil combustion, and leaded auto exhaust contributions.

All chemical element balances in the PACS were performed in the manner just elucidated. Though each has its own story to tell and is subject to interpretation, it is impossible to review every one here. Much more study is needed, obviously, of the PACS data in particular and of the chemical element balance receptor model application to it in general. But for the purpose of identifying and quantifying aerosol contributions for control strategy purposes, this chemical element balance receptor model application seems adequate. To verify this, it is necessary to examine the average source contributions to the fine and total suspended particulate matter at each of the PACS receptor sites.

6.3 INTERPRETATION OF AVERAGE SOURCE CONTRIBUTIONS TO THE PORTLAND AEROSOL

Source contribution averages analogous to the chemical concentration averages were calculated for the fine, coarse, and total suspended particulate by season, site, regime and flow pattern. The 24-hour unstratified source contribution averages for fine and total suspended particulate are presented in Tables 6.3.1a & b-6.3.6a & b.

A modification was necessary in the calculation of these values because the minimum detectable concentrations for source contributions were assumed to be zero. This is legitimate, and necessary in the absence of any other estimate of the minimum detectable limit. Each of the 20 source types, the 16 listed in Tables 3.1.12.2a & b and the four single constituent sources, could have been included in each chemical element balance. If it was not, then the chemical concentrations were adequately reproduced without it and its contribution was effectively equal to zero. Of course, if some of the eight basic source types had been left out, particularly the marine background or the continental/urban dust, other source type contributions might have been significant. But the fact that the basic source types fit so well in so many cases across the entire geographical region argues that these really are contributing in most cases, and that only those other contributions compatible with them should be allowed a value greater than zero.

Table 6.3.1a Source Contribution Averages at Sauvie Island, Background Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 1
COMPOSITE YEAR   FREQUENCIES

 SOU •••••••••••••••UG/M3•••••••••••••••••• #IN #CT•••••••••••••••••PERCENT•••••••••••••••••• #IN #CT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC•GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-----------------------------------------------------------------------------------------------------------------
MARIN  0.526( 2.350)          0.720( 0.570)  31  31•  3.683( 2 456)          5.368( 4 971)  31  31 0.007  15.42 MARIN
CDUST  0.386( 6 925)          1.156( 1.677)  31  26•  2 109( 9.619)          5.864( 5 007)  31  26 0.174  17.95 CDUST
UDUST  0.011( 1.970)          0.014( 0 000)  31   1•  0 012( 2.585)          0.063( 0.296)  31   1 0.049  11.00 UDUST
AUTPB  0.517( 2.311)          0.670( 0.398)  31  31•  3.610( 1.740)          4 087( 1 776)  31  31 0.097  15.45 AUTPB
RDOIL  0.007( 3.006)          0.130( 0.110)  31  29•  0.546( 2.924)          0.753( 0.474)  31  29 0.026  19.40 RDOIL
VBRN1  0.032(11.481)          0.922( 2.163)  31   6•  0 052(30.712)         10.765(24.242)  31   6 0.636  15.05 VBRN1
VBRN2  0.030(10.202)          0.520( 1.035)  31   8•  0.064(24.613)          3.624( 6 630)  31   0 0.071  43.93 VBRN2
KRAFT  0.010( 1.000)          0.000( 0.000)  31   0•  0.010( 1.000)          0.010( 0 000)  31   0 0.000   0.00 KRAFT
SULFT  0 032( 5.032)          0.146( 0.262)  31  10•  0.055(12.267)          0.653( 0 998)  31  10 0.145  33.60 SULFT
HOGFU  0.026( 5.935)          0.159( 0.332)  31   7•  0.039(12.925)          0.980( 1 966)  31   7 0.280  39.04 HOGFU
ALPRO  0.033( 5.377)          0.129( 0.230)  31  11•  0.064(12.007)          0.793( 1 541)  31  11 0.125  39.51 ALPRO
STEEL  0.011( 1.637)          0.005( 0 000)  31   3•  0.014( 2.669)          0 035( 0 000)  31   3 0.015  31.07 STEEL
FERMN  0 023( 2.513)          0.032( 0.040)  31  16•  0.060( 6.364)          0.239( 0.416)  31  16 0.015  31.55 FERMN
CARBO  0.010( 1.000)          0.000( 0.000)  31   0•  0.010( 1.000)          0.010( 0.000)  31   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)          0.000( 0.000)  31   0•  0 010( 1.000)          0.010( 0.000)  31   0 0.000   0.00 GLASS
CARBF  0.027( 5.097)          0.120( 0.274)  31   9•  0.044(10.059)          0.582( 1.107)  31   9 0.091  25.57 CARBF
NO3    0.001( 4.500)          1.453( 1.143)  31  20•  4.639( 5.743)          7.630( 4.026)  31  20 0.209  15.05 NO3
SO4    1.503( 2.542)          2.110( 1.604)  31  31• 10.517( 1.543)         11.413( 4.400)  31  31 0.291  15.69 SO4
VC     1.132( 9.940)          3.236( 2.702)  31  25•  5.379(17.269)         16.091(10.506)  31  25 0.002  20.27 VC
NVC    0.406( 4.237)          0.012( 0.594)  31  20•  2.847( 6.891)          5.296( 3.715)  31  20 0.266  34.51 NVC
CMASS 10.490( 1.053)         12.358( 6.599)  31  31• 73.479( 1.220)         74 927(14.673)  31  31 1.007   9.61 CMASS
MMASS 11.305( 4.105)         16.140( 9 060)  32  31•100 000( 1.002)        100.000( 0.000)  31  31 0.492   3.94 MMASS
-----------------------------------------------------------------------------------------------------------------
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Refer to Tables 6.1.1a & b for meanings of column headings

CMASS: Average of calculated mass loadings (sum of individual source contributions to a specimen).

MMASS: Average of measured mass loadings

Table 6.3.1b Source Contribution Averages at Sauvie Island, Background Site

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FACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 1
COMPOSITE YEAR   FREQUENCIES

 SOU ***************UG/M3****************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-----------------------------------------------------------------------------------------------------------------
MARIN  0.962( 3.397)          1.657( 2 028)  31  30*  3.109( 4.526)           7.209(11.342)  31  30 0.190  12.64 MARIN
CDUST  5.277( 7.514)         12.832(12 722)  31  29* 15.291( 0.082)          30.456(23.303)  31  29 1.014   0.90 CDUST
UDUST  0.014( 3.963)          0.307( 1.630)  31   2*  0.016( 5 959)           0.953( 4.171)  31   2 0.309   7.60 UDUST
AUTPB  0.567( 3.127)          0.820( 0.512)  31  30*  1.833( 3.532)           2 658( 1.572)  31  30 0.075   0.83 AUTPB
RDOIL  0.097( 3.375)          0.164( 0.148)  31  29*  0.297( 3.732)           0.484( 0.352)  31  29 0.016   0.40 RDOIL
VBRN1  0.046(14.140)          1.154( 2.536)  31   0*  0.070(29.510)           6.036(15.856)  31   0 1.002  25.73 VBRN1
VBRN2  0.030(10.202)          0.520( 1.035)  31   0*  0.054(10.723)           2.064( 3.935)  31   0 0.000   0.00 VBRN2
KRAFT  0.012( 2.295)          0.033( 0.103)  31   0*  0.012( 2.593)           0.075( 0.360)  31   0 0.000   0.00 KRAFT
SULFT  0.032( 5.032)          0.146( 0.262)  31  10*  0.043( 0.698)           0.331( 0.523)  31  10 0.000   0.00 SULFT
HOGFU  0.039( 9.112)          0.450( 1.064)  31   9*  0.055(15.999)           1.755( 4.358)  31   9 0.103   6.00 HOGFU
ALPRO  0.130( 0.080)          0.497( 0.553)  31  19*  0.272(12.789)           1.287( 1.327)  31  19 0.355  41.73 ALPRO
STEEL  0 030( 4.075)          0.079( 0.145)  31  13*  0.047( 6.104)           0.186( 0.259)  31  13 0.071  37.32 STEEL
FERMN  0.028( 2.755)          0.042( 0.053)  31  10*  0.054( 4.651)           0.145( 0.246)  31  10 0.013  14.74 FERMN
CARBO  0.010( 1.000)          0.000( 0.000)  31   0*  0.010( 1.000)           0.010( 0 000)  31   0 0 000   0.00 CARBO
GLASS  0.010( 1.000)          0.000( 0.000)  31   0*  0.010( 1.000)           0 010( 0.000)  31   0 0.000   0.00 GLASS
CARBF  0.107(10.239)          0.030( 0.952)  31  19*  0 359(15.034)           1 970( 1.041)  31  19 0.439  34.19 CARBF
NO3    2.015( 2.340)          2.706( 1.087)  31  31*  6 573( 1.700)           7.520( 3.479)  31  31 0.364  15.61 NO3
SO4    1.905( 2.516)          2.645( 1.944)  31  31*  6.215( 1.907)           7.401( 4.096)  31  31 0.339  13.54 SO4
VC     1.772( 9.902)          5.232( 5.394)  31  27*  4.692(12 006)          13.135( 9.766)  31  27 1.232  17.74 VC
NVC    0.630( 6.305)          1.473( 1.343)  31  27*  1.900( 8 623)           4.590( 4.193)  31  27 0.567  23.71 NVC
CMASS 26.926( 1.043)         31.597(16.982)  31  31* 86.285( 1.134)          86 943(10.899)  30  30 2.250   7.22 CMASS
MMASS 23.049( 4.660)         34.010(19.914)  32  31*100 000( 1.002)         100 000( 0.000)  31  31 0 620   2.13 MMASS
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Table 6.3.2a Source Contribution Averages at Industrial Air Products, Industrial Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 2
COMPOSITE YEAR   FREQUENCIES

 SOU ••••••••••••••••UG/M3•••••••••••••••••••• 0IN 0GT•••••••••••••••••PERCENT•••••••••••••••••• 0IN 0GT ARITH AV UNC
 RCE GEOM MEAN(STD)         ARITH MEAN(STD) AVG MDC•GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------------
MARIN  0.010( 4.250)         1 435( 1.217)  32  30•  2.719( 5.766)         5.774( 6.262)  32  30 0.233  10.74 MARIN
CDUST  0.010( 1.000)         0.000( 0.000)  32   0•  0.010( 1.000)         0.010( 0.000)  32   0 0.000   0.00 CDUST
UDUST  1.204( 5.077)         2.415( 2.372)  32  29•  3.740( 5.822)         7.389( 7.362)  32  29 0.207  13.26 UDUST
AUTPB  1.859( 2.044)         2.295( 1.414)  32  32•  6.749( 1.932)         8.076( 4.409)  32  32 0.327  14.50 AUTPB
RDOIL  0.335( 2.376)         0.457( 0.340)  32  32•  1.214( 2.173)         1.555( 0.994)  32  32 0.070  19.00 RDOIL
VBRN1  0 046(19.547)         3.502( 8.730)  32   7•  0.064(35.029)        11.684(24.721)  32   7 1.059  13.20 VBRN1
VBRN2  0.035(11 315)         0.915( 2.311)  32   7•  0.046(19.134)         2.984( 6.044)  32   7 1.725  47.22 VBRN2
KRAFT  0.047(19.444)         2.741( 5.735)  32   7•  0.059(30.249)         7.761(16.044)  32   7 1.499  13.36 KRAFT
SULFT  0.044( 7.283)         0.233( 0.367)  32  12•  0 064(11.604)         0.587( 0.859)  32  12 0.220  35.96 SULFT
HOGFU  0.015( 3.475)         0.074( 0.270)  32   3•  0.017( 5.270)         0.283( 0.939)  32   3 0.361  47.46 HOGFU
ALPRO  0.037( 6.459)         0.103( 0.314)  32  11•  0.057(11.722)         0.629( 1.071)  32  11 0.191  39.35 ALPRO
STEEL  0.435( 4.707)         0.767( 0.564)  32  28•  1.306( 6.073)         2.550( 1.580)  32  28 0.110  14.31 STEEL
FERMN  0 025( 4.675)         0.092( 0.105)  32   0•  0.032( 6.762)         0.213( 0.397)  32   0 0.100  32.14 FERMN
CARBO  0.010( 1.000)         0.000( 0.000)  32   0•  0.010( 1.000)         0.010( 0.000)  32   0 0.000   0.00 CARBO
GLASS  0.012( 3.107)         0.220( 1.245)  32   1•  0.013( 4.069)         0.807( 4.959)  32   1 1.100  16.06 GLASS
CARBF  0.013( 2.600)         0.026( 0.092)  32   3•  0.016( 4.074)         0.110( 0.349)  32   3 0.105  30.02 CARBF
NO3    1.017( 4.561)         1.937( 1.020)  32  29•  3.241( 5.227)         5.484( 3.945)  32  29 0.305  16.27 NO3
SO4    2.419( 2.583)         3.472( 2.750)  32  31•  8.650( 1.790)         9.982( 4.977)  32  31 0.605  20.09 SO4
VC     1 166(17.411)         5.306( 4.946)  32  24•  2.949(20.713)        15.913(11.265)  32  24 1.497  23.34 VC
NVC    0.531( 7.900)         1.370( 1.124)  32  26•  1.556(12.504)         4.819( 3.915)  32  26 0.537  37.01 NVC
CMASS 23.540( 1.023)        27.440(13.993)  32  32• 84.000( 1.146)        84.041(11.642)  31  31 2.216   0.32 CMASS
MMASS 27.549( 1.701)        31.600(14.979)  32  32•100.000( 1.003)       100.000( 0.000)  32  32 0.524   2.12 MMASS
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Table 6.3.2b Source Contribution Averages at Industrial Air Products, Industrial Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 2
COMPOSITE YEAR   FREQUENCIES

 SOU ***************UG/M3******************* #IN #CT*****************PERCENT****************** #IN #CT ARITH AV UNC
 RCE GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-----------------------------------------------------------------------------------------------------------------
MARIN  1.475( 2.663)           2.239( 2.107)  32  32*  2.370( 3.285)            4.645( 6.377)  32  32 0.217  12.10 MARIN
CDUST  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)            0.010( 0.000)  32   0 0.000   0.00 CDUST
UDUST 24.673( 2.901)          36.453(27.105)  32  32* 39.766( 1.597)           43.695(10.075)  32  32 2.135   6.27 UDUST
AUTPB  2.204( 2.161)           2.793( 1.742)  32  32*  3.552( 1.923)            4.319( 2.670)  32  32 0.260   0.00 AUTPB
RDOIL  0.398( 2.567)           0.562( 0.417)  32  32*  0.642( 2.337)            0.076( 0.667)  32  32 0.045   6.55 RDOIL
VBRN1  0.134(31.512)           5.717(11.375)  32  12*  0.160(41.403)            8.570(13.940)  32  12 3.100  31.29 VBRN1
VBRN2  0.035(11.315)           0.915( 2.311)  32   7*  0.039(13.674)            1.353( 3.287)  32   7 0.000   0.00 VBRN2
KRAFT  0.047(19.444)           2.741( 5.735)  32   7*  0.051(23.359)            4.174( 8.506)  32   7 0.000   0.00 KRAFT
SULFT  0.045( 7.509)           0.250( 0.449)  32  12*  0.045( 7.567)            0.261( 0.407)  32  12 0.046   2.39 SULFT
HOGFU  0.015( 3.475)           0.074( 0.270)  32   3*  0.016( 4.519)            0.102( 0.637)  32   3 0.000   0.00 HOGFU
ALPRO  0.100(12.819)           0.923( 1.392)  32  16*  0.134(15.414)            1.344( 1.954)  32  16 0.723  20.62 ALPRO
STEEL  1.130( 3.999)           1.770( 1.427)  32  30*  1.647( 4.171)            2.519( 1.090)  32  30 0.220  11.61 STEEL
FERMN  0.032( 5.422)           0.123( 0.204)  32  11*  0.034( 5.600)            0.141( 0.214)  32  11 0.022   5.62 FERMN
CARBO  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)            0.010( 0.000)  32   0 0.000   0.00 CARBO
GLASS  0.012( 3.107)           0.220( 1.245)  32   1*  0.012( 3.370)            0.311( 1.705)  32   1 0.000   0.00 GLASS
CARBF  0.098(13.310)           1.000( 1.793)  32  15*  0.109(14.094)            1.022( 1.537)  32  15 0.747  35.34 CARBF
NO3    1.071( 3.054)           3.210( 2.906)  32  31*  2.706( 3.311)            3.036( 2.305)  32  31 0.441  12.14 NO3
SO4    2.979( 2.507)           4.224( 3.410)  32  32*  4.001( 1.710)            5.497( 2.026)  32  32 0.400   9.26 SO4
VC     2.002(14.403)           7.009( 6.536)  32  25*  2.624(15.971)            9.029( 7.026)  32  25 1.691  12.99 VC
NVC    0.702( 9.397)           2.100( 1.900)  32  26*  1.009(10.265)            2.042( 2.290)  32  26 0.767  10.22 NVC
CMASS 50.096( 2.105)          72.437(43.676)  32  32* 91.905( 1.100)           92.450( 9.549)  31  31 3.960   5.35 CMASS
MMASS 62.044( 1.996)          75.470(43.957)  32  32*100.000( 1.003)          100.000( 0.000)  32  32 0.747   1.23 MMASS
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Table 6.3.3a Source Contribution Averages at Central Air Monitoring, Urban Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 3
COMPOSITE YEAR   FREQUENCIES

 SOU ****************UG/M3******************** 0IN 0GT******************PERCENT******************** 0IN 0GT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3    %
------------------------------------------------------------------------------------------------------------------
MARIN  0 434( 3.010)          0.734( 0.605)  32  30*  1.603( 4.793)          3.123( 3.924)  32  30 0.107  10.97 MARIN
COUST  0 010( 1.000)          0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 CDUST
UDUST  0.438( 0.699)          1.370( 1.551)  32  25*  1.150(13.686)          4.285( 4.864)  32  25 0.240  20.40 UDUST
AUTPB  3.439( 1.927)          4.210( 2.793)  32  32* 13.744( 1.533)         14.972( 6.160)  32  32 0.557  13.36 AUTPB
RDOIL  0.313( 2.643)          0.483( 0.467)  32  32*  1.252( 1.888)          1.460( 0.782)  32  32 0.079  17.46 RDOIL
VBRN1  0.109(23.359)          2.634( 4.653)  32  12*  0.200(54.040)         13.429(19.835)  32  12 1.216  21.15 VBRN1
VBRN2  0.113(20.034)          1.789( 2.539)  32  13*  0.177(34.285)          5.086( 6.982)  32  13 1.098  45.10 VBRN2
KRAFT  0.010( 1.000)          0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 KRAFT
SULFT  0.028( 5.410)          0.126( 0.246)  32   9*  0.040( 9.485)          0.411( 0.732)  32   9 0.154  35.35 SULFT
HOGFU  0.013( 3.221)          0.070( 0.336)  32   2*  0.015( 4.886)          0.412( 1.615)  32   2 0.516  41.07 HOGFU
ALPRO  0.039( 6.456)          0.280( 0.367)  32  12*  0.067(12.544)          0.789( 1.074)  32  12 0.199  51.07 ALPRO
STEEL  0.076( 9.012)          0.451( 0.707)  32  16*  0.135(14.934)          1.177( 1.560)  32  16 0.111  20.40 STEEL
FERMN  0.025( 4.300)          0.112( 0.350)  32  11*  0.040( 7.510)          0.305( 0.724)  32  11 0.035  10.51 FERMN
CARBO  0.010( 1.000)          0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 CARBO
GLASS  0 010( 1.000)          0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 GLASS
CARBF  0.012( 1.960)          0.010( 0.030)  32   2*  0.013( 2.999)          0.066( 0.236)  32   2 0.074  40.54 CARBF
NO3    1.074( 4.896)          2.172( 2.110)  32  30*  3.698( 5.371)          6.329( 4.565)  32  30 0.319  19.03 NO3
SO4    1.850( 3.004)          2.963( 2.444)  32  32*  7.427( 1.952)          0.879( 4.716)  32  32 0.486  10.50 SO4
VC     0 566(25.028)          4.776( 4.964)  32  20*  1.185(43.510)         14.269(14.098)  32  20 2.147  32.30 VC
NVC    0.469( 7.422)          1.174( 0.988)  32  25*  1.286(11.932)          3.990( 3.045)  32  25 0.545  44.01 NVC
CMASS 19.341( 1.922)         23.291(13.460)  32  32* 77.300( 1.234)         78.855(15.047)  32  32 2.301  10.01 CMASS
MMASS 25 020( 1.799)         29.211(15.769)  32  32*100.000( 1.003)        100.000( 0.000)  32  32 0.667   3.00 MMASS
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Table 6.3.3b Source Contribution Averages at Central Air Monitoring, Urban Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 3
COMPOSITE YEAR    FREQUENCIES

 SOU ****************UG/M3******************* #IN #GT*****************PERCENT***************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)            ARITH MEAN(STD) AVG MDC  UG/M3   %
---------------------------------------------------------------------------------------------------------------------
MARIN   1 010( 2.743)            1.646( 2.107)  32  32*  1.576( 3.324)           3 625( 6.200)  32  32 0.100   14.01 MARIN
CDUST   0.010( 1.000)            0.000( 0.000)  32   0*  0 010( 1.000)           0.010( 0.000)  32   0 0.000    0.00 CDUST
UDUST  23.474( 3.122)           36.562(29.132)  32  32* 36.630( 1.600)          40.519(14.919)  32  32 1.914    6.02 UDUST
AUTPB   5.204( 1.858)            6 218( 3.758)  32  32*  0 122( 1.714)           9.306( 4.924)  32  32 0.591    9.07 AUTPB
RDOIL   0.437( 2.837)            0.715( 0.719)  32  32*  0.602( 2.121)           0 059( 0.530)  32  32 0.079   10.71 RDOIL
VBRN1   0.512(20.262)            5.372( 6.413)  32  10*  0.600(37.604)          10.476(13.540)  32  10 1.989   22.76 VBRN1
VBRN2   0.137(20.754)            1.964( 2.711)  32  14*  0.147(22.755)           2.518( 4.022)  32  14 0.235    5.23 VBRN2
KRAFT   0.010( 1.000)            0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  32   0 0.000    0.00 KRAFT
SULFT   0 030( 5.530)            0.132( 0.245)  32  10*  0.035( 6.606)           0.100( 0.297)  32  10 0.011    6.24 SULFT
HOGFU   0.013( 3.221)            0.070( 0.336)  32   2*  0.014( 4.002)           0.193( 0.757)  32   2 0.000    0.00 HOGFU
ALPRO   0.124(11.749)            0.977( 1.751)  32  17*  0.160(13.615)           1.289( 2.037)  32  17 0.579   25.77 ALPRO
STEEL   0.191(11.463)            1.177( 1.717)  32  21*  0.213(10.921)           1.056( 1.330)  32  21 0.209   13.56 STEEL
FERMN   0.042( 5.375)            0.103( 0.400)  32  16*  0.053( 5.060)           0.106( 0.263)  32  16 0.043   14.71 FERMN
CARBO   0.010( 1.000)            0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  32   0 0.000    0.00 CARBO
GLASS   0.010( 1.000)            0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  32   0 0.000    0.00 GLASS
CARBF   0.102(16.932)            1.655( 2.360)  32  17*  0.215(19.390)           2.130( 3.093)  32  17 0.049   29.63 CARBF
NO3     2.501( 2.929)            3.041( 3.051)  32  31*  3.024( 2.001)           4.645( 2.717)  32  31 0.474   15.14 NO3
SO4     2.670( 2.061)            4.036( 3.334)  32  32*  4.179( 1.717)           4.710( 2.130)  32  32 0.437   15.07 SO4
VC      1 215(22.005)            7.441( 7.576)  32  23*  1.419(24.287)           0.377( 7.056)  32  23 2.075   26.06 VC
NVC     0.764( 6.485)            1.759( 1.719)  32  28*  1.032( 6.756)           2.185( 1.639)  32  20 0.515   16.55 NVC
CMASS  50.716( 2.074)           73.755(47.500)  32  32* 91.644( 1.124)          92.261(11.006)  32  32 4.102    5.03 CMASS
MMASS  64.070( 2.009)           79.050(49.116)  32  32*100.000( 1.003)         100.000( 0.000)  32  32 0.040    1.50 MMASS
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Table 6.3.4a Source Contribution Averages at Pacific Motor Trucking, Industrial/Urban Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 4
COMPOSITE YEAR   FREQUENCIES

 SOU ***************UG/M3******************* #IN #GT****************PERCENT***************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------------
MARIN  0.270( 4.772)           0.564( 0.544)  32  20*  0.987( 6.969)          2.403( 3.421)  32  20 0.091  21.60 MARIN
CDUST  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 CDUST
UDUST  0.928( 7.750)           2.611( 2.940)  32  28*  2.807(10.019)          7.345( 6.354)  32  28 0.319  15.02 UDUST
AUTPB  3.716( 1.931)           4.587( 3.235)  32  32* 13.242( 1.400)         14.005( 4.093)  32  32 0.626  13.66 AUTPB
RDOIL  0.189( 3.000)           0.300( 0.260)  32  32*  0.673( 2.029)          0.833( 0.521)  32  32 0.051  19.50 RDOIL
VBRN1  0.048(20.930)           4.251(10.070)  32   7*  0.059(30.614)          9.323(20.783)  32   7 2.167  22.27 VBRN1
VBRN2  0.001(16.056)           1.234( 2.202)  32  12*  0.134(30.406)          4.132( 6.005)  32  12 1.302  43.55 VBRN2
KRAFT  0.012( 2.827)           0.112( 0.632)  32   1*  0.012( 3.414)          0.335( 1.836)  32   1 0.564  15.77 KRAFT
SULFT  0.057( 7.107)           0.253( 0.368)  32  15*  0.107(13.119)          0.787( 0.945)  32  15 0.105  35.29 SULFT
HOGFU  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 HOGFU
ALPRO  0.018( 3.920)           0.083( 0.257)  32   6*  0.026( 7.676)          0.420( 1.143)  32   6 0.167  52.43 ALPRO
STEEL  0.085( 9.871)           0.498( 0.689)  32  17*  0.151(15.260)          1.309( 1.717)  32  17 0.125  20.40 STEEL
FERMN  0.021( 2.952)           0.035( 0.062)  32  13*  0.030( 5.636)          0.151( 0.220)  32  13 0.022  33.14 FERMN
CARBO  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 GLASS
CARBF  0.014( 2.753)           0.038( 0.104)  32   4*  0.018( 4.090)          0.153( 0.399)  32   4 0.104  47.49 CARBF
NO3    1.052( 3.562)           1.773( 1.640)  32  31*  3.617( 3.391)          5.005( 3.166)  32  31 0.314  19.66 NO3
SO4    1.725( 2.792)           2.578( 2.030)  32  32*  6.140( 1.075)          7.295( 3.998)  32  32 0.391  19.32 SO4
VC     1.886(14.064)           6.540( 5.699)  32  26*  5.873(23.377)         24.620(23.363)  32  26 1.762  24.41 VC
NVC    1.330( 3.433)           2.042( 1.692)  32  30*  4.574( 4.322)          9.040(15.164)  32  30 0.644  35.50 NVC
CMASS 22.044( 1.902)          27.492(16.550)  32  32* 77.832( 1.231)         79.401(15.656)  31  31 2.300   9.17 CMASS
MMASS 28.065( 1.869)          33.306(10.250)  32  32*100.000( 1.003)        100.000( 0.000)  32  32 0.540   2.12 MMASS
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Table 6.3.4b Source Contribution Averages at Pacific Motor Trucking, Industrial/Urban Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 4
COMPOSITE YEAR   FREQUENCIES

 SOU ****************UG/M3******************** #IN #GT*****************PERCENT***************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------------
MARIN  0.562( 4.794)           1.146( 1.393)  31  20*  0.716( 5.699)          1.963( 3.054)  31  20 0.190  19.52 MARIN
CDUST  0.010( 1.000)           0.000( 0.000)  31   0*  0.010( 1.000)          0.010( 0.000)  31   0 0.000   0.00 CDUST
UDUST 35.571( 3.184)          58.494(53.469)  31  31* 43.853( 1.659)         40.444(17.920)  31  31 2.982   5.70 UDUST
AUTPB  5.071( 1.950)           6.266( 4.306)  31  31*  6.252( 1.826)          7.352( 4.190)  31  31 0.620   9.63 AUTPB
RDOIL  0.219( 3.104)           0.365( 0.344)  31  30*  0.264( 2.507)          0.389( 0.337)  31  30 0.044  11.07 RDOIL
VBRN1  0.121(31.711)           5.849(11.923)  31  11*  0.120(31.613)          5.611(10.523)  31  11 1.983  20.23 VBRN1
VBRN2  0.009(16.922)           1.344( 2.273)  31  12*  0.102(20.344)          2.036( 3.354)  31  12 0.109   2.04 VBRN2
KRAFT  0.015( 4.365)           0.236( 0.913)  31   2*  0.014( 4.103)          0.195( 0.722)  31   2 1.640  43.95 KRAFT
SULFT  0.053( 7.066)           0.245( 0.371)  31  14*  0.059( 7.535)          0.271( 0.370)  31  14 0.003   1.52 SULFT
HOGFU  0.012( 3.067)           0.165( 0.920)  31   1*  0.012( 3.330)          0.271( 1.454)  31   1 1.177  22.97 HOGFU
ALPRO  0.124(13.554)           1.005( 1.700)  31  15*  0.143(14.512)          1.120( 1.394)  31  15 0.970  30.64 ALPRO
STEEL  0.107( 9.252)           0.534( 0.734)  31  19*  0.113( 8.937)          0.528( 0.669)  31  19 0.071  12.00 STEEL
FERMN  0.030( 4.525)           0.129( 0.294)  31  10*  0.044( 4.362)          0.122( 0.201)  31  10 0.046  13.25 FERMN
CARBO  0.010( 1.000)           0.000( 0.000)  31   0*  0.010( 1.000)          0.010( 0.000)  31   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)           0.000( 0.000)  31   0*  0.010( 1.000)          0.010( 0.000)  31   0 0.000   0.00 GLASS
CARBF  0.095(14.011)           1.078( 1.005)  31  13*  0.097(13.549)          0.881( 1.163)  31  13 1.046  39.26 CARBF
NO3    2.352( 2.453)           3.320( 2.715)  31  31*  2.980( 1.700)          3.281( 1.571)  31  31 0.484  17.22 NO3
SO4    2.335( 2.570)           3.301( 2.494)  31  31*  2.070( 1.682)          3.288( 1.820)  31  31 0.410  14.75 SO4
VC     3.319(10.757)           8.550( 6.310)  31  27*  4.206(11.417)         10.765( 8.396)  31  27 1.566  14.77 VC
NVC    2.086( 3.098)           3.076( 5.559)  31  31*  2.571( 2.350)          3.493( 2.587)  31  31 1.032  11.10 NVC
CMASS 68.315( 2.342)          93.352(73.344)  32  32* 89.270( 1.135)         89.964(11.463)  31  31 4.751   6.60 CMASS
MMASS 61.226( 5.770)         101.830(79.652)  32  31*100.000( 1.002)        100.000( 0.000)  31  31 0.957   1.10 MMASS
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Table 6.3.5a Source Contribution Averages at Flavel Park, Residential Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 5
COMPOSITE YEAR   FREQUENCIES

 SOU ***************UG/M3****************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3    %
-------------------------------------------------------------------------------------------------------------------
MARIN  0.236( 3.695)          0.416( 0.475)  30  27*  0.886( 6.060)          2.430( 4.199)  30  27 0.076  23.11 MARIN
CDUST  0.010( 1.000)          0.000( 0.000)  30   0*  0.010( 1.000)          0.010( 0.000)  30   0 0.000   0.00 CDUST
UDUST  0.641( 0.073)          1.714( 1.513)  30  24*  2.092(13.020)          7.002( 7.174)  30  24 0.210  14.10 UDUST
AUTPB  2.110( 2.433)          2.992( 2.573)  30  30*  9.347( 1.526)         10.142( 4.074)  30  30 0.412  13.92 AUTPB
RDOIL  0.003( 3.024)          0.140( 0.130)  30  30*  0.367( 1.959)          0.449( 0.279)  30  30 0.025  23.63 RDOIL
VBRN1  0.068(21.010)          2.638( 5.399)  30   8*  0.007(30.710)         10.515(21.737)  30   0 1.621  19.92 VBRN1
VBRN2  0.126(19.545)          1.791( 2.772)  30  13*  0.230(30.754)          6.440( 0.220)  30  13 1.501  39.67 VBRN2
KRAFT  0.012( 2.367)          0.037( 0.205)  30   1*  0.012( 3.017)          0.151( 0.772)  30   1 0.615  54.09 KRAFT
SULFT  0.053( 6.490)          0.206( 0.301)  30  14*  0.112(13.970)          0.004( 1.051)  30  14 0.150  34.64 SULFT
HOGFU  0.010( 1.000)          0.000( 0.000)  30   0*  0.010( 1.000)          0.010( 0.000)  30   0 0.000   0.00 HOGFU
ALPRO  0.024( 5.400)          0.146( 0.373)  30   7*  0.037(11.120)          0.731( 1.569)  30   7 0.190  33.69 ALPRO
STEEL  0.010( 1.261)          0.001( 0.000)  30   1*  0.011( 2.035)          0.026( 0.000)  30   1 0.000  23.26 STEEL
FERMN  0.025( 2.464)          0.036( 0.051)  30  20*  0.059( 3.032)          0.114( 0.113)  30  20 0.010  29.77 FERMN
CARBO  0.010( 1.000)          0.000( 0.000)  30   0*  0.010( 1.000)          0.010( 0.000)  30   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)          0.000( 0.000)  30   0*  0.010( 1.000)          0.010( 0.000)  30   0 0.000   0.00 GLASS
CARBF  0.013( 2.149)          0.014( 0.047)  30   3*  0.016( 3.959)          0.103( 0.297)  30   3 0.070  45.50 CARBF
NO3    0.634( 5.156)          1.296( 1.339)  30  27*  2.349( 6.905)          4.565( 3.241)  30  27 0.232  19.46 NO3
SO4    1.009( 3.449)          1.674( 1.267)  30  20*  4.350( 2.607)          6.106( 4.200)  30  20 0.301  25.61 SO4
VC     3.030( 0.420)          7.150( 5.979)  30  26* 11.689(11.716)         26.491(15.977)  30  26 2.006  26.97 VC
NVC    0.261( 0.006)          0.766( 0.696)  30  22*  0.780(14.730)          2.964( 2.160)  30  22 0.390  43.45 NVC
CMASS 17.529( 1.002)         21.025(12.500)  30  30* 77.651( 1.215)         79.041(14.014)  30  30 2.404  11.21 CMASS
MMASS 13.932( 7.293)         24.058(15.431)  32  30*100.000( 1.002)        100.000( 0.000)  30  30 0.503   2.51 MMASS
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Table 6.3.5b Source Contribution Averages at Flavel Park, Residential Site

```
PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 5
COMPOSITE YEAR    FREQUENCIES

 SOU ***************UG/M3****************** #IN #GT****************PERCENT**************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)         ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------
MARIN  0.701( 3.050)         1.475( 2.682)  32  31*  1.069( 4.313)          3.513( 7.400)  32  31 0.199  15.32 MARIN
CDUST  0.010( 1.000)         0.000( 0.000)  32   0*  0.010( 1.000)          0 010( 0.000)  32   0 0.000   0.00 CDUST
UDUST 22 442( 3.740)        30.793(33.613)  32  32* 34.900( 2.160)         42 663(20.885)  32  32 2.001   6.34 UDUST
AUTPB  3.670( 2.539)         5.352( 4.604)  32  32*  5.709( 1.705)          6.421( 2.025)  32  32 0.679  13.03 AUTPB
RDOIL  0.115( 3.091)         0.192( 0.174)  32  32*  0.170( 2.297)          0.238( 0.170)  32  32 0.033  15.16 RDOIL
VBRN1  0.204(31.237)         5.415( 0.501)  32  16*  0.340(30.525)          9.132(15.397)  32  16 2.130  26.93 VBRN1
VBRN2  0.112(19.953)         1.066( 2.950)  32  13*  0.131(24.546)          3.123( 5.504)  32  13 0.270   4.30 VBRN2
KRAFT  0.012( 2.303)         0.035( 0.190)  32   1*  0.012( 2.230)          0.039( 0.163)  32   1 0.000   0.00 KRAFT
SULFT  0.057( 6.992)         0.240( 0.340)  32  15*  0.070( 0.344)          0.320( 0.362)  32  15 0.053   6.90 SULFT
HOGFU  0.012( 2.474)         0.053( 0.297)  32   1*  0.012( 3.322)          0.280( 1.572)  32   1 0.296  17.60 HOGFU
ALPRO  0.192(13.027)         1.287( 1.600)  32  19*  0.247(15.869)          1.740( 2.327)  32  19 0.040  35.60 ALPRO
STEEL  0.016( 2.979)         0.034( 0.000)  32   5*  0.010( 3.463)          0 054( 0.101)  32   5 0.050  27.77 STEEL
FERMN  0.043( 3.333)         0.005( 0.119)  32  23*  0.057( 3.666)          0.113( 0.125)  32  23 0.036  23.90 FERMN
CARBO  0.010( 1.000)         0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)         0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 GLASS
CARBF  0.020( 6.306)         0.201( 0.054)  32   9*  0.034( 7.927)          0.453( 1.477)  32   9 0.314  31.50 CARBF
NO3    2.398( 2.705)         3.580( 2.993)  32  31*  3.678( 1.972)          4.402( 2.409)  32  31 0.545  15.53 NO3
SO4    1.713( 3.449)         2.760( 2.012)  32  32*  2.665( 2.210)          3.327( 1.702)  32  32 0.400  17.41 SO4
VC     3.003(10.560)         8.080( 6.545)  32  28*  4.367(11.377)         10.991( 7.032)  32  28 1.263  11.02 VC
NVC    0.316( 0.504)         0.996( 1.004)  32  24*  0.447( 9.675)          1 334( 1.055)  32  24 0.379  10.39 NVC
CMASS 56.295( 2.040)        70.525(46.708)  32  32* 87.565( 1.110)         80.897( 9.974)  32  32 3.603   5.59 CMASS
MMASS 64.290( 2.035)        88.555(53.996)  32  32*100.000( 1.003)        100.000( 0.000)  32  32 0.950   1.46 MMASS
--------------------------------------------------------------------------------------------------------------
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Table 6.3.6a Source Contribution Averages at Carus, Background Site

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FACS 24 HOUR ANNUAL UNSTRATIFIED FINE   PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 6
COMPOSITE YEAR   FREQUENCIES

 SOU ***************UG/M3****************** #IN #GT*****************PERCENT***************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)           ARITH MEAN(STD) AVG MDC  UG/M3   %
--------------------------------------------------------------------------------------------------------------------
MARIN  0.211( 3.769)           0.437( 0.652)  32  29*  1.559( 4.461)           3.411( 5.031)  31  29 0.060  23.43 MARIN
CDUST  0.153( 9.366)           1.200( 3.533)  32  22*  0.604(17.200)           4.649( 9.501)  31  22 0.205  23.00 CDUST
UDUST  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  31   0 0.000   0.00 UDUST
AUTPB  0.623( 2.092)           0.781( 0.484)  32  32*  4.490( 1.546)           4.917( 2.104)  31  31 0.112  14.67 AUTPB
RDOIL  0.030( 3.500)           0.059( 0.073)  32  20*  0.163( 4.237)           0.310( 0.291)  31  27 0.014  30.07 RDOIL
VBRN1  0.044(13.000)           1.014( 1.915)  32   0*  0.060(30.019)           0.149(19.375)  31   7 0.792  21.23 VBRN1
VBRN2  0.055(13.014)           0.760( 1.277)  32  10*  0.114(37.026)           7.592(13.550)  31  10 0.901  39.22 VBRN2
KRAFT  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  31   0 0.000   0.00 KRAFT
SULFT  0.039( 7.449)           0.276( 0.571)  32  11*  0.060(14.272)           1.032( 2.053)  31  10 0.220  32.95 SULFT
HOGFU  0.025( 5.076)           0.167( 0.300)  32   7*  0.036(11.560)           0.790( 1.670)  31   7 0.314  43.01 HOGFU
ALPRO  0.034( 5.533)           0.141( 0.252)  32  12*  0.075(13.535)           0.051( 1.359)  31  12 0.113  33.63 ALPRO
STEEL  0.011( 1.446)           0.003( 0.000)  32   2*  0.012( 2.316)           0.020( 0.070)  31   2 0.000  22.03 STEEL
FERMN  0.012( 1.917)           0.011( 0.031)  32   9*  0.023( 3.614)           0.064( 0.126)  31   9 0.010  42.00 FERMN
CARBO  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  31   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)           0.010( 0.000)  31   0 0.000   0.00 GLASS
CARBF  0.017( 3.276)           0.054( 0.200)  32   6*  0.025( 7.078)           0.296( 0.705)  31   6 0.000  36.20 CARBF
NO3    0.950( 3.191)           1.583( 1.432)  32  32*  6.696( 2.120)           0.574( 5.950)  31  31 0.217  19.59 NO3
SO4    0.540( 6.370)           1.265( 1.023)  32  20*  2.939( 9.932)           6.980( 4.950)  31  27 0.234  23.10 SO4
VC     0.939(12.642)           3.411( 3.246)  32  25*  3.020(27.006)          19.063(15.604)  31  24 0.941  27.10 VC
NVC    0.210( 5.161)           0.442( 0.390)  32  24*  0.960(11.132)           3.114( 2.702)  31  23 0.212  42.91 NVC
CMASS  9.322( 2.067)          11.611( 7.294)  32  32* 67.487( 1.312)          69.773(17.400)  31  31 1.175  11.53 CMASS
MMASS 12.036( 2.694)          16.174( 9.012)  32  31*100.000( 1.002)         100.000( 0.000)  31  31 0.514   4.53 MMASS
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Table 6.3.6b Source Contribution Averages at Carus, Background Site

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PACS 24 HOUR ANNUAL UNSTRATIFIED TOTAL  PARTICULATE SOURCE CONTRIBUTION AVERAGES AT SITE 6
COMPOSITE YEAR    FREQUENCIES

 SOU ***************UG/M3****************** #IN #GT***************PERCENT*************** #IN #GT ARITH AV UNC
 RCE GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC*GEOM MEAN(STD)          ARITH MEAN(STD) AVG MDC  UG/M3   %
-------------------------------------------------------------------------------------------------------------
MARIN  0.533( 3.972)           1 229( 2.324)  32  30*  1.981( 5 845)          6.786(13.697)  32  30 0.154  17.06 MARIN
CDUST  5.461( 4.087)          10.990(10.861)  32  32* 21 310( 2.227)         27.298(16.282)  32  32 0.070   9.13 CDUST
UDUST  0.012( 3.497)           0.372( 2.104)  32   1*  0 013( 4.340)          1.271( 7.134)  32   1 0.645   5.42 UDUST
AUTPB  0.013( 2.041)           1.006( 0.604)  32  32*  3.171( 1.641)          3.573( 1.000)  32  32 0.009   9.13 AUTPB
RDOIL  0.031( 3.574)           0.062( 0.080)  32  20*  0.102( 3.479)          0.177( 0.158)  32  20 0.004   2.71 RDOIL
VBRN1  0.045(14.019)           1.049( 1.970)  32   0*  0.063(25.809)          4.021(10.525)  32   0 0.107   2.32 VBRN1
VBRN2  0.055(13.014)           0.760( 1.277)  32  10*  0.007(26.494)          3.913( 7.460)  32  10 0.000   0.00 VBRN2
KRAFT  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 KRAFT
SULFT  0.040( 7.476)           0.276( 0.570)  32  11*  0.055(11.133)          0.607( 1.241)  32  11 0.003   3.69 SULFT
HOGFU  0.020( 6.123)           0.175( 0.379)  32   8*  0.037(10.169)          0.556( 1.154)  32   8 0.017   6.13 HOGFU
ALPRO  0.146( 7.402)           0.508( 0.652)  32  19*  0.324(11.579)          1.330( 1.436)  32  19 0.360  47.23 ALPRO
STEEL  0.020( 3.555)           0.055( 0.077)  32  14*  0.049( 5.028)          0.162( 0.193)  32  14 0.055  44.75 STEEL
FERMN  0.019( 2.970)           0.033( 0.057)  32  16*  0.035( 3.955)          0.002( 0.102)  32  16 0.026  29.97 FERMN
CARBO  0.012( 2.045)           0.116( 0.655)  32   0*  0.012( 3.305)          0.280( 1.520)  32   0 0.000   0.00 CARBO
GLASS  0.010( 1.000)           0.000( 0.000)  32   0*  0.010( 1.000)          0.010( 0.000)  32   0 0.000   0.00 GLASS
CARBF  0.133( 7.346)           0.470( 0.593)  32  22*  0.317(11.109)          1.191( 1.073)  32  22 0.353  51.76 CARBF
NO3    1.855( 3.059)           2.081( 2.309)  32  32*  7.239( 1.844)          0.450( 4.324)  32  32 0.362  13.34 NO3
SO4    0.731( 5.090)           1.572( 1.257)  32  28*  2.364( 7.073)          4.600( 3.100)  32  28 0.193  11.16 SO4
VC     2.409( 5.495)           4.035( 4.539)  32  29*  0.077( 6 449)         14.404(10.617)  32  29 1.062  23.44 VC
NVC    0.365( 5.212)           0.760( 0.674)  32  28*  1.210( 7.838)          3.190( 3.556)  32  28 0.230  19.82 NVC
CMASS 21.058( 2.251)          27.173(17.261)  32  32* 82.170( 1.146)         82.989(11.288)  32  32 1.980   7.01 CMASS
MMASS 25 627( 2 133)          32.281(19.658)  32  32*100.000( 1.003)        100.000( 0.000)  32  32 0.511   2.41 MMASS
-------------------------------------------------------------------------------------------------------------
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The prevalence of zero values poses a problem for the geometric mean, since the logarithm of 0 is undefined. This problem was eliminated though not successfully, by replacing 0 with .01 whenever it occurred. This value is of the order of the lowest contributions calculated in any of the PACS chemical element balances.

Comparing geometric to arithmetic means in Tables 6.3.1a & b-6.3.6a & b shows a large difference between the two, in contrast to their similarity when the chemical concentration means were calculated in section 6.1. This occurs because the geometric mean is very sensitive to low values, and when many .01 values enter into its calculation, it experiences a rapid attenuation. The arithmetic mean is perfectly comfortable with 0 values and it should be used in evaluating source contributions rather than referring to the geometric mean.

Of course, there is no empirical evidence to establish the distributions followed by source contributions, though one would expect them to be similar to the distributions of the chemical concentrations from which they are calculated. The arithmetic mean absolute and percent concentrations are not exact representations of contributions to the violation of the federal standard, but they are close enough.

Once again the unstratified annual means have been chosen because of their close similarity to the stratified means and the additional information contained in their format. The bottom two lines of the format contain the average calculated mass (CMASS) obtained by summing all source contributions and the average measured mass (MMASS) similar to that appearing in Tables 6.1.1a & b-6.1.6a & b. The difference in the treatment of minimum detectable concentrations causes MMASS to differ from the average in section 6.1. The results of 6.1 are preferred in these cases.

As far as assessing major contributors to the total suspended particulate at each site, Tables 6.3.1b-6.3.6b tell the whole story. For fine particulate contributors, Tables 6.3.1a-6.3.6a answer the question.

If chemical element balance receptor modeling was a proven methodology with an extensive track record, this section could end here. This is the first systematic application of this methodology to assess the cause of standard violations, however, and much of the interpretation of PACS results should be used to confirm or deny the existence and magnitudes of the source type contributions listed in these tables.

Hypotheses about each source type based on its spatial relationship to the receptor, the temporal variation of its emissions (both diurnally and annually), its dominant particle size range, its chemical composition and its similarity to other sources can be advanced, then tested against the information in sections 3.1 and 3.4 and the 6000 pages of data summaries, source summaries, flow pattern and regime averages.

A few examples of this procedure will be given in this section, but this short treatment should not be construed as the exhaustive examination which the PACS results require.

The most prominent source contribution to the total suspended particulate, and the source at which control efforts must be directed if the total suspended particulate level is to be reduced, is that of urban dust.

To confirm this contribution, we hypothesize that dust concentrations should be substantially higher in the city than they are at the background sites and the majority of their mass should occur in the coarse particulate. As an area source the contributions should be distributed more or less uniformly throughout the city. If they are caused by resuspension from moving motor vehicles, then those receptors in areas where more of this movement takes place should exhibit higher concentrations.

The results in Tables 6.3.1a & b-6.3.6a & b confirm all of these hypotheses. Average urban dust concentrations are three to five times higher in the city than background continental dust average concentrations. While UDUST accounts for an average of 40-48% of the total suspended particulate in the city, only 4-7% of the fine particulate fraction can be attributed to it. In most areas of the city its average total particulate concentration hovers around 38 $\mu g/m^3$, except at Pacific Motor Trucking (site 4) where the average movement of diesel trucks and trains is high above the norm for the rest of the city.

Urban dust is characterized by many chemical species, and there are no other source types or combinations which could have reproduced the concentrations observed on individual samples, so the UDUST presence is hard to doubt. The average percent uncertainty of each urban dust contribution of 5-6% is consistently lower than that for any of the other source types, attesting to the validity of these estimates of its contribution.

Other hypotheses could be advanced and checked by reference to PACS results. One would expect Sundays, when traffic volume is less, to exhibit lower urban dust contributions than weekdays in a similar meteorological regime if the real cause of urban dust is resuspension by traffic. If the contribution is due to re-entrainment by wind, then percent averages in high windspeed flow patterns 1 & 4 might be compared with percent averages in low windspeed flow patterns 3 & 6; the percentage contribution under high speed wind conditions should be greater if this is the case. If re-entrainment is doubted as the cause, then the results from rainy days, on which the dust would be harder to resuspend, should be contrasted with dry days, on which resuspension should be easier.

Excluding the single constituent source types for the moment, the next most abundant contributor to urban total suspended particulate averages is vegetative burning, the combination of VBRN1 and VBRN2. If this contribution is real it should be dominant in the fine particulate fraction. If it results from fireplace or woodstove burning for heating it should be more prevalent in the winter season than in the summer. The urban winter averages should outweigh the background winter averages and contributions should be greater in the residential areas.

The values in Tables 6.3.1a & b-6.3.6a & b show 70-80% of the urban averages for vegetative burns concentrated in the fine particulate mode. The average urban vegetative burn concentration is 3-4 times that of the average background site values. PACS seasonal averages show 30% of the fine particulate at site 5 composed of vegetative burn in the winter average, but only 7% in the summer average. The average vegetative burn contributions appear uniform at 4-6 $\mu g/m^3$ at all of the urban sites but are not significantly larger at the residential location, site 5.

It will be recalled from section 3.1 that this source type did not contain any unique chemical species, and that the variability of those that were detected was great. This is reflected in the high average uncertainties attached to VBRN1 and VBRN2 of approximately 20% and 40%, respectively. Doubt also exists about the validity of some of the source samples. Much more confirmatory efforts should be placed into the verification of these contributions than is necessary for the urban dust contribution. Particular days on which domestic, slash, and field burning were known to have taken place (see Table 4.2.6) should be compared to similar days without those impacts. If the burning appears with equal frequency on both types of day, then it may not really be a contributor (or some unknown vegetative burning took place on the non-impact days).

Though these vegetative burning contributions could be real, to confirm them by the chemical element balance will require more unique chemical constituents, ones which are surely present in the carbonaceous fraction of the ambient aerosol and vegetative burn emissions.

The third most abundant contributor to the urban annual average total suspended particulate is leaded auto exhaust. There is little doubt that this source exists because of its nearly unique Pb and Br contributions. Nevertheless, hypotheses could be advanced about the temporal variation of auto exhaust contributions. These conjectures could be tested by examining percentage contributions from sequential samples and comparing them to traffic volume cycles or by comparing element balances from high traffic weekdays to low traffic Sundays. The source contribution averages are 3-5 times higher at the urban locations than they are at background sites and the major portion occurs in the fine particulate fraction; all these facts are consistent with the auto exhaust source.

There might be some question about the magnitiude of the auto exhaust contribution, since the source composition was scaled to a 20% Pb concentration. Yet this is one of the lower estimates of the Pb value in Table 3.1.2.1c, so if anything, the auto exhaust contribution is overestimated. It was speculated in section 3.1.12 that this leaded auto exhaust component probably contains unleaded auto exhaust, diesel truck exhaust, and tire and brake wear.

The average marine contribution to the total suspended particulate hovers around 1.6 $\mu g/m^3$ at urban and background locations and is equally distributed between the fine and coarse particulate, consistent with expectations for this natural contributor.

The elevated value at site 2 is puzzling and can be attributed to a higher average Na concentration at site 2 than at the other sites as evidenced by Tables 6.1.1b-6.1.6b. Possibly another source of Na affects this receptor.

The remaining source contributions (still excluding those of a single constituent) comprise less than 1 $\mu g/m^3$ apiece of the average total suspended particulate, and from a control strategy point of view, they can be ignored, if the element balance is believed. They will be examined here as instructive features of the chemical element balance methodology.

Because residual oil combustion emissions are well characterized chemically, seasonal averages might confirm its use as a heating source as opposed to its uses in industrial processes; the use of these averages to confirm its impact does not seem necessary. Referring to section 3 of Table 3.1.1b allows an estimate of the total stationary fossil fuel combustion load, including natural gas and distillate oil combustion, to be made by use of Gartrell and Friedlander's (1975) emission inventory scaling. All of the sources in this category are used for the same purpose, space heating (near site 2 they are also prevalent in the production of industrial process heat). They are widely distributed area sources and follow the same diurnal and seasonal cycles. Thus, the contribution from the grouping as a whole will be roughly proportional to the residual oil combustion contribution. The best estimate of the proportionality constant is the inverse of the fraction of the group emissions contributed by residual oil combustion, 2.25. Even multiplying all residual oil combustion source contributions by this factor and using the result as an estimate of the average fossil fuel space heating impact shows this entire source grouping to have little effect on the total suspended particulate loading.

The industrial source types, the kraft mill, sulfite mill, hog fuel boiler, aluminum production, steel, ferromanganese and carbide furnaces, are also of little consequence to both the fine and total suspended particulate. In fact, it is doubtful that most of them are being detected at all in the presence of the eight basic source types. The average uncertainties of the sulfite mill, hog fuel boilet, aluminum production and carbide furnace rarely dip much below 30% in either size range at any of the sites. Their contributions are not larger at receptor sites closer to the sources (see Figures 3.4.1-3.4.6 and Table 3.4.2 to locate these industries in relation to the receptors). These source contributions are probably being fitted to differences between the ambient and calculated concentrations which are caused by uncertainties in the marine, urban dust, auto exhaust, and residual oil combustion contributions rather than the presence of the industrial sources. As such, the contributions in Tables 6.3.1a & b-6.3.6a & b are upper limits of the possible industrial contributions. This could be verified by simulation studies similar to those of section 3.3 with the source model contributions equal to the average values presented in this section. Even this upper limit is too small to merit consideration in the design of a control strategy.

By emission inventory scaling similar to that invoked for the space heating contributions, the sources in the forest products, aluminum processing and small point sources sections of Tables 3.1.1a & b can be eliminated as significant contributors.

Although the contributions of the steel electric arc and ferromanganese furnaces are small, they are not to be dismissed as fitting to the noise. These source types are located at points 41, 42, 43 and box B of Figures 3.4.1-3.4.6 and should have their greatest impacts at site 2 with contributions decreasing as sites become more distant from the sources.

This hypothesis is confirmed by average total suspended particulate contributions from STEEL of 1.8, 1.2, .5, and .03 $\mu g/m^3$ at sites 2, 3, 4, and 5, respectively. For the ferromanganese furnace it is not so pronounced.

If these source types are really affecting site 2, then their flow pattern 1, 2, and 3 (Figures 3.4.1-3.4.3) average percent contributions should exceed their flow pattern 4, 5, and 6 (Figures 3.4.4-3.4.6) averages. The PACS annual averages in these flow patterns do not support this hypothesis. The steel electric arc furnace contribution averages are 1.2%, 1.8%, and 3.0% in northerly flow patterns 1-3 and 3.1%, 2.2%, and 3.5% in southerly flow patterns 4-6, the opposite of what would be expected if the arc furnace was really affecting the receptor. Of course, this single observation does not exclude the arc furnace as a source, but it doesn't help to confirm it either. The ferromanganese furnace wind direction hypothesis is confirmed by the averages with .18%, .34%, and .56% average contributions in flow patterns 1-3, respectively, and 0.0, 0.0, and 0.07% contributions in flow patterns 4-6, respectively.

All in all, the surface windflow averaging is not too helpful in identifying sources in the Portland area because point sources of a directional nature simply do not make very large contributions. The seasonal and size range flow pattern averages should be examined to see if there are any surprises or patterns, but their use in confirming sources seems to be minimal. This is not to say that the concept is worthless. In an urban area with a heavier industrial base than that of Portland such averaging could be very effective, but in this particulat case that effectiveness has not been demonstrated.

The magnitudes of the single constituent source types, VC, NVC, NO_3^-, and SO_4^{-2}, comprise major fractions of the fine and total suspended particulate. Over 30% of the average total suspended particulate at background sites and over 20% at urban locations come from sources of these species not accounted for by the other source types. The fraction of the fine particulate comprised by these four contributors exceeds 40%.

Non-volatilizable carbon (NVC) is not a secondary aerosol and it cannot be placed in the same category with SO_4^{-2}, NO_3^-, and VC. The average uncertainty of this source type contribution in the fine particulate is always greater than 30%, so its presence there is subject to doubt. In the total suspended particulate, however, its average uncertaintiy, while still high at 20% (due mostly to the variability in the analysis technique), still places the non-volatilizable carbon contribution above minimum detectable limits. A clue pointing to one specific primary source of this component not included in Table

3.1.12.2 is found in the average NVC contribution to the total suspended particulate at Pacific Motor Trucking (site 4). Recall that the diesel truck exhaust source samples in Table 3.1.2.3 contain over 50% non-volatilizable carbon. The heavy truck traffic near site 4 shows evidence of its presence with the highest average non-volatilizable carbon concentrations of any of the other sites. Urban site 3 and industrial site 2 also demonstrate much higher NVC contributions than residential site 5 and both background locations. PACS results comparing workdays to holidays might support the hypothesis of diesel trucks as a major source of the single constituent non-volatilizable carbon contribution.

The single constituent volatilizable carbon source contributes a tremendous portion of the aerosol. At residential site 5 its contribution to the fine particulate averages 26%. Secondary sources of volatilizable carbon are photochemical in nature, and the portion of the total aerosol they comprise should be higher in the summer season, when sunlight is more prolonged and intense, than during the winter season. This is not confirmed by PACS results at site 5 which show the summer VC average contributing 17% to the fine particulate while the winter average is 24%.

Earlier, some surprise was registered that vegetative burning contributions were not higher at residential site 5, since fireplace and woodstove use would be concentrated in its vicinity. It may be that the uncertain source compositions of vegetative burning are underestimating that source contribution and that much of the single constituent

VC source contribution is really due to this burning. In the individual element balances, VBRN1 and VBRN2 always increased at the expense of the VC contribution, leaving the summed mass contribution nearly the same. If VC was eliminated as a source type, thereby making the volatilizable carbon concentration a fitting species, then the vegetative burn contribution always increased.

The vegetative burn/secondary organic source type controversy can be studied, but not resolved with present PACS results. Measurements of ions and elements are not sufficient to distinguish these sources because such species are not present in them to any great extent. The carbonaceous fraction of the sources and the ambient aerosol must be broken down into molecular components before a definitive distinction can be made.

Urban sulfate and nitrate absolute source contribution averages in the fine particulate are not much greater than the background site averages, indicating that little of these species is produced by secondary conversion of SO_2 and NO_x in the city. Much of these single constituent contributions is created outside of the airshed and they are not subject to local control.

On the average, 90% of the total suspended particulate at urban sites is accounted for by the chemical element balances and 83-87% is accounted for at the background locations. Most of the difference is due to underestimation of the fine particulate loadings. Only an average 78-84% of this fraction was accounted for in the city and 70-75% at the background locations.

This discrepancy is not surprising in the fine particulate portion because of the large role played by the single constituent source types. These constituents are usually attached to other species which were not quantified by PACS. Specifically, sulfate and nitrate are often present as NH_4SO_4 and NH_4NO_3, combinations which would increase their single constituent contributions by 1.19 and 1.29, respectively.

On the average, about three hydrogen atoms are associated with each carbon atom in organic compounds, and these compounds can also contain species, such as oxygen, which are not accounted for in the VC single constituent source type composition. A scaling factor in the range 1.2-1.5 might be appropriate for the VC source contributions.

The auto exhaust Pb and Br fractions could be scaled down by about 20%, and the carbon portions might be modified to better represent diesel truck and unleaded emissions, thus increasing its contribution slightly.

The emissions inventory scaling of the residual oil combustion contribution to encompass all stationary fossil fuel emissions will account for some of the measured mass, though not for much.

Some combination of these scalings can surely bring the calculated fine particulate contribution to with 10% of the measured value, and in future research some effort should be invested in the calibration of source compositions so that the calculated masses will equal the measured masses without external scaling.

This chapter has briefly outlined the production, scope, and uses of PACS results, while not attempting to study them all. Observations about the ambient data, the chemical element balance methodology applied to it and the possible source contributions to the Portland aerosol have been made in light of the previous chapters.

A recap of the findings and some projections of future areas of study will be helpful in putting this work into perspective.

CHAPTER SEVEN: SUMMARY, CONCLUSIONS, AND PROSPECTS

This document is an exploration of a methodology, even though it is highly colored by the Portland Aerosol Characterization Study of which it was a part. The conclusions in this chapter are not concerned with the contributions to Portland's aerosol so much as with the way in which those contributions were assessed. This chapter will summarize the work of the previous chapters, evaluate the successes and failures of the PACS, and reiterate some broad areas for future research.

At the outset several receptor models, which establish relationships between source and receptor on the basis of aerosol chemical composition, were derived and related to each other. These were the chemical element balance, the enrichment factor, time series correlation, multivariate models and spatial models. Emphasis was placed on their physical justification; limitations, ambiguities and constraints were noted.

The chemical element balance receptor model was chosen for further study because of its ability to quantify as well as identify source type contributions and because of its fundamental importance to the other models. Its major weaknesses were stated, then strengthened to a greater extent than ever before: most major aerosol sources within the airshed were identified and chemically characterized; a weighted least squares procedure for calculating source contributions was derived which took into account the variability in the dependent source compositions as well as that of the independent ambient concentrations;

the basic assumptions of this least squares chemical element balance were stated and the effects of deviations from several of them were assessed by a series of Monte Carlo simulation studies which provided insight into applications to ambient data; a crude source-receptor model hybridization by averaging source contributions within surface windflow patterns was proposed to identify specific point sources of aerosol.

The design of an experiment to obtain a representative sample of the airshed, one which would be directly relevant to violations of the federal annual total suspended particulate standard, was presented in regards to site selection, filter selection, sampler selection and sampling schedule. Standard operating procedures for source sampling, field sampling, filter handling and storage, filter weighing, filter cutting, x-ray fluorescence analysis, instrumental neutron activation analysis, ion chromatography and carbon analysis were defined and verified by interlaboratory and intermethod comparisons.

A mid-scale data management and quality assurance system for use by ordinary technicians on a mini-computer with minimal rapid access storage was developed.

Finally, the analytical results were summarized for each site in the form of seasonal and annual flow pattern and meteorological regime averages. A rapid methodology for application of the chemical element balance to each sample was devised which preserved human interaction and decision. Nearly 1700 individual chemical element balances were completed. These results were reduced to seasonal and annual flow pattern and regime averages for interpretation.

These annual average source contributions were examined at each receptor and the major primary aerosol contributors were found to be urban dust, vegetative burning and automobile exhaust. Industrial sources and stationary fossil fuel combustion were found to make only small contributions, if any, to the airshed's particulate levels.

It was not possible to attribute definitively the volatilizable carbon to secondary aerosol formation, and it was speculated that the vegetative burn could account for some of this if its contribution were underestimated. Sulfate and nitrate concentrations were not greatly enriched over background values and are probably not formed within the airshed.

As far as the goals of the PACS are concerned, the project must be considered a success. Very close to 100% of the aerosol can be accounted for by different aerosol source types and the major one contributing to the violation of the federal ambient standard has been identified with great precision. Whether or not the high urban dust concentration really deserves more control efforts than the fine particulate contributions from the more toxic and visibility degrading vegetative burning and automobile emissions is not an issue until some form of fine particulate standard is promulgated.

As far as the methodology is concerned, the PACS application of the chemical element balance experienced some difficulties.

Most of the source types tested did not contain very large quantities of the chemical species quantified, aside from carbon. Others, such as the carborundum plant, exhibited a composition that varied too much from sample to sample because of changes in the operating mode. The vegetative burn samples are close to falling into this category.

Industrial sources with large percentage compositions of several chemical species could not be detected in the presence of the basic source types, dust, residual oil combustion, marine background and auto exhaust.

Mainly because of this inability to detect these point sources, the source/receptor model hybridization of windflow pattern averaging could not be tested as a means of distinguishing individual emitters within a source type.

Probably the most important aspect of this study is the opportunity it has provided to determine the successes and failures of a receptor model application and to define the areas in which further work is required. Three broad topics have been covered in this document: source characterization, receptor modeling, and ambient aerosol characterization. Much more research needs to be perfommed within each one.

An emissions inventory of the area under study is essential to assembling a source matrix. In the source type groupings of Table 3.1.1 it can be used easily for emission inventory scaling to account for source types which cannot be included in the balance.

Once the important source types in the airshed have been identified, they must be assigned chemical compositions. It is in this area that a real need exists. No comprehensive reviews of sources directed toward the receptor modeler exist today. Certainly many such works have been published for the pollution control engineer, and a knowledge of the processes involved, the precursor material, average emission rates and control equipment contained in these works is important for the receptor modeler. But he needs more information about the chemical composition of emissions, its variation with source operating parameters, its possible fractionation in the atmosphere, and the likely dispersion characteristics of the source type. He needs to know if the source type has been identified by receptor models in other cities and with what difficulty. The chemical composition data must be complete (i.e. not just the results of one analysis technique), and its variability must be assessed.

Section 3.1 offers a taste of the form which these reviews might take, but it is much too sketchy and incomplete. Substantial original source testing will be required, and a standard operating procedure similar to that described in section 3.1 should be devised before such sampling is undertaken.

In addition to the elemental and ionic analyses, specific analysis of the carbon component is a must in such tests, as this constitutes a major portion of many source types, particularly those contributors to the increasingly important fine particulate regime. There is evidence that specific carbon species can label source types. Pierson and Brachaczek (1976) have identified styrene-butadiene rubber (SBR) in roadway gutter debris. This species only occurs in tires, and it might be useful in estimating the fraction of the urban dust contribution caused by vehicular resuspension. Appel, et al. (1976, 1979) assert that primary volatilizable organic carbon can be separated from the secondary source of this species by a combination of solvent extractions and carbon determinations. They (1976) broke down the primary fraction of some ambient aerosol samples from Pasadena into aliphatic, aromatic and polar molecular components. The same analysis of auto exhaust samples showed a very similar composition. Schuetzle, et al. (1973) speculate that the sources of organic fatty acids may be animal rendering and that chlorinated aromatics are tracers for pesticides. Cronn, et al. (1977) list many unique groupings of organic constituents and their possible aerosol sources.

On a more specialized plane, Currie and Murphy (1977) and Currie, et al. (1978) demonstrate the use of $^{14}C/^{12}C$ ratios to differentiate fossil fuel combustion carbon emissions from recently living vegetative burn emissions.

The top priority reviews would include the four basic source type groups, geological material, marine background, motor vehicle exhaust, and stationary fossil fuel combustion because of their ubiquitous nature; they are detected in almost every aerosol sample and will be found in most cities. Much information exists about these sources, some of it having been summarized in section 3.1. A certain amount of original source testing would be helpful, but it need not be as extensive as that required for other sources.

Of great importance in the Portland area, and of increasing interest nationwide, is the vegetative burning source. As fuel prices rise, wood is being looked to as a source of heat and the emissions from its combustion are on the increase. Very little information exists about the chemical composition of these emissions and much source testing is required, with primary emphasis on analysis of the carbonaceous fraction.

Of lower priority in Portland because of their small contributions, but of some consequence in certain urban situations, are the industrial point sources. The PACS source compositions could have been wrong by factors of 2 or 3 (they are much more accurate than this, in reality) and the contributions to ambient loadings would still be insignificant. But if these were major contributors, like urban dust or auto exhaust, then accuracy would have been essential. Reviews of these source types must be more explicit about industrial operating modes and their effects on emissions compositions, about the different precursor materials used, and about the different types of emissions within a single industry.

Finally, secondary aerosol species and their contributors must be identified and summarized with the receptor models in mind. The effects of meteorological parameters and interaction and interference with the primary aerosol should be defined.

A set of such reviews, one for each source type grouping in section 3.1, and probably other groupings as well, oriented toward the application of receptor models would remove a major hurdle in their application, that of inadequate source characterization. Such reviews would have to be updated periodically to keep up with changes in emissions compositions caused by legislation and technological advancement.

The second major topic to be dealt with is that of the receptor models themselves. Many questions were raised in chapter 2, more than were answered in the subsequent chapters. Even the chemical element balance receptor model, with its extensive examination in this document, requires more development. What about the basic assumptions stated in section 3.3 which were not tested, or the effects of greater deviations from the ones that were tested? The tracer solution method was not given close scrutiny, and linear programming techniques were given none at all. Non-negative linear least squares (Leggett, 1977) might be adapted to this application, thereby eliminating the physically impossible but mathematically common case of negative source contributions (though Gayle and Bennet, 1978, show that this is not as useful in some cases). At the very least, the simulation studies of section 3.3 should be rerun with the source model contributions equal to the PACS annual averages. This should indicate whether or not the small, industrial point source contributions could be due to uncertainty. Such simulations might allow minimum detectable limits to be specified for certain source type contributions in the presence of other sources.

It goes without saying that simulation studies should be performed for the other receptor models, above all for the orthogonal factor analysis.

Source/receptor model hybridization must be explored to incorporate windspeed and direction, emission rates, and possibly relative humidity and insolation. Each of these factors affects aerosol concentrations and their measurement is routine. It is possible that their effects can be useful in identifying sources. The crude application in the PACS says no, but a more rigorous examination might reverse that answer. The source model in section 3.3 could be replaced with a more sophisticated one, and simulations could be run to assess the effectiveness of the hybridization under the onslaught of model mis-specifications and random error.

Particle size has been shown to be a relevant parameter. Could additional size fractions be used to identify sources? Evidence has been cited in chapter 2 to suggest that this might be the case.

There seems to be a great misunderstanding about the powers and limitations of receptor models, particularly the multivariate ones. Here again, a series of reviews, more detailed and with more examples than chapter 2, is required to acquaint potential receptor model users with the subject.

Finally, the ambient aerosol study needs to be examined to provide a tested, standardized method of assessing source contributions. Here, a close examination of the PACS as an experiment, rather than of its results, could be of great help.

The objective of experimental design should be to get the most accurate picture of the annual aerosol contributions for the least cost. Thus, every aspect of the project should be examined. Dubious procedures should be upgraded, and operations which do not yield sufficient information should be done away with.

Average results from all sampling sites in the various meteorological regimes should be compared. If the information is duplicated, then it may be possible to eliminate some of the sites in future studies. Site selection criteria should be modified for receptor modeling purposes. For example, one receptor might be placed at the maximum concentration spot of an emissions source as determined by a source dispersion model. If the receptor model cannot detect the source type in that location, then it is probably fruitless to search for that source type's contribution in more distant sections of the airshed.

All questions about the filters should be resolved, particularly the conversion of gaseous NO_x and SO_2 to nitrate and sulfate. If necessary, samplers should be modified to remove these gases from the airstream as did Loo, et al. (1978) for SO_2.

The ERT sequential samplers did an excellent job for the PACS. The size cutoff of the fine particulate sampler was very sharp and subtraction of fine from total yielded very good values for the coarse particulate, as evidenced by the consistently excellent fits of geological material to the coarse particulate concentrations. Many field blank filters (i.e. those placed in the sampler but through which no air was pulled) were subjected to chemical analysis upon their return to the laboratory. Chemical concentration measurements due to particle fallout and filter handling can be assessed by examination of these results. Improvements to the sampler and filter handling procedures should result.

Additional ports for simultaneous sequential sampling on glass fiber filters for carbon analysis would provide more consistent carbon values than the hi-vol carbon measurements of the PACS. The timing system of the ERT sampler, which experienced reliability and accuracy problems, should be replaced with a microprocessor control which would not only sequence the samples more precisely, but could also continuously monitor the volume sampled and correct it for temperature and pressure changes.

The exhausts of hi-vol samplers should definitely be filtered to remove any possible copper contamination.

Results from PACS diurnal sequential samples need to be compared to decide whether or not a 24-hour average sample would be just as useful. At the background sites it appears that source contributions are somewhat constant throughout the day and that one daily sample would have sufficed. The number of continuous sequential samples available for the 8-hour specimens is so small that time series correlation is not possible. The 18 four-hour samples at site 3 which were presented in section 2.4 _do_ contain information, however, because a cyclic variation corresponding to that of an emissions source could be identified. Shorter sampling periods for more homogeneous wind direction averaging bought nothing for the PACS because of the lack of strong point source contributions.

The meteorological regime classification worked well for the selection of intensive chemical analysis days to represent the entire year, but it needs to be placed on a more objective footing. Source contribution averages from regimes with similar TSP loadings should be compared to see if some regimes might be combined.

PACS source test data need to be gone over once again. The sampling team has to be quizzed about the sources sampled and about additional details of specific samples to fill in Table 4.5.2. Their criticism of the source sampling apparatus should be recorded and improved upon. Minimum detectable concentrations need to be assigned to samples in section 3.1. Outlying values need to be weeded out and averages re-calculated.

In the area of standard operating procedures, the PACS has much to offer. With trained technicians, the system operated smoothly and efficiently. New rapid, multi-component analytical techniques for selected carbon species need to be developed, standardized and validated.

The PACS excelled in quality assurance, with duplicate analyses or standard reference materials run every 10-15 specimens. Multiple measurements of the same parameters offered a quality assurance check on every single specimen. The only improvement, which was not implemented for lack of resources, would be to re-analyze many of those samples in which the discrepancy could not be accounted for. PACS data summaries should be examined individually and the number and types of flags for each measurement should be tabulated and patterns sought. Standard operating procedures should be modified as a result.

The interlaboratory/intermethod comparisons were essential to the verification of the PACS data. These should be an integral and periodic part of any aerosol characterization study.

The PACS data management system is efficient, but inflexible. It was designed in piecemeal fashion without a picture of the entire program. It relies too much on low level programming to move data about.

Its advantages are that it can be handled by ordinary technicians with rudimentary programming skills (they do not remain rudimentary for long) and that it stores so much data in so little space. It has many interaction points where data integrity is checked by human beings and it incorporates checks of data reasonableness to alert the operator to possible errors.

Existing data management systems for air pollution information (Upchurch, 1978; Hedgepeth, 1978; Index Systems, 1976; Fair, et al., 1968; Research Triangle Institute, 1977; Zimmer, et al., 1973) deal with the final pollutant concentrations only, and not with the calculations necessary to obtain them. They are intended for huge data bases and require a substantial investment in computer storage, hardware and personnel. The record formats are long and redundant. Data interpretation is limited to averaging for the purpose of checking compliance or issuing permits. These systems require protracted installation and debugging periods and are meant for long-term monitoring. They perform their function well, but that function is not to assess sources of ambient aerosol.

The data management function is one of the most important of the whole aerosol study. It permeates every standard operating procedure, makes rapid quality assurance comparisons possible and dictates the ease and speed with which data interpretation takes place.

The PACS proves that a time sharing mini-computer with limited storage is equal to the task. In fact, it is desirable for the implementation of an aerosol study data management system. Most operations could be handled by a less expensive, dedicated micro-computer with floppy disk storage, though the computation times might be longer.

The latest in data base management (Whinston and Haseman, 1975; Yao, et al., 1978) should be studied and combined with the requirements of the aerosol study to implement a comprehensive data management structure in the scientific language FORTRAN which could be adapted to any time sharing mini-computer and run by personnel with minimal data management experience.

Very closely tied to the data management problem is the implementation of the receptor modeling. An important feature in the PACS is the interactive capability. The researcher is relieved of all data manipulation problems. With a few commands he can examine his data rapidly from many points of view. The power of this cannot be overstated; in the recognition of patterns and in the use of intuition, there is no computer equal to the human mind. For interpretation to be meaningful, the human manipulation, understanding and combination of the data must be preserved and enhanced.

Once the receptor models have been theoretically formulated and studied, they must be incorporated into this interactive mode. Maximum flexibility must be maintained so that the researcher can test any hypotheses he comes up with.

With such a system it will be easy to explore the application of many variations of different receptor models to the same set of data. Inconsistencies and anomolies should be sought out and resolved. Time-saving methods should be noted and communicated to others. For example, chemical element balances should be performed on the average chemical concentrations in each size range of the PACS data and compared with the averages of the source contributions obtained from individual specimens. Theoretically they should be the same. If they are, then a tremendous time savings could be realized by performing balances on these averages. This would give up information about the variability of the source contributions, however.

With such a system other receptor models should be applied to PACS data. Intensive analysis could be performed on samples from site 3, March 14, 15, 19, and 20, 1978, which would complete a ten day time series at little added expense. This data set of 60 four-hour specimens with high quality measurements would provide an excellent opportunity to examine the time series correlation and factor receptor models in the same way that the chemical element balance receptor model has been treated here. The chemical element balance results from these days would provide a good standard of comparison.

The PACS demonstrates that the chemical element balance, or better termed the chemical mass balance because of the non-elemental species involved, is a useful receptor model in assessing the presence of source contributions and estimating their magnitudes. But an important caveat needs to be re-emphasized: the receptor model expresses what could be there, and if all other possibilities can be eliminated, then, to paraphrase Conan Doyle, that which remains, no matter how improbable, must be the truth. This means that source characterization, receptor models and experimental results must be exhaustively explored and that no path can be left untrodden in narrowing down the list of suspected source types.

Future aerosol studies should dedicate a substantial portion of their resources to development in these three major areas before drawing definitive conclusions about major polluters. Receptor modeling methodology is still in its infancy and multi-billion dollar control policies should not be promulgated solely on its results until it has become established as a routine discipline!

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