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Estudo de Modelos para Identificação de Fontes de Emissão de Aerossóis a Nível de Receptor

(Recpetor Model)

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Review of the Chemical Receptor Model of Aerosol Source Apportionment

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There are two general types of aerosol source apportionment methods: dispersion models and receptor models. Receptor models are divided into microscopic methods and chemical methods. Chemical mass balance, principal component factor analysis, target transformation factor analysis, etc. are all based on the same mathematical model and simply represent different approaches to solution of the fundamental receptor model equation. All require conservation of mass, as well as source composition information for qualitative analysis and a mass balance for a quantitative analysis. Each interpretive approach to the receptor model yields unique information useful in establishing the credibility of a study's final results. Source apportionment sutdies using the receptor model should include interpretation of the chemical data set by both multivariate methods.

Urban aerosols are complicated systems composed of material from many different sources. Achieving cost-effective air particle reductions in airsheds not meeting national ambient air quality standards requires identification of major aerosol sources and quantitative determination of their contribution to particle concentrations. Quantitative source impact assesment, however, requires either calculation of a source's impact from fundamental meteorological principles using source oriented dispersion models, or resolving source contributions with receptor models based on the measurement of characteristic chemical and physical aerosol features. (1)

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Although source oriented dispersion models are invaluable predictive tools, their ability to quantify the impact of a source is limited. Receptor oriented methods of source apportionment, however, have evolved in recent years to the point where they now clearly form a new discipline of air pollution science. (1,2) This new discipline is distinctly different from dispersion modeling and has demonstrated that it can quantitatively apportion source contributions to particle levels. (3-7) Receptor models are not predictive tools and as such, have minimal applicability in estimating the effectiveness of future control strategies. These two models, however, are complementary in nature. Receptor models, for example, can provide a precise quantitative determination of the contribution each source type made to air particulate levels, the results of which can be used to calibrate a dispersion model to provide the highest level of confidence in its predictions. (8)

A variety of receptor oriented source apportionment tools have been developed, which can be grouped into two general categories as illustrated in Figure 1. (1) Microscopic methods include both optical and electron microscopic approaches which use morphology, color, and elemental content to qualitatively identify particles, while particle volume, density and number must be estimated for a quantitative analysis. The microscopic approach is the older of the two general receptor methods and an extensive library of "microscopic fingerprints" consisting of morphological, color and elemental features has been developed over the past few decades. Microscopic methods are limited primarily by their relatively poor precision and the high cost associated with analyzing a sufficient number of particles to adequately represent the entire group of particles collected on a filter.

The chemical method of receptor modeling is the most recent approach to source apportionment (1,4,9,10) and extensive libraries of source "chemical fingerprints" have yet to be established. Many different chemical methods have evolved over the past 10 to 15 years. Included in this category are chemical mass balance (CMB), factor analysis (FA), multiple regression, cluster analysis, enrichment factors, pattern recognition, principal component analysis, time series and spatial distribution analysis, target transformation factor analysis, etc. These methods of interpreting chemical data have evolved from different origins and are often perceived as distinctly different models when, in most cases, their only major differences are terminology and approach.

Chemical methods, in general, identify aerosol sources by comparing ambient chemical patterns or fingerprints (interelemental patterns, spatial or time variant patterns) with source chemical patterns. Source contributions are quantified by a least squares multiple regression analysis on either the total mass on different filters or the mass of individual chemical species on a single filter. Although similarities in the different chemical approaches are greater than their differences, they have been historically divided into two categories: chemical mass balance methods, which

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Introduction

Urban aerosols are highly complicated systems composed of material from many different sources. Achieving cost-effective air particulate reductions in airsheds not meeting national ambient air quality standards requires identification of major aerosol sources and quantitative determination of their contribution to particulate levels. Quantitative source impact assessment, however, requires either calculation of a source's impact from fundamental meteorological principles using source oriented dispersion models, or resolving source contributions with receptor models based on the measurement of characteristic chemical and physical aerosol features. (1)

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attempt to define the most probable linear combination of sources to explain the chemical pattern on a single filter; (1,4,11) and multivariate methods, which attempt to define the most probable linear combination of sources to explain either the time or spatial variability in ambient chemical patterns. (4,12-14)

Each source apportionment tool (Figure 2) has its unique strengths and limitations, and each can provide valuable insight into sources contributing to air particulate levels. The most cost effective tool or set of tools, however, will depend on the nature of the airshed, potential sources and the accuracy and precision of source apportionment required.

The information provided by these models is circumstantial in nature and the results from a single interpretive approach at this stage of model evolution may be insufficient to develop the level of confidence required to support strong action or clear decisions. The objective of source apportionment studies must be to build a strong enough bridge of circumstantial information (Figure 3) to quantitatively relate a source to an impact. Thus, the entire information base must support and be internally consistent with a study's conclusions to provide decision makers with confidence that their actions will result in improved air quality.

Recent publications (1,4,9,10) have provided extensive reviews of receptor models. The objective of this paper is to discuss selective aspects of the chemical receptor model.

The Chemical Receptor Model

Source-dispersion and receptor-oriented models have a common physical basis. Both assume that mass arriving at a receptor (sampling site) from source j was transported with conservation of mass by atmospheric dispersion of source emitted material. From the source-dispersion model point of view, the mass collected at the receptor from source j, M_j, is the dependent variable which is equal to the product of a dispersion factor, D_j (which depends on wind speed, wind direction, stability, etc.) and an emission rate factor, E_j, i.e.,

$$M_j = D_j E_j.$$

From the receptor model viewpoint, the total aerosol mass, M, collected on a filter at a receptor is the dependent variable and equal to a linear sum of the mass contributed by p individual sources,

$$M = \sum_{j=1}^{p} M_j.$$

The mass of individual chemical species, m_i, is also assumed to be a linear sum of the contributions of element i from each source,

$$m_i = \sum_{j=1}^{p} F_{ij} M_j, \qquad (1)$$

where F_{ij} is the fraction of the ith chemical species in emissions from the jth source. Equation (1) can be transformed to a fractional mass concentration form by dividing both sides of equation (1)

by the total deposit mass, M, multiplying by 100% and generalizing for the kth filter as shown in the following equation,

$$C_{ik} = \sum_{j=1}^{p} F_{ij} S_{jk}, \tag{2}$$

where C_{ik} is the percent concentration of the ith chemical species on the kth filter and S_{jk} is the percent of the total mass on the kth filter contributed by the jth source. The kth filter may be either one in a series of filters collected during different time intervals at one site or one in a series collected during the same time interval at different sites. The structure of the matrices noted in equation (2) are illustrated in Figures 4 and 5.

It needs to be emphasized at this point that a model is a mathematical representation of the real world. If two models have the same mathematical representation of the real world, they are, in fact, the same model. Chemical mass balance, principal component factor analysis, target transformation factor analysis, etc. have, for all practical purposes, identical mathematical representations (Equation 1) of the real world and start with the same input data matrices (Figure 4). The principal difference in these "different" receptor models is their approach to the solution of either Equation (1) or Equation (2).

The chemical mass balance method starts with a single column vector from the ambient data matrix, C_k. This vector represents the chemical concentrations for the kth filter, which is combined with the best available estimates of the source compositions from the fractional composition matrix, F_{ij}, to form a series of linear equations in which the M_j are the only unknowns. This set of equations is then solved by the least squares method to obtain the best fit of the ambient chemical data on a single filter.

Multivariate methods, on the other hand, resolve the major sources by analyzing the entire ambient data matrix. Factor analysis, for example, examines elemental and sample correlations in the ambient data matrix. This analysis yields the minimum number of factors required to reproduce the ambient data matrix, their relative chemical composition and their contribution to the mass variability. A major limitation in common and principal component factor analysis is the abstract nature of the factors and the difficulty these methods have in relating these factors to real world sources. Hopke, et al. (13,14) have improved the methods' ability to associate these abstract factors with controllable sources by combining source data from the F matrix, with Malinowski's target transformation factor analysis program. (15) Hopke, et al. (13,14) as well as Kleinman, et al. (10) have used the results of factor analysis along with multiple regression to quantify the source contributions. Their approach is similar to the chemical mass balance approach except they use a least squares fit of the total mass on different filters instead of a least squares fit of the chemicals on an individual filter.

Each method of data interpretation provides its own unique

insight into the nature of the aerosol sources. Which method will be most effective in resolving specific sources will depend on the airshed, sources of interest, and their characteristics. The method of data interpretation, however, should not necessarily be limited to a single approach but should include both mass balance and multivariate approaches which should yield the highest level of confidence in a study's conclusion.

Conservation of Mass

Source-dispersion and receptor-oriented models both assume that mass is conserved in transport of material from source to receptor. The validity of this assumption is a matter of degree and its utility depends on the specific source, airshed and model. The problems associated with this assumption are illustrated in Figure 6. Material emitted from a source can be either in the gaseous or aerosol phase. It may go through a number of chemical and physical changes before it is collected on a filter and measured. A portion of the aerosol phase, for example, may evaporate before it is collected or particles may be removed through sedimentation in transport. The gaseous phase, on the other hand, may contribute to the aerosol deposited on the filter by condensation or through atmospheric chemical reactions. In addition, filter artifact effects and evaporative losses may alter the material deposited on the filter before it is weighed.

These potential problems appear to substantially limit the validity of the conservation of mass assumption. Its validity, however, is a matter of degree and will depend on the specific source and how well the potential events noted above have been minimized through experimental design. The effect of these potential chemical and physical changes may be reduced by sampling source emissions with size selective samplers to minimize the effects due to changes in chemistry from sedimentation, and by using dilution sampling to mitigate the effect of condensation and evaporation. (16-18) This, plus selection of appropriate filters to limit artifact effects and a thorough knowledge of potential chemical reactions can minimize the effects of deviations from conservation of mass.

A substantial amount of confusion (9,10,13,14) has recently developed as to an approach's dependence on conservation of mass. As Cooper and Watson (1) have noted, the F_{ij} factors refer to the source chemistry as it arrives at the receptor. It is assumed with the conservation of mass that the F_{ij} as might be measured at a receptor, is the same as have been measured at the source. As noted above, this may not be valid depending on the source and the method used for source sampling. The chemical mass balance method incorporates the F_{ij} directly in its calculations and as a result is often perceived as having a greater dependence on this assumption than methods such as factor analysis which do not use F_{ij} values in their calculations. Factor analysis methods, however, identify abstract factors, which explain variability. It is impossible to attribute a common

source name to these abstract factors without additional information. The F_{ij} values derived from factor analysis, for example, have little relevance unless they can be associated with known or familiar F_{ij} values derived from prior studies of source emissions.

Examples of the dependence of factor analysis on prior knowledge of the chemistry of potential sources is clearly illustrated in the literature. Blifford and Meeker, (19) who were the first to apply factor analysis to an aerosol data set, resolved seven major factors from a set of five-year average elemental compositions from thirty cities. The largest factor found contained Fe, Mn and Ti and explained 21% of the variability. They attributed this source to heavy industry based on their prior knowledge of source chemistry in 1967. Although they considered the possibility of assigning this source to soil because of the strong Ti dependence, they ruled it out because this factor was highest in cities such as Birmingham, Cleveland and Pittsburgh, was not correlated with cities expected to have high wind blown dust, and was independent of population class. This factor, however, would probably be attributed today to road dust with the current knowledge of source and ambient aerosol chemistry and the typical level of impact from road dust. In addition, Hopke, et al. (20) in their factor analysis of a Boston data set, found a factor rich in Mn and Se for which they could not assign a common source identity because they had no knowledge of a source rich in these two elements.

More recent publications using factor analysis have recognized the above limitations, (13,14) but have concluded that less source information is required by factor analysis than chemical mass balance methods. It has also been suggested that factor analysis is less dependent on the conservation of mass assumption because it examines the variability in the chemistry at the source and is therefore less dependent on what happens between source and receptor. This concept, however, fails to recognize that the usual objective of a source apportionment study is to develop sufficient "confidence" in the results to stimulate "effective action" to reduce ambient particulate levels. Assume, for example, that the relative chemistry of material emitted by a specific source is substantially altered in transit to a receptor and that the effects of this source have been resolved by factor analysis. How much "confidence" can be attributed to an assignment of the resolved factor to this particular source, if the factor's chemistry differs substantially from what is known about the source's chemistry? The degree of confidence in source assignment is directly related to the degree of similarity between the factor's and the source's chemical composition.

The level of confidence in source assignment can be increased if other observables such as time variability, size dependence, etc. are consistent with prior knowledge of a source's emission characteristics. Confidence can also be enhanced by showing that the characteristics of other possible sources are inconsistent with the ambient observables. It follows that the highest level of confidence

in a study's conclusions will result when the characteristics of all possible sources in an airshed are known. These latter points emphasize the circumstantial nature of receptor model results which may require additional information to support the "level of confidence" required to attain the most effective action.

The Study and Source Resolution

Urban aerosols are complex mixtures of chemicals contributed by many different sources. One objective of an aerosol source apportionment study is to separate or resolve the contribution of specific sources or source types from the collection of all possible sources, and quantify their contributions.

There are three main phases of a source apportionment study, which includes sampling, analysis and interpretation. Each must be optimized to attain the highest level of source resolution and most accurate apportionment. The first phase, sampling, is as critical as the other two in contributing to the overall resolving power of a study. The sampling parameters which exert the greatest influence on source resolution, include selection of sampler, filter, sampling frequency and sampling duration. These parameters, however, are not independent and their choice will represent a compromise between maximizing analytical sensitivity, precisely defining the system's variability and available resources.

A dichotomous sampler with a fine to coarse cut point of about 2 µm is preferred because of the bimodal nature of the ambient aerosol and its sources. This type of physical separation according to particle size, is the first stage of source resolution since it separates the particles as well as sources into two broad classes. This particle sorting removes chemical interferences and increases analytical sensitivity. It also increases the level of confidence when most of a road dust contribution is, for example, found in the coarse fraction.

The filter material of choice is a thin teflon membrane since it minimizes artifact formation and maximizes analytical sensitivity by X-ray fluorescence analysis. Although X-ray fluorescence (XRF) may not be the only analytical technique used, it is generally accepted as being the most cost effective analysis for source apportionment. (2) Its background and therefore, analytical sensitivity, is dependent on the filters' surface density. The analytical sensitivity of XRF for aerosols deposited on a stretched teflon membrane with a density of about 0.3 to 0.4 mg/cm^2, for example, is about three times greater than an aerosol deposited on a cellulose based filter with a surface density of about 4 mg/cm^2. This difference can be translated into either more information for the same analytical costs or the same information for a lower analysis cost.

Selection of sampling frequency and duration will be determined primarily by the relevant standard, potential sources and resources. The current particulate standard is based on a 24-hour and annual average. Thus, sampling duration should probably not exceed 24 hours.

Sampling for less than 24 hours should substantially improve source resolution due to more precisely defined time dependence and enhanced signal to noise ratios. Sampling for less than 24 hours does increase cost substantially, and it may not be necessary for the first phase of a study.

The primary objective of the chemical analysis step is to accurately measure the major chemical components and key indicating species such as Pb for automotive exhaust, Ni and V for residual oil, Al and Si for road dust, etc. Although it is not essential that all of the major chemical species be measured, it greatly improves the credibility and confidence in the final results if most of the aerosol mass is explained. Carbon and silicon should be measured because they represent two of the most abundant chemical species present in a typical urban aerosol, (21) and because they are useful indicating elements (oxygen, which may at times be the most abundant element, is impractical to measure). In general, Na, Mg, Al, S, K, Ca, Fe and Pb should be measured because of their abundance and their roll in source fitting. Other elements such as P, Cl, Ti, V, Cr, Mn, Ni, Cu, Zn, Br, Rb, Sr, Zn, Cd, In, Sn, Ba, rare earths, etc. explain smaller portions of the total mass but may be key indicating elements. Chemical species such as ammonium and nitrate ions, and specific organic compounds, may also be useful. Measurement of specific organic compounds should be undertaken only after a thorough review of the expected source, transport, and analysis chemistries has shown the candidate compounds to have a reasonably constant production rate, a reasonable aerosol lifetime and measured by a relatively low cost analysis technique. The set of essential chemicals and preferred analytical techniques will be determined by the specific sources in each airshed. Selection of an optimum sampling and analysis protocol, based on a thorough understanding of the chemistry of potential sources, can result in substantial cost savings and greatly improved source resolution.

The interpretation stage consists of applying one or all of the chemical receptor model approaches to interpreting the chemical data generated. The objective of a source apportionment study is the support of effective control action. The level of confidence required to initiate this action may be established with a single receptor model interpretive approach or it may require information from additional interpretive approaches, wind sector analysis, (4, 22) dispersion models, microscopy, etc.

The first step of any source apportionment study should therefore include a thorough review of potential sources, their chemistry and time dependence, if the highest level of confidence is to be established in the final results.

Conclusions

The chemical receptor model is one of the most precise tools currently available for assessing the impact of aerosol sources. Each interpretive approach to the receptor model yields unique information useful in establishing the credibility of the final results.

A source apportionment study using the receptor model should include interpretation of the chemical data set by both multivariate and chemical mass balance methods. The most critical steps in a receptor model study are the initial review of potential source characteristics and the development of an appropriate study plan.

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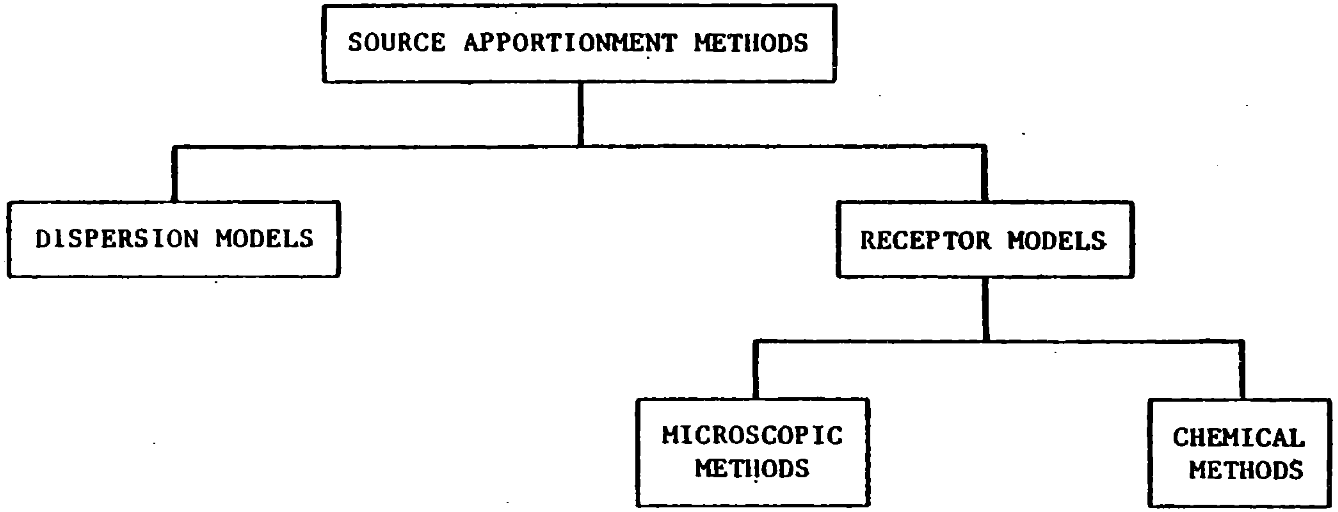


Figure 1. Schematic comparison of source apportionment methods

WHICH TOOLS SHOULD BE USED ?

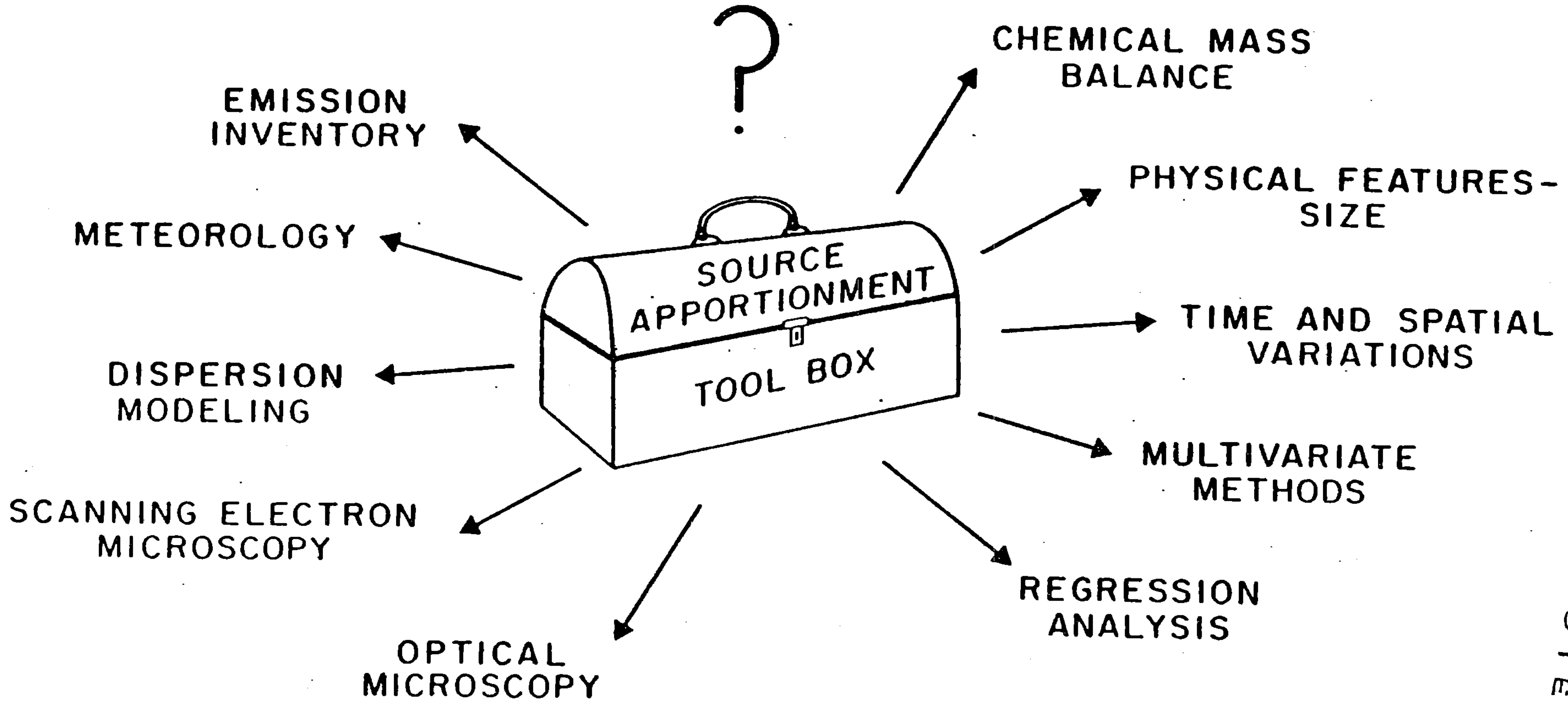
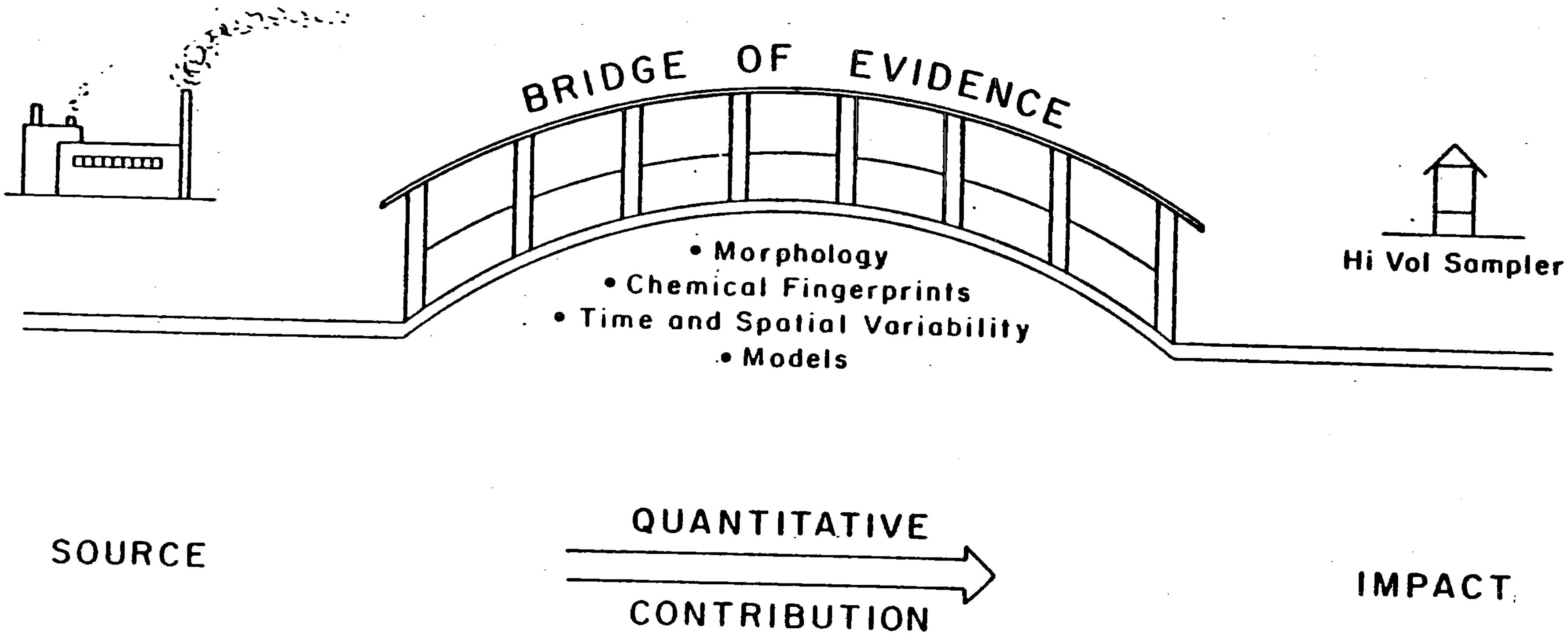


Figure 2

CIRCUMSTANTIAL SOURCE APPORTIONMENT INFORMATION



Contribution based on establishing other circumstances which afford reasonable inference of the source contribution

Figure 3

INPUT DATA

1. Ambient Chemical Data Set

$$C_{nxm} = \left|\begin{array}{llll} C_{11} & C_{12}\text{---}C_{1k}\text{---}C_{1m} \\ C_{21} & \\ \vdots & \\ C_{i1} & C_{i2}\text{---}C_{ik} \\ \vdots & \\ C_{n1} & C_{n2}\text{---}C_{nk}\text{---}C_{nm} \end{array}\right| = \left[C_{ik}\right]_{nxm} = \begin{array}{|lll|l} \multicolumn{3}{c}{\text{Time or Location} \longrightarrow} & \\ C_{Na,1} & C_{Na,2}\text{---}C_{Na,m} & & \text{Chemical Species} \downarrow \\ C_{Mg,1} & & & \\ C_{Al,1} & & & \\ \vdots & & & \\ C_{Pb,1} & & & \end{array}$$

2. Source Composition Data Set

$$F_{nxp} = \left|\begin{array}{llll} F_{11} & F_{12}\text{---}F_{1j}\text{---}F_{1p} \\ F_{21} & \\ \vdots & \\ F_{i1} & F_{i2}\text{---}F_{ij} \\ \vdots & \\ F_{n1} & F_{n2}\text{---}F_{nj}\text{---}F_{np} \end{array}\right| = \left[F_{ij}\right]_{nxp} = \begin{array}{|llll|l} \multicolumn{4}{c}{\text{Source} \longrightarrow} & \\ F_{Na,\,Auto} & F_{Na,Marine} & F_{Na,\,Kraft} & \text{---} & \text{Chemical Species} \downarrow \\ F_{Mg,\,Auto} & & & & \\ F_{Al,\,Auto} & & & & \\ \vdots & & & & \\ F_{Pb,\,Auto} & & & & \end{array}$$

Figure 4

UNKNOWN

$$S_{pxm} = \begin{vmatrix} S_{11} & S_{12} & --- & S_{1k} & --- & S_{1m} \\ S_{21} & & & & & \\ \vdots & & & & & \\ S_{j1} & S_{j2} & --- & S_{jk} & --- & S_{jm} \\ \vdots & & & & & \\ S_{p1} & S_{p2} & --- & S_{pk} & --- & S_{pm} \end{vmatrix} = \left[S_{jk}\right]_{pxm} = \begin{array}{c|ccc|c} & \multicolumn{3}{c}{\xrightarrow{\text{Time or Location}}} & \\ & S_{Auto,1} & S_{Auto,2} --- & S_{Auto,m} & \\ & S_{Marine,1} & & & \text{Source} \\ & S_{Kraft,1} & & & \downarrow \\ & \vdots & & & \\ & S_{p,1} & & & \end{array}$$

Figure 5

AEROSOL MASS BALANCE

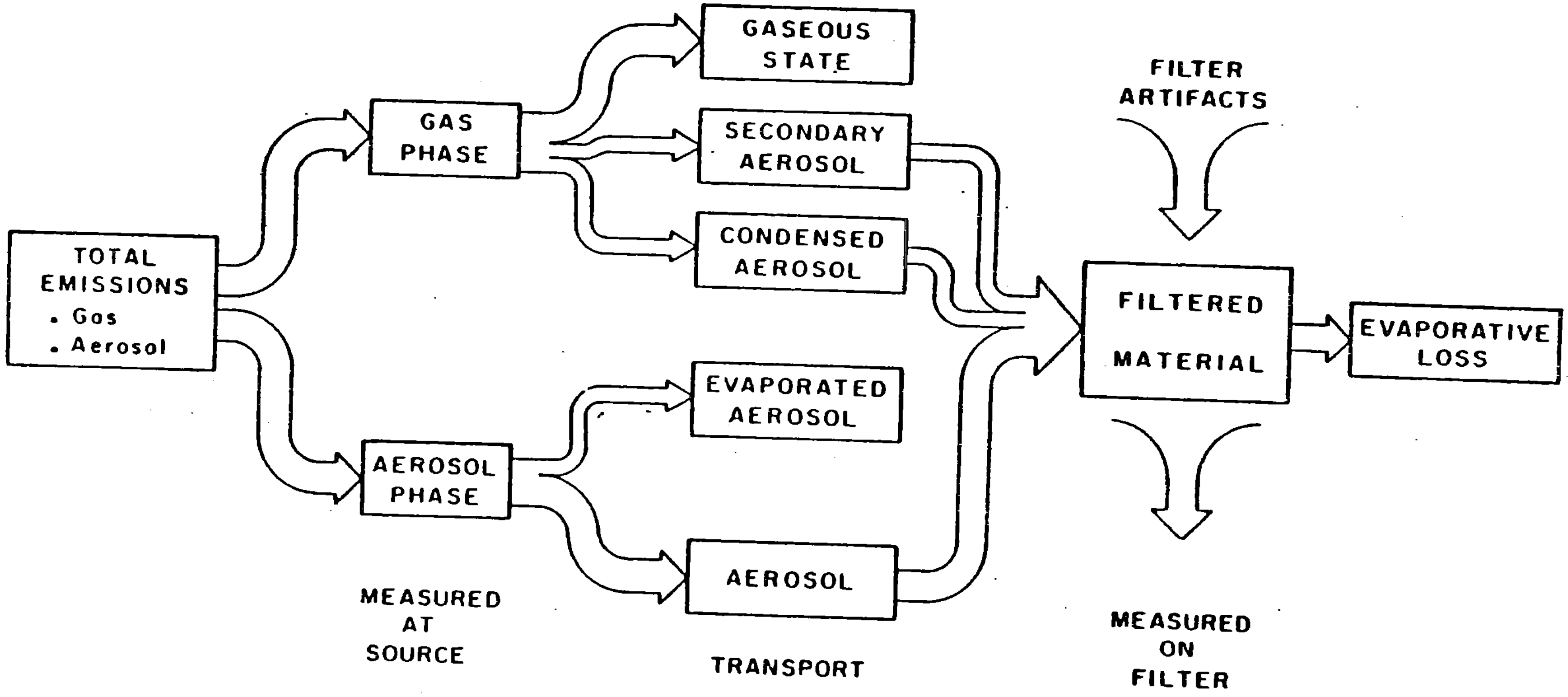


Figure 6

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RECEPTOR ORIENTED SOURCE APPORTIONMENT CAPABILITIES

Chemically oriented receptor methods measure chemical features of particulate material collected on ambient filters and quantitatively determine the contribution of possible sources on the basis of source chemical finger prints and the conservation of mass. This type of study requires:

1. Source sampling that simulates potential changes that are expected to take place as emissions are transported to the receptor.
2. Highly sensitive analytical procedures yielding documented quality results for both the most abundant and key indicating chemical species.
3. Interpretive procedures which yield realistic uncertainties on the reported source contributions.

NEA is the only organization with complete in house capabilities in all three areas.

SOURCE SAMPLING

Source sampling is generally recognized as the major source of uncertainty in chemical receptor models because of source variability and the possibility of chemical and/or physical transformations that can occur with emissions. These uncertainties can be minimized, however, by appropriate source sampling.

The major source sampling problems that need to be avoided include loss or addition of material due to evaporation or condensation and chemical fractionation due to sedimentation.

NEA is the only source apportionment laboratory using size-segregated dilution sampling to minimize chemical changes in source emissions due to evaporation, condensation and sedimentation. A schematic of its dilution stack sampler is attached. NEA also has special road dust samplers designed to sample even the fine particulate dust and the resuspension and sampling equipment to obtain fine (<2.5 μm) and coarse (>2.5μm, <15μm) road dust fractions to minimize chemical changes due to sedimentation in transport.

ANALYTICAL PROCEDURES

Source resolution, the ability to detect and quantify the impact of a source, depends strongly on the quality of input analytical data. If an analytical procedure, for example, lacks the analytical sensitivity to determine the concentration of lead on an ambient air filter, the receptor model used to apportion source contributions will be unable to resolve or see the impact of automotive exhaust. Instrumental neutron activation analysis would therefore be an inappropriate analytical tool to determine the contribution of automotive exhaust.

The appropriate analytical technique may be different for each airshed because of the chemical characteristics of the different sources. The two objectives generally of interest in selecting the analytical procedure to use is the need to:

1. Quantify all key indicating species from sources in the airshed under study and
2. Quantify all major chemical species so as to account for all of the deposit mass.

It was generally agreed at the Quail Roost Receptor Model Conference held in February 1980 that the most cost effective analytical procedure for aerosol receptor models is energy dispersive X-ray fluorescence. Other procedures such as neutron activation analysis, ion chromatography, X-ray diffraction, carbon, microscopic analysis, carbon-14, etc. are less cost effective and their utility is determined by the nature of the airshed.

NEA has a full range of analytical services related to receptor modeling and is the only laboratory with in house X-ray fluorescence and neutron activation analysis capabilities. The minimum detectable concentrations for these methods are attached. Ion chromatography, organic and elemental carbon and carbon-14 analyses are also avalable through NEA.

RECEPTOR MODELS AND INTERPRETIVE PROCEDURES

There are a wide variety of source apportionment tools available such as:

- Emission Inventory
- Dispersion Modeling
- Microscopy
- Chemical Mass Balance (CMB)
- Factor Analysis (FA)
- Regression Analysis (RA)

Each has its specific strengths and will contribute circumstantial information to build a strong conclusion regarding the contribution of specific sources. The most cost-effective procedure for providing QUANTITATIVE source apportionment information is the Chemical Mass Balance procedure. The utility of other methods depends on each airshed and the need for supportive information.

NEA specializes in receptor oriented models and offers all three interpretive methods including CMB, FA, RA and hybrid methods such as target transformation factor analysis. A key aspect of NEAs CMB programs is that it properly treats the source uncertainty and propagates uncertainties through to the final source contribution.

5

Receptor Oriented Methods of Air Particulate Source Apportionment

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Receptor models have evolved rapidly over the past 13 years but have just recently been recognized as a distinct discipline. The general category of receptor models includes both microscopic and chemical methods of apportioning source contributions to ambient air particulates. The number and variations of these methods have grown rapidly over the past few years and include such methods as automated scanning electron microscopy, chemical mass balance and multivariate procedures. These methods as well as hybrid procedures such as target transformation factor analysis, are reviewed and their boundary conditions, strengths, and weaknesses discussed.

Substantial progress has been made over the past 10 to 15 years in reducing air particulate pollution levels in many parts of the U. S. A large number of regions, however, are still not meeting the National Air Quality Standards despite costly and extensive control efforts.[1] Air pollution control strategies will be more critically evaluated in the future than they have been in the past as industry, government, and the public demand more effective programs in the face of high inflation rates and energy costs.

Development of air particulate control programs by state and federal agencies and evaluation of their effectiveness as new standards and sources are introduced, require an accurate understanding of the

- chemical and physical characteristics of air particulates,
- their origin, and
- the contribution of each source to air particulate levels.

Although a great deal of the data have been accumulated on the chemical and physical characteristics of air particulates, very little is known about their sources and contributions to specific receptor sites because of the inadequacy of previously available predictive tools.

Source oriented dispersion models based on emission inventories and meterological parameters have been the primary tool of control agencies to estimate the impact of a particular source at a receptor site. Estimation of source impact on ambient loadings at receptor sites, however, has been approximate at best because many of the variables required by these models, primarily meterological, are random in nature, vary with space and time and may combine with other variables in a nonlinear manner.

Over the past ten or more years, receptor oriented models have been examined as possible source impact assessment tools.[2-76] It has only been recently, however, that they have evolved to the point where they now form a distinct discipline and clear alternative to source oriented dispersion models. The number and variations of these receptor models have grown rapidly over the past few years without adequate evaluation or definition of their boundary conditions, strengths and weaknesses. It is the intent of this report to review these receptor models and discuss their boundary conditions, strengths and weaknesses.

Dispersion Models

The urban atmosphere is a highly complicated system composed of gaseous and particulate material. This atmospheric matter is made up of a wide variety of complex organic compounds, inorganic chemicals, and radionuclides with thousands of possible sources. Both natural and anthropogenic sources contribute to this complex mixture and include meteor dust, sea salt, forest fires, volcanoes, wind blown soil, agricultural tilling, transportation sources, space heating, cooking, industrial processes, etc.

Assessing the impact of individual sources depends on our ability to either predict the impact from fundamental meterological principles, source oriented models, or our ability to resolve the contributions of this large number of sources after the fact with receptor models as shown in Figure 1. Source oriented dispersion models start with emission rates and dispersion factors for a specific source and calculate the impact at a receptor site. Although source oriented models have the potential to assess the impact of specific sources, none are currently able to describe adequately the complicated random nature of dispersion in the atmosphere and the results in general have been considered only approximate.

Receptor Models

Receptor models, on the other hand, start with the measurement of a specific feature of the aerosol at the receptor and after the fact calculate the contribution of a specific source type. Measureable atmospheric features include particle size, shape and color, particle size distribution (number), component identification (organic, inorganic and radioactive), component chemical state and concentration, time and spatial variations. Although most of these features can be used to identify source types, the only measured parameters that can be used to determine quantitatively a source's contribution to air particulate levels are a component's concentration or number of particles of a specific type and size.

Receptor models can be conveniently grouped into two basic categories, microscopic and chemical methods, as illustrated in Figure 2. Microscopic methods have a high source resolving capability for sources with characteristic morphological features such as wood fiber, tire rubber, pollen, etc. To be quantitative, however, they must estimate the number of particles, their density and volume, and must analyze enough particles to be representative of the total sample. On the other hand, chemical methods require knowledge of the chemical composition of both the ambient and source particulates and are based on an assumed conservation of mass.

Microscopic Methods

Microscopic methods can be divided into three subcategories, optical, which is limited to particles greater than about 2 μm but can use such feautres as color to aid in its qualitative identification of particle type; scanning electron microscopy (SEM) which is applicable to smaller particles and may include a determination of the major elements to aid in qualitative particle type assignment; and automated SEM analysis which uses all of the same qualitative particle type identification features as the SEM analysis but has the capability of analyzing more particles because of its automation.[2] This latter method is the newest and promises to extend the general applicability of microscopic methods primarily because it provides for a more representative analysis. It needs to be evaluated further, however, and is still limited by many of the normal problems associated with microscopic methods. These include time and cost per analysis, lack of sensitivity for amorphous organic species which often account for a large fraction of the aerosol and large uncertainties associated with the basic assumptions required for quantitative analysis such as particle density and volume. There is no doubt that microscopic methods have been and always will be useful tools for air particulate source impact assessment but whether or not these methods become widely used for large scale quantitative assessment will depend on the results of their further evaluation, costs and the capabilities of alternate methods.

Chemical Methods

Chemical methods can be divided into five subgroups as shown in Figure 2. All of the chemical methods require knowledge of the chemical composition of both the ambient aerosol and possible sources. Enrichment factors, time, and spatial series analyses provide primarily qualitative information about possible sources whose contribution can only be determined quantitatively by applying a special case of the chemical mass balance model, i.e., the tracer method. Chemical mass balance and advanced multivariate data analysis methods are more likely to be widely used in the future for large scale source impact assessment studies.

Multivariate methods such as factor analysis were the first of the chemical receptor models to be used for air particulate source impact assessment.[3] These statistical methods were developed for problems in the social sciences, and applied to the physical sciences in the 1950s before Blifford and Meeker first applied them to air pollution problems in 1967.[3] The following year Prinz and Stratmann[4] also applied factor analysis to air quality problems. Winchester and Nifong analyzed the Chicago area aerosol pattern based on source emission inventories in 1969[5] and Hidy and Friedlander used a simple tracer form of the chemical mass balance method in 1970 to assess the impact of sources such as automotive exhaust and geological dust using Pb and Si as indicators.[6] Although five papers were published in 1971,[7-11] it wasn't until 1972 that the formalism of the chemical mass balance approach was firmly established by Miller, Friedlander, and Hidy[12] and by Friedlander in 1973.[13,14] Four additional papers appeared in 1972[15-18] and ten in 1973.[13,14,19-26] Numerous others have appeared since[27-76] (Table I) and within the past year it has become clear that chemical receptor models are coalescing into a clearly defined discipline.

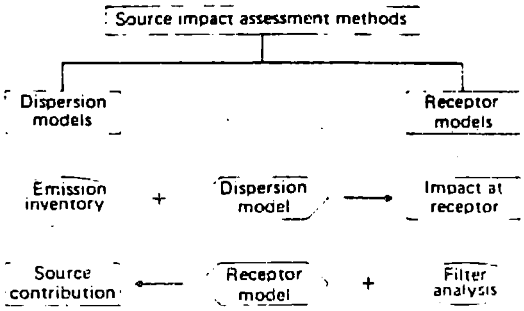

Figure 1. Schematic comparison of source assessment methods.

Chemical Mass Balance Method

The chemical mass balance (CMB) method is the basis for quantitative source impact determinations and is discussed first and in the greatest detail. It is based on the principles established by Miller, Friedlander, and Hidy[12] and Friedlander.[13,14]

Friedlander's CMB method of source type identification has been applied in Pasadena,[12] Chicago,[40] Fresno, Pomona, San Jose, Riverside,[39] New York,[15] Portland,[52,53] Washington, D.C.[57] and St. Louis[75]. These applications of the CMB methods suffered, however, major shortcomings related in part to the fact that the data sets to which they were applied were not developed with the needs of the CMB method in mind. These previous applications also suffered from the following shortcomings:

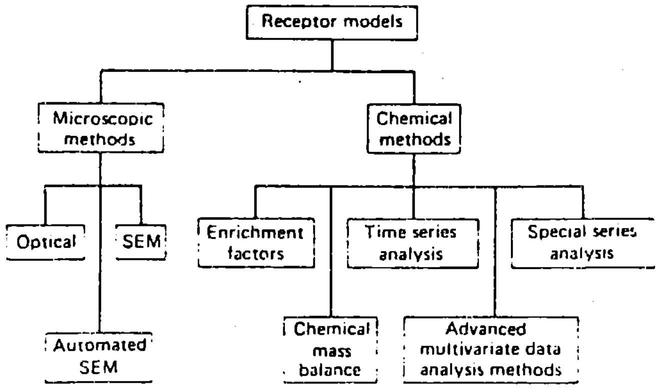

Figure 2. Schematic block diagram illustrating the relation between various types of receptor models.

- All major sources were not characterized at the time of the study.

TABLE I. Examples in the literature of chemical receptor model applications.

Ref.	Author	Date	Ref.	Author	Date
Chemical Mass Balance					
5	Winchester and Nifong	1969	39	Gartrell and Friedlander	1975
6	Hidy and Friedlander	1970	40	Gatz	1975
7	Winchester and Nifong	1971	52,53	Henry	1977
12	Miller, *et al.*	1972	57	Kowalczyk, *et al.*	1978
15	Kneip, *et al.*	1972	70	Throgmorton, *et al.*	1978
13,14	Friedlander	1973	71	Gordon	1979
19	Heisler, *et al.*	1973	75	Dzubay	1979
27	Hidy, *et al.*	1974	73	Watson	1979
38	Hammerle and Pierson	1975	74	Cooper and Watson	1979
Enrichment Factor					
8	Rahn	1971	41	Struempler	1975
16,17	Holtman and Duce	1972	42	Mroz and Zoller	1975
18	Tsunagni, *et al.*	1972	43	Duce, *et al.*	1975
20	Bogen	1973	46	Obrúsnik, *et al.*	1976
21	Gordon, *et al*	1973	45	Paciga and Jervis	1976
22	Zoller, *et al.*	1973	47	King, *et al*	1976
23	Wesolowski, *et al.*	1973	48	O'Donnell, *et al.*	1976
24	Bressan, *et al.*	1973	49	Neustadter, *et al*	1976
28	Heindryckx and Dams	1974	54	Moyers, *et al.*	1977
29,30	Zoller, *et al.*	1974	58	Lawson and Winchester	1978
27	Hidy, *et al.*	1974	59	Buat-Ménard and Arnold	1978
			70	Throgmorton, *et al.*	1978
Time Series Correlation					
8	Rahn	1971	38	Hammerle and Pierson	1975
23	Wesolowski, *et al.*	1973	49	Neustadter, *et al.*	1976
31	Giaque, *et al.*	1974	50	Pilotte, *et al.*	1976
32	Wedberg, *et al.*	1974	51	Moyers, *et al.*	1977
33,34,35	Johansson, *et al.*	1974	60	Tiao and Hilmer	1978
36	Winchester, *et al.*	1974	61	O'Conner, *et al.*	1978
37	Rahn, *et al*	1974	62	Pilotte, *et al.*	1978
41	Struempler	1975	63	Courtney, *et al.*	1978
			70	Throgmorton, *et al.*	1978
Multivariate Models					
3	Blifford and Meeker	1967	56	Gaarenstroom	1977
4	Prinz and Stratmann	1968	67	Barone, *et al.*	1978
9	Laamanen and Partanen	1971	64	Gatz	1978
38	Hammerle and Pierson	1975	70	Throgmorton, *et al.*	1978
49	Neustadter, *et al.*	1976	65	Dattner	1978
51	Hopke, *et al.*	1976	66	Tauber	1978
55	Kleinman	1977	71	Gordon	1979
52,53	Henry	1977	72	Gether and Seip	1979
			76	Alpert and Hopke	1979
Spatial Models					
3	Blifford and Meeker	1967	44	Scott Environ. Tech.	1975
10,11	Dams, *et al.*	1971	49	Neustadter, *et al.*	1976
25	Crozat, *et al.*	1973	48	O'Donnell, *et al.*	1976
26	John, *et al.*	1973	46	Obrúsnik, *et al.*	1976
28	Hendryckx and Dams	1974	68	Laird and Miksad	1978
40	Gatz	1975	69	Elmson	1978
			70	Throgmorton, *et al.*	1978

- Source uncertainties were not taken into account.
- The methods used had not been verified nor their sensitivities to variations in input parameters established.
- Ambient and source aerosol characterization was incomplete i.e., some of the major chemical species such as carbon, SO_4, NO_3, Si, etc. were not determined.

The basic principles of the CMB method as first presented by Friedlander[13,14] are illustrated schematically in Figure 3. The CMB method assumes that aerosol mass is conserved from the time a chemical species is emitted from its source to the time it is measured at a receptor. That is, if p sources are emitting M_j mass of particulates,

$$m = \sum_{j=1}^{p} M_j$$

where m is the total mass of the particulate collected on a filter at a receptor site.

The mass of a specific chemical species, m_i, is given by the following

$$m_i = \sum_{j=1}^{p} M_{ij} = \sum_{j=1}^{p} F'_{ij} M_j \qquad (1)$$

where M_{ij} is the mass of element i from source j and F'_{ij} is the fraction of chemical species i in the mass from source j collected at the receptor. It is assumed that the mass of each individual chemical component is conserved so that

$$F'_{ij} = F_{ij}$$

where F_{ij} is the fraction of chemical i emitted by source j as measured at the source. (This same assumption is required by dispersion models and most receptor models by varying degrees.) The degree of validity in this assumption depends on the chemical and physical properties of the species and its potential for atmospheric modifications such as condensation.

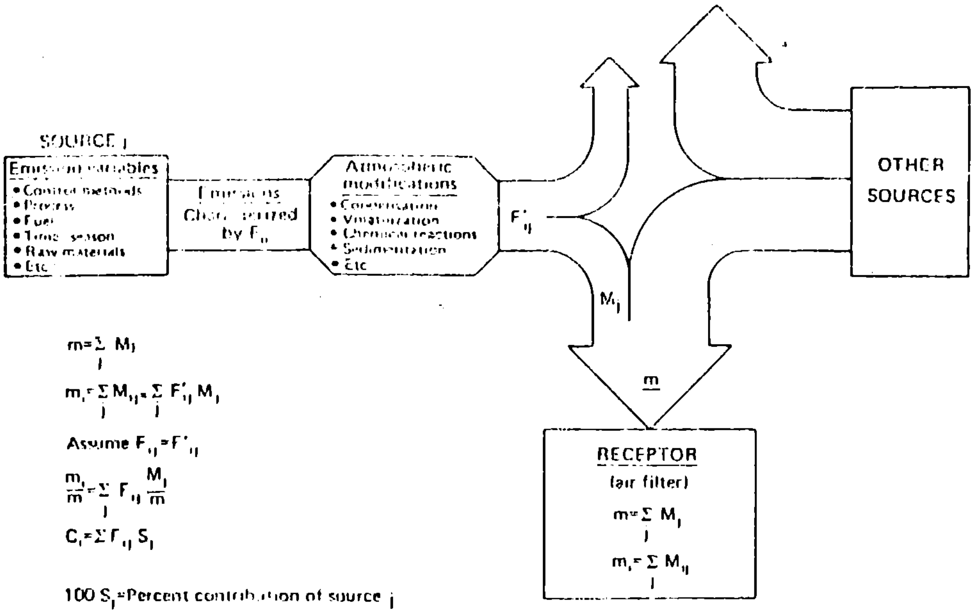

Figure 3. Schematic representation of chemical mass balance - methods.

volatilization, chemical reactions, sedimentations, etc.

Accepting this assumption and dividing both sides of Eq. (1) by the total mass of the deposit collected at the receptor site, it follows that

$$C_i = \sum_{j=1}^{p} F_{ij}\, S_j \tag{2}$$

where C_i is the concentration of the chemical component i measured at the receptor (air filter) and S_j is the source contribution; i.e., the ratio of the mass contributed from source j to the total mass collected at the receptor site. In practice, it is this fraction of particulate pollution measured at the receptor due to source j, S_j, which is of primary interest in CMB calculations.

If the C_i and the F_{ij} at the receptor for all p of the source types suspected of affecting the receptor are known, and $p \leq n$ (n = number of chemical species), a set of n simultaneous equations exist from which the source type contribution S_j may be calculated by least squares methods.[73]

The CMB method applies the maximum amount of source information to resolve the sources contributing to a single filter. Although normalized elemental source patterns can be used in the least squares fitting procedure,[77] the absolute concentration of at least one of the elements from each source type must be known for a quantitative analysis.

This fitting process can be more readily visualized by plotting both the source and ambient elemental patterns on semilogarithmic paper as illustrated in Figures 4–7. The atomic number is plotted in histogram form along the linear axis while the elemental composition, either $\mu g/m^3$, percent or normalized concentration, is plotted on the logarithmic axis. In this way the geometric shape of the distribution is independent of its level of contribution and can be considered similar to a fingerprint.

The source elemental fingerprints or spectra shown in Figure 4 were determined during the Portland Aerosol Characterization Study (PACS)[73,74] and illustrate the unique patterns many sources exhibit. Some sources, however, do not exhibit unique patterns and must be grouped into source types as illustrated in Figure 5.[73,74,75] Although there are distinct differences in the percent composition for some of the major elements, they cannot be resolved as distinct sources from an ambient aerosol composed of a complex mixture of these sources in the method's current stage of development.

The complexity of these patterns increases significantly when material from several different sources is combined to form an ambient aerosol, as shown in Figure 6.[74] The presence of some of the major sources, however, can still be easily identified by a simple visual inspection of the ambient patterns. For example, the automotive exhaust contribution is obvious from the Br and Pb in all 6 ambient spectra. The soil component is also apparent in all except the midnight to 8:00 A.M. sample collected on January 26, 1978, which has an unusual Al to Si ratio. The sample collected from midnight to 4:00 A.M. on January 27, 1978 is unusual because of its very high Mn concentration which must have been due to a significant impact from a ferromanganese furnace. This would also explain the high K and Na which were correlated with the Mn as can be seen from the time series spectra illustrated in Figure 7.[74] While the percent concentration of the Na, K and Mn were decreasing from midnight to noon, the soil-road dust components (Al, Si, Fe) and the Br and Pb were increasing as would be expected from the increase in traffic flow. The ambient distributions for October 17, 1977 and August 17, 1977 shown in Figure 6 are significantly impacted by kraft recovery boiler type emissions as can be seen by comparison with its elemental pattern in Figure 4.

Using least squares fitting methods, most of the major sources can be resolved or stripped from the ambient spectra.[73,74] This fitting of sourse distributions to a complex mixture of sources is analogous to the fitting or stripping of standard NaI(Tl) γ-ray spectra (energy histogram) from a γ-ray spectrum of a complex mixture of radionuclides.[79,80] Sources resolved from the ambient elemental spectra are not necessarily the unique solution. They are instead the best set of sources which when combined in the appropriate relative contributions come closest to reproducing the observed ambient elemental pattern. Absolute percent concentrations are not required to resolve sources and determine their fractional contribution to the ambient elemental pattern.[77] The absolute percent composition for at least one element or component in both the source and ambient aerosol, however, is required for a quantitative determination of a source's fractional contribution.

The most significant limitation to source resolution with the CMB method is the uncertainty (noise) in the F_{ij} values which can vary with time, location, raw materials, fuel type, etc. In the past, very little chemical data on source emissions were available. The catalog of source characteristics, however, is growing, and as it does so will the method's source resolving power.

Source resolution can also be improved by measuring additional components and by reducing the uncertainty in the measured components in both the ambient and source particles. The most cost effective set of components, however, has not been determined but will certainly depend on the sources expected to be major contributors to each airshed studied.

Multivariate Methods

Whereas CMB methods apply knowledge about source characteristics to a single filter data set to derive a source's contribution, multivariate methods such as factor analysis and pattern recognition methods extract information about a source's contribution on the basis of the variability of elements measured on a large number of filters. If two or more chemical components originate from the same source, their variability as a function of time as measured at a receptor will be similar. The objective of multivariate methods is to detect this common variability after the fact and imply source identity by comparing the elements with common variability to the elements associated with specific sources.[3,52,52,56,76]

The basis and starting point for advanced multivariate methods is the correlation matrix. Pattern recognition methods present the correlation matrix information in a more easily perceived graphical form. Source identity is inferred from the commonality of elements in a particular cluster or pattern and those known to be associated with a possible

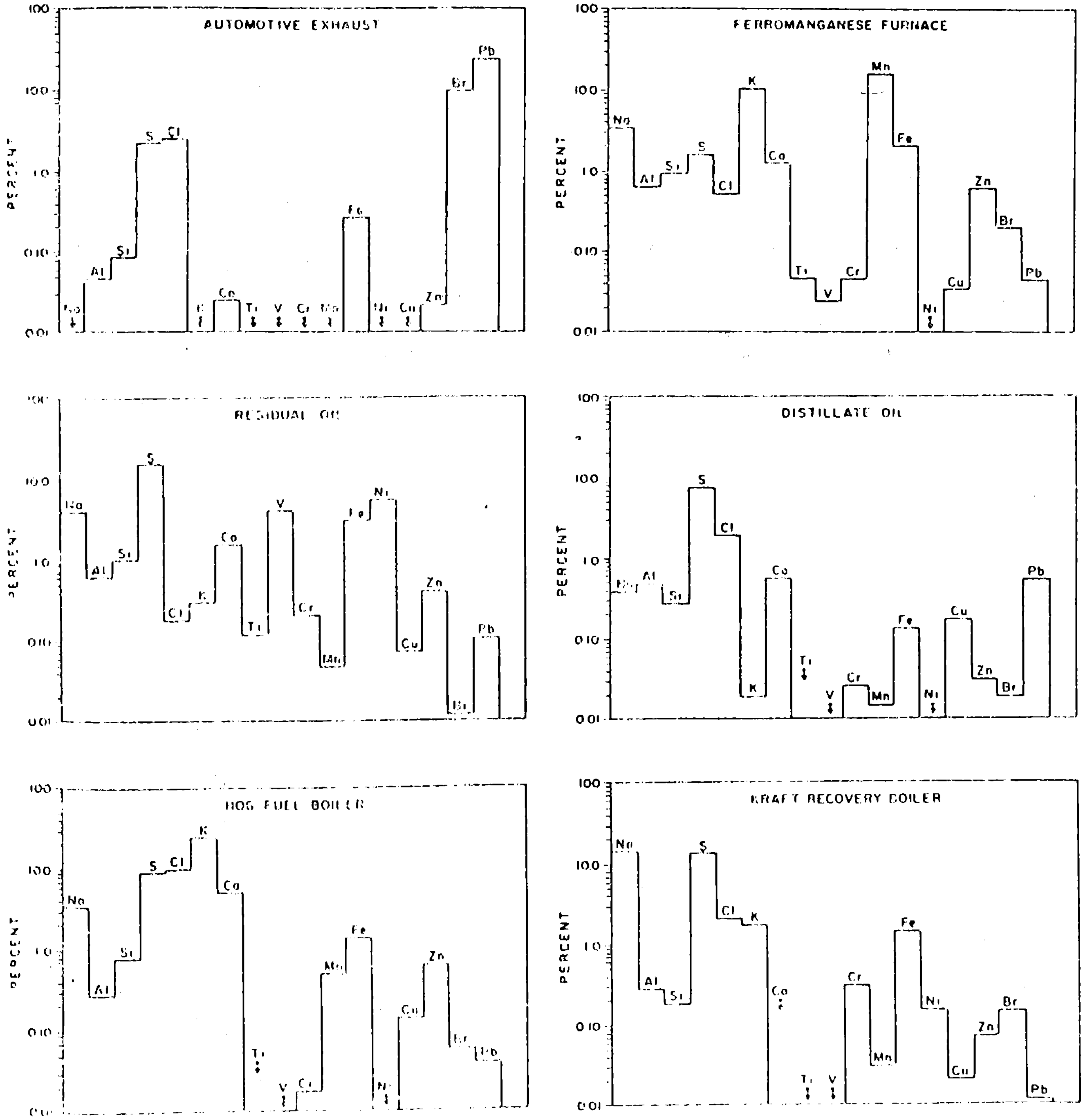

Figure 4. Comparison of selected fine particle (<2.5 μm) source composition patterns measured during the Portland Aerosol Characterization Study (PACS).[73,74] Particulate material from each of these sources can be distinguished on the basis of the unique elemental fingerprints.

source. Nothing new is learned, however, from this treatment of the data that could not have been learned from a careful study of the correlation matrix.[56]

On the other hand, factor analysis methods express each variable (concentration of element *i* on filter *k*) as a linear combination of factors. These factors are hypothetical variables selected so as to reproduce the measured variable correlations as well as possible with the fewest possible factors. The coefficients of these factors are determined by factor analysis starting with the correlation matrix of observed chemical components. A physical interpretation or source identification is possible by comparing the elements having a high loading on a particular factor with elements associated with known possible sources. Implicit in factor analysis are the assumptions that all major influences are reflected in the correlation matrix and that they are different enough not to be combinations of several influences. In addition, conservation of the major chemical characteristics of each source's emissions is necessary if each factor is to be correctly associated with a source by comparing chemical features. Thus, although factor analysis and pattern recognition methods require no prior knowledge of either the number of factors from a data set, or their characteristics, correctly labeling the resolved factors or patterns with common source names requires knowledge about the chemical characteristics of possible sources. In addition, factor analysis is unable to determine quantitatively the contribution of specific source types and cannot provide source information for individual filters.

Modifications of the basic factor analysis approach have recently been suggested[52,53,76] which provide quantitative

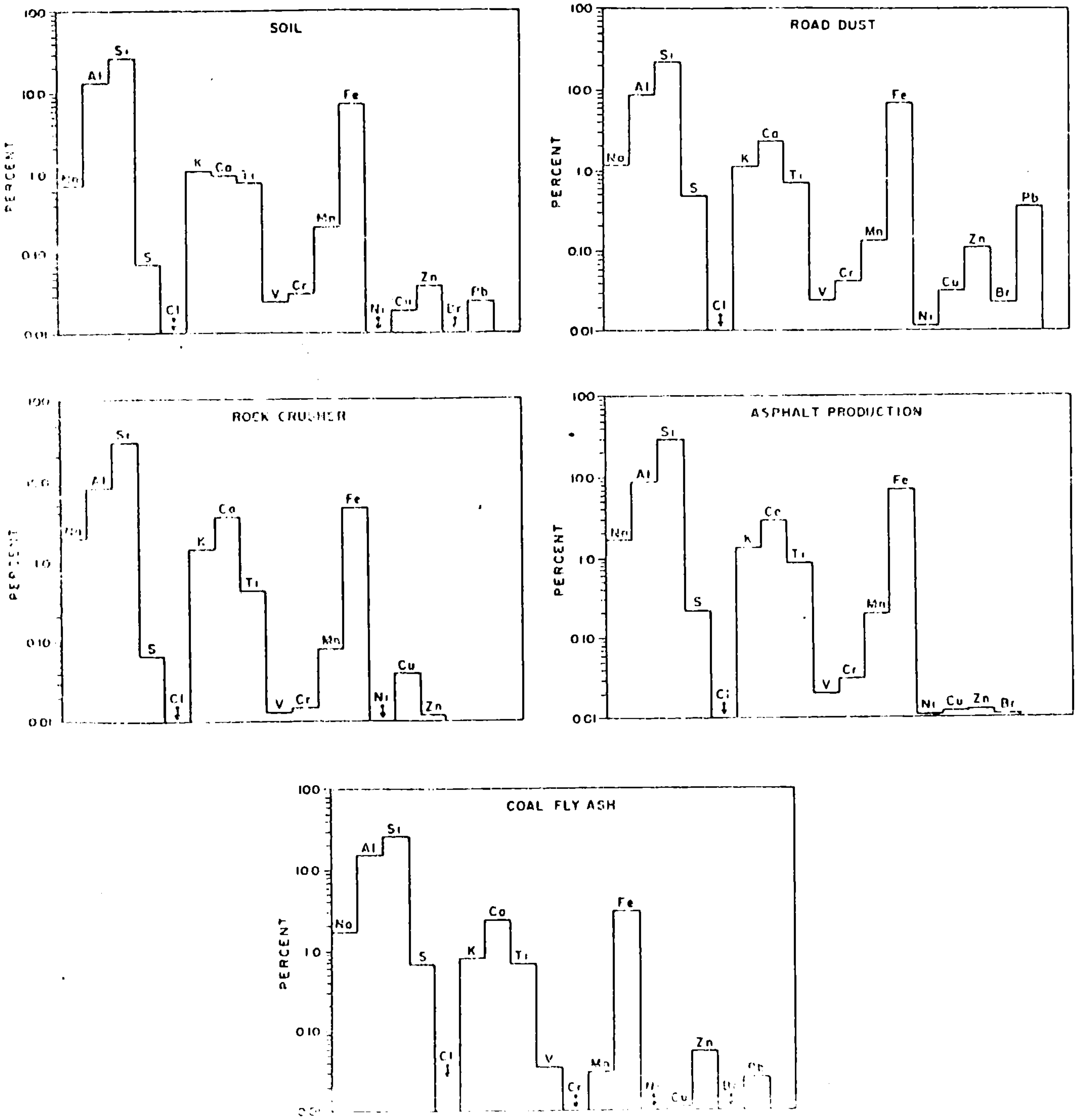

Figure 5. A comparison of [illegible] ns for sources which cannot be [illegible] into a common source category.[?]

analysis capabilities. Both methods, however, are a combination of the modified factor analysis and a mass balance calculation. Henry was the first to suggest this approach and applied it to a Portland, Oregon data set[52,53] developed prior to the Portland Aerosol Characterization Study (PACS).[73,74] Five target sources were used as input from which four source factors were derived. These four improved source factors were identified as "dust," "metallurgical," "plating," and "zinc." Two of the five target sources (auto and residual fuel oil) were not reported while an "unknown zinc" source was discovered. The suggested chemical composition of this unknown zinc source as well as the new plating source have surprisingly large absolute and relative amounts of Al and Si and their elemental patterns are unlike any observed two years later in the PACS[74] study which characterized 95% of the emission inventory.

Although there are sources of Zn in the Portland airshed as can be seen from the elemental spectrum shown in Figure 6, (January 26, 1978) factor analysis was not required to come to this conclusion. In addition, a simple three-filter time series analysis showed the Zn and Cl to be correlated and probably, in this particular case, related to galvanizing operations. The advantages of this new method were not clearly established with Henry's work.

In addition, the recent work of Hopke, *et al.*[51] and Alpert and Hopke[76] has not clearly demonstrated the advantages of factor analysis. Target factors, for example, based on the chemical characteristics of possible sources were required in their recent work.[76] Thus, the number and chemical composition of possible sources were required. New source chemical profiles were determined with factor analysis and source

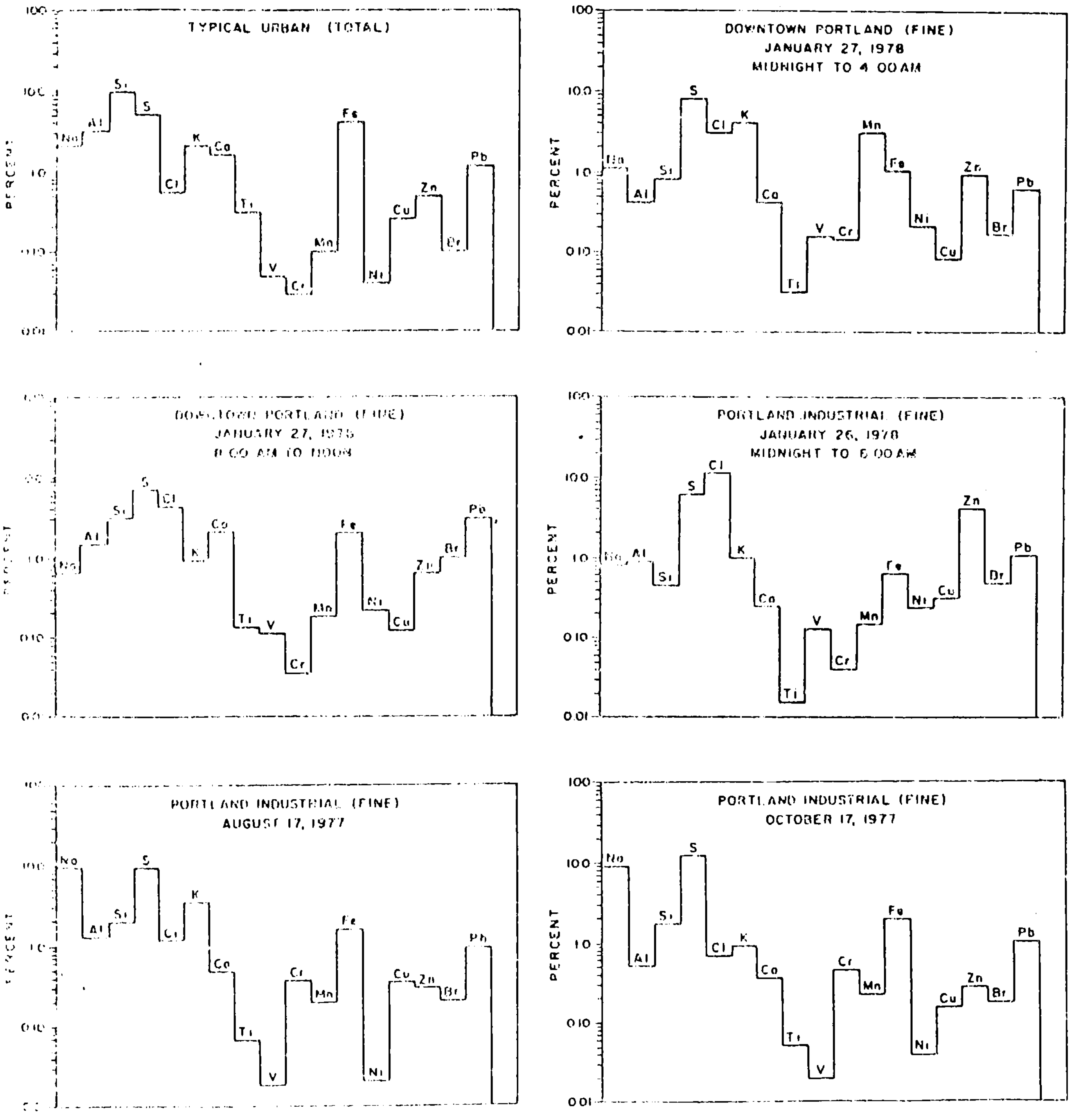

Figure 6. Comparison of the elemental composition pattern for a typical urban aerosol (total)[78] with ambient fine (<2.5 μm) particle samples collected during the Portland Aerosol Characterization Study (PACS).[73,74] The influence of some sources can be readily identified from these ambient patterns.

contributions calculated. Although fewer sources were found than were in the list of possible sources, the chemical composition of all the major elements was essentially the same as those in the target source compositions. It was not explained, however, why factors representing sources as determined from a statistical analysis of ambient data should be essentially identical to the input test vectors, particularly when these test vectors are based on data from other regions of the country. The advantages of target transformation factor analysis[76] over other receptor methods or hybrid combinations have yet to be established.

The CMB and factor analysis methods both require prior knowledge of the number of possible sources and their chemical features; both require the conservation of mass assumption, $F_{ij} = F'_{ij}$; and both are able to detect the presence of unknown sources. Chemical mass balance methods can determine the source contributions to a single filter and time series analysis of source contributions and elements may be just as revealing as the basic factor analysis. Correlation coefficients, the basis of factor analysis, indicate the degree of similarity between two variables, but not that there is or is not a causal relationship between them.

A critical evaluation of these advanced multivariate analysis methods has not yet been made. Although the advantages and disadvantages have been suggested by numerous authors, the unique utility of this approach relative to other methods has yet to be established. One of the major factors preventing a more thorough evaluation of these methods has been the lack of an adequate data set for comparison.[51-53,76]

Enrichment Factors

With the enrichment factor model, the elemental composition of the local ambient aerosol of interest relative to the concentration of an element characteristic of a background aerosol is compared with the relative elemental composition in the background aerosol. That is, the

$$\text{enrichment factor} = \frac{(C_i/C_n)\ \text{ambient}}{(C_i/C_n)\ \text{background}}$$

where C_n is the normalizing element assumed to be uniquely characteristic of the background and C_i is the element whose enrichment is to be determined. Elements with enrichment factors greater than 1 are assumed to be due to sources in the local or regional airshed of interest. Only a rudimentary understanding of the chemical composition of various sources is required to make possible source assignments. The enrichment factor approach has been most useful when there has been a limited amount of information available. Although it does not require absolute chemical concentrations, it cannot quantify a source's contribution, relies heavily on the assumed background composition and is not applicable to complex source mixtures where multiple local sources are contributing to the same element. This method is not likely to see large scale application to urban airsheds on a routine basis because other models have evolved over the past few years which provide more information; but it may still find considerable use in interpreting small data sets on a research basis.

Time Series

Time series analysis is based on the assumption that chemical species originating from the same source will have the same time dependence when measured at a receptor. Thus, if the elements measured at a receptor have a similar time dependence, they are said to be correlated and to have a similar source. Specific sources are inferred on the basis of correlated elements and a qualitative understanding of the composition of possible sources. Because the impact of dispersion conditions is often dominant, normalized or percent of total mass values are usually used. Short term studies based on hourly observations will yield information on short term variable sources such as automobile traffic, home heating, power demands, or industrial processes. Long term studies covering several years can often show clearly the impact of seasonally dependent sources or the implementation of control measures. Time series correlation studies provide qualitative information which can provide strong inferences as to possible sources and effect of control measures, but cannot provide a quantitative determination of specific source types. This type of analysis provides unique qualitative information which is extremely useful in evaluating the impact of control programs, directing the search for new sources and confirming source identities suggested by other models. It is expected to be very useful during the exploratory and transition period of the evolution of this discipline, but will be mainly used to monitor the effectiveness of control strategies during the period of routine application of receptor models.

Spatial Models

In spatial models, the measured concentrations on samples collected at the same time but from a number of different receptor sites of known geographical relationship are compared. Implications of source contributions are obtained by comparing the observed spatial distribution of measured elements with the location and chemical composition of known source emissions. These models have taken the form of spatial isopleths, spatial correlations, cluster analysis and pollution

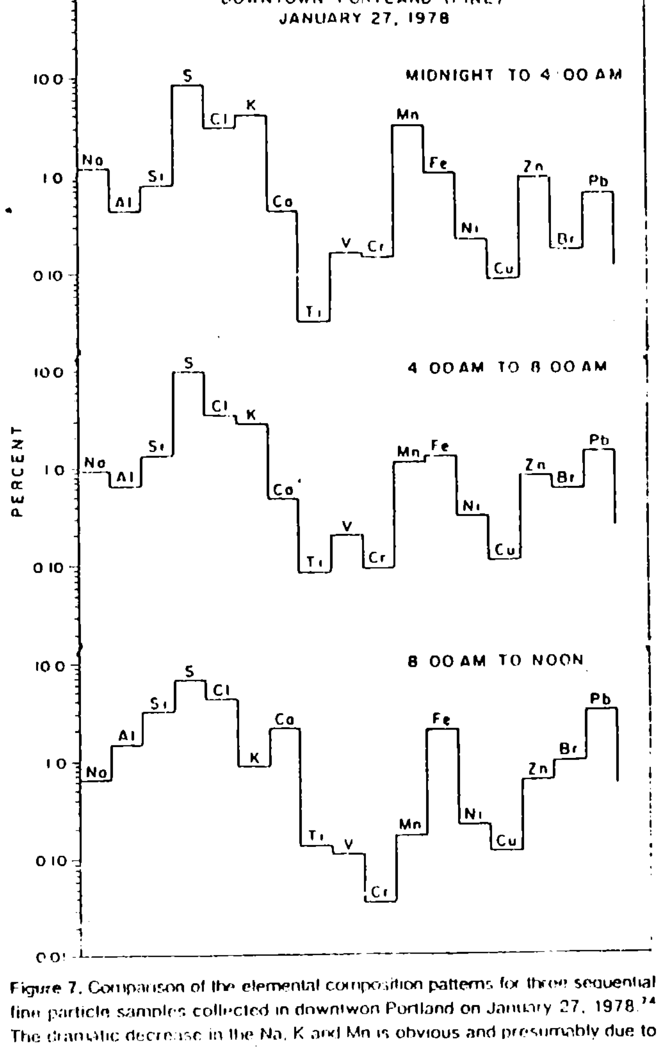

Figure 7. Comparison of the elemental composition patterns for three sequential fine particle samples collected in downtwon Portland on January 27, 1978.[74] The dramatic decrease in the Na, K and Mn is obvious and presumably due to the decreasing influence of emissions from a ferro-manganese furnace (Figure 4). The increase in the percent of Al, Si, Ca, Fe, Br and Pb is also apparent and likely due to increasing contributions from road dust and automotive exhaust

wind roses.[70] These methods have the advantage of possibly providing information on specific sources which might be unique to a given area. The information provided, however, is qualitative and depends strongly on the rather weak assumption of a constant wind direction and emission rate during the time of sampling. Nevertheless, these models are likely to be used considerably as part of hybrid models.

Conclusion

Chemical receptor models have evolved and improved considerably over the past 13 years but have only recently been recognized as a distinct discipline. In the four years from 1967 to 1970, for example, only four papers were published on chemical receptor models while over 13 were published in 1978. During this time, the total number of published articles has exceeded 70 and the CMB method has evolved from a simple tracer method to a sophisticated least squares fitting procedure which includes both source and ambient elemental pattern errors.[73] Factor analysis has evolved from the classic methods applied by Blifford and Meeker in 1967[3] to hybrid methods such as target transformation factor analaysis.[76] Although the entire set of boundary conditions for the application of these tools to source apportionment studies has not been defined completely, it is clear that it forms a new and very useful discipline for interpreting the very large number of complex chemical data sets that will be generated in the 1980s.

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Receptor Models - How Great Thou Art!(?)

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Introduction

As pressure to develop increasingly accurate control strategy analyses is brought to bear on State and local air pollution agencies, professionals responsible for management of our air resources increasingly find themselves searching for better source resolution methods. Faced with pressure from many interested groups, the control officer responsible for development of particulate attainment strategies must provide convincing evidence that he understands the relative importance of airshed emission sources to the problem. He must also propose cost effective control programs that he, and the community, can adopt with confidence. Unless an effective case can be made to demonstrate the magnitude and identity of particulate sources causing the nonattainment problem, considerable doubt as to the effectiveness of new control programs can exist.

Until quite recently, traditional approaches have dictated that source impacts be identified by dispersion (source) modeling based on emission inventory and meteorological data. While these techniques will remain as an important tool in the regulatory effort, dispersion models have not met several critical program requirements. For example, their ability to apportion source impacts during actual, 24-hour worst case episodes or to assess impact from sources in complex terrain, are limited by difficulties in developing accurate particulate emission inventories and meteorological data bases. Further limitations in the ability of source-oriented models to estimate source contributions to the "background" aerosol typically limit the dispersion model's ability to apportion source impacts to about one-half of the measured aerosol mass. These constraints severely limit the analyst's ability to understand the true mixture of source strengths and the nature of the incoming air.

Receptor models, those new and miraculous(?) methods now being hailed as a "new" alternative to dispersion modeling, have been seen by some as the remedy for this regulatory headache. But are they? Do the advantages of these techniques provide realistic alternatives to professionals charged with managing our air resources?

This paper focuses on the advantages, as well as the limitations, of current receptor models. Areas in which different kinds of receptor-oriented techniques compliment one another are also discussed in the hope that a realistic understanding of the technology will assist those considering the use of these new tools.

Particulate Source Apportionment Methods

As new papers are published and receptor model technology grows, those responsible for control strategy development have been increasingly tempted to view source apportionment methods as a solution to the seemingly impossible task of "sorting out" contributing sources. The data analysis techniques through which specific source impacts are identified are collectively referred to as source apportionment methods. These methods are commonly classified into source models, receptor models and emission inventory techniques. A further stratification of the various receptor model approaches is shown in Figure 1. While each of the techniques noted in Figure 1 has its own advantages, no single method should be considered

as the best approach. Instead, it is important to view the process of source impact identification as a total "system" consisting of the project design, field monitoring program, laboratory analysis and data interpretation phases in which a number of methods may be used to develop the necessary chain of evidence. Table I lists the most commonly used source apportionment tools, their advantages and disadvantages.

Although receptor models have been investigated as a method of particulate source apportionment during the past ten years, only recently have the techniques become recognized as a distinct, new discipline.[1] Unlike dispersion models which begin with measurements of emission rates, stack parameters and meteorology, receptor models "decode" ambient particle morphology, chemistry and variability information to identify source impacts.[2] Each of the major methods are briefly described in the Receptor Model Glossary, Appendix I. Selection of the most appropriate techniques largely depends on the analyst's objectives, resource constraints and knowledge of the receptor model technology available. For example, Table II lists a number of source apportionment techniques that may be useful in identifying inhalable particulate source impacts during air pollution episodes. The options listed provide the analyst with several choices of fine and coarse mode techniques which can provide qualitative, semiquantitative or quantitative results. Although the resource requirements noted are by necessity somewhat subjective, they reflect a general sense of the relative rankings between the methods.

Receptor model results are inexorably linked to the method of sample collection. Properly sited monitoring stations, operated in accordance with accepted quality assurance procedures, are a basic (and mandatory) requirement. An additional requirement which is frequently overlooked, however, is the sampling method.

The specifications of the sampler plays an important role in determining whether or not the objectives of the program are likely to be met. In addition to the importance of the sampler's upper (and lower) particle size cutpoint (discussed below), the sampler must reliably capture the desired size fraction under conditions of variable wind speeds and directions on the desired collection medium. Artifact sulfate, particle bounce between impactor stages, retention of coarse particles on the surface of the collection medium, and passive-mode accumulation are but a few of the potential problems to be aware of when interpreting ambient aerosol data.

Size resolution of the ambient aerosol into the fine (<2.5µm) and coarse (2.5-15µm) modes provides a simple, yet highly effective means of apportioning particles associated with combustion, secondary formation processes, condensation and controlled emission process losses from fugitive dust sources, grinding and crushing operations, and biological sources (pollen, leaf fragments). Recent development of reliable ambient sampling systems designed to gather size-resolved samples has significantly improved the receptor model's ability to separate, for example, sources of fine particle iron (e.g., steel mill emissions) from coarse mode iron (soil dust).

Receptor Models: A Closer Look

Source apportionment studies using receptor models have largely gained the attention of the air pollution community through journal publications and conferences reporting results of large scale, "big budget" aerosol studies. Many of these studies have gained national attention for their "success" in identifying source impacts. What may not be obvious, however, are the difficulties that must be overcome during the course of these studies, as well as the assumptions and judgments that must be applied to insure a successful program.

A closer look at typical case studies in which receptor models have been used provides an opportunity to more closely examine the assumptions and limitations of these methods. These examples are provided to promote a better understanding of the current technology, and to assist those interested in applying these new methods.

Case Study 1: Application of Polarized Light Microscopy to TSP Source Apportionment

In 1975, the EPA undertook a major program to assess the national particulate problem in urban areas. Case studies of 14 cities were conducted to provide information on the types of particles collected by hi-vol samplers and to identify likely source impacts.[3] Optical microscopy using polarized light was the primary analytical tool used to determine the mass percent contribution of major source categories. Several hundred samples collected during 1974 were examined to provide data representative of industrial, commercial and residential land use areas. Analytical quality control protocol included the use of two laboratories, multiple analysts at each lab and replicate analysis of blind samples taken from the same filter. Results of the quality control program, shown in Table III, summarize the filter analysis in percent by weight of the visible particles seen by the microscopist.[4]

While the results appear, at first glance, to provide clear conclusions regarding the sources causing the nation's TSP problem, a closer look at the quality assurance results indicates some uncertainty. Test results of identical samples analyzed by two different microscopists indicate agreement in only three of eight cases in which the mineral content was estimated and two of eight cases for which combustion products were examined.

Investigation into the related errors reveals particle identification, misassignment and analyst fatigue to be key factors. Misassignment, judged as the most important source of error, occurs because different microscopists may properly identify a particle, but assign it to a different common source name. Coal flyash, for example, is often assigned to the mineral group (rather than combustion products) because it contains substantial amounts of quartz and limestone. Other potential pitfalls may include:

° Failure of the analyst to view a sufficiently large number of fields to insure that a representative portion of the aerosol is examined. Since the mass of a single 20 μm particle may be equivalent to a thousand 2 μm particles, failure to locate large particles when viewing a sample at high magnification can provide very misleading results.

° The loss of organic aerosols of high volatility while being viewed in the vacuum required during scanning electron microscopy examination.

Although the 14 cities study detected disagreement among analysts, the differences tended to minimize systematic bias such that the composite results were meaningful. Subsequent improvements in analysis protocol have improved analytical reproducibility within the past three years, but experience has taught that heavy reliance on results from a single filter, by a single microscopist, should be avoided in preference to a composite of results. Supportive information, developed through the use of independent, complimentary identification techniques and good quality assurance programs provide increased confidence in results.

Case Study 2: Carbon-14 Analysis as an Indicator of Vegetative Burning Impact

Recent advances in radiocarbon analysis techniques and their application to apportionment of "contemporary" carbon sources has focused considerable attention on the use of $^{14}C/^{12}C$ isotope analysis as an "unequivocal" measure of vegetative burning impact.[5] The method provides an estimate of the portion of aerosol carbon associated with wood burning (residential wood stoves, fireplaces, forest fires, etc.) as opposed to sources of fossil carbon such as oil, coal, diesel, or gasoline combustion.

Although this approach seems, at first appearance, to offer a clear measure of urban impact from residential wood combustion (RWC) sources, a closer look into the assumptions required to build the "chain of evidence" between the $^{14}C/^{12}C$ measurement and an "unequivocal" measure of RWC impact reveals several uncertainties:

(a) Potential sources of "contemporary" carbon include a wide range of potential sources which include, but are not limited to, residential wood combustion. Table IV lists many possible source classes emitting "contemporary" carbon. Fortunately, several source categories can be distinguished from RWC emissions based on particle size if the ambient samples of fine particle carbon (<2.5μm) are available. Further narrowing of the possible source impact must be based on (1) evidence of source activity and transport, or (2) source impact estimates based on other indicators (e.g., absence of municipal incinerator chemical tracers). Given the difficulty in developing factual information on residential backyard burning, apartment incineration, structural wild fires and secondary vegetative carbon aerosol, an "unequivocal" estimate of residential wood combustion impact may be difficult to obtain. Estimates of the likely impact, based on known source activity may be more appropriate.

(b) Since RWC emissions are not pure, graphitic carbon, the $^{14}C/^{12}C$ measurement must either be corrected to account for the associated oxygen, hydrogen and inorganic ash components or used only as a conservative estimate of impact. Correction of the data requires that either the percent by weight of carbon in the emissions be known or that the C/(C+H+O) ratio be known. Unfortunately, considerable variability in the emission composition occurs between and within vegetative burning sources. Further, the C/(C+H+O) ratio is a function of the relative abundance of aliphatics, carboxylic acid and polynuclear aromatic hydrocarbons in the aerosol. Lacking specific information on the abundance of these compounds in wood

smoke, researchers have used a typical urban ratio (1.2) suggested by Van Vaeck[6] as a best estimate.

Studies conducted in Oregon have, in spite of these shortcomings, found carbon-14 estimates to agree reasonably well with source activity, light scattering measurements and other, more qualitative indicators. Care must be taken, however, to design the field program to minimize the potential from sources other than residential wood combustion. Typical "tricks" include fine particle monitoring during periods of cold weather in residential areas isolated from industrial sources.

Case Study 3: Chemical Mass Balance

Applications of the Chemical Mass Balance (CMB) receptor model have increased markedly within the past two years. Results from these studies have been used in the development of particulate control strategies as an aid to dispersion model validation and to identify previously unknown sources within particulate nonattainment areas.[7] A closer look at the apparent success of this method reveals that the chain of evidence used to identify source strengths in many studies includes a variety of techniques, of which CMB analysis is only one. Many of the methods listed in Table I can be used to supplement and support CMB source estimates, strengthening the analyst's conclusions. Although CMB is often the focus of the program, many of the more recent studies have gained "success" by developing a clear, complete and convincing case through the uses of several, independent approaches.

The ability of the CMB model to apportion source impacts is dependent on four frequently quoted factors: adequacy of the source emission composition data, field monitoring program design, quality of the ambient aerosol analytical data, and presence of reliable "tracer" species in the emissions from major sources. What is often not mentioned is that supplemental information on aerosol transport, emission inventory ratios among source categories, source activity and a working knowledge of the airshed are also required (but seldom acknowledged) factors in developing a successful program.

The importance of an accurate source composition data base can best be illustrated by examining a few applications of the CMB method in detail. Residual oil combustion and motor vehicle impacts have been selected for discussion because estimates prepared for these two source categories are often believed to be accurately predicted by CMB, because of the presence of unique tracers in their emissions. Failure to accurately characterize emissions from these two sources will introduce impact estimate errors which can be further compounded by emission inventory scaling techniques.

Residual Oil. Results of the Portland Aerosol Characterization Study (PACS) indicate a high degree of confidence in the CMB-estimated residual oil combustion impact estimates, based on chemical analysis of the emissions from seven local sources.[9] Results of tests conducted during the first quarter of 1978 reveal a vanadium/nickel ratio of 0.64, a figure consistent with the V/Ni ratio of PS400 residual oil used in Portland during that period. Since both elements are nearly unique tracers for residual oil combustion emissions in Portland, the CMB model estimates are heavily dependent on the accuracy of the V/Ni measurements. Analysis of

fuels marketed during 1977 and 1978, however, disclosed V/Ni ratios varying between 0.33 and 1.11. Had the source measurements been made during a period when the ratio was low, the estimated impacts would have been 50% higher than reported. Testing during a period when the ratio was 1.11 would have underpredicted the estimate by about one-third. Although these uncertainties appear large, the potential error in estimated impact in Portland would have been small, given the minimal impact ($<1 \mu g/m^3$ annual average) of this source. The key concept here is that care must be taken during the development of the source composition data if the analyst is expected to develop a convincing argument from CMB results.

Auto Exhaust. Impact estimates of transportation sources are of prime importance to the credibility of most source apportionment studies. Given the difficulties in source testing motor vehicles, published values of the chemical composition of auto exhaust are often used. Unfortunately, much of the literature is not self-consistent, nor are the details presented concerning how the data were developed. Table V summarizes exhaust composition data from the literature. Marked differences can be seen in the bromine values (normalized with respect to lead) and in the absolute values of Zn, Pb, Ba, and carbon. Because Pb and Br are used as the primary marker elements upon which motor vehicle exhaust impacts are calculated, the use of correct values is critical to the accuracy of the CMB analysis. Close examination of the research studies referenced in Table V serve to emphasize that these data sets are, in fact, "tuned" chemical composites intended to represent a mixture of leaded, unleaded and diesel exhaust characteristic of the airshed at the time the study was conducted. Direct use of these data sets must be viewed with caution and with the understanding that substantial error in the impact estimates are likely.

Source Nomenclature. One of the most difficult aspects of CMB (and factor) analysis is the application of the proper source name to the estimated source strengths when a number of chemically indistinguishable emissions occur within the same airshed. Since the CMB model only indicates what the likely source impacts may be (not necessarily what they are) based on the chemical "fingerprint" of the source, the analyst must decide which source name is the most appropriate. Table VI lists three source groups of similar chemical composition. Careless assignment of source nomenclature, conducted without supportive evidence, can mislead those charged with taking regulatory action.

The microscopy, radio-carbon analysis and chemical mass balance case studies discussed above provide a brief glimpse of the potential pitfalls of receptor modeling. Other techniques have their own associated perils. Factor analysis, for example, relies on the variability and chemical composition of emissions within the airshed to identify source impacts. Very strong, consistent impacts which coexist amidst weaker, more variable sources, may not be identified. Factor analysis results may also lump together two or more sources of similar variability and chemistry or ignore components associated with well-mixed "background" aerosol.

Regardless of the receptor model method used, the sum of the identified source impacts should provide a reasonable approximation of the measured aerosol mass. Failure to account for most of the mass may indicate omission of the background aerosol, important sources, or errors in the analysis.

Complimentary Applications

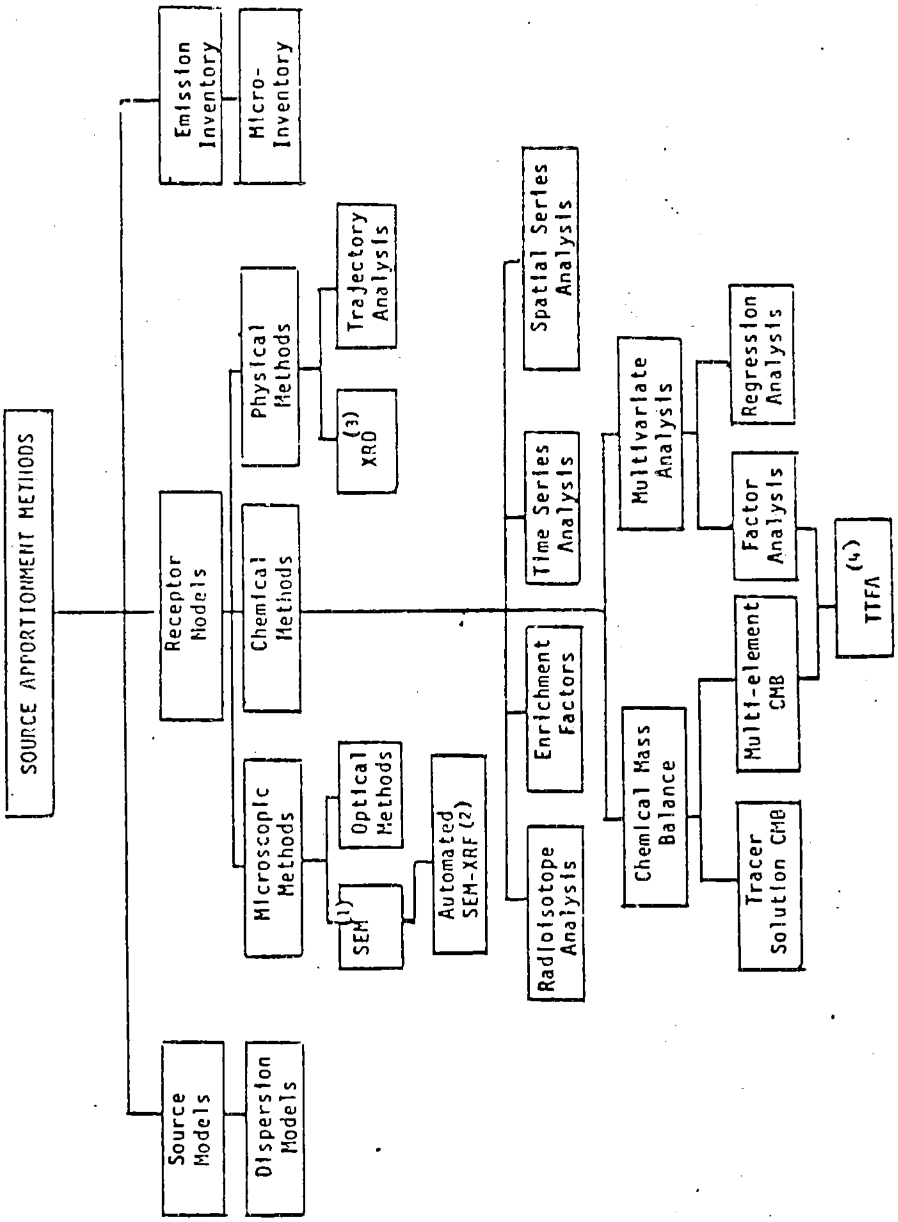
Perhaps the greatest advantage of the receptor model approach is the ability to identify the impact of particulate sources independent of the transport and emission inventory data required by dispersion models. These two methods can be used in concert to improve the strength of the dispersion model results. Validation of dispersion model results using selected receptor model results can identify weaknesses in emission inventory data and modeling assumptions. Core, et. al[7] have described work conducted by the State of Oregon Department of Environmental Quality in which selected chemical mass balance results were used to validate dispersion model results in three Oregon airsheds. The analysis identified major errors in fugitive dust inventories, source operating schedules and modeling assumptions. Following correction, systematic model underpredictions by the dispersion model were eliminated. Future applications of this approach to dispersion model validation could prove useful in a wide number of applications where complex terrain, uncertain emission factors and/or fugitive sources are important factors in model performance.

Other researchers have applied a number of receptor model approaches to apportion particulate mass, each selected to compliment results obtained from other methods. Factor analysis, for example, is being used to deduce the composition of major source emissions as input to chemical mass balance calculations. X-ray diffraction results can be used in concert with factor analysis estimates of the "geologic" source group to further apportion the sources based on the relative richness of mineral species in the aerosol and in nearby soil types. Optical microscopy can be of major importance in apportioning coarse-mode carbonaceous aerosol (such as pollen, wood fiber, paper fragments, etc.) which is difficult to identify by other methods. The most appropriate mix of tools must be selected on a case by case basis using the analyst's knowledge of the local source mix and meteorology, source constraints and program objectives.

Conclusions

Recent advances in receptor model technology have generated considerable interest among air pollution professionals responsible for the development of particulate control strategies. Application of these methods have included input to control strategy development, enforcement actions, dispersion model validation, demonstration control programs, and apportionment of light extinction between sources. Total, coarse, fine, and inhalable particulate fractions have been studied using these methods. Yet, as useful as receptor models are, each technique has definite limitations, requiring analyst understanding and judgment. As in other fields of science, receptor models can be inappropriately applied, misused, and results interpreted in such a way as to provide inaccurate conclusions. Properly applied, and with sufficient supportive evidence developed through independent approaches, receptor models can provide important new insights into the nature of the aerosol problem. As the technology expands, the costs associated with these methods will come within the reach of more users, providing an important new tool to regulatory agencies.

Figure 1.



(1) Scanning Electron Microscopy
(2) X-Ray Fluorescence
(3) X-Ray Diffraction
(4) Target Transformation Factor Analysis

Table I
Source Apportionment - Receptor Model
Advantages & Disadvantages

Source Apportionment Tools	Techniques Advantages	Disadvantages
RECEPTOR MODELS		
Microscopy		
Optical	Use of color, surface texture and optical properties to particle identification.	Limited to particles >2μm, semi-quantitative, highly dependent on operator skill.
SEM	Can be used with particles <1μm.	Costly to use on large numbers of particles, not quantitative if sample contains large variation in particle size.
Automated SEM-XRF	Classifies particles by size, shape and elemental composition. Analytical speed, ability to count large numbers of particles.	Still in early stage of development. Costly. Not reliable for organics. Coarse fraction only.
Chemical		
Enrichment Factors	Provides evidence of a source's impact by changes in aerosol composition. Simple.	Semi-quantitative method; requires source composition data. Often not specific.
Time Series Analysis	Provides clues to sources. Simple, inexpensive.	Generally does not provide specific source impact information.
Spatial Series Analysis	Provides clues to sources. Simple, inexpensive.	Does not provide source impact information.
Chemical Mass Balance	Provides quantitative estimates based on measured data. Impact uncertainties provided.	Source composition data required. Chemically similar sources cannot be independently identified.
Multivariate Analysis	No prior knowledge of sources needed to resolve element patterns. Source Compositon required to identify sources by common names.	Semi-quantitative method. Large data sets required, cannot provide short-term apportionment.
Radioisotope Analysis	Direct, quantitative measure of fossil carbon (e.g., coal or oil versus wood).	Costly. Limited to fossil-"modern" carbon apportionment.
Physical		
X-Ray Diffraction	Direct quantification of crystalline particles.	Coarse particles only, not useful for amorphous aerosols.
Trajectory Analysis	Helps identify approximate source location.	Cannot quantitatively estimate specific source impacts.
Traditional Methods		
Dispersion Modeling	Estimates impact from existing or proposed sources.	Difficulty in preparing accurate emission inventory and transport input data.
Emission Inventory	Traditional method of source contribution analysis. Simple to use.	Fugitive sources impossible to inventory, background aerosol not known; source impacts incorrectly assumed to be proportional to emissions.
Microinventory	A measure of the relative magnitude of nearby source impacts as an improved basis for dispersion modeling.	Does not provide source impact estimates directly.

Table II
Source Apportionment Technique Applications*

Method	Technique	Capabilities (1) Coarse Mode	Capabilities (1) Fine Mode	Application to Short Term Episodes	Resource Requirments (2) Manpower	Skill	Computer	Data
1	Optical microscopy	SQ	-	x	4	5	1	2
2	SEM microscopy	SQ	SQ	x	4	5	1	2
3	Automated SEM-XRF	Qn	-	x	5	5	3	2
4	Enrichment Factor	SQ	SQ	x	1	2	2	3
5	Time Series	QL	QL		1	2	2	3
6	Spatial series	QL	QL	x	1	2	2	3
7	Chemical Mass Balance	Qn	Qn	x	4	5	2	5
8	Multivariate methods	Qn	Qn		3	5	2	5
9	Dispersion modeling	Qn	Qn		2	4	3	5
10	X-ray diffraction	Qn	-	x	4	5	1	2
11	Microinventory	SQ	SQ		3	2	1	2

* After Throgmorton and Axtell[12]

(1) Source apportionment capabilities:
SQ = semi-quantitative
QL = qualatative
Qn = quantitative

(2) Judged on a scale of 1 to 5, 5 being the most resource intensive

Table III
Comparison of Mineral Content Estimates Between Analysts Using Optical Microscopy

	Analyst	Mineral Content* Mean	Mineral Content* Std. Dev.	t-test Result Significance Between Means
Case 1	1	69	22	not significant
	2	78	11	
Case 2	1	56	26	significant
	3	31	14	
Case 3	1	70	36	significant
	4	6	2	
Case 4	1	62	28	significant
	5	37	16	
Case 5	2	75	9	extremely significant
	3	36	10	
Case 6	2	77	16	extemely significant
	5	35	14	
Case 7	3	30	23	not significant
	4	5	0	
Case 8	3	38	10	not significant
	4	39	12	

* Percent of weight

Table IV
Potential Sources of Contemporary Carbon in Urban Atmospheres**

° Soil humus
° Paper fragments
° Spores, pollen, plant tissue
° Insect parts
° Starch and grain dust
° Sawdust
*° Residential wood combustion (fireplaces and wood stoves)
*° Structural wild fires
*° Forest fires, slash burning and grass burning
*° Agricultural land clearing
*° Residential backyard burning
*° Secondary vegetative carbon
*° Veneer dryer emissions
*° Hog fuel boiler emissions
*° Municipal incineration
*° Apartment, business or institutional incineration

* Fine particle sources

** All carbon associated with soil and road dust sources (carbonates, tire dust, oils, exhaust particles) assumed to be of fossil origin.

Table V
Motor Vehicle Exhaust Composition Summary From Literature Values

Specie	St. Louis, MO[a] % of Mass	Portland, OR[b] % of Mass	Washington, DC[c] % of Mass*	Medford, OR[d] % of Mass
Total Carbon	56.3 (3.80)**	53.8 (2.69)	-	62.26 (7.00)
Mg	0.6 (.04)	-	-	0.25 (.03)
Al	-	1.1 (.05)	-	0.06 (.01)
Si	-	0.82 (.04)	-	0.25 (.03)
P	0.09 (.006)	-	-	-
S	0.6 (.04)	0.4 (.02)	-	1.53 (.17)
SO_4	-	1.3 (.06)	-	1.49 (.16)
Cl	1.9 (.12)	3.0 (.15)	1.0 (.10)	1.53 (.17)
K	-	0.72 (.36)	-	-
Ca	-	1.25 (.06)	0.5 (.05)	0.69 (.07)
Mn	0.06 (.004)	-	-	-
Fe	1.0 (.06)	2.1 (.10)	0.5 (.05)	0.53 (.05)
Ni	-	0.018 (0.0)	-	-
Cu	-	0.073 (.003)	-	-
Zn	3.0 (.20)	0.350 (.017)	0.15 (.015)	0.28 (.03)
Br	3.7 (.25)	5.00 (.25)	3.8 (.38)	3.44 (.38)
Ba	0.09 (.006)	-	0.13 (.013)	-
Pb	14.80 (≡ 1.0)	20.00 (≡ 1.0)	(10.0)*(≡ 1.0)	8.89 (≡1.0)
NO_3	-	0.91 (.045)	-	12.60 (1.41)
Total	82.1%	90.8%	16.1%	93.8%

* Based on a lead content of 10% assumed by Kowalczyk
** ( ) normalized to lead content

(a) Dzubay, Reference 8
(b) Cooper, Reference 9
(c) Kowalczyk, Reference 10
(d) Cooper, Reference 11

Table VI
Chemical Mass Balance Source Groups

1. Geologic or Crustal
   - Shale
   - Paved road dust
   - Unpaved road dust
   - Windblown soil
   - Agricultural tilling
   - Coal flyash
   - Rock crusher
   - Asphalt production
   - Rock quarry dust
2. Calcium Sources
   - Limestone
   - Building demolition
   - Cement dust
   - Construction dust
   - Slag dust
   - Carbide furnace
3. Vegetative Burning
   - Residential fireplace
   - Residential wood stove
   - Residential backyard burning
   - Land clearing
   - Slash burning
   - Structural wild fires
   - Forest, brush and grass fires

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Appendix I
Receptor Model Glossary

Chemical Mass Balance

This method matches source particle size and chemical "fingerprints" to those measured at the receptor to back-calculate the impact of specific sources or source classes of similar chemical composition. Given data on the ambient concentrations of several chemical species and the percent by weight of these species in the emissions from the sources, a set of equations is prepared and solved to determine the source impacts.

Enrichment Factors

Ambient aerosol composition data is used in association with a reference element (usually a crustal element such as Fe, Al or Si) to provide an estimate of the degree to which a specific ambient aerosol element has been "enriched" by an anthropogenic source. If the "enriched" element is known to be a unique tracer for a specific source, and the concentration of the tracer in the source emissions is known, a crude estimate of the source's impact can be made.

Microscopic Methods

Particle identification by optical microscopy was one of the first, and the most widely used method of soruce apportionment. Current technology has expanded to include computer-driven scanning electron microscopy coupled with xray fluorescence analysis to provide a particle-by-particle analysis of ambient particulate filters. As a consequence, particle identification methods traditionally founded on particle size shape, color, bifringence, and surface properties has been expanded to include elemental composition and rapid, computer assisted analysis permitting large numbers of particles to be analyzed at minimum cost.

Multivariate Methods

Statistical methods that include factor analysis, regression methods, principle component and cluster analysis techniques. These methods extract information on source impacts on the basis of the variability of chemical species measured within a large set of particulate samples. Given the premise that chemical species emitted from a specific source will vary in time (as measured at the receptor) in the same manner, multivariate methods detect the common variability of the chemical species. The analyst then identifies the contributing source by comparing those species with similar variability to the chemical composition of sources within the airshed.

Radioisotope Analysis

Measurement of carbon-14/carbon-12 isotope ratios have recently been used to distinguish "modern" from fossil fuel carbon. Using this method, carbon emitted from contemporary sources (wood burning, leaf fragments, fireplaces) has been distinguished from auto and diesel exhaust, coal and fuel oil carbonaceous aerosols.

Spatial Series Analysis

Special relationships between aerosol chemistry measured at numerous receptors can provide important clues to likely contributing sources when viewed in relation to emission density maps and given a basic understanding of the chemical composition of source emissions.

Time Series Analysis

Qualitative indications of source impacts based on temporal variations in aerosol mass and chemistry can be used, in association with source emission activity and transport data, to gain insight into likely source impacts over time.

X-Ray Diffraction

Quantative identification of crystalline substances in the coarse mode ($>2.5\mu m$) by XRD has enabled analysts to determine impacts from fugitive emission sources with reasonable accuracy ($\pm 25\%$) for moderate to heavily loaded filters.

⑦

New models to control old pollution sources

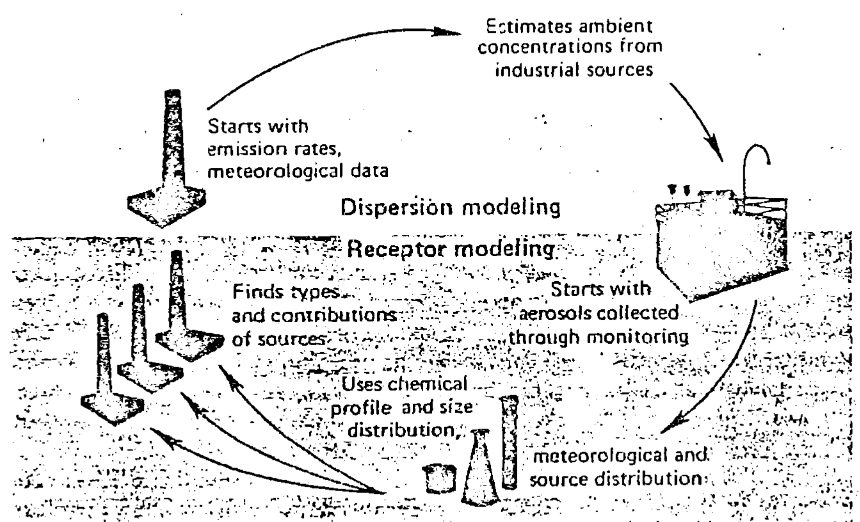
While models employed to permit new facilities are undergoing change, those used to curb existing pollution are being refined and improved by environmental specialists.

☐ People in industry who feel that there must be a better way to monitor and control air pollution can take comfort in the fact that many regulators agree and are doing something about it. The U.S. Environmental Protection Agency, for example, has funded a number of programs to develop new monitoring techniques, and air-pollution-control authorities throughout the nation are doing research, development and test work.

The various approaches that are being investigated fall under the common heading of "receptor modeling" (RM), a system whereby a monitoring station set up at a representative site (or sites) analyzes air samples and compares the results with collected data on the manmade and natural sources of emissions in the area.

"Within the next two years, we should have models in which about 90% of the origins of the aerosols are characterized, and then we will have documentation to permit state and local agencies to use the models for their own implementation plans," says Robert K. Stevens, chief of the inorganic-pollutant analysis unit at EPA's Environmental Science Laboratory (Research Triangle Park, N.C.).

Of course, receptor modeling is not now at the stage where it can predict pollution scenarios. As a consequence, it is not likely to become a requirement for permitting new sources in the near future. "What RM now does is go backward to figure out a control mechanism based on historical data," says an environmental consultant, adding that it doesn't "predict the future or consider the effects of adding a new source." As such, it is at present seen mainly as a tool to control existing pollution sources.



Dispersion and receptor modeling are complementary. The first begins with emission rates and dispersion characteristics, and estimates ambient-pollutant concentrations. Receptor modeling begins with chemical and size measurements of ambient aerosols, and estimates the contributions of each source-type to them.

Source: ERT Newsletter, Concord, Mass.

Differences between dispersion and receptor modeling — Fig. 1

In that role, however, RM might prove to be less expensive than the dispersion models widely employed by EPA to control existing pollution (see previous story for an analysis of another kind of EPA dispersion model—the kind used to predict new-source emissions). That is the opinion of Stuart Dattner, an environmental quality specialist with the Texas Air Control Board, Abatement Requirements and Analysis Div. (Austin, Tex.), who says that RM doesn't require industry to provide emissions data. "With RM, you don't need to know how many pounds per hour a plant is emitting at different hours of the day, every day of the year. In Houston, there are more than 1,000 major stacks, and some plants may have 75 major stacks—can you imagine the cost of having someone keep records on all that?"

RECEPTOR VS. DISPERSION—In the EPA dispersion models, air quality regulators make an emissions inventory by asking industries in the area to estimate their emissions of various pollutants. Then they develop a computer model that includes such factors as winds and the temperatures and velocities of emissions, in order to predict the dispersion of pollutants. The control strategy is based on this model.

Critics of dispersion modeling say that it is inaccurate and that it places an unfair burden on industry. "The problem is that it's extremely difficult to estimate exactly what's coming out," says Dattner. He notes that an oil refinery has only a few stacks, but thousands of valves from which the total leakage may be significant, and points out that emissions vary widely because processes fluctuate.

Dattner is also chairman of the Air Pollution Control Assn.'s Committee on Receptor/Source Apportionment, which is fostering development of RMs. The Committee is planning a session on this topic for APCA's national meeting in Philadelphia next June, and is working with EPA on plans for a series of workshops on RM that EPA hopes to hold next spring.

RM can produce some surprising results that are not predicted by dispersion models. For example, an RM

study done in Portland, Ore., about two years ago found that smoke from domestic wood fires was a major source of air pollution, especially in winter. Dust from paved roads and other sources was also more significant than had been anticipated.

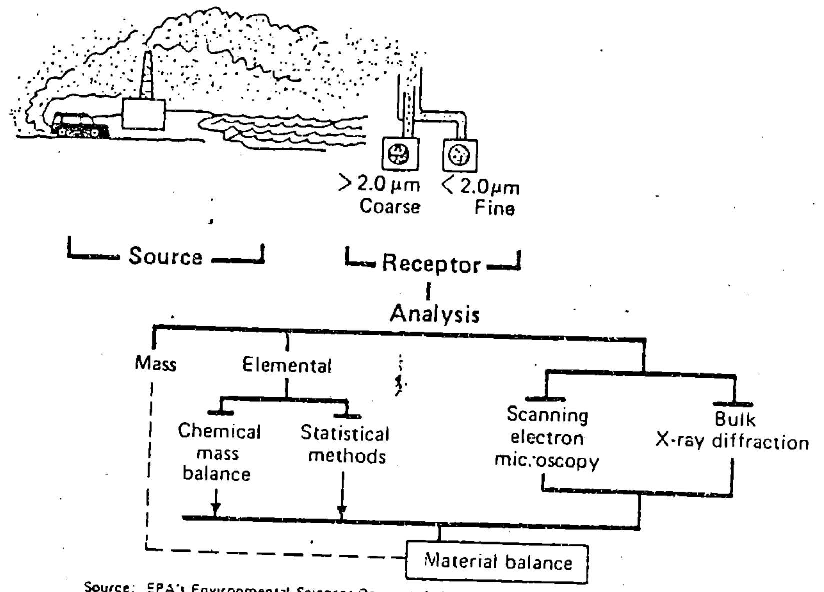
The study was prompted by the 1976 amendments to the Clean Air Act, which indicated that another round of controls might have to be imposed on Portland industries. However, industry there was already controlled to such a degree that it wasn't clear what could be done, says John Core, a supervisor in the Oregon Dept. of Environmental Quality's Air Quality Control Div.* Core is currently on a one-year assignment with EPA's Data Monitoring and Data Analysis Div. (Research Triangle Park), where one of his tasks is to write a guideline document on the chemical-mass-balance technique used in the Portland study.

This method, called the "chemical element balance," was developed some years ago by Sheldon K. Friedlander, of the chemical engineering department of the University of California at Los Angeles, and has been used in a number of studies. Its premise is that each type of source—e.g., automobile, power plant, ocean—emits a characteristic series of elements. The emissions from sources in the area are analyzed and the data compared with subsequent analyses of ambient pollutants that have been captured by a filter.

OTHER WAYS—Another technique used for elemental data is called factor analysis. In this case, a large number of filters measure the same elements, and patterns are sought for groups of elements. The relative occurrence of various elements permits attribution to the specific source for which the combination is characteristic.

A third method, target transformation factor analysis, is essentially a combination of chemical element balance and factor analysis.

While these methods have proved useful, as shown by the Portland experience, much development work remains to be done. "Among the things to be explored are how good are the models, what are their limitations, and how many elements does one need in order to identify an individual source," says Dattner.



Source: EPA's Environmental Sciences Research Laboratory, Research Triangle Park, N.C.

Various ways to validate receptor models

Fig. 2

Validation of the models is a major aspect of EPA's work in this area, and part of this effort is devoted to developing improved instrumentation. Stevens says that EPA development of dichotomous samplers in the 1970s was important for source apportionment. These samplers, now widely used, separate small particles (less than 2 µm) from larger particles. Stevens explains that large particles are mostly alkaline windblown dust, while small ones are often acid products of photochemical reactions and fossil-fuel burning. It is important to separate them, he notes, to avoid interaction on the sampling filters.

Currently, particles collected on filters are measured by atomic absorption, x-ray fluorescence or neutron activation, or by combinations of these techniques.

A more effective method is microscopic analysis, which identifies the shape and size of particles, but it is expensive and time-consuming. EPA is funding development of an automated method at New York University (Syracuse), which combines two types of monitoring techniques: a scanning electron microscope and x-ray fluorescence.

Other projects funded by EPA include:

- A study of the ability of the chemical-mass-balance method to identify the impact of specific emissions sources (University of Maryland, College Park).
- Source apportionment by factor analysis (University of Illinois, Urbana).
- Development of x-ray diffraction methods to analyze ambient aerosols (South Dakota School of Mines, Rapid City).
- Development of radiocarbon methods to distinguish between carbon derived from fossil fuels and "new" carbon resulting from wood-burning or land clearance (U.S. Bureau of Standards, Gaithersburg, Md.).
- Nondestructive methods of measuring carbon in air samples (as opposed to burning to get the measurement from the CO_2 or methane generated), so that the sample may be retained for other analyses (North Carolina State University, Raleigh).
- Analytical techniques to determine the amount of water in aerosol particles, since water swells particles and makes it difficult to ascertain chemical content (Duke University, Durham, N.C.).
- A comparison of the results of chemical mass balance and factor analysis (EPA in-house, and the Oregon Graduate Center for Research and Development, Beaverton).

Gerald Parkinson

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* In the aftermath of the study, the soil-dust allotment in the existing dispersion model's emissions inventory was increased by 600%, and 6,500 tons/yr was added for wood-burning emissions. The results are now included in plans for new air-quality regulations.

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Particulate Dispersion Model Evaluation: A New Approach Using Receptor Models

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PARTICULATE DISPERSION MODEL EVALUATION: A NEW APPROACH USING RECEPTOR MODELS,

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Recent advances in the development of receptor-oriented source apportionment techniques (models) have provided a new approach to evaluating the performance of particulate dispersion models. Rather than limiting performance evaluations to comparisons of particulate mass, receptor model estimates of source impacts can be used to open new opportunities for in-depth analysis of dispersion model performance. Recent experiences in the joint application of receptor and dispersion models have proven valuable in developing increased confidence in source impact projections used for control strategy development. Airshed studies that have followed this approach have identified major errors in emission inventory data bases and provided technical support for modeling assumptions.

This paper focuses on the joint application of dispersion and receptor models to particulate source impact analysis and dispersion model performance evaluation. The limitations and advantages of each form of modeling are reviewed and case studies are examined. The paper is offered to provide several new perspectives into the model evaluation process in the hope that they may prove useful to those that manage our nation's air resources.

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Introduction

During the past twenty years, the science of urban dispersion modeling has grown in sophistication, scope of application and importance as an air management tool. Dispersion models are widely used by regulatory agencies as a key tool in the development of program policy, enforcement actions and airshed management decisions that individually or collectively have major consequences to community economic growth and public health.

Since the courts have interpreted dispersion models to be legally binding mechanisms for establishing acceptable levels of emission control from sources, it follows that dispersion modeling results must provide the level of confidence that decision makers need to support their actions. Unfortunately, the use of dispersion models to provide accurate estimates of 24 hour and annual particulate concentrations, as required by current air quality regulations, pose many difficulties. Deficiencies in our knowledge of the basic processes controlling atmospheric dispersion include transport, particle deposition and transformation processes. In addition, uncertainties in emission rates and source activity levels for both stack and fugitive dust sources tend to further limit model performance.

Recent advances in receptor-oriented particulate apportionment techniques, however, provide new opportunities to advance the state-of-the-art in urban aerosol dispersion modeling. Receptor models are one of a number of approaches useful in identifying impacts from emission sources.[1] Other source apportionment methods include source (dispersion models) and emission inventory techniques. Further stratification of the various receptor model approaches is shown in Figure 1. Unlike dispersion models which begin with measurements of emission rates, stack parameters and meteorology, receptor models "decode" ambient particulate morphology, chemistry and variability information to identify source impacts. Perhaps the greatest advantage of these techniques is their ability to quantify particulate source impacts independent of the transport and emission inventory data required by dispersion models. The complementary relationship between these two approaches is shown in Figure 2.

The joint application of both source and receptor modeling techniques to air resource management and policy development has been demonstrated to be a cost-effective approach that can markedly increase community confidence in proposed regulatory action.[2] This paper focuses on the advantages and limitations of receptor and source-oriented models. New approaches useful in evaluating the performance of particulate dispersion models are proposed and case studies discussing the joint application of these techniques are presented.

Source and Receptor Oriented Models

Source-dispersion and receptor-oriented models have a common physical basis. Although many dispersion models incorporate particle deposition and secondary particle formation algorithms, the basic form of both models assumes that mass arriving at a receptor (sampling site) from source j was transported with conservation of mass by atmospheric dispersion of source emitted material. From the source-dispersion model point of view, the mass collected at the receptor from source j, M, is the dependent variable which is equal to the product of a dispersion factor, D_j, (which depends on wind speed, wind direction, stability, etc.) and an emission rate factor, E_j, i.e.,

$$M_j = D_j E_j.$$

From the receptor model viewpoint, the total aerosol mass, M, collected on a filter at a receptor is the dependent variable and equal to a linear sum of the mass contributed by p individual sources,

$$M = \sum_{j=1}^{p} M_j.$$

The mass of individual chemical species, m_i, is also assumed to be a linear sum of the contributions of element i from each source,

$$m_i = \sum_{j=1}^{p} F_{ij} M_j, \qquad (1)$$

where F_{ij} is the fraction of the ith chemical species in emissions from the jth source. Equation (1) can be transformed to a fractional mass concentration form by dividing both sides of equation (1) by the total deposit mass, M, multiplying by 100% and generalizing for the kth filter as shown in the following equation,

$$C_{ik} = \sum_{j=1}^{p} F_{ij} S_{jk}, \qquad (2)$$

where C_{ik} is the percent concentration of the ith chemical species on the kth filter and S_{jk} is the percent of the total mass on the kth filter contributed by the jth source. The kth filter may be either one in a series of filters collected during different time intervals at one site or one in a series collected during the same time interval at different sites.

Source (dispersion) and receptor-oriented models both assume that mass is conserved in transport of material from source to receptor. The validity of this assumption is a matter of degree and its utility depends on the specific source, airshed and model. Material emitted from a source can be either in the gaseous or aerosol phase and it may undergo a number of chemical and physical changes before it is collected on a filter and measured. A portion of the aerosol phase, for example, may evaporate before it is collected or particles may be removed through sedimentation during transport. The gaseous phase, on the other hand, may contribute to the aerosol deposited on the filter by condensation or through atmospheric chemical reactions. In addition, filter artifact effects and evaporative losses may alter the material deposited on the filter before it is weighed.

Chemical Receptor Modeling: State-of-the-Art

Chemical receptor models, in general, identify aerosol sources by comparing ambient chemical patterns or fingerprints (interelemental patterns, spatial or time variant patterns) with source chemical patterns. Source contributions are quantified by a least squares multiple regression analysis on either the total mass on different filters or the mass of individual chemical species on a single filter. Although similarities in the different chemical approaches are greater than their differences, they have been historically divided into two categories: chemical mass balance methods, which attempt to define the most probable linear combination of sources to explain either the time or spatial variability in ambient chemical patterns.[1]

The application of these approaches to particulate source apportionment and dispersion model evaluation has been supported by EPA because recent applications of these techniques have been found to be highly cost-effective. Recent studies by Cass suggest that joint receptor-dispersion modeling studies have had a 27:1 payoff in cost avoidance associated with misdirected control strategies.[2] Results from these studies indicate that quantitative estimates of source contributions to TSP, fine and coarse mode mass can be identified with relative uncertainties ranging from ± 5 to 30%.[8] Receptor models are typically able to apportion between 80 and 90% of the measured background or urban aerosol mass to specific sources, chemical classes or source groups (i.e., the crustal source group comprised of paved road dust, windblown soils and other sources of similar composition). To achieve this level of success, receptor models must be viewed not as an isolated computer program, but as a total "system" consisting of the project design, field monitoring program, laboratory analysis and data interpretation phase in which a number of methods may be used to develop the chain of evidence needed to quantify source impacts.

Receptor models, however, have distinct limitations which need to be recognized and dealt with during development of the experimental design phase of the project. Perhaps the most common limitations in the current technology are:

a. Inability of the models to estimate future air quality,

b. Difficulty in directly distinguishing impacts among sources of chemically or morphologically similar emissions,

c. Apportioning source contributions to secondary aerosols and

d. Our knowledge of the chemical composition of source emissions.

Development of better source emission characterization data bases will also be required before receptor models will be able to distinguish sources emitting several of the trace elements (e.g., Cu, Zn, Se, Sb, Sn) commonly measured in the ambient aerosols.

Perhaps the most important criteria in defining the state-of-the-art of receptor modeling is the intercomparison of results among several techniques using common synthetic and "real world" data bases. Although several comparisons have been reported in the literature, the first series of rigorous validation tests are only now being completed.[9]

Particulate Dispersion Models: State-of-the-Art

Just as receptor models have real advantages and limitations, so too do current particulate dispersion models. Their limitations may be grouped into four areas:

- The quality and relevance of the meteorological data
- The quality of the emissions data (especially for fugitive dusts)
- Quality and appropriateness of ambient measurements to model predictions
- Capabilities of the model algorithms to reproduce natural events in the atmosphere

In a recent overview of particulate dispersion models, Cramer and Bowers have reviewed these, and other difficulties.[10] Their review cites the generally poor correspondence between model predictions and hi-vol ambient

data, with the models typically accounting for 20-30% of the ambient concentrations. In contrast, both short-term and annual average SO_2 concentration estimates by dispersion models show agreement on the order of ± 10%.

Although dispersion models for predicting particulate concentrations have been under development for many years, the EPA Air Quality Models will need to be further improved to provide for gravitational settling, dry deposition and secondary particle formation before a comprehensive algorithm is available. The first step in this direction is development of EPA's Industrial Source Complex (ISC) model. ISC is designed to consider settling and deposition associated with emissions from stack or area sources including fugitive sources. Secondary particle formation is not included in the model. The most serious problem, however, arises from deficiencies in the emission and meteorological data bases for without major improvements in these areas, an objective evaluation of the performance of any dispersion model will be extremely difficult.

Dispersion Model Evaluation: New Perspectives

In recognition of the limitations of current dispersion models and because of the weight of the decisions that must be based on them, the Congress, in adopting Section 310 of the Clean Air Act Amendments of 1977, called for periodic reviews of dispersion modeling technology.[11] In response to these requirements, EPA and the American Meteorological Society (AMS) have jointly worked toward the development of dispersion model evaluation methods and the establishment of standards for judging model performance. The chief criteria upon which model performance is based have been described by Fox[12] and Wilson, et. al.[13] Both are based on statistical evaluations of (a) differences between measured and predicted values (model bias, variance and gross variability) and (b) correlation analysis of measured vs predicted values in time or in space.

Although several evaluation methods have been proposed, the use of statistical acceptance/rejection tests have not been widely adopted because of the large uncertainties associated with model inputs, algorithm limitations and inaccuracies imposed by the quality of ambient air quality data sets. As Fox suggests, the question facing regulatory decision-makers is whether model predictions reasonably approximate actual conditions. Given the numerous uncertainties that have been identified and the likely consequences of their actions, it is not surprising that decision-makers are demanding more credibility in dispersion modeling results.

Two authors have recently provided a new perspective on this problem. Hanrahan[14] and Core,[15] et. al. have suggested expansion of the concepts described by Wilson, et. al., to include direct comparison of actual impacts from specific sources (obtained by receptor model analysis) to those projected by dispersion modeling. This approach was adopted after it became clear that an independent means of evaluating specific source impacts developed by urban particulate dispersion models was needed to strengthen the credibility of proposed control strategies. The established practice of evaluating model performance by comparing ambient TSP measurements to dispersion model estimates (generated by inclusion of all sources) requires a "leap of faith" assumption that the dispersion model would reasonably predict impacts of specific sources, an assumption that many decision-makers

are increasingly reluctant to accept. By comparison of actual and predicted source impacts over time and space, major emission inventory errors have been identified and modeling assumptions have been evaluated. Most importantly, confidence in the ability of the dispersion model to reasonably approximate actual source impacts has been greatly strengthened.

Model Evaluation Protocol

The evaluation protocol consists of 5 steps, each of which are of key importance to developing confidence in the dispersion model's ability to simulate specific source impacts.

Step 1: Identification of "Target" Sources. The model evaluation process hinges upon the ability of the receptor model to quantify the impact of specific sources with a high degree of confidence. Sources that meet this requirement, called "target" sources, should ideally meet three criteria:

1. The chemical or morphological characteristics of the emissions should provide unique, consistent and chemically stable tracers for the source.
2. The source should be an important contributor to the airshed's particulate air quality.
3. The "target" source should be unique within the airshed.

The importance of the model's ability to realistically simulate both point and area source emissions requires that "target" sources in both categories be considered in the model comparison process. Sources that have been used in this way include those noted in Table I.

Step 2: Program Design. Experimental design is of central importance to the success of receptor model studies and, therefore, to the development of a credible source-receptor model evaluation program. Several of the program design elements of specific importance are discussed below.

1. Identification of key data elements required to support both dispersion and receptor modeling efforts. Example data elements might include those noted in Table II.
2. Development of concurrent source and receptor model data sets to insure that direct comparisons can be made by both models for the same time periods and receptor locations.
3. The sampling network design must (a) incorporate a sufficient number of receptors to provide an indication of model performance, (b) utilize instrumentation compatible with analytical requirements, (c) meet established EPA siting requirements and (d) include appropriate receptor locations. Receptor siting should meet the requirements noted in Table III.

Step 3: Dispersion Modeling. Based upon the emission inventory and meteorological data bases developed during the field monitoring program, an independent dispersion modeling analysis is conducted, predicted and observed aerosol mass comparisons are calculated and model performance is evaluated. After a "best-effort" analysis is completed, model simulations of impacts associated with only "target" source emissions are prepared for each location at which receptor model analysis has been conducted. Dispersion model prediction of "target" source impacts should be prepared for both 24 hour and annual averaging periods. Monthly or seasonal comparisons can be made, however, to minimize program costs.

Step 4: Receptor Modeling. The receptor modeling phase should focus on the application of those techniques believed to be most cost-effective in quantifying impacts associated with the "target" sources. In previous studies, chemical mass balance (CMB) source apportionment has served as the basis for the receptor modeling program. CMB results, however, may be compared to source impacts identified by factor analysis, x-ray diffraction, microscopy or any other techniques required to build the necessary level of confidence in the source apportionment results. The demonstrated ability of the receptor modeling result; to track known changes in spatial and temporal emission patterns can be a simple, yet reassuring, measure of the credibility of the receptor modeling study. Once the concurrent background and urban-site "target" source impacts are quantified, local source contributions may be calculated and averaged, providing a direct means of comparison to dispersion model predicted values.

Step 5: Model Comparisons. Comparison of dispersion and receptor model impact estimates requires (a) an understanding of the limitations and strengths associated with each model's impact estimate and (b) the strength of other independent data that may tend to support one method's impact estimate. By considering and weighing all of the available evidence, an informed judgment as to the true source impact can often be made, the adequacy of the dispersion model's performance evaluated and corrective action taken, if necessary. In the case studies described below, model comparisons of "target" source impacts identified major emission inventory, modeling assumptions and algorithm errors that normally would not have been identified. Control strategies adopted on the basis of these models would have been unable to achieve the level of air quality improvement projected, yet would have misdirected millions of dollars in industrial control technology.

Model Comparison Case Studies

Core, et. al.[12] and Hanrahan[13] have described joint applications of receptor and dispersion models in three Oregon airsheds. In each case, chemical mass balance source apportionment results for point and area "target" sources were quantified and compared to dispersion model results for the same site locations and time periods. Three models have been used in these comparisons; EPA's AQDM and CDMQC Gassian models and an Eulerian finite difference model. Several of the key findings of these programs are discussed below.

Source Impact Comparisons

Tables IV and V summarize "target" source comparisons of several area and point sources in two Oregon airsheds. Dust from paved and unpaved roads was compared because (a) of the overwhelming influence of fugitive dust sources to TSP mass and (b) the impact of fugitive dust sources (as a group) can be quantified to relative uncertainties of less than 10%. Motor vehicle exhaust serves as a second area source "target" that is extremely useful in evaluating a dispersion model's ability to simulate non-fugitive area source emissions. Residual oil and hogged fuel boiler point source emissions have served as a test of the model's ability to simulate point sources. The impacts associated with both of these sources can be confidently identified by the distinct elemental characteristics of their emissions.

Comparison of initial dispersion model predictions to those developed by the receptor model often identified important emission inventory deficiencies which, upon correction, can dramatically improve model performance. These comparisons have served to direct agency resources toward correction of fugitive dust emission inventories - a step which has led to major revisions in the emission inventory of both airsheds. In Portland, these changes included a 600% increase in Portland's paved road dust inventory and identification of a 6,500 ton per year residential wood combustion source class.

Early dispersion model predictions prepared for the Medford airshed were based on EPA's AQDM model which used a virtual point source algorithm. Although the AQDM TSP impact estimates and model statistics suggested satisfactory model performance, estimates of fugitive dust area sources highly underpredicted those indicated by the CMB model. Investigation into these discrepancies pinpointed the inability of the virtual point source algorithm to realistically simulate the area source emissions. Adoption of the CDQMC's finite difference area source algorithm, however, solved the problem. Had the CMB-AQDM fugitive dust impact comparison not been made, the predicted point source contributions to Medford's non-attainment problem would have been unrealistically high, providing a misleading assessment of the likely benefits of further point source controls.

Improved Dispersion Model Performance

Figures 3 and 4 illustrate model performance in two Oregon airsheds before and after completion of the model comparison and data base improvement processes. Although the Portland model predicted to observed correlation only improved from 0.5 to 0.7, systematic bias in the model was eliminated. The model predicted background aerosol concentrations improved to within 2 $\mu g/m^3$ of the measured value and, most importantly, the "target" source impacts were known to be predicted with good accuracy. As Figure 5 shows, major changes in the airshed emission inventory were also made as a result of the model comparison process, presenting an entirely new perspective of the relative importance of industrial point source emissions to Portland's TSP air quality.

Similar experiences evolved from the joint application of CMB and CDMQC results in the Medford, Oregon airshed. Performance of the CDMQC model improved markedly following improvements in the fugitive dust and residential wood space heating emissions, "target" source impact comparisons were markedly improved and community confidence in proposed control strategies were strengthened.

Summary and Conclusions

Cost-effective particulate control strategies must be based on dispersion models that have been shown to meet acceptable levels of performance. In the past, evaluations of model adequacy have been based on comparative analysis of predicted and observed particulate mass - comparisons that are compromised by difficulties in generating accurate emission inventories, by limitations in the accuracy of the air monitoring data and other factors. Comparisons of model bias, correlation in time or space and the degree of variability in measured and model-predicted data sets have served as the principal measures of acceptable performance.

Although the criteria are useful indicators of model performance, they provide little direct evidence of the dispersion model's ability to reasonably approximate actual impacts from specific sources, a point of central concern to those required to evaluate central strategy options. The joint application of receptor and dispersion models, however, provides a number of new opportunities to expand model performance criteria to comparisons of specific point and source impacts.

Concurrent analysis of particulate source impacts developed through independent dispersion and receptor modeling studies have led to major improvements in dispersion model performance. Perhaps more importantly, studies that have followed this protocol have led to new perspectives as to the relative importance of point and area sources to community air quality.

Acknowledgements

The concepts and program results reported herein were developed over a 5 year period by the many engineers and scientists associated with the design and conduct of the Portland and Medford, Oregon Aerosol Characterization programs. The pioneering efforts of the State of Oregon Department of Environmental Quality, Air Quality Division and U.S. EPA Region X Air Branch staff deserve special recognition.

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Table I

"Target" Sources Impact Uncertainties Associated With Chemical Mass Balance

Source	Source Type	Unique Tracer Property	Typical CMB Uncertainty (Relative %)
Residual Oil	Point	Ni, V*	± 10%
Hogged Fuel Boilers	Point	Na, Cl, K, SO_4^{-2}*	± 18%
Paved Road Dust	Area	Ca, Si, Al, Fe**	± 6%
Motor Vehicles	Area	Pb, Br*	± 10%
Wood Heating	Area	K, C*	± 17%

Notes:

* Fine fraction (< 2.5 μm)
** Coarse fraction (2.5-15 μm)

Table II

Typical Source-Receptor Modeling Data Requirements

- Meteorological Data (wind speed, wind direction, stability, etc.)
- Emission Inventory data representative of the field sampling period
- Records of unusual source activities near the sampling sites
- Spatially resolved area source emission inventories
- Ambient aerosol elemental, ion and carbon chemistry (size resolved)
- Background aerosol chemistry (size resolved elemental, ion and carbon composition data)
- Source emission chemical characterization (size resolved) representative of the field sampling period.
- Independent, supportive analysis (e.g., x-ray diffraction, factor analysis, microscopy)

Table III

Receptor Location Requirements

<u>Site Location</u>	
Background	The chemistry of the background aerosol is required to provide a basis for source apportionment. Once the source contributions are developed the background source impacts are subtracted from the urban source apportionment results to provide an estimate of "local" source contributions. The "local" impacts can then be directly compared to the dispersion model predictions.
"Target" Source Impact Areas	Sampling sites must be located in areas likely to be impacted by the "target" sources selected. This evaluation is often based on available modeling studies and simple transport analysis.
Non-attainment Locations	TSP non-attainment sites are often used to insure that program results are valid at the sampling locations which have historically exceeded NAAQS and upon which control programs are likely to be based.

Table IV

"Target" Area Source Impact Comparisons: Dispersion/Receptor Model Impact Estimates
($\mu g/m^3$)

Portland, Oregon[1]
Motor Vehicle Exhaust

Site	CMB Estimate	Eularian Model Initial	Eularian Model Final
1	1.8 ± 0.2	1.6	1.6
2	4.4 ± 0.4	4.6	4.6
3	3.4 ± 0.3	4.2	4.2
4	3.0 ± 0.3	1.6	1.8

Medford, Oregon
Motor Vehicle Exhaust

Season	CMB Estimate	CDMQC Final Estimate
Spring	1.0 ± 0.1	1.2
Summer	1.4 ± 0.1	1.4
Autumn	1.9 ± 0.2	1.9
Winter	1.9 ± 0.2	1.9
Annual	1.6 ± 0.2	1.6

Portland, Oregon[2]
Paved Road Dust

Site	CMB Estimate	Eularian Model Initial[3]	Eularian Model Final[4]
1	21.0 ± 1.2	3.5	19.0
2	19.7 ± 1.1	8.0	22.0
3	27.0 ± 1.6	5.5	28.5
4	13.5 ± 0.8	4.0	13.0

Medford, Oregon
Wood Space Heating

Site	CMB Estimate	CDMQC Model Initial[5]	CDMQC Model Final[6]
1	21.5 ± 6.4	11.1	19.4
2	5.8 ± 1.7	3.7	6.5

Notes:

[1] 1977 Annual Estimate
[2] Regime 7 (North winds)
[3] Based on uniform emission factor of 0.84 G/VMT (3145 TPY)
[4] Based on land-use specific emission factors which average 3.2 G/VMT (19,400 TPY)
[5] Initial emission factor 22 pound per ton (exclusive of condensible organics)
[6] Final emission rate used 38.5 pounds per ton (includes condensible organics)

Table V

"Target" Point Source Impact Comparisons
(Dispersion Receptor Models Impacts)
$\mu g/m^3$

Portland, Oregon[1]
Residual Oil Combustion

	CMB	Eularian Model	
Site	Estimate	Initial	Final[2]
1	0.13	0.21	0.17
2	0.20	0.25	0.17
3	0.90	0.34	0.16
4	0.04	0.24	0.05

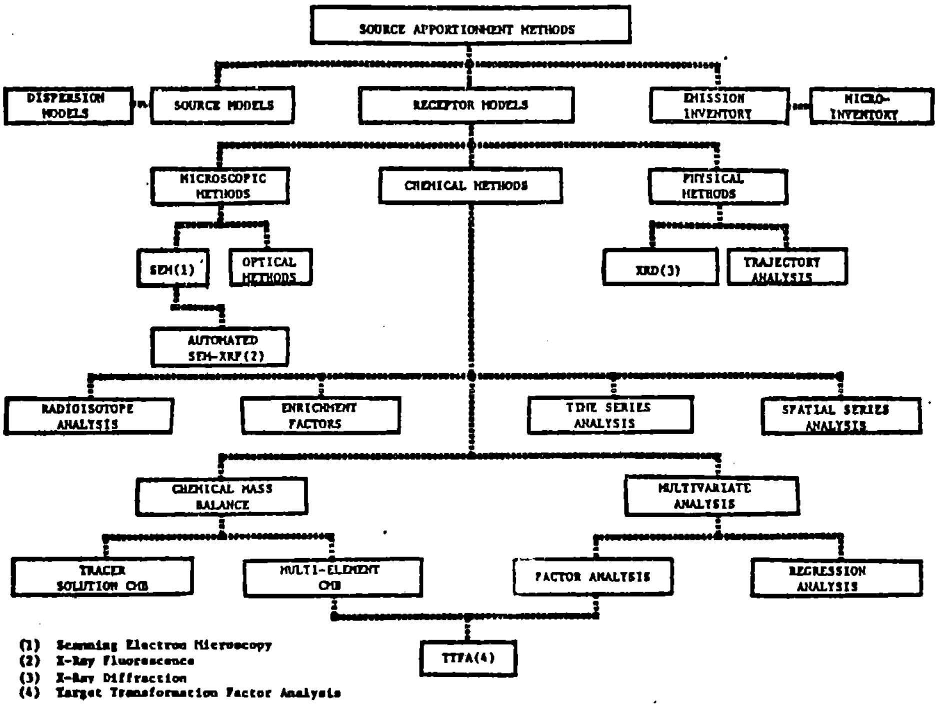
Medford, Oregon[3]
Hogged Fuel Boilers and
Particle Board Dryers

Site	CMB Estimate	CDMQC Estimate[4]
1	9.7 ± 1.7	7.5
2	8.0 ± 1.4	3.7

Notes:

[1] Regime 4 and 7 (north and south winds)
[2] Errors in boiler operating schedule corrected
[3] 1979 Annual predictions
[4] Initial CMDQC estimates were not revised

Figure 1



(1) Scanning Electron Microscopy
(2) X-Ray Fluorescence
(3) X-Ray Diffraction
(4) Target Transformation Factor Analysis

Figure 2

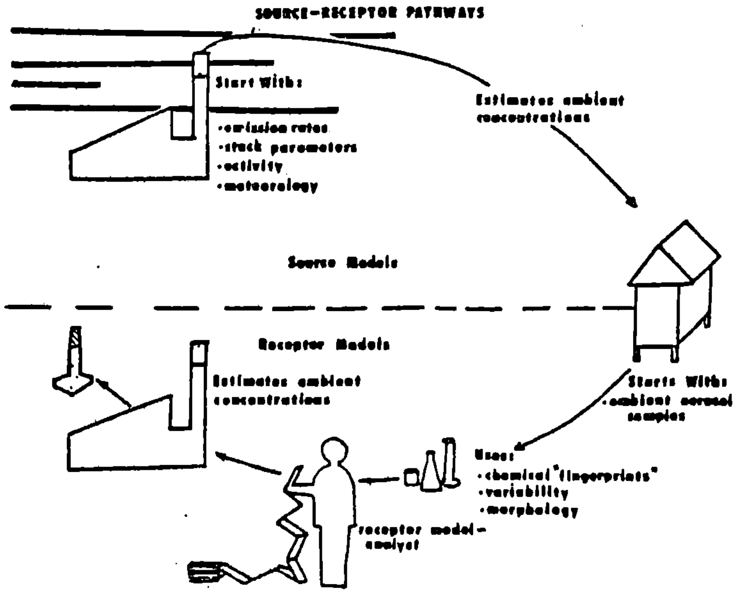


Figure 3

Portland, Oregon Dispersion Model

Annual Predictions

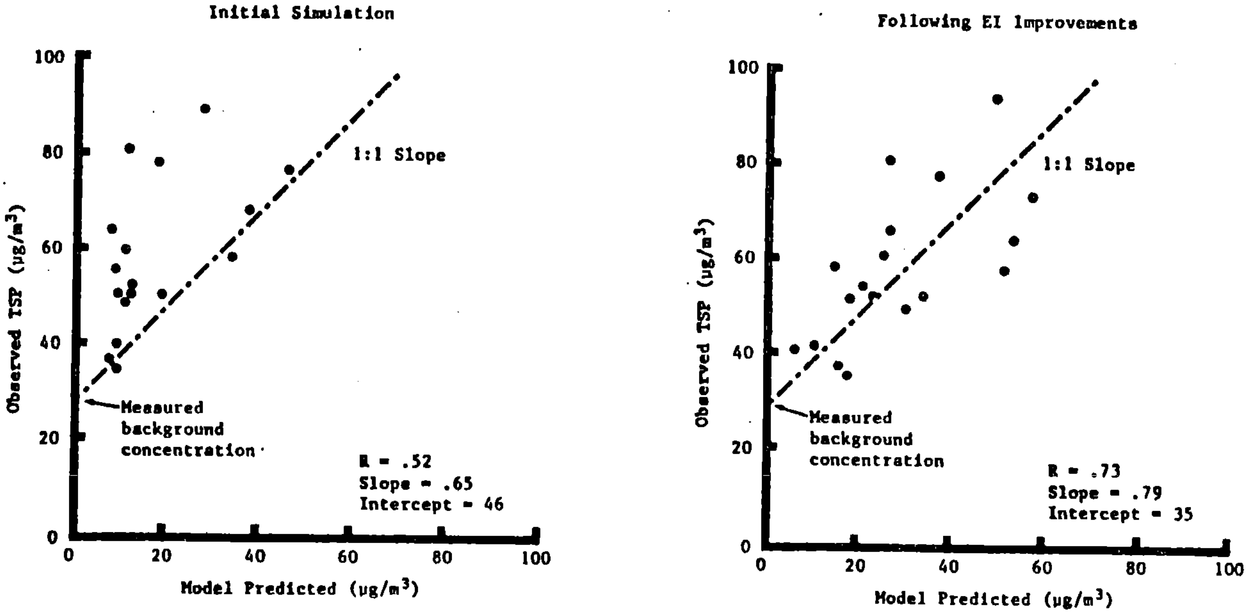


Figure 4

Medford, Oregon Dispersion Model

1978 Total Particulate (Arith. Mean)

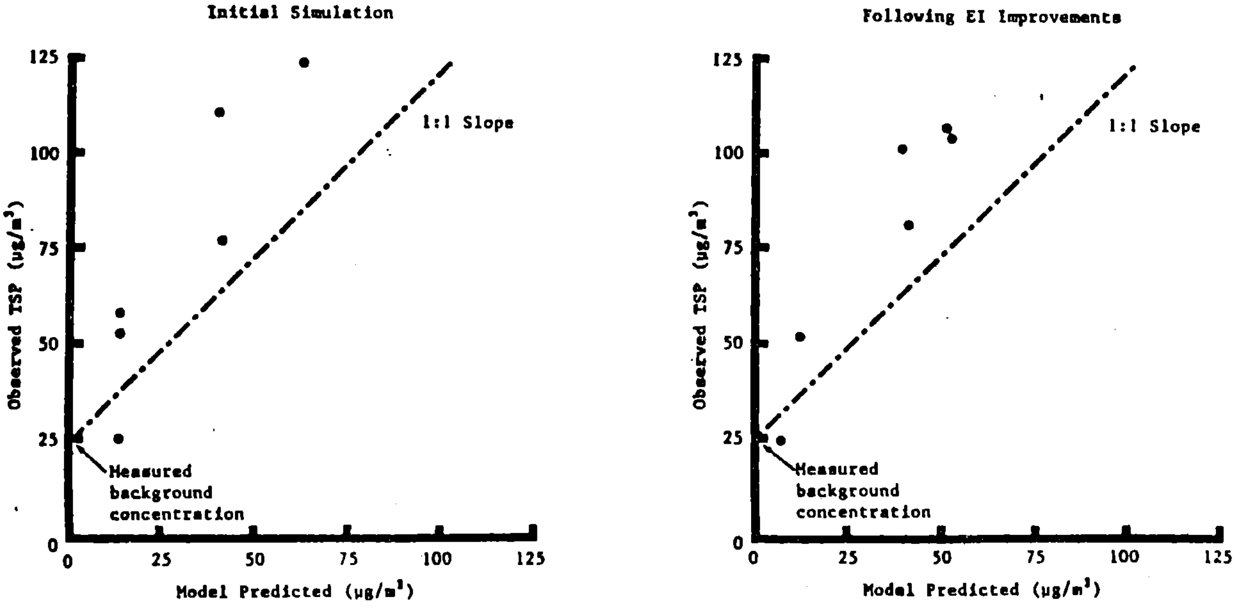
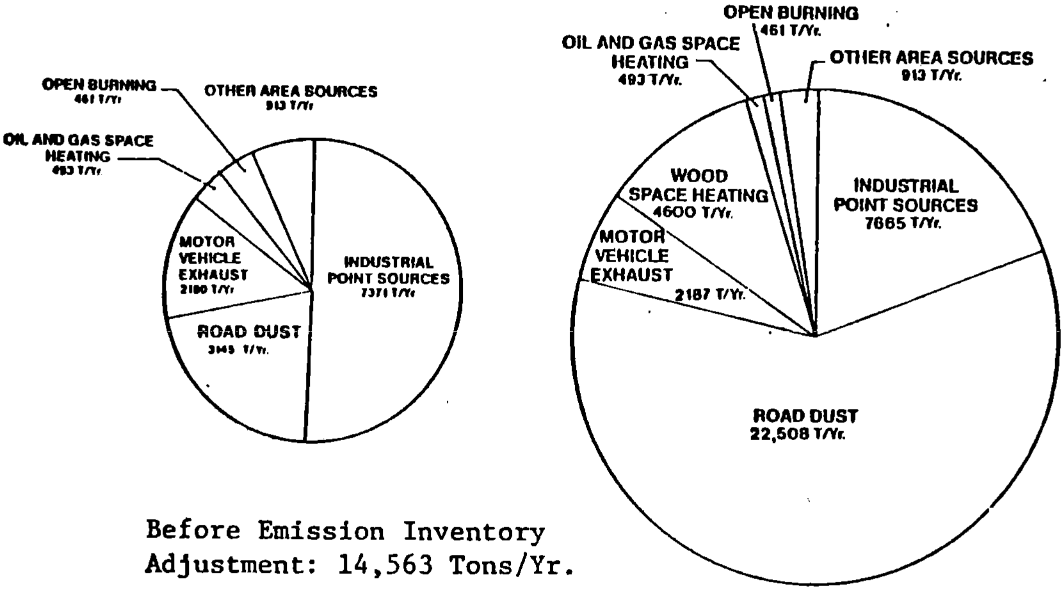


Figure 5

Portland AQMA Emission Inventory

1977 Total Particulate



Before Emission Inventory
Adjustment: 14,563 Tons/Yr.

After Emission Inventory
Adjustment: 38,827 Tons/Yr.

⑨

Minimizing the cost of air pollution control

Control strategies designed using advanced scientific and engineering methods could deliver better air quality at less cost

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A recent report by the Council on Environmental Quality (1979) places the cost of air pollution control in the U.S. at $19.3 billion annually. Cumulative abatement expenses are expected to total more than $300 billion over the decade ending in 1987. These high costs are coupled with an abatement program that has yet to achieve compliance with federal air quality standards (Table 1). There is mounting pressure to "solve" both the compliance and cost problems by relaxing air quality goals.

But restructuring air quality goals may not be the appropriate remedy. Today much more scientific information is available on how to describe and control complex air pollution problems than is routinely used to make emission control strategy decisions. Using this knowledge, engineers could improve the design of regional emission control programs and obtain better air quality at lower cost.

Would the economic gains from this careful control strategy design be large or small? The answer, of course, depends on local conditions, but a few examples that exist indicate large cost savings are possible.

Using the best available control technology on the largest sources in an airshed is often proposed as a way to make rapid air quality progress. In Figure 1, the cost of a control strategy developed with that approach is compared to a cost-conscious, or "economically optimized," control program constructed by considering all source types simultaneously along with their control costs and contributions to ambient concentration levels. The two control approaches may look similar, but at a hypothetical air quality target of 10 $\mu g/m^3$, the latter solution, obtained by use of advanced air quality models, careful consideration of economics, and examination of the problem as a whole would achieve the objective at half the cost. Atkinson and Lewis (1974) examined a similar case in St. Louis and reported even greater relative cost savings from careful control strategy design.

We will examine here the technical basis for the design of efficient air pollution control strategies, and will review prototype emission control strategy studies in which solutions to particular types of problems have been demonstrated. In addition, removal of barriers to the widespread use of advanced design methods by the engineering community will be addressed, as well as suggestions for future research.

The control strategy design problem

One way to conceptualize a polluted air basin is shown in Figure 2. Effluents enter the atmosphere and undergo transport, dilution, chemical reaction, and removal processes, and result in the atmospheric concentrations encountered by receptor populations. The task facing the emission control strategy design team is to devise a set of limitations on source emissions, spread among hundreds or thousands of sources, that will reduce pollutant concentrations at all community receptor points below the levels specified in air quality standards. In addition, these control plans should attain their objectives at the lowest possible cost.

Often, communities that would demand precise design of a new sewer system will adopt air pollution control programs costing hundreds of millions of dollars annually—programs that were selected by less than precise methods. This need not be the case. Over the past 15 years, techniques have been developed that permit systematic assignment of the least costly combination of air pollution control equipment needed to solve a regional air quality problem.

As shown in Figure 3, the approach taken is to construct a mathematical model of the emissions/air quality relationship in a particular airshed. Once verified, that model provides a flexible physical description of the air basin, which can be perturbed in order to study the effect of proposed emission control technologies in advance of their adoption. The air quality model then is matched to a description of the opportunities and costs of emission control for each relevant pollutant source in the air basin. Finally, mathematical programming techniques are used to select and sequence many single-source control measures into the least costly comprehensive control strategy.

In general, the least-cost control strategy problem assumes the form of a mathematical programming problem:

$$\text{select } x \tag{1}$$

$$\text{that minimizes } C[x] \tag{2}$$

subject to

$$Q[\mathrm{E}(r_0,t,x),\mathrm{M}(r,t),\mathrm{P}] \le s \tag{3}$$

A solution to this problem selects the control measures $x_i (i = 1, \ldots, n)$ that, when applied to an emission pattern, E, minimizes the cost of control, C, subject to air quality, Q, at all receptor points, r, remaining below air quality standards, s. The problem is complicated by the fact that Q is a function not only of emissions but also of meteorological events, M, that change over time, t, and chemical reaction parameters, P. Other constraints, such as limitations on available clean fuels, also may be incorporated.

As might be expected, there are many different ways to carry out the calculations. A variety of possible air quality modeling approaches and

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TABLE 1

Number of jurisdictions not attaining federal air quality standards

Pollutant	Counties [a]	Air quality control regions [b]
Ozone	538	80
Total suspended particulates	395	218
Carbon monoxide	161	— [c]
Sulfur dioxide	97	46
Nitrogen dioxide	7	4
Total	1198	

[a] Wagner and Deal (1980).
[b] Goldsmith and Mahoney (1978); evaluated using 1974 monitoring data, 247 air quality control regions possible.
[c] Data not provided.

FIGURE 1

Two different paths toward obtaining an air quality improvement. Available emission control technologies are the same in each case and are described by Cass (1978, 1981)

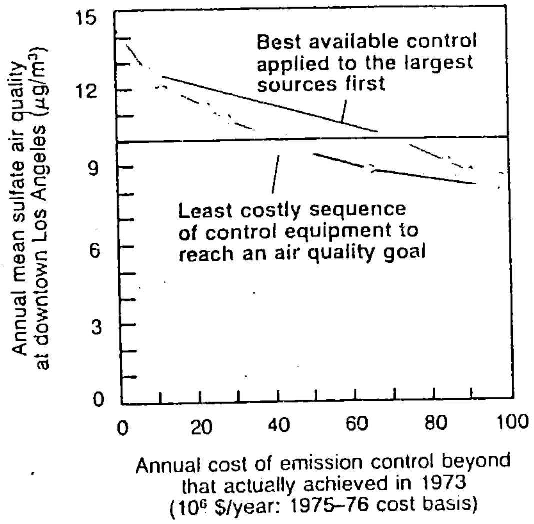
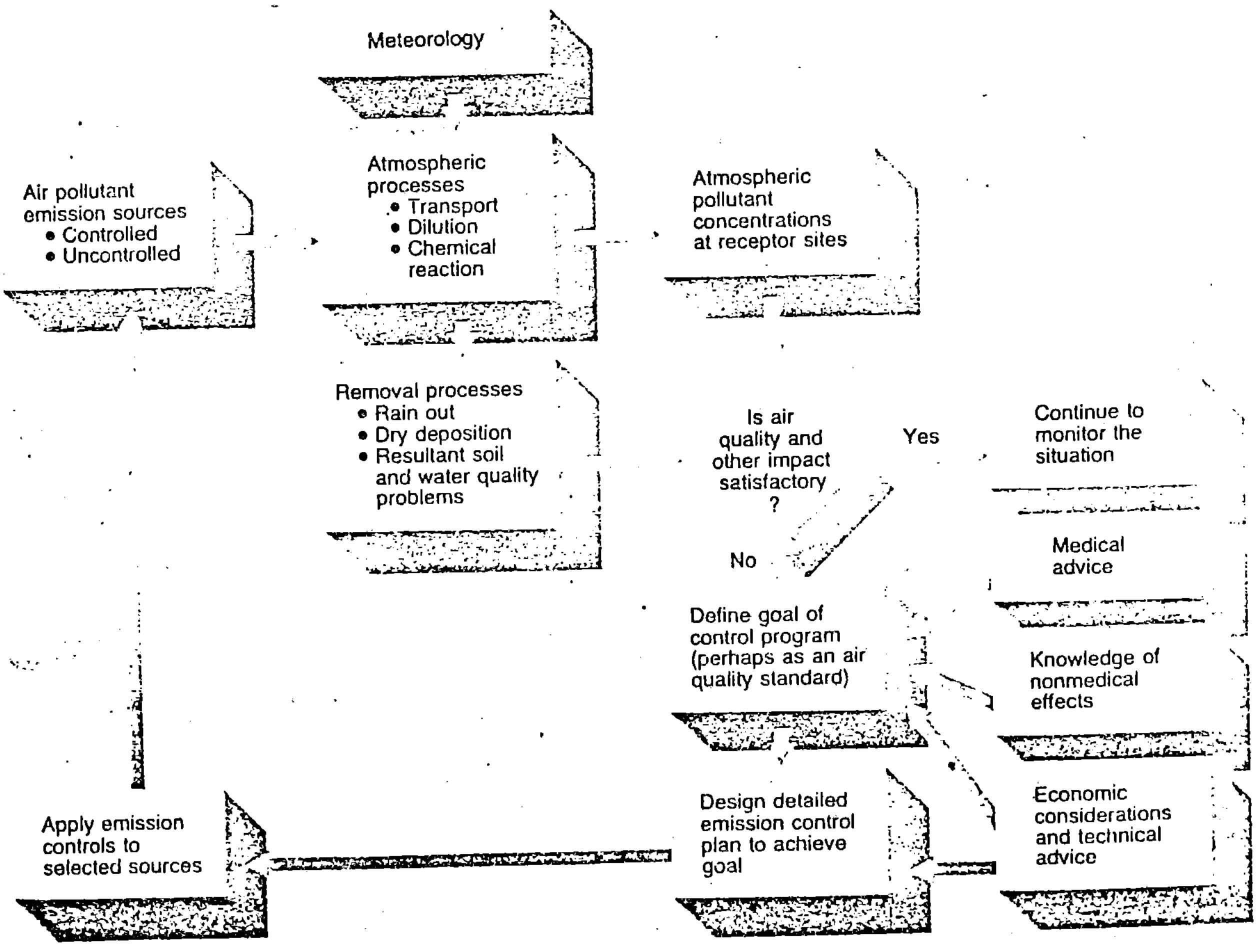


FIGURE 2

Some relationships in the air pollution control process as it is conventionally viewed



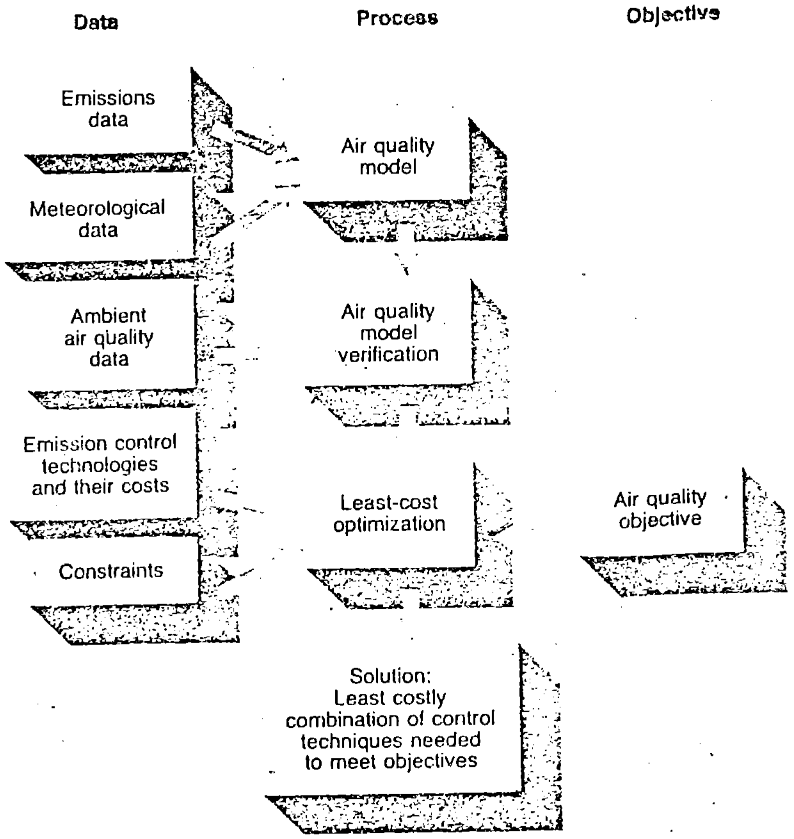


FIGURE 3

Simplified view of the steps involved in developing least-cost control strategies

mathematical programming methods that can be applied are indicated in Tables 2 and 3. Within the broad air quality modeling categories shown, specific calculation procedures with differing assumptions abound. For further description of air quality modeling methods, the reader is referred to reviews by: Roth et al. (1976), National Academy of Sciences (1977), Dimitriades (1977), Myrabo et al. (1977), and Turner (1979). Mathematical programming algorithms are presented by Franklin (1980), Shapiro (1979), and Wismer and Chattergy (1978).

One quickly sees that there is no shortage of air quality and economic modeling methods, but that more approaches exist than could be profitably pursued. A separate understanding of air quality and economic modeling methods does not solve the control strategy synthesis problem. Knowledge of particular approaches that have worked well in past applications, however, makes selecting a properly balanced combination of air quality modeling and cost minimization methods easier. Therefore, we will first summarize those types of problems for which prototype control strategy studies already have been successful. These studies communicate advances to air pollution control agencies and further demonstrate that the data requirements of particular modeling approaches can in fact be met. We will limit examples to cases in which data from identified airsheds were used for model evaluation, since hypothetical cases do not really test the practical barriers to the implementation of a particular design approach.

Prototype control strategy studies

In its simplest form, the least-cost control strategy problem is a matter of minimizing the costs of attaining a particular air basin-wide emissions level. One way to calculate the allowable basin-wide emissions, E_a, is to use a proportional linear rollback model (Chang and Weinstock, 1975; de Nevers and Morris, 1975):

$$\frac{E_a}{E_0} = \frac{s - b}{Q_0 - b} \qquad (4)$$

where Q_0 is the pollutant level at the receptor point with the highest measured pollutant concentration during an historical base time period; s is the ambient air quality goal; b is an estimate of background air quality due to nonanthropogenic sources and sources outside of the air basin; and E_0 is basin-wide emissions during the base time period.

If control opportunities are few, it is possible to solve this class of problem by enumeration, that is, by itemizing all possible combinations of control equipment and costs. One example of that sort of analysis is given by Siegel, Ehrenfeld, and Morgenstern (1975) for the case of sulfur oxides and particulate control in Boston. Emission control techniques also may be rank ordered on the basis of a cost-effectiveness index (e.g., dollars spent per unit of air quality improvement) in order to identify the least costly approach at any level of total emissions.

When the number of sources increases or the types of constraints on source operation become more complex, it becomes desirable to search for cost-minimizing solutions by more systematic methods. An efficient approach to cost minimization in the presence of a basin-wide emissions limit was demonstrated by Kohn (1970) in St. Louis. The least-cost control problem was solved by linear programming techniques:

$$\text{Minimize } C = c\,x \qquad (5)$$

$$\text{subject to B } x \geq r \qquad (6)$$

$$\text{subject to A } x \leq d \qquad (7)$$

$$\text{subject to } x \geq 0 \qquad (8)$$

where C is the cost of air pollution control; x is a vector of control method activity levels (e.g., x_i could be the number of barrels of low-sulfur oil substituted for high-sulfur oil at a particular source); c is a vector of control costs per unit activity level; r is a vector of pollutant emission reduction requirements ($r_j = E_0{}^j - E_a{}^j$ for the jth pollutant); B is a matrix whose elements b_{ji} indicate the emission reduction of pollutant j from one unit of control activity i; A is a matrix indicating the amount of fuel or emissions "consumed" when a control measure is selected; and d is a vector of current source magnitudes plus limits on available fuel supplies. Multiple emission control possibilities applicable to the same source in this case would be represented by multiple entries in the vector x, while constraints present in Expression 7 would prevent each source from being overcontrolled. A related application, lacking only the rollback air quality model, is presented by Jackson and Wohlers (1972) for the Delaware River Valley.

TABLE 2
Summary of different air quality modeling methodologies (grouped in order of increasing operational complexity)

Group [a]	Air quality modeling method	Selected references
1	None	
2	Linear rollback for inert pollutants and generalized procedures for reactive pollutants (upper limit curves and standard EKMA)	Chang and Weinstock (1975) de Nevers and Morris (1975) U.S. EPA (1971) Whitten and Hogo (1978)
3	Gaussian and multibox transport models	Martin and Tikvart (1968) Busse and Zimmerman (1973)
4	Empirical models for chemically resolved particulate air quality (chemical tracer and chemical element balance receptor models)	Friedlander (1973) Cooper and Watson (1980) Gordon (1980)
5	Empirical photochemical models with control isopleths derived from air monitoring or smog chamber data	Dimitriades (1977) Trijonis (1972, 1974) Myrabo, Wilson, and Trijonis (1977) Post and Bilger (1978)
6	Photochemical box models with components set for specific air basins (city-specific EKMA)	Whitten and Hogo (1978) McRae, Goodin, and Seinfeld (1981)
7	Airshed models with 2D or 3D transport and linear chemistry	Sheih (1977) Eliassen (1978), Cass (1978) Johnson, Wolf, and Mancuso (1978)
8	Photochemical trajectory models	Eschenroeder and Martinez (1972) Lloyd et al. (1979) McRae, Goodin, and Seinfeld (1981)
9	2D and 3D photochemical airshed models	Reynolds, Roth, and Seinfeld (1973) MacCracken et al. (1978) McRae, Goodin, and Seinfeld (1981)

[a] The order is based on the resource requirements needed to implement each procedure as part of a practical control strategy design.

TABLE 3
Summary of different optimization procedures (grouped in order of increasing operational complexity)

Group [a]	Control strategy optimization procedure
1	None
2	Cost-effectiveness index (graphical solutions)
3	Graphical solution of nonlinear problems
4	Linear programming
5	Integer programming
6	Multiobjective linear programming
7	Piecewise linear treatment of nonlinear problems using linear programming
8	Dynamic programming and optimal time sequencing
9	Constrained and unconstrained gradient search techniques, optimal control theory, nonlinear programming, sensitivity analysis

[a] The order is based on the resource requirements needed to implement each procedure as part of a practical control strategy design.

The preceeding studies focused on minimizing the "technological" cost of attaining a given emission level, based on the *direct* cost of acquisition and operation of emission control hardware or purchase of clean fuels. Secondary effects on expansion of the emission control equipment manufacturing industry, reduction in capital spending for plant expansion in the polluting industries, and resulting changes in labor productivity, unemployment, and personal income were ignored. Input-output models that include these macroeconomic effects have been formulated, and are reviewed by Rose (1981).

Using spatially resolved air quality models, it is possible to identify control strategies that selectively abate those sources responsible for local hot spots in an air basin. The earliest control strategy studies that attempted to account for atmospheric pollutant transport explicitly did so by using Gaussian plume air quality models. The simplest approach was to hypothesize a set of emission control regulations and then "test" the control strategy using the air quality model to see if air quality standards would be met. This approach was used in many early state implementation plans for sulfur oxides and particulate matter required by the 1970 Clean Air Act amendments. An example of control strategy testing in this vein is given by Morgenstern and Hagg (1972).

Gaussian plume air quality models generate linear source-to-receptor transport coefficients. Thus they can be readily combined with a linear programming formulation of the economic optimization problem, as demonstrated by Teller (1968), Kohn (1974), and Atkinson and Lewis (1974). The structure of the linear programming problem is similar to the

preceeding example by Kohn (1970) except that the emission reduction constraint of Expression 6 is replaced by one requiring that the air quality impact at each receptor location be held below applicable air quality standards.

The Atkinson and Lewis study (1974) is particularly interesting. They compared three alternative control strategy design procedures for particulate air quality using data from St. Louis. Abatement plans devised by minimizing basin-wide emission control costs in conjunction with a rollback air quality model were reported to be at least twice as expensive as those identified by minimizing the cost to attain a given air quality level in conjunction with a Gaussian plume air quality model. They also examined particulate abatement plans that employed a set of emission control regulations suggested nationwide for use in state implementation plans. Those abatement plans were much more expensive than solutions customized to local conditions by either the rollback/linear programming or Gaussian plume/linear programming formulations of the least-cost control problem.

Linear programming routines may result in least-cost solutions that specify use of a fraction of a control technique at the optimum (e.g., that half of a scrubber be applied to a particular power plant). Of course this is physically unrealistic. To prevent this problem, Burton and Sanjour (1970) combined integer programming techniques with a Gaussian plume air quality model. Sample calculations were worked for control of particulate matter and sulfur oxides in Washington, D.C., and Kansas City. Integer programming and linear programming approaches were compared by Gipson, Freas, and Meyer (1975) within the context of case studies in Louisville, Ky., New York City, and Buffalo, N.Y.

Atkinson and Lewis (1974) and many others indicate that very large savings in control cost for particulate abatement can be achieved by selective control of sources contributing to localized peak concentrations as identified by Gaussian plume models matched to linear programming algorithms. If cost savings are so large and air quality modeling procedures fairly simple, why don't we see many actual control strategies devised in this manner by air pollution control agencies?

The answer probably lies in a healthy skepticism toward overworking the economic analysis of a control strategy when one doubts the validity of the underlying air quality model application. In spite of considerable sophistication in optimization methods, control strategy conclusions for total suspended particulate matter (TSP) drawn from the preceeding studies are not likely to be correct. The reason? If data on direct emissions of particulate matter alone are supplied, rollback or Gaussian plume models usually will misrepresent observed air quality, because gas-to-particle conversion processes are not included in the model and because some fugitive emission sources are overlooked.

In Los Angeles, for example, roughly half of the material contributing to particulate concentrations often consists of sulfates, nitrates, ammonium ion, and secondary organics, which in large part were formed in the atmosphere from *gaseous* precursor emissions of SO_2, NO, NH_3, and hydrocarbons (Hidy et al., 1975). Large amounts of resuspended road dust are contributed by auto traffic without being reflected in conventional emission inventories (Core et al., 1980). When such sources are omitted and computed results do not match observations, Gaussian plume models are often "calibrated" (Busse and Zimmerman, 1973). Results are scaled up until the model appears to reproduce total suspended particulate concentrations completely. Short-circuiting the model evaluation procedure in this manner gives the appearance that an adequate air quality model and emission inventory are present when in fact the results are far from correct.

Control strategy design procedures for particulate matter have been developed that show considerable promise for correcting the worst of past abuses. The key to improvement lies in using data on the chemical composition of measured particulate air quality to assist apportionment of contributions to primary aerosol, gaseous precursor, and fugitive sources (Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1980).

The first full-scale emission control strategy study that capitalized on aerosol chemical composition was conducted by Trijonis et al. (1975). Ambient aerosol monitoring data throughout the Los Angeles basin were apportioned into sulfates, nitrates, ammonium ion, organics, sea salt, soil dust, and the remainder of the TSP. Then sulfates were related to SO_x emissions, nitrates to NO_x emissions, secondary organics to reactive hydrocarbon gaseous emissions, and the remainder of the TSP to primary aerosol

The relative amount of effort to be devoted to air quality modeling and to economic evaluation should be in reasonable proportion.

The level of accuracy inherent in the air quality and cost modeling procedures should match the quality of the input data available for model application.

Air quality models need to be verified in two ways. Individual components (like chemical mechanisms) should be compared to laboratory experiments or known analytical solutions. The completed air quality model must also be verified by application to an entire air basin over an historical time period to see whether or not it closely reproduces past observations. The latter exercise tests not only the air quality model but also the associated field data sets. When initiating a control strategy study, preference should be given to selecting an air quality model that can be verified against past events (many types of rollback and other empirical models cannot be verified easily). Secondly, ample resources should be allowed for testing that model in the context of the air basin of interest over an appropriate range of past events. Confidence in an analysis approach comes from practical demonstration, not only from increasing the nominal amount of physics and chemistry incorporated into the calculations.

The structure of the emission inventory affects the usefulness of the air quality model's results. The emission inventory should be organized around groups of like equipment that can be controlled under common regulations, and if possible, preference should be given to modeling approaches that deliberately display the air quality increment at each receptor arising from each source type.

A number of mutually compatible air quality modeling approaches, from simple to complex, should be used. The simpler methods can be used to perform initial control strategy screening calculations to find the neighborhood of a likely solution. The more resource-intensive models can be used to fine-tune that result.

emissions using linear rollback models applied within each source category. Emission control techniques were evaluated for gaseous precursor and primary aerosol sources and then ranked in order of incremental air quality improvement per dollar spent. The conclusion of these calculations was very interesting: The least expensive way to attain TSP air quality standards in Los Angeles was found to incorporate strict control of many sources of gas-phase particulate precursors. Such a conclusion could not have been reached using previous approaches because gaseous precursor sources were defined out of the aerosol problem during model construction. The study by Trijonis et al. (1975) should be examined by air pollution control agencies seeking to improve their implementation plans.

A second important advance in particulate air quality control strategy design procedures recently was demonstrated as part of the Portland Aerosol Characterization Study (Core, Hanrahan, and Cooper, 1980). Chemical element balance techniques were used with high accuracy to identify the actual source classes contributing to local particulate air quality. That information was used to identify and correct the local emission inventory and other problems present in a conventional air quality modeling study. The completed air quality models were combined with data on the marginal cost of available abatement techniques. A strategy was identified that emphasized traffic control and road cleaning in selected areas of the city, which would suppress fugitive road dust (accounting for half of local particulate emissions). This control strategy design procedure should be viewed as a prime candidate for duplication by air pollution control agencies elsewhere.

Chemical element balance or chemical tracer techniques can identify the sources contributing to a particulate air quality problem only to the extent that each source type is chemically distinct. Specific identification of the relative importance of different contributors to sulfate, nitrate, and secondary carbon particle air quality is impossible from routine analysis of filter samples alone. Air quality models for secondary aerosol formation are needed if we are to improve control strategy efficiency for secondary aerosol air pollutants.

A number of air quality models for sulfate formation have been reported. They fall into two classes: those that employ pseudo-first-order SO_2 oxidation at rates determined by field observation and those that describe SO_2 oxidation within an explicit chemical mechanism. Models that employ linear chemistry are readily suited to control strategy design studies, because the calculated air quality impact of each source is independent of other sources in the airshed and is linear in emissions. Least-cost control strategy design procedures for regional sulfate abatement using linear chemical models were developed by Cass (1978, 1981) and tested within a case study in Los Angeles. A second study emphasizing control of large power plants is provided by North and Merkhofer (1976). At present, the behavior of photochemical models for secondary aerosol formation may be studied by perturbation, but there is no systematic method for economic optimization of control strategy selection.

Procedures for estimating overall control requirements for oxidant abatement have been demonstrated using smog chamber data (Dimitriades, 1977), aerometric data analysis (Trijonis, 1972, 1974; Post, 1979), and mathematical box models that incorporate an explicit photochemical mechanism (Whitten and Hogo, 1978; Derwent and Hov, 1980). Each technique develops an isopleth map showing contours of constant ozone or oxidant concentration as a function of precursor reactive hydrocarbon (RHC) and NO_x emissions or early morning pollutant concentrations.

Trijonis (1972, 1974) devised a method for optimal control strategy selection using ozone isopleth maps and tested that procedure in Los Angeles. A piecewise linear programming approach was used to calculate isocost contours representing the most efficient combination of NO_x and hydrocarbon control equipment at a wide variety of NO_x-hydrocarbon ratios—given budget constraints of $100 million per year, $200 million per year, etc. The least-cost control strategy was selected by:

- superimposing the cost contours over the ozone isopleth map
- finding the NO_x level needed to attain NO_2 air quality objectives
- finding the intersection of that NO_x level with the oxidant isopleth corresponding to the oxidant air quality objective
- noting the degree of hydrocarbon control at that point
- finding the combination of emission controls on the isocost contour which passed through that combination of RHC and NO_x emissions.

The procedure is quite straightforward and can be executed graphically. To our knowledge, the Trijonis study and its extension by Kyan and Seinfeld (1974) provide the only economically optimized control strategy design procedures for photochemical smog demonstrated to date.

Sustained effort over the past decade has produced a number of air quality models that incorporate a detailed description of atmospheric photochemistry and that may include pollutant transport (see Table 2). The immense data requirements for verification and use of photochemical airshed models have restricted their use to testing two or three alternative control strategies. An airshed-specific photochemical box model was used to evaluate alternative automotive emission control regulations in England by Derwent and Hov (1980). Reynolds and Seinfeld (1975) assessed the likely effects on Los Angeles of the proposed 1977 U.S. Environmental Protection Agency (EPA) transportation control plan plus future light-duty vehicle emission control standards. Their study compared the answers obtained by linear rollback, modified rollback (Schuck and Papetti, 1973), the statistical model of Trijonis (1972), and the photochemical airshed model of Reynolds et al. (1973). Seinfeld and McRae (1979) evaluated the likely effect of tightened motor vehicle NO_x standards using photochemical trajectory models as well as EKMA (Whitten and Hogo, 1978) and rollback. Wada et al. (1979) used the LIRAQ model (MacCracken et al., 1978) to test three alternative control strategies as part of developing the current emission control program in the San Francisco Bay area. As part of that study, De Mandel et al. (1979) compared control strategy effectiveness using two types of rollback models, an upper limit curve approach, an aerometric empirical model, EKMA, and the LIRAQ photochemical airshed model.

In the studies in which comparisons have been made between oxidant modeling approaches, the two-dimensional and three-dimensional photochemical airshed models predicted greater ozone reductions from proposed control efforts than would be determined by more commonly used methods, such as upper limit curves. If that finding were true in general, then use of photochemical models in development of emission control programs could lead to less stringent control requirement estimates and thus lowered costs to attain present objectives.

Dynamic optimization techniques that minimize the cost of attaining

emission control objectives over time also have been explored. Patel (1973) used a repetitive linear programming approach together with a Gaussian plume air quality model to evaluate a short-term fuel switching strategy for SO_x abatement in Boston. Seinfeld and Kyan (1971) and Kyan and Seinfeld (1974) have addressed the problem of attaining and maintaining compliance with air quality standards over periods of successive years. The latter study used dynamic programming optimization techniques along with the empirical photochemical air quality model of Trijonis (1974) for the case of Los Angeles.

Areas for future research

In Figure 4, the prototype air pollution control strategy studies discussed above have been organized (approximately) by effort required for air quality modeling and economic analysis. One feature in particular is evident. No studies exist that combine the most advanced air quality models with economic optimization techniques.

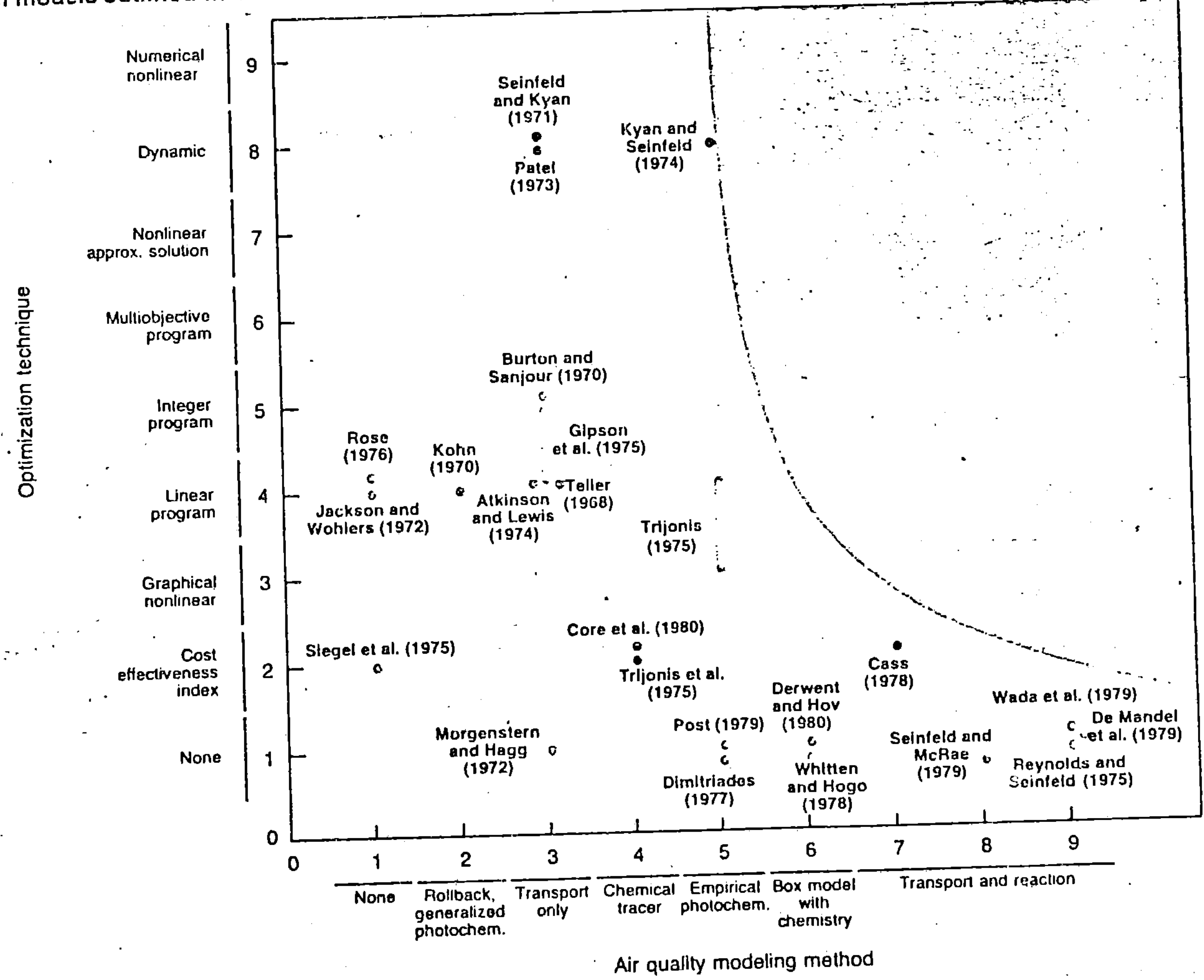
We suggest several areas for future research. The most obvious question is: How does one go about finding least-cost solutions to photochemical air pollution problems? The nonlinear chemistry embedded within photochemical air quality models is incompatible with traditional control strategy selection techniques. Nonlinear optimization schemes are needed to solve such problems. Possible approaches include piecewise linear approximate solutions, use of optimal control theory, or gradient search techniques employing the method of steepest descent.

Chemical element balance receptor models for particulate air quality generate linear source-to-receptor transfer estimates. It should be possible and attractive to address the "least-cost receptor modeling problem." A linear programming cost-minimization problem could be formulated around such a receptor air quality model in order to identify emission control strategies needed to meet air quality standards simultaneously at a large number of air monitoring sites. Particulate air quality models that describe transport and formation of secondary aerosols using linear chemical approximations also are well suited to linear programming economic optimization procedures.

Conflicting objectives continually pose problems for air and water pollution control agencies. When the conflict is spread among many emission source types (e.g., refineries, paper mills, and sewage treatment plants—all contributing to air and water quality problems), defining an appropriate trade-off between air and water quality control plans can become overwhelmingly complex. Multiobjective linear

FIGURE 4

Prototype air pollution control strategy studies organized by air quality and economic modeling approach. Numbers along the horizontal and vertical axes refer to those classes of models outlined in Tables 2 and 3



rogramming has been proposed as a means for mapping out efficient combinations of air and water quality utcomes. It would be interesting to xplore such an approach using data from an actual air basin.

Much attention has been focused on he difficulty of attaining current mbient standards for SO_2, ozone, and TSP. As a result, most practical experience has been gained in these reas, while very little has been learned bout control strategies for many related pollutants. Efficient approaches o abatement of urban NO_2 problems deserve more attention. In addition, a whole family of NO_x-related pollutants exists: Nitric acid vapor, PAN, ammonium nitrate, and nitrosamines, for example, have known or anticipated effects on health or welfare.

A second group of important carbon-containing unregulated air polutants includes aldehydes, polynuclear aromatic hydrocarbons, elemental carbon particles, and secondary organic aerosols. The desirability of preferentially abating some of these pollutants as part of ongoing oxidant and particulate control programs depends in part on whether it would be costly or cheap to do so. Such problems should be examined as a research question within the setting of actual air basins.

Barriers to practical application

While there is always a need for further research, it is important to recognize that much more is known about how to design cost-effective air pollution control strategies than is actually used in practice. Most state implementation plans developed under the Clean Air Act would fall into the lower left-hand corner of Figure 4. This is not to suggest that pollution control agencies are uninterested in developing more efficient and effective emission control strategies. Rather, there are some very serious practical problems that argue against the use of advanced engineering tools. These problems involve data resources, technology transfer, and time limits.

One reason why rollback air quality models are so popular is that their data requirements almost always can be met: All that is required is a basin-wide emissions estimate, a peak pollutant concentration at one monitoring site, and an estimate of background air quality. By comparison, a photochemical airshed model can require spatially and temporally resolved data on pollutant concentrations, wind speed, wind direction, inversion base height, terrain height, solar radiation, boundary and initial conditions, plus a spatially, temporally, and chemically resolved emission inventory.

In Figure 5, we examine a few control strategy studies for which we have access to the underlying data sets (Trijonis, 1972; Cass, 1978; McRae, 1981). Data requirements increase exponentially as more physical realism and flexibility in control strategy evaluation is attempted. A photochemical airshed model application in Los Angeles initially can require up to one million pieces of input data per day simulated. The mere task of organizing that much information in a format suitable for insertion into a computer program can take a surprisingly long time (several man-years of effort).

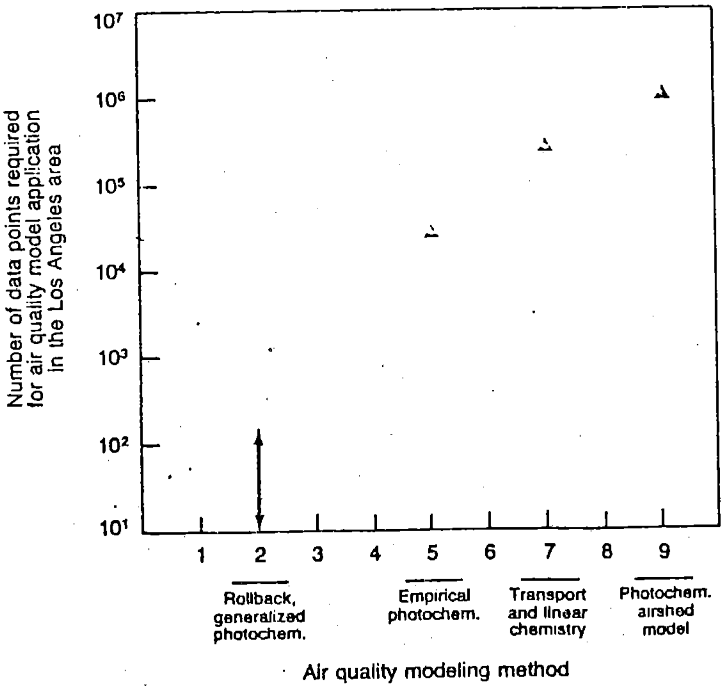
A further barrier to the spread of advanced air quality design procedures involves manpower resources and training. Recently, a national expert panel was asked whether or not the availability of skilled manpower limits the application of advanced air quality models to solve the nation's air quality problems. The panel answered "no" (Shutler, 1980). That response may be appropriate when looking at the nation's technical manpower pool as a whole. A question not being answered is whether or not air pollution control agencies have practical access to these skills. We suspect most do not.

In cases we are aware of, in which major advances were made in control strategies actually implemented by regulatory agencies, the studies were made possible by collaboration between the agency and an academic institution, a national laboratory, or a specialized consulting firm. Very few groups exist (perhaps about five) that could execute a photochemical oxidant control strategy study using realistic air quality models. When one considers the number of air basins in which photochemical oxidant problems are observed (Table 1), it becomes apparent that these skills need to be transferred to a wider group of people.

Finally, the question of time limitations must be addressed. Perhaps one reason why so little technical sophistication is exhibited in most air quality plans formulated to date is that the deadlines set by Congress for performing air quality analyses were impossibly short. The 1970 amendments to the Clean Air Act, Sec. 110 (a)(1), provided a statutory deadline of nine months following adoption of an air quality standard for states and localities to formulate a plan for attaining the air quality goal. From our experience, the time needed for a highly trained group of engineers to design a technically sound abatement plan for a single chemically reactive air pollution problem in a major city is about two to three years (not including time

FIGURE 5

Escalating data requirements for air quality model application. Numbers along the horizontal axis refer to model types listed in Table 2



for administrative review and approval). If a new field measurement program must be designed to gather data, or if inexperienced personnel must be trained first, then the time required for planning increases proportionately.

Problems with data management, present staff resources, and unrealistic time limits should not be permitted to constrain the choice of control strategy design procedures. The cost of overcoming these limitations is almost always much less than the cost to the economy of adopting an inefficient set of control regulations. An approach should be adopted which ensures that control programs devised use the best engineering procedures that are consistent with local problems.

Conclusions

A technical basis exists upon which efficient and effective air pollution control strategies can be built. Air quality modeling procedures are available and, if used, would increase the confidence that emission control programs will in fact deliver promised air quality improvements. By insisting on an accompanying economic analysis of control alternatives, least-cost emission control strategies can be identified. Persistence is needed, however, if better engineering methods are to be brought to bear to solve the nation's air quality problems. Data resource limitations must be resolved and new technologies must be transferred to the air pollution control agencies charged with drawing air quality plans.

Recent experience shows there is no choice but to tackle these problems directly. One set of state implementation plans was hurriedly solicited in the early 1970s. A second round of air quality maintenance plans was prepared in 1979; a step made necessary because many of the first plans failed to achieve their stated goals. By 1982, we expect a similar result, and a new set of emission reduction measures will be sought. In 10 years, we will have expended a great deal of effort on several consecutive unsuccessful cleanup efforts devised under unreasonable resource and time constraints. During the next few years, there is clearly enough time to develop technically defensible air quality plans at least once.

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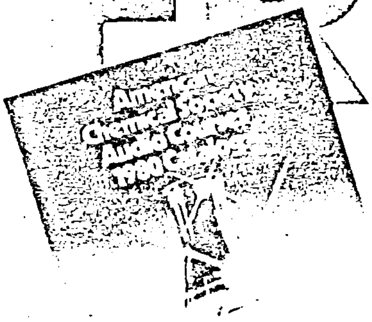

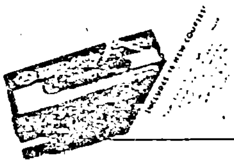

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Paper 82-61M.2

Dilution Sampling For Chemical Receptor Source Fingerprinting

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Mr. Larson is an environmental chemist with NEA, Inc. He has been involved in the field collection, laboratory preparation and analysis of aerosol samples. He has assisted in the calibration and construction of sampling equipment for use in CMB source apportionment studies.

Introduction

The chemical mass balance receptor method of source apportionment requires that the chemical composition of both ambient aerosols and particles from all major sources in a given airshed be measured for state-of-the-art results.[1] Generally, the limiting factor in chemical mass balance (CMB) studies is the size-resolved chemical characterization of the source particles, particularly stack aerosols. Literature values are available for some stack types, but due to the purpose or manner in which the samples were collected, the chemical fingerprints obtained frequently are not detailed enough for CMB source apportionment work. Often, literature tabulations of elemental data are incomplete or the elemental concentrations have been grouped together (e.g., total alkali metals). Most stack data have been obtained from baghouse dust, in-stack samplers or from EPA Method 5-type equipment. Samples collected in such a manner are not representative of the size distribution nor of the chemical composition of stack particles after they mix and cool in the atmosphere. Condensation, vaporization, agglomeration and secondary chemical reactions can significantly alter the size distribution and chemical composition of stack aerosols when ambient dilution and cooling occur.

The desire to obtain samples of particulate material in the form which it will have after it has been emitted into the atmosphere has stimulated the development of dilution/cooling systems.[2-6] The fundamental principles inherent in the design of a dilution/cooling system are: (1.) the isokinetic withdrawal of an aerosol stream from an industrial stack source, (2.) the mixing and cooling of the source aerosol with excess filtered ambient air and (3.) collection of size categorized particulate samples from the dilution chamber in a form compatible with standard methods of particulate analysis. The requirements of dilution sampling, the design of a pragmatic dilution/cooling system and data obtained with the system from several industrial stacks are presented here.

Requirements of Receptor-Oriented Dilution Sampling

The principal objective of receptor-oriented dilution sampling is to obtain chemical data representative of particulate emissions entering the environment from a point source. Unlike more traditional source sampling, in-stack gravimetric emission rates are of only secondary importance. This fundamental difference in objective requires modification of criteria which are typically considered most important for obtaining "good" stack test data. An adjustable dilution ratio, isokinetic flows, the maintenance of analytically clean sampling conditions, equipment portability, the ability to integrate emission variability and the collection of size-classified particles onto ambient filter media are the primary features which have been incorporated into the design of the dilution sampling system described here.

The dilution air/stack gas ratio must be adjusted for the general application of a dilution cooling system since characteristic temperatures, flow rates, particulate concentrations and water vapor content vary dramatically with stack type. Two opposing factors must be taken into consideration when selecting a dilution air/stack gas ratio. Enough dilution air is

required to achieve the primary objective of reducing the temperature to near ambient and, in addition, to prevent the condensation of water vapor. (Condensed water is deleterious to the collection of particulate samples on a filter medium.) However, the dilution ratio must also be adjusted low enough so that there is a sufficient particulate concentration in the diluted aerosol to collect adequate sample mass for analysis within a reasonable time frame. A workable compromise must be developed for each set of stack parameters.

The accurate control of linear and volumetric flow rates is critical for a dilution sampling system. The dilution ratio, as discussed, must be adjustable. Isokinetic conditions must be maintained at two points in the dilution sampling system. These are at the point of removal of the stack aerosol with a probe and at the point of removal of an aliquot of the diluted gas stream from the dilution chamber for size classification and sample collection. The size-classifying equipment (e.g., a dichotomous sampler or a cyclone) also requires a specific flow rate to maintain the correct size distribution. Finally, the ability to slow the overall sample collection rate is valuable if longer sampling times are needed to integrate the variability from stacks with non-uniform emission characteristics.

Dilution sampling to adequately reproduce atmospheric mixing requires a relatively large mixing volume and sample residence time. Unfortunately, spatial restrictions imposed by the approach structures to sampling stations as well as sampling platforms themselves often preclude the utilization of large equipment. Similarly, weight is critical as equipment must frequently be hand-carried up vertical ladders and stairways as well as through areas which are physically difficult to negotiate. To satisfy these requirements, a pragmatic dilution sampling system must be constructed in such a manner as to facilitate its disassembly and reassembly and be constructed with lightweight materials where possible.

To obtain detailed chemical fingerprints, including trace elements, from a variety of chemically dissimilar stacks in industrial surroundings, precautions must be taken to avoid external contamination and to insure analytically clean sampling conditions within the dilution system. Disassembly and laboratory cleaning between stack tests to prevent cross contamination are essential. Emissions from stacks are often caustic or corrosive in nature, hence materials used in the construction of a dilution sampler should not structurally degrade or leach with exposure or produce chemical artifacts. In addition, because sampling is often conducted in an area of high ambient particulate concentration and because of the high ambient air/stack gas ratio, it is also important that the dilution air be well filtered before entering the dilution chamber.

To parallel the size distribution typically obtained from ambient sampling equipment, the sample removed from the dilution chamber can be size categorized with either a dichotomous sampler or with a scalping cyclone followed by a back-up filter. In both cases, standard teflon membrane filters such as are used in the collection of ambient samples for inorganic analysis can be employed due to the low temperatures produced by dilution. If carbon or organic analyses are desired, glass fiber filters can be equally well used.

Uniform loading of between 0.5 and 3 mg of material on a teflon membrane filter is optimum for combined thin film x-ray fluorescence spectrometry and neutron activation analysis which are routine techniques for ambient filter analysis. Because these techniques are non-destructive, other analytical methods often used for the analysis of ambient aerosol filters, such as ion chromatography, atomic absorption spectrophotometry or microscopy, can also also be utilized.

The collection of samples in a form which permits the use of standard methods of air particulate analysis is advantageous for several reasons. New and untested preparatory and analytical protocals need not be developed for source samples if routine ambient aerosol techniques are applicable. Determinate errors often encountered when comparing data generated by different analytical techniques will be avoided when statistically comparing source and ambient (receptor) data during CMB calculations. Most importantly, both the source and ambient matrices contain the same set of quantified elements with similar associated uncertainties and detection limits for the same size categories of particles. The ability to form a detailed and uniform data set for both source and ambient particles is a key factor in conducting a state-of-the-art source apportionment study by CMB modelling.

The Dilution Sampling System

Figure 1 illustrates the dilution sampling system which has been developed for the chemical characterization of stack aerosols. The system can be divided into three principal parts: (1.) the sampling probe, (2.) the dilution chamber, and (3.) a particulate collector. The sampling probe and flexible hose connecting the probe with the dilution chamber can be heated to minimize wall condensation. The probe is constructed of stainless steel and the connecting hose is lined with teflon. Any standard sized buttonhook nozzle can be attached to the probe to permit a number of volumetric flow rates to be obtained at a given isokinetic linear flow velocity.

The dilution chamber is constructed of 10.2 cm (4 in.) polyvinyl chloride (PVC) pipe which has been fitted with several threaded unions to permit its disassembly for transport and cleaning. Because of its small "broken-down" size and light weight, the sampler can be sent as excess baggage on commercial airlines and hand carried or hand winched to stack sampling platforms. A turbulent mixing rather than a linear buoyant plume approach was taken because the ninety degree bends in the system permit it to be relatively compact while still maintaining a long dilution path length (approximately 3 meters). Turbulent conditions also maximize the mixing which occurs during the relatively short particle residence time within the dilution chamber (typically about 1-3 seconds). A high volume vacuum motor and blower independently controlled by variable transformers provide the vacuum necessary to withdraw the stack gas sample and provide the dilution air. The dilution air is filtered through a standard 20 cm X 25 cm (8 in. X 10 in.) glass fiber filter held in an in-line filter holder

Stack ambient and dilution chamber temperatures are measured with simple bimetal thermometers. Stack gas velocity is measured with a pitot tube. The velocity of gas within the dilution chamber is measured with a thermal anemometer. The difference in pressure between the dilution chamber and the stack must be measured and is accomplished with a Magnehelic gauge (trade name Dwyer Instruments, Inc.).

An aliquot of the gas flow within the dilution chamber is isokinetically withdrawn for size classification and particle collection by a stainless steel tube centered within the 10.2 cm PVC dilution chamber and aligned parallel with the gas flow. A virtual impactor was used for size classification and particle collection in the configuration illustrated in Figure 1. A scalping cyclone followed by a back-up filter has also been used with the dilution system. Cyclone particle cut points (D_{50}) of 15μ, 10μ, or 2.5μ would all be appropriate for use with receptor modelling depending on the specific requirements of the study.

The transfer of particulate bearing stack gases via the heated probe to the dilution chamber is accomplished by maintaining a pressure differential between the dilution chamber and the interior of the stack. From Bernoulli's equation of continuity it can be shown that the linear velocity of gas entering the buttonhook nozzle is dependent only on the pressure drop and density of the stack gas, i.e.,

$$V = \sqrt{\frac{\Delta P}{.5\,\rho}} \qquad (1)$$

Bernoulli's equation is only strictly applicable to idealized fluids but is illustrative for design considerations. A plot of actual flows measured in the laboratory with a mass flow meter versus those predicted by the pressure drop and Bernoulli's equation demonstrated the predictive capability of equation 1. A linear relationship (slope = .44, R = .98) was obtained between predicted nozzle velocity (abscissa) and measured nozzle velocity (ordinate) for measured velocities up to 40 meters/sec. Since the buttonhook sampling nozzle collects gas parallel with the direction of flow, the pressure value used to calculate ΔP in equation 1 must take into account the effect of velocity pressure, i.e.,

$$\Delta P = \left[P_{s,s} + \tfrac{1}{2}\,\rho_s V_s^2\right] - P_{d,s} \quad , \qquad (2)$$

where, $P_{s,s}$ is the static pressure within the stack,

ρ_s is the density of gas within the stack,

V_s is the linear velocity of gas within the stack, and,

$P_{d,s}$ is the static pressure within the dilution chamber.

Measurement of ΔP can be accomplished by the use of two commercially available sensor tips (one for static pressure and one for total pressure) connected to a Magnehelic gauge.

The reduced pressure and flow within the dilution chamber is produced by a high volume vacuum pump. If the blower is not used, each flow rate has a corresponding pressure drop associated with it. The vacuum pump flow rate can be regulated by controlling the pump motor with a variable transformer. Unfortunately, the pressure produced at high flow rates (high dilution ratios) is too high with the vacuum motor alone operating to permit isokinetic sampling (see equation 1). The addition of a high volume blower reduces the pressure drop and permits any combination of dilution chamber pressure and flow rate. For example, if a high dilution flow rate (i.e., high dilution ratio) and a low pressure drop (low linear velocity in sampling tip) is desired, the high volume vacuum pump is operated at near maximum power and the blower is adjusted until the pressure drop is lowered to the point where isokinetic sample velocities are obtained in the sampling tip. It should be noted that changing buttonhook nozzles ranging in size from 3.2 mm (1/8") to 12.7 mm (1/2") in diameter has a relatively small effect on dilution chamber pressure and hence the change in linear velocity with tip diameter is small. Volumetric flow and the subsequent dilution ratio will, however, change in proportion to the square of the nozzle radius.

Near the exhaust of the dilution chamber an aliquot of the diluted flow is transferred isokinetically into a dichotomous sampler or a scalping cyclone with a back-up filter for particulate collection. Particles have been collected on standard 37 mm or 47 mm filters and treated thereafter with the same protocol as ambient samples. Because the flow rate necessary to maintain the correct particle size cut point is fixed for both dichotomous samplers and cyclones, near isokinetic inlet velocities are obtained with a set of interchangeable stainless steel pipes of varying diameter. For example, if a dichotomous sampler is employed (correct flow 16.7 l/min.) and the desired dilution ratio dictates a flow of 1.7 M^3/min. inside the 10.2 cm diameter dilution chamber, an inlet pipe with an internal diameter of 11.2 mm would produce isokinetic conditions (2.9 M/sec.). Similarly a dilution chamber flow of 0.85 M^3/min. would require a dichotomous inlet pipe with a diameter of 14.2 mm to maintain isokinetic velocity (1.7 M/sec.).

The use of a dichotomous sampler without the aerosol inlet cap (D_{50} of 15μ) produces two size categories (< 2.5μ and > 2.5μ). The chemical composition of the greater than 2.5μ size fraction has been assumed to be approximately equivalent to the chemical composition of particles in the normal coarse size fraction (2.5-15μ) collected by a dichotomous sampler. The particle penetration efficiency through the dilution sampler decreases with size and it is unlikely that many particles greater than approximately 20μ reach the > 2.5μ filter. In addition, the bulk of most stack particles (especially those stacks with properly operating control equipment) have an aerodynamic diameter less than 15μ and chemical fractionation with size is less dramatic for larger particles.

Only three in situ measurements are required to operate the dilution sampler in the field once laboratory calibration of flow rate versus pressure drop has been performed. These are: (1.) stack gas velocity, (2.) the difference in internal pressure between the stack and the dilution chamber (equation 2) and, (3.) the velocity of air passing through the dilution chamber from which the dilution ratio can be determined. The stack, ambient

and dilution chamber temperatures are useful but not necessary. In addition, knowledge of the typical water vapor content contained in the stack emissions and the relative humidity of the ambient air are also useful so that enough dilution air is used to avoid water condensation. A dilution air/stack gas ratio of 20/1 has been found sufficient to avoid condensation in most cases.[2] If, however, the dilution air has a high relative humidity or the stack has a very high water vapor content, e.g., a lime kiln with a 50% water vapor content, a higher dilution ratio would be necessary. Generally stack data from previous tests are available so that approximate isokinetic velocity requirements can be anticipated and an appropriate dilution ratio can be selected prior to sample collection. Other factors such as the emission variability characteristic of the stack and typical particulate mass concentrations (grain/DSCF) are also useful in planning stack tests. Enough flexibility has been built into the sampling system to accommodate nearly all combinations of pressure, flow rate, temperature, water vapor content and mass concentration encountered in stack environments. Table I lists some typical stack parameters and the corresponding time required to collect a particulate sample for analysis. The sampling time estimates are based on the use of a 9.5 mm (3/8") I.D. sampling nozzle, a 20/1 dilution ratio and the collection of 3 mg of of particulate material with an interfaced dichotomous sampler.

Stack Tests and Analytical Procedures

The chemical composition of size categorized particles emitted from power boiler stacks, primary lead smelting stacks and a zinc fuming stack was determined from samples collected with the dilution sampling system. The power boiler samples were collected consecutively with two cyclone/back-up filter assemblies with cut-points at 2.5μ and 15μ used one after the other. The lead smelting and zinc fuming stack samples were collected by a dichotomous sampler with the 15μ aerosol inlet removed. The size categories thus obtained were: (1.) < 2.5μ for both the power boiler and lead smelting/zinc fuming stacks, (2.) < 15μ for the power boiler stacks and, (3.) > 2.5μ for the lead smelting/zinc fuming stacks. Teflon membrane filters were used to collect all samples. The mass of particles collected on each filter was measured with a Cahn Instruments Electrobalance. Thin film energy dispersive x-ray fluorescence spectrometry and instrumental neutron activation analysis were the analytical techniques used to determine the elemental concentrations.

The thin film x-ray fluorescence analyses were conducted with an Ortec TEFA III analyzer equipped with a Mo/W x-ray tube. Three excitation conditions were used: (1.) Mo tube, 50 KV tube voltage, Mo filter, (2.) Mo tube, 15 KV tube voltage, no filter and (3.) W tube, 35 KV tube voltage, Cu filter. A tube current of 100 μ amps and an analysis time (live) from 100 to 400 seconds were used in all conditions. Instrument calibration was obtained with commercial standards prepared by Micromatter, Inc. and Columbia Scientific Industries. A quality assurance standard and blank was run with each set of filters.

After the x-ray fluorescence analyses were completed, instrumental neutron activation analyses were performed on the filters. The filters were irradiated at 95% full power in a Triga Mark I 250 KW reactor. The neutron flux was 5×10^{12} neutrons/cm^2-sec. Copper flux monitors were used. Standards included

an NBS urban particulate reference material (SRM #1648), an IAEA soil standard (#5), a USGS basalt sample (BCR-1) and an Atlantic Richfield Hanford Company basalt sample (ARHCO-1). The samples were counted with an Ortec HPGe detector interfaced with a Norland IT-5400 multichannel analyzer. Both the power boiler samples and the lead smelting/zinc fuming samples were irradiated for 5 minutes, cooled for 10 minutes, and then counted for 200 seconds (live) time. The lead smelting/zinc fuming samples were then irradiated for an additional 8 hours and counted for 20 minutes after a 3 day cooling period and counted again for 1 hour after a total cooling period of 30 days.

Results and Discussion

Representative source fingerprints obtained from samples collected with the dilution sampling system are presented in Tables II and III. All concentration data are reported in weight percent along with analytical uncertainties. The concentrations of 22 elements have been reported for the power boiler stack particles and the concentrations of 28 elements have been reported for the lead smelting/zinc fuming stack particles. The concentration of approximately five additional elements were measured but are not listed in Tables II or III.

A multi-element source fingerprint which includes both the concentration or "less-than" values for trace elements as well as containing accurate concentration values for major elements is required for chemical mass balance modelling. A low concentration of a particular element in source particles is nearly as important as its presence at high concentration. For example, the contribution of a hog fuel boiler to ambient aerosol concentrations was easily distinguished from the contribution of a nearby residual oil fired boiler by CMB modelling since accurate elemental concentration data was produced. While the concentrations of all elements are used in the multi-component least squares approach, the differences in K, V and Ni concentrations between the two sources can illustrate this point. The hog fuel boiler has a very high K content and a very low V or Ni content in contrast to the residual oil fired boiler which emits particles containing V and Ni at the percent level and virtually no K. Similarly, the ambient contribution from the sinter stack, the zinc fuming stack and the blast furnace stack were distinguished from each other in a CMB airshed study due to the differences in their elemental fingerprints. Again, while the concentration of all elements is essential, the ratio of three elements (Cd, Zn and Fe) can illustrate the ability to distinguish stack particles based on differences in their elemental compositions. The Cd:Zn:Fe ratios are 0.2:0.7:1, 0.5:337:1 and 185:115:1 for the < 2.5μ size fraction of the particles emitted from the sinter stack, the zinc fuming stack and the blast furnace stack, respectively.

In addition to stack particles, the chemical composition of particles originating from all other major airshed sources (viz, fugitive sources) need to be characterized for a state-of-the-art CMB source apportionment study. While the differences in particles originating from two or three discrete sources, such as the stacks discussed here, can be qualitatively observed by

comparing concentration levels of several elements, it should be emphasized that complete and detailed fingerprints such as presented in Tables II and III are necessary to quantitatively identify the contribution of a given source among the multiplicity of particulate sources that are potential contributors to ambient aerosol concentrations. Besides accurate analytical measurements, the collection of particles with the dilution sampler in a form similar to that which they acquire after mixing and cooling with ambient air furthers the accuracy of the chemical fingerprint used to represent particles originating from them. The impact of both the power boiler stacks and lead smelting/zinc fuming stacks were determined in airsheds even when their contribution was minor as compared to the contribution from other (mainly fugitive) sources due to the detailed and representative source fingerprints obtained with the dilution sampler.

Conclusions

A pragmatic dilution sampling system for the collection of stack particles for use in receptor oriented chemical mass balance source apportionment studies has been developed. The system permits the accurate characterization of over thirty elements as well as other chemical species. The system is easily transportable, is relatively simple to operate and can collect particles in size categories which are compatible with existing and proposed ambient particulate categories (i.e., < 2.5μ, 2.5-15μ, 10μ, < 15μ and TSP). The system has been used to collect samples from a number of stacks in two airsheds where CMB source apportionment modelling was subsequently conducted with the data. In addition to CMB modelling of local airsheds, the dilution sampling system would be applicable to the collection of condensible organic compounds such as might be analyzed by gas chromatography/mass spectroscopy and would be useful for the collection of source samples used to model the long range transport of particles associated with the acid rain controversy.

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TABLE I - TYPICAL STACK PARAMETERS AND CALCULATED SAMPLING TIMES

Stack	Linear Flow Velocity (m/sec)	Particulate Loading (grain/DSCF)*	In-Stack Temperature (°C)	Sampling Time (min)
Hog fuel boiler	7.5	.07	69	41
Kraft recovery boiler	18.5	.02	129	120
Lead sinter stack	17.4	.06	81	35
Zinc fuming stack	12.0	.01	102	222
Residential wood stove	1.5	.2	300	17

* grain/ft^3 = 2.29 grams/m^3

TABLE II - THE ELEMENTAL COMPOSITION OF POWER BOILER PARTICULATE EMISSIONS

ELEMENT*	Hog Fuel Boiler		Residual Oil-Fired Boiler	
	<2.5μ	<15μ	<2.5μ	<15μ
Na	2.7 ± .2	3.1 ± .2	1.08 ± .07	4.2 ± .3
Mg	< .08	0.4 ± .1	< .07	< .1
Al	0.06 ± .01	0.24 ± .02	0.58 ± .03	0.90 ± .05
Si	0.83 ± .04	2.1 ± .1	0.77 ± .04	1.38 ± .07
S	5.5 ± .3	8.9 ± .5	9.4 ± .5	9.6 ± .5
Cl	2.8 ± .1	5.1 ± .3	< .005	.02 ± .01
K	20 ± 1	24 ± 1	0.061 ± .003	0.123 ± .008
Ca	3.0 ± .2	9.8 ± .5	0.58 ± .03	0.65 ± .03
Ti	0.041 ± .003	0.131 ± .008	0.043 ± .003	0.113 ± .007
V	0.011 ± .002	0.023 ± .003	1.88 ± .09	3.6 ± .2
Cr	0.013 ± .002	0.014 ± .002	0.021 ± .002	0.037 ± .006
Mn	0.19 ± .01	0.39 ± .02	0.028 ± .002	0.068 ± .004
Fe	0.19 ± .01	0.6 ± .2	1.20 ± .06	3.6 ± .2
Ni	0.005 ± .001	0.007 ± .002	3.3 ± .2	7.8 ± .4
Cu	0.068 ± .004	0.087 ± .006	0.010 ± .002	0.016 ± .007
Zn	0.75 ± .04	1.31 ± .07	0.109 ± .006	0.155 ± .008
As	0.036 ± .006	0.08 ± .01	0.003 ± .002	0.018 ± .006
Se	0.003 ± .001	0.006 ± .001	0.014 ± .009	0.022 ± .002
Br	0.015 ± .001	0.029 ± .002	0.0018 ± .0004	0.004 ± .001
Cd	0.05 ± .01	0.10 ± .02	< .004	< .02
Ba	0.10 ± .06	0.3 ± .1	< .03	< .1
Pb	0.127 ± .008	0.44 ± .02	0.062 ± .004	0.17 ± .01

*All values are in weight percent.

TABLE III - THE ELEMENTAL COMPOSITION OF LEAD SMELTING AND ZINC FUMING EMISSIONS

ELEMENT	SINTER STACK <2.5μ	SINTER STACK >2.5μ	ZINC FUMING STACK <2.5μ	ZINC FUMING STACK >2.5μ	BLAST FURNACE STACK <2.5μ	BLAST FURNACE STACK >2.5μ
Al	0.9 ± .2	1.0 ± .3	0.5 ± .1	0.3 ± .1	< .2	< .2
Si	3 ± 1	4 ± 1	1.5 ± .3	0.7 ± .2	< .4	< .4
P	0.30 ± .08	0.8 ± .1	0.16 ± .02	0.18 ± .02	0.76 ± .08	0.73 ± .07
S	16 ± 2	15 ± 2	2.6 ± .3	3.5 ± .4	13 ± 1	13 ± 2
Cl	1.0 ± .5	0.9 ± .2	1.7 ± .4	0.3 ± .1	5.0 ± .8	4.7 ± .5
K	0.59 ± .09	0.7 ± .1	0.56 ± .06	0.61 ± .06	2.1 ± .2	2.2 ± .2
Ca	2.6 ± .3	5 ± 1	0.2 ± .1	0.3 ± .1	0.56 ± .06	0.54 ± .07
Ti	0.17 ± .02	0.20 ± .03	0.025 ± .003	0.033 ± .003	0.027 ± .003	0.038 ± .007
V	0.004 ± .001	0.010 ± .003	< .0001	< .0001	< .002	< .005
Cr	0.046 ± .005	0.06 ± .01	0.011 ± .001	0.014 ± .002	0.020 ± .002	0.031 ± .006
Mn	0.38 ± .08	0.5 ± .1	0.002 ± .001	0.010 ± .005	0.007 ± .001	0.008 ± .001
Fe	5.8 ± .6	8 ± 1	0.16 ± .02	0.38 ± .04	0.13 ± .01	0.16 ± .02
Ni	0.082 ± .008	0.09 ± .02	0.10 ± .01	0.10 ± .01	0.060 ± .006	0.055 ± .008
Cu	1.5 ± .1	2.1 ± .3	0.21 ± .02	0.27 ± .03	0.35 ± .04	0.36 ± .04
Zn	4.2 ± .4	5.7 ± .8	54 ± 5	59 ± 6	15 ± 2	15 ± 1
As	4.9 ± .5	2.9 ± .4	1.4 ± .1	1.5 ± .2	3.0 ± .3	3.3 ± .3
Se	0.13 ± .01	0.08 ± .02	0.011 ± .002	0.012 ± .003	0.037 ± .008	0.018 ± .01
Br	0.08 ± .02	0.05 ± .01	0.006 ± .002	0.005 ± .001	0.13 ± .03	0.12 ± .02
Sr	0.20 ± .02	0.26 ± .04	0.006 ± .002	0.009 ± .004	0.010 ± .007	< .02
Pd	0.03 ± .02	< .06	0.13 ± .01	0.06 ± .01	0.20 ± .02	.025 ± .024
Ag	0.25 ± .03	0.23 ± .07	0.048 ± .006	0.04 ± .01	0.16 ± .02	0.15 ± .04
Cd	1.4 ± .1	1.1 ± .2	0.08 ± .01	0.06 ± .02	24 ± 2	21 ± 2
In	0.015 ± .003	0.015 ± .002	0.056 ± .003	0.03 ± .01	0.015 ± .003	0.05 ± .01
Sn	0.23 ± .05	0.12 ± .11	0.70 ± .07	0.71 ± .07	0.50 ± .05	0.48 ± .08
Sb	1.9 ± .2	1.6 ± .3	0.54 ± .05	0.59 ± .06	0.14 ± .06	< .2
Ba	< .3	< .8	< .04	< .1	0.17 ± .07	< .5
Hg	0.17 ± .02	0.14 ± .03	0.064 ± .006	0.061 ± .009	0.02 ± .01	0.025 ± .020
Pb	27 ± 3	27 ± 4	7.4 ± .7	10 ± 1	31 ± 3	30 ± 3

*All values are in weight percent

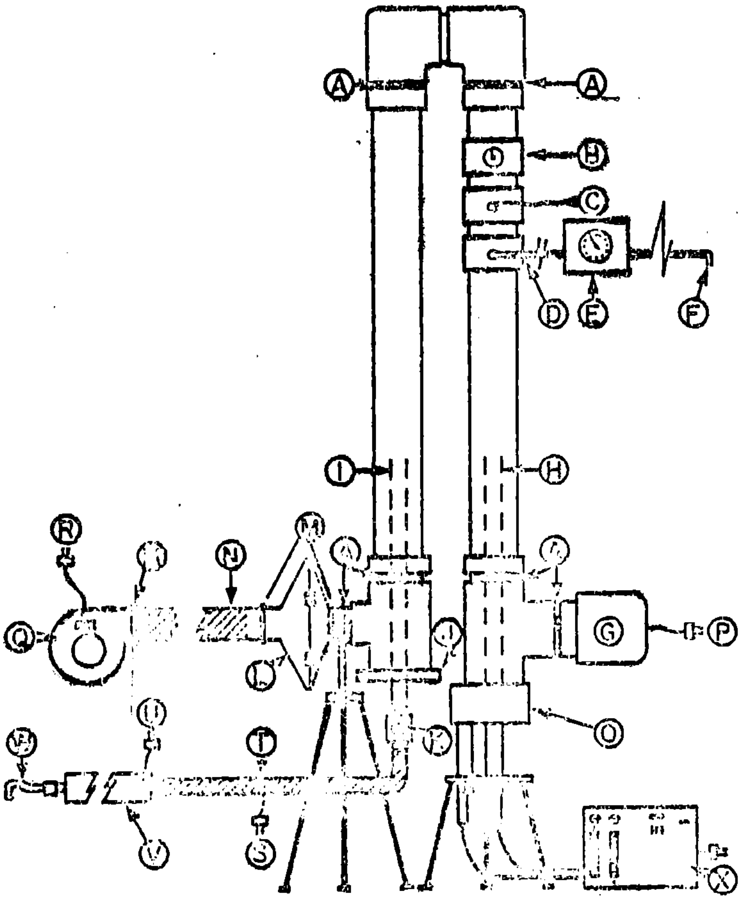


Figure 1. Dilution Source Sampler

(Not drawn to scale.) Height is approximately 2 meters, and unit is constructed with 10.2 cm (4 inch) diameter pipe. Design features include: (A) Threaded connectors for disassembly and transport, (B) thermometer, (C) gas velocity sensor to thermal anemometer, (D) static pressure sensor, (E) Magnehelic gauge, (F) total pressure sensor for in-stack measurements, (G) high volume vacuum motor, (H) interchangeable (0.64 to 2.54 cm I.D.) dichotomous inlet pipe, (I) stack gas inlet pipe, (J) stainless steel and asbestos end assembly, (K) threaded union with thermometer, (L) hinged 20 cm x 25 cm (8 inch x 10 inch) filter holder, (M) quick disconnect fittings, (N) flexible hose, (O) dichotomous sampler head, (P) power cord from high volume vacuum meter to a variable transformer, (Q) high volume blower, (R) power cord to a variable transformer, (S) power cord to heat tape, (T) insulated stainless steel teflon tubing, (U) power cord to heat tape, (V) 1.5 meter stainless steel stack probe, (W) button-hook sampling nozzle, and (X) dichotomous sampler control unit.

A STUDY OF PORTLAND'S AIRSHED
the sources and composition of suspended particles

A SUMMARY OF THE
PORTLAND AEROSOL CHARACTERIZATION STUDY (PACS)

WHY THE STUDY WAS DONE

Portland lies at the north end of the Willamette Valley, surrounded by mountains and hills. At times, when the weather is fair and the winds calm, a termperature inversion traps polluted air in the valley, reducing visibility and threatening the health of the community. As human activity in the valley has increased, the trapped air has become more and more polluted. Following the passage of the Federal Clean Air Act of 1970, Portland's air improved, because new standards were imposed on industry and limitations placed on new emissions and open burning. Still pollution has not been reduced as much as needed, and more controls are going to be necessary.

But no one knew exactly who was contributing how much of what to the airshed. A thorough study of the problem was needed to provide a good basis for decisions, so that controls could be imposed accurately, fairly, and effectively.

The Portland Aerosol Characterization Study (PACS) began in 1975, to fill the need for better information about particles suspended in the air. Other studies investigated other aspects of air pollution control in the area.

HOW THE STUDY WAS DONE

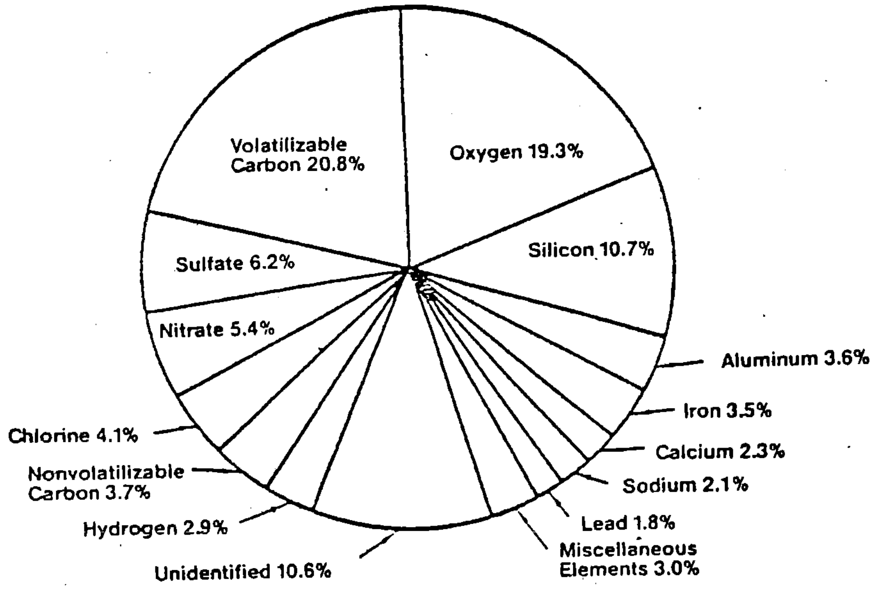
Air was sampled at six places in the Portland area. Two of the sites were at the outskirts of the city in the direction of the prevailing winds, so that particles blowing into Portland could be analyzed separately. The other sites sampled air in commercial, industrial and residential areas.

Samples were taken by vacuuming air through special filter paper. The particles trapped on the filters were then collected and analyzed. Over the course of a year, about 1300 samples were taken, under all kinds of weather conditions.

At the same time, samples were collected from 28 typical sources of particulate pollution. Twenty-seven different chemicals were found in many different combinations in these samples. Each source had a unique combination of chemicals which could be used to identify the particles from that source - a kind of "fingerprint". For example, a cement plant emits calcium; so do wood fired boilers, but with other chemicals that the cement plant does not emit. The characteristic "fingerprint" of auto exhaust shows a high proportion of lead in relation to other components.

Total Suspended Particulate

Chemical Composition



(Annual average at the Downtown Portland Sampling Site)

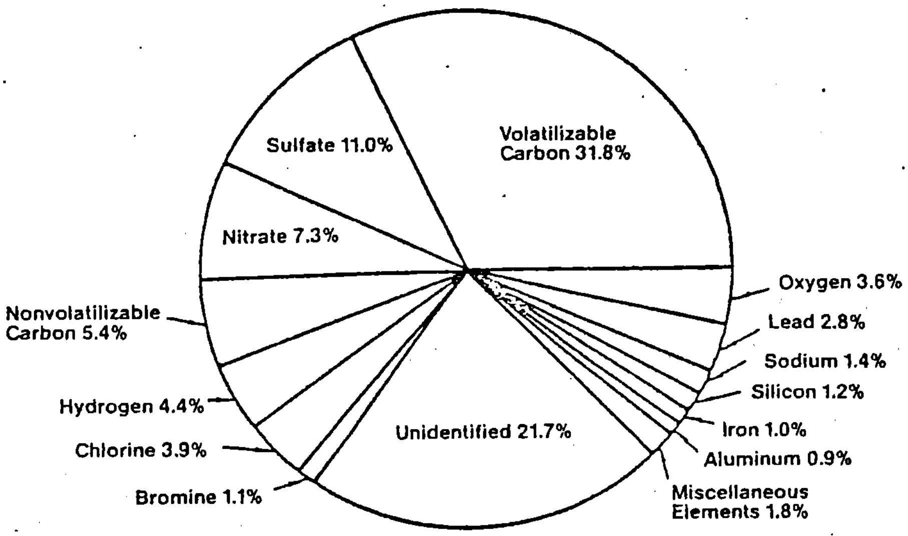
When all the data had been collected, a complex computer analysis called the "chemical mass balance" method was developed to match the source "fingerprints" with the collected air samples. The study was unique; no one anywhere before had so extensively or completely used these new, sophisticated techniques to analyze particulate pollution.

WHAT THE STUDY FOUND

About 40 percent of the total suspended particulate pollution comes from sources outside the Portland airshed. This portion of the local atmosphere is often called "background air". Its sources are roads, ocean spray, agriculture, slash burning, other cities, and the buildup of pollutants we share with the rest of the world.

Respirable Particulate

Chemical Composition



(Annual average at the Downtown Portland Sampling Site)

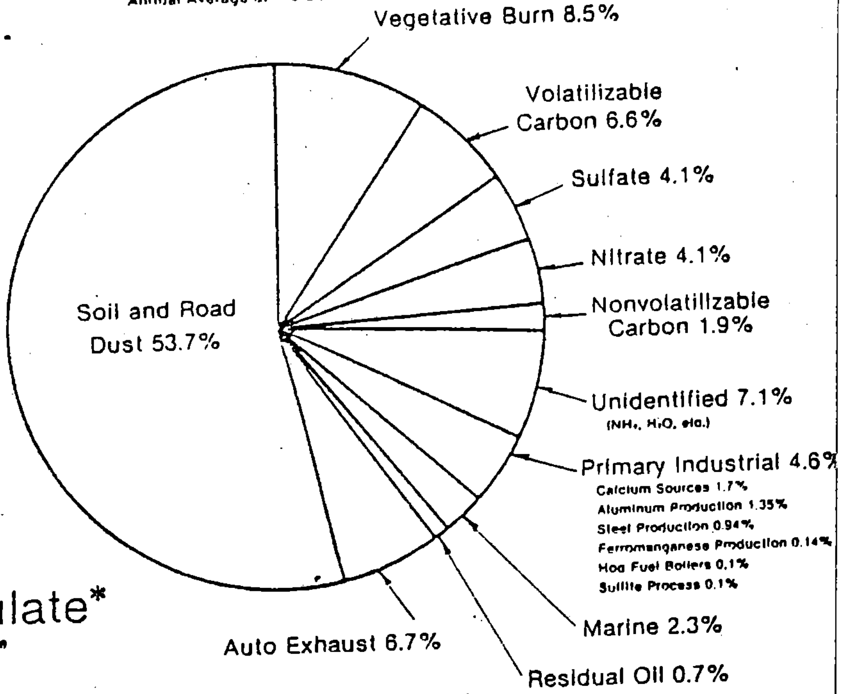
Particles can be thought about in two categories: those that are breathed in deeply by human beings are called respirable, and those that are not are called nonrespirable. The resipirable particles are extremely small, less than one micron in size. (A micron is one thousandth of a millimeter, or .00004 of an inch; a human hair is about 60 microns in diameter.) These tiny particles, invisible to the naked eye, are of the greatest concern because they affect visibility and health. The study showed that respirable particles accounted for about 31 percent of the total particulate pollution. Nonrespirable particles are larger and can be filtered or expelled by the nose and lungs before they do extreme harm.

TOTAL SUSPENDED PARTICLES

Of all the sources of particulate pollution, dust was the biggest offender, at 55 percent. Vegetative burning contributed 8.5 percent on the average to the total. Secondary particles are formed by reactions of gases like oxides with nitrogen and sulfur; these accounted for 8.2 percent of the total. The low share of emissions from industry, only 5 percent, was not surprising, because this source was relatively well controlled several years before the study was done.

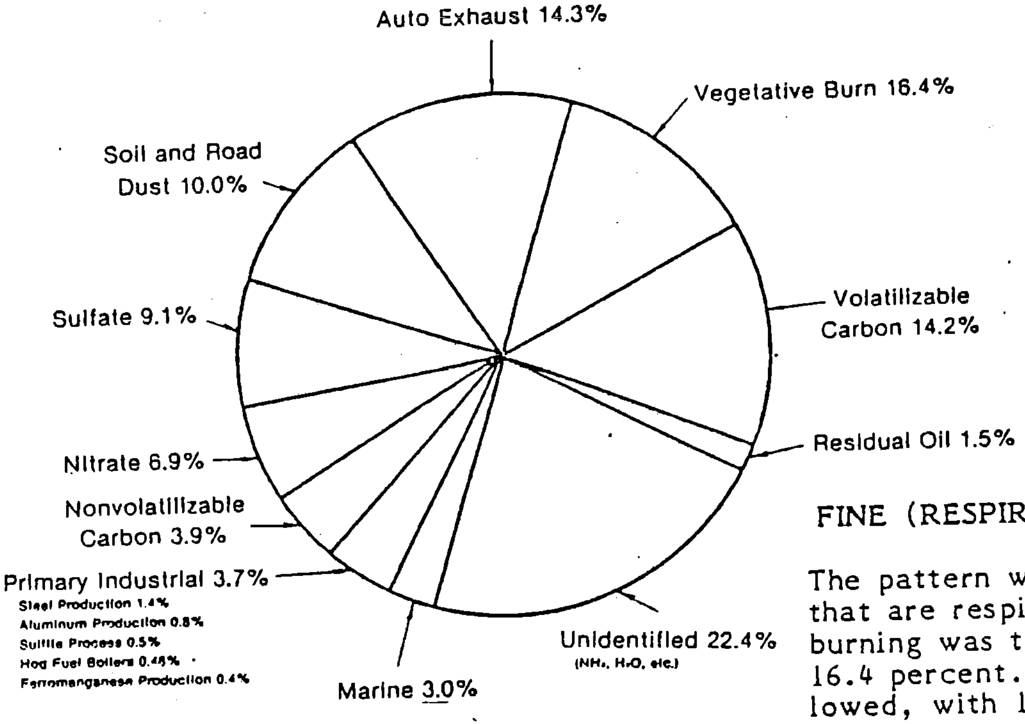
Sources of Total Particulate*

Annual Average at the Downtown Portland Sampling Site



Sources of Fine Particulate*

Annual Average at the Downtown Portland Sampling Site



FINE (RESPIRABLE) PARTICLES

The pattern was different for particles that are respirable. Here, vegetative burning was the largest contributor, at 16.4 percent. Secondary particles followed, with 15.2 percent, then auto exhaust at 14.3 percent. Industry contributed less than 4 percent. The rest came from many sources.

The one surprising piece of information was the 16 percent from vegetative burning. (On a cold winter day, this source accounted for as much as 22 percent of the total.) Most of this was suspected to be produced by local wood burning stoves and fireplaces. Wood smoke, with its potentially carcinogenic compounds, had been increasing with the rising prices of oil and natural gas. Subsequent studies indicate that it may continue to increase rapidly over the next few years, making attainment of air quality standards under the Clean Air Act an even more difficult task than first thought.

*The figures in the chart represent approximations of test results.

- For more information about the Portland Aerosol Characterization Study, the entire report is available from DEQ's Public Affairs Office. The language of the report is technical and detailed.

- If you heat with wood, you can find out about more effecient ways to operate your stove or fireplace. A brochure called "Wood Stoves: Energy Solution or Air Pollution?" is also available from DEQ.

- For these and other publications, call or write DEQ Public Affairs

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SUMMARY OF THE PORTLAND AEROSOL CHARACTERIZATION STUDY (PACS)

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with

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ABSTRACT

A brief summary of the Portland Aerosol Characterization Study (PACS), its methods and principal findings is presented. The body of information presented in this paper is directed to those individuals concerned with the identification of air pollution sources and their regulation. The objectives of the PACS were to determine quantitatively the contribution of major aerosol source types to the Portland airshed. A modified chemical mass balance method was used to quantify each source's contribution. Geological sources such as soil and road dust contributed about 40% of the TSP on an annual average while vegetative burning and automotive exhaust sources were the next two largest contributors. Primary industrial source emissions contributed only 4.9% of the TSP in downtown Portland. The results of this study are significant, not only for the information provided about Portland's aerosol but also because of the methodology developed.

INTRODUCTION

Portland, Oregon lies at the north end of the Willamette valley and is almost completely surrounded by mountains and hills. Temperature inversion frequently occurs trapping pollutants in the valley. The Portland AQMA frequently exceeds the federal primary standards for total suspended particulates on both a 24-hour and annual basis despite Portland's moderate population and pollution emission density. In 1972, Oregon adopted its Clean Air Act Implementation Plan as required by federal law which set standards for industrial sources and limited open burning. In 1974, Oregon's Environmental Quality Commission set interim standards limiting additional new particulate emissions to the Portland airshed. The consequences of this limitation to the economic growth of the region were significant. The inadequacies in the data base upon which this first plan was established were apparent and a data base improvement project (DBIP) was established to improve the data base sufficiently to quantitatively assess the impact of various source types on Portland's air quality. The PACS was one of four major studies in the DBIP, which also included emission inventory, meteorological data and air quality monitoring improvements.

Large scale studies examining the nature and sources of urban aerosols have been conducted in Los Angeles (ACHEX)[1], St. Louis (RAPS)[2] and in New York (NYSAS)[3]. The results of these studies, however, are not generally applicable to Portland because of specific differences in source types and meteorological conditions in addition to incomplete source and ambient chemical data sets.

The primary objectives of the PACS were to identify the major aerosol source types in the Portland AQMA and quantitatively determine their contribution to particulate levels and visibility degradation. A variation of the CMB method first established by Friedlander[4] was used to quantify each source's contributions. These earlier studies applied the CMB method only on limited data sets and their large scale deployment and the extent of their sensitivity to ambient and source composition errors were never adequately established.

Although these methods have had only limited success in previous applications, the PACS represents the first time a study was designed from the beginning to provide all of the essential data required by the CMB method. In this study, both the fine and coarse particle fractions from 37 sources representing 95% of the emission inventory in the Portland AQMA were chemically characterized for 27 chemical species. Over 2000 individual fine and total ambient air particulate filter samples collected over a one-year period where chemically characterized for the same 27 chemical species which accounted for 90% of the ambient aerosol mass. In addition, the CMB methodology was extended to include source uncertainties in addition to uncertainties in the ambient aerosol measurements and the validity of this method and the effective variance least squares method of fitting were verified through simulation studies. Over 1700 CMBs have been determined with this method and averages and standard deviations of aerosol source contributions and chemical compositions for each meteorological regime, flow pattern, season, size range and site determined. This study has not only characterized Portland's aerosol and determined its major sources, but has verified the general applicability

of the CMB methodology to source assessment problems, developed the methodology for its routine application and clearly defined a new environmental discipline of receptor models.

This report briefly summarizes the methods used and developed in this study, presents the most significant results and briefly discusses their implications.

EXPERIMENTAL METHODS

Chemical Mass Balance Method

The CMB method is based on the assumption that the mass of the material deposited on a filter at a receptor site is a linear combination of the mass contributed from each of the sources and that mass and chemical speciation are conserved from the time of emission to the time it is measured at a receptor site. If this is the case, it can be shown that[4]

$$C_i = \sum_j F_{ij} S_j \qquad (1)$$

sigma

where

C_i = concentration of the ith chemical species measured on an air filter at a receptor site;
F_{ij} = fraction of the ith chemical species in the aerosol emitted by the jth source;
S_j = fraction of the mass collected at a receptor site contributed by the jth source.

The C_i and F_{ij} components are empirically determined by chemical analysis of ambient and source air filters and the S_j source contributions determined by an effective variance method of least squares solution to the resulting over-determined set of simultaneous equations. The details of the method have been described by Watson, et al.[5,6]

Sampling Sites

Six sampling sites were located within the Portland-Vancouver Interstate AQMA as illustrated in Figure 1. Sites 1 and 6 were located in a rural area about 15 miles from downtown Portland and represent upwind and downwind background sites. These were used to estimate the flow of pollutants into and out of the AQMA. The objective of these sites was to distinguish between locally (within the AQMA) generated particles and those generated outside the AQMA. The results obtained at these sites on days with clearly defined northerly or southerly wind flows may be reasonable estimates of the AQMA background air mass. The results obtained on days during relatively long periods of air stagnation may be significantly impacted not only by the local background site specific sources but also by a spreading urban plume.

Site 2 sampled an industrial area, site 3 the downtown Portland urban core, site 4 an urban-industrial-residential area and site 5 a residential section of the airshed. Thus, each important land use element in the airshed was represented.

Ambient Air Particulate Samplers

The major objective of the sampling and analysis part of the

program was to characterize chemically about 90% of the material deposited on a standard hi-vol sampler. Air particulate samples, however, had to be collected on substrates suitable both for elemental analysis and carbon analysis. Four samplers were used to collect simultaneous fine and total particulate samples at all six sites. These included

- a standard hi-vol sampler to collect standard TSP samples on glass fiber type A/E filters for mass and carbon analysis;
- a hi-vol sampler with a Sierra Model 235 cascade impactor head modified to collect an aerosol mass similar to that collected by the fine particle fraction of a dichotomus virtual impactor;
- A modified ER & T sequential lo-vol sampler designed to collect nearly the same total mass as the hi-vol TSP sampler;
- A modified ER & T sequential lo-vol sampler fitted with a cyclone to remove coarse particles greater than 2 µm in aerodynamic diameter as determined empirically in the laboratory. mu

Both lo-vol samplers collected particulates on Millipore 1.2 µm cellulose acetate filters. The collection efficiencies of the ER&T total particulate samplers averaged 83% of the standard hi-vol sampler. The ER&T fine particle sampler and the after-filter of the high-vol Sierra impactor collected an average of 35% and 39% respectively of the hi-vol total mass concentration.

Source Sampling

Fine and coarse particle samples were collected from 37 sources identified by an emission inventory as potential aerosol contributors. The basic sampling unit consisted of a virtual impactor of the Lawrence Berkeley Laboratory design which was connected to a ball joint fitting for coupling to a sampling probe; the entire unit including a pump and rotameter was housed in an insulated case whose temperature could be varied from ambient to 60°C. A total of 356 fine and coarse filter samples were obtained for chemical characterization from the 28 source types listed below

Rock Crusher
Asphalt Batching
Road Dust
Soil
Automotive Exhaust
Diesel Truck Exhaust
Diesel Train Exhaust
Residual Oil
Distillate Oil
Natural Gas
Slash Burning
Fireplace
Wood Stoves
Carbide Furnace
Domestic Incineration
Field Burning
Kraft Recovery Boiler
Sulfite Recovery Boiler
Car Shredder
Hog Fuel Boiler
Flour Mill
Grain Elevators
Aluminum Production
Alumina Handling
Steel Foundry
Ferromanganese Production
Carborundum Production
Glass Furnace

Ambient Air Sampling Scheme

The PACS sampling program was based on the frequency of occurrence of surface wind flow patterns.[6] To ensure collection of samples representing each wind flow regime and type of day with their typical frequency, it was necessary to sample for 94 days during the year. A

32 day subset was selected for intensive chemical characterization. Samples were usually collected over a 10-day period each month with time in between to allow for instrument calibration, maintenance, etc. Selection of days for intensive chemical analysis was guided by a desire to match the regime frequency of occurrence, provide a representative sampling of rainy days and week ends, special impact days on which permits were issued, three "worst case" days and the degree of data completeness.

Analytical Methods

Analytical methods used for chemical characterization included ion chromatography (F, Cl, Br, NO_3 and SO_4), carbon analysis by a volatilization and flame ionization method[7], energy dispersive X-ray fluorescence (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cd, Ba, and Pb), and neutron activation analysis (Al, Br, Cl, Mg, Mn, Na, Ti, V and K).[9] A significant aspect of the entire analysis scheme was the high level of quality assurance established for every filter analyzed through intermethod and interlaboratory comparisons.

RESULTS

Composition of the Ambient Aerosol

The 24-hour annual unstratified arithmetic average chemical compositions of fine and total aerosol in downtown Portland are schematically illustrated in Figure 2. About 90% of the total particulate mass collected on the ERT-TSP sampler has been characterized. The O, Si, Al and Fe account for almost 40% of the total particulate mass, but only about 7% of the fine particle mass. Carbon accounts for 37.2% of the fine particulate mass. About 30 to 50% of the TSP consists of fine particles. The upwind "background" sites accounted for about 40% of the urban TSP and about 49% of the urban fine particulate mass.

The average percent composition of the Portland aerosol is compared with that predicted on the basis of emission inventory and a typical urban aerosol[8] in Table I. The standard deviation of the mean and the average uncertainty of a single determination is also listed. The composition of Portland's aerosol is, in general, similar to that observed in other urban areas and quite close to that predicted on the basis of emission inventories. The largest differences are in the Cl values where the Portland value is over an order of magnitude greater than the typical urban value and the emission inventory NO_3 value which is 7.5 times less than measured.

Sources of Portland's Air Particulates

The major sources contributing to the air particulate levels in downtown Portland (site 3) are schematically illustrated in Figure 3. The most surprising results relative to what was expected on the basis of the emission inventory are the relatively low contribution of primary industrial emissions and the large geological (primarily soil and road dust) and vegetative burn contributions. Over 90% of the TSP sampled by the ER&T TSP sampler has been explained with primary and secondary sources.

The source contributions to the TSP at the six PACS sampling sites are summarized in Table II. It is obvious from this comparison that the percent of source contributions are generally similar at all of the urban

sites. The largest single source to the TSP at all sites and on "worst case" days is the geological (primarily soil and road dust) source catagory, followed by the vegetative burn and automotive exhaust sources.

The geological source category includes soil, road dust, rock crushers and asphalt production because of their similar chemical and physical character. It is assumed, though, to be primarily composed of soil or continental dust plus urban road dust because of their emission inventory values. This source is characterized by many chemical species and there are no other source types or combinations which could have produced the elemental concentrations observed on individual samples. The average 5-6% relative uncertainty in each urban dust contribution is lower than that for any other source type. In addition, the geological contribution is substantially higher in the city than at the background sites, relatively uniform throughout the urban sites, highest at site 5 where the largest amount of automotive movement takes place and 80 to 90% of the mass is in the coarse fraction as would be expected from an urban road dust source. Thus, although the geological source cannot be unequivocally identified as urban road dust, it is likely the dominant source making up this particular category.

The vegetative burn category is the second largest contributor to the TSP and the largest contributor to the fine particle fraction. This category includes slash, field and backyard burning and home heating with wood. It is possibly one of the most significant air pollution sources in the area, not only because of its magnitude but also because of its fine particle nature, potential carcinogenic compounds and possible difficulties of control.

Although there is considerable uncertainty in the relative contributions of the specific source types to the vegetative burn category, the general order of magnitude of this contribution is supported not only by the CMB results but also by carbon-14 studies[10] and the lack of other significant sources of fine particulate volatilizable carbon. The average urban vegetative burn concentration is 3-4 times that of the average background site and 30% of the fine particulate in the residential area, site 5, is composed of vegetative burn in the winter, while only 7% is in the summer.

Carbon-14 measurements have shown unequivocally that about half of the TSP carbon collected in downtown Portland on October 10, 1977, was biogenic and presumably due primarily to a slash fire in the Gifford Pinchott National Forest. Similarly, 100% of the fine particulate mass at background site 1 and 80% of the fine fraction at site 3 were biogenic on the same day, strongly supporting the large vegetative burn impact in the fall due to slash burning. Wood heating was also shown to be a significant source of air pollution by this same method. For example, 62% of the fine particulate carbon on January 23, 1978 was biogenic and 45% of the TSP in downtown Portland was biogenic. This was in the winter period when the only source of biogenic carbon is expected to be from wood smoke. The vegetative burn contribution on this day accounted for 20-30 $\mu g/m^3$ of particulate mass at both sites.[10]

The most significant source of concern in this category is home heating with wood which may represent the newest air pollution problem of the future in Portland and probably many other areas of the country.

The third most abundant contributor to the urban annual average

TSP is leaded automotive exhaust. There can be little doubt that this source exists because of its nearly unique Pb and Br contributions and its dominance in the fine particle fraction. The magnitude of this source was scaled to a 20% Pb concentration.

The relatively small contribution of the Primary Industrial category was surprising. The largest subgrouping of sources contributing to this category is the so-called "Ca Sources" which average about 1% throughout the airshed. The carbide furnace source composition was used for fitting this category of sources. It is, however, about 30% Ca and since its concentration is an order of magnitude greater than the next most abundant element, Si, it was essentially fitting a pure Ca source to the excess Ca. Its particle size distribution, with over 90% of its mass occurring in the coarse fraction, and its abundance at other non-industrial sites suggests that this subgroup is probably made up of other calcium-type sources such as Portland Cement manufacturing and handling, concrete production, lime manufacturing and handling, general construction, etc.

The steel contribution shows a clear high in its contribution in the industrial area, site 2, where such sources are located. In addition, about half of the source contribution is assigned to the fine particle fraction and its contribution drops off rapidly as the sampling sites get farther from the source.

The secondary aerosol has not been specifically considered. However, the SO_4, NO_3, and volatilizable carbon source categories are what is left after accounting for primary emissions from the identified sources and may be the result of gas-to-particle conversion reactions.

Only 8% of the TSP is unaccounted for by the sources listed. This unidentified category will include such sources as ammonia emitters, water and miscellaneous small sources like galvanizing operation, etc.

CONCLUSION

This study represents the first time chemical mass balance methods have been applied to a data set specifically designed from the beginning to provide the data necessary for CMB interpretation methods. The chemical nature of Portland's aerosol has been determined and the contribution of source categories established. The results of this study are significant not only for the information it has provided about Portland's aerosol, its chemical character and its sources, but also because of the methodology developed.

FIGURE CAPTIONS

1. PACS sampling sites (X with large number) and meteorological stations (O with small number) in the Portland airshed.
2. Schematic illustration of the chemical composition of fine and total air particulates in downtown Portland.
3. Schematic illustration of the sources of the fine and total air particulates in downtown Portland.

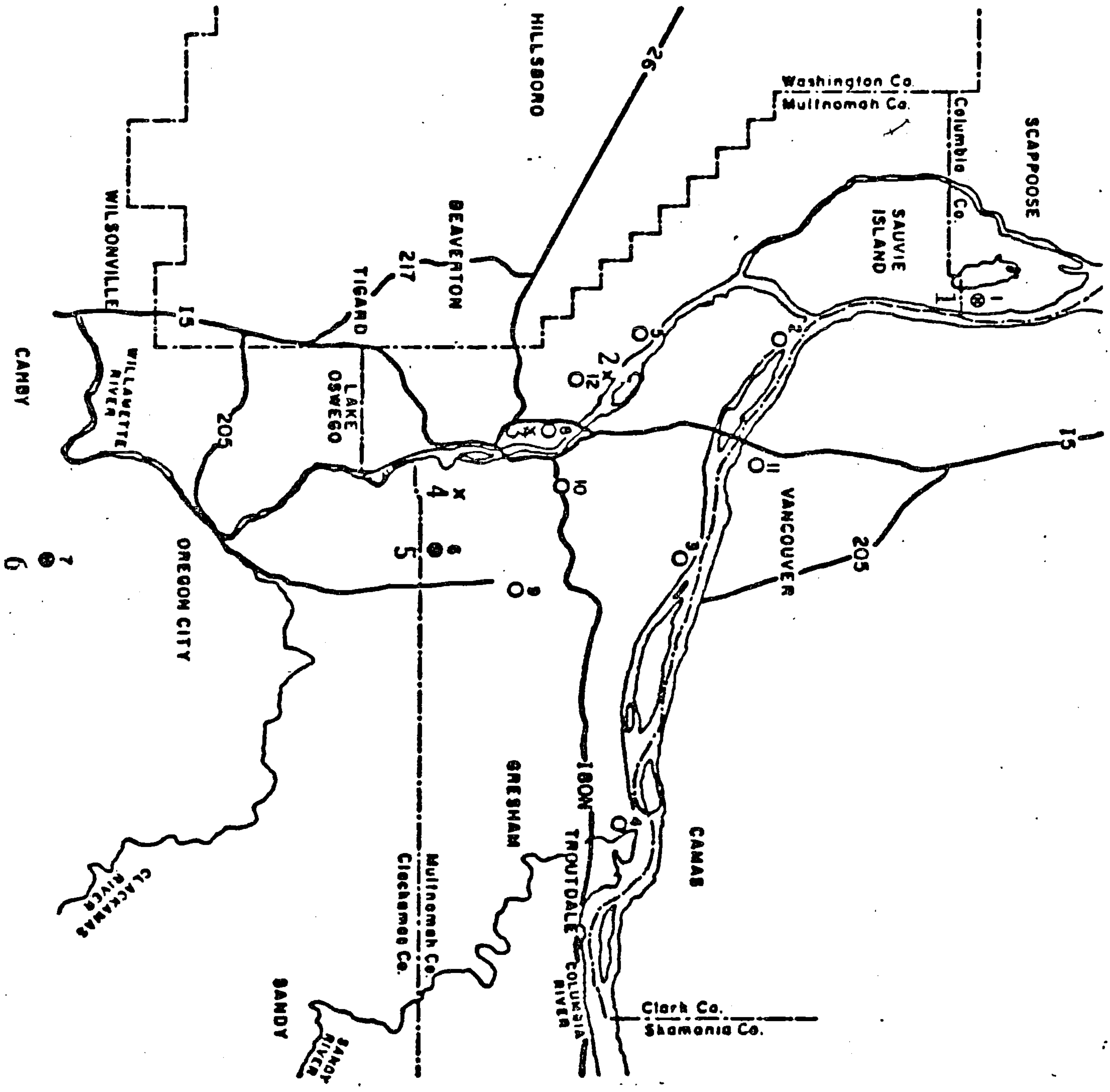

Figure 1. PACS sampling sites (x with large number) and meteorological stations (o with small number) in the Portland Airshed.

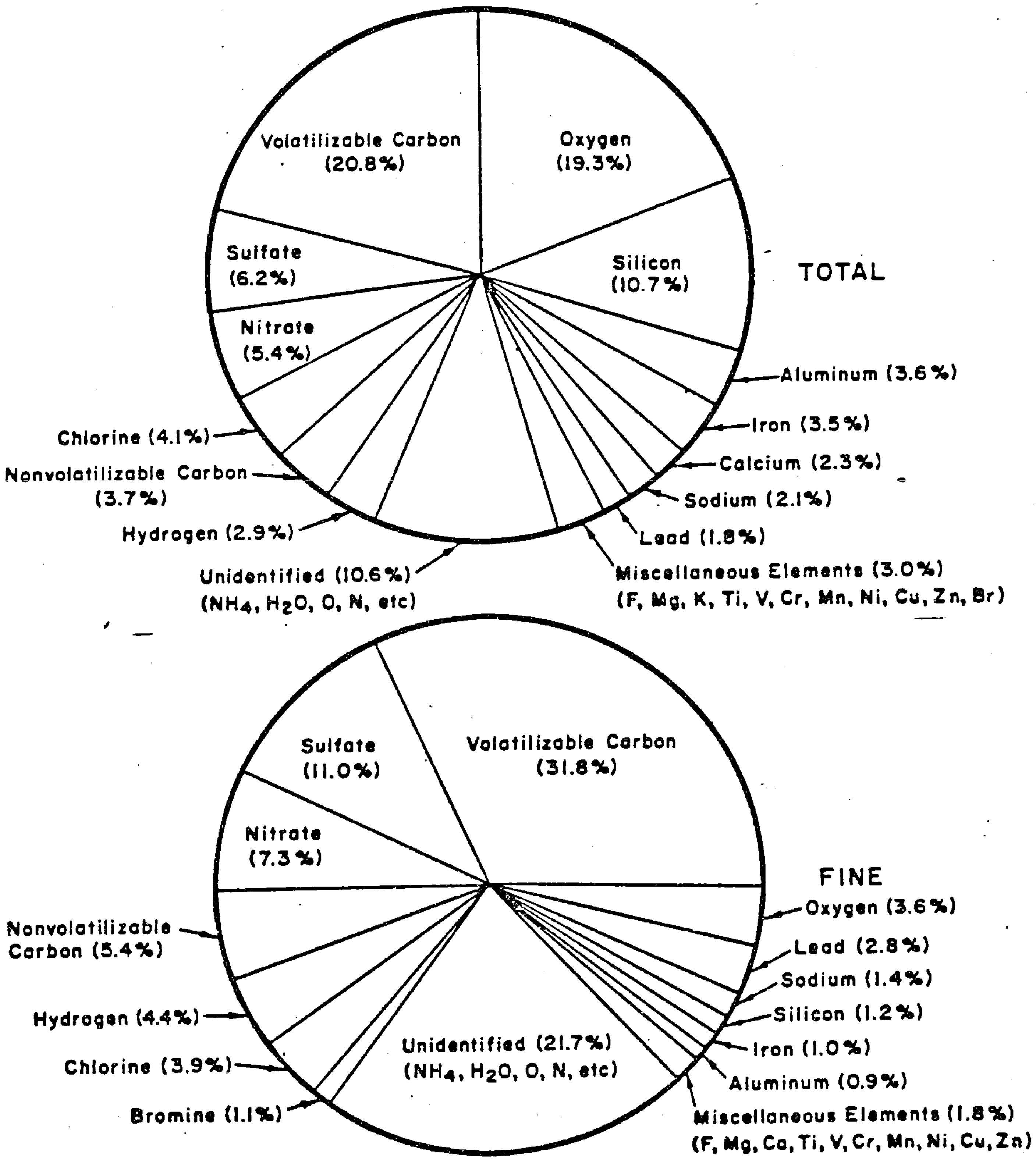

Figure 2. Chemical Composition of Aerosol in Downtown Portland, Annual Unstratified Arithmetic Average. Volatilizable and non-volatilizable carbon are operational definitions which approximately correspond to organic and elemental carbon respectively.

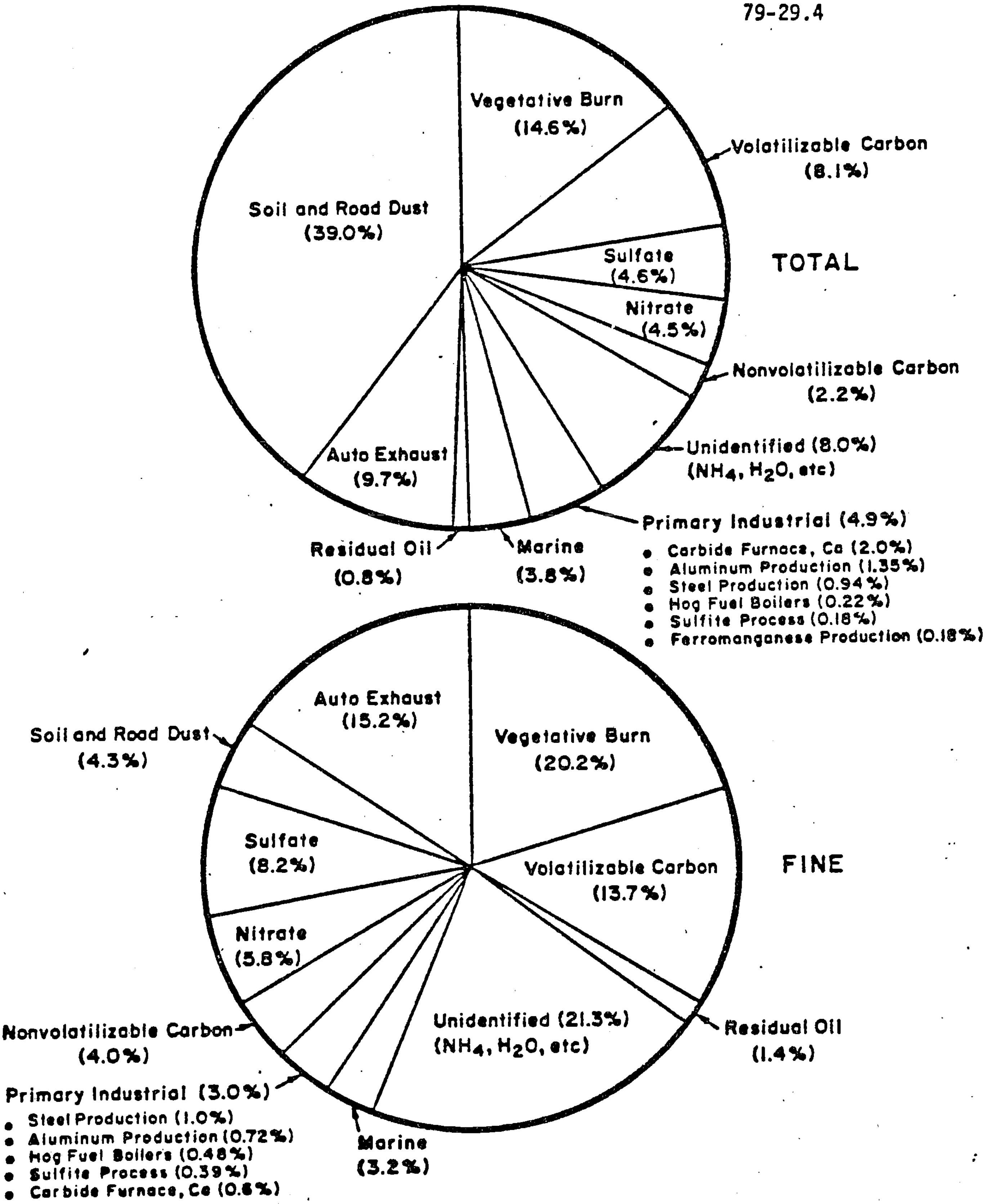

Figure 3. Aerosol Source in Downtown Portland, Annual Stratified Arithmetic Average. Does not include the 17%, on the average, of material collected with the standard hi-vol sampler which was not collected and characterized with the ERT-TSP sampler. Volatilizable and non-volatilizable carbon are operational definitions which approximately correspond to organic and elemental carbon respectively.

TABLE I

CHEMICAL COMPOSITION OF DOWNTOWN PORTLAND'S AEROSOL COMPARED WITH THAT PREDICTED FROM EMISSION INVENTORY AND A TYPICAL URBAN AEROSOL

(PERCENT, TSP)

			Downtown Portland		
Chemical	Emission Inventory	Typical Urban	Mean	St. Deviation of Mean	Average Uncert. of Single Det.
VC *	17.2	--	20.8	6.7	2.8
NVC*	7.3	--	3.7	2.1	0.8
Total C	24.5	26	24.5	--	--
NO_3	0.72	--	5.4	2.5	0.4
SO_4	8.7	--	6.2	1.9	0.3
F	0.38	--	0.16	0.14	0.03
Na	2.0	1.3	2.1	2.1	0.08
Mg	1.2	1.3	0.67	0.34	0.14
Al	4.2	2.6	3.6	1.4	0.12
Si	8.3	6.5	10.7	3.8	0.4
S	2.2	3.2	2.3	0.6	0.1
Cl	2.2	0.32	4.1	5.1	0.2
K	3.1	1.3	0.75	0.14	0.04
Ca	2.3	3.2	2.3	1.0	0.08
Ti	0.27	0.2	0.30	0.12	0.02
V	0.10	0.03	0.04	0.02	0.0015
Cr	0.06	0.01	0.05	0.03	0.005
Mn	0.26	0.06	0.17	0.11	0.008
Fe	2.3	2.6	3.5	1.5	0.13
Ni	0.17	0.02	0.06	0.03	0.004
Cu	0.05	0.2	0.15	0.09	0.006
Zn	0.20	0.4	0.22	0.10	0.008
Br	1.0	0.2	0.62	0.36	0.02
Pb	2.7	0.77	1.81	0.80	0.07

*VC: "Volatilizable carbon"; NVC: "Non-volatilizable carbon." These are operational definitions which correspond approximately to organic and elemental carbon respectively.

TABLE II

COMPARISON OF PERCENT SOURCE CONTRIBUTIONS OBTAINED FROM PACS-CMB METHODS AND EMISSION INVENTORY

(Total Particulate Fraction, Annual Stratified Arithmetic Average)

Source	Emission Inventory	Percent Contribution					
		Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
Geological	26.1	32.7	41.8	39.0	46.9	41.7	27.7
"Vegetative Burn"	2.9	9.1	9.4	14.6	7.7	13.9	9.2
Automotive Exhaust	10.8	2.6	4.5	9.7	7.7	6.3	3.6
Volatilizable* Carbon	--	12.2	9.3	8.1	11.4	11.0	15.0
Sulfate	--	6.9	5.3	4.6	3.3	3.2	4.3
Nitrate	--	7.3	3.7	4.5	3.3	4.3	7.9
Marine	--	7.5	5.0	3.8	2.0	3.9	7.4
Nonvolatilizable* Carbon	--	4.7	2.9	2.2	3.4	1.4	3.4
Residual Oil	2.1	0.46	0.91	0.83	0.38	0.24	0.16
Primary Industrial	(34.8)	(5.4)	(10.6)	(4.84)	(3.27)	(3.03)	(4.24)
• "Ca Sources"	.02	1.71	0.84	1.97	0.80	0.43	1.12
• Aluminum Production	9.8	1.29	1.41	1.35	1.17	1.80	1.42
• Steel	1.54	0.18	2.63	0.94	0.50	0.05	0.15
• Kraft Recovery	2.1	0.03	4.70	--	0.15	0.04	--
• Sulfite Recovery	1.7	0.28	0.24	0.18	0.26	0.31	0.58
• Hog Fuel Boiler	11.9	1.77	0.20	0.22	0.26	0.29	0.56
• Ferromanganese	--	0.14	0.12	0.18	0.13	0.11	0.08
• Carborundum	5.0	---	0.06	--	--	--	0.33
• Glass	0.68	--	0.37	--	--	--	--
Unidentified	--	11.1	7.6	7.8	10.6	11.0	17.1
• Diesel	2.4						
• Distillate Oil	1.69						

*VC: "Volatilizable carbon"; NVC: "Non-volatilizable carbon." These are operational definitions which correspond roughly to organic and elemental carbon respectively.

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