MODEL AND DATA BASE DESCRIPTION FOR CALIFORNIA'S LEVEL I PM_{10} ASSESSMENT PACKAGE

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ABSTRACT

A Level I PM_{10} Assessment Package is described which will allow initial estimates to be made of the source contributions to PM_{10} receptor concentrations. The package consists of the Principal Components Analysis, Chemical Mass Balance, and Industrial Source Complex-Short Term models implemented on IBM/PC compatible microcomputers. This software is applicable to existing data sets and is consistent with EPA's protocols for application and validation of the CMB receptor model and for reconciling differences among receptor and dispersion models.

This document describes the models which are included in the Level I PM_{10} Assessment Package, the measurement methods which are commonly applied to obtain model input data, and the availability of these data in the state of California. A companion users' manual provides step-by-step instructions on the application of this package to real data.

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Ms. Patty Patton, Ms. Beverly Brooks and Ms. Susan Grobman of DRI typed, edited, and produced the users' manual and model and data base description. A large number of scientists and regulatory personnel tested the software and commented on the documents. Their recommendations have been incorporated into the final software and documentation to the greatest extent possible.

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1.0 INTRODUCTION

1.1 Background

The United States Environmental Protection Agency has promulgated a primary ambient air quality standard which would control particles smaller than 10 microns (μm) in aerodynamic diameter (PM_{10}) rather than total suspended particulate matter (Federal Register, 1987a, 1987b, 1987c, 1987d and 1987e). These standards allow PM_{10} concentrations in an air quality maintenance area to reach an annual arithmetic average of 50 $\mu g/m^3$ and a 24-hour average of 150 $\mu g/m^3$.

The California Air Resources Board approved PM_{10} standards which became effective on August 19, 1983. These California standards require 24-hour PM_{10} concentrations of less than 50 $\mu g/m^3$ and an annual geometric average of less than 30 $\mu g/m^3$.

The U.S. EPA has also proposed policies and guidelines for the creation of State Implementation Plans (SIPs) for air quality maintenance areas which exceed PM_{10} standards (Federal Register, 1987a; U.S. EPA, 1987b; 1987c; Anderson et al., 1984). These guidelines rely on the application of both source and receptor models to quantify the major contributors to excess PM_{10} concentrations and linear rollback to estimate the effects of alternative emissions controls. While these guidelines recognize the need to control gaseous precursors of secondary components of PM_{10}, they are most specific for the primary aerosol components. U.S. EPA's Office of Air Quality Planning and Standards, in a cooperative agreement with the Desert Research Institute (DRI) of the University of Nevada, has prepared receptor model software to complement the UNAMAP source model software in support of these guidelines (Axetell et al., 1987). Model validation and reconciliation protocols (Pace and Watson, 1987; U.S. EPA, 1987a) have also been developed to allow users of these PM_{10} assessment methods to evaluate their appropriateness for a particular application.

In order to facilitate its application of these protocols, the California Air Resources Board (ARB) commissioned DRI to integrate the EPA version of the Chemical Mass Balance (CMB) receptor model with Principal Components Analysis (PCA) and the Industrial Source Complex-Short Term (ISC-ST) dispersion model in a microcomputer-based Level I PM_{10} assessment package. This software is interfaced to ARB's emissions, meteorological, and PM_{10} data bases in order to execute the composite modeling approach developed by Chow (1985) and to carry out the model reconciliation protocol of U.S. EPA (1987a). This modeling package requires meteorological, emission rate, ambient chemical speciation and source composition data in order to determine the contributions of California's pollution sources to PM_{10} receptors.

The Level I PM_{10} Assessment Package is designed to: 1) draw the most information out of existing data bases; 2) help define the needs for new data; 3) be easily updated to take advantage of new research findings; 4) be easy to use; 5) provide at least minimal estimates of the uncertainties

of its results; and 6) be acceptable as the basis for state implementation plans. This package is applicable to existing and future data from the air basins with the highest probability of violating a PM_{10} standard such as the South Coast, Southeast Desert, southern San Joaquin Valley, and Great Basin Valleys.

1.2 PM_{10} Assessment Levels

The U.S.EPA has issued guidelines for PM_{10} implementation plans (U.S. EPA, 1987a) which recommend the use of more than one type of air quality model in devising controls for PM_{10}. Both source and receptor models are specified as appropriate, particularly when they can be used in a complementary fashion. The EPA document "Receptor Model Technical Series, Volume V: Source Apportionment Techniques and Considerations in Combining Their Use" (Anderson et al., 1984) describes the different PM_{10} assessment methods in great detail and the list will not be repeated here. Volume V describes three levels of effort, each one more costly but supplying more accurate and precise information than the previous level.

Level I uses existing data. The models are standardized and are commonly available. In Level I assessment, the major contributors are identified and the minor ones are excluded from further consideration. If the sources contributing to the high concentrations of PM_{10} are apparent and sufficiently certain, no further work will be needed beyond Level I. Otherwise, the Level I effort serves to narrow down the areas to be studied in greater detail under Level II. The example presented in the "Level I PM_{10} Assessment Package Users' Manual" (Freeman et al., 1987), which accompanies this document, provides a good illustration of Level I assessment.

Level II involves additional chemical analyses on existing samples, acquisition of new samples from existing sampling sites, more detailed emissions characterization, and applications of the same standard models used in Level I. All measurement and modeling methods are of a standard nature. Level II fills in gaps in the existing data bases used in Level I. The State of Nevada Air Pollution Study (SNAPS) (Chow et al., 1987) provides a good example of a Level II study.

Level III involves the acquisition of new data from special sampling activities and the use of site-specific air quality models. Level III programs can involve a dense spatial distribution of aerosol samplers and meteorological sensors, specific source testing, experiments to differentiate between chemical reaction pathways, and complex gridded air quality models of both the source and receptor variety. The South Coast Air Quality Study (SCAQS) (Blumenthal et al., 1987) provides a good example of a Level III study.

Though Volume V (Anderson et al., 1984) describes an approach to each level, it does not include software to implement these approaches. Because it is a generally applicable document, it does not specify which data bases

are available in California for a Level I effort. The results of this project are intended to fulfill these needs.

1.3 Project Objectives

The objectives of California's Level I PM_{10} Assessment Package are:

- To integrate existing EPA source and receptor models, with error propagation, into a composite modeling framework on commonly available desktop computers.
- To provide access to existing ARB and other data bases which are required by this composite model.
- To identify other models and measurements which could be incorporated into the framework in order to increase the accuracy and precision of PM_{10} source apportionment.

1.4 Report Contents

This report emphasizes breadth rather than depth. It is meant to give the reader an overview of the models, their limitations, the data they require, the availability of those data in California, and the limitations of existing data. It will point the reader to the data sources, publications and technical experts who can help him with his problems, but it cannot solve those problems.

The information contained here is a snapshot of the situation at the date of the report. The report has been structured to accommodate new information as it becomes available. Future revisions will be necessary to keep it current. This report also limits itself to Level I assessment and the alternative measurement methods which might be considered for Level II. It is not intended to evaluate all possible modeling and measurement options which might be included in a Level II study. The software associated with the Level I assessment package is described in a separate users' manual (Freeman et al., 1987) which is a companion to this model and data base description.

Section 1 states the objectives of this project and defines the three levels of PM_{10} assessment. The software components which comprise the Level I PM_{10} Assessment Package are presented in Section 2. Each model is described with respect to its history and fundamentals, the procedures it follows to produce results, and current knowledge regarding the effects of deviations from model assumptions.

A fundamental theme of the Level I analysis is that the results it provides can be no more accurate or precise than the input data with which it is supplied. Each model is capable of providing quantitative estimates of this "measurement uncertainty." The measurement alternatives from which input data are derived must be understood in order to place confidence

limits on the input data. Section 3 describes these measurement methods, the assumptions they make, and the effects of deviations from these assumptions.

A key input data component in this Level I package is the source profile, i.e., the fractional chemical composition of emissions from each contributing source type. In many areas of California, this profile may change between source and receptor owing to the conversion of gaseous materials to particles. The mechanisms for this conversion and the signs of its occurrence are described in Section 4.

California contains a wealth of existing size and chemically speciated receptor data, source profile data, meteorological data, and emissions data, in addition to those contained in the data bases maintained by the Air Resources Board. These data bases, their contents, their limitations and their availability are presented in Section 5.

Any model and data base description such as this one will reveal many areas where modeling methods, measurement methods, and data bases could be improved. Recommendations for further efforts in the development of the Level I PM_{10} Assessment Package, and the data upon which it operates, are contained in Section 6.

2.0 COMPONENTS OF THE LEVEL I PM_{10} ASSESSMENT PACKAGE

2.1 Overview

Air quality models have been developed to determine the contributions of emission sources to receptor concentrations and to estimate the effect of emissions reductions. The selection of a model is commonly dictated by study objectives, existing data bases and the preferences of the investigator. Gaussian plume dispersion models have been the principal tool used for many policy actions. These models combine dispersion parameters with source emission rates to estimate the potential pollutant impact at downwind receptors.

Source-oriented dispersion modeling applied by itself to suspended particulate matter concentrations has not yielded credible results owing to the difficulties in compiling reliable emissions inventories and the inability to simulate atmospheric chemistry and particle dispersion/ deposition. Recent advances in ambient air quality monitoring and laboratory analysis techniques have resulted in chemical receptor modeling methods for source apportionment studies.

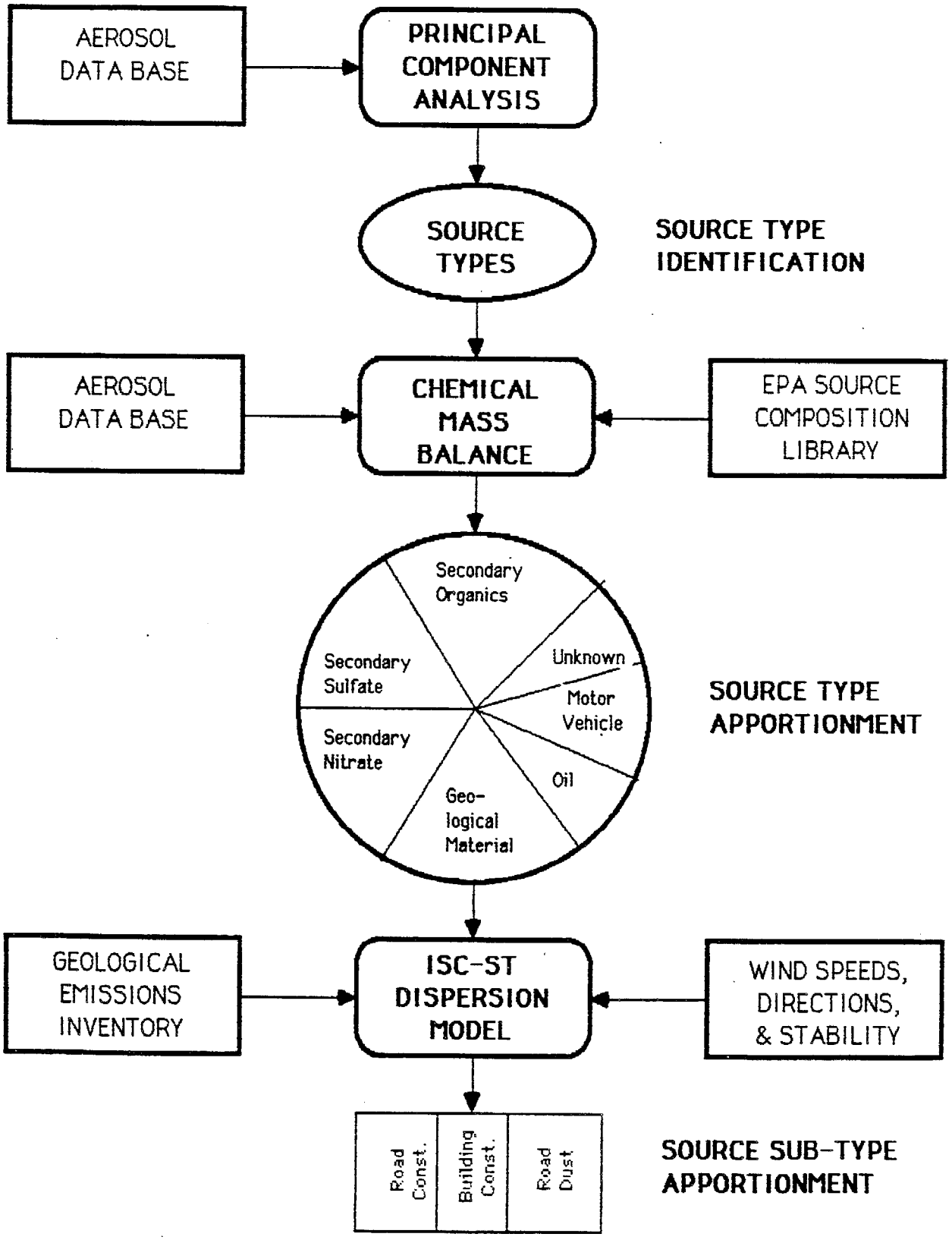
In contrast to source modeling, receptor modeling uses chemical and physical characteristics measured at the receptor to identify and quantify the emission source contributions to ambient particulate matter concentrations. This technique has been applied in the past decade as a valid and cost-effective method for developing local pollution control strategies. However, these models are often unable to apportion the impacts of specific sources from the same source group due to the similarity of chemical compositions.

No single model represents reality under all circumstances. In all likelihood, a combination of several types of source and receptor models would improve the reliability of the calculated source contributions to receptor concentrations. Better resolution of source contributors might allow pollution controls to be optimized.

The models included in California's Level I PM_{10} Assessment Package are:

- Principal Components Analysis (PCA) receptor model for urban- and regional-scale contributors.
- Chemical Mass Balance (CMB) receptor model for urban- and regional-scale contributors.
- Industrial Source Complex Short-Term (ISC-ST) dispersion model for urban-scale contributors.

Figure 2.1.1 illustrates the framework of California's Level I PM_{10} Assessment Package. This framework uses: 1) principal components analysis, along with the emissions inventory, to identify the major contributors to the fine and coarse particles measured at a receptor;


AEROSOL DATA BASE
PRINCIPAL COMPONENT ANALYSIS
SOURCE TYPES
SOURCE TYPE IDENTIFICATION
AEROSOL DATA BASE
CHEMICAL MASS BALANCE
EPA SOURCE COMPOSITION LIBRARY
Secondary Organics
Unknown
Motor Vehicle
Oil
Geo-logical Material
Secondary Nitrate
Secondary Sulfate
SOURCE TYPE APPORTIONMENT
GEOLOGICAL EMISSIONS INVENTORY
ISC-ST DISPERSION MODEL
WIND SPEEDS, DIRECTIONS, & STABILITY
Road Const.
Building Const.
Road Dust
SOURCE SUB-TYPE APPORTIONMENT

2) the chemical mass balance to attribute the measured PM_{10} to source types; and 3) the ISC-ST dispersion model to attribute the largest source-type contributors to sub-types.

The source identification step applies PCA to particulate chemical concentrations to identify the probable source types as a function of particle size. The species associated with each principal component are used in conjunction with available source composition information and emissions inventories to associate each principal component with a source type. The sources identified by PCA are used to verify and add to the source types in the emissions inventory to select source profiles as input to the CMB analysis.

The source-type contributions for each receptor sample are quantified by the CMB along with the primary contributions to ammonium, sulfate, nitrate and organic species. The secondary contributions to these constituents are determined by including single-constituent source types as proposed by Watson (1979) and recommended in Pace and Watson (1987). The effective variance least squares solution used in this model has been shown to provide realistic uncertainty estimates (Watson et al., 1984) when the measurement uncertainties of the input data are known. The CMB determines those source types which are major contributors and those which are not. Only the major contributors are subjected to dispersion modeling. The CMB also identifies the fraction of PM_{10} which can be accounted for using existing measurements. If this fraction is low, then additional species must be quantified as part of a Level II assessment.

The apportionment of the major source-type contributions into more specific sub-types is accomplished by the Industrial Source Complex-Short Term (ISC-ST) dispersion model. With the emission rates and dispersion parameters, the relative contributions from sources to the receptor can be obtained for each source sub-type. Mathematically,

$$S_{lj} = S_j \times \frac{M_{lj}}{\sum_{l=1}^{L} M_{lj}}, \quad j=1,J \; ; \; l=1,L \qquad (2.1\text{-}1)$$

where:

S_{lj} = contribution of sub-type l in source-type j to the total contribution from source-type j

S_j = total contribution to source-type j determined by the CMB model

M_{lj} = the absolute contribution of sub-type l to source-type j calculated by ISC-ST

L = the number of sub-types in source type j

J = the number of source types determined by the CMB

The ISC-ST is applied separately to emissions inventories of each major source type which were quantified by the CMB. In this way, errors in the inventories of other source types do not affect the ISC-ST results. By considering the relative as opposed to the absolute contributions within the source type, systematic biases in the dispersion parameters and emission rates partially compensate for each other. The absolute contribution from the source type calculated by the ISC-ST can also be compared to the corresponding contribution derived from the CMB as a validation test. The EPA's model reconciliation protocol (U.S. EPA, 1987a) can then be followed to determine the causes of an excessive disagreement and to modify models and input data to minimize the differences.

These three models are included in this PM_{10} Assessment Package because: 1) they are the most widely recognized and used as regulatory air quality models; 2) their computer codes are reliable, well-tested and available on microcomputers; and 3) they are compatible with the existing PM_{10} data collected by ARB. The strengths, weaknesses and availability of each component of the California's Level I PM_{10} Assessment Package are summarized in Table 2.1-1. Model input data requirements are identified in Table 2.1-2.

There are many variations on these models, and the Level I assessment package has been constructed in a modular fashion to allow other software to be easily substituted. In particular, the ISC-ST can be replaced with several other dispersion models which may be more appropriate for a given situation. The following subsections present a detailed description of the models contained in the current package.

2.2 Principal Components Analysis Receptor Model

2.2.1 Model History and Fundamentals

Principal components analysis (PCA) has been proposed and applied (Henry and Hidy, 1979, 1982; Lioy et al., 1982; Thurston, 1983; Wolff and Korsog, 1985; Malm, 1985; Chow, 1985; Chow and Spengler, 1986) as an objective method of removing the highly intercorrelated nature of variations in atmospheric measurements. The variability in an aerosol concentration which arises from the variability of a number of observables is apportioned among the various principal components.

The PCA receptor model is meant to classify variables into groups which can then be associated with factors which contribute to PM_{10} levels measured at receptors. These factors can be identified as emissions sources, chemical interactions or meteorological phenomena, depending on the data sets which have been submitted to the PCA. Many of these variables are indicative of more than one causative factor. By themselves,

Table 2.1-1

Strengths and Weaknesses of the Components in California's Level I PM_{10} Assessment Package

Model	Features/Strengths	Weaknesses	Availability on Microcomputers
PCA (Principal Components Analysis)	Handles correlated variables. Simplifies large, correlated data sets to small, uncorrelated factors. Can use chemical and meteorological data simultaneously. Identifies contributing source types, chemical character and direction with respect to receptors. Dependent variables can be linearly regressed on principal components.	Principal components rarely account for the total variance. Not effective if data set has small variability in time and space. Cannot distinguish among components which are highly correlated with each other. Requires a large (>75 cases) data set. Lacks necessary physical constraints to determine source compositions and source contributions.	BMDP, statistical software SPSS, statistical software SAS, statistical software Stratgraphics, statistical software
CMB (Chemical Mass Balance)	Quantifies contributions of source types to PM_{10}. Does not require emission rates or detailed dispersion parameters. Incorporates effective variance weighting and error propagation to estimate confidence intervals of source contributions. Uses singular value decomposition to identify excessive collinearity and uncertainty.	Requires detailed and accurate source composition data which are not always available. Source compositions as perceived at the receptor may differ from those measured at the sources. Cannot distinguish among individual sources with similar chemical compositions.	EPA Version 6 NEA Labs Desert Research Institute Tom Dzubay, EPA/ASRL

Table 2.1-1 (continued)

Strengths and Weaknesses of the Components in California's Level I PM_{10} Assessment Package

Model	Features/Strengths	Weaknesses	Availability on Microcomputers
ISC-ST (Industrial Source Complex-Short Term)	Handles multiple point, area and volume sources. Incorporates aerodynamic wake effects, terrain adjustment, momentum and buoyant plume rise algorithms and wind profile exponentiation calculations. Estimates dry deposition, gravitational settling and exponential decay. Applies to both urban and rural areas for either short- or long-term estimations. DRI version includes error propagation formulae (Freeman et al., 1986). Groups individual sources into source types.	Results are very sensitive to minor changes in input measurements. Absolute calculated concentrations often differ significantly from measured concentrations. Validity of model results is highly dependent upon validity and completeness of emissions inventory.	Bowman Engineering Trinity Consultants Desert Research Institute (with error propagation)

Table 2.1-2

Model Input Data Requirements for California's Level I PM_{10} Assessment Package

Model Input	PCA Receptor Model	CMB Receptor Model	ISC-ST Dispersion Model	Primary Data Source
Meteorological Data				
Upper Air Data				National Climate
- Mixing height			X	Center (Ashville, NC) National Weather Service
Surface Weather Data				
-Wind speeds			X	"
-Wind directions			X	"
-Ambient temperature			X	"
-Atmospheric stability			X	"
-Wind profile exponent			X	"
Source Data				
Point and Area Emissions Inventory				ARB Emissions Inventory
-Source Type				
-Source location (UTM)			X	"
-Emission rates			X	"
-Release height			X	"
-Elevation of base of stack (point source)			X	"
-Stack height (point source)			X	"
-Stack inner diameter (point source)			X	"
-Stack exit temperature (point source)			X	"
-Stack exit velocity (point source)			X	"
-Effluent particle size distributions			X	"
-Obstructions in close vicinity of emissions point			X	ARB Site Surveys
Source Composition Data				
-Source Library	X	X		Core et al. (1984)
-Source Characterization	X	X		ARB, SCAQMD

Table 2.1-2 (continued)

Model Input Data Requirements for California's Level I PM_{10} Assessment Package

Model Input	PCA Receptor Model	CMB Receptor Model	ISC-ST Dispersion Model	Primary Data Source
Ambient Data				
Mass Concentrations	X	X		ARB Dichotomous Sampler Network
Particle Compositions				
-Elements	X	X		ARB Dichotomous Sampler Network
-Ion	X	X		No data source
-Carbon	X	X		No data source
Particle Size Fractions				
-PM_{10} (0 to 10 μm)	X	X		ARB Dichotomous Sampler Network
-$PM_{2.5}$ (0 to 2.5 μm)	X	X		ARB Dichotomous Sampler Network
-Coarse (2.5 to 10 μm)	X	X		ARB Dichotomous Sampler Network

they cannot be used to distinguish the influence of one factor from another.

Several causative factors have been identified in air pollution studies. Photochemical factors were found in measurements from Los Angeles, CA; New York, NY (Henry and Hidy, 1979); St. Louis, MO (Henry and Hidy, 1982); and Lewisburg, WV (Lioy et al., 1982). These photochemical factors were consistently associated with daily average and maximum O_3, maximum temperatures and absolute humidity.

Relative humidity (RH) factors were found for Los Angeles data (Henry and Hidy, 1979) and were highly correlated with daily maximum and minimum RH measurements. Local source factors were found for Salt Lake City (Henry and Hidy, 1982) and Los Angeles (Henry and Hidy, 1979) and were highly correlated with SO_2 and the wind frequency distributions from different quadrants. Dispersion/stagnation factors were found for St. Louis, Salt Lake City, and Lewisburg. The variables correlated with the dispersion/stagnation factor were NO, NO_2, wind speed at midnight and noon, average wind speed, morning mixing height, maximum hourly precipitation, and average precipitation. Each of these factors resulted from the application of PCA to gaseous, particle chemistry and meteorological measurements. The Level I PM_{10} Assessment Package restricts itself to applications to chemically speciated particulate measurements.

The mathematical formulation of PCA in matrix form is:

$$C^S = FS^S \qquad (2.2\text{-}1)$$

where C^S is an IxK matrix of I "normal deviate" chemical species measurements taken over K days, F is an IxJ matrix of "factor loadings" for J source types, and S^S is a JxK matrix of "factor scores." The only measurements required are the ambient chemical concentrations, C. F and S^S are calculated following the procedures described in Section 2.2.2. The number of measurements (K) of an ambient concentration should exceed the number of species measured (I) by 50 to 100 cases (Henry et al., 1984; Preisendorfer, 1977). A large data set taken over a long period of time is required to obtain a stable set of factor loadings and factor scores.

Henry (1977a) and Watson (1979) describe the conditions under which F can be related to the source composition (A) and S^S can be related to the source contribution vectors (S) in the CMB. These conditions can be only partially met in practice, though Hopke (1982) and Thurston (1983) have proposed methods to approximate them. The purported advantage of factor analysis is that it can determine the number of contributing source types and source compositions without source profile measurements. This information is critical for a subsequent application of the CMB. For the PCA to accomplish this, a large number of receptor measurements is needed and additional model assumptions are imposed that may not be adequately met in practice.

The following assumptions apply to the PCA model:

Assumption 1. Compositions of source emissions are constant over the period of ambient and source sampling.

Assumption 2. Chemical species concentrations add linearly.

Assumption 3. Measurement errors are random and uncorrelated.

Assumption 4. The case-to-case variability of actual source contributions is much larger than the variability due to other causes, such as measurement uncertainty or changes in source profiles due to process and fuel changes.

Assumption 5. Causes of variability that affect all sources equally (such as atmospheric dispersion) have much smaller effects than causes of variability for individual source types (such as wind direction or emission rate changes).

Assumption 6. The number of cases exceeds the number of variables in the PCA to an extent that statistical stability is achieved.

Assumption 7. Eigenvector rotations are physically meaningful.

The PCA is dogged by an elaborate terminology that tends to obscure its inherent simplicity when applied to air quality situations. The following descriptions of key terms are an attempt to relate them to physically meaningful phenomena.

2.2.1.1 Normal Deviate Transformations

Normal deviate transformations place each variable on a common scale by subtracting the average of a set of measurements from each individual measurement and dividing by the standard deviation of that measurement set. PCA operates on these normalized variables and therefore evaluates the causes of variability rather than the absolute values of atmospheric observables. Without this normalization, the PCA results would depend on the measurement units and would be dominated by variables which take on large numerical values. Transformed variables are treated as vectors in a multidimensional space with dimension equal to the number of cases (i.e., sampling days) contained in the PCA. These variable vectors are described in terms of projections onto the axis of this "case space."

2.2.1.2 Correlation Matrix

The correlation matrix is a square matrix whose columns and rows correspond to the variables included in the PCA. Each element of this matrix is termed a "correlation coefficient" and expresses the degree to

which values for a pair of variables change in the same way. The correlation coefficient is the sum of the products of the normal deviate transformed measurements, divided by the number of products in the sum.

A correlation coefficient of 1.0 indicates that both variables increase and decrease in exactly the same proportions. A correlation of -1.0 indicates that the value for one variable increases in exact proportion to a decrease in the other variable. A correlation of zero means there is no common variability between the two variables. Owing to limited sample sizes and random measurement errors, values of -1.0, 0.0, and 1.0 are rarely found in practice. Previous PCA studies have empirically established ranges of significance for these correlation coefficients. Correlation coefficients greater than 0.75 or less than -0.75 are considered high. Correlation coefficients between -0.40 and 0.40 are considered low. Values between these extremes may or may not describe a meaningful relationship between the two variables. Though a statistical significance can be attached to correlation coefficients, the statistical distributions of ambient data rarely meet the assumptions required for the significance tests to be valid. The empirical ranges cited above are more meaningful than statistical tests.

2.2.1.3 Eigenvalues and Eigenvectors

Eigenvalues measure the variance explained by each principal component. Eigenvectors define a hypergeometric space which defines the principal components. The normalized measurements of a variable in a data set define the coordinates of a vector in a multidimensional space, the dimensions being equal to the number of cases. The correlation coefficient is geometrically equivalent to the cosine of the angle between two of these vectors. High correlations indicate vectors which point in nearly the same direction, while low correlations denote vectors which are nearly orthogonal. If the common causes of the variability expressed by these vectors are less than the number of cases and the number of variables, which is often the case in a physical situation, then the dimensions of this space can be reduced considerably. This reduced-dimension space is defined by eigenvectors.

Coordinates of the first eigenvector are determined by maximizing the sums of the squares of the projections of each variable vector on this eigenvector. Since the coordinates of all vectors are in terms of variabilities, this first eigenvector denotes the dimension which explains the maximum amount of the variance of the entire data set. This variance, the sum of the squares of the projections, is termed the eigenvalue for that dimension. Subsequent eigenvectors and eigenvalues are those which are orthogonal to the preceding vectors and explain a maximum amount of the remaining variance. A large fraction of the variance of the measurements can usually be explained by a small number of these eigenvectors. Often, those vectors with eigenvalues less than 1.0 are ignored. The remaining eigenvectors define the space which contains the factors responsible for most of the variability in the data. These vectors are specified in terms of their projections onto the variable vectors.

2.2.1.4 Rotated Factors

Eigenvectors are rotated in the reduced space defined by the eigenvalue to form factors which can be identified as physically interpretable contributors to aerosol concentrations. The eigenvectors define a multidimensional space, but an infinite number of other vectors also define the same space. The set is sought which will most closely correspond to some of the physical causes of aerosol levels defined prior to performing the PCA. The rotation imposes a mathematical constraint which associates the factor vectors with clusters of the projections of the variable vectors in the reduced multidimensional space. Several mathematical criteria have been proposed as appropriate for this rotation:

- No Rotation: Uses the eigenvectors as the factors.
- Varimax: Maximizes the projections of as few variables as possible on each factor vector with all factor vectors orthogonal to one another.
- Quartimax: Minimizes the number of factor vectors on which a variable has a projection with all factor vectors orthogonal to one another.
- Equimax: Represents a compromise between Varimax and Quartimax in which factor vectors are orthogonal to one another.
- Oblimin: Is similar to Equimax but without the orthogonality constraint.

Hopke (1981) proposes a target rotation in which the factors are aligned with a pre-selected set of target vectors in the reduced space. These target vectors are selected based on a physical model of the causative factors which they are intended to represent. Though each of these rotations is considered equally valid, the varimax rotation has been arbitrarily selected for most air pollution applications of PCA.

The components of each factor vector are termed "factor loadings." These loadings equal the correlation coefficient between the factor and each variable. When a number of variables is highly correlated (high factor loading) with a factor, the variable vectors are in the cluster represented by that factor. These factor loadings are evaluated to assign each mathematical factor vector to a physically meaningful causative factor.

2.2.1.5 Factor Scores

Factor scores express the relative influence of a factor on a specific sample. One factor score is associated with each factor for each case. The largest positive factor scores are highly influenced by the factor associated with that score. Factor scores near zero indicate an

average influence of the corresponding factor. A negative factor score indicates a lower-than-average influence of the corresponding factor.

2.2.1.6 Communalities

Communality is the sum of the squares of the projections of each variable vector on the factors. It indicates the extent to which linear combinations of the factors describe the variable. Specifically, the communality of a variable is the fraction of its variance which is explained by the factors. Previous studies have empirically found that communalities of 0.75 to 1.0 are high and 0.45 to 0.75 are moderate. These ranges are empirical rather than theoretical and they should be used as "rules of thumb." None of the variable vectors will be completely contained in the reduced space which is defined by the rotated factors.

The preceding explanations are complex and are better understood within the context of the examples given in Freeman et al. (1987).

2.2.2 Principal Components Analysis Procedures

The PCA procedure is as follows: 1) select the chemical species and measurement cases to be included; 2) calculate the correlation coefficients between the species; 3) calculate the eigenvectors and eigenvalues of the correlation matrix; 4) select eigenvectors to be retained; 5) rotate these eigenvectors into a more physically meaningful space; and 6) interpret the rotated vectors as air pollution sources based on the chemical species with which they are highly correlated. The BMDP (Dixon et al., 1985) set of statistical computer programs is used to perform principal components analysis in the Level I Assessment Package. This set of programs performs all of the operations required for the PCA and returns: 1) correlation coefficients; 2) eigenvectors and eigenvalues; 3) rotated factor loadings; 4) factor scores; and 5) communalities.

The mathematical structure implied by this verbal procedure is explained by Henry and Hidy (1979) and has been derived from first principles for air quality applications by Watson (1979). While this procedure appears to be straightforward in principle, it consists of a nearly infinite number of variations in practice. No systematic study applied to air pollution data has been performed to determine the extent to which these procedural differences affect the conclusions drawn from the PCA. An assessment of these procedural variations should be part of every use of this receptor model.

2.2.3 Effects of Deviations from PCA Model Assumptions

The PCA model has been tested with respect to: 1) variables which are selected; 2) number of components rotated; 3) type of rotation; and 4) number of cases included. Consistency of conclusions despite these

variations lends confidence that unassessed procedural differences will not significantly affect the conclusions drawn from the selected procedure.

It is often assumed that all available variables which might be associated with the physical factors affecting ambient air quality values should be submitted to the PCA and that they will automatically migrate to the appropriate mathematical factor. PCA model testing shows that it may be wiser to limit the number of variables because:

- Very highly correlated variables (greater than $\pm$ 0.98) can produce a singular correlation matrix.

- Highly correlated ($\pm$ 0.8 to $\pm$ 0.98) variables of similar quantities are redundant and may result in mathematical factors which are not related to physical factors.

- If one causative factor is represented by many more variables than another factor, the factor associated with the greater number of variables will always appear to explain a greater amount of the total variance.

- Since PCA operates on complete data sets, a larger number of variables increases the likelihood that one or more measurements will be missing and cases will be eliminated. The statistical reliability of the eigenvectors, eigenvalues, factor loadings, factor scores and regression coefficients decreases with the difference between the number of cases and the number of variables.

Other results of PCA model testing include the following:

- Mathematical factors derived from the PCA are not necessarily associated with physical factors. The selection of variables is the most important determinant of the factors derived from the PCA.

- A minimum of 75 to 100 cases is required to extract clearly defined and reliable mathematical factors that can clearly be associated with physical factors. These cases must include a wide range of intensities in physical factors.

- An association of mathematical factors with physical factors provides a better method of selecting the number of eigenvectors for rotation than do purely mathematical selection criteria.

Javitz and Watson (1986) applied PCA to simulated data sets that introduced deviations from assumptions with respect to source strength variability, source profile uncertainty, and correlation among source contributions. They found that even when all uncertainties and intersource correlations were equal to zero, the usual criterion for selecting the

number of sources (i.e., the number of eigenvectors with eigenvalues greater than 1.0) resulted in three instead of the actual four sources. Intersource correlations of up to 0.9 could be tolerated by the model, however.

Javitz and Watson also showed that when all assumptions were met, the calculated F values could indeed approximate true source profiles, though they were unable to reproduce them exactly. With the higher uncertainties associated with the source profiles used to generate the simulated data, however, the PCA did not adequately identify the correct number or the chemical character of the source types known to be present.

Ito et al. (1986) introduced random errors of up to 30 percent of their model input data and determined that, while the factor loadings shifted somewhat, the selection of independent predictor variables for their Multiple Linear Regression model was unaffected. They also selected subsets of data from their original 138 cases. While the 70-case subsets did not result in significantly different factors, qualitatively different solutions were observed in the 35-case subset. This finding is in agreement with those of Henry (1984) and Watson et al. (1987). Henry et al. (1984) recommend that the number of cases exceeds half the number of variables included in the PCA by at least 32. PCA performed on random numbers by Preisendorfer (1977) indicates that more than 100 cases are required for 10 to 15 variables in order to obtain eigenvalues typical of random variations.

2.3 Chemical Mass Balance Receptor Model

2.3.1 Model History and Fundamentals

The chemical mass balance (CMB) receptor model (after Friedlander, 1973) obtains values for the source contributions from a set of simultaneous equations which express the chemical concentrations in each size range as a sum of products of source compositions and source contributions.

The CMB receptor model consists of a solution to the set of equations:

$$C_i = \sum_{j=1}^{J} F_{ij} S_j, \quad i=1 \text{ to } I \qquad (2.3\text{-}1)$$

C_i is the concentration of species i at a receptor, F_{ij} is the mass ratio of species i in source-type j, S_j is the mass contribution of source j to the receptor sample and J is the number of contributing source types. If a set of C_i and F_{ij} is measured, Equations 2.3-1 can be solved for the S_j with the following assumptions:

Assumption 1. Compositions of source emissions, as seen at the receptor, are constant over the period of ambient and source sampling.

Assumption 2. Chemical species concentrations add linearly.

Assumption 3. All sources with a potential for significantly contributing to the receptor have been identified and had their emissions characterized.

Assumption 4. The source compositions are linearly independent of each other.

Assumption 5. The number of sources J is less than or equal to the number of pollutant properties I.

Assumption 6. Measurement errors are random, uncorrelated and normally distributed.

The chemical mass balance model and its assumptions are well understood, but it is only recently that the solutions to Equations 2.3-1 have become widely accepted. These solutions consist of: 1) a tracer solution; 2) a linear programming solution; 3) an ordinary weighted least squares solution with or without an intercept; 4) a ridge regression weighted least squares solution with or without an intercept; and 5) an effective variance weighted least squares solution with or without an intercept. An estimate of the uncertainty associated with the source contributions is an integral part of several of these solution methods. The tracer solution assumes that each source type possesses a unique chemical component, or "tracer," which is not common to any other source type. This approach has been applied by Kneip et al. (1972), Miller et al. (1972), Hidy et al. (1974a; 1974b), Gatz (1975), and Hammerle and Pierson (1975).

The additional assumption imposed by this solution is that the concentration of chemical species i comes only from source j. This assumption is rarely met in practice, and the tracer solution is only used for the most rudimentary source apportionment studies.

The linear programming method applied to Equations 2.3-1 was proposed, then abandoned, in a material balance of gaseous hydrocarbons by Mayrsohn and Crabtree (1976). Henry (1977a) first applied it to the CMB and it was later resurrected by Hougland (1983). This solution uses an algorithm, such as that described by Hadley (1962), to maximize S_j subject to constraints that require: 1) each S_j to be greater than zero but less than the total mass concentration; 2) each calculated concentration to be less than the measured concentration within experimental uncertainty; and 3) the sum of the S_j to be less than the measured mass concentration.

The measurement uncertainty of the calculated S_j can be obtained by randomly perturbing the C_i and F_{ij} by amounts proportional to their

uncertainties (Tiwari and Hobbie, 1976), but this computationally intensive method has not yet been used with this solution applied to chemical mass balance calculations.

The most general solution to the chemical mass balance equations results from the minimization of the weighted sums of the squares of the difference between the right and left hand side of Equations 2.3-1, as explained by Britt and Luecke (1973). The C_i and F_{ij} are weighted by the inverse squares of their uncertainties.

Weighted linear least squares solutions are preferable to the tracer and linear programming solutions because: 1) theoretically they yield the most likely solution to Equations 2.3-1, providing model assumptions are met; 2) they can make use of all available chemical measurements, not just tracer species; and 3) they are capable of analytically estimating the uncertainty of the source contributions.

Several variants of the linear least squares solution to the chemical mass balance equations can be derived from the general solution described above: 1) the Britt and Luecke (1973) exact solution; 2) the effective variance solution, originally proposed independently by Clutton-Brock (1967) and Hust and McCarty (1967) and applied to the chemical mass balance receptor model by Watson et al. (1984); and 3) the ordinary weighted least squares solution. Williamson and Dubose (1983) have included an intercept term and added a ridge regression option.

The Britt and Luecke (1973) exact solution consists of an iterative application of the weighted least squares solution. With each iteration, the F_{ij} and the S_j are adjusted to their more probable values. The iteration as applied by Watson et al. (1984) stops when every S_j differs by less than 1% of its value in the previous iteration. The unique feature of this solution is the adjustment of the measured F_{ij}. It is not clear that this adjustment really results in a more valid solution than one in which the F_{ij} retain their measured values. The effective variance solution is identical to the Britt and Luecke (1973) solution except that the F_{ij} are kept equal to their measured values throughout the iteration process. This solution has been used extensively in practical applications and, when verified with synthetic data as discussed below, it has exhibited the following advantages with respect to other solutions:

- Realistic estimates of the uncertainties of the source contributions are calculated when the absolute uncertainties of the receptor concentrations and source compositions are known.

- Chemical species with higher precisions in both the source and receptor measurements are given greater influence than are species with lower precisions when the relative uncertainties of the receptor concentration and source composition are known.

The second advantage is particularly important in that it allows a large number of chemical species to be used in the least squares solution without biasing the results.

The ordinary weighted least squares solution was introduced by Friedlander (1973) and has been used to solve chemical mass balance equations by Gartrell and Friedlander (1975) and Kowalczyck et al. (1978, 1982). This solution assumes that the uncertainties of the source compositions, the F_{ij}, are insignificant when compared to the uncertainties of the receptor measurements, the C_i. However, in most cases, the source composition uncertainties are much larger than those of the receptor measurements. Watson (1979) shows, using simulated data, that ordinary weighted least squares and effective variance model results are equivalent when measurement uncertainties are less than 10%. For larger uncertainties, Watson (1979) shows that the effective variance solution provides more accurate results as well as a better estimate of the uncertainty of those results.

Williamson and Dubose (1983) proposed ordinary and effective variance weighted least squares solutions with the addition of a constant term, or an intercept, to Equations 2.3-1. This is effectively the same as adding a source type for which all F_{ij} are equal to unity. Williamson and Dubose (1983) believe that this intercept term "...represents a discrepancy between the measured concentration...and the sum of its parts. If all important sources are included and there are no severe data errors, the value of [the intercept] should be small...including the [intercept] simply provides a check. However, it is not required that it be included." Yfantis and Pitchford (1984) argue that linear least squares models "...should be consistent with the real world or the underlying physics," and they show several examples to illustrate this. Physical reality argues against the addition of an intercept term to Equations 2.3-1 since, when all source contributions, the S_j, approach zero, so should the receptor concentrations, the C_i.

Watson (1979) observed that individual sources with similar F_{ij}, such as different soils and road dusts, would yield unreliable values if included in the same chemical mass balance. Henry (1982) proposed a quantitative method of identifying this interference between similar source compositions, which is known as "collinearity." Henry's (1982) "singular value decomposition" defines an "estimable space into which resolvable sources should lie." The source types which do not fall into this estimable space are collinear or too similar to be resolved from a combination of one or more of the source types which do lie within the estimable space. Henry (1986) further proposed that linear combinations of source contributions resulting from collinear source compositions would be more representative of the summed contributions of these sources.

Williamson and Dubose (1983) believe that ridge regression, a variant of the weighted least squares solution in which a bias is introduced to the source compositions, is capable of reducing collinearities. The magnitude of this bias is somewhat arbitrary and subject to controversy. Henry (1982) applied the ridge regression bias to the separation of urban and

continental dust and found that the bias resulted in physically unrealistic negative values for several of the F_{ij}.

2.3.2 Chemical Mass Balance Procedures

The CMB modeling procedure requires: 1) identification of the contributing sources types; 2) selection of chemical species to be included; 3) estimation of the fraction of each of the chemical species which is contained in each source type (i.e., the source compositions); 4) estimation of the uncertainty in both ambient concentrations and source compositions; and 5) solution of the chemical mass balance equations. These procedures are described in greater detail in an operations manual (Axetell et al., 1987) and in an applications and validation protocol (Pace and Watson, 1987) which accompany EPA's Version 6 of the CMB receptor model software.

2.3.3 Effects of Deviations from CMB Model Assumptions

Assumptions 1 through 6 for the CMB model, stated in the beginning of Section 2.3, are fairly restrictive and will never be totally complied with in actual practice. Fortunately, the CMB model can tolerate reasonable deviations from these assumptions, though these deviations increase the stated uncertainties of the source contribution estimates.

The CMB model has been subjected to a number of tests to determine its abilities to tolerate deviations from model assumptions (Watson, 1979; Gordon et al., 1981; Henry, 1982; Currie et al., 1984; Dzubay et al., 1984; Watson and Robinson, 1984; DeCesar et al., 1985a, 1985b; Watson et al., 1985c; Javitz and Watson, 1986; and Watson et al., 1987b). These studies all point to the same basic conclusions regarding deviations from the above-stated assumptions.

With regard to Assumption 1, source compositions, as seen at the receptor, are known to vary substantially among sources, and even within a single source over an extended period of time. These variations are both systematic and random and are caused by three phenomena: 1) transformation and deposition between the emissions point and the receptor; 2) differences in fuel type and operating processes between similar sources or the same source in time; and 3) uncertainties or differences between the source profile measurement methods. Evaluation studies have generally compared CMB results from several tests using randomly perturbed input data and from substitutions of different source profiles for the same source type. The general conclusions drawn from these tests are:

- The error in the estimated source contributions due to biases in all of the elements of a source profile is in direct proportion to the magnitude of the biases.

- For random errors, the magnitude of the source contribution errors decreases as the number of components increases.

With regard to the nonlinear summation of species, Assumption 2, no studies have been performed to evaluate deviations from this assumption. While these deviations are generally assumed to be small, conversion of gases to particles and reactions between particles are not inherently linear processes. This assumption is especially applicable to the end products of photochemical reactions and their apportionment to the sources of the precursors. Further model evaluation is necessary to determine the tolerance of the CMB model to deviations from this assumption.

A major challenge to the application of the CMB is the identification of the primary contributing sources for inclusion in the model, Assumption 3. Watson (1979) systematically increased the number of sources contributing to his simulated data from four to eight contributors while solving the CMB equations assuming only four sources. He also included more sources in the least squares solutions than those which were actually contributors, with the following results:

- Underestimating the number of sources had little effect on the calculated source contributions if the prominent species contributed by the missing sources were excluded from the solution.

- When the number of sources was underestimated, and when prominent species of the omitted sources were included in the calculation of source contributions, the contributions of sources with properties in common with the omitted sources were overestimated.

- When source types actually present were excluded from the solution, ratios of calculated to measured concentrations were often outside of the 0.5 to 2.0 range, and the sum of the source contributions was much less than the total measured mass. The low calculated/measured ratios indicated which source compositions should be included.

- When the number of sources was overestimated, the sources not actually present yielded contributions less than their standard errors if their source profiles were significantly distinct from those of other sources. The over-specification of sources decreased the standard errors of the source contribution estimates.

Recent research suggests that Assumption 3 should be restated to specify that source contributions above detection limits should be included in the CMB. At this time, however, it is not yet possible to determine the "detection limit" of a source contribution at a receptor since this is a complicated and unknown function of the other source contributions, the source composition uncertainties and the uncertainties of the receptor measurements. Additional model testing is needed to define this "detection limit."

The linear independence of source compositions required by Assumption 4 has become a subject of considerable interest since the publication of Henry's (1982) singular value decomposition (SVD) analysis. As previously noted, this analysis provides quantitative measures of collinearity and the sensitivity of CMB results to specific receptor concentrations. These measures can be calculated analytically in each application. Henry (1982) also proposed an optimal linear combination of source contributions that have been determined to be collinear.

Other "regression diagnostics" have been summarized by Belsley et al. (1980) and have been applied to the CMB by DeCesar et al. (1985a, 1985b). At this point, the exact values of these diagnostics that correspond to intolerable degrees of collinearity are unknown, though this is an area of active research.

Tests performed on simulated data with obviously collinear source compositions typically result in positive and negative values for the collinear source types. Unless the source compositions are nearly identical, the sum of these large positive and negative values very closely approximates the sum of the true contributions.

With most commonly measured species (e.g., ions, elements and carbon) and source types (e.g., motor vehicle, geological, residual oil, sea salt, steel production, wood burning and various industrial processes), from five to seven sources are linearly independent of each other in most cases.

Gordon et al. (1981) found instabilities in the ordinary weighted least square solutions to the CMB equations when species presumed to be "unique" to a certain source type were removed from the solution. Using simulated data with known perturbations ranging from 0 to 20 percent, Watson (1979) found: "In the presence of likely uncertainties, sources such as urban dust and continental background dust cannot be adequately resolved by least squares fitting, even though their compositions are not identical. Several nearly unique ratios must exist for good separation." It is widely recognized at this time that a substantial amount of research is needed to minimize the effects of source composition collinearity in the CMB.

With regard to Assumption 5, the true number of individual sources contributing to receptor concentrations is generally much larger than the number of species that can be measured. It is therefore necessary to group sources into source types of similar compositions so that this assumption is met. For the most commonly measured species, meeting Assumption 4 practically defines these groupings.

With respect to Assumption 6 (the randomness, normality, and the uncorrelated nature of measurement uncertainties), there are no results available from verification or evaluation studies. Every least squares solution to the CMB equations requires this assumption, as demonstrated by the derivation of Watson et al. (1984). In reality, very little is known about the distribution of errors for the source compositions and the ambient concentrations. If anything, the distribution probably follows a log-normal rather than a normal distribution. Ambient concentrations can

never be negative, and a normal distribution allows for a substantial proportion of negative values, while a log-normal distribution allows no negative values. For small errors (e.g., less than 20%), the actual distribution may not be important, but for large errors, it probably is important. A symmetric distribution becomes less probable as the coefficient of variation of the measurement increases. This is one of the most important assumptions of the solution method that requires testing.

2.4 Industrial Source Complex Gaussian-Plume Model

2.4.1 Model History and Fundamentals

The transport and dispersion of air pollutants depends on the physical nature of the pollutants, emissions conditions, source configurations, wind speed, wind direction, atmospheric stability and the level of turbulence (Seinfeld, 1975). Source-oriented dispersion models attempt to mathematically simulate atmospheric plume dispersion and estimate the source contributions at a specific downwind receptor. These models often assume a Gaussian distribution of the pollutants and homogeneous turbulence. Dispersion models also solve advection-diffusion equations involving eddy diffusivities (Pasquill, 1974).

Depending upon the method used to simulate pollutant dispersion, these dispersion models can be classified as (Bowne and Londergan, 1983): 1) kinematic; 2) first-order closure; and 3) second-order closure.

Kinematic models are the least complex representations of pollutant transport, both mathematically and conceptually. These models simplify the non-linear equations of turbulent motion, thereby permitting a closed analytical approximation to describe pollutant concentrations (Green et al., 1980). First-order closure models are based on the assumption of an isotropic pollutant concentration field. Consequently, turbulent eddy fluxes are estimated as being proportional to the local spatial gradient of the transported quantities. The Eulerian grid models, Lagrangian particle models and trajectory puff/plume models are included in this category. Second-order closure models involve a series of algorithm transformations of the equations of state, mass continuity, momentum and energy by using Boussinesque approximations and Reynold's decomposition theory (Holton, 1979).

Currently, computer codes for several kinematic models are available. First- and second-order closure models are not commonly used in regulatory applications owing to lack of appropriate input data, the high cost of computing, and the proprietary nature of such models. Nevertheless, research is being conducted to make these models more practical and accessible.

Lupini and Tirabassi (1979) have proposed a link between the Gaussian-plume model and advection-diffusion equations. Their "modified" Gaussian-plume model allows variations of advection and dispersion with height. Evaluation studies of first- and second-order closure models

performed by Liu et al. (1983) and Lewellen et al. (1983), respectively, as part of the EPRI Plume Model Validation program, are intended to determine the minimum input data which are needed. Egan (1979) notes that there is hope for improving the treatment of pollutant dispersion in complex meteorological situations.

Since the Gaussian-plume kinematic model is presently the one which is most applicable to existing data bases, it has been included in the Level I PM_{10} Assessment Package. As the first- and second-order closure models reach a standardized stage of development, they should be considered as a replacement for the less realistic Gaussian-plume formulation.

Guidelines on Air Quality Models (Tikvart and Slater, 1978) and the Guidelines for Air Quality Maintenance Planning and Analysis (Budney, 1977) present generalized approaches for the selection and application of air quality models and data bases. It is generally agreed that none of these "guideline" dispersion models can take into account all possible factors involved in the air quality impacts of a complex set of sources (American Meteorological Society, 1978; Thurston, 1979; Schewe, 1981). Prior to using a model, the study objectives, emissions characteristics, source configuration and terrain features need to be examined within the context of the model assumptions to ensure appropriate model selection and application.

The Industrial Source Complex (ISC) model (Bowers et al., 1979; 1981) is the most comprehensive Gaussian-plume dispersion model in EPA's UNAMAP system. The ISC is designed to evaluate the air quality impacts of emissions from a wide variety of sources. Most other UNAMAP models are subsets of the ISC-ST.

The ISC Gaussian-plume model has the following features (Tikvart and Slater, 1978; Hanna et al., 1982):

- It produces results that agree with experimental data (within measurement uncertainties) as well as other models, even ones with greater complexity when model assumptions are reasonably met.
- Its mathematical formulae are relatively simple.
- It averages the random turbulent nature of atmospheric motion.
- It is a legitimate solution to the Fickian diffusion equation, given the proper boundary conditions and physical assumptions.
- It has been widely accepted for regulatory purposes.
- It has been coded and tested.

The ISC dispersion model is based on the following assumptions (Stern, 1977; Spengler, 1982):

Assumption 1. Plume constituents are Gaussian (normally) distributed over the crosswind (y) and vertical (z) directions.

Assumption 2. Time-averaged concentrations rather than instantaneous behavior are described.

Assumption 3. Emissions are continuous, non-heated and inert and come from near surface point sources.

Assumption 4. No plume mass is absorbed or generated from chemical/ physical processes or by the ground (i.e., perfect reflection of the plume).

Assumption 5. The atmosphere is steady-state and uniform.

- -- Dispersion in the x-direction is negligible (i.e., no downwind diffusion).
- -- The plume centerline follows a straight line originating at a point and is parallel to the ground (i.e., straight line and horizontal flow).
- -- Mean wind speed varies uniformly throughout the diffusion layer (i.e., no wind shear).
- -- The speed of the plume is described by the empirical dispersion coefficients (α_y and α_z for crosswind and vertical directions, respectively) as a function of distance, stability class, and is constant in the diffusion domain.

Several deviations from these assumptions can be accommodated, albeit in a rudimentary form, by the ISC-ST model (i.e., first-order transformations, tilted plumes, ground-level absorption).

The ISC dispersion model can be applied to both rural and urban areas for either short- (ISC-ST) or long-term (ISC-LT) estimates. The model combines and enhances components of other dispersion models in a single package. It includes the Briggs plumes rise equations (Briggs, 1975) which are used by the RAM model (Turner and Novak, 1978). It incorporates the terrain adjustment features of the single source CRSTER model (U.S. EPA, 1977c). It uses sequential hourly meteorological inputs to calculate ground-level concentrations as does the CRSTER model in its short-term option. Statistical wind summaries (STAR Summaries) from the Climatological Dispersion Model (CDM) (Busse and Zimmerman, 1973) can be used in the ISC-LT version to calculate seasonal and annual averages. ISC calculates concentrations over averaging times ranging from one hour to one year. It applies trigonometric relationships to accomplish the physical separation of multiple point sources. It adjusts wind speed with height by using wind profile exponents, accommodates aerodynamic building wake effects (downwash), and estimates dry deposition and gravitational settling

for particles and dry deposition for gaseous pollutants. Time-dependent exponential decay can be represented, as can curvilinear and elevated line sources with variable emission rates. Variable area and volume source configurations can be simulated.

Examples of actual ISC dispersion modeling applications for gaseous and particulate pollutants in various types of industrial plants are enumerated by Bowman (1981), Marker et al. (1981) and Bowers et al. (1981).

2.4.2 ISC-ST Modeling Procedures

The ISC-ST modeling procedures are presented in great detail by Bowers et al. (1979). The Level I PM_{10} Assessment Package uses the UNAMAP Version 6 adapted to the IBM-PC. The computer code has been enhanced with an input data error propagation scheme (following Freeman et al., 1986) and outputs which combine emissions source sub-types into the source types used in the CMB.

The procedures followed in a typical application of this model are: 1) select point, area and mobile sources to be modeled and reformat emissions data into input files; 2) select representative wind and stability data and reformat meteorological data files into input files; 3) select model input data; 5) apply the model to calculate the absolute and relative contributions of source contribution sub-types to the contribution of each source type.

As with the PCA and CMB models, numerous variations on these basic procedures exist. Part of the validation of model results should include an application of the model to a number of these variations. This validation step will allow the effects of model choices on source apportionments to be quantified.

2.4.3 Effects of Deviations from Gaussian-Plume Model Assumptions

Testing for Gaussian-plume models such as the ISC model has focused on the comparison of model predictions to measured concentrations (Fox, 1981).

These evaluations of model performance are a critical need (Sklarew, 1979; Hamburg, 1979). Bencala and Seinfeld (1979) proposed a computer package (AQMPAP) to evaluate air quality model performance. This package includes statistical techniques for analyzing residual, trends, and common air quality indices. A workshop on "Judging Air Quality Model Performance" was held by the American Meteorological Society in September 1980, at Woods Hole, Massachusetts, to discuss model evaluation, to recommend model performance evaluation measurements and methods, and to set standards for model performance (Fox, 1981).

The Electric Power Research Institute (EPRI) has initiated a Plume Model Validation and Development (PMV&D) program (Hilst, 1978) which

provides a data base and an operational and diagnostic validation of plume models. The outcome of these evaluations of model performance identifies several shortcomings of plume models (Bowen, 1981). Sensitivity analyses indicate that, relatively, the vertical dispersion coefficient (σ_z) (Bohac et al., 1974), plume rise algorithms, and mixing height are the key parameters and have greater effects on the predicted ground-level concentrations than do other model input variables. Discrepancies between Gaussian-plume model predictions and corresponding measured concentrations can be attributed to three general causes (Liu and Moore, 1984):

- Deviations from fundamental Gaussian-plume model assumptions.
- Inaccuracies of the parameters used in the model, such as the plume dispersion parameters.
- Uncertainty and inaccuracy of the model input data, such as the estimated emission rates and meteorological measurements.

The atmospheric dispersion modeling of particles by Gaussian-plume models was assessed by Cramer and Bowers (1980), where model calculations accounted for only 20 to 30% of the total suspended particulate concentrations measured at receptors with high-volume samplers, even though SO_2 predictions agreed within $\pm$ 10% of the observed annual average.

In McTaggart's (1981) complex aluminum plant study, observed SO_2 concentrations were compared at four monitoring sites with calculations of the ISC, BLP (Buoyant Line and Point) (Schulman and Scire, 1980), and MPTER (Multiple Point Gaussian Dispersion Algorithm with Operational Terrain Adjustment) (Pierce and Turner, 1980) dispersion models. This study revealed limitations of the ISC model with respect to building downwash effects, line source plume rise, and wind shear factors. The ISC model underpredicted the concentrations for low-level sources which were subject to downwash. Additionally, it overpredicted the maximum concentrations for a low-level line source and a smelter complex.

Similar results were found by Scire and Schulman (1981). They compared the ISC and BLP models with SF_6 tracer data and SO_2 measurements at two aluminum production plants. Once again, plume rise and building downwash effects in the line, volume and area source algorithms of the ISC model appeared to be the major cause of discrepancies. The use of multiple point sources in the ISC model to simulate line sources could also have contributed to the unfavorable comparisons.

Schreiber and Hurt (1981) conducted model/model intercomparisons between the ISC and BLP models. ISC overpredicted volume source impacts when compared to buoyant line source emissions.

Gschwandtner et al. (1982) found substantial differences among concentrations calculated from ISC-ST, PAL (a Gaussian Plume Algorithm for Point, Area, and Line Sources; Peterson, 1978), and RAM (Turner and Novak, 1978) models as the receptor grid spacing, physical dimensions of area sources, and their relative release heights varied. This study suggests

that receptor grid spacing should not exceed twice the area source width for area sources with release heights below 20 meters. Otherwise, the location of maximum concentration predicted by the model becomes less accurate. Even with identical input data, different Gaussian-plume model algorithms resulted in significantly different results in the Gschwandtner et al. (1982) study.

Eldridge and Gschwandtner (1984) compared the contributions of line source calculated by the ISC-ST and PAL models. Significantly lower concentrations were obtained from the ISC model as compared to the PAL model with line source release heights less than the wind measurement height (usually 10 meters), except for wind speeds less than or equal to one meter per second (calm period). However, the predictions were comparable for emission release heights over 25 meters. Eldridge and Gschwandtner (1984) advocate obtaining wind speed measurements at the source release height, rather than relying on nearby weather data and a power law distribution.

The long-term ISC model (ISC-LT) with and without deposition algorithms predicted TSP concentrations which were compared with CDM (Busse and Zimmerman, 1973) model predictions by Komp et al. (1984). This study attempted to select an appropriate method for the determination of air quality impacts from surface mining. The results suggest that the ISC model offers considerably more advantages and greater flexibility than the CDM model in this situation.

Bowman and Crowder (1984) discovered discrepancies of 40% and larger between ISC short-term and long-term concentrations calculated from the same data. They hinted that the different algorithms used in the two versions act in a synergistic manner to cause these discrepancies. Apparently the long-term ISC model, which uses averaged meteorological values, is not equivalent to the short-term ISC modeling approach, which uses discrete hourly values. Version 6 of the ISC is said to return more consistent results for equivalent applications of the long- and short-term versions.

Roffman and Norton (1981) identified the following areas which need further testing in the ISC model:

- Incorporation of the initial vertical dispersion of the plume in dispersion calculations for area and line sources. The idea is to account for the effects of surface roughness, mechanical turbulence and thermal convection in large industrial plants.

- Sensitivity analyses to test the ISC model in complex terrain.

- Determination of the number of subdivisions for area and line sources that will yield concentrations which asymptotically approach the true value. An iterative scheme uses the ratio of source-receptor distance (L) to source length (R). The L/R ratio is the deviation from the true concentration as a function of the number of subsources.

In conclusion, the ISC is a model with broad applications but many limitations. The model evaluations summarized in this section do not show a good temporal and spatial agreement between model predictions and receptor measurements. These evaluations do show, however, that the relative contributions from several sources predicted by the model are consistent with those of other models and measurements.

3.0 MEASUREMENTS FOR MODEL INPUT DATA

Suspended particles are complex entities with characteristics which depend on their chemical composition, size, and equilibrium with the surrounding environment. No particle measurement system in existence today can truly represent the ambient aerosol concentration under all conditions. It is possible to obtain comparable values within reasonable degrees of measurement precision, however, when measurement methods are comparably specified. This comparability must be established for any measurement process which will be used to determine compliance or non-compliance with an ambient air quality standard and to obtain the size and chemically characterized data needed for the PCA and CMB receptor models. If one measurement process exhibits a systematic bias with respect to another process, if that bias exceeds typical precision intervals, and if the bias cannot be corrected, then the data may not yield valid source assessments, no matter how good the models. Measurement processes which are needed to supply input data to the models described in Section 2 fall into the categories of: 1) receptor sampling; 2) source sampling; 3) chemical analysis; 4) meteorology; and 5) emission rates.

3.1 PM_{10} Receptor Sampling

PM_{10} sampling differs from that of total suspended particulate matter (TSP). Table 3.1-1 compares measurement requirements for TSP measurements, and the EPA PM_{10} reference method. The new reference method opens up many possibilities for using compliance-oriented monitoring samples for the chemical characterization required by receptor models. High volume sampling on glass fiber filters is not amenable to such analyses.

3.1.1 Size-Selective Inlets

Six PM_{10} size-selective inlets have been developed and tested (Watson and Rogers, 1986a, 1986b). These are:

- **The Wedding high volume (hivol) inlet**: Operating at 1132 l/min (40 cfm), this inlet is cylindrically symmetrical to eliminate wind directional dependence, as are all of the PM_{10} inlets described here. This inlet uses an inner, coaxial cyclone as the main fractionating device; the cyclone's inner surface is lined with porous material impregnated with oil (Wedding and Weigand, 1985).

- **The Sierra-Andersen hivol inlet** (retrofitted SA-321A or SA-1200): Operating at 1132 l/min, the SA-1200 inlet is similar to the earlier and discontinued Models SA-321 and SA-321A. This inlet uses stages of opposing impaction jets to steepen the sampling effectiveness curve and to further reduce the transmission of particles 20 μm in size and larger (McFarland et al., 1984). The SA-1200 contains a greased impaction surface to mitigate against the re-entrainment of

Table 3.1-1

Comparison of TSP and Proposed PM_{10} Measurement Requirements (from Watson and Rogers, 1986)

Criteria	TSP (U.S. EPA, 1977)	PM_{10} (Federal Register, 1987a, 1987e)
Sampler Inlet and Sampling Device	Inlet must be "rectangular in shape with a gabled roof" and allow effective particle capture air velocity between 20 and 30 cm/sec	Three replicate measurements of 3, 5, 7, 9, 10, 11, 13, 15, 20 and 25 μm liquid particles at 2, 8 and 24 km/hr wind speeds in a wind tunnel Calculated sampling efficiency within $\pm$ 10% of prescribed ideal sampler and specified size distribution 50% cut-point size (D_{50}) between 9.5 and 10.5 μm Sampling effectiveness for solid particles <5% higher than sampling effectiveness at 25 μm. Independence of wind direction Horizontal filter Twenty-four-hour sampling range of 0 to 300 $\mu g/m^3$
Air Volume	Manual or automatic control Sample time precision $\pm$ 30 min. in 24 hours Flow rate 1.1 to 1.7 m^3/min Convert to standard temperature and pressure	Flow control device Sample time precision $\pm$ 15 min Convert to 25°C and 101.3 kPa Average flow rate within $\pm$5% of initial flow rate Any single flow rate measurement in a 24-hour sample within $\pm$ 10% of initial flow rate Accuracy of transfer standard <2%

Table 3.1-1 (continued)

Comparison of TSP and Proposed PM_{10} Measurement Requirements (from Watson and Rogers, 1986)

Criteria	TSP (U.S. EPA, 1977)	PM_{10} (Federal Register, 1987a, 1987e)
Filter Media	DOP test > 99%	DOP test > 99%
	Weight loss not to exceed 2.4 mg	Weight gain or loss not to exceed equivalent of $\pm$ 5 $\mu g/m^3$
		Alkalinity < 25 microequivalents/gm
Sample Handling	Guidelines	Guidelines
Filter Weighing	Temperature 15° to 30°C	Temperature 15 to 30 $\pm$ 3°C
		Relative humidity 20 to 45 $\pm$ 5%
	Temperature variation $\pm$ 3°C	0.1 mg balance sensitivity for flow rates > 0.5 m^3/min
	Relative Humidity < 50%	< 0.1 mg for high volume samplers and better for lower volume samplers
	< 0.1 mg balance sensitivity	
	Equilibrate filter for 24 hours	
Operating Precision	Coefficient of variation of collocated sampler < 15%	Standard deviation for 3 collocated samplers $\leq$ 5 $\mu g/m^3$ for PM_{10} < 80 $\mu g/m^3$ and $\leq$ 7% for PM_{10} > 80 $\mu g/m^3$ for ten 24-hour measurements
Maintenance Schedule	Two or three times per year; 400-500 hour motor brush replacement	Defined in operator's manual by sampler manufacturer
Calibration and Performance Test Schedule	Variable	Defined in operator's manual by sampler manufacturer
Audit Schedule	Variable	Not Specified

large particles. A retrofit kit is available for SA-321 and SA-321A inlets which inserts a greased plate below the impaction jets.

- **The Wedding medium-volume inlet**: This omni-directional cyclonic inlet operates at 113 l/min (4 cfm). The cyclonic particle removal mechanism is similar to that of the Wedding high volume inlet. Large particles deposit on an inner tube (Wedding and Carney, 1983).

- **The Sierra-Andersen medium-volume inlet** (SA-254): This inlet is designed to operate at a 113 l/min. Opposing jets are the primary fractionating device (Olin and Bohn, 1983). This inlet is being used for PM_{10} sampling in the ARB's South Coast Air Quality Study (SCAQS) and the California Acid Deposition Monitoring Program (CADMP).

- **The Wedding low-volume inlet**: This inlet is designed to operate at 18 l/min and is similar in concept to the Wedding hivol inlet, except that the central, coaxial cyclone does not utilize an oiled surface in this case (Wedding and Weigand, 1982).

- **The Sierra-Andersen low-volume inlet** (SA-246): This inlet is designed to operate at 16.67 l/min, is cylindrically symmetrical, and utilizes an acceleration jet issuing into an impaction chamber as the main fractionating device (Andersen Samplers, Inc., 1985).

PM_{10} inlets designed and manufactured by two different companies, Sierra-Andersen and Wedding and Associates, have been the subject of controversy recently. Most of this controversy centers around the high volume inlets. Each designer has presented arguments and data (Wedding et al., 1985; McFarland and Ortiz, 1985a, 1985b, 1985c, 1985d, 1985e; Wedding et al., 1986; Rodes et al., 1985) identifying weaknesses of the other's inlet.

The cut-point of the Wedding hivol inlet has been said to decrease with time, and that after the equivalent of four months' exposure at 60 $\mu g/m^3$ PM_{10} concentration, the 50 percent cut-point of the Wedding inlet is reduced to 6.6 μm (McFarland and Ortiz, 1985a, 1985b). McFarland and Ortiz (1985b) suggest that this shift in cut-point is due to the buildup of particles in the central, oil-coated duct of the Wedding inlet, which acts as the barrel of a cyclone separator. Such deposits were observed and cut-point shifts were inferred during the four-city ambient sampling program described by Rodes et al. (1985). One of the participating Wedding inlets examined following this study was found by Ranade and Kashdan (1984a, 1984b, 1984c) to exhibit a D_{50} of 6.6 μm.

Wedding et al. (1985a) have responded to this criticism by reanalyzing data from the four-cities study (Rodes et al., 1985). They

assert that PM_{10}/TSP ratios for the Wedding inlet are reasonably consistent with time, and that no significant cut-point shift, beyond perhaps 0.5 μm, is indicated. Furthermore, referring to the inlet tested by Ranade and Kashdan (1984), Wedding (1985) states:

> "---We have in our possession and have tested the inlet utilized by EPA at the Phoenix II study and found effectively no change in cut-point, certainly not the 3μm value as published by RTI (Ranade and Kashdan). These tests were performed during a site visit by Dr. Ranade of RTI.---"

Wedding et al. (1985b) found that solid aerosol particles much larger than D_{50} penetrated an SA-321A inlet by the mechanism of particle bounce. The pass-through of particles much larger than D_{50}, in the SA-321A, is hypothesized to be due to an erosion-saltation process within the inlet (Wedding, 1985). In the course of the four-cities study, Rodes et al. (1985) observed that "the SA-321A inlet was added in Rubidoux [to correct an apparent dry-particle bounce problem in the SA-321]." (The SA-321 uses a single stage of particle classification jets, while the SA-321A incorporates two stages.)

Additionally, Miller et al. (1985), reporting the results of an intercomparison in Ohio sponsored by the American Iron and Steel Institute, found evidence of 80 μm particles in microscopic examination of filters exposed using the SA-321A inlet. McFarland and Ortiz (1985c) cite field tests of collocated SA-321A inlets, using oiled surfaces in one of the units to preclude particle bounce, which show no evidence of particle bounce in the un-oiled sampler and the potential collection of particles less than 10 μm, which should pass through to the filter, in the oiled inlet.

Whatever the physical mechanisms responsible, comparisons of SA-321A and Wedding high volume inlets collocated in ambient sampling usually show that aerosol mass loadings derived from the SA-321A sampler exceed those derived from the Wedding inlet. Sweitzer (1985), summarizing 32 sampling days in Granite City, IL, an industrialized area, found the difference in mass concentration to be about 15% in favor of the SA-321A. Rodes et al. (1985) calculated linear regression coefficients of the SA-321A data onto the Wedding inlet data. For the only two cities where the SA-321A measurements were available, Rubidoux and Phoenix, the regression slopes (SA-321A/Wedding) were 1.02 and 1.30, respectively. Only seven pairs of measurements were available in Rubidoux and only eleven pairs were available in Phoenix, and broad conclusions are not justified based on such limited data. Other intercomparisons of PM_{10} inlets are reported by Mathai et al. (1985) and Honcoop (1985a,b). Other than this, very little independent testing data is available.

Wind tunnel investigations have not always produced comparable effectiveness curves under low wind speed and clean inlet conditions. Wedding shows the SA-321A oversampling at various wind speeds (e.g., Wedding et al., 1985b). McFarland and Ortiz (1985a, 1985b), and Ranade and

Kashdan (1984) show substantial D_{50} shifts of the Wedding high volume PM_{10} inlet after a few weeks of ambient sampling.

A recent intercomparison by Purdue et al. (1986) used various combinations of greased and ungreased impaction surfaces and cleaned and uncleaned inlets. The SA-321A yielded up to 15% higher PM_{10} concentrations when compared to samples taken through the Wedding inlet, even when both samplers were clean and greased.

More than ever, the recommendations of Watson et al. (1981b) should be heeded, that "Present wind tunnel testing of inlets provides useful comparisons of [sampling] effectiveness. It is not certain that all such tests are equivalent. Standardized methods of evaluating [sampling] effectiveness and efficiencies should be devised and applied to all samplers used for evaluating compliance with a standard."

The 17 l/min and 113 l/min inlets have not undergone such detailed scrutiny, though their sampling effectiveness curves measured in the two wind tunnels are much more similar than those of the 1132 l/min inlets.

Several types of sampling devices have been developed to sample fine particles in the 0 to 2.5 μm size range. These devices differ from one another with respect to their specified flow rates, steepness of sampling effectiveness curves, degree of characterization, operating principle, and commercial availability. These size-selective sampling inlets and their relevant features are:

- **Sierra-Andersen Slotted Impactor**. This cascade impactor operates at 1132 l/min and has well defined size cuts, one of which is in the neighborhood of 2.5 μm (Willeke, 1975). It requires slotted fiber filters between stages, though it has been used in a single stage mode to sample fine particles on 8 x 10 in. filters (Watson, 1979). These impactors are commercially available, but they are expensive.

- **Bendix Unico 240 Cyclone**. This cyclone has been shown to have a sharp cut-point at 2.5 μm (Chan and Lippman, 1977; Mueller et al., 1983) in laboratory tests and operates at 113 l/min. It is the most widely used of fine particle cyclones, having seen service in the Sulfate Regional Experiment (SURE), Portland Aerosol Characterization Study (PACS), Western Regional Air Quality Study (WRAQS), Sub-Regional Cooperative Electrical Utility, National Park Service, Environmental Protection Agency Study (SCENES), State of Nevada Air Pollution Study (SNAPS), South Coast Air Quality Study (SCAQS), California Acid Deposition Monitoring Program (CADMP), and many other aerosol studies. These cyclones are commercially available at a cost of a few hundred dollars apiece.

- **Bendix Unico 18 Cyclone**. This cyclone has a sharp cut-point at 2.5 μm as measured by Chan and Lippman (1977). It operates at 18 l/min and is slightly less costly than the Bendix Unico 240.

- **Air Industrial Hygiene Laboratory (AIHL) Cyclone**. This cyclone was developed by Dr. Walter John of the Air Industrial Hygiene Laboratory to operate at 22 l/min (John and Reischl, 1978). It has a sharp cut-point near 2.5 μm as shown in laboratory tests. It is not currently manufactured commercially, though it has been used in the Research on Operational Limiting Visual Environment (RESOLVE) visibility study, the Interagency Monitoring and Protected Visual Environment (IMPROVE) visibility network, and the SCAQS.

- **Virtual Impactor**. The most commonly used virtual impactor is the Sierra-Andersen 241 (also in 244 and 245 models). This design has a sharp cut-point at 2.5 μm with flow rates of 15 l/min through the fine particle filter (Mueller et al., 1983). Virtual impactors are commercially available, but they are very expensive. Both fine and coarse samples have been measured with these units in many programs, including EPA's Inhalable Particulate Network (Watson et al., 1981b), the Harvard Air Pollution Respiratory Health Study (Chow and Spengler, 1986), and the ARB dichotomous sampler network (Watson et al., 1987).

- **Stacked Filter Unit**. Large pore Nuclepore filters have been placed in series to eliminate particles larger than 2 or 3 μm in diameter (Cahill et al., 1979; Heidam, 1981). The sampling effectiveness curve is very broad at 10 l/min. These units have been used in numerous studies in California and in the Western Fine Particle Network by researchers at the University of California at Davis. This unit can be constructed from Nuclepore filters and Nuclepore filter holders.

A recent intercomparison study (Mathai et al., 1985) compared fine particle measurements from the virtual impactor, the AIHL Cyclone, and the Bendix Unico 240 cyclone. Concentrations measured with each inlet appeared to be comparable for simultaneous samples.

3.1.2 Volumetric Measurement

Four general methods of sampler air flow control are used in air quality samples: 1) manual volumetric; 2) automatic mass; 3) differential pressure; and 4) critical orifice.

- **Manual Flow Control**. Manual control is accomplished when the operator initializes a setting, such as a valve adjustment, and then relies on the known and constant functioning of sampler components, such as pumps, to maintain volumetric flows within

specifications. Manual flow settings generally change over a sampling period as the collection substrate loads up and presents a higher pressure drop.

- **Automatic Mass Flow Control.** Mass flow controllers employ thermal anemometers to measure the heat transfer between two points in the gas stream. To a first approximation, the heat transfer is proportional to the flux of gas molecules between the two points, and hence the mass flow controller is able to sense the flux of mass. The feedback signal from the mass flow controller is then used to modulate the rotation rate of an air mover such as a hivol blower. Mass flow controllers require compensating circuitry to avoid errors due to absolute temperature variations of the gas itself as well as the controller sensing probe. Wedding (1985) observes that the size-selective properties of inlets require the consistency of volumetric, rather than mass, flow properties of the atmosphere. Wedding estimates potential differences in excess of 10% between mass and volumetric measurements of flow rates.

- **Differential Pressure Volumetric Flow Control.** Constant pressure is maintained across an orifice (usually a ball valve which can be adjusted for a specified flow rate) by a diaphragm-controlled valve located between the filter and the orifice. The diaphragm is controlled by the pressure between the orifice and the pump. When this pressure increases (as it does when filters load up), the diaphragm opens the valve and allows more air to pass. Variations on this type of flow control are used in the Sierra-Andersen 244 dichotomous sampler, the old MISCO high volume samplers, and the RESOLVE particle sampler.

- **Critical Orifice.** A critical orifice consists of a small circular opening between the filter and the pump. When the downstream pressure at the minimum flow area downstream of the orifice is less than 53% of the upstream pressure, the air velocity attains the speed of sound and it will not increase, regardless of changes in pressure. Critical orifices provide very stable flow rates, but they require large pumps and low flow rates (typically less than 20 l/min with commonly available pumps) to maintain the high pressure differences. Wedding et al. (1986) report a diffuser arrangement which allows recovery of over 90% of the energy which is normally expended in back pressure behind a critical orifice. This design allows higher flow rates to be obtained with a given pump.

Most filter samplers rely on setting and maintaining a specified volumetric flow rate because the cut-points of size-selective inlets, and other operational physics of the sampler, are often designed for specified velocities of the sample gas stream. Some concentration differences are

therefore inevitable because ambient temperatures and pressure changes vary between settings, and these affect the flow rates and the flow controllers.

In the case of a perfect mass flow controller, as temperatures rise above the set point temperatures, this device accelerates the sampler's air mover (such as the blower on a hivol) to achieve a constant air mass flux as air density decreases. The true volumetric flow becomes larger than the assumed flow. As ambient temperatures fall below the set-point temperature, the mass flow controller decelerates the air mover and the volumetric flow is less than that which is assumed.

Wedding et al. (1985) calculated a 26.6% discrepancy between true volumetric and assumed volumetric flow rates in an example case involving a temperature change of 126°F and a pressure change of 20 inches H_2O. Differences of 4% to 11% in PM_{10} can result from infrequent flow controller setting for a sampler located at a desert site with plausibly large seasonal and diurnal temperature and pressure fluctuations.

A mass flow controller should be set at some temperature between the extremes, i.e., mid-morning or twilight, in which case the difference between mass-flow controlled and true volumetric flow rates is significantly reduced. At least a seasonal re-adjustment is prudent. A 5% flow rate bias does not significantly affect the inlet cut-point, but it can bias the PM_{10} concentration in a positive or negative direction by the same percentage.

3.1.3 Measurement Interferences

PM_{10} samplers are subject to systematic biases caused by specific physical mechanisms which constitute interferences in the measurement process. These include the following:

- **Passive Deposition.** Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling. Positive biases of approximately 10 to 15% have been found with peaked roof inlets (Bruckman and Rubino, 1976) on TSP samplers. Studies for other inlets are insufficient for quantification. This interference can be minimized by shortening the passive period or by using commercially available covers which protect the filter until air flow starts.

- **Inlet Loading and Re-entrainment.** Material collected in size-selective inlets can become re-entrained in the sample flow. Controlled studies are insufficient to quantify this interference. It can be minimized by greasing or oiling inlet impaction surfaces, though this may change the size-selective properties. A better approach is to disassemble and clean inlets on a regular basis.

- **Recirculation.** Recirculation occurs when the blower exhaust, which contains carbon and copper particles from the armature

and brushes, is entrained in the sampled air. Positive biases of 0.15 $\mu g/m^3$ have been measured (Countess, 1974) which are insignificant mass interferences but which may affect carbon and copper measurements. Copper and elemental carbon levels as high as 20 $\mu g/m^3$ have been found just prior to blower failure, however. Recirculation can be minimized by assuring a tight seal between the blower and the sampler housing or by ducting blower exhaust away from the sampler. Blowers should be serviced or replaced on a regular schedule.

- **Filter Artifact Formation.** Sulfur dioxide, nitrogen oxides, nitric acid and organic vapors can be absorbed on the filter media along with the suspended particles, thereby causing positive biases. Samples taken in the presence of high SO_2 concentrations have been shown to yield up to 10 $\mu g/m^3$ of excess sulfate on glass fiber filters (Appel et al., 1984). Quartz, Teflon membrane, and Teflon-coated glass fiber filters have been shown to minimize NO_x and SO_2 absorption and denuder inlets have been used to minimize nitric acid absorption. Very little information is currently available regarding organic artifacts.

- **Filter Conditioning.** Filter conditioning environments can result in different mass measurements as a function of relative humidity (RH). Soluble particles take on substantial quantities of water as RH increases, especially above the deliquescent point of 70% RH. Increased mass deposits of 50% or more have been observed as RH increases to 100% (Tierney and Connor, 1967). The hysteresis effect as RH decreases does not assure a constant mass measurement unless samples are equilibrated at an RH of less than 30% prior to and after exposure. EPA procedures call for 20 to 45 $\pm$5% RH during equilibration. Twenty-four hours at constant RH is considered adequate for sample equilibration.

- **Filter Integrity.** Filter integrity is compromised by handling which causes some of the filter to be lost after the pre-exposure weighing. This result is a negative bias to the mass deposit. Quartz filters are the most prone to loss of material while Teflon membrane filters retain their integrity with normal handling (Rehme et al., 1984). Filters can be loaded into a filter cassette in the laboratory for transport to the field to minimize losses of the filter material.

- **Particle Loss During Transport.** Particle loss during transport occurs when filters are heavily loaded with large, dry aerosols (Dzubay and Barbour, 1983). It is more prevalent on membrane than on fiber filters. Particle loss is minimized by shorter sample duration in heavily polluted environments, use of fiber as opposed to membrane filters, folding the filter during transport, and careful shipping procedures. Oiling the

surfaces of Teflon filters prior to sampling has also been attempted.

3.1.4 PM_{10} Measurement Precision

Measurement precision is determined by both error propagation of the mass and volume uncertainties (Watson et al., 1983a) and by collocated sampling. Though the propagated precisions do not necessarily include all of the sources of measurement uncertainty, they can be determined for each sampling site from routine performance test data, while collocated sampling can only be performed at a few sites.

McKee et al. (1972) conducted a hivol sampling collaborative testing program with 12 laboratory groups participating. The mean coefficient of variation of the results from 11 of the 12 groups (the results from one group were deemed outliers) was 3.8% for particulate matter concentrations in the 70 to 140 $\mu g/m^3$ range. The mean coefficient of variation of mass measurements made with two collocated standard hivol samplers in another study (Shaw et al., 1983) was 4.1% in the 50 to 180 $\mu g/m^3$ range.

Shaw et al. (1983) compared Beckman dichotomous samplers and concluded: "...over a broad mass range, fine fraction aerosol mass can be collected using the standard commercial inlets with a reproducibility of 5% or better. Coarse fraction aerosol mass can be collected with a reproducibility of 10% or better except for very light mass loadings (less than 200 μg). Fine and coarse masses can be collected with a reproducibility of 5% or better." They found that the mass measurement precision dominates the precision attainable below approximately 200 μg (or 8 $\mu g/m^3$) loadings.

Watson et al. (1981b) examined collocated hivol and PM_{15} sampler data from various sites in EPA's Inhalable Particulate Network. They found:

- 80% of all hivol measurements were within $\pm$ 10% and all were within $\pm$ 20% of each other.

- 53% of dichotomous sampler with 2.5 to 15 μm measurements were within $\pm$ 10%, 87% were within $\pm$ 20%, and all were within $\pm$ 30% of each other. These larger differences may reflect some of the filter handling losses discusses in Section 3.1.3.

- 80% of the dichotomous sampler with 0 to 2.5 μm measurements were within $\pm$ 10%, 93% were within $\pm$ 20%, and all were within $\pm$ 30% of each other.

- 60% of the dichotomous sampler PM_{15} measurements were within $\pm$ 10%, 93% were within $\pm$ 20% and all were within $\pm$ 30% of each other.

- Hivol size-selective samplers exhibited an average difference of 4.5%.

Rodes et al. (1985) found "...the precision of the majority of PM_{10} samplers and measurement fractions is within ± 10%."

It appears that precision required by EPA can be accommodated by most PM_{10} samplers. It is also clear that several of the potential biases reported previously may exceed this uncertainty and could have a significant effect on PM_{10} measurement comparability. These precisions must be estimated by collocated sampling or by error propagation to accompany all chemical concentrations determined from PM_{10} samples. These precision estimates are essential input data to the CMB model.

3.1.5 Potential Differences Among PM_{10} Sampling Methods

Table 3.1-2 summarizes the factors which could cause differences among PM_{10} measurements and which could occur within the constraints of the EPA Reference Method. In all cases, the magnitude of these biases depends on environmental as well as sampler variables. Where possible, quantitative estimates of the range of PM_{10} gain or loss have been given. These values are intended only to provide an order-of-magnitude estimate. In some cases (e.g., pump exhaust recirculation and filter integrity) these biases may not be considered significant. In other cases, theoretical and experimental data are insufficient to provide an estimate.

The differences listed in Table 3.1-2 do not necessarily add linearly. For example, the relative biases of flow rate, altitude and inlet are multiplicative rather than additive. Some factors are also speculative. For example, the effect of "dirt" in inlets is still controversial and the maximum bias reported in Table 3.1-2 (due to reduction of the inlets' D_{50} by whatever cause) may be found to be over-estimated when this controversy is resolved. The effects of these measurement uncertainties on model results is not quantified at this time.

3.1.6 Existing PM_{10} Sampling Systems

Several filter sampling systems have been developed for research studies and the determination of compliance with air pollution standards. These systems combine size-selective inlets with filter handling systems and flow movers. Some of these instruments can accommodate more than one particle size range, different filter media and gaseous absorbing substrates. These samplers represent not only potential hardware for PM_{10} measurements, they also provide evidence of proven technologies which might be combined to better meet PM_{10} measurement needs. Several of these samplers have sequential features which automatically switch samples at pre-determined intervals.

- **Wedding and Associates High Volume Sampler.** This sampler uses a Wedding high volume PM_{10} inlet with sonic choking volumetric flow control. It samples on an 8" x 10" fiber filter at 1132 l/min.

Table 3.1-2

Potential Differences Among Different PM_{10} Measurement Methods

Bias	Might Depend On	Potential Differences[a] Relative[b]	Absolute[b] ($\mu g/m^3$)
1. Sampling Efficiency	o Ambient particle size distribution (Rubidoux assumed). o Wind tunnel test method. o Dirt in inlet. o Wind speed. o Inlet geometry. o Oiling of impaction surfaces.	± 15%	± 30
2. Mass Flow Control	o Pressure and temperature differences between set-time and sampling time. o Ambient temperature and pressure variations over sampling period.	-10% to +10%	-20 to +20
3. Passive Deposition	o Wind speed. o Large particle loading. o Filter orientation.	unknown	unknown
4. Re-entrainment	o Sampling time between inlet cleaning. o Ambient large particle loading.	unknown	unknown
5. Pump Exhaust Recirculation	o Type of pump. o Filtration or ducting. o Pump wear and maintenance	0 to 10%	+0.2 to 20

Table 3.1-2 (continued)

Potential Differences Among Different PM_{10} Measurement Methods

Bias	Might Depend On	Potential Differences[a] Relative[b]	Absolute[b] ($\mu g/m^3$)
6. Filter Artifact	o Filter alkalinity. o Filter type. o Ambient gas and particle constituents.	unknown	unknown
7. Volatilization	o Atmospheric gas and particle compositions. o Face velocity. o Filter medium. o Temperature history.	-0.35% to	-0.7 to
8. Filter Equilibration	o Fraction of soluble aerosol (assume 20 $\mu g/m^3$ of NH_4SO_4). o Relative humidity at time of sampling. o RH between sampling and equilibration. o Equilibration RH.	0% to +10%	0 to +20
9. Filter Integrity	o Filter type. o Handling.	-1.5% to 0%	-3 to 0
10. Filter Handling	o Sample loading. o Size fraction, 2.5-10 μm (coarse) (assume 50% of PM_{10} coarse). o Filter type (Teflon).	-15% to 0%	-30 to 0

Table 3.1-2 (continued)

Potential Differences Among Different PM_{10} Measurement Methods

Bias	Might Depend On	Potential Differences[a] Relative[b]	Absolute[b] ($\mu g/m^3$)
11. Volume Correction to Standard	o Elevation of sampling site	0 to +25%	0 to +50 $\mu g/m^3$

[a] Assumes a high PM_{10} concentration of 200 $\mu g/m^3$ typical of Rubidoux, CA.

[b] Based on theoretical and empirical evidence presented in Watson and Rogers (1986) for a 200 $\mu g/m^3$ PM_{10} measurement at Rubidoux, CA.

- **Sierra-Andersen High Volume Sampler.** This sampler uses an SA-321A or SA-1200 high volume PM_{10} inlet with either hot-wire anemometric mass flow control or sonic choking volumetric flow control. It samples on an 8" x 10" fiber filter at 1132 l/min. The mass-flow controlled version of this sampler with ungreased SA-321A inlets (10.2 μm cut-point) is currently being used in ARB's compliance sampling network.

- **Sierra-Andersen Series 240 Dichotomous Samplers.** This sampler operates at 16.7 l/min and uses an SA-246 PM_{10} inlet and a virtual impactor $PM_{2.5}$ inlet. It samples on 37 mm filters in fine and coarse particle size ranges. Ten percent of fine particles deposit on the coarse filter, and corrections must be made. The Model SA-245 can switch among up to 20 pairs of samples without operator intervention. Flow rates are controlled by a differential pressure regulator. These units are produced commercially and are used with Teflon membrane substrates in ARB's dichotomous sampler network.

- **Wedding 2x4 Sampler.** This sampler was developed for the RESOLVE visibility program (Trijonis et al., 1987) and consists of two separate units which sample three separate $PM_{2.5}$ samples through John cyclones at 22 l/min and one PM_{10} sample through a Wedding low volume inlet at 18 l/min. Up to six sequential samples may be taken without operator intervention, and fine particle samples may be taken on up to three different media. Seven of these samplers were constructed and they are currently deployed in the California Desert. Differential pressure regulators are used to maintain automatic flow control.

- **WRAQS Samplers.** AeroVironment developed the WRAQS sampler for EPRI's Western Regional Air Quality Studies (Tombach et al., 1987). The most recent version of this sampler involves drawing air through an SA-320 high volume inlet (with a 15 μm cut-point) with a high volume sampler blower. Samples are drawn isokinetically from the airstream onto filters or through Bendix 240 cyclones at 113 l/min. Various medium and low volume sample lines can be drawn from the high volume flow to obtain samples on several filter media in different size ranges. Each sample is drawn by a separate Sierra-Andersen mass-flow-controlled carbon vane pump. Samples are changed manually. Eleven of these samplers were originally constructed and two are still in use in the SCENES (Mueller et al., 1986) program.

- **ERT Sequential Filter Sampler.** Environmental Research and Technology, Inc., designed and built this sampler for the PACs (Watson, 1979) and SURE (Mueller and Hidy, 1983) studies. It consists of a plenum to which a medium or low volume size-selective inlet is attached. Up to 12 sampling ports controlled by solenoid valves accept filters which have been

pre-loaded into Nuclepore filter holders. A timer and stepper switch sequence the filters for unattended operation. Two or more filter media can sample simultaneously by dividing the flow. The RESOLVE differential pressure volumetric flow controller has been adapted to split the flow between filters and maintain a constant flow rate despite filter loading (Chow et al., 1986b). Forty-one of these samplers were originally manufactured for the PACS, SURE, and Denver Winter Haze programs, and 20 of them are still in operation today with a variety of configurations. Oregon and Nevada have equipped the sequential filter sampler with SA-254 PM_{10} inlets for PM_{10} monitoring.

- **Size Classifying Isokinetic Sequential Aerosol Sampler (SCISAS).** The SCISAS, developed at DRI, combines elements of the WRAQS sampler and the Sequential Filter Sampler to provide for up to six sequential samples in two size ranges on two filter media (Rogers et al., 1984). Air is drawn through a SA-320 (PM_{15}) inlet into a 10-inch stack from which each sample is drawn directly onto a filter or through a Bendix 240 cyclone. A Chrontrol timer allows programming of sample start and stop times and sample duration via activating or deactivating solenoid valves in the sample lines. The SCISAS pulls air through the filters with a GAST 1022 carbon vane pump attached to each filter. The current manual flow control can be replaced with the RESOLVE differential pressure system of the 2x4 or with the mass flow controlled Sierra-Andersen carbon vane pumps. Seven SCISAS of various configurations are currently operating at seven SCENES sampling sites.

- **SCAQMD/CIT Acid Aerosol Sampler.** The California Institute of Technology (CIT) has taken gaseous and acidic gas measurements at seven sites in the SoCAB using a system designed by Dr. Glen Cass. In this system, fine particles are collected after passage through an AIHL cyclone and PM_{10} is collected through an SA-246 inlet. Flows are split into parallel paths to collect PM_{10} and $PM_{2.5}$ on one quartz and two Teflon membrane filters. A make-up flow in the fine particle sample is drawn through a nylon filter, an LiOH-impregnated filter, and a denuder tube prior to presentation to parallel Nylon and LiOH-impregnated filters. Flow rates are controlled with critical orifices. This system provides for gaseous as well as particulate species sampling and analysis.

- **South Coast Air Quality Study (SCAQS) Sampler.** AeroVironment developed the SCAQS sampler for the measurement of chemically-speciated PM_{10}, $PM_{2.5}$ and gaseous constituents as part of the SCAQS field experiment. This sampler is similar to the SCAQMD/CIT sampler. PM_{10} is sampled on one quartz and two Teflon filters through an SA-254 inlet while a similar set of $PM_{2.5}$ samples is obtained through a Bendix 240 cyclone. A parallel sampling system draws air through a Teflon-coated AIHL

cyclone and through a set of denuders and impregnated filters to quantify the gas and particle phases of labile compounds. Flow rates are controlled by critical orifices.

The 2x4, WRAQS, and SCISAS samplers were recently compared with each other and were found to return similar measurements for fine particles (Mathai et al., 1985). The WRAQS and SCISAS were equipped with SA-320 inlets and returned virtually identical PM_{15} measurements. The 2x4 used a PM_{10} inlet, so it collected a lower mass concentration than the other samplers.

These samplers illustrate the features which are desirable in a PM_{10} sampling system for use with Level I and Level II PM_{10} assessments: 1) existing and proven hardware; 2) gaseous as well as particulate capabilities; 3) ample flow rates for 24-hour samples; 4) automatic flow control; 5) multi-substrate capabilities; 6) proven sample handling and changing methods; 7) sequential sample switching; and 8) reasonable cost. None of these samplers by itself possesses all of these qualities. Several of these systems have been used to acquire PM_{10} data in California.

3.2 PM_{10} Source Sampling

Receptor models require the chemical composition of emissions from contributing sources (Watson, 1984). These "source profiles," the percent of each chemical species in emitted particulate matter, are especially difficult to obtain for fugitive and area sources because no single emitter is representative of the entire population of emitters. Storage piles, materials handling, street dust, residential heating, wood and waste burning, motor vehicle, as well as many industrial emissions need to be characterized to provide input data to the PCA and CMB models. This section identifies different source sampling methods (Chow et al., 1986a; Gordon et al., 1984). In each case, emitted particulate matter is collected on substrates which are then submitted to chemical analyses.

The ideal source sampling method would allow for chemical and physical transformations of source emissions to occur prior to sample collection. Lacking this ideal, the sampling would at least quantify the precursors of the receptor profile so that a theoretically or empirically derived transformation could be applied. These transformations are discussed in Section 4, and only the measurement aspects of source characterization are treated here. Methods used to sample source emissions in receptor model studies include: 1) hot exhaust sampling; 2) diluted exhaust sampling; 3) plume sampling from airborne platforms; 4) ground-based sampling of single-source dominated air; and 5) grab sampling and resuspension.

3.2.1 Hot Exhaust Sampling

Hot exhaust sampling is well established for determining the emission rates of criteria pollutants, including suspended particulate matter. These

samples are not taken on substrates amenable to extensive analysis nor are they generally size-specific. Components of these compliance-oriented methods have been incorporated into other exhaust sampling procedures. Hot exhaust sampling does not necessarily provide a chemical speciation representative of the source profile perceived at the receptor because it does not account for transformations which take place when the emissions cool. Several sources must be tested to obtain a composite profile of a source type.

3.2.2 Diluted Exhaust Sampling

Dilution samples draw hot exhaust gases into a chamber where they are mixed with filtered ambient air. After a few minutes of aging, the particles are drawn through a size-selective inlet and onto the substrates. Multiple substrates for different chemical analyses are obtained simultaneously or via sequential sampling of the same gas stream. Houck et al. (1982a) have developed such a system which draws the diluted sample through a virtual impactor to provide particle size fractionation. McCain and Williamson (1984) performed tests on this sampler which showed losses of large particles owing to inertial impaction and electrostatic charging. They recommended design changes to minimize these losses. Harris (1986), Huynh et al. (1984), Heinsohn et al. (1980), Stiles (1983), and Cooke et al. (1984) offer variations of the same principle. Rau and Huntzicker (1985) used the natural dilution of ambient air to sample woodstove effluents.

None of these samplers has been adequately examined theoretically with respect to: 1) sampling efficiencies; 2) required dilution ratios and residence times to attain an ambient equilibrium; and 3) their ability to measure the full range of particle sizes, chemical constituents, and precursor gases which would be needed to estimate the fractionation of source profiles between source and receptor. Each current design is optimized to sample only certain species, and there is currently no method which is capable of obtaining simultaneous samples which are amenable to analyses for all of the species and precursor gases needed for receptor modeling.

Developmental work is needed to combine the best elements to these dilution samplers. While dilution sampling provides a better source profile for individual sources, it still requires many single-source tests to represent a large number of individual sources and requires ducted emissions.

3.2.3 Airborne Sampling

Source sampling from airborne platforms to characterize the chemical and physical properties of emissions has been performed from airplanes (Small et al., 1981; Richards et al., 1981, 1985), tethered balloons (Armstrong et al., 1981) and helicopters. It has also been proposed that model airplanes be used to carry ultra-light sampling payloads.

Sampling components of appropriate weight and packaging are elevated above the emissions, usually on the order of 100 to 500 meters, to draw samples of the effluent. All of the approaches to airborne sampling are unestablished, lacking widely scrutinized and accepted standard operating procedures and intercomparison results.

The major advantage of airborne sampling for source characterization is that source profile fractionating might be determined if the sample can be taken at a time after emission (i.e., distance) sufficient to have allowed transformation to take place. The drawbacks of airborne plume sampling are:

- It is difficult to know when the sampler is in the plume and when it is in ambient air. SO_2 monitors, condensation nucleus counters and nephelometers are often used in aircraft to detect plume constituents which differentiate the plume from background air. Such sensors are heavy, however, and can only be used on aircraft. Many sources do not emit such unique species.

- It is difficult to stay in the plume long enough to obtain a sample. For fixed platforms, such as helicopters or balloons, the plume wanders away from the sampling position. Airplanes must always keep moving, so a plume cross-section can only be sampled for a few minutes at a time. High volume, size-resolved samples (Soloman et al., 1983) may be able to alleviate this limitation to some extent.

- Ambient air mixes with the plume, so the source profile is really a combination of emissions and ambient air. This is especially true at large distances from the emission point, and this mixing negates the major advantage of obtaining fractionated source profiles if adequate corrections cannot be made. Upwind values of the background concentrations can be subtracted from plume measurements, but the uncertainty introduced by this process has not been assessed.

Development efforts required for airborne sampling are: 1) design, construction, and testing of very light sampler payloads; 2) feasibility testing of balloon- and drone-borne samplers; and 3) evaluation of past aircraft data to determine whether or not fractionated source profiles can be corrected for mixing with ambient air. Airborne sampling is most applicable to forest fires, large dust storms, and tall smokestack emissions. Balloon or model aircraft sampling might be useful above roof monitors over storage piles and transfer facilities.

3.2.4 Ground-Based Source Sampling

Ground-based source sampling is identical to receptor sampling, but it is applied in situations for which the air being sampled is known to be dominated by emissions from a given source. The requirements of this

method are: 1) meteorological conditions and sampling times conducive to domination by a particular source; 2) samples short enough to take advantage of those conditions; and 3) a minimum of other interfering source contributions. Pierson and Brachaczek (1983) and Hering et al. (1984) have characterized motor vehicles in tunnels. Rheingrover and Gordon (1980) characterized several point sources using ambient virtual impactor measurements when the sampling was downwind of the source. Chow et al. (1986b) propose characterizing wood-smoke source by sampling in a community with few industrial sources on cold winter nights with low inversions when traffic is at its lowest.

Chow (1985) examined the effects of an elevated coal-fired power plant emission on ground-based samples in a rural environment. She could identify the presence of the plume from corresponding SO_2 and wind direction measurements, but she could not discern other chemical concentrations contributed by the power plant owing to an overwhelming abundance of geological material in her 24-hour sample. This method may be much better for fugitive and area sources, however, because their influence is more constant over time.

The advantages of ground-based sampling are: 1) it is representative of fractionated (presuming transformations are complete) and composite (for area sources such as home heating, motor vehicles, and resuspended dust) source profiles; 2) it is relatively economical; and 3) it is compatible with other receptor samples. The disadvantages are: 1) sampling times may be too short to obtain an adequate deposit; and 2) contributions from other source types interfere with the source profile.

Developmental work requires simultaneous ground-based sampling with diluted exhaust sampling and measurements of more unique species to determine whether or not this is a viable alternative.

3.2.5 Grab Sampling

Grab sampling involves: 1) removal of a precipitated residue or precursor of the emissions; 2) resuspension and sampling onto substrates through size-selective inlets; and 3) analysis for the selected species. A simple sample swept, shoveled, or vacuumed from a storage pile, transfer system, or roadbed can be taken to represent these source types. Five to ten different samples from the same source are averaged to obtain a representative source profile. This method is semi-established, or at least as established as the chemical and physical analyses applied to it, because procedures are widely accepted and results are reproducible within a method, though not necessarily among methods (Chow et al., 1982).

The main advantages of this method are that it is simple, reliable, and relatively inexpensive. The major disadvantage is that the residue does not necessarily possess the same source profile or the same size distribution as the particulate emissions to the atmosphere. There may, however, be an adequately consistent relationship between the residue source profile and the emissions source profile. If such a relationship

exists, then expensive dilution samples and airborne plume samples might be required only intermittently to confirm it, while relatively frequent and inexpensive grab samples could be taken to apply it.

Developmental work is needed to re-examine past data in which both exhaust and grab samples have been taken, as well as inclusion of these measurements in future source testing studies. The exhaust and residue profiles should be correlated with each other to determine whether or not a constant relationship exists between them and, if so, the form of that relationship.

3.2.6 Source Sampling Conclusions

No single source sampling method is adequate for every source type. Grab sampling is best suited for materials handling, tilling, and resuspended road dust. Airborne or ground-based sampling is best suited for large fires and dust storms. Ground-based sampling in tunnels is most suitable for motor vehicle emissions, though these values should be compared with diluted exhaust sampling of individual vehicle emissions to eliminate road dust contributions. Residential heating by oil, gas or wood burning should be characterized by ambient sampling under cold, stable meteorological conditions at times and places for which other source influences are negligible. These profiles should be compared with those obtained from diluted exhaust sampling.

A Level I PM_{10} assessment normally uses source profiles which have been measured by one or more of these methods, but at sources which are not representative of the study area. The Level I assessment will identify those source profiles which are in need of better characterization (Pace and Watson, 1987), and a combination of the methods described here can be directed toward this additional sampling.

3.3 PM_{10} Sample Analysis

This section describes the alternatives for chemical analyses of PM_{10} source and receptor samples which can be used to provide input data to the PCA and CMB receptor models. It identifies the options which must be considered with respect to sampling substrates, mass, elemental, ion and carbon analyses. Many other chemical and physical properties can be characterized to determine source contributions, but these are only appropriate for a Level III assessment. Table 3.3-1 summarizes the observables, measurement alternatives, precisions, accuracies, lower quantifiable limits and interferences of chemical analyses available for Level I and Level II source assessment.

Table 3.3-1

LABORATORY ANALYSIS METHOD CHARACTERISTICS

Observable	Measurement Method	Typical Ambient Concentration Range	Precision[a]	Accuracy[b]	LQL[c]	Interferences
1. Suspended Particulate Mass[d]	a. Electrobalance	5-300[e]	10 μg (1)	10 μg (1)	20 μg	Static Electricity, Filter orientation, air density changes
	b. β-Gauge	5-300[e]	20 μg	20 μg		
2. Elements in Particles	a. Atomic Absorbtion	See Table 3.3-2	2%	NA	See Table 3.3-2	Absorption lines of other elements, variable extraction efficiencies
	b. Inductively coupled Plasma Emission	See Table 3.3-2	5%	NA	See Table 3.3-2	Emission lines of other elements, variable extraction efficiencies
	c. Instrumental Neutron Activation	See Table 3.3-2	20% (3)	NA	See Table 3.3-2	Spectral interferences of other elements
	d. Proton Induced X-ray Emission (PIXE)	See Table 3.3-2	5%	20%	See Table 3.3-2	Large particle absorption for low atomic number, spectral interferences
	e. Photon Induced X-ray Fluorescence (XRF)	See Table 3.3-2	2%	NA	See Table 3.3-2	Large particle absorption for low atomic number, spectral interferences
3. Ions in Particles and Absorber Extracts	a. Automated Colorimetry	.See Table 3.3-3	~5%	~5%	See Table 3.3-3	Non-linearity at low concentration, spectral interferences
	b. Ion Chromatography	See Table 3.3-3	5%	~5%(8)	See Table 3.3-3	NA
	c. Ion selective elect de	See Table 3.3-3	5%	NA	See Table 3.3-3	NA
4. Carbonaceous Material in Particles	a. Light atten. w/temp program combustion in O_2	See Table 3.3-3	NA	NA	NA	NA
	b. HNO_3 digest. w/ pyrolysis-oxidation		NA	NA	NA	NA
	c. Step-wise thermal oxid. over HNO_2		0.2 μg/m^3 (9)	NA	0.1 μg/m^3 (9)	NA

Table 3.3-1 (continued)

LABORATORY ANALYSIS METHOD CHARACTERISTICS

(a) ± 1 standard deviation, per filter, unless otherwise specified.

(b) ± absolute error.

(c) LQL = Lower Quantifiable Limit; often determined by variability in blank analysis or minimum detectable limit - whichever is greater. Values given are per filter.

(d) Values given are for 37 mm PTFE filters having 1 mg/cm^2 real density.

(e) Assumes 24-hr sample at 113 l/min for PM_{10} and $PM_{2.5}$ mass, elements, ions and carbon. Values based on Western Fine Particle Network measurements from Aug 19 through Sep 08 at Grand Canyon (Pitchford, 1982); range of average monthly values.

(f) Numbers in parentheses refer to references below.

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3.3.1 Aerosol Sampling Filter Media

As a fiber or membrane filter is used to collect particles, the choice of filter type results from a compromise among the following filter attributes: 1) mechanical stability; 2) chemical stability; 3) particle sampling efficiency; 4) flow resistance; 5) loading capacity; 6) blank values; 7) artifact formation; 8) compatibility with analysis method; and 9) cost and availability. U.S. EPA filter requirements for PM_{10} sampling specify 0.3 μm DOP (dioctyl phthalate) sampling efficiency in excess of 99%, weight losses or gains due to mechanical or chemical instability of less than a 5 $\mu g/m^3$ equivalent, and alkalinity of less than 25 microequivalents/gm to minimize sulfur dioxide (SO_2) and nitrogen oxides (NO_x) absorption (Federal Register, 1987a). Summaries and experimental evaluations of these attributes for various filter media have been prepared (Lippman, 1983). The most commonly used filter media for atmospheric particle sampling are cellulose fiber, glass fiber, Teflon-coated glass fiber, Teflon membrane, Nuclepore, and quartz fiber. None of these materials is perfect for all purposes.

- **Cellulose fiber filters** meet requirements in most categories with the exception of sampling efficiency and water vapor artifacts. Sampling efficiencies below 50% in the submicron region have been observed, but these are highly dependent on the filter weave. Cellulose fiber is hydroscopic and requires precise relative humidity control in the filter processing environment to obtain accurate mass measurements. This substrate has low elemental blanks and is commonly used for chemical speciation of the deposit. Because this substrate is carbon-based, it is not normally used for carbon analyses.

- **Glass fiber filters** meet requirements in most categories with the exception of artifact formation and blank levels (Witz et al., 1983). Sampling efficiency is very high for all particle sizes. The high alkalinity of these substrates causes sulfur dioxide, nitrogen oxides, and gaseous nitric acid to be absorbed. Blank levels for most elements of interest are extremely high and variable. Particulate nitrate and ammonium losses have been observed when these samples are stored at room temperature for long periods, but this is probably true of deposits on all types of filter media. Glass fiber filters may exhibit volatilizable carbon artifacts.

- **Teflon-coated glass fiber filters** meet requirements in all categories except blank element and carbon levels. Though a small nitric acid artifact has been observed, it is tolerable in most situations. These filters are excellent for ion analyses but not for carbon analyses owing to their Teflon coating.

- **Teflon membrane filters** meet requirements in all categories except flow resistance and carbon blank levels. Because of their low porosity, it is not usually possible to attain the

flow rates needed by the size-selective inlets in high volume sampling, though it is possible to obtain flow rates required for lo-vol and med-vol inlets. These filters cannot be analyzed for carbon because of its presence in the filter material, though they have very low blank levels for ions and elements. Most nondestructive multi-elemental analysis methods use Teflon membrane filters. The deposit of particles on the filter surface makes these substrates especially amenable to x-ray fluorescence and proton induced x-ray emission analyses.

- **Nuclepore membrane filters** have low sampling efficiencies, even for small pore sizes (Liu and Lee, 1976; Buzzard and Bell, 1980). They have low elemental blank levels. Nuclepore filters hold an electrostatic charge (Engelbecht et al.,1980; Chow, 1985) which influences mass measurements unless substantial effort is invested in discharging them. Nuclepore filters are most appropriate for electron microscopic and elemental analyses. Ion analyses are also possible. Carbon analyses are not performed on these substrates because the filter material contains carbon.

- **Quartz fiber filters** meet requirements in most categories and have artifact properties which are significantly lower than those for glass fiber filters, though these substrates may exhibit volatilizable carbon artifacts. Trace element blank levels are too variable for most elemental analyses, though these filters are widely used for carbon analyses. The greatest drawback of quartz fiber filters is their fragility, which requires extremely careful handling for accurate mass measurements. New formulations are under development to minimize this drawback (Lundgren and Gunderson, 1975; Witz and Wendt, 1981; West, 1985; McMann, 1986). Various quartz-filter formulations have been shown to have low carbon blank levels, though there is evidence that these substrates absorb organic vapors.

- **Nylon filters** are used almost exclusively for the collection of nitric acid. These filters were not originally manufactured for this purpose, however, and there is a substantial difference between the properties of filters from different manufacturers. Nylon filters have high flow resistances, which increase rapidly with filter loading.

No single filter medium is adequate for all measurements. Simultaneous sampling on both Teflon membrane and quartz fiber filter substrate represent the most viable compromise for elemental, ionic, and carbon analyses. Most high volume samplers cannot accommodate a Teflon membrane filter owing to its large flow resistance. Medium and low volume samples are more appropriate sampling devices for use with these substrates.

3.3.2 Mass Determination Alternatives

The analytical determination of particulate matter mass concentrations collected on filters is the most widely made measurement on aerosol filter samples. Several techniques have been used to determine aerosol mass:

- Gravimetric analysis (Habibi, 1970; Lee et al., 1971).
- β-ray attenuation (Mitchell and Engdahl, 1968; Lilienfeld, 1970).
- Light scattering and light transmission (Channell and Hanna, 1963).
- Piezoelectric crystal mass monitors (Herling, 1971; Hinds, 1982).
- Thermal precipitation (Bush, 1964).

Krost et al. (1977) summarize the limitations of each of these mass measurement techniques. Only the β-ray attenuation and gravimetric analysis methods are applied to routine aerosol studies.

The β-ray attenuation (also known as β-gauge) method for the determination of aerosol mass is based on the attenuation which a β-particle spectrum undergoes when traveling through a thin-film of matter. The β-gauge consists of a β-ray source (^{174}Pm, half life, $t_{1/2}$ = 2.623 years, E_{bmax} = 224 keV), a β-ray detector, and counting electronics. It is used to measure the mass of an object between the source and the detector. The source is chosen such that β-particle emission is the predominant mode of decay. The total number of electrons transmitted through a thin, uniform foil in a continuous β-particle spectrum emanating from a radioisotope source can then be described (Jaklevic et al., 1981; Courtney et al., 1982).

The β-gauge was developed to: 1) minimize the handling of a fragile filter; 2) diminish the risk of filter contamination; and 3) facilitate the rapid measurement of samples. Limitations of β-gauge mass measurements are: 1) the filter must be oriented in exactly the same way for each mass determination; 2) changes in air density affect calibration; and 3) the devices are expensive and not commercially available.

The β-gauge has been employed in air monitoring the Regional Air Pollution Study (RAPS) and the Harvard Air Pollution Respiratory Health Study (Macias and Husar, 1976; Ferris et al., 1980; Dzubay and Barbour, 1983; Thurston et al., 1984; Chow, 1985). Several continuous β-attenuation monitors are currently being tested as equivalent methods for *in situ* PM_{10} measurements.

Husar (1974) reports a precision of $\pm$ 10 $\mu g/m^3$ for measuring aerosol concentrations of approximately 100 $\mu g/m^3$ over a one-hour interval. The precision of the β-gauge depends on counting statistics and electronic stability for calibration standards and samples. It can also be affected by misalignment of the filter (standard or sample) in the instrument. The accuracy of the results depends on the quality of the standards, the validity of the calibration procedure, particle size effects, filter substrate inhomogeneity, and the atomic number dependence of the mass absorption coefficients.

The gravimetric analysis method determines aerosol mass by weighing the filter before and after sampling with an electrobalance in a temperature and relative humidity controlled environment. Both unexposed and exposed filter samples are allowed to equilibrate for at least 24 hours in a control box before weighing. The sensitivity of the electrobalance is about $\pm$ 0.001 mg. Tolerances within $\pm$ 0.010 mg can be obtained in replicate weighings. The main interference in gravimetric analysis of filters results from electrostatic effects. Engelbrencht et al. (1980) found that residual charge on a filter could produce an electrostatic interaction between the filter on the pan and the metal casing of the electrobalance. The small electrostatic force on the pan can produce erroneous gravimetric measurements. Electrostatic charge is removed by a radioactive polonium source before sample weighing.

Feeney et al. (1984) examined the gravimetric measurement of lightly loaded membrane filters and obtained excellent precision and accuracy. Use of the electrobalance has the advantage of being relatively inexpensive, with values independent of filter orientation, laboratory air density, and the elemental composition of the particles and filter substrate.

An intercomparison study between the β-gauge and gravimetric analysis for the determination of atmospheric aerosol mass concentrations (Jaklevic et al., 1981) revealed an equivalent accuracy and precision for both techniques as they were used in that study. Courtney et al. (1982) found β-gauge and gravimetric mass measurements to differ by less than $\pm$ 5%. The precision of β-gauge measurements has been shown to be $\pm$ 5 $\mu g/cm^2$ or better for counting intervals of one minute per sample, which translates into $\pm$ 32 μg/filter for 37 mm diameter substrates. This is less precise than the $\pm$ 6 μg/filter precisions determined by gravimetric analysis using an electrobalance (Feeney et al., 1984).

Gravimetric analysis is used to measure mass concentrations in ARB's high volume and dichotomous PM_{10} sampling networks.

3.3.3 Elemental Determination Alternatives

Table 3.3-2 compares the minimum detectable limits for aerosol samples submitted to atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP/AES), instrumental neutron activation analysis (INAA), proton induced x-ray emission spectroscopy (PIXE), and x-ray fluorescence analysis (XRF). These data were taken from

Table 3.3-2

TYPICAL CONCENTRATION RANGE AND MINIMUM DETECTION LIMITS FOR PM_{10} ELEMENTAL ANALYSIS [a]

Element	Typical Ambient Concentration Range ($\mu g/m^3$)	Minimum Detectable Limit ($\mu g/m^3$)[b]				
		AAS[e]	ICP/AES[e]	INAA[f]	PIXE[g]	XRF[h]
Na	0.7 - 6.7[c]	0.0028	0.00028	0.00056	NA[i]	NA[i]
Mg	0.4 - 3.5[c]	0.00014	0.001	0.069	NA	NA
Al	1.0 - 5.0[c]	0.042	0.0028	0.00056	0.085	0.028
Si	0.08 - 0.34[d]	0.14	0.0014	0.1389[j]	0.084	0.021
P	NA	NA	0.056	NA	NA	0.024
S	0.15 - 1.06[d]	NA	0.0028	NA	0.080	0.074
Cl	0.3 - 11.2[c]	NA	NA	0.0069	0.067	0.050
K	0.3 - 1.7[c]	0.0003	0.0028	0.028	0.036	0.017
Ca	1.0 - 2.8[c]	0.0014	0.00010	0.56	0.050	0.017
Ti	NA	0.13	0.00040	0.014	0.033	0.0042
V	0.005 - 0.911[c]	0.014	0.0083	0.00030	0.032	0.0028
Cr	0.006 - 0.015[c]	0.0042	0.0014	0.042	0.031	0.0028
Mn	0.017 - 0.093[c]	0.0042	0.0010	0.000014	0.029	0.0042
Fe	0.94 - 3.38[c]	0.0069	0.0069	0.26	0.028	0.0042
Ni	0.006 - 0.067[c]	0.0069	0.0083	0.097	0.022	0.0069
Cu	0.012 - 1.5[c]	0.0028	0.0014	0.00028	0.021	0.0028
Zn	0.097 - 0.46[c]	0.0028	0.0028	0.014	0.018	0.0028
Se	NA	0.14	0.042	0.0014	0.042	0.0028
Br	0.2 - 1.2[c]	NA	NA	0.00040	0.046	0.0028
Pb	0.87 - 3.9[c]	0.014	0.011	0.069[k]	0.083	0.015
As	NA	0.14	0.056	0.00070	0.032	0.0028
Sr	NA	0.014	0.000018	0.00070	0.083	0.013
Zr	NA	6.94	0.0069	0.11	NA	0.09
Mo	NA	0.042	0.0069	0.014	NA	NA
Cd	NA	0.0014	0.0028	0.00070	NA	0.039

(a) Analytical Instruments:
AAS = Atomic Absorption Spectrophotometry
ICP/AES = Inductively Coupled Plasma Atomic Emission Spectrometry
INAA = Instrumental Neutron Activation Analysis
PIXE = Proton Induced X-ray Emission
XRF = X-ray Fluorescence

(b) Minimum Detectable Limits are calculated assuming sampling at 30 l/min flow rates for 4-hrs

(c) Typical concentration ranges are based on ACHEX Final Report Volume IV (Hidy et al, 1974b), 24-hr TSP concentrations

(d) Based on Ouimette's (1981) measurements at Zilnez Mesa, AZ, June-July 1979; sampling at 21 l/min for 24-hrs

(e) Fassell and Kniseley (1974). Assumes extraction of entire filter in 10 ml of solvent

(f) Sensitivities quoted by General Activation Analysis

(g) T. Cahill, personal communication. Assumes active area of filter is 11.3 cm^2, 100-second analysis run

(h) J. Cooper, personal communication-excitation. Assumes active area of filter is 11.3 cm^2

(i) NA - Not Available by this method at appropriate level

(j) Fast neutrons, fission spectrum

(k) Reactor pulse

various sources and they will vary depending on the instrument configuration and analysis protocol. Values are missing from the tables either because the methods have not been sufficiently characterized to provide them or because the data were not available.

AAS, ICP/AES, PIXE, and XRF have all been applied to elemental measurements of aerosol samples. These methods all have adequate sensitivity for the types of samples expected from the PM_{10} sampling. The criteria used to select the most appropriate method for this program usually include: 1) species measured; 2) interferences; 3) sample integrity; and 4) cost.

Atomic absorption spectrophotometry (Ranweiler and Moyers, 1974), requires individual analyses for each element, is destructive of the sample, and is subject to inaccuracies owing to the variable extraction efficiencies of different compounds (Chow et al., 1980). For these reasons, AAS analysis is not normally applied to aerosol samples. Although it is capable of measuring a number of elements simultaneously, inductively coupled plasma atomic emission spectrometry (ICP/AES) (Lynch et al., 1980) is also destructive and has variable extraction efficiencies. These methods are best applied to the water-soluble fraction of particulate matter, which has just recently been recognized as a potential addition to the species in source profiles. The remaining analysis techniques are nondestructive, allowing multiple analyses to be performed on single samples.

The minimum detectable limits and lack of interferences of instrumental neutron activation analysis (INAA) (Zoller and Gordon, 1970; Dams et al., 1970) for many elements such as Al, Cl, V, Mn, Cu, Se, Br, As, Sr, and Cd are better than those of XRF and much better than those of PIXE (Ahlberg and Adams, 1978; Gordon et al., 1984). As presently performed, INAA requires more sample handling and interpretation of results than does XRF or PIXE, so INAA is more costly per sample. INAA does not quantify several important elemental species, such as Si, Ni, Sn, and Pb. INAA uncertainties include: sample contamination, self-shielding during radiation, inhomogeneity of neutron flux, interference from Compton edge radiation, and interference from daughter isotopes or competing parent isotopes (Radiological Health Handbook, 1970; Lapp and Andrews, 1972; Malissa, 1977; Colome et al., 1978; Leaderer et al., 1978).

The minimum detectable limits, species measured, and costs of XRF and PIXE analyses are roughly comparable. XRF and PIXE are rapid and inexpensive, but they cannot be used to quantify elements in particulate filter samples lighter than aluminum (Al). In XRF, a secondary fluorescer system, similar to that used by EPA (e.g., Jaklevic et al., 1980), provides greater sensitivity than primary excitation systems.

In x-ray fluorescence analysis, an x-ray tube with a metal anode generates x-rays which can be filtered or focused on a secondary target to produce nearly monochromatic radiation. In PIXE analysis, a beam of protons is used. The x-rays or protons excite an atom in the sample from its ground state to a higher energy level, thereby creating a vacancy in

the inner atomic shell. A higher-energy electron drops into the lower energy orbit and releases a fluorescent x-ray to remove excess energy (Jaklevic et al., 1977). The release energy is characteristic of the emitting element and it is used to identify the element. The area of the fluorescent x-ray peak (intensity) in the spectrum is proportional to the number of atoms in the sample and is used to quantitatively determine a specific element's concentration through a direct comparison with standards (Dzubay and Stevens, 1975).

The most commonly used filter substrate for elemental analysis is the polytetra-fluoroethylene (PTFE) Teflon membrane filter with a pore size of two microns and a supporting polyolefin ring. Teflon is preferred because of its high purity, low initial pressure drop, minimal water retention, negligible particle penetration and minimal tendency to react with gaseous pollutants (Dzubay and Rickel, 1978). This type of filter also has excellent sampling and analysis characteristics. Stevens and Dzubay (1978) found a more than 99% efficiency in collecting particles greater than 0.01 μm. The low weight per unit area (1 $\mu g/cm^2$), the chemical inertness, and the homogeneous particle distribution make the filter suitable for XRF or PIXE analysis. X-ray fluorescence analysis has been used to determine elemental concentrations in ARB's dichotomous sampler network.

3.3.4 Ion Determination Alternatives

Generally, the ionic composition of filter deposits is determined by analyzing the aqueous extract of the filter samples, though some efforts have concentrated on the development of nondestructive spectroscopic techniques for the characterization of aerosol particles collected on filters (Rohl et al., 1982).

Table 3.3-3 lists the typical concentration range and the commonly used methods for measuring the ionic composition of aqueous extracts from filter samples. Although the sensitivity, accuracy, and versatility of ion chromatography, ion selective electrodes, and automated colorimetry are comparable, these methods are destructive, require an extraction step, and may even alter the chemical composition of the species of interest. Ion selective electrode measurements require a separate analysis for each type of ion.

The automated colorimetric technique uses the Technicon Auto-analyzer II system (Technicon Instruments Corporation, Tarrytown, NY) for the analysis of inorganic anions and cations in aqueous extracts. The Technicon Auto-analyzer analyzes up to 30 samples per hour simultaneously for sulfate ($SO_4^=$), nitrate (NO_3^-), chloride (Cl^-) and ammonium (NH_4^+) with minimal operator attention and relatively low maintenance and material costs. Large-scale analysis of high volume filter samples was performed in the Sulfate Regional Experiment (SURE) (Mueller and Hidy et al., 1983) and Eastern Regional Air Quality Study (ERAQS) (Mueller and Watson et al., 1982) in which more than 150 samples were processed per day. Like most other analytical instruments, this one requires a periodic standard calibration and the use of daily prepared reagents. Each analysis method

Table 3.3-3

Typical Concentration/Range and Detection Limits for PM_{10} Ion Analysis

Ion Species	Typical Ambient Concentration Range ($\mu g/m^3$)[a]	Minimum Detectable Limit ($\mu g/m^3$)		
		Automated Colorimetry	Ion Chroma-tography	Ion Selective[b] Electrode
$SO_4^{=}$	0.5 - 25	0.42	0.025	NA[c]
NO_3^-	0.5 - 30	0.14	0.015	0.14
NH_4^+	0.5 - 25	0.0056	0.011	0.028

a Typical concentration ranges are based on ACHEX Final Report Volume IV (Hidy et al., 1974b), 24-hr TSP concentraton

b Assumes no dilution factor, 10 ml extract volume, sampling at 30 l/min for 4-hrs

c NA - Not Available

is subject to certain interferences and ranges of sensitivity. As indicated in Table 3.3-3, lower quantifiable limits of automatic colorimetry for sulfate and nitrate are an order of magnitude higher than those of ion chromatography. However, new technology in automatic colorimetry is being developed (Fung, 1987). It might eventually achieve the equivalent lower quantifiable limits as those in the ion chromatographic analysis, although further evaluation is required.

Ion chromatography is subject to fewer interferences from substances commonly found in aerosol samples when compared to specific ion electrodes and automated colorimetry. This chromatographic approach was developed by Small et al. (1975) and has been applied to aerosol measurements since the mid-1970's (Mulik et al., 1976, 1977, 1978; Butler et al., 1978; Mueller et al., 1978; Rich et al., 1978; Small, 1978).

An ion-exchange column separates the sample ions for individual quantification by a conductimetric detector. Prior to detection, the column effluent enters a suppressor column where the chemical composition of one component is altered, resulting in a matrix of low conductivity. The ions are identified by their elution/retention times and are quantitated by the conductivity peak area (Steele et al., 1981). Recent studies have explored the application of Fourier Transform Infrared (FTIR) transmission spectroscopy to the analysis of ambient aerosols collected on Teflon filters for ammonium, sulfate and other compounds (Miller and Jacobson, 1978; Gendreau et al., 1980; McClenny et al., 1985).

The FTIR system offers spectral multiplexing, high optical throughput, precise wavelength control, and computerized data processing. The advantages of the FTIR technique are (McClenny et al., 1985): 1) it provides direct molecular information; 2) it is nondestructive and requires no sample preparation; and 3) it is rapid and amenable to automation. However, this technique has not been applied to routine quantification of ambient samples. FTIR has unquantified interferences due to the presence of nitrate and unneutralized sulfate. FTIR detection limits for sulfate and ammonium are orders of magnitude higher than those of ion chromatography. Most commonly used filter materials are relatively opaque to infrared radiation, which further limits sensitivity. FTIR transmission spectroscopy is not yet well developed enough for Level I or Level II ion measurements.

Intercomparison studies between FTIR, automated colorimetry (AC) and ion chromatography have been conducted in different analytical laboratories (Butler et al., 1978; Mueller et al., 1978; Fung et al., 1979; Pyen and Fishman, 1979). Butler et al. (1978) found excellent agreement between sulfate and nitrate measurements by automated colorimetry and ion chromatography. Comparable results were also obtained between IC and AC methods by Fung et al. (1979). The choice between the two methods for sample analysis may be dictated by sensitivity, scheduling, and cost requirements. The automation of the ion chromatograph by interfacing to an automatic sampler which can conduct unattended analysis of as many as 400 samples at a time (Tejada et al., 1978) seems to be a cost-effective alternative to handle large sample loads with minimal labor requirements.

Ion chromatography also offers the opportunity to measure a number of anions and cations (e.g., $SO_4^{=}$, NO_3^-, NO_2^-, F^-, Cl^-, Br^-, PO_4^{-3}, NH_4^+ Na^+, and K^+) and is widely used in the analysis of precipitation samples. ARB applies ion chromatography to the measurement of sulfate and nitrate in its high volume PM_{10} sampling network.

3.3.5 Carbon Determination Alternatives

Carbon has long been recognized as an important atmospheric aerosol constituent due to its potential effects on health, materials, visibility, and deposition (Delumyea et al., 1980; Shah, 1981; Mueller et al., 1982; Hidy, 1982; Novakov, 1982). Typical concentrations of organic, elemental and total carbon at urban and non-urban sites are summarized in Table 3.3-4.

Standard methods for the collection and analysis of carbonaceous species are still being developed (Cadle et al., 1983). The analytical uncertainties for the determination of carbonaceous aerosol on filter samples include:

- Sampling errors (i.e., sample volume calibration, system leakage, non-uniformity of the sample deposits).
- Adsorption of gas-phase organics on the filter substrate (McDow, 1986). Cadle et al. (1983) found that adsorption of organic compounds on glass fiber, quartz fiber and silver membrane backup filters equaled 15 to 30% of the deposit on the front filter.
- Loss of carbon particles during filter handling (Thurston, 1983; Spengler and Thurston, 1983).
- Volatilization of organic carbon prior to analysis.
- Instrument error, including non-quantitative oxidation or methanation, peak integration, calibration bias, reproducibility of the temperature program, etc.
- Errors in the separation of organic and elemental carbon such as: variation in pyrolytic conversion due to variation in oxygen; contamination; and variation in the properties of atmospheric carbonaceous particles (Grosjean, 1980; Chang et al., 1982).
- Interferences from carbonate carbon or other inorganic species.

The chemical, adsorptive and catalytic characteristics of carbon particles depend greatly on their crystalline structure, surface composition and electronic properties, all of which vary among pollution sources. A complex set of questions concerning the adsorption of gas-

Table 3.3-4

Carbon Analysis Method Characteristics

Typical Ambient Concentration Range ($\mu g/m^3$):

Urban sites (0 to 2.5 μm)[d] -	OC 2.7 to 12.9 EC 0.9 to 7.0 TC 3.6 to 19.9
Non-urban sites (0 to 2.5 μm)[d] -	OC 1.2 to 4.3 EC 0.5 to 2.2 TC 1.5 to 6.0

Measurement Method	Precision[a]	Accuracy[b]	LOL[c]	Advantages and Disadvantages
Solvent Extraction	5 to 15%[e]	20 to 54%[e]	NA[e]	Only 30 to 50% of organic carbon is removed Underestimates organic carbon and overestimates elemental carbon by 9 to 20% Pyrolytical conversion of organic to elemental carbon is minimized These methods require significant quantities of sample, are time consuming and expensive
Nitric Acid Digestion	1.4 to 5.8%[e]	15 to 32%[e]	NA[f]	Some elemental carbon is measured as organic carbon because nitric acid converts elemental carbon to organic carbon

Table 3.3-4 (continued)

Carbon Analysis Method Characteristics

Measurement Method	Precision[a]	Accuracy[b]	LQL[c]	Advantages and Disadvantages
Integrating Plate Method	NA[f]	NA[f]	NA[f]	Relies on poorly determined absorption coefficients and is subject to interferences Contains interference from non-absorbing species such as $(NH_4)_2SO_4$
Thermal Combustion Method	10%[g]	15%[g,h]	0.3μg/cm^2 for OC 0.5μg/cm^2 for EC	Different thermal combustion analyzers with different procedures often yield different values for identical material Elemental carbon is overestimated due to the carbonization of organic material Organic carbon is underestimated due to the conversion to elemental carbon at high temperatures
Thermal/ Optical Method	10%[j]	15%[k]	0.5 μg/cm^2[j] for OC 0.2 μg/cm^2 for EC	Separates organic from elemental carbon Corrects for pyrolysis of organic to elemental carbon Carbonate carbon is measured as organic and elemental carbon if present as more than %5 at total carbon

Table 3.3-4 (continued)

Carbon Analysis Method Characteristics

Notes

[a] ± 1 standard deviation, per filter, unless otherwise specified.

[b] ± absolute error.

[c] LQL = Lower Quantifiable Limit; often determined by variability in blank analysis or minimum detectable limit - whichever is greater.

[d] From Shah, 1981.

[e] From Cadle and Groblicki, 1982.

[f] NA = not available.

[g] From Mueller and Hidy et al., 1983.

[h] From Watson et al., 1982.

[i] From Stevens et al., 1982.

[j] From Johnson, 1981.

[k] From Rau, 1986.

* OC: Organic Carbon
EC: Elemental Carbon
TC: Total Carbon

phase organics on filter substrates, the equilibrium between vapor and solid phases, and the carbonization of organics during analysis are still awaiting answers.

Three classes of carbon are commonly measured in ambient aerosol samples collected on quartz fiber filters: 1) volatilizable or organic carbon; 2) elemental carbon; and 3) carbonate carbon. Carbonate carbon (i.e., K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCO_3$) can be determined on a separate filter section by measurement of the carbon dioxide (CO_2) evolved upon acidification with phosphoric acid (H_3PO_4) (Johnson et al., 1981). If carbonate is present in samples, the acid pretreatment will eliminate it. Carbonate is measured primarily as organic carbon during the carbon analysis if it is not removed by pretreatment, and the carbonate fraction of total carbon can be estimated by analyzing acidified and non-acidified samples.

Organic and elemental carbon categories are operational (i.e., method dependent) rather than absolute (Grosjean, 1980). Several analytical methods for the separation of organic and elemental carbon in ambient and source particulate samples have been developed and applied (Cadle and Groblicki, 1980; Stevens et al., 1982). These methods include:

- Solvent extraction of the organics followed by total carbon analysis (Gordon, 1974; Grosjean, 1975, 1985; Appel et al., 1976, 1977; Daisey et al., 1979; Muhlbaier and Williams, 1982).

- Nitric acid digestion of the organics followed by total carbon analysis (McCarthy and Moore, 1952; Kukreja and Bove, 1976; Pimenta and Wood, 1980).

- Absorption of radiation using an integrating plate to determine elemental carbon. Infrared absorbance (Smith et al., 1975), Raman spectroscopy (Rosen et al., 1978) and visible absorbance (Lin et al., 1973; Weiss et al., 1979; Gerber, 1982; Heintzenberg, 1982) are variations of this method.

- Thermal combustion including both temperature-programmed (Muhlbaier and Williams, 1982) and step-wise pyrolysis followed by oxidation using either CO_2 or CH_4 detection (Mueller et al., 1971; Patterson, 1973; Merz, 1978; Johnson and Huntzicker, 1979, Johnson et al., 1979; Malissa, 1979; Cadle et al., 1980a, 1980b; Heisler et al., 1980a, 1980b; Mueller et al., 1981; Wolff et al., 1982).

- Combination of thermal and optical methods (Appel et al., 1976; Dod et al., 1979; Macias et al., 1979; Cadle et al., 1980a, 1980b; Johnson et al., 1981; Novakov, 1982; Rosen et al., 1982; Huntzicker et al., 1982).

Organic and elemental carbon measurements obtained by these methods have been shown to correlate with each other, but the different methods

sometimes give significantly different carbon concentrations when applied to the same sample. None of them represents an ideal separation procedure of organic from elemental carbon.

Cadle and Groblicki (1980) determined the removal of organic carbon from six ambient particulate samples by solvent extraction, acid digestion and thermal combustion. Solvent extraction removed only 30 to 50% of the organic carbon. Nitric acid digestion was found to convert some elemental carbon into pyrolyzable carbon. The integrating plate method relies on poorly determined absorption coefficients and is subject to interferences from non-absorbing species. The thermal methods may overestimate elemental carbon due to the carbonization of the organic material (Cadle and Groblicki, 1982).

Stevens et al. (1982) compared elemental carbon obtained from thermal combustion methods and nondestructive optical measurements (e.g., photoacoustic measurements). Least-squares linear regression calculations showed consistently higher values for thermal combustion methods for samples from Houston, Texas. Similar characteristics were observed for Shenandoah Valley samples; however, the slope of the linear regression equation was one-fourth the value obtained for the Houston study. The uncertainty in calibration of the photoacoustic technique for low elemental carbon loadings, the interference of iron oxide present in the sample which biases the optical measurement, and the conversion of organic carbon to elemental carbon during the combustion process present unquantifiable interferences which could be the cause of intermethod differences.

Johnson (1981) compared elemental carbon derived from thermal/optical analysis and the integrating plate method. The average thermal/optical to integrating plate ratio of elemental carbon obtained by these two methods for six sampling sites was 0.88 + 0.06. Elemental carbon values determined from solvent extraction and thermal/optical carbon analysis were also compared. Johnson (1981) concluded that: 1) the solvent extraction method overestimates elemental carbon by 9 to 20% with respect to the thermal/optical method because unextracted organic carbon left on the filter is presumed to be in the elemental category; and 2) the amounts of pyrolytically produced elemental carbon are reduced by 58 to 79% using an extraction procedure.

In addition, a mass balance for total carbon on the samples was performed by Johnson (1981) to ensure that there were no major problems in the extraction procedure. An average loss of 15% was found, which can be attributed to non-quantitative transfer (e.g., loss of elemental carbon) and volatilization during solvent removal (e.g., loss of volatilizable carbon) (Gundel et al., 1979).

Watson (1979) reported the first results of an interlaboratory comparison for total carbon as part of the Portland Aerosol Characterization Study (PACS), using the thermal method developed at the Oregon Graduate Center (OGC) and a total carbon measurement conducted by the Oregon Department of Environmental Quality (DEQ) and the Environmental Protection Agency (EPA) at Corvallis, Oregon (Watson, 1979; Cooper et al.,

1979a; 1979b). The results of this intercomparison indicated a reasonable equivalence between the EPA and OGC measurements (slope = 1.02, correlation = 0.907). Comparison with DEQ yielded a higher correlation (correlation = 0.990), but exhibited a multiplicative bias (slope of DEQ/OGC = 0.83).

Heisler et al. (1980a) and Mueller and Hidy et al. (1983) also conducted a carbon interlaboratory comparison study between the General Motors Research Laboratory (GMR) and Environmental Research and Technology, Inc. (ERT) for the 1978 Denver Winter Haze Study (Heisler et al., 1980a; 1980b) and the Sulfate Regional Experiment (SURE) (Mueller and Watson, 1981; Mueller et al., 1981; Mueller and Hidy et al., 1983). The paired comparison was done with 151 filters with an average loading of 208 μg carbon per 47 mm quartz filter. High correlations (0.96 to 0.99) resulted, with the largest discrepancies observed in the analysis of elemental carbon (slope of GMR/ERT, b = 0.76). Furthermore, GMR's results were systematically higher than ERT's measurements.

Similar interlaboratory studies were carried out among OGC, DEQ, and GMR laboratories on a set of 10 ambient samples (Johnson, 1981; Shah, 1981). A high correlation was found among total carbon values; however, the slopes of GMR/OGC were 1.46 for volatilizable carbon and 0.74 for elemental carbon. Results of the least squares fit to the data for OGC, EPA, DEQ, GMR, and ERT laboratories are summarized in Table 3.3-5 for comparison.

Stevens et al. (1982) performed an interlaboratory comparison of thermal combustion techniques between the two laboratories on 28 aerosol samples. They reported average values of 0.85 and 0.37 $\mu g/m^3$ for elemental carbon, and 1.89 and 3.52 $\mu g/m^3$ for organic carbon for laboratories I and II, respectively. These differences were attributed to variations in the thermal combustion analyzers and different analytical procedures.

Cadle and Groblicki (1982) conducted an intermethod comparison of carbon analyses. Their agreement was best for total carbon (organic plus elemental), the results ranging from - 15% to + 26% of the mean, and worst for elemental carbon, ranging from - 57% to + 179% of the mean.

These differences among laboratories accentuate the uncertainties about different carbon analysis methods. The ARB carbon intercomparison study (Countess, 1987) is expected to further quantify differences among carbon analysis methods.

Because widely accepted primary standards for carbon in ambient aerosols do not exist, it is difficult to determine which of the available techniques is "best." A controversy exists over whether or not volatilization with simultaneous oxidation is preferable to volatilization followed by oxidation. Volatilization of organic carbon without simultaneous oxidation could convert some of the organic material to a char, thereby increasing the apparent elemental carbon and decreasing the apparent organic carbon measured. On the other hand, there is a concern that some of the inorganic carbon may oxidize along with the organic carbon

Table 3.3-5

Summary of Carbon Analysis Interlaboratory Comparison Results
Linear Regression Slope and Correlation Coefficient
(number in parentheses)

Carbon Species	GMR/ERT[b]	GMR/OGC[b]	DEQ/OGC[b][c]	EPA/OGC[c]
Elemental Carbon	0.76[a] (0.09651)	0.74[b] (0.9305)	NA[d]	NA
Organic Carbon	0.93[a] (0.989)	1.46[b] (0.9902)	NA	NA
Total Carbon	0.92[a] (0.994)	1.14[b] (0.9856)	1.07[b] (0.9938)	1.02[c] (0.907)
			0.83[c] (0.990)	

(a) From: Heisler et al., 1980a; and Mueller and Hidy et al., 1983. (Data converted when X and Y axes are switched with King's approach, 1977.)

(b) From Johnson, 1981.

(c) From Watson, 1979.

(d) NA - Information not available.

* ERT - Environmental Research and Technology, Inc., as independent variable.
GMR - General Motors Research Laboratories, as dependent variable.
OGC - Oregon Graduate Center, as independent variable.
DEQ - Oregon Department of Environmental Quality, as dependent variable.
EPA - Environmental Protection Agency, Corvallis, OR, as dependent variable.

if oxidation is simultaneous with heating of the sample. Step-wise thermal oxidation appears to be the most viable approach, though further evaluation is required to determine whether or not simultaneous heating and oxidation is preferable to volatilization followed by oxidation.

The thermal/optical method developed at the Oregon Graduate Center (OGC) for the analysis of carbonaceous aerosol on quartz or glass fiber filters (Johnson, 1981; Johnson et al., 1981; Shah, 1981; Huntzicker et al., 1982; Rau, 1986) has been subjected to rigorous development and testing efforts as those reported by Watson (1979), Johnson and Huntzicker (1979), Johnson (1981), Johnson et al. (1981), Shah (1981), Huntzicker et al. (1982), and Rau (1986). It appears to be one of the most promising methods for the carbon analysis of PM_{10} samples.

The OGC technique is based on the preferential oxidation (step-wise thermal analysis) of organic and elemental carbon to CO_2. The CO_2 is mixed with hydrogen and passed through a methanator (hydrogen-enriched nickel catalyst) where it is reduced to methane (CH_4) for detection by a flame ionization detector (FID) which responds linearly to CH_4. The reflectance of the sample is continuously monitored throughout the analysis by a He-Ne laser and photo detector which permits a quantitative correction for the pyrolytic production of elemental carbon that occurs during the organic analysis. This correction has been shown to be significant and cannot be ignored. In approximately 200 filters collected from nine sampling sites, Johnson et al. (1981) reported that an average of 22% of the organic carbon was pyrolytically converted to elemental carbon as evidenced by reflectance corrections. The precision of the pyrolytic conversion has been found to be $\pm$ 10% in both organic and elemental carbon (Johnson et al., 1981).

Pure substances, source mixtures and ambient samples have been analyzed by Cadle et al. (1980a, 1980b, 1983), Heisler et al., (1980a), Johnson (1981), and Groblicki et al. (1983). An average recovery of 99 $\pm$ 6% was obtained from the known amounts of 12 different pure compounds analyzed by Johnson (1981).

The accuracy of the thermal/optical reflectance method for total carbon determined by analyzing a known amount of carbon is reported to be between 2 and 6% (Rau, 1986), though these specifications seem overly optimistic. Accuracy of the organic/elemental carbon split is reported to be between 5 and 10%. The precision of this analysis has been reported to range from 2 to 4% (Johnson, 1981).

The lower quantifiable limits of carbon combustion methods depend upon the variable carbon content of the blank quartz filters rather than the analysis method. For better lower quantifiable limits, the unexposed filter should be pre-fired in an oven at 600 to 700°C for several hours to remove any residual carbon contamination (Fung, 1986; Huntzicker, 1986; Rau, 1986). For well-cleaned quartz filters, the standard deviation of the blanks for both organic and elemental carbon is on the order of 0.2 to 0.3 $\mu g/m^3$ (Fung, 1986). The ARB currently conducts benzene-soluble organics analysis on samples from its high volume PM_{10} monitoring network.

3.4 Meteorological Data

Meteorological measurements are used by receptor models to identify sources (e.g. wood burning on cold winter days) and to determine the potential for source profile fractionation. Meteorological measurements are used by dispersion models to explicitly estimate the movement and transformation of emissions between source and receptor. Hoffnagle et al. (1981) identified the following variables as those needed for these purposes:

- Mean horizontal wind speed ($\bar{u}$) and mean wind direction reported as the hourly resultant vector direction (θ) at 10 meters (m) and at source height.
- Harmonic mean wind speed $(1/\bar{u})^{-1}$ between source height and effective plume height, used for calculating initial dilution and plume rise.
- Standard deviation of horizontal and vertical wind fluctuations (σ_θ, σ_φ) at 10 m, calculated from variations in wind direction.
- Temperature (T) at 2 m.
- Temperature difference (ΔT) between 2 m and 10 m.
- Heights of the convectively mixed layer (h_c) and the mechanically mixed layer (h_m) created by surface heating and wind-generated turbulence, respectively.
- Average surface roughness length (z_o), derived from wind speed profile data or estimated from site description.
- Friction velocity (u_*).
- Bulk Richardson number (Ri_B), Monin-Obukhov length scale (L), turbulent heat flux (H_F), and convective velocity scale (w_*), all estimated from temperature and wind measurements.
- Water vapor content (e_w) between source height and effective plume height, derived from measurements of temperature dew point (T_d) and ambient temperature.

The meteorological variables which can be measured directly are listed in Table 3.4-1 with their recommended instrument heights, accuracy, resolution, sampling times and response times. The dependence of derived quantities and the measured variables is listed in Table 3.4-2.

Hoffnagle et al. (1981) also identified the following meteorological variables as desirable for more accurate modeling in certain situations including complex terrain and long-range transport:

Table 3.4-1

METEOROLOGICAL VARIABLES WHICH AFFECT DISPERSION OF POLLUTANTS IN THE ATMOSPHERE

Measurement[a]	Height	Accuracy	Resolution	Averaging Time	Response Time
u^b	10 m, source,	0.2 m/s $\pm$ 5%	---	1-5 sec	distance const. $<$ 5 m
	plume	0.5 m/s	---	---	---
θ^b, ϕ^b	10 m, source	absolute 5°	---	1-5 sec	distance const. $<$ 5 m
		relative 1°			damping ratio $>$0.4
ΔT	2-10 m	0.1°C	0.02°C	30 sec	1 min
h_c	50-2000 m	50 m	10 m	---	10 sec
h_m	0-200 m	10-50 m	10 m	---	10 sec
T_d[c]	source, plume	1.5°C	0.1°C	$>$1/2 of response time	1-30 min
T	2 m, source, plume	0.5°C	0.1°C	30 sec	1 min

a Symbols are defined in text.

b Or equivalent wind measurements u, v, w.
Requirements specified are for threshold speeds $<$0.5 m/s.

c Required only when cooling tower plumes are modeled.

Table 3.4-2

Interdependence of Derived and Measured Meteorological Parameters

Symbol	Sampling Duration	Parameters Needed for Derivation	Comments
$\bar{u}_v$, $\bar{u}_s$	1 h	u, θ:10 m, source	--
$\bar{\theta}_v$	1 h	u, θ:source	--
	1 h	u:source	1 min samples of u
$\sigma\theta$, $\sigma\phi$	1 h	θ:10 m	--
	3 min	θ:10 m	Optional, depending on source characteristics
ΔT	1 h	ΔT:2-10 m	--
h_c	1 h	h_c	--
h_m	1 h	h_m	--
z_o	1 h	u:2 m, 10 m, 20 m	Derived from wind profile measurements or estimated from site description
Ri_B	1 h	ΔT, u(10 m), T(2 m)	--
L	1 h	R_i, z_o	--
u_*	1 h	z_o, u(10 m), L	--
H_F	1 h	ΔT, L, u_*, T(2 m)	--
w_*	1 h	H_F, T(2 m), h_c, ΔT	--
e_w	3 h	T_d, T:source	--
$\sigma(1/u)$	1 h	u:source	1 min averages of u
$\bar{\theta}_v$	1 h	u, θ:plume	--
$\sigma\theta$, $\sigma\phi$	1 h	θ, ϕ:source	--
	3 min	θ, ϕ:source	Optional, depending on source characteristics
ΔT	1 h	ΔT:source-plume	Vertical profile
Sr	1 h	Q*:1 m	Total solar and net radiation
$\bar{w}$	1 h	w:10 m	Useful for complex terrain modeling
Fr	1 h	ΔT, u:Profile	Useful for complex terrain modeling
U_g	3 h	NWS p,T	Useful for long-range transport modeling
State of the ground	3 h	Observation	--

- Standard deviation of the reciprocal of the wind speed at source height ($\sigma(1/u)$).

- Mean wind direction at plume height (Θ_v) requiring remote sensing or tall tower observations.

- Standard deviation of horizontal and vertical wind fluctuations at source height (σ_Θ, σ_ϕ).

- Temperature gradient from source height to effective plume height (ΔT) obtained from temperature profiles obtained once per hour.

- Total solar radiation (SR) measured with pyranometers with 50 W/m^2 accuracy and resolution of 10 W/m^2.

- Mean vertical velocity ($\bar{w}$).

- Froude number (Fr), which requires vertical profiles of temperature and velocity to heights exceeding local terrain elevation.

- Geostrophic wind (U_g), calculated from 3-hour NWS observations near the site.

- State of the ground over which the plume travels.

The values derived from meteorological measurements at a single point are usually taken to be representative of the three-dimensional modeling domain. The greatest cause of uncertainty in these values is not the uncertainty of the meteorological measurement device, but the uncertainty of extrapolating the point measurements to a wider domain. Table 3.4-3 lists the typical monitoring devices, precisions, and accuracies for meteorological variables. The remainder of this sub-section will focus on this extrapolation, and the cautions which must be observed, rather than on the measurement hardware.

3.4.1 Upper Air Measurements

Winds aloft can be tracked by following superpressure balloons (i.e., constant level balloons, also called tetroons, and using Doppler sodar (e.g., acoustic sounder) systems. Ascending free balloons (e.g., pibals, rawinsondes) provide data on flow trajectories over a finite time interval. Since the balloon does not exactly follow an air parcel when vertical motion is involved, the results must be interpreted cautiously.

The Doppler sodar technique may be used in either the monostatic or the bistatic mode. Measurements of wind components aloft are accurate to about 0.5 m/sec. These measurements routinely provide information to heights of 500 m, and sometimes to heights above 1000 m.

Table 3.4-3

Typical Performance Specifications of Meteorological Instruments

Wind Speed	Coaxial cup anemometer (Weather Measure W1034) Threshold: 0.3-0.5 m/sec Distance Constant: 1.5 m Accuracy: ± 1%
Wind Direction	Damped Wind Vane (Weather Measure W1034) Threshold: 0.3 m/sec Linearity: 0.5% Resolution: 0.7^{o} Distance Constant: 1.1 m
Temperature	Power-aspirated thermistor (Weather Measure T622R) Accuracy: ± $0.3^{o}C$ Sensitivity: ± 0.1% fullscale
Dew Point	Power-aspirated dewall (General Eastern 1200 MPS/1100 MPS) Accuracy: ± 0.2 to ± $0.4^{o}C$ Sensitivity: ± $0.03^{o}C$
Solar Radiation	Pyranometer (Eppley 8-48) Sensitivity: 11 $\mu v/w\text{-}m^{-2}$ Linearity: ± 1% Spectral Range: 285-2800 nm
Winds Aloft	Balloon theodolite: ± 0.10

The major uncertainties of upper air data are caused by the sparse temporal spatial and temporal resolution of the measurements. The National Weather Service (NWS) rawinsonde network measures temperature, wind speed, wind direction and moisture every 12 hours at 70 sites across the continental U.S. This provides upper level winds at a horizontal resolution of the order of 400 kilometers, considerably less than the grid spacing required in air quality simulation modeling.

A more precise three-dimensional wind field can be attained by releasing and tracking pilot balloons (pibals) at points within a study area. Pibals may be tracked using either single or double theodolite methods. Of the two, the double theodolite method is more accurate because is does not rely on the assumption of a constant ascension rate of the balloon as does the single theodolite method. Apart from errors in reading angles and the timing of the readings, the best observations can give wind speeds accurate to $\pm$ 1 m/sec and wind directions accurate to $\pm$ 2° at altitudes to 3 or 4 km. At 5 km distance from the observer these uncertainties are doubled.

Upper air temperature measurements are used to derive mixing heights. The lower atmosphere usually exhibits a decrease in temperature with altitude; any reversal of this condition is termed an inversion. The inversion base is the point on the vertical temperature profile where warming with height begins; the inversion top is the warmest point on the profile and marks the resumption of cooling with altitude. More than one inversion layer may exist in the first several thousand meters of the atmosphere. Low-level inversions generally occur near the ground when it is cold. As the ground warms up during the day and heats up the lower portion of the atmosphere, the inversion base rises and in many instances the low level surface inversion is broken altogether. Irregular terrain and non-uniform surface heating affect the height of the inversion base inland. For example, the inversion may break up over the slopes and crests of the mountains while inland valleys retain a strong inversion with a low base.

The height of the inversion base of the inversion layer nearest the surface is termed the mixing height. Mixing heights are either estimated from surface temperatures and a single temperature sounding or measured from a detailed vertical temperature profile. Soundings are made with both monastatic and bistatic sodars as well as aircraft, towers and balloons instrumented with thermistors. In the absence of detailed soundings, mixing heights are generally calculated from surface temperatures. Afternoon mixing heights are estimated from the maximum surface temperature and a measured sounding by constructing a dry adiabatic lapse rate which intersects the sounding. The morning mixing height is estimated by increasing the minimum surface temperature by $5^{o}C$ and determining the intersection of an adiabatic lapse rate with the sounding. Both techniques can lead to overestimating the mixing height.

The mean AM and PM mixing heights for 19 sites throughout California are given in Table 3.4-4 as a function of season. The lowest mixing heights occur in the winter months due to the preponderance of long nights with clear skies that allows maximum radiational cooling of the ground.

Table 3.4-4

Mean Morning and Afternoon Mixing Heights in California[a]

Station	Mean Mixing Height in Meters							
	Winter		Spring		Summer		Fall	
	AM	PM	AM	PM	AM	PM	AM	PM
China Lake	595	>1200	>1200	>1200	675	>1200	140	>1200
Edwards AFB	840	>1200	645	>1200	180	>1200	105	>1200
El Monte	240	>1200	460	>1200	285	1100	225	>1200
Fresno	150	630	230	>1200	175	>1200	115	1135
LAX	>1000	>1200	805	>1200	525	665	335	510
Lakeport	--	--	--	--	60	1195	55	655
Oakland	>1100	>1200	>1200	>1200	550	660	530	925
Pt. Mugu	95	>1200	420	945	150	450	95	815
Red Bluff	95	520	160	>1200	325	>1200	110	1185
Rialto	--	--	--	--	--	1170	--	785
Sacramento	135	395	190	1035	155	1120	150	845
Salinas	225	>1200	485	>1200	505	665	325	945
San Bernardino	70	>inv	255	>inv	150	>inv	90	>1200
San Diego	705	>1200	930	>1200	705	815	420	>1200
San Nicholas Island	260	530	610	630	440	560	360	1080
Tahoe City	80	650	--	--	--	--	--	--
Thermal	80	1180	105	1105	140	>1200	85	>1200
Vandenberg AFB	530	>1200	1055	990	395	415	270	445
Ukiah	250	815	255	>1200	215	>1200	170	975

[a] From Smith et al. (1984); utilizes 1979-1980 ARB data base for 19 sites.

During the summer, in the peak of the photochemical season, many areas of California experience inversion bases of less than 400 meters. Ninety percent of the time the inversion base is less than 800 meters, a level that indicates a limited potential for the dispersion of pollutants.

Upper air measurements can also be examined to determine the extent to which the dispersion model assumptions are met. Although the inversion base limits vertical mixing, there are several mechanisms that function to trap pollutants aloft in the inversion layer. This can occur when:

- The sea breeze undercuts a polluted layer, bringing with it an inversion at a lower level.
- The return flow of air aloft from mountain ridges transports pollution into the air above the inversion base of the coastal regions.
- Buoyant plumes from elevated stacks penetrate the inversion base.
- A surface inversion is formed by radiational cooling of the land below an existing inversion.

Pollution can exist in stratified layers aloft within the inversion proper as well as in a layer at the surface. Unless winds aloft transport the pollution trapped in the inversion layer away from the area, these aged pollutants can be brought back to the surface with sufficient vertical mixing caused by surface heating and mix with fresh emissions.

Elevated concentrations of both ozone and sulfates are favored by the presence of moderately low (< 800 m), strong (> $\Delta 7^{o}C$) inversions. The daily absolute concentrations of sulfates are also controlled by daily fluctuations in the sulfur emissions and by an apparent carry-over of sulfates in the atmosphere from the previous day. For instance, with an established marine layer that has an inversion base and strength that does not change appreciably for several days, sulfate concentrations may increase each day until the basic weather pattern changes.

3.4.2 Temperature

Temperature, as the key factor in the climatology of California, is interrelated with relative humidity, wind flow in three dimensions, and stability as discussed in the following sections. Temperature is measured with aspirated, shielded thermistors.

The time of the daily maximum temperature of a site during the summer varies more or less with its distance from the ocean. The maximum most often occurs during the late morning to about noon at the coast, and mid-afternoon in inland valleys.

The offshore and onshore winds that occur in the coastal plains are the product of temperature differentials between the relatively constant ocean air temperature and the uneven heating and cooling that takes place inland over widely varying topography. Another phenomenon associated with temperature is the upslope flow that occurs at the higher terrain inland due to solar heating of the surface. This upward air flow can transport pollutants to extremely high altitudes. The wind direction aloft can either transport these pollutants long distances downwind of the source or they can be trapped in the inversion and mixed downward to the surface the following day as a result of surface heating.

Temperature also controls the extent of vertical mixing and thus the daily air quality. As each day progresses, the sun heats the surface, creating updrafts or "thermals" that mix the air between the surface and the base of the inversion. This process mixes upper air, which may have a different pollutant mix, downward as the inversion base rises. Eventually the surface temperature reaches a maximum and the daily maximum mixing height is attained, representing the greatest vertical mixing of the day. With sufficient surface heating, the inversion may be broken, resulting in virtually unlimited vertical dispersion.

Although there is a positive correlation between high temperatures and elevated ozone concentrations, the relationship may be misleading if the conclusion is drawn that the high temperatures alone account for the high ozone values. Meteorological conditions favorable to the production and accumulation of maximum ozone concentrations include the presence of a low, intense inversion and strong solar radiation. Both conditions are accompanied by high temperatures at the surface and aloft, masking the role of temperature in the photochemical process.

3.4.3 Relative Humidity and Dew Point

High relative humidity affects chemical reaction rates and contributes to the growth of hygroscopic aerosols (e.g., ammonium sulfate and sulfuric acid) at relative humidities above 70%. Relative humidity and dew point are measured with hygrometers and cooled mirror or aspirated dew cells, respectively. These methods provide different measurements of the moisture content of the air.

Relative humidity is a measure of the relative amount of water vapor existing in the air compared to the amount the air could hold if saturated; dew point is defined as the temperature to which air must be cooled in order for saturation to occur. With diurnal changes in temperature, the relative humidity will show a diurnal fluctuation even though the actual moisture content of the air at the surface remains nearly constant. On many days the dew point throughout a region may be approximately constant while the relative humidity, which is temperature dependent, will be higher at the coast than in the hotter interior.

3.4.4 Rainfall

The influence of rainfall on contaminant levels may vary with the type and intensity of rain. Winter rains from warm air masses that are stable near the surface can cause some wash-out of pollution if precipitation is heavy. Unstable summer thunderstorms can provide excellent dispersion that masks any wash-out effects. If the inversion is not broken by a major weather system, high contaminant levels can persist even in areas of light showers. On the other hand, heavy cloud shields associated with outbreaks of tropical air minimize photochemical aerosol formation because of inadequate sunshine. Rainfall is measured with a tipping bucket or weighing rain gauge.

3.4.5 Solar Radiation

Ozone and many aerosol precursors are formed by photochemical reactions that involve the interaction of radiation, visible or ultraviolet, with airborne gaseous pollutants. The amount of cloud cover as well as the sun angle and duration of sunlight, determines seasonal radiation received at the surface of the earth. Both are important to photochemistry and to solar heating and cooling. A heavy cloud cover will retard photochemical aerosol formation even during the summer, whereas even with clear skies during the winter, weak radiation limits the amount of photochemical activity. Solar radiation is measured with a pyranometer.

3.4.6 Wind Speed and Direction

Just as the inversion base limits vertical dispersion of contaminants, the direction and speed of the wind determine horizontal dispersion and transport of pollutants.

Wind direction is generally measured with a wind vane, wind speed with a cup anemometer. However, at very low wind speeds (i.e., <3 knots), the response of many airport cup or propeller anemometers is not very good; thus "calm" conditions may merely represent a speed of less than 3 knots.

Surface wind measurements represent air movement in the layer from the surface to the base of the inversion, where most pollution is found. During the day, surface winds are good indicators of the wind flow in the mixed layer. However, at night, surface winds are light, thus indicating stagnation or drainage. Winds aloft may indicate very different conditions.

The regions of predominantly light morning wind speeds (i.e., <2 knots) include the Ukiah/Santa Rosa area, the March Field/San Bernardino area, Gillespie Field and the Inyokern area. Other areas of the state which experience light morning winds several weeks a year include the Salinas Valley, the South Coast Air Basin and much of the Mojave Desert.

Hayes et al. (1984) present detailed streamline maps of major wind flow patterns within California for each season. These patterns are greatly influenced by local terrain. Mountains accelerate air mass due to deflection and/or convergence. Parts of the Mojave Desert also have very high average wind speeds, caused by local changes in terrain and thermal gradients.

Because of stronger sea breezes, coastal areas generally have higher average wind speeds than inland locations. In California, there are a limited number of routes by which coastal winds can flow through to the interior. These include:

- Carquinez Straits, which serve as the major transport corridor into the Central Valley in northern California;
- Mountain passes such as Soledad Canyon, Cajon Pass and San Gorgonio Pass on the perimeter of the South Coast Air Basin;
- Tehachapi Pass at the southeast end of the San Joaquin Valley.

In addition to the dominant flow patterns in California documented by Hayes et al. (1984), there are a number of regional flow patterns described by Smith et al. (1984) that serve to redistribute pollutants both horizontally and vertically. They include:

- Eddy structures which result from blocking of the flow by terrain or opposing winds such as occur in the southern Sacramento Valley, San Joaquin Valley and the Santa Barbara Channel.
- Upslope flows created by strong heating of mountain ridges during the afternoon in areas such as the southern slopes of the San Gabriel and San Bernardino Mountains in the South Coast Air Basin.
- Convergence zones with strong updrafts produced by terrain and pressure gradients (e.g., the Elsinore and San Fernando Valley Zones).
- Marine air intrusions caused by the sea breeze transporting a shallow layer of cool, moist air inland which undercuts the existing mixed layer and creates a layer aloft out of the top of the existing mixed layer. In most areas of the state, the marine air intrusion brings with it cleaner air from offshore. However, in both the South Central and South Coast Air Basins the marine air may bring in recirculated pollutants from offshore.

Interbasin transport has been investigated in California over the past decade by analysis of wind data and the release of inert tracers. Details of these studies are discussed by Smith et al. (1984). Trajectories are documented from:

- San Francisco Bay Area to the Sacramento and San Joaquin Valleys.
- San Francisco Bay Area to the North Central Coast Air Basin.
- Sacramento Valley to Mountain Counties and Lake Tahoe Air Basins.
- San Joaquin Valley to Southeast Desert Air Basin.
- South Central Coast Air Basin to South Coast Air Basin, and vice versa.
- South Coast Air Basin to Southeast Desert and San Diego Air Basins.
- San Diego Air Basin to Southeast Desert Air Basin.

3.4.7 Ventilation Factors

Holzworth (1972) developed an urban dispersion model to be used with climatological data to generate statistics on air pollution potential. The model assumes that pollutant concentrations are a direct function of the area emission rate and vary inversely with the wind speed and mixing height. The product of the average wind speed in the mixed layer and the mixing height is referred to as the "ventilation factor." Low wind speeds and low mixing heights result in small ventilation factors which translate into large pollution potential. The combination of low inversion heights, high terrain inland, and a strong diurnal heating cycle in California channel the summer flow patterns into a highly repeatable daily cycle. Since the source areas are largely fixed in location, the receptor areas also tend to be similar each day due to minor fluctuations in wind speed and mixing height.

Smith et al. (1984) have calculated the ventilation factors for each of the 19 sounding locations in California during the period of 1979 to 1980 which includes the following observations:

- Morning ventilation factors are highest along the coast and higher in the Central Valley than other inland areas.
- Ventilation is greatest during summer afternoons, with higher values inland than along the coast.
- The ventilation factor correlates almost as well with peak ozone as with the 850 mb temperature.
- Better mixing height statistics are needed for Santa Rosa, the Salinas Valley, the southern San Francisco Bay Basin, San

Bernardino/Riverside, and the inland areas of the San Diego Air Basin.

- Uncertainties in predicting high air pollution potential from ventilation factors include poor estimates of mixing height, inaccurate wind speeds at the lower limit of the anemometer range, and the neglect of directional pollutant transport by the wind.

3.5 Emissions Inventory Data

An emissions inventory is an itemized list of emission data for both stationary point and area sources as well as mobile sources of air pollution in a given area. The spatial resolution of these inventories varies -- it can range from a 10 km by 10 km grid, to a county, to an air basin, or to the entire state.

Ideally, an emissions inventory should identify and quantify the emissions from each source as a function of time and location. The data should be structured so that the inventory can serve as a base for forecasting emissions, provide data for modeling, and provide a basis for developing and prioritizing emission control strategies. The requirements and methods for assessing and maintaining a data inventory vary because of the wide variety of sources that must be evaluated.

3.5.1 Emissions Sources

A point source is a sizable emissions source that has a specific location (i.e., stationary source). Point sources vary in size and complexity, ranging from a simple source, such as a store that has one boiler, to a complex industrial facility, such as a refinery that contains hundreds of devices that emit pollutants. Facilities with emissions greater than 25 tons per year are classified as point sources. The information compiled for point sources is obtained primarily from local air pollution control districts.

The term "area source" is used to describe sources that individually emit small amounts but collectively result in significant emissions. Sources that emit less than 25 tons per year are usually classified as area sources. However, some districts have chosen to treat as point sources facilities with emissions less than 25 tons per year. Therefore, a more universal definition of an area source is a source that is not treated as a point source.

Because area sources are collections of individual sources, it is common to separate them into categories based on similar characteristics. Each category is then assigned a five-digit code.

Motor vehicles are divided into six categories: 1) light duty passenger vehicles; 2) light duty trucks with gross vehicle weight (GVW)

less than 6001 pounds; 3) medium duty trucks (GVW) from 6001 to 8500 pounds); 4) heavy duty gasoline trucks (GVW greater than 8500 pounds); 5) heavy duty diesel trucks (GVW greater than 8500 pounds); and motorcycles. Vehicles in the first three categories may be equipped with catalytic converters; vehicles in the last three are not.

3.5.2 Emission Factors

Emission factors are used for estimating air pollutant concentrations from different stationary and mobile sources. An emission factor is an average value which relates the quantity of a pollutant to activity associated with the release of that pollutant. It is usually expressed as the weight of pollutant divided by a unit weight, volume, distance or duration of the activity that emits the pollutant (e.g., kilograms of particulate emitted per megagrams of coal combusted).

In most cases, emission factors are simply averages of all available data of acceptable quality, generally without consideration of the influence of various process parameters such as temperature, reactant concentrations, etc. In a few cases, empirical formulae have been developed which can relate emissions to such variables as temperature and wind velocity. Emission factors correlated with such variables tend to yield more precise estimates than factors derived from broad statistical averages.

Also, because these factors are averages obtained from data of wide range and varying degrees of accuracy, emissions calculated this way for a given facility are likely to be different from that facility's actual emissions. Emission factors can yield emission rates which are higher than actual emissions for some sources and lower than actual for others. Only on-site source tests can estimate the actual emission rates under the conditions existing at the time of the test.

Emission factors for motor vehicles are specific to cold and hot starts, different speeds, vehicle type, model year, ambient temperature, and the type of fuel. The major sources of emissions from motor vehicles are exhaust emissions and evaporative emissions. Other sources are crankcase components (controlled on most cars), tire wear, and resuspended road dust.

The U. S. EPA (1985) evaluates the reliability of emission factors (using grades of A through E, with A being the best). Subjective schemes are used to assign these ratings, depending upon data availability, source characteristics, etc. Because these ratings are subjective and take no account of the inherent scatter among the data used to calculate factors, they should be used only as approximations to infer error bounds or confidence intervals about each emission factor. At most, a rating should be considered an indicator of the accuracy and precision of a given factor used to estimate emissions from a large number of sources.

The factors for calculating emissions for a process may be derived in various ways. Source tests of a device provide the best emission factors for that device. Tests can be made over a range of operating conditions of the process and the control equipment. If source test data are not available for a specific device, an alternative is to use average emission factors for similar devices. These factors are usually derived by averaging the results of many tests of similar sources. Such factors are published for a wide variety of devices by the Environmental Protection Agency in its publication Compilation of Air Pollutant Emission Factors, AP-42 (U.S. EPA, 1985). The published emission factors are usually for devices without control equipment, and it is therefore necessary to adjust the emission factors to account for the control equipment being used.

3.5.3 Determining Emissions from Various Sources

Estimates of emissions are made for each process that results in emissions from a facility or aggregate of sources. These estimates are based on a measure of activity, usually a process rate or throughput for a device, and an emission factor that relates how much of a pollutant is emitted per unit of throughput.

Emissions from a process can in some cases be determined by conducting a materials balance, that is by determining the amounts of materials entering and leaving a process. For example, in a painting process it is reasonable to assume that all the solvent used in the coating eventually evaporates into the air. This technique is also used in estimating the sulfur oxides (SO_x) emissions from combustion processes because it is assumed that all of the sulfur in the fuel is transformed to SO_x in the combustion process.

The process rate data used to calculate emissions from a source can vary significantly from year to year as well as during the year. Therefore, information on the yearly, weekly and daily variations of the process rate is necessary for estimating emissions during a particular season or period of poor air quality.

For those area source categories that aggregate many individual sources, the total emissions estimates are based on composite activity emission factors. In determining a measure of the area source activity, it is sometimes necessary to use the national statistics concerning a specific product and apportion the emissions to each county based on population.

3.5.4 PM_{10} Emissions Inventory Data

The emission factors for size-segregated particulate matter have, for the most part, been derived from source tests utilizing multi-stage impactors, size fractionating inlets and cyclones to collect material in different size fractions. Most emission factors for fugitive dust sources (agricultural tillage, unpaved roads, heavy construction activities and

aggregate storage piles) are based on tests conducted by Cowherd et al. (1974).

Significant atmospheric dust arises from the mechanical disturbance of granular material. Dust generated from these open sources is termed "fugitive" because it is not discharged to the atmosphere in a confined flow stream. The dust generation process is caused by two physical phenomena:

- Pulverization and abrasion of surface materials by application of mechanical force through implements (wheels, blades, etc.).

- Entrainment of dust particles by the action of turbulent air currents, such as wind erosion of an exposed surface by wind speeds over 19 kilometers per hour (12 mph).

The basic measurements of Cowherd et al. (1974) consisted of isokinetic dust exposure profiles with specially designed sampling equipment, TSP dust concentrations with conventional high-volume samplers and particle size classification with high volume cascade impactors. For each source type, emissions were related to meteorological and source parameters, including properties of the emitting surface and characteristics of the vehicle or implement which causes the emission. This information is used to derive factors which adjust basic emission factors to reflect regional differences in climate and surface properties. According to Cowherd et al. (1974), estimation of the fugitive dust emissions is not easily accomplished because:

- The sources are not well defined in area.

- Emissions are highly erratic with time due to changes in source activity.

- Great variations in emission rates result from meteorological factors, which are quite variable themselves (e.g., length of time between rains, frequency of high winds, occurrence of atmospheric turbulence, etc.).

The reliability rankings of PM_{10} emission factors for fugitive dust sources are summarized in Table 3.5-1, along with the various parameters used to adjust the emission factors for non-site specific sources. PM_{10} emission factors can be determined using the following approaches:

- Extrapolation of particle size distribution data to the PM_{10} size range combined with a total mass emission factor. For some sources, particle size distribution data are not available in the size range of interest (i.e., $< 10\ \mu m$), but they are available for larger particle size ranges. In these situations, an estimate of the PM_{10} emission factor can be obtained by superimposing a PM_{10} inlet sampling effectiveness curve on the size distribution of the primary particulate

Table 3.5-1

Reliability of PM_{10} Emission Factors for Fugitive Dust Sources[a]

Source Category	Measure of Extent	Adjustment Parameter	Emission Factor Ranking
Unpaved Roads	Vehicle miles travelled, by road type	o Mean vehicle weight and speed o Mean number of wheels o Silt content of road surface	A if site specific, other B
Agricultural	Area by crop	o Silt content of surface soil o Particle size multipler	A for TSP B for PM_{10} C if not site specific
Aggregate Handling and Storage Piles	Aggregate tonnage	o Age of pile o Moisture content o Proportion of aggregate fines o Mean wind speed o Drop height o Dumping device capacity o Particle size multiplier	
Heavy Construction	Area of active construction, by construction type	o Silt content of soil o Soil moisture o Activity index o Particle size multiplier	B or C
Paved Roads	Vehicle miles travelled, by roadway category	o Traffic volume o Surface dust loading o Base emission factor for specific roadway category o Particle size multiplier	A if site specific, other B

[a] AP-42: Compilation of Air Pollutant Emission Factors (U.S. EPA, 1985).

emissions. This is straightforward if the emissions closely fit a log-normal distribution. In this case, plotting the particle size data on log-probability graph paper allows one to make a linear extrapolation of the data to the particle size of interest, namely 10 μm.

The PM_{10} emission factor is calculated by multiplying the percentage of emissions less than 10 μm diameter by the total suspended particulate mass emission factor available from AP-42 (U.S. EPA, 1985). This technique provides only a rough estimate of the emission factor because the extrapolation of the particle size data may misrepresent the actual size distribution. However, in the absence of any particle size data in the range of interest, the technique provides a first approximation.

- A measured mass fraction of particles less than 10 μm combined with a total mass emission factor. This technique is applied when the mass fraction of particles less than 10 μm has been measured. To compute the PM_{10} emission factor, the mass fraction of particles smaller than 10 μm is multiplied by the total mass emission factor.

- Estimation of emission factors by generic grouping of source categories. For sources which lack particle size distributions, the mass fraction of PM_{10} in uncontrolled source emissions may be estimated by generic grouping of source categories according to particulate generation mechanisms. For example, process fugitive emissions may be assigned the same PM_{10} mass fraction as the uncontrolled ducted emissions for the same sources. Also, it has been shown that open dust sources within the same generic source category have nearly the same proportion of PM_{10} in the emissions plume. Some source emissions consist entirely of particles less than 10 μm (e.g., condensation of metal fumes). In addition, it is usually a good approximation to treat controlled particulate as PM_{10} since control devices typically remove most of the particulate mass consisting of particles larger than 10 μm.

Development of PM_{10} emissions inventories requires the calculation of PM_{10} emission rates for various sources, both uncontrolled and controlled. Emission rates for uncontrolled sources are readily determined by multiplying the PM_{10} emission factor by the process rate. Two alternative procedures may be used to calculate a controlled PM_{10} emission rate.

In the first approach, the mass fraction of particles smaller than 10 μm in the uncontrolled emission stream is multiplied by the uncontrolled total mass emission factor for the specific source yielding an uncontrolled PM_{10} emission factor. Next, the controlled PM_{10} emission factor is multiplied by the PM_{10} collection efficiency for the specific control device applied to that source. Finally, the controlled PM_{10} emission rate

is calculated by multiplying the process rate by the controlled PM_{10} emission factor.

The second approach for calculating a controlled PM_{10} emission rate requires the particle size distribution in the uncontrolled emission stream, the uncontrolled total mass emission factor, the penetration curve for the specific control device, and the process rate. This procedure requires a more sophisticated calculation program to determine the controlled emission factor -- it combines the uncontrolled emission factor and the corresponding particle size distribution with the control device penetration curve.

Many of the same PM_{10} emission factors have been used by U.S. EPA in establishing the National Emissions Data System (NEDS) and the Emission Assessment Data System (EADS) and by ARB and local Air Quality Management Districts (AQMDs) in deriving the latest versions of the PM_{10} emissions inventories for the state and local air basins. While the NEDS data base has been criticized in the past for lack of complete coverage and questionable reliability, it nonetheless represents the largest and most complete emissions file available. The major limitation of current PM_{10} emission rate data relates to limited particle size measurements. PM_{10} emission factors and control efficiencies of various air pollution control devices for PM_{10} are currently being updated by EPA's Office of Research and Development (ORD) staff.

At an Air Pollution Control Association (APCA) sponsored workshop in 1980 it was the consensus of the participants that:

- AP-42 is inadequate in its current form; including size specific information by way of some universal PM_{10} conversion factors would make the problem worse.

- AP-42 needs experimental error bounds associated with emission factors.

- The majority of the previous work to develop emission factors used unestablished methodologies and equipment and non-comparable size fractions.

- Very few PM_{10} emission factors have been measured directly.

- Aerosol precursors and condensable gases are not dealt with by primary PM_{10} emission factors.

Major uncertainties in the PM_{10} emission factors and emission rates stem from:

- Errors in measurement methods. Examples include uncertainties in the sampling efficiency of the sampler, recirculation of pump exhaust, particle bounce in cascade impactors, filter artifacts, non-isokinetic flow sampling, single sampling points in a ducted source, and neglect of condensable fractions of

emissions. Under controlled conditions, simultaneous tests run to collect particle mass and size distribution data with the SASS train, Joy train with cyclones, standard EPA Method 5 procedure, and an Andersen cascade impactor indicate a precision for measuring particulate mass emissions of ± 30%.

- Paucity of data. Most of the available particle size data is confined to ducted sources, whereas data on process fugitive emissions and on open dust sources is sparse.

- High degree of variability in emission rates. Emissions from the same source may vary significantly with time due to changes in process rates and operating conditions, or due to degradation of control equipment.

- Extrapolation of size distribution data. Aerosols generated by a single formation mechanism tend to be log-normally distributed which allows extrapolation of PM_{10} data from particle size measurements of other size ranges. However, because more than one mechanism may be active within a given source type, bimodal particle size distributions may be present. This is very common with plumes that contain a large amount of condensable gases as well as primary emissions of PM_{10}. In the case of bimodal size distributions, it is almost impossible to extrapolate size distribution data to calculate a PM_{10} fraction with any accuracy.

- Variable PM_{10}/TSP ratios. It used to be common to calculate PM_{10} emission rates from TSP emission rates using a universal fudge factor or ratio of ~0.6. However, recent particle size measurements for different sources show that this ratio is highly source dependent and ranges from about 0.4 to 1.0.

4.0 CHANGES IN CHEMICAL COMPOSITION BETWEEN SOURCE AND RECEPTOR

Receptor-oriented models, including the CMB model, require the source composition as it is perceived at the receptor. This is nearly always impossible to measure since the receptor represents a mixture of source contributions and the source composition can change between source and receptor. Most source compositions are therefore determined directly from samples taken at the source. If the chemical species that are measured at the source do not change in their relative proportions between source and receptor, then there is no difference between the relative measurement at the source and that perceived at the receptor. Unfortunately, the physical and chemical phenomena of sedimentation, diffusion, impaction, interception, evaporation, condensation, oxidation, reduction and precipitation scavenging can change the relative proportions of chemical species between source and receptor. This change in relative proportions of source compositions was termed "fractionation" by Miller et al. (1972).

Fractionation is a function of the atmospheric conditions along the path between source and receptor and the travel time along that path. Methods for accurately estimating source profiles as they appear at a receptor (when fractionation is important) are still under development. Source-oriented models are also concerned with changes of chemical composition between source and receptor. In particular, these models must accurately represent the same physical and chemical phenomena as receptor models.

Gas-to-particle transformations have a major impact on changing the PM_{10} source profiles between source and receptor and will be the major focus of this chapter. We will summarize the current knowledge of the mechanisms and rates that transform gases to particles between source and receptor, thereby resulting in source profile fractionation. Also, we will help the model user identify situations in which source profile fractionation may be important.

4.1 Chemical Transformations in Source and Receptor Models

Primary particulate matter is defined as particulate matter emitted into the atmosphere at the source. Some gases are transformed to particulate matter by the physical and chemical processes occurring between the source and the receptor. This particulate matter is defined as secondary. Measured PM_{10} includes contributions from both primary and secondary particulate matter. This discussion will focus on the major secondary contributors to PM_{10} in California, which are sulfates, nitrates and, to a lesser extent, organics. These particulate species are formed in the atmosphere from emitted SO_2, NO and NO_2, and reactive organic gases, respectively. These secondary contributors to PM_{10}, and their associated ions, must be included in any modeling approach because together they can often account for one-third to one-half of the total PM_{10} mass.

Table 4.1-1 shows the ARB annual average PM_{10} mass, sulfate and nitrate concentrations for 1985. Sulfate and nitrate ion concentrations

Table 4.1-1

Annual Arithmetic Average Concentrations of PM_{10} Mass, Sulfate and Nitrate (in $\mu g/m^3$) at California Sampling Sites in 1985

Air Basin/Location	Mass	Sulfate	Nitrate
S.F. Bay Area			
Bethel Island	33.4	2.59	1.66
San Jose	52.5	3.25	3.73
South Central Coast			
Santa Maria	35.5	4.63	1.65
Piru	31.7	3.23	2.45
Simi Valley	45.8	6.35	3.72
South Coast			
Azusa	66.8	5.76	7.30
Burbank	70.1	6.79	7.54
L.A.-No. Main	70.3	6.79	7.67
North Long Bech	54.6	6.87	4.68
El Toro	46.8	5.21	4.32
Los Alamitos-Orange	56.4	5.93	5.24
Riverside-Rubidoux	96.1	6.43	18.92
Fontana-Arrow Hwy	74.3	4.23	17.29
Ontario APT	73.6	6.18	12.91
San Joaquin Valley			
Five Points	46.9	2.97	4.24
Fresno-Cal St. #2	48.8	2.56	1.69
Fresno-Olive	63.6	4.07	5.38
Bakersfield	76.7	7.63	12.20
Oildale	74.2	10.40	12.58
Taft	64.2	5.92	3.93
Corcoran	66.4	2.95	2.99
Hanford	58.3	3.59	3.36
Kettleman City	15.3	4.63	1.68
Madera	56.4	3.08	2.51
Merced	50.9	2.69	1.25
Stockton	52.3	3.43	5.12
Modesto	46.0	3.11	4.14
Visalia	67.8	4.39	6.10
Southeast Desert			
Brawley	61.5	2.45	2.59
El Centro	55.8	3.45	2.31
Mojave	64.2	2.93	1.38
Banning	51.5	4.61	9.00
Indio	67.7	3.68	4.48
Barstow	40.9	2.31	1.74
Trona	70.9	9.15	2.61
Victorville	53.3	2.83	4.95

account for a significant portion of the measured PM_{10}, averaging from 12 to 27%. Most of the measured sulfate and nitrate is assumed to be of secondary origin. A few sources (e.g., coal-fired power plants and sulfuric acid plants) emit approximately 1 to 4% and up to 15%, respectively, of their total sulfur emissions as primary sulfate, but this generally contributes little to the average sulfate receptor concentrations shown in Table 4.1-1.

The contributions of secondary sulfate and nitrate to PM_{10} mass are actually higher than these measurements indicate, due to associated ions and nitrate losses during sampling. For example, if ammonium ion is assumed to neutralize all of the sulfate and nitrate at Azusa, CA, the contribution of sulfate and nitrate (now as ammonium sulfate and ammonium nitrate) to average PM_{10} mass increases from 19.6 to 27.6%. Associated ammonium at Kettleman City, CA, increases the contribution from 41.2 to 61.4%.

Actual nitrate values may be even higher than measured because a significant amount of the nitrate in the atmosphere may have evaporated from the sample substrate before analysis. Preliminary estimates indicate that South Coast Air Quality Management District (SCAQMD) nitrate concentrations may be twice as high as measured (SCAQMD PM_{10} Modeling Approach, 1986). The SCAQMD and ARB are evaluating nitrate losses from PM_{10} samples. They will measure PM_{10} mass, sulfate, nitrate, ammonium and chloride on fresh filter samples taken at three stations and then repeat the analyses on each filter about three more times during 1987. The results should be available by the end of 1987.

Table 4.1-2 shows the average fine particle (< 2.1 μm) mass, elemental carbon and organic carbon measured for 11 SoCAB sampling sites in 1982. Gray et al. (1986) show that aerosol carbon species accounted for approximately 40% of the fine mass at most monitoring sites in this study. The elemental carbon is of primary origin, while the organic carbon is part primary and part secondary. Gray et al. (1986) estimate that 27 to 38% of the average organic carbon in the eastern portion of the basin is due to secondary aerosol formation. Thus, secondary carbon contributed only about 4% to the fine particulate mass in a photochemical system like the South Coast Air Basin for the study period. This is significantly less than the sulfate and nitrate contributions.

However, measurements of fine aerosols in the California Desert during August 1983 to August 1985 (Trijonis et al., 1987) may indicate a larger contribution from secondary organics. There, organic carbon averaged 32% of the fine mass (< 2.5 μm) versus the 21% measured by Gray et al. (1986). Also, the total carbon to elemental carbon ratio of 6.8 was significantly higher than the 3.2 measured by Gray et al. (1986). Trijonis et al. (1987) also found a large portion of their organic carbon to be attributable to the adsorption of organic vapors on the quartz fiber substrates.

In summary, secondary sulfate and nitrate components of PM_{10} average 12 to 27% of the measured PM_{10} in California. However, ions associated with

Table 4.1-2

Fine Particle Mass and Aerosol Carbon Data for the Los Angeles Area, 1982

Station	Number of Carbon Samples	Concentrations in $\mu g/m^3$			
		OC[a] Sample Population Mean	EC[b] Sample Population Mean	TC[c] Sample Population Mean	Particulate Mass Concentration
Azusa, CA	60	5.73	3.30	9.03	29.6
Burbank, CA	58	8.71	5.04	13.74	28.6
Long Beach, CA	59	6.11	3.75	9.86	27.5
Lennox, CA	61	6.18	4.51	10.69	28.5
Pasadena, CA	60	6.79	3.95	10.73	28.5
West Los Angeles, CA	58	5.84	3.61	9.44	24.8
Los Angeles, CA	61	7.29	4.87	12.16	32.7
Upland, CA	56	5.36	3.14	8.51	27.7
Rubidoux, CA	55	5.20	3.03	8.23	42.1
Anaheim, CA	57	5.35	3.18	8.53	23.1
San Nicolas Island, CA	46	1.73	0.28	2.02	6.8

[a] OC is organic carbon concentration.

[b] EC is elemental carbon concentration.

[c] TC is total carbon concentration.

these secondary components and the loss of nitrate before measurement increase the contribution of secondary components to the PM_{10} mass. Secondary organic components may contribute only a small percentage to the measured PM_{10} mass. Also, the often significant non-controllable contributions to PM_{10} mass increase the importance of the (controllable) secondary component contributions. Thus, any modeling approach must be able to account for the transformation of primary gases to secondary PM_{10} components.

The mechanisms and rates of transformation for each of these classes of secondary species (sulfate, nitrate and organics) will be discussed in more detail in the following sections.

4.2 Transformation Mechanisms

There are a number of mechanisms which transform primary gases such as SO_2, NO_x and hydrocarbon gases to secondary PM_{10} particulate matter. These mechanisms are complex and not yet completely understood. Physical and chemical properties of the atmosphere also affect transformation rates. The level of current understanding of the transformation rates differs for sulfate, nitrate and organic species.

4.2.1 Sulfur

The conversion of gaseous SO_2 to particulate sulfate is a complex process involving both chemical conversion of SO_2 to sulfate and the incorporation of sulfate into the particles. These processes are interconnected and both influence the rate of transformation and the size of the final particulate sulfate.

SO_2 can be oxidized in the gas-phase or in aqueous droplets. The controlling mechanism is different, depending on the conditions of the atmosphere. The gas-phase photochemical reaction with the hydroxyl radical dominates SO_2 oxidation in the presence of sunlight and the absence of clouds or fog. SO_2 oxidation is faster in the presence of clouds or fog, when the aqueous-phase reactions of hydrogen peroxide (H_2O_2) or metal catalysts dominate.

In the gas phase, photochemically produced radicals such as OH, HO_2 and CH_3O_2 can oxidize SO_2. Typically, the hydroxyl radical (OH) is estimated to dominate the gas-phase oxidation of SO_2. At very high alkene concentrations another mechanism may dominate, the reaction of SO_2 with intermediate biradicals formed from ozone-alkene reactions (Atkinson and Lloyd, 1984). Reactions of SO_2 with RCHOO, CH_3O and O(3P) are probably less important. In the presence of even trace amounts of water, the gas-phase products of these reactions quickly form a sulfate aerosol or attach to pre-existing particles. The radicals and atoms that drive these reactions are produced by the NO_x-O_3-hydrocarbon photochemical cycle and are expected to exist in polluted urban air, in "clean" rural air, and in

diluted stack plumes. However, the concentrations of these ions and atoms have not, in general, been measured in any of these atmospheres.

The rate constants for these gas-phase photochemical reactions have been measured in the laboratory with pure components or estimated from first principles. However, the intermediate species formed in these reactions are not well understood and their concentrations have not been measured in either laboratory or real atmospheres. Direct measurement of these reactive intermediates is an important step in confirming and improving understanding of homogeneous gas-phase SO_2 oxidation mechanisms.

SO_2 oxidation can also occur via reactions of dissolved sulfur constituents (sulfite and bisulfite) with dissolved H_2O_2, ozone or oxygen. Trace metals can also catalyze these aqueous-phase reactions. The oxidation of sulfite and bisulfite in aqueous droplets by H_2O_2 may be the dominant process under acidic conditions (Schwartz, 1983) because the rates of reaction by ozone and oxygen decrease rapidly as acidity increases. Recent measurements of Los Angeles Basin cloudwater (Richards et al., 1987) demonstrated sufficiently high H_2O_2 concentration levels to sustain this reaction at a rate about 100 times faster than other processes.

Oxidation by dissolved ozone might be important in urban or rural air, but this mechanism should not be significant in plumes where the ozone has been removed by excess NO. The catalyzed oxidation of sulfite and bisulfite in solution by transition metals ions (i.e., Fe and Mn), is probably important when high concentrations of the catalysts are present in the droplets.

4.2.2 Nitrogen

NO_x is oxidized in the gas phase by either OH radicals during the daytime or by the NO_3 radical at night. Most of the oxidation products remain in the gas phase and do not form secondary particulate matter.

NO_x oxidation is strongly dependent on the gas-phase photochemical system of reactive organic gases/NO_x/O_3 and is generally 5 to 10 times more rapid than SO_2 oxidation. Nitrogen oxides are oxidized to nitric acid and organic nitrates (including peroxyacetylnitrate, PAN). As with SO_2 oxidation, the reaction of NO_2 with the OH radical (to produce nitric acid) is the major daytime oxidation method, but it occurs at a rate about eight times faster than with SO_2. At night, on the other hand, NO_3 radical formation and subsequent reactions with NO_2 and organics produce nitric acid. Most of the oxidized nitrogen oxides, including PAN, do not form particulate nitrate. In smog chambers, the total amount of NO_x oxidation linearly increases with an increase in the ratio of non-methane hydrocarbon (NMHC) to NO_x. The fraction of the oxidized products which is nitrates also increases with an increase in the NMHC/NO_x ratio (Spicer, 1983).

Gas-phase nitric acid can combine with ammonia gas to form either solid or aqueous ammonium nitrate (NH_4NO_3). However, this process is

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Education

Sc.D	Environmental Science	1985	Harvard University, MA
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Experience Related to Proposed Project

Dr. Judith C. Chow is an Assistant Research Professor in the Energy and Environmental Engineering Center (EEEC) at the Desert Research Institute (DRI) where she conducts air quality measurement and source apportionment studies. These studies involve program planning, field sampling, laboratory analysis, data management, quality assurance, source/receptor modeling, and control strategy evaluations. Dr. Chow is also in charge of EEEC's environmental analysis facilities which include gravimetric, x-ray fluorescence, neutron activation, automated colorimetric, atomic absorption spectrophotometric, gas and liquid chromatographic, ion chromatographic, thermal/optical carbon, filter transmittance, and microscopic analyses. Other current projects include sampler design and testing for California's Acid Deposition Monitoring Program, receptor and source sampling in several western states for PM_{10}, State Implementation Plan development, and the 1987-88 Metro Denver Brown Cloud Study.

Prior to coming to DRI, Dr. Chow was a research fellow in the department of Environmental Science at Harvard University. In this program, Dr. Chow interpreted data from the Harvard Air Pollution Respiratory Health Study by combining Principal Component Analysis (PCA), Chemical Mass Balance (CMB), Branching Atmospheric Trajectory (BAT), Industrial Source Complex-Short Term (ISC-ST), and first-order chemical transformation models. This combination of models attributed ambient air pollution concentrations to local and regional sources in the midwest. Dr. Chow also contributed to various indoor air pollution studies at Harvard University.

Before returning to school, Dr. Chow worked as an Environmental Scientist for nine years at Environmental Research and Technology, Inc. (ERT) and North Carolina State University. At ERT, Dr. Chow managed a major field monitoring program in Puerto Rico, created an aerosol data base and data management system, interpreted data from the USEPA Inhalable Particulate Matter (IPM) Network and performed laboratory analyses on aerosol samples from the Sulfate Regional Experiment (SURE) and Eastern Regional Air Quality Study (ERAQS). At North Carolina State University, Dr. Chow performed chemical analyses of contaminated soil and waste water samples.

Professional Experience

1985 to Present	Assistant Research Professor, Energy and Environmental Engineering Center, Desert Research Institute
1982-1985	Environmental Consultant, Environmental Research & Technology, Inc., Concord, MA
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1977-1982	Environmental Scientist and Chemist, Environmental Research & Technology, Inc., Concord, MA
1976-1977	Chemistry Technician, Soil Science Department, North Carolina State University, Raleigh, NC
1974-1976	Biology and Health Science Teacher, Dominican High School and Chin-Ching Junior High School, Kaohsiung, Taiwan

Memberships

Air Pollution Control Association (APCA)
APCA, Source Apportionment and Receptor Modeling Technical Committee
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JOHN G. WATSON
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Education

Ph.D.	Environmental Sciences	1979	Oregon Graduate Center
M.S.	Physics	1974	University of Toledo
B.A.	Physics	1970	State University of New York at Brockport

Experience Related to Proposed Project

Dr. Watson supervises a group of scientists performing advanced aerometric measurements of trace gases, suspended particulate matter, wet and dry deposition, meteorological variables, and visibility. Dr. Watson also performs original research in the development and evaluation of measurement processes, receptor models, and the effects of measurement uncertainty on model results.

Dr. Watson's current projects include the development of receptor modeling software and its integration with source and receptor data bases, a visibility source apportionment study in Denver, CO, regional receptor modeling for the SCENES 1986 Winter Intensive, and evaluation of PM_{10} control strategy development in various western states. He has recently completed program plans for the South Coast Air Quality Study (SCAQS), the SCENES Visibility Study, the State of Nevada Air Pollution Study (SNAPS), the 1987-88 Metro Denver Brown Cloud Study, and the California Acid Deposition Monitoring Program. Dr. Watson is also on the program planning team for the San Joaquin Valley Air Quality Study.

Prior to his employment at the Desert Research Institute, Dr. Watson was a Senior Environmental Scientist at Environmental Research and Technology, Inc., where he played major roles in the Electric Power Research Institute's Eastern Regional Air Quality Studies (ERAQS), the Sulfate Regional Experiment (SURE), the Denver Winter Haze Study, and the interpretation of data from EPA's Inhalable Particulate Network. He also organized and conducted EPA's Quail Roost I Receptor Model Workshop.

Dr. Watson was technical manager of the Portland Aerosol Characterization Study (PACS) at the Oregon Graduate Center where he developed routine procedures for sequential aerosol sampling systems, and x-ray fluorescence, neutron activation, ion chromatography, and carbon analyses of aerosol samplers.

Before entering the field of environmental sciences, Dr. Watson was a physics instructor at the college level. He currently works with physics graduate students at the University of Nevada.

Professional Experience

1986-Present	Research Professor, Energy and Environmental Engineering Center, Desert Research Institute, University of Nevada, Reno, NV.
1982-1986	Associate Research Professor, Atmospheric Sciences Center, Desert Research Institute, University of Nevada, Reno, NV.
1979-82	Sr. Environmental Scientist, Environmental Research and Technology, Concord, MA.
1975-79	Research Fellow, Oregon Graduate Center, Beaverton, OR.
1974-75	Physical Science Instructor, University of Illinois, Urbana, IL.
1973-74	Physics Teaching Assistant, University of Toledo; Toledo, OH.
1970-73	Pysics Instructor, Teachers College, Chiclayo, Peru, as a member of the U.S. Peace Corps.

Memberships

Air Pollution Control Association
Chairman, Control Program Administration Division
Member, International Affairs Committee, Critical Review Committee, Receptor/Source Apportionment Committee
Technical Chairman, 1988 APCA International Specialty Conference on Receptor Models in Air Resources Management
Association of Environmental Scientists and Administrators
American Association for the Advancement of Science
American Chemical Society

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Watson, J.G., N.F. Robinson and H.S. Javitz (1986). "The Feasibility of the Chemical Element Balance Applied to Regional-Scale Source Apportionment." Presented at the Cooperative Institute for Research in the Atmosphere (CIRA) Workshop on Acid Deposition.

Chow, J.C. and J.G. Watson (1987). "Relationships Between Secondary Aerosols and Photochemical Factors in California's San Joaquin Valley." Paper 87-61.7, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Watson, J.G. and J.C. Chow (1987). "PM_{10} Sampling and Analysis Alternatives for Receptor Modeling." Paper 87-63.3, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Watson, J.G. and T.G. Pace (1987). "A New Method to Reduce Uncertainties of Receptor Models to Apportion PM_{10} to Sources." Paper 87-74.3, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Freeman, D.L., J.G. Watson, N.R. Robinson. J.C. Chow and R.T. Egami (1987). "Uncertainty Reduction Through Use of Combined Source-Receptor Models in a PM_{10} Assessement Package." Paper 87-74.2, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Gertler, A.W., C.F. Rogers, N.F. Robinson and J.G. Watson (1987). "Uncertainites in the Measurement of Deposition Velocities in an Urban Environment." Paper 87-72.5, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Pace, T.G. and J.G. Watson (1987). "Protocol for Improving Model Estimates by Combining Receptor Modeling and Dispersion Modeling." Paper 87-73B.5, presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 21-26 June 1987.

Major Scientific Reports:

Watson, J.G. (1979). "Chemical Element Balance Receptor Model Methodology for Assessing the Sources of Fine and Total Suspended Particulate Matter in Portland, OR." Ph.D. dissertation, Oregon Graduate Center, Beaverton, OR.

Cooper, J.A., J.G. Watson and J.J. Huntzicker (1979). "Portland Aerosol Characterization Study: Application of Chemical Mass Balance Methods to the Identification of Major Aerosol Sources in the Portland Airshed." Prepared for the Oregon Department of Environmental Quality at the Oregon Graduate Center, Beaverton, OR.

Heisler, S.L., R.C. Henry, J.G. Watson and G.M. Hidy (1980). "The 1978 Denver Winter Haze Study." Environmental Research and Technology Report P5417-1, prepared for the Motor Vehicle Manufacturer's Association of the United States.

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reversible and an equilibrium is established between nitric acid, ammonia and ammonium nitrate:

$$HNO_3(g) + NH_3(g) \underset{}{\overset{K}{\rightleftharpoons}} NH_4NO_3 \text{ (s or aq)} \qquad (4.2\text{-}1)$$

where:

s = solid

aq = aqueous

g = gas

$K = [NH_4NO_3 \text{ (s or aq)}]/[HNO_3 \text{ (g)}]\ [NHO_3 \text{ (g)}]$

The equilibrium constant, K, is dependent on temperature and relative humidity in a very non-linear fashion. Particulate nitrate concentrations are limited by the availability of ammonia because ammonia is preferentially scavenged by sulfate.

4.2.3 Organic Species

The transformation of organic gases to secondary PM_{10} particulate organics is a poorly understood process. This is true for a number of reasons, including: 1) the large number of individual organic gas species emitted by sources; 2) the even larger number of possible reactions of these emitted gases; 3) the difficulty of measuring all of the complex organic species that exist in the atmosphere; 4) sampling artifacts; and 5) disagreement over the analytical separation of organic and elemental particulate carbon.

Qualitatively, reactive organic gases are oxidized by ozone, H_2O_2, OH radicals and other species in the photochemical mixture. Some of these products can continue to oxidize or react, but eventually the concentration of a gas-phase species exceeds its vapor pressure. That species begins to condense, usually on existing particulate matter. This produces particles (generally smaller than 1 or 2 μm in size) which contain secondary organic material. Temperature and the concentration of the condensable species are the controlling parameters in this transformation, since the atmosphere almost always provides sufficient pre-existing particles for the condensable organic species to condense upon.

Smog chamber studies reveal that both chemical reaction in the gas phase and the physical process of condensation contribute to the transformation of organic gases to secondary carbon particles. Atmospheric studies have identified a host of polyfunctional oxygenates, including dicarboxylic acids, as particulate end products of hydrocarbon photo-

oxidation. Often only a small percentage of the individual carbon particulate compounds can be identified (besides elemental carbon).

This general area is the focus of much current research effort. Relevant efforts which will result in new knowledge about the fractionation of organic species include the ARB-sponsored carbon intercomparison (Lawson, 1986), the SCAQMD-sponsored carbon PM_{10} measurement program by the California Institute of Technology (CIT) and the cooperative SCAQS program (Blumenthal et al., 1987). Each of these programs will greatly improve understanding of the transformation of organic gases to secondary organic particulate matter.

4.3 Transformation Rates

Though a full mathematical description of gas-to-particle transformations is not available, empirical estimates of the rates at which SO_2, NO_x and reactive organic gases are transformed to PM_{10} sulfate, nitrate and organic carbon have been determined. These rates are estimated using model simulations, laboratory experiments and field measurements. These are reasonable estimates that can be used for screening calculations and to determine whether or not fractionation of the source profile between a source and a receptor might bias the results of a CMB application. These rates can also be used as input data to source-oriented models, such as the ISC-ST, which include first-order transformation of gases to particles.

4.3.1 Sulfur

Transformation rates for SO_2 have been estimated using measurements in laboratory and smog chamber experiments, in the Los Angeles atmosphere, and in powerplant and urban plumes in the Southwest and Midwest. These studies give a reasonably consistent picture of the transformation of SO_2 to particulate sulfate.

Cass (1981) has estimated the transformation rate of gaseous SO_2 to particulate sulfate in the Los Angeles Basin. His extensive measurement and modeling study provides monthly average rates for 1972 to 1974. For October through February, the SO_2 oxidation rate was between 0.5 and 3% per hour. During late spring, summer and early fall, SO_2 oxidation rates increase to about 6% per hour. A number of studies in Los Angeles (Cass, 1975, 1981; Sander and Seinfeld, 1976; Richards et al., 1987) indicate that the aqueous-phase mechanisms for SO_2 oxidation must have a major influence on this average rate, especially in the presence of stratus clouds or persistent fog.

Recent estimates of the transformation of SO_2 to particulate sulfate have been made in urban and powerplant plumes in the Midwest and Southwest (McMurry and Wilson, 1983) and in powerplant plumes in the Midwest (Gillani et al., 1981, 1983a, 1983b). These studies provide information on the rate of SO_2 transformation as a function of relative humidity and as the dominant mechanism changes from gas-phase photochemical to aqueous-phase.

Both studies indicate that the gas-phase photochemical mechanism is dominant below 75% relative humidity and that the aqueous-phase mechanism dominates above 75%. For the Columbus, OH, urban plume, McMurry and Wilson (1983) used aerosol formation rates to estimate the gas-phase conversion of SO_2 to be only 0 to 5% per hour, while they observed liquid-phase rates of up to 12% per hour. Sunlight was necessary for aerosol to form during their studies.

Gillani et al. (1981) have parameterized the sulfur conversion rate for dry summertime conditions (relative humidity < 75%) as a function of sunlight, plume dilution and reactivity of the background air, as shown in the following equation:

$$k_{SO_2} = (0.03 \pm 0.01)\ (R \bullet \Delta Z_p \bullet [O_3]) \qquad (4.3\text{-}1)$$

where:

k_{SO_2} = pseudo-first-order rate constant for SO_2 (%/hour)

R = solar radiation (kilowatts/hour)

ΔZ_p = vertical spread of the plume (meters)

$[O_z]$ = background ozone concentration (ppm)

Generally, Gillani et al. (1987) estimated sulfur dioxide to sulfate conversion rates of about 3% per/hour for dry conditions.

At higher relative humidities (> 75%) and in clouds and fogs, Gillani et al. (1983a, 1983b) estimated that the sulfate formation rate was approximately 12 ± 6% per/hour. He estimated that in the Midwest, such cloud/fog situations are likely to occur less than 10% of the long-range transport time of a plume. Although it is likely that similar situations exist in California, more study is needed to apply these estimates to California's climates.

For use in their AQMP revisions in September 1987, the SCAQMD is presently sponsoring a study by Environmental Research and Technology, Inc. (ERT) to develop parameterized, first-order chemical transformation rates of SO_2 to PM_{10} sulfate and NO_x to PM_{10} nitrate which are applicable in the South Coast Air Basin. ERT will generate rate constants for the following reactions, as a function of important atmospheric parameters:

$$SO_2(g) \xrightarrow{k_1} SO_4^{=}(s) \qquad (4.3\text{-}2)$$

$$NO_x(g) \xrightarrow{k_2} \alpha\ HNO_3(g) + \beta\ RNO_3(g) \qquad (4.3\text{-}3)$$

$$HNO_3(g) \underset{}{\overset{k_3/k_4,\ NH_3}{\rightleftharpoons}} NO_3^{-}(s) \qquad (4.3\text{-}4)$$

where:

k_1 = pseudo-first-order reaction rate for SO_2, the sum of gas- and aqueous-phase rates

k_2 = pseudo-first-order reaction rate for NO_x

ERT will use photochemical box model simulations to estimate the nitrate and photochemical sulfate reaction rates for a range of important parameters. These parameters include solar radiation, temperature, relative humidity and initial concentrations of NH_3, NO_x, reactive organic gases and ozone. A range of typical (Los Angeles) values for each of the parameters for both daytime and nighttime will be used in the photochemical simulations.

Then, ERT will analyze these simulation results by stepwise linear regression. This will produce a parameterized pseudo-first-order rate constant for NO_x and for the photochemical portion of SO_2. The aqueous portion of the SO_2 rate will be estimated from the known reaction rates of SO_2 with H_2O_2, O_3, and O_2 in solution and estimated concentrations of H_2O_2, O_3, iron and manganese, H^+ and liquid water. This study will be finished by August 1987.

4.3.2 Nitrogen

Transformation rates for NO_x have been estimated using measurements in laboratory and smog chamber experiments, in the Los Angeles atmosphere, and in powerplant and urban plumes in the Southwest and Midwest.

Russell et al. (1985) have estimated the net nitrogen oxide flux for a simulated 24-hour trajectory across the Los Angeles Basin for June 28, 1974. For this simulated day, 7% of the NO_x emitted into the simulated air parcel ended up as airborne nitric acid. Thus, depending on the ammonia gas concentration and the sulfate concentration, anywhere from 0 to 7% of the emitted NO_x could end up as nitrate aerosol after 24 hours.

4.3.3 Organic Species

Transformation rates for organics are much harder to estimate than the rates for SO_2 and NO_x. Only a few estimates have been made, based on sampling of ambient aerosols in Los Angeles. Grosjean and Friedlander (1975) estimated that an average of only 1 to 2% of the total non-methane, non-acetylene hydrocarbons exist in the particulate phase. This, combined with estimates of air-mass travel times, provides an upper limit of about 2% per hour for the gas-to-aerosol conversion rate in a photochemical atmosphere.

For use in their Air Quality Management Plan (AQMP) revisions in September 1987, the SCAQMD is presently sponsoring a review by Daniel Grosjean and Associates and CIT to estimate the fraction of specific organic gases which are likely to result in secondary carbon particulate matter. They will use detailed organic particulate analyses from past smog chamber and ambient measurements in combination with past photochemical model simulations. Important parameters that will affect the estimated fractional transformation will be the initial NO_x concentration, the NO_x to total reactive hydrocarbon gases ratio, and the temperature.

4.3.4 Summary of Transformation Rates

Table 4.3-1 shows estimated pseudo-first-order transformation rates for SO_2, NO_x and reactive organic gases. Different rates are shown when there are significant differences due to atmospheric conditions and the existing data support such distinctions.

For the SO_2-to-sulfate transformation, the table shows the estimated rate and range of rates for five different atmospheric conditions. The presence of fog or clouds increases the rate dramatically. For the NO_x-to-nitrate transformation, the table shows four different rates. The availability of ammonia is the critical factor which produces particulate nitrate from gas-phase nitric acid.

Less is known about the transformation of organics. However, the transformation rate is estimated to increase with photochemical activity.

4.4 Source Profile Fractionation

The previous sections of this chapter have discussed the range of physical and chemical phenomena which affect fractionation of emissions on the way to a receptor and the details of a major contributor to that fractionation -- gas-to-article transformation. This section will help the model user determine if fractionation might be influencing a particular situation.

Table 4.3-1

Estimated Average Transformation Rates (pseudo-first order)

	Daytime	Nighttime
SO_2 to $SO_4^{=}$		
Relative Humidity <75% (no clouds or fog)		
Photochemical	<1%/hr.	0%/hr.
Non-photochemical	3%/hr. (0.5 to 6%/hr.)	0%/hr.
Relative Humidity >75% (some clouds or fog)	6%/hr. (0 to 12%/hr.)	6%/hr. (0-12%/hr.)
- - - - - - - - - -		
NO_x to NO_3		
Excess Ammonia		
Available	5%/14 hrs	3%/12 hrs
Not Available	0%/hr.	0%/hr.
- - - - - - - - - -		
Reactive Organic Gases to Organic Particles		
O_3> .08 ppm	1-2%/hr.	1-2%/hr.
O_3< .08 ppm	<1%/hr.	<1%/hr.

To do this evaluation, the model user will need to know something about the chemical composition of the source emissions, the time and distance of travel from the emissions source to the receptor, and the air quality and meteorological conditions during transport.

If the chemical species being modeled change in a similar way during transport to the receptor, then fractionation is not much of a problem. In this case, relative fractionation between two or more such components will be identical and the present Level I PM_{10} Assessment Package should work quite well.

On the other hand, if the chemical species being modeled react during transport, or if a number of other processes occur during transport, then fractionation may be quite important. A number of keys can be used to indicate when fractionation may be significant. For PM_{10}, these keys include:

- Reactive gases in the emissions (SO_2, NO_x, reactive organics).
- Large numbers of very small (less than 0.1 μm) particles in the emissions.
- Other emission sources of similar components but with different relative concentrations.
- Reactive gases (ozone, OH, H_2O_2, etc.) in the dilution air along the path to the receptor.
- Reactive particles (like basic soil dust) in the dilution air along the path to the receptor.
- Long transport times.
- Precipitation, clouds or fog during transport.
- Large changes in temperature during transport.

Some general guidelines can be used to determine if any of these types of keys might lead to important fractionation effects. The best method to do this is to separate these keys into three general temporal-spatial scales, as follows:

- The near field, in which chemical transformations and deposition are not significant and the fractionation coefficients are close to unity. This is most likely the case for transport times of less than a few hours and when there are no large changes in the atmospheric conditions along the transport route.
- The far field, where all transformation and deposition processes have run their course and all source profiles have reached constant proportions. Fractionation coefficients may differ markedly from unity, but they are at least constant with respect to time and

space. This case is most likely when transport or residence times are greater than one day.

- The intermediate field, where transformation and deposition processes are in progress. Here, fractionation coefficients are changing in time and space. This is generally the case when transport times are between 3 and 24 hours.

We can develop more specific guidelines for those cases which include reactive components such as SO_2, NO_x, and reactive organics, using the information in Table 4.3-1.

Gas-to-particle transformation is probably not significant for SO_2 emissions when:

- $O_3 < 0.08$ ppm, RH < 75%, transport time < 10 hours, daytime.
- $O_3 > 0.08$ ppm, RH < 75%, transport time < 3 hours, daytime.
- any O_3, RH > 75%, transport time < 1 hour, daytime.
- any O_3, RH < 75%, transport time < 12 hours, nighttime.
- any O_3, RH > 75%, transport time < 1 hour, nighttime.

Gas-to-particle transformation is probably not significant for organic species when:

- $O_3 < 0.08$ ppm, transport time < 5 hours.
- $O_3 > 0.08$ ppm, transport time < 10 hours.

Gas-to-particle transformation is probably not significant for NO_x emissions when excess ammonia is not available or when transport times are less than 24 hours, even if excess ammonia is available.

When gas-to-particle transformation is not a problem, some of the other phenomena which affect the gaseous precursor concentrations also become unimportant. However, when models are improved to handle gas-to-particle transformation, they also need to account for deposition to the ground. This deposition may account for large losses of precursor gases before they can change to particulate matter. For example, Russell et al. (1985) estimated that almost 60% of the originally emitted NO_x was lost by deposition to the ground over their 24-hour simulated trajectory. This is a much larger quantity than the amount estimated to remain airborne as nitric acid and potentially convert to particulate nitrate. Similar losses result with SO_2 and with reactive organic gases.

5.0 SOURCES OF MODEL INPUT DATA APPLICABLE TO CALIFORNIA'S LEVEL I PM_{10} ASSESSMENT PACKAGE

The Level I PM_{10} Assessment Package requires input data from PM_{10} monitoring networks, source composition measurements, meteorological monitoring networks and emissions inventories. Section 3 identified the different methods which can be used to acquire these data and the potential uncertainties and inequivalencies associated with these methods. This section identifies data bases applicable to the state of California which were acquired via an application of a subset of those measurement methods.

5.1 PM_{10} Data

Since 1982 ARB has operated PM_{10} samplers at several existing TSP monitoring stations. PM_{10} measurements with high volume samplers using SA-321A size-selective inlets were taken at 47 monitoring stations in 1984, 54 stations in 1985, and 76 stations in 1986, covering 12 air basins in California. These samples are not amenable to extensive chemical characterization, however, so they do not provide the data needed for the Level I PM_{10} Assessment Package.

PM_{10} samples have also been collected with Sierra-Andersen virtual impactor dichotomous samplers in the fine and coarse particle size ranges at several sites in the ARB's high volume sampling network. Mass, nitrate and sulfate concentrations by automated colorimetry have measured on the high volume PM_{10} samples, while mass and elemental concentrations by x-ray fluorescence (XRF) have been quantified on the dichotomous PM_{10} samples.

In addition, the South Coast Air Quality Management District (SCAQMD) has also operated a seven-station network between August 1985 and August 1986, in the South Coast Air Basin. Mass and chemical composition data will be available in 1987 for the application of a Level II PM_{10} assessment (Liu, 1987).

The RESOLVE (Research on Operations Limiting Visual Extinction) study also provides a long-term (August 1983 to August 1985) size-classified (PM_{10} and $PM_{2.5}$) chemical composition data base in the Southeast Desert Basin (Trijonis et al., 1987).

Mass and chemical measurements from several sampling sites in the state of California from 1979 through 1985 have been assembled in the WOGA Aerosol Data Base (Dea and Watson, 1985; Watson et al., 1985b), which is available in specified formats on IBM/PC compatible floppy disks. This data base contains size and chemically speciated PM_{15} data from 1979 through 1982 and has recently been updated with PM_{10} data from the ARB dichotomous sampler network and the RESOLVE visibility study.

Table 5.1-1 summarizes PM_{10} measurements available from these long-term monitoring networks in California. Sampling sites and monitoring periods for five California Air Basins are listed in Table 5.1-2. These

Table 5.1-1
SUMMARY OF PM_{10} MEASUREMENTS IN CALIFORNIA

	WOGA Data Base	ARB Dichot	ARB PM_{10}	SCAQMD PM_{10}	Westside Operators PM_{10}	RESOLVE Study
Sampler (Inlet)	• HIVOL • HIVOL/SSI • Virtual Impactor	Sierra Anderson Virtual Impactor (SA-246)	HIVOL/SSI (SA-321A)	Cal Tech. Sampler (SA-246)	HIVOL/SSI (SA-321A)	• RESOLVE 2x4 (Wedding lo-vol)
Particle Size	PM_{40}, PM_{15}, $PM_{2.5}$	PM_{10}, $PM_{2.5}$	PM_{10}	PM_{10}, $PM_{2.5}$	PM_{10}	PM_{10}, $PM_{2.5}$
Filter Substrate	• Glass Fiber on HIVOL & HIVOL/SSI • Ghia Teflon membrane on Dichot	Gelman Teflon Membrane	Whatman EPM-2000 Quartz Fiber	• Gelman Teflon Membrane • Pallflex Quartz Fiber	Pallflex Teflon-Coated Glass Fiber	• Gelman Teflon Membrane • Pallflex Quartz Fiber
Sampling Frequency	Every 6th day for 24 hours	Every 6th day for 24 hours	Every 6th day for 24 hours	Every 6th day for 24 hours	Every 6th day for 24 hours	• Daily for 24-hr (RESOLVE Sampler)
Data Base Contact	Dr. John Watson DRI P.O. Box 60220 Reno, NV 89506 (702) 972-1676	Ms. Kathy Hsiao ARB 9528 Telstar Ave. El Monte, CA 91731 (818) 575-6829	Mr. Gary Honcoop ARB 11021 Q Street P.O. Box 2815 Sacramento, CA 95812 (916) 323-8372	Mr. Art Davidson South Coast Air Quality Management Dist. 9150 Flair Dr. El Monte, CA 91731 (818) 572-6200		Mr. John O'Gara Naval Weapons Ctr. Code 2692 China Lake, CA 93555 (619) 939-3411
Analysis Method (species)	• Gravimetric (Mass) • Automated Colorimetry ($SO_4^=$, NO_3^-) • Optical Emission Spectroscopy (V, Mn, Fe, Ni, Cu, Zn, As, Pb)	• Gravimetric (Mass) • Energy Dispersive X-ray Fluorescence (Elements Al to Pb)	• Gravimetric (Mass) • Turbidimetric or Ion Chromatography ($SO_4^=$) • Brucine Colorimetric or Ion Chromatography (NO_3^-)	• Gravimetric (Mass) • Ion Chromatography ($SO_4^=$, NO_3^-) • Energy Dispersive X-ray Fluorescence (Elements Al to Pb) • Thermal/ Optical Carbon Analysis (EC, OC)	• Gravimetric (Mass) • Ion Chromatography ($SO_4^=$)	• Gravimetric (Mass) • Ion Chromatography ($SO_4^=$, NO_3^-) • Energy Dispersive X-ray Fluorescence (Elements Al to Pb) • Proten-Induced X-ray Emission Spectroscopy (PIXE for Elements) • Thermal Combustion Light Absorption, Optical Absorption (EC, OC)

Table 5.1-2

SUMMARY OF EXISTING PM_{10} DATA AVAILABILITY IN SIX CALIFORNIA AIR BASINS

Basin/Sampling Site	WOGA Data Base	ARB PM_{10} Dichot Sites	ARB PM_{10} Sites	SCAQMD PM_{10} Sites	Westside Operators PM_{10}	RESOLVE Sampling Site
• San Francisco Bay Area						
Bethel Island	- - -	- - -	- - -	- - -	- - -	- - -
San Jose	79-82	- - -	12/84-12/86	- - -	- - -	- - -
• South Center Coast						
Santa Maria	- - -	- - -	12/84-12/86	- - -	- - -	- - -
Piru-2SW	- - -	- - -	10/85-12/86	- - -	- - -	- - -
Simi Valley	- - -	- - -	9/85-12/86	- - -	- - -	- - -
Simi Valley 5400	- - -	- - -	7/85-12/86	- - -	- - -	- - -
• South Coast						
Azusa	79-82	- - -	11/84-12/86	- - -	- - -	- - -
Burbank	79-82	- - -	11/84-12/86	8/85-12/86	- - -	- - -
LA - NO. Main	- - -	- - -	4/85-12/86	8/85-12/86	- - -	- - -
Long Beach	- - -	3/84- 6/86	- - -	- - -		
North Long Beach	79-82	- - -	10/84-12/86	8/85-12/86	- - -	- - -
El Toro	- - -	- - -	11/84-12/86	- - -	- - -	- - -
Los Alamitos-Orange	- - -	- - -	11/84-12/86	- - -	- - -	- - -
Riverside-Rubidoux	79-82	8/85- 6/86	11/84-12/86	8/85-12/86	- - -	- - -
Riverside-Magnolia Av.	79-82	3/83- 8/84	- - -	- - -	- - -	- - -
Fontana-Arrow Hwy.	- - -	- - -	10/85-12/86	- - -	- - -	- - -
Ontario Airport	- - -	- - -	11/84-12/86	- - -	- - -	- - -
San Bernardino	- - -	- - -	1/86-12/86	- - -	- - -	- - -
Glendora	79-82	1/83- 6/86	- - -	- - -	- - -	- - -
San Nicolas Island	- - -	- - -	- - -	8/85-12/86	- - -	- - -
Lennox	- - -	- - -	- - -	8/85-12/86	- - -	- - -
Anaheim	- - -	- - -	- - -	8/85-12/86	- - -	- - -
Lancaster	- - -	1/83- 6/84	- - -	- - -		
• San Joaquin Valley						
Five Points	79-82	- - -	10/85-12/86	- - -	- - -	- - -
Fresno-Cal St #2	79-82	- - -	10/85-12/86	- - -	- - -	- - -
Fresno-Olive	- - -	3/83-12/83	9/84-12/86	- - -	- - -	- - -
Bakersfield	79-82	3/83- 1/85	9/84-12/86	- - -	- - -	- - -
(collocated)	- - -	- - -	(9/85-12/86)	- - -	- - -	- - -

Table 5.1-2 (continued)

SUMMARY OF EXISTING PM_{10} DATA AVAILABILITY IN SIX CALIFORNIA AIR BASINS

Basin/Sampling Site	WOGA Data Base	ARB PM_{10} Dichot Sites	ARB PM_{10} Sites	SCAQMD PM_{10} Sites	Westside Operators PM_{10}	RESOLVE Sampling Site
• San Joaquin Valley (continued)						
Oildale	- - -	- - -	9/84-12/86	- - -	- - -	- - -
Taft	- - -	- - -	3/85-12/86	- - -	- - -	- - -
Corcoran	- - -	- - -	4/84-12/86	- - -	- - -	- - -
Hanford	- - -	- - -	3/85-12/86	- - -	- - -	- - -
Kettlemen City-Cal	- - -	- - -	12/85-12/86	- - -	- - -	- - -
Madera-Library	- - -	- - -	11/85-12/86	- - -	- - -	- - -
Merced	- - -	- - -	10/85-12/86	- - -	- - -	- - -
Stockton-Hazelton S.	- - -	- - -	10/84-12/86	- - -	- - -	- - -
Modesto-Oakdale Rd.	- - -	- - -	10/84-12/86	- - -	- - -	- - -
(collocated)	- - -	- - -	(6/85-12/86)	- - -	- - -	- - -
Visalia-Church St.	- - -	- - -	9/84-12/86	- - -	- - -	- - -
Kernridge	79-82	- - -	- - -	- - -	1/83- 6/86	- - -
McKittrick	79-82	- - -	- - -	- - -	1/83- 6/86	- - -
• Southeast Desert						
Brawley-401 Main St.	- - -	- - -	9/85-12/86	- - -	- - -	- - -
El Centro-Broadway	- - -	- - -	10/84-12/86	- - -	- - -	- - -
Mojave	- - -	- - -	11/85-12/86	- - -	- - -	- - -
Banning-Allesandro	- - -	- - -	11/84-12/86	- - -	- - -	- - -
Indio-Jackson	- - -	- - -	11/84-12/86	- - -	- - -	- - -
Barstow	- - -	- - -	10/85-12/86	- - -	- - -	- - -
Trona-Market St.	- - -	- - -	11/84-12/86	- - -	- - -	- - -
Victorville-Fairgro	- - -	- - -	10/85-12/86	- - -	- - -	- - -
China Lake	79-82	9/83- 2/86	- - -	- - -	- - -	8/83- 8/85
Edwards AFB	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
Randsburg Wash	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
Fort Irwin	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
Tehachapi Pass	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
Soledad Pass	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
Cajon Pass	- - -	- - -	- - -	- - -	- - -	8/83- 8/85
• Sacramento Valley						
Yuba City	79-82	12/82- 6/86	10/84-12/86	- - -	- - -	- - -

existing PM_{10} mass and chemical composition data can serve as a starting point for the application of the Level I PM_{10} Assessment Package.

5.2 Source Composition Data

Obtaining the source-type composition data can be the most costly part of a receptor model application if carried to its extreme. The Level I approach to obtaining this information is to compile and examine existing information, determine its inadequacies and focus the sampling and analysis resources which are available on alleviating those inadequacies in a Level II assessment.

Very limited information is available with regard to size and chemical-specific source profiles in California. Most of the existing profiles are based on tests performed by Taback et al. (1979), using hot exhaust sampling.

Watson (1979), Anderson et al. (1984), Core et al. (1984), Chow (1985), Hopke (1985), and Javitz and Watson (1987) identify a large number of source characterization results from various studies. Most of these source profiles possess the following weaknesses:

- The species measured are more often those which are convenient rather than those which differentiate among sources.
- The types of species and size fractions measured are not the same for different source types and are not equivalent to the types of measurements made at receptors.
- Measurement methods are non-standard and do not generate equivalent results for the same species.
- Source characteristics, fuels and operating parameters are inadequately documented.
- Source profile uncertainties are not reported.
- Source samples are not necessarily representative of source profiles as monitored at the receptor (i.e., the source profile after modification by transformation, as explained in Section 4).
- Data are not available in formats which can be conveniently interfaced to modeling software.

The EPA Source Composition Library (Core et al., 1984) has been established as a central repository for source profile data. This library uses a source type classification and numbering system and data quality criteria. It is intended that this data base will be updated on a period basis by EPA's Office of Air Quality Planning and Standards (OAQPS). The

Level I PM_{10} Assessment Package contains a reformatting program which allows source profiles to be selected from the computerized version of this library (which contains several hundred profiles in its current revision) and placed into input data formats for the CMB receptor model. Source profile data from other data bases must be manually entered into the CMB input format. For the majority of Level I assessments, the EPA Source Composition Library is adequate.

The ARB is conducting a study to determine the chemical composition of particulate material in four size ranges (<1 μm, 1 to 2.5 μm, 2.5 to 10 μm, and > 10 μm) for selected sources in the Great Basin Valleys, San Joaquin Valley, and Southeast Desert Air Basins. The source types being tested: agricultural tillage, paved and unpaved roads, construction and demolition, livestock operations, wind-blown dust, vehicular diesel combustion, forest fires, agricultural burning, wood stoves and fireplaces, oil-field internal combustion engines, and heavy crude combustion. These source profiles are expected to become available by the middle of 1988 and could be added to this package at that time.

The SCAQMD has conducted source tests in support of their PM_{10} work plan to be submitted to EPA Region IX (Liu, 1987). Program elements of this work plan are summarized in Table 5.2-1 as an illustration of the PM_{10} assessment efforts being undertaken at the local district level and to identify the source profiles which will be available. This source characterization in South Coast Air Basin will provide 40 to 50 source profiles in 0 to 2.5 μm, 2.5 to 10 μm and, 0 to 10 μm size ranges.

5.3 Meteorological Data Bases for California

This section summarizes the sources of meteorological data for California. A partial list of the sources that compile information on surface observations is given in Table 5.3-1.

The services available from these sources are:

- National Weather Service Facsimile Network (NAFAX). Provides daily facsimile transmissions of weather analyses and observations, as well as predictions for surface and upper air levels, including upper air charts of wind and temperature at 850 mb, gradient wind flow, maximum and minimum surface temperature, sea level pressure, and significant weather, prepared and transmitted by the National Meteorological Center (NMC) of NOAA.

- Geostationary Operational Environmental Satellite (GOES). Provides high quality images of clouds and dust layers and the underlying surface via telephone line from the Satellite Field Services Station at Redwood City, California.

Table 5.2-1

Program Elements of SCAQMD PM_{10} Plan

Program Element	Time Frame
Establish PM_{10} Monitoring Network	1985 - Present
Determine PM_{10}/TSP ratios	
Obtain detailed chemical speciation information	
Derive relationship between PM_{10} concentrations and meteorology	
Size Segregated Source Sampling	1986 - 1987
Utility boilers (4 tests)	
Industrial boilers (4 tests)	
Paved roads (6 tests)	
Unpaved roads (4 tests)	
Construction sites (4 tests)	
Rock crushing plant (1 test)	
Petroleum coke calcining kiln (1 test)	
Vehicles (Tunnel tests)	
Misc. (landfill, agricultural tillage, IC engines)	
Preparation of PM_{10} Emissions Inventory	1987
Modeling	
PM_{10} concentration predictions	1985 - 1987
Control strategies	
PM_{10} implementation plan	

Reference: Personal Communication, Art Davidson, SCAQMD, May 1986

Table 5.3-1

Major Meteorological Data Resources for California Surface Data

Resources	Contact[a]	Phone
Federal Agencies		
National Weather Service	John Hughes	704-259-0682
United States Coast Guard		
United States Forest Service	Neil Berg	415-486-3457
National Park Service		
Bureau of Reclamation	Judith Bonds	303-234-3203
National Oceanographic and Atmospheric Administration		
State Agencies		
California Air Resources Board	Arndt Lorenzen	916-322-7454
Local Air Pollution Control Districts		
San Francisco Bay Area	Mike Basso	415-771-6000
South Coast	Joe Cassmassi	
California Department of Transportation	Ken Pinkerman	916-739-2322
Other Sources		
Nowcasting, Inc.	Dennis Lundy	916-895-5082
Pacific Gas and Electric	Sam Altshuller	415-820-2000
Southern California Edison	Carol Ellis	818-302-1866
Naval Weapons Center, China Lake	Tom Dodson	714-939-3411
Electric Power Research Institute	Peter Mueller	415-855-2586

[a] Where available

- WSI Corporation. Provides meteorological data from a worldwide network on a continuous, round-the-clock basis in tabular and map form via modem.

- National Climatic Data Center (NCDC) (Asheville, North Carolina 704-259-0862). Provides meteorological records in both magnetic tape ($99) and hard copy ($5 and up) formats for all the sites operated by the National Weather Service.

  Climatological information is published in several formats including:

  -- Climatological Data by State - daily, monthly, seasonal and annual data of maximum and minimum temperatures, precipitation, soil temperature, wind movement for all sites in a given state for the period 1914 to the present.

  -- Local Climatological Data - hourly, 3-hourly, daily, monthly and annual data of temperature, dew point, relative humidity, degree days, precipitation, pressure, wind, amount of sky cover, visibility for the period 1897 to the present for 248 airport locations in the US.

  -- Surface Weather Observations - hourly or 3-hourly aviation weather observations (ceiling, visibility, weather type, sea level pressure, temperature, dew point, wind speed and direction, relative humidity, amount of sky cover) for NWS, U.S. Coast Guard (USCG), U.S. Air Force and U.S. Navy airports for the period 1948 to the present.

- National Weather Service/FAA Flight Service (in Los Angeles: 213-209-7211/213-215-2338). Recorded messages of local weather are provided.

- NOAA/U.S. DOD. Sounding data from rawinsondes are available for several airports in California.

- Local Air Quality Management Districts. These districts operate extensive networks of aerometric and meteorological monitors as part of state and local air monitoring sites (SLAMS) and national air monitoring sites (NAMS). For instance, the SCAQMD operates a 30- to 40-site network that records basic climatological values (temperature, relative humidity, wind) which are telemetered automatically to the District's data acquisition system. In addition, the SCAQMD supports daily early-morning temperature soundings and pibal releases (which yield wind speed and direction at 500-foot increments) at Loyola-Marymount University. During the May to October smog season, these data are supplemented with a mid-day

pibal release and a temperature sounding as well as a morning aircraft temperature sounding at El Monte.

Stations that provide surface observations of the primary meteorological variables (temperature, wind speed, wind direction, relative humidity, dew point, pressure, sky cover, precipitation) in California are identified in Table 5.3-2.

These stations which are operated by the Air Force, Navy, Coast Guard, FAA and the National Weather Service make observations at least eight times per day. Meteorological records from past years are available on magnetic tape from the National Climatic Data Center.

Miscellaneous reports on California meteorology that are relevant to the PM_{10} assessment package are identified below:

- Title: Summary of California Upper Air Meteorological Data
  Author: A. Lorenzen, ARB
  Reference: Final Report to ARB, TS-79-003, December 1979
  Contents: Summary statistics of inversion heights, upper air wind speed and direction, and stability index for 22 sites in California.

- Title: Winds in California
  Author: J.D Goodridge and E.G. Bingham
  Reference: Department of Water Resources, Bulletin #185, January 1978
  Contents: Annual statistical summaries of wind records in California.

- Title: Temperature Inversion Summaries of U.S. Weather Bureau Radiosonde Stations in California
  Author: G. Holzworth, G. Bell and G. DeMarrais
  Reference: California Department of Public Health Report, 1963
  Contents: General summary of inversion heights.

- Title: Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Continental United States
  Author: G. Holzworth
  Reference: EPA, Office of Air Programs, Publication #AP-101, 1972
  Contents: General summary of mixing layers by time of year and regions (isopleths).

Table 5.3-2

Stations That Provide Surface Meteorological Observations in California

Stations	Operator
Alameda	N
Arcata	F
Bakersfield/Meadows Field	W
Bishop	W
Blue Canyon	O
Blythe/Riverside Co. AP	F
China Lake/Inyokern	N
El Toro	N
Fresno/Hammer Air Terminal	W
Imperial Beach/Ream	N
Lemoore	A
Long Beach/Daugherty	A
Los Angeles International AP	W
Miramar	N
Mt. Shasta/WBO	W
Oakland/Metro International AP	W
Point Mugu	N
Red Bluff	W
Sacramento/Executive	F
San Bernardino/Daggett	F
San Clemente Island	N
San Diego/Lindbergh	W
San Diego/North Island	N
San Francisco International AP	W
San Nicholas Island	W
Santa Ana	N
Santa Maria/Public	W
Stockton Metro AP	W
Sunnyvale/Moffett Field	N

A = Air Force
N = Navy
O = US Coast Guard
F = FAA
W = National Weather Service

- Title: Application of Climatological Analysis to Minimize Air Pollution Impacts in California
  Author: T.B. Smith, W.D. Saunders and D.M. Takeuchi
  Reference: Final Report to CARB, Contract #A2-119-32, August 1984
  Contents: Comprehensive compilation of air quality climatology for California; utilizes 1979-1980 ARB statewide data base.

- Title: California Surface Wind Climatology
  Author: T.P. Hayes, J.J.R. Kinney and N.J.M. Wheeler
  Reference: CARB Report, June 1984
  Contents: Statistical summary of surface winds for 176 locations in California.

- Title: Climatological, Meteorological and Dispersion Study of Regional and Selected Local Environments of Northern California
  Author: T.B. Smith, D.E. Lehman, W.R. Knuth, and D.L. Blumenthal
  Reference: Sonoma Technology, Inc., Report #90034-24, March 1985
  Contents: Monthly and seasonal summaries of surface winds, ventilation factors and local flow patterns for selected areas of northern California.

5.4 Emissions Inventories for California

The 1983 calendar year emissions inventory is the most current complete emissions inventory for California compiled by ARB, accounting for approximately 15,000 emissions sources. It include emissions estimates for total organic gases, reactive organic gases, oxides of nitrogen, oxides of sulfur, carbon monoxide and total suspended particulates. The ARB has also prepared a draft inventory for size-resolved particulate matter in four size classes for the 1983 calendar year.

The statewide inventory is the product of the efforts of a number of local and state agencies. At the local level, the principal agencies contributing to the inventory are the air pollution control districts (APCD's), air quality management districts (AQMD's), and councils of governments (COG's). At the state level, the principal agencies contributing to the inventory are the California Department of Transportation (Caltrans) and the ARB. Within the ARB, several divisions develop data for the statewide inventory, including the Stationary Source Control Division, the Mobile Source Control Division, the Haagen-Smit Laboratory Division, the Enforcement Division and the Research Division.

The point source data file includes sources that emit more than 25 tons per year of particulate matter, oxides of nitrogen, sulfur oxides or total organic gases; 250 tons per year of carbon monoxide; or 5 tons per year of lead. The ARB's documentation to support the point source

inventory is maintained in their Emission Data System. The information documented in the point source data system includes:

- Company name, address, type of business and contact person.
- Description of individual devices and processes that produce emissions and associated air pollution control equipment.
- Process rate data, emission factors and estimated annual emissions.

The ARB staff estimates emissions for each county from information that is made available from the local AQMD's or from studies made on a statewide basis. The emission factors used in both the point source and area source emission assessment processes are obtained from U.S. EPA (1985); special studies conducted for EPA or ARB; source tests conducted by the districts, ARB or others; and studies and tests made by universities.

The main sources of motor vehicle use data are Caltrans, the Department of Motor Vehicles (DMV) and regional transportation planning agencies. The ARB staff collects vehicle statistics from DMV and vehicle miles traveled (VTM) and vehicle-trip data from Caltrans and regional planning agencies. These data are fed into computer models used to compute composite emission factors and statewide motor vehicle emissions.

Motor vehicle emission factors are assembled by the ARB staff and are based on data and analyses done by ARB and EPA staff. The motor vehicle emission factors are derived from dynamometer tests of California vehicles, an EPA emission factor model, and other data specific to the operation of vehicles in California, including the makeup of the vehicle fleet, estimates of misfueling, and the extent and effect of mandatory vehicle inspection.

Besides the collection and analysis of point source, area source, and motor vehicle emission data, discussed above, supplemental data are collected by ARB to prepare spatial (e.g., 10 km x 10 km grids), temporal (e.g., daily and monthly profiles) and organically speciated and particle size inventories. The latter two types of inventories rely heavily on source tests conducted by Taback et al. (1979) in the South Coast Air Basin. These inventories are also supplemented by data assembled by the ARB staff. Representative organic species profiles are associated with each source category in the inventory, and the data have been used to estimate reactive organic gas emissions as a function of reactivity class for air quality photochemical models.

The national size-resolved particle emissions inventory compiled by the EPA is based on measured size distribution profiles of TSP emissions for different source categories in each of four size ranges: less than 1 μm, 1 to 3 μm, 3 to 10 μm, and greater than 10 μm. The size-resolved particulate matter (PM) inventory developed by ARB uses particle size profiles which represent the weight fraction of the total suspended

particulate emissions in four size ranges: less than 1 μm, 1 to 2.5 μm, 2.5 to 10 μm, and greater than 10 μm.

Emissions for a particular size range are calculated by multiplying the weight fraction for a given size range by the total suspended particulate matter emissions, with appropriate adjustments made for particulate matter control devices. To generate the size-resolved inventory, the sources of particulate matter were separated into a number of source categories. A particle size and composition profile has been assigned to each PM category based upon available source test and other published data. For each particle size profile, the chemical composition within the four size ranges is specified. Chemical analysis of the particulates consists of x-ray fluorescence analysis for elemental composition, wet chemistry for nitrate and sulfate content, and carbon analysis for volatile, carbonate and total carbon content.

The amount of information available on particle size and chemical composition profiles is currently very limited, as discussed in Section 5.2. Because of this lack of data, the same particle size and chemical composition profile is sometimes used for more than one category (e.g., for both Stationary IC Engines burning gasoline and Vehicular Sources burning gasoline).

As noted in Section 3, some emissions are controlled using various control devices. To adjust the particle size fraction for the effects of the control device, ARB has grouped together control equipment of similar effectiveness. The efficiency of various types of air pollution control equipment for removing particulates is shown in Table 5.4-1 as a function of particle size. The draft California particulate matter (PM) inventory for the 1983 calendar year is considered preliminary and subject to change. Categories, size profiles, chemical profiles and the various temporal and spatial inventories will be updated as new information is developed and analyzed (Yotter, 1986).

Major PM categories included in the statewide inventory are combustion, evaporation, process loss and fugitive dust. The inventory includes an unspecified category for which the size profile that is used approximates the weighted size distribution of emissions from the known PM sources in the state; no chemical composition profile is assigned. Emission rates in the ARB inventory are assigned a quality rating ranging from 1 (reliable) to 5 (unreliable). Of the 67 subcategories in the PM inventory, only coal/coke combustion has a reliability rating of 1; nine subcategories (residual fuel consumption, residual utility boilers, gaseous material combustion, solid material combustion, wood waste combustion, incineration of solid fuel, cement product/concrete batching, lime manufacturing and glass melting furnace) have a rating of 2, 33 have a rating of 3, 20 have a rating of 4, and 4 (unplanned structural fires, evaporation, coating material evaporation, and unspecified) have a rating of 5.

The daily size-resolved PM emissions inventory by major source categories for California for 1983 is summarized in Table 5.4-2. The single largest source of PM_{10} is from miscellaneous processes that include

Table 5.4-1

Effect of Various Particulate Matter Control Equipment for Different Particle Size Ranges

Air Pollution Control Equipment	Control Efficiency as a function of Particle Size, %			
	<1 μm	1-2.5 μm	2.5-10 μm	>10 μm
Gravity Collector	0	2	13	60
Centrifugal Collector, Low & Med. Eff.	25	63	83	91
Wet Scrubber/Dust Supression	8	47	92	98
Centrifugal Collector, High Eff.	80	88	97	99
Venturi Scrubber	77	96	97	99
Dry Scrubber	91	95	99	99
Electrostatic Precipitator	97	98	99	99
Fabric Filter	99	99	99	99

Table 5.4-2

Daily Size-Resolved Particulate Emissions for California (1983 base year)

Source Category	Particle Size Fraction (Tons/Day)					
	<1 μm	1-2.5 μm	2.5 μm	PM_{10}	TSP	PM_{10}/TSP
1) Stationary Sources						
Fuel Combustion	70.4	8.4	9.4	88.2	105.7	0.83
Waste Burning	41.6	5.1	2.5	49.2	50.2	0.98
Solvent Use	0.9	<0.1	<0.1	1.0	1.1	0.94
Petroleum Process/ Storage/Transfer	6.2	0.6	0.8	7.6	13.8	0.55
Industrial Processes	31.9	17.5	34.8	84.2	152.8	0.55
Misc. (farming, construction, fires, road dust)	505	267	1614	2386	5002	0.48
Subtotal	656	299	1662	2617	5326	0.49
2) Mobile Sources						
On Road Vehicles	109	15.5	11.0	135.5	210	0.64
Other (trains, ships, etc.)	56.6	0.9	1.3	58.8	61.0	0.96
Subtotal	166	16	12	194	271	0.72
TOTAL	822	315	1674	2811	5597	0.50

farming operations (498 tons/day), construction and demolition (423 tons/day),re-entrained road dust (1416 tons/day) and unplanned fires (47 tons/day). In total, these processes account for 85% of the daily PM_{10} emissions in the state.

The earlier 1981 PM emissions inventory for California included a breakdown by chemical species for each of the major source categories in four size ranges: 0 to 1 μm, 0 to 2.5 μm, 0 to 10 μm, and total suspended particulates. The chemical composition of the size-resolved PM emissions for an average day in 1981 are summarized in Table 5.4-3. By far the largest portion of the PM_{10} emissions are uncategorized in terms of their chemical composition.

ARB has recently assembled a PM_{10} emissions inventory for each of the counties for the Great Basin Valleys, San Joaquin Valley and Southeast Desert Air Basins for the 1983 calendar year (Yotter, 1986). In addition, the South Coast AQMD recently published a TSP emissions inventory for the South Coast Air Basin for the 1983 calendar year (Davidson, 1986). Using the PM_{10}/TSP ratios shown in Table 5.4-2, one can calculate a PM_{10} inventory for the SoCAB. The results for the SoCAB are summarized in Table 5.4-4 along with those for the three air basins prepared by the ARB staff.

As part of the Southern California Air Quality Study (SCAQS, Blumenthal et al., 1987) the ARB and other sponsors (WOGA, MVMA, and EPRI) are supporting emissions inventory enhancements for the SoCAB. This work will result in an updated, quality assured time- and species-resolved gridded inventory for the major pollutant species, including organic and inorganic gases and primary particles. The emphasis will be on those species most important for oxidant and aerosol formation. This inventory uses available inventories for 1987 as a foundation and includes the results of special inventory characterization studies. This inventory will provide hourly-averaged emissions for each of the SCAQS intensive study days.

Only two gridded emissions inventories have been prepared by ARB for dispersion modeling purposes: Kern County and the South Coast Air Basin. The Kern County inventory is used as an example of a Level I PM_{10} assessment in the accompanying User's Guide.

Table 5.4-3

Daily Size-Resolved PM Emissions by Chemical Species for California (1981 base year)

	Particle Size Fraction (Tons/Day)			
Chemical Species	0-1 μm	0-2.5 μm	0-10 μm	TSP
Aluminum	36.5	56.0	92.0	156.0
Calcium	17.5	23.4	34.7	51.9
Carbon	106	125	139	201
Chlorine	8.21	8.25	8.27	8.32
Iron	18.1	26.3	40.5	65.3
Lead	0.71	0.84	1.07	1.48
Manganese	2.7	4.0	6.5	10.9
Nickel	1.65	1.82	2.09	2.56
Nitrates	1.61	1.64	1.67	1.73
Potassium	16.3	22.1	31.7	48.1
Silicon	106	160	260	441
Sulfates	81.6	82.6	83.7	85.8
Titanium	2.70	4.05	6.55	11.0
Zinc	1.08	1.46	1.86	3.51
Other Elements	3.29	3.75	5.43	7.00
Other	470	643	953	1516
Unkown	111	269	577	802
TOTAL	985	1433	2245	3414

Table 5.4-4

Direct PM_{10} Emissions in Tons per Day by Source Category for Four California Air Basins for 1983*

Source Category	GBVAB[a]	SJVAB[b]	SEDAB[c]	SoCAB[d]
Unpaved Road Dust	30.9	39.9	41.1	27.5
Paved Road Dust	6.0	133.9	37.4	90.4
Agricultural Tillage Dust	1.5	152.1	30.4	35.1
Construction Dust	1.3	62.1	11.2	84.2
Windblown Dust	..... Not estimated			
Vehicular Diesel Combustion	0.3	21.3	10.2	--
Fireplaces/Woodstoves	0.2	0.9	0	--
Cattle Feedlot Dust	0	14.6	35.5	--
Forest Fires	0	17.7	4.4	3.3
Agricultural Burning	0	5.2	1.8	0.5
Other Sources	0.8	45.3	16.6	104.8
TOTAL	41.0	493.2	188.6	345.8

* Uncertainities range from ±15% to ±100%
[a] GBVAB = Great Basin Valleys Air Basin, by ARB
[b] SJVAB = San Joaquin Valley Air Basin
[c] SEDAB = Southeast Desert Air Basin
[d] SoCAB = South Coast Air Basin, calculated from ARB TSP and PM_{10}/TSP ratios from Table 5.4-2

6.0 SUMMARY AND RECOMMENDATIONS

6.1 Summary

This model and data base description has identified the Principal Components Analysis (PCA) receptor model, Chemical Mass Balance (CMB) receptor model, and the Industrial Source Complex-Short Term (ISC-ST) dispersion model as parts of a Level I PM_{10} Assessment Package. This package is implemented on IBM/PC microcomputers using software provided by commercial developers and the U.S. EPA. The advantage of these software systems is that they will be maintained by their suppliers long after this project has been completed. The disadvantage is that the PCA must be obtained from its suppliers (BMDP) and a licensing fee is required.

The principal components analysis (PCA) receptor model acts on many days of chemically speciated fine (0 to 2.5 μm), coarse (2.5 to 10 μm), or PM_{10} (0 to 10 μm) measurements. Each principal component can be associated with a source contributor by comparing the chemical species on which it has high factor loadings with the typical chemical compositions of source emissions. The PCA confirms the presence of sources which are identified in the emissions inventory for an area. It may also identify the potential contributions of sources which have not been inventoried. All contributing sources are not necessarily identified by the PCA. This will be the case if the contributions from an included source do not vary by more than the measurement uncertainty, or if the species measured at the receptor have not been measured in those sources. Additional sources may be selected for inclusion in subsequent analyses based on their contributions from the emissions inventories.

The chemical mass balance (CMB) receptor model is applied to single daily fine, coarse or PM_{10} ambient chemical data and to fine, coarse or PM_{10} source composition data. The sources included in a CMB analysis are those which were identified from the PCA and the emissions inventory. PM_{10} chemical measurements at the receptor can be acquired via filter sampling through size-selective inlets and subsequent chemical analyses. Source composition data is usually derived from a source library for Level I PM_{10} assessment. The CMB yields the contribution to PM_{10} from source types such as motor vehicles, residual oil combustion, geological material and secondary sulfate. Other source type contributions may be identified if a sufficient mixture of chemical species has been quantified at source and receptor. Detailed guidance for the application of the CMB and the validation of its results has been prepared by the EPA's Office of Air Quality Planning and Standards (Axetell et al., 1987; Pace and Watson, 1987).

The ISC-ST dispersion model is applied to individual source sub-types with the major source type contributions identified by the CMB. This model uses emission rates, atmospheric stability class, mixing height, wind speed and wind direction as input. It yields absolute and relative contributions from the included sources as output.

Two types of uncertainty are associated with the results of these modeling components: modeling and measurement. Modeling uncertainty results from deviations from model assumptions in an actual application. The major model assumptions for the PCA, CMB, and ISC-ST have been identified, but the effects of deviations from them have been only minimally quantified. One advantage of applying all three models to the same situation is that several of these deviations can be identified and appropriate measures taken. EPA has issued a protocol for reconciling differences among receptor and dispersion models which describes these measures (U.S. EPA, 1987a).

Measurement uncertainty is that which results from the imperfection of the model input data. These data contain uncertainty which is caused by random events and biases in the measurement process. Lack of standardization with respect to PM_{10} sampling results in different values achieved with different methods used at receptors. Source profiles may differ, even when taken at the same emissions point, owing to the sampling and analysis methods as well as to changes in the profile between source and receptor. These uncertainties are largely unquantified at this time but sufficient tests have been conducted to assure that they are significant. A thorough description of the measurement methods which supply model input data, and the differences between them, has been presented as part of the model and data base description.

Data bases needed for the application of this Level I PM_{10} Assessment Package are: 1) size- and chemically-speciated PM_{10} receptor measurements; 2) size- and chemically-speciated PM_{10} source emissions measurements; 3) meteorological data; and 4) emissions data. Some of this data is currently available in various forms for some parts of California. However, this data is often incomplete and the available formats often make it difficult to use in the models described here.

PM_{10} receptor data is available from the WOGA Aerosol Data Base, ARB's dichotomous sampling network and the RESOLVE visibility study. Data from the South Coast Air Basin will soon be available from the South Coast Air Quality Management District and from the southern California Air Quality Study.

PM_{10} source profile data is available from EPA's Source Composition Library. The South Coast Air Quality Management District is just completing a source sampling program for the South Coast Air Basin. ARB is sponsoring the sampling and chemical characterization of sources in the San Joaquin Valley, Southeast Desert and Great Basin Valleys.

Meteorological data is available from the National Weather Service, several military bases and several of the air quality management districts.

Emissions inventories are compiled and maintained by the ARB. Only Kern County and the South Coast Air Basin currently have urban-scale gridded inventories which are appropriate for the ISC-ST dispersion model.

6.2 Recommendations

Recommendations for PM_{10} assessment in California fall into three categories: 1) models; 2) measurements; and 3) the PM_{10} Assessment Package. With respect to the models, the following research is needed:

- All models need to be subjected to greater evaluation to determine the quantitative effects of deviations from assumptions in practical situations.

- Additional models need to be developed which would be more accurate than the ones currently contained in the assessment package. This is especially true of the dispersion model component. The ISC-ST model is inadequate for most applications. A more realistic grid-based model would be more appropriate. These models should be implemented on microcomputers and, with recent advances in microcomputer technology, this is totally feasible.

- Error propagation and uncertainty estimation methods need to be better developed, understood and applied. The CMB and ISC-ST models have been equipped with rudimentary error propagation formulae. The adequacy of these formulae needs to be verified.

- Sensitivity studies and applications to synthetic data are required to determine the tradeoffs on temporal and spatial data density and measurement uncertainty. Models need to be used as design tools to optimize the measurements taken for Level II and Level III PM_{10} assessment.

- Chemical models which accurately transform primary particulate matter and precursor gases into the fractionated source profile perceived at the receptor need to be formulated and tested. This will allow the secondary aerosol portion of PM_{10} to be more accurately apportioned to its sources.

With respect to measurements, the following research is needed:

- Standardized procedures for PM_{10} receptor sampling, source sampling and chemical characterization need to be established and their equivalency demonstrated.

- Source profile fractionation coefficients need to be quantified empirically in controlled environments such as smog chambers, urban plumes or single-source-dominated sampling regions.

- Emissions inventories require more accurate emissions factors and better estimates of emissions variability.

- The representativeness of meteorological data needs to be assessed for each application and more representative measurements of air transport, temperature, stability and

relative humidity need to be developed. Remote sensing may be the only practical alternative to current, but inadequate, ground-based measurements.

With respect to the Level I PM_{10} Assessment Package:

- Future data bases to be used for PM_{10} assessment need to consider the needs of the PM_{10} assessment models. A standardized network design would help to accomplish this.

- Software interfaces to other computerized data bases need to be developed. The RESOLVE, SCAQS and SCAQMD data bases could be used in this package if such an interface existed.

- A data base of source compositions needs to be established and maintained which will complement the EPA Source Composition Library. This data base would be specific to sources in California.

- Additional modeling software needs to be interfaced to the package for Level II and Level III assessments. Linear regression of secondary species on principal components and CMB source contributions can provide valuable insights into the mechanisms and pathways of these species. Chemically reactive dispersion models could better apportion PM_{10} subgroups and estimate source profile fractionation.

- A central data base of all potential input data should be established, maintained and distributed to state and local agencies for the preparation of state implementation plans.

- This model and data base description should be revised on an annual basis to reflect changes in the state of the art of models, measurements and data bases.

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