MEASUREMENTS OF CARBONACEOUS AEROSOL ACROSS THE U. S.: SOURCES AND ROLE IN VISIBILITY DEGRADATION

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DEDICATION

This work is dedicated to my parents and family who have sacrificed so much to put me through school.

J. J. S.

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ABSTRACT

MEASUREMENTS OF CARBONACEOUS AEROSOL ACROSS THE U.S.: SOURCES AND ROLE IN VISIBILITY DEGRADATION

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This dissertation has three sections which cover analytical measurements, source apportionment, and visibility impact of carbonaceous aerosols. The samples from 46 urban and 20 rural National Air Surveillance Network (NASN) sites were analyzed for organic, elemental, and carbonate carbon to establish a data base for carbonaceous aerosol. Exploratory data analysis was performed on the NASN results to gain an understanding of the nature, magnitude, and relationship of carbon with other constituents of ambient aerosol. Urban centers with high carbonaceous aerosol concentration were Burbank, Chicago, Dallas, East Chicago, Gary, Houston, Los Angeles, New York City, Pasadena, Phoenix, San Bernardino, Santa Ana, and Torrence.

The chemical element balance (CEB) and multiple linear regression (MLR) receptor models were evaluated for source apportionment of carbonaceous aerosol measured at Portland, Oregon, during 1977-78. The chemical element balance method on an average accounted for 87% of the fine mass and 83% of the carbon for each filter. The major sources of carbonaceous aerosol were vegetative burning and automobile exhaust. The results of receptor models were compared with the carbonaceous aerosol emission inventory (EI). The agreement between the chemical element balance method and the emission inventory shows that well constructed EI's can be used for seasonal or annual source apportionment.

The automotive contribution by MLR agreed with that of the CEB; however, the residual oil combustion and vegetative burning contributions were significantly different. The correlation between vanadium and vegetative burning and the inability of potassium to represent vegetative burning in the MLR were the primary reasons for the discrepancy between MLR and CEB. Because the MLR method relies solely on tracers, the presence of sources without good tracers limits MLR's ability to perform accurate source apportionment.

A regression model was applied to the Portland Aerosol Characterization Study data set to determine the sources of visibility degradation. The contributions of chemical species to the scattering coefficient were studied by a linear model, and it was found that all the major chemical components had to be included for the scattering efficiency evaluation. Sulfates, nitrates, and carbon were found to be equally efficient scatterers with a scattering efficiency of around 5 m^2/g. This is in contrast to other cities where sulfates have been found to be the most efficient scatterers.

CHAPTER I. INTRODUCTION

As the laws of gravitation had to be understood before Man could go to the moon, environmental pollution must be understood before Man can cope with its consequences. In accordance with Newton's Third Law environmental pollution may be viewed as the equal and opposite reaction to modernization. The environmental problems of centuries ago had obvious, albeit primitive, solutions; but as human demand became more sophisticated, the complexity of environmental problems and their repercussions increased correspondingly. Examples of modern problems include: depletion of stratospheric ozone, acid rain, global DDT and PCB contamination, urban smog, climatic effects, the Love Canal incidnet, the Three Mile Island accident, and others, including many more yet unknown to us today.

We have adjusted our life styles to their present "modern" status and feel quite comfortable with them. However, we must also accept responsibility to clean up the waste and to solve the problems generated by our modernization. Our vulnerability to environmental problems is considerable; therefore, we must seek solutions to avoid becoming an endangered species.

Air pollution, readily recognized by smell or reduced visibility, has been studied for many years. Since the atmosphere is vast and as complex as it is vast, it cannot be understood quickly. Advancements in science and technology, aided by researchers' steadfastness and increased public awareness and involvement have made inroads to the understanding of air pollution. Legislative acts have been passed to protect the wilderness and reduce air pollution in urban areas to bring air quality within accepted standards. This dissertation is focused on the carbonaceous aerosol -- a small part of air pollution.

The major constituents of urban fine aerosols ($d_p < 2.5$ μm) are carbonaceous aerosols, ammonium sulfate and related acidic sulfates, nitrates, lead compounds, and trace elements. The carbonaceous material present in the atmospheric aerosol is comprised of a number of organic compounds, elemental carbon, and inorganic carbon (carbonate salts). Approximately 10-30% of the particulate mass in a typical urban airshed is carbonaceous. Organic carbon forms the biggest fraction constituting 50-70% carbon with the rest as elemental carbon. Less than 2% of the total carbon is in the form of carbonate; therefore, the term "carbonaceous aerosol" will be used to address only organic and elemental carbon in the rest of the dissertation.

The importance of carbonaceous aerosol is three-fold. Carbonaceous aerosol makes up a large fraction of the total aerosol loading; it ranks high in terms of its potential hazards to health, and it may play an important role in various atmospheric processes.

The health hazards associated with carbonaceous aerosol were recognized as early as 1775 when Sir Percivall Pott related scrotal cancer in chimney sweeps with their exposure to soot (Pott, 1775). Many organic compounds present in the atmopshere have been found to be carcinogenic and co-carcinogenic (Daisey, 1980; Grosjean, 1975;

Pitts et al., 1979; Peters, 1974). A summary of different research evaluating carcinogenicity is given by Hoffman and Wynder (1977). They found the organic fractions containing polycyclic aromatic hydrocarbons (PAH) to be primarily responsible for the carcinogenicity. Daisey (1980) found the mutagenic character of the organic fraction, indicated by the presence of biologically active compounds, to be present in the polar as well as the nonpolar fraction. The health effects of carbonaceous aerosol are further emphasized by its size distribution. The Task Group on Lung Dynamics (1966), among others, has pointed out the importance of aerosol size distribution in determining its deposition in the respiratory tract. Pierce and Katz (1975) found PAH aerosol to be not only highly dependent upon its size but also with maximum concentration in the respirable size range.

Carbonaceous aerosol may also be relevant to several atmospheric processes. Ketseridis et al. (1976) pointed out that surface active organic compounds have an effect on uptake or evaporation of water, thus influencing the process of cloud formation. Light-absorbing aerosol such as elemental carbon are important in the radiation balance determining the temperature of the earth. Bergstrom et al. (1980) showed that the presence of soot in the atmosphere (at a level of 5 $\mu g/m^3$) reduces the horizon brightness substantially at all wavelengths. Carbonaceous aerosols from vehicle exhaust and other combustion processes have been shown to have large surface areas (up to 100 m^2/gm or more), suggesting a porous structure and making them efficient absorbers of other materials (Pierson, 1979). Scanning Electron Micrographs (SEM) of soot material confirm the agglomerated sphere structure of elemental carbon. The possible involvement of elemental carbon in sulfate formation in the atmosphere has been investigated by Freiberg (1979), Novakov et al. (1974), Chang et al. (1979), and Eatough et al. (1979). Possible mass transfer mechanisms enhancing the concentration of dissolved gases absorbed by elemental carbon via water vapor condensation have been studied by Matteson (1979).

Incomplete combustion of fossil fuel, wood- and coal-burning, agricultural activities, and photochemical activity are the major anthropogenic sources of carbonaceous aerosol in an urban environment and are schematically represented in Figure 1.1.

Organic aerosols are the result of direct emissions into the atmosphere (primary component) and atmospheric reactions (secondary component) usually involving photochemistry. Organic aerosol found in the atmosphere is comprised of hundreds of compounds whose analysis is laborious, requiring sophisticated equipment and laboratory techniques. The classes of identified primary organic compounds include linear and branched alkanes and aklenes, substituted benzenes and styrenes, phenols, cresols, phthalates, fatty acids, carbonyl compounds, and some pesticide compounds (Grosjean, 1977; Daisey, 1980).

The formation of organic aerosol as a result of photochemical reactions of hydrocarbons, ozone, and oxides of nitrogen has been observed in urban and rural atmospheres (Grosjean et al., 1975; O'Brien et al., 1975a). Classes of secondary organic aerosol compounds in-

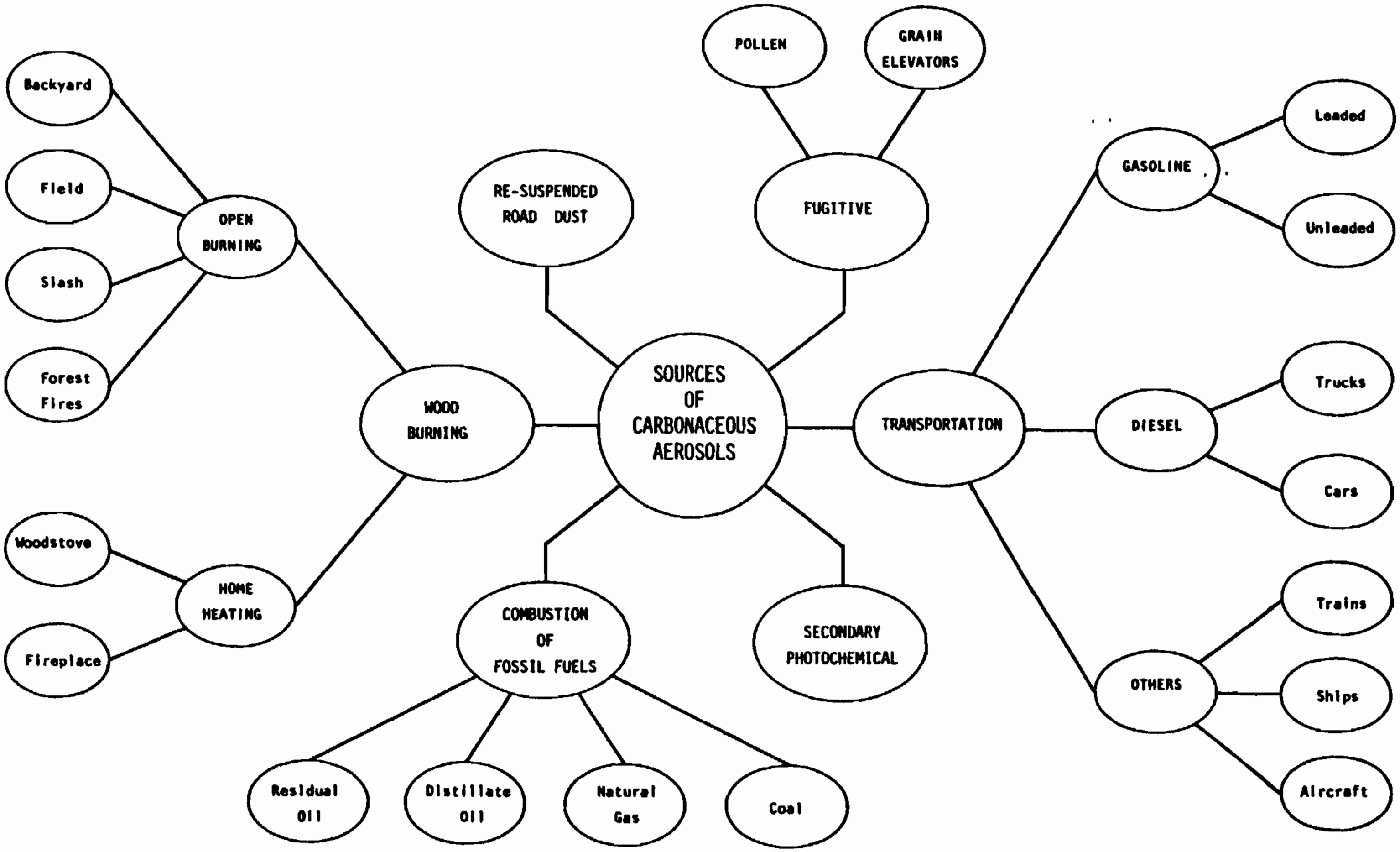

Figure 1.1. Sources of carbonaceous aerosol.

clude aliphatic organic nitrates, carbocyclic acids (e.g., adipic and glutaric acid (O'Brien et al., 1975b)), terpene-derived oxygenates, and nitrate esters. Smog chamber experiments to identify and study secondary organic aerosol have been carried out by many researchers. For detailed accounts of organic aerosol the reader is referred to reviews given by Grosjean (1977, 1979), Daisey (1980), and Hoffman and Wynder (1977).

Elemental carbon (EC) (also referred to as graphitic carbon, particulate elemental carbon, soot, free carbon, black carbon) is produced as the result of incomplete combustion. Sources of elemental carbon include industrial emissions from combustion processes, vehicle exhaust, and space heating. Elemental carbon is primary in origin.

Rosen et al. (1979) used Raman spectroscopy to show the presence of a physical structure similar to activated carbon in ambient and source samples. They also demonstrated that the blackness of the sources and ambient samples was due to the graphitic soot content of the aerosol. The amount of light-absorbing species was found to be proportional to the graphitic soot content of the samples.

A knowledge of relative abundance of primary and secondary components of carbonaceous aerosol is essential for the design of optimal control strategies. Gartrell and Friedlander (1975) found that secondary organic aerosol, estimated by a Chemical Element Balance (CEB), accounted for about 80% of aerosol carbon during several days in the Los Angeles Basin. Other studies (many of them also carried out in the Los Angeles Basin) support these findings (O'Brien et al., 1975b; Grosjean et al., 1975; Heisler and Friedlander, 1977; Wilson et al., 1972). However, Hansen et al. (1979) found no evidence for substantial production of secondary organic aerosol in either the Los Angeles area or the San Francisco Bay area. Novakov and his co-workers (Novakov, 1981) have emphasized the importance of the primary contribution and have argued that it can account for the majority of ambient particulate carbon. The analysis of organic and elemental carbon at several urban and rural sites reported here may contribute to a resolution of this controversy.

The purpose of the present work is to generate a data base for organic and elemental carbon in the atmopsheric aerosol by analyzing samples from different parts of the United States. Another major purpose is to evaluate two methods, chemical element balance and multiple linear regression, for source apportionment of carbonaceous aerosol. The role of carbonaceous aerosols in visibility degradation is also evaluated.

The analytical methods for carbonaceous aerosol and a description of the thermal/optical method developed at the Oregon Graduate Center are reviewed in Chapter II. The results of the carbonaceous aerosol measurements for 46 urban and 20 rural NASN sites are presented and discussed in Chapter III. The goal of this part of the research was to establish a data base for organic, elemental, and total carbon.

Exploratory data analysis was performed on each site to answer general questions on carbonaceous aerosol. Detailed graphical representations are given in Appendix B.

Two methodologies, chemical element balance (CEB) and multiple linear regression (MLR), were evaluated for their applicability to the source apportionment of the carbonaceous aerosol in Portland, Oregon. Results of the carbon balance are discussed in Chapter IV. The emissions inventory and source matrix for Portland are given in Appendix A. Sources of carbon are also evaluated for New York City by the MLR method and are included in Appendix C. In Chapter V sources of visibility degradation for Portland, Oregon, are evaluated, and the importance of carbonaceous aerosol contributions to visibility degradation is assessed and compared with the importance of sulfates and nitrates.

Finally, in Chapter VI the results of this dissertation are summarized and conclusions are drawn.

CHAPTER II. ANALYTICAL METHODS

Carbonaceous aerosol has long been recognized as a major fraction of atmospheric aerosols (10-30%); however, the measurement of organic and elemental carbon is relatively new. Part of the reason for the scarcity of instrumentation is due to the complexity of the measurements. Although sophisticated methods have been developed which are capable of analyzing specific compounds present at an extremely low level in the atmosphere, as pointed out by Cunningham (1979), development of a low cost measurement method for specific compounds and classes of compounds is necessary to obtain a quantity of data sufficient to evaluate the relative importance and sources of carbonaceous aerosol in the atmosphere. At the Oregon Graduate Center, an instrument has been developed which separates carbonaceous aerosol into organic, elemental, and carbonate carbon (Johnson et al., 1979; Huntzicker et al., 1980).

Analytical procedures for carbonaceous aerosol can be grouped into the following classes:

1. Thermal Methods
2. Optical Methods
3. Extraction Methods
4. Digestion Methods
5. Hybrid Methods
6. Other Special Techniques

The category "Others" includes specialized techniques to identify a specific component (e.g., C^{14}) of the carbonaceous aerosol. A schematic representation of the methods and a partial list of the references is given in Figure 2.1.

Optically Assisted Thermal Analyzer for Carbonaceous Aerosols

Instruments using thermal combustion techniques are based on the principle of preferential oxidation of organic and elemental carbon to CO_2 followed by analysis of the CO_2 evolved. The methods differ in their determination of CO_2 and the steps they employ to separate organic and elemental carbon. Because elemental carbon is non-volatile even at high temperatures in an inert atmosphere, separation between organic and elemental carbon can be achieved by volatilizing organic carbon at high temperatures. The organic carbon is then oxidized to CO_2 and analyzed. The elemental carbon is oxidized in an oxygen atmosphere and analyzed. The methods frequently used for CO_2 analysis are: 1) infrared absorption; 2) thermal conductivity detection (TCD); and 3) flame ionization detection (FID) after reducing CO_2 to methane.

There are three modes of operation in the thermal/optical method:

1. 350°C in He/O_2(2%) mixture;
2. 600°C in helium;
3. 400-600/700°C in He/O_2(2%) mixture.

The system is shown schematically in Figure 2.2. Several filter disks (0.25 cm^2 each) are placed vertically in the quartz boat (insert, Fig-

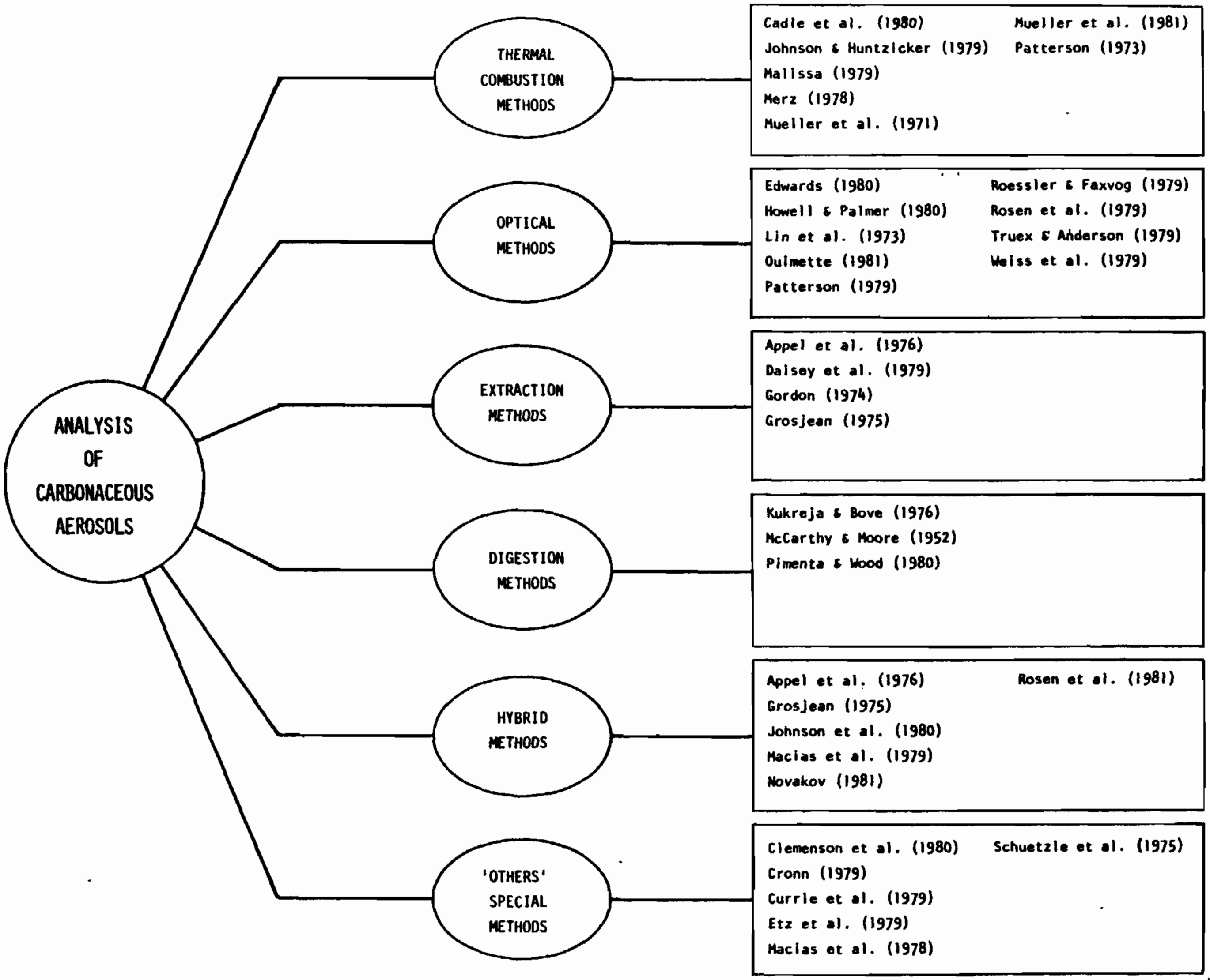

Figure 2.1. Methods for analysis of carbonaceous aerosols.

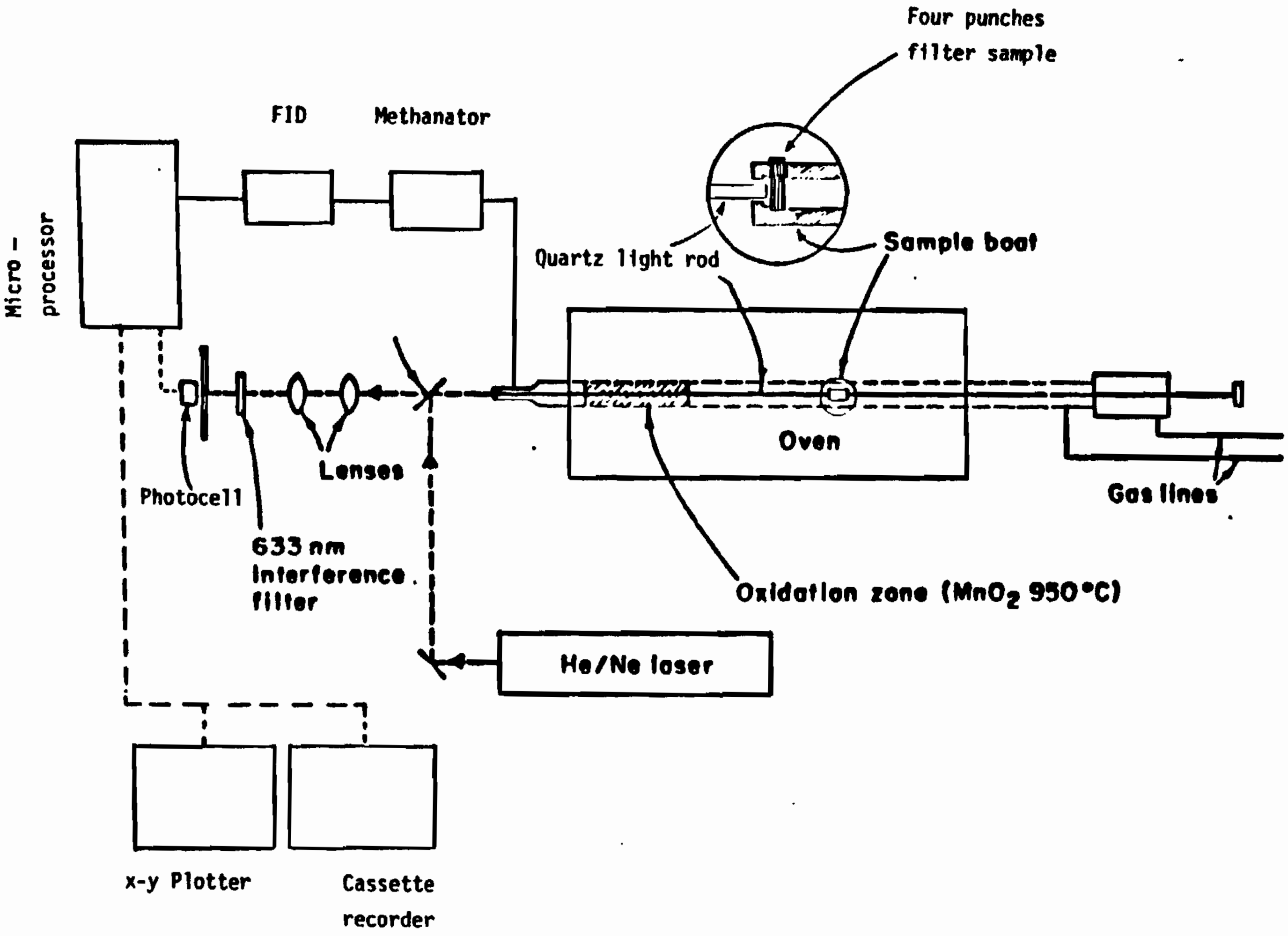

Figure 2.2. Schematics of thermal/optical method.

ure 2.2). After the initial purge with He/O_2, the boat is inserted in the oven which is at 350°C. The volatile carbon evolved at this temperature is oxidized to CO_2 by MnO_2 at 950°C, reduced to CH_4, and measured by a flame ionization detector. The oven temperature is raised to 600°C after purging the oven with helium. The remaining organic carbon is volatilized and measured by an FID. The oven temperature is dropped to 400°C and the carrier gas flow is changed to He/O_2. The oven temperature is now raised to 600°C in steps to oxidize elemental carbon. Evolved CO_2 is converted to CH_4 and measured. Calibration is carried out by injecting a known amount of CH_4 into the oven and measuring the FID output. During the calibration the oven is cooled to 350°C for the beginning of the next run.

The reflectance of the filter sample is monitored throughout the analysis by the optical system as shown in Figure 2.2. A graphical representation of the FID output, the filter reflectance, and the oven conditions for a typical sample is shown in Figure 2.3. The filter reflectance is fairly constant during the first mode of operation (350°C, He/O_2); however, as the temperature is raised to 600°C, the reflectance decreases, indicating higher absorption by the filter sample. This increased absorption is due to pyrolytic conversion of organic to elemental carbon. The correction for the pyrolytic conversion of organic carbon is determined by measuring the amount of carbon evolved before the filter reflectance returns to its initial value during the elemental carbon oxidation step. This assumes that the re-

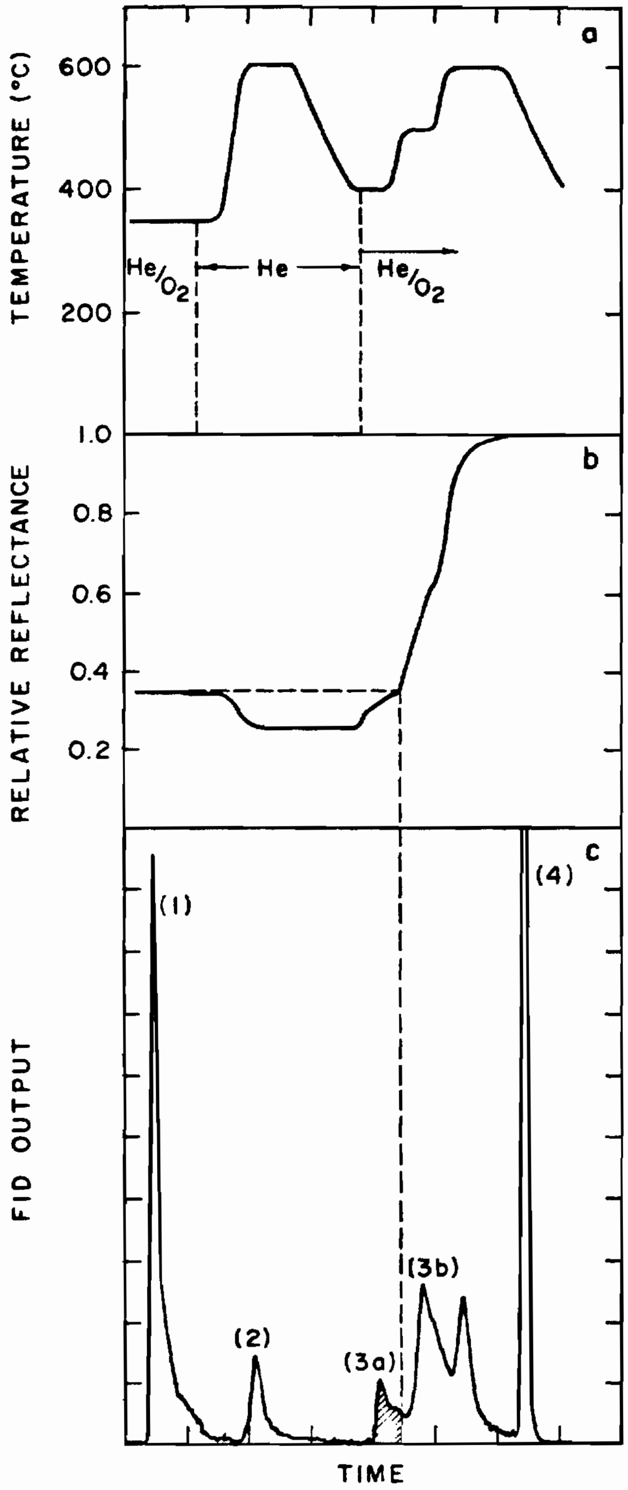

Figure 2.3. Graphical output of thermal/optical method.

flectance (or absorptivity) of original and pyrolytically produced elemental carbon to be the same. The temperature increases in the third step are carried out in steps to slow the oxidation of elemental carbon and to produce a slow initial rise in the reflectance. The correction procedure is shown in Figure 2.3. The shaded area 3A corresponds to pyrolytically produced elemental carbon and is added to peaks 1 and 2 to give total organic carbon. Peak 3B is the amount of original elemental carbon on the filter.

The analytical system is automated and under the control of a microprocessor. All electronic outputs including FID output, reflectance, oven temperature, integrated peak areas, pyrolysis correction, and time are stored on a cassette tape which can be analyzed at a later date on the OGC PRIME 350 computer.

Carbonate carbon is determined in a separate system by measuring the amount of CO_2 evolved upon acidification (20 ml 1% H_3PO_4) of a filter segment at 50°C. Most of the samples analyzed for this work did not show significant amounts of carbonate carbon.

Instrument Characterization and Validation

Extensive experiments conducted to characterize and validate the instrument are discussed by Johnson (1981). The average recovery of 99 ± 6% (Table 2.1) was obtained for the known amounts of pure compounds. Interlaboratory comparisons have been conducted with the De-

Table 2.1. Average recovery of known amounts of pure compounds.

Compound	% Recovered as Organic Carbon	% Recovered as Elemental Carbon	% Total Carbon Recovered
Tetracosane	103	0	103
Tetradecane	102	0	102
Tetratriacontane	106	0	106
Coronene	92	0	92
Perylene	103	1	104
Glutaric Acid	103	2	105
Oleic Acid	92	0	92
Stearic Acid	90	1	91
Humic Acid	72	9	81
DOP	95	1	96
Mannitol	92	6	98
Lampblack	1	97	98

partment of Environmental Quality (DEQ), Portland, and with General Motors Research Group (Groblicki). Good agreement was found for the total carbon values; however, organic carbon values obtained at GM were consistently higher and elemental carbon values were consistently lower than values obtained at OGC. Reasons for this discrepancy are currently being evaluated.

The precision of the analytical methods was assessed by repeated analysis of a filter sample. The average organic, elemental, and total carbon concentrations and their standard deviations for two sets of analyses are presented in Table 2.2. The larger propagated errors by the program are the conservative estimates (Johnson, 1981).

The major limitation on the analytical sensitivity is the uncertainly associated with blank filters. For glass fiber filters (Gelman A/E) the blank values are 2.8 ± 1.4 μgC/cm^2 for organic carbon and 0.2 ± 0.1 μgC/cm^2 for elemental carbon. For Pallflex QAST quartz filters the respective values are 1.0 ± 0.5 and 0.3 ± 0.2 μgC/cm^2. For the NASN filters (glass fiber) the organic and elemental blank values are 6.6 ± 1.2 and 0.9 ± 0.5 μgC/cm^2. Another major source of uncertainty in the chemical speciation is associated with the pyrolysis correction. As pointed out by Grosjean (1975), current definitions of elemental carbon are method-dependent ("operational"). An inter-method comparison by Johnson (1981) found that the thermal/optical method gives elemental carbon concentrations which are higher by 10 ± 10% with respect to the

Table 2.2. Repeat analysis of AG12** and AG13** samples.

Sample Name & Number of Observations	Carbon Fraction	Average Conc. µg/cm^2	Observed Standard Deviation µg/cm^2	Program Error Estimate µg/cm^2
AG12F	OC	68	4 [a]	7 [b]
N = 21	EC	33	3	7
	TC	101	6	10
AG13	OC	56	4	7
N = 18	EC	24	2	4
	TC	81	4	8

** 24-hour hi-volume samples on Gelman AE filter.

a) Standard deviation for the multiple runs.

b) Standard propagation of errors method (Johnson, 1981).

integrated plate method (Lin et al., 1973) and combined solvent extraction-thermal/optical analysis. Unfortunately, there is no reference method for the measurement of elemental carbon.

Interlaboratory comparison studies presently under way will make judging of different methods easier. The current uncertainties in organic, elemental, and total carbon measurements are approximately 15%, 20%, and 10%, respectively.

Quality Assurance

A special effort was directed to quality assurance. Every sample was individually calibrated. A standard filter was analyzed at the beginning of each day, and its values were compared with the standard values, which were obtained by multiple analyses before its use as a standard filter. Any deviations in the standard were checked and corrected before proceeding with routine analysis. The accuracy of the analytes was checked regularly by analysis of external standards, which were prepared by depositing known amounts of organic, elemental, and carbonate carbon.

CHAPTER III. MEASUREMENTS OF CARBONACEOUS AEROSOL ACROSS THE UNITED STATES

The importance of carbonaceous aerosol has been recognized for some time; however, there are no long term data available for ambient organic and elemental carbon concentrations. The development of a data base is necessary for understanding and evaluating the role of carbonaceous aerosol in the air quality. Benzene-soluble organic compounds (BSO) have been measured since 1960 at selected urban and rural NASN sites (Faoro, 1975). However, as pointed out by Grosjean (1975), benzene extraction removes only part of organic carbon from the aerosol samples. The BSO fraction of the total organic carbon depends on the types of organic compounds present and thus is not a reliable measure of the total organic content of the aerosol.

Recent advances in optical techniques have made the estimation of elemental carbon easier. Short-term studies in different cities show that elemental carbon, as estimated by optical methods, comprises a significant fraction of total aerosol (Pierson and Russell, 1979; Conklin et al., 1981; Delumyea et al., 1980; Heisler et al., 1980), but no long term data are available.

Because of the need for a data base for carbonaceous aerosol, ambient samples from 46 urban and 20 rural sites were analyzed for organic, elemental, and carbonate carbon by the thermal/optical system described in Chapter II. These samples were collected by the National Air Surveillance Network (NASN) during the year 1975. The NASN began its sampling in 1953 and is now a part of the Environmental Protection Agency (EPA). The samples were collected by hi-volume samplers on glass fiber filters for a 24-hour duration every 12th day, starting with 6th January. Thus, sampling was done on the same days for most sites, and enough weekday-weekend samples were collected to make an annual average representative of the weekly cycle of human activities.

A comparative study conducted in 1957 (PHS Publication 637), based on the data for TSP that were collected nearly every day during 1955-56, concluded that a reliable measure of air pollution in a specific area may be obtained by sampling on a limited basis. Akland (1972), in his study of TSP data collected at Buffalo for 1960-1966, reported the average percent deviation of the biweekly sample mean from the population mean to be 2.9% for systematic biweekly sampling (similar to the NASN sampling schedule for 1975).

The objective of the measurement phase was to survey and establish a data base for the organic (OC), elemental (EC), and total carbon (TC) concentrations in the aerosol samples collected at several urban and rural locations. Exploratory data analysis was performed to gain insight into the following questions:

1. What are the typical urban and rural concentrations and how do they vary during the year?
2. What are the geographical areas of high carbon concentration?

3. How do carbonaceous aerosol concentrations compare (magnitude, time, and spatially) with other constituents ($SO_4^=$, and Pb) of aerosol?
4. How do carbonaceous aerosol and its constituents differ between urban and rural locations?
5. What fraction of OC, EC, and TC are fine aerosol ($d_p < 2.5$ μm)?
6. What are the major sources of carbonaceous aerosols?
7. What is the role of carbonaceous aerosol in visibility degradation?

The last three questions were evaluated using data generated in other studies which are discussed in Chapters 4 and 5.

It should be noted that the aerosol samples were collected during 1975, stored at room temperature, and were not analyzed until 1980-81. There is some evidence indicating that part of the organic aerosol is lost during extensive storage and handling. Samples collected during the Portland Aerosol Characterization Study (PACS) lost about 20% of the total carbon over the 3-year period (Figure 4.3). Thus, any conclusions concerning organic carbon from this study must be considered as strictly qualitative.

Over 1300 ambient samples from 46 urban and 20 rural sites were analyzed for organic, elemental, and carbonate carbon. Average concentrations for organic carbon (OC), elemental carbon (EC), total carbon (TC), total suspended particulate matter (TSP), sulfate (SUL), and lead (Pb) are compiled in Tables 3.1 and 3.2 for the urban and rural sites. The TSP and sulfate values were obtained from the monitoring data analysis division, National Air Data Branch, EPA, N.C. (Mr. H. Barkhau). The lead data were obtained from the quarterly composite lead values reported in the EPA document entitled "Air quality data for metals 1975 from the NASN" (EPA, 1978). The NASN site names, state, site code, analysis date, population, and population per square mile for the urban and rural sites are given in Tables 3.3 and 3.4 (County and City Data Book, 1977). Because of the possibility of losses or organic carbon during storage, the values for OC listed in Tables 3.1 and 3.2 should be regarded as lower limits.

Graphical Representation

The results of the analysis are graphically represented in different forms to give a better understanding of levels of carbonaceous aerosols, their variations at each site, and their concentrations across the United States.

In order to present the distributional information in one figure, a modified version of the box plot (Tukey, 1977) is used. This presentation was used by EPA in 1975 (EPA, 1976, 1977). Box plots depict the 10th 25th, 50th (median), 75th, and 90th percentiles of the data, along with the composite average. The average and the median both show the typical behaviour; however, the median has the advantage of not being affected by a few extreme observations. Several charac-

Table 3.1. Annual average concentration in $\mu g/m^3$ for the 46 urban sites.

	NAME	No.[a]	OC	EC	TC	TSP	SUL	PB
1	Anchorage	26	5.3	2.4	7.7	78	1.3	1.2
2	Atlanta	13	4.3	2.8	7.0	52	10.2	0.9
3	Baton Rouge	14	5.1	2.0	7.0	57	8.4	0.8
4	Berkeley	28	3.4	2.4	5.7	42	4.8	0.7
5	Birmingham	10	6.6	4.1	10.7	68	11.3	0.7
6	Boston	14	4.5	3.8	8.3	61	7.4	-
7	Burbank	23	12.9	7.0	19.9	132	17.8	3.0
8	Camden	25	7.0	4.5	11.5	87	13.3	1.1
9	Charleston	16	5.9	4.1	10.0	101	13.5	0.8
10	Charlotte	13	5.2	3.0	8.2	45	8.9	0.7
11	Cheyenne	20	2.9	1.7	4.6	37	2.6	0.4
12	Chicago	19	7.9	5.5	13.3	125	17.2	1.2
13	Cincinnati	28	4.5	4.1	8.7	77	13.3	0.8
14	Columbia	13	6.3	4.4	10.7	59	9.2	1.0
15	Dallas	28	12.5	5.6	18.2	120	13.2	2.8
16	Denver	16	7.6	4.1	11.7	108	3.9	-
17	Des Moines	27	5.0	2.0	7.0	76	6.4	0.9
18	Detroit	26	5.7	3.1	8.8	84	14.0	1.0
19	East Chicago	26	6.4	5.7	12.1	119	17.3	2.7
20	Elizabeth	29	6.3	3.7	10.0	65	12.7	-
21	Gary	22	8.6	4.2	12.7	107	15.1	1.0
22	Helena	17	2.7	0.9	3.6	30	3.1	-
23	Houston	20	9.7	3.0	12.7	87	9.7	1.9
24	Jackson	13	5.5	2.3	7.9	62	9.4	0.6
25	Little Rock	26	5.7	3.0	8.7	65	8.5	0.8
26	Los Angeles	26	8.7	5.5	14.2	116	12.0	2.1
27	Miami	11	3.6	1.9	5.5	52	4.8	1.1
28	Milwaukee	25	5.9	3.1	9.0	70	11.1	1.0

a = number of filters analyzed.

Table 3.1. (continued):

	NAME	No.[a]	OC	EC	TC	TSP	SUL	PB
29	Nashville	9	6.0	3.3	9.3	81	14.3	0.8
30	New Orleans	24	5.8	3.2	9.0	67	10.5	0.9
31	New York	21	10.4	7.7	18.1	88	12.2	0.9
32	Newark	27	5.5	4.3	9.8	59	9.4	1.1
33	Pasadena	28	8.4	4.2	12.7	85	10.8	1.7
34	Philadelphia	26	5.3	4.5	9.8	69	11.6	1.0
35	Phoenix	19	13.4	4.5	18.0	129	4.0	2.1
36	Pittsburgh	25	5.6	4.2	9.8	77	11.0	0.8
37	Portland	23	4.1	3.1	7.2	49	5.4	0.8
38	Providence	25	5.4	4.2	9.6	64	10.1	1.2
39	St. Louis	24	7.6	4.0	11.6	98	16.2	0.9
40	Salt Lake City	28	6.5	3.4	9.8	75	7.3	1.1
41	San Bernardino	28	10.0	4.6	14.6	135	13.0	1.4
42	Santa Ana	26	8.4	4.2	12.5	96	11.6	1.6
43	Seattle	26	5.3	3.7	9.0	46	6.4	1.1
44	Sioux Falls	16	3.8	1.8	5.5	58	4.7	-
45	Torrance	26	8.3	4.4	12.7	100	12.9	2.0
46	Youngstown	30	6.5	4.4	10.9	84	8.0	0.6
47	Urban Average	1005	6.6	3.8	10.3	79	10.0	1.2

a = number of filters analyzed.

Table 3.2. Annual average concentrations in μg/m^3 for the 20 NASN rural sites.

	NAME	No.	OC	EC	TC	TSP	SUL
1	Acadia	17	1.6	1.0	2.6	22.5	6.6
2	Calvert	24	2.6	2.2	4.9	29.8	8.5
3	Clarion	16	2.0	1.5	3.5	37.0	11.7
4	Coos	23	2.6	2.1	4.6	28.3	7.3
5	Cumberland	15	2.8	1.3	4.1	58.0	9.0
6	Curry	15	1.5	0.8	2.3	51.4	3.2
7	Fort Howes	19	1.2	0.5	1.6	15.7	1.8
8	Glacier	19	1.2	0.6	1.8	10.2	1.8
9	Jefferson	22	2.3	1.2	3.5	28.4	9.7
10	Kent	6	2.9	1.4	4.3	34.3	7.0
11	Monroe	21	3.4	1.4	4.8	50.1	14.9
12	Orange	27	3.1	1.8	4.9	39.6	12.8
13	Parke	11	4.3	1.8	6.0	45.3	6.6
14	Richland	19	3.3	1.6	4.9	28.1	6.6
15	Shannon	26	3.0	1.1	4.1	28.8	10.4
16	Shenandoah	16	2.8	1.4	4.2	27.7	2.0
17	Thomas	19	1.7	0.8	2.5	21.2	7.1
18	Washington	24	2.6	1.4	4.0	26.6	6.5
19	Wythe	25	2.7	1.5	4.2	22.1	1.8
20	Yellowstone	17	1.2	0.3	1.5	8.9	12.0
21	Rural Average	386	2.4	1.3	3.7	30.7	7.4

Table 3.3. Urban site information.

URBAN SITE	STATE	NASN SITE CODE	POPULATION	P/M^2 *	DATE YY/MM/DD/I **
Anchorage	Alaska	020040003A01	161,018	3,170	80/08/11 A
Atlanta	Georgia	110200001A01	276,273	3,345	80/08/12 A
Baton Rouge	Louisiana	190280002A01	294,394	6,146	80/10/28 A
Berkeley	California	050740001A01	110,465	10,421	80/05/30
Birmingham	Alabama	010380003A01	276,273	3,345	80/08/11 B
Boston	Massachusetts	020240001A01	636,725	13,842	80/08/10 B
Burbank	California	050900002A01	86,001	5,029	80/11/17 A
Camden	New Jersey	010720001A01	89,214	9,913	80/10/24 A
Charleston	South Carolina	500280001A01	67,348	2,449	80/10/16 A
Charlotte	North Carolina	340700001A01	281,417	2,596	80/08/09 B
Cheyenne	Wyoming	520140001A01	46,677	3,705	80/10/20 A
Chicago	Illinois	141220001A01	3,099,391	13,911	80/07/22 A
Cincinnati	Ohio	361220001A01	412,564	5,283	80/05/27
Columbia	South Carolina	420760001A01	111,616	1,028	80/08/13 A
Dallas	Texas	451310002A01	812,797	3,006	80/08/14 A
Denver	Colorado	060580001A01	484,531	5,090	80/05/12
Des Moines	Iowa	161180001A01	194,168	3,020	80/09/26 A
Detroit	Michigan	231180001A01	1,335,085	9,675	80/08/18 A

* population/square mile; ** I = instrument code, A or B.

Table 3.3. Urban site information (continued).

URBAN SITE	STATE	NASN SITE CODE	POPULATION	P/M^2 *	DATE YY/MM/DD	I **
East Chicago	Indiana	151180001A01	44,186	3,592	80/07/23	A
Elizabeth	New Jersey	311300002A01	104,405	8,924	81/05/04	A
Gary	Indiana	151520001A01	167,546	3,924	80/08/19	A
Helena	Montana	270720001A01	26,251	2,652	80/10/15	A
Houston	Texas	452560001A01	1,326,809	2,744	80/08/21	A
Jackson	Mississippi	251260002A01	166,512	2,590	80/10/21	A
Little Rock	Arkansas	041440001A01	141,143	2,481	80/08/11	B
Los Angeles	California	054180001A01	2,727,399	5,879	80/05/25	
Miami	Florida	102700002A01	365,082	10,644	80/10/17	A
Milwaukee	Wisconsin	512200001A01	665,796	7,008	80/08/22	A
Nashville	Tennessee	442540001A01	446,941	881	80/09/26	A
New Orleans	Louisiana	192020002A01	559,770	2,840	80/08/26	A
New York	New York	334680014A01	7,481,613	24,964	80/10/26	A
Newark	New Jersey	313480001A01	339,586	14,450	80/10/22	A
Pasadena	California	055760002A01	108,220	4,685	80/06/06	
Philadelphia	Pennsylvania	397140004A01	1,815,808	14,131	80/07/25	A
Phoenix	Arizona	030600002A01	664,721	2,467	80/08/29	A
Pittsburgh	Pennsylvania	397260001A01	458,651	8,309	80/07/27	A

* population/square mile; ** I = instrument code, A or B.

Table 3.3. Urban site information (concluded).

URBAN SITE	STATE	NASN SITE CODE	POPULATION	P/M^2 *	DATE YY/MM/DD	I **
Portland	Oregon	381460001A01	356,732	3,815	80/05/19	A
Providence	Rhode Island	410300001A01	49,636	3,732	80/09/01	A
Saint Louis	Missouri	264280001A01	524,964	8,578	80/09/03	A
Salt Lake City	Utah	460920001A01	169,917	2,445	80/08/28	A
San Bernardino	California	056680001A01	102,076	2,005	80/11/12	A
Santa Ana	California	057180001A01	177,304	6,519	80/11/17	A
Seattle	Washington	491840001A01	487,091	5,826	80/07/20	A
Sioux Falls	South Dakota	431480001A01	73,925	2,207	80/08/10	A
Torrance	California	058260001A01	139,776	6,818	80/11/25	A
Youngstown	Ohio	367760001A01	132,203	3,935	80/09/04	A

* population/square mile; ** I = instrument code, A or B.

Table 3.4. Rural site information.

RURAL SITE	STATE	NASN SITE CODE	P/M^2 *	DATE YY/MM/DD	I **
Acadia	Maine	200010001A03	25	80/08/23	B
Calvert	Maryland	210280001A03	123	80/08/26	B
Clarion	Pennsylvania	391760001A03	68	80/08/27	B
Coos	Vermont	300140001A03	19	80/08/28	B
Cumberland	Tennessee	440680001A03	36	80/09/01	B
Curry	Oregon	380440001A03	9	80/09/02	B
Fort Howes	Montana	271240008A03	1	80/09/02	B
Glacier	Montana	270570001A03	5	80/09/04	B
Hawaii	Hawaii	120080001A03	19	80/09/05	B
Jefferson	New York	333340001A03	70	80/09/26	B
Kent	Delaware	080060001A03	153	80/10/06	B
Monroe	Indiana	152800001A03	230	80/10/06	B
Orange	New Hampshire	470360001A03	29	80/12/11	B
Parke	Indiana	153260001A03	39	80/10/13	B
Richland	South Carolina	421900002A03	8	80/12/12	A
Shannon	Missouri	264480002A03	331	80/12/17	A
Shenandoah	Virginia	482890001A03	-	80/12/22	A
Thomas	Nebraska	282480001A03	1	80/12/24	A
Washington	Rhode Island	410380002A03	257	80/11/14	A
Wythe	Virginia	483440001A03	51	80/11/12	A
Yellowstone	Wyoming	520860001A03	3	80/12/22	A

* population/square mile; ** I = instrument code, A or B.

teristics of the data are thus represented in a compact manner as shown in Figure 3.1. Box plots for all the urban and rural sites were plotted and are presented in Appendix B. Sites from different regions were grouped to facilitate comparisons. Box plots of the annual arithmetic average concentrations (Tables 3.1 and 3.2) for the urban and rural sites are presented in Figures 3.2 and 3.3.

The OC and EC fractionation for the urban and rural sites are graphically represented in Figures 3.4 and 3.5. Because of the possibility of volatilization losses of organic carbon during storage, the organic and elemental fractions shown in Figures 3.4 and 3.5 should be regarded as lower and upper limits, respectively.

Results

The average concentration of organic carbon (OC) varied from 2.7 to 13.4 $\mu g/m^3$ for the urban sites and 1.2 to 4.3 $\mu g/m^3$ for the rural sites. The average fractional concentration of OC varied from 5.9% (of TSP) to 11.8% at the urban sites, and 2.0% to 13% at the rural sites. The highest 24-hour OC concentration was 57 $\mu g/m^3$ for a sample collected in Phoenix on 14 November 1975. The lowest urban OC concentration was 1 $\mu g/m^3$ for a sample collected in Helena on 2 November 1975. The average OC concentrations were 6.6 and 2.4 $\mu g/m^3$ for all the urban and rural sites respectively.

The average elemental carbon (EC) concentration varied from 0.9 to 7.7 $\mu g/m^3$ and from 0.3 to 2.1 $\mu g/m^3$ for the urban and rural sites respectively. The fractional concentration varied from 2.6 to 8.8%

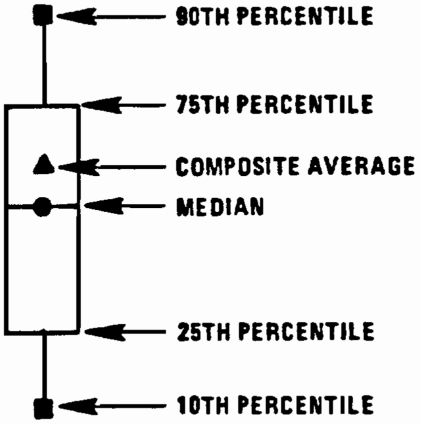

Figure 3.1. Sample illustration of plotting conventions for box plots.

Source: EPA-451/1-77-002.

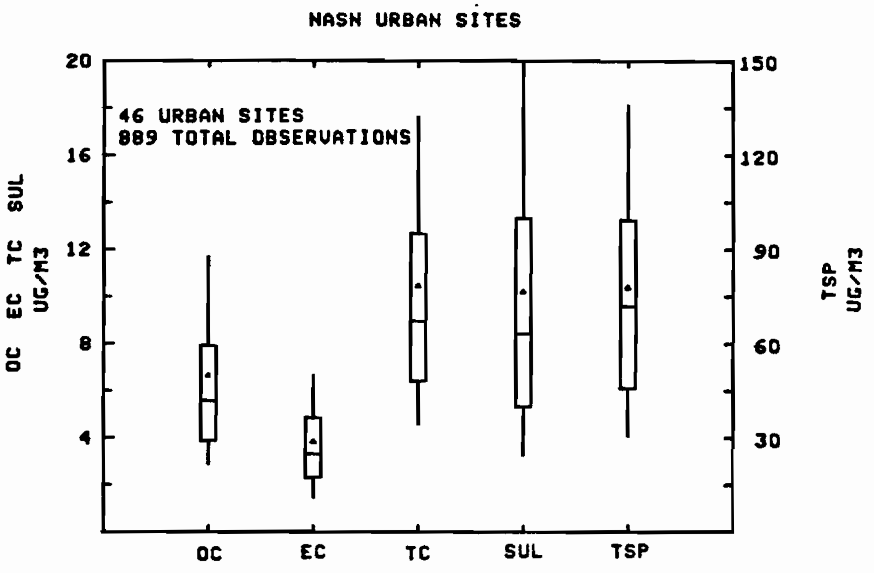

Figure 3.2. Box plots for annual arithmetic average urban concentrations.

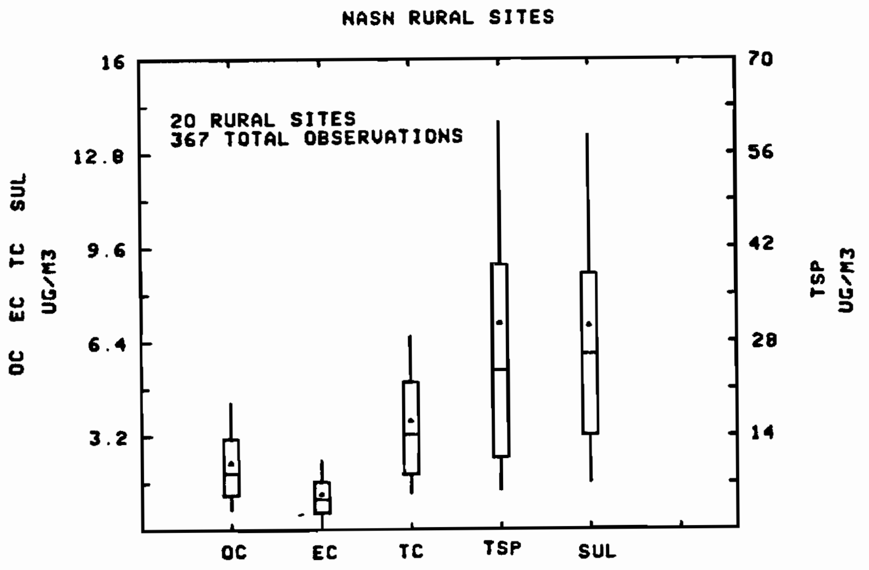

Figure 3.3. Box plots for annual arithmetic average rural concentrations.

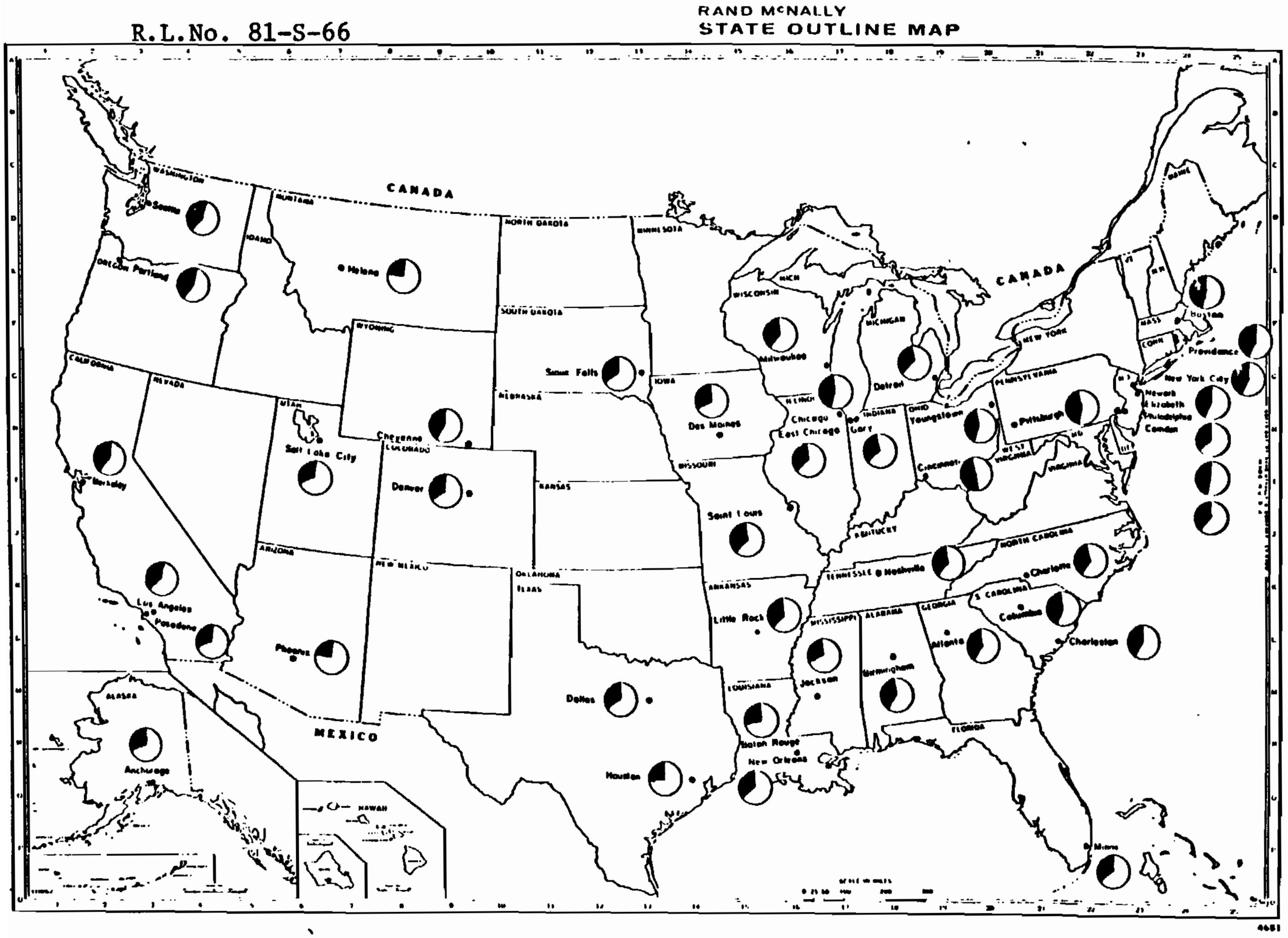

Figure 3.4. Organic and elemental carbon fractionation for the urban sites. The shaded area is the elemental carbon fraction.

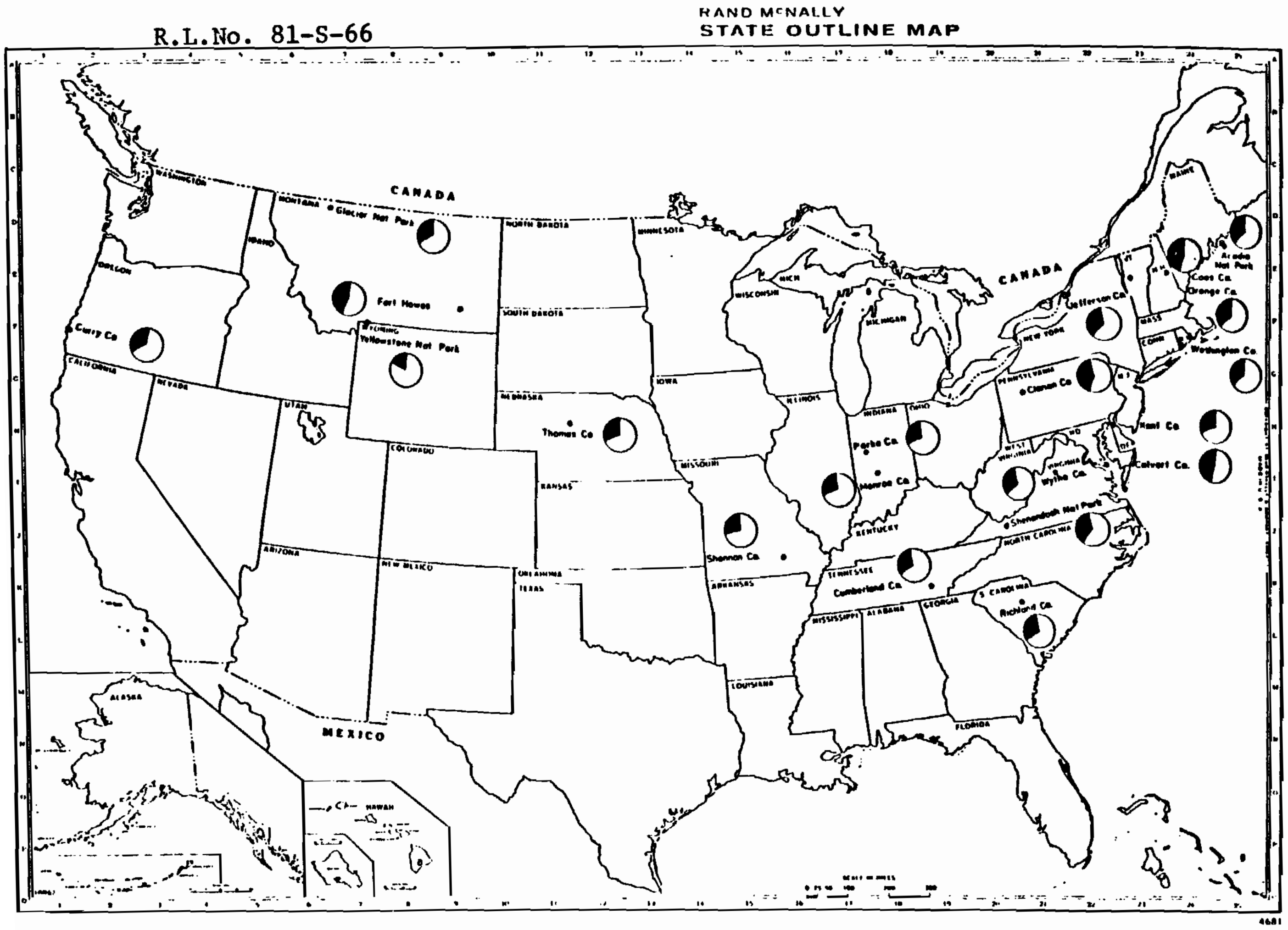

Figure 3.5. Organic and elemental carbon fractionation for the rural sites. The shaded area is the elemental carbon fraction.

(of TSP) for the urban sites and from 1.0 to 7.0% for the rural sites. The highest urban EC concentration was measured at 19 μg/m^3 for a sample collected on 18 January 1975 in New York City. The lowest EC concentration was 0.2 μg/m^3 for a sample collected in Helena on 2 November 1975 (the lowest OC, TC, $SO_4^=$, and TSP were found on the same filter). The average urban and rural EC concentrations were 3.8 and 1.3 μg/m^3. The elemental fraction of carbonaceous aerosol was maximum during fall and winter, and minimum during summer.

Measurable amounts of carbonates were found only at Miami (urban), Hawaii (rural), and Cumberland County (rural). The average carbonate concentrations were 1.63, 0.13, and 1.2 μg/m^3 for Miami, Hawaii, and Cumberland County respectively.

The annual average concentrations of OC, EC, TC, SO_4^{-2}, and TSP for the urban and rural locations are tabulated in Table 3.5 for comparison. The absolute concentrations of all components are lower for the rural locations. The OC, EC, and TC as a mass fraction of TSP are the same for the urban and rural locations. For sulfate, however, the rural mass fraction is a factor of two larger than at the urban sites. This shows that OC, EC, and TC at rural sites are probably due to transport from urban centers while sulfates are transported and produced en route from urban to rural locations. Thus, secondary formation of sulfate aerosol appears to be more important on a fractional basis than secondary formation of organic aerosol.

Table 3.5. Annual average carbon concentration and standard deviation for the urban and rural locations in $\mu g/m^3$.

	OC	EC	TC	SUL	TSP
URBAN (46 sites)	6.6 ± 2.5	3.8 ± 1.3	10.3 ± 2.4	10.0 ± 4.1	79 ± 26
RURAL (20 sites)	2.4 ± 0.8	1.3 ± 0.5	3.7 ± 1.2	7.4 ± 3.8	31 ± 13

The geographical areas of high carbon concentrations can be located with the help of the average concentration Table 3.1. Cities with total carbon concentrations of more than 15 $\mu g/m^3$ were Burbank, Dallas, New York City, and Phoenix. Some of the other cities with high carbon concentrations were Chicago, East Chicago, Houston, Los Angeles, Pasadena, St. Louis, San Bernardino, and Santa Ana.

Because all NASN sites follow the same sampling schedule, the national averages of OC, EC, and TC for the sampling days were obtained. Time series plots of OC and EC as a fraction of TC are plotted in Figures 3.6 and 3.7, for urban and rural sites, to show the national yearly trend of organic and elemental carbon. As seen in these figures, the organic fraction is highest during summer and lowest during winter. The elemental carbon is the mirror image of OC by definition $(\frac{EC}{TC} = 1 - \frac{OC}{TC})$. The higher contribution by the organic fraction during the summer months might be due to the decline in space heating emissions relative to other sources and possibly due to the contribution by secondary organic aerosols. This trend is observed for both urban and rural sites. The peaking of the organic fraction is more pronounced for the rural locations.

The relationship between elemental carbon and sulfate was also explored. Although there was considerable scatter in the relationship between elemental carbon and sulfates for the individual urban and rural locations, the correlation between the average EC and $SO_4^=$ for the urban sites was 0.63. Also, a correlation of 0.41 was obtained

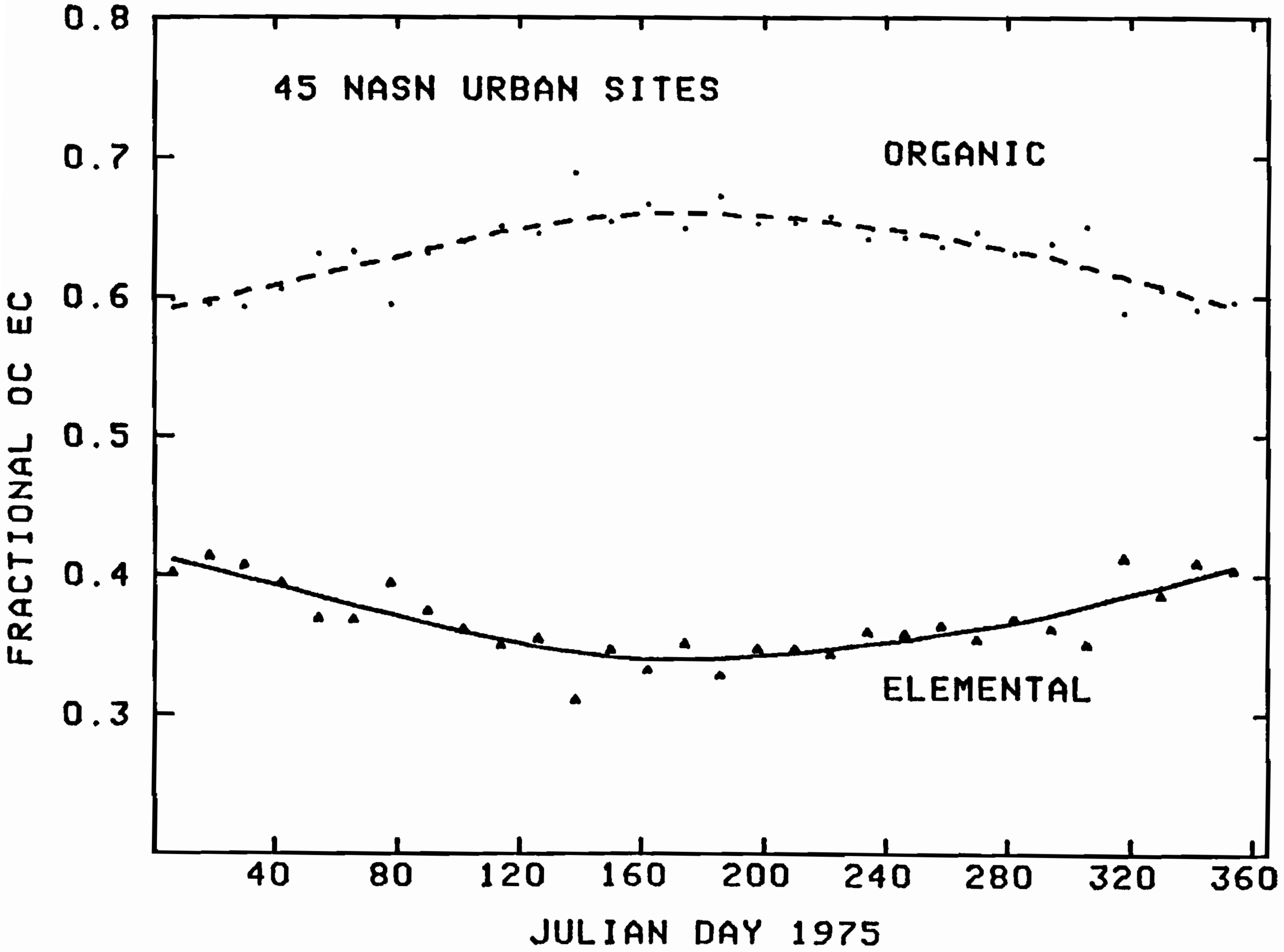

Figure 3.6. National yearly trend for urban sites (800 observations at 45 sites).

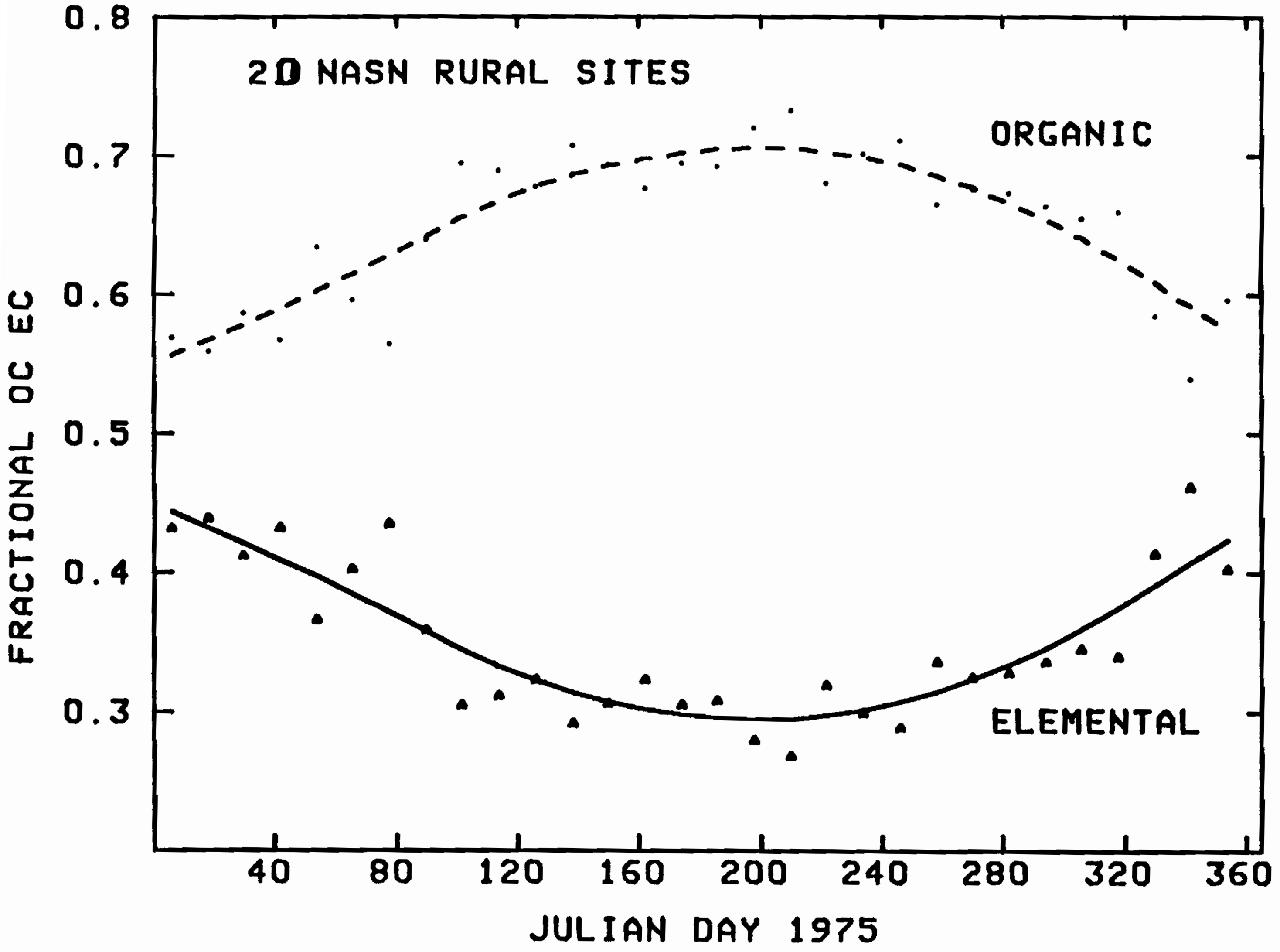

Figure 3.7. National yearly trend for the rural sites (300 observations at 20 sites).

for $SO_4^=$/TSP vs. EC/TSP (division by TSP reduces the intercorrelation resulting from common meteorological dispersion (Henry, 1977)). These observations imply that elemental carbon and sulfate have intrinsic commonality in the urban atmosphere. This may be due to the fact that EC and $SO_4^=$ (or SO_2) are emitted by the same sources, or that their emissions follow similar temporal patterns, or because of elemental carbon's involvement in sulfate formation.

Size distributional information on carbonaceous aerosol could not be obtained for the NASN sites because size segregated samples were not obtained. However, FINE and TOTAl aerosol samples have been collected simultaneously for the Portland Aerosol Characterization Study (PACS) and the Medford Aerosol Characterization Study (MACS) by Sierra Impactors and hi-volume samplers. The PACS samples collected at a downtown site were re-analyzed for this study while the MACS carbon data were obtained from Rau (1981). It was found that organic compounds in fine particles constituted from 66% to 82% of the OC in TSP, and FINE elemental carbon constituted 45% to 66% of total elemental carbon. A summary of these findings at different sites is given in Table 3.6.

Conclusions

Samples from 46 urban and 20 rural NASN sites were analyzed for organic (OC), elemental (EC), and carbonate carbon to establish a data base. These samples were collected during 1975 and were not analyzed until 1980-81, during which they were stored at room temperature. Be-

Table 3.6. Carbon in FINE (dp < 2.5 μm) fraction.

	Site	OC	EC	TC	MASS
PACS	Site 3 (downtown)	66%	51%	59%	37%
	Site 1 (background)	N.A.[a]	N.A.	59%	48%
	Site 5 (residential)	N.A.	N.A.	69%	33%
	Site 6 (background)	N.A.	N.A.	67%	50%
MACS	Justice Building	76%	58%	70%	47%
	Floyd Lay Road	72%	45%	62%	36%
	Dodge Road (background)	82%	66%	78%	42%

[a] Not available.

cause of the strong possibility of loss of organic compounds during storage, the organic carbon values should be viewed as lower estimates.

The average OC and EC concentrations were 6.6 and 2.4 $\mu gC/m^3$ for the urban sites, and 3.8 and 1.3 $\mu gC/m^3$ for the rural sites. The OC, EC, and TC constituted 8.4%, 4.8%, and 13.2% of TSP for urban sites, and 7.7%, 4.2%, and 11.9% of TSP for rural sites. The difference between urban and rural aerosol concentrations suggests that secondary formation of organic aerosol is less important than secondary production of sulfate aerosol.

On an average 74% of organic, 55% of EC, and 66% of TC were in fine aerosol ($d_p < 2.5$ µm) fractions.

CHAPTER IV. CARBON BALANCE

Understanding the nature of the aerosol and its sources is the starting point for the study and control of air pollution. The physical and chemical nature of aerosols has been investigated for many years; however, source identification using measured elemental information is relatively new. Control strategies in the past were designed mainly on the basis of emission inventories (EI) which are at best approximate. Most available emission inventories are not appropriate for the identification of the sources of aerosol (particularly carbonaceous aerosol) at the receptor because they do not take into account gas to particle conversion, size distribution of the particles emitted, fugitive emissions, and source fluctuations. For New York City, Daisey and Kneip (1980) found that controls based on emission inventories were effective in reducing total aerosol; however, they were not effective in reducing the organic aerosol.

Dispersion models evaluating source impact at receptors on the basis of emission inventory (EI) are limited because of the shortcomings of the EI and the complex nature of atmospheric dispersion. Receptor models have been evaluated over the past few years to assess their applicability for source apportionment. Advances in the art of source apportionment for urban aerosol using measured elemental concentrations have been reported by Friedlander (1973), Henry (1977), Watson (1979), Cooper and Watson (1980), and Gordon (1980).

The recent advances in measurement techniques along with better understanding of receptor models have made identification of the sources of carbonaceous aerosols feasible. The major sources of carbonaceous aerosol in an urban environment include automotive exhaust, combustion of fuel oils, coal and vegetative burning, urban dust, and secondary formation (Figure 1.1).

Literature Review

One of the earliest applications of the chemical element balance technique was reported by Miller, Friedlander, and Hidy (1972) for the Pasadena aerosol. Their analysis showed that 19% of the Pasadena aerosol was carbon. They concluded that further breakdown of the carbon fraction was not possible at that time because the sources of carbon did not have definite tracers and secondary production of carbon was not well understood. Friedlander (1973) constructed one of the first carbon balances to account for the 19% of the Pasadena aerosol. The assumptions made then may not stand up to scrutiny now. However, carbon was recognized as a large component of aerosol whose sources needed to be understood. One of the main reasons for the inability of the earlier investigators to carry out a carbon balance was the unavailability of a reasonable and reliable method to analyze for the carbon fractions in the aerosol.

Daisey and Kneip (1980) used a multivariate model to identify the sources of extractable organic aerosol. They analyzed weekly aerosol samples (fines) for 1977-79 by sequential extraction with increasingly polar solvents. The concentrations of two of the soluble organic fractions were then used in a multivariate model with source tracers for source identifcation and apportionment. They found that oil burning was the principal source and accounted for 40% of the extractable organics. Transportation and soil resuspension accounted for 19% and 15% respectively. Comparison of the results from the multivariate model with source emission data fared well, promising the applicability of such models as a source apportionment method.

It is only recently that we can analyze aerosol for organic, elemental, and carbonate carbon with a high level of confidence. As a first step towards understanding the carbonaceous fraction of the aerosol, the samples were analyzed from 46 cities and 20 rural sites in the U.S. as described in Chapter 3. The next step in understanding the carbon fraction is to identify and understand its sources. With this in mind, a mass balance for carbon (carbon balance) was performed for the samples collected in Portland, Oregon. The main purpose of this study was to evaluate the applicability of two receptor modeling techniques, namely multiple linear regression and chemical element balance, for the carbon balance.

Theory

Source Apportionment Methods

As described by Cooper and Watson (1980b), the source apportionment methods can be schematically summarized and represented as shown in Figures 4.1 and 4.2. Receptor models start with elemental measurements at the receptor and then calculate the contribution by various sources using elemental information on source emissions. The dispersion model starts with the emission inventory and meteorological information and calculates source impact at the receptor.

The use of receptor models for the design of optimal control strategies is relatively new. Since Watson (1979) has described the major receptor models, their theoretical basis, and their application in great detail in his dissertation, they will be covered in brief only. Some of the major advantages and disadvantages of CEB and multivariate methods are discussed.

As implied by its name, chemical element balance (CEB) is based on the principal of conservation of mass. The CEB method was primarily established and applied to characterize Pasadena aerosol by Friedlander and co-workers (Miller et al., 1972). A CEB equation for each element measured at the receptor can be written as

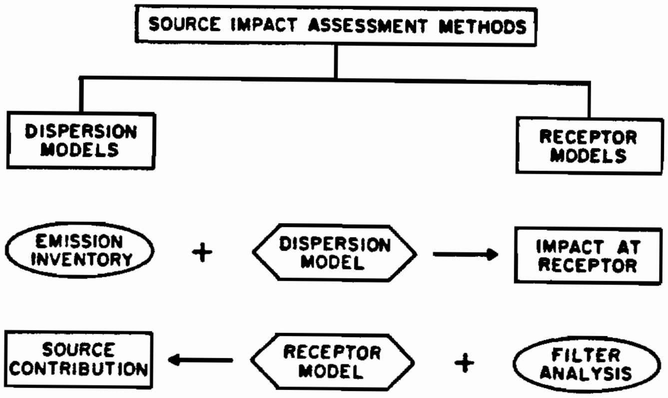

Figure 4.1. Source impact assessment methods.

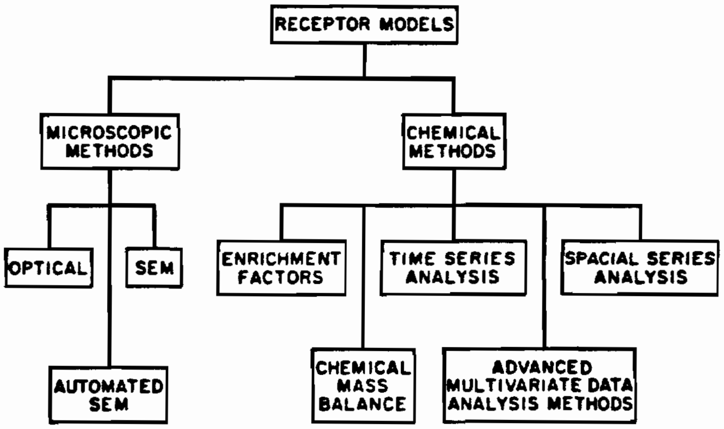

Figure 4.2. Receptor models.

Source: Cooper and Watson (1980)

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

or in normalized form

$$C'_{ik} = \sum_{j=1}^{P} a_{ij} \quad S'_{jk} \qquad i = 1,n \tag{2}$$

where C_{ik} is the concentration of element i during sampling period k, contributed by P sources. a_{ij} is the fraction of element i in the source contribution by source j. S_{jk} is the mass concentration at the receptor during time period k due to source j. C'_{ik} and S'_{jk} are the fractional concentration obtained by dividing C_{ik} and S_{jk} by the total mass concentration at the receptor during time period k.

The limitations of CEB as applied to date are primarily in the a_{ij} values for source j. In equation (1) a_{ij} is the fraction of element i in the source contribution by source j <u>at the receptor</u>. It is generally assumed that the composition of the contribution by source j at the receptor is the same as it is at the point of emission. The validity of this assumption depends on the chemical composition, size distribution, and atmospheric processes (sedimentation, chemical reaction, condensation, vaporization, etc.) for the aerosol during its transport to the receptor. The error introduced by this assumption under different circumstances is yet to be evaluated. For example, the Br/Pb ratio in fresh auto exhaust is similar to that in the fuel; however, this ratio decreases rapidly with time. Thus the source matrix assembled by source or tunnel samples of automotive exhaust would not be the same at the receptor. Such changes in the emissions from major sources need to be studied extensively before a "true" source matrix can be constructed (Friedlander, 1973).

The chemical characteristics of sources and their variability must be assessed by elaborate sampling of all major sources. During the Portland Aerosol Characterization Study (PACS) extensive source sampling was conducted; however, much more needs to be done. Major shortcomings of the PACS source matrix were with respect to sources with "nondescript" chemical composition. Their importance cannot be evaluated by CEB without further chemical characterization (e.g., specific organic compounds) which allows their differentiation from other sources. An emission inventory can be used to aid the construction of the source matrix by supplying scaling factors relating nondescript to specific sources whose contribution can be calculated by CEB (Henry, 1977; Miller et al., 1972).

Multivariate methods refer to statistical methods such as factor analysis, principal component analysis, pattern recognition, MLR, and cluster analysis. These methods evaluate the source contributions based on the observed commonality among elements measured on several filters. The limitations of these statistical techniques lie in the assumption that all significant variations are distinctive and are reflected in the correlations. In air pollution measurements correlations among chemical elements measured are due to common emission sources and meteorological dispersion; however, it is not an easy task to separate the two effects. Meteorological dispersion depends on atmospheric conditions, location of source, type of source, and the emission characteristics (size distribution of various chemical elements). Henry (1977) showed that substantial intercorrelation in the chemical elements due to the common atmospheric dispersion could be minimized by dividing the elemental concentration by the total aerosol mass. The observed correlations include meteorological dispersion effects while normalized correlations (obtained by using TSP normalized concentrations) have an unknown error introduced by normalization procedures. (There is no perfect normalization procedure!) Also, because the source apportionment is carried out on the complete data set, the overall pattern tends to be distorted by extreme values. Special effort must be devoted to locate and evaluate such points. This is further discussed in the data analysis section.

Users of multivariate methods (factor analysis) claim that no *a priori* assumption or knowledge about the number and composition of sources is necessary (Hopke et al., 1976; Gordon, 1980); however, identification of factors resulting from statistical analysis requires some knowledge of the chemical compositions of possible sources. Factors resulting from a factor analysis may not all be physically interpretable. Many researchers have used factor analysis to determine the number and choice of tracers to be used in a regression model to quantitatively assess source contributions (Kleinman et al., 1980; Daisey and Kneip, 1980). The same choice of tracers can also be made by careful study of the literature and understanding of major sources for the area under investigation (Appendix C).

Graphical representation of factor analysis results (also cluster analysis and pattern recognition) allows visualization and sometimes helps to understand complex relationships existing in the data set. The advantages of factor analysis include the capability to (1) handle correlated variables, (2) simultaneously use chemical and meteorological data, (3) incorporate secondary aerosols to an extent, and (4) use all available information at once.

The multiple linear regression method using source tracers has been applied for source apportionment (Kleinman et al, 1980; Kleinman, 1977). A general MLR equation for any chemical component can be written as

$$F = \sum_{i=1}^{P} a_i C_i + a_o \qquad (3)$$

where P is the number of sources, C_i is the concentration of tracer element for source i, a_i is the regression coefficient to be determined, and F is the concentration of the chemical component in question. For n observations ($n \geqslant P$) a set of simultaneous equations can be obtained to solve for a_i's.

The regression model thus developed can be used for the prediction of chemical components in the future. The regression coefficients may be modified to reflect the changes in the source emissions. (For example, the use of leaded gasoline is declining as more unleaded cars are introduced. This will change the coefficient for Pb, which is used as a tracer for automotive contribution.)

The usefulness of MLR and CEB were evaluated by applying them to the data set obtained during the PACS project. A carbon balance using MLR was also conducted for New York City and is discussed in Appendix C.

Experimental

Most of the data used for the carbon balance were obtained during the Portland Aerosol Characterization Study (PACS). The PACS sampling program was designed to obtain representative samples and to record relevant meteorological data to be used for chemical element balance (CEB) analysis. Sampling was done at six sites. Two sites were located in rural areas about 24 km from the downtown, representing upwind and downwind (prevailing winds) background sites. Sampling was carried out for 93 days between July 1977 and April 1978, and a 32-day subset was selected for intensive chemical analysis. Selection of days for the intensive chemical characterization was guided but not controlled by the desire to represent the entire year with respect to meteorology. Analytical methods used for chemical characterization included ion chromatography (F^-, Cl^-, Br^-, NO_3^-, and $SO_4^=$), carbon analysis by the OGC thermal method (Johnson et al., 1979), energy dispersive x-ray fluorescence (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cd, Ba, and Pb), and neutron activation analysis

(Al, Br, Cl, Mg, Mn, Na, Ti, V, and K). A significant aspect of the entire analysis scheme was the high level of quality assurance established for every filter analyzed through intermethod and interlaboratory comparisons (Watson, 1979).

Many source samples were collected and analyzed to obtain a representative source matrix for all the major sources in the area. A transportation source matrix was constructed with the use of tunnel (Pierson, 1981) data and tunnel samples analyzed for organic (OC) and elemental (EC) carbon.

Re-analysis (1980-81) of all the 24-hour samples from the downtown site for OC and EC by the new thermal/optical (Johnson et al., 1981) method showed total carbon to be consistently lower by about 20%. The correlation coefficient for total carbon measurements between original analysis and new analysis was 0.98 (Figure 4.3). This decrease in the total carbon was presumably due to loss of organics off the filter. Because elemental carbon is a conservative species, the organic carbon values were obtained by sutracting EC from the original TC measurements. This was necessary because the organic/elemental speciation obtained in the original PACS analysis was incorrect. Further experimental details are discussed in Chapter V and by Watson (1979) and Cooper and Watson (1979).

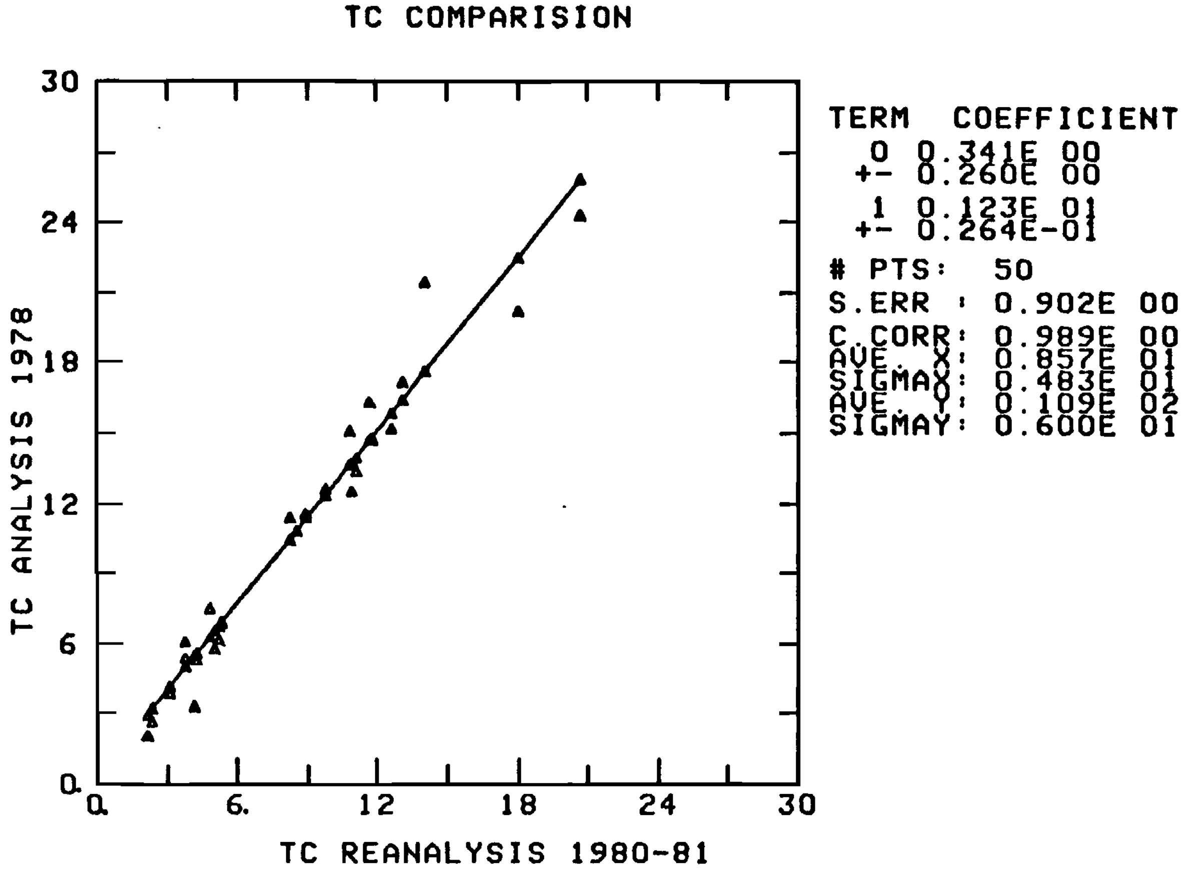

Figure 4.3. Comparison of total carbon analysis done in 1978 and 1980-81.

Data Analysis

An MLR model as described by equation (3) was applied to the downtown site of the Portland data set to evaluate the sources of carbonaceous aerosol. The coefficients in equation (3) were calculated using a stepwide regression routine. Stepwise regression and its advantages have been discussed by Draper and Smith (1966).

On the basis of the PACS results, which indicated that vegetative burning, automobiles, residual oil combustion, and road dust were the principal sources of carbonaceous aerosol, K, Pb, V, Si/Ti were selected as their respective tracers. The use of K as a tracer for vegetative burning is not ideal because it is not a major component, it is highly variable, and is not unique. However, nothing else was available. The average concentrations for the chemical species are listed in Table 4.1.

The initial regression analysis was performed using all the data points. However, it was noted that the regression coefficients were very sensitive to some of the data points. To identify these points, the observed carbon concentrations were compared with those calculated from the regression analysis. Those points which differed greatly from the calculated values were deleted to obtain a refined data set for which new regression coefficients were obtained. This process was continued until the regression coefficients for the model reached stable values (Table 4.2). Seven points had to be deleted before the model

Table 4.1. Average concentrations of trace metals and carbonaceous aerosol in $\mu g/m^3$. Downtown site, 25 observations, PACS 1977-78, Portland, Oregon (Cooper and Watson, 1979).

Element	Concentrations in fine aerosol samples - $\mu g/m^3$
OC	7.33
EC	3.54
TC	10.87
$SO_4^=$	3.36
NO_3^-	2.42
Pb	0.77
Br	0.30
Fe	0.33
Si	0.36
K	0.18
V	16×10^{-3}
Ni	30×10^{-3}
Zn	80×10^{-3}
Cu	27×10^{-3}
Mn	63×10^{-3}
Ti	14×10^{-3}
Cr	14×10^{-3}
Fine Mass	27.58
Av. Temp.	12°C
Av. R.H.	77%

Table 4.2. Sensitivity of regression coefficients to selective removal of data points. Dependent variable, total carbon.

Number of Points	Multiple Correlation Coefficient	b_o	Regression Coefficient for V	Pb	K
25	0.86	2.22	159±70[a)]	2.2±2.3	16.9±6.3
24	0.88	1.61	119±77	2.3±2.5	23.4±6.7
23	0.87	2.03	215±77	--	22.9±7.3
22	0.82	0.98	147±80	4.7±3.6	16.5±6.7
21	0.91	-0.39	60±63	8.7±2.9	19.9±5.0
20	0.92	-0.65	266±112	6.7±2.8	14.5±5.2
19	0.93	-0.07	362±104	5.3±2.5	7.1±5.3
18	0.93	-0.01	390±116	4.7±2.7	6.8±5.5

a) standard error

stabilized. The overall fit and the form of the model improved, as seen in Table 4.2, when the extreme values were deleted. Such points were usually associated with either an unusual value for one of the chemical components in the model or extreme meteorological conditions (heavy rain, snow, or very low inversion). It was noted that most extreme points also had northerly to southeasterly flow with low wind speed. This procedure allowed the underlying pattern in the data set to be explored and explicitly rejected "atypical" observations.

The stability of the regression coefficients was further checked by deleting one observation at a time from the refined data set and performing the regression on n-1 observations. The data points in the refined set did not have significant effects on the overall relationship or any specific coefficient.

The carbon balance (CB) on each 24-hour averaged filter for fine aerosol was performed by the chemical element balance (CEB) method, using the effective variance least square fitting procedure with as many fitting elements as possible (Tables 4.3, 4.4). The carbon balance routine *CEBCB was based on the original *CALCEB routine written by Watson (1979). The *CEBCB performs the mass balance and carbon balance while the original *CALCEB performed the mass balance only. The source matrix used for the CB is presented in Table A.2 and discussed in Appendix A.

Table 4.3. Example of mass balance output.

```
FILTER IDS  FINE: N2220    TOTAL:
DATE: 78 321 SITE: 3 SEQUENCE: 7
UPWIND BACKGROUND SITE: 6 SEQUENCE: 4
SITE 3 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: F/C BACKGROUND: _/_        FINE    PARTICULATE FRACTION
SITE 6 METHOD FLAGS:  FINE/TOTAL FIELD: _/_ MASS: _/_ SIZE: _/C BACKGROUND: _/_
REGIME:  2

EFFECTIVE VARIANCE FITTING.  REDUCED CHI SQUARE:   0.147 DEGREES OF FREEDOM:  7
CODE SOURCE FLG      UG/M3              %
---------------------------------------------------------------------------------------------------------
  1   MARIN   *   0.770+- 0.142    2.052+- 0.380
  3   UDUST   *   1.627+- 0.176    4.337+- 0.475
  4   TRANS   *   3.351+- 0.459    8.932+- 1.232
  5   RDOIL   *   0.378+- 0.069    1.008+- 0.184
  7   VBRN2   *   2.655+- 1.237    7.075+- 3.300
 11   ALFRO   *   1.419+- 0.859    3.783+- 2.289
 12   STEEL   *   1.217+- 0.149    3.243+- 0.402
 13   FERMN   *   0.564+- 0.127    1.504+- 0.339
 17   NO3     *   5.697+- 0.639   15.184+- 1.721
 18   SO4     *   6.531+- 0.785   17.408+- 2.111
 20   WOODS   *  10.017+- 3.569   26.699+- 9.520
---------------------------------------------------------------------------------------------------------
TOTAL:           34.227+- 4.041   91.224+-10.860

     SPE FIT BA    FINE   SUSPENDED PARTICULATE  ** LESS BACKGROUND   CALCULATED       RATIO
CODE CIE FLG FLG       UG/M3            PERCENT   **        UG/M3          UG/M3
---------------------------------------------------------------------------------------------------------
  1  OC   *          7.790+- 1.500  20.763+- 4.011 **   7.790+- 1.500   8.895+- 1.979  1.142+-0.336  OC
  2  EC   *          3.360+- 0.800   8.955+- 2.137 **   3.360+- 0.800   2.732+- 0.645  0.813+-0.273  EC
  3  NO3  *          5.827+- 0.280  15.532+- 0.786 **   5.827+- 0.280   5.827+- 0.574  1.000+-0.110  NO3
  4  SO4  *          7.240+- 0.392  19.296+- 1.080 **   7.240+- 0.392   7.240+- 0.677  1.000+-0.108  SO4
  5  F    *          0.130+- 0.014   0.369+- 0.038 **   0.130+- 0.014   0.130+- 0.048  1.001+-0.360  F
  6  NA   *          0.454+- 0.010   1.210+- 0.050 **   0.454+- 0.010   0.456+- 0.043  1.005+-0.102  NA
  7  MG                    < 0.104         < 0.277 **   0.052+- 0.104   0.290+- 0.104  5.571+-011.3  MG
  8  AL       )      0.307+- 0.010   0.818+- 0.031 **   0.307+- 0.010   0.570+- 0.123  1.856+-0.405  AL
  9  SI   *          0.485+- 0.020   1.292+- 0.058 **   0.485+- 0.020   0.484+- 0.031  0.998+-0.077  SI
 10  S               1.673+- 0.057   4.460+- 0.168 **   1.673+- 0.057   2.387+- 0.220  1.427+-0.140  S
 11  CL   *   )      0.685+- 0.028   1.827+- 0.081 **   0.685+- 0.028   0.661+- 0.157  0.964+-0.233  CL
 12  K    *          0.274+- 0.010   0.730+- 0.028 **   0.274+- 0.010   0.289+- 0.122  1.055+-0.446  K
 13  CA   *          0.239+- 0.008   0.638+- 0.023 **   0.239+- 0.008   0.236+- 0.040  0.987+-0.171  CA
 14  TI   *          0.016+- 0.001   0.042+- 0.003 **   0.016+- 0.001   0.016+- 0.004  1.004+-0.205  TI
 15  V    *          0.015+- 0.001   0.040+- 0.001 **   0.015+- 0.001   0.015+- 0.003  1.029+-0.198  V
 16  CR   *          0.031+- 0.002   0.081+- 0.005 **   0.031+- 0.002   0.027+- 0.017  0.884+-0.560  CR
 17  MN   *          0.213+- 0.012   0.566+- 0.033 **   0.213+- 0.012   0.212+- 0.013  0.999+-0.082  MN
 18  FE   *          0.535+- 0.021   1.426+- 0.060 **   0.535+- 0.021   0.540+- 0.040  1.009+-0.084  FE
 19  NI   *          0.033+- 0.002   0.088+- 0.005 **   0.033+- 0.002   0.032+- 0.005  0.973+-0.157  NI
 20  CU              0.045+- 0.002   0.121+- 0.006 **   0.045+- 0.002   0.009+- 0.002  0.191+-0.042  CU
 21  ZN              0.090+- 0.003   0.241+- 0.010 **   0.090+- 0.003   0.033+- 0.005  0.367+-0.055  ZN
 22  BR   *          0.205+- 0.007   0.547+- 0.020 **   0.205+- 0.007   0.224+- 0.044  1.092+-0.217  BR
 23  PB   *          0.617+- 0.022   1.645+- 0.064 **   0.617+- 0.022   0.579+- 0.106  0.938+-0.174  PB
 24  SE                    < 0.002         < 0.007 **
 25  AS       *            < 0.008         < 0.021 **
 26  CD                    < 0.028         < 0.074 **
 27  BA                    < 0.182         < 0.485 **
---------------------------------------------------------------------------------------------------------
SITE 3 LOVOL/HIVOL, UG/M3:  FINE  37.5+- 0.6/ 47.0+- 1.7 COARSE 103.4+- 1.2/113.0+-10.0 TOTAL 140.9+- 1.0/160.0+-17.9
```

Table 4.4. Example of carbon balance output.

```
CONTRIBUTIONS TO ORGANIC AND ELEMENTAL CARBON
                  in μg/m3

March 31, 1978            OC       OC ERR          EC       EC ERR
 1 MARINF                0.000 ± 0.000           0.000 ± 0.000
 3 UDUSTF                0.111 ± 0.041           0.017 ± 0.009
 4 TRANS3                4.511 ± 0.725           1.975 ± 0.666
 5 RDIOLF                0.057 ± 0.046           0.023 ± 0.019
11 ALPROF                0.026 ± 0.026           0.016 ± 0.007
12 STEELF                0.073 ± 0.000           0.012 ± 0.001
13 FERMNF                0.015 ± 0.002           0.003 ± 0.000
17 NO3  F                0.000 ± 0.000           0.000 ± 0.000
18 SO4  F                0.000 ± 0.000           0.000 ± 0.000
19 DOMEST                5.801 ± 3.581           0.900 ± 0.740
MEASURED                10.000 ± 1.900           5.690 ± 1.020
CALCULATED              10.595 ± 3.654           2.946 ± 0.996
RATIOS                   1.060 ± 0.417           0.518 ± 0.198

March 21, 1978
 1 MARINF                0.000 ± 0.000           0.000 ± 0.000
 3 UDUSTF                0.192 ± 0.070           0.030 ± 0.015
 4 TRANS3                1.454 ± 0.234           0.637 ± 0.215
 5 RDOILF                0.029 ± 0.023           0.012 ± 0.009
 7 VBRN2F                1.173 ± 0.993           0.191 ± 0.218
 1 ALPROF                0.055 ± 0.055           0.033 ± 0.014
 2 STEELF                0.110 ± 0.000           0.018 ± 0.002
13 FERMNF                0.051 ± 0.005           0.008 ± 0.001
17 NO3  F                0.000 ± 0.000           0.000 ± 0.000
18 SO4  F                0.000 ± 0.000           0.000 ± 0.000
20 WOODST                5.830 ± 1.693           1.803 ± 0.567
MEASURED                 7.790 ± 1.500           3.360 ± 0.800
CALCULATED               8.895 ± 1.979           2.732 ± 0.645
RATIOS                   1.142 ± 0.336           0.813 ± 0.273
```

Results

The final regression equations for OC, EC, and TC are given in Table 4.5. The multiple correlation coefficient for all the regression equations was greater than 0.9 (see Figure 4.4). The average source contributions to OC, EC, and TC calculated using the regression coefficients and average tracer concentrations are listed in Table 4.6. The major contributors to TC, according to the MLR method, were residual oil combustion (55%), transportation (33%), and vegetative burning (12%).

The CEB and CB were performed for each intensive sampling day. Their typical outputs are given in Tables 4.3 and 4.4. The chemical element balance accounted for 87% of the fine mass on an average. Most of the elemental ratios $(\frac{\text{calculated conc.}}{\text{measured conc.}})$ were close to unity. The reduced X^2 for the mass balances were low and the overall fit was impressive. The carbon balance by CEB was also successful and on an average accounted for 114 ± 21% of organic and 71 ± 18% of elemental carbon. The average source contributions for all the intensive sampling days were calculated from the carbon balance output for each day and are listed in Table 4.6. The major contributors to TC according to CB were vegetative burning (51%), transportation (29%), and others (20%).

The validity of the CEB and MLR can be assessed by

i) comparison with an emission inventory;

ii) comparison of MLR's regression coefficients with the ratio of carbon to tracer element concentration in the source emissions;

Table 4.5. MLR model for carbonaceous aerosol. Fine aerosol. 18 observations, 1977-78, Portland, Oregon. All concentrations in $\mu g/m^3$.

$$TC = (4.7 \pm 2.7^{a})\,Pb + (390 \pm 110)\,V + (6.8 \pm 5.5)\,K - 0.01$$

$$(r = 0.93;\ \overline{TC} = 7.86)$$

$$OC = (3.1 \pm 1.8)\,Pb + (216 \pm 78)\,V + (7.4 \pm 3.7)\,K + 0.3$$

$$(r = 0.93;\ \overline{OC} = 5.42)$$

$$EC = (1.6 \pm 1.1)\,Pb + (168 \pm 39)\,V - 0.3$$

$$(r = 0.91;\ \overline{EC} = 2.44)$$

---

a = standard error

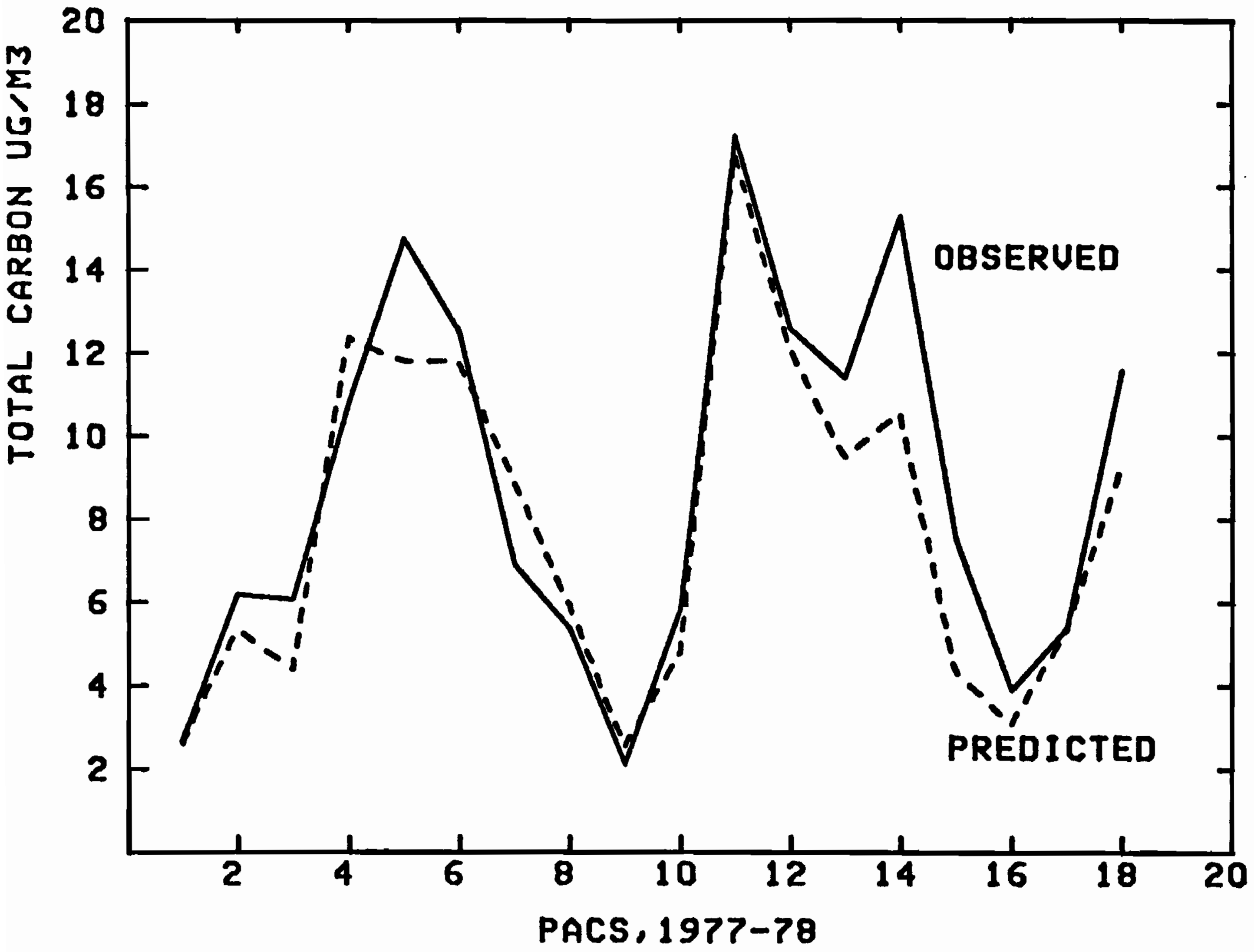

Figure 4.4. Example of goodness of fit for the MLR model.

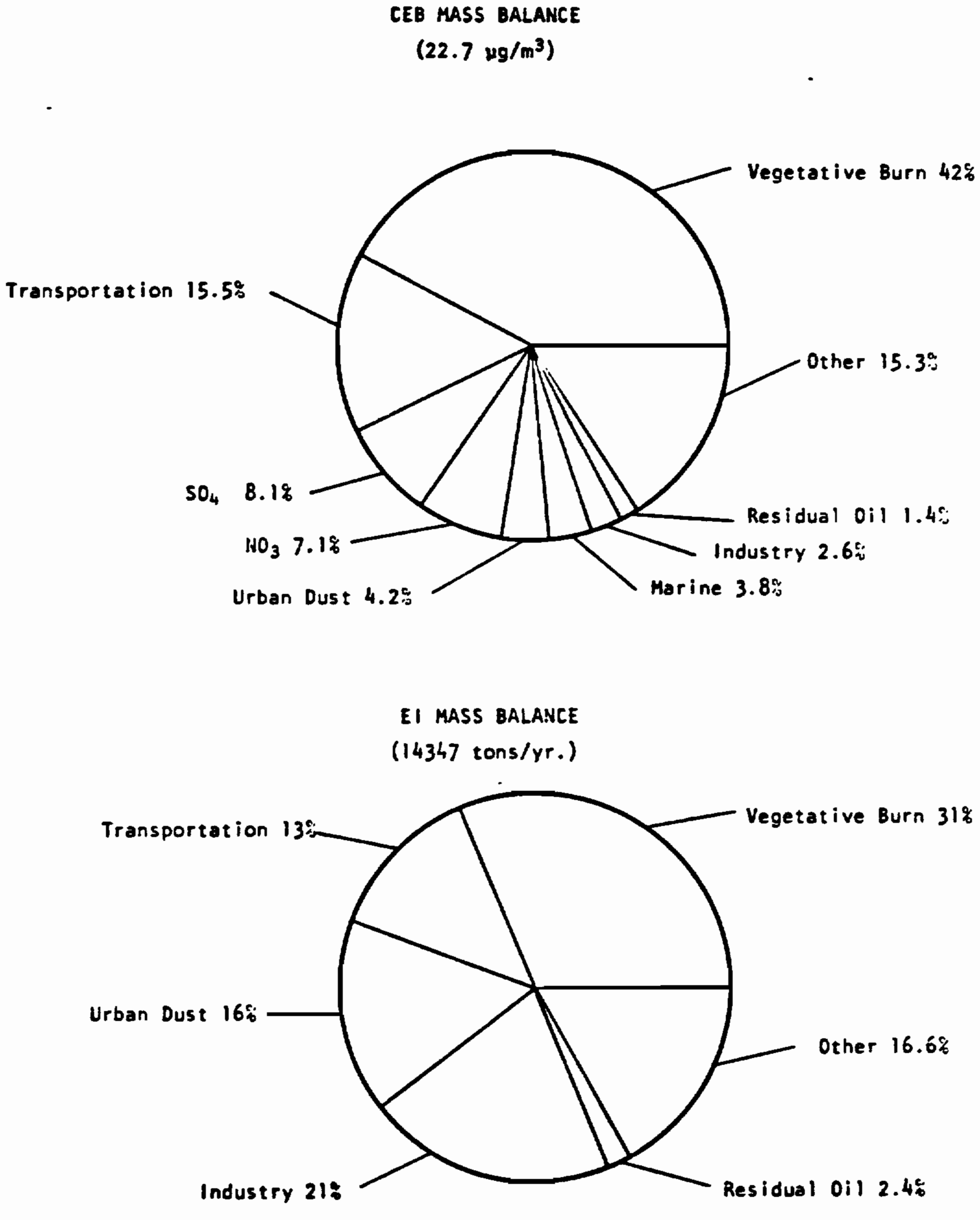

Figure 4.5 Annual average mass balance for 18 fine fraction samples taken at CAMS sampling station, Portland, Oregon, 1977-78.

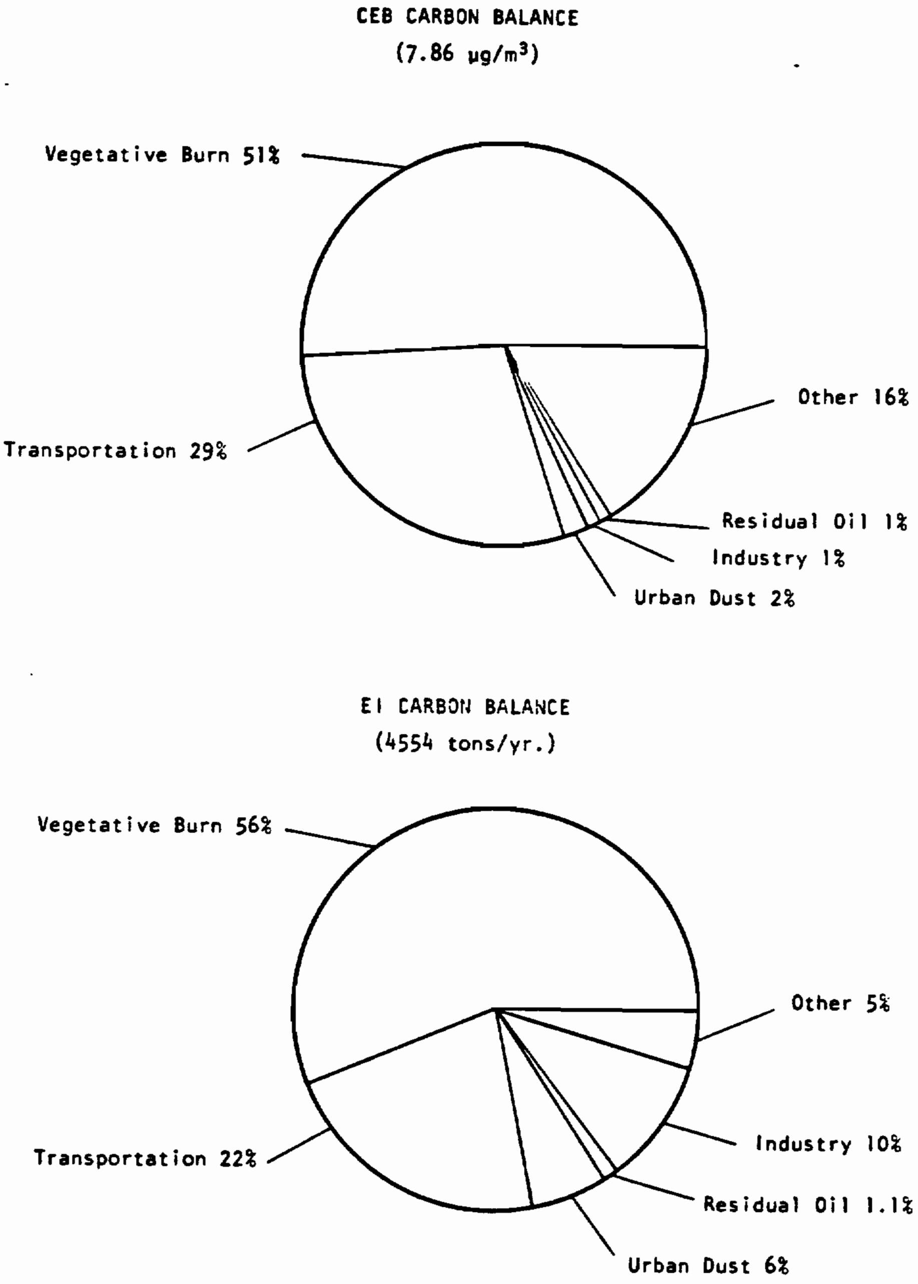

Figure 4.6 Annual average carbon balance for 18 fine fraction samples taken at CAMS site, Portland, Oregon, 1977-78.

iii) checking the predictive capability of the MLR at other sites; and

iv) comparing with the results of different source apportionment techniques for the same data.

The models developed for the present study (MLR and CEB) were compared with the best estimates of emission inventory, present knowledge of source emissions, and with each other. Results of the MLR, CEB, and emission inventory estimates (Appendix A) are listed in Table 4.6 for comparison.

The source contributions calculated by CEB and emission inventory agreed reasonably well. Part of the agreement is due to the fact that similar emission data were used for the source contributions to OC, EC, and TC. The automotive contribution calculated by MLR is in reasonable agreement with CEB results; however, the residual oil combustion and vegetative burning contributions are totally inconsistent. The use of K as a tracer for the vegetative burning was questionable and was probably responsible for the discrepancy in the contribution by vegetative burning.

The validity of the MLR model was checked by comparing regression coefficients to ratios of carbon to tracer element in the source emission measurements. Such a comparison is given in Table 4.7. The regression coefficients for Pb and K for OC, EC, and TC were within the range of values expected from source data, but the regression coefficient for V was an order of magnitude or more higher. The unusually high value for the V regression coefficients and the resultant

Table 4.6. Source contributions to OC, EC, and TC. Calculated by MLR, CEB, and Emission Inventory.

Source Category	Contribution to OC Calculated by			Contribution to EC Calculated by			Contribution to TC Calculated by		
	MLR	CEB[b]	Emission Inventory	MLR	CEB	Emission Inventory	MLR	CEB	Emission Inventory
Automotive	32 ± 19[a]	29 ± 10	19 %	35 ± 25	30 ± 14	31 %	33 ± 19	29 ± 10	22 %
Vegetative Burn	19 ± 10	63 ± 30	61 %	--	27 ± 14	43 %	12 ± 10	51 ± 24	56 %
Residual Oil	44 ± 16	1 ± 0.2	1 %	76 ± 18	1 ± 0.1	1 %	55 ± 16	1 ± 0.2	1 %
Urban Dust	--	3 ± 1	7 %	--	1 ± 1	2 %	--	2 ± 1	6 %
Others	5.0	18	12 %	-12.0	12	23 %	0.1	17	15 %

a) Errors calculated using the standard error of the regression coefficient.

b) The average contribution and its standard deviation for the days included in the MLR model.

Table 4.7. Carbon to tracer element ratios.

Source and Tracer	Carbon Fraction	Range of Carbon/Tracer Ratios Found in Source Measurements a)	Range Found by Regression
Automotive	TC	2.8 - 6.7	4.7 ± 2.7
Pb	OC	2.5 - 6.0	3.1 ± 1.9
	EC	0.3 - 6.0	1.6 ± 1.1
Residual Oil	TC	0.7 - 34	389 ± 116
V	OC	0.4 - 27	259 ± 78
	EC	0.3 - 14	168 ± 39
Vegetative Burning	TC	7 - 100	6.8 ± 5.5
K	OC	6 - 90	7.4 ± 3.7
	EC	1 - 25	--

a) These values were calculated by reanalyzing samples obtained during the PACS Study (Watson, 1979).

contribution from fuel oil combustion as calculated by MLR being inconsistent with CEB and EI raises serious doubts about MLR. The V in the MLR model is possibly tracing sources not included in the model. One of the main disadvantages of linear least square fitting procedure is that when all the major sources are not included in the model, inflated contributions for the sources included are obtained. It is possible, but not very likely, that the source matrix and emission inventory for emissions from residual oil combustion are both in error by an order of magnitude.

It was hypothesized that the V coefficient was unusually high because of its correlation with vegetative (wood) burning which was included in the regression but not well represented by the use of tracer element K. To check this hypothesis, the vegetative burning contribution to OC and EC as calculated by CB were subtracted from the measured OC and EC for each day. When the MLR was performed on the modified OC* ($OC_{measured} - OC_{veg.\ burning}$) and EC*, the V coefficient dropped to 0 while the Pb coefficient remained the same. This exercise supported the hypothesis that the high V coefficient and, in turn, the large fuel oil contribution were due to the correlation of V with vegetative burning. Moreover, the fact that the Pb coefficient remained the same adds confidence to the automotive contribution calculated by MLR. The correlation between V and vegetative burning is not too surprising because both residual oil usage and vegetative burning (i.e., firewood) are expected to follow heating demands.

The automotive contributions calculated by CEB, MLR, and EI were in general agreement. This is mainly because the automotive source is well characterized, and Pb is a good tracer. The lower estimate for the automotive contribution by the emission inventory was due to a lower value used for the percent carbon in the automotive exhaust. (43% of the automotive exhaust was assumed to be carbon.)

The main limitations of CEB are in the source matrix (i.e., a_{ij} values in equation (1)), which is constructed by emission measurements at the source, and the assumption of invariability in the composition of source contributions between sources and receptor. The MLR method can be used to check the validity of the source matrix. For example, the C to Pb ratio in the automotive source matrix was 3.7 while the regression coefficient for the MLR was 4.7 ± 2.7. Fractional OC:EC in the transportation source matrix was 70:30, while the MLR calculations indicated it to be 66:33.

About 30% of the elemental carbon could not be attributed to any source by the CEB method. The sources of this unexplained elemental carbon included jet fuel, diesel train, and distillate oil combustion. These sources could not be included in MLR or CEB because of nondescript source matrices.

Conclusions

The multiple linear regression (MLR) and chemical element balance (CEB) methods have been used to perform a carbon balance in Portland, Oregon. The CEB approach is more elaborate and needs a representative source matrix and analysis of many elements for accurate analysis. The MLR is relatively simple and is easy to use but requires good tracers for the major sources in question. Strong intercorrelation between the tracers can be a serious problem for the MLR. The CEB approach calculates a carbon balance on individual filters while the MLR method performs analysis on the complete data set which makes it susceptible to extreme values and necessitates sensitivity analysis to locate atypical points and obtain a stable model.

The agreement between source contributions calculated by CEB and emission inventory (EI) improves our trust in well constructed EI's. It also illustrates that seasonal and yearly average source apportionment can successfully be carried out with an EI.

The automotive contribution to OC, EC, and TC by MLR agreed with the CEB results; however, residual oil combustion and vegetative burning contributions by the two methods were significantly different. The reasons for the high regression coefficient for V and high contribution by residual oil combustion were i) the correlation between V and vegetative burning (which includes residential wood burning), and ii) the inability of K to represent vegetative burning in the MLR. Because the MLR method relies solely on tracers, the presence of sources without good tracers limits MLR's ability to perform accurate source apportionment.

The mass balance and the carbon balance by the CEB method accounted for 87% of the fine mass and 83% of the total carbon on an average. The most prominent sources of fine mass and carbon were vegetative burning (which includes fireplace, woodstove, domestic, backyard, field, and slash burning) and vehicle exhaust, contributing 51 ± 24% (4.0 $\mu g/m^3$) and 29 ± 10% (2.3 $\mu g/m^3$) of total carbon respectively.

Because of the inherent limitation of different receptor models and the importance of accurate source apportionment in control strategy development, it would be prudent to utilize a set of models (e.g., MLR and CEB, or MLR, CEB, and dispersion models) to determine source contributions.

CHAPTER V. SOURCES OF VISIBILITY DEGRADATION

Visibility degradation is the most readily apparent symptom of urban air pollution. Visual range without any aerosol would be about 200 km; however, visibility of a few kilometers is frequent in urban and industrial areas today. There is concern that the future industrial and population growth with added energy demand will not only lead to further visibility degradation in urban areas but will extend to remote and global levels. These concerns are reflected in the 1977 Clean Air Act amendments which contain provisions for the prevention of significant deterioration and protection of visibility in scenic areas (designated as Class I). Urban visibility degradation is primarily a result of scattering and absorption of light by aerosol particles. In most cases the light absorption component is small in comparison with the light scattering component.

A linear relationship between the scattering coefficient (b_{scat}) and atmospheric aerosol mass concentrations was originally proposed by Charlson et al. in 1967 and was shown to have a narrow distribution at various locations. This relationship has been investigated in a number of studies, and correlation coefficients in the range 0.4-0.9 have been found (Charlson et al., 1969; Noll et al., 1968; Lippmann et al., 1978; Heisler et al., 1980; White and Roberts, 1977).

The relationship between light scattering and aerosol chemical components has been studied by a number of researchers (White and Roberts, 1977; Eggleton, 1969; Lundgren, 1970; Cass, 1976; Leaderer and Stokwijk, 1979; Pierson et al., 1980; Grosjean and Friedlander, 1975). White and Roberts isolated the relative importance of various chemical species to light scattering in the ACHEX study conducted in the Los Angeles basin. A linear relationship between the b_{scat} and chemical components (sulfate, nitrates, and organics) was employed. They found that sulfate was the largest contributor to reduced visibility with lesser contributions from nitrates and other aerosol components. Relative humidity was found to affect only the nitrate scattering efficiency.

Like many other cities in the United States, Portland, Oregon, has a particulate problem, and compliance with state and federal ambient air quality standards has required regulatory actions which could have a serious impact on future growth. Using data generated in the Portland Aerosol Characterization Study (PACS), we have investigated the sources of visibility degradation during 1977-78.

Experimental

The sampling program was designed to obtain representative samples and to record relevant meteorological data to be used for chemical element balance (CEB) analysis (Cooper and Watson, 1979; Watson, 1979). Sampling was done at six sites (Figure 5.1). Two

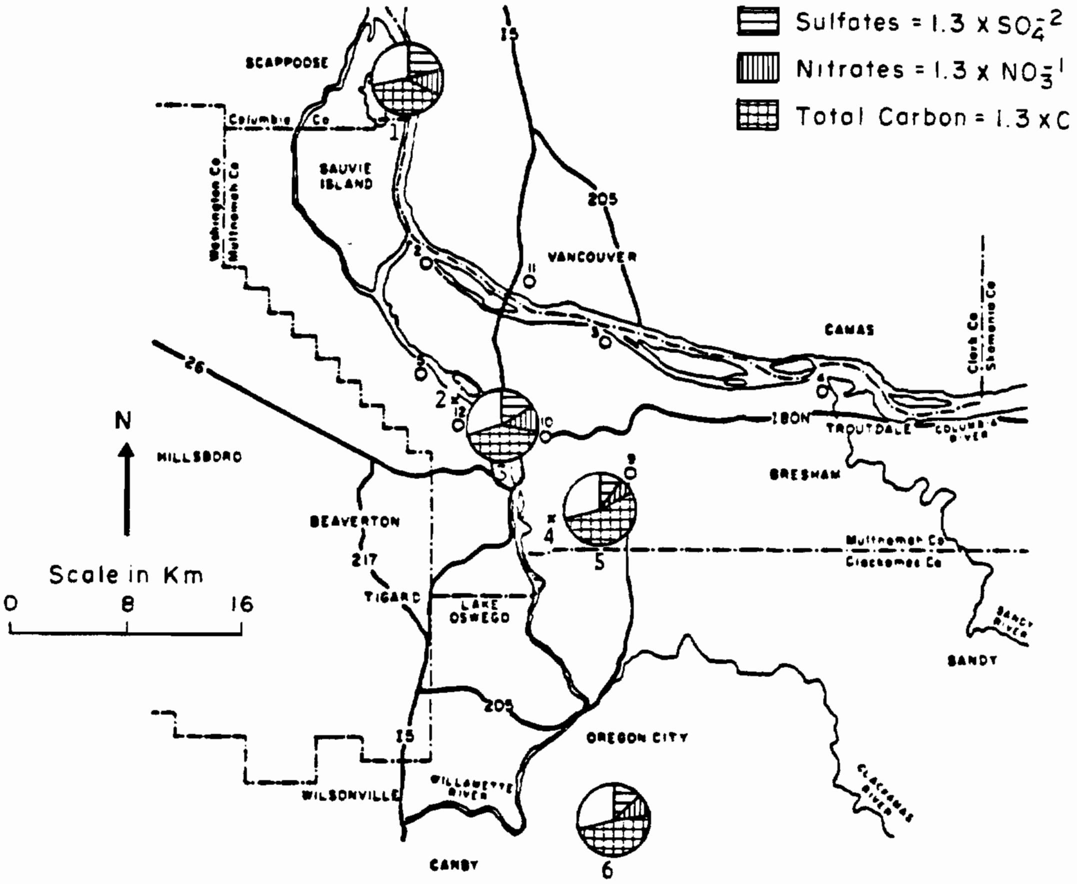

Figure 5.1. PACS sampling sites (x with large number) and estimated breakdown of the aerosol mass by components (average of 24-hour samples) and meteorological stations (o with small number) in the Portland Airshed.

sites were located in rural areas about 24 km from the downtown, representing upwind and downwind (prevailing winds) background sites. The light scattering coefficient b_{scat} was measured at four sites (downtown, residential, and two background) using integrating nephelometers (Meteorology Research, Inc., Model 1550). The nephelometers were calibrated with Freon-12 and were adjusted to read 0.23×10^{-4} m^{-1} when filled with aerosol-free air. All nephelometers were provided with an inlet heater, designed to keep relative humidity inside the nephelometers below 65%, thus minimizing the effect of relative humidity on b_{scat} measurements.

Four samplers were used to collect samples of fine ($d_p < 2$ μm) and total aerosol simultaneously at all sites:

- a standard high-volume sampler to collect samples for a 24-hour period on glass fiber (Gelman A/E) filters for mass and carbon analysis;
- a high-volume sampler with a Sierra Model 235 cascade impactor head to collect particles with aerodynamic diameter less than 2.5 μm (24-hour duration);
- a modified ER&T sequential low volume sampler (Watson, 1979) to collect samples on cellulose ester filters (either 4- or 8-hour sampling periods).
- an ER&T sequential low volume sampler with a cyclone separator to remove coarse particles greater than 2 μm in aerodynamic diameter (either 4- or 8-hour sampling periods).

Sampling was carried out for 93 days between July 1977 and April 1978, and a 32-day subset was selected for intensive chemical analysis. Selection of days for the intensive chemical characterization was guided but not controlled by the desire to represent the entire year with respect to meteorology.

Analytical methods used for chemical characterization included ion chromatography (F^-, Cl^-, Br^-, NO_3^-, and $SO_4^=$), carbon analysis by a thermal method (Johnson and Huntzicker, 1979), energy dispersive x-ray fluorescence (Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Cd, Ba, and Pb), and neutron activation analysis (Al, Br, Cl, Mg, Mn, Na, Ti, V, and K). A significant aspect of the entire analysis scheme was the high level of quality assurance established for every filter analyzed through intermethod and interlaboratory comparisons (Cooper and Watson, 1979).

Statistical Procedure

A linear regression approach was used to evaluate the relationship between b_{scat} and aerosol components and sources. The analysis consisted of three types:

1. regression of b_{scat} against fine and total aerosol mass concentrations;
2. regression of b_{scat} against the concentrations of the chemical components (e.g., sulfates, nitrates, total carbon, etc.) using the regression models of Equations 1 and 2:

$$b_{scat} = \sum_{i=1}^{n} C_i M_i \qquad (1)$$

$$\frac{b_{scat}}{MASS} = \sum_{i=1}^{n} C_i \frac{M_i}{MASS} \qquad (2)$$

(In these equations M_i is the mass concentration of the ith chemical species, MASS is the aerosol mass concentration, and C_i is the ith regression coefficient which can be viewed as the light scattering efficiency of the ith component (White and Roberts, 1977).

3. regression of b_{scat} against the aerosol mass concentrations contributed by individual source types using Equations 1 and 2. (In this case M_i is the aerosol mass concentration contributed by the ith source type as determined by chemical element balance.)

Ionic concentrations of SO_4^{-2}, NO_3^{-1} and carbon were multiplied by 1.3 to account for associated ions that make up the rest of the aerosol (White and Roberts, 1977). The factor 1.3 accounted for ammonium ions in sulfates and nitrates. If the carbon content of organic compounds is taken to be 67%, organics measured as carbon must be multiplied by 1.5 (i.e., 1/0.67) to obtain organics concentration (White and Roberts, 1977). Analysis of Portland aerosol (Chapter 4) has shown that about 60% of carbon is organic and 40% is elemental; thus, an average factor for total carbon is 1.3 (= 1.5 x 0.6 + 1 x 0.4). The average chemical composition for the fine fraction of aerosol is shown in Figure 5.1).

The coefficients in Equations 1 and 2 were calculated using a step regression routine. A step regression is a modified form of multiple linear regression in which variables are selectively added and re-examined in single steps (Draper and Smith, 1966). This process is continued until no more variables can be entered into or rejected from the regression based on preselected criteria of significant contribution. The step regression procedure starts with a correlation matrix and enters the variable with highest correlation coefficient with the dependent variable. Next, the partial correlation coefficients for the variables not in the regression are evaluated, and the variable with the highest partial correlation is entered. The variables entered so far are evaluated, and variables providing a non-significant contribution are removed. This is an important step since variables entered earlier may be ineffective after a few more steps because of their relationship with other variables entered. Some of the advantages of the step regression are:

- The final equation contains only significant variables.
- It is capable of handling intercorrelated variables.
- It provides an important role in the model building process.

Results

Relationship Between Light Scattering and Mass

Atmospheric mass concentrations of fine and total aerosol were measured by various samplers as described earlier. Because the b_{scat} included Rayleigh scattering due to air molecules and scattering due to aerosol, a linear regression of the form

$$b_{scat} = b_0 + b_1 \cdot \text{mass} \tag{3}$$

(b_{scat} in 10^{-4} m^{-1} and mass in $\mu g/m^3$)

was performed on various mass fractions measured by different sampling devices. The data were separated into two sets, one with relative humidity <70% and the other with >70%, to evaluate the importance of relative humidity. The relationship between b_{scat} and mass fractions was consistent from one site to another. Results of the regression for all sites combined are presented in Table 5.1. As expected, fine mass correlates best with b_{scat}. In most cases, the correlation coefficient between b_{scat} and mass improved when the data set was stratified with respect to relative humidity. The slope of the linear regression line for the subset with relative humidity <70% was less than the slope of the regression line for the data set with relative humidity >70%. This indicates a higher scattering efficiency at higher relative humidities. Water associated with aerosol at higher relative humidity is mainly responsible for the added scattering efficiency.

TABLE 5.1

Relationship between b_{scat} and mass for 8-hour observations from all sites combined.

$$b_{scat} = b_o + b_1 \text{ mass}$$

(b_{scat} in 10^{-4} m^{-1} and mass in $\mu g/m^3$)

MASS FRACTION	RELATIVE HUMIDITY	NUMBER OF OBSERVATIONS	CORRELATION COEFFICIENT	b_o INTERCEPT	b_1 SLOPE
Fine Mass	< 70%	329	0.878	0.146	0.0471
	> 70%	770	0.931	0.162	0.0495
	All	1099	0.930	0.135	0.05
Total Mass	< 70%	334	0.783	0.393	0.114
	> 70%	769	0.866	0.345	0.0184
	All	1101	0.797	0.377	0.0151

The linear relationship between b_{scat} and fine mass for the intensive sampling days for all the sites is plotted in Figure 5.2. The regression line has a slope of 0.0474 and an intercept of 0.113.

$$b_{scat} = 0.113\ (\pm 0.026) + 0.0474\ (\pm 0.0009)\ \text{mass} \qquad (4)$$
$$(n = 404,\ r = 0.93)$$

For all sites for the entire study period the relationship between b_{scat} and both mass fractions (fine and total) was:

$$b_{scat} = 0.135 + 0.05\ \text{mass}\ (\text{fine},\ n = 1099,\ r = 0.93) \qquad (5)$$

$$b_{scat} = 0.377 + 0.015\ \text{mass}\ (\text{total},\ n = 1107,\ r = 0.80) \qquad (6)$$

The difference in the slopes for the fine and total mass fractions reflects the lower scattering efficiency for the particles greater than 2.0 μm included in the total mass fraction (Figure 5.3).

Relationship Between b_{scat} and Chemical Components

If the size distribution for each chemical component were known and the mass contribution by sources to each size range were available, it would be possible to calculate the fractional light scattered by each chemical component and by aerosols from each source (Friedlander, 1977). Usually, however, such detailed size distribution or source contribution information is not available. Therefore, statistical procedures calculating the scattering efficiencies of chemical components and sources were employed. The results of regression (Eq. 1)

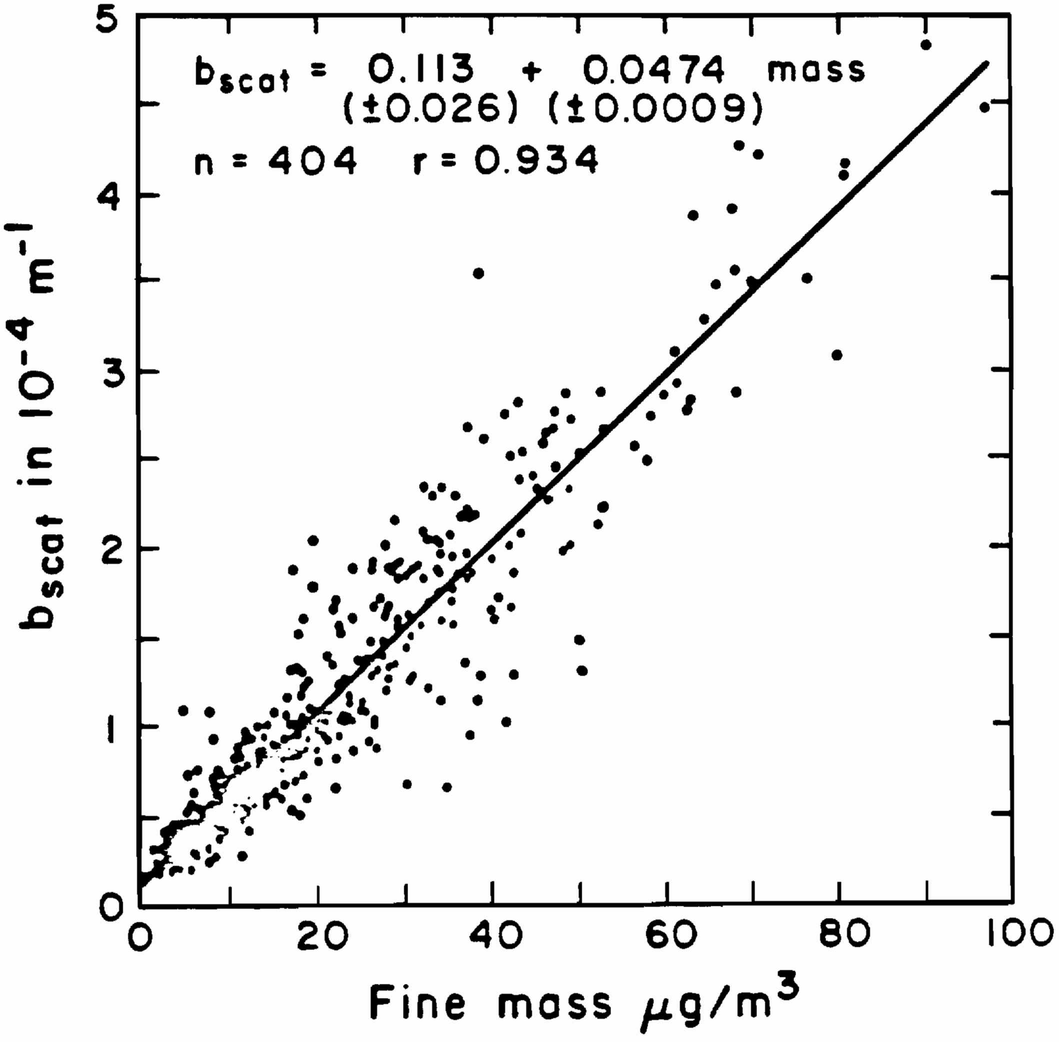

Figure 5.2. Relationship between light-scattering coefficient and fine aerosol mass for 8-hour samples from all the sites for the intensive sampling days. Solid line represents the linear regression of b_{scat} on mass.

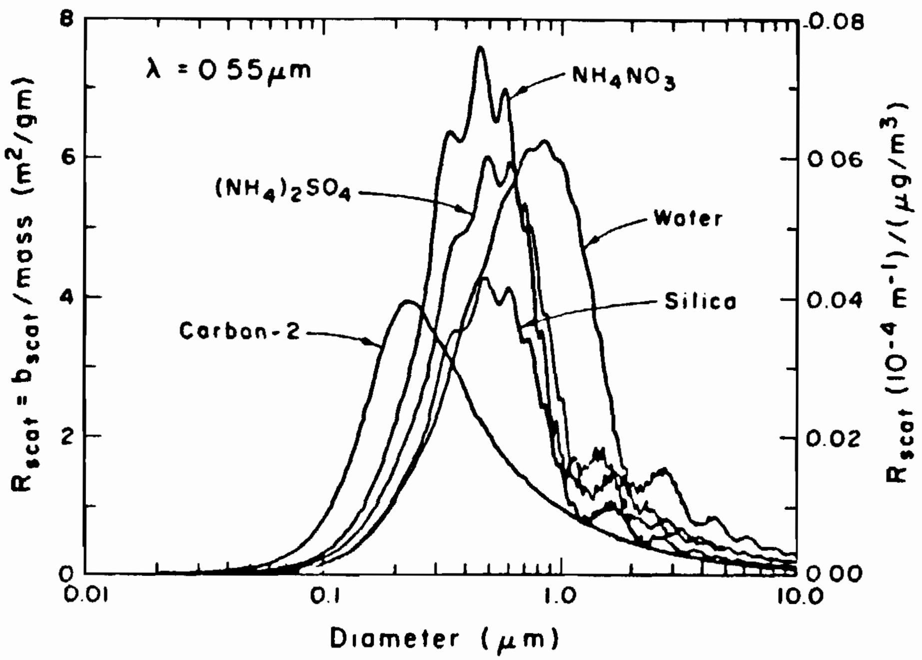

Figure 5.3. The calculated scattering cross-section per unit mass R_{scat} (scattering efficiency) at a wavelength of 0.55 μm for absorbing and non-absorbing materials as a function of diameter for single-sized particles. The refractive indices and densities (g/cm^3) used: carbon-2 ($m = 1.96-0.66i$, $\rho = 2$), $(NH_4)_2SO_4$ ($m = 1.52$, $\rho = 1.77$), NH_4NO_3 ($m = 1.61$, $\rho = 1.73$), water ($m = 1.33$, $\rho = 1.0$), and silica ($m = 1.55$, $\rho = 2.66$). (Figure supplied by Dr. Davis M. Roessler from the General Motors Research Laboratory, Warren, Michigan.)

using chemical species concentrations in the fine aerosol are presented in Tables 5.2 and 5.3 and are summarized as follows:

1. The average scattering efficiencies for the sulfates, nitrates, and carbon were approximately 5 m^2/g. Contrary to findings of other researchers (White and Roberts, 1977; Leaderer and Stokwijk, 1979), light scattering was not dominated by sulfates. High values of b_{scat} were not uniquely associated with high values of sulfate, nitrates, or carbon.
2. The scattering efficiencies for sulfates and carbon were relatively site-independent. For nitrates it varied from negligible at Site 1 (background) to a high of 9.7 m^2/g at Site 3 (downtown). The nitrate results are difficult to interpret, however, because of the possibility of artifact nitrate (from HNO_3) on the filters (Spicer and Schumacher, (1979).
3. Carbon, sulfates, and nitrates were the major contributors to both fine mass and light scattering. On an average they accounted for 76% of the fine mass and 86% of the light scattering due to aerosol (using the regression coefficients of Table 5.2).

The importance of including all the major chemical components in the step regression analysis is apparent when the results for the 8-hour samples are compared with those for 24-hour samples. For the former no carbon analyses were performed, and thus the regression equation

Table 5.2

Summary of step regression between b_{scat} and chemical components

Fine fraction, 24-hour samples †

$$b_{scat} = b_o + b_{SO_4^=} \text{ sulfates} + b_{NO_3^-} \text{ nitrates} + b_{TC} \text{ carbon} + b_{\Delta mass} \, \Delta mass$$

SAMPLING SITE	CORRELATION COEFFICIENT	b_o	$b_{SO_4^=}$	$b_{NO_3^-}$	b_{TC}	$b_{\Delta mass}$
1	0.87	0.166	0.0897 ±0.0314	N.S.	0.0538 ±0.0793	N.S.
3	0.93	0.28	0.0501 ±0.0285	0.0792 ±0.0305	0.0388 ±0.0112	0.0375 ±0.0180
5	0.95	0.238	0.0746 ±0.0419	0.0326 ±0.0382	0.0503 ±0.0052	0.0200 ±0.0117
6	0.94	0.1886	0.0726 ±0.0287	0.0286 ±0.0226	0.0487 ±0.0076	0.0207 ±0.006
All	0.94	0.173	0.0561 ±0.0136	0.0477 ±0.0161	0.0250 ±0.003	0.0225 ±0.0057

† 26 to 31 observations per site.

includes only sulfates, nitrates, and "Δ mass." The principal difference between the two sets of results as shown in Tables 5.2 and 5.3 is the added importance attached to nitrates and "Δ mass." Although the increased importance of "Δ mass" is expected, the higher coefficients for nitrates are a consequence of the intercorrelation between nitrates and carbon which results from common atmospheric dispersion. Similar results were found when carbon was included in "Δ mass" for the 24-hour analyses.

The importance of eliminating dispersion-related correlations among the chemical elements before attempting data analysis has been pointed out by Henry (1977) and Watson (1979). During his evaluation of chemical composition and its relation to visibility, Eggleton (1969) cautioned against ascribing cause and effect relationships to parameters with high correlations since they could merely reflect a common relationship to a third variable (e.g., atmospheric dispersion). In their analysis of ACHEX data, White and Roberts (1977) discussed the importance of factoring out the correlation with mass in judging the importance of the scattering efficiency of sulfates and nitrates.

Although normalizing elemental concentrations by the fine mass concentration has proven to be a successful way of reducing such intercorrelation (Henry, 1977), the results of step regression on Equation 2 using normalized concentrations were surprisingly poor for 8-hour and 24-hour samples. None of the normalized chemical components explained any variability in $\frac{b_{scat}}{mass}$. This undoubtedly resulted from the

Table 5.3

Summary of step regression between b_{scat} and chemical components
Fine fraction, 8-hour samples †

$$b_{scat} = b_o + b_{SO_4^=}\ \text{sulfates} + b_{NO_3^-}\ \text{nitrates} + b_{\Delta mass}\ \Delta\text{mass}$$

SAMPLING SITE	CORRELATION COEFFICIENT	b_o	$b_{SO_4^=}$	$b_{NO_3^-}$	$b_{\Delta mass}$
1	0.88	0.239	0.0783	0.0793	0.0172
			±0.0144	±0.0368	±0.0066
3	0.94	0.207	0.0532	0.1003	0.0387
			±0.0073	±0.0098	±0.0025
5	0.96	0.138	0.0275	0.0329	0.0504
			±0.0200	±0.0226	±0.0023
6	0.89	0.194	0.0662	0.0653	0.0319
			±0.0193	±0.0182	±0.0032
All	0.94	0.119	0.0495	0.0828	0.0429
			±0.0055	±0.0011	±0.0014

† 74 to 90 observations per site; site 3, 3 to 160 observations.

high degree of correlation between fine mass concentration and both b_{scat} and chemical component concentrations. This is further evidence for the lack of dominance of light scattering in Portland by a single chemical species such as sulfate.

Relationship of Aerosol Sources to Light Scattering

Source apportionment of the Portland aerosol was accomplished in the Portland Aerosol Characterization Study by means of the chemical element balance method (Cooper and Watson, 1979). The principal primary sources of fine aerosol included vegetative burning (e.g., of wood), automotive exhaust, other combustion sources, resuspended dust, and to a lesser extent industrial process emissions. Most of the sulfate and nitrate and about 20% of the carbon could not be explained by primary emissions. These were attributed to secondary sources (i.e., gas to particle conversion). When source contributions were expressed as mass fractions (i.e., $\frac{M_i}{MASS}$) and regression Equation 2 used, the only significant contribution from the primary aerosol sources to b_{scat} was from vegetative burning, which was the major primary source of carbon. This accounted for approximately 18% of the light scattering. Because the primary precursors of secondary sulfate, nitrate, and carbon were not identified in the chemical element balance calculations, such sources were not included in the regression. Further progress in source apportionment of visibility degradation in Portland will require the identification of these sources of carbon and secondary aerosols.

Summary and Conclusions

The major conclusions can be summarized as follows:

1. All the major chemical components of the fine aerosol must be included in the scattering efficiency evaluation.

2. Sulfate, nitrates, and carbon were found to have scattering efficiencies of about 5 m^2/g. On an average they constituted 76% of the fine mass and contributed 86% of light scattering by aerosols.

3. The aerosol scattering coefficient b_{scat} correlates strongly with the fine fraction of aerosol mass ($r = 0.93$, $n = 1129$) and to a lesser degree with the total mass fraction ($r = 0.87$, $n = 1124$).

4. The values for the intercept and the slope of the relationship $b_{scat} = b_0 + b_1$ mass were similar for all the sites. This suggests that mass loading in this area (especially the fine fraction) could be estimated by nephelometer measurements, providing, of course, that both the chemical concentration and the particle size distribution of the aerosol do not change significantly.

5. Relative humidity had a small but statistically significant effect on the relationship between b_{scat} and mass. The data set with relative humidity >70% consistently showed a higher correlation between b_{scat} and fine mass at all sites and had a slightly higher slope than the data set with relative humidity <70%, implying higher scattering efficiency at higher relative humidity.

CHAPTER VI. SUMMARY AND CONCLUSIONS

The fundamental goal of this study was to obtain a better understanding of carbonaceous aerosol. Analytical measurement, source apportionment, and visibility impact of carbonaceous aerosol were the three main topics covered in this dissertation. The purposes of this chapter are to summarize the research and evaluate its shortcomings.

An instrument measuring organic, elemental, and carbonate carbon has been developed at the Oregon Graduate Center and was used for the analysis. A brief description of the thermal/optical system for the measurement of carbonaceous aerosol was given in Chapter II.

The data base for the organic, elemental, and carbonate carbon was constructed by analyzing over 1300 hi-volume samples from 46 urban and 20 rural National Air Surveillance (NASN) sites. Exploratory data analysis was performed to gain a better understanding of the nature, magnitude, and relationship of carbon with other constituents of ambient aerosol. The average organic and elemental carbon concentrations were 6.6 and 3.8 $\mu g/m^3$ for the urban sites and 2.4 and 1.3 $\mu g/m^3$ for the rural locations. The urban centers with high carbon concentrations (>12 $\mu g/m^3$) were Burbank, Chicago, Dallas, East Chicago, Gary, Houston, Los Angeles, New York City, Pasadena, Phoenix, San Bernardino, Santa Ana, and Torrance.

The national yearly trend for the organic fraction of total carbon was maximal during summer and minimal during winter. The summer maximum was due to the contribution of secondary aerosols and to the decline of space heating emissions relative to other sources.

A measurable amount of carbonate carbon was found only at the Miami, Hawaii, and Cumberland County sites. In general, carbonate carbon constitutes less than 2% of total carbon.

The evaluation of sources of carbonaceous aerosol was the second phase of this study. Chemical element balance (CEB) and multiple linear regression (MLR) receptor models were evaluated for their applicability to perform mass balance for carbon for the data set obtained during the Portland Aerosol Characterization Study (PACS). The chemical element balance proved to be very useful because of its ability to identify and quantify the sources for individual filters, while the multiple linear regression method was selected because of its simplicity.

The chemical element balance (CEB) and carbon balance (CB) were performed for 25 sampling days. The CEB and CB were considered a success because most of the elemental ratios $(\frac{\text{calculated concentration}}{\text{measured concentration}})$ were close to unity, the reduced X^2 for the mass balances were low and on an average accounted for 87% of the fine mass by the CEB and 83% of carbon by the CB. The major sources of carbonaceous aerosol were vegetative burning (51%) and automotive exhaust (29%).

The sources of 30% unexplained elemental carbon include distillate oil combustion, diesel train, jet aircraft, and others which could not be included in the element balance because of nondescript source matrices.

For the MLR model, K, Pb, V, and Si/Ti were selected as tracers for vegetative burning, automobile exhaust, residual oil combustion, and road dust respectively. The use of K for vegetative burning was found unsuitable. A sensitivity analysis was performed on the data set prior to the final MLR application to identify the points for which regression coefficients were very sensitive. This procedure allowed the underlying pattern in the data set to be explored and explicitly rejected "atypical" observations.

The results of the receptor models (CEB and MLR) were compared with the emission inventory (EI). The average source contributions calculated by CEB and EI agreed well. This suggests that carefully constructed IE's can be used for a seasonal or annual source apportionment.

The automotive contribution by MLR agreed with CEB and EI; however, the residual oil combustion and vegetative burning contributions were significantly different. Correlation between vanadium and vegetative burning and inability of potassium to represent vegetative burning in the MLR were the primary reasons for the discrepancy between MLR and CEB. Because the MLR method relies solely on tracers, the presence of sources without good tracers limits MLR's ability to perform accurate source apportionment.

The main limitations of CEB are in the source matrix, which is constructed by emission measurement at the source, and the assumption of invariability in the composition between source and receptor.

Another major shortcoming was with respect to sources with nondescript chemical composition. Their importance cannot be evaluated by CEB without further chemical characterization which allows their differentiation from other sources. An emission inventory can be used to aid the construction of a source matrix by supplying scaling factors relating nondescript sources to specific sources whose contribution can be calculated by CEB. Diesel vehicle exhaust was included in this manner for the Transportation source matrix.

Because of the inherent limitations of different receptor models and the importance of accurate source apportionment in control strategy development, it would be prudent to utilize a set of models (e.g., MLR and CEB, or MLR, CEB, Factor Analysis, and dispersion models) to determine source impact.

A regression model was applied to the Portland Aerosol Characterization Study (PACS) data set to determine the sources of visibility degradation. The light scattering coefficient and the size segregated aerosol mass concentration were measured at four sites within Portland, Oregon, for 92 sampling days, extending from July 1977 to March 1978. A subset of 32 "intensive days" was selected for extensive chemical characterization. The contributions of chemical species and source types (as determined by CEB calculations) to the scattering coefficient were studied by a linear model.

Atmospheric scattering coefficient b_{scat} correlated strongly with the fine fraction of aerosol mass ($r = 0.93$, $n = 1129$) and to a lesser degree with respirable mass ($r = 0.87$, $n = 1124$). Sulfates, nitrates, and carbon were found to have a scattering efficiency of about 5 m^2/gm. On an average they constituted 76% of the fine mass and contributed 86% of the light scattering by aerosol. All the major chemical components of the fine aerosol must be included in the scattering efficiency evaluation to avoid erroneous conclusions.

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APPENDIX A.

EMISSION INVENTORY OF CARBONACEOUS AEROSOLS

There are several classes of mobile and stationary sources of carbonaceous aerosol which can schematically be represented as shown in Figure 1.1. Emission inventories of organic and elemental carbon are virtually nonexistent. A detailed account of emission rate, size distribution, and chemical composition of sources is generally not available. Cass et al. (1981) gave one of the first in-depth accounts of the carbonaceous aerosol emissions for metropolitan Los Angeles.

An emission inventory for the carbonaceous aerosols was constructed for the following reasons:

1. To understand the sources of carbonaceous aerosol and their relative importance for the Portland AQMA.
2. To evaluate the applicability of different source apportionment methods (CEB and multivariate analysis) by comparing their results with the emission inventory.

The importance of a comprehensive emission inventory, especially for carbonaceous aerosol, became evident after PACS. The CEB method was able to resolve most sources effectively; however, there was always excess organic and elemental carbon (50% on an average) which could not be attributed to any source. Since the PACS project, the emission inventory has been updated (Core et al., 1980). Source samples collected during PACS have been re-analyzed and a better understanding of transportation (Pierson, 1981) and wood combustion sources (Cooper, 1980) has been gained from the literature. With this new information, an emission inventory for carbonaceous aerosol for Portland was constructed and is summarized in Table A.1. Graphical representation of sources of fines, OC, EC, and TC are given in Figures A.1 and A.4. The fine particulate annual emissions add up to 14,347 tons. Fine organic and elemental carbon add up to 3307 tons (23.1% of fines) and 1247 tons (8.7 of fines), respectively. The major sources of total carbon are transportation (22.2%), combustion of fossil fuels (3.5%), road dust (6%), vegetative burning (56.0%), carborundum (5.8%), and miscellaneous (6.5%).

The source matrix used to perform the mass balance and carbon balance was obtained by modifying the source matrix used in PACS. The leaded automobile source matrix was replaced by transportation source matrix, which was constructed using tunnel data (Pierson, 1981) and the knowledge that diesel vehicles accounted for 5.0% of vehicle miles traveled (Batson, 1981) and emit 3 times the amount emitted by automobiles (EPA, 1976). The sources entitled fireplace, domestic, woodstove, and home heating were added because vegetative burn 1 and vegetative burn 2 did not represent all possible vegetative burning adequately. A composite source matrix for home heating from the Medford Aerosol Characterization Study (MACS) was also included. Most of the available source samples from PACS were re-analyzed for organic and elemental carbon. The OC and EC values in the source matrix represent the newer

TABLE A.1

Emission inventory for fine mass and carbonaceous aerosol, Portland, Oregon

						CARBON PRESENT AS		FINE ORGANIC CARBON			FINE ELEMENTAL CARBON			FINE TOTAL CARBON		
SOURCE TYPE	FINES TONS/YR 1977-78 PORTLAND	% MAJOR SOURCE TYPE	% OF ANNUAL FINE EMISSION	% FINES dp < 2.5 µm	% CARBON IN FINE FRACTION	% OC	% EC	TONS/YR	% MAJOR SOURCE TYPE	% TOTAL ORGANIC EMISSION	TONS/YR	% MAJOR SOURCE TYPE	% TOTAL ELEMENTAL EMISSION	TONS/YR	% MAJOR SOURCE TYPE	% TOTAL CARBON EMISSION
Transportation	1818	100	12.7	--				622	100	18.8	387	100	31.0	1009	100	22.2
Auto-Leaded	1094^{c}	60.0	7.6	80^{b}	43^{a}	89	11^{j}	419	67.4	12.7	51	13.2	4.1	470	46.6	10.3
-Unleaded	74^{c}	4.1	0.5	86^{b}	52^{a}	55	45^{k}	21	3.4	0.6	18	4.7	1.4	39	3.9	0.9
Diesel-Trucks	339^{c}	18.6	2.4	90^{b}	85^{f}	20	80^{j}	58	9.3	1.8	230	59.4	18.4	288	28.5	6.3
-Train	124^{b}	6.8	0.9	95^{b}	85^{a}	77	23^{a}	81	13.0	2.4	24	6.2	1.9	105	10.4	2.3
Misc.-Tire, Brake, Ship, Jet, etc.	187^{b}	10.3	1.3	13.5^{b}	57^{g}	40	60^{g}	43	6.9	1.3	64	16.5	5.1	107	10.6	2.3
Fossil Fuel	781	100	5.4	--				69	100	2.1	90	100	7.2	159	100	3.5
Residual Oil	343^{b}	44	2.4	92^{b}	15^{h}	78	22^{k}	40	58	1.2	11	12.2	0.9	51	32.0	1.1
Distillate Oil	271^{b}	35	1.9	76^{b}	34^{a}	18	82^{k}	16	23.2	0.5	76	84.4	6.1	92	57.9	2.0
Coal	11^{b}	1	0.1	--	--	--	--	--	--	--	--	--	--	--	--	--
Natural Gas	156^{b}	20	1.1	99^{b}	10^{l}	83	17^{l}	13	18.8	0.4	3	3.3	0.2	16	10.1	0.4
Geological	2291	100	16.0	--				242	100	7.3	29.4	100		271	100	6.0
Asphalt Produc.	40^{b}	1.7	0.3	92^{b}	3^{a}	70	30^{a}	1			0.4	1.4	--	1.2	0.4	--
Street Dust	2251^{b}	98.3	15.7	10^{b}	12^{a}	90	10^{n}	241	100	7.3	29	98.6		270	99.6	6.0
Vegetative Burning	4464	100	31.1	--				2007	100	60.7	541	100	43.4	2548	100	56.0
Slash Burning	14^{b}	0.3	0.1	99^{b}	63^{a}	90	10^{n}	8	0.4	0.2	1	0.2	--	90	0.4	0.2
Field Burning	9^{b}	0.2	0.1	98^{b}	52^{a}	91	9^{a}	4	0.2	0.1	1	0.2	--	50	0.2	0.1
Domestic "	370^{b}	8.2	2.6	55^{b}	34^{a}	55	45^{k}	69	3	2.1	57	12.0	4.6	126	4.9	2.8
Fireplace	2932^{d}	65.7	20.4	85^{d}	60^{a}	80	20^{m}	1407	71	42.5	352	650	28.2	1759	69.0	38.6
Woodstove	1139^{d}	25.5	7.9	99^{d}	57^{a}	80	20^{n}	519	26	15.7	130	24	10.4	649	25.5	14.3
Aluminum Proc.	1023^{b}	100	7.1	60^{b}	56^{a}	63	37^{a}	36	100	1.1	21	100	1.7	57	100	1.3
Vegetative-Grain Elevators	242^{b}	100	1.7	19^{b}	29^{a}	85	15^{k}	60	100	1.8	10	100	0.8	70	100	1.3
Flour Proc.	8^{b}	100	0.1	89^{b}	26^{a}	98	2^{a}	2	100	0.1	--	100	--	2	100	--
Forest Products Industries	2197^{b}	100	15.3	--					100			100			100	
Hog Fuel Boiler	1207^{b}	54.9	8.4	73^{b}	9.3^{a}	54	46^{n}	61	100	1.8	51	100	4.1	112	100	2.5
Carborundum	758^{b}	100	5.3	89^{b}	35^{a}	61	39^{k}	161	100	4.9	104	100	8.3	265	100	5.8
Others, Miscellaneous	765^{b}		5.3	63^{b}	8^{g}	77	23^{g}	47	100	1.4	14	100	1.1	61	100	1.3
TOTAL ANNUAL EMISSIONS	14347		Σ 100					3307		Σ 100.1	1247		Σ 100	4554		Σ 100.1

NOTES FOR TABLE 1:

a) PACS source sampling and analysis.

b) Department of Environmental Quality (DEQ), Portland, estimates and PACS source sampling.

c) Calculated as follows: Portland AQMA 4 x 10^6 miles/av. day highway VMT with 7% diesel and 11 x 10^6 miles arterial VMT with 4% diesel (based on DEQ estimates (Batson, 1981)).

Emissions Gasoline Powered Vehicles: There are 22% unleaded vehicles (volume basis) which contribute 30% of VMT. Using EPA emission factor of 0.34 g/mile for leaded cars and light trucks and 0.05 g/mile for unleaded cars, emission for leaded cars = 14,280,000 x 0.70 x 0.34 x 365/10^3 x 907.19 = 1368 tons/year ∴ fine emission leaded cars = 1368 x 0.8 = 1094 tons/yr. For unleaded cars emission = 14,280,000 x 0.30 x 0.05 x 365/10^3 x 907.19 = 86 tons/yr ∴ fine emission unleaded cars = 86 x 0.86 = 74 tons/yr.

Diesel emissions: Total diesel VMT = 720,000 using EPA emission factor of 1.3 g/mile. Emissions per year come to 377 tons, of which 90% is in fine ∴ fine emissions diesel = 377 x 0.9 = 339 tons/yr.

d) Based on a survey by Hatchard and Day (1980), particulate emission due to home heating amounts to 4600 tons/yr. 10% residences use woodstove burning, 1.4 cord/yr, and 40% residences use fireplace burning, 1.1 cord/yr. This amounts to 25% emissions from woodstove and 75% emissions from fireplace burning. Considering that 85% of fireplace emissions are in fine and 99% of woodstove emissions are in fine fraction, fire fireplace emissions = 2932 tons/yr. and woodstove emissions = 1139 tons/yr.

e) Average of PACS and Pierson (1981) tunnel experiments.

f) Pierson et al. (1981) tunnel data.

g) Based on the knowledge of carbon fraction in the emissions of sources contributing to this category.

h) Based on PACS and Taback et al. (1979) PA-8.

i) Average based on Taback et al. (1979) PA-29, and Muhlbauer and Williams (1980).

j) Based on re-analysis of PACS samples and Tuscarora tunnel samples.

k) Re-analysis of PACS source samples.

l) Based on equal usage by residential customers (emissions, OC 67% and EC 37%) and industrial usage (emissions mostly OC).

m) Source sampling, Medford Aerosol Characterization Study (MACS).

n) Average of PACS and MACS source sampling.

Fine Particulate Emissions, Portland (AQMA), 1977-78.

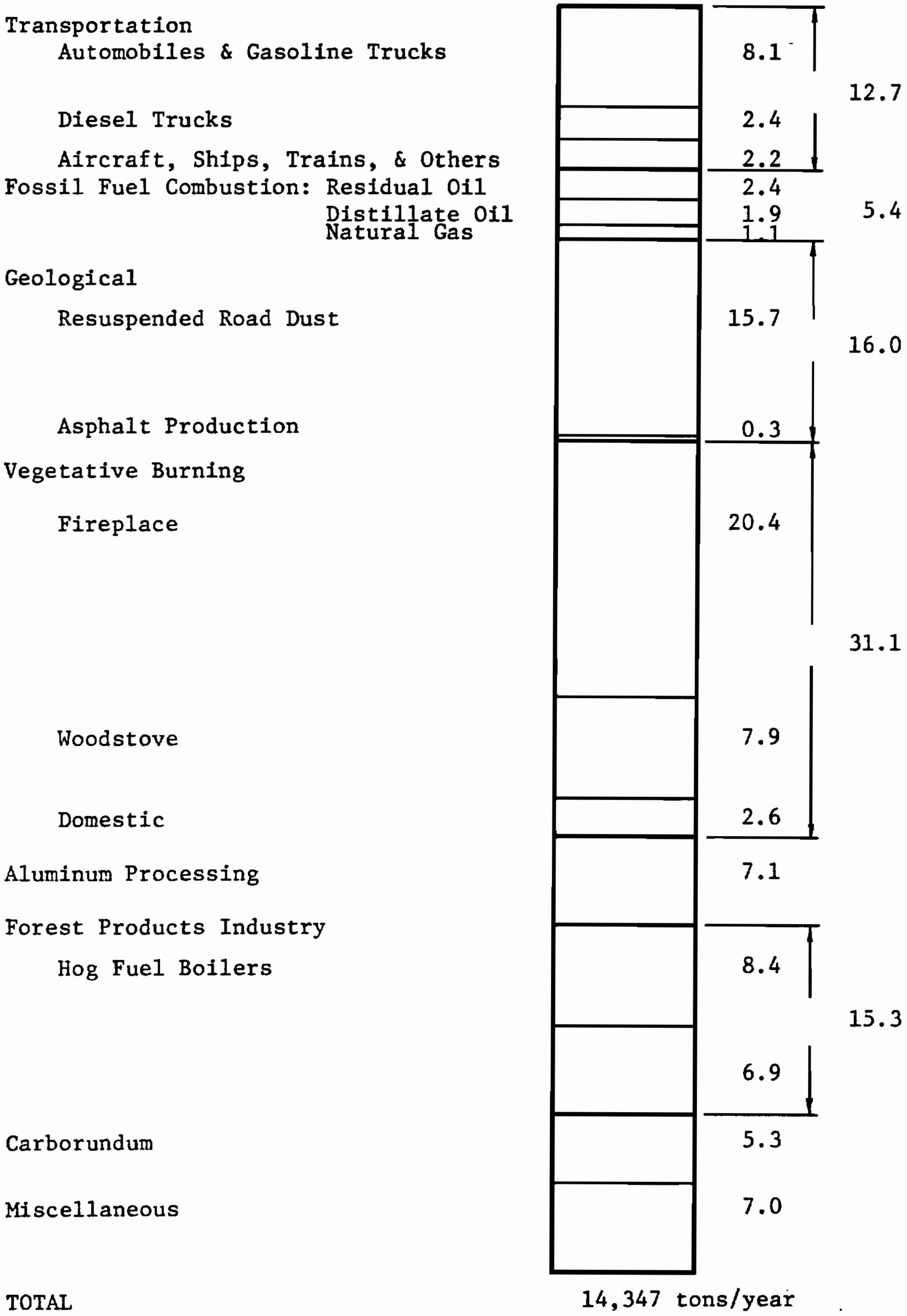


Figure A.1.

Fine Primary Organic Carbon Emissions, Portland, Oregon, 1977-78.

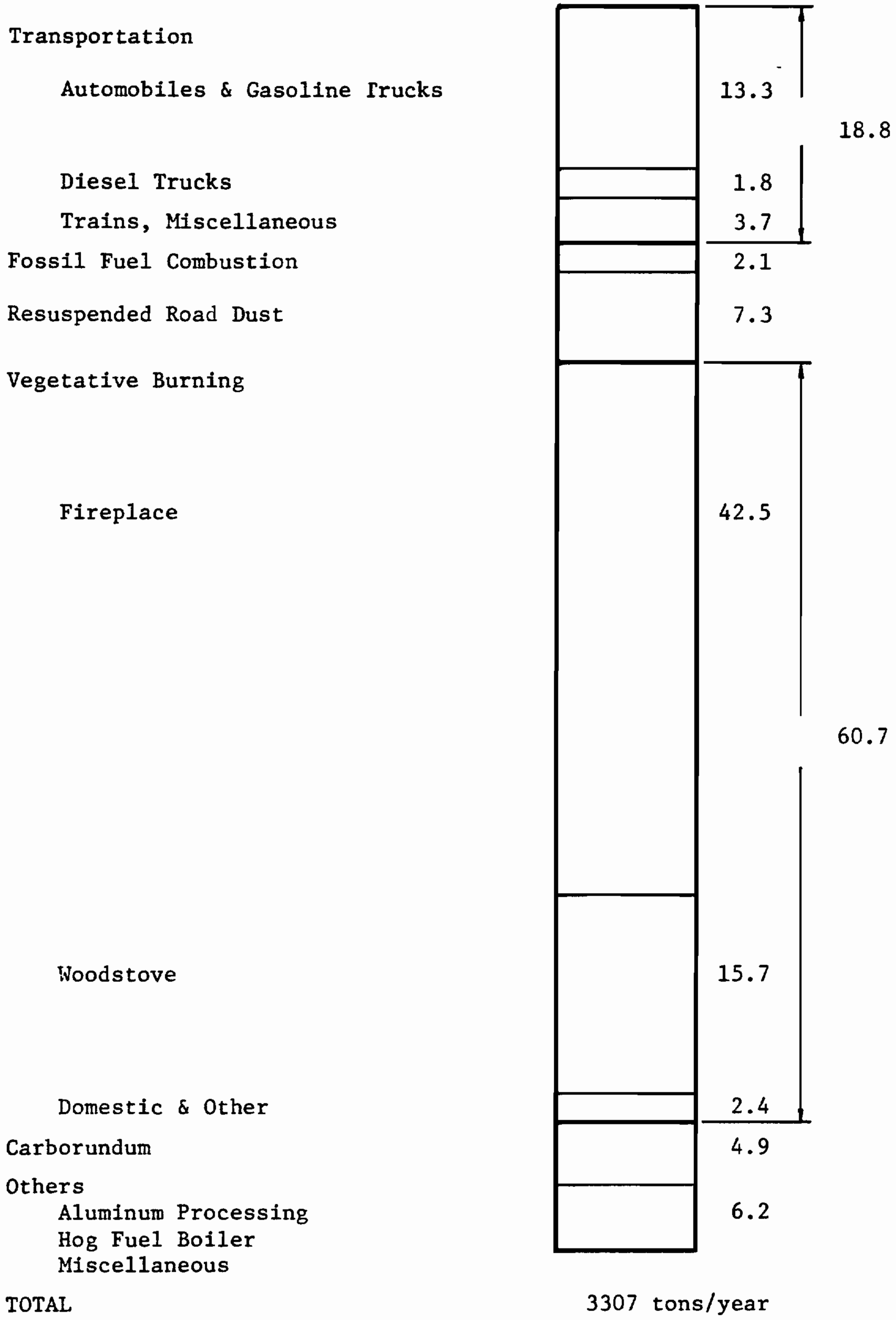
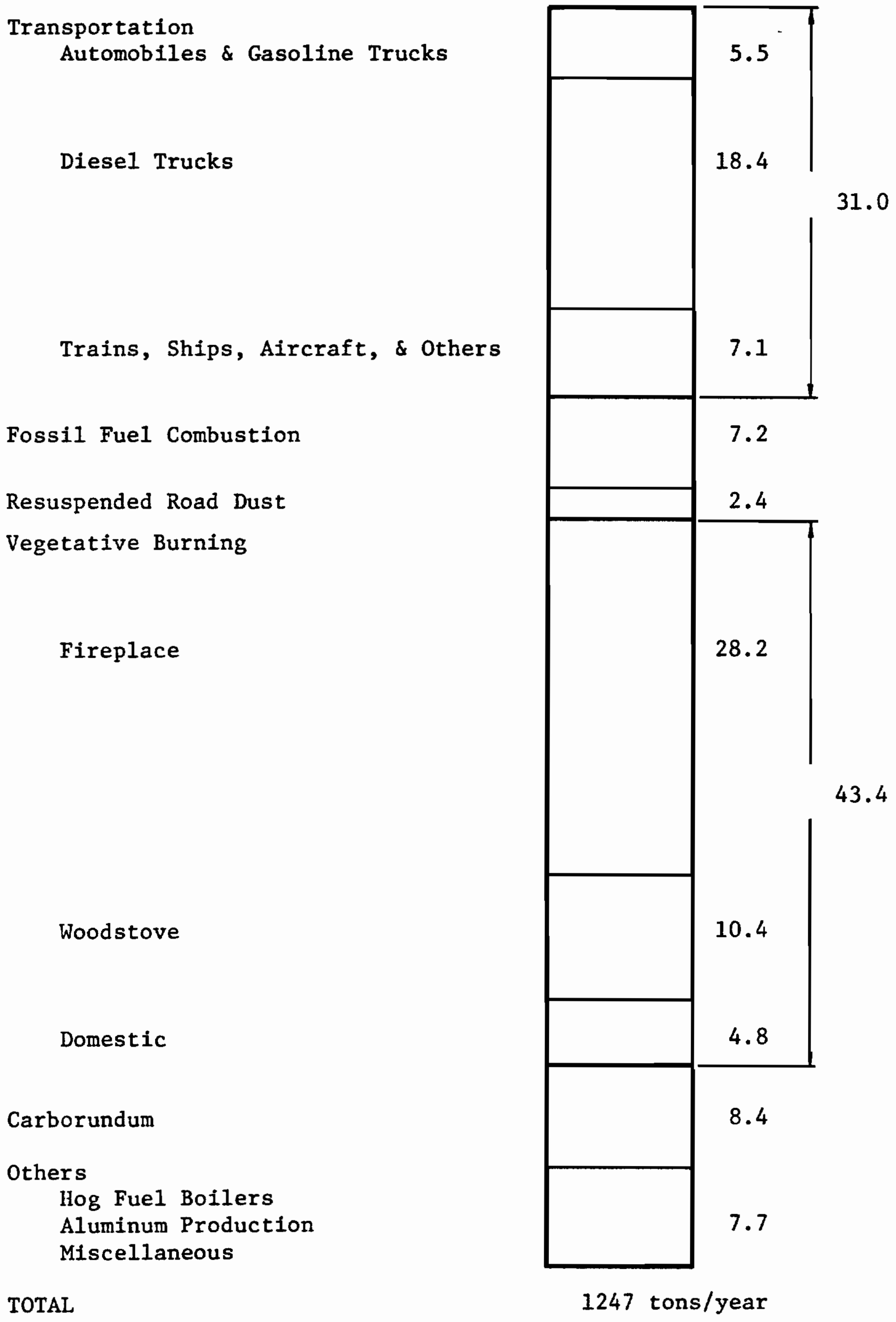


Figure A.2.



Fine Elemental Carbon Emissions, Portland, Oregon, 1977-78.

Figure A.3.

Fine Carbonaceous Emissions, Portland, Oregon 1977-78

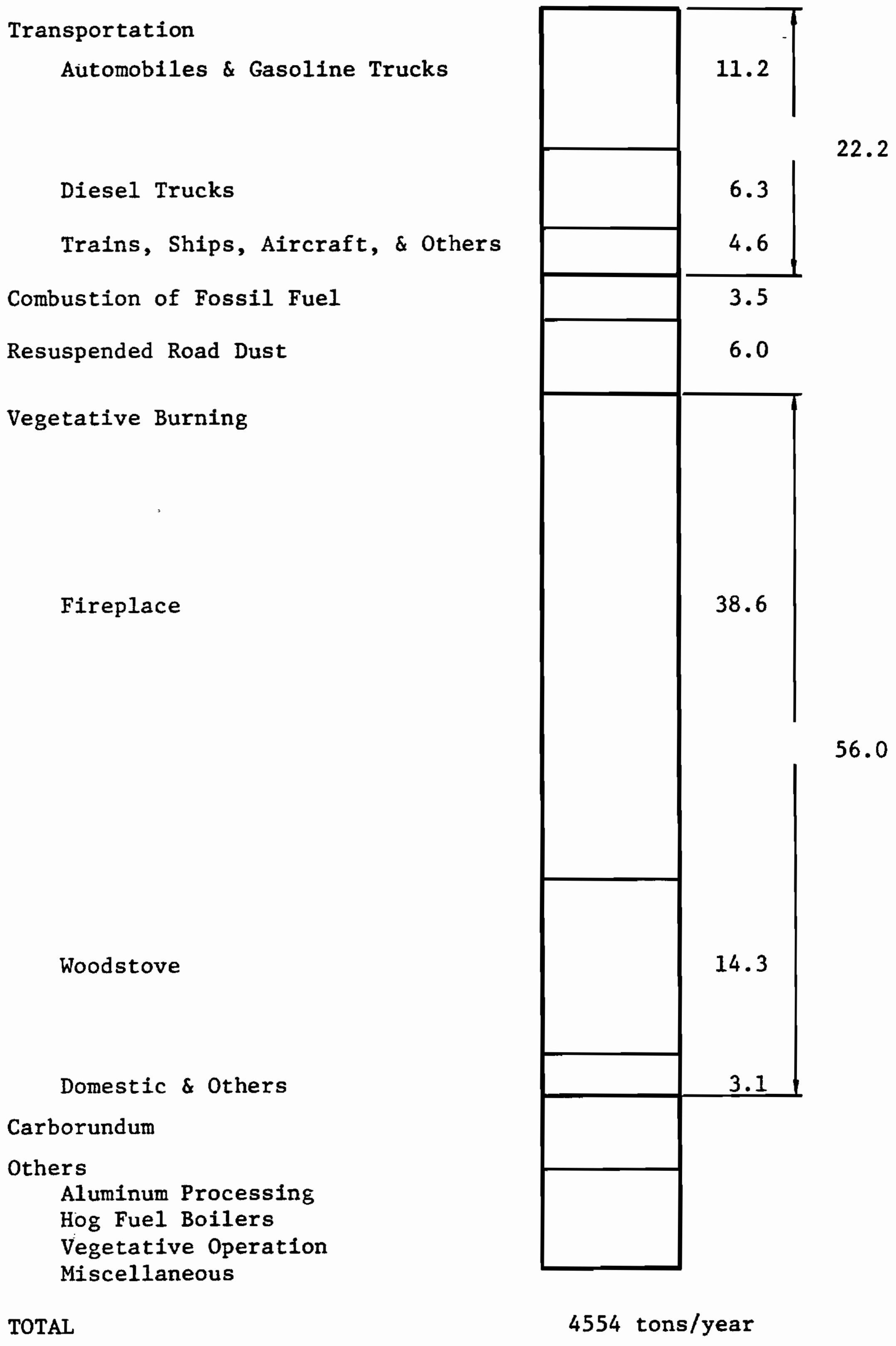
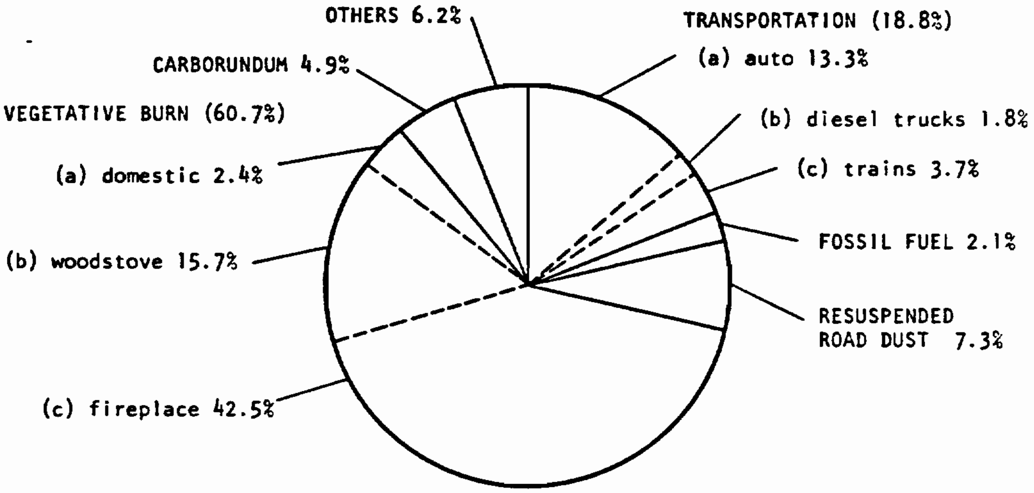


Figure A.4.

PACS EMISSION INVENTORY, FINE FRACTION 1977-78

FINE PRIMARY ORGANIC CARBON EMISSIONS
(3307 tons/yr.)



FINE ELEMENTAL CARBON EMISSIONS
(1247 tons/yr.)

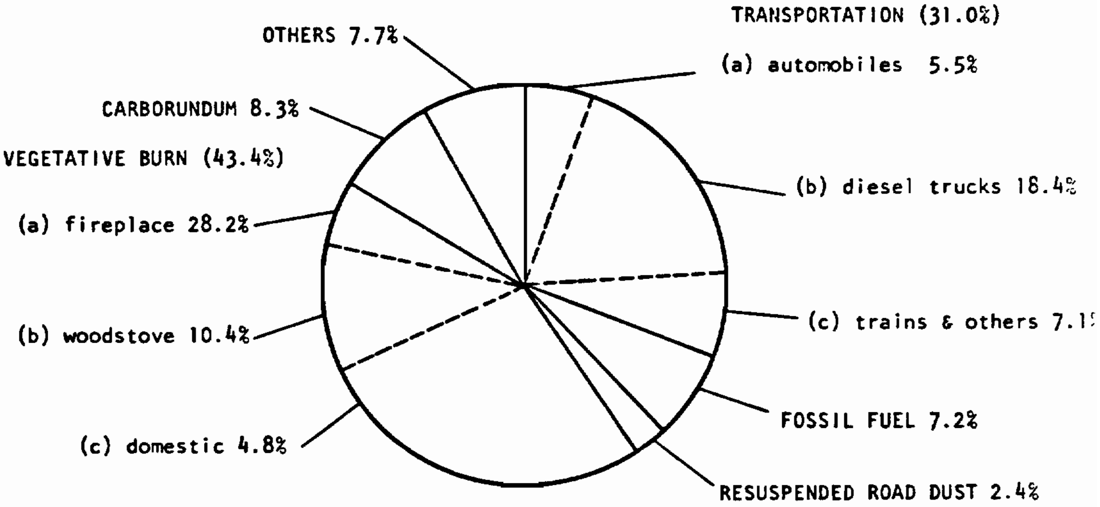


Figure A.5.

estimation of organic and elemental carbon. The final source matrix is given in Table A.2.

Table A.2. Source Matrix.

Chemical Element Balance Source Composition Matrix, Fine Particulate Composition

	Mnemonic		OC	EC	NO_3	SO_4	F	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	Percent Fine
			Percent																							
Marine	MARINF	Avg.	0.0	0.0	0.0	10	0.0	40	4.8	0.0	0.0	3.3	40	1.4	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	.2	0.0	
		Std*				4		4	.9			1.3	10	.2	.2									.05		
Continental Dust	CDUSTF	Avg.	4.32	.59	0.0	0.0	0.0	.69	1.76	11.7	25.4	.07	0.0	1.0	.93	.76	.025	.03	.20	6.8	.0092	.02	.041	0.0	.006	
		Std*	1.7	.38	.1	.05	.01	.38	.67	2.2	3.4	.03	.01	.28	.37	.24	.006	.008	.09	2.3	.004	.004	.026	.01	.002	
Urban Dust	UDUSTF	Avg.	11.8	1.85	0.0	.42	0.0	1.25	1.30	8.84	22.3	.37	0.0	1.03	2.44	.64	.023	.045	.123	6.0	.0093	.030	.11	.020	.37	~10
		Std*	4.3	.91	.1	.31	.01	.34	.27	2.71	1.1	.14	.01	.06	.40	.12	.005	.017	.017	.6	.0033	.012	.037	.0056	.15	
Transportation	TRANSF	Avg.	43.4	18.97	0.81	5.61	0	0.26	1.126	0.46	0.988	1.04	1.10	0.266	1.916	0	0	0	0.118	0.548	0.076	0.059	0.35	6.54	16.77	80
		Std*	6.98	6.41	0.3	1.95	0.01	0.1	1.004	0.239	0.406	0.38	0.42	0.118	0.866	0.07	0.001	0.001	0.051	0.235	0.008	0.027	0.13	1.30	3.15	
Residual Oil Combustion	RDOILF	Avg.	7.8	2.42	.65	48.1	.053	3.5	0.0	.51	.96	13.3	0.0	.28	1.58	.11	3.44	.047	.046	2.97	5.36	.075	.40	.013	.11	90
		Std*	6.2	2.5	44	11.9	.019	1.7	3	.24	.48	2.4	.1	.10	.64	.038	.75	.015	.013	.61	1.21	.025	.18	.021	.064	
Vegetative Burn 1	VBRN1F	Avg.	53.75	8.75	5.1	1.6	0.0	.65	0.0	1.44	.89	.43	5.55	.60	1.07	0.0	0.0	0.0	.12	.19	0.0	.09	0.0	.053	0.0	~99
		Std*	10	5.0	2.5	.88	1	.14		.83	1.1	.30	1.47	.013	.38				.12	.11		.04		.044		
Vegetative Burn 2	VBRN2F	Avg.	44.2	7.2	2.0	5.0	.32	.33	0.0	.45	.49	1.6	9.9	6.5	.92	.07	0.0	.012	.047	.054	0.0	.054	0.0	.045	0.0	~99
		Std*	37	8.2	2.5	5.4	.15	.34	1	.51	.78	1.5	5.1	4.5	.98	.07		.007	.042	.060		.060		.045		
Kraft Recovery Boiler	KRAFTF	Avg.	1.7	.22	0.0	40	0.0	12.7	.63	.25	.15	11.7	1.8	1.5	0.0	.006	.001	.28	.03	1.2	.13	.021	.069	.13	.013	87
		Std*	.21	.23	.3	2.1	.1	.71	.53	.014	.014	1.0	.42	.14	.5	.002	.001	.08	.004	.11	.014	.013	.021	.06	.011	
Sulfite Recovery Boiler	SULFTF	Avg.	0.0	0.0	.3	56	0.0	2.5	.73	0.0	.40	12	.58	30	2	.01	0.0	0.0	.054	.066	0.0	.016	.017	0.0	0.0	~90
		Std*						.8	.52		.15	2	.1	10	.2	.001	.001	.001	.070	.036	.001	.017	.002	.005	.01	
Hog Fuel Boiler	HOGFUF	Avg.	0.0	0.0	.51	33.8	.15	3.4	0.0	.24	.76	8.8	9.5	22.4	5.6	0.0	0.0	.015	.51	1.76	.0067	.12	.71	.055	.42	73
		Std*			.23	9	.05	2.9	1.0	.18	.37	2.4	4.9	11.2	4.0	.06	.002	.006	.34	.88	.0042	.06	.34	.03	.22	
Aluminum Processing	ALPROF	Avg.	3.9	2.3	.41	4.4	6.0	4.1	2.8	27	.34	1.4	1.33	.22	.33	.04	.064	0.0	.011	.45	.19	.044	.015	.037	.012	56
		Std*	3.9	1.0	.18	3.9	2.3	1.7	1.8	8	.34	.21	.84	.06	.03	.03	.016	.01	.008	.29	.085	.007	.011	.054	.010	
Steel Electric Arc	STEELF	Avg.	9	1.5	0.0	2.5	0.0	1.26	6.5	.65	5.0	1.95	1.85	.92	6.2	.20	.06	2.1	8.7	32	.7	.28	1.2	0.0	.76	92
		Std*	.9	.15	1.4	1.3	.5	.48	.71	.16	.21	.07	.78	.07	.57	.02	.01	1.4	.9	3	.07	.03	.12	.1	.07	
Ferromanganese	FERMNF	Avg.	9	1.5	5.7	4.2	.29	3.1	0.0	.64	.99	1.7	.42	10.5	1.3	.046	.024	.042	17.3	2.1	0.0	.036	.58	.16	.045	92
		Std*	.9	.15	2.8	.4	.08	.3	4	.13	.30	.35	.16	3.9	.14	.007	.019	.0028	.99	1.4	.005	.004	.25	.22	.016	
Carborundum	CARBOF	Avg.	21.4	13.67	1.6	16	.05	.12	.78	.35	3.5	4.8	1.7	.79	.14	.014	.007	.009	.035	.33	.004	.019	.004	.017	0.0	82
		Std*	7.4	13	2.1	25	.03	.10	1.2	.40	4.3	6.6	1.5	1.1	.13	.019	.008	.011	.041	.61	.007	.023	.004	.010	.01	
Glass Furnace	GLASSF	Avg.	0.0	0.0	.62	65	.054	9.2	0.0	.19	.25	11.3	.06	1.37	.3	0.0	.0047	.19	.0021	.02	0.0	.0047	.011	.0063	.38	93
		Std*			.35	9.9	.023	1.0	1	.014	.07	2.3	.006	.28	.03	.005	.0002	.035	.0007	.002	.01	.0017	.0019	.0053	.06	
Carbide Furnace	CARBFF	Avg.	7.3	1.2	.57	3.2	0.0	.92	2.4	.58	2.5	1.6	1.05	1.25	30	0.0	.006	0.0	.042	.54	.022	.020	.015	0.0	.008	55
		Std*	1.3	.28	.24	.42	.1	.10	.35	.11	.07	.42	.07	.35	4	.02	.0005	.01	.0035	.08	.008	.011	.007	.01	.004	
Fireplace	FIREPF	Avg.	45.9	12.9	.13	.11	.38	.037		.024	.024	.037	0.61	.53	.055				.0015	.0023	.00048	.019	.12	.007	.011	61.5
		Std*	5.5	5.2	.04	.07	.064	.045	.01	.018	.024	.034	0.057	.11	.0071	.004	.00006	.0008	.00071	.00035	.00032	.021	.16	.0057	.012	4.5
Domestic	DOMESF	Avg.	29.0	4.5	.88	1.2	.28	.096		.13	.53	.28	1.35	1.66	.21			.0018	.003	.017		.014	.050	.0080	1.8	54.9
		Std*	17.9	3.7	1.7	1.3	.16	.17	.009	.21	.93	.46	2.11	1.75	.19	.001	.001	.0029	.0018	.030	.05	.023	.067	.0065	2.5	22.6
Woodstove	WOODSF	Avg.	58.2	18.8	0.033	.055	.43	.060	.75	.018			.094	.053	.037		.0013		.012	.0035		.0025		.0021		99.
		Std*	16.9	5.66	0.011	.02	.34	.023	1.06	.003	.005	.01	.0049	.043	.0021	.003	.0011	.001	.015	.00071	.004	.00071	.01	.0023	.005	99.
Home Heating	HOMEHF	Avg.	47.5	12.8		0.289		0.083	0.013	0.021		0.182	0.509	0.86	0.061								0.037			90
		Std*	13.8	8.4		0.021		0.012	0.017	0.01		0.019	0.031	0.096	0.006								0.002			

APPENDIX A

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APPENDIX B.

Graphical Representation of NASN Results for Urban and Rural Sites.

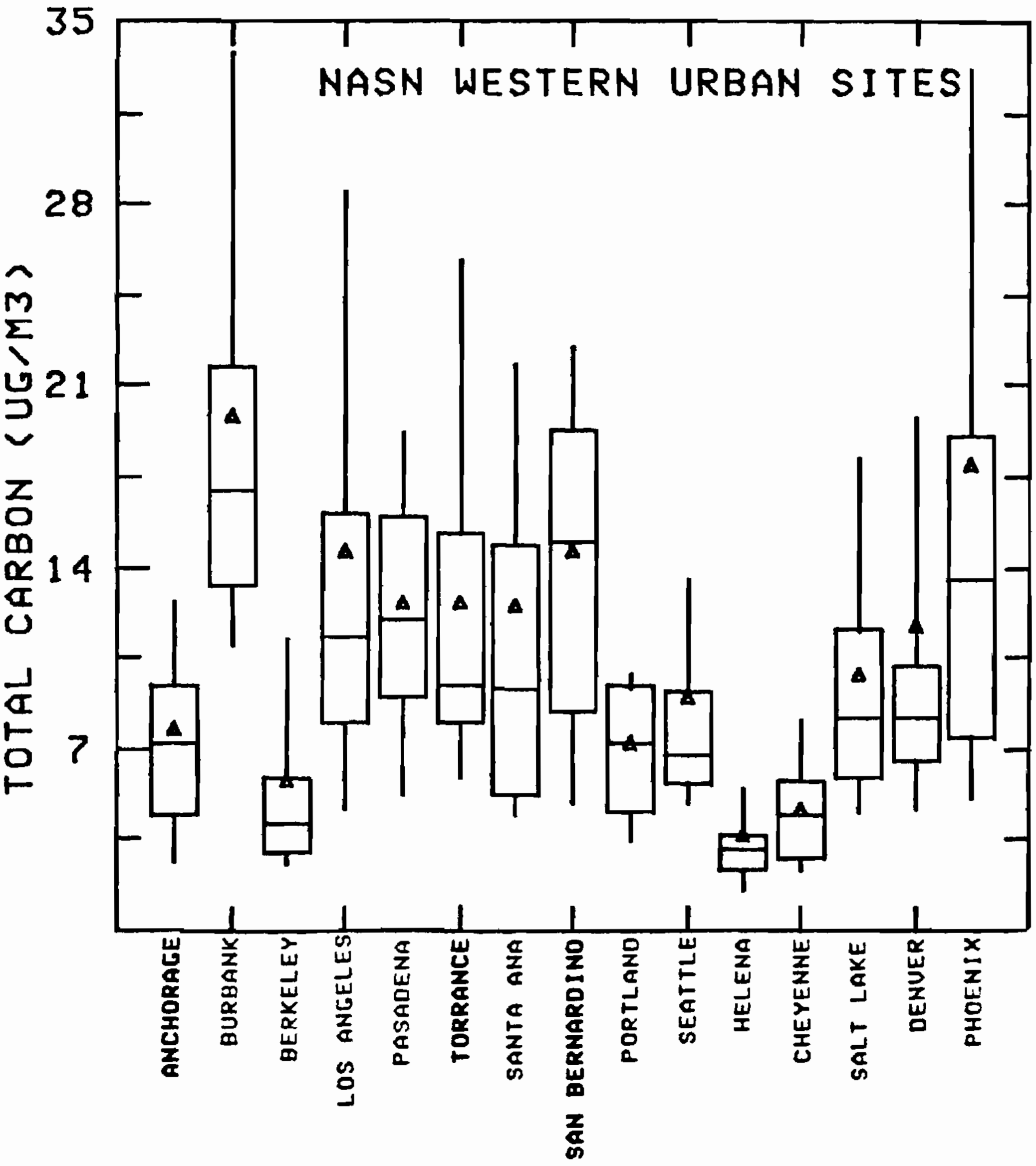

Figure B.1.a

Box plot of total carbon for NASN western urban sites.

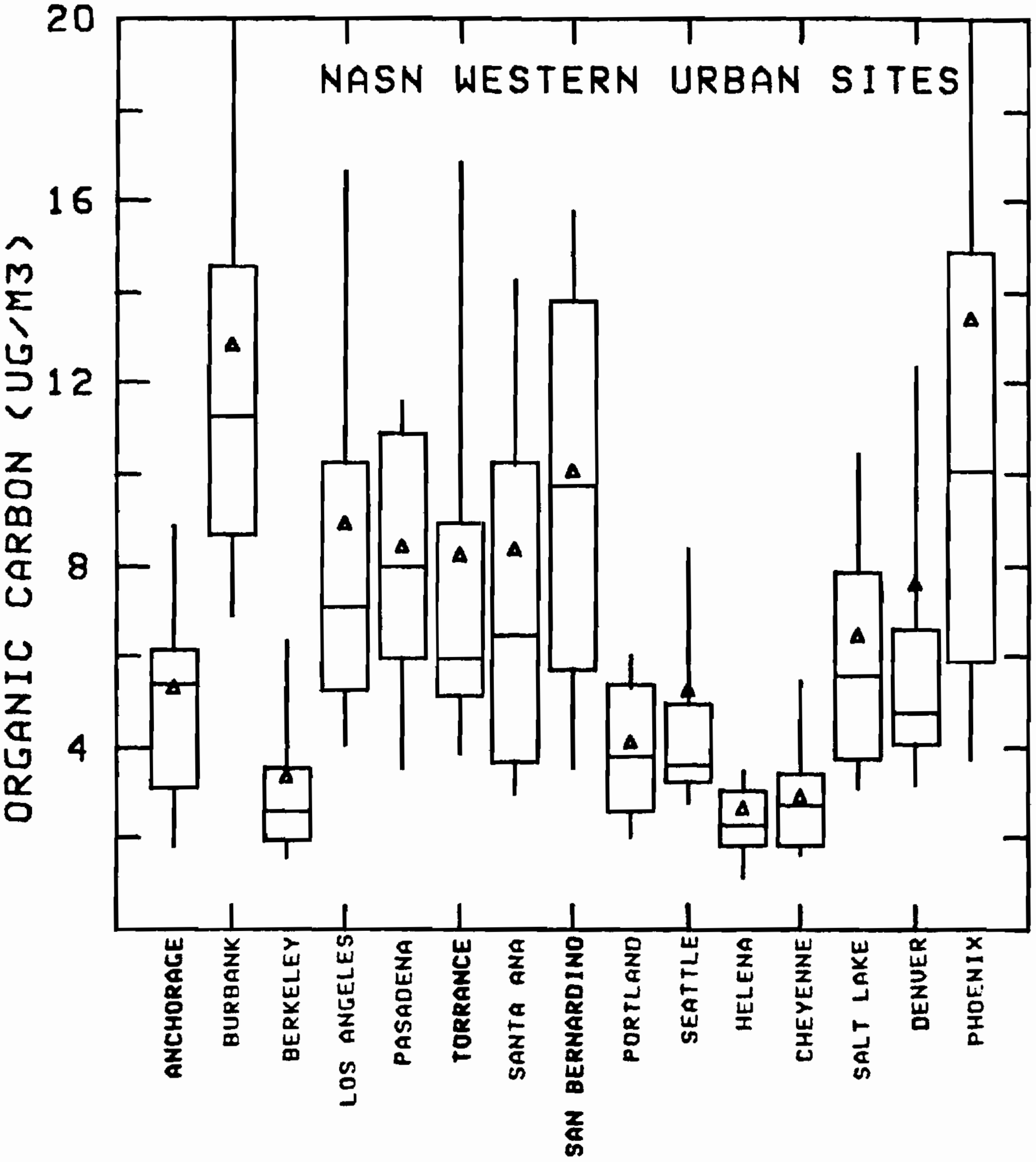

Figure B.1.b

Box plot of organic carbon for NASN western urban sites.

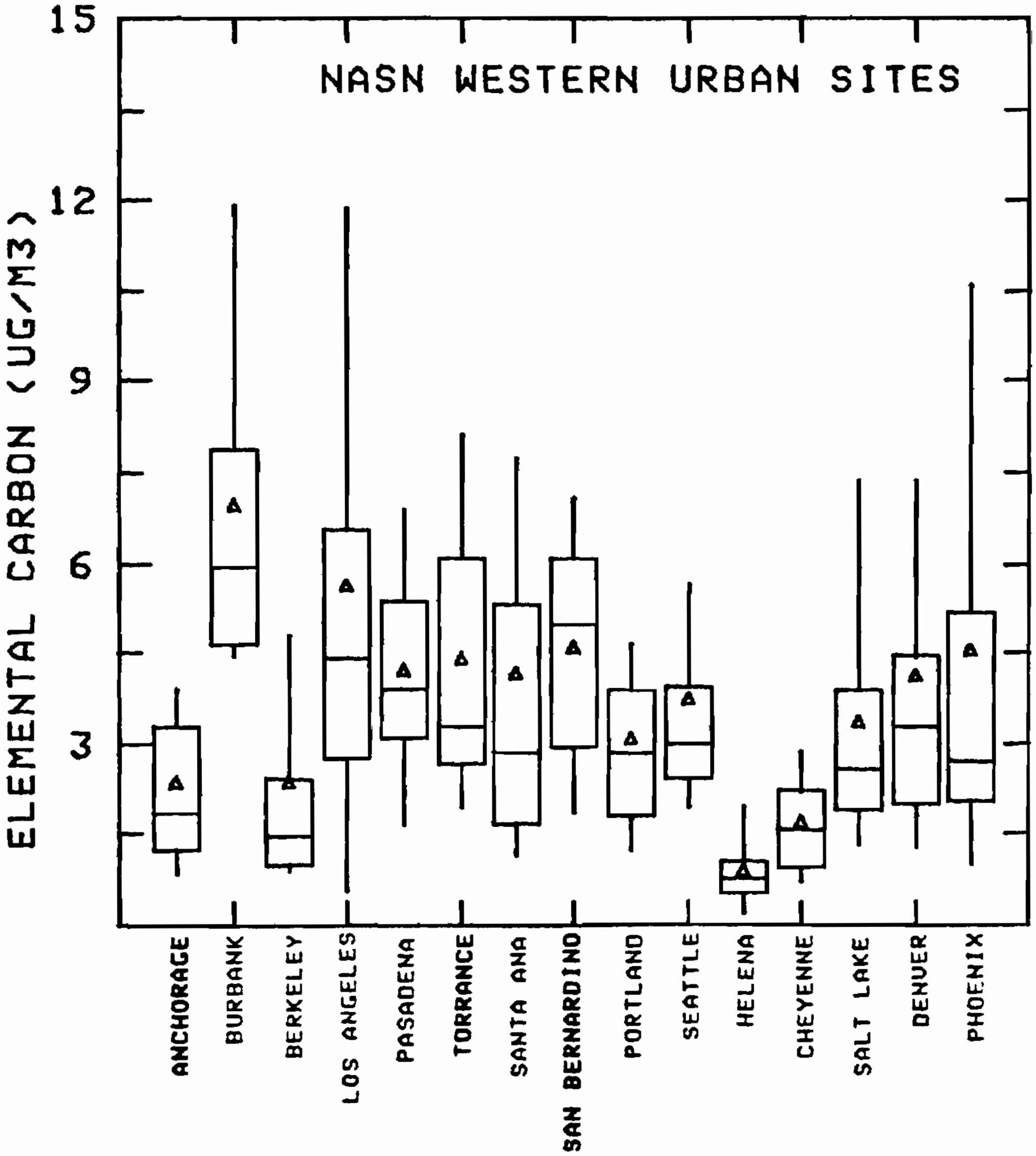

Figure B.1.c

Box plot of elemental carbon for NASN western urban sites

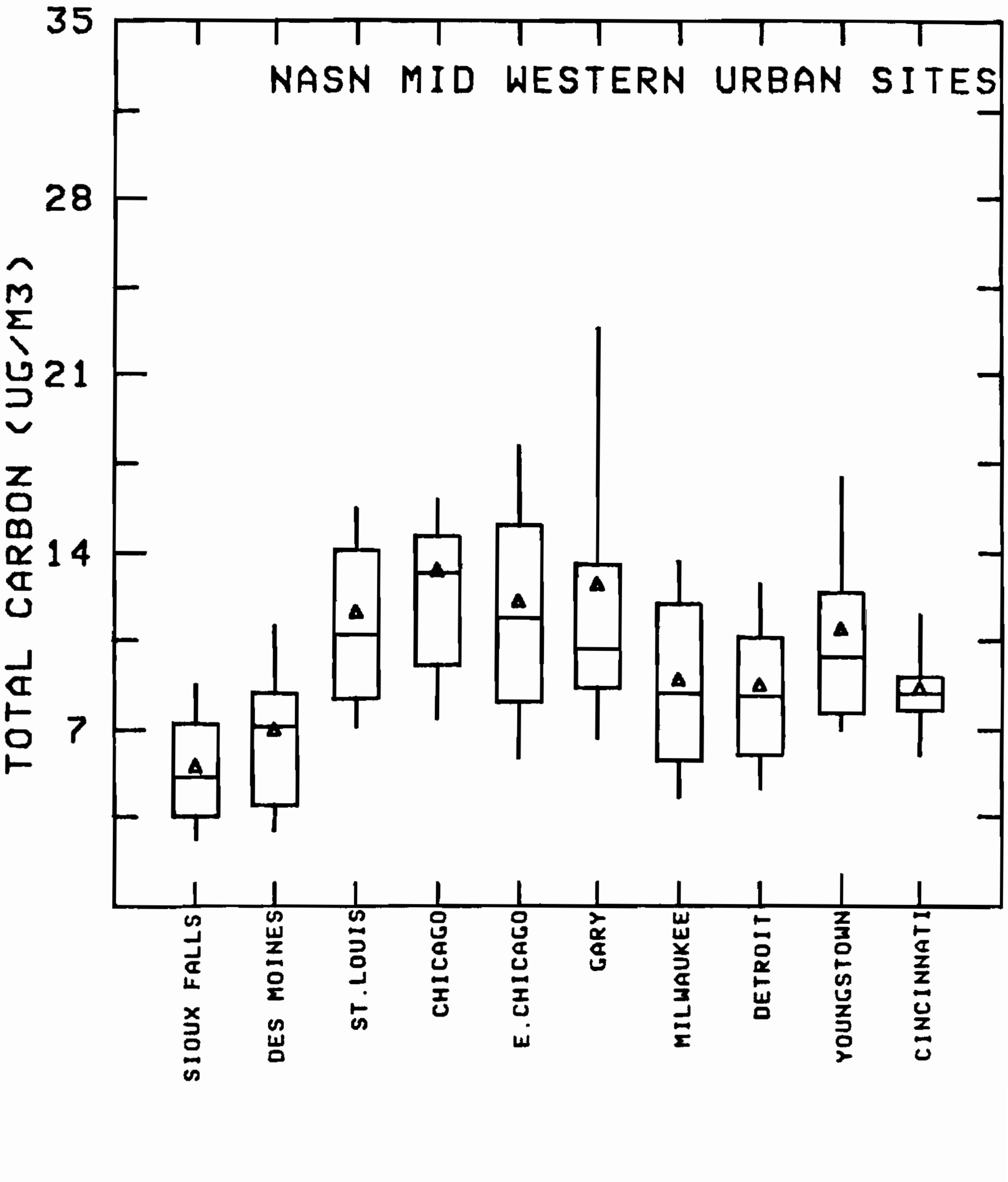

Figure B.2.a

Box plot of total carbon for NASN mid-western urban sites

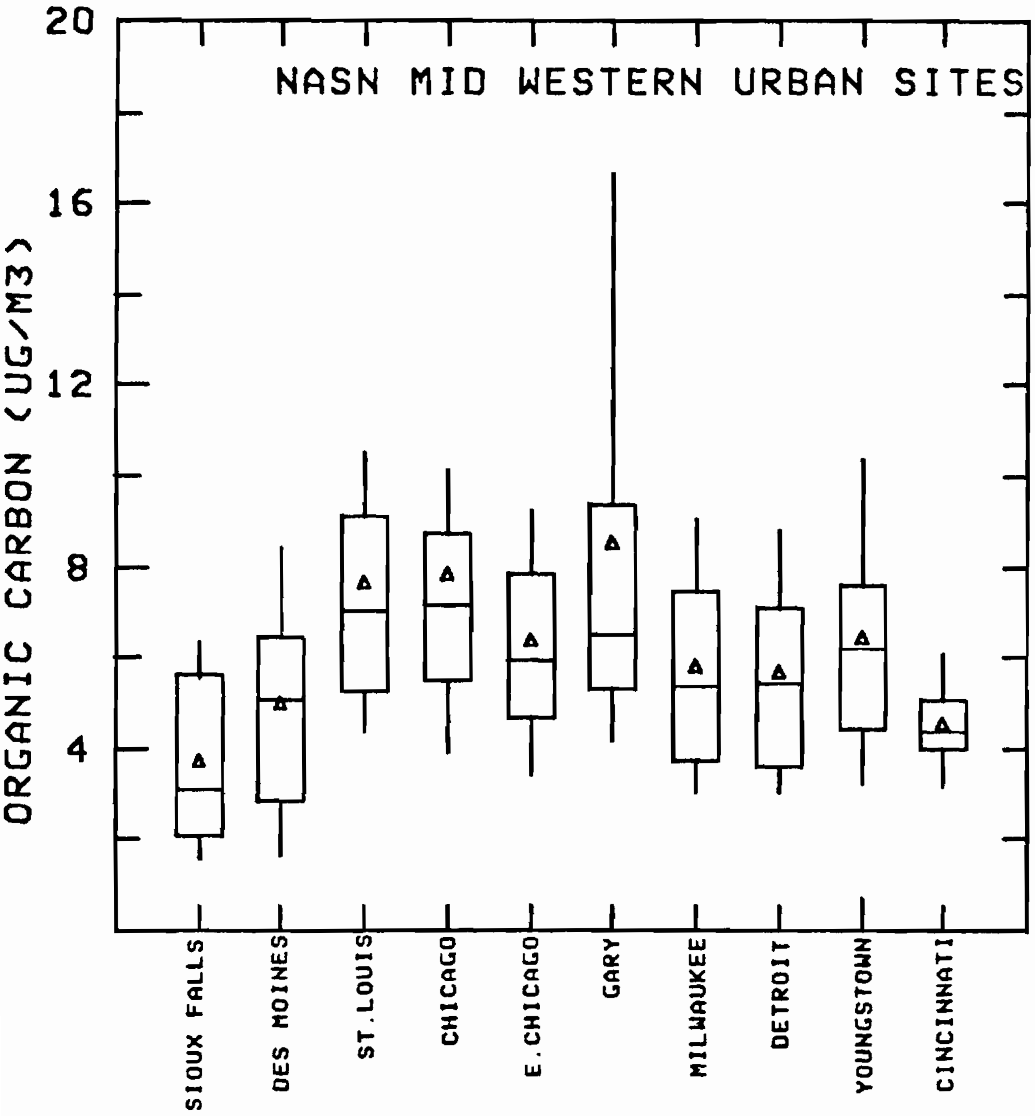

Figure B.2.b
Box plot of organic carbon for NASN mid-western urban sites

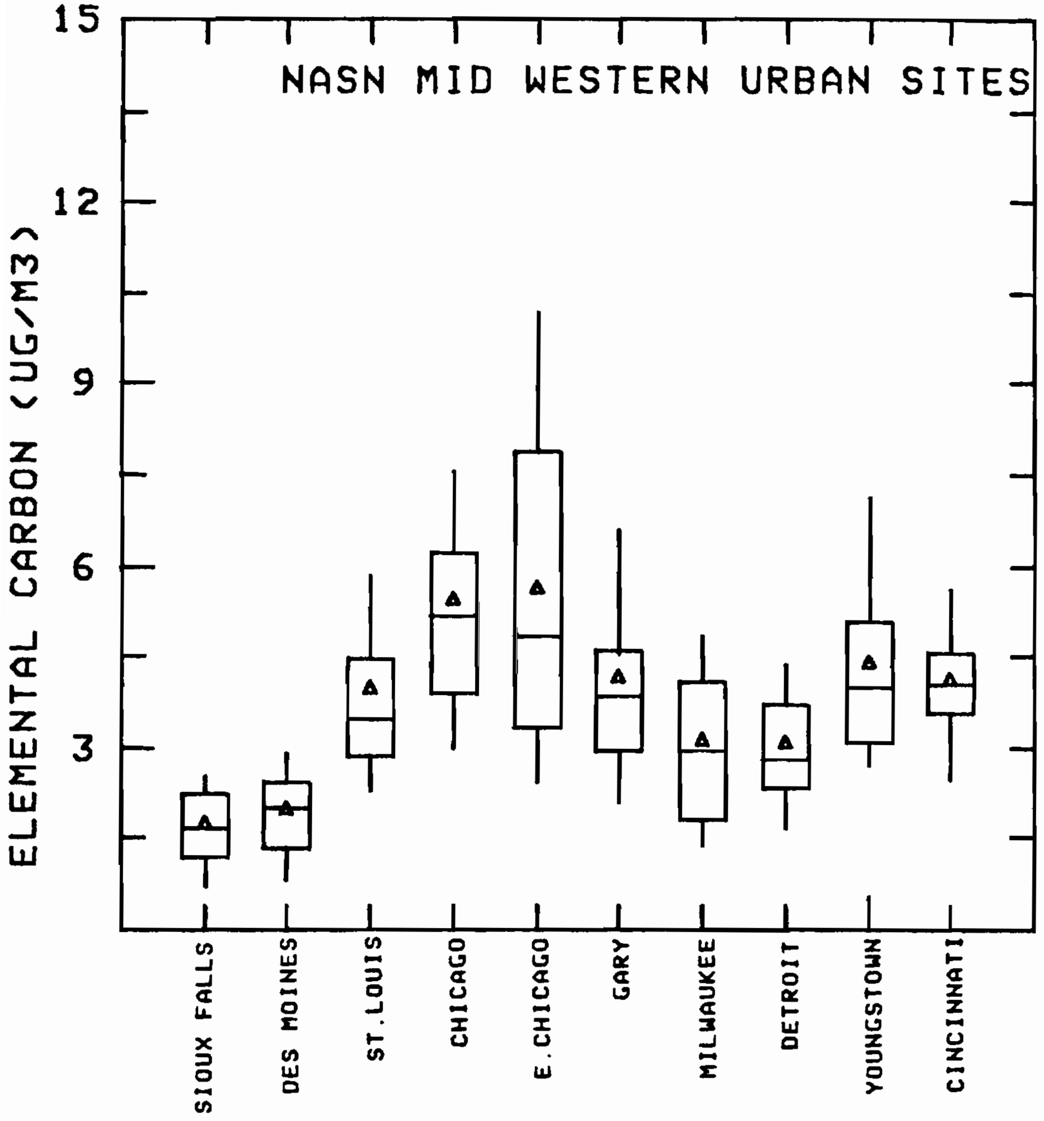

Figure B.2.c

Box plot of elemental carbon for NASN mid-western urban sites

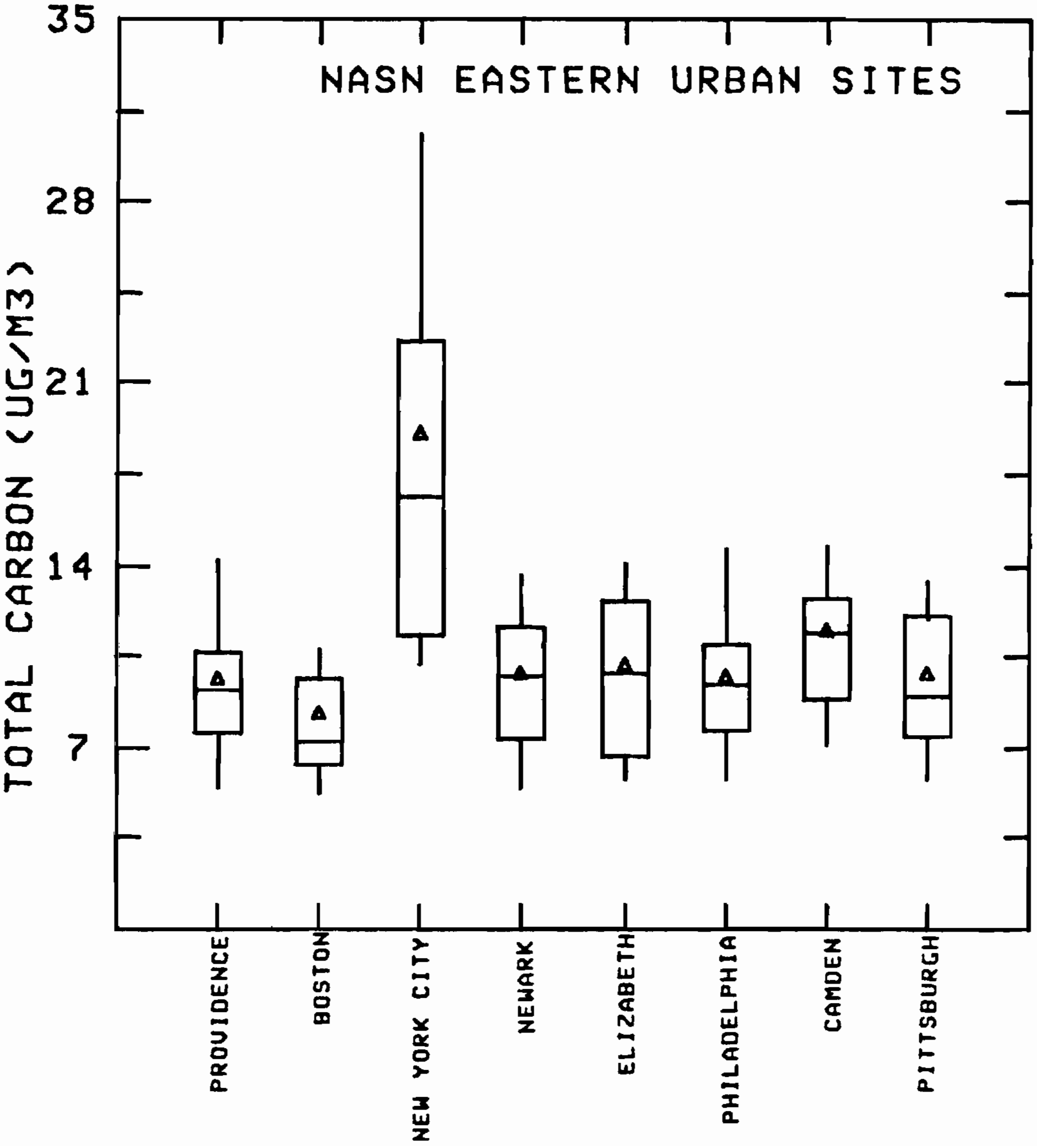

Figure B.3.a

Box plot of total carbon for NASN eastern urban sites.

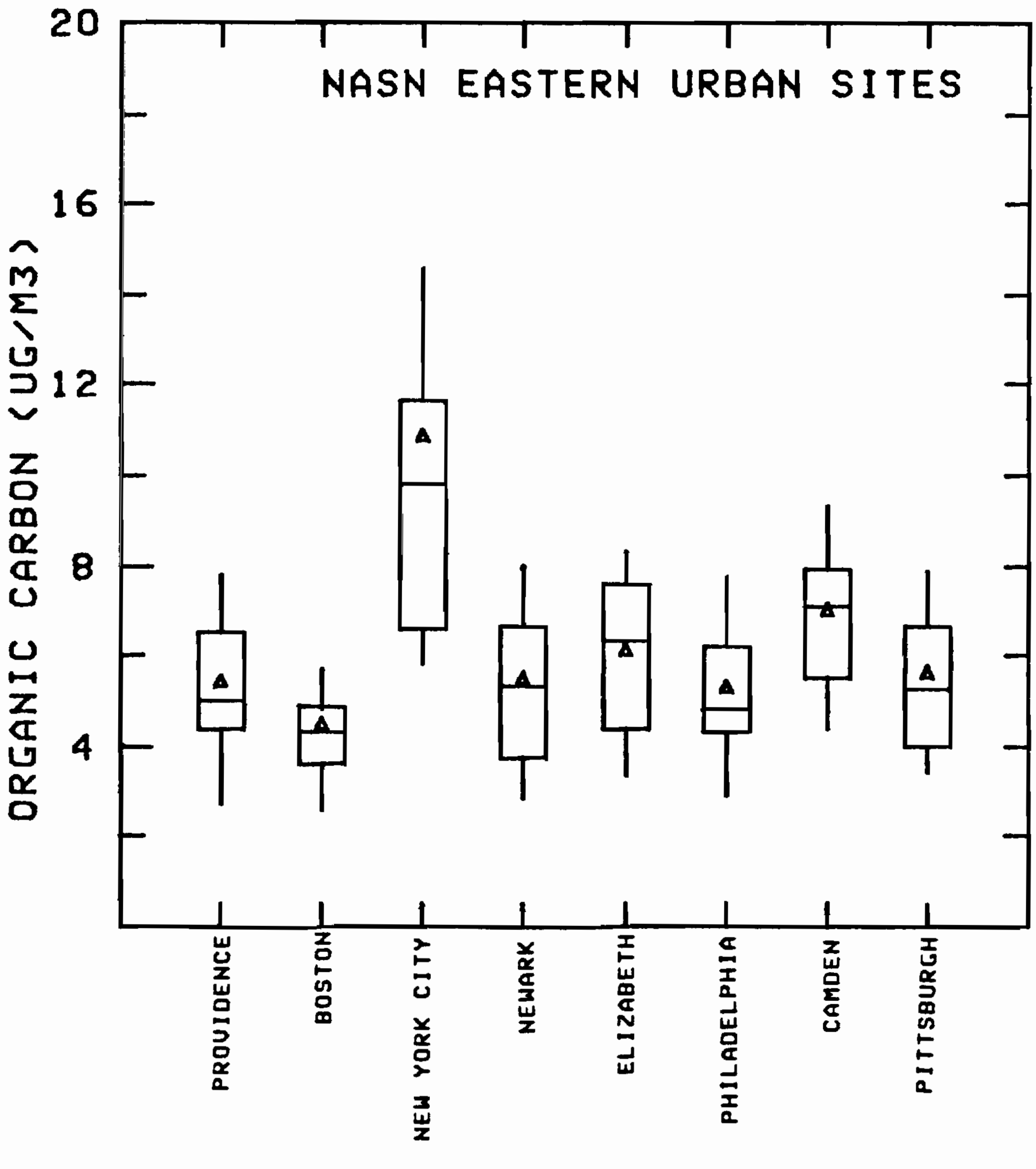

Figure B.3.b

Box plot of organic carbon for NASN eastern urban sites.

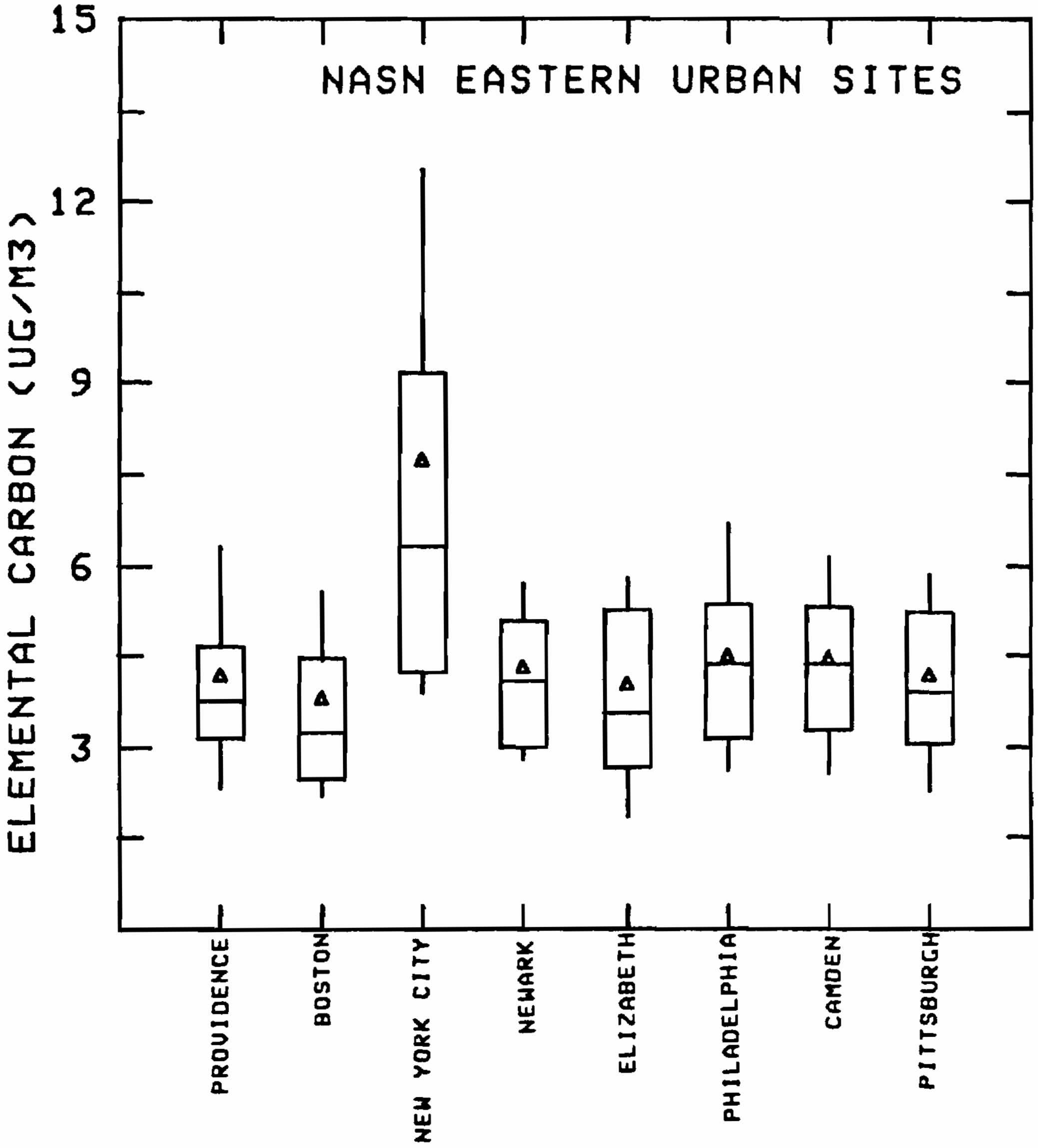

Figure B.3.c

Box plot of elemental carbon for NASN eastern urban sites.

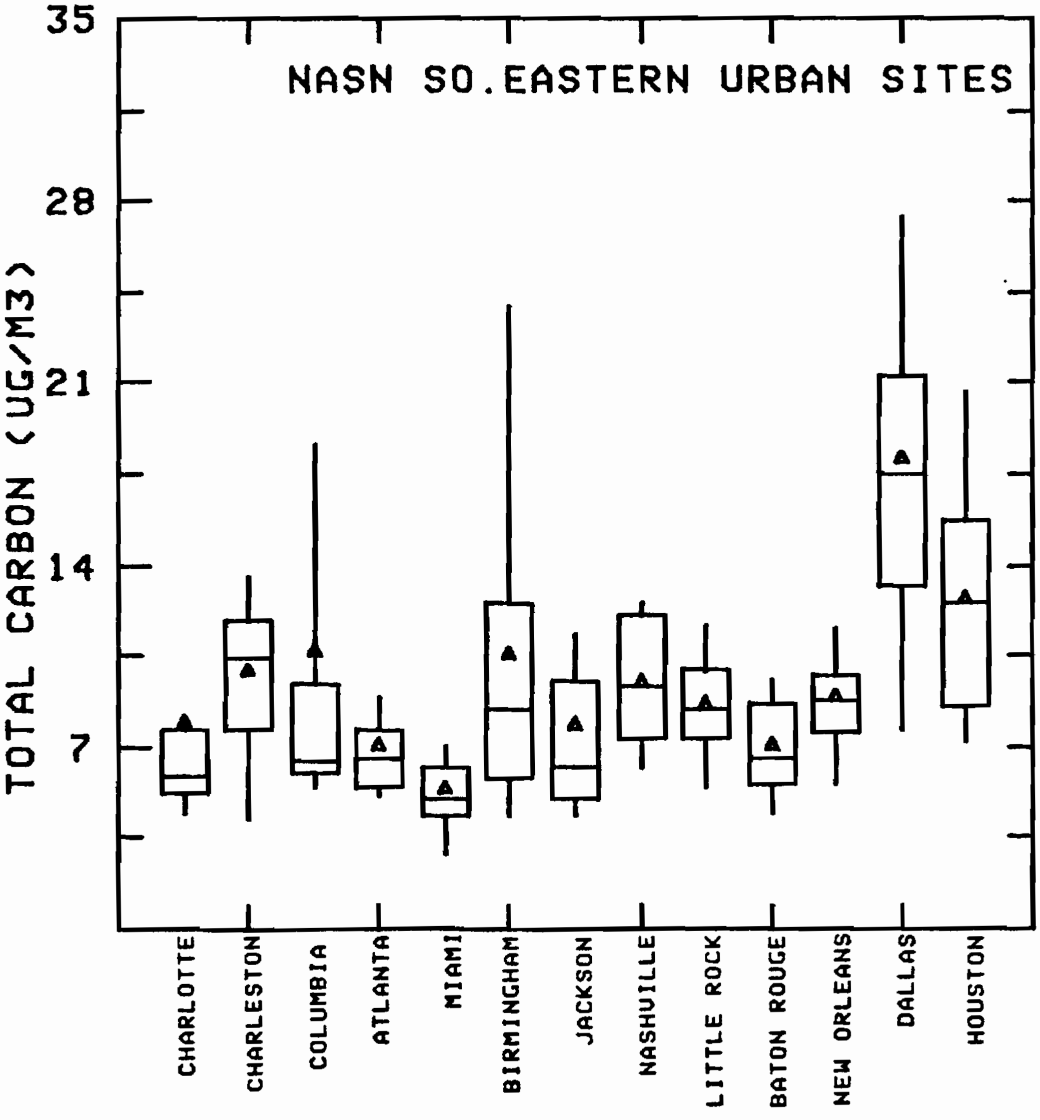

Figure B.4.a

Box plot of total carbon for NASN south-eastern urban sites

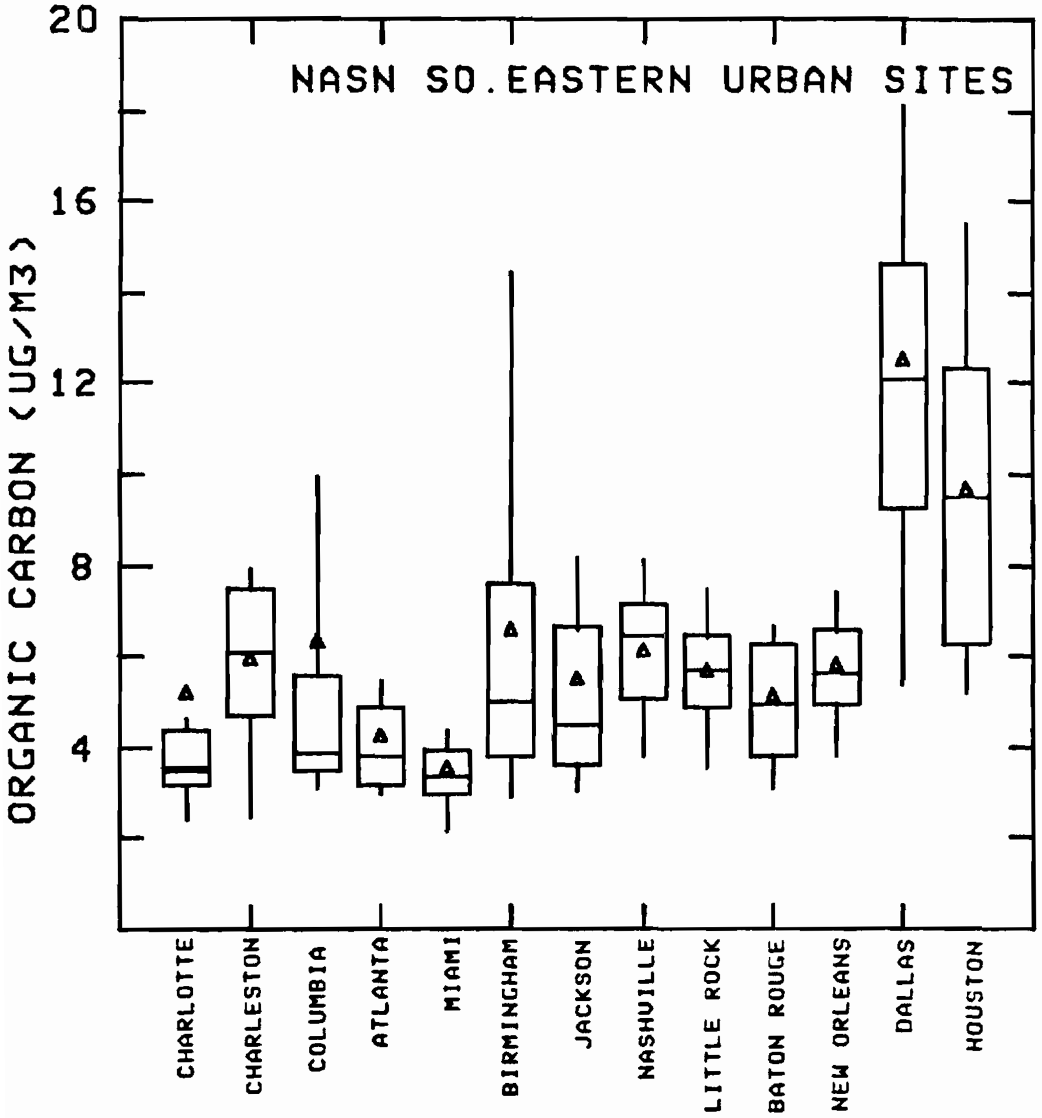

Figure B.4.b

Box plot of organic carbon for NASN south-eastern urban sites.

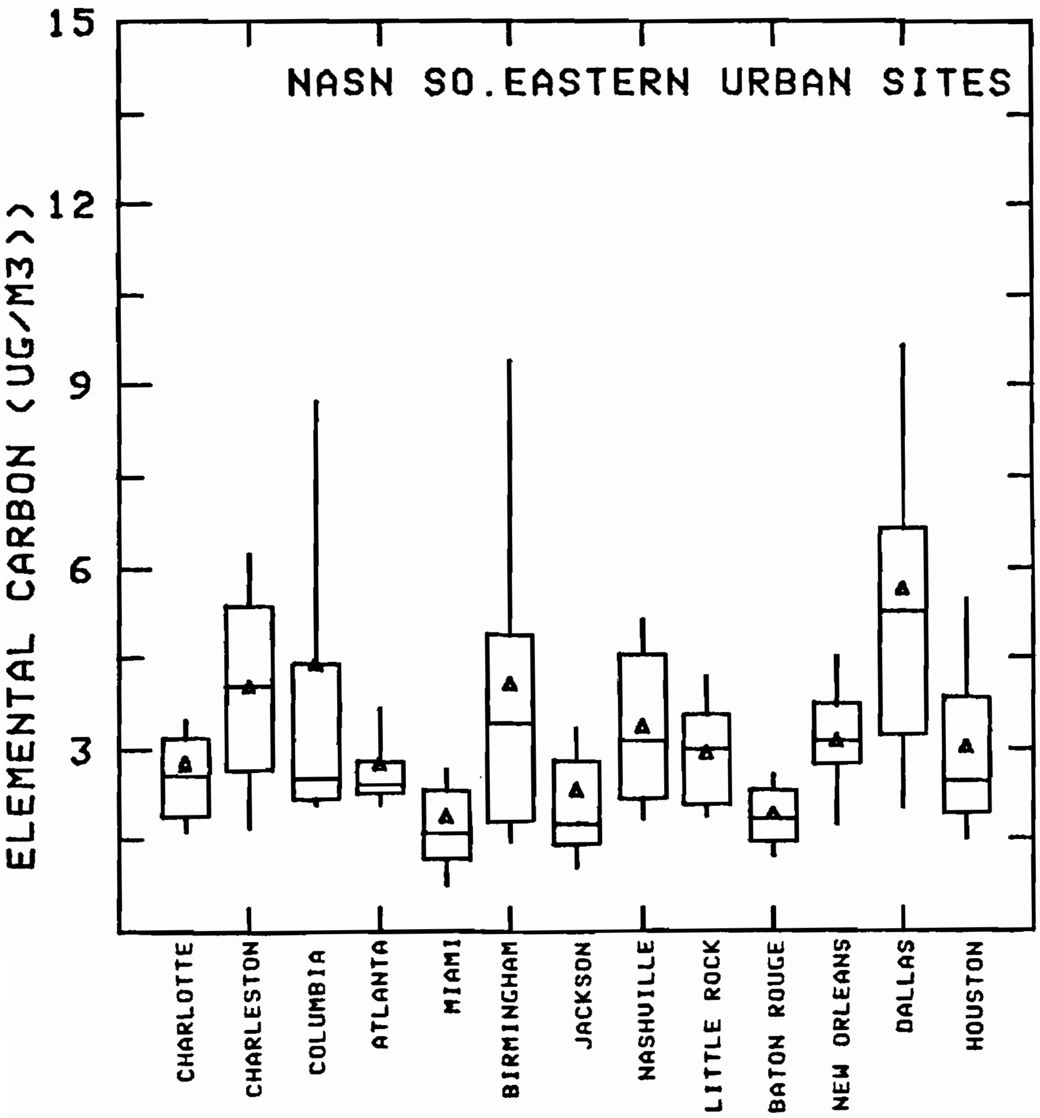

Figure B.4.c

Box plot of elemental carbon for NASN south-eastern urban sites.

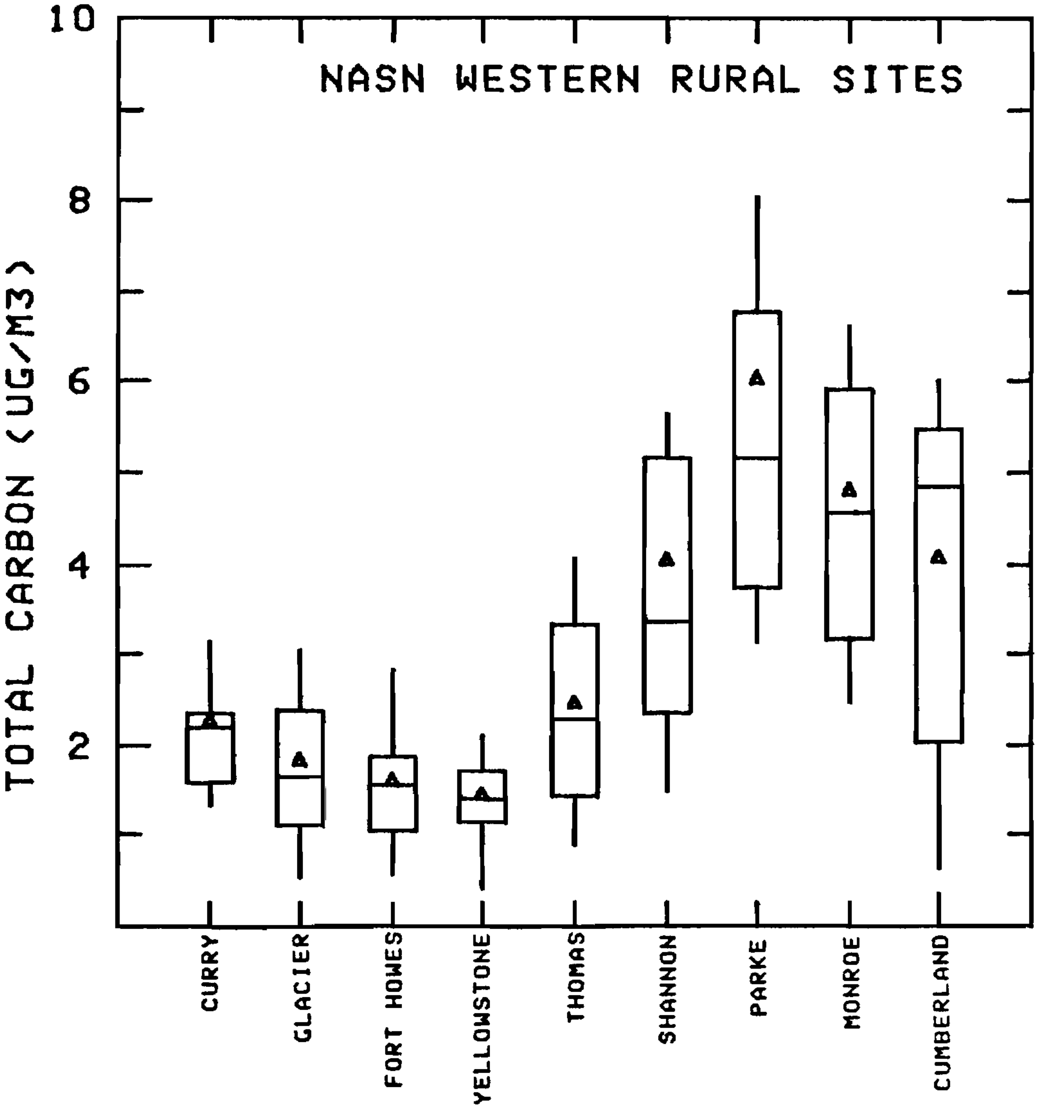

Figure B.5.a

Box plot of total carbon for NASN western rural sites.

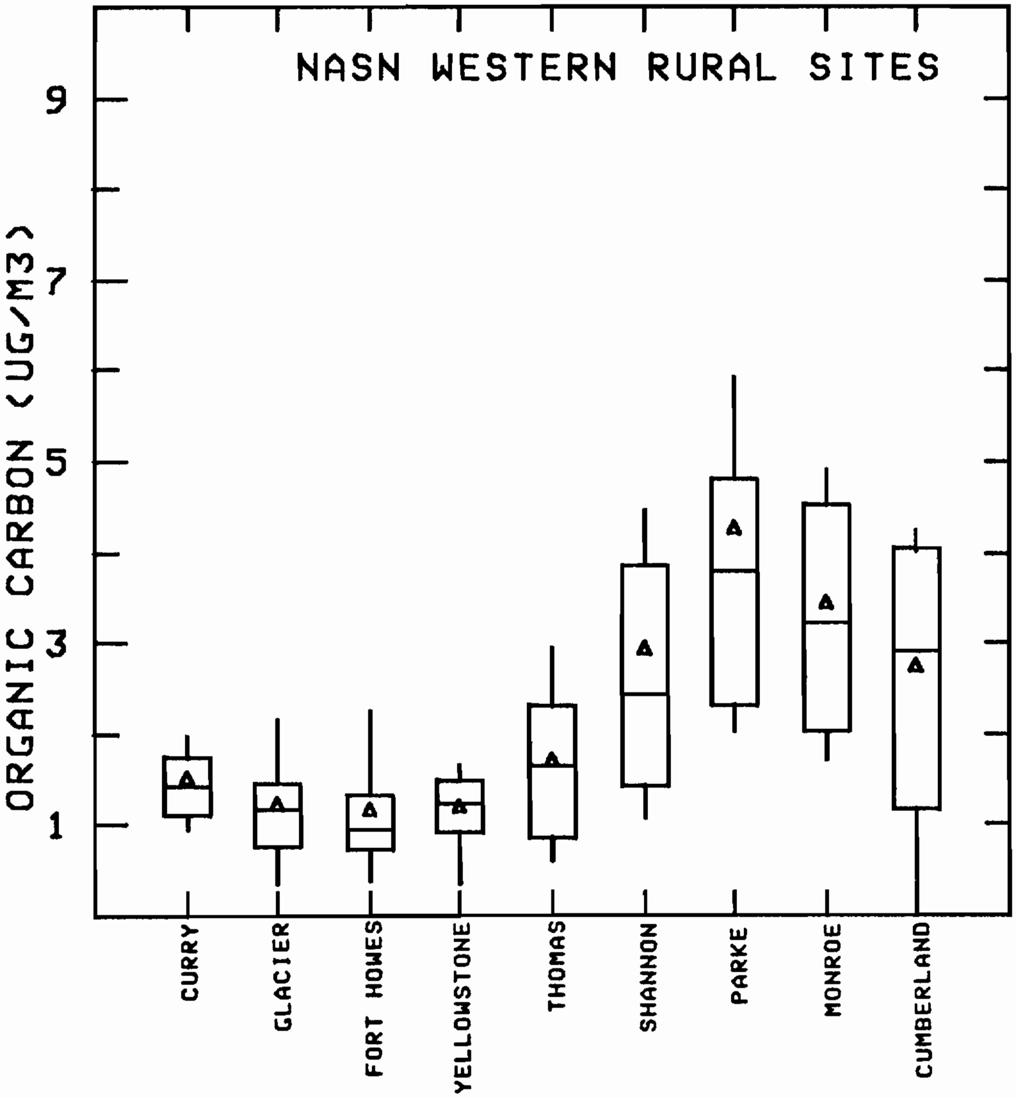

Figure B.5.b

Box plot of organic carbon for NASN western rural sites.

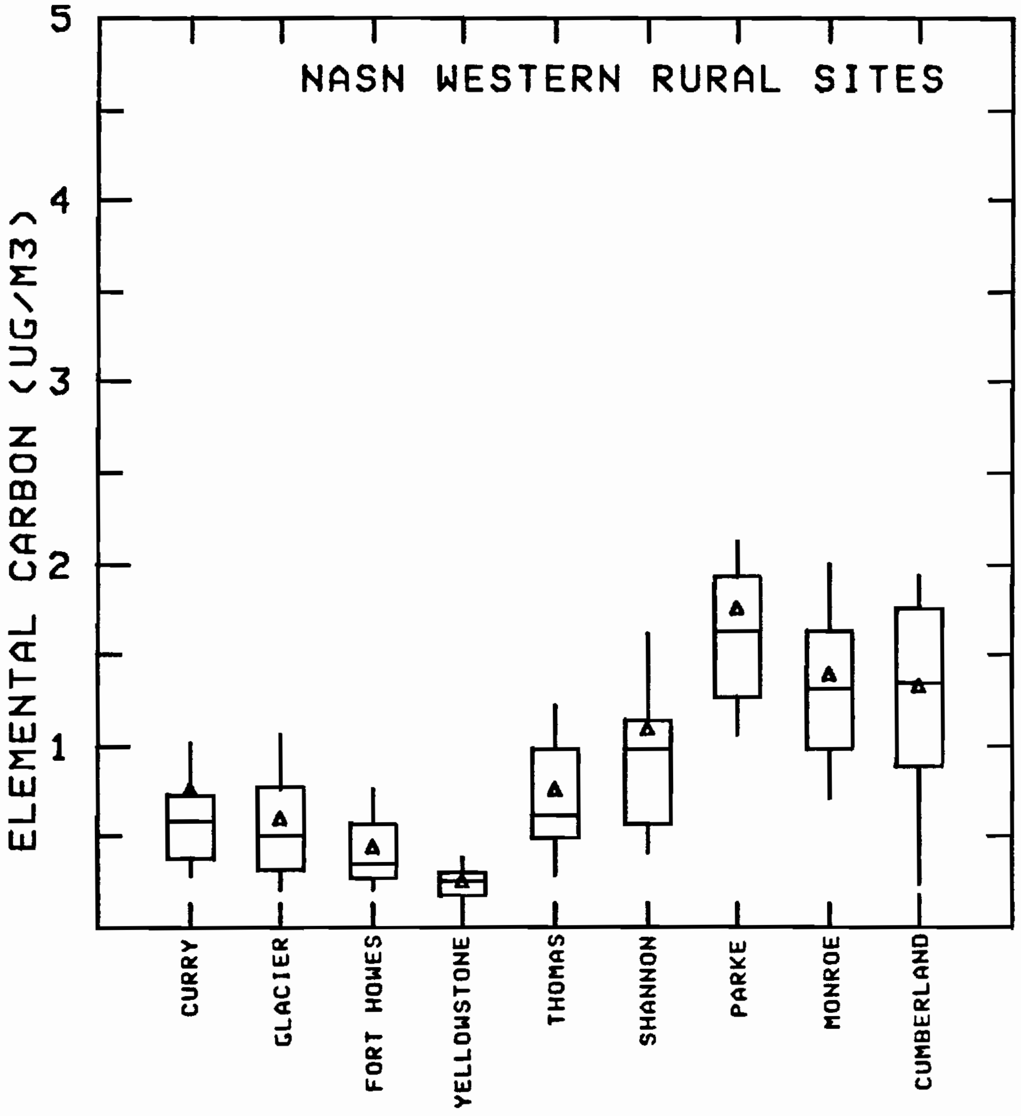

Figure B.5.c
Box plot of elemental carbon for NASN
western rural sites.

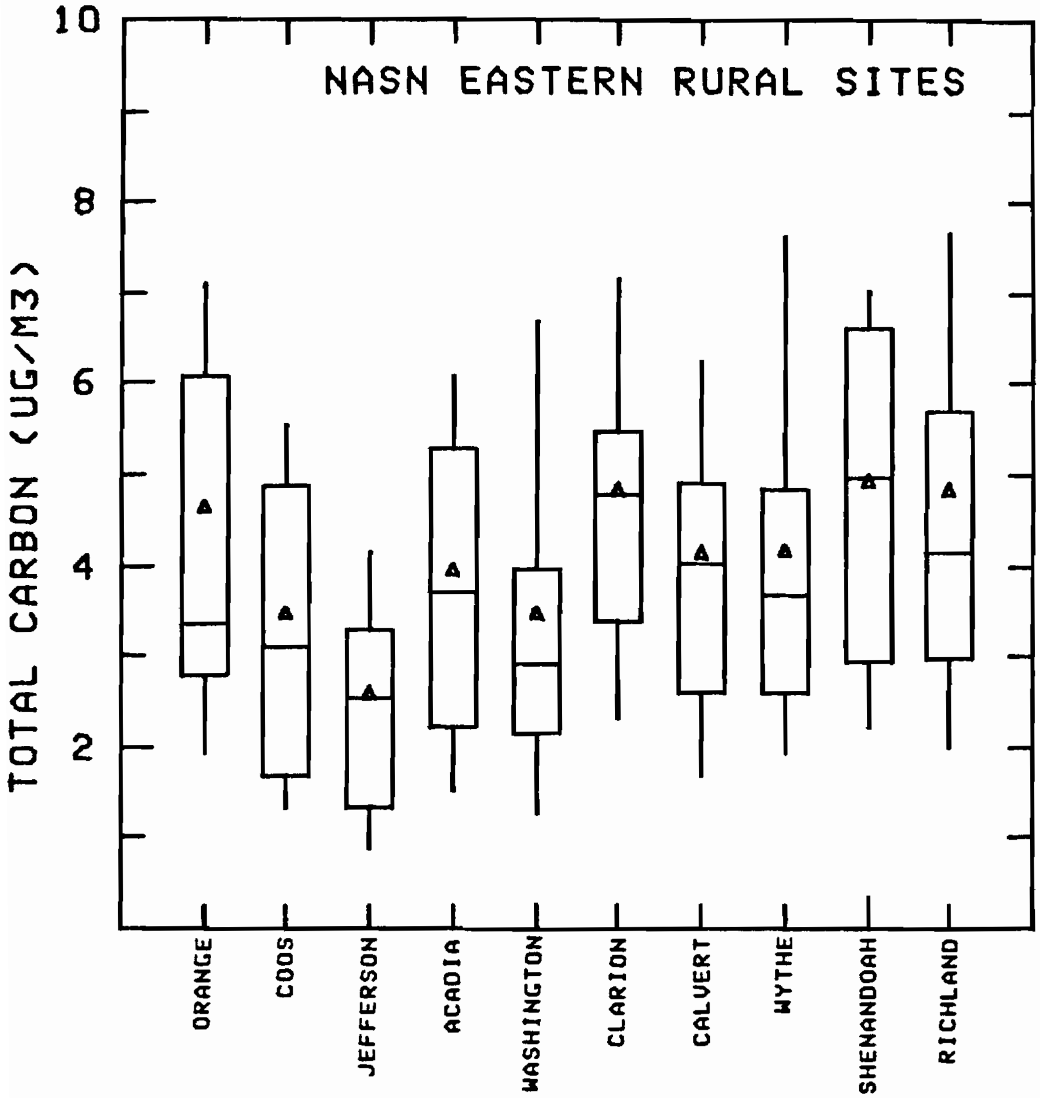

Figure B.6.a

Box plot of total carbon for NASN eastern rural sites.

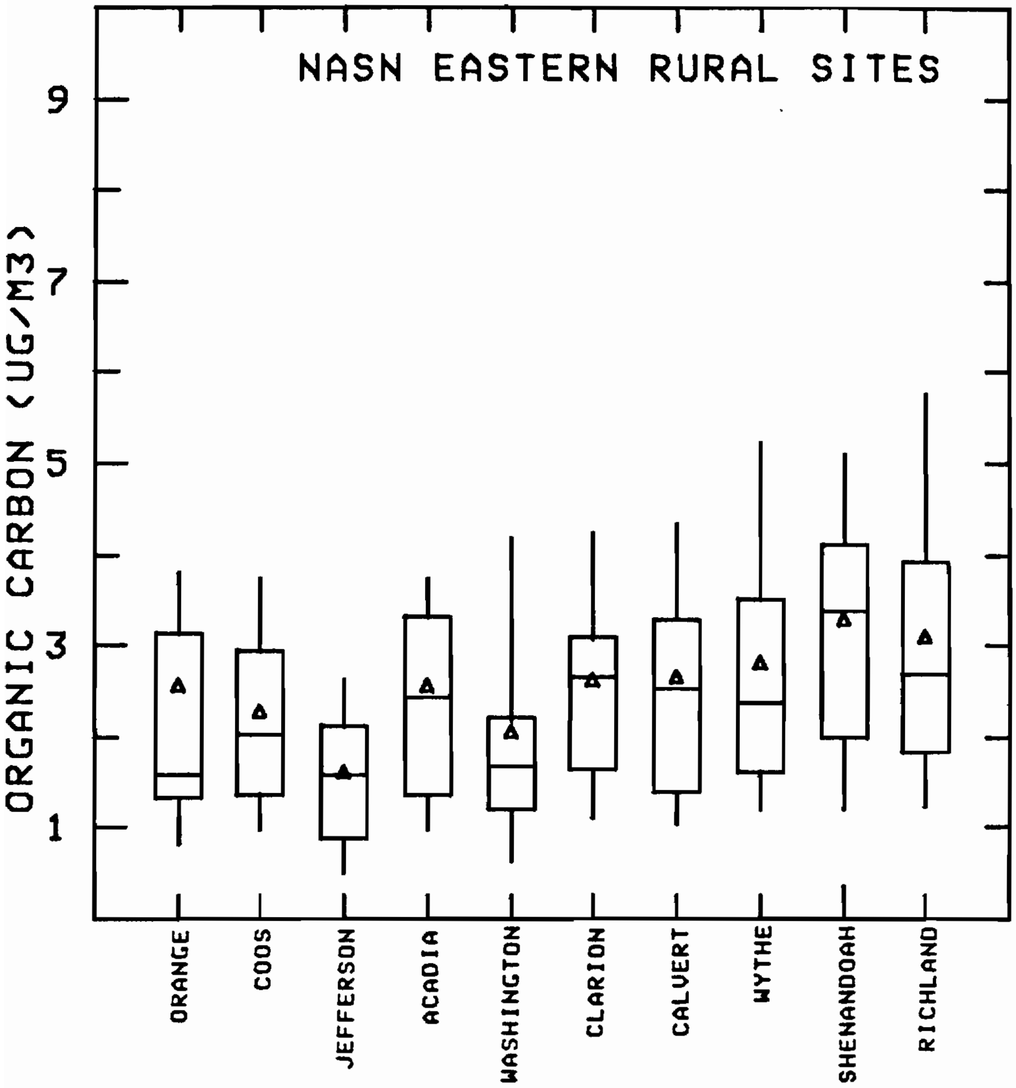

Figure B.6.b

Box plot of organic carbon for NASN eastern rural sites.

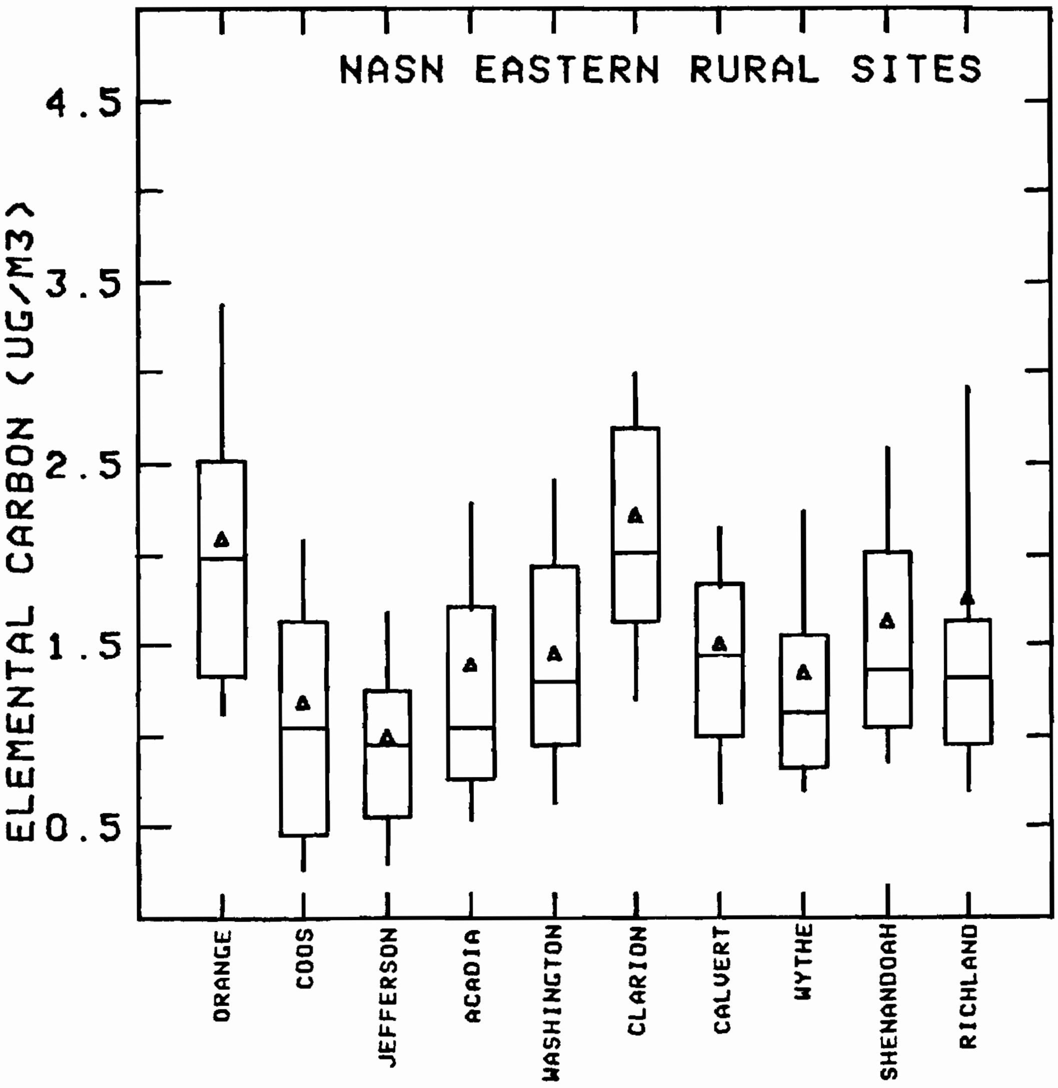

Figure B.6.c

Box plot of elemental carbon for NASN eastern rural sites

APPENDIX C

SOURCES OF CARBONACEOUS AEROSOL IN NEW YORK CITY

Introduction

The goal of the research reported here was to evaluate the applicability of the multiple linear regression method for the determination of the sources of organic (OC), elemental (EC), and total carbon (TC) in aerosol samples.

Experimental

Weekly samples of total aerosol (TSP) for 1975 and fine aerosol ($d_p < 3.5$ μm) for the period June 1978 to June 1979 were obtained from the New York University Medical Center (NYUMC). Samples were collected on the roof of a residence hall 14 stories high located on East 30th Street between 1st Avenue and the FDR Drive in Manhattan. The 1975 TSP samples were collected on Gelman type A glass fiber filter paper. Weekly fine aerosol samples during 1978-79 were collected on pre-fired Gelman type A/E glass fiber filters for carbon analysis. Simultaneous samples of fine aerosol and TSP were also collected on Gelman Spectrograde filters for trace metal and sulfate analysis during 1978-79. The sampling systems and location have been described in detail by Kleinman (1977).

The 1975 samples were analyzed for Pb, V, Mn, Cu, Fe, Cd, Ni, Cr, Zn, Na, and K by atomic absorption spectrometry and the 1978-79 samples for Pb, V, Mn, and Cu. The samples were also analyzed for organic and elemental carbon by a thermal/optical technique (Johnson et al., 1980, Chapter 2).

Data Analysis

A multiple linear regression model for carbonaceous aerosol can be written as:

$$F = \sum_{i=1}^{P} a_i C_i + a_o \qquad (1)$$

where F is the carbon concentration (OC, EC, or TC), P is the number of sources, C_i is the concentrations of the ith tracer, and a_i is the ith regression coefficient to be determined. For n observations ($n \geqslant P$), a set of simultaneous equations can be obtained to solve for the a_i's. The coefficients in Equation 1 were calculated using a stepwise regression routine (Chapter V).

Tracer elements were chosen on the basis of previous studies of New York aerosol which indicated that the principal sources of TSP and carbonaceous aerosol for New York City were automobiles, incinerators, fuel oil combustion, and resuspended road dust (Kleinman et al., 1980, Kleinman, 1977). On the basis of factor analysis results obtained by Kleinman and Dailey (Kleinman, 1977; Daisey and Kneip, 1980), Pb, Mn/Fe, Cu/Zn, and V were selected as tracers for automobile exhaust, resuspended road dust, incinerators, and fuel oil combustion sources, respectively. For the 1975 data set Fe and Zn were selected as tracers for resuspended road dust and incinerators. For the 1978-79 data set fine Mn could not be used because of a strong association between Pb and Mn (r = 0.73) which was probably due to the use of methylcyclopentadienyl tricarbonyl (MMT) as an octane booster for unleaded gasoline during part of the sampling period (Daisey and Kneip, 1980). The use of Si or Ti as a tracer for resuspended soil would have been preferable; however, these samples were not analyzed for Si or Ti. Average concentrations for the chemical species are listed in Table C.1.

The initial regression analysis was performed using all the data points. However, it was noted that the regression coefficients were very sensitive to some of the data points. To identify these points, the observed carbon concentrations were compared with those calculated from the regression analysis. Those points which differed greatly from the calculated values were deleted to obtain a refined data set for which new regression coefficients were obtained. This process was continued until the regression coefficients for the model reached stable values (Table C.2.). About 10 points had to be deleted from each data set before the model stabilized. The overall fit and the form of the model improved, as seen in Table C.2., when the extreme values were deleted. Such points were usually associated with either an unusual value for one of the chemical components in the model or extreme meteorological conditions (heavy rain, snow, or very low dispersion factor).

Table C.1. Concentration of trace metals and carbonaceous aerosol in New York City for the weekly samples in $\mu g/m^3$.

Element	1975 TSP Samples	1978-79[a] Fine Samples
Organic carbon	5.42	5.14
Elemental carbon	4.71	3.12
Total carbon	10.13	8.27
Sulfates	7.7	6.35
Pb	1.087	0.665
V	39.5×10^{-3}	46.2×10^{-3}
Mn	19.7×10^{-3}	6.2×10^{-3}
Cu	44.6×10^{-3}	20×10^{-3}
Ni	26.4×10^{-3}	--
Fe	1.088	--
Mn(C)[b]		21.3×10^{-3}
Mass concentration	51.7	26.5

[a] Fine ($d_p < 3.5$ μm) concentrations.

[b] Mn concentration as measured on total aerosol filter.

Table C.2. Sensitivity of total carbon regression coefficients to selective removal of data points (1975 data).

Number of Points	Correlation Coefficient	b_o	Regression Coefficient for Pb	V	Fe	Zn
36	0.57	5.5	1.1	38	1.74	--
32	0.71	3.8	2.6	40	1.8	--
30	0.79	2.3	3.4	49	1.7	2.5
28	0.82	2.3	3.3	46	1.4	4.5
26	0.86	1.6	3.7	44	1.5	4.6

The stability of the regression coefficients was further checked by deleting one observation at a time from the refined data set and performing the regression on n-1 observations. The data points that had significant impact on the overall relationship or any specific coefficients were flagged. The overall fit for the model improved slightly and the constant term was reduced when the flagged values were deleted from the data; however, the relationship did not change. This procedure allowed the underlying pattern in the data set to be explored and explicitly rejected "atypical" observations.

Results

The final regression equations for organic, elemental, and total carbon are given in Table C.3 for the 1975 data and in Table C.4 for the 1978-79 data. The average source contributions were calculated using the individual regression equations and the average tracer concentrations and are listed in Tables C.5 and C.6. For the 1975 data automotive emissions accounted for 35% (3.5 $\mu g/m^3$), residual oil combustion for 17% (1.7 $\mu g/m^3$), resuspended road dust 14% (1.4 $\mu g/m^3$), and incinerators for 13% (1.3 $\mu g/m^3$) of total carbon. For the 1978-79 fine aerosol data the automotive contribution was 26% (2.1 $\mu g/m^3$) of total carbon with residual oil, resuspended soil, and incinerators accounting for 20, 25, and 7% respectively. The large contribution of road dust to fine carbon is unusual. It is likely that the tracer element (coarse Mn) was influenced by emissions of Mn from automobiles burning gasoline with MMT as a fuel additive and was not appropriate for soil. When coarse Mn was not included in the regression model, the automotive contribution rose to 32%, and the contributions from residual oil combustion and incinerators were 16%.

The source contributions to organic and elemental carbon are also listed in Tables C5 and C6. For 1975 automotive emissions were the principal source of organic carbon, but for 1978-79 the source contributions were more evenly distributed. For both data sets approximately 20% of the total carbon could not be explained. This unexplained carbon was primarily elemental and comprised 40-50% of elemental carbon.

Table C.3. Regression model for carbonaceous aerosol in New York City during 1975. Total aerosol samples, 28 observations. All concentrations in $\mu g/m^3$.

$$\mathrm{TC} = (3.28 \pm 1.04\,[b]) \times \mathrm{Pb} + (46.2 \pm 15.6) \times \mathrm{V} + (1.39 \pm 0.78) \times \mathrm{Fe} + (4.53 \pm 2.75) \times \mathrm{Zn} + 2.26$$

$$(r = 0.82,\ \overline{\mathrm{TC}} = 10.1)$$

$$\mathrm{OC} = (3.05 \pm 0.96) \times \mathrm{Pb} + (17.5 \pm 10) \times \mathrm{V} + (1.3 \pm 0.5) \times \mathrm{Fe} + (1.21 \pm 1.68) \times \mathrm{Zn} - 0.027$$

$$(r = 0.84,\ \overline{\mathrm{OC}} = 5.23)$$

$$\mathrm{EC} = (0.23 \pm 1.4)\,[a] \times \mathrm{Pb} + (30.4 \pm 14) \times \mathrm{V} + (0.09 \pm 0.9)\,[a] \times \mathrm{Fe} + (3.3 \pm 2.5) \times \mathrm{Fn} + (2.5)\,[a]$$

$$(r = 0.52,\ \overline{\mathrm{EC}} = 4.88)$$

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[a] Values obtained by difference (i.e., TC - OC = EC).

[b] Standard error.

Table C.4. Regression model for carbonaceous aerosol in New York City for 1978-79. Fine aerosol samples, 24 observations. All concentrations in $\mu g/m^3$.

With Mn(C) in the equation:

$$TC = (2.29 \pm 0.47^{a}) \times Pb + (26.7 \pm 5.5) \times V + (94.4 \pm 24.4) \times Mn(C) + (20 \pm 13.8) \times Cu + (1.8206)$$

$$(r = 0.95,\ \overline{TC} = 7.98)$$

$$OC = (1.62 \pm 0.42) \times Pb + (17.6 \pm 5.0) \times V + (61.0 \pm 22.3) \times Mn(C) + (24 \pm 12.6) \times Cu + (0.5048)$$

$$(r = 0.93,\ \overline{OC} = 4.93)$$

$$EC = (0.72 \pm 0.26) \times Pb + (8.6 \pm 3) \times V + (29.8 \pm 12.3) \times Mn(C) + (1.28)$$

$$(r = 0.85,\ \overline{EC} = 3.06)$$

B. Without Mn(C) in the equation:

$$TC = (2.86 \pm 0.58) \times Pb + (21.4 \pm 7) \times V + (47 \pm 16) \times Cu + (2.93)$$

$$(r = 0.92,\ \overline{TC} = 7.98)$$

$$OC = (1.99 \pm 0.46) \times Pb + (14.2 \pm 5.6) \times V + (41.4 \pm 12.5) \times Cu + (1.22)$$

$$(r = 0.90,\ \overline{OC} = 4.93)$$

$$EC = (0.84 \pm 0.28) \times Pb + (7.8 \pm 3.3) \times V + (1.8496)$$

$$(r = 0.80,\ \overline{EC} = 3.06)$$

[a] Standard error.

Table C.5. Source contributions to carbonaceous aerosol for 1975 in percent. Average organic, elemental, and total carbon concentration of 5.35, 4.88, and 10.2 $\mu g/m^3$. (Total aerosol)

Source	Selected Tracer	% Contribution to Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)
Automobile	Pb	60 ± 13[b]	5 ± 30[a]	34 ± 11
Residual Oil	V	12 ± 7	23 ± 10	17 ± 6
Resuspended Soil	Fe	26 ± 10	2 ± 20[a]	14 ± 8
Incinerators	Zn	7 ± 9	20 ± 15	13 ± 8
Others		-5	51	22

[a] Values obtained by difference (i.e., EC = TC - OC).

[b] Errors calculated using the standard error of the regression coefficient.

Table C.6. Source contributions to carbonaceous aerosol for 1978-79 in percent (fine aerosol). Average organic, elemental, and total carbon concentrations of 4.93, 3.06, and 7.98 μg/m^3.

		% Contribution to		
Source	Tracer	Organic Carbon (OC)	Elemental Carbon (EC)	Total Carbon (TC)
Automobile	Pb	30 ± 8[b]	21 ± 8	26 ± 5
Residual Oil	V	21 ± 6	16 ± 6	20 ± 4
Resuspended Soil	Mn(C)	26 ± 10	21 ± 9	25 ± 7
Incinerators	Cu	13 ± 7	--	7 ± 5
Others		10	42	23

[b] Same as Table C.5.

The sources of this unexplained carbon undoubtedly include combustion of diesel and distillate oils. Such sources were not included in the model because suitable tracers are not available. In evaluating these results, it is important to note that the relative uncertainties in the source apportionment are large(20% to >100%). Thus, the absolute contributions of individual source types must be viewed with caution.

The source apportionment results for organic carbon (Tables C.5 and C.6) are in contrast with the results of Daisey and Kneip (1980) who found residual oil combustion to be the principal source of extractable organics. In our analysis many data points were deleted during sensitivity analysis. These included periods corresponding to extremely cold conditions during which the combustion of residual oil for space heating would be large. This is a possible cause of the discrepancy. Another possibility concerns inherent limitations in the multiple linear regression method of source apportionment. Several tests of the method follow.

The regression coefficients listed in Tables C.3 and C.4 should correspond to ratios of carbon to tracer element (e.g., C/Pb) for the sources which the tracers represent. Thus, comparison of the regression coefficients with actual source composition data should give some measure of the quality of the regression results. Table C.7 provides such a comparison. With the exception of the vanadium coefficient for 1975, all the regression coefficients fall within the range of measured compositions. The decrease in the Pb regression coefficient from

Table C.7. Carbon to tracer element ratios.

Tracer	Range from Source Data	Regression Results 1975	Regression Results 1978-79
Pb	2.8-6.7(1,2,11)	3.3 ±1	2.3 ±0.5 2.9 ±0.6[a]
V	0.7-34(1,12)	46 ±15	27 ±6
Mn	40-170(1)	--	94 ±24
Fe	0.7-3.5(1)	1.4	--

[a] Without Mn(C) in the regression model.

1. Analysis of source samples
2. Watson (1979)
11. Pierson (1981)
12. Miller et al. (1972)

1975 to 1978-79 is difficult to understand, however. The increased use of unleaded gasoline and the decreasing concentration of lead in gasoline during the 1975 to 1979 suggest an increase in the regression coefficient over this period. This apparent discrepancy might simply reflect different size distributions for auto exhaust lead and carbon. (For 1975, total (i.e., TSP) aerosol data were used as contrasted to 1978-79, for which fine aerosol data were used.) Alternatively, the discrepancy could be associated with limitations in the regression model arising from intercorrelation among the tracer elements and failure to include all significant sources with their appropriate tracers.

Another test of the regression model is to compare the regression results for the organic-elemental split for different sources with actual measured values from source samples. Such a comparison is shown in Table C.8 in which the percentage of total carbon which is organic (i.e., OC/TC) is listed for the various sources. Within the limits of uncertainty there is general agreement between the regression results and the source measurements, although the large uncertainties in the regression results do not lend much confidence to such comparisons. No physical conclusions regarding the difference in the regression results between 1975 and 1978-79 can be drawn because of the large uncertainties in the regression results.

One final point can be noted from the regression analyses. Tables C.5 and C.6 indicate a factor of two decrease in the automotive contribution to organic carbon between 1975 and 1978-79. This is presumably associated with the large growth in the number of catalyst-

Table C.8. Calculated and measured organic carbon fractions (OC/TC).

Source	Regression Results 1975	 1978-79	Source Measurements
Automobile	93 ±42	71 ±23	89 ±4(1,2,11) (leaded) 59 ±8(1,2,11) (unleaded) 22 ±4(1,2,11) (diesel)
Residual Oil	38 ±25	66 ±23	70 ±30(1)
Soil Dust	94 ±64	65 ±29	90 ±10(1)

1. Analysis of source samples.
2. Watson (1979)
11. Pierson (1981)

equipped vehicles during that period. Such vehicles emit substantially less particulate matter in general than vehicles without catalytic control devices. Such reasoning is complicated, however, by the use of total aerosol for 1975 and fine aerosol for 1978-79.

Conclusions

The multiple linear regression methodology has been used to calculate the contributions of various sources to carbonaceous aerosol in New York City. The important question which must be asked concerning these results, however, is: how well can they be validated? Comparison of the regression coefficients to elemental ratios (e.g., C/Pb) determined from actual source measurements gave reasonable agreement. However, no conclusions from the organic-elemental speciation could be drawn because of the large propagated uncertainties. Relative uncertainties in the source apportionment results were also substantial and ranged from a minimum of about 20% to more than 100% for sources with relatively small contributions. Because of the importance of accurate source apportionment in control strategy development, it would seem prudent to utilize a set of receptor models (e.g., multiple linear regression and chemical element balance) to determine source impacts. Comparison with emission inventory methods and dispersion model results would also be useful. Finally, careful evaluation of the attendant uncertainties in the model results is necessary to determine the level of confidence which can be attached to the results.

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VITA

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