Source Apportionment
and
Characterization of Ambient Fine Particles
in
Delhi, Mumbai, Kolkata, and Chandigarh

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1.0. Executive Summary

The objective of this study is to characterize fine particle air pollution in the three Indian megacities of Delhi, Mumbai, and Kolkata and quantify how major sources impact the observed levels. During the months of March, June, October, and December of 2001, atmospheric fine particle samples were collected over consecutive 24-hour periods in those cities. Samples were also taken during the summer at Chandigarh, a background site upwind of Delhi. Peaks of the average fine particle mass concentrations occurred during the winter and the lowest concentrations occurred during the summer in all of the three megacities sampled. Average fine particle mass concentrations during the winter season in the cities were 230.9±1.6 μg m^{-3} in Delhi, 88.9±0.5 μg m^{-3} in Mumbai, and 304.5±1.1 μg m^{-3} in Kolkata. Average fine particle mass concentrations during the summer were 49.5±0.6 μg m^{-3} in Delhi, 21.0±1.4 μg m^{-3} in Mumbai, 26.5±0.5 μg m^{-3} in Kolkata, and 29.2±0.7 μg m^{-3} in Chandigarh. Low rainfall, air stagnation, and atmospheric inversions during the winter months lead to increased fine particle mass, whereas the monsoon rains scavenge particles during the summer, reducing the atmospheric concentrations during that time. Most of the observed $PM_{2.5}$ concentrations in Delhi and the wintertime $PM_{2.5}$ concentrations in both Mumbai and Kolkata exceeded the U.S. EPA 24-hour average $PM_{2.5}$ standard of 65 μg m^{-3} signifying unhealthy air quality during that time. Moreover, the apparent fine particle annual average concentrations for the cities sampled are well above the annual US standard of 15 μg m^{-3}.

Organic carbon (OC), elemental carbon (EC), NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, and trace metals, were analyzed. During winter, OM and EC were respectively 58% and 8% in Delhi, 53% and 9% in Mumbai, and 67% and 9% in Kolkata. Sulfate was the next largest contributor. Detailed organic speciation using GC/MS techniques was further conducted to characterize the composition of organic carbon. Fifty-five organic compounds were quantified in this study, including n-alkanes, polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, and levoglucosan. Annual average concentrations for four seasonal periods were determined for three out of the four sites. Summertime concentrations for levoglucosan, picene, and the sum of hopanes and steranes were respectively 210±42 ng/m^3, 0.3±0.06 ng/m^3, and 8.5±1.7 ng/m^3 (for Delhi); 75±15 ng/m^3, 0.3±0.06 ng/m^3, 15±3 ng/m^3 (for Kolkata); 140±28 ng/m^3, 0.2±0.04

ng/m^3, and 41±8 ng/m^3 (for Chandigarh).   Wintertime concentrations for the same compounds were respectively 5260±1052 ng/m^3, 5.1±1.0 ng/m^3, and 80±16 ng/m^3 (for Delhi); 5490±1098 ng/m^3, 7.1±1.4 ng/m^3, 110±22 ng/m^3 (for Kolkata); 910±180 ng/m^3, 0.9±0.2 ng/m^3, 23±5 ng/m^3 (for Mumbai). Summertime Mumbai and wintertime Chandigarh measurements were not available. The higher amounts of levoglucosan and picene in the winter suggest increased amount of wood and coal used for home heating purposes during the colder months. Almost no cholesterol was detected in any of the samples suggesting that the amount of meat cooking is minimal and negligible. This is reasonable as most Indians are vegetarian and thus meat consumption is low in the country compared to other countries.

Relative contributions of crustal oxides or dust to the fine particle mass reached a peak during the spring and the summer time in all of the three cities. These crustal elements were probably emitted in these cities principally in the form of fugitive dust from local sources and long range transport of desert dust (Carrico et al., 2003). It is interesting to note that the annual average lead concentrations were 0.58±0.03 μg m^{-3}, 0.14±0.01 μg m^{-3} and 0.86±0.04 μg m^{-3} in Delhi, Mumbai, and Kolkata respectively. Lead concentrations seem to increase during the colder months leading to concentrations as high as 2.39 μg m^{-3} in Delhi (January 4, 2002), 0.48 μg m^{-3} in Mumbai (December 11, 2001), and 3.36 μg m^{-3} in Kolkata (December 17, 2001). Unleaded petrol was introduced in Delhi in 1995 to cut lead emissions, and by September 1, 1998 Delhi became lead free with the complete phase out of leaded petrol. However, our results show that lead is still present in these cities, probably from re-entrainment of lead-laden dust or from smelter activities.

Finally, the results obtained from organic speciation analysis were used in a Chemical Mass Balance (CMB) model, along with organic emissions profiles and key organic tracers typical of urban sources, to quantify the primary source contributions to the PM$_{2.5}$ mass concentrations in each of those four cities. Five important sources were identified and quantified: diesel (or compression ignition CI) exhaust, gasoline exhaust, road dust, coal combustion, and biomass combustion. It should be noted, here, that diesel exhaust in this study comprises all forms of diesel combustion products since the organic tracer techniques used cannot distinguish between the different sources of diesel combustion or usage of slightly different fuels. Important trends in the seasonal and spatial patterns of the impact of

these five sources were observed. Primary emissions from fossil fuel combustion (coal, diesel, and gasoline) were responsible for 22-33% of $PM_{2.5}$ mass in Delhi, 23-29% in Mumbai, 37-70% in Kolkata, and 24% in Chandigarh. These figures can be compared to the biomass combustion contributions to ambient $PM_{2.5}$ of 9-28% in Delhi, 12-21% in Mumbai, 15-31% in Kolkata, and 9% in Chandigarh. Our results suggest that fossil fuel combustion seems to dominate in each of these cities with significant contributions from biomass and soil dust.

These measurements provide important information about the seasonal and spatial distribution of fine particle-phase inorganic and organic compounds in India as well as quantifying source contributions leading to the fine particle air pollution in Indian cities. Uncertainties in this work come from the small number of samples taken for each city throughout the seasonal periods specified, from the usage of source profiles from other parts of the world, other uncertainties and variabilities in source profiles, and measurement uncertainties.

2.0 Introduction

Air pollution from particulate matter in developing countries, like China and India, has worsened dramatically in the last several decades. Rapid industrialization and urbanization during this time have led to an increase in anthropogenic emissions from both fossil fuel and biomass combustion. Ramanathan et al. (2001) and other researchers participating in the INDOEX study have observed a large anthropogenic haze spreading over most of the North Indian Ocean, and South and Southeast Asia between December and April. In fact, ground level fine particle concentrations as high as 24.7 ± 0.2 μg m^{-3} were reported during INDOEX at a remote island off the coast of India (Chowdhury et al., 2001). Such high PM levels are comparable to the fine particle concentrations observed in many US cities, like Atlanta, Houston, and Los Angeles. In India, the Central Pollution Control Board (CPCB) and the National Environmental Engineering Research Institute (NEERI) have focused their efforts on measurements of PM_{10} and TSP (NEERI 2000). Studies have shown that it is $PM_{2.5}$ instead of PM_{10} that contribute to the visibility problem and are likely responsible for respiratory and cardio-pulmonary diseases like asthma, bronchitis, and heart disease (Dockery et al., 1993 Pope et al., 2002). However, $PM_{2.5}$ has not been historically measured in India. Except for the study conducted in Mumbai by Venkataraman et al. (2002) during INDOEX, there have not been other studies in measuring the mass and chemistry of the fine particulate matter in Indian cities.

In the absence of detailed measurements of fine particulate matter, detailed emission inventory, and appropriate emission factors for South Asian-city specific sources, quantitative identification of major anthropogenic sources responsible for the worsening of air pollution in key Indian cities has been difficult to achieve. A different approach to identifying sources is to use receptor-based techniques which rely on identification of key tracers in sampling sites (receptors). Such a receptor-based source apportionment has been carried in Bangladesh using inorganic elemental analysis of $PM_{2.5}$ (Begum et al., 2004). In India, no such work has been published. Models using primarily inorganic elements have limitations when examining fine particulate mass since a significant fraction of the fine particulate mass in the urban atmosphere is from combustion sources. These sources emit fine particles largely comprised of organic carbon with only trace levels of inorganic

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elements. The trace elements present in the fine particle emissions from several important urban air pollution sources are not sufficient to provide unique fingerprints that can be used to properly distinguish the sources in a source-receptor model. The organic compounds present in fine particles emitted from cooking meat, burning wood, combustion of automotive fuels, and cigarette smoking are very different. These differences can be exploited by receptor models to determine their respective contributions to the atmospheric concentrations of fine particulate matter (Schauer et al., 1996).

Motivated by the INDOEX findings, in this study, a detailed analysis of ambient $PM_{2.5}$ has been carried out in Delhi, Mumbai, Kolkata, and Chandigarh. These measurements serve many purposes. First, they provide a description of the mass and chemical characteristics of fine particulate matter conducted for the first time ever in those four cities. Second, the data obtained have been used to quantify sources in these cities using Chemical Mass Balance modeling.

3.0. Experimental Setup

3.1. Sampling Protocol

One year's worth of ambient sampling was conducted in Delhi, Mumbai, and Kolkata-- three of the megacities located in India. Four months from the entire year were selected to represent the seasonal pattern observed in the region. Five samples every six days were taken for each of the four months sampled. The selected four months were:

1. March to represent spring,
2. June to represent summer,
3. October to represent autumn, and
4. December to represent winter.

Besides the above listed three sites, a fourth site, Chandigarh, upwind of Delhi was also selected to represent background conditions for India. After analyzing five years of backwind trajectories from NOAA, Chandigarh appeared to be suitable as a background site upwind to Delhi. It is a smaller city with a population of 809,000 located in the northern side of India. Suitable power supplies, availability of trained personnel, cost of transportation, and ease of communication were limiting factors in selecting Chandigarh as the background site. Inspite

of efforts to take samples for four seasons, only five samples during the summer season were obtained; the rest of the sampling protocol could not be completed.

Figure 1 shows the location of the four cities in the Indian subcontinent where the samples were taken and Table I describes the sites. The sites at Delhi, Mumbai, and Kolkata were carefully selected to avoid undo influence of emissions coming from heavy city traffic or industrial work, yet they were located within the metropolitan cities, thus enabling the capture of the cities emissions throughout the day and the night. In each location, the samplers were placed either on rooftops or in the middle of open fields to ensure that the sampler inlet was able to sample wind coming from all directions. The Chandigarh site needed to be outside the limit of the main town and thus was located at the Postgraduate Institute of Medical Education and Research on a rooftop on the fourth floor. Figure 2 shows the sampling schedule that was followed during the year 2001. Sampling started on March 4, 2001 and continued until January 16, 2002. Samples were collected at ambient temperatures and relative humidities for 24 hours starting at midnight local time every sixth day for each of the months sampled. After the completion of the sampling campaign, the number of useful samples were: 21 for Delhi, 25 for Mumbai, 20 for Kolkata, and 5 for Chandigarh.

3.2. Instrumental Setup

A Caltech-built, $PM_{2.5}$ filter sampler was used at each of the four sites. Sampling equipment is shown schematically in Figure 3. Fine particulate matter was collected on one quartz fiber filter (Pallflex, 2500 QAO, 47 mm diameter), two pre-washed Nylon Filters (Gelman Sciences, Nylasorb, 47 mm diameter), and on two PTFE filters (Gelman Sciences, Teflo, 1.0 μm pore size). (Refer to Table II for characteristics of the filter substrates used.) Ambient air was drawn at a rate of approximately 22.5 lpm through an acid-washed Pyrex glass inlet line to a Teflon-coated Air and Industrial Hygiene Laboratory (AIHL)-design cyclone separator (John and Reischl, 1980), which removed large particles with a collection efficiency curve having a 50% aerodynamic cutoff diameter at 2.5 μm before the air passed through the filters. The nylon filter located downstream of the MgO-coated diffusion denuder was used in conjunction with the nylon filter downstream of the cyclone alone to measure gas-phase nitric acid, hydrochloric acid, and fine particle nitrate by the denuder

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difference method. The air flowrate through each filter was measured before and after each 24-hour sampling period with a calibrated rotameter.

3.3. Analytical Methods:

3.3.1. Inorganic Chemical Analysis:

Both unexposed filters and exposed samples were kept in individual Petri dishes and sealed with Teflon tape. To ship filters and samples by FedEx between the United States and India, ice-coolers with blue-ice packets were used to ensure that the temperature of the filters during shipment would remain cool enough to prevent sample degradation. All PTFE filters were gravimetrically analyzed at Georgia Tech by the same operator by repeated weighing before and after the experiment on a Mettler Toledo microbalance maintained in a temperature- and humidity-controlled environment ($20.5 \pm 0.2^{\circ}C$, $39 \pm 2\%$ RH). Once weighing was completed, samples were stored in freezers until ready for chemical analysis.

One of each pair of PTFE filter samples was analyzed by ion chromatography (Dionex Corp, Model 2020i) for the anions NO_3^-, SO_4^{2-}, and Cl^- (Mulik, 1976) and by an indophenol colorimetric procedure for NH_4^+ (Bolleter, 1976) using an Alpkem rapid flow analyzer (Model RFA-300). The second set of each of these sample sets was analyzed for trace elements using X-Ray Fluorescence (XRF) by the Desert Research Institute (DRI). Quartz fiber substrates were analyzed for elemental and organic carbon content using the thermal-optical carbon analysis method of Huntzicker et al. (1982) as modified by Birch and Cary (1996). In the thermal evolution and combustion method of Birch and Cary (1996), elemental carbon is defined as carbon that resists volatilization up to a temperature of $900^{\circ}C$ in an inert atmosphere in a manner similar to graphite, and also is black. In this report, we will use the term Elemental Carbon (EC) to define the carbon detected by the method used. Variations in elemental carbon values between alternative methods can arise due to differences in the way that alternative methods correct for charring of the samples during analysis. Table III lists the analytical methods being used to analyze the various samples.

3.3.2. Organic Chemical Analysis:

Extraction of particle-phase organic compounds collected on quartz fiber filters was based on the methods described by Mazurek et al. (1987) and further refined by Schauer et al. (1996) and Zheng et al. (2002). Samples were combined by season and extracted in annealed glass jars with Teflon-lined lids. Mumbai summertime samples did not contain enough organic carbon (OC) for acceptable GC/MS analysis and thus were not analyzed. In addition, filter blanks as well as lab blanks were analyzed. Filter blanks were prepared, stored, shipped in the same manner as the samples, and lab blanks were used to identify possible contaminants from handling samples in the laboratory. Results from both field and lab blanks were carefully analyzed and subtracted before reporting the final results. In total, 23 samples were analyzed including field and laboratory quality assurance/quality control (QA/QC) blanks.

The samples were first spiked with an internal standard mix containing 16 deuterated compounds. These deuterated internal standards as well as standard mixtures were provided by the Wisconsin State Hygiene Laboratory. The deuterated internal standards were: dodecane-*d*26, hexadecane-*d*34, eicosane-*d*42, octacosane-*d*58, hexatriacontane-*d*74, benzaldehyde-*d*6, decanoic acid-*d*19, heptadecanoic acid-*d*33, phthalic acid-3,4,5,6-*d*4, acenaphthene-*d*10, 4,4′-dimethoxybenzophenone-*d*8, dibenz(ah)anthracene-*d*14, chrysene-*d*12, ααα-20R-cholestane-*d*4, cholesterol-2,2,3,4,4,6-*d*6, and levoglucosan-13C6. These internal standards provided internal quantification references for the key particle phase organic compounds covering their range of mass spectral fragmentations, polarity, and reactivitiy with derivatization reagents. About 250 μL of the internal standard mix was spiked per milligram of OC. The amount of spiked internal standard mix was proportional to the amount of the OC present in the sample. Samples were extracted under mild sonication (20 minutes) twice with hexane (Fischer Optima Grace), followed by three successive extractions using a 2:1 mixture of benzene and isoproponal (benzene—high purity lots of E&M Scientific Omnisolv; isopropanal—Burdick & Jackson). High purity benzene was further distilled in the laboratory to remove the small fraction of impurities and tested for purity by GC/MS prior to use. The extract was filtered to remove loose filter materials, and the volume was reduced to about 5 mL using a rotary evaporator. Finally, it was blown down

close to the volume of injected internal standard using ultrapure N_2. The extract was split into two fractions. One fraction was derivatized with diazomethane to convert organic acids to their methyl ester analogues which are better identitied and quantified using GC/MS.

A Hewlett-Packard GC/MSD (6890 GC and 5973MSD) equipped with a 30 m l. x 0.25 mm i.d. x 0.25 μm film thickness HP 5 MS capillary column was used. The operation conditions were: isothermal hold at 65°C for 2 min, temperature ramp of 10°C min^{-1} to 300°C, isothermal hold at 300°C for 22 min, GC/MS interface temperature 300°C. The flow of the carrier gas, He, was 1 mL min^{-1}. The injection volume was 1 μL for each sample. The scan range was 50-500 amu, and the sample was analyzed under electron ionization mode (70 eV). These same instrumental settings were used by Zheng et al. (2002). Not all organic compounds were solvent extractable, nor were they all elutable from a GC column. Hundreds of authentic standards have been prepared for the positive identification and quantification of the organic compounds available from the Wisconsin Hygene Laboratory. Estimated measurement uncertainties of the measured organic compounds by GC/MS techniques as found by Schauer et al (1999a) used in the present study were ±20% (1 sigma).

3.4 Chemical Mass Balance Modeling:

Chemical Mass Balance (CMB 8.0) (Watson et al., 1990) modeling was used to apportion $PM_{2.5}$ particles to various sources. The CMB receptor model consists of a solution to linear equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profile abundances (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the CMB model. In order to distinguish among source type contributions, the measured chemical and physical characteristics must be such that they are present in different proportions in different source emissions and changes in these proportions between source and receptor are negligible or can be approximated. The CMB calculates values for the contributions from each source and the uncertainties of those values.

The CMB is applicable to multi-species data sets, the most common of which are

chemically characterized particulate matter (PM) and volatile organic compounds (VOCs). Although not perfect, source apportionment modeling is a powerful tool for inferring sources of atmospheric PM given a high quality set of observations and the needed source profiles. Refer to Watson et al. (1990) for the mathematics involved in CMB modeling. Model assumptions, as described by Watson et al. (1990) are:

1) Compositions of source emissions are constant over the period of ambient and source sampling
2) Chemical species do not react with each other, rather they add linearly
3) All sources with a potential for contributing to the receptor have been identified and have had their emissions characterized
4) The number of sources or source categories is less than or equal to the number of species
5) The source profiles are linearly independent of each other, and
6) Measurement uncertainties are random, uncorrelated, and normally distributed.

CMB can tolerate reasonable deviations from these assumptions, though deviations increase the stated uncertainties of the source contribution estimates (Cheng and Hopke, 1989).

In the present study, CMB was conducted using organic compounds as molecular markers. An important aspect of molecular marker source apportionment is the selection of organic compounds that can be properly used as tracer species in the model. Fifty-five organic compounds, along with Al, Si, and elemental carbon (EC) have been quantified in this study by using the methods described by Mazurek et al. (1987) and further refined by Schauer et al. (1996). These compounds have been selected carefully so they can be used as tracer species in the CMB model. These species do not form, do not significantly react, nor have other selective removal processes (i.e. volatilization) in the atmosphere. Table IV has a list of the compounds (along with their major urban sources) that have been quantified. The above compounds were identified for each season and used as input to the CMB model. After repeated analysis, out of the fifty-five identified organic compounds, thirty-two were selected as fitting species (see Table V). Source profiles are the key parameters used in CMB modeling. Eighteen source profiles, as described in Table VI, were selected for this study. These source profiles were put together at California Institute of Technology using the same laboratory procedures described previously for atmospheric samples using the same quantification standards as used in this study. Whenever possible, source profiles from the Indian Subcontinent were selected. Five source profiles selected from Bangladesh were:

coconut leaves, rice straw, cow dung, jackfruit wood, and biomass briquette. Sheesley et al. (2003) describes in detail these five sources from Bangladesh. Source profiles for diesel engine exhaust, gasoline-powered vehicle exhaust, road dust, and natural gas combustion were obtained from previous studies in North America and applied to this study (Hildemann et al., 1991; Rogge et al., 1993b; Schauer, 1998; Schauer et al., 1999a, 1999b, 2002a; Zheng et al., 2002). The coal source profile was obtained from the analysis of fine particulate matter emitted from the burning of Datong coal in China (Zheng et al., in preparation). Given that not all of the source profiles have been directly measured in India, the model inputs serve as best estimates of the actual emission profiles based on available data. However, tracer species are limited to a few characteristic tracers per source and so they are more specific to the sources than to the locations. It should be noted in here that the identification of sources carries a lot less uncertainties than the quantification since CMB can over quantify source contributions. The results and uncertainties in the modeling work are explained in the following sections in more details.

4.0. Results and Discussion

4.1. Regional Meteorology and Particulate Matter Concentrations:

Monsoon winds and rains control the extent of pollution seen over many of the South and East Asian countries, like India and China. Monsoon winds, which come from the Southeast and Southwest during the months of June, July, August, and part of September, are characterized by heavy rain and winds. The monsoon gathers moisture along its source region over the Indian Ocean and releases it in the form of rain over South and Southeast Asia. Conversely, the predominant wind direction during the winter is from the Northeast, and is characterized by a dry airmass producing almost no rain as the airmass travels over continental landmass. Because of this regional wind pattern, wet deposition of aerosol dominates during the summer causing a decrease in concentrations of the fine particles. This trend of decreasing aerosol mass during the summer monsoon has been captured in the present study and can be seen in Figures 4 and 5 which show the seasonal variations of the fine particle mass and chemical composition over Mumbai, Delhi, Kolkata, and Chandigarh.

Average fine particle mass concentrations during summer were 49.5 ± 0.6 μg m^{-3} in Delhi, 21.0 ± 1.4 μg m^{-3} in Mumbai, 26.5 ± 0.5 μg m^{-3} in Kolkata, and 29.2 ± 0.7 μg m^{-3} in Chandigarh. It was surprising to see summertime ambient fine particulate matter concentrations in Chandigarh exceeding those of Mumbai and Kolkata. Both Mumbai and Kolkata are located near the Arabian Sea and the Bay of Bengal respectively; whereas Delhi and Chandigarh are located in the middle of the Indian subcontinent. Proximity to the ocean and the influence of diurnal land and sea breezes aid in the dilution of the aerosol concentration seen in both Mumbai and Kolkata since ocean air is cleaner than continental air. Furthermore, five years (Jan 1995 to Dec 1999) of backwind trajectory analysis conducted by NOAA revealed that 62% of all trajectories arriving at Delhi during that time period experienced stagnation. Air stagnation reduces mixing, worsening the air quality in the northern Indian cities. In fact, Delhi records the highest fine particle mass concentrations throughout the year except for the month of December when Kolkata's fine particle mass concentrations exceed those observed in Delhi.

The highest concentration of aerosol mass is seen during the month of December, representing the winter season in all of the three cities sampled (no sample was taken in Chandigarh during winter). Average fine particle mass concentrations during the winter were 230.9 ± 1.6 μg m^{-3} in Delhi, 88.9 ± 0.5 μg m^{-3} in Mumbai, and 304.5 ± 1.1 μg m^{-3} in Kolkata. During the winter month of December, more stagnation of wind occurs in cities like Delhi, causing aerosol particles to remain suspended over the city for an extended period of time. Also, the lower temperatures during the winter months lead to lower atmospheric inversion layers where pollutants become trapped close to the ground, further increasing fine particle concentrations. Low rainfall, air stagnation, and atmospheric inversions during the winter months lead to increased fine particle mass in December. Understanding regional meteorology significantly aid in explaining the seasonal changes in air quality in these Indian cities.

India has yet to set a fine particle standard. In the absence of a fine particle standard, the US EPA's 24-hour $PM_{2.5}$ standard of 65 μg m^{-3} can be used to show the severity of the particulate pollution in India. The current study shows that most of the observed $PM_{2.5}$ concentrations in Delhi and the wintertime $PM_{2.5}$ concentrations in both Mumbai and Kolkata exceed the daily EPA $PM_{2.5}$ standard. Table VII shows the US EPA's pollutant standard

index for $PM_{2.5}$ which can be used for general assessment of health risks from existing air quality. 24-hr average of $PM_{2.5}$ concentration in the range of 40.5-65.4 $\mu g \ m^{-3}$ is considered as unhealthy for sensitive groups, 65.5-150.4 $\mu g \ m^{-3}$ as unhealthy, 150.5-250.4 $\mu g \ m^{-3}$ as very unhealthy, and above 250 $\mu g \ m^{-3}$ as hazardous. Wintertime air quality in Kolkata, Delhi, and Mumbai can be considered to be hazardous, very unhealthy, and unhealthy, respectively. Out of 21 samples collected in Delhi, the $PM_{2.5}$ concentrations from 16 samples are in the "unhealthy" or worse than "unhealthy" range. $PM_{2.5}$ is responsible for respiratory problems such as asthma and bronchitis, as well as reduction in visibility (Dockery et al., 1993). In a local Indian newspaper, Ms. Anumita Roy Chowdhury, a researcher at the Delhi-based Center for Science and Environment (CSE), mentioned that each year, air-pollution-related diseases claim some 52,000 lives in 36 Indian cities, including the capital New Delhi where the toll is 10,000. Particle pollution is so widespread that many visitors landing in Delhi by air during the winter time observe the thick haze over the city. Because of low visibility, flights to and from Delhi may be cancelled during the wintertime.

4.2. Fine Particle Chemical Analysis Results:

Seasonal variations in organic matter (OM) and elemental carbon (EC) were observed. OM and EC concentrations increase during the winter season compared to the rest of the year (see Figure 5 and Table VIII). Organic matter has been calculated by multiplying organic carbon by 1.4 to account for the H, O, N, and other elements typically found in organic matter. The percentage of OM and EC in the fine particle mass are 45.6% OM and 8.2% EC in Delhi during the summer and 58.1% OM and 7.5% EC in Delhi during the winter; 11.0% OM and 5.2% EC in Mumbai during the summer and 52.8% OM and 9.2% EC during the winter; 41.1% OM and 24.9% EC in Kolkata during the summer and 67.4% OM and 8.7% EC in Kolkata during the winter; and 34% OM and 4.5% EC in Chandigarh for the summer. Approximately half of all measured $PM_{2.5}$ is organic in nature and the concentrations for both OM and EC increase during the winter. To explain this seasonality in OM and understand the sources of this organic matter, it is important to conduct organic speciation and observe target organic compounds individually by season. The results of this work are described in the next section.

Elemental carbon (EC) and organic matter (OM) are emitted mostly from burning fossil fuels and biomass (Andreae, 1995). From previous source testing, we found that biomass burning has a lower ratio of EC to OC whereas fossil fuel burning emits more EC compared to OC (Chowdhury et al., 2004). The ratio of EC to OC is highest during the month of June for all the sites. This ratio reaches unity during June in both Mumbai and Kolkata, whereas in Delhi this ratio is approximately 0.3. However, the EC to OC ratio decreases to 0.2 to 0.4 during the remainder of the year in all three sites. A high EC to OC ratio signifies the dominance of fossil fuel burning over biomass burning. From this ratio analysis, it appears biomass burning increases during the winter leading to a lower EC to OC ratio during the winter.

Of the fine particle mass, sodium and potassium contribute 0.03-0.60% and 0.9-2.1% respectively in Delhi, 0.2-6.6% and 0.9-1.6% respectively in Mumbai, 0.01-1.0% and 1.2-2.0% respectively in Kolkata, and 0.5% and 2.0% in Chandigarh. High sodium concentrations are predominantly seen during the summer, indicating presence of marine aerosol (sea salts in the form of NaCl) in all of the cities, especially in Mumbai where 6.6% of the fine particle mass during June is from sodium ion. South east and south west monsoons carry sea salts from both the Bay of Bengal and the Arabic Sea. The presence of potassium during the year is an indication that biomass burning occurs in all four cities since potassium is an inorganic tracer for biomass. Biomass burning appears to peak during the winter month of December. A closer look at the organic speciation results in the next section will reveal more information on the extent of biomass burning.

Crustal oxide has been calculated by adding the oxides of aluminum, silicon, calcium, titanium, iron, and phosphorous. Relative contributions of crustal oxides or dust to the fine particle mass reach a peak during the spring and summer in all of the cities. During this time, contributions of dust to the fine particle mass are 6.28-12.7% in Delhi, 16.0-16.4% in Mumbai, 9.6-11.3% in Kolkata, and 13.3% in Chandigarh. These crustal elements are probably emitted principally in the form of fugitive dust. Al and Si are used as markers for dust as they are present as alumino-silicates or clay minerals. Carrico et al. (2003) conclude that in Nepal, long range transport of desert dust from arid regions is observed to the Indian subcontinent: they hypothesize that this dust comes from West India, the Middle East and perhaps as far as the Sahara. Saharan dust production peaks in March (Marticorena et al.,

1997). African dust transported eastward into the Middle East peaks in April (Ganor, 1994; Moulin et al., 1998). Effects of long range transport of desert dust may be present in these samples during peak dust seasons. However, Mumbai seems to experience high dust concentration throughout the year, possibly because of the heavy roads and buildings construction in the city.

The non-crustal metals analyzed in this study include Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Tl, Pb, and U. The percent contribution of non-crustal metals to the fine particle mass in all of the three cities is only about 1%, yet these metals are important in understanding the influence of anthropogenic activities. Energy production, industrial metal production, and vehicular traffic have brought about a serious increase in trace element emissions in the atmosphere. To compare these emissions with trace elements released from natural sources, one must take into account the scale of pollutant perturbations. According to Pacyna (1983), for some trace elements, such as Se, Hg, and Mn, global natural emissions exceed total releases from anthropogenic sources. Pacyna (1983) further explains that global emission inventories show that anthropogenic Be, Co, Mo, Sb, and Se are chiefly emitted from coal combustion. On the other hand, Ni and V are released mainly during oil firing. Smelters and secondary nonferrous metal plants emit the largest amounts of As, Cd, Cu, and Zn when compared with other sources. Cr and Mn are released mainly from factories producing iron, steel, and ferroalloys (Pacyna, 1983). It is interesting to note that the annual average lead concentrations were 0.58 ± 0.03 μg m^{-3}, 0.14 ± 0.01 μg m^{-3} and 0.86 ± 0.04 μg m^{-3} in Delhi, Mumbai, and Kolkata respectively. Lead concentrations seem to increase during the colder months leading to concentrations as high as 2.39 μg m^{-3} in Delhi (January 4, 2002), 0.48 μg m^{-3} in Mumbai (December 11, 2001), and 3.36 μg m^{-3} in Kolkata (December 17, 2001). In 1992, Shahandra in Delhi recorded the highest annual average of 8.5 μg m^{-3} (Aggarwal, 2001). Studies by Huntzicker et al. (1975) and Kowalczyk et al. (1978) suggested that lead emissions historically could serve as a tracer for all vehicle derived emissions, including both gasoline and diesel powered vehicles. Cass and McRae (1983) found that lead constitute 21.1% of the mass of fine particulate matter emitted from cars burning leaded gasoline. The fate of lead in gasoline has been studied extensively. Lead has been added traditionally to petrol to raise its octane level. Removing the lead from petrol can virtually eliminate the

largest source of lead in the cities using leaded fuel since it is the primary source of airborne lead emissions in such cities. Unleaded petrol was introduced in Delhi in 1995 to cut lead emissions, and by September 1, 1998 Delhi became lead free with the complete phase out of leaded petrol. However, our results show that lead is still present in these cities, probably from re-entrainment of lead-laden dust, from smelter activities, or residual lead in automobile systems.

Vehicular traffic in most Indian cities is disproportionately dominated by extremely polluting vehicles (Aggarwal et al., 1999). In December 1998, Saifuddin Soz, then the Union Minister for Environment and Forests, issued a white paper on Delhi's pollution mentioning that while the relative contribution of industries and domestic sources to total air pollution load in Delhi has been steadily declining since 1970, the contribution of automobile emissions has been increasing dramatically. Emission regulations have been very weak, particularly in the case of vehicular emissions and fuel quality. The vehicles manufactured are viewed as emitting high levels of pollutants even when they are new (Aggarwal et al., 1999). Under Supreme Court orders, the Ministry of Petroleum and Natural Gas (MPNG) introduced diesel with a 500 ppm wt sulfur content in the severely polluted cities of Delhi, Mumbai, and Kolkata. Table IX describes the changes of sulfur specifications that took place during the year 2001 in all of the three Indian megacities. All three Indian cities have switched sulfur content for all vehicles from 2500 ppm wt to 500 ppm wt at different months during the year 2001. As seen in Figure 6, reduction in sulfur content of diesel fuel appears to have decreased the ambient measured sulfate in all three cities. Continuation of similar measurements would support the validity of this finding.

4.3. Organic Speciation Results:

Results from organic speciation for all four cities are displayed in Figure 7, and are further analyzed and presented with key organic tracers in Figure 8. Organic speciation for the summertime Mumbai samples could not be conducted because of the low organic carbon levels.

Hopanes and steranes are organic markers that are present in heavy petroleum distillates such as lubricating oil (Simoneit, 1985, 1999; Simoneit et al., 1999). In the

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southern California atmosphere, these compounds have been shown to be predominately from the exhaust emissions of gasoline and diesel-powered motor vehicles and result from the presence of lubricating oil in PM emissions (Rogge et al., 1993ab, 1996, Schauer and Cass, 2000, Schauer et al., 2002). Wood smoke contributes to carbonaceous aerosol concentrations but not to hopane and sterane concentrations. Diesel vehicles are important sources of both elemental carbon and hopanes and steranes, while gasoline-powered vehicles are important sources of hopanes and steranes and smaller contributors to elemental carbon concentrations. On the other hand, levoglucosan is a major component of wood smoke aerosol and has been shown to be a good tracer for wood burning (Schauer and Cass, 2000, Simoneit et al., 1999, Schauer et al., 2001), whereas silicon and aluminum are markers for road dust. Table IV lists organic species along with their potential urban sources.

Summertime levoglucosan concentrations for Delhi, Kolkata, and Chandigarh are 210 ± 42 ng/m^3, 75 ± 15 ng/m^3, and 140 ± 28 ng/m^3 respectively; whereas wintertime levoglucosan concentrations for the Delhi, Kolkata, and Mumbai are, respectively, 5260 ± 1052 ng/m^3, 5490 ± 1098 ng/m^3, 910 ± 180 ng/m^3. Summertime Mumbai and wintertime Chandigarh measurements were not available. Ratios for levoglucosan to the sum of hopanes and steranes follow a seasonal trend: ratios are at least three to ten times higher during the colder months compared to the warmer months for all the cities in this study. This seasonal trend in levoglucosan, a proven biomass smoke marker, may suggest increased amount of wood used for home heating. Also, stigmasterol, a suggested marker for cowdung combustion smoke, has been detected in all cities. Very low income households use cowdung patties along with tree leaves and branches to cook or heat their surroundings.

Picene concentrations in the summer in Delhi, Kolkata, and Chandigarh were 0.3 ± 0.06 ng/m^3, 0.3 ± 0.06 ng/m^3, 0.2 ± 0.04 ng/m^3, respectively, and wintertime concentrations in Delhi, Kolkata, and Mumbai are 5.1 ± 1.0 ng/m^3, 7.1 ± 1.4 ng/m^3, 0.9 ± 0.2 ng/m^3 respectively. Concentrations of picene, which is a coal marker, increased during the winter, particularly because of air stagnation and because of a decrease in wet deposition. Three thermal power plant stations are present in Delhi: Indraprastha (284 MW capacity, burning 11,50,000 MT/yr of pulverized coal with 39.4% ash and 0.36% sulfur content in the coal), Rajghat (135 MW capacity, burning 876,000 MT/yr of pulverized coal with a 35-42% ash and 0.50% sulfur content in the coal), and Badarpur (720 MW capacity, burning

3,940,000 MT/yr of pulverized coal with a 28-32% ash and 0.35% sulfur content). Although electro static precipitators (ESPs) are present in each of these power generating facilities, poor maintenance has often been blamed for high loads of fly ash (Aggarwal et al., 1999). The New Cassipore power generating facility has often been blamed for the dark cloud of haze over the city of Kolkata (Aggarwal et al., 1999). However, such implications have not been conclusively demonstrated.

Cholesterol concentrations were below the instrument detection limit in almost all the samples suggesting that the amount of meat cooking is minimum and negligible. This is consistent with most Indians being vegetarian and thus meat consumption is low in the country compared to other countries.

4.4. CMB Results:

Results from CMB modeling (Figures 9-12) show that there is no single dominant source of $PM_{2.5}$ and a number of sources contribute to the fine particle concentrations. Gasoline combustion is primarily from mobile sources, but the diesel contribution is from both stationary and mobile sources. It is not possible to attribute secondary sulfates, nitrates, and ammonium to specific primary sources using CMB, though sulfates can likely be linked to the sulfur in fossil fuels. Secondary particulate formation comprised approximately one-tenth to one-fifth of $PM_{2.5}$. Broadly, mobile sources and biomass combustion appear to contribute substantially and in several cases approximately in equal proportions. Road dust can also be significant. Predictably, the contributions of biomass and coal, presumably used for heating, are high in winter in Delhi and Kolkata. Out of the 12 samples that underwent CMB analysis, road dust was the largest contributor in three, whereas, biomass combustion in two, and unidentified sources in the remaining three. Unidentified hydrocarbons and water are two potential sources of the unidentified mass. Diesel exceeds gasoline in all cases, which is not surprising, given the relatively higher emission rates for diesel compared to gasoline and the higher consumption of diesel compared to gasoline in India. It should be pointed out that although the source profile for diesel is from medium-duty diesel trucks, it is not possible to distinguish between diesel exhaust from vehicles and diesel emissions from stationary sources. The use of diesel in small power generators is not insignificant in the

Indian cities studied because of frequent power outage. Therefore, not all diesel-derived $PM_{2.5}$ is from mobile sources. Gasoline, in contrast, is used almost exclusively in vehicles, and can be attributed to mobile sources with little error. By summing the contributions from diesel, gasoline, and coal, we find that in most cases fossil fuel combustion exceed biomass combustion (see Figure 13). It is interesting to note that the sum of the identified sources from the CMB results from spring (107%), summer (130%), and autumn (120%) seasons in Kolkata exceeded the measured mass of $PM_{2.5}$. Total mass concentrations from identified sources should equal approximately 100%, although values ranging from 80 to 120% are acceptable (Watson et al., 1990). If the measured mass is very low (< 5 to 10 $\mu g/m^3$), percent mass may be outside of this range because the precision of the mass measurement is on the order of 1 to 2 $\mu g/m^3$. Also, higher levels can be due to larger ratios of total $PM_{2.5}$ to specific tracers than are actually present, or propagation of the various uncertainties involved in this process (Zheng et al, 2002). Traditional application of CMB often leads to greater mass apportioned than measured.

5.0 Fuel-Based Particulate Matter Emissions:

An initial confirmation of the CMB-based source apportionment was conducted by comparing the results here for fuel oil, diesel, and gasoline emissions to the results obtained from National Environmental Engineering Research Institute (NEERI)'s yearly fuel usage and fuel-based emissions factors in Mumbai for the year 2001. Emission factors were obtained from Reddy and Venkataraman (2002). The emission factor for gasoline vehicles is a weighted average between the emission factor for non-catalytic vehicles using unleaded gasoline reported by Reddy and Venkataraman (2002) and for motorcycles (EPA, 2000). As seen from Table X, a first order approximation, it appears that diesel contribution to fine particle emission in Mumbai is an order of magnitude higher than gasoline and fuel oil. This is comparable to our results obtained from CMB. In addition, gasoline and diesel emissions from vehicular activity are directly emitted at ground level and thus have a proportionally greater effect on urban air quality. Reddy and Venkataraman (2002) find that utility coal burning has the largest emissions nationally in India. Such emissions are not concentrated as much in cities as are motor vehicle emissions. Further, those emissions, along with the

emissions from burning fuel oil are often injected into the atmosphere well above the mixed layer. Thus, one expects fuel oil and coal sources to have smaller impact, relative to their total emissions rate, on urban, ground level particulate measurements as apportioned here

It is also of interest to conduct an order of magnitude approximation of the expected levels of PM from the various sources. Using an approximate size of greater Mumbai of 50 x 50 km, an average mixing height of 200 m, and an average wind speed of 2 m/s, and assuming instant mixing in to the whole airshed, the above emissions estimates would suggest PM levels from the three sources would be <u>about</u> 5 $\mu g/m^3$ for diesels, 0.3 $\mu g/m^3$ for gasoline fueled vehicles and 0.2 $\mu g/m^3$ for furnace oil. While all of these values appear low (due to the approximations in the calculation and possible underestimates in the emissions factors for the various sources), it does suggest that it is not surprising that our source apportionment does not find significant levels of PM coming from furnace oil, kerosene and other liquid and gaseous fuel used in industrial, external combustion boilers. Again, gasoline fueled vehicles emit near the ground, similar to where the monitors are sampling air, and will have a greater impact, particularly at night when the mixing depths are much lower.

6.0. Uncertainties

Receptor modeling of the type performed here is open to uncertainties, albeit not so large as other approaches relying on less detailed information. Indeed, the use of organic molecular markers provides significant extra information than is typically available. Further, the agreement with other approaches of estimating sources of $PM_{2.5}$ conducted above is also encouraging, as is the agreement with other studies (e.g., Reddy and Venkataraman, 2002). Still, it is important to recognize the uncertainties and possible sources of error.

First, as a receptor modeling approach, errors in the measurements will manifest themselves directly in the source apportionments, and possibly be magnified if the source profiles are similar. It can be shown that if two source profiles are similar, small variations of the measurements in the source profiles can lead to large uncertainties in the source apportionment results. Second, errors, omissions and/or variations in the source profiles will impact the source apportionment. For example, in this study, it was found that using all of the available, and possibly applicable biomass burning profiles led to the CMB model giving

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erroneous results (some of the sources had negative strengths), so a single profile for the various biomass burning sources had to be used. This involved judgment as to what mixture of profiles for biomass burning would be best. More subtle is that a source in one location can have a different profile than ostensibly the same source in another location, for example, diesel trucks. The source profile used was developed in the United States. The engine type, age, condition, duty cycle, additional controls, maintenance, fuel type and lubricating oil can all impact the source profile. The profile for coal was taken from a Chinese coal. Subtler still is the assumed uncertainties in the measurements and profiles can impact results. Parameters chosen for the CMB application can affect results. Finally, the measurements taken were for a limited period. Without additional monitoring it is difficult to say if the analysis is representative over longer periods.

While the above list seems daunting, it is important to remember that even without applying the CMB, one can look at the measured organics and identify which sources are most likely to have a major impact because emissions from fossil fuel combustion in internal combustion (IC) engines has certain characteristics very distinct from biomass burning, which is distinct from meat cooking, all of which are distinct from road dust. Thus, the uncertainties within, say, apportioning the amount of PM from compression ignition versus spark ignition engines may be relatively large, organic carbon from biomass burning has distinctly different compounds, so the uncertainty between fossil fuel and biomass combustion is not so uncertain. Thus, while it is more difficult to say with great confidence how much PM is coming from gasoline-fueled automobiles vs. diesel vehicles, one can say with greater confidence how much is coming from IC engines. A formal error analysis is beyond the scope of this work. Again, it is reassuring the consistency of the results from the receptor modeling with those from the fuel-based estimates and other estimates for India.

Reducing the uncertainties requires significant effort. In particular, it would be very beneficial to measure source profiles for the various sources specific to India, e.g., measure the source profiles for Indian diesels, automobiles, two wheelers and coal. Second, monitoring for another year or two would be useful to assess the representativeness of the current observations. Such monitoring could be limited to less detailed organic speciation. Third, more detailed emissions inventory work, and/or comparison with other available estimates would be useful. Ultimately, the emissions inventory will be used for policy

setting and control strategy development, so it is important that the sources and resulting impacts on air quality be reconciled.

7.0 Opportunities for Future Research

Two of the major limitations of this work contributing to large uncertainties in the results are the lack of regional source profiles and the lack of statistically significant number of samples for each season. There is a need to conduct several source tests for diesel and gasoline combustion using vehicles representing the local vehicle fleet (diesel trucks, three-wheel auto-rickshaws). Coal source tests using Indian and Bangladeshi coals have been conducted, however, organic speciation work was not completed by the publication of this report. Emissions from local soil profiles (paved road dust as well as non-paved road dust) are necessary to refine the results from this work. Additional fine particle sampling is needed to identify the magnitude of seasonal variability. Finally, it is important to reconcile the observations and source apportionment work done here with results that would be achieved using a source-based model in order to evaluate the emissions inventories developed for the various regions. Our order of magnitude calculation for Mumbai suggests that the two will give consistent results, though may differ quantitatively. This latter work is important for identifying possible missing sources and to provide a defensible, more first-principles, approach to policy-makers that can directly link specific sources to their air quality and health impacts.

8.0 Conclusions

Chemically-detailed particulate matter characterization and detailed source apportionment for Delhi, Mumbai, Kolkata, and Chandigarh were conducted using receptor-based chemical mass balance modeling. For the period studied, average fine particle mass concentrations during the winter season in Delhi was 230.9 ± 1.6 μg m^{-3}, in Mumbai was 88.9 ± 0.54 μg m^{-3}, and in Kolkata was 304.5 ± 1.13 μg m^{-3} and average fine particle mass concentration during the summer in Delhi was 49.5 ± 0.64 μg m^{-3}, in Mumbai was 21.0 ± 1.38 μg m^{-3}, and in was Kolkata 26.5 ± 0.45 μg m^{-3}. Measured concentrations of organic carbon

species, elemental carbon, and metals from the four sampling sites were used in a molecular marker source apportionment model to quantify the primary source contribution to the $PM_{2.5}$ mass concentrations at those sites. Five important sources of primary $PM_{2.5}$ were quantified: diesel exhaust, gasoline exhaust, road dust, coal combustion, and biomass combustion. Important trends in the seasonal and spatial patterns of the impact of these five sources were observed. Primary emissions from fossil fuel combustion (coal, diesel, and gasoline) were 22-33% in Delhi, 23-29% in Mumbai, 37-70% in Kolkata, and 24% in Chandigarh. These figures can be compared to the biomass combustion of 9-28% for Delhi, 12-21% for Mumbai, 15-31% for Kolkata, and 9% for Chandigarh. Road dust was also significant. Further study of the situation is warranted, and a variety of further avenues were suggested, in particular closer study of the source profiles in India, and a study to compare results between the receptor model approach and emissions inventory-based approaches.

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TABLE I. Description of the sampling sites.

City	Site Address	Location Type	Site Description	Source of Pollution
Mumbai	NEERI Zonal Laboratory 89/B, Dr. Annie Basen Rd. Worli, Mumbai-400018 India	Urban Residential	Sampler placed 3 m above ground on a rooftop. A four-story building and slum areas near-by.	City traffic typically seen in residential and business areas, and cooking by slum dwellers.
Delhi	National Physical Laboratory Dr. K. S. Krishnan Marg New Delhi - 110012 India	Urban Residential	Sampler placed 5 m above ground on an office building rooftop in the NPL campus. Unobstructed space around.	City traffic typically seen in residential and business areas, and cooking by slum dwellers.
Kolkata	NEERI Zonal Laboratory I-8, Sector-C, East Kolkata P.O. Box Haltu, Kolkata 700078 India	Urban Residential	Sampler on a 2 meter platform located in an open field. Ruby General Hospital and a diesel truck garage nearby.	City traffic typically seen in residential and business areas, cooking by slum dwellers, and some emission from combustion by diesel trucks parked in nearby garage.

TABLE II. Characteristics of filter substrates used for collecting samples.

Filter Type	Details
Quartz Fiber Filter	Pallflex, 2500 QAO, 47-mm diameter
Poly Tetra Fluoro Ethylene (PTFE) filter	Gelman Sciences, Teflo, 47-mm diameter, 1.0-μm pore size
Nylon Filter	Pall Gelman, Nylasorb filters, 47-mm diameter

TABLE III. Analytical methods used on the filter substrates.

Species of Interest	Instrument Used	Method Used
Mass	Mettler model M-55-A mechanical microbalance	Gravimetric Analysis by repeated weighing before and after the experiment. Microbalance maintained in a temperature and humidity-controlled environment (21.0 ± 0.2°C, 39 ± 3% RH)
Sulfate Ion	Dionex Corporation, Model 2020i	Ion Chromatography described by *Mulik et al.,* 1976
Chloride Ion		
Nitrate Ion		
Ammonium Ion	Alpkem rapid flow analyzer (Model RFA-300)	Indophenol Colorimetric Procedure described in *Bolleter et al.,* 1961
Elemental Carbon	Carbon Analyzer	Thermal-optical carbon analysis method of *Huntzicker et al.* [1982] as modified by *Birch and Cary* [1996]
Organic Carbon		
Trace Elements	XRF	X-Ray Fluorescence Analysis by Desert Research Institute (Wolfe and Flocchini, 1977; Van Espen et al., 1981; Adams et al., 1983)
Organic Speciation	GCMS	Schauer et al., 1996, 1999a, 1999b, 2000, 2001, 2002a, 2002b.

TABLE IV. Molecular Markers and Their Likely Sources Used in This Study.

SN	Category	Molecular Marker	Major Urban Sources
1	Alkanes	n-Pentacosane	Gasoline, Diesel, and Fuel Oil combustion
2	Alkanes	n-Hexacosane	Gasoline, Diesel, and Fuel Oil combustion
3	Alkanes	n-Heptacosane	Gasoline, Diesel, and Fuel Oil combustion
4	Alkanes	n-Octacosane	Gasoline, Diesel, and Fuel Oil combustion
5	Alkanes	n-Nonacosane	Vegetative Detritus combustion
6	Alkanes	n-Triacontane	Gasoline combustion
7	Alkanes	n-Hentriacontane	Vegetative Detritus, Cigarette Smoke
8	Alkanes	n-Dotriacontane	Varieties of Combustion Sources
9	Alkanes	n-Tritriacontane	Vegetative Detritus, Cigarette Smoke
10	Alkanes	n-Tetratriacontane	Tire Wear Debris
11	Alkanes	n-Pentatriacontane	Tire Wear Debris
12	Branched Alkanes	Anteiso-Triacontane	Cigarette Smoke
13	Branched Alkanes	Iso-Hentriacontane	Cigarette Smoke
14	Branched Alkanes	Anteiso-Hentriacontane	Cigarette Smoke
15	Branched Alkanes	Iso-Dotriacontane	Cigarette Smoke
16	Branched Alkanes	Anteiso-Dotriacontane	Cigarette Smoke
17	Branched Alkanes	Iso-Tritriacontane	Cigarette Smoke
18	Steranes	20S&R-5α(H), 14β(H), 17β(H)-Cholestanes	Gasoline, Diesel, and Fuel Oil combustion
19	Steranes	20R-5α(H), 14α(H), 17β(H)-Cholestane	Gasoline, Diesel, and Fuel Oil combustion
20	Steranes	20S&R-5α(H), 14β(H), 17β(H)-Ergostanes	Gasoline, Diesel, and Fuel Oil combustion
21	Steranes	20S&R-5α(H), 14β(H), 17β(H)-Sitostanes	Gasoline, Diesel, and Fuel Oil combustion
22	Hopanes	22, 29, 30-Trisnorneohopane (T m)	Gasoline, Diesel, and Fuel Oil combustion
23	Hopanes	17α(H), 21β(H)-29-Norhopane	Gasoline, Diesel, and Fuel Oil combustion
24	Hopanes	17α(H), 21β(H)-Hopane	Gasoline, Diesel, and Fuel Oil combustion
25	Hopanes	22S-17α(H), 21β(H)-30-Homohopane	Gasoline, Diesel, and Fuel Oil combustion
26	Hopanes	22R-17α(H), 21β(H)-30-Homohopane	Gasoline, Diesel, and Fuel Oil combustion
27	Hopanes	22S-17α(H), 21β(H)-30-Bishomohopane	Gasoline, Diesel, and Fuel Oil combustion
28	Hopanes	22R-17α(H), 21β(H)-30-Bishomohopane	Gasoline, Diesel, and Fuel Oil combustion
29	Alkanoic Acids	n-9-Hexadecanoic acid	Meat Cooking
30	Alkanoic Acids	Hexadecanamide	Biomass (cowdung) combustion
31	Alkanoic Acids	Octadecanamide	Biomass (cowdung) combustion
32	Resin Acids	Pimaric acid	Softwood Burning
33	Resin Acids	Isopimaric acid	Softwood Burning
34	PAH	Benzo[b]fluoranthene	Varieties of Combustion Sources
35	PAH	Benzo[k]fluoranthene	Varieties of Combustion Sources
36	PAH	Benzo[e]pyrene	Varieties of Combustion Sources
37	PAH	Indeno[1,2,3-cd]fluoranthene	Varieties of Combustion Sources
38	PAH	Indeno[1,2,3-cd]pyrene/o-Phenylenepyrene	Varieties of Combustion Sources
39	PAH	Picene	Coal Combustion
40	PAH	Coronene	Gasoline combustion from Noncatalyst Cars
41	Other Compounds	Beta-tocopherol	Biomass Combustion
42	Other Compounds	Coprostanol	Biomass (cowdung) Combustion
43	Other Compounds	Stigmastan-3,5-dien	Biomass (cowdung) Combustion
44	Other Compounds	Vitamin E	Biomass Combustion
45	Other Compounds	Cholestanol	Biomass (cowdung) Combustion
46	Other Compounds	Campesterol	Biomass Combustion
47	Other Compounds	Stigmasterol	Biomass Combustion
48	Other Compounds	(3beta, 5 beta) Stigmastan-3-ol	Biomass Combustion
49	Other Compounds	Beta-Sitosterol	Biomass Combustion
50	Other Compounds	(3beta, 5alpha) Stigmastan-3-ol	Biomass Combustion
51	Other Compounds	Stigmasta-3,5-dien-7-one	Biomass Combustion
52	Other Compounds	Cholesterol	Meat Cooking
53	Other Compounds	Levoglucosan	Hardwood Burning, Softwood Burning
54	Other Compounds	Galactosan	Biomass Combustion
55	Other Compounds	Mannosan	Biomass Combustion
56	Inorganic	Elemental Carbon	Diesel, Gasoline, Coal and Fuel Oil Combustion
57	Inorganic	Aluminum	Crustal Material
58	Inorganic	Silicon	Crustal Material

TABLE V. List of compounds used for source apportionment modeling.

Elemental Carbon	n-Dotricontane	Octadecanamide
Aluminum	20S&R-5α(H), 14β(H), 17β(H)-Cholestanes	Benzo[b]fluoranthene
Silicon	20R-5α(H), 14α(H), 17α(H)-Cholestane	Benzo[k]fluoranthene
n-Pentacosane	20S&R-5α(H), 14β(H), 17β(H)-Ergostanes	Benzo[e]pyrene
n-Hexacosane	20S&R-5α(H), 14β(H), 17β(H)-Sitostanes	Indeno[1,2,3-cd]fluoranthene
n-Heptacosane	22, 29, 30-Trisnorneohopane	Indeno[1,2,3-cd]pyrene
n-Octacosane	17α(H), 21β(H)-29-Norhopane	Picene
n-Nonacosane	17α(H), 21β(H)-Hopane	Coronene
n-Triacontane	n-9-Hexadecenoic acid	Stigmasterol
n-Hentriacontane	Isopimaric acid	Levoglucosan
n-Dotricontane	Hexadecanamide	

TABLE VI. List of source profiles used in this study.

SN	Source Profile Name	Description	Used in Final Analysis
1	Medium Duty Diesel Trucks		Yes
2	Non-Catalyst Gasoline Powered Motor-Vehicle		No
3	Catalyst Equipped Gasoline Powered Motor-Vehicle		No
4	Average of Gasoline Vehicle: 83% Non-Cat, 17% Cat	Weighted average of #2 and #3	Yes
5	Meat Cooking		No
6	Road Dust from Fresno, CA		No
7	Road Dust from Bakersfield, CA		No
8	Road Dust from Kern Wildlife Refuge, CA		No
9	Average of Road Dust	Average of #6 to 8	Yes
10	Fuel Oil		No
11	Beijing Coal		Yes
12	Natural Gas		No
13	Coconut Leaves from Bangladesh		No
14	Rice Straw from Bangladesh		No
15	Cow Dung from Bangladesh		No
16	Biomass Briquette from Bangladesh		No
17	Jackfruit Branches from Bangladesh		No
18	Average of Bangladeshi Biomass	Average of #13 to 17	Yes

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TABLE VII. Health risks from air quality in Delhi, Mumbai, and Kolkata using EPA's pollutant standard index.

	Unhealthy for Sensitive Groups[*1]	Unhealthy[*2]	Very Unhealthy[*3]	Hazardous[*4]
Delhi (21 samples)	Jul 2, 8	March 4, 10, 16, 22, 28 June 8, 14 Oct 11, 17	Oct 5 Dec 17, 23, 29 Jan 10, 16	Jan 4
Mumbai (25 samples)	Mar 4, 19 Dec 23	Oct 17, 23, 29 Nov 4, 10 Dec 5, 11, 17, 29 Jan 4, 10		
Kolkata (19 samples)	Mar 22, 28 Apr 3 Oct 11, 23	Mar 16		Dec 5, 11, 17, 23, 29

[*1] Unhealthy for Sensitive Groups: Increasing likelihood of respiratory symptoms in sensitive individuals, aggravation of heart of lung disease and premature mortality in persons with cardiopulmonary disease and the elderly.

[*2] Unhealthy: Increased aggravation of heart or lung disease and premature mortality in persons with cardiopulmonary disease and the elderly; increased respiratory effects in general population

[*3] Very Unhealthy: Significant aggravation of heart or lung disease and premature mortality in persons with cardiopulmonary disease and the elderly; significant increase in respiratory effects in general population.

[*4] Hazardous: Serious aggravation of heart or lung disease and premature mortality in persons with cardiopulmonary disease and the elderly; serious risk of respiratory effects in general population.

Table VIII. Seasonal Chemical Composition and Percentage Contribution to Fine Particle Mass in (a) Delhi, (b) Mumbai, (c) Kolkata, and (d) Chandigarh.

(a)

Delhi	Spring	% of PM2.5	Summer	% of PM2.5	Fall	% of PM2.5	Winter	% of PM2.5
Unidentified	12.9	11%	5.5	11%	29.9	19%	7.6	3%
Nitrate	2.5	2%	1.5	3%	3.6	2%	16.8	7%
Chloride	8.8	8%	0.5	1%	1.4	1%	15.3	7%
Ammonium	7.2	6%	2.0	4%	4.4	3%	12.1	5%
Sulfate	9.6	8%	5.2	10%	10.1	6%	18.8	8%
Sodium	0.2	0%	0.3	1%	0.1	0%	0.1	0%
Potassium	2.0	2%	0.7	1%	3.3	2%	2.1	1%
Non-Crustal Metals	1.3	1%	1.0	2%	2.0	1%	2.1	1%
Crustal Oxides	7.7	7%	6.3	13%	12.4	8%	4.5	2%
Organic Matter	52.9	46%	22.6	46%	80.3	50%	134.1	58%
Elemental Carbon	9.1	8%	4.0	8%	11.5	7%	17.4	8%
Avg PM2.5	114.2	100%	49.5	100%	159.1	100%	230.9	100%

(b)

Mumbai	Spring	% of PM2.5	Summer	% of PM2.5	Fall	% of PM2.5	Winter	% of PM2.5
Unidentified	4.2	12%	5.5	26%	10.0	16%	4.5	5%
Nitrate	0.7	2%	0.9	4%	1.9	3%	2.9	3%
Chloride	0.1	0%	2.4	12%	0.6	1%	0.7	1%
Ammonium	1.2	3%	0.4	2%	2.3	4%	4.2	5%
Sulfate	5.6	16%	3.1	15%	7.9	12%	10.9	12%
Sodium	0.3	1%	1.4	7%	0.2	0%	0.2	0%
Potassium	0.6	2%	0.2	1%	0.9	1%	1.2	1%
Non-Crustal Metals	0.4	1%	0.3	1%	0.8	1%	1.0	1%
Crustal Oxides	5.9	16%	3.4	16%	5.7	9%	8.1	9%
Organic Matter	13.3	37%	2.3	11%	28.1	44%	47.0	53%
Elemental Carbon	3.7	10%	1.1	5%	5.6	9%	8.2	9%
Avg PM2.5	35.9	100%	21.0	100%	63.9	100%	88.9	100%

(c)

Kolkata	Spring	% of PM2.5	Summer	% of PM2.5	Fall	% of PM2.5	Winter	% of PM2.5
Unidentified	2.0	4%	0.8	3%	1.2	3%	15.9	5%
Nitrate	1.1	2%	0.8	3%	0.5	1%	9.1	3%
Chloride	0.4	1%	0.2	1%	0.2	0%	8.7	3%
Ammonium	2.2	4%	0.5	2%	1.3	3%	10.2	3%
Sulfate	8.7	16%	3.0	11%	4.0	9%	13.2	4%
Sodium	0.3	1%	0.3	1%	0.1	0%	0.0	0%
Potassium	1.1	2%	0.4	1%	0.8	2%	3.7	1%
Non-Crustal Metals	0.5	1%	0.4	2%	1.1	2%	3.8	1%
Crustal Oxides	6.2	11%	2.5	10%	1.9	4%	8.0	3%
Organic Matter	26.3	48%	10.9	41%	24.7	55%	205.3	67%
Elemental Carbon	6.1	11%	6.6	25%	9.1	20%	26.5	9%
Avg PM2.5	54.7	100%	26.5	100%	44.7	100%	304.5	100%

(d)

Chandigarh	Summer	% of PM2.5
Unidentified	4.6	16%
Nitrate	0.7	2%
Chloride	0.2	1%
Ammonium	1.9	7%
Sulfate	4.7	16%
Sodium	0.2	1%
Potassium	0.6	2%
Non-Crustal Metals	1.1	4%
Crustal Oxides	3.9	13%
Organic Matter	10.0	34%
Elemental Carbon	1.3	5%
Avg PM2.5	29.2	100%

TABLE IX. Diesel sulfur specifications in Delhi, Kolkata, and Mumbai.

City	Private diesel vehicles	All diesel vehicles
Delhi	2500 ppm wt until April 2000, 500 ppm wt thereafter	2500 ppm wt until March 2001, 500 ppm wt thereafter
Kolkata	2500 ppm wt until July 2001, 500 ppm wt thereafter	2500 ppm wt until October 2001, 500 ppm wt thereafter
Mumbai	2500 ppm wt until January 2001, 500 ppm wt thereafter	2500 ppm wt until October 2001, 500 ppm wt thereafter

TABLE X. First order approximation of particulate emission from Mumbai using a fuel-based approach. The estimate for gasoline is sensitive to the assumed fraction of fuel use by motorcycles and the emissions factor for that source.

	Yearly Consumption	Emission Factor	Density	Fuel-Based PM Emission	CMB PM Emission	Reddy and Venkataraman
	10^6 l	g/kg	kg/l	Kg/Day	% of Fine	Entire India
Furnace Oil	424	0.65	0.95	620	Negligible	Negligible
LSHS	1845	0.3	0.95	1400	Negligible	Negligible
Diesel (automotive + industrial)	1140	4.2	0.85	11,000	22%	10%
Gasoline	565	0.6	0.75	700	3%	Negligible
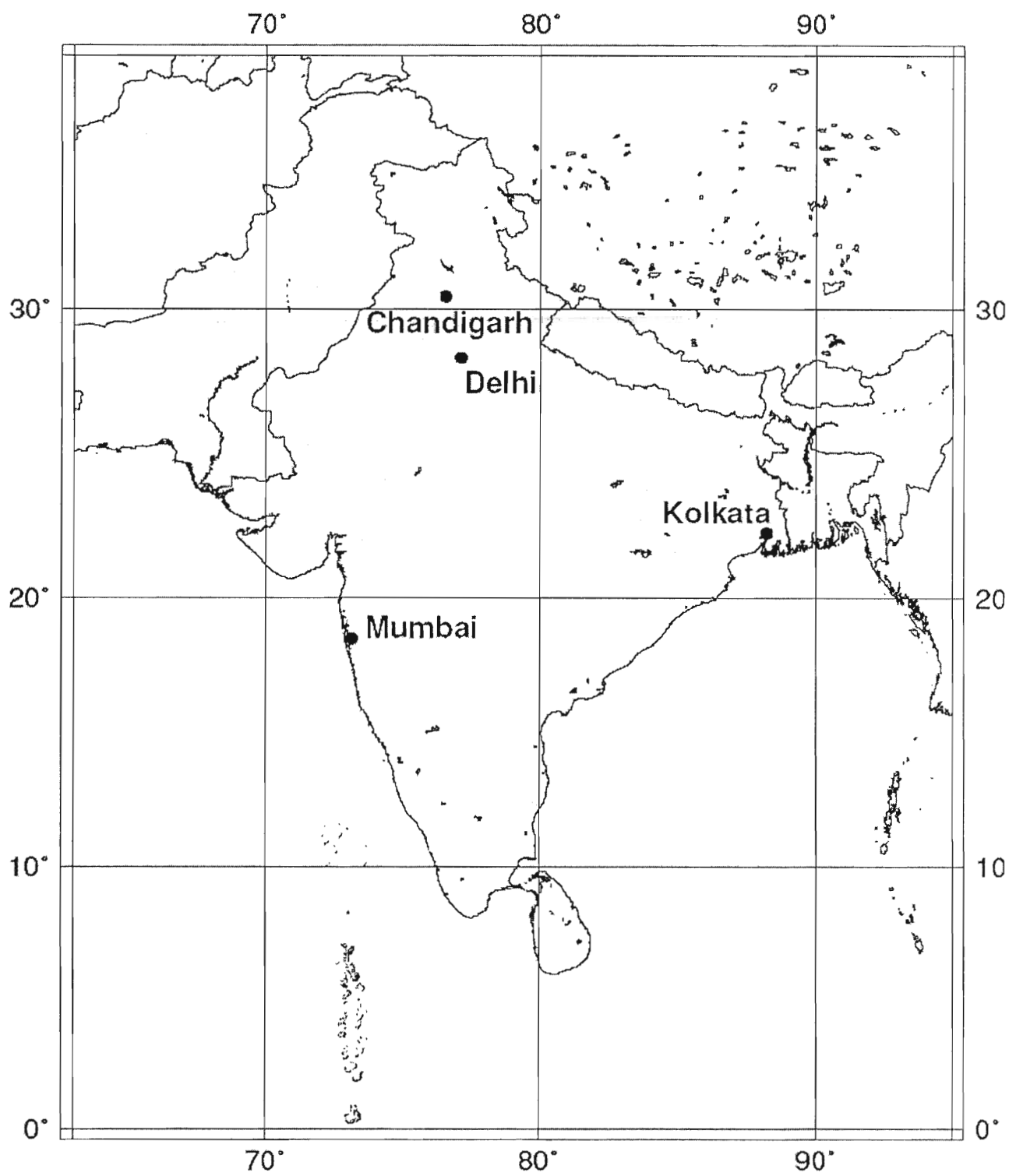
Figure 1. Location of the Four Sampling Sites: Delhi, Mumbai, Kolkata, and Chandigarh.

	March '01						April '01		June '01				July '01			October '01					Nov '01		December '01					January '02		
	4	10	16	19	22	28	3	9	8	14	20	26	2	8	14	5	11	17	23	29	4	10	5	11	17	23	29	4	10	16
Delhi																														
Mumbai																														
Kolkata																														
Chandigarh																														

Legend Key:

Spring

Summer

Fall

Winter
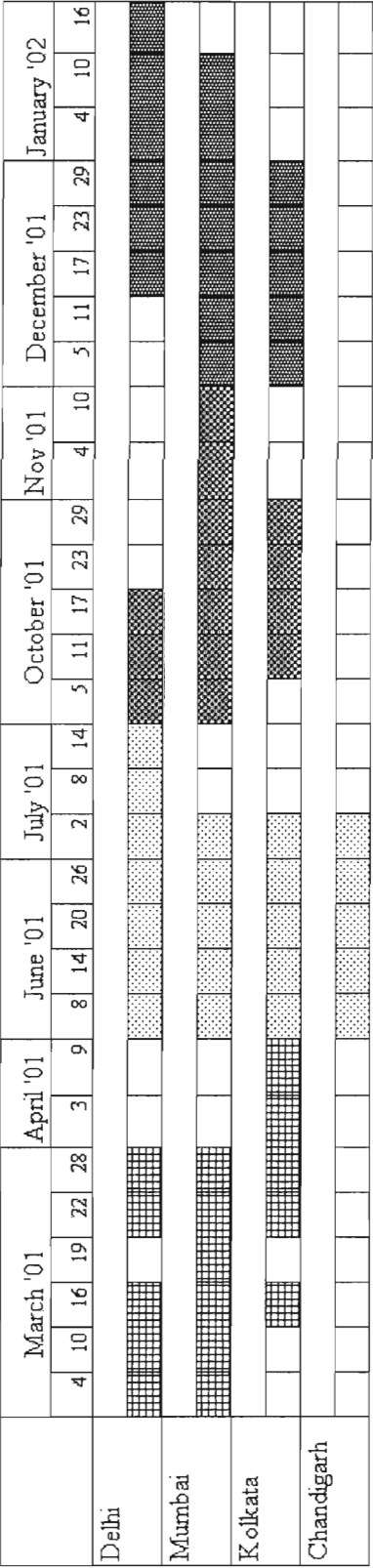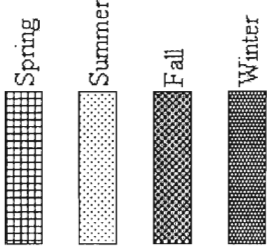
Figure 2. Diagram of the 24-hr averaging sampling schedule at four Indian cities.
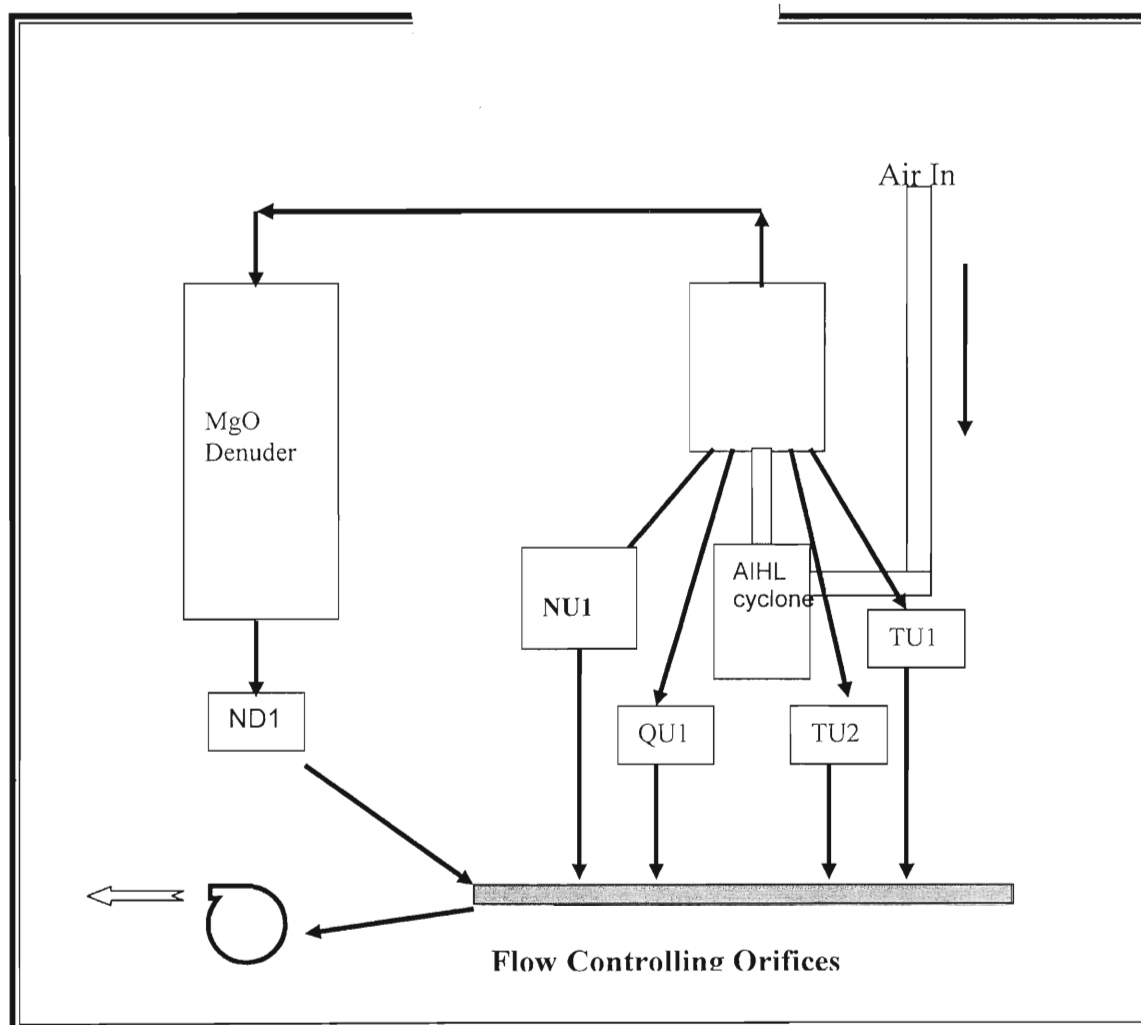
Figure 3. Schematic diagram of the sampling unit. TU1 and TU2 are teflon filters, NU1 and ND1 are undenuded nylon filter and denuded nylon filter respectively, and QU1 is a quartz fiber filter.
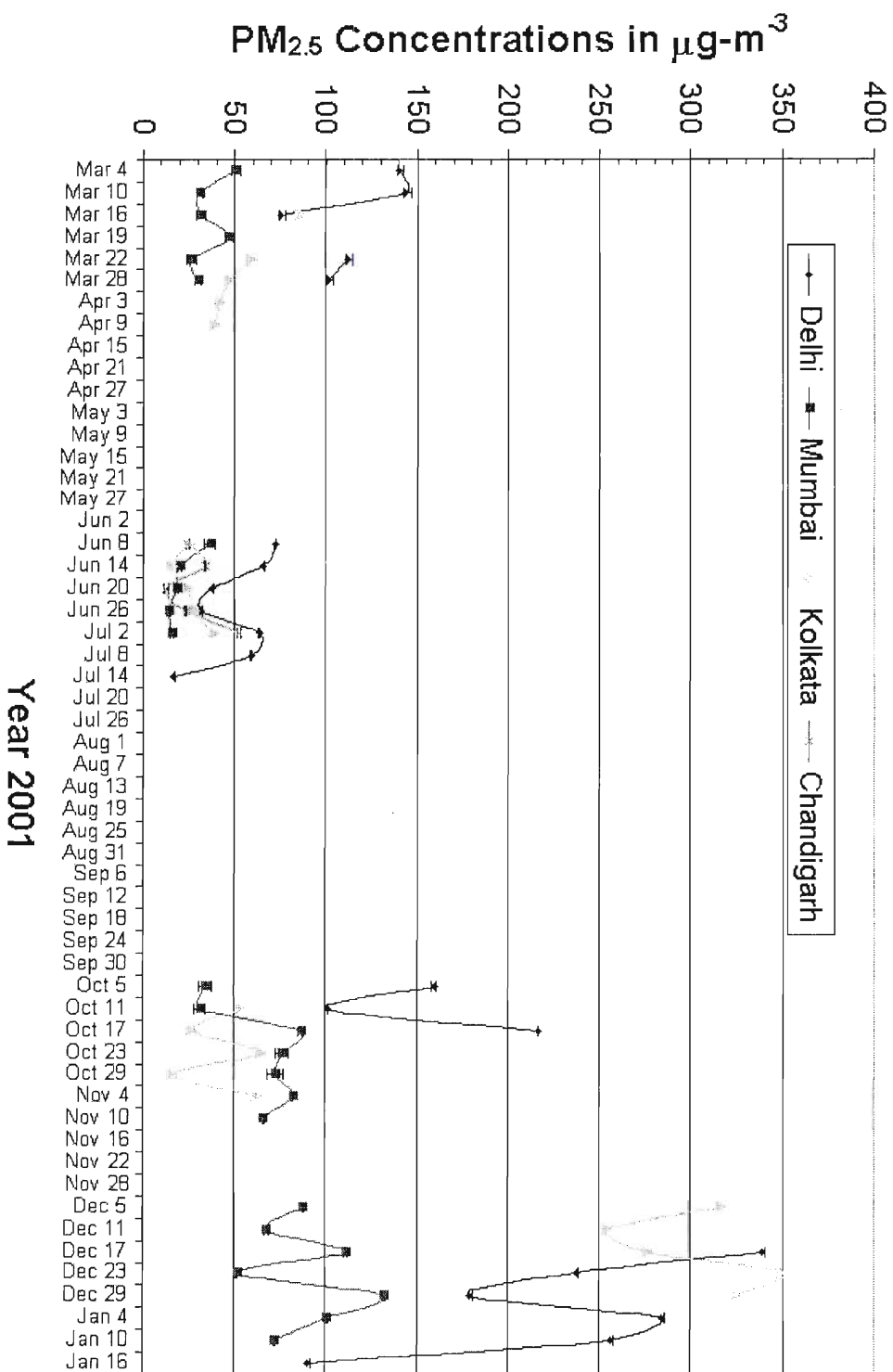
Figure 4. Fine Particulate matter concentrations comparison among Delhi, Mumbai, Kolkata, and Chandigarh for the Year 2001.

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(a)

(b)

(c)
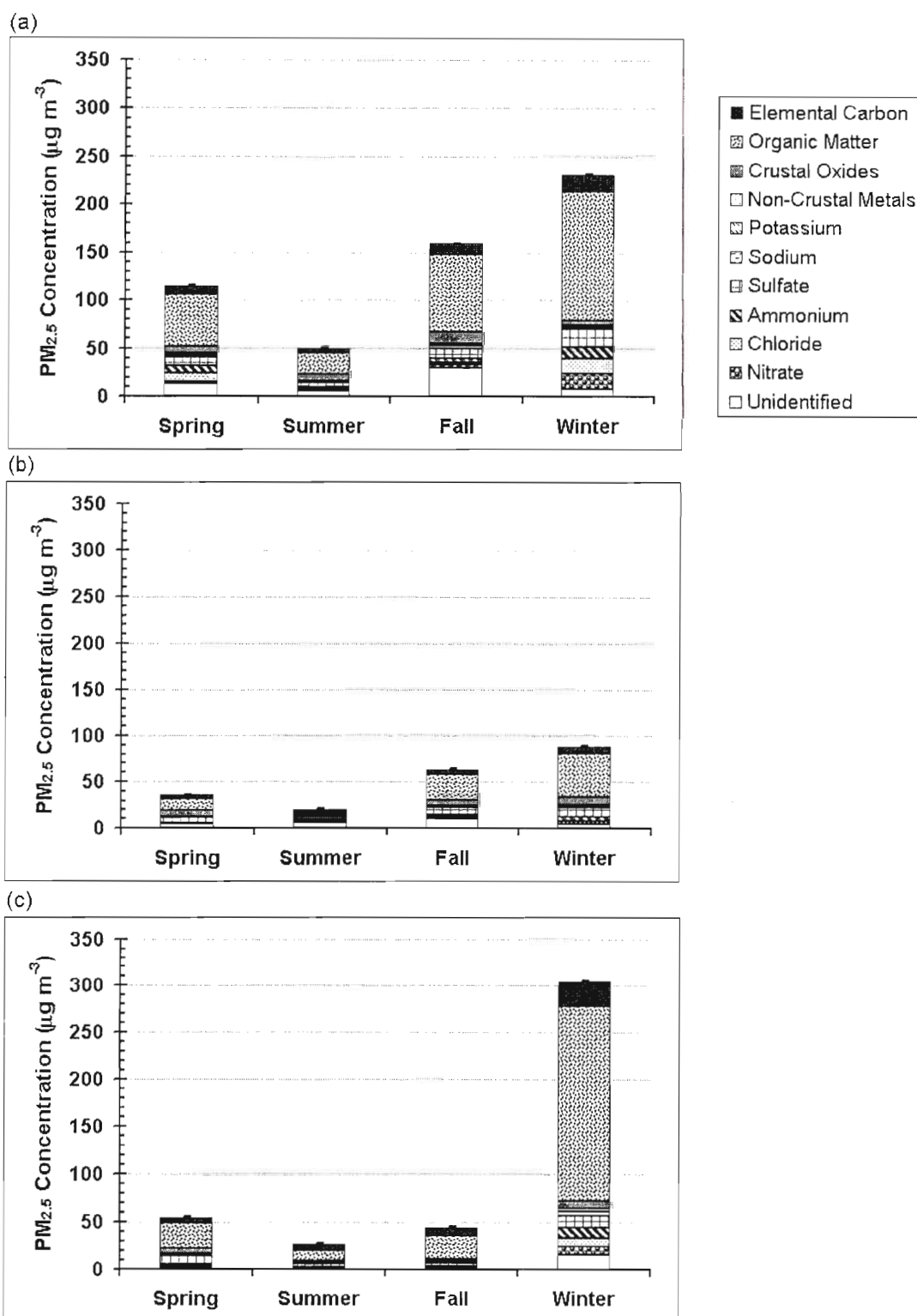
Figure 5. Chemical composition and seasonal variation of the fine particle mass in Delhi, Mumbai, and Kolkata.
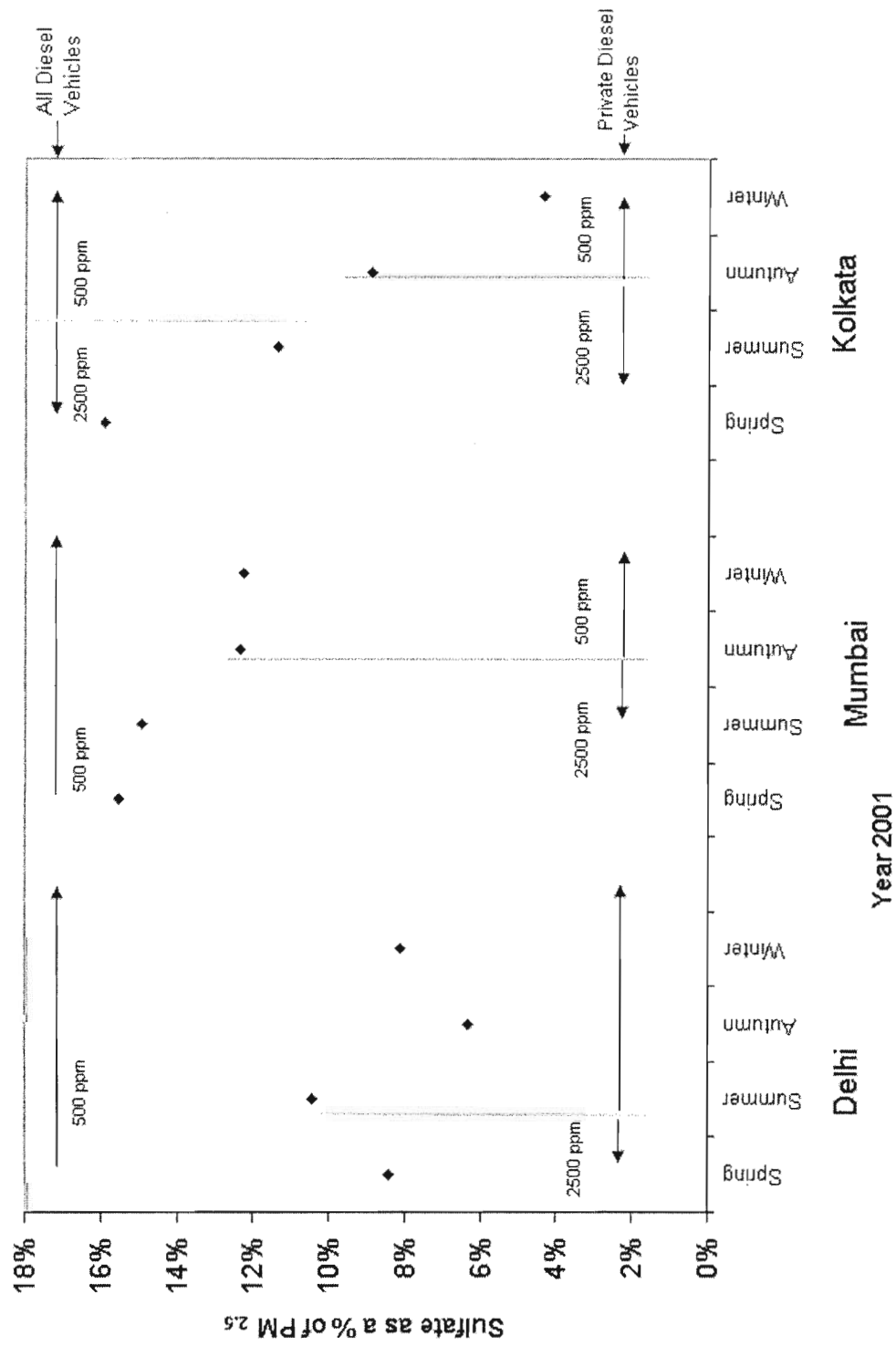
Figure 6. Effect on particulate sulfate from changes in diesel sulfur specifications in India.

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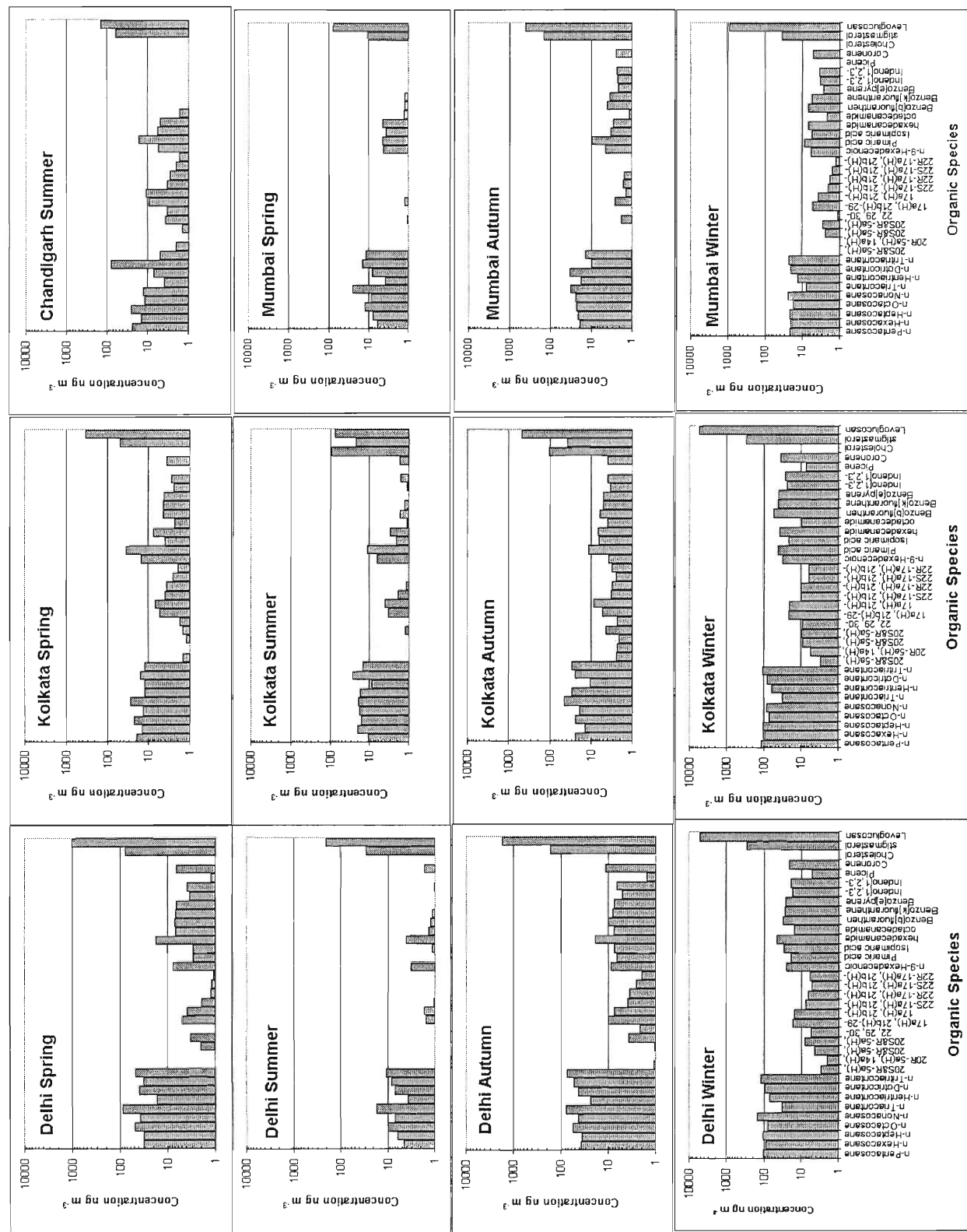
Figure 7. Concentrations of organic species in fine particles for four Indian cities as identified by Gas Chromatography Mass Spectrometry.

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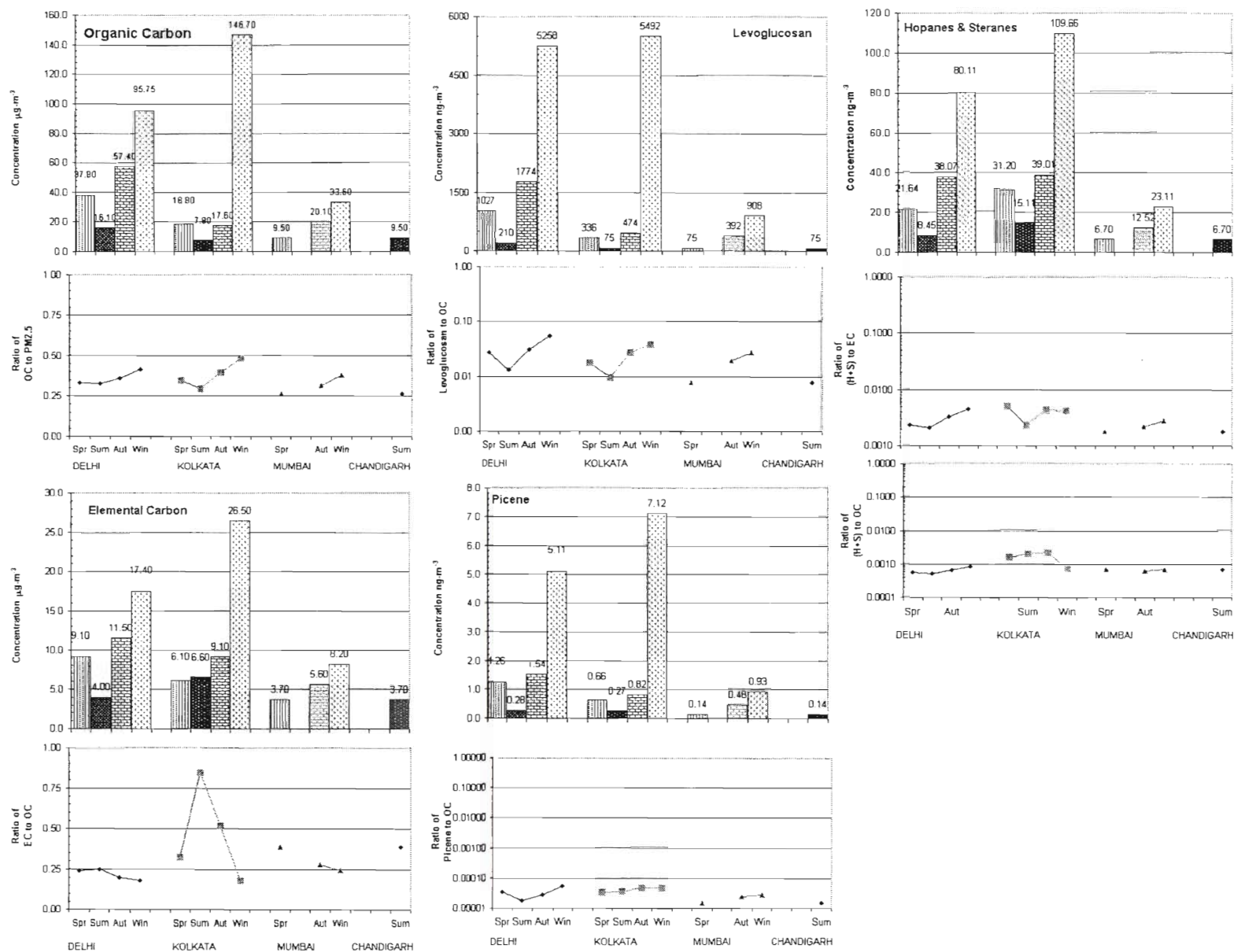
Figure 8. Seasonal variations of elemental carbon, organic carbon, levoglucosan, picene, hopanes and steranes, and alkanes for Delhi, Mumbai, Kolkata, and Chandigarh.

Figure 9. Fine particle emission pattern from diesel combustion, gasoline combustion, road dust, coal combustion, and biomass combustion.
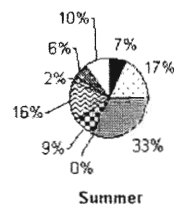
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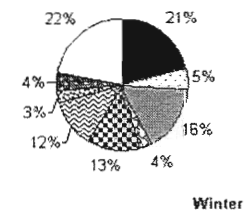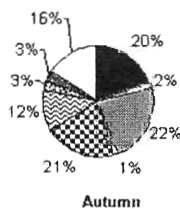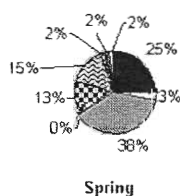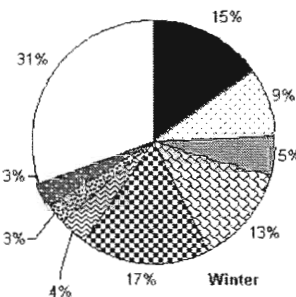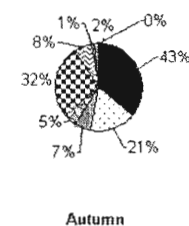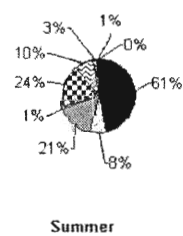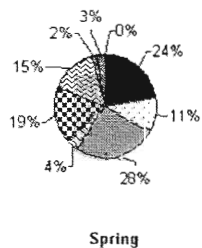
Figure 10. Source contribution to the ambient fine particles in Delhi, Mumbai, Kolkata, and Chandigarh.
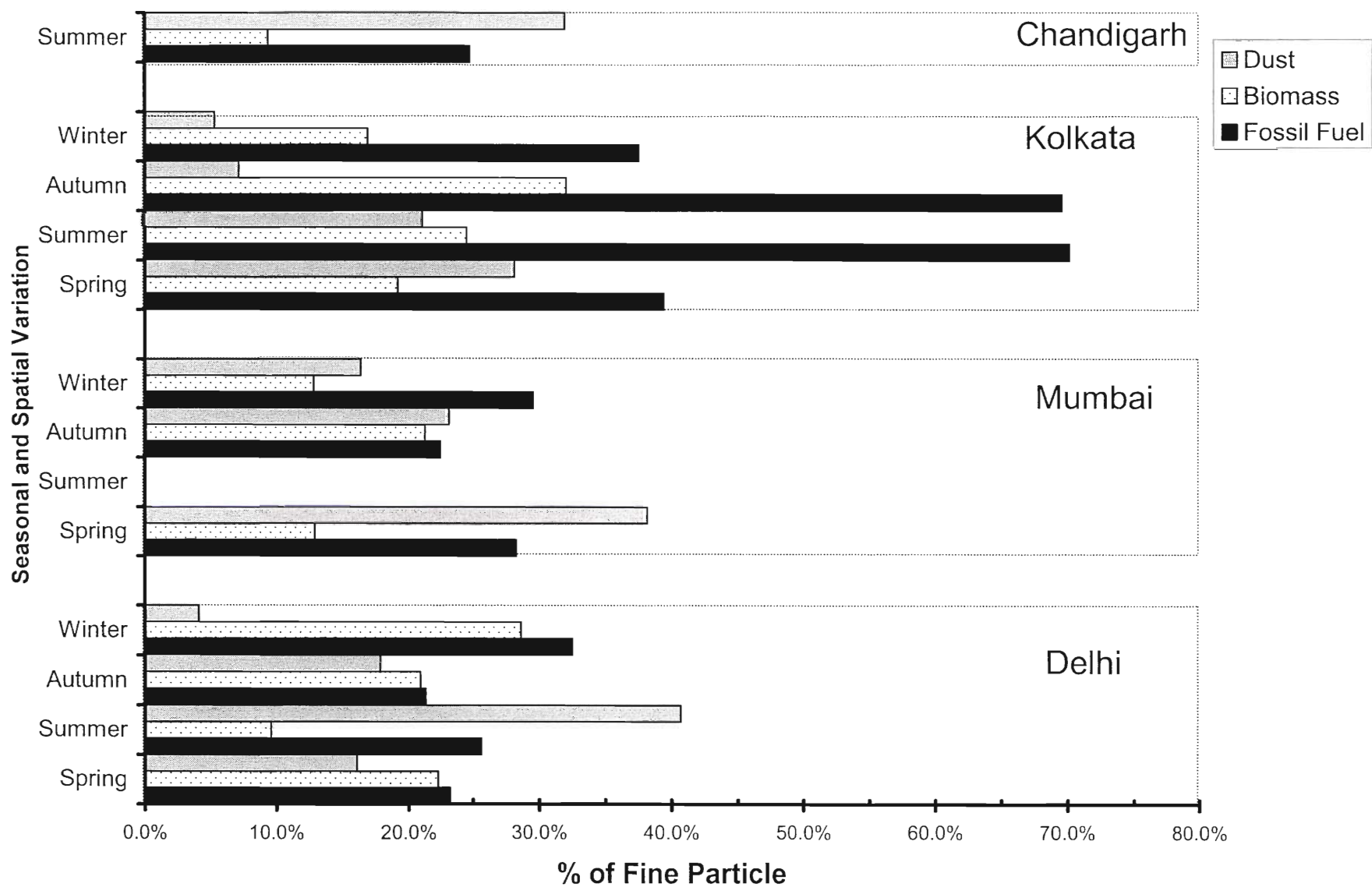
Figure 11. Seasonal and spatial variation of the predominant sources in Delhi, Mumbai, Kolkata, and Chandigarh.