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Chemical Characterization and Mass Closure of Fine Aerosol for Different Land Use Patterns in Mumbai City

Abba Elizabeth Joseph^{1,2*}, Seema Unnikrishnan¹, Rakesh Kumar²

¹ National Institute of Industrial Engineering, Mumbai, Vihar Lake, Mumbai–400087, India

² National Environmental Engineering Research Institute (NEERI), Mumbai, 89/B, Dr. A. B. Road, Worli, Mumbai–400018, India

ABSTRACT

Air quality management in India is being studied with more rigor. A detailed chemical analysis of fine particles helps to identify the sources of pollution and to predict potential health effects and climate change. In the present study, fine particles were measured at four locations in Mumbai city, India, during 2007–2008. The fine particles were measured using MiniVol portable air samplers. After gravimetric measurement, ions, elements, elemental carbon and organic carbon were analyzed. The average PM_{2.5} mass concentrations at control (C), kerb (K), residential (R) and industrial (I) sites were 69 ± 20, 84 ± 31, 89 ± 33 and 95 ± 36 µg/m³ respectively. The average OC contributions at C, K, R and I sites were 30%, 34%, 35% and 31% respectively while EC contributions were 7%, 11%, 9% and 8% respectively. The non-sea salt contributions of SO₄²⁻, K⁺ and Ca²⁺ were over 85% suggesting anthropogenic sources. Pb and Zn were highly enriched (> 1000). Reconstruction of mass of PM_{2.5} in Mumbai city includes organic matter (36–52%), secondary inorganic aerosols (21–27%), crustal (6–12%), noncrustal (4–8%) and sea salt (6–11%). The present study aims to improve the scientific understanding of aerosols.

Keywords: Fine aerosol; Elemental and organic carbon; Ions; Elements; Mumbai.

INTRODUCTION

Many toxic compounds, organic and inorganic, are associated with ambient air particulate matter (Oanh *et al.*, 2000). The epidemiological studies have found an association between fine particle concentrations and increased human health effects (Pope *et al.*, 2002; Pope and Dockery, 2006). Because of health concerns, Indian Ministry of Environment and Forest Notification, 2009, regulated National Ambient Air standards (24 hours) for PM_{2.5} as 60 µg/m³ also known as Central Pollution Control Board (CPCB) standards. Fine aerosols also influence climate directly by the scattering and absorption of solar radiation indirectly through their role as cloud condensation nuclei (Seinfeld and Pandis, 1998).

The study by Ramanathan and Ramana (2003) pointed out the need for reliable global inventory of aerosol emissions rates, lifetime, concentrations and importance of black carbon emissions from Asia. As per Intergovernmental Panel on Climate Change, the level of scientific understanding of aerosols is low (IPCC, 2001). The sources are becoming more complex day by day so are the emissions. Air quality

management in India is being studied with more rigor than before. The country has also progressed in its understanding of total suspended particulates and PM₁₀ sources, but the amount of information available on fine particulate pollution in India is very limited. A detailed chemical analysis of particulate matter samples provides data useful in pinpointing sources of pollution and in predicting potential health effects.

The objectives of the present study is to determine the concentrations of PM_{2.5} in ambient air representing different land use pattern in Mumbai city, to carry out chemical speciation of PM_{2.5} (metals, ions, elemental carbon and organic carbon), to do mass closure of speciated particles and to understand the sources. Mumbai is transforming into a city with increasing commercial activities compared to its past character of an industrial city known in the past. This change has led to high vehicular usages and acute congestions. Kerb site air quality shows high deterioration. Therefore, a kerb site/mixed site was chosen to examine the effect of increased traffic on air quality and compare the same with a residential location as well as an industrial location.

METHODS

Study Area

Mumbai is the commercial and industrial capital of India. The increase in number of vehicles from 1993 to

* Corresponding author. Tel.: +91-022 24973521;
Fax: +91-022 24936635
E-mail address: abbaelizabeth@gmail.com

2003 was 50% with 1604704 vehicles in 2008 (Transport Commissioners Office, 2008). This transformation shows high vehicular usages; therefore, kerb site/mixed site was chosen to examine the effect of increased traffic on air quality and compare the same with a residential location as well as an industrial location.

The study area map represents four categories of sampling sites (Fig. 1). Air monitoring was carried out at four locations representing control (C), kerb site (K), residential (R) and industrial (I) sites in Mumbai. The sampling was done in the year 2007–2008 representing three different seasons

i.e. winter, summer and monsoon. The control site was located at Colaba, which was selected to assess background levels as it is in close proximity to the seacoast and the effect of sea breeze can be distinctly felt, with minimum traffic and its three sides surrounded by the sea. Dadar was selected as a kerb site/mixed, because of heavy traffic and commercial activities; other emission sources are flyovers, petrol pump, bus terminals etc. Khar, which is a popular residential area located in the western suburbs, has a variety of sources, i.e. public transport and private buses, auto rickshaw plying on Western Express Highway, along



Fig. 1. Sampling Sites in Mumbai City.

with many hotels/restaurants, bakeries and airport. Mahul, designated as Industrial site has major industries like refineries, fertilizer and thermal power plant located in the vicinity. Other sources include unpaved roads, heavy duty vehicles, tankers, residential areas and sea coast as the contributors of air pollution.

Measurements

In the present study, ambient fine particles were measured for mass, ions, elements, organic carbon (OC) and elemental carbon (EC). The atmospheric fine particles were measured for a period of over 24 hours for 15 days in a season. The fine particles were measured using MinVol portable air samplers (Air Metrics, Eugene, USA) at the rate of 5 liters per minute for 24 hours on Whatman PTFE, polypropylene ring supported Teflon filter (46.2 mm and 2.0 μm Pore Size) and Pallflex tissue quartz filters, 47 mm.

EC and OC Analysis

The Desert Research Institute's (DRI) Thermal/Reflectance Optical Carbon Analyzer (Model 2001 A, Protocol Improve A) was used for measuring Organic Carbon (OC) and Elemental Carbon (EC). This method is based on preferential oxidation of organic carbon and elemental carbon compounds at different temperatures. The principal function of the optical component of the analyzer is correction for pyrolysis of organic carbon. The eight fractions OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OPC (Pyrolyzed Organic Carbon) are reported. The IMPROVE protocol defines OC as OC1 + OC2 + OC3 + OC4 + OPC and EC as EC1 + EC2 + EC3 – OPC (DRI, 2000). A filter punch is submitted to volatilization at 120, 250, 450, and 550°C in a 100% helium atmosphere, then to combustion at 550, 700, and 800°C in 2% oxygen and 98% helium atmosphere (DRI, 2000). The analysis is based on liberating carbon compounds at different temperatures. The sample boat having a punch of 0.5-cm² area is passed through oxygenator containing heated MnO₂ at 900°C. Here, volatilized carbon compounds get converted to CO₂. A Methanator having hydrogen-enriched Nickel catalyst reduces CO₂ to CH₄ at 425°C. The CH₄ concentration is detected using a Flame Ionization Detector (FID) at 125°C. CH₄ concentration is equivalent to elemental and organic carbon present in the sample. The results are noted in terms of reflectance based upper split values for regular OC, regular EC and TC in $\mu\text{g}/\text{filter}$. The analyzer was calibrated with known quantities of carbon dioxide. Replicate analyses were performed at the rate of 1 per 10 samples. The precision for OC is 1.2% and for EC is 5.0%. The punch for analysis was always taken from the centre of the filter paper in order to get a representative sample. The EC and OC analysis was performed at NEERI, Delhi Zonal Centre.

Ion Analysis

The first Teflon filter was used to analyze ions after mass determination. For the ion analysis, Teflon membrane filters were extracted in DI water using an ultrasonicator and then submitted for IC analysis. The target ions Cl⁻, NO₃⁻, SO₄²⁻, K⁺, NH₄⁺, Na⁺, and Ca²⁺ were analyzed by Ion Chromatograph, DIONEX-100 with a cation exchange

column, Ionpac CS12 and an anion exchange column, Ionpac AS4 A-SC with a conductivity detector. The eluant used for anion was 1.8 mM Na₂CO₃/1.7 mM NaHCO₃ and for cation 18 mM Methanesulphonic Acid (MSA) with the regenerant flow rate of 1 mL/min was used. Filter blanks were determined and considered for the calculation purposes. The ions were estimated at NEERI, Nagpur, India. Ionic difference percentage was 37%, 52%, 45%, 30% at C, K, R and I which is an acceptable criterion for samples ≤ 50 as per World Meteorological Organization quality assurance criteria (WMO, 2004).

Elemental Analysis

The samples collected on Teflon filter were extracted in a clean and labeled 100 mL beaker by adding 5 mL aqua regia (15 mL GR grade concentrated HCl and 5 mL of GR grade concentrated HNO₃). Refluxing was done for 4–5 hours at 90°C without allowing the sample to dry. It was then allowed to cool. The beaker was rinsed with deionized (DI) water and the final volume of 25 mL was made by DI water. The sample was then analyzed on Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP–AES), (Model-Horiba Jobin-Yvon, Ultima, 2000). The operating conditions of ICP–AES were: temperature of the instrument lab at 20°C, inert gas of Argon, line pressure for plasma at 6 to 7 kg/cm², line pressure for purge at 1 to 2 kg/cm², and sample uptake flow rate at 1 mL/min. The instrument was calibrated using NIST traceable standards (multi-elemental standards) every time before start-up. All reagents used for digestion of samples (acids, DI water) were analyzed for background elemental concentrations. Field blanks and laboratory blanks were also digested along with the exposed filters and analyzed for background concentration of elements. The elemental analysis was carried out at Indian Institute of Technology, Bombay (IITB).

RESULTS AND DISCUSSION

A total of 174 samples of PM_{2.5} were collected at four monitoring sites in Mumbai city during the study period. The four sigma test was used to identify potential outlier in the dataset. According to Chebyshev's theorem, ± 4 standard deviation is used to ensure that at least 94% of the data fall inside the interval. Outliers were removed by 4 sigma test and latter subject to statistical analysis (Gupta *et al.*, 1996). One outlier at Colaba, Dadar and Mahul and four outliers at Khar were observed. The three season's average PM_{2.5} mass and chemical components in fine aerosol are given in Table 1.

PM_{2.5} Levels

The average PM_{2.5} mass concentrations at C, K, R and I site were 69 ± 20 , 84 ± 31 , 89 ± 33 and 95 ± 36 $\mu\text{g}/\text{m}^3$ respectively. The mean concentration of PM_{2.5} measured at industrial sites was higher than the other three sites. The next highest concentration was measured at residential location. In India, land use patterns are mixed and simply do not represent residential activities. The PM_{2.5} levels estimated at Colaba was less than the other sites which represents background site.

Table 1. Concentrations of PM_{2.5} Chemical Speciation During 2007–2008.

| | Colaba | (±) Stdev | Dadar | (±) Stdev | Khar | (±) Stdev | Mahul | (±) Stdev |
|-----------------------------------|--------|-----------|-------|-----------|-------|-----------|-------|-----------|
| PM _{2.5} | 69 | 20 | 84 | 31 | 89 | 33 | 95 | 36 |
| OC | 20.40 | 7.51 | 28.40 | 14.12 | 31.30 | 14.69 | 29.10 | 15.06 |
| EC | 5.00 | 2.71 | 9.20 | 4.35 | 7.70 | 4.83 | 7.20 | 3.95 |
| TC | 25.40 | 9.74 | 37.60 | 17.54 | 39.10 | 18.52 | 36.40 | 18.28 |
| OC1 | 1.10 | 0.84 | 1.60 | 1.41 | 1.60 | 1.05 | 1.40 | 1.02 |
| OC2 | 6.30 | 2.39 | 9.70 | 4.99 | 12.40 | 6.27 | 9.70 | 4.84 |
| OC3 | 5.20 | 1.65 | 7.70 | 4.31 | 8.40 | 3.56 | 8.00 | 4.17 |
| OC4 | 3.50 | 1.82 | 3.80 | 2.03 | 4.30 | 2.36 | 4.70 | 3.05 |
| EC1 | 8.60 | 3.64 | 13.50 | 8.22 | 11.40 | 7.52 | 11.50 | 7.24 |
| EC2 | 0.60 | 0.26 | 1.00 | 0.93 | 0.90 | 1.41 | 0.80 | 0.55 |
| EC3 | 0.10 | 0.09 | 0.30 | 0.16 | 0.10 | 0.16 | 0.20 | 0.23 |
| OPC | 4.30 | 1.64 | 5.60 | 4.80 | 4.70 | 4.14 | 5.30 | 4.28 |
| Ca ²⁺ | 0.80 | 0.39 | 0.80 | 0.38 | 0.80 | 0.54 | 2.00 | 1.89 |
| Cl ⁻ | 5.00 | 2.96 | 6.20 | 3.75 | 3.30 | 2.87 | 4.70 | 3.35 |
| K ⁺ | 1.50 | 0.68 | 1.00 | 0.53 | 1.10 | 0.42 | 2.10 | 1.30 |
| Na ⁺ | 2.20 | 1.17 | 3.50 | 1.11 | 2.30 | 1.31 | 2.70 | 1.84 |
| NH ₄ ⁺ | 4.90 | 2.30 | 2.70 | 2.43 | 2.40 | 1.68 | 3.30 | 2.67 |
| NO ₃ ⁻ | 2.70 | 2.40 | 4.40 | 4.24 | 1.80 | 1.12 | 3.50 | 2.88 |
| SO ₄ ²⁻ | 13.20 | 5.56 | 11.50 | 7.90 | 11.20 | 8.69 | 12.90 | 8.35 |
| Al | 0.07 | 0.06 | 0.04 | 0.03 | 0.04 | 0.03 | 0.08 | 0.11 |
| As | 0.06 | 0.02 | | | | | 0.04 | 0.01 |
| Ba | 0.04 | 0.03 | 0.05 | 0.05 | 0.02 | 0.02 | 0.05 | 0.04 |
| Ca | 2.57 | 1.62 | 3.46 | 2.21 | 1.31 | 1.00 | 2.59 | 2.23 |
| Cd | | | 0.02 | | 0.03 | 0.01 | 0.08 | 0.08 |
| Cu | 0.02 | 0.01 | 0.04 | 0.04 | 0.04 | 0.02 | 0.04 | 0.03 |
| Cr | 0.04 | 0.02 | 0.06 | 0.07 | 0.04 | 0.04 | 0.04 | 0.03 |
| Fe | 2.78 | 2.12 | 2.89 | 1.93 | 1.22 | 0.82 | 2.62 | 2.49 |
| In | 0.60 | 0.39 | 0.50 | 0.46 | 0.38 | 0.24 | 0.64 | 0.49 |
| K | 1.65 | 0.74 | 1.44 | 0.46 | 1.30 | 0.78 | 2.29 | 1.51 |
| Mg | 0.38 | 0.26 | 0.31 | 0.19 | 0.19 | 0.07 | 1.06 | 1.13 |
| Mn | 0.05 | 0.04 | 0.04 | 0.03 | 0.04 | 0.05 | 0.06 | 0.05 |
| Na | 1.52 | 1.08 | 0.95 | 0.63 | 0.54 | 0.22 | 1.99 | 1.41 |
| Ni | 0.04 | 0.02 | 0.10 | 0.09 | 0.02 | 0.01 | 0.04 | 0.02 |
| Pb | 0.42 | 0.25 | 0.32 | 0.23 | 0.40 | 0.23 | 0.59 | 0.58 |
| Se | 0.04 | 0.01 | 0.02 | 0.01 | 0.03 | 0.01 | 0.04 | 0.03 |
| Si | 0.95 | 0.93 | 0.50 | 0.39 | 0.68 | 0.36 | 0.88 | 0.66 |
| Sr | 0.01 | | 0.01 | | 0.01 | 0.01 | 0.01 | 0.02 |
| Ti | 0.03 | 0.02 | 0.04 | 0.02 | 0.02 | 0.01 | 0.05 | 0.04 |
| V | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 |
| Zn | 0.81 | 0.66 | 0.61 | 0.46 | 0.52 | 0.38 | 0.78 | 0.68 |
| nss-Ca ²⁺ | 0.75 | 0.38 | 0.6 | 0.39 | 0.7 | 0.52 | 1.9 | 1.89 |
| nss-K ⁺ | 1.40 | 0.68 | 0.9 | 0.52 | 1.0 | 0.41 | 2.1 | 1.30 |
| nss-SO ₄ ²⁻ | 12.64 | 5.49 | 10.6 | 7.84 | 10.6 | 8.51 | 12.2 | 8.28 |
| ss-Ca ²⁺ | 0.08 | 0.04 | 0.1 | 0.04 | 0.1 | 0.05 | 0.1 | 0.07 |
| ssK ⁺ | 0.08 | 0.04 | 0.1 | 0.04 | 0.1 | 0.05 | 0.1 | 0.07 |
| ss-SO ₄ ²⁻ | 0.55 | 0.29 | 0.8 | 0.27 | 0.6 | 0.32 | 0.7 | 0.45 |
| Count | 44 | | 44 | | 41 | | 44 | |

* Mean of three seasons concentrations in $\mu\text{g}/\text{m}^3$.

The levels remained within CPCB standard in summer season at three sites (C, K and R) except for industrial locations. During post monsoon and winter seasons, the 24-hour average concentration of PM_{2.5} exceeded CPCB Standards (Fig. 2). During winter, lower temperature, calm conditions, lower mixing depth, and temperature inversion restrict and confine pollutants dispersion and dispersal. The

percentage exceedances of PM_{2.5} standards (CPCB) at C, K, R and I site were 59, 76, 67 and 80% respectively. A seasonal percent contribution of chemical components in PM_{2.5} is given in Table 2. Average total carbon contribution to PM_{2.5} is about 40%, whereas remaining was inorganic, elements and ions. Anion percent contribution was higher at control and kerb site as compared to residential and

industrial site. High anion concentration at control could be due to sea coast, proximity to dock activities (use of diesel) and secondary ions getting transported from other part (Industrial) site. Kerb site has highest heavy duty vehicles plying as compared to other sites which may lead to high

contribution of nitrates and sulphates. Percentage contribution of OC and EC increases during post monsoon and winter. During summer season, increased mixing depths lead to dilution of the pollutants whereas in winter, temperature inversions play a significant role in building up carbon

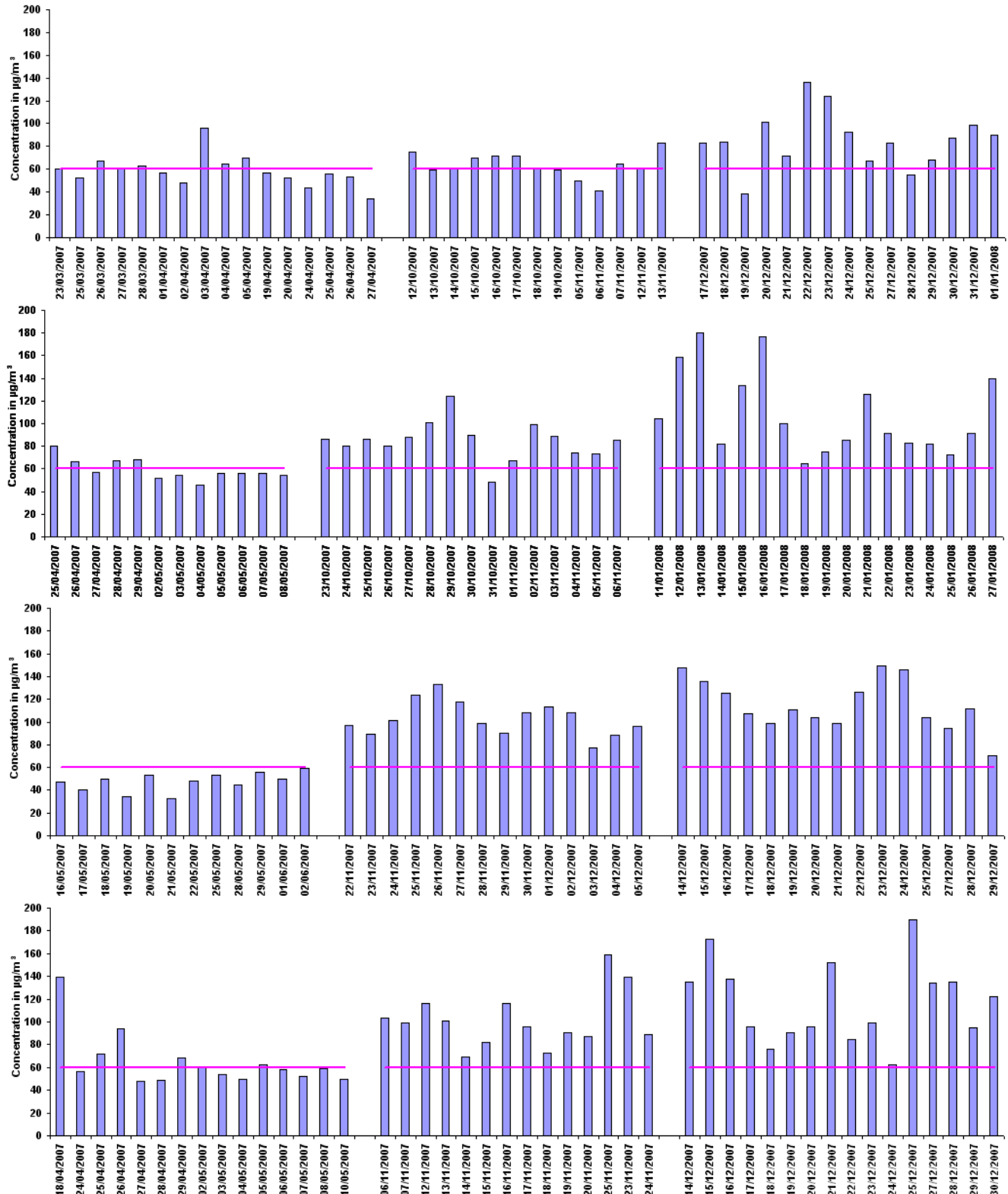


Fig. 2. Concentration of $\text{PM}_{2.5}$ During Summer, Post Monsoon and Winter.

Table 2. Seasonal Percent Contributions of Chemical Components in PM_{2.5}.

| | Control | Kerb | Residential | Industrial |
|--|---------|------|-------------|------------|
| Summer | | | | |
| PM _{2.5} (µg/m ³) | 58 | 59 | 47 | 65 |
| OC | 21 | 27 | 33 | 19 |
| EC | 4 | 10 | 6 | 5 |
| TC (OC + EC) | 26 | 37 | 39 | 25 |
| Sum Cations | 19 | 9 | 12 | 16 |
| Sum Anions | 27 | 27 | 12 | 22 |
| Crustal | 9 | 18 | 5 | 5 |
| Non Crustal | 8 | 5 | 4 | 9 |
| Post Monsoon | | | | |
| PM _{2.5} (µg/m ³) | 64 | 85 | 103 | 101 |
| OC | 34 | 29 | 37 | 32 |
| EC | 9 | 10 | 10 | 9 |
| TC (OC+EC) | 43 | 40 | 47 | 40 |
| Sum Cations | 13 | 11 | 6 | 11 |
| Sum Anions | 31 | 26 | 17 | 22 |
| Crustal | 12 | 8 | 4 | 12 |
| Non Crustal | 10 | 8 | 4 | 12 |
| Winter | | | | |
| PM _{2.5} (µg/m ³) | 85 | 109 | 115 | 117 |
| OC | 32 | 41 | 35 | 36 |
| EC | 8 | 11 | 9 | 8 |
| TC (OC + EC) | 40 | 52 | 44 | 44 |
| Sum Cations | 10 | 9 | 7 | 8 |
| Sum Anions | 31 | 26 | 22 | 23 |
| Crustal | 7 | 3 | 3 | 3 |
| Non Crustal | 6 | 3 | 4 | 5 |

Values expressed in percent except PM_{2.5} concentration

concentrations. In summer season, due to high temperature, volatilization of OC leads to losses that may also affect OC concentrations. At kerb site, continuous vehicle movement leads to resuspension of road dust. Summer being a dry season, particles get resuspended naturally. Therefore, highest crustal contribution was estimated at kerb site during summer months.

Carbonaceous Fraction

EC is often used as a tracer for diesel exhaust particles (Götschi *et al.*, 2002). OC can be emitted from primary emission sources and generated from chemical reactions among primary gaseous organic carbon species in the atmosphere. Primary OC is emitted directly from combustion of fossil fuels, biomass burning, vegetative detritus and meat cooking. Secondary Organic Aerosols (SOC) are formed from the oxidation products of Volatile Organic Compound (VOC) gases (Seinfeld and Pandis, 1998).

OC concentrations ranged between 7.1–33.8 µg/m³, 11.7–67.5 µg/m³, 9.7–63.4 µg/m³ and 9.0–57.5 µg/m³ and corresponding EC concentrations ranged from 1.3–15.6 µg/m³, 4.6–28.3 µg/m³, 1.6–18.7 µg/m³ and 1.8–16.6 µg/m³ at C, K, R and I respectively. The average OC contributions at C, K, R and I sites were 30%, 34%, 35% and 31% respectively while the EC contributions were 7%, 11%, 9% and 8% respectively. The EC contribution at kerb site was higher than the other sites due to heavy duty vehicles on

the road. The EC levels would also be high next to kerb site as the EC is a by-product of high temperature combustion, which is due to vehicles engines burning diesel and petrol at high temperature. At industrial location, coal and oil burning, refineries and heavy duty vehicles could be the probable sources for TC. At residential sites, the possible sources for Total Carbon (TC) are vehicles, biomass burning, bakeries, etc. A significant correlation ($p = 0.01$) was obtained between OC and EC and they were 0.77, 0.67, 0.73 and 0.77 at C, K, R and I sites, indicating coexistences of sources e.g., vehicles, coal and biomass burning.

Eight Carbon fractions in PM_{2.5}

The carbon fraction abundances in a source category may be useful for source discrimination (Chow *et al.*, 2004). The average percentage of OC-EC in TC was about 80–20% except kerb site with 75–25%. The eight fractions are in the order of increasing volatility. OC1 compounds are more likely to be VOCs that are adsorbed by the filter matrix while OC2 and OC3 are semi-volatile compounds of increasing molecular weights.

The EC1 percentage in TC was highest (36%) at kerb site. EC1 is the soot commonly seen in urban atmosphere. It includes both automotive and some diesel soot. The difference in the carbon composition of source profiles for diesel- and gasoline-powered vehicles studied by Watson *et al.* (1994) indicated that EC1 in the gasoline-fueled

sample is larger, whereas EC2 is most abundant in exhaust of diesel fuel vehicles as compared to gasoline fuel vehicles. The fuel emission survey has indicated that, in Mumbai, 59% of the vehicles are fueled by petrol and 41% by diesel (NEERI, 2009). EC2 was 2–4% in TC at all sites. In general, EC2 and EC3 are much smaller than EC1. EC3 was present in modest traces. As per IMPROVE protocol; OC evolved in a ‘Helium only’ atmosphere at 120°C is defined as VOC. The percentage of OC1 in TC was 4% in TC. The high percentage of VOCs is due to vehicles and industries like refineries. The percentage of OC2 fraction in TC was 24%, 26%, 32% and 27% at C, K, R and I sites, while OC3 in TC was 20–22% and OC4 in TC was between 10–14% (Cao *et al.*, 2006) indicated that high OC2 and OC3 are associated with presence of gasoline and liquefied petroleum gas emissions and secondary organic carbon. The OC4 components may consist of a mixture of high boiling point hydrocarbons e.g PAHs. The Pyrolyzed Organic Carbon (OPC) in TC was 17%, 15%, 12% and 15% at C, K, R and I sites. OP is associated with water soluble organic carbon (Cao *et al.*, 2004).

Secondary Organic Carbon

The secondary organic aerosol cannot be detected directly; the minimum OC/EC ratio is used to estimate the amount of secondary organic carbon. EC is emitted from primary combustion sources. It is used as a tracer of primary organic carbon (Turpin and Huntzicker, 1995). The lowest OC/EC ratios contain exclusively primary carbonaceous compounds (Na *et al.*, 2004). Particulate OC/EC ratios larger than 2.0 have been used to identify SOC formation (Chow *et al.*, 1996). The OC/EC ratio may vary depending upon the sources present. Estimation of OC/EC is a challenge. Gray (1986) conducted organic particulate emission inventory and found OC/EC ratio of 2.4. Another method used by Turpin *et al.* (1995) include measurement of ambient OC/EC ratio at a time when secondary organic aerosol formation is expected to be less on days with low ozone concentrations, lack of sun, unstable air mass suggesting that photochemical activity would be minimum. The ratio determined by Turpin *et al.* (1995) was 2.2. Thus, the true primary OC/EC ratio was likely to be lower than 2.2. (Strader *et al.*, 1999).

Authors (Turpin *et al.*, 1995; Castro *et al.*; 1999) used the following equation to estimate:

$$\text{SOC} = \text{OC}_{\text{tot}} - \text{EC} (\text{OC/EC})_{\text{min}}$$

SOC = Secondary Organic Carbon, OC_{tot} = Total organic carbon in the sample

EC = Elemental carbon, $(\text{OC/EC})_{\text{min}}$ = minimum ratio observed in all sample

The average SOC concentration at C, K, R and I was 9.8 ± 5.0 , 13.5 ± 11.8 , 17.5 ± 5.1 , and 10.4 ± 5.7 $\mu\text{g}/\text{m}^3$ accounting for 48%, 48%, 56% and 36% of OC.

The OC/EC ratio at all the sites was larger than 2 with mean ratio of 4.3, 3.2, 4.5, and 4.2 at C, K, R and I site respectively. The OC/EC ratio was less at kerb site than the other site. The ratio larger than 2 implies that SOC is formed in Mumbai city. The OC/EC ratio ranged from 3 to 5 at all sites. A similar ratio between 2.0 to 4.7 was observed in China (Cao *et al.*, 2004). A study by Castro *et al.* (1999)

observed a ratio between 2.4 to 7.3 in coastal area of Areao, Brazil; 10.8 at Mace head, Ireland; and a very low ratio at Birmingham, UK. Various OC/EC ratios were reviewed by Na *et al.* (2004) in US cities, which ranged between 1.7 to 8.1. The OC/EC ratio in the present study is more comparable to studies in China. Previous studies by Cachier *et al.* (1995); Castro (1997) indicated that wood burning emissions are characterized by a higher value of OC/EC ratio. An OC/EC ratio of 4.15 for residential wood combustion was estimated by Watson *et al.* (2001) which is similar to the ratio observed in the present study. More research is needed on OC/EC ratio and SOC for Indian cities to better understand their formation mechanism.

Ions

Water soluble fraction of atmospheric aerosols contains many important compounds, which can change the size, composition, number and lifespan of aerosols owing to their hygroscopic nature. The anion percent contributions in $\text{PM}_{2.5}$ were 30%, 26%, 18% and 22% whereas cation contributions were 12%, 9%, 18% and 9% at C, K, R and I respectively.

Among the four sites, the highest ionic concentration was determined at control and lowest at residential. At control site, the high ionic contribution may be due to sea coast, sewage treatment plant and fishing vessels operating on diesel close to sampling station. And also during winter season, wind direction is mainly easterly and wind transports secondary ions from an industrial site and pollutes Colaba, which is situated downwind of the industrial site. The sources of precursor gases of ions like industries, dock activity was low at residential site leading to lower ion contribution. In India, all the sites, though associated with a particular zone, are in a broader sense mixed zones.

Sulphur dioxide is a primary pollutant. Sulphate formation mechanism includes direct photochemical oxidation or heterogeneous reaction. The primary oxidized reactive nitrogen compounds are nitric acid and particulate nitrate. Nitric acid is produced through gas phase oxidation of NO_x (Zhuang, 1999) which is emitted directly into the atmosphere from anthropogenic activities like the combustion of fossil fuels. Ambient concentrations of sulphate and nitrate are not necessarily proportional to quantities of direct emissions. Their formation is also enhanced due to photochemical reactions. Among the anionic components, sulphate was the major component at all sites. The possible sources of sulphate include fuel combustion in vehicles and industries. Sea spray and photochemical activity are also sources for sulphate. The average percentage of SO_4^{2-} in $\text{PM}_{2.5}$ was estimated as 19%, 14%, 13%, and 14% at C, K, R and I site respectively.

Ionic constituents such as SO_4^{2-} , K^+ and Ca^{2+} are derived from both marine or non-marine origins, i.e. anthropogenic and soil emission. Hence, it is necessary to discriminate sea salt (ss) from non-sea salt (nss) contributions for a city like Mumbai, which has marine environments on three sides. The non-marine component is evaluated from the Na^+ concentration on an assumption that all sodium ions originated from the sea. The marine sea salt (ss) and non-sea salt (nss) contributions were calculated using ratios like

$\text{SO}_4^{2-}/\text{Na}^+$, K^+/Na^+ , and Ca^{2+}/Na in bulk sea water using the formulae (Keene *et al.*, 1986). The nss contributions of SO_4^{2-} , K^+ and Ca^{2+} were over 85% suggesting other anthropogenic sources. The equivalent ratio of Cl^- , Ca^{2+} , SO_4^{2-} and K^+ with Na^+ is greater than the sea water ratio. The percentages of NO_3^- in $\text{PM}_{2.5}$ were 4%, 5%, 2% and 4% at C, K, R and I respectively. Maximum NO_3^- concentration of $23 \mu\text{g}/\text{m}^3$ was measured at kerb site. The concentrations of NO_3^- were high in winter and low in summer. The lower temperature in winter would favor the shift from the gas phase of nitric acid to the particle phase of ammonium nitrate which could lead to high concentration of NO_3^- . Good correlations between NO_3^- and SO_4^{2-} at C, K, R and I were 0.48, 0.81, 0.66, and 0.80 ($p = 0.01$) respectively, indicating common sources like vehicle, industries and secondary inorganic aerosol formation.

Na^+ and Cl^- are also major components of airborne particulates in coastal areas. Na^+ and Cl^- concentration were 7.2, 9.6, 5.6 and $7.4 \mu\text{g}/\text{m}^3$ at C, K, R and I respectively. Significant correlations ($p = 0.01$) between Na^+ and Cl^- were 0.92, 0.49, 0.47, 0.65 at C, K, R and I respectively indicating influence of sea spray in Mumbai.

Potassium ion commonly found in plants as a constituent of chlorophyll is tracer for biomass burning and it is extensively found in fine particles (Chow, 1995). The nss K^+ contributed 95%, 91%, 93%, and 97% of the total K^+ . The nss K^+/K^+ ratio were 0.85, 0.63, 0.77 and 0.90 respectively, indicating that K^+ accounts for major portion of the total K. A significant correlation between nss K^+ and K as 0.99 at all sites proves that K exists in fine aerosol mainly as soluble K^+ .

Minor contribution by calcium about 1–2% of mass was observed at all sites. Calcium is generally derived from soil/crustal material. Construction activity is also a source of calcium.

Ammonium percentages in $\text{PM}_{2.5}$ were 7%, 3%, 3% and 4% at C, K, R and I sites respectively. The $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio was 2.0, 1.3, 1.1 and 1.4 at C, K, R and I sites respectively. Total Ammonia/Total Sulphate (TA/TS) molar ratio is used to evaluate that the cases are ammonia- rich (non acidic) or ammonia- poor (acidic). Seinfeld and Pandis (1998), reported that if (Total Ammonium) TA/(Total Sulphate) TS is < 0.5 , then aerosol particles exists as H_2SO_4 solution. If the ratio is between 0.5–1.25, then NH_4HSO_4 is the dominant component. For ratio between 1.25–1.5 it exists as NH_4HSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ letovicite and, if the ratio is equal to 2 then all the ammonia is fully neutralized with sulphate present and therefore $(\text{NH}_4)_2\text{SO}_4$ is present. In the present study, none of the ratios were less than 0.5. At Control, ratio is 2 indicating particles may be in the form of $(\text{NH}_4)_2\text{SO}_4$ whereas, at the rest NH_4HSO_4 may be the dominant component.

Elements

In the present study, 21 elements were analyzed by ICP-AES starting from Al to Zn. Crustal particles are introduced into the atmosphere either naturally by wind or as resuspended dust due to movement of vehicles. The crustal components include common elements in Earth's crust like Al, Si, Ca and Fe; non-crustal contribution is obtained by

excluding crustal elements. Crustal contribution was 9%, 8%, 4% and 7% whereas non-crustal accounted for 7%, 5%, 4%, and 8% at C, K, R and I, respectively. Non crustal contribution was highest at industrial site and crustal at control site.

The Indian Ministry of Environment and Forests Notification, November 2009, revised standards for Pb making it more stringent as $0.5 \mu\text{g}/\text{m}^3$ for industrial, residential, rural and ecologically sensitive areas. The averages of three seasons for Pb were 0.423, 0.316, 0.403, and $0.591 \mu\text{g}/\text{m}^3$ at C, K, R and I site respectively. Pb levels were within CPCB standards at C, K and R except industrial site. Maximum lead concentration of $2.262 \mu\text{g}/\text{m}^3$ was recorded at Industrial site during winter season. Gasoline lead phase out programme in India started in June 1994 with 0.15 g/L in metro to 0.013 g/L, phase 7 in February 2000 for the entire country. Although unleaded gasoline is used in the entire country, lead is still dispersed in the particles that are resuspended by strong winds and traffic. Significant correlations at the level of $p = 0.01$ were obtained between Pb and Zn ($r = 0.43, 0.77$ and 0.59) indicating vehicular sources (road dust and tire wear) at C, K and I respectively (USEPA, 2004).

The most prominent markers for oil combustion identified in the previous studies were V and Ni (Huang *et al.*, 1994). Cr as a heavy fuel oil marker was identified by Hosiokangas *et al.* (1996). In the present study, significant correlation was obtained between Ni and V (0.81, 0.63, $p = 0.01$) at control and kerb sites. At control site, nearby dock activities may be responsible, and at kerb site vehicular activities and smelters in the vicinity of sampling station could be likely sources. Ni correlated well with Cr ($r = 0.63, p = 0.01$) at industrial site indicating oil combustion as the source. Significant correlations were also observed among crustal species like Fe, Ca, Si, Ti, Sr, Mg, at all sites indicating common crustal source.

Past studies have associated Se with coal burning. The average concentrations of Se were 0.037, 0.023, 0.034 and $0.043 \mu\text{g}/\text{m}^3$ at C, K, R and I sites respectively. The highest concentration was observed at Mahul which has a coal-based thermal power in the vicinity of sampling station. Concentration of As, $0.039 \mu\text{g}/\text{m}^3$ was estimated at Mahul during post-monsoon season which is also considered tracer for coal combustion.

Enrichment Factor

Enrichment factor is a type of receptor model that accounts for increase in rate of chemical concentration in the atmosphere relative to the same ratios in a reference material associated with a source. The concept of enrichment factor (EF) is based on the fact that metals originating from relatively well known sources such as Al, Si or Fe originating from the earth crust can be distinguished from other metals derived by different sources (Sharma, 1994). To estimate whether the presence of certain element in $\text{PM}_{2.5}$ aerosol is due to anthropogenic or natural processes, the enrichment factor of elements was determined with reference to Si. If $\text{EF} \geq 10$ (Wang *et al.*, 2006), the element X in aerosol is considered to emerge from anthropogenic pollution.

As seen in Fig. 3, the EF of Al and Ti was low (< 10), thereby suggesting non-enriched elements because of crustal origin. Ca, Fe, Mn, Na, K, Cr, were moderately enriched ($10 > EF < 1000$) because their main sources are of natural origin like soil and sea salt. These elements are also emitted from re-suspension of road dust and construction activities. Pb and Zn were highly enriched (> 1000) suggesting anthropogenic sources like vehicle, industries and tire wear. Elements with high EF generally have low concentrations.

Mass Closure

Mass closure refers to a simple mass balance modeling procedure that can be used for apportioning particulate matter to its component (Vallius *et al.*, 2008). In chemical mass closure method, the gravimetric mass is compared with the chemical mass obtained by summing up individual chemical components. The basis for mass closure is the analysis of particulate matter for a number of chemical components, which can then be used as tracers of major aerosol constituents (Harrison *et al.*, 2003).

Mass closure analysis in the present study is adopted from Chow *et al.* (2002). Crustal matter originates from soil which is expressed as its oxides. The organic matter reconstruction procedure used in the present study was based on a value of 1.4 for the OC multiplier (Turpin *et al.*, 2001). The factor 1.4 corrects the organic carbon mass for other elements like O, H, N associated with organic carbon. The mass of elemental carbon as measured by TOR, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 assumed to be the main forms of secondary ions in urban environment were included in the mass closure. The chloride in the aerosol was assumed to come solely from sea and sea salt was used in the calculation.

The material balance equation is as follows:

$$\begin{aligned} \text{PM Mass} = & \text{Geological } [(1.89 \times \text{Aluminium}) + (2.14 \times \\ & \text{Silicon}) + (1.4 \times \text{Calcium})] + (1.43 \times \text{Iron}) + \\ & \text{Organic Matter } (= 1.4 \times \text{Organic Carbon}) + \\ & \text{Elemental Carbon} + \text{Ammonium Nitrate } (= 0.29 \times \\ & \text{Nitrate}) + \\ & \text{Ammonium Sulfate } (= 1.375 \times \text{Sulphate}) + \\ & \text{Sea Salt } (= 1.65 \times \text{Chloride}) + \\ & \text{Trace Elements (Excluding geological elements)} + \\ & \text{Unidentified} \end{aligned}$$

A material balance is a preliminary source apportionment that allocates $\text{PM}_{2.5}$ to geological material, OM, EC, sulphate, nitrate, ammonium and marine salt. (Watson *et al.*, 2002). The average attribution of $\text{PM}_{2.5}$ to each aerosol type is given in Fig. 4. The major components in $\text{PM}_{2.5}$ in Mumbai city contain organic matter (36, 42, 52, 43%), secondary inorganic aerosols (27, 23, 21, 23%), crustal (12, 11, 6, 10%), noncrustal (7, 5, 4, 8%) and sea salt (10, 11, 6, 8%) at C, K, R and I respectively. The contributions by crustal, non crustal and sea salt were low as compared to organic matter and secondary inorganic aerosol (SIA). The higher percentages of NO_3^- and EC at kerb site indicate influence of diesel vehicles. NO_x emissions arise from road traffic (Hutchinson and Clewley, 1996). The heavy duty vehicles operating on diesel are high in number at kerb site. Compared to gasoline engine, diesel emissions are lower in carbon monoxide (CO), hydrocarbon (HC) and carbon dioxide (CO_2), but higher in oxides of nitrogen (NO_x) and particulate matter (CPCB, 2011) NO_x is a precursor gas for the formation of nitrate particles and it may be derived from diesel combustion in the vicinity of sampling station.

The highest organic carbon concentration and significant SOC formation at residential site indicates strong sources of organic carbon. Possible sources could be wood-burning activities in bakeries and crematoria, biomass burning, vehicles and photochemical activity (NEERI, 2009).

The secondary inorganic aerosol (ammonium nitrate and ammonium sulphate) were highest at the control site. The sulphate contribution is greater than 15% at all sites. The EC contribution was highest at the kerb site. The gravimetric mass exceeded sum of the chemical components at residential site and industrial site by 6% and 1%, whereas at control and kerb site the mass was less than the sum of the chemical components by 12%. Mass closure can also be used for quality assurance of data. Pearson correlation was done between $\text{PM}_{2.5}$ gravimetric mass and sum of the chemical components. The r values were 0.8, 0.94, 0.95, and 0.88 at C, K, R and I respectively, showing that calculated and measured mass is explained well.

In Mexico, mass closure analysis shows OM-45%, SIA-29%, EC-14% and geological-14% (Chow *et al.*, 2002). In the United States, the contributions of sulphate-30%, OM-31%,

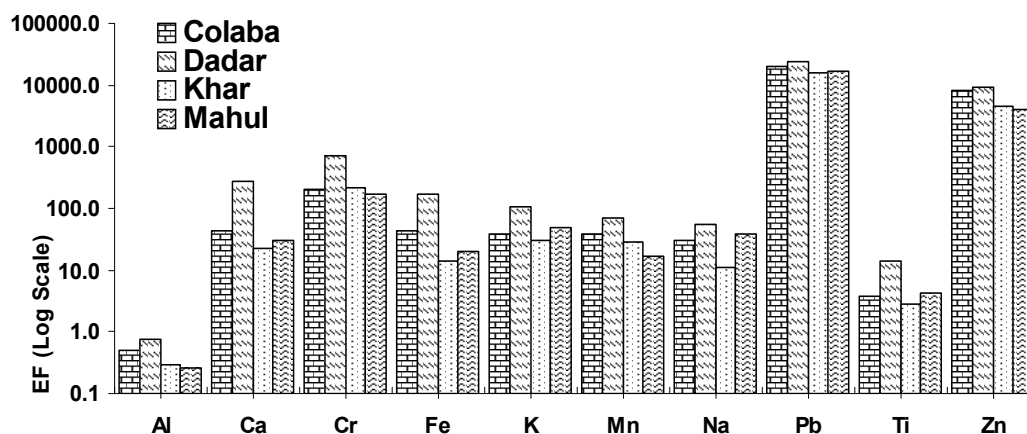


Fig. 3. Spatial Variation of Enrichment Factor of Elements.

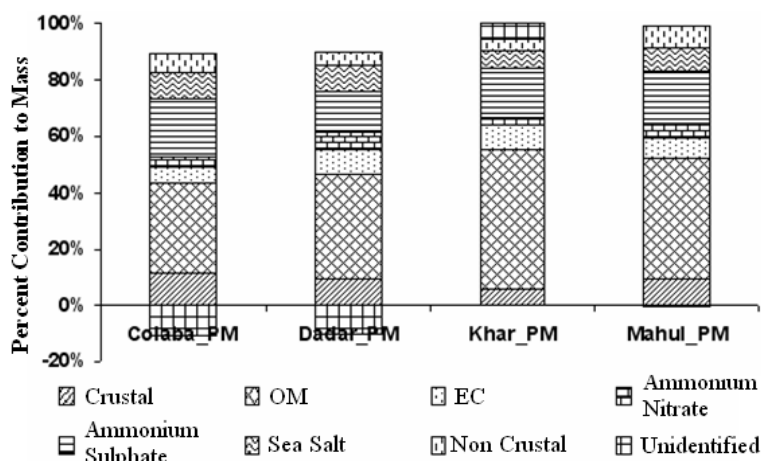


Fig. 4. Mass Closures at Different Sites in Mumbai.

EC-4%, crustal -10%, were estimated at Cincinnati whereas contributions of OM-23%, EC-3%, SIA-45%, crustal-10% at Pittsburgh were observed (Martuzevicius *et al.*, 2004; Rees *et al.*, 2004). In Shanghai, China, OC-30%, SIA-40% and crustal 10% were observed while in Macao, China, OM-40%, EC-7%, SIA-28% were determined (Wu *et al.*, 2003). In Europe, fine particles show SIA-39%, OM-35%, and EC-7% (Sillanpää *et al.*, 2006). The contribution of SIA in Europe and US is higher as compared to organic matter, whereas in India and Mexico, organic matter contribution is higher as compared to secondary inorganic aerosols. China, India and Mexico also have higher OC and EC contribution as compared to the US and Europe.

CONCLUSIONS

Accurate measurement and speciation is essential in air quality management. Determination of chemical composition of particulate matter facilitates the identification of major source categories in a given airshed. The percentage exceedances of $PM_{2.5}$ standards (CPCB) at C, K, R and I site were 59%, 80%, 71% and 80% respectively. More than 50% exceedances show the non-attainment of the CPCB standard for $PM_{2.5}$. In order to meet the $PM_{2.5}$ standards, it is necessary to generate time series data and plan in future to regulate the attainment standards. It is very essential to understand the background levels of fine particles also. EC contribution at kerb site was higher than the other sites due to heavy duty vehicles. The OC/EC ratio in the environment at all the sites was larger than 2 indicating SOC formation. Among the four sites, the highest ionic concentration was determined at control and lowest at residential. The nss contribution of SO_4^{2-} , K^+ and Ca^{2+} was over 85% suggesting anthropogenic sources. The equivalent ratios of Cl^- , Ca^{2+} , SO_4^{2-} and K^+ with Na^+ were greater than sea water ratio indicating anthropogenic sources. The good correlation of Na^+ and Cl^- at all sites indicates influence of sea spray in Mumbai. nss K^+ was > 90 of the total K^+ , which is a tracer for biomass burning.

Pb and Zn were highly enriched (> 1000) suggesting sources like vehicle, industries and tire wear. The reconstruction of

$PM_{2.5}$ mass in Mumbai city includes organic matter (36–52%) and secondary inorganic aerosols (21–27%). The contributions by crustal (6–12%), noncrustal (4–8%) and sea salt (6–11%) were low as compared to organic matter and SIA.

Mass closure and chemical mass balance model contribution reveal that a significant component of fine particles in Mumbai is organic in nature. About 30 to 50% OC is secondary in nature. The Indian Ministry of Standards has introduced mass-based standards for $PM_{2.5}$, but particulate research shows that toxic characteristics may depend on some properties other than mass. An improvement in the understanding of the ratio of carbon mass to total mass of OC is required. The typical ratio of converting organic carbon to organic matter is 1.2 to 1.6. There is a need of an appropriate factor. A major portion of SO_4^{2-} and K^+ is anthropogenic in nature. In Indian National Ambient Air Quality Monitoring Programmes along with mass measurement, a long-term speciation study is required. In addition to heavy metal characterization, OC, EC, anions like SO_4^{2-} , NO_3^- , Cl^- , cations like NH_4^+ , Na^+ , K^+ , and crustal components need to be speciated. In India, the development of standard methodologies and expertise in organic speciation is also required. A spatial understanding of sources of various regions in India is needed.

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