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Chemical Composition of $PM_{2.5}$ in metropolitan cities in India: Results from extensive winter campaign

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Introduction

- Atmospheric PM is a complex mixture of elemental and organic carbon, ions, mineral dust, trace elements

- Natural or anthropogenic origin and can be emitted directly into the atmosphere, or formed in the atmosphere from gaseous precursors

- Study of particle concentrations, and chemical composition at defined receptors is essential to elucidate the sources of the aerosols (Wang et al., 2003, Cheng et al., 2005, Yin and Harrison, 2008, Putaud et al., 2010)

- Concentration and chemical composition of PM can be influenced by processes on a regional scale & by long-range pollution transport

Objectives of the study

- This presentation focuses on the

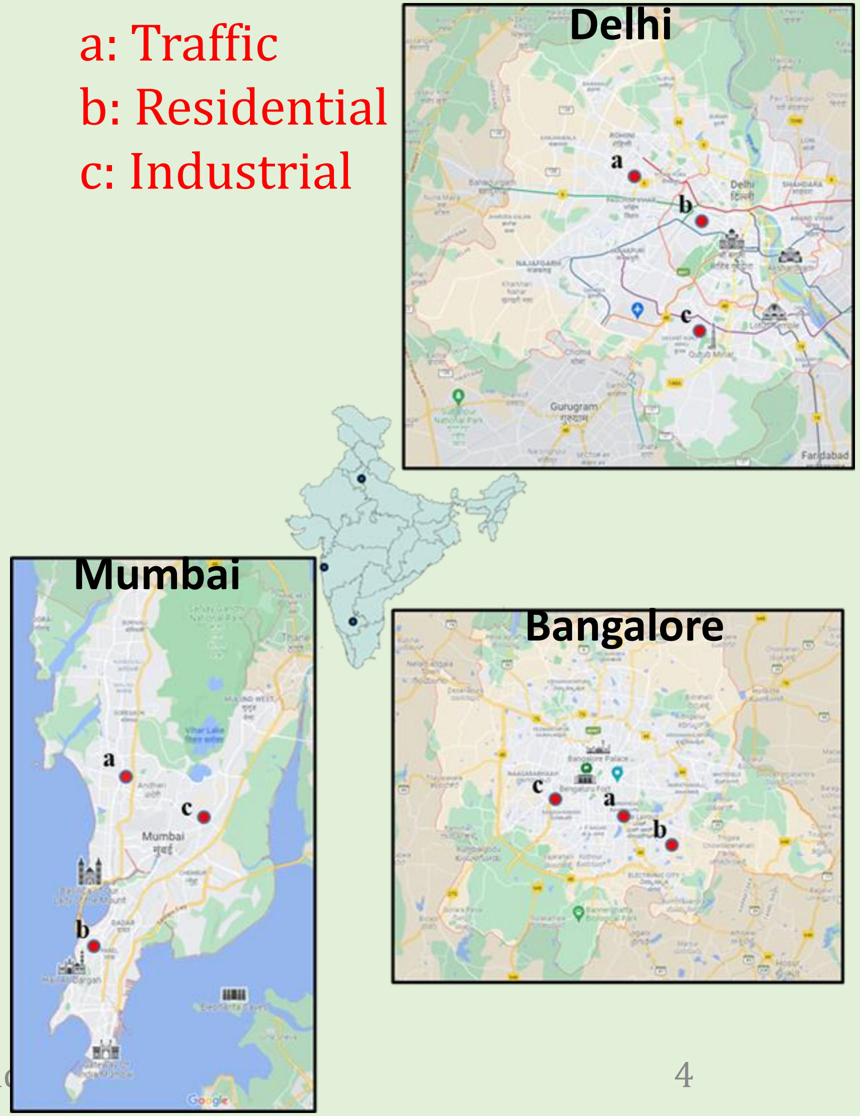
  - Determination of the concentration

  - Chemical characterization

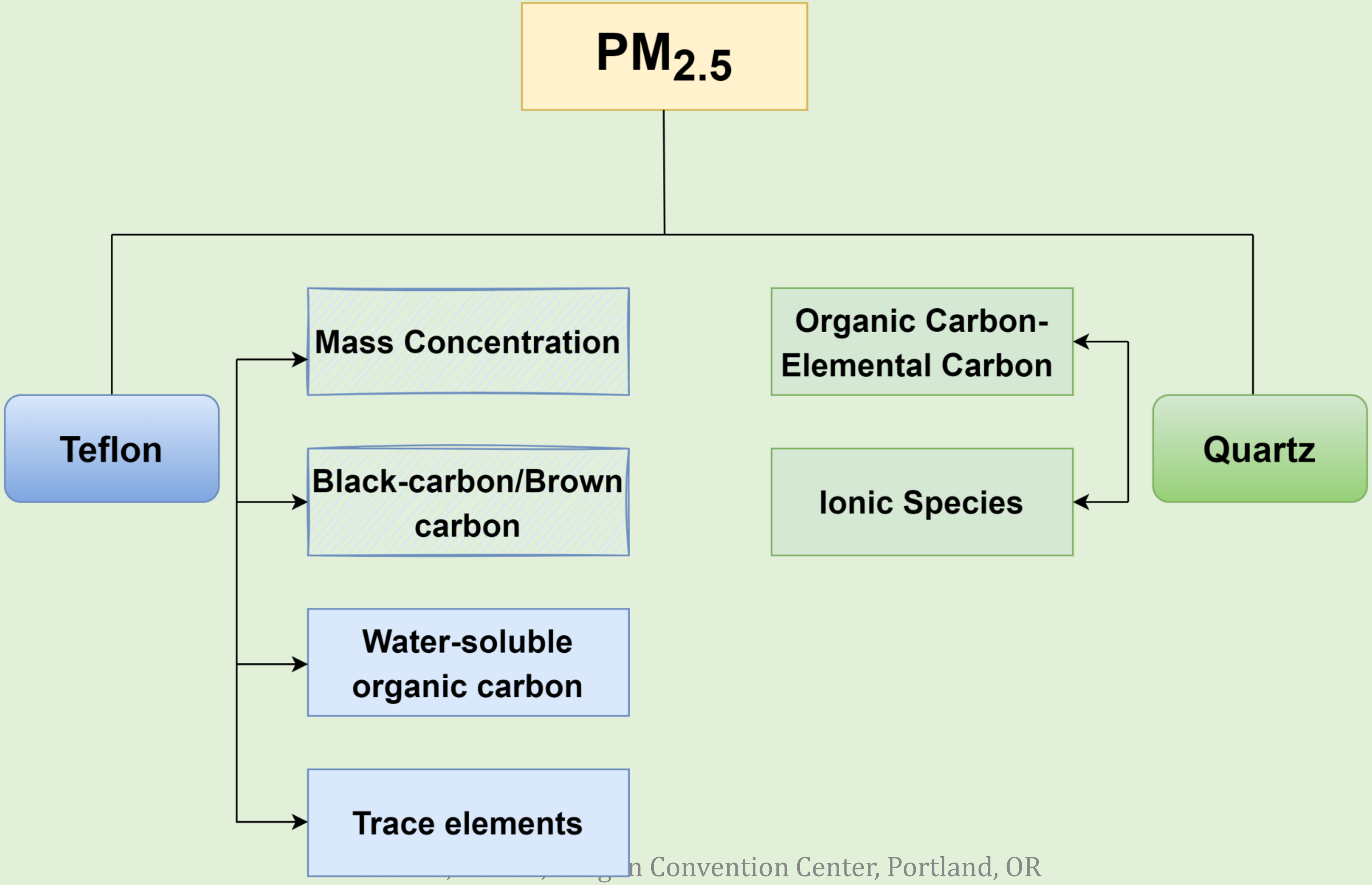
  - Sources of atmospheric $PM_{2.5}$ at traffic, industrial and residential sites in three metropolitan cities in India

Methodology

- Part of CASAI study (1500 women from 3 cities)
- Sites should be sufficient to capture the anticipated spatial variation of air pollutants in this area
- Three sites selected- traffic, residential and industrial
- MiniVol Tactical Air Sampler used to collect bi-weekly $PM_{2.5}$ samples at 5 l/min for 24 hrs

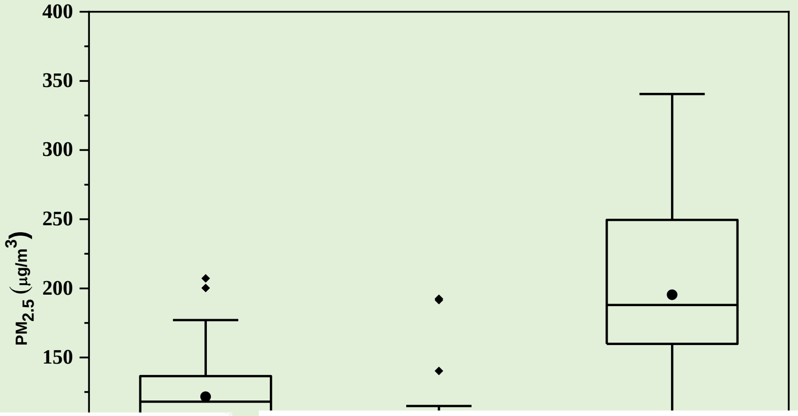


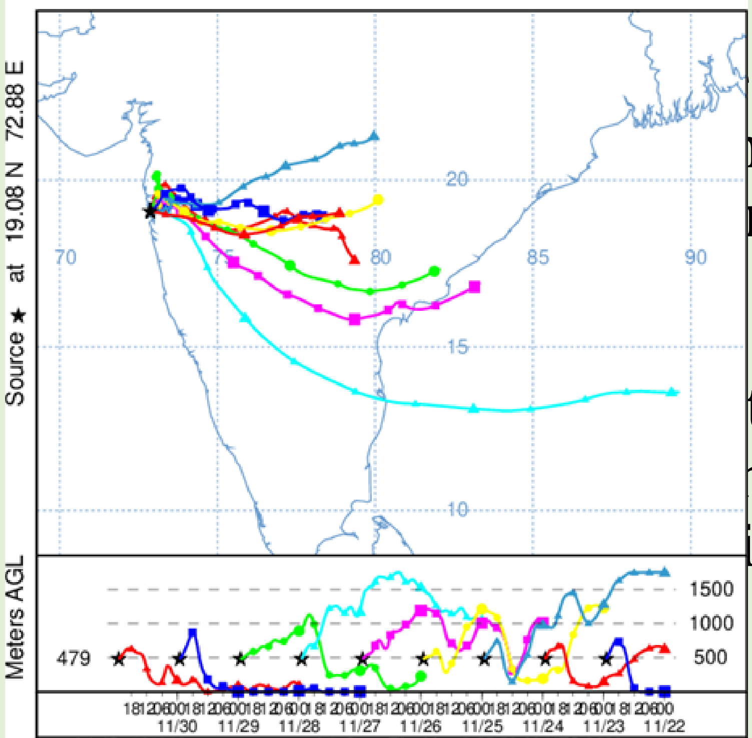
Methodology- Chemical Analysis

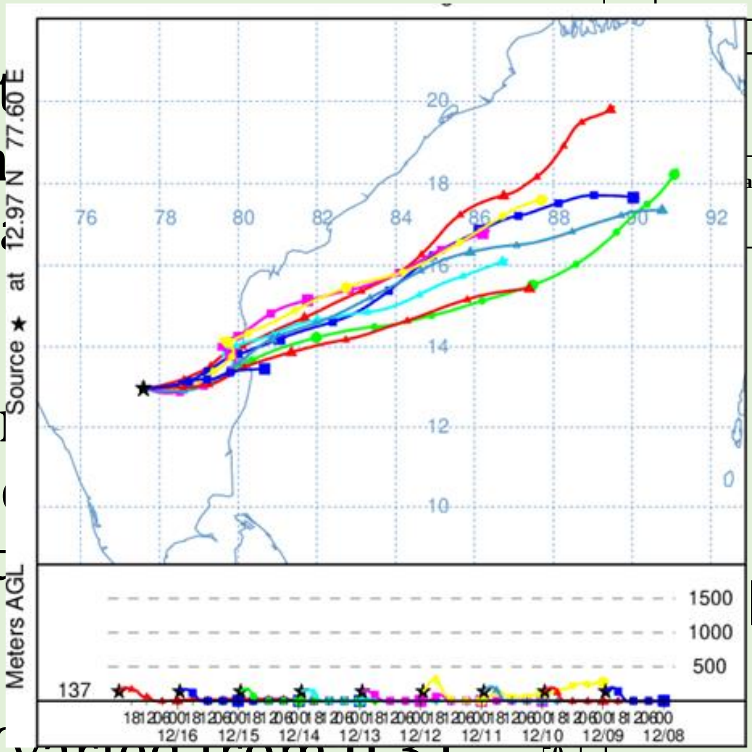


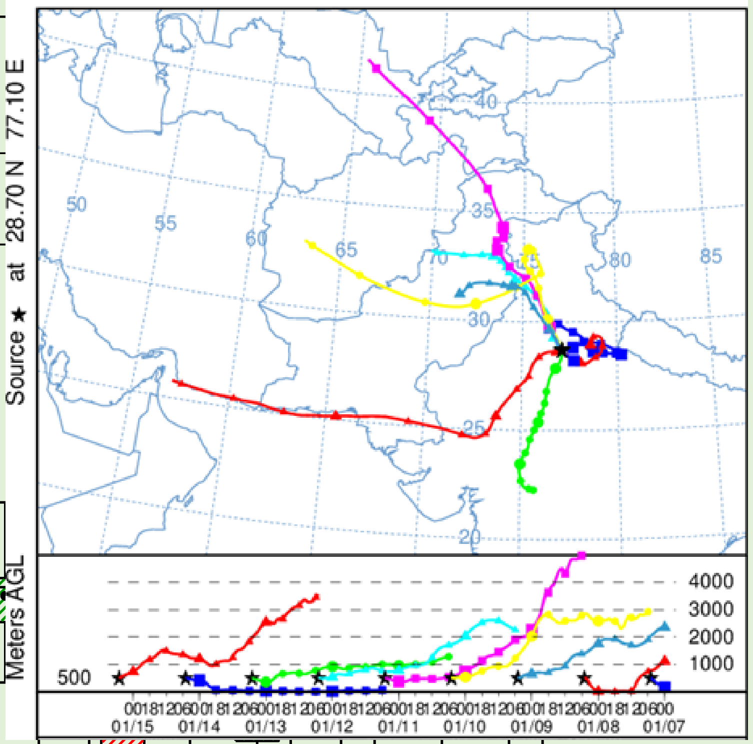
Results and Discussions

- Monitored $PM_{2.5}$ concentrations were 3-4 times higher than NAAQS averages









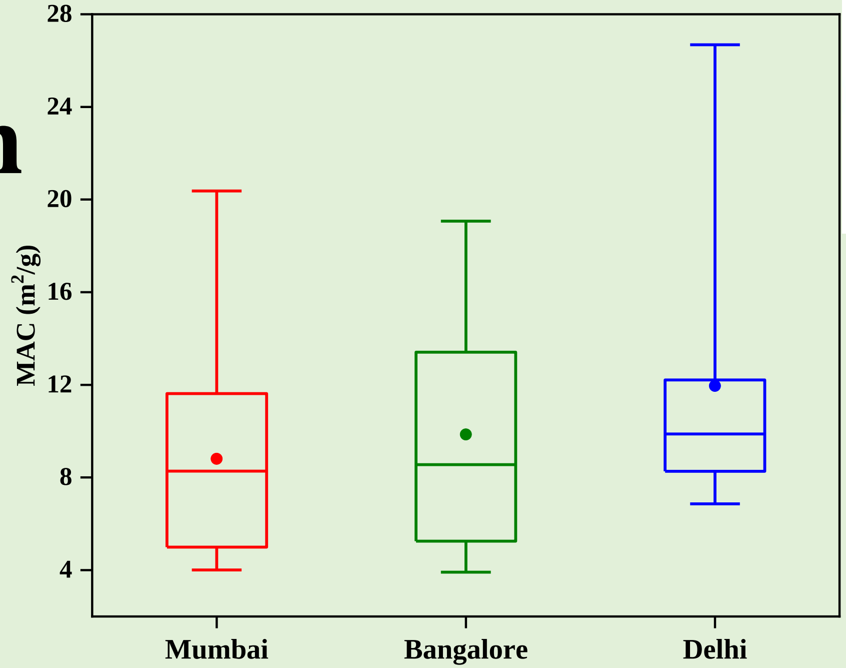
- Mean COD values ~0.38 (varied from 0.31 to 0.50) indicating moderate spatial heterogeneity

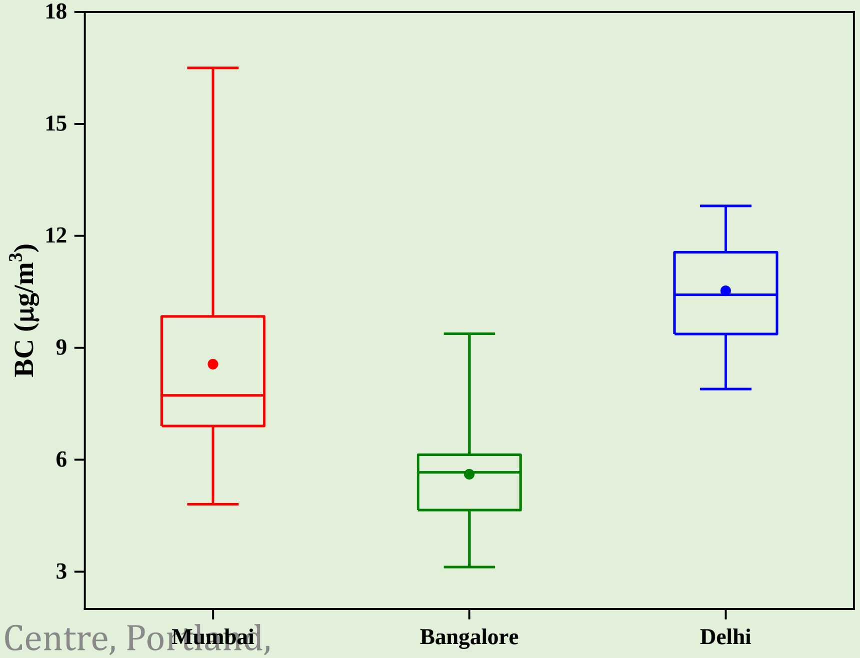
Black Carbon (BC) variation

- This study presents first-time measurements of absorption properties of aerosols emitted from residential outdoor locations

- Most of these studies used an assumed value of MAC

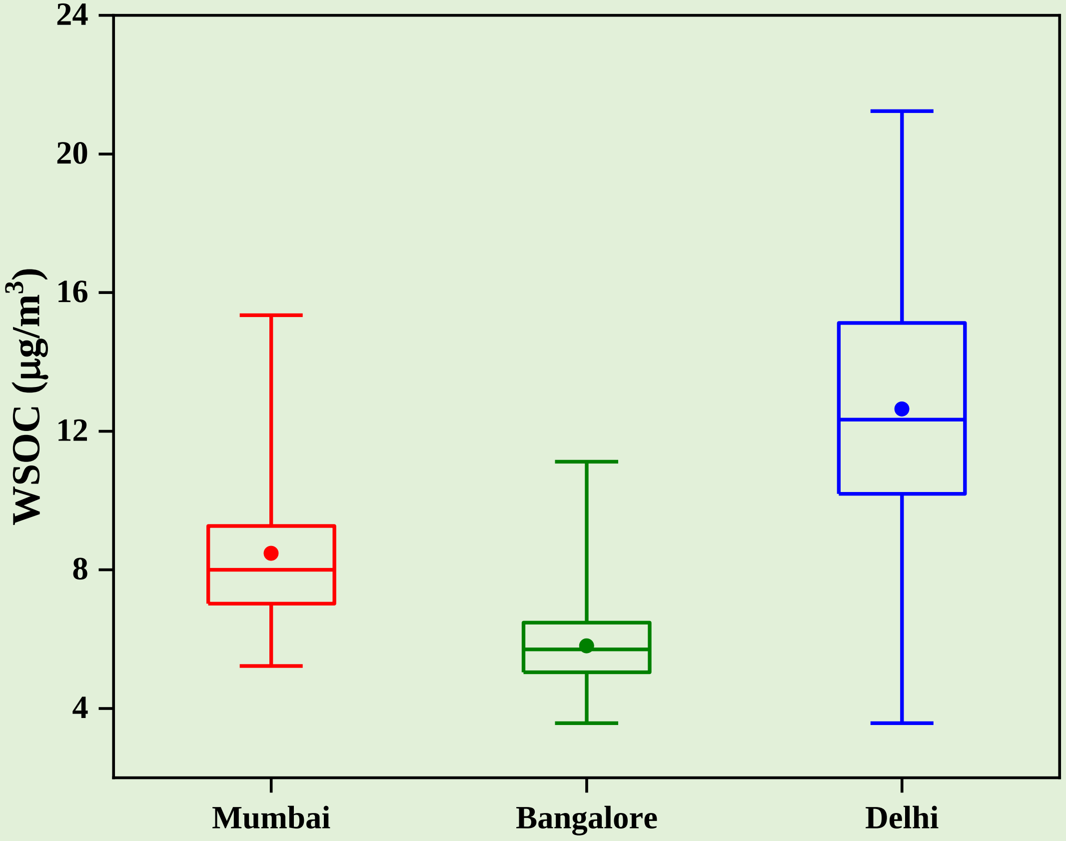
- We focus specifically on evaluating MAC by region





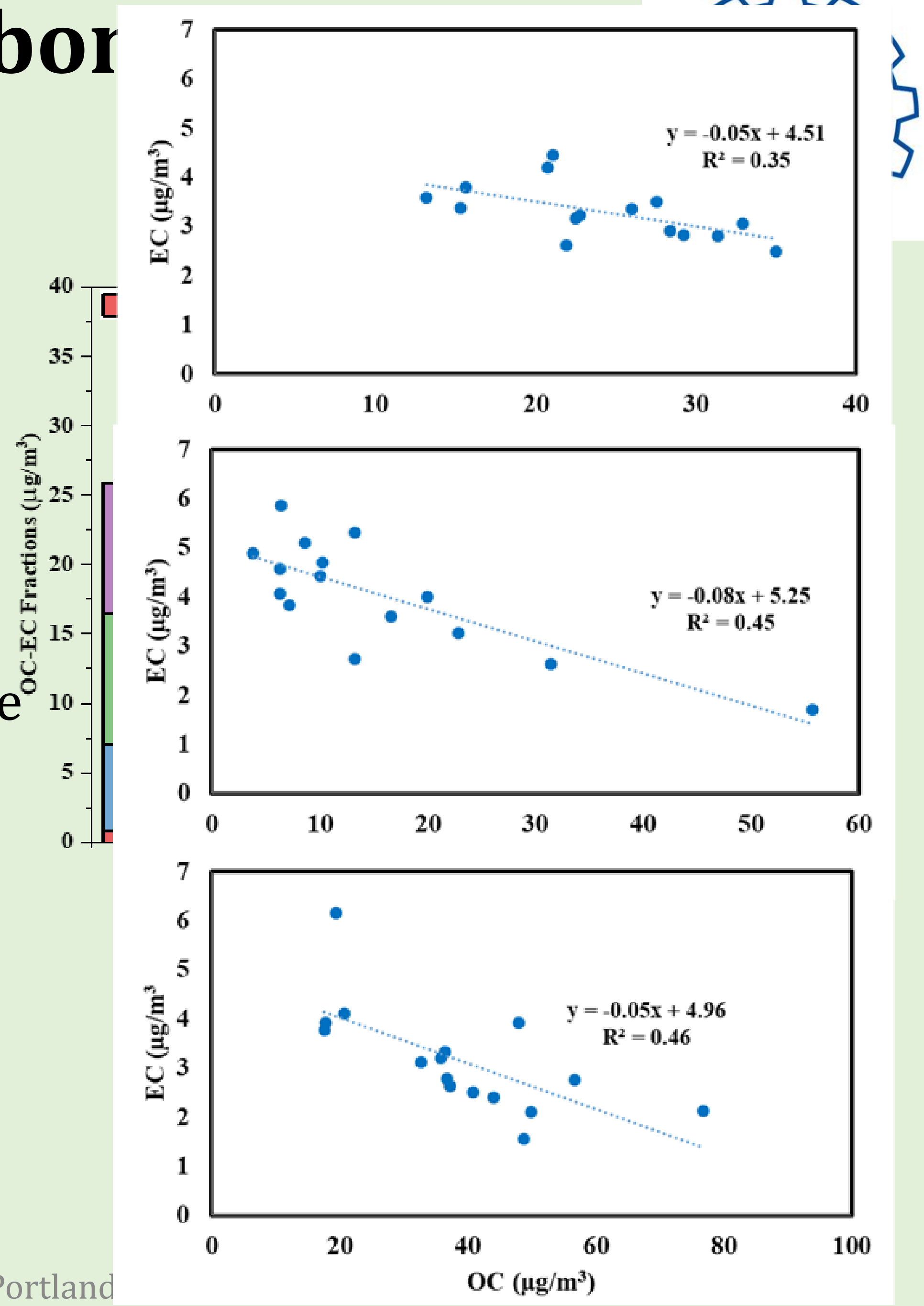
Water Soluble Organic Carbon (WSOC) variation

- Average WSOC at Delhi had the highest concentrations, while the lowest was found at Bangalore city
- Potential sources of the WSOC in fine particles include both primary and secondary sources (Huang et al., 2012)
- Often associated with polar organic compounds correlated with SOA formation (Huang et al., 2012, Rogge et al., 1993)



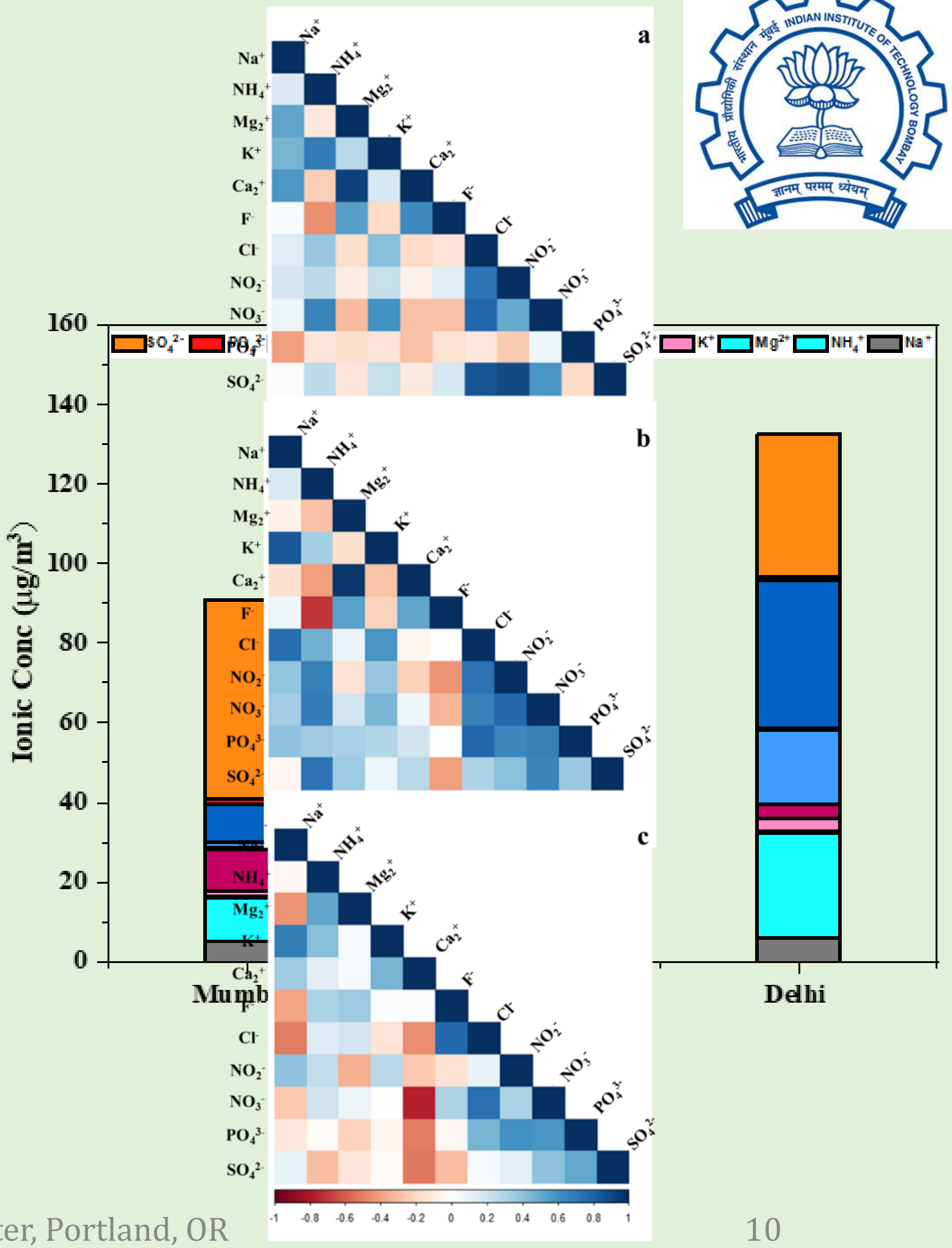
Organic Carbon- Elemental Carbon (OC-EC)

- % OC in $PM_{2.5}$ and EC showed a lesser magnitude and percent in $PM_{2.5}$ mass was less (Bawase et al., 2021)
- TCA was the predominant part, contributing 57.1%, 47.3% and 39.4% of $PM_{2.5}$ mass
- Most abundant fraction EC1- emitted from incomplete combustion of fuel (Kim et al., 2011) and motor vehicles (Watson et al., 1994)
- OC4 and OC3 were highest after EC1 shows the contribution of road dust (Cao et al, 2005)
- OC2 fraction higher- industrial influenced residential urban homes due to coal combustion



Ionic Composition

- Sulfate is the most abundant species ~32%, ~29% and ~34%
- Transport of sulfur pollutants to the relatively long lifetime of tropospheric sulfate aerosols (He et al. 2016) indicated by the air mass backward trajectory
- SNA contributed around 60-70% of the total ionic species for the three cities
- Good correlation (r > 0.70) between NO_3^- and SO_4^{2-} indicates that a portion of these may have originated from a similar source



Ratios between chemical constituents

City	OC/EC	K^+/OC	K+/EC	NO_3^{2-}/SO_4^{2-}	Cl-/Na^+
Mumbai	7.3±2.6	0.18±0.08	0.39±0.19	0.97±0.56	3.01±2.64
Bangalore	3.5±3.0	0.17±0.19	0.30±0.24	0.18±0.13	0.47±0.13
Delhi	14.8±9.5	0.27±0.27	0.57±0.52	0.47±0.45	0.33±0.20

- **OC/EC** for Delhi is higher indicating the strong influence from biomass and coal combustion combined with the aging of emissions in the atmosphere (Cao et al. 2012; Niu et al. 2016)
- For combustion sources such as biomass combustion are characterized by K^+/OC ratios ranging from 0.08 to 0.10 (Echalar et al. 1998) and K^+/EC from 0.04 to 0.13 (Andreae and Merlet 2001)
- Lowest WSOC/OC was found at the traffic emissions and highest for the sites influenced with industrial emissions (Rengarajan et al. 2007; Ram et al. 2011; Rai et al. 2020)

Ratios between chemical constituents

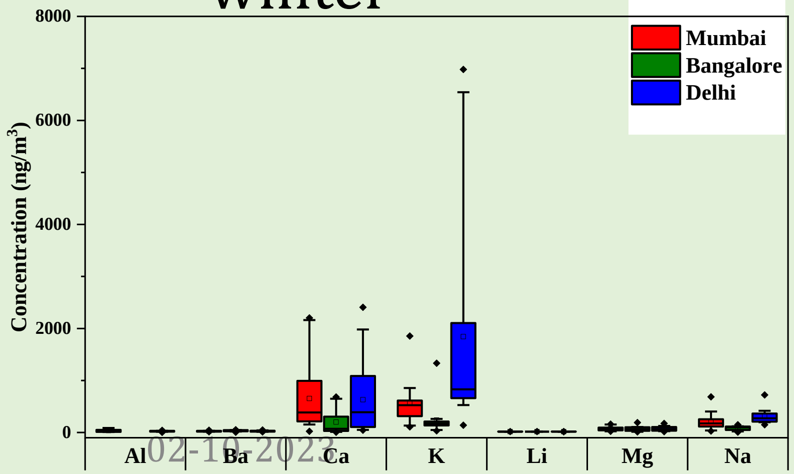
- Average Cl^-/Na^+ >1.8, implies the anthropogenic origin of Cl− ions. Low due to loss of Cl- through reactions with atmospheric nitric acid, sulfuric acid and SO_2
- Also higher due to burning of MSW or trash or open burning involving plastics (Sharma and Dikshit, 2016)
- NO_3^-/SO_4^{2-} to assess the relative contributions from stationary versus mobile sources of PM (Arimoto et al. 1996). Ratio closer to unity indicate significant contributions from vehicle exhaust emissions coupled with enhanced ammonium nitrate formation (Bhati et al. 2018)

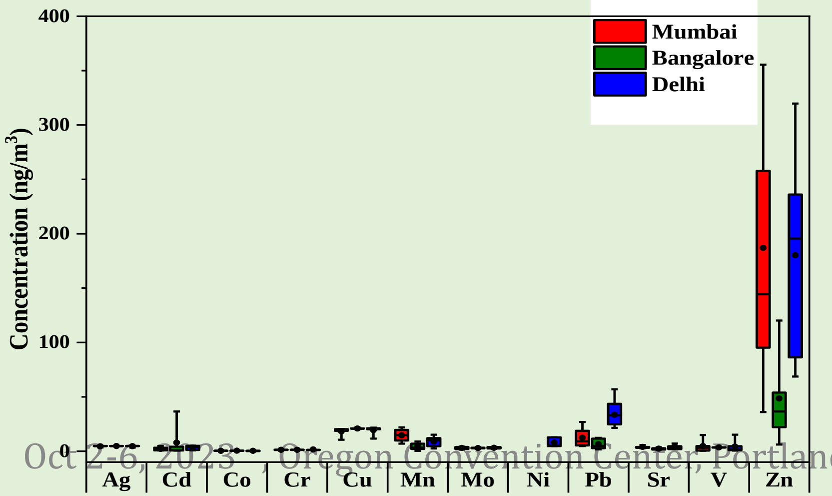
Trace elements

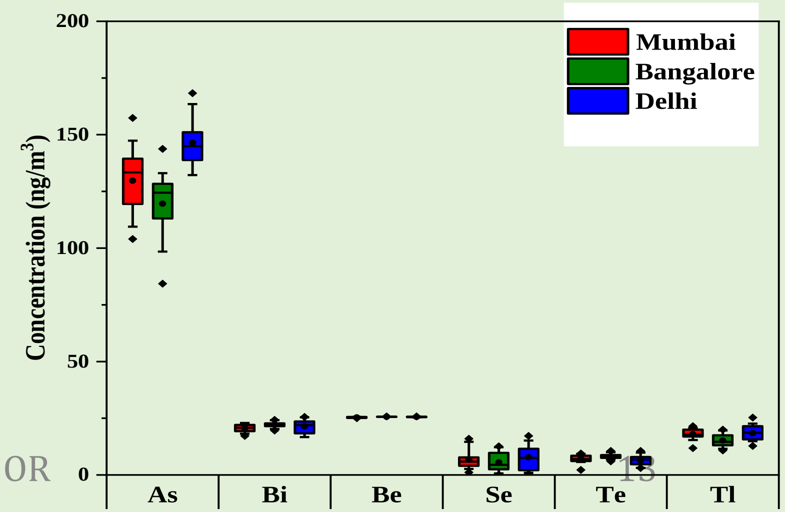
- Summed mass concentrations of the metals showed higher for Delhi, followed by Mumbai and Bangalore (3429.8 > 2055.7> 947.0 ng/m^3)

- Crustal material contribution to $PM_{2.5}$ mass loadings is lower (3-9%) (Bawase et al., 2021)

- Much lower values in winter explained by stable atmospheric conditions coupled with low wind speed, high relative humidity and higher soil moisture during winter

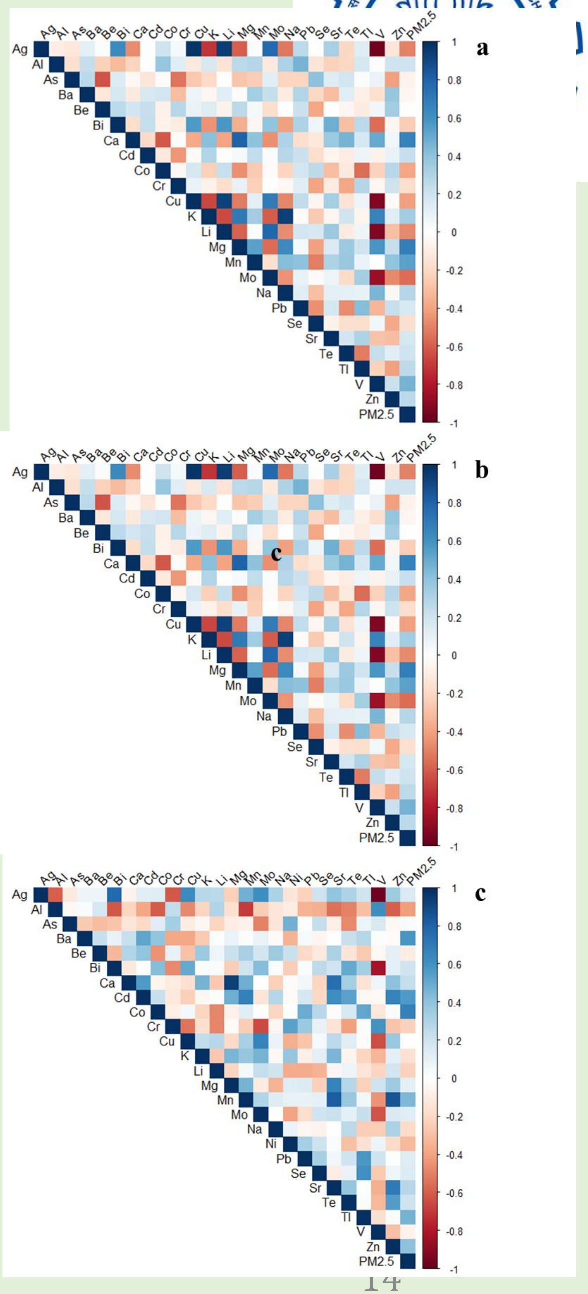




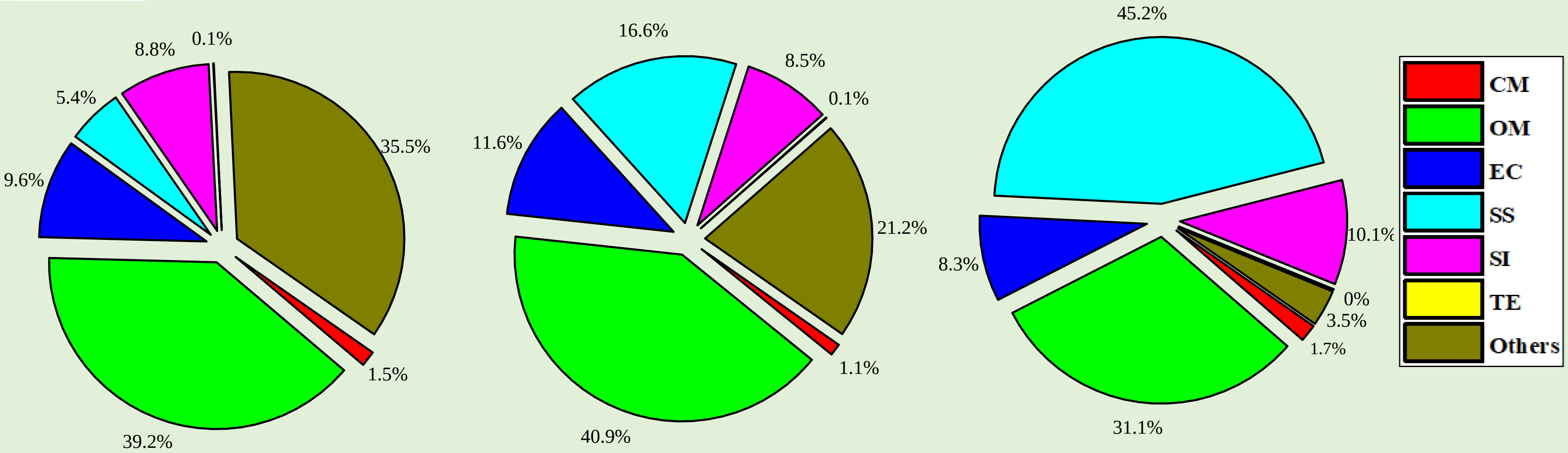


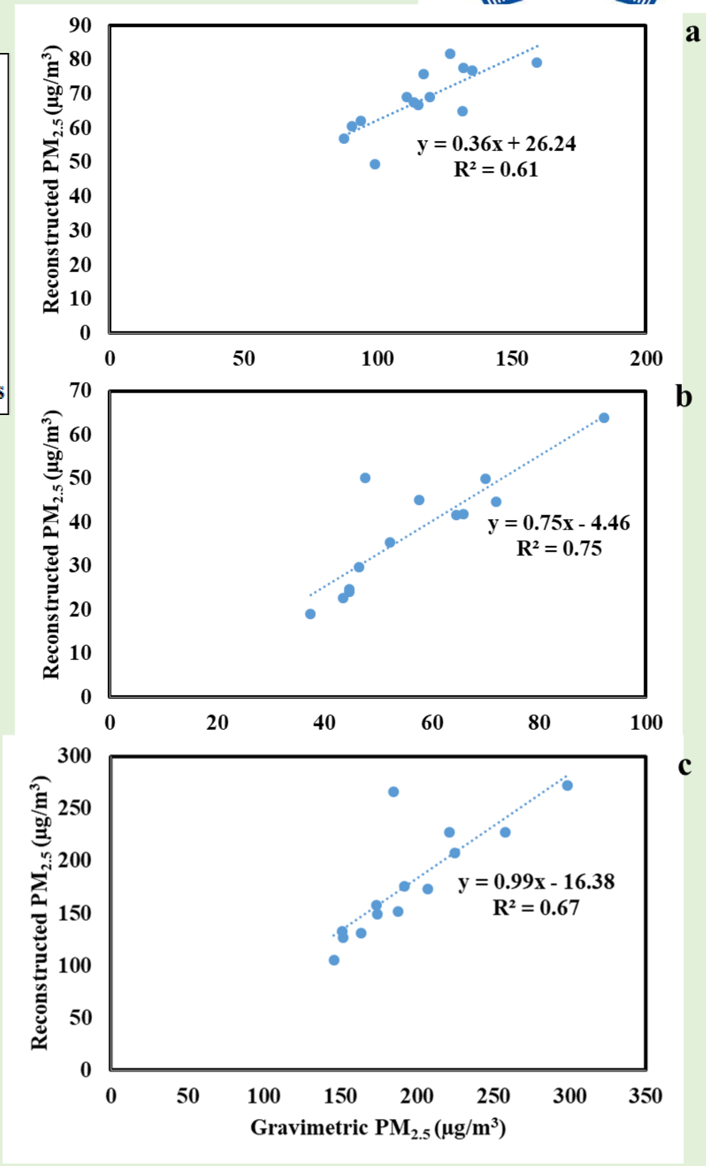
Correlation between trace elements

- Correlation of Zn with Cd, Mn, K suggests that coal burning, biomass combustion, soil dust and vehicular emissions
- K, important marker of biomass burning activities, was found to correlate with most anthropogenic elements (Mg V Na Cr Zn Cd)
- V and Ni showed moderate correlation as these are the byproducts of oil combustion
- Ca and Mg were correlated as they are from crustal origin
- Cu and As were inversely correlated (Patrycja, 2020)



$PM_{2.5}$ mass reconstruction





- For Mumbai and Bangalore, OM was the most abundant species
- For Delhi, factors such as traffic induced resuspended dust, road and other construction activities and long range transport of aerosols
- Sulfate, followed by OM secondary ions and EC

Summary

- Monitoring campaign was conducted on Mumbai, Bangalore and Delhi and $PM_{2.5}$ samples were collected during winter season
- This study presents the first comprehensive data set of chemical composition of fine $PM_{2.5}$ at residential locations in three metropolitan cities in India
- Average±SD daily $PM_{2.5}$ concentrations (in $\mu g/m^3$) were 131.3±71.8 for Mumbai, 75.2±33.4 for Bangalore and 192.2±75.5 for Delhi which is due to meteorology and seasonal regional emissions of both anthropogenic and natural sources
- Average WSOC was highest in Delhi, while the lowest levels were found in Bangalore similar to the $PM_{2.5}$ trend

Summary

- Sulfate most abundant species among inorganic ions contributing ~38%, ~39% and 37% consistent with previous studies (~43%) of SNA in $PM_{2.5}$ fraction

- Gravimetric and reconstructed mass concentrations R^2 ranging from 0.54–0.64. ~60% of the total mass was explained for Mumbai (50% for summer), 67% for Bangalore and 91% for Delhi during the winter period

- Further source apportionment using PCA/PMF is underway

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