



Chemical Characterization and Source Identification of Particulate Matter at an Urban Site of Navi Mumbai, India

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ABSTRACT

Particulate matter samples were collected using a dichotomous sampler at a residential area of Vashi situated in Navi Mumbai, India during the period of 2008. The sampler facilitates the simultaneous collection of atmospheric particulates in coarse and fine size fractions. The filter samples collected were analysed for trace elements using Proton Induced X-ray Emission (PIXE) technique. The particulate matter trends show higher concentration during winter season compared to other seasons. High concentrations of elements related to soil and sea salt were found in the coarse fraction of particulate matter. Enrichment Factor (EF) analysis with respect to Fe showed enrichment of Cu, Cr, and Mn only in the fine fraction suggesting their origin from anthropogenic sources. The EF value was observed to be maximum for As, Pb and Zn in the fine particulates. However, crustal and marine derived elements showed very low EF values indicating their origin from soil and sea salt respectively. The Principal Component Analysis (PCA) based multivariate studies identified soil, sea salt and combustion as common sources for coarse and fine particles. Additionally a source contributing to coarse fraction Br concentration as well as an industrial and Se source contributing to fine fraction particles has been identified.

Keyword: PM_{2.5-10}; PM_{2.5}; PIXE; EF analysis; PCA.

INTRODUCTION

The awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and the determination of pollution sources. Atmospheric aerosols influence many atmospheric processes including cloud formation, visibility variation and solar radiation transfer, (Pueschel *et al.*, 1986) and play a major role in the acidification of clouds, rain and fog. Both gaseous pollutants and atmospheric aerosols contribute to the deterioration of air quality (Parmar *et al.*, 2001). Many Asian cities face environmental crisis due to severe air pollution. Deteriorating air quality is a result of rapid economic expansion, population growth, increased industrial output and an unprecedented surge in motor vehicle traffic. Urban air pollution problems are the results of combined effects of gaseous air pollutants such as sulphur dioxide, oxides of nitrogen, ozone and particulate matter. Medical researchers have defined the respirable fraction as those particles with diameters less than 10 µm (Cohen, 1998). Particularly air borne particulates with aerodynamic diameter 2.5 to 10 µm

are referred as coarse particles (PM_{2.5-10}) and less than 2.5 µm as fine particles. Fine particles (PM_{2.5}) are mainly generated by combustion processes including emissions from motor vehicles, fossil fuel burning for power generation and large industrial processes such as ore and metal smelting. They may also include natural emissions such as fine windblown soils, emission from volcanos, sea spray and smoke from biomass burning (Cohen *et al.*, 2002). Studies of Chow *et al.* (1992) and Andrade *et al.* (1993) showed geological sources such as fugitive dust from tilling, roadways, construction, soil dust and industrial emissions are the main contributors of the coarse particulates. The behaviour of particulate matter in the atmosphere and within the human respiratory system is determined by various physical and chemical properties of particulates. In specific chemical composition and size of the particulates can provide valuable insights into the sources of airborne particles, and these parameters also determine the atmospheric behaviour and fate of particles and influence on human health effects. Few studies reveal that there is a significant correlation between airborne particulate matter levels and increased adverse health effects (Pope *et al.*, 1995; Pope, 2000). Also ambient particulate matter particularly, fine particulate matter has received worldwide attention for its adverse impacts on human health, visibility degradation and global climate change (Laden *et al.*, 2000; Ramanathan *et al.*, 2001; Watson, 2002; Li *et al.*, 2009).

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The rate of increase of air pollutant concentrations in developing countries such as India are higher than those in developed countries and hence atmospheric pollution is often severe in cities of developing countries all over the world (Mage *et al.*, 1996; Bhaskar and Mehta, 2010). Indian megacities are among the most polluted in the world. Air concentrations of a number of air pollutants are much higher than the levels recommended by the World Health Organization (WHO) as well as the National Ambient Air Quality Standards (NAAQS), India (Milind and Gurumurthy, 2000; WHO, 2005; NAAQS, 2009). The air quality guidelines stipulated by WHO and NAAQS are presented in Table 1. In India major sources of urban air pollution include coal combustion, oil refineries and industrial manufacturing facilities (Murray *et al.*, 2001; Dubey and Pervez, 2008). The most polluted metropolitan cities of India are Mumbai, Kolkata and Delhi. The mass concentration levels of particulate matter in the Indian mega cities were discussed by Gupta and Kumar (2006). Particularly in Mumbai there are many studies carried out to monitor the particulate matter of size less than 10 μm (Sadasivan and Negi, 1990; Sharma and Patil, 1994; Kumar *et al.*, 2001; Venkataraman *et al.*, 2002; Tripathi *et al.*, 2004) and most of these studies showed very high concentrations of particulate matter. This paper presents a comprehensive study on particulate pollution carried out at Vashi in Navi Mumbai, a site very close to Thane-Belapur industrial belt. Particulate Matter of two size fractions: Coarse particles ($\text{PM}_{2.5-10}$) and fine particles ($\text{PM}_{2.5}$) were collected for the present study. The characterization of the filter samples was carried out using PIXE technique. The work carried out was mainly focussed to evaluate $\text{PM}_{2.5-10}$, $\text{PM}_{2.5}$ concentration levels and their composition at Vashi. Furthermore, data derived from the study has been utilized for Enrichment Factor Analysis and statistical analysis using principal component analysis based receptor model technique to identify the possible sources contributing to the particulate matter concentration in the study area.

MATERIALS AND METHODS

Sampling

Atmospheric particulate matter samples were collected at Vashi in Navi Mumbai and the sampling was performed at a height about 15 m. Although the sampling site is

located at a residential area, it is near to Thane Belapur industrial area and a national highway passes 2 km from the site. The Navi Mumbai region is covered by hills in the East and the West is covered by Thane Creek as well as by Mumbai city. North to Navi Mumbai is the Thane – Belapur industrial belt and towards South is the newly developed Panvel city. Thane-Belapur industrial estate mainly comprises of a number of major, medium and small scale industrial units largely involved in the manufacture, storage and use of chemicals, petrochemicals, pharmaceuticals, fine chemical products and pesticide formulation etc. The percentage of industries in various categories are presented by Anjali and Dipanjali (2007). For air sampling Gent sampler (Maenhaut *et al.*, 1994; Hopke *et al.*, 1997) developed at Ghent University in Belgium was used. The sampler is equipped with stacked filter unit (SFU) that can carry two 47 mm filters. Nuclepore polycarbonate filters of 8 and 0.4 μm pore sizes were used in each of the two stages. The air was sampled at a rate of 16 L/min, which allowed the collection of coarse particles with Aerodynamic Diameter (AD) between 10 and 2.5 μm ($\text{PM}_{2.5-10}$) in the first stage and fine particles with AD 2.5 μm ($\text{PM}_{2.5}$) in the second stage. A total of 109 samples were collected and sampling of each sample was carried out for a period of 24 h, on a twice or thrice-a-week basis from 1 January 2008 to 22 December 2008. The particulate load in the filter was measured by gravimetry using a Mettler balance with 10 μg sensitivity in an air conditioned room at a temperature of 22°C and relative humidity of 50%.

Analysis

Particle Induced X-ray emission (PIXE) was used to determine elemental concentrations from elements heavier than magnesium by exposing the filter samples to a proton beam accelerated with 2.5 million volts from the Van-de-Graaff accelerator at GNS Science, New Zealand (Trompeter *et al.*, 2005). While all elements heavier than boron emit K X-rays, the production of them become too few to satisfactorily measure for elements heavier than strontium. Elements heavier than strontium are detected via their lower energy L X-rays. The X-rays were detected by means of a Si(Li) detector. The sensitivities were further improved by using two X-ray detectors, one for light element X-rays and the other for heavier element X-rays, each with different filtering and collimation. The

Table 1. Air quality standards stipulated by WHO and India.

#WHO Air Quality Guide line			
S. No.	Pollutant	Time Weighted Average	Concentration in Ambient Air
1	$\text{PM}_{2.5}$	Annual	10 $\mu\text{g}/\text{m}^3$
		24 hour	25 $\mu\text{g}/\text{m}^3$
2	PM_{10}	Annual	20 $\mu\text{g}/\text{m}^3$
		24 hour	50 $\mu\text{g}/\text{m}^3$
*National Ambient Air Quality Standards, India			
1	PM_{10}	Annual	60 $\mu\text{g}/\text{m}^3$
		24 hour	100 $\mu\text{g}/\text{m}^3$

World Health Organization Air Quality Guideline, 2005

* National Ambient Air Quality Standards for residential area, Central Pollution Control Board, 1998.

proton beam size used for this analysis is 5 mm high and 3mm wide and the intensity of the beam is constant over the area of $3 \times 5 \text{ mm}^2$. The typical beam current used in this study is 5–7 nA and charge collected is $10 \text{ } \mu\text{C}$. The exact limits of detection of each element depend on the method of detection, filter composition, sample composition, the detector resolution, and spectral interference from other elements. GUPIX (Maxwell *et al.*, 1995) was used to determine the concentration of each element by background subtraction and peak area fitting. Mainly the peaks of light elements in the spectra that have interferences or backgrounds from other elements present in the air particulate matter, or filter matrix itself, have higher limits of detection. Measurements of blank filters were performed to correct for filter derived analytical artefacts as part of the QA/QC procedures. Typical LODs achieved by PIXE for each element are shown in Fig. 1.

Enrichment Factor Analysis

Enrichment factor (EF) is widely used to identify the anthropogenic source of metallic elements and it is generally applied to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material or Sea salt (Gao *et al.*, 1992). In this study crustal EF's are calculated with Fe as reference element while EF values for sea salt were evaluated using Na as reference element. The elemental concentrations of soil in Mumbai are used from Mahadevan (1986). Whereas, sea water composition is referred from Pytkowicz and Kester (1971). The formula used for enrichment factor calculation is: $\text{EF}_i = (i/j)_{\text{air}} / (i/j)_{\text{crust}}$, where EF_i is the enrichment factor of species i , j is a reference element for crustal material, $(i/j)_{\text{air}}$ is the ratio of species i to species j in the aerosol sample and $(i/j)_{\text{crust}}$ is the ratio of species i to species j in the crust (Quiterio *et al.*, 2004).

Principal Component Analysis

Source identification analysis of particulate matter was performed based on the principal component analysis method, a method widely used to factorize the input concentration data of different species assuming a linear relationship between total mass concentration and the individual concentrations of different species (Carmine *et al.*, 1999; Bongiovanni *et al.*, 2000). The multivariate mathematical method involves several steps to group the elemental data. In the first step the concentration data are transformed in to a dimensionless form by standardization, which is given as,

$$X_{it} = \frac{C_{it} - C_i}{d_i} \quad (1)$$

where C_{it} is the concentration of the variable i in the sample t , C_i and d_i are the arithmetic mean and standard deviation of the variable i for all samples included in the analyses. The PCA model is expressed as,

$$X_{it} = \sum_{j=1}^N L_{ij} S_{jt} + E_{it} \quad (2)$$

where L_{ij} is the factor loading of the variable i in the source j with N number of sources, S_{jt} is the factor score of the source j for sample t and E_{it} is the residual of variable i in the sample t not accounted by the j sources or factors. This equation is then solved by eigenvector decomposition. A Varimax normalised rotation is applied to maximise (or minimise) the values of the loading factors of each compound analysed in relation to each rotated principal component and this provides the most interpretable structure to the factors.

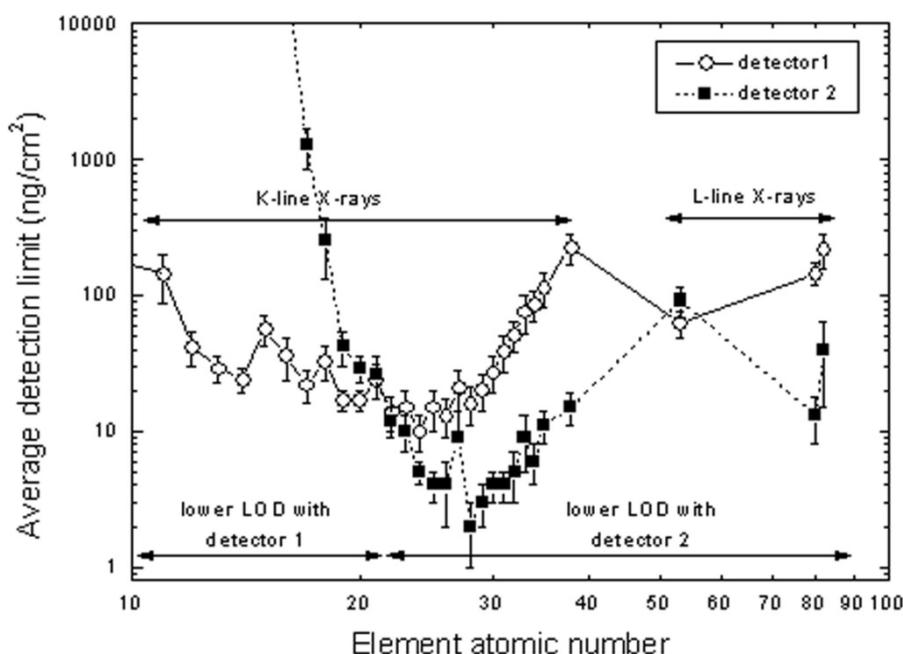


Fig.1. Elemental limits of detection achieved at the GNS IBA facility.

RESULTS AND DISCUSSION

Particulate Matter Concentration

The summary of the coarse and fine particulate matter collected at the sampling site during 2008 is presented in Table 2. The average concentration of $PM_{2.5-10}$ and $PM_{2.5}$ were $70 (\mu\text{g}/\text{m}^3)$ and $41 (\mu\text{g}/\text{m}^3)$ and the highest concentration was observed to be $140 (\mu\text{g}/\text{m}^3)$ and $76 (\mu\text{g}/\text{m}^3)$ respectively. The time series plot of the particulates in both the size fractions is presented in Fig. 2. At Mumbai the period between October to February is the season of winter. From March the temperature gradually increases and it becomes very hot just before the monsoon break at the middle of the June and the rainy season lasts up to September. The time series plot clearly indicates that the concentrations of $PM_{2.5-10}$ and $PM_{2.5}$ in the season of winter were about two times higher than the concentrations during summer and monsoon seasons because it is well known that during winter due to lower temperatures the mixing height becomes

Table 2. Summary of Coarse and Fine Particulate Matter.

Parameter	$PM_{2.5-10} (\mu\text{g}/\text{m}^3)$	$PM_{2.5} (\mu\text{g}/\text{m}^3)$
Mean	71	42
Median	70	39
Standard deviation	22	11
Maximum	140	76
Minimum	34	17
No. of samples	95	

lower and the particulate matter gets trapped nearer to the ground level and it has been identified and discussed in few of the previous studies (Gupta and Kumar, 2006).

The time series plot of ratio between $PM_{2.5}$ and $PM_{2.5-10}$ is presented in Fig. 3. It was observed that there was an insignificant variation in the fine to coarse ratio with respect to the seasons of the year and the average $PM_{2.5}$ to $PM_{2.5-10}$ ratio is 0.59 ± 0.09 with the range of 0.35–0.78. The average ratio evaluated is in the lower end of the

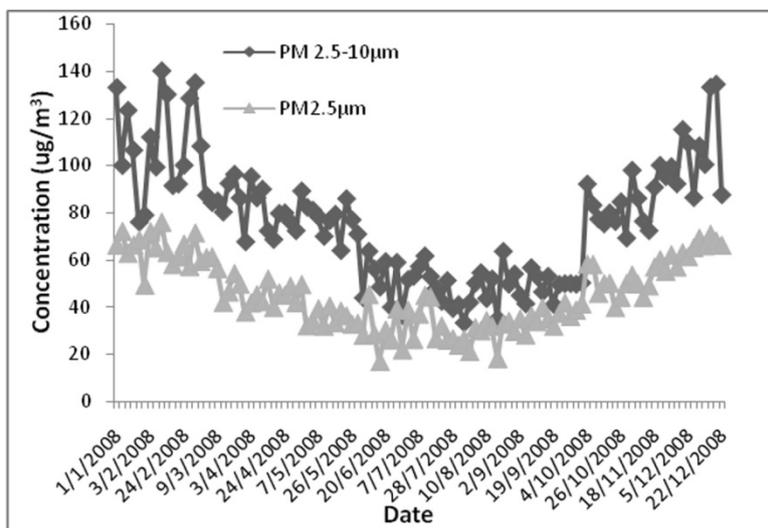


Fig. 2. Time series plot of $PM_{2.5-10}$ and $PM_{2.5}$ mass concentrations during the study period.

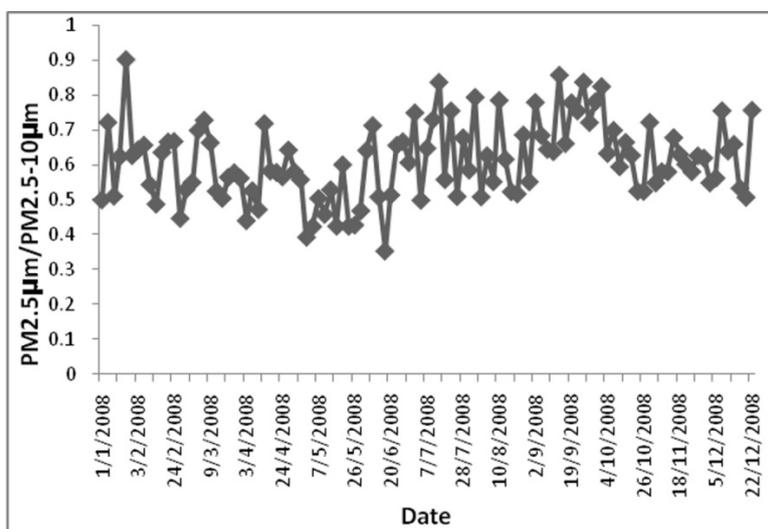


Fig. 3. Time series plot of $PM_{2.5}/PM_{2.5-10}$ ratio during the study period.

results reported by Chow *et al.* (1996; 1999) and Lin (2002) and in their studies the range of the ratio obtained were 0.41–0.81 and 0.57–0.71 respectively. Therefore, the results show comparatively low $PM_{2.5}$ to $PM_{2.5-10}$ ratio and indicate that the domination of fine particles over the coarse particles is marginal or insignificant. The correlation coefficient between the two size fractions was found to be 0.8 (Fig. 4) which is suggesting that there could be some common sources contributing to the particulate matter in the size range from 2.5 to 10 μm and $\leq 2.5 \mu m$ in the sampling region.

Tracemetal Concentrations in Particulate Matter

Elemental concentrations of particulate matter were obtained by PIXE technique with the sensitivity in the order of a few ng/m^3 . Table 3 summarizes mean chemical concentration of each species in the coarse and fine fractions of particulate matter along with their standard deviation. The elemental concentration in the coarse fraction ranged from 0.0023–4.1 $\mu g/m^3$ and in the fine fraction it was from 0.0014 to 1.5 $\mu g/m^3$. From the results we can note that the concentration of elements typical of marine aerosol (Na, K and Cl) and of soil-related (Al, Si, Ca, Mg, Fe) were higher in the coarse fraction than the fine mass fraction. Subsequently the abundance of elements such as Sulphur and Zinc found to be higher in comparison with the crustal and marine derived elements. While, Cu, Cr, Se and As were found as minor elements contributing very less to the total mass concentrations of particulates. The standard deviation presented for each element is very high suggesting significant temporal variation in the concentrations. Trend analysis was also performed for the elements. A typical time series plot for sulphur in fine mass fraction is presented in Fig. 5, which displays increased concentrations during January and February (winter) and lower concentrations during June and July months (fall) similar to the trend of particulate matter.

Enrichment Factor Analysis

The analyzed elements can be divided into three major groups: earth crust elements or soil tracers, marine tracers and anthropogenic tracers. Therefore, the separation of natural and anthropogenic components is one of the basic tasks of aerosol measurements. Enrichment Factor (EF) analysis is conventionally used for separating soil derived or marine derived elements from the anthropogenic components (Yuanxun *et al.*, 2006). Therefore to verify the contributing elements of crustal and marine sources associated with $PM_{2.5-10}$ and $PM_{2.5}$, EF was calculated for each element. In this study Fe is used as a reference element to determine the EF with respect to crustal abundance and the elemental concentrations of soil used were the average background values of soil in Mumbai (Mahadevan, 1986). Whereas Na is used as a reference element to determine the marine based EF values. Conventionally, a cut off for the enrichment of the respective element is considered as 10 to distinguish other elements from the crustal and marine based elements. It is believed that the element should be enriched as if the EF of each element is greater than 10, indicating that atmospheric particulate matters come mainly from human activities. The greater value of enrichment factor shows the greater possibility of air pollution from anthropogenic sources (Huang *et al.*, 2010). Fig. 6 shows EF values obtained for the trace elements of coarse and fine particulate matter related to crustal concentrations. The plot shows EF values of Al, Ca, Mg, Si in both the size fractions are small indicating their origin from crustal source. Few elements such as Ni and V were found to possess EF values in the range of 14 to 37. As, Br, Pb and Zn in the fine fraction exhibit the maximum enrichment ranging from 685–1164, whereas in the coarse fraction except Zn, the EF of other three elements are within 100. Elements like Mn, Cr, and Cu are showing enrichment only in the fine fraction which indicates their anthropogenic origin from traffic or industrial

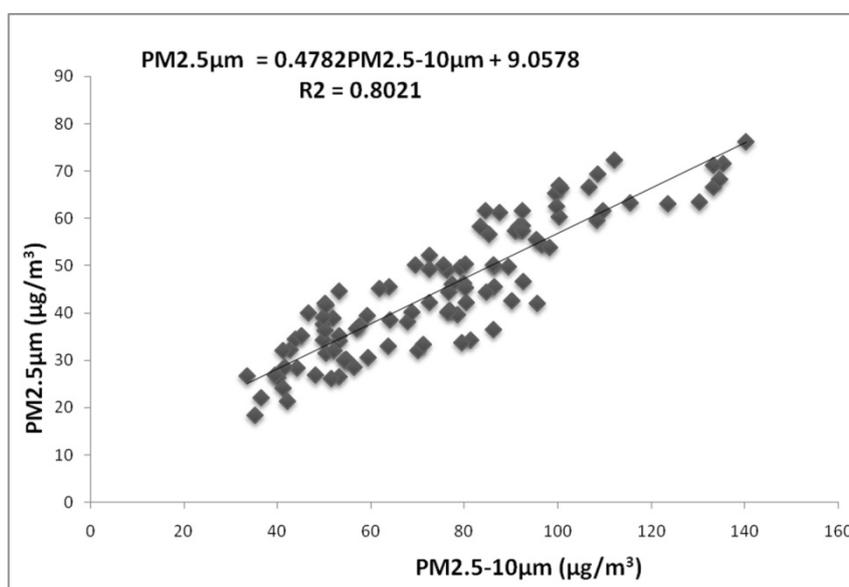


Fig. 4. Correlation between $PM_{2.5-10}$ and $PM_{2.5}$ during the study period.

Table 3. Concentration of elements in coarse and fine particulate matter at Vashi.

Parameter ($\mu\text{g}/\text{m}^3$)	PM _{2.5-10}		PM _{2.5}	
	Mean	S.D.	Mean	S.D.
Na	1.33	0.86	0.46	0.30
Mg	0.68	0.50	0.22	0.21
Al	1.65	1.33	0.45	0.21
Si	4.1	3.1	0.84	0.67
S	0.99	0.65	1.503	1.32
Cl	2.3	1.76	0.26	0.19
K	0.43	0.22	0.28	0.13
Ca	2.4	1.68	0.31	0.14
Ti	0.17	0.14	0.023	0.019
V	0.0072	0.0031	0.0091	0.0031
Cr	0.026	0.018	0.044	0.024
Mn	0.041	0.033	0.0092	0.0041
Fe	1.9	1.48	0.31	0.22
Ni	0.0023	0.0012	0.0063	0.0022
Cu	0.019	0.011	0.0062	0.0043
Zn	0.084	0.012	0.064	0.042
As	0.0054	0.0014	0.0071	0.0031
Se	0.0039	0.0011	0.0032	0.0011
Br	0.011	0.0052	0.012	0.0083
Pb	0.024	0.014	0.036	0.019
P	0.044	0.022	0.028	0.021
Ga	0.0023	0.0013	0.0014	0.0011
Ge	0.0051	0.0012	0.0042	0.0012
Rb	0.011	0.0063	0.011	0.0032
Sr	0.018	0.011	0.014	0.0053
Mo	0.053	0.019	0.023	0.0081
Ba	0.132	0.034	0.27	0.049

* S.D. is Standard Deviation.

emissions. Enrichment of Na, K and Cl can be attributed to sea salt. Marine enrichment factors calculated for the elements considering Na in bulk sea water as reference

element is presented in Fig. 7. EF values found to be greater than 10 for K and Mg. Other elements such as Al, As, Cr, Cu, Mn, Pb, Ni, Se, V, Fe and Ti found to possess EF around or greater than 100000. The above set of elements showing very high EF values comprise both crustal derived as well as anthropogenically originated elements.

Source Identification

Principal Component Analysis with varimax rotation (Salvador *et al.*, 2003) was performed with selected twenty elements which was found to be abundant in all the samples to extract the major sources of the trace elements and the technique yielded a number of key factors associated with the finger print elements of different sources. The factor loadings obtained for coarse and fine particles are presented in Table 4 and Table 5 respectively. The analysis of trace elemental data set of the coarse particles showed strong correlation among the finger print elements of crustal source and has been labeled as soil. The second factor with the group of trace elements which are considered as the major components of sea water has been identified as sea salt. The third source identified was found to be a mixture of combustion and industrial emission sources. The last factor was found with high loadings of Br which could be from the nearby Liquid bromine and sodium bromide manufacturing industries. Similarly soil, sea salt, combustion, industries and Se sources have been identified from the multivariate analysis of fine fraction data set. There are various drug and chemical manufacturing industries in the surrounding areas of sampling site, among them few industries at Vashi are involved in selenium salts and compounds manufacturing and hence this could be one of the source contributing to the fine Se in the study area. Also, in the PCA study of fine particles a source of industries has been resolved separately other than the combustion source identified in the coarse

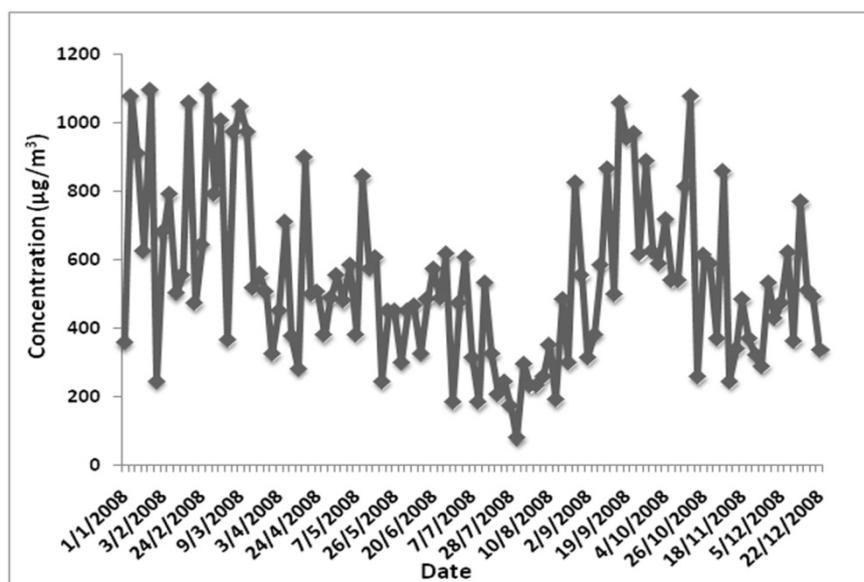


Fig. 5. Time series plot of Sulphur in fine mass fraction during the study period.

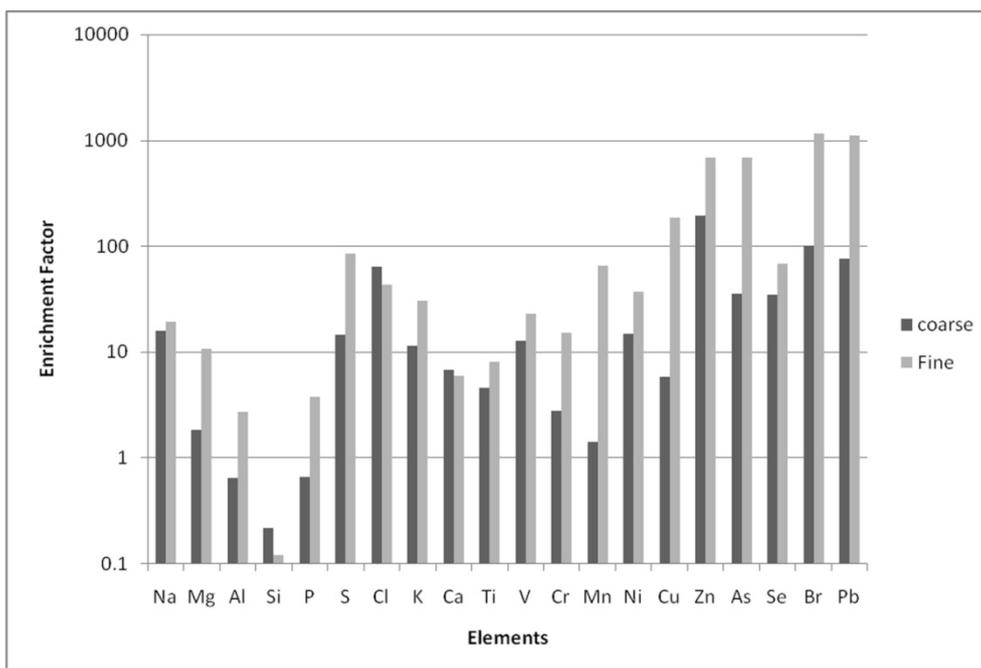


Fig. 6. Crustal Enrichment Factors of elements in $PM_{2.5-10}$ and $PM_{2.5}$.

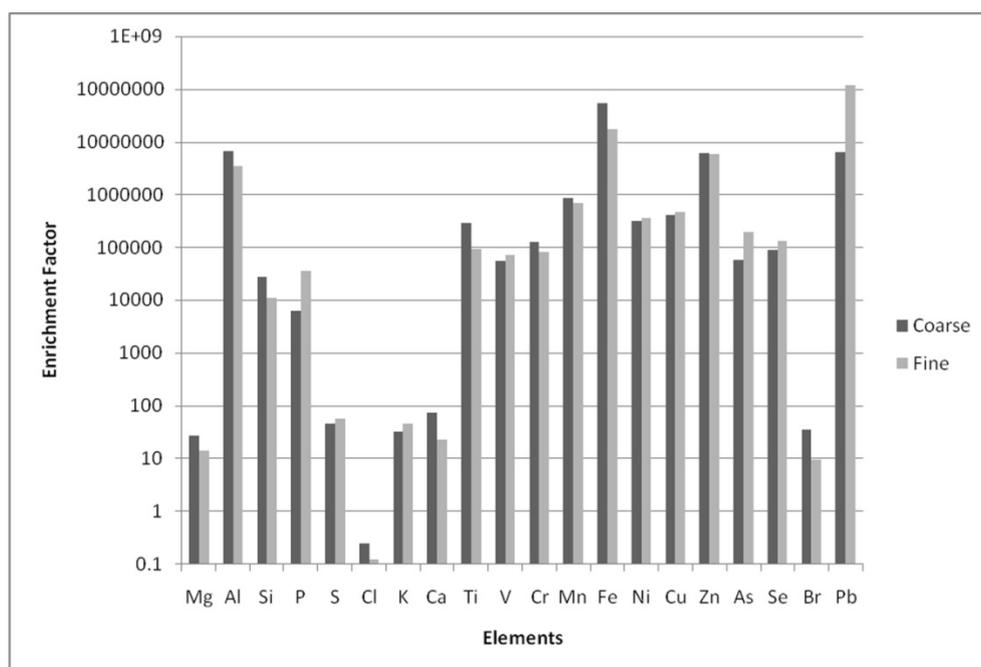


Fig. 7. Marine Enrichment Factors of elements in $PM_{2.5-10}$ and $PM_{2.5}$.

particulate matter and was comprising trace elements such as Cu and Cr. Since Cu and Cr complexes are mostly used in abundance in the industries of textile, dyes and intermediates, it is suspected that this could be the source of emission for these elements having high loadings in the fourth factor of fine particulates. Also about 6% of the industries in the nearby industrial belt comprise dye and textile industries (Srivastava and Som, 2007). Elements such as Cu and Cr showed comparatively high enrichment in the fine fraction and have been resolved as a separate

source in the PCA studies confirming their anthropogenic origin. Previous source apportionment studies performed in the study area provided similar kind of source profile (Kothai et al., 2008), however in the present study a bromine source in the coarse fraction and a selenium source in the fine fraction were identified additionally in the multivariate data analysis of the elemental concentrations of particulate matter. Also the tracer elements of vehicular emission such as Zn and S (Xudong et al., 1994) found to be merged along with the combustion source and was not resolved as a separate

Table 4. Varimax rotated PCA factor loadings for coarse particles.

Elements	Soil	Sea salt	Combustion	Br source
Na	0.131	0.95	-0.172	0.061
Mg	0.87	0.53	0.19	0.082
Al	0.94	0.042	0.19	0.023
Si	0.95	0.061	0.23	0.06
S	0.36	0.19	0.83	0.24
Cl	-0.69	0.96	0.25	-0.091
K	0.53	0.61	0.22	0.074
Ca	0.93	0.37	0.073	-0.035
Ti	0.95	-0.112	0.26	0.035
V	0.140	-0.43	0.82	0.23
Cr	0.74	-0.171	0.44	0.25
Mn	0.86	-0.092	0.42	0.113
Fe	0.95	-0.071	0.26	0.024
Ni	0.041	0.053	0.73	-0.14
Cu	0.76	-0.28	0.37	0.24
Zn	0.69	-0.28	0.59	0.23
As	0.172	-0.114	0.81	-0.021
Se	0.58	0.092	-0.113	0.21
Br	0.124	0.48	-0.062	0.96
Pb	0.38	-0.24	0.84	0.113
Eigen Value	12.2	4.96	1.96	1.55
% Var	52.53	17.43	6.95	5.9

Table 5. Varimax rotated PCA factor loadings for fine particles.

Element	Soil	Sea salt	combustion	Industries (Pigment)	Se source
Na	0.44	0.78	-0.154	0.121	0.132
Mg	0.84	0.31	-0.122	0.35	0.112
Al	0.86	0.132	0.26	-0.082	-0.141
Si	0.95	0.27	0.074	0.061	0.144
S	-0.061	0.29	0.79	0.44	-0.133
Cl	-0.12	0.79	-0.171	0.46	0.21
K	0.58	0.58	0.42	-0.21	-0.33
Ca	0.94	0.36	0.21	0.074	0.081
Ti	0.93	-0.081	0.112	-0.163	0.062
V	0.39	-0.144	0.79	0.192	-0.42
Cr	-0.062	0.193	0.044	0.93	0.15
Mn	0.42	-0.113	0.76	-0.081	-0.22
Fe	0.96	0.115	0.153	-0.042	-0.123
Ni	0.121	0.26	0.92	0.051	0.091
Cu	0.36	-0.134	0.39	0.76	-0.161
Zn	0.45	-0.112	0.75	-0.063	-0.081
As	0.140	0.043	0.85	-0.034	0.22
Se	-0.143	0.144	0.37	0.34	0.85
Br	-0.26	0.73	0.24	0.24	-0.144
Pb	0.35	-0.21	0.74	0.191	-0.23
Eigen Value	11.1	6.14	2.42	1.55	1.67
% Var	45.9	22.5	7.46	3.53	4.64

factor. Similar studies conducted on source identification at various places of Mumbai region also indicated crustal matter and sea salt as the main sources contributing to particulate pollution along with other sources such as oil combustion, road dust, metal industries and coal combustion (Sadasivan *et al.*, 1984; Sharma and Patil, 1994; Kumar *et al.*, 2001; Tripathi *et al.*, 2004).

CONCLUSIONS

Coarse and fine particulate matter (PM_{2.5-10} and PM_{2.5}) was collected at a residential site situated near an industrial area to know the impact of their emissions in the ambient air. PIXE technique has been used to determine the concentration levels of trace elements in the filter samples

containing only few hundred μg of total dust load. Time series analysis of particulate matter revealed a seasonal trend with high concentrations during winter season. Concentrations of crustal and sea salt derived elements found in high levels. The EF analysis showed very high enrichment for elements As, Pb, Zn in the fine fraction and Mn, Cr, and Cu found to be enriched only in the fine particles which indicate their nature of origin could be from any anthropogenic sources and has also been confirmed by PCA studies. PCA studies explained three common contributing sources of coarse and fine particulates such as soil, sea salt and combustion. Additionally a source with high loadings of Br is identified for coarse particles. In the case of the fine particle fraction a source related to industrial emission and a source of Se has also been identified.

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REFERENCES

- Andrade, F., Orsini, C. and Maenhaut, W. (1993). Receptor Modeling for Inhalable Atmospheric Particles in Sao Paulo, Brazil. *Nucl. Instrum. Methods Phys. Res., Sect. B* 75: 308–311.
- Anjali, S. and Dipanjali, S. (2007). Hazardous Air Pollutants in Industrial Area of Mumbai – India. *Chemosphere* 69: 458–468.
- Bhaskar, B.V. and Mehta, V.M. (2010). Atmospheric Particulate Pollutants and their Relationship with Meteorology in Ahmedabad. *Aerosol Air Qual. Res.* 10: 301–315.
- Bongiovanni, S.F., Prati, P., Zucchiatti, A., Lucarelli, F., Mando, P.A., Ariola, V. and Bertone, C. (2000). Study of the Aerosol Composition in the Town of La Spezia with Continuous Aampling and PIXE Analysis. *Nucl. Instrum. Methods Phys. Res., Sect. B* 161–163: 786–791.
- Carminie, P.D., Lucarelli, F., Mando, P.A., Valerio, M., Prati, P. and Zucchiatti, A. (1999). Elemental Composition of Size-fractionated Urban Aerosol Collected in Florence, Italy; Preliminary Results. *Nucl. Instrum. Methods Phys. Res., Sect. B* 150: 450–456.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P. A., Magliano, K.L., Ziman, S.D. and Richards, L.W. (1992). PM_{10} Source Apportionment in California's San Joaquin Valley. *Atmos. Environ.* 26A: 3335–3354.
- Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Hackney, B., Magliano, K., Lehrman, D. and Smith, T. (1999). Temporal Variations of O_3 , PM_{10} and Gaseous Precursors during the 1995 Integrated Monitoring Study in Central California. *J. Air Waste Manage. Assoc.* 49: 16–24.
- Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H. and Magliano, K. (1996). Descriptive Analysis of $\text{PM}_{2.5}$ and PM_{10} at Regionally Representative Locations during SJVAQS/AUSPEX. *Atmos. Environ.* 30: 2079–2112.
- Cohen, D.D. (1998). Characterisation of Atmospheric Fine Particles Using IBA Techniques. *Nucl. Instrum. Methods Phys. Res., Sect. B* 136: 14–22.
- Cohen, D.D., Stelcer, E. and Garton, D. (2002). Trace Elements in Street and House Dust: Source and Speciation. *Nucl. Instrum. Methods Phys. Res., Sect. B* 190: 466–470.
- Dubey, N. and Pervez, S. (2008). Investigation of Variation in Ambient PM_{10} Levels within an Urban-Industrial Environment. *Aerosol Air Qual. Res.* 8: 54–64.
- Gao, Y., Arimoto, R., Duce, R.A., Lee, D.S. and Zhou, M.Y. (1992). Input of Atmospheric Trace Elements and Mineral Matter to the Yellow Sea during the Spring of a Low-dust Year. *J. Geophys. Res.* 97: 3767–3777.
- Gupta, I. and Kumar, R. (2006). Trends of Particulate Matter in Four Cities in India. *Atmos. Environ.* 40: 2552–2566.
- Hopke, P.K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W., Artaxo, P. and Cohen, D. (1997). Characterization of the Gent Stacked Filter Unit PM_{10} Sampler. *Aerosol Sci. Technol.* 27: 726–735.
- Huang, L., Wang, K., Yuan, C.S., and Wang, G. (2010). Study on the Seasonal Variation and Source Apportionment of PM_{10} in Harbin, China. *Aerosol Air Qual. Res.* 10: 86–93.
- Kothai, P., Saradhi, I.V., Prathibha, P., Hopke, P.K., Pandit, G.G., and Puranik, V.D. (2008). Source Apportionment of Coarse and Fine Particulate Matter at Navi Mumbai, India. *Aerosol Air Qual. Res.* 8: 423–436.
- Kumar, A.V., Patil, R.S. and Nambi, D.S.V. (2001). Source Apportionment of Suspended Particulate Matter at Two Traffic Junctions in Mumbai, India. *Atmos. Environ.* 35: 4245–4251.
- Laden, F., Neas, L.M. and Dockery, D.W. (2000). Association of Fine Particulate Matter from Different Sources with Daily Mortality in Six U.S. Cities. *Environ. Health Perspect.* 108: 941–947.
- Li, W., Bai, Z., Liu, A., Chen, J., and Li, C. (2009). Characteristics of Major $\text{PM}_{2.5}$ Components during Winter in Tianjin, China. *Aerosol Air Qual. Res.* 9: 105–119.
- Lin, J.J. (2002). Characterization of Water-Soluble Ion Species in Urban Ambient Particles. *Environ. Int.* 28: 55–61.
- Maenhaut, W., Francois, F. and Cafmeyer, J. (1994). The “Gent” Stacked Filter Unit (SFU) Sampler for the Collection of Aerosols in Two Size Fractions: Description and Instructions for Installation and Use. Applied Research on Air Pollution Using Nuclear-related Analytical Techniques, Report on the First Research Co-ordination Meeting, Viennam Austria, 30 March–2 April 1993, NAHRES-19, IAEA, Vienna, p. 249–263.
- Mage, D., Ozolins, G., Peterson, P., Webster, A., Orthofer, R., Vandeweerd, V. and Gwynne, M. (1996). Urban Air Pollution in Mega Cities of the World. *Atmos. Environ.* 30: 681–696.
- Mahadevan, T.N. (1986). Studies on Aerosol Size Distribution and Chemical Composition in Urban, Rural

- and Marine Environments and Their Deposition through Precipitation. Ph.D. Thesis Submitted to University of Bombay, p. 321–322.
- Maxwell, J.A., Teesdale, W.J. and Campbell, J.L. (1995). The Guelph-PIXE Software Package-II. *Nucl. Instrum. Methods Phys. Res., Sect. B* 95: 407–421.
- Milind, K. and Gurumurthy, R. (2000). The Causes and Consequences of Particulate Air Pollution in Urban India: A Synthesis of the Science. *Annu. Rev. Energy Env.* 25: 629–684.
- Murray, F., McGranahan, G., and Kuylensstierna, J.C.I. (2001). Assessing Health Effects of Air Pollution in Developing Countries. *Water Air Soil Pollut.* 130: 1799–1804.
- National Ambient Air Quality Standards (1998). Central Pollution Control Board, India.
- Parmar, R.S., Satsangi, G.S., Kumari, M., Lakhani, A., Srivastava, S.S. and Prakash, S. (2001). Study of Size Distribution of Atmospheric Aerosol at Agra. *Atmos. Environ.* 35: 693–702.
- Pope, C.A. (2000). Epidemiology of Fine Particulate Air Pollution and Human Health: Biologic Mechanisms and Who's at Risk. *Environ. Health Perspect.* 108: 713–723.
- Pope, C.A., Bates, D. and Raizenne, H. (1995). Health Effects of Particulate Air: Time for Reassessment? *Environ. Health Perspect.* 103: 472–480.
- Pueschel, R.F., Van Valin, C.C., Castillo, R.C., Kandlech, R.C. and Ganor, E. (1986). Aerosols in Polluted versus Non Polluted Air Masses: Long Range Transport and Effect on Clouds. *J. Climate Appl. Meteor.* 25: 1908–1917.
- Pytkowicz, R.M. and Kester, D.R. (1971). The Physical Chemistry of Sea Water. *Oceanogr. Mar. Biol. Ann. Rev.* 9: 11–60
- Quiterio, S.L., Da Silva, C.R.S., Arbilla, G. and Escaleira, V. (2004). Metals in Airborne Particulate Matter in the Industrial District of Santa Cruz, Rio de Janeiro, in an Annual Period. *Atmos. Environ.* 38: 321–331.
- Ramanathan, V., Crutzen, P. J., Lelieveld, J., Mitra, A.P., Althausen, D., Anderson, J., Andreae, M.O., Cantrell, W., Cass, G.R., Chung, C.E., Clarke, A.D., Coakley, J.A., Collins, W.D., Conant, W.C., Dulac, F., Heintzenberg, J., Heymsfield, A.J., Holben, B., Howell, S., Hudson, J., Jayaraman, A., Kiehl, J.T., Krishnamurti, T.N., Lubin, D., McFarquhar, G., Novakov, T., Ogren, J.A., Podgorny, I.A., Prather, K., Priestley, K., Prospero, J.M., Quinn, P.K., Rajeev, K., Rasch, P., Rupert, S., Sadourny, R., Satheesh, S.K., Shaw, G.E., Sheridan, P., Valero, F.P.J. (2001). Indian Ocean Experiment: An Integrated Analysis of the Climate Forcing and Effects of the Great Indo-Asian Haze. *J. Geophys. Res.* 106: 28371–28398.
- Sadasivan, S. and Negi, B.S. (1990). Elemental Characterization of Atmospheric Aerosols. *Sci. Total Environ.* 96: 269–279.
- Sadasivan, S., Negi, B.S. and Mishra, U.C. (1984). Composition and Sources of Aerosols at Trombay, Bombay. *Sci. Total Environ.* 40: 279–286.
- Salvador, P., Artinano, B., Alonso, D.G., Querol, X. and Alastuey, A. (2004). Identification and Characterization of Sources of PM₁₀ in Madrid (Spain) by Statistical Methods. *Atmos. Environ.* 38: 435–447.
- Sharma, V.K. and Patil, R.S. (1994). Chemical Mass Balance Model for Source Apportionment of Aerosols in Bombay. *Environ. Monit. Assess.* 29: 75–88.
- Srivastava, A. and Som, D. (2007). Hazardous Air Pollutants in Industrial Area of Mumbai, India. *Chemosphere* 69: 458.
- Tripathi, R.M., Kumar, A.V., Manikandan, S.T., Bhalke, S., Mahadevan, T.N. and Puranik, V.D. (2004). Vertical Distribution of Atmospheric Trace Metals and their Sources at Mumbai, India. *Atmos. Environ.* 38: 135–146.
- Trompeter, W.J., Markwitz, A. and Davy, P. (2005). Air Particulate Research Capability at the Newzealand Ion Beam Analysis Facility Using PIXE and IBA Techniques. *Int. J. PIXE* 15: 249–255.
- Venkataraman, C., Reddy, C.K., Josson, S. and Reddy, M.S. (2002). Aerosol Size and Chemical Characteristics at Mumbai, India during the INDOEX-IFP (1999). *Atmos. Environ.* 36: 1979–1991.
- Watson, J.G. (2002). Visibility: Science and Regulation. *J. Air Waste Manage. Assoc.* 52: 628–713.
- World Health Organization. (2005). Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulphur Dioxide, Global Update 2005.
- Xudong, H., Ilhan, O., Namik, K.A. and Glen, E.G. (1994). Emission of Trace Elements from Motor Vehicles: Potential Marker Elements and Source Composition Profile. *Atmos. Environ.* 28: 1385–1391.
- Yuanxun, Z., Yuanmao, Z., Yingsong, W., Delu, L., Aiguo, L., Yan, L., Guilin, Z., Yifei, Z. and Zuci, S. (2006). PIXE Characterization of PM₁₀ and PM_{2.5} Particulate Matter Collected during the Winter Season in Shanghai City. *J. Radioanal. Nucl. Chem.* 267: 497–499.

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