

Characterization of Atmospheric Particulate Matter using PIXE Technique

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Abstract—Coarse and fine particulate matter were collected at a residential area at Vashi, Navi Mumbai and the filter samples were analysed for trace elements using PIXE technique. The trend of particulate matter showed higher concentrations during winter than the summer and monsoon concentration levels. High concentrations of elements related to soil and sea salt were found in PM10 and PM2.5. Also high levels of zinc and sulphur found in the particulates of both the size fractions. EF analysis 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 derived elements showed very low EF values indicating their origin from soil. The PCA based multivariate studies identified soil, sea salt, combustion and Se sources as common sources for coarse and additionally an industrial source has also been identified for fine particles.

Keywords—EF analysis, PM10, PM2.5, PIXE, PCA.

I. INTRODUCTION

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. Particularly air borne particulates with aerodynamic diameter 2.5 to 10 μm are referred as coarse particles (PM10) and less than 2.5 μm as fine particles. Fine particles (PM2.5) 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 metals smelting. They may also include natural emissions such as fine windblown soils, emission from volcanoes, sea spray and smoke from biomass burning [2]. Studies of Chow et al [3] and Andrade [4] 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 parameters 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 [5], [6].

Indian megacities are among the most polluted in the world. Air concentrations of a number of air pollutants are much higher than levels recommended by the World Health Organization [7]. In India major sources of urban air pollution include coal combustion, oil refineries and industrial manufacturing facilities [8], [9]. The most polluted metropolitan cities of India are Mumbai, Kolkatta, and Delhi. 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 (PM_{2.5-10 μm}) and fine particles (PM_{2.5 μm}) 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 PM10, PM2.5 concentration levels and their composition at Vashi. Furthermore, data derived from the study has been utilized for various statistical analyses.

II. SAMPLING PROGRAM

The particulate sampling system was installed at Vashi in Navi Mumbai and the sampling was performed at a height about 15m. Although the sampling site is located at a residential area, the city is near to Thane belapur industrial area and a highway passes 2 km from the site. The Navi Mumbai region is covered by parsik 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. For air sampling Gent PM10 sampler developed at Gent University in Belgium was used. The sampler is equipped with a NILU (Norwegian Institute for Air Research) 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 lpm, which allowed the collection of coarse particles with Effective Cut off Diameter (EAD) between 10 and 2.5 μm (PM10) in the first stage and fine particles with EAD 2.5 μm (PM2.5) 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. The particulate load in the filter was measured by gravimetry using

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a Mettler balance with 10 μ g sensitivity.

III. ANALYSIS

Multielement analyses of the filter samples collected during the study period were performed using Proton Induced X-ray Emission (PIXE) at the Institute of Geological and Nuclear Sciences (IGNS), New Zealand. An 8 mm diameter, 10 nA beam of 2.6 MeV protons was used to obtain the PIXE spectra and the x-ray spectra obtained from PIXE measurements were analysed using the computer code GUPIX developed by Guelph University. Calibration of the PIXE system was performed by irradiating suitable thin target standards in the similar experimental conditions. As the filters were thin, concentrations were obtained in ng/cm² on the filter and were then converted to ng/m³ of air sampled, by multiplying by the exposed filter area (in cm²) and dividing by the volume of air sampled in 24 h (in m³).

IV. ENRICHMENT FACTOR ANALYSIS

Enrichment factor (EF) is widely used to identify the anthropogenic source of metallic elements. The equation for enrichment factor is: $EF_i = (i/j)_{air} / (i/j)_{crust}$, where EF_i is the enrichment factor of species i , j is a reference element for crustal material, $(i/j)_{air}$ is the ratio of species i to species j in the aerosol sample and $(i/j)_{crust}$ is the ratio of species i to species j in the crust [10].

V. RESULTS AND DISCUSSION

A. Concentrations of Particulate Matter

Table I presents the summary of the coarse and fine particulate matter collected at the sampling site. The average concentration of PM₁₀ and PM_{2.5} were 76.34 (μ g/m³) and 45.67 (μ g/m³) and the highest concentration was observed to be 140.23 (μ g/m³) and 76.24 (μ g/m³) respectively. The time series plot of the particulates in both the size fractions over the three seasons of Mumbai was presented in Fig. 1. 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 PM₁₀ and PM_{2.5} in the season of winter were about two times than the concentrations during summer and fall seasons because it is well known that during winter due to lower temperatures the mixing height becomes 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 [11].

The time series plot of ratio between PM_{2.5} and PM₁₀ is presented in Fig. 2. 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 PM₁₀ 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 results reported by Chow et al [12], [13] and Lin [14] 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 PM₁₀ 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. 3), which indicate there might be similar kind of sources contributing to the particulate matter in the sampling region.

TABLE I
SUMMARY OF COARSE AND FINE PARTICULATE MATTER

Parameter	PM _{2.5-10μm} (μ g/m ³)	PM _{2.5μm} (μ g/m ³)
Mean	76.34	45.67
Median	76.82	44.44
Standard deviation	25.78	14.47
Maximum	140.23	76.24
Minimum	33.56	17.16
No. of samples	109	

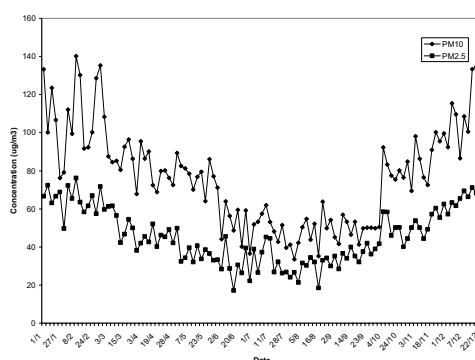


Fig. 1 Time series plot of PM₁₀ and PM_{2.5} mass concentrations during the study period

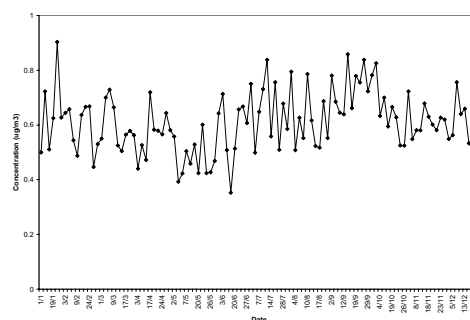


Fig. 2 Time series plot of PM_{2.5}/PM₁₀ ratio during the study period

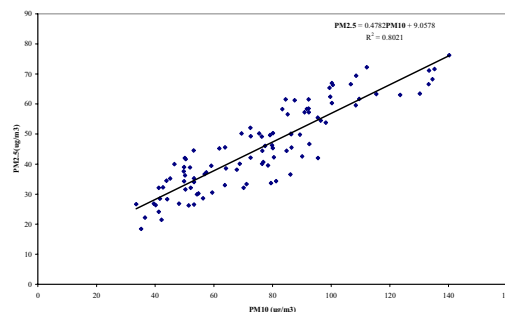


Fig. 3 Correlation between PM₁₀ and PM_{2.5} during the study period

B. Concentrations of Metals in Particulate Matter

Table II presents the mean and standard deviation of concentration levels of few metals in the coarse and fine fractions of particulate matter. Among the 25 elements Na, K, Cl, Si, Al, Mg, Ca, and Fe are found to be the most abundant metals where the major contributing source of first three elements could be sea salt and others could be originated from soil dust. In the coarse fraction concentration of metals ranged from 0.017 -6.77 $\mu\text{g}/\text{m}^3$ and in the fine fraction it was from 0.008 to 2.134 $\mu\text{g}/\text{m}^3$. A high concentration of sulphur and Zinc was observed in both the sizes of particulates except the high levels of elements, which are considered to be originated from natural sources. Also marginally higher levels of Cu, Cr, Se, Co and As was observed in the particulate samples. The standard deviation presented for each element is very high suggesting significant temporal variation in the concentrations.

TABLE II
SUMMARY OF CONCENTRATION OF ELEMENTS IN COARSE AND FINE PARTICULATE MATTER

Parameter ($\mu\text{g}/\text{m}^3$)	PM _{2.5-10μm}		PM _{2.5μm}	
	Mean	S.D.	Mean	S.D.
Na	1.239	0.497	0.462	0.386
Mg	1.122	0.291	0.264	0.140
Al	3.208	0.858	0.696	0.604
Si	6.770	1.797	1.095	0.627
P	0.044	0.025	0.028	0.020
S	2.682	0.832	2.134	0.868
Cl	0.565	0.381	0.100	0.027
K	0.909	0.453	0.561	0.815
Ca	3.783	1.068	0.457	0.283
Sc	0.024	0.023	0.014	0.009
Ti	0.347	0.096	0.046	0.026
V	0.018	0.008	0.008	0.004
Cr	0.046	0.019	0.013	0.008
Mn	0.104	0.035	0.018	0.011
Fe	3.657	1.031	0.489	0.290
Co	0.039	0.019	0.009	0.007
Ni	0.017	0.009	0.008	0.005
Cu	0.050	0.026	0.018	0.012
Zn	0.380	0.193	0.148	0.069
As	0.026	0.012	0.033	0.024
Se	0.023	0.014	0.012	0.007
Br	0.043	0.018	0.031	0.017
I	0.089	0.050	0.035	0.020
Hg	0.059	0.037	0.024	0.017
Pb	0.158	0.097	0.131	0.125

C. Enrichment Factor Analysis

The separation of natural and anthropogenic components is a basic task of aerosol measurements. Enrichment Factor (EF) analysis is conventionally used for separating soil derived and anthropogenic components [15]. Therefore to verify the contributors of crustal and non-crustal sources for trace elements associated with PM10 and PM2.5, the EF was calculated for each element. In this study Fe is used as a reference element and Fig.3 shows EF values obtained for the trace elements of coarse and fine particulate matter. The plot shows EF values of Al, Ca, Mg, Sc, Si in both the size fractions are very less indicating their origin from crustal source. The anthropogenic elements such as P, Ni and V were enriched to a lesser extend ($1 < \text{EF} < 10$). As, Br, Pb and Zn in the fine fraction exhibit the maximum enrichment ($\text{EF} \leq 1000$), whereas in the coarse fraction except Zn, the EF of other three

elements are within 100. Few elements like Mn, Cr, and Cu are showing enrichment only in the fine fraction, which indicates their anthropogenic origin from traffic emissions or smelters. Enrichment of Na, K, Br and Cl can be attributed to sea salt.

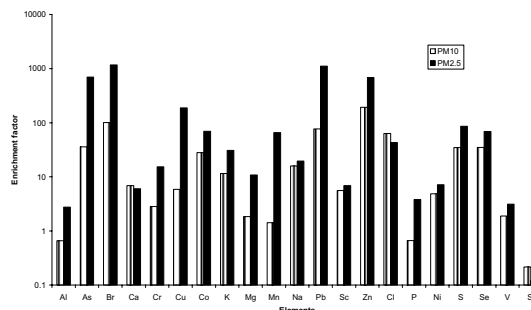


Fig. 4 Enrichment factors of elements in PM10 and PM2.5

D. Sources of Trace Metals in Ambient Air

A multivariate Principal Component Analysis [16] was used to extract the major sources of the trace elements and the technique yields a number of key factors associated with the finger print elements of the sources. From the analysis of the trace elemental data of the coarse particles the first source with the finger print elements of crustal has been interpreted 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. Finally a source of Se was identified separately and the respective industry in the surrounding area has to be delineated. Similarly soil, sea salt, combustion and Se sources have been identified from the multivariate analysis of fine fraction data set. Also, in the PCA study of fine particles the sources of combustion and industrial emission has been resolved separately and a source comprising Cu, Cr and Ni has been grouped together. There were four sources found to be common for both the fractions supporting the strong correlation between fine and coarse particle concentrations. Similarly elements such as Cu and Cr showed high enrichment only in the fine fraction and has been resolved as a separate source in the PCA studies confirming their anthropogenic origin.

TABLE III
SOURCES OF COARSE PARTICLES

Source	Elements
Soil	Mg, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu
Sea salt	Na, Cl, K, Br, I
Combustion	S, Ni, As, Zn, Pb
Se source	Se

TABLE IV
SOURCES OF FINE PARTICLES

Source	Elements
Soil	Mg, Al, Si, K, Ca, Ti, V, Fe, Co, Zn
Sea salt	Na, Cl, K, Br, I
Combustion	S, V, Zn, As, Mn
Industries	Cu, Cr, Ni
Se source	Se

VI. CONCLUSIONS

Particulate matter in two sizes (PM₁₀ and PM_{2.5}) was collected at a residential site situated near an industrial area and a highway 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. 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, 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 the major contributing sources of coarse and fine.

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