

Chemical Characterization of Submicron Aerosol in Kanpur Region: a Source Apportionment Study

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Abstract—Several studies have shown the association between ambient particulate matter (PM) and adverse health effects and climate change, thus highlighting the need to limit the anthropogenic sources of PM. PM Exposure is commonly monitored as mass concentration of PM₁₀ (particle aerodynamic diameter < 10µm) or PM_{2.5} (particle aerodynamic diameter < 2.5µm), although increasing toxicity with decreasing aerodynamic diameter has been reported due to increased surface area and enhanced chemical reactivity with other species. Additionally, the light scattering properties of PM increases with decreasing size. Hence, it is important to study the chemical characterization of finer fraction of the particulate matter and to identify their sources so that they can be controlled appropriately to a large extent at the sources before reaching to the receptors.

Keywords— PM₁, PCA, source apportionment.

I. INTRODUCTION

KANPUR is one of the most polluted cities in India today. Kanpur's climate can be characterized by a very hot and dry summer and very cold winter, the temperature during summer can go up to 50 °C and winter it's dropped below 0°C. The city's population is around 6 million at present and it is dangerously congested and overcrowded and due to the onset of leather industries pollution levels have risen dangerously high, according to the CPCB (central pollution control board) the RSPM (respirable suspended particulate matter) concentration in the city is 178µg/m³ which is far more than the specified under the National Ambient Air Quality Standards (NAAQS). Alarming vehicular and population growth rate, frequent traffic jams and not much improvement in the quality and number of roads has resulted in a significant rise in the RSPM (respirable suspended particulate matter) level of Kanpur. However, although vehicles and industries are two of the biggest contributors to the Kanpur's ambient RSPM level but contributions from other pollution sources, such as roadside dust, trans-boundary migrations, power plants, solid waste and local sources can't be ruled out. Particulate matter from these sources may contain hazardous pollutants and can have carcinogenic and mutagenic effects. Thus, identification of the sources is important. In India there are very few studies are conducted on characterization of fine particulate matters (PM_{2.5} or less), but their characterization and source identification is very much important as these particles can remain suspended in air for

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long time and can be transported a long distance with wind and can easily go into our respirable tract. Several methods are used to estimate sources including principle component analysis (PCA or Factor Analysis), multiple linear regression analysis (MLR) and the Chemical Mass Balance (CMB) Receptor Model, Positive Matrix Factorization (PMF), Molecular Marker method etc. In the present investigation, we have applied PCA for the source apportionment of PM₁ in the ambient air of Kanpur.

II. OBJECTIVES

To carry out the chemical characterization of PM₁ and with the help of chemical characterization data identification of possible sources of PM₁ using statistical tools such as PCA or Factor analysis.

III. MATERIALS AND METHOD

A. Sampling Site

Sampling was carried out during monsoon (July-august) and in post monsoon season (sep-oct) inside the IIT Kanpur. The sampler was placed on the roof a building around 12m high. The sampling was performed between 18th July and 23rd of October. The sampling period was 8hr from 9 am to 5 pm. During the sampling days maximum temperature was 38°C and minimum was 24°C and max and min relative humidity were 60% and 96% respectively.

Sampling Site	Season	Sampling Time	No. of Samples
IIT KANPUR	Monsoon	8hr	15
IIT KANPUR	Post Monsoon	8hr	15

B. Sampling Procedure

The sampling was done using a single stage impactor type sampler developed in IIT Kanpur itself. Flow rate maintained through the sampler was 10LPM using a vacuum pump and a Rota meter. The samples were collected on Whatman PTFE (Teflon) filters of 47mm diameter and 2µm pore size, since the collected mass were of very low quantity so extreme care was taken during sampling and analysis of the samples to avoid any contamination, the PTFE filters were chosen because of their 1. Chemical inertness 2. Very less moisture absorption 3. Stability to withstand changing weather conditions. All the filters are pre-conditioned at 25°C and 60% relative humidity before sampling and post-conditioned after

sampling at same condition, 10% of the total no of samples were always kept as a blank. The blank filters were kept at same condition as the actual samples. After the sampling filters were immediately transferred to a sealed plastic container and kept in refrigerator till further analysis

C. Quality Control

- Clear forceps are used to handle the filters and each time the forceps were cleaned with ethanol to avoid any contamination.
- Filters were kept in sealed plastic containers in the refrigerator until the analysis was done.
- Flow rate was checked at every 30min interval to avoid any fluctuation in air flow.
- All the glass wares were acid washed and oven dried before use.
- All the working standards and sample solutions were prepared using ultra pure (resistivity 18.2 MΩ/cm) water.
- Each instrument was calibrated before sample analysis.
- After every 10 samples analyzed the instrument performance was checked against the working standards and if the recovery was not found between (90-110) % ranges then the instrument was re-calibrated.

D. Chemical Analysis

Chemical analysis of the exposed filters is carried out in the following way:

Each exposed filter is cut into half portion and then one half portions is cut into several small fragments and kept in a digestion vessel which was a round bottom flask of 100ml capacity. Then 20ml of conc. Nitric acid (65%, Merck GR grade) was poured into the digestion vessel and it is then placed over a hot plate and kept for around 2hr at 180°C until the most of the Nitric acid is evaporated but not completely dried the vessel. The residual is then filtered through .22µm Teflon filter and diluted to 100ml for elemental analysis. Each blank filtered is digested in the same way as the sample filters. The elemental analysis is performed in ICP-OES(Inductively coupled plasma optical emission spectrometry),the instrument uses a superheated Argon plasma of 7000-10000K excite the atoms of the different elements and then identifies the elements from the characteristic wavelength they emits during the excitation process, it's a fairly rapid process and can identify up to 60 elements simultaneously . We have selected 13 metals for our analysis-As, Ca, Co, Cr, Cd, Mg, Fe, Ni, Pb, Cu, Zn, V, Se, out of these metals 11 were found be present in the samples as other metals were found to be below the detection limit of the instrument. Samples are analyzed for 5 anions- F⁻,Cl⁻,NO₃⁻,SO₄²⁻,PO₄³⁻ by Ion Chromatography (Metrohm, Compact IC 761). For Ion analysis the remaining half of the filter was cut into small pieces and placed inside a test tube after that 20ml ultra pure water was poured into the test tube. The test tubes were then placed in a sonication bath and ultrasonication was done for 20 minutes to extract the water soluble anions, this extracted solution then diluted to 100 ml with ultrapure water and kept in refrigerator till further analysis.

IV. RESULTS AND DISCUSSIONS

The PM₁ concentration in the samples varies significantly

from monsoon to post monsoon season. During monsoon season due to high relative humidity, heavy rainfall and less turbulence in the atmosphere PM₁ concentration is found to be significantly lower than post monsoon .Elements which are of mainly crustal origin and mostly associated with coarse-medium size range like-Ca, Mg, Fe found to be higher in post monsoon also the PM₁ mass concentration increases significantly from monsoon to post monsoon season due to low humidity, less rainfall which allows the resuspension of crustal dust.

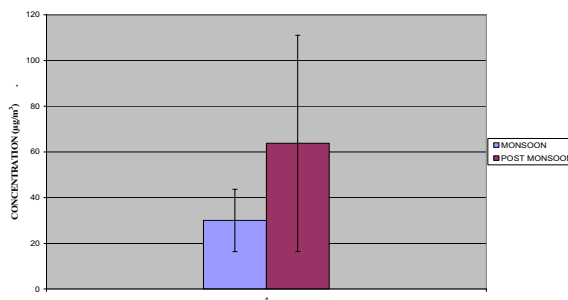


Fig. 1 Seasonal variability in average pm₁ mass concentration

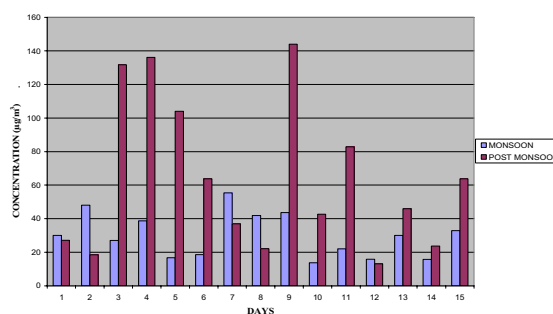


Fig. 2 Seasonal daily variation in pm₁ concentration

TABLE I

Season	Average PM ₁ mass concentration (µg/m ³)	Standard deviation (µg/m ³)
Monsoon	30.03	13.71
Post monsoon	63.75	47.26

In the post monsoon season the variability in PM₁ concentration is higher than in monsoon season because in monsoon season almost all the days are calm and cloudy while in post monsoon season some of the days are cloudy and other days are sunny and windy.

A. Elements

Elemental concentration of the elements found to be higher in post monsoon than in monsoon season this is mainly due to the partial washout by heavy rainfall and high relative humidity which prevents the resuspension of settled dust; this is especially true for crustal elements like-Ca, Mg, Fe as their concentration significantly increase in post monsoon. Elements like-Ni, Pb, Zn, V, Se which are mainly originated from anthropogenic activities showed very little difference in

concentration and from this observation we can say that at PM₁ size range washout by rainfall played lesser role than other larger size fractions and it is well documented in the literature that as the particle size goes down wet deposition become less and less effective due to inefficient entrapment of the particulate matter by rain droplets and quick resuspension after deposition[1].

TABLE II
ELEMENTAL CONCENTRATION IN MONSOON

ELEMENTS	AVERAGE CONCENTRATION(ng/m ³)
Ca	556.67
Mg	610.03
Fe	378.04
Cr	38.44
Cu	184.54
Cd	36.67
Pb	93.48
Ni	78.12
Se	93.87
Zn	109.07
V	7.3

TABLE III
ELEMENTAL CONCENTRATION IN POST MONSOON

ELEMENTS	AVERAGE CONCENTRATION(ng/m ³)
Ca	796.21
Mg	753.47
Fe	763.46
Cr	88.63
Cu	197.64
Cd	59.59
Pb	101.63
Ni	97.22
Se	121.46
Zn	136.96
V	10.10

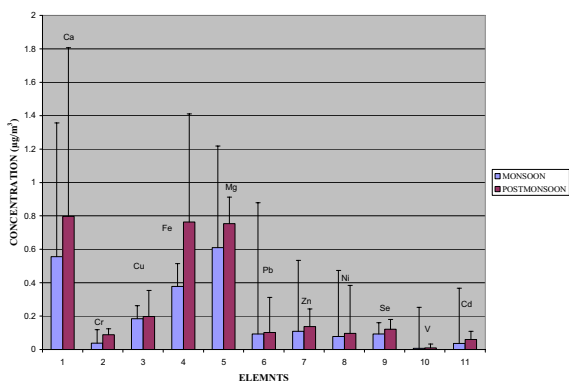


Fig. 3 Seasonal elemental concentrations

B. Anions

Anion concentrations also showed significant seasonal variability as elements. Anion concentration found to be significantly higher in post monsoon season than in monsoon and the reasons could be the same as for elements. Nitrate (NO₃-) in both the season is the dominating ion species followed by sulfate (SO₄²⁻) which indicates that vehicular emission is one of the major sources of PM₁ at this region. Fluoride (F-) and Phosphate (PO₄³⁻) mainly found in the post

monsoon season, from literature review it can be that the Fluoride is associated with coarser size fractions when the relative humidity is very high in the atmosphere as in case of monsoon, so washout by rainfall may leads to depletion of Fluoride. Phosphate is mainly associated with coarser size fractions so it's also not found in monsoon samples [2], [3]. Chloride (Cl-) is detected in both the season but in very low concentration and this is mainly due to absence of any significant quantity of marine aerosol since Kanpur is located in much interior part of India far from any sea, so chloride detected may be present in form of NH₄Cl formed by the neutralization of NH₃ with HCl originated mainly from coal combustion [4].

TABLE III
MONSOON ANION CONCENTRATIONS

ANION	AVERAGE CONCENTRATION(µg/m ³)
F ⁻	.0017
Cl ⁻	.240
SO ₄ ²⁻	4.46
NO ₃ ⁻	9.8

TABLE IV
POST MONSOON ANION CONCENTRATIONS

ANION	AVERAGE CONCENTRATION(µg/m ³)
F ⁻	.291
Cl ⁻	.760
SO ₄ ²⁻	12.70
NO ₃ ⁻	16.92
PO ₄ ³⁻	.485

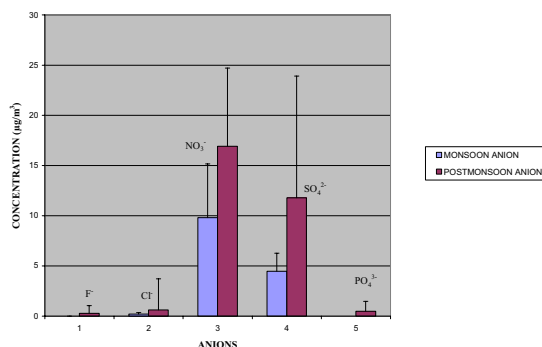


Fig. 4 Seasonal variability in anion concentrations

V. SOURCE APPORTIONMENT

For source apportionment we used PCA (Principle Component Analysis) or Factor analysis method. To identify the sources of PM₁ particles PCA or factor analysis method was applied. PCA was executed by the Varimax Rotated Factor Matrix method, based on orthogonal rotation criterion which maximizes the variance of the squared elements in the column of a factor matrix, using a statistical package SPSS (version 9). Metals and Anion concentrations are used as input variables. This method focuses on cleaning up the factors [5] - [8]. It produces factors that have high correlations with one smaller set of variables and little or no correlation with another set of variables.

The results of the PCA analysis shown below:

Component	TOTAL VARIANCE EXPLAINED					
	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.073	50.912	50.912	3.102	38.776	38.776
2	1.784	22.304	73.216	2.601	32.518	71.294
3	1.212	15.148	88.364	1.366	17.070	88.364
4	.527	6.585	94.949			
5	.263	3.290	98.239			
6	.080	.999	99.238			
7	.055	.686	99.924			
8	.006	.076	100.000			

SPSS software extracted factors with eigenvalues greater or equal to 1 as a principle component or factor [9],[10]. The above Total Variance Explained Table shows that first three components or factors with eigenvalues greater than 1 explained 88% of the total variance of entire data set so we extracted these three factors as the main factors for source identification. The factor loadings associated with these factors are then orthogonally rotated to get more interpretable factor loadings to identify possible sources.

Metals	FACTOR 1	FACTOR 2	FACTOR 3
Zn	.942		
Cu	.941		
Mg	.789		.689
Ca	.781	.514	.568
Ni		.966	
Pb	.287	.889	
Cr		.762	.436
Se		.423	.204
Fe			.900
SO ₄ ²⁻	.452	.879	.301
NO ₃ ⁻	.768		.312
Cl ⁻	.201	.282	.202
SOURCE	VEHICULAR	INDUSTRIAL	CRUSTAL DUST

Factor 1: Factor 1 shows very good correlation with Zn, Cu and Pb and NO₃⁻, these chemical species are very good indicators for vehicular emission. Cu can be emitted from break linings of a vehicle specially while stop and go kind of traffic situation happens. Zn can be emitted from vehicle exhaust. Pb can be emitted when leaded petrol is used as fuel. NO_x is formed during combustion inside the engine which later converts to NO₃⁻ via photochemical reactions so this source represents vehicular emission [11].

Factor 2: Factor shows high loadings on Ni, Pb, Cr, SO₄²⁻ these species are mainly of anthropogenic origin and generated from various industrial processes like coal combustion, metal production, fertilizer etc. Since in Kanpur, there are various kinds of industries and coal and oil fired

power plant so these metals more likely to be generated from those sources. So this factor represents industrial emission [12].

Factor 3: Factor 3 shows high correlation with Fe, Mg and Ca. These species are predominantly of crustal origin so this factor represents crustal or soil resuspension.

VI. CONCLUSION

It is observed that a significant amount of metals associated with the PM₁ are of anthropogenic origin which suggests that as the particle size goes down significant enrichment of anthropogenic metals and anions occurred in the particulate matters and vehicular emission is one of the most significant source that contributes at this fine particulate matter size range. Most of the metals like Ni, Cr, Pb, Zn are harmful for humans and can cause serious health concerns and as they are associated with PM₁ they can easily inhaled and retained in our respiratory system for longer duration making it more serious concerns. So there is an urgent need to control the emission of PM₁ particles into the atmosphere.

REFERENCES

- [1] R. Chester a, M. Nimmo b, P.A. Corcoran, Rain water-aerosol trace metal relationships at Cap Ferrat: A coastal site in the Western Mediterranean, *Marine Chemistry* 58 (1997) 293-312
- [2] Young-Ji Hana, Tae-Sik Kimb, Hekap Kim, Ionic constituents and source analysis of PM_{2.5} in three Korean cities, *Atmospheric Environment* 42 (2008) 4735-4746
- [3] P. Chandra Mouli a, S. Venkata Mohanb, S. Jayarama Reddya, A study on major inorganic ion composition of atmospheric aerosols at Tirupati, *Journal of Hazardous Materials B96* (2003) 217-228
- [4] M. J. Willison, A. G. Clarke and E. M. Zeki, Chloride aerosols in central northern England, *Atmospheric Environment* Vol. 23, No. 10, pp. 2231-2239, (1989)
- [5] Srivastava A, Gupta S, Jain V K, Source Apportionment of Total Suspended Particulate Matter in Coarse and Fine Size Ranges Over Delhi, *Aerosol and Air Quality Research*, 8(2), 188-200 (2008).
- [6] Paulo A, Pedro O, Roberto M, Aerosol composition and source apportionment in Santiago de Chile, *Nuclear Instruments and Methods in Physics Research*, 150 (B), 409-416(1999).
- [7] Guor-Cheng F,U, Cheng Nan C, Yuh Shen W, Peter Pi-C F, Ding G Y, Chia C C, Characterization of chemical species in PM₁₀ and PM_{2.5} aerosols in suburban and rural sites of central Taiwan, *The Science of the Total Environment*, 234(5), 203-212(1999).
- [8] Beceiro GonzBlez E, Andrade Garda J.M., Serrano Velasco E, P. Lbpez M, Metals in airborne particulate matter in La Corufia (NW Spain), *The Science of the Total Environment*, 196, 131-139(1997)
- [9] Ho K.F, Caob J.J, Lee S.C, Chak K, Source apportionment of PM_{2.5} urban area of Hong Kong, *Journal of Hazardous Materials*, B 138, 73-85 (2006)
- [10] Gupta A.K, Karar K, Srivastava A, Chemical mass balance source apportionment of PM₁₀ and TSP in residential and industrial sites of an urban region of Kolkata, India, *Journal of Hazardous Materials*, 142, 279-287(2007)
- [11] Kare K, Trends and sources for heavy metals in urban atmosphere, *Nuclear Instruments and Methods in Physics Research*, B 189, 227-232 (2002)
- [12] Fung Y. S. and Wong L. W. Y, Apportionment of air pollution sources by Receptor Models in Hong Kong, *Atmospheric Environment* 29(16), 2041-2048 (1999).