

Chemical characterization of atmospheric particulate matter in Delhi, India, Part II: Source apportionment studies using PMF 3.0

Suresh Tiwari,¹ Shamsh Pervez,^{2,*} Perrino Cinzia,³ Deewan Singh Bisht,¹ Atul Kumar Srivastava¹ and Dilip Chate¹

¹Indian Institute of Tropical Meteorology

Pune 411008, India

²School of Studies in Chemistry

Pt. Ravishankar Shukla University

Raipur 492010, India

³Atmospheric Sciences

C.N.R. Institute of Atmospheric Pollution

Monterotondo 29 300 00015, Italy

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ABSTRACT

World Bank reports Delhi as a second most polluted megacity in the world for particulates pollution. In Delhi, PM₁₀ (d ≤ 10 μm) aerosol samples were monitored throughout 2008 and their characterization for major chemical elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb, Cd, Sn and Sb) and ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) have been documented in an earlier study. To resolve complexity in source apportionment for chemical constituents in PM₁₀, UNMIX 6.0 and Positive Matrix Factorization (PMF 3.0) models are applied. Four factors were derived to explain routine sources of PM₁₀ (crustal origin, road-traffic and secondary aerosols). Factor-1, designated as road-traffic source, has been determined by temporal correlation among Pb, Cu, Zn, Ni and V with strong correlation between Pb and Zn. This source factor-1 has shown more than 60% contribution to receptor site. Factor-2, referred as crustal origin due to strong inter-relationship among Si, Fe, Al, Ca and Mg, has also shown to be significant contribution to similar species in receptor matrix. Factor-3 (NH₄⁺, NO₃⁻) has been differentiated due to contribution of secondary aerosols in the receptor region. This factor-3 has indicated major fraction of these ionic species for their uniform percentage variability, where mean values have been projected close to 75th percentile. Surprisingly, source factor-4 has explained the specific chloride source in the region with major contribution of 86%. For policymakers, results presented would serve as benchmark of source apportionments in Delhi.

INTRODUCTION

Presented work is the second part of the study on status and characterization of ambient PM₁₀ in Delhi that focused on source signatures of ambient PM₁₀ using USEPA receptor models. The first part of the study was focused on characterization of ambient PM₁₀ [1]. Occurrence of higher uncertainties in the chemical characterization of ambient particulate matter (PM), especially PM₁₀ measured at different environmentally defined microenvironments of various urban areas in India

has shown higher degree of multi-complexity in the particulate source signatures [2-10]. Most of Indian source apportionment studies conducted earlier was based on simple factor evaluation from the chemical data of PM [11-14]; some of the studies conducted using this method have shown various types of sources for the pollutants, for instance, fossil fuel combustion contributes Al, Fe, Ca, Mg, K, Na, As, Pb, Cd, Sc and Hg elements [15-17], elements of Pb and Zn are contributed by wood combustion [18-30], vehicular traffic contributes Cd, Cr, Cu, Ni, Pb, Zn [5], electroplating contributes Cr [31], and metal

*Corresponding author
Email: shamshpervez@gmail.com

alloy industries emits Cd, Cr, Al, Fe, Ni, Zn, Pb, Cu [32]. Simple factor analysis has been described in effective in precise extraction of source factors due to non-optimal data scaling [33]. Very selective studies of source apportionment using chemical mass balance by least square approaches viz. Positive Matrix Factorization (PMF 3.0), Effective Variance-Chemical Mass Balance (EV-CMB) and UNMIX 6.0 of USEPA have been reported [2-4,34-45]. EV-CMB is useful if the pollution sources are known and the compositions of the emissions measured [2-4,45]. However, in many cases, the sources have not been identified or their emissions characterized. If the source information is not known, UNMIX and/or PMF can be applied. These models estimate the number and nature of the sources from only the ambient data. UNMIX developed by others [46,47] applies non-negative constraints of source profile and source contribution externally to the eigenvector analysis used to identify the number of underlying source profiles. PMF uses a least squares approach to solve the factor analysis problem and can integrate the non-negativity constraints into the optimization process [48,39-45].

Beside these basic inventories work, inventory work of this study (PART I) has dealt the chemical mass fractions of 21 elemental species in ambient PM₁₀ during 2009-2010 in Delhi [1]. Earlier studies on source apportionment of ambient PM₁₀ in Delhi have shown that wind blown dust, secondary aerosol, coal combustion, traffic exhausts and biomass burning were major contributor to PM [49]. The transport sector of Delhi shares ~72% to total airborne pollutants [50,51]. A fundamental step towards the identification of the sources of atmospheric particles is constituted by the chemical characterization of PM. In the scientific literature there are only few papers dealing with the source apportionment of ambient PM in India with special reference to PMF [9,39,52-54]. Recently, Perrino et al. [1] analyzed macro-components in PM₁₀ aerosols samples in the atmosphere of Delhi during two short periods of 2009 and 2010 for obtaining the mass closure. Also, strength of the main sources of PM is estimated for the soil, secondary reactions, combustion processes and organic matter. However, detailed source apportionment studies for Delhi atmosphere using maximum analyzed ionic radicals in PM concentrations is expected for better understanding of their sources. For instance, qualitative predictions of source signatures of ambient PM₁₀ based on source indicator/tracer species have shown the multi-complexity in source contributions of ambient PM₁₀. The principal aim of the present study is in resolving the complexity in source identification and apportionment of the measured ionic constituents in PM₁₀ aerosol over

Delhi which is performed by statistical models called UNMIX 6.0 and PMF 3.0.

MATERIALS AND METHODS

1. Site Description with Sampling and Analysis

Delhi which is 160 km south of the Himalaya has a semi-arid climate with extremely hot summers, heavy rainfall in the monsoon season and very cold winters. The annual mean temperature is 25.3 °C and rainfall is 715 mm [55]. Wind direction is normally north-westerly during January-April period, while it is south-easterly in June and July. Wind speeds are typically higher in summer and monsoon; mostly calm in winter. Pre-monsoon dust storms are westerly from the Great Indian Desert, carrying large concentrations of total suspended particulate (TSP) into the ambient air of Delhi. Inversion conditions mostly prevail in winters, increasing the pollution concentration [56]. Delhi has three coal based Thermal Power Plants - the Rajghat, the Indraprastha and the Badarpur, and two natural gas based plants - the Indraprastha Gas Turbine and the Pragati Power. Delhi is among the ten most polluted cities in the world and the second largest Indian megacity with an average population growth rate of 3.85% per year [13]. Consequently, vehicular growth rate on an average is 5.85% per year [57]. This alarming vehicular growth rate has resulted in a significant rise in the TSP level over Delhi. Although the vehicles are the biggest contributor to the ambient TSP level, significant contributions from other sources such as industries, roadside dust, trans-boundary migration, power plants and local biomass burning sources have also been observed [58]. The sampling site was inside the premises of the Indian Institute of Tropical Meteorology Pune (New Delhi Branch), located in New Rajinder Nagar, area in Central Delhi (28.63° N, 77.18° E; ~216 m above mean sea level). It is bordered by the Central Ridge Protected Forest on the south and Indian Agricultural Research Institute on the west with a major road carrying vehicular traffic. The daily traffic density is moderate to high with peak periods found during morning and evening hours. The experimental site is located in the heart of Delhi and no major industries are located within 5 km radius around.

Sampling of aerosol was carried out using single stage PM₁₀ aerosol samplers, which provides information about aerosol mass concentrations of sizes up to 10 µm. Aerosol samples were collected once a week on Whatman, Teflon Micro fibre filter papers (2 µm PTFE) of the size 46.2 mm using APM 541 samplers (Envirotech, India) for PM₁₀. The sampling cycle was 24 h with a flow rate of 1 m³ h⁻¹

collecting sufficient mass of aerosols. The filter papers, used for aerosol sampling, were subjected to 24 h desiccation before and after the sampling, to remove the moisture content of the filter papers. The desiccated filter papers were weighted using electronic microbalance (Model GR202, A&D, Japan) with 0.01 mg resolution. The particle concentrations were determined gravimetrically by the difference in their weights before and after the sampling [1].

The collected aerosol samples were analysed by ED-XRF (energy dispersion X-ray fluorescence), a non-destructive method for the determination of major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb), by using a ED-XRF spectrometer mod (X-Lab 2000, Spectro, Italy). Cd, Sn and Sb were in principle detectable, but their atmospheric concentrations were generally below the instrumental detection limits (0.006, 0.052, 0.068 $\mu\text{g m}^{-3}$, respectively). After XRF analysis, the Teflon filters were extracted in deionised water and analysed by ion chromatography (IC model DX-100, Dionex, Italy) for Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . The detection limits, detail analysis and quality control for all analysed radicals are reported in [1].

2. Methodology for Source Identification

Qualitative predictions of source signatures of ambient PM_{10} based on source indicator/tracer species have shown the multi-complexity in source contributions of ambient PM_{10} as already discussed in earlier studies. Receptor models are used to quantify source contributions that affect the mass concentration by using selective particles' macro ensembles properties viz. variability of chemical composition, particle size, and concentration variations in space and time framework [59]. UNMIX [43,44,46] and PMF [48,60,62] to solve the CMB equations [61] by identifying source-related "factors" in the dataset. Nonnegative factor loadings and scores are derived simultaneously and interpreted as source profiles and source contributions, respectively. PMF typically requires large ambient datasets, e.g., more than 100 samples distributed across time and space, for which the underlying source profiles are relatively constant and for which there is large independent variability among actual source contributions. However, small dataset e.g., above 50 samples can also be capable of extracting generalized and more prone source profiles underlying the dataset [39,52]. Description of sampling, chemical and statistical analysis of ambient datasets used here (53 samples during 2008) have been described in an earlier study [1]. Extractable factors from the data set have been

evaluated using UNMIX 6.0 where uncertainty weighting coefficients are not required [43,44,46].

Dataset has been first analyzed using UNMIX 6.0 to evaluate factors underlying the dataset and PMF 3.0 been executed thereupon using evaluated factors from UNMIX 6.0. Among all model execution patterns (i.e., combinations of species and number of factors) that provided UNMIX solutions, solutions were sought that: 1) maximized the number of species concentrations; 2) maximized the number of factors; and 3) avoided species with low signal to noise ratio for the same number of factors. These combinations were also analyzed by PMF using the inverse analytical uncertainty of ambient concentrations as weighting coefficients. In subsequent tests, additional species were included and the number of factors was adjusted (-2 to +2) in PMF, as suggested by Reff et al. [40], to achieve source factors that could be associated with measured source profiles. Bootstrap and Fpeak model run has been executed with maintaining the Q (robust values) at optimum levels. Variation in factors has also been checked using correlation values between the selected factors. Strong positive correlation in temporal variation of longitudinal data of selected species groups representing specific source types has been observed in the preliminary analysis of PMF execution data and presented in Fig. 1. Model extracted factors from base, bootstrap and Fpeak run using four factor solutions have been assigned to four major source categories of the ambient PM_{10} chemical data. These factor-source assignments have been done using chemical species grouping described in extracted factors. Results of factor-source profiles extracted in base, bootstrap and Fpeak run along with temporal variation of their contribution to receptor profile are shown in Figs. 2a-2d. Species source apportionment of receptor chemical data (ambient PM_{10}) is presented in Table 1.

RESULTS AND DISCUSSION

1. Mass Concentrations of PM_{10} over Delhi

During the study period, the arithmetic mean concentrations of PM_{10} was $161 \pm 80 \mu\text{g m}^{-3}$ ranged from 42 (August) to 355 $\mu\text{g m}^{-3}$ (December). The mean concentration is considerably higher than the Indian, World Health organization (WHO) and European Union air quality annual PM_{10} standard standards of 100, 50 and 40 $\mu\text{g m}^{-3}$ respectively. The average mass mean PM_{10} during different season were in the order of: post- monsoon (Oct.-Nov: 250 $\mu\text{g m}^{-3}$) > winter (Dec. to March: 204 $\mu\text{g m}^{-3}$) > summer (April-June: 127 $\mu\text{g m}^{-3}$) > monsoon (July to Aug.: 94 $\mu\text{g m}^{-3}$). PM mass concentrations were remarkably higher in post monsoon and winter

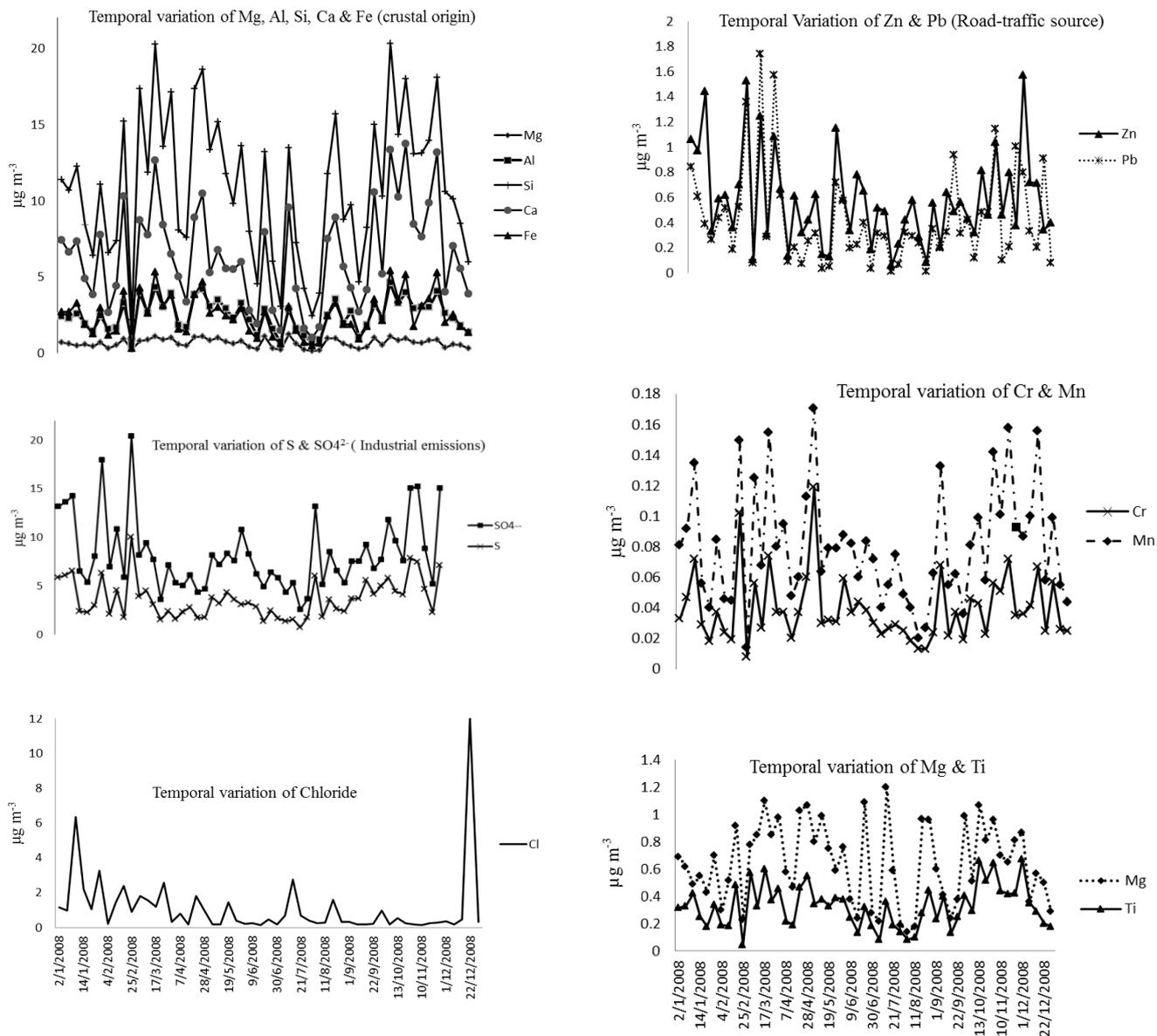


Fig. 1. Relationship of temporal variation between selected marker species (concentration in $\mu\text{g m}^{-3}$).

than those in summer and monsoon. The mean concentration of PM_{10} over Delhi is lower than the results reported at Delhi $234 \pm 125 \mu\text{g m}^{-3}$ during 2000-2006 [63,64] and is close to the results ($219 \pm 84 \mu\text{g m}^{-3}$) of Kulshrestha et al. [65] studied during 2007. Tiwari et al. [66] have also studied the running mean of PM_{10} , $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ mass concentrations at Delhi during the August to December 2007 by optical instrument (GRIMM) and found that the PM levels in monsoon were lower than those in winter. The pronounced concentration during winter was due to meteorological effect such as low relative humidity and temperature including Deewali fireworks which are generally celebrated in post monsoon season in India. They have also suggested that low concentrations during monsoon were due to washout/scavenging effect of PM_{10} aerosols. In the

other city such as Chennai, Srimuruganandam and Nagendra [67] have reported very low concentrations (In winter season: $98 \mu\text{g m}^{-3}$; monsoon: $87 \mu\text{g m}^{-3}$ and summer: $77 \mu\text{g m}^{-3}$) during different seasons as compared to the present study.

2. Source Apportionment

The analyzed chemical constituents were presented by [1] and the same data were used for the study of their sources identification by receptor model UNMIX 6.0 and PMF 3.0 and their results are depicted in Table 1. Four factors have been determined that explained the usual sources of ambient PM_{10} (crustal origin, road-traffic and secondary aerosols) with exception of chloride source. Significance of four factors solution has been re-checked

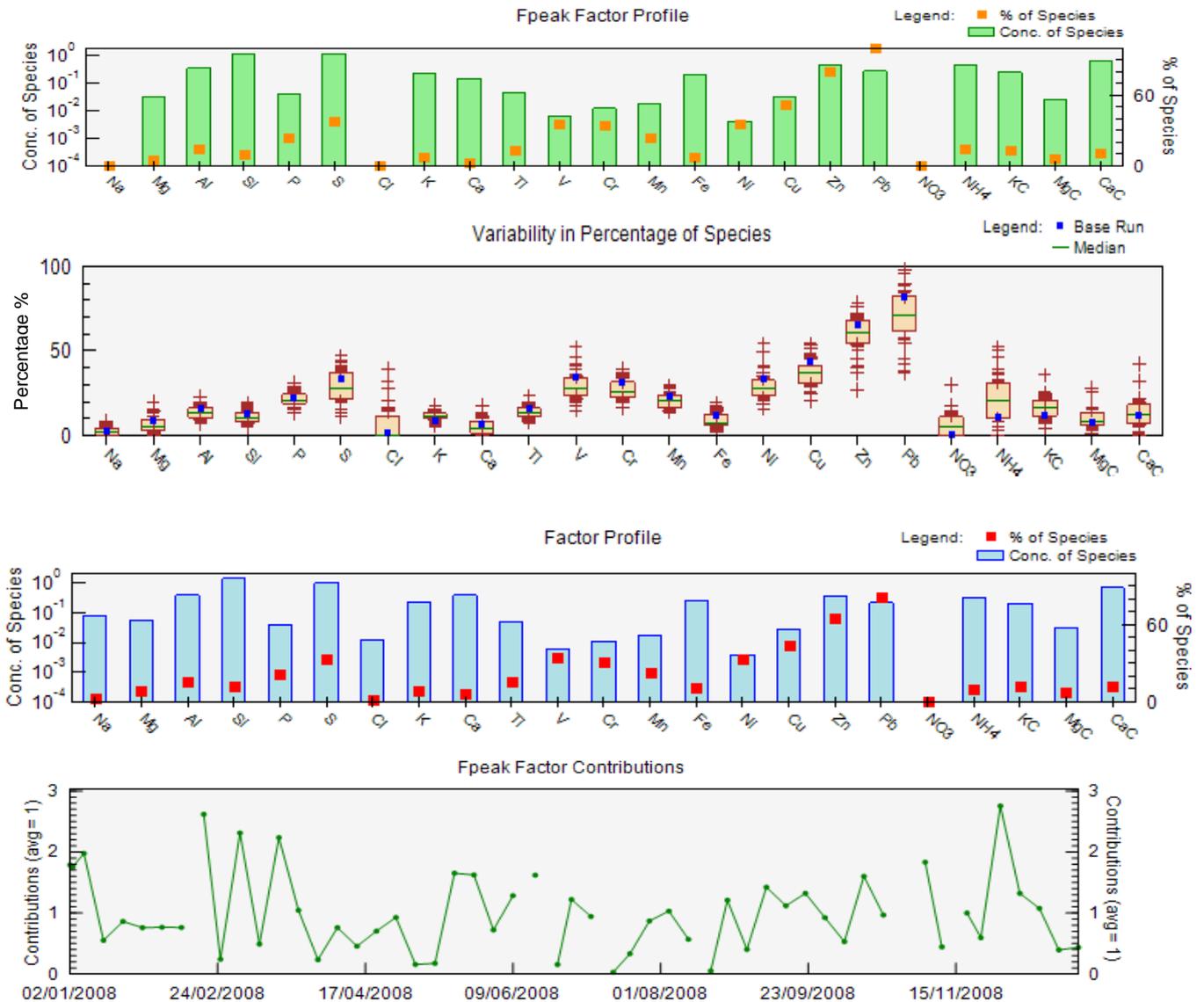


Fig. 2a. PMF extracted source profile [Factor-1: Pb, Zn, Ni, V (Road-Traffic)] and temporal variation in its contribution to receptor ambient PM₁₀ of Delhi. Concentration in $\mu\text{g m}^{-3}$.

by investigation of relationship between species concentration-time series. Markers of crustal origin (Si, Fe, Al, Ca, and Mg) have shown uniform temporal variation; similarly markers of road-traffic origin (Zn and Pb) have shown good correlation in their temporal variation (Fig. 1). S and SO₄²⁻ have also shown moderate relationship between their temporal variation attributing to earlier outcome of secondary sulfate formation from sulfur and sulfur dioxide [68]. Catalytic metals used in industrial processes (Cr and Mn) have also shown good correlation between their temporal variations, whereas Titanium has shown moderate relation with markers of crustal origin.

Factor analysis results have shown that factor-1, designated as road-traffic origin by the observation of major contributors (Pb, Cu, Zn, Ni, V) [38] is mainly sharing Pb and Zn with more than 60% of their concen-

tration at receptor site. Only Ni has shown similar contribution from crustal origin. The bootstrap solutions have shown that Pb, Zn and Cu are projecting uniform mean value of their percentage share close to 75th percentile and lower outlier projections faraway from 25th percentile compared to upper outliers. Sulfur, Vanadium, Chromium and Nickel have also shown significant share in Factor-1 (Road-traffic origin).

Factor-2 has been designated as Crustal origin due to higher share of Si, Fe, Al, Ca and Mg. Na, P, Ti, Cr and Mn have also shown significant share in the modeled chemical profile of crustal origin but only Ti and P have shown similar percentage variability as major constituents (Si, Fe, Al, Ca). Higher variability pattern shown by Cr, Mn, Ni and ionic fractions of Ca and Mg might be due to their alternate potential sources

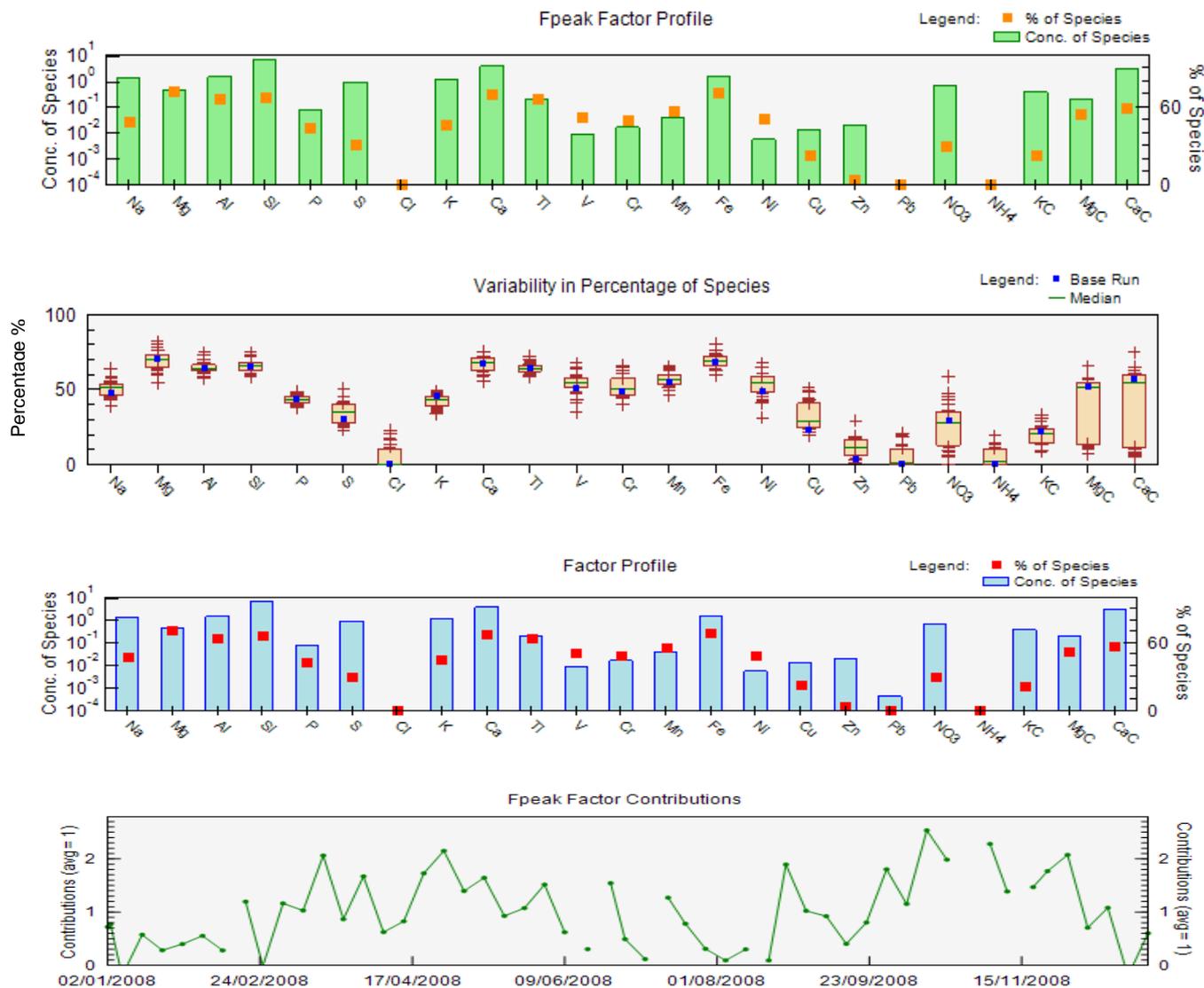


Fig. 2b. PMF extracted source profile [Factor-2: Si, Ca, Mg, Al, Fe, Na, Mn, Cr, Ca^{2+} , Mg^{2+} (Crustal origin)] and temporal variation in its contribution to receptor ambient PM_{10} of Delhi. Concentration in $\mu\text{g m}^{-3}$.

viz. road-traffic origin. Secondary aerosols of NH_4NO_3 and KNO_3 have been evaluated to be the Factor-3 due to major share of respective ionic species and their uniform percentage variability, where mean values have been projected close to 75th percentile. Interestingly, Na and K have shown their potential source from crustal origin. Chloride has been identified as another potential source (Factor-4) of ambient PM_{10} in the study region with projection of its mean of percentage share close to 75th percentile. Sodium has also shown another potential source of ambient PM_{10} as Factor-4. As far as Fpeak factor contribution is concern, crustal origin and road-traffic origin have shown significant contribution of throughout the sampling period, whereas Factor-4 (Chloride) has shown higher contribution during summer and winter period with selective exception in the

a month of post-rainy period.

In case of species source apportionment, more resolved picture of source apportionment of ambient PM_{10} has been observed (Table 1). Si, Fe, Al, Ca and Mg have shown major reception with $\sim 3/4$ th contribution from Crustal origin, whereas road-traffic and Factor-4 have shown very low contribution in comparison to crustal origin. Ionic species known for secondary aerosols (NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , SO_4^{2-} , Br^- , etc.) have shown their major reception from another factor designated as secondary aerosols with highest contribution from NH_4^+ (83%) followed by NO_3^- (65%), Br^- (64%) and K^+ (59%). Ca^+ , Mg^+ have shown two major sources; secondary aerosols (31 and respectively), whereas SO_4^{2-} has shown similar trend of source signatures compared to sulfur with three source origins: road-traffic (S-33%, SO_4^{2-} -45%); crustal

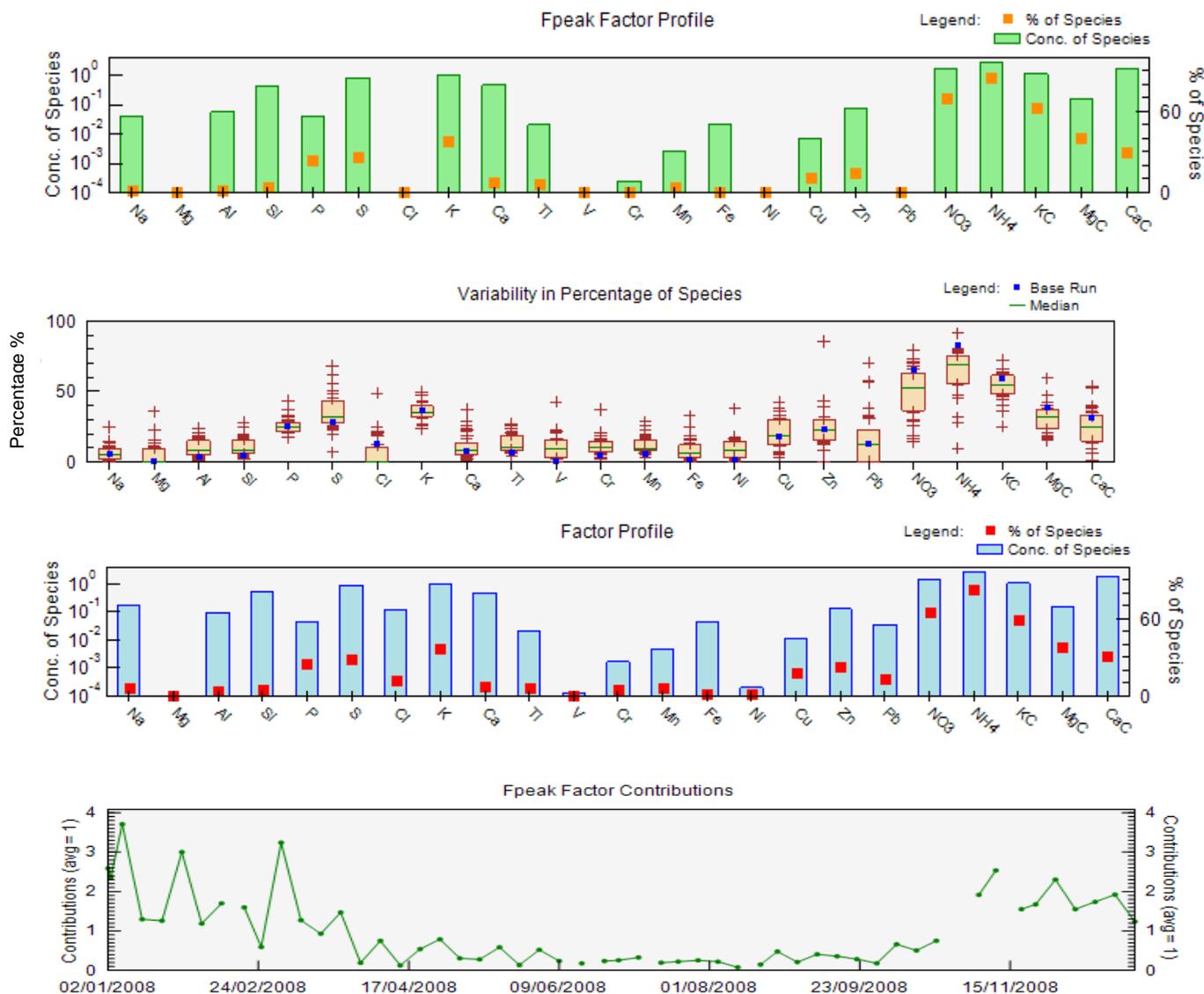


Fig. 2c. PMF extracted source profile [Factor-3: NH₄, NO₃, K⁺ (Secondary aerosols)] and temporal variation in its contribution to receptor ambient PM₁₀ of Delhi. Concentration in $\mu\text{g m}^{-3}$.

origin (S-30%, SO₄²⁻-18%) and secondary aerosols (S-29%, SO₄²⁻-23%). Significant sulfur contribution from secondary aerosols including small share of Cu, Pb, As and Ba in species source apportionment results has explained the marginal overlapping of two source profiles extracted from ambient PM₁₀ receptor compositional profile by PMF 3.0 and attributed to the need for execution of CMB for higher degree of precision in species source apportionment [41,45,67]. Markers of crustal origin (Si, Fe, Al, Ca and Mg) have shown about 3/4th contributions to ambient PM₁₀, however, Na and K have been enriched aerosols, respectively. Interestingly, Factor-4 has shown from one more source of chloride origin and secondary major contribution of chloride (86%) with 44% contribution of Na that explained the two possible sources of chloride: 1) NaCl-aerosols and 2) chloro based

industrial sources in the region. Other species have shown marginal contribution from Source Factor-4 that justifies the Factor-4 as unique source of chloride in ambient PM₁₀ of Delhi.

CONCLUSIONS

The 24-h average PM₁₀ mass concentrations measured during a yearlong in 2008 and the arithmetic mean concentrations was found ($161 \pm 80 \mu\text{g m}^{-3}$) to be varied from 42 to 355 $\mu\text{g m}^{-3}$ which was considerably higher than the Indian National Ambient Air Quality Standards (100 $\mu\text{g m}^{-3}$), WHO (50 $\mu\text{g m}^{-3}$) and European Union air quality annual PM₁₀ (40 $\mu\text{g m}^{-3}$) standards.

Based on the chemical macro-components in PM₁₀ in the atmosphere of Delhi during 2008, source ap-

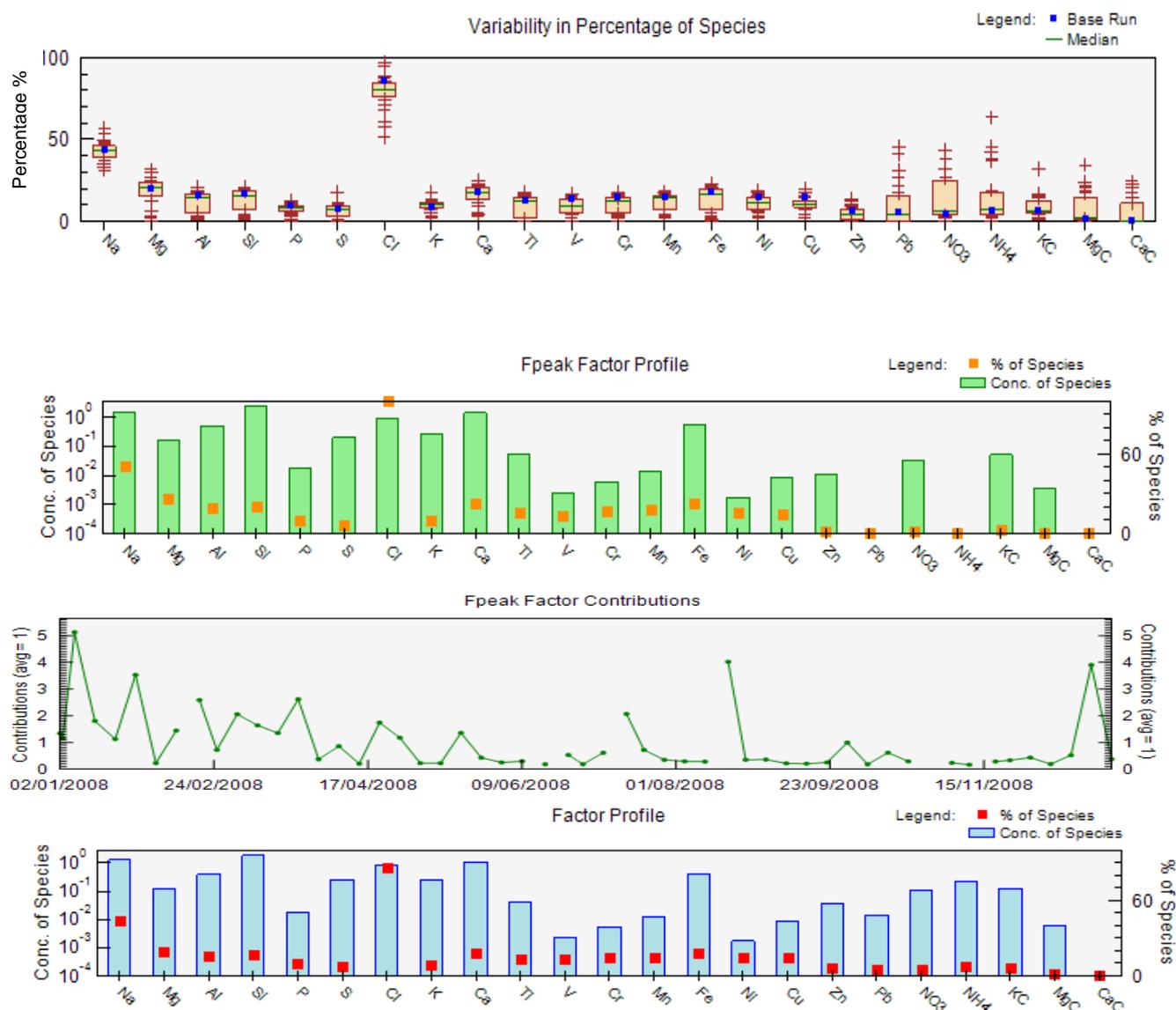


Fig. 2d. PMF extracted source profile [Factor-4: Cl^- , Na^+ (Chloride origin)] and temporal variation in its contribution to receptor ambient PM_{10} of Delhi. Concentration in $\mu\text{g m}^{-3}$.

portionments are carried out by applying UNMIX 6.0 and PMF 3.0 models to resolve their source origins.

Tracers of crustal origin (Si, Fe, Al, Ca, Mg) indicates uniform temporal variation, while markers of transport sectors (Zn and Pb) have shown good correlation. For ionic species, secondary aerosols (NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- , SO_4^{2-} , Br^- , etc) have shown their major reception from another factor designated as secondary aerosols with the highest contribution from NH_4^+ (83%) followed by NO_3^- (65%), Br^- (64%) and K^+ (59%). Ca^+ and Mg^+ indicated two major sources as secondary aerosols (31 and 38%, respectively) and crustal origin (57 and 53%) respectively. Significant sulfur contribution from secondary aerosols including minor Cu, Pb, As and Ba species source apportionment results has explained the marginal overlapping of two source profiles extracted

from ambient PM_{10} receptor compositional profile by PMF 3.0 and attributed to the need for execution of CMB for higher degree of precision in species source apportionment.

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Table 1. Species source apportionment results of ambient PM₁₀, Delhi using PMF 3.0

Chemical Species	Factor 1 (Road traffic)	Factor 2 (Crustal origin)	Factor 3 (Secondary aerosols)	Factor 4 (Chloride factor)
Si	1.408 (13)*	7.259 (66)	0.527 (5)	1.845 (17)
Fe	0.270 (11)	1.621 (69)	0.044(2)	0.417 (18)
Al	0.394 (16)	1.594 (64)	0.095 (4)	0.389 (16)
Ca	0.391 (6)	4.138 (68)	0.487(8)	1.076 (18)
Mg	0.057 (9)	0.442 (71)		0.123 (20)
Na	0.081 (3)	1.377 (48)	0.172 (6)	1.258 (44)
K	0.239 (9)	1.274 (46)	1.022 (37)	0.256 (9)
S	1.027 (33)	0.940 (30)	0.893 (29)	0.254 (8)
SO ₄ ²⁻	1.751 (45)	0.693 (18)	0.889 (23)	0.579 (15)
P	0.038 (22)	0.075 (43)	0.043 (25)	0.018 (10)
Ti	0.049 (15)	0.206 (64)	0.022 (7)	0.042 (13)
Cl	0.012 (1)		0.119 (13)	0.816 (86)
NO ₃ ⁻		0.685 (30)	1.498 (65)	0.113 (5)
NH ₄ ⁺	0.328 (10)		2.614 (83)	0.225 (7)
K ⁺	0.214 (12)	0.406 (22)	1.081 (59)	0.122 (7)
Na ⁺	0.143 (16)	0.488 (54)	0.170 (19)	0.098 (11)
Mg ²⁺	0.030 (8)	0.207 (52)	0.152 (38)	0.006 (2)
Ca ²⁺	0.704 (12)	3.294 (57)	1.793 (31)	
Cr	0.011 (31)	0.017 (49)	0.002 (5)	0.005 (15)
Mn	0.018 (23)	0.043 (56)	0.005 (6)	0.012 (15)
V	0.006 (34)	0.009 (51)	0.0001 (1)	0.002 (14)
Cu	0.026 (44)	0.013 (23)	0.011 (18)	0.009 (15)
Ni	0.004 (34)	0.006 (49)	0.0002 (2)	0.002 (15)
Zn	0.363 (66)	0.021 (4)	0.129 (23)	0.038 (7)
Pb	0.219 (81)	0.0004 (0.2)	0.035 (13)	0.014 (5)
As	0.014 (35)	0.003 (7)	0.020 (50)	0.003 (8)
Br	0.002 (6)	0.005 (16)	0.019 (64)	0.005 (15)
Ba	0.087 (31)	0.114 (41)	0.030 (11)	0.048 (17)

*Values in parenthesis are percentage (%) of source contribution

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