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Original article

Chemical characterization of atmospheric particulate matter and their source apportionment at an emerging industrial coastal city, Visakhapatnam, India



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ABSTRACT

In the present study, particulate matter (PM₁₀) was collected from two different locations viz. Jogannapalem and Parawada sites of Visakhapatnam. During study period, PM₁₀ concentrations were found in the range from 34.8 to 109.7 $\mu\text{g}/\text{m}^3$ and from 32.3 to 137.3 $\mu\text{g}/\text{m}^3$ at Jogannapalem and Parawada sites respectively. Chemical characterization of PM₁₀ was carried out to estimate the concentration levels of various particle bound chemical species (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Cd, Cl⁻, F⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺). Among different species, Al was observed to have highest average concentration (4.1 $\mu\text{g}/\text{m}^3$ at Jogannapalem and 3.8 $\mu\text{g}/\text{m}^3$ at Parawada) at both the sampling sites followed by K at Jogannapalem and Ca at Parawada. PM₁₀ concentration as well as trace metals concentration (except Mn and Fe) was observed to have higher concentrations at Parawada site as compared to Jogannapalem site, indicating higher pollution at Parawada.

Source apportionment study carried out using PMF (USEPA PMF5.0) receptor model identified six major sources at Jogannapalem and seven predominant sources at Parawada, which are contributing to collected PM. The two study locations share five common sources viz. crustal, sea salt spray, coal combustion, fuel oil combustion and metal industry. The other sources include biomass burning at Jogannapalem; road traffic and secondary aerosols at Parawada. At Jogannapalem, biomass burning (35%) is the predominant source, whereas coal combustion (22.6%) is dominating at Parawada. PMF factor profiles were observed to have similar elemental profiles obtained at different industrial locations of Visakhapatnam.

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1. Introduction

In recent years, India's dramatic economic rise, rapid industrialization, urbanization, population growth and increased vehicular emissions critically affected the atmospheric environment, especially with regards to contamination of atmospheric particulate matter (PM) (Singh et al., 2014; Das et al., 2015). Previous studies have indicated the adverse influence of PM on visibility, global climate and human health (Correia et al., 2013). Particularly, PM₁₀

(aerodynamic equivalent diameter lower than 10 μm) fraction was studied as a carrier of many harmful chemicals into the human respiratory system and are therefore more likely to increase the incidence of respiratory and cardiovascular diseases (Padoan et al., 2016). According to the global burden of disease study, 3.2 million people died from air pollution in 2010 (Lim et al., 2012). Based on the mounting epidemiological evidence, CPCB (Central Pollution Control Board) has legislated daily limit (100 $\mu\text{g}/\text{m}^3$) as well as annual limit (60 $\mu\text{g}/\text{m}^3$) for PM₁₀ in India (MoEF, 2009). However, with increased industrial and vehicular emissions, PM₁₀ concentrations have been found to exceeding the CPCB limits in most of the Indian cities such as Delhi, Kanpur, Mumbai, Hyderabad, Agra etc. This situation raises concern about the exposure of a large proportion of the Indian population to dangerous levels of PM pollution. However, most recent reviews agree that, the human health effects should not be attributed simply to the total PM

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concentration, but to the toxic chemical component's concentration associated with PM (Valavanidis et al., 2008; Stanek et al., 2011). Metal ions on PM surfaces may trigger free radical production in living organisms, which leads to oxidative damage of lung cells and DNA (Song et al., 2015). Hence chemical characterization of PM is an important aspect of particulate matter air pollution research study to estimate the health effects due to inhalation.

PM₁₀ can be contributed by wind-suspended component, mainly from natural sources such as sea salt spray, surface soils and also from some anthropogenic sources like construction activities, traffic generated re-suspension and mechanical processes, such as tire and brake emissions. Identification of PM emission sources is important in planning efficient abatement strategies for PM pollution and in verifying of their effectiveness. Receptor oriented models based upon mass balance analysis with mass conservation are generally used to assist in the identification and the apportionment of sources of observed pollutants (Liu et al., 2014). Various approaches for source apportionment are currently available in the literature (Viana et al., 2008). Among these, PMF (Positive Matrix Factorization) has been shown to be a powerful technique and commonly used receptor model that is effective in resolving PM sources and was successfully used in many studies, since it has inherent added advantages over factor analysis technique (Contini et al., 2014; Indrani et al., 2012).

In the present study, PM₁₀ monitoring and their source apportionment was carried at two different locations (Jogannapalem and Parawada) of coastal industrial city Visakhapatnam, which is the second largest city after Hyderabad in Andhra Pradesh, India. The city is densely populated and well-developed with a lot of major, minor industries around. The city is situated on the sea shore of Bay of Bengal with natural geographic conditions that hinder pollutant dispersion leading to the high pollution. At Visakhapatnam, very few literature studies have been reported on PM monitoring, their chemical characterization studies and till date no study was reported on source apportionment of PM. Present study will be helpful in knowing the air quality status at study locations, sources contributing to PM and also in applying stringent emission strategies for healthy environment.

2. Materials and methods

2.1. Study area

Topography of Visakhapatnam is surrounded by hill ranges on three sides and sea on the other side and is often called as bowl area for assessment of environmental related issues (Srinivas and Purushotham, 2013). Visakhapatnam is presently witnessing a boom in industrialization and a consequent explosion in population (Growth over the decade 2001–2011 was 11.89%). Fig. 1 illustrates the two PM sampling locations (about 30 Kms away from each other) along with their surrounding industries.

Site 1: Jogannapalem is a rural area in Atchuthapuram Mandal with a Bay of Bengal on one side and residential area with paddy fields on the other side. Many industries such as alloy industry, equipment manufacturing industry, metal manufacturing industry, granite industry, power plant, metal extraction plant, textile industry etc., are present near to this sampling site. At this site, people were mostly dependent on wood and wood coal burnings for cooking and other purposes.

Site 2: Parawada is a suburb Mandal in Visakhapatnam district and surrounded by many industries such as steel plant, thermal power plant (TPP), fertilizer industries, cement industries, petroleum industries, metal smelters, chemical, pharma industries etc. This site is far away from Bay of Bengal as compared to Jogannapalem site. Visakhapatnam port is also near to this site as compared

to Jogannapalem site. Being suburban location, vehicular emissions are also higher at this site.

Atmospheric conditions: At Visakhapatnam, predominantly three seasons are experienced i.e. summer (March to June), monsoon (July to October) and winter (November to February). The average high temperatures (33–35 °C) were observed during March to June, whereas average minimum temperatures were found in the range of 18–19 °C during December and January. The wet season at Visakhapatnam persists mainly during the southwest monsoon with a total annual precipitation of 955 mm (38 inches). The maximum rainfall was observed in the range of 133 to 179 mm, during July to October months. Relative humidity was in the range of 68–78% with least value during May month. Wind speed was observed in the range of 4.3 to 6.4 m/s with annual average of 5.4 m/s. Highest wind speed is observed in July (6.4 m/s) and August (6.3 m/s) months followed by June (6.1 m/s) and April (5.8 m/s). The predominant wind directions at Visakhapatnam are SW and NE with 37.9% and 17.6% respectively.

2.2. Sampling protocol

PM₁₀ samples were collected simultaneously at both the sites from April 2010 to December 2011. The sampling frequency was twice a week and sampling was carried out for 24 h with an average flow rate of 1.1 m³/min. At both the sites, sampler was located on the roof of a building at about 15 m from the ground and PM₁₀ samples were collected on Whatman GF/A (8" × 10") glass fiber filters using High-volume samplers (Respirable Dust High volume Sampler, Model 460NL, Envirotech Pvt. Ltd.). A total of 160 samples were collected at each study location. In the present study, weighing of glass fiber filters was carried out in Mettler (Model AE163) weighing balance. The filter papers used for the collection of PM₁₀ samples were preconditioned (48 h in desiccators under the conditions of temperature of 25 ± 2 °C and relative humidity 50 ± 5%) before and after sampling. Weighing was carried out by mild folding of filter paper and final PM₁₀ concentrations were determined gravimetrically by subtracting the pre-sampling filter weigh from post sampling filter weight.

2.3. Chemical processing and analysis

One fourth of the sample filters were soaked in 15 ml of mixed acid (HNO₃ and HClO₄) and kept on a hot plate at high temperature until the mix solution was boiled and clarified (Huang et al., 2010). After complete digestion, sample solution was slowly reduced to near dryness at low temperature to remove excess acid. Then, 0.25% HNO₃ was added to the above sample and resulting solution was filtered into 25 ml volumetric flask. A separate digestion procedure was used for Arsenic extraction using high purity concentrated HCl and HNO₃ as discussed by Guor-Cheng et al. (2011). Filter blank was prepared by using field blank filter following the above same procedure. Metal (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb and Cd) analysis was carried out using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Jobin Yvon, Model ULTIMA 2), flame atomic absorption spectrometry (AAS, GBC-Avanta) system and Metrohm make Autolab Potentiostat instrument (Model 693 VA Processor equipped with a 663 VA stand). ICP-AES was used for the analysis of Al, Mn, Cr, V, Fe, Ni, and Zn, whereas analysis of Pb, Cu, Cd was carried out using voltammetry system and As was analyzed using AAS by hydride generation technique.

Another one fourth of the glass fiber filters were treated with deionized water (resistivity 18.2 MΩ) for extraction (Alharbi et al., 2015) of water soluble ions bound to PM₁₀ viz. chloride (Cl⁻), nitrate (NO₃⁻), sulfate (SO₄²⁻), sodium (Na⁺), potassium (K⁺), calcium (Ca²⁺) and Magnesium (Mg²⁺). Ion Chromatography (Metrohm

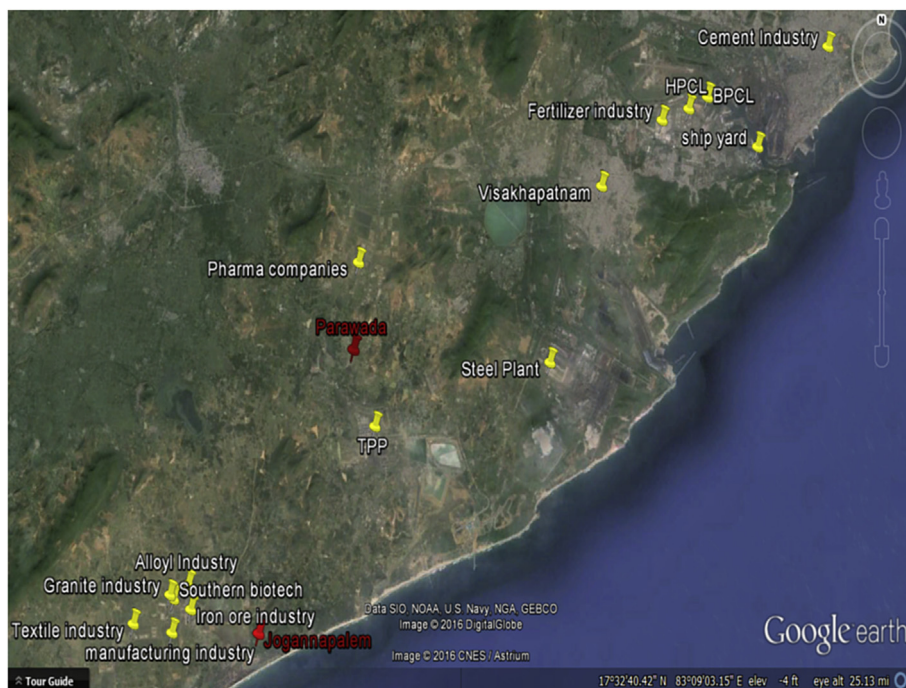


Fig. 1. PM sampling locations Viz. Jogannapalem and Parawada along with surrounding industries.

make, Model IC 733) was used for the analysis of these ions under optimized conditions. In the present study, anion analysis was carried out using metro SepA Supp5 column, whereas for cation analysis Metrosep cation 1–2 column was used.

2.4. Analytical quality control

To validate the metal extraction procedure used, NIST SRM 1649a (urban dust) was processed in the same way as the PM samples. After chemical processing, reference material sample solutions were analyzed for various trace and toxic metals using different analytical techniques. The percentage recovery of individual metal of interest from SRM 1649a is given in Table 1. Percentage recoveries of ions and other metals were estimated by spiking known amounts of chemical components on glass fiber filter.

During metal analysis ICP-AES was calibrated for each metal using set of three to five standards (VHG labs make). The calibration curve was checked frequently by injecting the known standard solution. Field blanks were analyzed and the data was subsequently blank-corrected to determine accurate results of chemical species.

3. Results and discussion

Table 2 gives the detailed statistical summary of PM₁₀ and particle bound chemical constituents observed at both the sites. During the study period, the mean concentration of PM₁₀ was found to be 65.4 $\mu\text{g}/\text{m}^3$ at Jogannapalem and 74.7 $\mu\text{g}/\text{m}^3$ at Parawada. These values were exceeded the annual PM₁₀ National Ambient Air Quality Standard (NAAQS) (60 $\mu\text{g}/\text{m}^3$) prescribed by the CPCB, India (MoEF, 2009). The daily PM₁₀ NAAQ standard (100 $\mu\text{g}/\text{m}^3$) was observed to be violated about 6.8% and 21.3% of the sampling days at Jogannapalem and Parawada sites respectively and throughout the study period, the PM₁₀ concentrations were observed to be high at Parawada site as compared to Jogannapalem. This could be due to the high vehicular movement and large industrial emissions at Parawada site as compared to Jogannapalem site.

Among major metals (Al, Fe, Ca, K, Mn and Na) highest mass concentration was observed for Al at both the sampling sites followed by $\text{K} > \text{Fe} > \text{Ca} > \text{Na} > \text{Mg} > \text{Mn}$ at Jogannapalem, whereas at Parawada, the observed order was found to be $\text{Ca} > \text{Fe} > \text{K} > \text{Na} > \text{Mg} > \text{Mn}$. Al and Fe concentrations were observed to be high at Jogannapalem site as compared to Parawada site and higher concentration of Ca at Parawada could be due to construction activities near the sampling site. At Jogannapalem, K

Table 1

Percentage recoveries of different metals of interest from NIST SRM 1649a and of spiked chemical species.

Element	Percentage recovery	Chemical species spiked	Percentage recovery
As	96.0 \pm 1.4	Cl^-	98.5 \pm 5.1
Cu	99.5 \pm 2.1	SO_4^{2-}	97.3 \pm 4.1
Cd	88.5 \pm 3.5	NO_3^-	98.2 \pm 4.3
Cr	93.7 \pm 2.0	Na^+	97.8 \pm 3.3
Fe	87.3 \pm 2.8	Ca^+	98.3 \pm 5.1
Mn	95.5 \pm 2.1	K^+	97.1 \pm 2.5
Ni	99.6 \pm 2.0	Mg^{2+}	98.1 \pm 3.2
Pb	97.0 \pm 1.4	Al	99.1 \pm 4.1
V	99.5 \pm 2.1		
Zn	94.9 \pm 2.3		

was found to be the second highest contributing metal to PM₁₀ after Al, this could be due to the high biomass burning been carried out at nearby agricultural lands and also in the houses for cooking, heating purposes. As suggested by Chan et al. (1997), “K-smoke” was estimated to indicate the presence of K contributed by biomass burning and is taken equal to (K-0.6 × Fe). As expected, an excess K-smoke value was observed at Jogannapalem (1511.6 ng/m³) as compared to Parawada site (950.7 ng/m³).

Among anions, sulfate was found to have highest concentration at both the sampling sites followed by Cl⁻ > NO₃⁻ > F⁻ and NO₃⁻ > Cl⁻ > F⁻ at Jogannapalem and Parawada sites respectively. Interestingly, Cl⁻ concentration at Jogannapalem was observed to be 1.9 times that observed at Parawada, this could be due to its close proximity to sea shore. Also, Cl⁻/Na⁺ ratio was found to be 1.5 and 1.4 at Jogannapalem and Parawada sites respectively, which is close to the actual value of 1.8 in sea water (Contini et al., 2014) indicating that these could be originated from sea salt spray. Slightly lower Cl⁻/Na⁺ ratio at sampling sites could be due to the fact that, Cl⁻ concentration can diminish through reactions between the marine aerosol and nitric acid, sulfuric acid and SO₂.

Sulfate can also be contributed from sea salt as sea water contains significant concentration of sulfate. In the present study, non-sea-salt sulfate (nssSO₄²⁻) was calculated to know the contribution of sulfate from other sources by using nssSO₄²⁻ = SO₄²⁻ - 0.25 × Na⁺ equation. Where, 0.25 is the typical ratio of SO₄²⁻ to Na⁺ in sea water. It was found that, about 89% and 94% of observed sulfate was contributed from non-sea-salt sources at Jogannapalem and Parawada respectively. Further a significant correlation (R² = 0.86) was observed between NO₃⁻ and SO₄²⁻ which suggest that, these anions could have originated from identical sources.

In the case of trace and toxic metals, highest concentration was observed for Zn at both the sites, whereas least concentration was observed for As followed by V at Jogannapalem and Cd followed by V at Parawada sites. In the present study, As and Zn concentrations observed at Parawada was 2.1 times and 1.4 times that observed at Jogannapalem respectively and all the other metal concentrations were also observed to be high at Parawada site as compared to Jogannapalem site. CPCB (MoEF, 2009) has also given annual safety limits for some toxic metals such as As (6 ng/m³), Ni (20 ng/m³), Pb (500 ng/m³) and Cd (5 ng/m³), in the present study, no mean metal concentration was observed to exceed the CPCB safety limit.

Table 3 presents the PM₁₀ annual averages of different locations across India along with present study data for comparison purpose. The average PM₁₀ concentration at rural study site (Jogannapalem) was observed to be less than or equal to literature reported value. Whereas, the average PM₁₀ concentration observed at Parawada (Sub-urban) was found to be less as compared to the values reported at other parts of the country.

3.1. Seasonal variation of PM₁₀ and particle bound chemical species

As shown in Fig. 2, clear seasonal trends were observed for PM₁₀ and particle bound chemical species (i.e., highest concentrations during winter followed by summer and monsoon season) during study period, except for F⁻, V, Ni and K at Jogannapalem site and for F⁻, V, Ni and Cu at Parawada site. These species were observed to have high concentrations during monsoon as compared to summer season, which could be due to the significant contribution of these species from a specific source activity which is predominantly been carried in monsoon season. In the present study, wood/coal burning is one such activity predominantly being carried out in monsoon and winter seasons as compared to summer season.

Observed least concentrations in monsoon season could be due to wash out of PM and its associated (especially with coarse PM) chemical species along with rain water. Also, relatively higher

Table 2

Statistical summary of PM₁₀ and Particle bound chemical constituents at Jogannapalem and Parawada sites.

	Jogannapalem Parawada							
	Min.	Max.	Mean	Stdev.	Min.	Max.	Mean	Stdev.
PM ₁₀	34.8	109.7	65.4	17.9	32.3	137.3	74.7	26.2
Al	1109.7	8873.2	4079.5	1980.9	729.1	9877.9	3828.0	1923.5
Ca ²⁺	223.1	6399.9	2361.1	1371.1	300.0	6880.0	2501.5	1137.5
Cr	0.8	31.1	7.4	6.7	0.9	53.9	9.6	9.5
Cu	0.6	20.8	3.5	3.2	0.2	53.4	9.9	9.9
Ni	0.7	34.8	6.2	6.8	0.8	28.3	7.3	4.8
Pb	1.6	27.6	9.1	4.7	1.1	83.2	23.0	15.7
Mn	7.1	797.6	154.2	153.9	0.3	62.8	18.2	13.2
Zn	79.9	1909.2	676.8	407.4	60.4	3686.8	927.5	692.2
V	0.3	16.2	3.5	3.1	0.6	18.3	5.2	3.4
Fe	63.9	7538.5	2741.0	1406.5	287.6	5646.9	2350.8	1270.9
As	0.2	7.3	2.5	1.6	0.2	24.3	5.3	5.3
F ⁻	0.5	177.0	54.3	31.1	4.8	1260.0	127.5	141.5
Cl ⁻	105.7	4951.5	1805.3	1394.5	306.9	2584.3	948.4	384.8
NO ₃ ⁻	386.0	1669.0	840.3	291.9	400.3	4256.0	1833.3	840.5
SO ₄ ²⁻	1199.0	5336.0	2854.6	1056.0	717.2	7336.0	3194.8	1432.0
K ⁺	398.4	11,716.5	3156.2	2323.5	240.0	5874.0	2361.2	1061.1
Na ⁺	88.3	2971.9	1229.7	672.6	226.8	1980.1	710.1	291.5
Mg ²⁺	85.1	963.6	351.1	201.6	55.0	760.0	287.9	151.7
Cd	<0.01	<0.01	<0.01	<0.01	0.04	8.0	1.9	1.6

*Chemical species values are expressed in ng/m³; PM₁₀ values are in μg/m³.

humidity in this season resists the PM to suspend in ambient air, leading to lowest concentrations. In contrary, some metals which are associated with very fine particles cannot be scavenged by the rain water droplets. This can result a higher concentration in this season (like Ni, V, Cu K and F⁻ in present study) and contribution from specific activities in monsoon season can lead to higher concentration of some species as discussed above. In this season, lowest concentration was observed for Cd (1.6 ng/m³) followed by As (2.9 ng/m³) at Parawada site, whereas at Jogannapalem site, As (1.5 ng/m³) was observed to have lowest concentration. None of the sampling day was observed to exceed the CPCB daily PM₁₀ limit, suggesting lowest pollution in this season.

Highest concentrations observed in winter season (November to February) could be due to the temperature inversion effect in this season, which favors the trapping of PM and associated chemical species near to earth's surface leading to highest concentrations in this season (Khillare and Sarkar, 2012). And also, the increased anthropogenic activities (biomass burning, space heating etc.), low wind speed and low temperature might be leading to poor dispersion conditions which increases the concentration of these species in winter. Most of the metal concentrations observed in winter season were twice that observed in monsoon season. But Cr and As concentration in winter was observed to be 4 times and 3 times that in monsoon season at Jogannapalem site. Whereas Zn and As were observed to have 3 times and 4 times that observed in monsoon at Parawada site. K being assumed to be contributed from biomass burning was observed to have highest concentration in winter season followed by monsoon and summer at Jogannapalem, which could be due to the highest use of biomass burning (for heating purposes) during winter. Nitrate was also reported to have higher concentration in winter and generally attributed to the low thermal stability of nitrate in summer season (Contini et al., 2010).

Intermediate concentrations were observed in the summer season (March to June), which could be due to decrease in wet precipitation. This causes a reduction in the cleaning effect on the atmosphere and consequently a greater concentration in the ambient air. Also high temperatures during this season lead to increased dryness of the air, which favors the re-suspension of soil substrate in the area (Khillare and Sarkar, 2012).

Table 3
Comparison of PM₁₀ observed at different locations of India with present study data.

Location	Type of Environment	PM ₁₀ Annual average (µg/m ³)	Reference
Delhi, Delhi	Urban	166.5 ± 54.7	Khillare and Sarkar, 2012
Gopalprasad, Odisha	Rural	63 ± 18	Roy et al., 2012
Jagannathpur, Odisha	Urban	114 ± 34	Roy et al., 2012
Agra, UP	Rural	180.2 ± 59.7	Massey et al., 2013
Vashi, Mumbai	Urban	113 ± 33	Kothai et al., 2011
Jogannapalem, AP	Rural	68 ± 15	Present study
Parawada, AP	Urban	80 ± 29	Present study

3.2. Source apportionment of PM using positive matrix factorization (PMF) model

PMF is a multivariate receptor model that has been described in detail by Paatero (1997) and implemented in the PMF program. PMF model is based on the principle that, there exists a relationship between sources and receptor when mass conservation can be assumed (Paatero and Hopke, 2003). When chemical analysis data of ambient PM is available, a mass balance equation (1) of the following form can be written:

$$X_{ij} = \sum_{h=1}^p g_{ih}f_{hj} + e_{ij} \quad (1)$$

where X_{ij} is the j th species concentration measured in i th sample, g_{ih} is the particulate mass concentration from the h th source contributing to the i th sample, f_{hj} is the j th species concentration contributed from h th source and p is the total number of independent sources. The objective of this model is to identify p independent factors representing different PM sources, their main tracers, their contribution to the total determined PM and their contribution to the total concentration of specific species.

PMF decomposes speciated data matrix X of i by j dimensions (i number of samples –160 and j chemical species-19) into two sub-data matrixes, the factor profiles and factor contributions based on the correlation between the different components. PMF estimates 'g' and 'f' by minimizing the residual error 'e' and allowing each data point to be individually weighed. This feature allows the analyst to adjust the influence of each data point, depending on the confidence in the measurement. Further the elements are constrained to be non-negative. For this, a weighted least square approach is used, which involves minimization of an objective function Q , given as

$$Q = \sum_{i=1}^n \sum_{j=1}^m \frac{e_{ij}^2}{s_{ij}^2} \quad (2)$$

subject to $g_{ih} \geq 0$, $f_{hj} \geq 0$. Where s_{ij} is an uncertainty estimate in the j th species measured in the i th sample.

The procedures of Polissar et al. (1998) were applied to estimate the uncertainty matrix for the PMF analysis. The below detection limit (DL) values were replaced with the value DL/2 and $(5/6) \times DL$ was used as corresponding uncertainty values. Missing values of a species for a measurement included in the sample were replaced by the geometric mean for that species and the uncertainty was magnified to three times the geometric mean concentration of the species to decrease its impact on the model.

In the current study, a range of solutions were examined with different number of factors (varied from 3 to 9) and different number of base runs (varied from 20 to 100). In each case, the model was run in the robust mode with number of repeat runs to insure the model least-squares solution represented a global rather than local minimum and the rotational FPEAK variable was held at the default value of 0.0. Thirty-five base runs were performed and the run with the minimum Q value was selected as the base run solution. In the case of 3 and 4 factor solutions, no meaning full sources were identified as there was a mixing of most of the trace elements, but 6 and 7 factor solutions were observed to have profiles that are interpretable in terms of the nature of the sources in the study area and their known physical meaning. Good agreement between Q_{TRUE} and Q_{ROBUST} values was discovered at Jogannapalem (9413 and 13,806) and Parawada (11,705 and 15,987) sites respectively at optimized number of factor solutions. Again, beyond 7 factor solutions, the sources were observed to split further leading to no meaning full solutions. The sources were identified and named based on the appearance and percentage contribution of marker elements in particular factor profile.

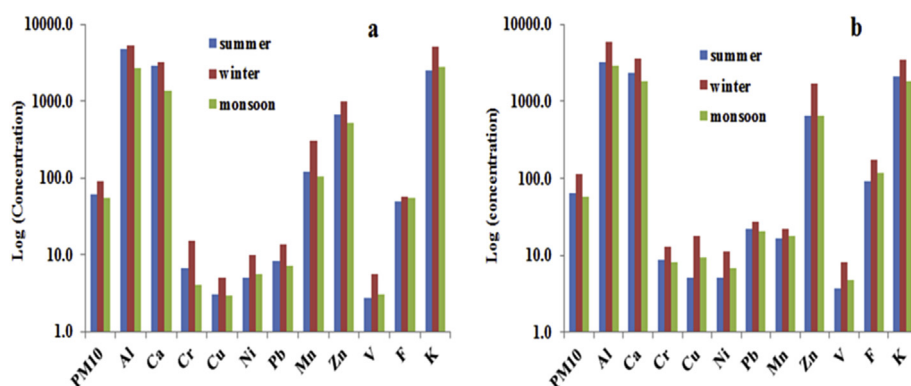


Fig. 2. Seasonal variation of PM₁₀ (µg/m³) and metals (ng/m³) associated with PM at (a) Jogannapalem (b) Parawada sites.

3.3. PMF results

In the present study, we have used EPA PMF 5.0 software and a total of 19 variables viz. F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , Mg^{2+} , K^+ , Al , Ca^{2+} , V , Cr , Mn , Fe , Cu , Ni , Zn , As , Cd and Pb were considered for the PMF study. All species included in the matrix were qualified as “strong” (signal to noise: $S/N > 2$). PMF results suggest that, at Jogannapalem majorly six sources were contributing to PM_{10} , whereas seven sources were found to contributing to PM_{10} at Parawada. Sources were identified and named based on the marker elements present in the source profiles provided by the PMF model. Figs. 3 and 4 shows the source profiles observed in the model at both the sampling sites. In figures, the red dot indicates the percentage contribution and the bar indicates the concentration of a species.

3.3.1. Coal combustion source

Elemental profiles of factor 1 at Jogannapalem site and factor 3 at Parawada site were predominantly contributed by As , Cr and Zn . Literature studies indicate arsenic (As) as one of the important tracer of coal fired thermal power plant emissions (Dai et al., 2012) and Cr , Zn were also typical for combustion of coal sources (Song et al., 2015; Hedberg et al., 2005). Hence the factor was named as coal combustion source. Coal fired thermal power plant near Parawada site might have contributed to these metals observed in PM .

3.3.2. Sea salt spray

Enhanced percentage contribution of Cl^- and Na^+ was observed in factor 2 at Jogannapalem and in factor 4 at Parawada, additionally contribution of Mg was observed at Jogannapalem site. These tracers are mainly associated with the sea salt particles (Kothai et al., 2011). A good correlation ($R^2 > 0.85$) was observed between Na^+ and Cl^- at both the sites with Cl^- to Na^+ ratio close to actual sea salt ratio, which further supports the PMF model results. At Jogannapalem site, low percentage contribution of SO_4^{2-} and NO_3^- was also observed in sea salt spray source; similar observation was made by Aldabe et al. (2011). This could be due to higher $ss-SO_4^{2-}$ contribution to PM_{10} at Jogannapalem site as compared to Parawada site as discussed above.

3.3.3. Biomass burning

Factor 3 at Jogannapalem site was dominated by K , F^- and a minor contribution of SO_4^{2-} , NO_3^- , was also observed. Various authors (Indrani et al., 2012; Hang and Oanh, 2014) indicated the contribution of K from biomass burning sources. Observed contribution of SO_4^{2-} and NO_3^- in this factor could be due to wood combustion been carried out for heating and cooking purposes at sampling site (Zhang et al., 2014). Metals observed in this source could be contribution from the miscellaneous source, which may include the industrial emission and coal combustion. Similar observation was made by Hang and Oanh (2014).

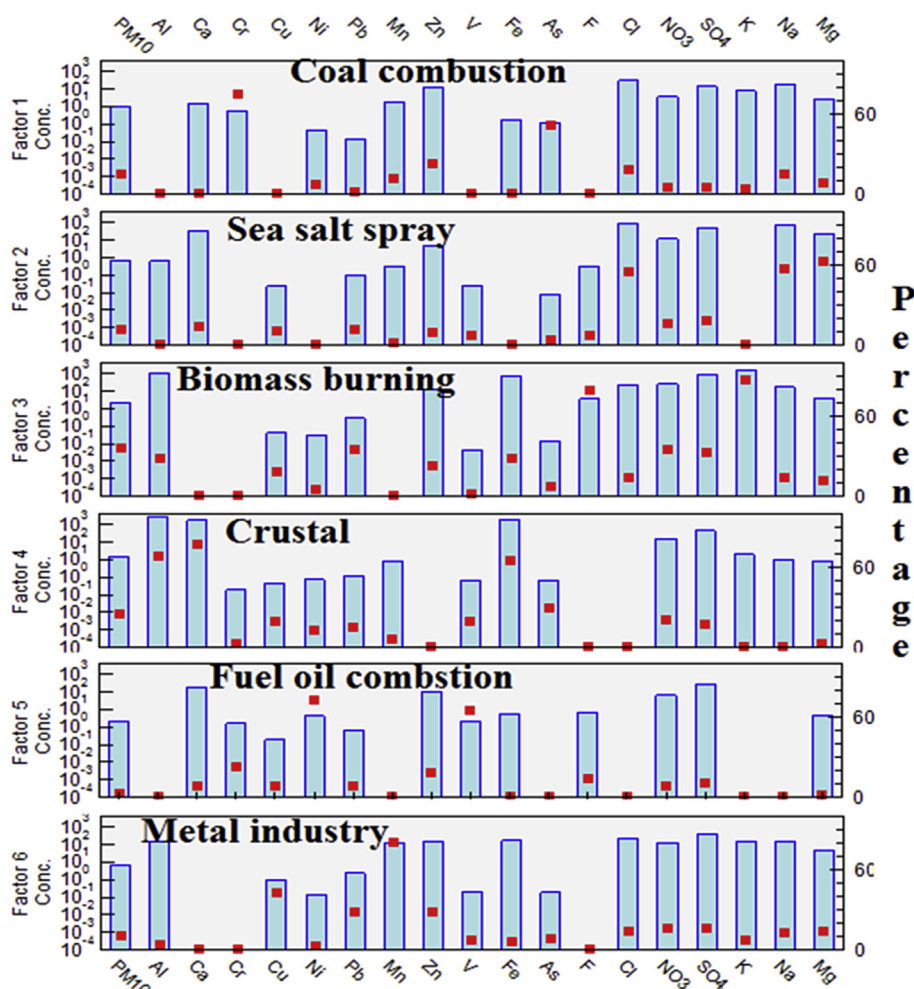


Fig. 3. The calculated source profiles for the PM_{10} dataset showing the contribution of each species in the factor profiles at Jogannapalem site.

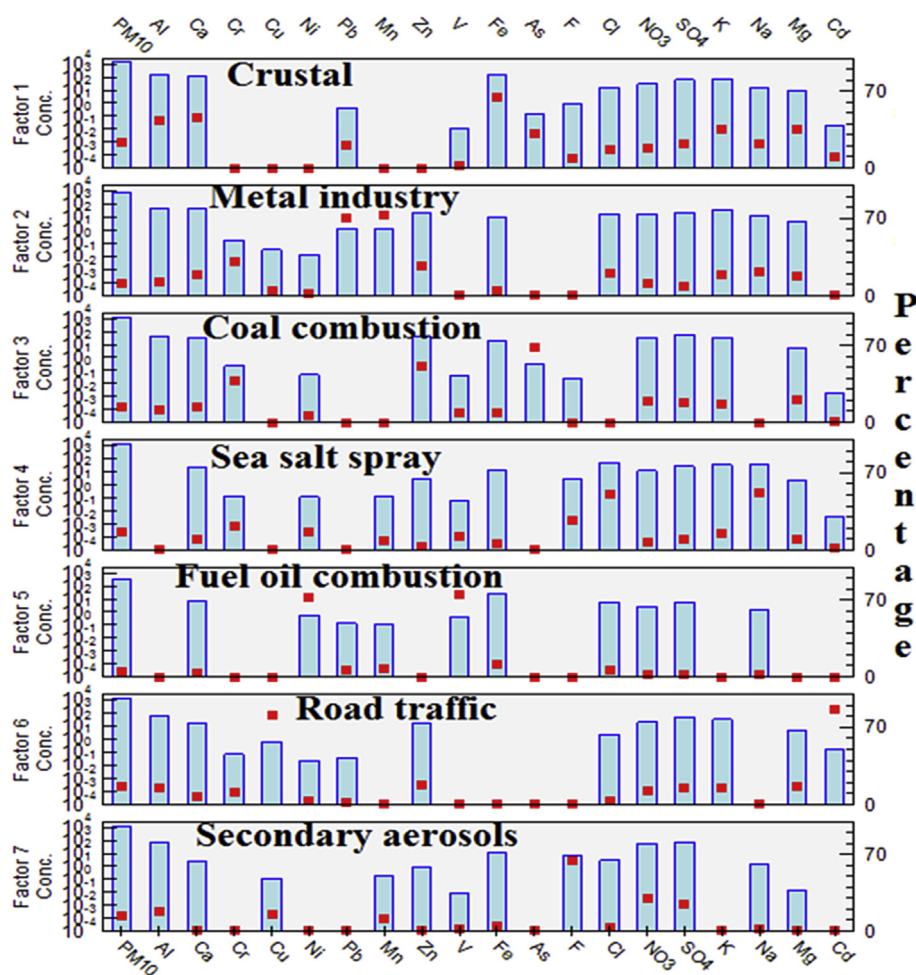


Fig. 4. The calculated source profiles for the PM₁₀ dataset showing the contribution of each species in the factor profiles at Parawada site.

3.3.4. Crustal

Highest percentage contribution of major metals like Al, Ca and Fe was observed in elemental profiles of factor 4 at Jogannapalem and factor 1 at Parawada. The major source of these metals at both the sampling sites could be re-suspension of regional dust and hence named this factor as crustal source. Many researchers have also reported crustal material contribution to PM (Kothai et al., 2011; Cheng et al., 2015). In present study, Ca to Al ratio was found to be 0.58 and 0.73 at Jogannapalem and Parawada sites respectively. Ratio observed at Parawada site is higher than the reference value (0.44); this could be due to the additional contribution of Ca from anthropogenic sources.

In addition to these metals, the factor was also contributed by other metals; this could be due to the presence of these chemical components in soil dust due to the contamination from nearby industrial activities. Aldabe et al. (2011) also indicated the presence of other metals in crustal material.

3.3.5. Fuel-oil combustion

At both the sampling sites, the elemental profiles of factor 5 were characterized by significant percentage contribution of V and Ni. Typical emission of these metals could be from fuel oil combustion sources such as shipping emissions, emissions from crude oil refineries and industrial power plants using heavy oil (Minguillón et al., 2014). In present study, these metals might be contributed from petroleum industries present at study sites and

also could be contributed from ship emissions, as Visakhapatnam contains one of the leading port in India.

3.3.6. Metal industry

High percentage contributions of Mn, Zn and Pb were observed in elemental profiles of factor 6 at Jogannapalem and factor 2 at Parawada. Additionally, Cu and Cr were observed in elemental profiles of Jogannapalem and Parawada sites respectively. This cluster of metals could have contributed from sources such as metal manufacturing industries (Minguillón et al., 2014; Mooibroek et al., 2011). The soil samples collected around various metal processing/production industries at Visakhapatnam were also observed to have enriched concentrations of Mn, Zn, Pb, Cr and Cu (Sandeep et al., 2014), which further supports the model results.

3.3.7. Road traffic

Predominant contribution of Cu, Cd and Zn was observed in elemental profiles of factor 6 at Parawada site. This factor was identified as road/vehicular traffic, as dust originated from motor brake wears and tire wear contains Cu, Cd and Zn (Minguillón et al., 2014). Wang et al. (2013) have mentioned the contribution of Cd to PM₁₀ from the metal smelting industry. As Parawada site is close to major metal industries, the contribution of these industries cannot be neglected. This source was not observed at Jogannapalem site as it is rural residential area with negligible vehicular movement.

3.3.8. Secondary aerosols

Factor 7 at Parawada was found to have highest loadings of F^- , SO_4^{2-} and NO_3^- . These marker species were identified as secondary aerosol component in many source apportionments studies performed (Srimuruganandam and Nagendra, 2012). The origin of SO_4^{2-} and NO_3^- could be from the oxidation of SO_2 and NO_2 emitted by combustion processes (Hang and Oanh, 2014) and from long range transport. Airborne Fluoride (F^-) mostly emitted in gaseous form from anthropogenic sources, but at sampling site, we observed F^- in particulate form; this could be due to the gas to particle conversion phenomena.

3.4. Comparison of PMF source profiles with elemental profiles observed at various industries of Visakhapatnam

In our earlier studies (Sandeep et al., 2014), we have collected soil samples at Visakhapatnam around different industries viz. thermal power plant, metal manufacturing industries and oil refineries to get the emission elemental profiles of these industries. Collected soil samples were analyzed for various metals like Mg, Al, K, Ca, V, Ti, Cr, Mn, Fe, Cu, Ni, Zn, As and Pb and elemental profiles were compiled for each industrial site. The elemental profiles observed in the present study for thermal power plant, oil combustion sources and metal industries using PMF model were well in agreement with the elemental profiles observed in the soil samples collected from these industrial locations, which further confirms the PMF results.

3.5. PM_{10} source contributions determined by PMF model at study locations

The percentage contribution of each source to PM_{10} at Jogannapalem and Parawada sites are given in Fig. 5. At Jogannapalem site, highest contribution to PM_{10} was observed from biomass burning (35%) followed by crustal source (22.5%), coal combustion source (14%), sea salt spray (9.7%), metal industry (5.1%) and fuel oil combustion (1.5%). Whereas at Parawada, highest contribution to PM_{10} was observed from coal combustion (22.6%) followed by crustal source (22.5%), road traffic (14.0%), secondary particles (12.9%), metal industry (7.8%), sea salt spray (5.5%) and fuel oil combustion (3.5%). The unexplained fraction was found to be 12.3% at Jogannapalem and 11.2% at Parawada; which could majorly include organic carbon, elemental carbon and other unaccounted components like Si, NH_4^+ .

As Jogannapalem site is rural area, biomass burning activity is common for daily activities like cooking and heating purposes. This could be the reason for observed highest contribution of this source to PM. Sea salt spray contribution was observed to be higher at Jogannapalem site as this site is close to the sea shore as compare to Parawada site. Whereas, coal combustion source contribution was observed to be high at Parawada as the sampling site is close to the thermal power plant. Similarly, metal industries and fuel oil combustion source contribution was observed to be more at Parawada site as compared to Jogannapalem site. It was found that, the sum of all anthropogenic source contributions at Jogannapalem (55.4%) was observed to be comparable to that observed at Parawada site (60.8%).

The present study demonstrated important source apportionment results which can be taken in mind in the design of future pollution reduction strategies. For example, at Jogannapalem, biomass burning (wood and wood coal burning) was found to be most dominating source, which can be reduced by educating the people about the advantages of using modern equipment for cooking and heating purposes. Also, some control strategies for industrial sources includes, cleaner fuel substitution, change in basic production processes and pollution abatement through flue gas treatment modifications of exit gas characteristics. Most coal power plants use low grade coal with high ash content, which can be replaced by low ash content coal for improving the air quality.

4. Conclusion

Present study gives detailed insight into the concentration levels of PM_{10} , various chemical species bound to PM_{10} and the sources contributing to collected PM_{10} . Study results suggest that average PM_{10} mass concentrations observed at Jogannapalem ($65.4 \mu\text{g}/\text{m}^3$) and Parawada ($74.7 \mu\text{g}/\text{m}^3$) were exceeding the CPCB annual limit ($60 \mu\text{g}/\text{m}^3$). PM and associated chemical species pollution was observed to be high during winter (Nov–Feb) season and lowest during monsoon season (Jul–Oct). Chemical analysis results suggest that most of the trace and toxic metals (except Mn and Fe) were observed to be more at Parawada as compared to Jogannapalem. Annual average concentration of toxic metals such as As, Ni, Pb and Cd were observed to be well within the CPCB annual limits.

Further, source apportionment studies using PMF model identified six potential sources (crustal, sea salt spray, coal combustion, metal industries, fuel oil combustion and biomass burning) at Jogannapalem, whereas seven significant sources (crustal, sea salt

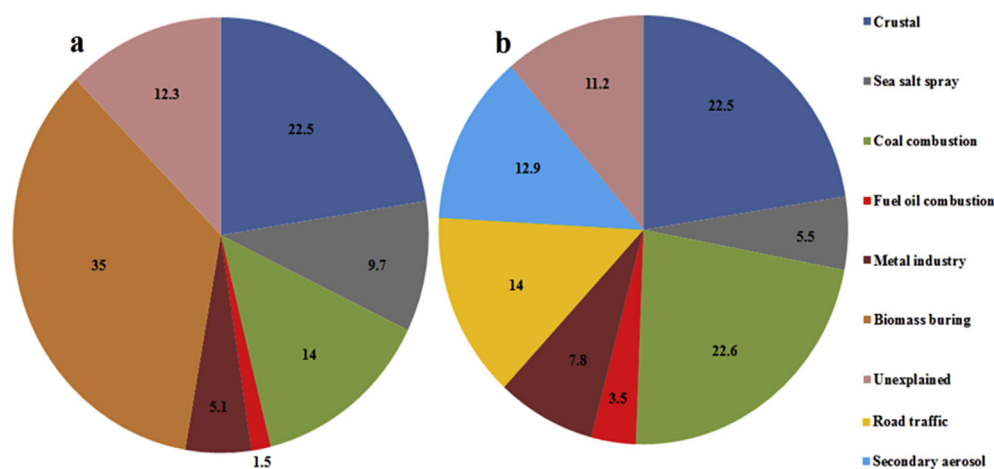


Fig. 5. Percentage contribution of each source to PM_{10} at (a) Jogannapalem (b) Parawada.

spray, coal combustion, metal industries, fuel oil combustion, road traffic and secondary aerosol) at Parawada. It was interesting to observe that, biomass burning is the major source (35%) at Jogannapalem, whereas at Parawada, coal combustion is the major source (22.6%) followed by crustal material (22.5%) contributing to PM₁₀. Though the Jogannapalem is a rural site, the sum of all anthropogenic source contributions was observed to be similar to that observed at sub-urban industrial (Parawada) sites.

Conflict of interest

It is hereby declared that there is no conflict of interest.

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