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Source Apportionment of Total Suspended Particulates in an Arid Area in Southwestern Iran Using Positive Matrix Factorization

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Abstract The present study sough to apportion the possible sources of TSP in Ahvaz, southwestern Iran. A high correlation coefficient existed between measured and predicted values ($R^2 = 0.99$), indicating that the data were well modeled. Seven factors were resolved by the model: crustal dust (56%), road dust (7%), motor vehicles (8%), marine aerosol (9%), secondary aerosol (7%), metallurgical plants (4.5%), and finally petrochemical plants & fossil fuel combustion (8.5%). In contrast with crustal dust having higher relative contributions during spring and summer, motor vehicles had higher contributions during fall and winter. In addition, the latter had higher contributions during weekdays than weekends.

Keywords PMF · Source apportionment · TSP · Ahvaz

Since particulate pollution is of primary concern in air pollution studies due mainly to its considerable effects both on human health and the environment (Perez et al. 2008; Satheesh and Krishna Moorthy 2005), it seems necessary to carefully assess the potential sources of particulate matters in order to develop an efficient air quality management scheme (Lim et al. 2010). Therefore, several methods, such as principal component analysis (PCA), have been developed to identify sources of particulate matters. Nevertheless, these methods have some disadvantages, including improper handling of uncertainties and inability to deal with noisy data sets (Paatero and Hopke 2003). Consequently, a new approach, called Positive Matrix Factorization (PMF), has been developed to overcome these limitations, while retaining the advantages of the previous methods. PMF has been successfully used to define the possible sources of fine particles (Alleman et al. 2010; Lim et al. 2010; Yue et al. 2008). However, only few studies have applied PMF for source apportionment of coarse particles (Wang and Shooter 2005) or in the areas which are subject to severe air pollution episodes (Kim et al. 2003).

Ahvaz is a city of 1.3 million located in an arid area in southwestern Iran. This city is subject to severe dust storms due to its proximity to major dust storms areas in the Middle East, namely, Iraq, Kuwait, and Saudi Arabia (Shahsavani et al. 2012). However, our precise knowledge of different sources and their quantitative contributions to the total mass of particulate matters (TSP) is quite limited mainly because of the limited number of studies in this area, particularly regarding source apportionment and development of emission inventories. The present study, therefore, sought to investigate the possible sources of TSP and their relative contributions in Ahvaz using the EPA PMF version 3 model, applied to data collected between

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April 2010 and March 2011. For this purpose, a large set of species, including 28 elements (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, Si, Sn, Sr, Li, Ti, V, Zn, Mo, and Sb) and 4 ions (NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}), was selected to allow precise apportionment of possible sources.

Materials and Methods

The sampling location was located in Ahvaz, Khuzestan, southwestern Iran, a region known for its strong surface winds, high ambient temperatures, highly humid weather, and ultimately low vegetation cover. The sampling site was located at the center of the city on the flat roof of Health Research Center (10 m above the ground). Twenty-four-hour TSP samples were collected at 6 day intervals over the period from April 2010 to March 2011. Additional sampling was also done during the occurrence of dust storms in the study area. TSP samples were collected on fiberglass filters using a high volume air sampler (Model: Anderson) with an operational flow rate of 1 m^3/min. Filter conditioning before and after the sampling was carried out according to the procedure presented by Zhang et al. (2010). TSP concentrations were calculated by gravimetric method after the sampling.

For determining concentrations of the water-soluble ions in TSP, one-fourth of each filter paper was used. For this purpose, an ion chromatography instrument (Model: Metrohm 850 Professional IC, Switzerland), operating at a flow rate of 0.7 mL/min, was used. Detailed description of the procedure applied for preparing the samples can be found in Cheng et al. (2008). Nitric acid 3.2 mM was used as the cationic solvent, while sodium bicarbonate 1.7 mM combined with sodium carbonate 1.8 mM was used as the anionic solvent. For each analysis, the solvents were injected into the ion chromatography instrument at specific rates (10 µL of the cationic solvent and 20 µL of the anionic solvent). Finally, a recovery rate of 80–120% was obtained for each ion. Another one-fourth of each filter paper was used for quantitative analysis of the trace elements by inductively coupled plasma (ICP). Before the ICP analysis, samples were prepared according to the method presented by Sun et al. (2004).

PMF can be described as a weighted least squares fit of a dataset. In this matrix, the expert can modify these weights according to the experimental uncertainties (for example, uncertainties due to analytical errors or those occurring during sampling) for each individual value in the matrix. The final goal of PMF is to resolve a number of potential sources (p), a factor profile (f) for each of the sources, and contribution of different factor sources (g) to the total mass of the pollutant measured. The following is the general equation of PMF (USEPA 2008):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where, g_{ik} is the concentration contributed by kth factor to the ith sample, f_{kj} is the relative fraction (%) of jth element in factor k, and e_{ij} is the residual concentration of each sample which is not resolved by the model. The PMF model solution is based on minimizing a weighted sum of the squared residuals function (Q) taking into consideration the uncertainties in the data (USEPA 2008):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} \cdot f_{kj}}{u_{ij}} \right]^2 \tag{2}$$

where, u_{ij} corresponds to the concentration uncertainty.

In the present study, unexposed blank filters repeatedly underwent the analytical procedure during the study period to quantify the background concentration of each of the species in the study area. MDL value for each species was also calculated using blank values by adding three standard deviations to the average values of filter blanks (Alleman et al. 2010). Values below MDL for each species were replaced by half of the MDL for that species and the uncertainty for that value was set to five sixth of the MDL (Polissar et al. 1998). In addition, missing values were replaced by the geometric mean of the same species (Polissar et al. 1998). However, since this replacement can artificially change the correlations existing among the elements, the uncertainty of these values was set as for times the geometric mean in order to reduce their weights (Alleman et al. 2010).

Results and Discussion

The overall mean TSP concentration was 1289.86 ± 1440.23 µg/m^3. Table 1 presents a variety of critical parameters for each species used as input to PMF. As given in the table, the percent of missing values was generally low mainly because of a strong control over data collection during the sampling and analytical period. This, combined with low percent of values below MDL, gave high signal to noise (S/N) ratios for most of the elements. Only in the case of species such as K, Ni, Li, Mo, Cl^-, NO_3^-, and SO_4^{2-} for which the percent of either missing values or values below MDL or both is high, the S/N ratio is low. Nevertheless, even in these cases the S/N ratios are higher than the desired value of 2 (Paatero and Hopke 2003). It is noteworthy that the high correlation between measured and

Table 1 Summary statistics for critical parameters of PMF speciated input data

Species	Missing values (%)	MDL (μg/m^3)	Values below MDL (%)	S/N ratio[b]	Species	Missing values (%)	MDL (μg/m^3)	Values below MDL (%)	S/N ratio[b]
TSP	0.00	–	0.00	98.86	Ni[a]	20.83	1.170	19.44	5.27
Al	2.70	0.400	0.00	48.69	P	2.70	0.020	0.00	35.88
As[a]	0.00	0.100	6.94	22.15	Pb[a]	0.00	0.008	0.00	33.48
B	13.80	3.000	11.10	15.49	Se[a]	0.00	0.070	0.00	29.07
Ba	0.00	0.100	0.00	31.49	Si[a]	5.50	0.090	0.00	32.33
Be	2.70	0.015	6.94	23.95	Sn[a]	0.00	0.020	0.00	31.25
Ca	0.00	5.000	0.00	32.23	Sr[a]	0.00	0.015	0.00	32.31
Cd[a]	6.94	0.075	0.00	47.63	Li	13.8	0.025	12.50	6.91
Co[a]	0.00	0.015	0.00	32.15	Ti[a]	0.00	0.070	1.38	47.35
Cr[a]	0.00	0.200	0.00	44.02	V[a]	0.00	0.100	0.00	36.73
Cu[a]	0.00	0.070	0.00	32.26	Zn[a]	8.33	0.180	0.00	38.91
Fe	8.33	1.700	6.94	14.23	Mo[a]	2.70	0.200	25.00	7.64
Hg[a]	0.00	0.300	0.00	34.28	Sb[a]	0.23	0.000	0.00	17.94
K	5.50	3.000	9.72	7.63	NH_4^+	6.94	0.000	0.00	19.82
Mg	0.00	1.000	0.00	25.77	Cl^-	13.8	0.000	27.77	5.43
Mn[a]	0.00	0.360	1.38	46.88	NO_3^-	18.05	0.000	9.72	6.14
Na	0.00	0.350	0.00	89.75	SO_4^{2-}	20.83	0.000	4.16	8.54

[a] The MDL values for the species are presented in ng/m^3

[b] *S/N Ratio* $\frac{1}{2}\sqrt{\frac{\sum x_{ij}^2}{\sum s_{ij}^2}}$ (Lim et al. 2010)

predicted values, $R^2 = 0.99$, suggests that the speciated input data were well modeled by PMF.

The model was repeatedly run applying different number of factors, F peak values, and extra model uncertainties in order to resolve the most physically reasonable source profiles. By evaluating different source profiles resolved by each run, it was found that the seven-factor solution, with Fpeak value of 0.1 and extra model uncertainty of 10%, is the most justifiable solution. Figure 1 indicates the species profile for each of the factors resolved by the model. Note that bars represent concentrations of the elements in each factor with a scale on the left axis, while solid circles represent the percentage of each element in that factor and should be read from the right axis. In addition, major elements and ions for each factor are marked by darker bars. Figure 2a, b depicts seasonal box plots for factors 1 and 3. Figure 2c indicates a day-of-the-week box plot for factor 3. Since distinct trends were not detected for other factor profiles, they are not presented in this figure.

The first factor is mainly dominated by Al (63%), Si (58%), Ca (35.9%), Fe (23.1%), K (19.5%), Mg (18.7%), and Mn (21%). These elements have been considered as good markers of “crustal dust/soil” (Alleman et al. 2010; Kim et al. 2003; Santoso et al. 2008; Lim et al. 2010). In addition, this factor had the highest contribution (56%) to the total mass of TSP among the other factors. According to Fig. 2a, this factor had greater contributions in spring and summer compared to fall and winter. In some days (in the late June, for example), the contribution of this factor increased up to about 95% of the total mass of TSP. This period (spring and summer) is the time during which several severe dust storms occur in the study area (Shahsavani et al. 2012). These dust storms are believed to be due mainly to the westerly Shamal wind which blows during spring and summer and carries great amounts of mineral dusts from desert areas located at southwestern Iraq (Goudie and Middleton 2006). Therefore, this verifies that the first factor best suits the crustal dust source category. The second factor belongs mainly to Al (22.1%), Ba (31.2%), Si (23.3%), Pb (21%), Cu (14.8%), Fe (13.9%), K (14%), and Zn (9.4%), contributing to 7% of the total mass of TSP. The main origin of this source category is transportation of motor vehicles in paved or non-paved roads (Lim et al. 2010). This can cause to vehicular emissions (e.g., exhaust emissions, tire abrasion, and emission of oils from places other than exhaust) combined with resuspension of road dusts which have been previously deposited on the roads (Kim and Henry 2000). Considering the arid climate of Ahvaz as well as high number of non-paved roads in this area, existence of this source can be validated.

The dominant elements in the third factor are Ba (45%), Cd (33.6%), Pb (33.2%), Zn (44%), Cl (29.6%), and Sb (24.5%). Ba, Cd, and Cl have been widely used as good markers of “motor vehicle” source category (Lim et al.

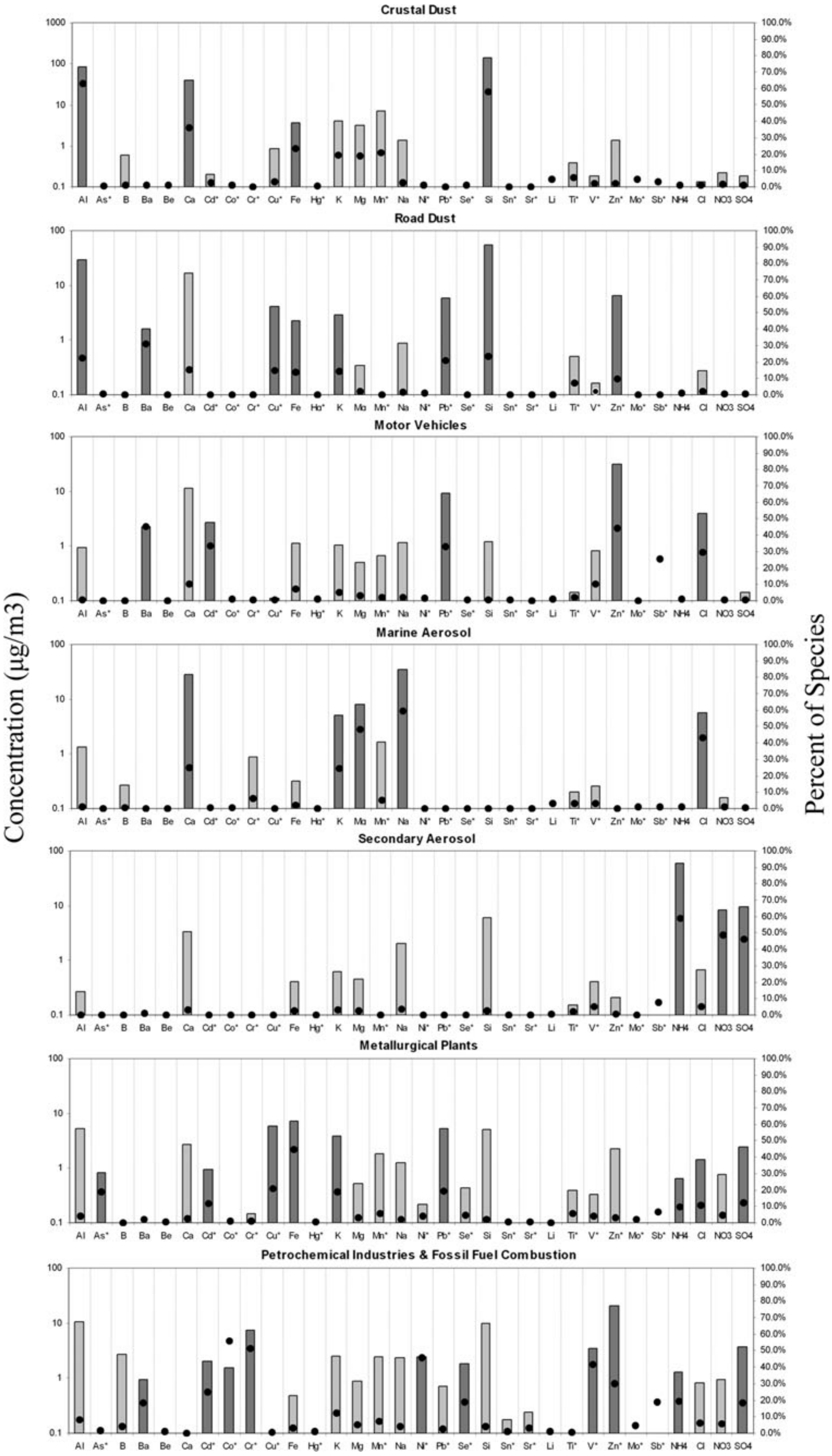

Fig. 1 Species profile of the factors resolved by PMF (*bars* have a *scale* on the left axis, while *solid circles* should be read from the right axis; the species marked by the *asterisk* are presented in ng/m^3)

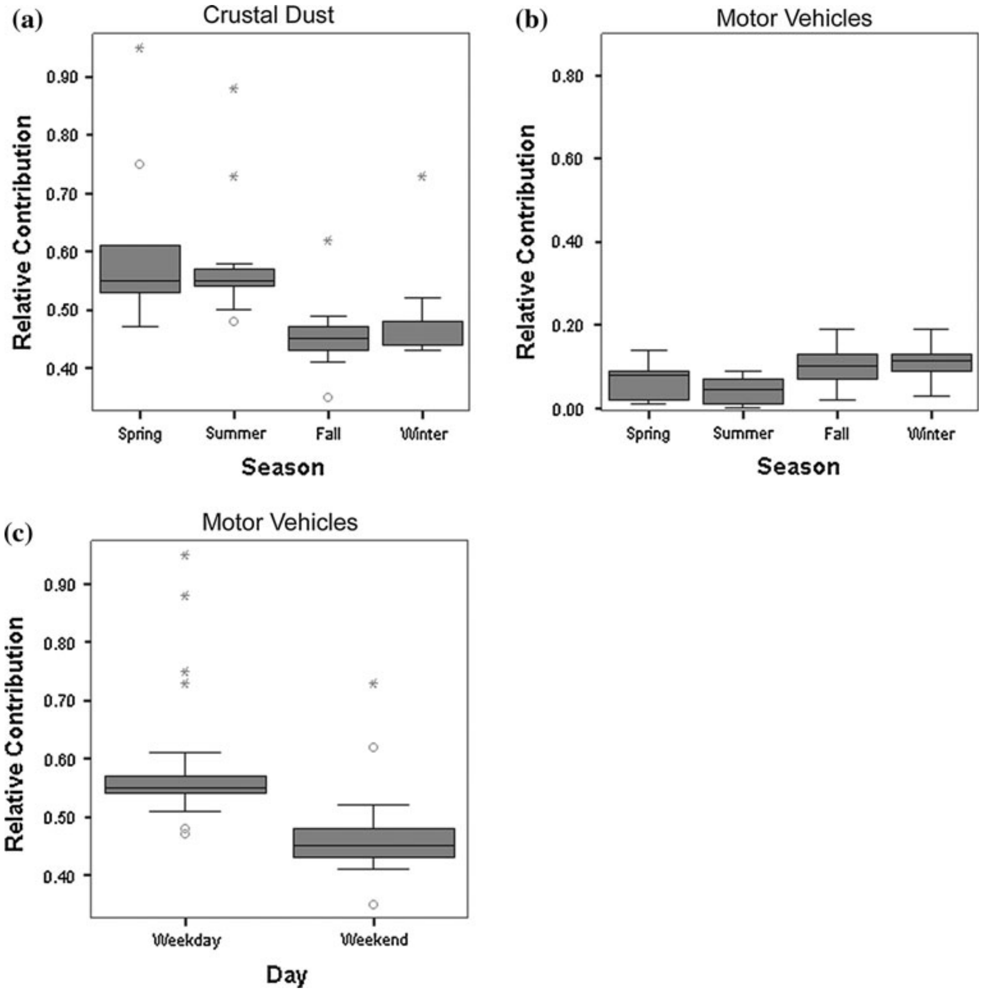

Fig. 2 Seasonal and day-of-the-week *box plots* for factors 1 (**a**) and 3 (**b**, **c**)

2010). This source category accounted for 8% of the total mass of TSP. It had greater contributions during fall (nearly 11%) and winter (about 13%) compared to spring (well below 10%) and summer (below 5%) (Fig. 2b). This is due mainly to the fact that low atmospheric temperature enhances the transformation of exhaust emissions into solid particles (Wehner et al. 2000). Atmospheric stability and consequently possible temperature inversions can also be considerable factors that would increase the contributions of this factor in fall and winter. Finally, this factor had greater contributions in weekdays than in weekends (Fig. 2c), which is typical of emissions due to motor vehicles. The forth factor is typical of "seasalt/marine aerosol" since it has high levels of Na (59.2%) and Cl (43.1%), Ca (25%), K (24.6%), and Mg (48%) (Santoso et al. 2008; Alleman et al. 2010). Since Ahvaz is located near coastal regions in southwestern Iran, presence of this source was expected. It contributed to 9% of the total mass of TSP. Finally, as expected according to the previous studies, the profile of this source (not shown) did not have significant temporal variations since its origin exists constantly during the whole year.

The fifth factor is dominated by only three ions, namely NH_4^+ (59%), NO_3^- (47.8%), and SO_4^{2-} (46.4%). Previous studies have linked the presence of NH_4^+ and NO_3^- to secondary nitrate aerosols (Kim et al. 2003). In addition, presence of high concentrations of SO_4^{2-} combined with NH_4^+ is a good marker of secondary sulfate aerosols (Santoso et al. 2008). It can, therefore, be concluded that this factor best suits "secondary aerosol" source category. It contributed to 7% of the total mass of TSP. It is also noteworthy that precise allocation of possible sources of secondary aerosols is difficult, mainly due to the fact that these particles are produced as a consequence of transformations between pollutants directly released into the atmosphere. Hence, complementary information on the meteorological conditions as well as spatio-temporal analysis of the pollutants are required for this purpose (Lim et al. 2010). The sixth factor belongs to a number of metallic elements, namely, As (19%), Cd (11.6%), Cu (21%), Fe (5.44%), K (18.7%), and Pb (19.4%) and to a lesser extent to three ions, i.e., NH_4^+ (9.8%), Cl^- (10.9%), and SO_4^{2-} (12%). These species have been previously associated with "metallurgical Plant" source category

(Alleman et al. 2010; Kim et al. 2003; Lim et al. 2010). There are some metal manufacturing and smelting plants in the study area, but their emissions are not well known, neither quantitatively nor qualitatively, mainly as a result of lack of air pollution studies in this area. Overall, these plants accounted for 4.5% of the total mass of TSP. The last factor mainly consists of Ba (18.5%), Cd (25%), Co (56%), Cr (51.2%), Ni (45.9%), Se (19%), V (41.7%), Zn (29.8%), NH_4^+ (19.4%), and finally SO_4^{2-} (18.3%), which are representatives of "petrochemical industries & Fossil fuel combustion" (Alleman et al. 2010). The Ni/V ratio of 1.05, which is in the range of that observed by Alleman et al. (2010), can also be used as another indicator of this source category. The existence of this factor seems reasonable since there are a large number of oil extraction and refinery plants as well as continuous combustion of natural gas in numerous flares in the region. This factor made up of these two sources constituted 8.5% of the total mass of TSP measured over the study period.

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