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Characterization of ionic composition of TSP and PM₁₀ during the Middle Eastern Dust (MED) storms in Ahvaz, Iran

Abbas Shahsavani · Kazem Naddafi · Nematollah Jaafarzadeh Haghhighifard ·
Alireza Mesdaghinia · Masud Yunesian · Ramin Nabizadeh · Mohamad Arhami ·
Maryam Yarahmadi · Mohammad Hossein Sowlat · Maryam Ghani ·
Ahmad Jonidi Jafari · Mahmood Alimohamadi · Seyed Abbas Motevalian ·
Zahra Soleimani

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Abstract Because of the recent frequent observations of major dust storms in southwestern cities in Iran such as Ahvaz, and the importance of the ionic composition of particulate matters regarding their

health effects, source apportionment, etc., the present work was conducted aiming at characterizing the ionic composition of total suspended particles (TSP) and particles on the order of ~10 μm or less (PM₁₀)

A. Shahsavani · K. Naddafi (✉) · A. Mesdaghinia ·
M. Yunesian · R. Nabizadeh · M. Yarahmadi ·
M. H. Sowlat · M. Ghani · A. Jonidi Jafari ·
M. Alimohamadi
Department of Health Engineering, School of Public
Health, Tehran University of Medical Sciences,
16 Azar St., Enghelab Sq.,
Tehran, Iran

e-mail: knadafi@tums.ac.ir

A. Shahsavani
e-mail: ashahsavani@gmail.com

A. Mesdaghinia
e-mail: mesdaghinia@sina.tums.ac.ir

M. Yunesian
e-mail: yunesian@tums.ac.ir

R. Nabizadeh
e-mail: rnabizadeh@tums.ac.ir

M. Yarahmadi
e-mail: m.yarahmadi86@gmail.com

M. H. Sowlat
e-mail: hsowlat@gmail.com

M. Ghani
e-mail: ghani.maryam@yahoo.com

A. Jonidi Jafari
e-mail: ahmad_jonidi@yahoo.com

M. Alimohamadi
e-mail: m_alimohammadi@tums.ac.ir

N. Jaafarzadeh Haghhighifard · Z. Soleimani
Department of Environmental Health,
Ahvaz Jondishapour University of Medical Sciences &
Environmental Technology Research Center,
Ahvaz, Iran
e-mail: na.haghhighifard@gmail.com

Z. Soleimani
e-mail: ronak_soleimani@yahoo.com

K. Naddafi · M. Yunesian
Institute for Environmental Research(IER),
Kargar St., Enqelab Sq.,
Tehran, Iran

M. Arhami
Department of Civil Engineering,
Sharif University of Technology,
Azadi St.,
Tehran, Iran
e-mail: arhami@sharif.edu

S. A. Motevalian
Department of Biostatistics and Epidemiology, School
of Public Health, Tehran University of Medical Sciences,
16 Azar St., Enghelab Sq.,
Tehran, Iran
e-mail: amotevalian@yahoo.com

during dust storms in Ahvaz in April–September 2010. TSP and PM₁₀ samples were collected and their ionic compositions were determined using an ion chromatography. Mean concentrations of TSP and PM₁₀ were 1,481.5 and 1,072.9 µg/m³, respectively. Particle concentrations during the Middle Eastern Dust (MED) days were up to four times higher than those in normal days. Ionic components contributed to only 9.5% and 11.3% of the total mass of TSP and PM₁₀, respectively. Crustal ions were most abundant during dust days, while secondary ions were dominant during non-dust days. Ca²⁺/Na⁺ and Cl⁻/Na⁺ ratios can be considered as the indicators for identification of the MED occurrence. It was found that possible chemical forms of NaCl, (NH₄)₂SO₄, KCl, K₂SO₄, CaCl₂, Ca(NO₃)₂, and CaSO₄ may exist in TSP. Correlation between the anionic and cationic components suggests slight anion and cation deficiencies in TSP and PM₁₀ samples, though the deficiencies were negligible.

Keywords The Middle Eastern Dust storm · TSP · PM₁₀ · Water-soluble ions · Ahvaz

Introduction

Dust storm has high priority in air quality management schemes, because it has considerable impacts in local, regional, and even global scale both in short- and long-term (Husar et al. 2001; Wang et al. 2005; Fairlie et al. 2007). It is believed that 800 Tg particulate matter is annually transported through dust events in Asia (Zhang 1995). The number for Sahara alone is about one billion tons (Kwon et al. 2002). These huge numbers have been associated with adverse effects on human health such as hospitalization due to cardiovascular and respiratory diseases (Meng and Lu 2007; Kwon et al. 2002; Chan et al. 2008). Several other impacts have also been reported such as effects on the radiation budget of the earth, photochemical, and dynamic processes, which take place in the atmosphere, agricultural activities, traffic,

etc. (Kurosaki and Mikami 2003; Liao et al. 1999; Satheesh and Krishna Moorthy 2005)

Of the total mass of the particles released due to occurrence of dust storms, ionic composition of dust storm particles is of high priority due to several reasons. For example, knowledge of water-soluble ions helps us in creating emission inventories used in source apportionment, investigating possible health effects of dust storms, and enhancing pollution control strategies (Shen et al. 2009). In addition, it has been suggested that they have considerable impact on the environmental (mostly climatic) change and if deposited on the ocean, they can increase its biogenic productivity (Goudie and Middleton 2001; Hughes et al. 1998). Besides, it is believed that water-soluble ions can influence formation, growth, and evolution processes of the particles, so they can be better indicators of reactions occurring on the particle surface compared to their elemental counterparts (Wang et al. 2006).

Therefore, a great number of studies have been conducted in the areas facing frequent occurrence of dust storms, especially in the eastern Asia, for assessing chemical composition of Asian dust storms (Chen et al. 2004; Cheng et al. 2005; Kang et al. 2009; Lee et al. 2006; Lia et al. 2008; Shen et al. 2009; Tsai and Chen 2006; Wang et al. 2007; Wang et al. 2006; Xiao and Liu 2004). In the recent years, studies have shown the occurrence of major dust storms in the Middle East with particles on the order of ~10 µm or less (PM₁₀) concentrations of up to a few thousands of micrograms per cubic meter (Draxler et al. 2001). According to the study of Leon and Legrand (2003), the major sources of these dust storms, called the Middle Eastern Dust (MED) storms, are believed to be Arabian Peninsula, Kuwait, Iraq, and parts of Iran. However, no studies have been performed for evaluation of the ionic components in particulate matters during the MED storms, which are increasingly happening in the aforementioned areas and affecting the air quality of the region and people's life. Therefore, the present study aimed to characterize the ionic composition of total suspended particles (TSP) and PM₁₀ during the MED storms in Ahvaz, Iran (which is closely located near the mentioned sources of the MED storms in this region). The study was conducted over the period from April to September 2010, as this is the time period with

K. Naddafi
Enghlab Square, 16 Azar Street, TUMS,
Tehran, Iran

highest number of dust storms in this region (Leon and Legrand 2003).

Materials and methods

Sampling

The air sampling was performed in Ahvaz, an arid area located at southwest of Iran, the characteristics of which are low vegetation cover, strong surface winds, high temperatures, and humidity, and being surrounded by large deserts, all of which are known as the major causes of dust storm (Kurosaki and Mikami 2003). With a surface area of 220 km², it has a total population of 1.3 million. The most important feature is proximity to arid countries such as Kuwait, Saudi Arabia, and Iraq, which are believed to be the major sources of dust storms in this region (Goudie and Middleton 2001; Leon and Legrand 2003).

The sampling station was located at an urban background area in the city on the roof top of the Health Research Center at the height of 10 m above the ground. The sampling height was selected to minimize the potential effects of natural and anthropogenic features on the air stream, and therefore, particle concentrations.

Twenty-four-hour TSP and PM₁₀ samples were collected every sixth day from 1 April to 31 September 2010, which is believed to be the time period with the most frequent occurrence of dust storm in this region (Leon and Legrand 2003; Kouyoumdjian and Saliba 2006). In addition, further sampling was also conducted in the case of dust storm occurrence. TSP and PM₁₀ sampling was conducted using two separate high-volume air samplers (model: Anderson) operating at a flow rate of 1 m³/min. The fiberglass filters used to capture particles were preconditioned before sampling by being washed with deionized water in order to remove potential impurities (Yao et al. 2002). They were then put into an oven (50°C for 10 h) and subsequently kept in room temperature for 24 h and weighted using an analytical balance (model: Sartoris 2004 MP) with a reading precision of 10 µg (Zhang et al. 2010). Then, they were put into covers until the sampling time (Y. Wang et al. 2007). After the sampling, particle concentrations were obtained by

gravimetric method. The filters were kept in the refrigerator at 4°C till the chemical analysis (Shen et al. 2009).

Chemical analysis of water-soluble ions

Filter samples were used for determination of the ionic species, including five anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, and SO₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺). To do this, one-fourth of each filter paper was cut and shredded into a 100-ml vial containing 50 ml distilled-deionized water (with a resistivity of 18 Ω), and then shaken for 2 h to extract the ionic components. All the extracts were then filtered through a 0.2-µm pore size membrane (Schleicher & Schuell) and kept in plastic vials at 4°C until chemical analysis (Chen et al. 2004; Cheng et al. 2008). Finally, the ionic components were determined by using an ion chromatography (model: Metrohm 850 Professional IC, Switzerland) which was operating at a flow rate of 0.7 ml/min.

Cationic and anionic solvents used were nitric acid 3.2 mM and sodium hydrogen carbonate 1.7 mM combined with sodium carbonate 1.8 mM, respectively. For each analysis, 20 µl of the anionic sample and 10 µl of the cationic sample were injected into the ion chromatography. It is noteworthy that the recovery rate for each ion was in the range of 80–120%. The relative standard deviation of each ion was less than 2% for the reproducibility of the tests. In order to determine the background concentrations of each species during the study period, blank samples (i.e., unexposed control filters) were chemically analyzed routinely. Then, the real concentration of each species was calculated by subtracting the blank values from the results of the chemical analysis conducted on the exposed filters (Shen et al. 2009).

Statistical analyses

In order to determine the possible chemical forms of the ionic components, bivariate correlations were made among the anions and cations present in TSP. Generally, a *R*² value of about 0.5 was considered a good correlation between the selected ions, indicating the possibility of the formation of that specific chemical form (Wang et al. 2006).

Results and discussion

Mass concentration of TSP and PM₁₀ and their ionic components

Fifty-eight samples were collected for each pollutant at the sampling station in Ahvaz during the study period. Table 1 presents summary statistics of TSP and PM₁₀ mass concentrations and their ionic composition. Mean TSP mass concentration was 1,481.5 µg/m³ during the entire study period. In addition, its mass concentrations were considerably higher during dust days compared with non-dust days (1,857.3 versus 542.1 µg/m³). For PM₁₀, average mass concentration was found to be 1,072.9 µg/m³, with concentrations of 1,353.6 and 371.3 µg/m³ during dust days and non-dust days, respectively. It is noteworthy that the particle concentrations observed in the present study during the Middle Eastern Dust storm are generally higher than those observed during the Asian dust (AD) storms (Chen et al. 2004; Shen et al. 2009) and only in the case of Beijing higher mean TSP concentration of 1,949 µg/m³ was observed (Wang et al. 2006). This implies the high level of air pollution during occurrence of the MED in Ahvaz and the importance of its impact on the air quality of the region.

According to Table 1, ionic components contributed to only 9.5% and 11.3% of the total mass of TSP and PM₁₀, respectively, indicating that the ionic

components are more concentrated in the coarse fraction of the MED particles. This is consistent with the results of other studies, in which the ionic contribution to total particle mass were reported to be in the range of 5–15% during AD storms (Cheng et al. 2005; Shen et al. 2009; Wang et al. 2006). As shown in Table 1, mass concentrations of the ionic components in TSP were in the following order: SO₄²⁻ > Ca²⁺ > NO₃⁻ > Mg²⁺ > Cl⁻ > Na⁺ = NH₄⁺ > K⁺ > F⁻ > NO₂⁻; the order for the ionic components in PM₁₀ were: Ca²⁺ > NO₃⁻ > SO₄²⁻ > Mg²⁺ > Cl⁻ > Na⁺ > NH₄⁺ > K⁺ > F⁻ > NO₂⁻. This shows that Ca²⁺, Mg²⁺, NO₃⁻, SO₄²⁻, and Cl⁻ are the most frequently found constituents in TSP and PM₁₀ in the study area.

Figure 1a–d illustrates relative contributions of ionic components to the total mass of TSP and PM₁₀ during dust storm days (DSDs) and non-dust storm days (NDSDs). As can be seen from the figure, ionic components in TSP during dust storm days were in the following order of Ca²⁺ > SO₄²⁻ > NO₃⁻ > Mg²⁺ > Na⁺ > Cl⁻ > NH₄⁺ > K⁺ > F⁻ > NO₂⁻ (Fig. 1a); the ionic components in PM₁₀ followed approximately the same order of Ca²⁺ > SO₄²⁻ > Mg²⁺ > NO₃⁻ > Cl⁻ > Na⁺ > NH₄⁺ > K⁺ > F⁻ > NO₂⁻ (Fig. 1c). It can be implied that for both TSP and PM₁₀, Ca²⁺, Mg²⁺, NO₃⁻, and SO₄²⁻ were the most frequent ionic components during the MED storms. In addition, Ca²⁺, Mg²⁺, and Na⁺, which are believed to be the crustal ions (Wang et al. 2006), contributed to 48% and 51% of the total mass of TSP and PM₁₀,

Table 1 Summary statistics for mean total mass concentrations of TSP and PM₁₀ and their ionic components over the study period in Ahvaz

Species	TSP (µg/m ³)				PM ₁₀ (µg/m ³)			
	Mean	SD	Min	Max	Mean	SD	Min	Max
Mass	1,481.5	1,713.1	293.2	7,535.6	1,072.9	1,123.0	210.0	5,012.7
Na ⁺	9.1	8.3	0.1	28.0	8.5	6.5	1.4	25.6
NH ₄ ⁺	9.1	12.4	0.5	47.7	4.5	5.5	0.6	25.6
K ⁺	2.5	2.6	0	9.6	2.5	2.2	0.2	7.2
Mg ²⁺	19.0	18.2	0.15	81.7	18.0	2.0	0.2	47.8
Ca ²⁺	30.6	22.0	1.8	89.9	27.6	16.9	3.8	73.8
F ⁻	0.3	0.5	0.0	3.1	0.3	0.4	0.0	2.0
Cl ⁻	18.9	45.9	2.2	208.0	15.0	26.7	1.2	104.2
NO ₂ ⁻	0.01	0.02	0.00	0.10	0.01	0.01	0.00	0.04
NO ₃ ⁻	27.5	56.9	0.0	287.5	22.6	47.7	0.0	220.6
SO ₄ ²⁻	33.5	50.2	7.1	254.3	22.3	33.5	0.6	153.0

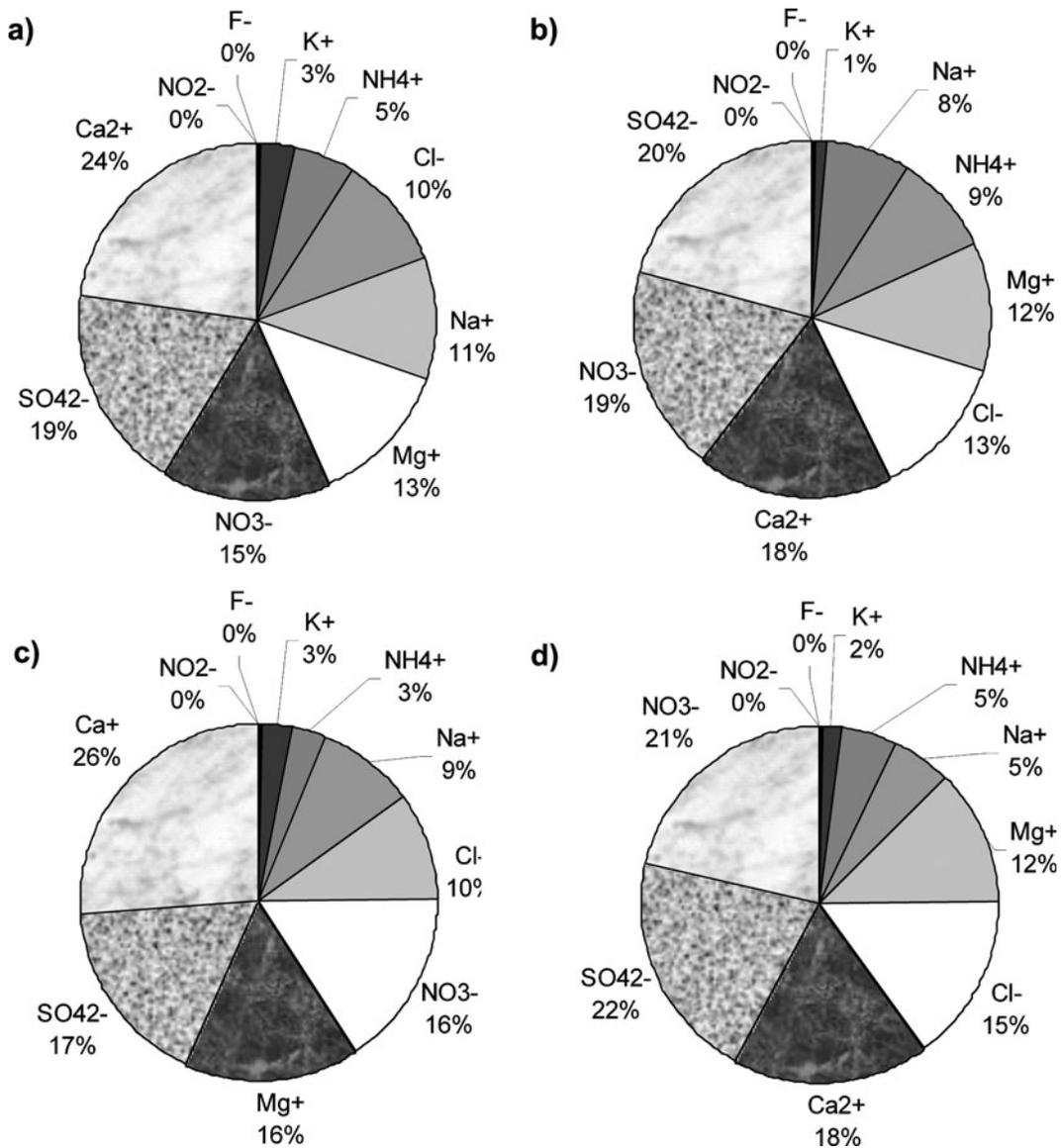


Fig. 1 Relative contributions of the ionic components to the total mass of TSP and PM₁₀ during dust storm days (DSDs) and non-dust storm days (NDSDs): **a** ions in TSP during DSDs; **b**

ions in TSP during NDSDs; **c** ions in PM₁₀ during DSDs; and **d** PM₁₀ during NDSDs

respectively. These percentages are much higher than those found by other studies during normal days as well as Asian dust days (Lee et al. 2002; Lia et al. 2008; Shen et al. 2009; Wang et al. 2006; Xiao and Liu 2004). Therefore, they can be used as indicators to identify the occurrence of the MED in the study area.

The order of mass concentration of the ionic components in TSP during non-dust storm days were in the following order of SO₄²⁻ > NO₃⁻ >

Ca²⁺ > Cl⁻ > Mg²⁺ > NH₄⁺ > Na⁺ > K⁺ > F⁻ > NO₂⁻ (Fig. 1b); the order for the ionic components in PM₁₀ were NO₃⁻ > SO₄²⁻ > Ca²⁺ > Cl⁻ > Mg²⁺ > Na⁺ > NH₄⁺ > K⁺ > F⁻ > NO₂⁻ (Fig. 1d). It can, therefore, be implied that during normal days pollution as well as pollution-crustal ions (according to the categorization of Wang et al. (2006) that classified chemical species of particulate matters into three categories of crustal, pollution, and pollution-crustal species based on their origins) most contributed to the

total mass of TSP and PM₁₀. It is noteworthy that the relative contribution of Cl⁻ ion, which is the indicator of sea salt particles (Cheng et al. 2005), is usually high, most probably due to proximity of the study area to the sea. Finally, it can be concluded that crustal ions were most abundant during dust storm days, while secondary ions were dominant during non-dust storm days. This difference is possibly due to the fact that the anthropogenic sources are abundant during non-dust storm days, while their effects considerably decrease by dilution of anthropogenic pollutants

by mineral dusts during dust storm days (Guo et al. 2004).

Trends of particle mass concentrations

Figure 2a shows temporal trend of TSP and PM₁₀ concentrations with respect to wind speeds over the entire study period in Ahvaz. As shown in the figure, TSP and PM₁₀ mass concentrations were generally high due to the occurrence of the MED in the area. In addition, four major dust storms with TSP mean

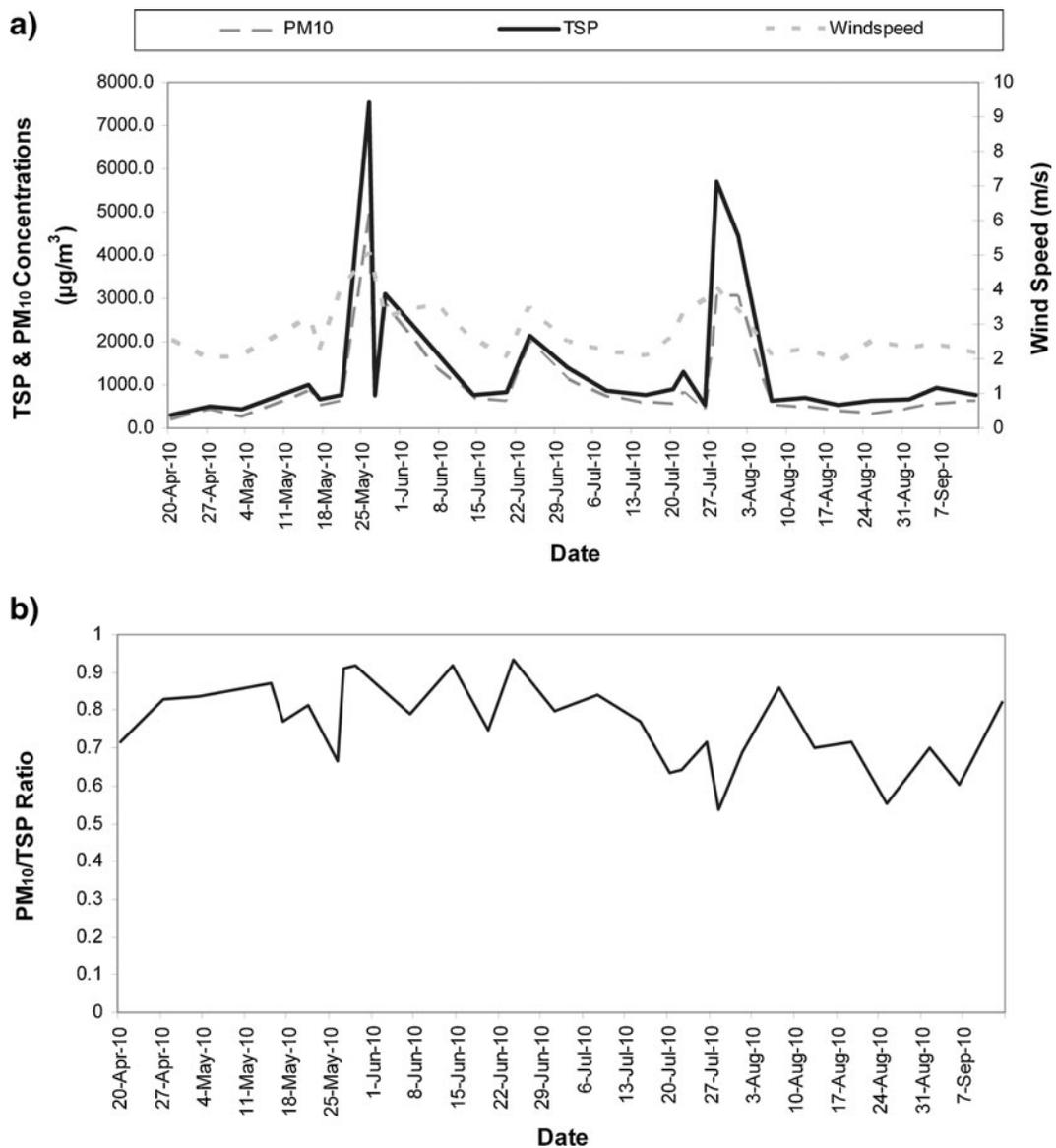


Fig. 2 Temporal trends for: a TSP and PM₁₀ concentrations; and b TSP/PM₁₀ ratio

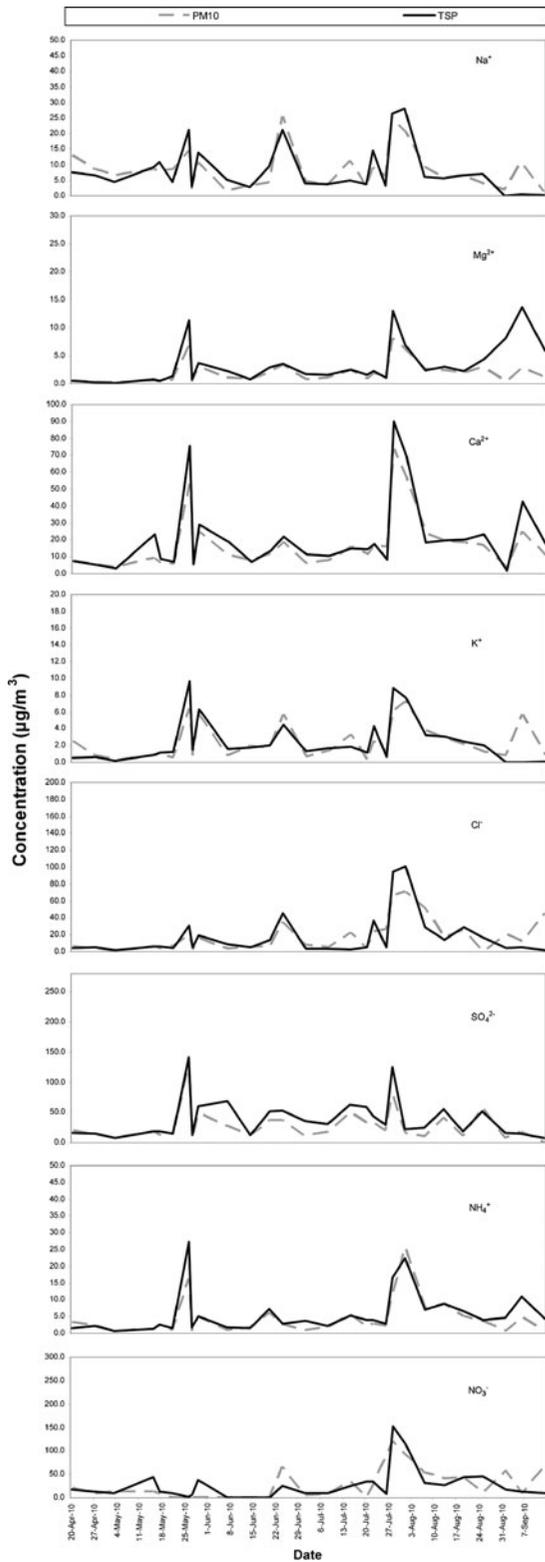


Fig. 3 Temporal trends of mass concentrations of the major ionic components in TSP and PM₁₀

24-h concentrations of up to 7,535.6 µg/m³ occurred, which has highly affected the air quality of the area. Corresponding value for PM₁₀ was 5,012.7 µg/m³, which is over 30 times higher than USEPA standards (USEPA 1997). According to the temporal trend of wind speeds, which is closely related to the trends of TSP and PM₁₀ mass concentrations, these pollution episodes were associated with the highest wind speeds, implying the major effect of meteorological conditions, especially wind speed, on dust storm occurrence.

It is noteworthy that TSP and PM₁₀ concentrations are closely associated during the study period. However, during the two sharp peaks of TSP (i.e., 25 May and 3 August 2010, as seen in Fig. 2a), PM₁₀ concentrations deviated from those of TSP, which can be seen more easily in the temporal trend of TSP/PM₁₀ ratios (Fig. 2b). Therefore, it can be implied that the MED storm particles mostly consist of large particles.

Trends of ionic components in TSP and PM₁₀

Temporal variations of the eight major ionic components in TSP and PM₁₀ are illustrated in Fig. 3. In general, no distinct temporal trend is observed for any of the components and their concentrations have small fluctuations during the year. The sharp peaks observed for most of the components match temporally with the mentioned major dust storms occurred during the study period (Fig. 2a). It is noteworthy that the mass concentrations of ionic components in TSP and PM₁₀ were closely related and followed the same pattern.

In the case of Ca²⁺, Mg²⁺, and Na⁺, which are the ions with crustal origin (Wang et al. 2006), the ionic concentrations are generally low except during the occurrence of dust storms. Na⁺ which can also originate from sea salt particles has less sharp peaks

Table 2 Matrix of correlation coefficients (R^2) among the ionic components in TSP

Species	F ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ²⁻
Na ⁺	0.19	0.56	0.04	0.38	0.26
NH ₄ ⁺	0.40	0.45	0.24	0.23	0.49
K ⁺	0.45	0.58	0.16	0.36	0.56
Mg ²⁺	0.26	0.24	0.12	0.24	0.29
Ca ²⁺	0.41	0.64	0.10	0.54	0.50

Table 3 $\text{NO}_3^-/\text{SO}_4^{2-}$, $\text{Ca}^{2+}/\text{Na}^+$, and Cl^-/Na^+ ratios in non-dust storm days (NDSs) dust storm days (DSDs)

Day situation	$\text{NO}_3^-/\text{SO}_4^{2-}$				$\text{Ca}^{2+}/\text{Na}^+$				Cl^-/Na^+			
	TSP		PM_{10}		TSP		PM_{10}		TSP		PM_{10}	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
NDSs	0.64	0.20–1.85	0.86	0.01–2.10	1.60	0.78–19.06	1.57	0.67–4.2	1.72	0.32–26.55	2.12	0.26–7.13
DSDs	0.54	0.01–1.50	0.30	0.01–1.13	3.07	0.95–89.21	2.7	0.85–9.35	0.55	0.35–7.52	0.49	0.19–2.05
Overall	0.59	0.01–1.85	0.58	0.01–2.10	2.36	0.78–89.21	2.13	0.67–9.35	0.86	0.32–26.55	1.30	0.19–7.13

during dust storms. Therefore, Ca^{2+} and Mg^{2+} can be considered better indicators of the MED.

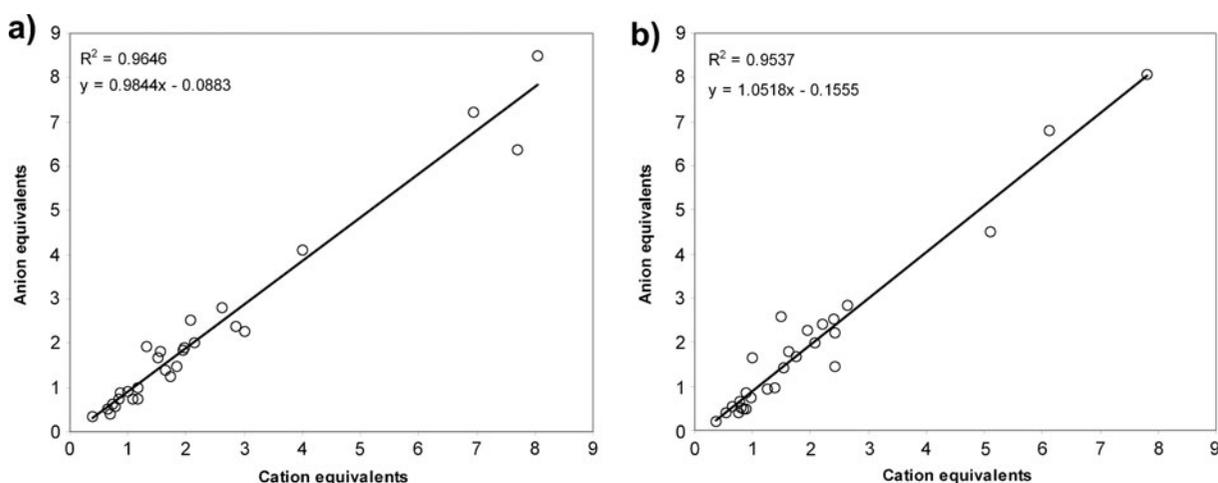
Ions with both crustal and pollution origin, i.e., Cl^- , K^+ , and SO_4^{2-} (Wang et al. 2006), had higher fluctuations during the study period. Although their concentrations peaked during dust storms, their relative contributions to the total mass of TSP and PM_{10} were lower than those of crustal ions (Fig. 1a, c) possibly because of their higher concentrations during the occurrence of dust storms. High Cl^- concentrations could originate from sea salt particles, since the study area is close to marine environment. Considerably high SO_4^{2-} concentrations in both TSP and PM_{10} could be associated with proximity of the sampling location to oil extraction and refinery plants, which are frequently found in this area.

Concentrations of NO_3^- , which mainly originates from fossil fuel combustion by motor vehicles (Wang et al. 2006), were evenly distributed during the study period and only a nearly sharp peak was observed during the dust storm that occurred in late July, when

concentrations of other ionic components were also high. Variations of NH_4^+ mass concentrations were closely related to those of NO_3^- , implying that NH_4^+ most probably originated from the neutralization between acidic components and NH_3 (Wang et al. 2006).

Possible chemical forms of the ionic components

As mentioned in “Material and methods,” to determine possible chemical forms of the ionic components, bivariate correlations were made among the anions and cations present in TSP. Table 2 presents matrix of correlation coefficients among the ionic components in TSP. As can be seen from the table, good correlations exist between Na^+ and Cl^- , NH_4^+ and SO_4^{2-} , K^+ and Cl^- , K^+ and SO_4^{2-} , Ca^{2+} and Cl^- , Ca^{2+} and NO_3^- , and finally Ca^{2+} and SO_4^{2-} , implying that forms of NaCl , $(\text{NH}_4)_2\text{SO}_4$, KCl , K_2SO_4 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and CaSO_4 may exist in TSP. Similar chemical forms have been reported by

**Fig. 4** Correlations between anionic and cationic components in: **a** TSP and **b** PM_{10}

other studies (Lia et al. 2008; Wang et al. 2006; Xiao and Liu 2004).

To investigate the possible indicators which can be used for identification of the MED storm, several ionic ratios were calculated and compared during DSDs and NDSs, of which $\text{NO}_3^-/\text{SO}_4^{2-}$, $\text{Ca}^{2+}/\text{Na}^+$, and Cl^-/Na^+ ratios had the highest differences between DSDs and NDSs and could therefore be used for this purpose (Table 3). $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio used to determine the relative importance of mobile sources versus stationary sources of N and S (Arimoto et al. 1996) was 0.64 and 0.54 during DSDs and NDSs, respectively, implying the higher importance of stationary sources of SO_4^{2-} and NO_3^- in the area. This can be further verified by the fact that several industries exist in the area which release their emissions into the atmosphere. $\text{Ca}^{2+}/\text{Na}^+$ ratios varied from 0.78 to 19.06 during NDSs and from 0.95 to 89.21 during DSDs. Because of these significant differences, this ratio can be considered as an indicator of the MED occurrence. Cl^-/Na^+ ratio which fluctuates from 0.32 to 26.55 during NDSs and from 0.35 to 7.52 during DSDs can also be considered useful for this purpose.

Finally, Fig. 4a, b illustrates correlations between anionic and cationic components in TSP and PM_{10} . As can be seen from the figure, strong correlations exist between anionic and cationic components both in TSP and PM_{10} . However, since the slope of the regression line for TSP is slightly lower than the unity, it shows that there might be slight anion deficiencies in TSP samples, which is possibly due to the fact that carbonate and bicarbonate ions were not measured in the present study (Meng and Lu 2007). For PM_{10} , in contrast, the higher-than-unity slope of the regression line implies possible existence of cation deficiencies in the PM_{10} samples. This can be attributed to vaporization of NH_4^+ into the gas phase during the experiments (Y. Wang et al. 2006). Since these deviations from the unity slope are negligible, TSP and PM_{10} samples can approximately be considered neutral.

Conclusions

Results of the present study revealed that concentrations of both TSP and PM_{10} during dust storm days were considerably higher than those during non-dust storm days, that the maximum PM_{10} concentration was over

30 times higher than USEPA standard during the most polluted dust storm. Besides, the particle concentrations during the MED storm were generally higher than those observed during the Asian dust storms, indicating the high level of air pollution during the occurrence of the MED in Ahvaz and the importance of its impact on the air quality of the area. In addition, concentrations of water-soluble ions were also higher during dust storm days. Ionic components were more concentrated in PM_{10} rather than TSP, though the ionic contribution to the total particle mass was not considerable. Ion proportions differed during dust storm days and non-dust storm days; crustal ions were most abundant during dust storm days, while secondary ions were dominant during non-dust storm days. This is mainly due to the difference between the origins of the two mentioned ion types. Results of this study suggested possible existence of chemical forms such as NaCl, $(\text{NH}_4)_2\text{SO}_4$, KCl, K_2SO_4 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and CaSO_4 in TSP. $\text{Ca}^{2+}/\text{Na}^+$ and Cl^-/Na^+ ratios were found to be useful as the indicators for identification of the MED occurrence. Both TSP and PM_{10} samples could be considered neutral with respect to the electric charge of the particles, though negligible derivations from neutral conditions existed. Further studies are necessary in order to evaluate the chemical composition of finer fractions of particulate matters (i.e., $\text{PM}_{2.5}$ and PM_1) during the Middle Eastern Dust storms mainly because of their fundamental role in human health effects.

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