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Effect Wind Speed and Dehydration Hamoun Wetland on Characterization of Ionic Composition of Tsp and Pm during the 120 Day Winds of Sistan, Iran

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ABSTRACT

Characterizing the ionic composition of total suspended particles (TSP) and particles on the order of ~2.5 µm or less ($PM_{2.5}$) during dust storms in Zabol in Jun to October 2014.TSP and $PM_{2.5}$ mass concentrations were considerably higher in period after dry wetland (ADW) compared with period during dry wetland (DDW) (1358.19 versus 1967.25 µg/m³ for TSP and 354.49 and 392 µg/m³ for $PM_{2.5}$). Mass concentrations of PM and TSP were ~6 times higher than USEPA standards. The percentage of the total aerosol mass contributed by the ions was higher in DDW than in ADW, showing that water soluble ions were more concentrated in the during dry wetland. Mg^{2+}/K^+ and Ca^{2+}/Mg^{2+} ratios were found to be useful as the indicators for identification of DDW and ADW and day with difference speed wind (D1 to D3) in during the 120 day winds. Results of the present study revealed that concentrations of both TSP and PM during days with speed >10 m/s were considerably higher than those during dust storm with speed wind <5 m/s. Calculation of enrichment factors for TSP and $PM_{2.5}$ relative to soil region indicated that K^+, NH_4^+, NO_3^- and NO_2^- mainly originated were mostly attributed for the anthropogenic activities.

Keywords: 120 day winds, TSP, $PM_{2.5}$, Water-soluble ions, Sistan, Zabol

INTRODUCTION

Dust storm is a weather phenomenon in which strong winds blow up a great deal of dust and sand causing local district visibility decreasing to less than 1 km [1]. Dust particles affect both regional and global environment in reducing visibility, changing of radioactive forcing and harming human health. Particulate matter (PM) has been given much attention in recent decades due to its potential adverse health impact and the subsequent need to have a better control or regulate these pollutants. The sources, characteristics and potential health effects of the larger or coarse particles (>2.5 mm in diameter) and smaller or fine particles (<2.5 mm in diameter) are very different; the latter can more readily penetrate into the lungs and are therefore more likely to increase respiratory and mutagenic diseases [2]. There is a widely accepted hypothesis that chemical components of particles and their capacity to carry potentially toxic substances may be the main factors for health effects, but it is not yet clear as to which factors are determinant. It was reported that water-soluble ions such as sulfate, nitrate and other acid-rain-related pollutants had severe effects on human health [3]. Dust particles would have harmful effects on human health, as ions are easier to be absorbed by human body [4].

The Hamoun basin, located on the Iran-Afghanistan border, has attracted scientific interest during recent years, since it constitutes a major dust source region in southwest Asia, often producing intense dust storms that cover the Sistan region of eastern Iran, southwest Afghanistan and Pakistan [5-8]. Particles from dust storms might also cover farm and grasslands to result in damage to crops and fill the rivers and water channels with aeolian material. After the extreme drought of 1999, the dust activity over Sistan appears to be increasing in both frequency and severity. Over recent years, ten thousands of people have suffered from respiratory diseases during months of devastating dust storms in the Sistan basin, especially in the cities of Zabol and Zahak and the surrounding villages [9]. However, no studies have been performed for evaluation of the ionic components in particulate matters during the 120 day winds, 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 $PM_{2.5}$ during the dust storms in Zabol, Iran. The study was conducted over the period from Jun to October 2014, as this is the time period with highest number of dust storms in this region. Also in this study the effect of dewatering the wetland and the wind speed was invested on TSP and $PM_{2.5.}$

MATERIALS AND METHODS

Study area

Sistan is a densely populated enclave in the scarcely populated south-eastern part of Iran and lies between the Latitudes 30°450′N to 31°30′N and the Latitudes 60°510′E to 62°50′E (Figure 1). It covers an area of approximately 15,197 km^2 and has a population of about 400,000. The Sistan region includes 980 villages and four cities. The climate is arid, with low annual average precipitation of ~55 mm occurring mainly in the winter (December to February) and evaporation exceeding ~4000 mm $year^{-1}$ [10]. Hamoun Lake lying on the north of Sistan plain is recharged by the Hirmand River, which flows from the Paghman Mountains just west of Kabul to end in Sistan after a journey of 1,400 km [11]. Hirmand River, at the boundary of Iran and Afghanistan, is divided into two branches (Sistan and Parian). The Sistan branch travels through the Sistan plain and flows to the southwest part of lake (Hamoun Hirmand and Hamoun Saburi). That is, the Parian branch travels along the boundary of Iran and Afghanistan and finally flows into the east part of Lake (Hamoun Puzak) Water in the Hamoun lakes is rarely more than 3 m deep, and the size of the lakes varies both seasonally and intra-annually. Maximum expansion takes place in late spring, following snowmelt in the mountains. In years of exceptionally high runoff, the Hamoun lakes overflow their low divides and create one large lake that is approximately 160 km long and 8-25 km wide with ~5700 km^2 surface area and a volume of 13,000 million m^3 [12]. It is a major oasis of freshwater cover in a very dry region surrounded by hundreds of kilometers of arid plains, where potential evapo-transpiration is more than 4m annually. This makes for a system that is very vulnerable to climatic fluctuations and modifications of water inflow by humans. As the annual perspiration varies less in the Sistan area, drought can occur in the form of hydrological drought, when the amount of water flow by Hirmand River declines. Fluctuation in incoming water and repetitive droughts are mainly due to natural elements (e.g. climatological drought in Afghanistan) and human activities such as water flowing control by dams. The plentiful natural flow of the Hirmand River is reduced by the irrigation dams in Afghanistan; the Arqhandab and Kajaki dams extract about half of the 12 billion m^3, which enters into the Afghan plain. Severe droughts during the past decades, especially after 1999, have caused desiccation of the Hamoun lakes [13] leaving a fine layer of sediment that is easily lifted by the wind [14], thus modifying the basin to one of the most active sources of dust in southwest Asia [15]. During summer, the area is under the influence of a low pressure system attributed to the Indian thermal low that extends further to the west as a consequence of the south Asian monsoon system. These low pressure conditions are the trigger for the development of the Levar northerly wind, commonly known as the ''120 day winds''. The most important meteorology-atmospheric phenomenon over the region that controls the dust activity, air quality and human health which causes frequent dust and sand storms, especially during June–August.

Sampling

Source samples were collected at Hamoun Puzak, Hamoun Saburi. Each surface sample was collected using a shovel to scrape the top 5 cm from the ground surface within an area of 30 cm^2. A total of 1 to 1.5 kg of each sample was collected and placed into plastic bags at each site and sealed [16]. Samples were sieved through Tyler 30, 50, 100, 200 and 400 mesh sieves to obtain about 5 g of material. The nominal geometric diameter is <38.5 μm for the 400 mesh sieve, which is equivalent to the aerodynamic diameter of TSP [17]. Then, they were put into covers until the sampling time [18].

The sampling station was located at an urban background area in the city on the roof top of the Zabol Department of Environmental Protection at the height of 5 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 $PM_{2.5}$ samples were collected Three days in a week from 24 June to 2 October 2015, which is believed to be the time period with the most frequent occurrence of dust storm in this region [19]. In addition, further sampling was also conducted in the case of dust storm occurrence. TSP and $PM_{2.5}$ sampling was conducted using two separate low-volume samplers equipped with cyclones that had a cut-off size of <10 µm and TSP (Model Chrono, Zambelli, Italy) operating at a flow rate of 16.7 L/min. For each sample, prevailing temperature and pressure during each sampling campaign was used to determine the actual air volume under standard conditions (25°C and 1 atm). Teflon filters (0.45 µm pore size and 47 mm i.d.) were used and weighted using an analytical balance (ae ADAM model: A°C AA 160LE) with a reading precision of 0.1 mg [20]. Then, they were put into covers until the sampling time [18]. After the sampling, particle concentrations were obtained by gravimetric method. The filters were kept in the refrigerator at 4°C till the chemical analysis [21].

Chemical analysis of water-soluble ions

The filters were cut into four pieces using cleaned scissors. After that, ¼ fraction of each filter of each sample filter was ultrasonically extracted for 60 min with 10 ml of 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 cellulose acetate filter (Sartorius) and kept in plastic vials with a temperature of 4°C until the chemical analysis [22]. Water soluble inorganic ions of the water extract were analyzed using a Shimadzu ion chromatograph system equipped with Shimadzue HPLC pump model LC 10AD and the conductivity detector model CDD-6A. The concentration of the cations (Na^+, NH_4^+ and K^+) was determined through the use of a Shim-pack IC-C1 (Shimadzu DGU-12A), using a 5 mM nitric acid solution as an eluent. The anions (SO_4^{2-}, NO_3^-, NO_2^- and Cl^-) were separated by a Shim-pack ICA1 (Shimadzu DGU-12A), using 2.5 mM phethalic acid combined with 2.4 mM tris-(hidroximetil) aminometano as the eluent [23]. The concentration of Ca^{2+} and Mg^{2+} was determined by a flame atomic absorption spectrometer (Philips, PU9400X, England). A pH meter (Hana 83141 pH meter, Europe, Romania) was used for measuring the pH of aqueous solutions. Unused filters were also extracted to determine the blank values. Sample quantities exceeding the LOD were quantified and blank quantities were corrected by subtracting the mean blank amount from the sample amount. The detection limit was utilized to determine the lowest concentration level that could be detected, which is statistically different from a blank. In this study, the detection limits of the ions (S/N=3) were 0.06, 0.03,0.02, 0.16, 0.15, 0.02, 0.001, 0.02 and 0.01 mg l^{-1} for Cl^-, NO_3^-, NO_2^-, SO_4^-, Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}, respectively. The quality of the measurements made via ion chromatography and atomic absorption spectrometry was checked through calibration after every 10 samples and deviations of ≥ 5% were adjusted by running new standard solutions. So as to calculate the recovery efficiencies, the samples were evaluated by their spiking with a known amount of ion standard solution. The analytical procedure for the recovery test was the same as that for field samples. Sample spike recoveries were within the acceptable range of 81.0%–100.7%. The relative standard deviation was less than <5% for the above ionic species.

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, R 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 [24].

RESULTS AND DISCUSSION

Mass concentration of TSP and PM2.5 and their ionic components

Eighty-four samples were collected for each pollutant at the sampling station in Zabol during the study period. Mean TSP and $PM_{2.5}$ mass concentration was 1365.8 and 322.1 µg/m^3 during the entire study period (Table 1). It is noteworthy that the particle concentrations observed in the present study during the 120 day winds Sistan are generally higher than those observed during the Asian dust (AD) storms [24–26] and only TSP in the case of Beijing with concentration 1,949 µg/m^3 and $PM_{2.5}$ in Xian in haze and straw days with concentration 351.2 and 404.1 have higher mean than this study [21,24]. Mass concentrations of the ionic components in TSP and PM were in the following order: Ca^{2+}>NH $^{4+}$>K^+>SO_4^{2-}>Cl^->Na^+>NO^{3-}>Mg^{2+}=NO^{2-}. This shows that Ca^{2+}, NH^{4+}, K^+ and SO_4^{2-} are the most frequently found constituents in TSP and $PM_{2.5}$ in the study area.

The effects of dehydration wetland on TSP and PM and their ionic components

During 2014, Sistan experienced abnormally high precipitation and the Hirmand catchment area contributed to increased water surface in the lakes and ~20% of the wetland was drained (Figure 2b) and again dry in 13 July 2014 (Figure 2c). To compare the effect of water entering the wetland on the quantity and quality TSP and PM2.5 in this

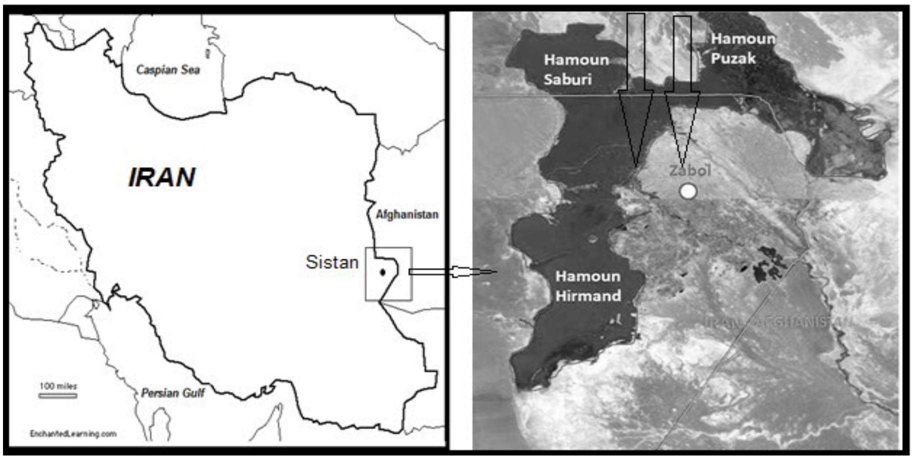

Figure 1: Sampling site location, wind direction in Sistan

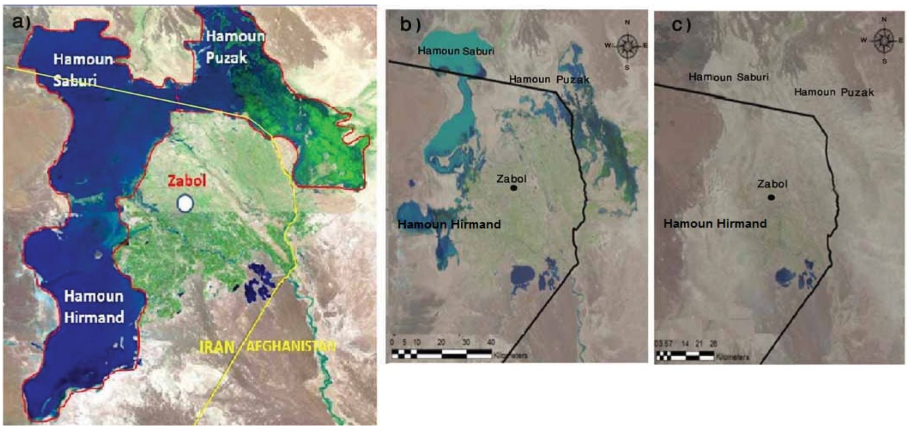

Figure 2: (a) Position of the Hamoun wetland in Iran and Afghanistan, showing a maximum inundation period. (b) Position and level water of the Hamoun wetland in 12 May, 2014. (c) Position and level water of the Hamoun wetland in 12 July, 2014

Table 1: Summary statistic for mean ± SD total mass concentration of TSP and $PM_{2.5}$ and their ionic component over the study period in Sistan

Species	TSP (µg/m³)		$PM_{2.5}$ (µg/m³)	
	Mean	SD	Mean	SD
Mass	1365.8	1745.9	322.1	362.1
Na^+	5.7	8.1	3.1	4.1
$NH4^+$	12.1	12.1	7.5	5.1
K^+	10.4	10.4	6.9	5.3
Mg^{2+}	1.2	0.8	0.8	0.5
Ca^{2+}	14.8	10.6	10.1	6.8
Cl^-	6.1	9.5	2.3	3.2
NO_2^-	1.2	2.3	0.6	1.1
NO_3^-	2.5	2.3	1.5	1.1
SO_4^{2-}	7.7	7.4	4.1	2.4

study days with wind speeds identical were compared with each other's in during the drying wetlands (DDW) and after dry wetland (ADW) (Figure 2).

TSP and $PM_{2.5}$ mass concentrations during the drying wetlands (DDW) and after dry wetland (ADW) are given in Table 2. TSP mass concentrations were considerably higher in ADW compared with DDW (1358.19 vs. 1,867.25 µg/m³). For $PM_{2.5}$, average mass concentration was found to be 354.49µg/m³ and 392 µg/m³ during DDW and ADW, respectively. Compared with the daily average of the "standard value" of 300 µg/m³ for TSP and the daily average of 65 µg/m³ for PM (US EPA, 1997), Although $PM_{2.5}$ and TSP before and after drying wetland was higher than the standard USEPA, mass concentrations of PM and TSP were very higher than the standards in ADW period, with mean 392 and 1867.25 µg/m^3 which is ~6 times higher than USEPA standards for $PM_{2.5}$ and TSP that showing $PM_{2.5}$ and TSP particle pollution was a very serious issue in Sistan especially in after drying wetland Hamoun period.

Through months of devastating sand storms in Sistan Basin, especially the cities Zabol and surrounding villages. With the storm lasting about 5 days, more than 3,000 people suffering from allergy and respiratory diseases went to hospitals or health centers. Miri et al. [9] showed that 63% of the people of Zabol suffer from respiratory diseases with the majority coming from villages rather than the city. Miri et al. [9] indicated that 132,000 people have been considered as patients suffering from respiratory diseases related to the dust storms. The health damages to the population were estimated at over US $66.7 million in the period 1999–2004. The information obtained from hospitals indicated that most of the patients who visited hospitals suffered from chronic obstructive pulmonary disease (COPD) and asthmatic diseases with the peak of incidence during the summer season (June, July and August) when the severest dust storms occur. It is estimated that 90% of the population living in the region suffered from respiratory problems in June, July, August and September. Medical costs for patients for the period of study exceeded US $166.7 million [9]. Asthma Mortality of Iran the rate of asthma in Zabol is higher than in other cities in Sistan and Baluchistan Provinces [27]. The ratios of $PM_{2.5}$ to TSP mass concentrations for DDW and ADW were 0.26 and 0.2, therefore in the period DDW the windstorm in Sistan had the greatest proportion of $PM_{2.5}$ particles. $PM_{2.5}$ concentration during DDW not many changes but TSP has more changes. It shows the bottom of the wet land is a source of TSP particles in the Sistan region.

Concentration ions of DDW and ADW periods shown in Table 2. The TSP total ion mass concentration was 55.55 and 76.62 µg/m^3 on average during DDW and DW, and this accounted for 6.48% and 7.83% of the TSP mass in DDW and ADW. The $PM_{2.5}$ total ion mass concentration was 28.03 and 44.76 µg/m^3 on average during DDW and ADW, and this accounted for 12.18% and 18.04% of the $PM_{2.5}$ mass. In general, the percentage of the total aerosol mass contributed by the ions was higher in PM than TSP, showing that water soluble ions were more concentrated in the coarse particle, also the percentage of the total aerosol mass contributed by the ions was higher in DDW than in ADW, showing that water soluble ions were more concentrated in the during dry wetland.

To investigate the possible indicators which can be used for identification in ADW and DDW in during the 120-day winds Sistan, several ionic ratios were calculated and compared during ADW and DDW, of which Mg^{2+}/K^+ ratios had the highest differences between ADW and DDW and could therefore be used for this purpose (Table 3). Mg^{2+}/K^+ ratios varied from 0.09 to 1.05 during DDW and from 0.02 to 0.39 during ADW for TSP and 0.06 to 1.88 during DDW and from 0.02 to 0.88 during ADW for $PM_{2.5}$. Because of these significant differences, this ratio can be considered as an indicator of DDW and ADW in region Sistan.

The effects of wind speed on TSP and PM2.5 and their ionic components

To compare the wind speed on the intensity of dust in this region, just days after drying wetland compared with each other. The 120 day winds in Sistan were classified into three groups based on their wind speed, winds with a speed

Table 2: Mean ± SD TSP and $PM_{2.5}$ in during dry wetland (DDW) and after dry wetland (ADW)

Species	Number	Mass	Na^+	$NH4^+$	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
$PM_{2.5}$											
DDW	7	354.49 ± 336.41	1.44 ± 0.69	5.15 ± 1.89	4.76 ± 2.17	0.59 ± 0.36	9.66 ± 8.38	1.20 ± 1.03	0.20 ± 0.32	1.24 ± 0.71	3.80 ± 2.97
ADW	20	392.00 ± 424.53	4.53 ± 5.20	9.50 ± 5.67	8.65 ± 6.35	0.82 ± 0.57	11.07 ± 6.85	3.09 ± 4.15	0.84 ± 1.26	1.77 ± 1.42	4.54 ± 2.62
TSP											
DDW	7	1358.19 ± 1245.33	3.31 ± 2.69	12.76 ± 17.68	7.86 ± 7.67	1.45 ± 1.33	16.86 ± 15.57	1.87 ± 2.94	1.30 ± 2.83	2.62 ± 3.21	7.61 ± 8.65
ADW	20	1967.25 ± 2062.67	8.31 ± 10.22	14.15 ± 11.60	13.05 ± 12.58	1.22 ± 0.68	16.82 ± 8.95	9.38 ± 11.89	1.37 ± 2.74	2.82 ± 2.45	9.50 ± 8.06

Table 3: Mg^{2+}/K^+ ratios in during dry wetland (DDW) and after dry wetland (ADW)

Day situation				
Mg^{2+}/K^+				
	PM2.5		TSP	
	Mean	Rang	Mean	Rang
DDW	0.32	0.06-1.88	0.28	0.09-1.05
ADW	0.15	0.02-0.88	0.13	0.02-039

of 1 to ≤ 5 m/s (D1), winds with a speed of >5 to 10 m/s (D2) and winds with a speed >10 m/s (D3). The winds were blowing from the north for all of the sampling periods.

During 120 day winds in Sistan, the mass concentration increased with the increase of wind speed in $PM_{2.5}$ and TSP, which indicated that more re-suspended particles from the local sources were brought to the dust air. Concentration ions in D1, D2 and D3 shown in Table 4. The TSP total ion mass concentration was 12.74, 13.61 and 7.27 µg/m^3 on average during D1, D2 and D3 and this accounted for 5.95%, 1.29% and 0.22% of the TSP mass in D1, D2 and D3. The $PM_{2.5}$ total ion mass concentration was 29.18, 37.61 and 50.63 µg/m^3 on average during D1, D2 and D3 and this accounted for 19.62%, 18.49% and 7.39 % of D1, D2 and D3 in the PM mass. In general, the percentage of the total aerosol mass contributed by the ions was higher in $PM_{2.5}$ than TSP, showing that water soluble ions were more concentrated in the coarse particle, also the percentage of the total aerosol mass contributed by the ions decrease with increase speed wind in Sistan in during 120 day winds.

During 120 day winds in Sistan, the concentration NO_3^- increased with the increase of wind speed in $PM_{2.5}$ of D1 to D2, but don't increase of D2 to D3. It shows when the wind speed is less than 10 m/s natural resources and anthropogenic resources similar fossil fuel combustion by motor vehicles are the most important source NO_3^- but when the wind speed >10 m/s natural resources have a greater role in the production of NO_3^- than anthropogenic resource in this region.

For $PM_{2.5}$, average mass concentration was found to be 135.99, 271.36 and 1226.05 µg/m^3 and for TSP was found to be 201.14, 926.09 and 3198.22 in during D1, D2 and D3, respectively. Compared with the daily average of the "standard value" of 300 µg/m^3 for TSP and the daily average of 65 µg/m^3 for $PM_{2.5}$ (US EPA, 1997), Although TSP in D1 higher than the standard USEPA, mass concentrations of TSP were very higher than the standards in D2 and D3, with mean 926.09 and 3198.22 µg/m^3 which is 3 and 10 times higher than USEPA standards for TSP. For $PM_{2.5}$ mass concentration was 3 and 10 times higher than USEPA standards in D2 and D3, which show $PM_{2.5}$ and TSP particle pollution were a very serious issue in Sistan especially with increase wind speed after drying wetland Hamun period.

The ration PM /TSP in D1, D2 and D3 was 0.71, 0.21 and 0.22, respectively. Also, according to the temporal trend of wind speeds, which are closely related to the trends of TSP and PM 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 (Figure 3a). It is noteworthy that TSP and $PM_{2.5}$ concentrations are closely associated during the study period. However, during the six sharp peaks of TSP (i.e., 25 June, 17 July, 2 August and 17 August, 3 September, 17 September and 29 September, 2014, as seen in Figure 3b), PM concentrations deviated from those of TSP, which can be seen more easily in the temporal trend of $PM_{2.5}$/TSP ratios (Figure 3b). Therefore, it can be implied that the 120 wind day of Sistan particles mostly consist of large particles (Figure 3).

Also Mg^{2+}/Ca^{2+} ratios varied from 4.27 to 12.15 during D1 and from 5.68 to 32.55 during D2 and from 8.29 to 57.4 during D3 for $PM_{2.5}$ and also, 2.06 to 7.70 during D1 and from 8.05 to 23.31 during D2 and from 7.06 to 31.14 during D3 for TSP (Table 5). Because of these significant differences, this ratio can be considered as an indicator from D1 to D3 in Sistan in during 120 days wind in region Sistan.

Table 4: Mean ± SD, TSP and $PM_{2.5}$ in winds with a speed of 1 to ≤ 5 m/s (D1), winds with a speed of >5 to 10 m/s (D2) and winds with a speed >10 m/s (D3)

Species	Number	Mass	Na^+	$NH4^+$	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
$PM_{2.5}$											
D1	7	148.72 ± 60.88	1.78 ± 1.17	4.24 ± 2.71	4.56 ± 3.03	1.45 ± 0.76	10.54 ± 6.75	2.13 ± 1.74	0.53 ± 0.80	1.30 ± 0.41	3.07 ± 1.84
D2	18	203.36 ± 137.78	3.14 ± 3.38	8.86 ± 4.17	7.84 ± 4.28	0.73 ± 0.55	8.64 ± 5.24	2.30 ± 3.34	0.61 ± 1.07	1.71 ± 1.41	3.88 ± 2.11
D3	8	691.22 ± 604.91	5.90 ± 7.39	9.29 ± 8.40	8.67 ± 9.53	0.82 ± 0.52	13.97 ± 8.28	3.69 ± 5.01	1.10 ± 1.39	1.77 ± 1.18	5.43 ± 2.93
TSP											
D1	7	207.14 ± 67.21	2.71 ± 1.37	4.81 ± 2.25	4.63 ± 1.98	1.58 ± 1.10	8.39 ± 9.70	3.30 ± 2.22	0.90 ± 0.76	1.69 ± 1.05	3.30 ± 2.36
D2	18	926.09 ± 130.14	6.51 ± 9.66	13.56 ± 9.80	12.23 ± 9.06	1.04 ± 0.65	13.28 ± 8.34	6.67 ± 11.32	0.82 ± 0.98	2.37 ± 1.76	6.78 ± 4.50
D3	8	3198.22 ± 2695.02	8.63 ± 9.90	12.40 ± 3.66	12.32 ± 17.29	1.45 ± 0.53	20.42 ± 8.08	11.26 ± 10.75	2.36 ± 4.38	3.58 ± 3.17	13.36 ± 11.29

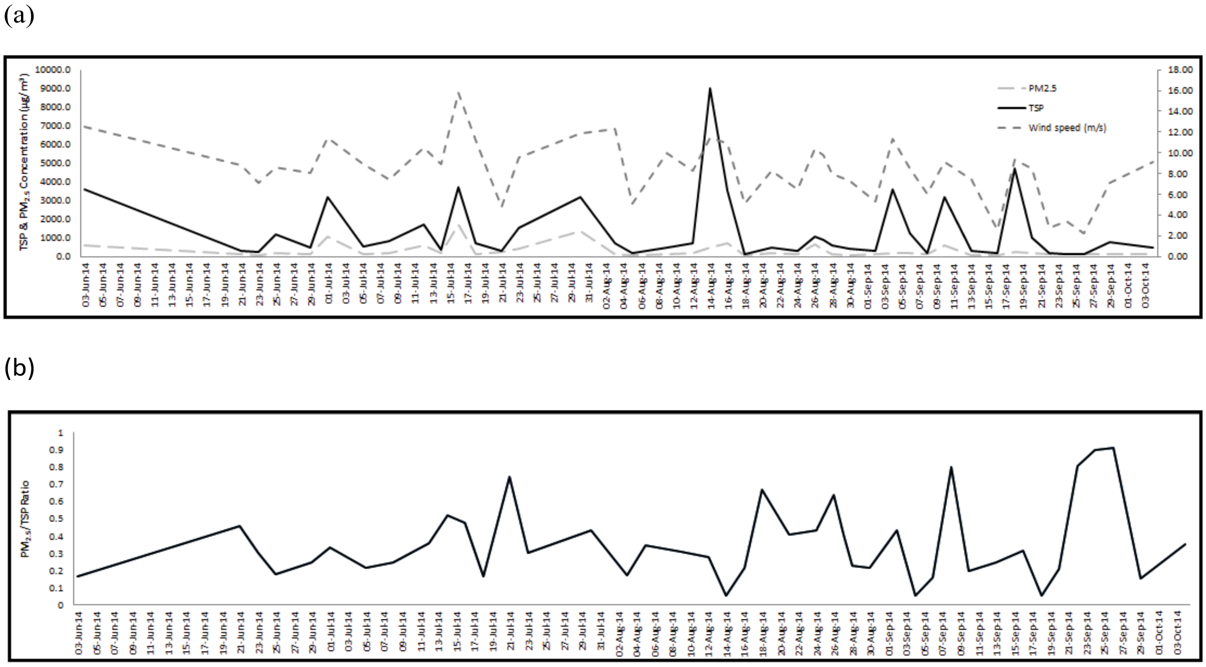

Figure 3: Temporal trends for: (a) TSP and $PM_{2.5}$ concentrations; and (b) $PM_{2.5}$/TSP ratio

Table 5: Ca^{2+}/Mg^{+} TSP and $PM_{2.5}$ in winds with a speed of 1 to ≤ 5 m/s (D1), winds with a speed of >5 to 10 m/s (D2) and winds with a speed >10 m/s (D3)

Day situation				
	Ca^{2+}/Mg^{+}			
	PM2.5		TSP	
	Mean	Range	Mean	Range
D1 (n=5)	7.74	4.27-12.15	5.00	2.06-7.70
D2 (n=20)	13.2	5.68-32.55	13.17	8.05-23.31
D3 (n=8)	19.69	8.92-57.40	15.27	7.06-31.14

Enrichment factor

The EF for the elemental component of PM can be calculated using the following equation:

$$EF=\{[C]_A/[Ca]_A\}/\{[C]_B/[Ca]_B\}$$

where $[C]_A$ and $[Ca]_A$ are the concentrations of the component samples and the reference element in the dust storms, while $[C]_B$ and $[Ca]_B$ are the mean concentrations of component and the reference component in the soil samples this region. Reference component in this study was Ca [28,29].

The EF of NH_4^+, K^+, Mg^{2+}, Na^+, SO_4^{2-}, NO_3^-, Cl^- in the aerosol samples collected in D1 to D3 are given in Table 6. According to with category EF the major water-soluble ions could be classified into three groups (Table 7) [30]. The mean EF for particulate is also higher in the ADW than in the DDW except Mg^{2+} that higher in DDW and may be this is due to the presence of water in Saburi and Pozak Hamoun (Table 6).

The EF high NH_4^+, K^+, NO_2^- and NO_3 concentrations suggest the effect of local anthropogenic emissions .The mean EF high NH_4^+, K^+, NO_2^- and NO_3 decrease in D3 with increase wind speed in compare with wind speed in D1 and D2 in region (Table 8). The EF NH_4^+, K^+, NO_2^- and NO_3 in samples D1 and D2 decreased significantly when the wind speed >10 m/s in this region in samples D3. This result suggested that NH_4^+, K^+, NO_2^- and NO_3 mainly originated from the local pollution sources and diluted by the invaded dust storm with speed >10 m/s (Table 4). Concentrations of NO_3^- and NO_2^- mainly originate from fossil fuel combustion by local motor vehicles.

Particulate NH_4^+ is formed by the neutralization between ammonia gas and acidic species and the major sources for ammonia gas includes animal farming, fertilizers and organic decomposition. It was clear that over the surrounding regions of Zabol city in Sistan, there are many fields for agricultural cultivation and the chemical nitrogenous fertilizers, such as carbamide, NH_4HCO_3, NH_4NO_3 and NH_4Cl, are the prevailing fertilizers. In summer, the dry weather with

Table 6: EF values TSP and $PM_{2.5}$ in during dry wetland (DDW) and after dry wetland (ADW)

EF		Na^+	NH4+	K^+	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
TSP DDW	Mean	1.33	6.82	10.08	1.53	0.49	6.87	5.52	0.65
	Min	0.16	1.99	3.34	0.43	0.04	0.00	1.52	0.17
	Max	3.32	15.93	20.59	4.67	0.99	21.91	9.21	1.03
TSP ADW	Mean	1.59	7.07	13.12	0.90	2.25	7.43	5.09	0.77
	Min	0.42	1.36	2.61	0.38	0.45	0.00	2.85	0.38
	Max	4.64	14.27	32.69	1.67	12.11	43.68	12.16	2.00
$PM_{2.5}$ DDW	Mean	0.84	6.07	10.58	0.97	0.48	4.43	5.01	0.59
	Min	0.28	1.73	1.65	0.57	0.17	0.00	2.29	0.23
	Max	1.88	11.72	19.94	2.27	0.83	19.32	9.34	0.87
$PM_{2.5}$ ADW	Mean	1.47	8.83	15.67	0.94	1.05	7.19	5.30	0.66
	Min	0.27	1.89	1.14	0.21	0.24	0.00	0.88	0.10
	Max	5.08	20.39	51.37	2.08	4.28	34.53	12.59	1.49

Table 7: Enrichment categories on the basis of EF values

EF<2	Deficiency to minimal enrichment
EF<2	Deficiency to minimal enrichment
$2 \leq EF<5$	Moderate enrichment
$5 \leq EF<20$	Significant enrichment
$20 \leq EF<40$	Very high enrichment
$EF \geq 40$	Extremely high enrichment

Table 8: EF values TSP and $PM_{2.5}$ in winds with a speed of 1 to ≤ 5 m/s (D1), winds with a speed of >5 to 10 m/s (D2) and winds with a speed >10 m/s (D3)

EF		Na^+	NH4+	K^+	Mg^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
$PM_{2.5}$ D1	Mean	0.91	4.89	9.47	1.74	1.12	8.40	5.36	0.58
	Min	0.06	0.61	1.22	0.97	0.07	0.00	1.21	0.07
	Max	1.87	12.24	19.58	2.76	2.61	37.06	11.55	1.39
$PM_{2.5}$ D2	Mean	1.35	9.78	17.88	1.01	0.99	5.88	6.34	0.74
	Min	0.16	1.83	0.86	0.36	0.24	0.00	0.88	0.10
	Max	5.08	23.82	51.27	2.08	4.28	18.49	11.86	1.59
$PM_{2.5}$ D3	Mean	1.38	6.18	11.14	0.78	0.94	8.81	4.61	0.61
	Min	0.27	1.89	1.14	0.21	0.29	0.00	2.29	0.42
	Max	4.16	17.72	30.29	1.32	2.01	34.53	12.59	1.13
TSP D1	Mean	2.74	13.04	23.87	2.55	3.35	25.44	15.64	1.43
	Min	0.80	9.23	16.92	1.07	0.50	7.65	5.85	0.52
	Max	4.71	18.65	34.72	5.74	6.81	59.39	36.12	3.41
TSP D2	Mean	1.46	7.33	14.37	1.04	2.08	7.60	5.46	0.77
	Min	0.07	0.78	1.23	0.38	0.07	0.00	1.20	0.09
	Max	4.64	14.27	32.62	3.01	12.11	43.68	12.16	2.00
TSP D3	Mean	1.29	5.01	8.60	1.01	1.85	5.74	4.53	0.68
	Min	0.42	2.22	4.15	0.70	0.67	0.00	2.78	0.50
	Max	2.67	11.41	21.57	1.67	6.84	19.09	8.31	0.99

wind could lead these lands to be the seasonal aerosol sources, from which those aerosols originated would contain more ammonium and easily transport to Zabol. In a rural area, a high concentration of NH_4^+ is usually an indication of agricultural activities [31,32]. Therefore, it is thought that the fertilizer put in the fields might have its effects on concentration NH_4^+ this region. This shows the importance of the fertilization effect on the NH_4^+ concentration found in a rural atmosphere during the period studied here. Lee et al. [33] and Seto et al. [34] have also found similar results in Hiroshima, Japan and in the Korean peninsula, respectively.

The major natural sources for particulate K^+ are sea salts and soils, and biomass burning constitutes the major part of its anthropogenic source [35]. There isn't industrial plant and source anthropogenic in Sistan region for K^+. Biomass burning by villagers is the most important source of K^+ in Zabol and the use of biomass fuel in stormy days and dilution K^+ to the strong wind in the region is decrease EF potassium in D3.The results show that although the concentration of NH_4^+, K^+ and NO_3 with increasing wind speed increases, but the impact of human activities by increasing the wind speed decreases in the Sistan region.

Ion balance and carbonate calculation

Correlations between anionic and cationic components in $PM_{2.5}$ in DDW and ADW were (R^2=0.89 and R^2=0.90) and for TSP in DDW and ADW were (R^2=0.93 and R^2=0.81). As can be seen strong correlations exist between anionic and cationic components both in TSP and $PM_{2.5}$ difference period in Sistan. However, since the slope of the regression line for TSP and $PM_{2.5}$ is slightly lower than the unity, it shows that there might be slight anion deficiencies in TSP and $PM_{2.5}$ samples, which is possibly due to the fact that carbonate and bicarbonate ions were not measured in the present study. Therefore, the anion deficit could be the indicator of carbonate ion in aerosol, i.e., the alkalinity of aerosol. The correlation between total equivalents of cations and anions in the two cases of TSP and $PM_{2.5}$ aerosols were very different in ADW period. In ADW period $PM_{2.5}$ samples, a good correlation was achieved with a R^2=0.90, while in TSP samples, the R^2=0.81, which indicated that the alkalinity of aerosols increased significantly with the increase of the particle size in ADW period.

Mineral dust is the main source for aerosol carbonate [36,37] and when relatively high concentrations of this ion are present, aerosol acidity can be buffered [38]. Unfortunately, carbonate cannot be directly determined by our analytical methods because carbonate is contained in the chromatographic eluent. However, estimates of the carbonate concentration can be made based on the differences in the measured cations minus anions (in µg m^3) as follows [39]:

$CO_3^{2-}=(Na^++NH_4^++K^++Ca^{2+}+Mg^{2+})-(Cl^-+NO_3^-+NO_2^-+SO_4^{2-})$

The calculated CO_3^{2-} mass concentration averaged 20.03 and 26.05 µg/m^{-3} for $PM_{2.5}$ and TSP the entire study, and this would account for 6.21% and 1.9% of the total $PM_{2.5}$ mass and TSP mass.

The concentrations of Ca^{2+} in $PM_{2.5}$ were strongly correlated with those of the calculated CO_3^{2-}(R=0.83, P<0.01) in DDW period but in ADW period NH^{2+} were strongly correlated with those of the calculated CO_3^{2-} (R=0.87, P<0.01) and this implies that the CO_3^{2-} and NH_4^{2+} and CO_3^{2-} and Ca^{2+} likely originated from the same source in period DDW and ADW, most likely mineral dust. Also, the concentrations of Ca^{2+} in TSP were strongly correlated with those of the calculated CO_3^{2-} in DDW (R^2=0.86) and NH_4^{2+} and CO_3^{2-} in ADW period and (R=0.67) and this implies that the $CO_3^{2-}$and NH_4^{2+} and CO_3^{2-} and Ca^2 likely originated from the same source in period DDW and ADW, it indicates that Ca_2CO_3 and $(NH_4)_2CO_3$ were the form for CO_3^{2-} in the TSP samples.

Carbonate concentrations in the $PM_{2.5}$ of D1 to D3 increase wind speed in region of 15.5, 20.6 and 26.6 but for TSP increase of D1=12.9 to D2=29.9 and decrease in D3=24.6. In total in D1, D2 and D3 correlation $CO_3^{2-}$and NH_4^{2+} in TSP and $PM_{2.5}$ was (R^2=0.67 and R^2=0.80). Therefore, airborne $CaCO_3$ may provide the important atmospheric alkaline component for buffering acid aerosol in Sistan region from Iran.

The titration test represents samples which include 27% to 42.6% carbonate minerals in soil Sistan [40] and shows the amount of carbonate in soil is very high and can be resource carbonate in $PM_{2.5}$ and TSP samples.

CONCLUSION

TSP mass concentrations were considerably higher in ADW compared with DDW (1358.19 vs. 1967.25 µg/m^3). For $PM_{2.5}$, average mass concentration was found to be 354.49 µg/m^3 and 392 µg/m^3 during DDW and ADW, respectively. Mass concentrations of $PM_{2.5}$ and TSP were very higher than the standards in ADW period, with mean 392 and 1967.25 µg/m^3 which is ~6 times higher than USEPA standards for $PM_{2.5}$ and TSP. the percentage of the total aerosol mass contributed by the ions was higher in DDW than in ADW, showing that water soluble ions were more concentrated in the during dry wetland. Mg^{2+}/K^+ and Ca^{2+}/Mg^{2+} ratios were found to be useful as the indicators for identification of DDW and ADW and in D1 to D3 in during the 120 day winds respectively. Results of the present study revealed that concentrations of both TSP and $PM_{2.5}$ during days with speed >10 m/s were considerably higher than those during dust storm with speed wind <5 m/s, that the maximum $PM_{2.5}$ concentration was over 27 times higher than USEPA standard during the most polluted dust storm. Besides, the particle concentrations during 120 day winds were generally higher than those observed during the Asian dust storms, indicating the high level of air pollution during the occurrence of the 120 day winds in Zabol and the importance of its impact on the air quality of the area. Ionic components were more concentrated in PM rather than TSP, though the ionic contribution to the total particle mass was not considerable. Calculations of enrichment factors for TSP and $PM_{2.5}$ relative to soil region indicated that K^+, NH_4^+, NO_3^- and No_2^- mainly originated were mostly attributed for the anthropogenic activities in the study area. The observed low correlation between anion and cation found in ADW and DDW were ascribed to carbonate, which was not measured but is known to be another component of mineral dust. Indeed, a strong relationship between CO_3^{2-} and NH_4^+ in ADW and CO_3^{2-} and Ca^{+2} in DDW in PM and TSP implies that Ca_2CO_3 and $(NH_4)_2CO_3$ was the major form for the aerosol carbonate. Also, a strong relationship between CO_3^{2-} and Ca^{2+} in D1 to D3 in TSP and $PM_{2.5}$ implies that Ca_2CO_3 was the major form for the aerosol carbonate in TSP and $PM_{2.5}$ in 120-day winds after dry Hamoun wetland in Sistan region.

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