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# **Original article**

# Determination of the Concentration and Composition of PM10 during the Middle Eastern Dust Storms in Sanandaj, Iran

# Gilas Hosseini (MSc)<sup>a</sup>, Pari Teymouri (MSc)<sup>a</sup>, Behzad Shahmoradi (PhD)<sup>b</sup>, and Afshin Maleki (PhD)<sup>b\*</sup>

<sup>a</sup> Environmental Health Research Center and Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran

ABSTRACT

<sup>b</sup> Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

## ARTICLE INFORMATION

Article history: Background: The present study investigated the effect of the Middle East dust storm episodes on the concentration and composition of PM<sub>10</sub> during April to September 2013 in Sanandaj City, Received: 22 June 2015 western Iran. Revised: 10 August 2015 Accepted: 02 September 2015 Methods: Sampling was once every six days, and on dusty days using an Omni air sampler. The PM<sub>10</sub> sample was collected on polytetrafluoroethylene filters. Average of 24 h values of Available online: 09 September 2015 PM<sub>10</sub> mass concentrations was determined. Half of each sample filter and blank filter was ana-Keywords: lyzed for water -soluble ions and the other half was digested for metal analysis. Water-soluble ions Results: The average PM<sub>10</sub> concentration was 160.63 µg/m<sup>3</sup>. The lowest and highest concen-Metal trations of PM<sub>10</sub> were in May and June respectively. The average PM<sub>10</sub> concentration during the PM10 non-dusty days was 96.88 (µg /m3). Nevertheless, it increased by 4.8 times during the dusty days. Ca<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and Na<sup>+</sup> accounted for 71% of total water-soluble ions on the dusty Air pollution days. During the dusty days, the dominant elements in PM<sub>10</sub> were Na, Ca, Mg, Al, and Fe contributing to 95.72% of total measured metals. The correlation coefficient and enrichment factor analysis have shown that on dusty days, AI, Ca, Fe, K, Mg, Na, Sr, and V were the elements \* Correspondence with the crustal sources. Afshin Maleki (PhD) Tel: +98 87 33626969 Conclusions: Concentrations of PM<sub>10</sub> during dusty days were considerably higher than that Tel: +98 87 33625131 during non-dusty days. In addition, concentrations of water-soluble ions and metals were also higher during dusty days. E-mail: maleki43@yahoo.com

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# Introduction

s a meteorological phenomenon, dust event usually occurs in arid and semi-arid areas<sup>1</sup> after strong winds, and carries large amounts of dust and sand from sparsely vegetated dry deserts<sup>2</sup>. Areas known as dust prone locations are those with the annual average rainfall of  $\leq 100$  mm. On a global scale, the main source of dust emissions have been reported from Sahara, Middle East, Taklamakan, South west Asia, Central Australia, the Etosha and Mkgadikgadi parts of Southern Africa, the Salar de Uyuni (Bolivia), and Great Basin of the USA.

Dust events in the atmosphere have direct and indirect impacts on climate change. The direct effects include the absorption and scattering of sunlight and this condition affects the Earth's radiation budget<sup>3</sup>. Indirectly it can affect clouds' lifetime by changing their properties<sup>4</sup>. Reduction in visibility due to atmospheric dust is another main problem that causes an increased challenge in aviation industry<sup>5</sup>. A large amount of particles are suspended in the air can also affect human health. Many epidemiological studies have shown a relationship between daily changes in the levels of particulate matter (PM) and health consequences such as cardiovascular and respiratory diseases and hospital admissions<sup>6</sup>. Each 10 microgram per millimeter cubed ( $\mu$ g/m<sup>3</sup>) increase in the mass concentration of PM<sub>10</sub> causes a 5% increase in the total number of premature deaths<sup>7</sup>.

The range of environmental and health effects of PM depends on its chemical and physical nature. Therefore, exploring the physical and chemical properties of PM is of great importance<sup>8</sup>. Water-soluble ions are composed up to about 30% of the particulate mass in the outer atmosphere<sup>9</sup>. Ionic composition of the particulates is important due to several reasons. First, water-soluble ions can determine the contribution of each source of particulate emissions; second, they can show the health effects of particulates; and third, they can change pollution control strategies from general control mode into specialized mode<sup>10</sup>. In addition, deposition of ions such as  $K^+$ ,  $NH^+$ ,  $PO_4^{-3-}$ ,  $NO_3^-$ , and  $Fe^{2+}$  may improve the biogenic fertility of the oceans and cause changes in the environment<sup>11</sup>. However, the dissolved ions in water could be attributed to several factors including formation, growth, and evolution processes of the particulates. Thus, they could be better indicators of reactions occurring on the particulate surface compared with their elemental counterparts<sup>12</sup>. PM contains various metallic elements, which can be absorbed by lung through inhalation<sup>13</sup> and can cause harm.

Studies have shown the occurrence of huge dust storms with high concentrations of  $PM_{10}$  in the Middle East. Severity and frequency of these storms were higher especially during the spring<sup>14,15</sup>. The major sources of Middle Eastern Dust (MED) storms include the Arabic Peninsula, Iraq, Kuwait, and some parts of Iran<sup>16</sup>. According to WHO, Sanandaj was ranked the third polluted city in the world in term of  $PM_{10}^{17}$ . The existence of PM10 pollution in Sanandaj City on one hand the lack of data on its quantitative and qualitative characteristics on the other hand bold necessity of carrying a scientific research work on this issue. Moreover, preparing a comprehensive database is crucial for the authorities concerning with control, planning, and increasing people's knowledge in order to contribute to their protection against the hazardous effects of pollutants. The chemical composition of dust storms has impact on the environment and human health; however, few studies have been conducted in this regard. Since 2009, dust event phenomenon has frequently been occurring in Sanandaj and there have been an increased mortality and morbidity attributable to PM<sub>10</sub> exposure<sup>18</sup>. Schools, airports, and offices have also been closed. In addition, there is no report on qualitative analysis of  $PM_{10}$  in Sanandaj City. Therefore, this study aimed to determine the atmospheric PM<sub>10</sub> concentration of Sanandaj City and its ionic and metallic contents during April to September of 2013.

# **Methods**

# Study area

Sanandaj is a developing and non-industrialized city located in northwestern Iran, with a population of around 450,000 people. Its longitude and latitude are 47°00' E and 35°32' N respectively and its elevation is about 1500 meters above sea level. The city is influenced by dust storms coming from several countries, such as Iraq, Kuwait, and Saudi Arabia<sup>11,14</sup> (Figure 1).



Figure 1:  $PM_{10}$  Sampling site, Kurdistan University of Medical Sciences, Sanandaj, Iran

# Meteorology in Sanandaj

Meteorological parameters including temperature (°C), wind speed (m/s), relative humidity (RH) (%), rainfall (mm) and visibility were obtained from Kurdistan Province Meteorological Organization and were used to show the climatic characteristics of Sanandaj City. With an average temperature of 28.54 $\pm$ 1.6°C and humidity of 21.82  $\pm$  1.69% RH, August was the hottest and driest month in Sanandaj City. April was the coolest (14.06  $\pm$ 1.56°C) month while May was the most humid (55.27  $\pm$ 16.84% RH) month. During the study period, the lowest and the highest reported wind speeds were 1.88  $\pm$ 0.41 m/s and 2.66  $\pm$ 1.24 m/s, respectively.

#### Instruments and measurement schedule

The concentration of  $PM_{10}$  was measured using a low-volume air sampler (FRM  $OMNI^{TM}$  Air Sampler, multi-cut inlet; BGI, Inc., USA) operating at a flow rate of 5 1 min<sup>-1</sup>. This instrument is small and light (<10 kg), so that it can be mounted on power poles, fence posts, rooftops, and tripods in areas that are inaccessible to the high volume and low volume devices. Moreover, it is inexpensive and can be used to assess air quality in areas with high concentrations of pollutants. During April to September 2013, 28 PM<sub>10</sub> samples were collected once in every six days in a 24 hours (h) period. Besides, 25 dusty days (DDs) samples were collected on days reported dusty by the Kurdistan Province Meteorological Organization. Out of the total 53 samples collected, 44 samples belonged to non-dusty days (NDDs) with concentrations of  $PM_{10} < 250 \ \mu g/m^3$  and the rest nine were samples represented concentration of  $PM_{10}>250 \ \mu g/m^3$  (DDs sam $ples)^{15}$ .

## Filter analysis and chemical determination

The PM<sub>10</sub> samples were collected on polytetrafluoroethylene (PTFE, Teflon) filters with 47 mm diameter and 2 mm pore size, from SKC. Before sampling, the filter was kept at normal room temperature and relative humidity for 24 h. It was weighed three times before and after sampling by an analytical balance (Sartorius 2004 MP). The average 24 h values of PM<sub>10</sub> mass concentrations were obtained by subtracting the initial mass of the blank filter from the final mass of the sampled filter and dividing the difference by the total volume of air passing through the filter<sup>19</sup>. After gravimetric analysis, all filter samples were stored in a  $-20^{\circ}$ C freezer before subsequent analysis of water-soluble ions and metals.

## Analysis of Water-Soluble Ions

Half of each sample filter and blank filter was cut and shredded into a glass vial. Since PTFE filters are hydrophobic and direct dissolution of the samples in water is not possible, to overcome this problem 0.1ml of isopropanol was added in the glass vial<sup>20</sup>. After 15 minutes, about 15ml double–distilled water was added to it. The vial was then shaken for at least 60 min and subsequently ultrasonicated for 30 min to complete the extraction. All the extracts were then filtered through a 0.2 micrometre (µm) pore size membrane (Schleicher and Schuell) and the filtrates were stored at 4 °C in clean tubes until chemical analysis was done<sup>21</sup>. A total of nine species of water-soluble ions in the aqueous extracts of the PM<sub>10</sub> samples including  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were analyzed using a Metrohm 850 Professional ion chromatography (IC), Switzerland.

# Metal Analysis

The other half of each sample filter was digested at 170 °C for 4 h in high-pressure Teflon digestion container using a mixture of 3 mL HNO<sub>3</sub>, 1 mL HClO<sub>4</sub>, and 0.1 mL HF. After elapsed time, each solution was dried at 95-100°C, and then diluted to 10 ml by adding hydrochloric acid and ultrapure water (18 M $\Omega$  cm<sup>-1</sup> of specific resistivity) at a ratio of 1:9 V%<sup>20</sup>. The obtained solution was filtered through a Whatman-42 filter paper. Twenty-one (21) elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sn, Sr, Te, Tl, V, Zn) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Arcous, Germany).

#### **Enrichment Factors of trace metals**

Enrichment Factor (EF) was used to determine and evaluate the source of trace elements in ambient aerosols. Al is commonly used as crustal source indicator element<sup>22,23</sup>.  $\text{EF}_{\text{crust}}$  value for element (X) was calculated according to the Equation (1):

# $EF_{crust} = (C_{X-aerosol}/_{CAl-aerosol})/(C_{X-crust}/C_{Al-crust})$ (Equation1)

Where,  $C_{X\text{-}aerosol}$  and  $C_{Al\text{-}aerosol}$  are concentrations of elements X and Al in aerosol respectively and  $C_{X\text{-}crust}$  and  $C_{Al\text{-}crust}$  are their concentrations in average crustal material<sup>24</sup>. Based on the values of their  $EF_{crust}$ , elements are classified into two groups.  $EF_{crust} < 10$  indicates that the element in the aerosol has crustal source. These are known as non-enriched elements (NEE). In contrast, the value of  $EF_{crust} > 10$  indicates a significant share of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE)<sup>25</sup>.

## Composition of PM<sub>10</sub>

Their concentrations were estimated using concentration of measued ions and elements and calculated as: 1) crust=Al/0.08, because Al accounts for about 8% by weight of average crust and composion of mineral dust is assumed to be similar to average crust, 2) seconary =  $NH_4^++NO_3^-+SO_4^{2^-}$ , 3) sea salt = 2.54×(Na-0.3Al), in whitch Na-0.3 Al stands for the seasalt originated Na, 4) smoke = K-0.25 Al, here smoke is in fact nonecrustal K, 5) metals = is the total mass of all non-crustal/non seasalt elements measured by ICP-AES, and 6) micellaneous, which is the remaining content of PM10 that does not belong to the above mentioned groups.

# Data analysis

The statistical package for social sciences (SPSS) software version 16.0 (Chicago, IL, USA) was used for statistical evaluation. All graphs were plotted using Microsoft Excel 2010.

# **Results**

## Concentration of PM<sub>10</sub>

Table 1 shows  $PM_{10}$  concentrations during different months of the study period. The overall mean value of  $PM_{10}$ was 160.63 µg/m<sup>3</sup>. The highest and lowest concentrations of  $PM_{10}$  were 837.12 and 31.14 µg/m<sup>3</sup> and were recorded in June and May respectively. The Iranian national  $PM_{10}$  standard is the same as WHO guideline, which is 50 µg/m<sup>3</sup> for daily average. The findings revealed that the daily mean  $PM_{10}$  concentrations exceeded the WHO guidelines in 77% of the days sampled. Figure 2 shows the temporal trends for mean values of  $PM_{10}$  concentrations. Figure 3 shows the comparison between  $PM_{10}$  concentration and meteorological parameters. Figure 3a indicates that the  $PM_{10}$  concentration decreased with increasing wind speed. In Figure 3b and 3d with increasing relative humidity (RH) (%) and rainfall, the  $PM_{10}$  concentrations decreased. Figure 3c shows that  $PM_{10}$  concentration decreased with increasing temperature. In Figure 3e, as  $PM_{10}$  concentration increased, the visibility decreased.

Table 1: Comparison of PM<sub>10</sub> concentrations (µg/m<sup>3</sup>)

| Month     | Mean ±SD            | Min   | Max    |
|-----------|---------------------|-------|--------|
| April     | 146.37 ±28.42       | 97.56 | 183.02 |
| May       | $104.40 \pm 110.70$ | 31.14 | 329.18 |
| June      | 273.49 ±214.68      | 85.04 | 837.12 |
| July      | 90.74 ±43.47        | 37.80 | 156.52 |
| August    | $64.92 \pm 41.06$   | 34.48 | 133.77 |
| September | $37.75 \pm 7.98$    | 33.44 | 51.99  |
| Overall   | 160.63 ±166.07      | 31.14 | 837.12 |



Figure 2: Temporal trends in daily average  $PM_{10}$  concentrations over the study period in Sanandaj City, western Iran



Figure 3: Comparison between  $PM_{10}$  concentration and meteorological parameters: a: Wind speed, b: RH, c: Temperature, d: Rainfall, e: Visibility

# Concentration of chemical composition in PM<sub>10</sub>

Table 2 presents the mass concentration and chemical composition of  $PM_{10}$  in the collected samples during the DDs and NDDs. Ions contributed in 21.69% and 32.334% of  $PM_{10}$  mass during the DDs and NDDs respectively. On the DDs,  $Ca^{2+}$ ,  $Cl^-$ ,  $NO_3^-$  and  $Na^+$  were the highest concentrations in the  $PM_{10}$ , which accounted for 71% of total water-soluble ions. All water-soluble ions had their highest concentrations

during the DDs. The ratio DDs to NDDs ions content of sampled  $PM_{10}$  are shown in Figure 4a. The highest increase in ion on the DDs was for  $Ca^{2+}$  ( $C_{DD}/C_{NDD}$  =3.87) compared to other ions, in which  $C_{DDs}$  and  $C_{NDDs}$  were the concentrations of the specific ion on the DDs and NDDs periods respectively. The highest ion concentrations next to  $Ca^{2+}$  were for  $Cl^{-}$ ,  $SO_4^{2-}$  and  $NO_3^{-}$  (3.66, 3.39 and 3.35) respectively.

Table 2: Mass Concentrations of PM<sub>10</sub> and its chemical composition during the dusty days and non-dusty days

|                                      |                          | DDs                             | NDDs                  |                                 |  |
|--------------------------------------|--------------------------|---------------------------------|-----------------------|---------------------------------|--|
| Species                              | Mean ±SD                 | Average mass ratio to $PM_{10}$ | Mean ±SD              | Average mass ratio to $PM_{10}$ |  |
| $PM_{10} (\mu g/m^3)$                | $472.28 \pm 178.96$      | -                               | $96.88 \pm 53.92$     | -                               |  |
| $F(\mu g/m^3)$                       | 1.54 ±0.83               | 0.00326                         | $0.88 \pm 0.41$       | 0.00908                         |  |
| $Cl^{-}(\mu g/m^{3})$                | $19.90 \pm 11.90$        | 0.04214                         | 5.44 ±2.63            | 0.05615                         |  |
| $NO_3(\mu g/m^3)$                    | $16.89 \pm 13.26$        | 0.03576                         | $5.04 \pm 2.52$       | 0.05206                         |  |
| $SO_4^{2-}(\mu g/m^3)$               | $12.30 \pm 8.60$         | 0.02604                         | $3.63 \pm 3.54$       | 0.03744                         |  |
| $Na^+(\mu g/m^3)$                    | $15.86 \pm 3.65$         | 0.03358                         | 4.75 ±4.02            | 0.04903                         |  |
| $K^{+}(\mu g/m^{3})$                 | $0.09 \pm 0.07$          | 0.00019                         | $0.08 \pm 0.63$       | 0.00078                         |  |
| $NH_{4}^{+} (\mu g/m^{3})$           | $3.60 \pm 2.32$          | 0.00762                         | $1.96 \pm 1.06$       | 0.02023                         |  |
| $Ca^{2+}(\mu g/m^{3})$               | $20.86 \pm 3.95$         | 0.04417                         | $5.39 \pm 4.85$       | 0.05564                         |  |
| $Mg^{2+}(\mu g/m^3)$                 | $11.39 \pm 5.03$         | 0.02412                         | 4.17 ±3.81            | 0.04304                         |  |
| A/C Ratio                            | 0.93 ±0.36               | -                               | 1.04 ±0.24            | -                               |  |
| Al (ng/m <sup>3</sup> )              | 9990.21 ±2079.98         | 0.02115                         | $3124.24 \pm 1424.11$ | 0.03225                         |  |
| As (ng/m <sup>3</sup> )              | 225.65 ±23.58            | 0.00048                         | $182.45 \pm 65.87$    | 0.00188                         |  |
| Ca(ng/m <sup>3</sup> )               | $17252.05 \pm 3594.16$   | 0.03653                         | $4344.84 \pm 2175.84$ | 0.04485                         |  |
| Cd (ng/m <sup>3</sup> )              | $15.45 \pm 5.90$         | 0.00003                         | 5.27 ±3.25            | 0.00005                         |  |
| Co (ng/m <sup>3</sup> )              | $54.54 \pm 19.99$        | 0.00012                         | $31.91 \pm 21.76$     | 0.00033                         |  |
| Cr (ng/m <sup>3</sup> )              | $267.09 \pm 173.17$      | 0.00057                         | $108.27 \pm 23.44$    | 0.00112                         |  |
| Cu (ng/m <sup>3</sup> )              | $99.00 \pm 116.98$       | 0.00021                         | $85.24 \pm 12.37$     | 0.00088                         |  |
| Fe $(ng/m^3)$                        | $5860.39 \pm \! 1890.78$ | 0.01241                         | $3430.17 \pm 1180.32$ | 0.03541                         |  |
| $K (ng/m^3)$                         | $107.13 \pm 106.68$      | 0.00023                         | $84.16 \pm 56.81$     | 0.00087                         |  |
| Li (ng/m <sup>3</sup> )              | $27.99 \pm 15.78$        | 0.00006                         | 9.54 ±4.21            | 0.00010                         |  |
| Mg (mg/L)                            | $13781.56 \pm 1124.82$   | 0.02960                         | $4714.71 \pm 1014.26$ | 0.04867                         |  |
| Mn (ng/m <sup>3</sup> )              | $26.56 \pm 15.83$        | 0.00006                         | $9.56 \pm 3.43$       | 0.00010                         |  |
| Mo (ng/m <sup>3</sup> )              | $198.69 \pm 89.64$       | 0.00042                         | $120.91 \pm 48.34$    | 0.00125                         |  |
| Na (ng/m <sup>3</sup> )              | $19107.34 \pm 6792.87$   | 0.04046                         | $6602.54 \pm 5636.60$ | 0.06815                         |  |
| Ni (ng/m <sup>3</sup> )              | 119.46 ±59.33            | 0.00025                         | $68.00 \pm 32.98$     | 0.00070                         |  |
| $Sn (ng/m^3)$                        | 544.32 ±322.89           | 0.00115                         | 299.27 ±121.32        | 0.00309                         |  |
| Sr (ng/m <sup>3</sup> )              | 142.32 ±66.16            | 0.00030                         | $117.82 \pm 61.38$    | 0.00122                         |  |
| Tl (ng/m <sup>3</sup> )              | 8.18 ±5.79               | 0.00002                         | $6.10 \pm 4.12$       | 0.00006                         |  |
| Te $(ng/m^3)$                        | 988.91 ±721.90           | 0.00209                         | 539.09 ±326.95        | 0.00556                         |  |
| $V (ng/m^3)$                         | 39.33 ±17.77             | 0.00008                         | $16.09 \pm 11.72$     | 0.00017                         |  |
| Zn (ng/m <sup>3</sup> )              | $94.67 \pm 48.93$        | 0.00020                         | $57.18 \pm 31.86$     | 0.00059                         |  |
| $\Sigma Ions/PM_{10}$ (%)            | 21.69                    | -                               | 32.34                 | -                               |  |
| $\Sigma$ Metals/PM <sub>10</sub> (%) | 14.64                    | -                               | 24.73                 | -                               |  |



Figure 4: Ionic (a) and Metal (b) components in  $PM_{\rm 10}$  on dusty days and non-dusty days

# NO<sub>3</sub><sup>-/</sup>SO<sub>4</sub><sup>2-</sup> ratio

Figure 5 shows the average  $NO_3^{-7} SO_4^{-2-}$  ratio in the studied months and seasons. As shown in Figure 5, sulfur had higher concentration during summer, especially in June, due to higher formation of  $SO_4^{2-2}$ .



Figure 5: The average  $NO_3^{-7}/SO_4^{-2-}$  ratio in the studied months and seasons

## Chemical forms of major ionic species

Bivariate correlation was used to identify the chemical forms of studied anions and cations. Table 3 depicts the correlation coefficients among the major ions. Based on the correlation coefficients, NaCl, KCl, NH<sub>4</sub>Cl, CaCl<sub>2</sub>, MgCl<sub>2</sub> NaNO<sub>3</sub>, KNO<sub>3</sub>, and Ca(NO<sub>3</sub>)<sub>2</sub> on the DDs and K<sub>2</sub>SO<sub>4</sub><sup>-1</sup> on both the DDs and NDDs were the major ionic species.

Table 3: The correlation coefficients among major ions in the PM<sub>10</sub>

|                   | F    |       | CI.  |      | NO <sub>3</sub> <sup>-</sup> |      | <b>SO</b> <sub>4</sub> <sup>2-</sup> |      |
|-------------------|------|-------|------|------|------------------------------|------|--------------------------------------|------|
| Species           | DDs  | NDDs  | DDs  | NDDs | DDs                          | NDDs | DDs                                  | NDDs |
| $Na^+$            | 0.24 | 0.05  | 0.88 | 0.15 | 0.72                         | 0.49 | 0.19                                 | 0.11 |
| $\mathbf{K}^+$    | 0.34 | 0.45  | 0.72 | 0.23 | 0.43                         | 0.15 | 0.53                                 | 0.51 |
| $\mathrm{NH_4}^+$ | 0.37 | 0.32  | 0.59 | 0.48 | 0.51                         | 0.43 | 0.48                                 | 0.34 |
| Ca <sup>2+</sup>  | 0.21 | 0.004 | 0.71 | 0.41 | 0.50                         | 0.08 | 0.48                                 | 0.23 |
| Mg2+              | 0.30 | 0.07  | 0.55 | 0.07 | 0.17                         | 0.13 | 0.31                                 | 0.26 |

## Metal concentration of PM<sub>10</sub>

The results of metals concentration analysis in  $PM_{10}$  are listed in Table 2. The sums of percentages of metals in  $PM_{10}$ were 14.64% and 24.73% on the DDs and NDDs respectively. The dominant elements in  $PM_{10}$  were Na, Ca, Mg, Al, and Fe during the DDs (contributing for 95.72%) and NDDs (contributing for 92.73%) of the total measured metals. The ratio of DDs to the NDDs of metal contents of the studied  $PM_{10}$  samples is displayed in Figure 4b. Accordingly, all metal elements have increased on the DDs compared to the NDDs. Cruscal elements of Ca, Al, Mg, and Na (3.97, 3.20, 2.97 and 2.89, respectively) had the highest increase on the DDs compared to the NDDs.

#### Enrichment Factors of trace metals

Figure 6 shows the  $\text{EF}_{\text{crust}}$  distribution of elements over the periods of the DDs and NDDs.  $\text{EF}_{\text{crust}}$  values for all elements in PM<sub>10</sub> were lower on the DDs. It is noteworthy that the long-range transport particles of PM<sub>10</sub> were diluted by anthropogenic heavy metals, relative to locally suspended particles. In addition, as shown in Figure 6, Al, Ca, Fe, K, Mg, Na, Sr, and V on the DDs had lower  $\text{EF}_{\text{crust}}$  values than 10. That means, there were the elements with the crustal sources. The other elements were of anthropogenic sources.



#### Elements

Figure 6:  $\text{EF}_{\text{crust}}$  values for analyzed elements in PM  $_{10}$  during dusty days and non-dusty days

## Composition of PM<sub>10</sub>

Chemical species in  $PM_{10}$  were groupt into six classes including crust, secondary, sea sult, smoke heavy metals and

micellaneous. Figure 7 presents the composition of  $PM_{10}$  on the DDs and NDDs. It shows that there was no non-crustal K in the studied  $PM_{10}$  samples. During the DDs concentration of all groups inceased about 3 times, except for the sixth group, which had a 9 fold increase. This constituent of  $PM_{10}$  contributed to 57.35% of the total  $PM_{10}$  concentratin. It could be comprised of carbonaceous components,  $H_2O$  and/or other unmeasured ions and elements in the  $PM_{10}$ .



Figure 7: Composition of PM<sub>10</sub> during the dusty days and non-dusty days

#### Discussion

Previous report by Shahsavani et al.<sup>15</sup> showed that the highest concentrations of  $PM_{10}$  (5337.6 µg/m<sup>3</sup>) during June. Similarly, Draxler et al<sup>.14</sup> reported the highest concentrations of  $PM_{10}$  in June from Kuwait, Iraq, and Saudi Arabia. Since the current study area was nearby to the dust-producing countries in the Middle East such as Iraq, Kuwait, and Saudi Arabia, it is possible that the changes in  $PM_{10}$  concentrations follow the same trends as in those regions<sup>14</sup>. Most dust events in the Middle East occur in late spring and early summer. This event can be caused by the Shamal wind, a hot northwesterly wind that can carry large amounts of dust from southern areas of Iraq and increases the concentration of particulates<sup>26</sup>.

The decrease in  $PM_{10}$  concentration with increase in wind speed can be attributed to the fact that the main source of dust in Sanandaj is Iraq. The city is not surrounded by desert. In the direction of the winds, dust source did not exist. Therefore, increasing the wind speed does not increase the concentration of  $PM_{10}$ , rather an increase in wind speed caused the dispersion of the particulates in the city and thus, the PM<sub>10</sub> concentration decreased. The decrease in PM<sub>10</sub> concentration was associated with an increase in temperature. As temperature increased, the airborne particulates expanded, resulting in a well vertically mixed up particles. This research showed no strong correlation between PM<sub>10</sub> and meteorological parameters, except for PM<sub>10</sub> and visibility (negative correlation of -0.502). As shown in Figure 3e, visibility was down on the DDs. The average visibility on the NDDs (9993 meters) was 1.7 times higher than in the DDs.

In a study conducted by Yadav and Rajamani<sup>27</sup>, PM<sub>10</sub> concentrations during dust events in summer was 2907  $\mu$ g/m<sup>3</sup>, which is 10-25 times higher than in the non-dust events. The results of another study showed that during the Asian dust events in 2000, the PM<sub>10</sub> concentration in Beijing was higher than 1500  $\mu$ g/m<sup>3</sup>. The concentration was more than 5-10 times higher during DDs compared to NDDs<sup>28</sup>. Rodriguez et al<sup>29</sup> reported that daily average of PM<sub>10</sub> concentrations in Sahara during dust events might be 10-23 times higher than the standard increase in Southern

Spain. Another study conducted in Lanzhon (China) found that the average  $PM_{10}$  concentration in April and the average concentration of  $PM_{2.5}$  and  $PM_1$  in December to be the highest values. Furthermore, sand dust events in spring were found to have carried greater amount of coarse particles than fine particles<sup>30</sup>.

Anions such as  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $Cl^{-}$ , and carboxylates were responsible for acidic atmosphere while cations such as  $NH_4^{+}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were reported to be the causes of basic atmosphere. The ratio of the summation of equivalent concentration of cations ( $\mu eq/m^3$ ) to summation of equivalent concentration of anions ( $\mu eq/m^3$ ) (C/A), which is known as ionic balance, can be used to study the acidity of the atmosphere<sup> $\perp$ </sup>. In this study the ratio of DDs/NDDs (C/A) was 1.07/0.96. The ratio is almost close to one and indicates that there were some other ions that should be measured. Slope of the regression line of A/C (reverse C/A ratio) plot for the NDDs was slightly higher than unity. This might be due to the attribution of uncalculated  $H^+$  or vaporization of  $NH_4^+$ into gas phase. For the DDs, the slope was lower than unity, which implies the probable existence of carbonate or bicarbonate anions<sup>15</sup> that have not been considered in this study.

To study the relative importance of mobile versus stationary sources of nitrogen and sulfur in the atmosphere, the ratio of  $NO_3^{-7}/SO_4^{-2-}$  was used because  $NO_3^{-}$  and  $SO_4^{-2-}(\mu eq/m^3)$  are indicators of mobile and stationary emissions respectively. This ratio of DDs and NDDs are found to be 0.78 and 0.79 respectively. This indicates that stationary sources had higher contribution in atmospheric pollution than mobile ones.

As shown in figure 4b, all metal elements have increased on the DDs compared to the NDDs. Cruscal elements of Ca, Al, Mg, and Na had the highest increase on the DDs compared to that of the NDDs. These findings are in agreement with the results reported by Tsai et al.<sup>22</sup> and Wang et al.<sup>1</sup>, in which Ca<sup>2+</sup>, Ca, and Al were the species with the highest increase in atmospheric concentration during Asian dust storms. The long-range transport of particles of PM<sub>10</sub> was diluted by anthropogenic heavy metals, relative to locally suspended particles. Therefore, EF<sub>crust</sub> was reduced on the DDs. However, this does not mean that the absolute concentrations of these metals in the air on the DDs were lower than those on the NDDs.

The strong correlation between Al and Fe on DDs (r = 0.98) shows the crustal origin of Fe. The average ratio of Fe/Al was 0.59 on the DDs, which is closer to the ratio of Fe/Al (0.68) in crust<sup>24</sup>. This shows that the bulk Fe could be due to crustal source. Besides the strong correlation between Al and V on the DDs (0.81), the very low  $\text{EF}_{\text{crust}}$  (2.70) for this element implies that V has a crustal source<sup>31</sup>. On the other hand, the mean ratio of V/Al (0.004) is close to what is stated in the crust (0.001). This in turn can confirm the crustal source of this element. Again the strong correlation between Al and Ca (r=0.78), Al and K (r=0.67), Al and Mg (r=0.64) Al and Mn (r=0.64), Al and Mg (r=0.53) confirms that all these elements have crustal source.

The Al on the DDs has a correlation coefficient of less than 0.5 with As, Cd, Cr, Li, Mo, and Ni and their  $EF_{crust}$  is above 10 can indicate that these elements have anthropogenic sources. In both DDs and NDDs, Al and Cu have low correlation coefficient (< 0.5). This may indicate that Cu is a metal with anthropogenic source, which probably has local

sources of pollution because on the NDDs it has a higher  $EF_{crust}$  than the DDs. The high correlation (0.5 to 0.98) of Cu with trace elements, such as As, Cd, Cr, Li, Mo, and Ni, imply non-crustal source, having identical source for all of them.

The crustal source of Al, Fe, Mn, and Cr elements and trace metals such as Pb, Cd, and Zn were derived from noncrustal sources with EF>  $10^{27}$ . Correlation coefficient between Al and Co, Sn, Tl, and Zn elements were 0.81, 0.75, 0.94, and 0.68, respectively. EF<sub>crust</sub> over 10 for Co, Sn, Tl, and Zn refers to their dominant pollution sources. However, high correlation of these elements with Al refers to the fact that portion of these elements could be from the crustal source or the resuspended polluted crustal dust. Tahir et al.<sup>25</sup> and Hsu et al.<sup>32</sup> reported that Al, Na, Mg, K, Ca, Sr, Ba, Ti, Mn, and Co in PM<sub>10</sub> of Taipei atmosphere were the elements with the crustal origin. It should be mentioned that on the NDDs, all elements with a correlation coefficient higher than 0.5, could be derived from an identical source.

## Conclusions

During the study period, average PM<sub>10</sub> concentration was 160.63  $\mu$ g/m<sup>3</sup>. The highest and lowest concentrations of PM<sub>10</sub> were found in June and May with the values of 837.12 and 31.14  $\mu$ g/m<sup>3</sup> respectively. Moreover, the average PM<sub>10</sub> concentrations on the NDDs and DDs were 96.88 and 472.28  $\mu g$  /m³, respectively. Ca²+, Cl¯, NO3¯, and Na+ accounted for 71% of the total water-soluble ions. The ratio of  $NO_3^{-7}/SO_4^{-2}$ revealed that stationary sources had higher contribution in atmospheric pollution than mobile ones. During the DDs, the dominant elements in PM<sub>10</sub> were Na, Ca, Mg, Al, and Fe contributing to 95.72% of the total measured metals. The correlation coefficient and enrichment factor analyses revealed that Al, Ca, Fe, K, Mg, Na, Sr, and V on the DDs were the elements with the crustal sources. The classification the PM<sub>10</sub> composition into six groups revealed that the concentration of all the classified groups including crustal, secondary, sea salt, metals and other, increased during the DDs. However, non-crustal K did not exist on the DDs or NDDs. Finally, it is suggested that other components of  $PM_{10}$ , especially by considering their health effects and carbonaceous contents should be studied in future.

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# **Conflict of interest statement**

The authors have no competing interest.

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