# $PM_{10}$ CONCENTRATION AND ITS COMPOSITION IN SANANDAJ, IRAN

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## ABSTRACT

The present study, investigated the effect of the Middle East dust (MED) storm episodes on the concentration and composition of $PM_{10}$ in Sanandaj city, Iran, from April to September, 2013. Sampling was once on every six days, and also on dusty days (DDs) using an Omni air sampler. The average $PM_{10}$ concentration was160.63 μg/m$^3$. The lowest and highest concentrations of $PM_{10}$ were found in May and June, respectively. The average$PM_{10}$ concentration during the non-dusty days (NDDs) was 96.88 (μg /m$^3$). But, it increased by 4.8 times during the DDs. $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $Na^+$ had accounted for 71 % of total water soluble ions on the DDs. During the DDs,the dominant elements in $PM_{10}$were Na, Ca, Mg, Al and Fe contributing to 95.72% of total measured metals. Based on the correlation coefficient and enrichment factor analyses it was found that Al, Ca, Fe, K, Mg, Na, Sr and V on DDs were the elements with crustal sources.

**Keywords:** Air pollution, water soluble ions, metal, middle eastern dust storms, $PM_{10}$

## 1. Introduction

Dust event is a meteorological phenomenon usually occurring in arid and semi-arid areas (Squires 2001; Wang et al. 2005). It mainly occurs during strong winds and carries large amounts of dust and sand from sparsely-vegetated dry lands (Jayaratne et al. 2011). Generally, dust prone locations are those with annual average rainfall of ≤ 100 mm. On a global scale, the main source regions for dust emissions have been reported from Sahara, Middle East, Taklamakan, Southwest Asia, Central Australia, the Etosha and Mkgadikgadi parts of Southern Africa, the Salar de Uyuni (Bolivia), and the Great Basin of the USA.

Dust events in the atmosphere have direct and indirect impacts on climate. With regard to direct effects of atmospheric dust, it absorbs and scatters sunlight and affects the Earth's radiation budget (Baker et al. 2006; Ramanathan et al. 2001; Wang et al. 2011). It also can indirectly affect clouds' life time by changing their properties (Lim et al. 2012). Dust events also can cause other problems. One of the major problems is reduced visibility, which would cause increased problems in aviation industry, etc. (Maghrabi et al. 2011). In addition, they may affect agriculture (Kurosaki and Mikami 2003), marine ecosystems (Jickells et al. 2005) and tropospheric ozone (Arimoto 2001). During dust events, large amounts of particles are suspended in the air, which can affect human health. Meanwhile, many epidemiological studies have shown a relationship between daily changes in levels of particulate matter (PM) and health consequences such as cardiovascular and respiratory diseases and hospital admissions (Berghmans et al. 2009; Gharehchahi et al. 2013). It has been reported that each 10 μg/m$^3$ increase in the mass concentration of $PM_{10}$ causes a 5% increase in total number of premature deaths (Putaud et al. 2004).

The range of environmental and health effects of particulate matters depends on their chemical and physical nature; therefore, exploring physical and chemical properties of the particles are of great importance (Ali et al. 2012). Generally, water-soluble ions compose up to about 30 percent of the particles mass in the rural atmosphere (Zheng et al. 2005). Ionic compositions of the particles are 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 particles. And third, they can change pollution control strategies from general control mode into specialized mode (Shen et al. 2009). However, it is believed that the dissolved ions in the water could be attributed to several factors including formation, growth and evolution processes of the particles. Thus, they could be better indicators of reactions occurring on the particle surface compared to their elemental counterparts (Wang et al. 2006). Also, it is well known that PM contains various metallic elements, which can be absorbed by lungs through inhalation (Quiterio et al. 2004) and cause damage.

Studies have shown that in recent years huge dust storms with high concentrations of $PM_{10}$ have occurred in the Middle East. Severity and frequency of these storms were higher especially in the spring (Draxler et al. 2001; Shahsavani et al. 2012). Major sources of Middle Eastern Dust (MED) storms include the Arabic Peninsula, Iraq, Kuwait and some parts of Iran (Léon and Legrand 2003). Furthermore, the chemical composition of dust storms has an impact on the environment and human health; however, few studies have been conducted in this regard. Since 2009, dust events have frequently occurred in Sanandaj and caused increased mortality and morbidity attributable to $PM_{10}$ exposure in this city (Hosseini et al. 2014). Therefore, this study aims to determine $PM_{10}$ concentration and its ionic and metallic contents during April to September of 2013 in Sanandaj city, Kurdistan, Iran.

## 2. Materials and methods

### 2.1. Study area

Sanandaj is a developing and non-industrialized city located in the North-Western Iran, with a population of around 450000 people. Its longitude and latitude are 47°00′ E and 35°32′ N, respectively and its elevation is about 1500 meters above sea level. As mentioned before, the city is influenced by dust storms coming from several countries, such as Iraq, Kuwait, and Saudi Arabia (Draxler et al. 2001; Givehchi et al. 2013; Goudie and Middleton 2001) (Fig. 1).


**Figure 1:** Sampling site

### 2.2. Instruments and measurement schedule

The concentrations of $PM_{10}$ were 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 l min$^{-1}$. These instruments are small and light (<10 kg), so they can be mounted on power poles, fence posts, rooftops, and tripods in areas that are inaccessible to the high volume and low volume devices. They are also inexpensive and therefore can be used to assess air quality in areas with high concentrations of pollutants. $PM_{10}$ samples were collected, once in every six days, during a 24-h period, from April through September 2013 (28 samples). Dusty days (DDs) samples were collected on days that were reported dusty by the Kurdistan Province Meteorological Organization (25 samples). From

53 collected samples, 44 samples were belong to non-dusty days (NDDs) (concentrations of $PM_{10}$<250 µg/$m^3$) and 9 of them were belong to the DDs (concentration of $PM_{10}$>250 µg/$m^3$) (Shahsavani et al. 2012).

### 2.3. Filter analysis and chemical determination

The $PM_{10}$ was collected on polytetrafluoroethylene (PTFE, Teflon) filters (47mm diameter and 2mm 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 (model: Sartoris2004 MP). The average 24h values of $PM_{10}$ mass concentrations was found by subtracting the initial mass of the blank filter by the final mass of the sampled filter and dividing the difference by the total volume of air passing through the filter (Chao and Wong 2002). After gravimetric analysis, all filter samples were stored in a –20°C freezer before subsequent analysis of water soluble ions and metals.

#### 2.3.1. Analysis of Water Soluble Ions

One half of each sample filter and blank filter was cut and shredded in to a glass vial. Since PTFE filters are hydrophobic and direct dissolution of the samples in water is not possible, to solve this problem 0.1ml isopropanol was added in the glass vial (Herner et al. 2006). After 15 minutes, about 15 ml doubled–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-µm pore size membrane (Schleicher &Schuell) and the filtrates were stored at 4 °C in clean tubes until chemical analysis (Zhang et al. 2011). A total of nine species of water-soluble ions in the aqueous extracts of the $PM_{10}$ samples including$F^-$,$Cl^-$, $NO_3^-$, $SO_4^{2-}$,$Na^+$, $K^+$,$Ca^{2+}$ and $Mg^{2+}$ were analyzed using a Metrohm 850 Professional IC, Switzerland.

#### 2.3.2. 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 $HNO_3$, 1 mL $HClO_4$ and 0.1 mL HF. After elapsed time, the solutions were dried at 95-100° C, and then diluted to 10 ml by adding hydrochloric acid and ultrapure water (18MΩ$cm^{-1}$ of specific resistivity) with a ratio of 1:9 V%) (Celo et al. 2010; Herner et al. 2006; Sun et al. 2004). The obtained solution was filtered through a Whatman-42 filter paper. 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, Model: Arcous, Germany).

### 2.4. Data analysis

The SPSS software version 16.0 was used for statistical evaluation. All graphs were plotted using Microsoft Excel 2010.

## 3. Results

### 3.1. Concentration of $PM_{10}$

The overall mean value of $PM_{10}$ was 160.63 µg/$m^3$. The Highest and lowest concentrations of $PM_{10}$ were 837.12 and 31.14 µg/$m^3$ in June and May, respectively.

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 particles (Goudie and Middleton 2006). Figure 2 shows the temporal trends for mean values of $PM_{10}$ concentrations.

Table 1 presents the mass concentration and chemical composition of $PM_{10}$ in the collected samples during the DDs and NDDs. It is clear that the average$PM_{10}$ concentration on the DDs has a 4.8 fold increase.

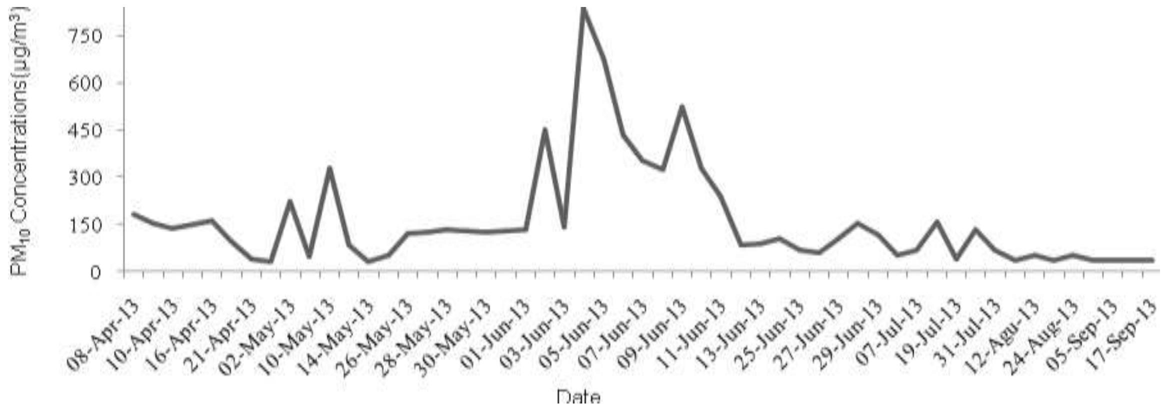


**Figure 2:** Temporal trends in daily average $PM_{10}$ concentrations over the study period in Sanandaj

**Table1:** Mass Concentrations of $PM_{10}$ and its chemical composition during the DDs and NDDs
Reviewer note: Reporting two decimal digits has no significance.

| Species | DDs | | NDDs | |
|---|---|---|---|---|
| | mean±SD | Average mass ratio to $PM_{10}$ | mean±SD | Average mass ratio to $PM_{10}$ |
| $PM_{10}$ (µg/m$^3$) | 472.3±179 | - | 96.9±53.9 | - |
| $F^-$ (µg/m$^3$) | 1.5±0.8 | 0.00326 | 0.9±0.4 | 0.00908 |
| $Cl^-$ (µg/m$^3$) | 19.9±11.9 | 0.04214 | 5.4±2.6 | 0.05615 |
| $NO_3^-$(µg/m$^3$) | 16. 9±13.3 | 0.03576 | 5.0±2.5 | 0.05206 |
| $SO_4^{2-}$(µg/m$^3$) | 12.3±8.6 | 0.02604 | 3.6±3.5 | 0.03744 |
| $Na^+$(µg/m$^3$) | 15.9 ±3.6 | 0.03358 | 4.8±4.0 | 0.04903 |
| $K^+$(µg/m$^3$) | 0.1±0.1 | 0.00019 | 0.1±0.6 | 0.00078 |
| $NH_4^+$ (µg/m$^3$) | 3.6±2.3 | 0.00762 | 2.0±1.1 | 0.02023 |
| $Ca^{2+}$(µg/m$^3$) | 20.9 ±4 | 0.04417 | 5.4±4.9 | 0.05564 |
| $Mg^{2+}$(µg/m$^3$) | 11.4±5.0 | 0.02412 | 4. 2±3.8 | 0.04304 |
| A/C Ratio | 0.9±0.4 | - | 1.0±0.2 | - |
| Al (ng/m$^3$) | 9990.2±2080.0 | 0.02115 | 3124.2±1424.1 | 0.03225 |
| As (ng/m$^3$) | 225.6±23.6 | 0.00048 | 182.4±65.9 | 0.00188 |
| Ca(ng/m$^3$) | 17252.0±3594.2 | 0.03653 | 4344.8±2175.8 | 0.04485 |
| Cd (ng/m$^3$) | 15.4±5.9 | 0.00003 | 5.3±3.2 | 0.00005 |
| Co (ng/m$^3$) | 54.5±20. | 0.00012 | 31.9±21.8 | 0.00033 |
| Cr (ng/m$^3$) | 267.1±173.2 | 0.00057 | 108.3±23.4 | 0.00112 |
| Cu (ng/m$^3$) | 99.0±117.0 | 0.00021 | 85.2±12.4 | 0.00088 |
| Fe (ng/m$^3$) | 5860.4±1890.8 | 0.01241 | 3430.3±1180.3 | 0.03541 |
| K (ng/m$^3$) | 107.1±106.7 | 0.00023 | 84.2±56.8 | 0.00087 |
| Li (ng/m$^3$) | 28.0±15.8 | 0.00006 | 9.5±4.2 | 0.00010 |
| Mg (mg/L) | 13781.6±1124.8 | 0.02960 | 4714.7±1014.3 | 0.04867 |
| Mn (ng/m$^3$) | 26.6±15.8 | 0.00006 | 9.6±3.4 | 0.00010 |
| Mo (ng/m$^3$) | 198.7±89.6 | 0.00042 | 120.9±48.3 | 0.00125 |
| Na (ng/m$^3$) | 19107.3±6792.9 | 0.04046 | 6602.5±5636.6 | 0.06815 |
| Ni (ng/m$^3$) | 119.5±59.3 | 0.00025 | 68.0±33.0 | 0.00070 |
| Sn (ng/m$^3$) | 544.3±322. 9 | 0.00115 | 299.3±121.3 | 0.00309 |
| Sr (ng/m$^3$) | 142.3±66.2 | 0.00030 | 117.8±61.4 | 0.00122 |
| Tl (ng/m$^3$) | 8.2±5.8 | 0.00002 | 6.1±4.1 | 0.00006 |
| Te (ng/m$^3$) | 988.9±721.9 | 0.00209 | 539.1±327.0 | 0.00556 |
| V (ng/m$^3$) | 39.3±17.8 | 0.00008 | 16.1±11.7 | 0.00017 |
| Zn (ng/m$^3$) | 94.7±48.9 | 0.00020 | 57.2±31.9 | 0.00059 |
| ΣIons/$PM_{10}$ (%) | 21.7 | - | 32.3 | - |
| ΣMetals/$PM_{10}$ (%) | 14.6 | - | 24.7 | - |

In a study conducted by Yadav and Rajamani (2006), $PM_{10}$ concentrations during dust events in summer were 2907 μg/m$^3$, 10-25 times higher than non-dust events. The results of another study showed that during the Asian dust events in 2000, $PM_{10}$ concentration in Beijing was higher than1500 μg/m$^3$. Concentrations during dust days compared to non-dust days increased by more than 5-10 times (Meng and Lu 2007). Rodriguez et al. (2001) reported that daily average of $PM_{10}$ concentrations in Sahara during dust events may be 10-23 times higher than the standard increase in Southern Spain. In another study conducted in Lanzhon (China), it was found that the average $PM_{10}$ concentration in April and the average concentration of $PM_{2.5}$ and $PM_1$ in December had the highest values. Furthermore, in studying the differences between coarse and fine particles, the results showed that sand dust events in spring carry greater amount of coarse particles than fine particles (Wang et al. 2009).

### 3.2. Concentration of water soluble Ions in $PM_{10}$

Table 1 shows the concentration of water soluble ionic species in $PM_{10}$. Ions contributed in 21.7%and 32.3% of $PM_{10}$ mass during the DDs and NDDs, respectively. On the DDs, $Ca^{2+}$, $Cl^-$, $NO_3^-$ and $Na^+$ had the highest concentrations in $PM_{10}$, respectively, which accounted for 71 % of total water soluble ions. All water soluble ions had their highest concentrations during the DDs.

Figure 3a Shows the ratio of ions content of sampled $PM_{10}$ on the DDs to NDDs. $Ca^{2+}$ had the highest increase on the DDs ($C_{DD}$/ $C_{NDD}$ =3.87) compared to the other ions, which here $C_{DDs}$ and $C_{NDDs}$ are the concentrations of the specific ion on the DDs and NDDs periods, respectively. $Cl^-$, $SO_4^{2-}$ and $NO_3^-$ (3.66, 3.39 and 3.35) had the next ranks.

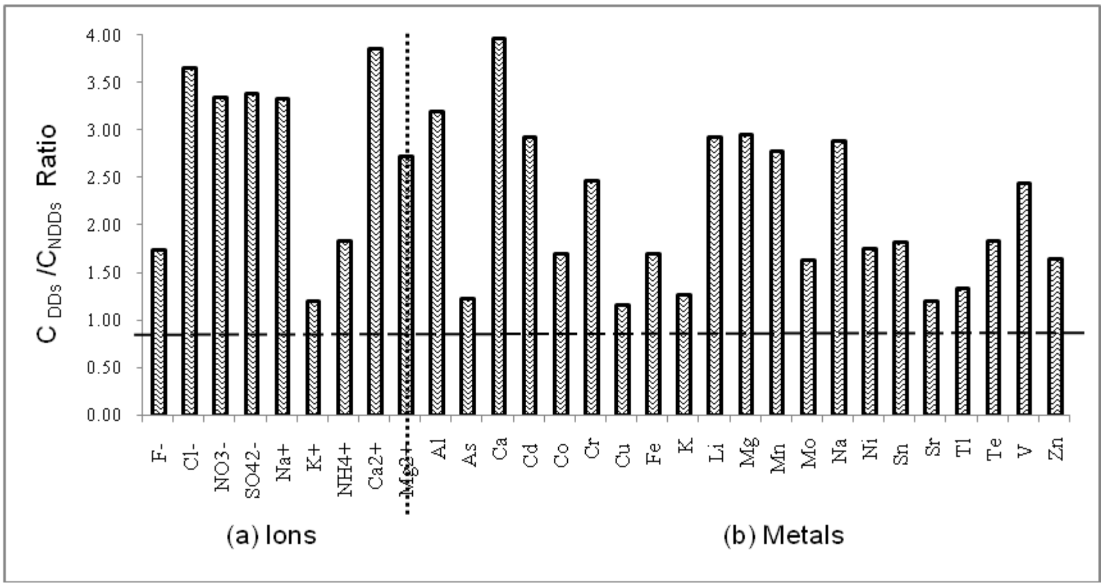


**Figure 3:** Ionic (a) and metal components (b) in $PM_{10}$ on the DDs and NDDs

#### 3.2.1. Chemical forms of major ionic species

Bivariate correlation was used to identify the chemical forms of studied anions and cations.

**Table 2:** The correlation coefficients among major ions in the $PM_{10}$

| Species | $F^-$ | | $Cl^-$ | | $NO_3^-$ | | $SO_4^{2-}$ | |
|---|---|---|---|---|---|---|---|---|
| | 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 |
| $K^+$ | 0.34 | 0.45 | 0.72 | 0.23 | 0.43 | 0.15 | 0.53 | 0.51 |
| $NH_4^+$ | 0.37 | 0.32 | 0.59 | 0.48 | 0.51 | 0.43 | 0.48 | 0.34 |
| $Ca^{2+}$ | 0.21 | 0.004 | 0.71 | 0.41 | 0.5 | 0.08 | 0.48 | 0.23 |
| Mg2+ | 0.30 | 0.07 | 0.55 | 0.07 | 0.17 | 0.13 | 0.31 | 0.26 |

Table 2 shows the correlation coefficients among these major ions. It can be seen that based on their correlation coefficient, NaCl, KCl, $NH_4Cl$, $CaCl_2$, $MgCl_2$ $NaNO_3$, $KNO_3$, $Ca(NO_3)_2$ on the DDs and $KSO_4^2$ on both the DDs and NDDs are the major ionic species.

### 3.3. Metal concentration of $PM_{10}$

The results for metals concentration in $PM_{10}$ were also listed in Table 2.The sums of percentages of metals in $PM_{10}$ were 14.6% and 24.7% on the DDs and NDDs, respectively. In general, the dominant elements in $PM_{10}$ were Na, Ca, Mg, Al and Fe during the DDs and NDDs, contributing to 95.7% (for the DDs) and 92.7% (for the NDDs) of total measured metals. Figure 3b shows the ratio of metal contents of the studied $PM_{10}$ samples on the DDs to the NDDs. According to this figure, all metal elements have increased on the DDs compared to the NDDs. Crustal elements of Ca, Al, Mg, Na had the highest increase on the DDs compared to the NDDs (3.97, 3.20, 2.97and 2.89, respectively). These results are in agreement with the results obtained by Tsai et al. (2012) and Wang et al.(2005), which reported $Ca^{2+}$, Ca and Al as the species with the highest increase in their studied atmosphere during Asian dust storms.

#### 3.3.1. Enrichment Factors of trace metals

Enrichment Factor (EF) is used to determine and evaluate the source of trace elements in ambient aerosols. Al is commonly used as crustal source indicator element (Chester et al. 1997). $EF_{crust}$ value for element (X) is calculated according to Equation 1.

$$EF_{crust} = (C_{X\text{-aerosol}}/C_{Al\text{-aerosol}})/(C_{X\text{-crust}}/C_{Al\text{-crust}}) \quad (1)$$

In which, $C_{X\text{-aerosol}}$ 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 (Taylor 1964). 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 that a significant share of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE) (Tahir et al. 2009).

Figure 4 shows the $EF_{crust}$distribution of elements over the periods of the DDs and NDDs. $EF_{crust}$ values for all elements in $PM_{10}$ are lower on the DDs. It is noteworthy that the long-range transport particles of $PM_{10}$ were diluted by anthropogenic heavy metals, relative to locally suspended particles. Therefore, $EF_{crust}$ is reduced on the DDs. Nonetheless, this does not mean that absolute concentrations of these metals in the air on the DDs were lower than those on the NDDs. Also according this figure, Al, Ca, Fe, K, Mg, Na, Sr and V on the DDshad lower $EF_{crust}$values than 10, meaning that these are elements with the crustal sources. Other elements are of anthropogenic sources.

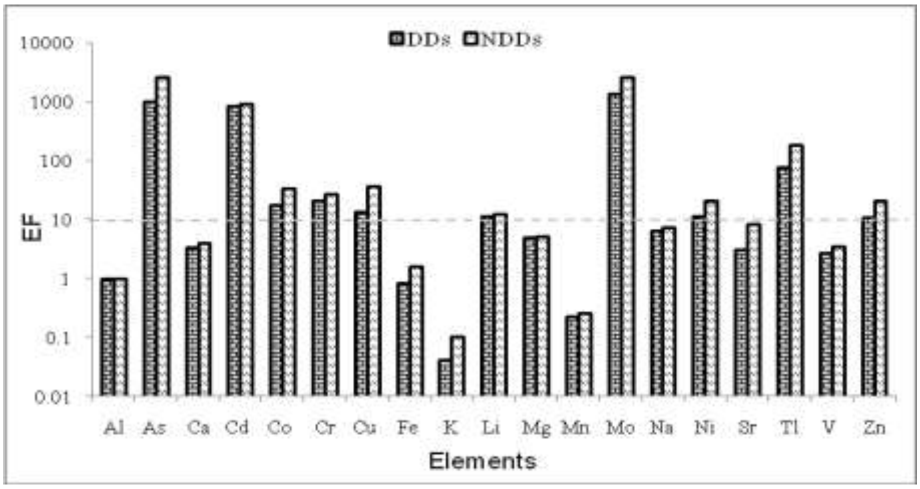


**Figure 4:** $EF_{crust}$ values for analyzed elements in $PM_{10}$ during DDs and The NDDs

In this study, bivariate correlation analysis showed that there was a strong correlation between Al and Fe on DDs (r = 0.98 [Reviewer comment please report r2 rather than r]), which shows the crustal origin of Fe. The average ratio of Fe/Al was 0.59 on the DDs, which was close to that in crust (Fe/Al = 0.68, Taylor 1964). This shows that the bulk Fe could be due to crustal source. Strong correlation between Al and V on the DDs (0.81) and also very low $EF_{crust}$ (2.70) for this element implies that V has a crustal source (Sun et al. 2005).On the other hand, mean ratio of V/Al=0.004 is close to what is stated in the crust (0.001). This in turn may confirm the crustal source of this element. Strong correlations 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=0.58), Al and Sr (r=0.53) also confirm that all these elements have crustal sources.

Since Al on the DDs have a correlation coefficient [Reviewer comment please report r2 rather than r] of less than 0.5 with As, Cd, Cr, Li, Mo and Ni and their $EF_{crust}$is above 10; thus, these elements may have anthropogenic sources. Al and Cu on the both DDs and NDDs had also a low correlation coefficient [Reviewer comment please report r2 rather than r] (0.5>). This indicates 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. Cu has a high correlation [Reviewer comment please report r2 rather than r] (0.5 to 0.98) with trace elements including As, Cd, Cr, Li, Mo and Ni with non-crustal source, showing their identical source.

Tahir et al. (2009) reported the crustal source of Al, Fe, Mn and Cr elements and trace metals Pb, Cd and Zn were derived from non-crustal sources with EF> 10. Correlation coefficient between Al and Co, Sn, Tl and Zn elements were [Reviewer comment please report r2 rather than r] 0.81, 0.75, 0.94, and 0.68, respectively. $EF_{crust}$Over 10for 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. 2009). Hsu et al. (2004) reported that Al, Na, Mg, K, Ca, Sr, Ba, Ti, Mn and Co in $PM_{10}$ 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.

## 4. Conclusion

During the study period, average $PM_{10}$ concentration was160.6 μg/m$^3$. The highest and lowest concentrations of $PM_{10}$ were found in June and May with the values of 837.1 and 31.1 μg/m$^3$, respectively. Also, the average $PM_{10}$ concentrations on the NDDs and DDs were 96.9 and 472.3 μg /m$^3$, respectively.$Ca^{2+}$, $Cl^-$, $NO_3^-$ and $Na^+$ had accounted for 71% of total water soluble ions. During the DDs the dominant elements in $PM_{10}$ were Na, Ca, Mg, Al and Fe contributing to 95.7% of total measured metals. Based on the correlation coefficient and enrichment factor analyses, it was found that Al, Ca, Fe, K, Mg, Na, Sr and V on the DDs were the elements with the crustal sources. Finally, it is suggested that other components of $PM_{10}$, especially, considering their health effects, its carbonaceouscontents get studied in future works.


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