

# Inorganic chemistry, granulometry and mineralogical characteristics of the dust fall over phosphate mine adjacent area, central Jordan

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**Abstract** Eight selected heavy metals and phosphorus (Fe, Zn, Pb, Cu, Cr, Cd, Ni and P) were analyzed in the dust fall samples collected from the surrounding areas adjacent to Al-Hisa phosphate mine central Jordan during summer 2008. The chemical analysis was done using the ICP-AES, after being digested with ( $\text{HNO}_3/\text{HCl}/\text{HF}$ ) acid mixture, beside the identification of their mineral constituents using the XRD. Moreover, the particulate matter (PM) size was investigated and divided into four fractions ( $\text{PM}_{2.5}$ ,  $\text{PM}_{2.5-10}$ ,  $\text{PM}_{10-100}$  and  $\text{PM}_{>100}$ ). The  $\text{PM}_{10}$ – $\text{PM}_{100}$  were found to be the most abundant in the local atmosphere followed by  $\text{PM}_{2.5}$ – $\text{PM}_{10}$ , while the respirable fraction ( $\text{PM}_{2.5}$ ) and giant fraction ( $\text{PM}_{>100}$ ) showed lower levels. The studied samples contain less  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  particulates (9.39 and 28.67), respectively, than samples located far from the mine area (blank samples) (17.32 and 51.7) for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ , respectively. The meteorological effects, mainly the prevailing wind direction beside the distance to emission sources affect the distribution of dust particle sizes. Heavy metal contents in studied samples are similar to some extent to those found in Isa Town (Bahrain), which related to similar arid and low precipitation climatic conditions. The effect of phosphate mining activities was obvious as indicated from the presence of apatite as the main mineral phase and the higher P contents. Moreover, the studied samples contain higher Zn, Ni, Cu and to lesser extent Cr than blank samples. They exhibited

a significant positive correlation with P, as they are usually associated with the phosphate rocks.

**Keywords** Dry deposition · Heavy metals · Apatite ·  $\text{PM}_{2.5}$  · Phosphate mine · Jordan

## Introduction

Dust fall not only adversely affects urban air quality but also directly threatens public health (Fergusson and Kim 1991; Tian and Zhou 1994; Harrison et al. 1997), and thus it is important to study the characteristics beside the temporal and spatial variations of dust fall. Compared to suspended dust, the temporal and spatial variations of pollutant concentrations in dust fall tend to be more sensitive to emission and meteorological conditions. Fang and Lee (2008) measurement results demonstrated that particulate concentrations of total suspended particles (TSP), in particular the particulate matter ( $\text{PM}_{2.5-10}$  and  $\text{PM}_{2.5}$ ) in spring and winter were higher than those in other seasons. Koliadima et al. (1998) identified that the concentration, composition, and size of TSP at a given site were determined by factors such as meteorological features of the atmosphere, topographical influences, emission sources, and by particle parameters such as density, shape, and hygroscopicity.

In recent years great progress has been made in the study of air pollution by investigating the urban airborne particulate pollution (Harrison et al. 1997; Chen et al. 1999; Yang and Chen 2002; Hu et al. 2007). Previous studies have concentrated on elemental content and source identification of dust fall (De Miguel et al. 1997; Nagerotte and Day 1998; Soylak et al. 2000; Yang and Chen 2002; Hueglin et al. 2005; Kim et al. 2007). Salvador et al. (2004)

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found traffic to be the main contributor to PM<sub>10</sub> mass in Madrid, because it is characterized by low industrial activities. The PM<sub>10</sub> poses serious health problems, such as affecting the breathing and respiratory systems, damaging lung tissue, cancer and premature death, and also is a major cause of reduced visibility as reported in the Environmental Protection Agency (EPA 1987). Botkin and Keller (2007) reported that there is a direct relationship between particulate pollution and increased hospital admissions for respiratory distress. The chemical and physical compositions of particulate matter vary widely depending on the sources from where they originated. These sources could be anthropogenic such as fuel combustion, industrial processes, mining, and transportation, etc.; or natural such as unpaved roads, forestry activities, wind erosion, wildlife's and managed burning.

In Jordan, considerable work has been done to investigate the air pollution in major cities such as Amman (Momani et al. 2000); beside that Jiries et al. (2002) have investigated the mineralogical and chemical composition of dry deposition in the central and southern highlands of Jordan. El-Hasan et al. (2008) studied the effect of the Dead Sea on the dry deposition chemical and mineralogical composition. Moreover, Momani et al. (1997) have determined the concentration of the water-soluble inorganic species in the airborne particulate matter of urban areas in Jordan. They used the term non-inhalable for the particles with diameter <11–0.45, and <0.45 μm, they called in the inhalable particles. However, they found that most of water-soluble species (e.g. F, NO<sub>3</sub>, SO<sub>4</sub>, Na, K, Mg and Ca) are higher in the inhalable, while Cl and NH<sub>3</sub> are higher in the non-inhalable particles.

Al-Hisa phosphate mineworker's town was chosen for this study to elucidate the extent of air pollution at arid climate areas characterized by low rainfall and the main source of emission is the phosphate mining activities. Phosphate ore deposits as Al-Abyad and Al-Hisa areas are of shallow marine nature. It was found that the initial bone materials were carbonate hydroxyapatite (Dahlite) modified by early diagenetic process into carbonate flourapatite (Francolite) (Khaled et al. 1990; Abed and Fakhouri 1995). Abu-Jaber (1993) has investigated the rare earth elements (REE) concentration in the Jordanian phosphates (JP), and found that they contain higher concentrations of REE than other authigenic sediments, which was attributed to the deposition under anoxic environment as indicated from the negative Ce anomaly. Sadaqa et al. (2001) investigated the deposition of the phosphate ores using C<sup>14</sup> and O<sup>18</sup> stable isotopes in Jordan, where they found to be of authigenic origin. The concentration of heavy metals and toxic elements in the Jordanian phosphate rocks is lower than several phosphate deposits worldwide (Ghosheh and Dodeen 1993). Moreover, the low content of heavy and

toxic elements in the JP was recently confirmed (Al-Hwaiti et al. 2001).

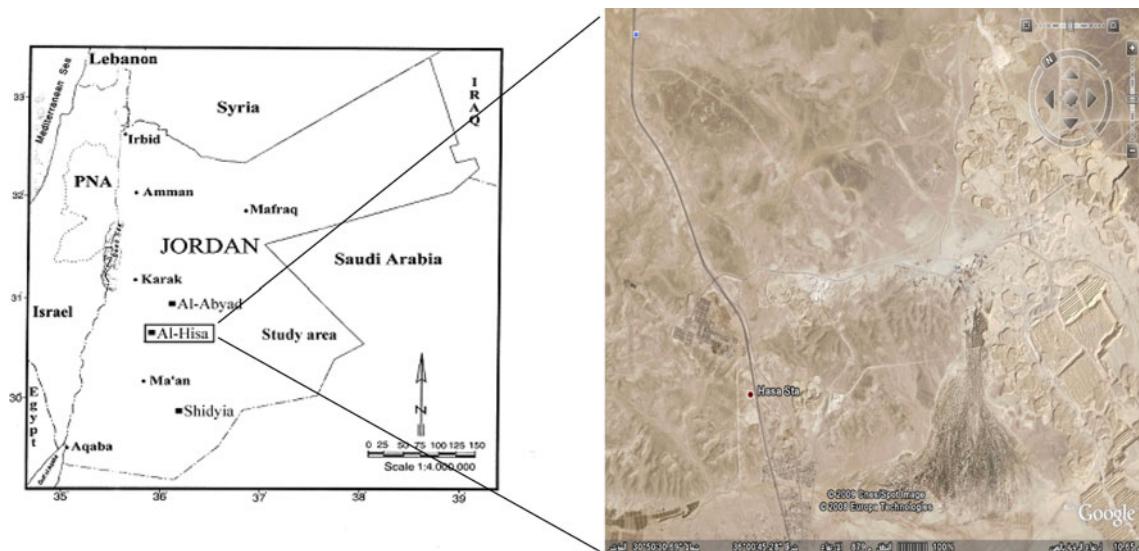
Offer and Azmon (1994) found several industrial plants contributing to the elemental composition of the Aeolian dust. The phosphate industry is one of the most contaminating sources to the environment, which contributes to soil, water and air pollution (Vandenhoove 2002; Jiries et al. 2004). Therefore, the present study is aimed to determine the abundances and distribution of the heavy metals in the dry deposition at the adjacent areas to active phosphate mine in central Jordan. The study will investigate the distribution of particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) beside their mineral constituents. The goal is to assess their toxicity risk for human health and environment at this particular area by analyzing its heavy metal concentrations.

## Study area settings

The study area is located to the west of Al-Hisa phosphate mine, Central Jordan (Fig. 1). The dust fall samples were collected from the rooftops of 18 houses in Al-Hisa mineworker's town. The town population is more than 2,000, where all of them are employees of the Jordanian Phosphate Mine Company (JPMC) with their families. The town is situated exactly 7.5 km to the west of Al-Hisa phosphate mine and about 24 km to the south west of Al-Abyad mine. The total number of houses at the town is 250 house, the 18 houses were randomly selected to cover the whole town in order to evaluate the wind direction effect. Therefore, samples were collected to investigate the impact of mines pollutant emissions on the town.

The study area is dominated with Mediterranean climate that is characterized by dry and hot summer seasons from May to September with a max temperature of 34°C and wet winter season extending from October to April with a mean temperature of 14°C. The mean annual rainfall is about 300 mm/year, the average wind speed is about 7.2 km/h and the evaporation average is 13.3 mm/day (Jordanian Phosphate Mines Company, JPMC 1998).

The geology of Al-Hisa mine area is characterized by a thick succession of sedimentary rocks from Cambrian to Recent ranges between 2,000 and 3,000 m. The lower part of its lithological column is composed of sandstones and claystones of Paleozoic to lower Mesozoic age, whereas the upper part is composed of carbonate rocks of Mesozoic to Cenozoic age. The studied mine area intruded by two major fault zones, such as the NW–SE (Al-Karak–Al-Fiha fault and Al-Hisa fault), and ENE–WSW (Silwan fault) (Bender 1974; Abed 1982; JPMC 1998). The aquifers at the study area are Amman/Wadi Es-Sir formations (B2/A7), which is described as massive limestone unit (Bender 1974). It is highly fractured and jointed, which increase its



**Fig. 1** Location map of the study area (modified after Batarseh and El-Hasan 2009)

permeability, all the wells of the mines were drilled into this aquifer, their depths ranges from 60 to 200 m. This unit is outcropping at the western parts of the mining area that have high precipitation, considering as good recharging inlets.

## Material and analytical methods

The samples were collected randomly from houses all over the whole town. For comparison blank samples were collected from a remote reference site, at which no influence of phosphate mining as well as limited anthropogenic activities is dominating. Roof dust deposits were sampled from each house rooftop using a clean plastic bucket to capture the dust deposition. A clean plastic dustpan, brush, and scoop were used to remove the samples from the buckets. Samples were then dried in an oven at 110°C, sieved through a 2 mm sieve to remove extraneous materials, and retained for further analysis. 0.2 g of the sample was accurately weighed and digested for total heavy metal analysis using the wet digestion procedure. The sample was transferred to a 100 ml polyethylene bottle and digested by adding 4 ml HCl, 4 ml HNO<sub>3</sub> and 2 ml of HF. The mixture was heated using water bath at 70°C for 2 h after which 50 ml of H<sub>3</sub>BO<sub>3</sub> was added to the mixture. The mixture was heated again about 1 h until the solution becomes clear. Then the volume was completed with distilled water to exactly 100 ml. The solutions were stored in sealed polyethylene bottles prior to analysis. The heavy metals (Pb, Zn, Ni, Fe, Al, Cr, and Cd) were determined using ICP-AES (model optima 2000 DV, Perkin Elmer, UK). Concentration of PO<sub>4</sub> in the samples was determined using

Ion Chromatography model D × 120. All materials used for analysis (e.g., bottles and glassware) were washed thoroughly, rinsed with 1% HNO<sub>3</sub>, and finally rinsed with distilled water.

The mineral constituents of the studied samples were determined using X-ray diffraction system (XRD) (Philips-X'pert MpD). The fine powder samples were mounted on special slides and then scanned between 2° and 65°, using Ni-filtered Co K- $\alpha$ -radiation, 40 kV/40 mA, divergent and scattering slits of 0.02 mm, a receiving slit of 0.15 mm, with stepping of 0.01° and scanning speed of 3°/min. The grain size analysis was done using the laser particle size analyzer (Analysette 22 Compac/FRISCH).

## Results and discussion

Eight heavy metals beside phosphorus were analyzed; the complete analytical results are shown in Table 1. The blank represents areas that are not influenced by phosphate mining activities from remote sites in northern and central Jordan. The difference was obvious between studied and blank samples as shown in Fig. 2. This difference was found in all studied samples; especially it bears high P, Zn, Cd, and Ni. This would indicate the influence of phosphate mining activities from which the particulate is more likely to be originated.

The mineral constituents of the studied samples were analyzed using the XRD technique. The effect of the phosphate mining was clear as all samples contain apatite as one of the major mineral phases as shown in Table 2. There are clear differences in mineralogical constituents between studied samples and the blank samples as the average

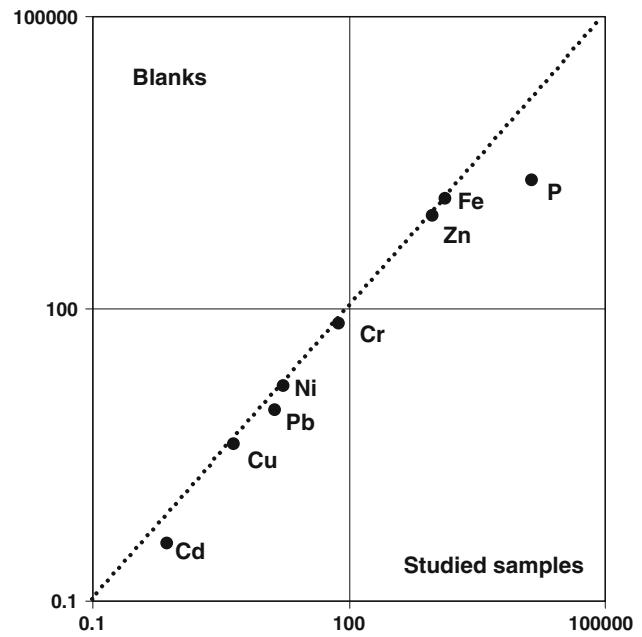
**Table 1** The ICP-AES results of the analyzed heavy metals and P in all studied samples and three blank samples (below)

Samples	Zn	Fe	Ni	Cr	Cd	Pb	P	Cu
Studied samples								
S1	8,815	1,414	19.6	1.2	1.2	7.4	14,947	6.5
S2	865	1,353	16.5	82.7	0.7	10.5	1,3655	5
S3	1,092	1,337	17	78.6	0.7	12.4	14,849	4
S5	–	1,276	16.9	65.2	0.9	12.9	14,103	3.5
S6	455	1,261	16.4	62.5	0.7	15.3	14,409	4.5
S7	610	1,395	17.5	91	0.8	12.4	13,876	45
S8	1,058	1,274	16.9	64.6	0.5	17.1	15,306	5
S9	619	1,240	16.8	66.6	0.6	16.5	13,215	3.5
S10	878	1,360	17.8	81	0.8	11.3	12,307	4.5
S11	721	1,235	15.7	69.9	0.6	12.3	12,649	3.5
S12	811	1,328	16	73.2	0.7	14.4	14,601	5
S13	812	1,294	15.5	64.7	0.9	13.3	13,785	3.5
S14	694	1,275	16.3	69.8	0.5	15.5	12,307	3.5
S15	1,200	1,330	16.9	76.5	0.7	10.6	13,293	4
S16	1,187	1,303	16.1	68.1	0.7	11.7	14,067	3.5
S17	854	1,266	16.7	65.8	0.6	15.1	14,865	3.5
S18	–	1,349	17.3	86.6	1.1	16.1	13,774	6.5
Average	949	1,312	16.9	75.7	0.7	13.2	13,846	4.4
Max.	8,815	1,414	17.8	86.6	1.2	17.1	15,306	6.5
Min.	455	1,235	15.5	62.5	0.5	7.4	12,307	3.5
SD	230.3	53.3	0.7	9.0	0.2	2.2	948.9	11.3
Blank samples								
B7	688	1,365.5	16.5	72.5	0.5	6.9	3,700	3.5
B8	873	1,343	17.0	73.9	0.4	10.7	387	4.0
B9	1,141	1,381.5	15.5	68.9	0.4	10.0	2,158	5.0
Average	900	1,364	16.3	71.6	0.4	9.17	2,081	4.1
Max.	1,141	1,368.5	17.0	73.9	0.5	10.7	3,700	5.0
Min.	688	1,343	15.5	68.4	0.4	6.9	387	3.5
SD	227.8	19.3	0.8	2.6	0.1	2.0	1,657.8	0.8

Values are in ppm

apatite contents were 17.5 and 11% in studied and blank samples, respectively. The blank samples bear lower apatite and dominating dolomite phase, beside calcite and quartz. Whereas studied samples composed mainly from calcite and quartz, have higher apatite and little dolomite as shown in Table 2. The XRD chart represents one studied sample compared with one blank sample, where the apatite peaks are lacking in the blank sample is illustrated in Fig. 3a, b.

The collected samples and the blank samples were analyzed for their grain size using the laser particle size analyzer. The studied samples contain PM<sub>2.5</sub> and PM<sub>10</sub> (9.39 and 28.67), respectively. However, the blank samples have 17.32 and 51.7 for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively, as shown in Table 3. This might be attributed to the wind direction and the distance between the study area and the particulate pollution emission source where the sample

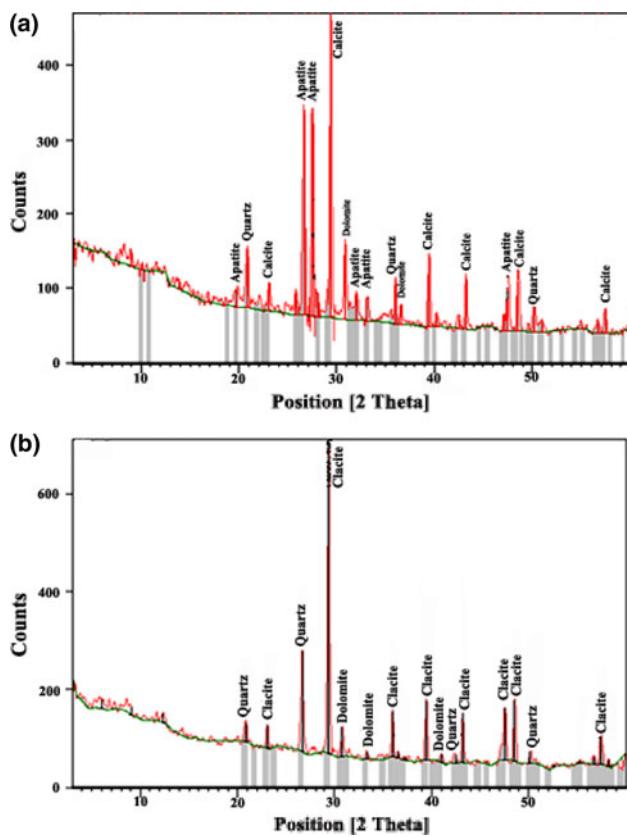


**Fig. 2** 1:1 ratio scatter plot showing the relative depletion and enrichment of the heavy metals and P between studied samples and blank sample

**Table 2** Generalized table showing the mineral constituents as percentages in the studied samples

Samples	Calcite	Qz	Apatite	Dolomite	Graphite	Ankerite	Total%
1	0.45	0.32	0.23				100
2	0.43	0.35	0.22				100
3	0.39	0.34	0.13	0.15			101
4	0.40	0.30	0.13	0.17			100
5	0.44	0.37	0.19				100
6	0.51		0.18		0.31		100
7	0.38	0.32	0.30				100
8	0.53	0.30	0.17				100
9	0.37	0.31	0.15		0.17		100
10	0.47	0.34	0.19				100
11	0.47	0.40	0.13				100
12	0.42	0.32	0.12			0.14	100
13	0.50	0.32	0.18				100
14	0.45	0.38	0.18				101
15	0.40	0.34	0.26				100
16	0.50	0.39	0.11				100
17	0.44	0.41	0.14				99
18	0.37	0.31	0.14	0.18			100
B7	0.55	0.32	0.11	0.07			105
B8	0.48	0.26	0.12	0.14			100
B9	0.32	0.26	0.10	0.14		0.13	95

collection sites are all at the workers town that is located to the west of Al-Hisa phosphate mine (pollution emission source), therefore, as the prevailing winds direction is



**Fig. 3** X-ray diffraction chart for **a** one studied dust sample No. (13), and **b** one blank sample No. (B7)

toward the southeast (JPMC 1998), eventually this will result in moving the smaller air particulates toward the southeast. And only when steady calm wind-days prevailing these smaller air particulates can reach and accumulated at the workers town.

The distribution of dust particle sizes was controlled by meteorological effect, mainly the prevailing wind direction and the lower precipitation rates.

**Table 3** Generalized table showing the percentages of PM<sub>2.5</sub> and PM<sub>10</sub> in the studied samples and blank samples

	Min	Max	Mean
<b>Samples</b>			
PM <sub>2.5</sub>	6.65	14.55	9.37
PM <sub>10</sub>	19.70	44.80	28.67
≤PM <sub>2.5</sub> /≤PM <sub>10</sub>	0.26	0.43	0.36
<PM <sub>10</sub> />PM <sub>10</sub>	0.25	0.81	0.41
<b>Blank</b>			
PM <sub>2.5</sub>	10.25	24.35	17.32
PM <sub>10</sub>	31.60	68.4	51.7
≤PM <sub>2.5</sub> /≤PM <sub>10</sub>	0.31	0.36	0.33
<PM <sub>10</sub> />PM <sub>10</sub>	0.46	2.16	1.28

**Table 4** Correlation coefficient matrix showing the inter-elemental relationships between the analyzed heavy metals and phosphorus

	Zn	Fe	Ni	Cr	Cd	Pb	P	Cu
Zn	1							
Fe	0.08	1						
Ni	0.05	<b>0.78</b>	1					
Cr	0.04	<b>0.90</b>	<b>0.86</b>	1				
Cd	-0.04	<b>0.76</b>	<b>0.80</b>	<b>0.87</b>	1			
Pb	-0.20	<b>-0.64</b>	-0.43	<b>-0.61</b>	-0.44	1		
P	0.44	0.23	<b>0.48</b>	0.32	0.29	0.16	1	
Cu	-0.07	<b>0.73</b>	<b>0.74</b>	0.77	<b>0.83</b>	-0.24	0.43	1

Values indicated in bold represents the 95% confidence level at  $n = 18$  (0.455)

The correlation coefficient values presented in Table 4 show that Ni, and to lesser extent Zn, Cu, and Cr have significant positive correlation values with P, which might indicate their association within the apatite mineral lattice. While Fe, Cd, and Pb have lower positive correlation with P that reflects their association with other mineral phases than apatite most likely calcite and clay minerals. Pb looks unique because it shows very negative correlations with all heavy metals except with P and Cu (0.29 and 0.83), respectively; this might be due to different source of Pb. This might be attributed to the unleaded fuels emissions associated with mining process and transportation.

The comparison with dry deposition from other different cities with various climatic conditions around the world showed an obvious difference in heavy metal content between the study area and Uijeongha and Koyang cities (S. Korea) and Coventry city (UK). Meanwhile there are many similarities in heavy metal contents between the study area and Isa town (Bahrain) as shown in Table 5. This might be attributed to the influence of climate. As our study area and Isa town (Bahrain) bears similar semi-arid climatic conditions, S. Korea and the UK have different

**Table 5** Comparison in heavy metal contents between the studied samples and other dry deposition samples from around the world

	Zn	Fe	Ni	Cr	Cd	Pb	Cu
Studied samples	52.91	1,311	14.29	29.13	3.01	0.47	14.65
Uijeongha S. Korea <sup>a</sup>	334	nd	29	41	1.2	nd	124
Koyang S. Korea <sup>a</sup>	265	nd	39	43	1.8	nd	83
Isa City Bahrain <sup>b</sup>	58	nd	4.05	3.2	0.29	1.2	21.5
Coventry UK <sup>c</sup>	336	nd	66.4	nd	3.3	nd	141

All values are in ppm

nd Not detected

<sup>a</sup> Chon et al. (1998)

<sup>b</sup> Ali-Mohammed (1991)

<sup>c</sup> Charlesworth and Lees (1999)

climatic parameters mainly higher rainfall. However, slight differences between our study area and Isa city of Bahrain can be noticed, where our study area is enriched in Zn, Cd, and Cr, while it is depleted in Pb and Cu, which might be due to the local effect of the phosphates mines emissions that indicate it as the main source of pollution in the area. Meanwhile, higher Pb and Cu in Isa city samples reflect the effect of the vehicular emissions.

Although the studied samples contain less PM<sub>2.5</sub> and PM<sub>10</sub> than blank samples, by revising the files of patients who had visited the health center of the town during 2008, it was found that 40% of them were found suffering from respiratory system health problems, which mainly attributed to the phosphate dust (Al-Hisa Health Center, personal communication). Moreover, the impacts of phosphate mines dust were known not only at Al-Hisa mine but also at other phosphate mines in Jordan such as Rusiehah and Al-Byad mines. Similar health problems were reported in Egypt for phosphate mineworker's ([Zidan, Alsharqal-awsat 9463](#)). The granulometry and chemical characteristics of the dust could explain the adverse health impacts, as the dust contains solid particulates that are not easily dissolved in water, thus remain attached to reparatory tissues and alveoli.

## Conclusions

The dust fall over the adjacent areas to Al-Hisa phosphate mine is enriched with Pb, Cd, and P, beside that it is dominated with calcite and apatite, which indicates the phosphate mining industry as the main anthropogenic pollution source. The median diameter of particulate matter in dust varied between <2.5 and 45 µm. These particles are small enough to enter the alveoli of lung. The grain size analysis show lower PM<sub>2.5</sub> and PM<sub>10</sub> percentages relative to blank samples, this might be attributed to the effect of the prevailing wind direction and the distance to emission source. Moreover, the comparison with heavy metal contents in dry deposition samples world-wide revealed that our studied samples bear similar heavy metal contents as Isa Town (Bahrain), which might be due to similar climatic conditions.

The health impacts are clear and indicate that phosphate dusts are the main reason for adverse health effects in the study area. However, this study should be followed by further investigations to characterize the mineral and chemical contents for each grain size, also to execute a continuous seasonal monitoring.

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