Releases of phosphate fertilizer industry in the surrounding environment: Investigation on heavy metals and polonium-210 in soil

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Received 21 September 2009; revised 26 October 2009; accepted 27 November 2009

Abstract

Distribution of Cu, Zn, Pb, Cr, Ni, Mn concentrations and the activity of polonium-210 in the surrounding area of a phosphate fertilizer industry located on the eastern coast of the Mediterranean Sea has been determined. Nineteen sampling sites were distributed around the industrial zone on a surface area of about 100,000 m². Atomic absorption spectroscopy and Alpha spectroscopy were used to quantify the heavy elements and polonium-210, respectively. Investigation on a particle scale was conducted by TEM and SEM coupled to EDX and X-ray cartography to determine the nature of heavy elements carriers and their distribution. Heavy elements were mainly concentrated inside the particle size fraction < 50 µm. Their levels decreased with distance increasing from the industry. According to the reference soil, enrichment factors were about 10, 15, 32 and 100 times for Zn, Pb, Cu, and Cr, respectively inside the particle size fraction < 50 µm on the closest sites to the industry. The main contaminant sources were transport and storage of raw materials and the free release of phosphogypsum waste. Heavy elements were entrapped inside agglomerates of sulfates, phosphates and iron oxihydroxides in a diffused shape. Polonium-210 with an enrichment factor of about 56, showed the same behavior of the spatial distribution of the trace elements.

Key words: heavy elements; phosphogypsum; fertilizer industry; polonium-210; Alpha spectrometry

DOI: 10.1016/S1001-0742(09)60247-3

Introduction

The non-organic chemical fertilizers are mainly composed of phosphate, nitrate, ammonium and potassium salts. Phosphate fertilizer industries are considered to be a potential source of natural radionuclides and heavy metals contamination (Al-Masri et al., 2004). Extensive studies have been carried out through the world to evaluate the impact of the phosphate fertilizer industry production in the environment (McDonald et al., 1991; Barisic et al., 1992; McCartney et al., 1992; Rutherford et al., 1994; Hamam and Landsberger, 1994; Martinez et al., 1994; Bolivar et al., 1994; Carvalho, 1995; Marovic and Sencar, 1995; Martinez and Garcia, 1996; Timmrmanas and Van der Steen, 1996; Al-Marsi et al., 2004).

Phosphate fertilizers produced are derived from phosphate ores. In addition to phosphate minerals, these ores contain a wide range of heavy metals like Hg, Cd, As, Pb, Cu, Ni, and Cu (Al-Masri et al., 2004), and natural radionuclides like 238U, 232Th, and 210Po (Al-Masri et al., 2002; Othman et al., 1994). Exploiting, transporting of phosphate ores, production and using of phosphate fertilizers are ways in which workers, public and the environment are exposed to enhanced contamination by natural radionuclides and heavy elements (UNSCEAR, 1993; IAEA, 2004). Most of the contaminants are found in the solid waste of the phosphate fertilizer industry which is mainly constituted from CaSO₄ known as phosphogypsum (Kroschwitz and Howe-Grant, 1995). During production processes, some amounts of contaminants are transferred from used ores to produced phosphoric acid and to fertilizers (Brigden et al., 2002). Nevertheless, many of these contaminants are transferred to the effluents and mainly to phosphogypsum (Brigden et al., 2002; Rutherford et al., 1994). It contains impurities such as Al, P, F, Si, Fe, Mg as well as many trace elements, including rare earth elements and naturally occurring radioactive materials (226Ra and 210Po). Hence, disposing phosphogypsum directly into the environment without any treatment or its storage as piles exposed to weathering processes may lead to chemical and radioactive contamination (Becker, 1985). Leaching of phosphogypsum with water showed that Cu and Cd are easily transferred to water and then to the surrounding environment (Al-Marsi et al., 2004). According to Arocena and Rutherford, particle fraction of phosphogypsum lower than 20 µm generally concentrates the heavy metals (Arocena, 1995; Rutherford, 1996). Carvalho showed that the concentration of 210Po in the rich phosphogypsum
sediments increases inversely with the size of the sediment; on the other hand, increasing sand in soil was found to have a diluting effect on the concentration of Pb, since it is considered as a non-reactive agent in soil (Carvalho, 1995). According to Al-Masri’s study, trace elements are always concentrated in the fine particle fraction (Al-Masri et al., 2004). Variation of parameters such as temperature, pressure and concentrations of salts affect the distribution of elements. Al-Masri et al. (2004) sustained this conclusion in his survey of the distribution of the elements traces in the Syrian phosphogypsum.

In this study, the distribution of polonium-210, as a natural occurring radionuclide, Pb, Zn, Cu, Cr, Ni, and Mn is investigated around a phosphate fertilizer industry which is storing and disposing its solid waste directly in the surrounding environment without any pretreatment. Contaminants are studied inside two main particle fractions, less and higher than 50 µm. The main goal is to evaluate the impact of such waste on soil and sediments and to identify the most influencing factors on contaminants distribution.

1 Experimental

1.1 Study area

The study was conducted around a chemical fertilizer company which produces a large range of phosphate based fertilizers. The industry is producing simple, triple superphosphate and phosphoric acid. It is located in the eastern coast of the Mediterranean Sea, near a small town, at 46 kilometers to the north of Beirut, the capital of Lebanon. At several altitudes around the industrial complex, many residential units are distributed intermittently. Small industries of food-oil, metallurgy and stones tiling are located at the north and the north-east of the fertilizer industry. The region is limited by the sea at the west and low altitude levels (10–40 m) of mountain frontiers at the east (Fig. 1). Winds are mostly blowing from the south or the south-west and occasionally from the north especially during the fall season. The soil type in the study area was reported in the Lebanese soil map as calcivertisol and calciluvisoil (Darwish, 1998). The area chosen for this study was selected among the most “hot spots” of the Mediterranean Sea because of the high contamination levels found in the region (UNEP, 1999).

The annual production in the manufacture of fertilizers is 230 tons of simple superphosphate, 31 tons of triple superphosphate and 160 tons of phosphoric acid (Al Hajj and Muscat, 2000). Effluents originated from solid waste leaching are discharged directly into the Mediterranean Sea. As reported by MoE/Envirotech (1999), phosphogypsum production is estimated to 950 tons per year.

**Fig. 1** Locations of the sampling sites (1–19).
1.2 Sampling sites

In order to evaluate the environmental impact of the fertilizer industry, the chosen area for this study was subject to three main sampling campaigns from April 2006 until January 2007 (Fig. 1). About 200–300 g samples were collected from 19 different sampling sites located in the continental part around the industry and inside the populated area as shown in Fig. 1. Sites from 1 to 14 were chosen close to the frontier of the fertilizer industry; sites 15, 16, 17, 18 and 19 were 250–300 m far from the frontiers of the factory. Three reference soil samples were collected in a non urban region located at about 15 km from the east of the study area far from the anthropogenic influences. The reference soil was also a calcivertisoll. Soil samples were collected from 20 cm × 20 cm of a surface layer section of 10 cm depth. Samples from each site were homogenized, stones and plant debris were removed from the samples manually before oven drying at 90°C for 24 hr. Homogenized samples were sieved through a 50 µm mesh and separated in two size fractions: less than 50 µm (F1) and greater than 50 µm (F2) to quantify the heavy metals and phosphogypsum-210. Fraction higher than 50 µm was ground for 20 min inside an agate mortar. A 50 µm sieve was selected since the mean size diameter of disposed phosphogypsum is 30–44 µm (Sfar Felfoul et al., 2005) and the most reactive components in soils are silts and clays that are less than 50 µm. Al-Masri et al. (2004) used a 45-µm sieve also to separate particle fractions of phosphogypsum.

1.3 Heavy metals analysis

Heavy metals were quantified using an atomic absorption spectroscopy (AAS, A Analyst 100, HGA 800, Perkin Elmer, USA). A well homogenized size fraction sample duplicate of 2 g was ashed for 6 hr at 550°C inside a muffle furnace (48000 Barnstead Thermolyne, Thermo Fisher Scientific Liberty, USA), then dissolved in a combination of mineral acids (nitric and hydrochloric acid) for at least 72 hr. All used glasses were well washed by 5% HNO₃ solution. In a covered borosilicate beaker of 100 mL, samples were dissolved in 25 mL of concentrated nitric acid (14 mol/L) (Analar, BDH), heated at 80°C and stirred gently for at least 24 hr; about 10 mL of concentrated hydrochloric acid (12 mol/L) (Analar, BDH) was added as drops from time to time during this procedure. Acids were evaporated to near dryness, and then 15 mL of concentrated hydrochloric acid (12 mol/L) (Analar, BDH) was added to the sample. Once the sample is totally dissolved, hydrochloric acid was evaporated and replaced by 15 mL of concentrated nitric acid. This operation was repeated three to four times before dissolving the residual salts in 25 mL of nitric acid (14 mol/L). The final solution was filtered through 0.45 µm PTFE membrane filters (Millipore, USA), the volume was adjusted to 25 mL with deionized water then stored at 4°C until AAS analysis. Zn, Cu, Pb, Cr, Mn, Ni were quantified by using an Atomic Absorption Spectrometry (A Analyst 100, HGA 800, Perkin Elmer, USA) in a flame mode or graphite furnace when necessary. Standard solution containing the same matrix as the samples was made up at appropriate concentrations for each element. Standard metal solutions used for the determination were CertiPur solutions obtained from Merck, USA. Total heavy metals solubilization was based on the method reported in the handbook for soil analysis (Pansu and Gautheyrou, 2003). The same heavy elements were quantified also inside produced phosphogypsum of the industry by using the same digestion method. Phosphogypsum was prepared by mixing and homogenizing four equal amounts of collected samples generated from different production dates and released in the surrounding environment.

1.4 Electron microscope investigation

Electronic microscope observations were performed with a Philips Cm20 Transmission Electron Microscopy (TEM, Philips-FEI Company, USA) (200 kV) coupled with an EDAX energy dispersive X-ray spectrometer (EDX), and with a S-2500 Hitachi SEM (Scan Electron Microscopy, Hitachi, Japan) equipped with a Kevex 4850-S EDX (KEVEX Company, USA). Trace element carriers were identified from elemental analysis of individual particles.

About 50 mineral particles from fraction F1 (< 50 µm) of samples from each sampling site were examined over the period of study (400 SEM-EDX spectra and 200 TEM-EDX spectra). For TEM imaging and micro-analysis, the sample was re-suspended in ethanol under ultrasonification, and a drop of suspension was evaporated on a carbon-coated copper grid (EuroMEDEX, Mesh200-Car#CF200CU, Electron Microscope Sciences Company, USA). A spot size of about 70 nm was used to record EDX spectra with a counting time of 40 sec. EDX calibration standards were run to obtain quantitative analyses of major and trace elements with a detection limit of about 100 ppb. Samples for SEM-EDX examination were sprinkled onto 2 cm² plates and carbon coated. Backscattered electron imaging (BEI) was used to locate the particles of interest. In that mode, brightness is related to the average atomic number of materials, and the mineral particles appear as bright spots within the matrix. It should nevertheless be noted that this procedure largely overlooks mineral phases with low-atomic-number elements. In order to increase the emission of backscattered electrons, the SEM microscope was generally operated with a beam current of 3 pA and an accelerating voltage of 20 kV (analyzed micro-volume of about 6 µm³). However, to improve the quantification of low atomic number elements, EDX analysis was sometimes carried out at an accelerating voltage of 10 kV (sample volume of 3 µm³).

1.5 Polonium-210 analysis

Concentrations of ²¹⁰Po were measured using the silver disc technique (Harley, 1978; Al-Masri et al., 2002). Five grams of each sample were spiked with a known amount of ²⁰⁸Po (0.2 Bq) as a yield tracer. Each sample was digested using a combination of mineral acids (nitric and hydrochloric acid simultaneously) for at least 24 hr. When the solution was clear, the sample was gently evaporated...
to dryness. This procedure is repeated three times. The residue was dissolved in 100 mL of 0.5 mol/L hydrochloric acid. The solution was heated to 80°C under agitation. Ascorbic acid was added for the reduction of iron and 210Po was spontaneously plated onto a rotating prewashed silver disc. Alpha counting of 208Po (5.15 MeV) and 210Po (5.3 MeV) was performed using an alpha spectrometer (Alpha Analyst™, Canberra, USA) with a passive ion implanted silicon detector (active area 300 mm²) and a minimum depletion thickness of 100 mm. 210Po activity was corrected for recovery by comparison with measured activity of the 208Po yield tracer and for radioactive decay to the time of sampling. Polonium-210 was quantified inside a reference phosphogypsum obtained from the industry.

2 Results and discussion

2.1 Particle size fractions and volatile matter

For each sampling site, weight percentages of particle size fractions < 50 µm (F1) and > 50 µm (F2) and their corresponding volatile matter amounts are presented in Table 1. The particle size fraction less than 50 µm provides relatively weak weight percentages in almost all the sampling sites whereas the most important amounts of particles were greater than 50 µm. F1 varies between 2% and 18% of the total mass of the samples around the industry. The higher proportions of F1 (18%, 15% and 12%) were observed respectively in samples collected from sites 19, 1, 8 and 9. Sites 1, 8 and 9 are next to the main road and they are mostly influenced by deposits coming from vehicles transporting raw and industrialized materials. These values are analogous to the values obtained by Rutherford (1996). In his work, the sediments with fraction size less than 50 µm obtained from different phosphate industries represented about 10% of the total mass.

Table 1 also shows the weight percentage of ashes. Weight loss is related to the contents of some volatile matter such as organics and some waters in hydrated minerals present in the samples. According to ash weights inside the particle size fraction less than 50 µm, volatile matter is always greater than 10% of the total mass in almost all the sites (Table 1). On the other hand, 14 sampling sites showed volatile matter percentages less than 8% for F2. Two sets of sites can be distinguished according to the percentages of ashes. The first set corresponding to sites 2, 6, 8 and 13 is characterized by a homogeneous distribution of mass loss in the two size fractions. The second set corresponds to sites of a heterogeneous distribution of mass loss inside the particle size fraction greater than 50 µm.

Mainly, it is the fraction (F1) that concentrates the large fraction of organic matter and hydrated minerals. The organic matter may have some anthropogenic sources in the studied area, particularly due to several urbanized sectors located near the industry. Nevertheless, the nature of soil (calciuluvisoil rich in silts and clays) and the presence of a weak vegetation cover dispersed in the area enhance the natural origins of such volatile matter.

2.2 Heavy elements quantification

Figure 2 shows Zn, Pb, Cu, Cr, Mn and Ni total mean contents in all the sampling sites inside the two size fractions less and greater than 50 µm. Zinc is distributed in both size fractions but preferably inside the F1 except for sites 10, 11 and 12 located near the tile factory and the phosphogypsum storage area. In some sampling sites (8, 13, 15 and 18), Zn is fairly distributed between the two size fractions (Fig. 2). Inside F1, Zn content was between 40 and 1000 mg/kg, whereas F2 provided 50 to 80 mg/kg Zn.

With regards to Zn levels, contents of Pb are found in less important levels inside the two size fractions. Lead is mostly concentrated in the fine fraction (F1). This is in agreement with Carvalho (1995) findings where Pb levels in rich phosphogypsum deposits are inversely proportional to particle size. Moreover, Carvalho (1995) has reported that sands in soil have a diluting effect on the concentration of Pb. However, some sites provided equivalent amounts or slightly more abundant levels in Pb inside the greater size fraction (F2) like sites 10, 11 and 19 (Fig. 2). Equivalent metal contents indicate their homogeneous distribution in these sites.

Like Zn and Pb, the highest level of Cu is inside the fine fraction (F1) (Fig. 2). This size fraction shows concentrations between 38 and 940 mg/kg. The difference between the Cu levels in the two size fractions of the same sampling site is significant especially in sites 3, 4, 5, 6, 7, and 9 where F1 provides the most important levels of Cu.

Chromium has significant levels in almost all the sites close to the industry. Chromium levels vary between 64 and 1510 mg/kg in size fraction F1 while 637 mg/kg is the highest concentration F2 (Fig. 2). Also Mn is mostly

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Particle size fraction &lt; 50 µm</th>
<th>Particle size fraction &gt; 50 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight (%)</td>
<td>Volatile matter (wt.%/wt.%)</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>12.23</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>13.43</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>13.82</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>11.24</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>15.08</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>12.02</td>
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<td>7</td>
<td>3</td>
<td>16.77</td>
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<td>8</td>
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<td>2</td>
<td>21.67</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>17.08</td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>11.32</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>25.55</td>
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<tr>
<td>14</td>
<td>9</td>
<td>11.31</td>
</tr>
<tr>
<td>15</td>
<td>2</td>
<td>19.10</td>
</tr>
<tr>
<td>16</td>
<td>6</td>
<td>11.31</td>
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<tr>
<td>17</td>
<td>7</td>
<td>13.99</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>9.70</td>
</tr>
<tr>
<td>19</td>
<td>18</td>
<td>12.07</td>
</tr>
</tbody>
</table>
stored inside F1 (Fig. 2); sites 2, 8, 10, 11, 18 and 19 provide slightly higher levels of Mn inside F2. Compared to the concentrations of the studied heavy metals, Ni is less abundant elements. The fine fractions of various sites concentrate Ni more than F2 except for sites 2, 10, 11 and 15 (Fig. 2).

Fig. 2  Zn, Pb, Cu, Cr, Mn, and Ni concentrations in F1 and F2 at different sampling sites.

Compared to metal contents inside the selected soil references and phosphogypsum, all sampling sites show clear enrichment levels in all studied metals especially for sites that are closer to the fertilizers industry (Table 2). It must be highlighted that the total metal contents in the reference soils reported in Table 2 were close to the mean standard values reported for natural soils (Kabata-Pendias and Pendias, 2000). With regards to soil references, the most enriched sites with heavy metals are sites from 1 to 14 for Zn and Cr, from 1 to 9 for Pb and Cu, and finally from sites 1 to 19 for Ni and Mn. Therefore, two main groups of sampling sites can be distinguished: (1) the first group from sites 1 to 14 located directly near the phosphate industry and along the main road, (2) the second group from sites

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Phosphogypsum</th>
<th>Size fraction</th>
<th>Ref. 1</th>
<th>Ref. 2</th>
<th>Ref. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (mg/kg)</td>
<td>24.0 ± 2.8</td>
<td>&lt; 50 µm</td>
<td>22.0 ± 3.2*</td>
<td>27.0 ± 6.0</td>
<td>18.0 ± 4.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>10.0 ± 2.5</td>
<td>13.0 ± 2.9</td>
<td>11.0 ± 1.8</td>
</tr>
<tr>
<td>Zn (mg/kg)</td>
<td>74.0 ± 4.8</td>
<td>&lt; 50 µm</td>
<td>92.0 ± 3.0</td>
<td>85.0 ± 2.0</td>
<td>60.0 ± 3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>34.0 ± 3.5</td>
<td>41.0 ± 3.2</td>
<td>44.0 ± 2.9</td>
</tr>
<tr>
<td>Cu (mg/kg)</td>
<td>12.0 ± 2.7</td>
<td>&lt; 50 µm</td>
<td>35.0 ± 2.8</td>
<td>30.0 ± 2.5</td>
<td>15.7 ± 6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>21.0 ± 1.1</td>
<td>22.0 ± 1.7</td>
<td>9.0 ± 0.9</td>
</tr>
<tr>
<td>Ni (mg/kg)</td>
<td>3.0 ± 1.1</td>
<td>&lt; 50 µm</td>
<td>1.2 ± 0.5</td>
<td>0.8 ± 0.4</td>
<td>3.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>Cr (mg/kg)</td>
<td>34.0 ± 3.1</td>
<td>&lt; 50 µm</td>
<td>15.0 ± 2.0</td>
<td>18.5 ± 2.1</td>
<td>10.2 ± 3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>5.0 ± 0.5</td>
<td>4.0 ± 0.3</td>
<td>5.0 ± 0.7</td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>5.3 ± 1.1</td>
<td>&lt; 50 µm</td>
<td>810.0 ± 23.0</td>
<td>850.0 ± 31.0</td>
<td>942.0 ± 28.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>122.0 ± 12.0</td>
<td>117.0 ± 10.0</td>
<td>116.0 ± 12.0</td>
</tr>
<tr>
<td>210Po (Bq/kg)</td>
<td>289.0 ± 8</td>
<td>&lt; 50 µm</td>
<td>17.0 ± 0.5</td>
<td>15.0 ± 0.5</td>
<td>18.0 ± 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 50 µm</td>
<td>0.5 ± 0.1</td>
<td>0.0 ± 0.3</td>
<td>1.2 ± 0.2</td>
</tr>
</tbody>
</table>

Data are expressed as mean ± SD (n = 4). DL: detection limit. Ref. 1, 2, and 3 are the reference soils collected at 15 km far from the industrial sampling sites.
15 to 19 distributed relatively at long distances from the industry. Sites 7, 8 and 9 are the most enriched sites in heavy metals. The metal enrichment factor is defined as the metal concentration inside a particulate size fraction in a given site ($M_{\text{site}}$) to the mean contents of this metal inside the same particulate size fraction of the reference soil ($M_{\text{ref}}$). This factor is given as the enrichment factor $= \frac{M_{\text{site}}}{M_{\text{ref}}}$.

Almost all the sampling sites especially in the sector around the industry (sites 1–14) have Zn concentration levels clearly higher than reference soils and released phosphogypsum (Table 2). Sites 7 and 9 have an enrichment factor of zinc greater than 10 inside the fine fraction.

Compared to the mean levels of Pb in reference soils and phosphogypsum (Table 2), samples in almost all the sites are clearly enriched in Pb or at least have equivalent contents. According to reference soils, Pb is enriched more than 15 times in the fine fraction of sites 6 and 7. Copper and chromium have enrichment factors greater than 32 and 100 respectively in the fine fraction of site 9. Enrichment factor is 1.5 for Mn inside the fine fraction of sites 3, 4, 6 and 7.

Removing the highest value of Ni obtained in the fine size fraction of site 8, the average of Ni in the sampling sites will become around 4 mg/kg. According to the study by Brigden et al. (2002) conducted in the same industrial area, the concentration of Ni in the phosphogypsum is lower than 2 mg/kg, which is an agreement with values reported for phosphogypsum in Table 2. It explains the relatively low level of Ni in the studied samples. However, an enrichment factor greater than 2 can be recorded for sites 1–7 inside the fine size fraction.

Sites enrichment in heavy metals may have many reasons. Large vehicles transporting raw materials, phosphogypsum storage, and smelters are the most important sources of metal enrichment. Lead may be emitted from transporting vehicles and can be associated with aerosols as PbSO$_4$ impurities inside (NH$_4$)$_2$SO$_4$ (Harrison and Jones, 1995). Such reaction can take place especially under high relative humidity which is the main atmospheric condition at the Mediterranean coast. Particulate materials from smelters contain PbS, PbSO$_4$ and PbO-PbSO$_4$ (Seiler et al., 1988). Phosphate loading activities and phosphogypsum storing are considered as the main source of Zn, Cu, Cr and Pb since they are very concentrated in phosphogypsum (Table 2). Zinc compounds are usually used for wheel manufacturing, metal alloys and are present in some ores such as phosphate minerals (El Samrani et al., 2004; Al-Masri et al., 2006). Therefore, it is expected to observe high levels of Zn in soils near the phosphate industry and the surrounding environment. Such concentrations are most probably attributed to eroded wheels, to vehicles transporting raw materials as well as to stored phosphogypsum under atmospheric conditions. According to Al-Masri et al. (2004), Zn is the most transferred element from phosphate ores to phosphogypsum. Transfer of Zn from raw materials to solid waste depends on the process of production and the origin of the ores.

Compared to the analysis results of Lebanese phosphogypsum by Brigden et al. (2002), it can be evidenced that Ni made an accumulation in the soil all around the industry. Much more accumulation is observed far from the industry (sites 15–19). Such results enhance the presence of another mechanism of transportation. However, such mechanism is difficult to be explained since the methods used for investigation are insufficient. Manganese enrichment was insignificant since that the soil of the studied region is a calciluvisoil as reported in the map described by Darwish (1998); clay and silts are rich ferromagnesian oxihydroxides compounds. Hence, any Mn enrichment cannot be evidenced in such a rich matrix.

Metal elements enrichment can take place since phosphogypsum can be leached many times during the wet weather periods and releases its metal content to the soil. In fact, it is reported that dehydrated gypsum and semi-hydrated gypsum solubility are respectively 2 and 9 g/L at 20°C. The log$K_s$ of gypsum is $-4.58$ (Johnson et al., 1981). Under such conditions, releasing metals from phosphogypsum becomes very expected and enrichment can take place under such conditions.

The amounts of different heavy metals in the 19 studied sites decreases in the following order: Zn > Mn > Cr > Cu > Pb > Ni. Several parameters can give explanation for this difference; as the composition of the sediments, the sources of metals, the state of oxidization, the pH and the size of the particles (Sfar Felfoul et al., 2002; Arocena et al., 1995). It can be noticed that heavy metal contents in the samples depend strongly on the size of the particles. The large size particles provide less metal contents than small particles for almost all the sites. However, in some sampling sites, heavy metals where more associated to the greater size fraction (F2). Such result is most probably related to the matrix of the sample where small size particles are aggregated and cemented together resulting larger size fraction. This may be attributed to the presence of clays colloids and some precipitated salts as sulfates, carbonates and phosphates. This behavior was significantly observed in sites 10, 11 for Zn, Pb, Cr, Mn and Ni. It is reported that the fine fraction in phosphogypsum generally concentrates the heavy metals (Carvalho, 1995; Arocena et al., 1995). The site 11 represents the most important exception since the coarse fraction has the most important amounts of heavy metals (Fig. 2).

### 2.3 Electron microscope investigation

Figure 3 shows typical particles identified inside the particle size fraction < 50 µm. They were identified inside the sites from 1 to 13. Phosphate minerals were identified at almost all the sampling sites except for sites 14 to 19. They were found as nanoparticle agglomerates (Fig. 3a) or precipitates (Fig. 3b). Most of the calcium phosphate particles contained more than 28% of fluorine. Phosphate rocks, according to their origin, and phosphogypsum waste may contain fluorine (Arocena et al., 1995; Camelo et al., 1997). In fact, the presence of fluorine can be used as an indicator to explain the relation between phosphate raw materials and the origin of heavy elements distribution in the surrounding area. Other typical particles were formed.
mainly from iron oxyhydroxides contaminated with zinc and associated to some amounts of silicates and calcium sulfates (Fig. 3c). This kind of particles is most probably related to the natural components of the soil. In addition to the above TEM micrographs demonstrating the phosphate row materials dispersion on the sampling sites and incorporating soil components as silicates and iron oxyhydroxides, strontrium sulfates aerosols were identified by SEM-EDXS (Fig. 3d). Such particles are most probably originated from phosphogypsum waste. This origin may be reinforced by a previous finding that demonstrated that strontrium content in sulfates and oxyhydroxides was about 56% of the total strontrium in the phosphogypsum waste (Pérez-López et al., 2007). In the present work, the most abundant rate of strontrium was transferred from phosphate rocks to phosphogypsum. Another proof to the diffusion distribution of trace elements can be observed in Fig. 3e, where BEI shows aggregated microparticles entrapping Sn, Pb, and Cu. Other kind of particles was found to have no heavy elements. It was mainly composed from sulfates and phosphates particles recovered by some clays particles (Fig. 3f).

An X-ray emission cartography of O, Al, Si, Ca, Fe, and Zn, realized by TEM-EDX on a typical aggregate found in sampling site 10 is shown in Fig. 3g. The main goal of presenting this figure is to demonstrate the homogenous distribution of metals inside the particles. Hence, focusing EDX analysis on an individual particle inside the aggregate will result in a diffused contamination by heavy elements.

Electron microscope investigations always raise the problem of results representativity. Clearly, the number of particles examined here remains infinitesimally small compared to the total amount of particles dispersed in the surrounding environment of the phosphate fertilizer industry. Extreme caution should then be exerted as to the conclusions inferred from microscopical observations. Still, our results strongly suggest that: (1) heavy metal contamination is in a diffused state in the particles. The electron microscope investigation is a very complementary technique to the total heavy metal determination since it demonstrates the state of the contamination by using an individual particle scale; (2) strontrium and fluorine are considered as indicators that demonstrate the dispersion of phosphate row materials and phosphogypsum waste in the surrounding area.

2.4 Spatial distribution of heavy elements

The distribution of total Pb, Zn, Cu, Ni, Cr, and Mn inside the two particle size fractions all around the fertilizer industry is achieved at a spatial scale (Fig. 4). Longitudes and latitudes of the extreme sampling sites located to the south, north, east and west of the industry constituted the limits of this spatial scale. Site number 18 was excluded from the mapping data as it is extremely isolated site especially from the west and this may disturb the trace metal distribution maps. Another part of the maps was excluded;
it corresponds to the sea area that is not included in our study. Surfer-8 software was used in the metal distribution mapping as a function of sampling sites longitudes and latitudes. The mapped area was about 100,000 m².

The behaviors of Cu, Pb, Zn and Cr are fairly similar (Fig. 4). Copper in fine fraction (F1) shows two maximum contents located at the south-west and north-west of the industry that coincide with the main road conducting to the industry. In the coarse fraction (F2), Cu is more likely dispersed from the SW of the industry. It shows a particular collapse at the NW of the industry.

The profile of zinc inside the fine fraction shows three main highest contents located in the south-west and the north-west of the industry. The greatest content of Zn is observable close to the industry, in the south and the southwest where two great accumulations can be identified. The closer Zn accumulation to the industry is sharper (Fig. 4). The third main Zn accumulation is located at the NE of the map at a longer distance from the industry. Such behavior suggests more than one source of Zn dispersion load; the first load is related to the main road and row material and product transport from and to the industry whereas the second load of Zn is much more related to wind deposits close to the storage area of phosphogypsum waste. This can be enhanced by observing the distribution of Zn in the coarse fraction where the third maximum content of Zn in the NE disappears from the map of zinc in F2. Based on the particle size, the coarse fraction is hardly removable whereas the fine fraction is transportable to longer distances. So the transfer is identifiable from the SW to the NE of the industry.

Since it is concentrated in the south-west of the industry, lead in F1 is dispersed all around the industry from this point without showing any accumulation to the north-east. Lead in F2 is largely accumulated in the south-west and distributed gradually in all directions before rejoining the geochemical background. Based on such gradual decrease in Pb content, physical migration cannot be assigned to the entirely transportation mode. Taking into account the phosphogypsum solubility, a transfer of Pb by solubilization of the fine fraction and readsoption and precipitation on the large size particles can occur. Taking into account the chemical composition of phosphogypsum, leaching rich phosphogypsum deposits in an environment greatly influenced by humidity and marine sprays may dissolve a significant part of the heavy metals. Hence, transfer by chemical exchange and physical transportation are two possible ways of metal transfer.

Chromium in F1 and F2 show an important accumulation closed to the industry at the south and the south-west then a gradual decrease in all the map direction. A significant accumulation of Cr inside F1 can be observed to the north-east of the industry like Zn and Cu. Even its high concentration near the industry, mapped Ni in F1 shows a weak spatial variation with values very close to the geochemical background. As for F1, Ni load inside F2 disappeared completely near the industry demonstrating that phosphogypsum waste and phosphate row materials are not significant participants in Ni load around the industry.

Maps of Mn in F1 and F2 showed no important loads of this metal from the industry as its content was much close to the geochemical background determined in the soil references (Table 2) and since the studied phosphogypsum provided negligible manganese contents.

Mapping the distribution of heavy elements in F1 and F2 evidences their transfer and their accumulation around the fertilizer industry. Four facts can be highlighted from this mapping: (1) excepting Ni, increasing distance from the industry is accompanied with content decreasing in heavy elements especially for metals in F2; (2) metals in F1 are more likely accumulated in the south and the north-east of the industry. The most important contamination is coming from the row materials and waste transport along the main road conducting to the industry, then come the waste stored at atmospheric conditions that enhance the contaminant distribution. Waste leaching may also contribute to exchange metals between size fractions. Moreover, wind direction at the studied area is western and south-western. It enhances transporting fine particulate metals coming from the smelters of the industry to the north and the north-east. The topography of the studied region, limited at the east by a mountain frontier, contributes also in the entrapment and accumulation of heavy metals in the north-east. In a previous study, wind direction has been identified as the most important dispersing factors of air suspended matter (Othman and Al-Masri, 2007).

2.5 Polonium-210

Radioactivity of 210Po in F1 of the studied sites varied between 56 and 936 Bq/kg (Fig. 5a). Almost all the studied sites presented 210Po levels upper than 100 Bq/kg. Sites 3, 5, 9, 10 and 13 provided the higher levels in 210Po. An enrichment factor of 210Po was about 56 in the F1 of the site 13. The 210Po enrichment factor is defined as the 210Po activity inside F1 in a given site to the average of the 210Po activity inside F1 of the reference soil (210Po site/210Po ref.).

They were located in the area close to the industry (sites 9 and 10), to the main road (sites 3 and 5) and to the storage zone (site 13) as it is observable in Fig. 5a. Compared to the level of 210Po in reference soils (about 18 Bq/kg) and phosphogypsum (289 Bq/kg) (Table 2), a significant enrichment in 210Po and transfer from phosphogypsum to soil become evident in all the sampling sites. Compared to previous studies, the activity of the 210Po in the sediments of phosphogypsum varied between 355 and 1765 Bq/kg (Santos et al., 2005; Lardineye, 1982; Brigden et al., 2002). Working on the impact of fertilizer industry on the environment, Al-Masri (2006) found that radioactivity of 210Po ranged between 148 and 1479 Bq/kg in deposits and sediments collected around the phosphate fertilizer industries in Syria (Al-Masri et al., 2006). These activities are slightly higher than the levels range obtained in this work (Fig. 5a).

Since the atmospheric transportation is the most important origin of 210Po in soil (Coppen et al., 2004), it becomes much probable that dust contributes in the increase of 210Po.
in the upper level of soil in both the transportation and the storage area. It is reported that $^{210}\text{Po}$ would be mainly concentrated in the upper layer of soils (Coppin et al., 2004). Therefore, the distribution and enhancement of this radionuclide in the surrounding environment are mainly attributed to the fallout of phosphate dust generated during

![Fig. 4 Maps of Cu, Zn, Pb, Cr, Ni and Mn levels distribution around the fertilizer industry inside F1 and F2 particle size fractions.](image)

**Fig. 5** $^{210}\text{Po}$ activity inside F1 fraction as a function of sampling sites (a), maps of $^{210}\text{Po}$ activity levels distribution around the fertilizer industry inside F1 particle size fractions (b).
the loading and processing of phosphorus ores.

Radioactivity levels of $^{210}\text{Po}$ inside F1 are mapped as a function of latitudes and longitudes (Fig. 5b). Three greatest increases of $^{210}\text{Po}$ are identified at the south, the south west and at the north of the industry (Fig. 5b). At the north of the industry, dusts from storage of fertilizing materials are the most important sources of $^{210}\text{Po}$ whereas transportation remains the most important sources at the south and south west of the industry. Behavior of $^{210}\text{Po}$ is similar to behaviors of Cu, Zn and Cr inside F1 around the industry.

The metal and $^{210}\text{Po}$ mapping has a great importance since the accumulation zones were identified on a spatial scale of about 10,000 m² well represented by 18 experimental sampling sites. This distribution enabled us to follow the direction of heavy element dispersion rates. The studied area was relatively flat and weakly waterproofed by the local urbanization and by the presence of some minor hills dominated by limestone and dolomite outcrops. Such geomorphology may contribute to create some preferable accumulation zone mainly influenced by wind direction and leaching during wet weather. Moreover, the industry is planted on a continental shelf surrounded by the sea at the west and by elevated reliefs at the East. Hence, the wind blowing from the south and the south west during a long period of the year makes a turbulent movement along the reliefs and transports the various pollutants to the north of the industry.

3 Conclusions

This work gives detailed information about heavy elements and $^{210}\text{Po}$ distribution and enrichment around a phosphate fertilizer industry. The survey of the contaminants release by the industry was evidenced on the near environment and supported by studying the mechanisms of transportation and accumulation. Greatly elevated contaminations by Pb, Zn, Mn, Ni, Cr, Cu, and $^{210}\text{Po}$ were recorded inside the fine particle size fraction (< 50 μm). Studied contaminants decreased with the distance increasing from the industry. The survey revealed three main sources of contamination: (1) storage and vehicles transport of raw materials, (2) phosphogypsum waste free releases, and (3) dust deposits from smelters. Transfer of contaminants was governed by two major mechanisms: a physical transfer by winds and leaching, and a chemical transfer by dissolving the contents of phosphate ores and phosphogypsum in the fine fraction. Mapping the contaminants shows the source of emission and the accumulation sector of each contaminant. In fact, the phosphate industry is the main source of enhancement of naturally occurring radionuclides in the surrounding environment. This survey demonstrated that the region is certainly contaminated and protective measures that assure the public and workers security must be taken. Following this survey, transport and storage of raw materials and releases of phosphogypsum waste must be done with respect to the norms applied on environment protection.

Acknowledgments

This work was supported by the research grants program of the Lebanese Council for Scientific Research. The authors wish to express their sincere thanks to the National Council for Scientific Research.

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