A PRELIMINARY EVALUATION OF THE INORGANIC CHEMICAL COMPOSITION OF ATMOSPHERIC TSP IN THE SELAATA REGION, NORTH LEBANON

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ABSTRACT

The inorganic chemical composition of atmospheric total suspended particles (TSP) was studied in the region of Selaata, around a phosphate fertilizer factory, between April and June, 2008. Water soluble anions and metal analysis were conducted using ion chromatography (I.C.) and inductively coupled plasma-mass spectrometer (ICP-MS) respectively. The results showed moderate industrial contribution to the anions loads, but mostly in nitrates which were linked to gas-particle conversion of NO_2 *emitted from heavy duty machinery. High metals content were verified with a remarkable enrichment in the downwind sites. The enrichment factor analysis showed high values for P, Ca, V, Ni, Cu, Zn, Cd, Pb, and Cr. This enrichment resulted from many anthropogenic sources in the area, from which dry milling of phosphate rocks, chemical reactions used for fertilizer production, and vehicles activities were the most prominent.*

Keywords: atmospheric total suspended particles, trace metals, chemical fertilizer factory, ion chromatography, ICP-MS, Lebanon

INTRODUCTION

Atmospheric pollution in Lebanon has been the focus of many scientific studies in recent years. The majority of these researches have dealt with gaseous pollutants such as transport related emissions in big cities (El-Fadel & Bou-Zeid, 1999; 2000; Chaaban *et al.,* 2001; Sbayti *et al.,* 2002; Moussa *et al.,* 2006), precisely green house gas emitted by vehicles and atmospheric lead emissions related to the use of lead concentrated gasoline, and finally industrial related gaseous emissions (El-Fadel *et al.,* 2001). On the other hand, atmospheric aerosols have been studied recently by Shaka' and Saliba (2004), Saliba *et al.* (2006), Kouyoumdjian and Saliba (2006), Saliba *et al.* (2007; 2009), in an attempt to evaluate the air quality in Lebanon, mostly in the heavily urbanized capital Beirut.

Few studies were concerned with the industrial particulate matter emissions in Lebanon, especially in the northern section of the country, where several cement and local factories are located in the cities of Chekka and Selaata, respectively. Few attempts to evaluate the pollution caused by these industries have been conducted, most of which concentrated on atmospheric particulate matter emitted in the region of Chekka (Ministry of Environment, 2001; Karam & Tabbara, 2004; Kfoury *et al.*, 2009), and on effluents coming from the chemical fertilizer factory in Selaata (Brigden *et al.*, 2002; Nakhlé, 2003). Up to our knowledge, there is no study of the chemical composition of atmospheric aerosols in Selaata, despite the presence of local factories, and the fact that a link between exposure, respiratory diseases and proximity to the industrialized region in Chekka and Selaata has been proven (Kobrossi, 2000).

The phosphate chemical fertilizer factory in Selaata is known to produce simple superphosphate (SSPh), triple superphosphate (TSPh) and phosphoric acid. The production line in the factory uses phosphoric and sulfuric acids mixed with phosphate rocks to produce the fertilizer (Nakhlé, 2003). The phosphate rock (mainly $Ca_{10}(PO_4)_6F_2$) used in the production of phosphate based chemical fertilizer contains calcium, phosphate and fluorine in large quantities. In addition, many studies proved that impurities including major elements (Mn, Mg, Na, K…) and minor elements (Co, Cu, Ni, Cr, Pb, Cd, Zn …) can be found at higher concentration in the phosphate rock (Pantelica *et al.*, 1997; Martin *et al.*, 1999; Al-Masri *et al.*, 2004; Sabiha-Javied *et al.*, 2008; 2009). The load of these elements in the rock varies depending on the geographic location of the phosphate mines from which these rocks were imported. The most common phosphate rock exporting countries are Morocco, Tunis, Jordan, Syria, Senegal, Algeria, Israel, United States of America, Russia, Pakistan, Egypt and Togo. In the case of the chemical fertilizer factory of Selaata, phosphate raw materials are imported from Syria (Nakhlé, 2003).

As for fertilizer production, it revolves mainly around the reaction of phosphate rocks with sulfuric and phosphoric acid to produce SSPh and TSPh respectively (USEPA, 1995). The factory also produces its own phosphoric acid by reacting sulfuric acid with the same raw material used for fertilizer production, but with different reaction conditions (USEPA, 2009). The most important byproduct resulting from these reactions is gypsum effluents, also known as phosphogypsum, which was found to be concentrated with toxic trace elements and radioactive matter in many studies (Martin *el al.*, 1999; Al-Masri *et al.*, 2004; Mourad *et al.*, 2009). The case of Selaata was not different since toxic trace elements were also found concentrated in the marine waters and sediments located in the vicinity of the chemical fertilizer plant and accumulated in marine organisms living in the same zone. The source of this pollution was linked to phosphogypsum effluents that are dumped in seawater (Brigden *et al.*, 2002; Nakhlé, 2003; Abi-Ghanem *et al.*, 2009).

Gaseous emissions from phosphate fertilizer factories have been assessed by the United States Environmental Protection Agency (USEPA). It was found that CO_2 which was produced from limestone ($CaCO_3$) reaction with sulfuric acid (USEPA, 2009), hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) from the reaction of phosphate rocks with sulfuric and phosphoric acids as well as particulate matter were among the major pollutants (USEPA, 1995).

Up to our knowledge, there is no previous evaluation of atmospheric suspended particulate matter in the region of Selaata, precisely around the chemical fertilizer plant.

Therefore, the aims of this study are to obtain preliminary information concerning the inorganic chemical composition of atmospheric total suspended particles in the region, taking in consideration the area stretching from Kfaraabida (South) to Hannouch (North), and to identify the nature as well as the possible sources of atmospheric particulate pollution.

MATERIALS AND METHODS

Study area

The coastal region of Selaata is located in north Lebanon, approximately 50 km from the capital Beirut. It is surrounded by Mount Sha'aa (north) and the city of Batroun (south). The area is divided into a moderately urbanized village and an industrial area that covers most of its coastal line. The climate is similar to the typical Lebanese coastal climate: mediterranean type exhibiting a rainy winter and a hot dry summer (Administration Centrale de la Statistique, 2006).

In general, Lebanon is affected by airborne dust coming regularly from Africa in spring (Kubilay *et al.,* 2000) and the Arab peninsula in autumn (Dayan, 1986; Dayan *et al.,* 1991). These air masses usually pass over Egypt then into the Lebanese atmosphere (Dayan, 1986; Goudie & Middleton, 2001) and are loaded with crustal particles (Querol *et al.,* 2009). As for the studied area, it can be affected by many sources of particulate matter emissions: local chemical fertilizer factory (including point and non-point sources), sea spray coming from the adjacent Mediterranean Sea, air masses holding secondary aerosols from long range transport mechanism, local transport vehicle exhaust (cars, trucks and ships), and air masses coming from the Arab peninsula or Africa.

Sampling methodology

The sampling strategy implicated seven sampling points, from the south to the north: "Kfaraabida", "Dunkin", "Batroun", "Koubba", "Koubba-coast", "Selaata", and "Hannouch" (Figure 1). The first three sites are subjected to moderate to high light vehicle traffic (cars), and are relatively distant from the fertilizer factory compared to "Koubba-coast" and "Koubba", which are in the middle and next to the industrial zone respectively. "Koubba-coast" site is subjected to heavy duty vehicle emissions (trucks and ships), local particulate emissions from dry milling of phosphate rocks, and local dust particles re-suspension. The remaining two sites, Selaata and Hannouch, are located downwind, to the north of the chemical fertilizer factory, and therefore are expected to be highly influenced by the emissions, since on the local level, the observed wind direction at each site was South-West (SW).

The sampled sites were divided into two groups, characterized by their relative position towards the chemical fertilizer factory: the southern group includes sites located upwind ("Koubba", "Batroun", "Dunkin", and "Kfaraabida"), and the remaining sites are downwind ("Koubba-coast", "Selaata", and "Hannouch") and were enclosed in the northern group. Table 1 summarizes the characteristics of the sampling sites.

The sampling campaign covered the period from April 22nd to June 6th (2008). At each site, sampling occurred once per day, during two different days, using a mobile sampling truck provided by the University Of Balamand (Lebanon). A high volume sampling pump

(Staplex® TFIA-2) was used to collect atmospheric particles on pre-cleaned Staplex® cellulose filters, each sample represents 4 hours collection at each site, from 9 am to 1 pm, with a 68 m^3/h air flow rate. In total, 14 samples were collected under local SW wind and total absence of precipitation. After sampling, all filters were placed in a properly washed Petri dish and sealed with Parafilm® ribbons, then conserved at -20°C before analysis.

TABLE 1

Sampling Site, Geographic Position, Sampling Date and Local Wind Direction

Site	**Geographic position**		**Sampling dates and local wind direction**			
	Lat	Long	1st day	Direction	2nd day	Direction
Hannouch	34.30468	35.67432	29/05/2008	SW	04/06/2008	SW
Selaata	34.29297	35.67023	30/04/2008	SW	22/05/2008	SW
Koubba-coast	34.27623	35.65678	27/05/2008	SW	06/06/2008	SW
Koubba	34.27295	35.66305	22/04/2008	SW	14/05/2008	SW
Batroun	34.26416	35.65859	19/05/2008	SW	26/05/2008	SW
Dunkin	34.24975	35.65969	02/05/2008	SW	03/06/2008	SW
Kfaraabida	34.23918	35.65962	20/05/2008	SW	02/06/2008	SW

Filters preparation and contamination reduction

Unwashed Staplex® cellulose filters used for sampling present many trace metals contents, especially Fe (up to 5µg per filter). The reduction of such elements was applied using the technique described in Ledoux *et al.* (2006) for Fe analysis, in which cellulose filters were submerged in 0.5M HCl and 0.5M HNO_3 for 24h, rinsed with ultrapure water (MilliQ®, Millipore; resistivity = 18.2 MΩ.cm), desiccated under a laminar flow hood (Class 100, US Federal Standard 209a), and finally conserved in previously washed Petri dishes and stored at -20°C. This treatment was applied to the filters before sampling to lower Fe concentration under 0.1µg per filter, and the concentration of all other metals below detection limit.

Chemical analysis

Ion chromatography (I.C.) and inductively coupled plasma-mass spectrometer (ICP-MS) were used to obtain the concentrations of different water soluble anions and metals respectively for each of the 14 samples. For water soluble anions (Cl^-, NO_3^-, SO_4^{2-}) a Dionex DX500 equipped with an AS14A analytical column and a conductivity detector were used.

The eluent was a mixture of sodium carbonate and sodium hydrogen carbonate (Na_2CO_3 3.5mM / $NaHCO_3$ 1mM) with 1.2 mL/min flow rate. The standard solution used for calibration covered a concentration range of 0.5 – 100 ppm.

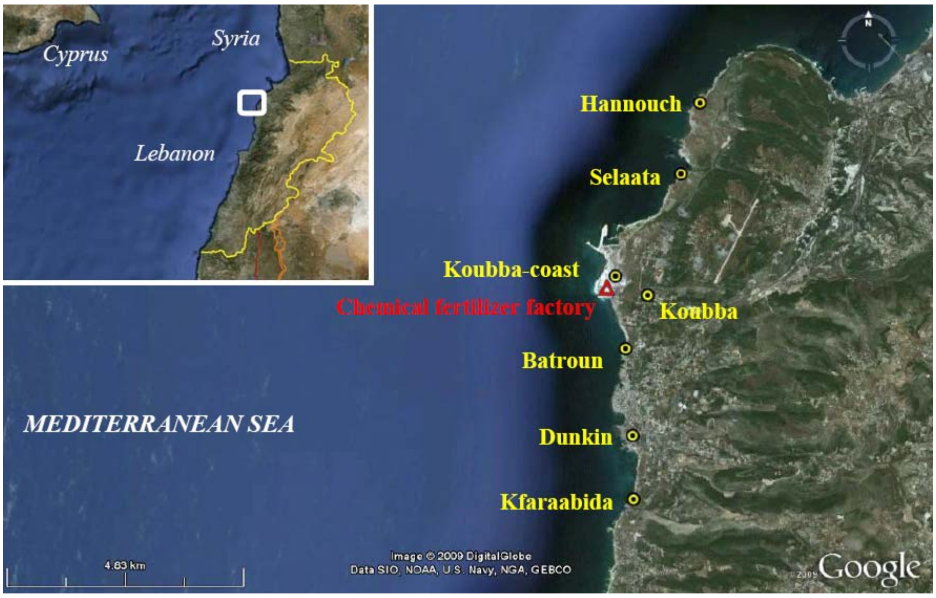

Figure 1. Satellite image showing the main emissions source in Selaata and the sampling sites (source: Google™).

Metal analysis was conducted using a Varian® 820-MS equipped with a collision reaction cell to minimize polyatomic interferences. The list of metals that were analyzed was restricted to: Na, Mg, Al, P, K, Ca, Fe, Ti, V, Cr, Mn, Ni, Cu, Zn, Pb, and Cd. Standard solutions were prepared from a multi-element stock solution and covered a concentration range from 0.2 to 100 ppb. A blank filters concentration was found negligible for all the analyzed elements. Quality control and measurements accuracy tests are included in Kfoury *et al*., 2009.

Samples preparation

Water soluble anions were extracted by leaching about 200 mg of the total filter, using an ultrasonic treatment for 30 min in 10 mL of ultra-pure water (MilliQ®, Millipore; resistivity=18.2 MΩ.cm). The leachate was filtered on a cellulose acetate membrane (porosity 0.45 µm) in a polyethylene flask and the volume adjusted to 20 mL, in each flask, by adding ultrapure water. The final solutions were conserved at 4°C before injection in the analytical column.

The analysis was realized after acid digestion in a high temperature medium following the method described in Kfoury *et al*. (2009). Approximately 1/6th of each cellulose filter was deposited into a PTFE flask (Savillex® Corp.) and digested with 5.5 mL $HNO_3/HF/HClO_4$ (4: 1: 0.5 v/v/v, Suprapur®, Merck®) at 130°C for 4h using a heating plate, then acids were evaporated under 170°C for 3h. Ultrapure water was added to the residue and heated at 110°C for 1h, after which the solution was placed aside for cooling. A final dilution was applied to the solution using ultra-pure water (up to 10 mL of final volume), added with 20 µL of nitric acid, and then filtered on PTFE membrane (0.45 µm) in a polyethylene flask. Finally, the solutions were conserved at 4°C before analysis.

RESULTS AND DISCUSSIONS

The results of ICP-MS and I.C. analysis showed different concentrations for metals and water soluble anions. Between analyzed metals, Na, Mg, Al, P, K, Ca, and Fe exhibited high concentrations and were assembled in the "major metals" group. The remaining metals (Ti, V, Cr, Mn, Cd, Ni, Cu, Zn, and Pb) were found in lower concentrations and were included in the "minor metals" group.

Comparison of total average concentrations with other studies

The total average concentration for each metal was compared with those found in other studies conducted in sites around the mediterranean basin, most of which analyzed PM_{10} (Güllü *et al*., 2000; Koçak *et al*., 2007 ; Saliba *et al*., 2007 ; Sanchez de la Campa *et al*., 2007; Koulouri *et al*., 2008; Mamane *et al*., 2008 ; Kfoury *et al*., 2009).

Major metals

Table 2 displays the comparison between this study's metals average concentrations and other studies. Average levels of Na (4551 ng/m^3), Mg (1643 ng/m^3), Al (2225 ng/m^3), and K (14862 ng/m^3) are found higher than all the compared studies. These elements are usually concentrated within TSP (especially PM > 10 µm), that are sampled using high volume sampling methods like the one applied in this study.

Elemental phosphorous exhibits a very high average (10663 ng/m^3) in Selaata when compared to the remaining studies. In the same time, Ca average (13528 ng/m^3) in this study exceeds all the other results found in the Mediterranean, and doubled the amount found in Beirut (6612 ng/m^3) where a crustal source, arriving to the area with air masses movements, was behind this high load.

Fe average concentration (1801 ng/m^3) is found higher than in the other comparison sites including Ashdod (1210 ng/m^3) but lower than in Beirut (2157 ng/m^3) where crustal enrichment was behind high Fe levels. Since no dust storms were observed during the sampling period, this high Fe source can be linked to resuspended dust in the industrial area.

Minor metals

The analysis of minor metals showed a total average concentrations of Ti (157 ng/m^3), V (76 ng/m^3), Cr (50 ng/m^3), Cd (2 ng/m^3), and Ni (34 ng/m^3) higher than all the other Mediterranean sites, between which only Ashdod exhibited high values for these elements (Table 2).

TABLE 2

Comparison of Major and Minor Metals Average Concentrations (in ng/m^3) with Those Found in other Studies

	Present study	***SD***	**Kfoury *et al.* 2009 (Chekka-Lebanon)**	**Saliba *et al.,* 2007 (Beirut - Lebanon)**	**Sanchez de la campa, 2007 (Huelva - Spain)**	**Koulouri *et al.*, 2008 (Crete Island - Greece)**	**Koçak *et al.,* 2007 (Erdemli-Turkey)**	**Mamane *et al.*, 2008 (Ashdod-Israel)**	**Güllü *et al.*, 2000 (Antalya-Turkey)**
Na	4551	± *3307*	516	-	1000	-	-	692	1900
Mg	1643	± *1813*	164	-	300	-	-	523	365
Al	2225	± *2534*	250	-	-	-	-	776	540
P	10663	± *25183*	-	-	64	-	-	95	-
K	14862	± *31597*	2091	533	600	-	360	630	365
Ca	13528	± *20081*	1021	6612	1400	1548	1888	4655	2100
Fe	1801	± *2379*	185	2157	700	598	351	1210	390
Ti	157	± *154*	18	-	55	43	27	113	40
V	76	± *132*	2	-	7	8	9	39	3
Cr	50	± *94*	3	-	3	9	6	22	4
Mn	35	± *35*	5	-	12	12	8	38	9
Cd	2	± *3*	0	-	1	0	-	-	-
Ni	34	± *31*	3	-	4	4	4	15	3
Cu	12	± *11*	2	-	50	3	-	14	-
Zn	132	± *145*	12	174	30	29	10	165	21
Pb	14	± *7*	3	-	-	9	-	49	21

Mn average concentration in Selaata (35 ng/m^3) is found higher than in all the other sites except Ashdod (38 ng/m^3). However, Cu concentration in this study (12 ng/m^3) is comparable to that of Ashdod (14 ng/m^3), but is much lower than the corresponding value found in Huelva (50 ng/m^3) where metallurgic activities were behind these concentrations.

On the other hand, Zn average concentration (132 ng/m^3) is smaller than in Ashdod (165 ng/m^3) and Beirut (174 ng/m^3), which both represent heavier traffic conditions.

Finally, Pb concentration in Selaata (14 ng/m^3) was lower than in Ashdod (49 ng/m^3) and in Antalya (21 ng/m^3) which are subjected to more traffic emissions.

Water soluble anions

Table 3 compares chloride, nitrate, and sulfate average concentrations in this study with those found in other studies that covered mediterranean regions as well (Erduran & Tuncel, 2001; Galvas *et al.*, 2008 ; Güllü *et al.*, 2000 ; Koçak *et al.*, 2007; Koulouri *et al.*, 2008 ; Kfoury *et al.*, 2009 ; Prodi *et al.*, 2009). Chloride average concentration in Selaata (705 ng/m^3) is comparable to that found in Chekka (650 ng/m^3) but lower that in other coastal sites like Crete Island (1509 ng/m^3), Antalya (4300 ng/m^3), and Erdemli (5492 ng/m^3). On the other hand, nitrate average concentration (1032 ng/m^3) is higher than in Patras (400 ng/m^3), comparable to Antalya (1180 ng/m^3) in 2000, and lower than all the other sites. The case of sulfates is different, where it is found lower than all the comparison sites in the Mediterranean.

Comparison of upwind (South) to downwind (North) average concentrations

Table 4 compares the average concentrations for metals and water soluble anions between upwind and downwind samples in the Selaata region.

Major metals

The results of major metals analysis show that Na concentrations didn't vary much between upwind (4389 ng/m^3) and downwind (4767 ng/m^3). However, Mg, Al, and Fe present an increase in their average concentrations between southern and northern samples, which may be due to their abundance in coarser fraction of the TSP (> 10 µm), sampled in this study. On the other hand, elemental phosphorus shows an important increase in the downwind sites (24626 ng/m^3) when compared to the upwind ones (191 ng/m^3). This remarkable difference verifies the contribution of the phosphate fertilizer factory to the phosphate concentrations in the region.

Another increase can be seen in the case of potassium where the northern downwind average concentration (15983 ng/m^3) was higher than the southern upwind one (14021 ng/m^3). This potassium loads could not be generated by the activities of the phosphate fertilizer factory. In fact high K concentrations were observed in different upwind and downwind sites in a non-prominent fashion. These chronologically and geographically independent K peaks indicates that the origin is a non-point source of emissions similar to the one observed in the nearby region of Chekka (Kfoury *et al.*, 2009). The Ca load in the northern samples (21343 ng/m^3) was 2.8 times higher than the load in the southern ones (7667 ng/m^3), which points at an anthropogenic contribution, most probably resulting from calcium loaded dust re-suspension from heavy machinery activities and/or rocks grinding in the factory.

Minor metals

The results of minor metals average concentrations (Table 4) show that Ti, V, Cr, Ni, and Mn average concentrations are higher in the northern downwind samples (178 ng/m^3, 140 ng/m^3, 97 ng/m^3, 50 ng/m^3, and 45 ng/m^3 respectively) than in the southern upwind group (Ti: 142 ng/m^3, V: 27 ng/m^3, Cr: 14 ng/m^3, Ni: 21 ng/m^3, and Mn: 27 ng/m^3). This increase indicates an anthropogenic contribution in the northern downwind zone. Possible sources of atmospheric Ti, Cr, Ni and Mn can range from the impurities in phosphate rocks (Pantelica *et al.,* 1997; Martin *et al.,* 1999; Sabiha-Javied *et al.,* 2009), soil dust re-suspension for Ti (Dordević *et al.,* 2005), and finally oil combustion for V and Ni (Okuda *et al.,* 2007).

On the other hand, Zn average concentration in the southern samples (73 ng/m^3) is found lower than the northern one (209 ng/m^3). For this reason, Zn enrichment is verified, and might be linked to particles emitted from wheels of transport vehicles (Chow *et al.,* 1996) and/or to resuspended dust containing Zn impurities coming from Syrian phosphate rocks (up to 269 ± 5 ppm) used in the fertilizer plant (Pantelica *et al*., 1997). This idea is backed up by Al-Masri *et al*. (2006), who concluded that dust generated from phosphate loading activities contributed to the atmospheric loads of Zn in Tartous (Syria).

Cu average concentration increases from the southern (9 ng/m^3) to the northern (15 ng/m^3) samples. The possible sources of Cu can range from crustal and traffic related sources (Saliba *et al.,* 2007) to impurities in phosphate rocks. However, copper concentration in phosphate rocks is found to be 8.7 ± 0.3 ppm on average (Sabiha-Javied *et al.,* 2009), indicating a moderate possibility of phosphate rocks dust contribution in Cu loads.

Lead mean concentrations for the southern and northern group are found to be 12 ng/m^3 and 17 ng/m^3 respectively. This increase proves the contribution of the industrial activities in the emission of Pb loaded particles most probably through heavy machinery emissions.

Finally, the northern Cd level (3 ng/m^3) is found much higher than the southern one (1 ng/m^3). This implies the possibility of an enrichment coming from the fertilizer factory, especially from impurities within Syrian phosphate rocks used in the Selaata fertilizer factory (Nakhlé, 2003; Al-Masri *et al*., 2004).

Water soluble anions

Chloride averages in the southern and northern samples are found to be 713 ng/m^3 and 695 ng/m^3 respectively. These values are relatively close to each other, showing that there is no obvious anthropogenic contribution to chloride concentrations in the area.

Nitrate average in the southern group (562 ng/m^3) is found lower than the northern one (1658 ng/m^3). This difference between northern and southern nitrate averages is probably not related to dust emissions, but most likely to gaseous NO_2, precursor of NO_3^- formation by gas-particle conversion mechanism, emitted by heavy duty vehicles and/or engines used in the industrial site.

TABLE 3

Comparison of Water Soluble Anions Average Concentrations (in ng/m^3) with Those Found in Other Studies

			Kfoury *et al.*, 2009	**Prodi *et al.*, 2009**	**Koulouri *et al.*, 2008**	**Galvas *et al.*, 2008**	**Koçak *et al.*, 2007**	**Erduran & Tuncel, 2001**	**Güllü *et al.*, 2000**
	Present study	***SD***	**(Chekka - Lebanon)**	**(Venice - Italy)**	**(Crete Island - Greece)**	**(Patras - Greece)**	**(Erdemli - Turkey)**	**(Antalya - Turkey)**	**(Antalya - Turkey)**
Cl^-	705	± *134*	649	167	1509	120	5492	4300	-
NO_3^-	1032	± *765*	2958	3503	1731	400	1857	2280	1180
SO_4^{2-}	580	± *103*	1937	4423	5478	3200	4953	2350	5540

Finally, sulfate ions mean concentrations did not vary much between upwind (510 ng/m^3) and downwind (674 ng/m^3) samples. Modest contribution in sulfate emissions can be generated from the production line in the Selaata factory, despite the use of sulfuric acid, because the latter will combine with calcium to produce phosphogypsum effluents.

TABLE 4

Comparison of Metals and Water Soluble Anions Average Concentrations (in ng/m^3) between Downwind and Upwind Samples

	Downwind	*SD*	**Upwind**	*SD*
Na	4767	± *3798*	4389	± *3153*
Mg	2404	± *2657*	1073	± *437*
Al	2561	± *3672*	1973	± *1458*
P	24626	± *35205*	191	± *137*
K	15983	± *36889*	14021	± *29669*
Ca	21343	± *30209*	7667	± *2333*
Fe	2445	± *3603*	1318	± *785*
Ti	178	± *234*	142	± *65*
V	140	± *189*	27	± *27*
Cr	97	± *135*	14	± *5*
Mn	45	± *52*	27	± *13*
Cd	3	± *5*	1	± *1*
Ni	50	± *43*	21	± *9*
Cu	15	± *17*	9	± *2*
Zn	209	± *195*	73	± *54*
Pb	17	± *9*	12	± *3*
Cl^-	695	± *162*	713	± *120*
SO_4^{2-}	674	± *828*	510	± *103*
NO_3^-	1658	± *56*	562	± *64*

Enrichment factors analysis

To be able to distinguish the difference between anthropogenic and natural crustal sources of metals in the aerosol samples, an enrichment factor (EF) for these elements was calculated using the same formula in Saliba *et al.* (2007), taking into consideration aluminum as a reference element:

$$\frac{[X]_{aerosol}/[REF]_{aerosol}}{[X]_{crustal}/[REF]_{crustal}}$$

[X] = studied metal concentration; [REF] = reference metal concentration.

The upper continental crust elements concentrations were retrieved from Wedepohl (1995). Only one sample from each site was taken in consideration. Consequently, seven samples were chosen: “Hannouch 1” (29/5/2008), “Selaata 2” (22/5/2008), “Koubba-coast 1” (27/5/2008), “Koubba 1” (22/4/2008), “Batroun 2” (26/5/2008), “Dunkin 2” (3/6/2008), and “Kfaraabida 2” (2/6/2008). The results of EF calculations are illustrated in Figure 2.

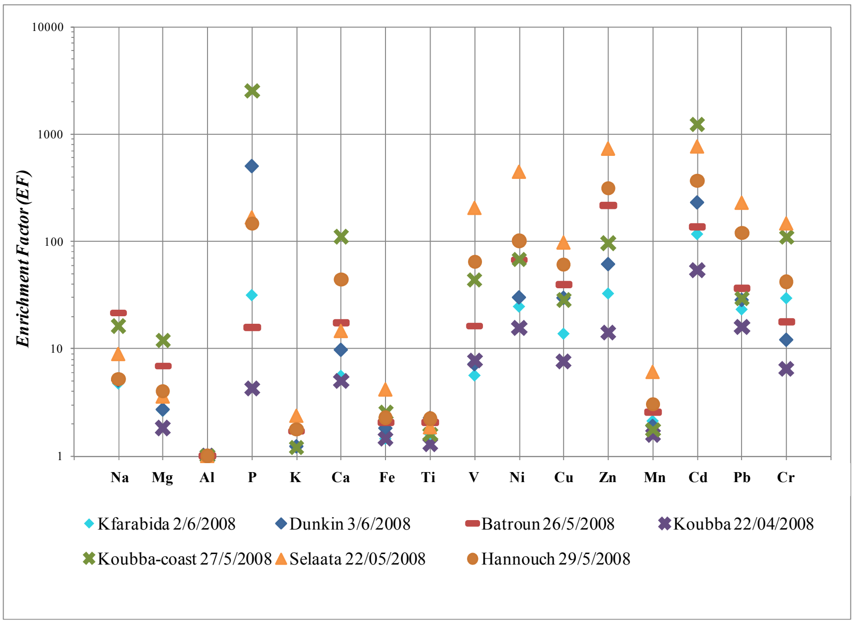

Figure 2. Metal’s enrichment factor in seven chosen samples, calculated with Aluminum as a reference element.

EF of Na is low even though air mass back trajectories show that most of the air masses in the region have marine origins. However, wind roses verify wind speed was not strong enough to carry sea salt aerosols in all the sampling sites.

The enrichment factors for Mg, K, Fe, Ti and Mn are low (EF < 10) in all the samples showing that they are most likely coming from crustal sources and no point emission enrichment was detected. Moreover, Ti can exist in small concentrations in the phosphate rocks, and it usually ranges between 0.025% and 0.04% (Martin *et al.*, 1999).

Phosphate showed high EF, especially for the three northern samples (“Koubba-coast”, “Selaata”, and “Hannouch”). However, phosphate EF in “Kfaraabida” (31) and

"Dunkin" (505) was found moderate and high respectively. Up to our knowledge, there are no emissions sources of phosphate in these sites, and their upwind locations discard the possibility of an industrial influence. One possible explanation can be in the accumulation of phosphate loaded dust in the area from a previous period, when a northern wind was dominant, carrying particles from the factory to these sites.

On the other hand, Ca is found moderately enriched in "Batroun" and "Selaata", and highly enriched in "Koubba-coast" and "Hannouch". Air mass back trajectories show that a typical southwesterly wind was dominant, and particles coming from the southwest had passed over the factory before getting to "Selaata" and "Hannouch", which may explain the source of Ca in the particles as originating from milling activities and point source emission of Ca particles. On the opposite, in "Batroun" and "Koubba-coast" sites, the local high Ca concentration is probably linked to dust re-suspension and dry milling of phosphate rocks in the factory respectively.

Zn and Cd enrichment factors are found high in "Selaata", "Hannouch", and "Koubba-coast" indicating that an addition to the crustal particles load is resulting from the plant's activities. In fact, Zn and Cd concentrations in the Syrian rocks used in the plant of Selaata were analyzed by Pantelica et *al.* (1997) and cited in Martin et *al.* (2004) respectively, with values of 269 ± 5 ppm (Zn) and 10 ppm (Cd). It is highly possible that a part of Cd and Zn impurities within the phosphate rocks has been emitted in the atmosphere which we were able to determine in the sampled particles. However, Zn enrichment can also be linked to heavy-duty vehicles used in the factory, as Zn can be emitted from wheels (Chow et *al.,* 1996). On the other hand, "Batroun" sampling site exhibited high Zn enrichment factor which can be mostly attributed to car traffic in this site.

Cu enrichment factor shows high values (30 < EF < 100) in southern sites ("Dunkin" and "Batroun") as well as in northern ones ("Koubba-coast", "Hannouch", and "Selaata"). Cu can be generated by the excessive use of disk brakes in vehicles (Saliba *et al.,* 2007) especially when Cu/Zn are well correlated. In this study a good correlation ($R^2 = 0.75$) was found between Cu and Zn, pointing at vehicles traffic contribution in the region with emphasis on heavy-duty vehicles in the north.

Atmospheric Pb shows high EF in almost all the samples and particularly in "Selaata" and "Hannouch" (EF > 100). Since these two sampling sites are downwind, the Pb load in the particles can therefore result from phosphate rocks handling and/or vehicles exhaust emissions, especially since lead emissions from the transport sector is still high in Lebanon (Hashisho and El-Fadel, 2004) despite the banning of the use of leaded fuel. On the other hand, Martin *et al.* (1999) and Sabiha-Javied *et al.* (2009) measured Pb content in phosphate rocks extracted from many mining sites around the world. The average of all the values in both references was found to be 45 ppm, proving that Pb can be found in atmospheric particles emitted during dry milling of phosphate rocks.

Ni, V, and Cr enrichment factors ranged from low to moderate in some upwind sites, but were high in the northern downwind ones. In 2007, Okuda *et al.* studied the correlations between Ni-V and Ni-Cr that can point at oil combustion and mechanical abrasion/erosion of metallic surfaces as a source of particles respectively. This might explain the good correlations obtained in this study for Ni-V ($R^2 = 0.872$) and Ni-Cr ($R^2 = 0.778$), as originating from oil combustion and mechanical activities which are two typical anthropogenic signatures heavily present in the fertilizer factory.

CONCLUSION

This study aimed at identifying the composition and possible sources of atmospheric TSP in the region of Selaata, around a phosphate chemical fertilizer factory. When compared to other studies, the inorganic chemical analysis of the sampled aerosols showed moderate levels of anions in the region but high levels of metals in the downwind samples which indicated an enrichment caused by the factory. This enrichment was verified by the enrichment factor analysis that showed high values in downwind samples. Elements such as P, Pb, Ca, and Zn were possibly generated by the dry milling process of phosphate rocks in the factory. The chemical reactions within the factory probably participated in the loads of Cd, Ca, and Zn. On the other hand, Cu, Ni, V, Pb, and Zn also resulted from vehicles activities including disk brakes, oil combustion, leaded fuel and wheels rubber. Vehicles activities also contributed to the high Ca enrichment concentrated in resuspended dust. Finally, Cr was enriched in the downwind samples and was linked to mechanical erosion of metallic surfaces in the industrial site.

REFERENCES

Abi-Ghanem, C., Chiffoleau, J.F., Bermond, A., Nakhlé, K., Khalaf, G., Borschneck, D., Cossa, D. 2009. Lead and its isotopes in the sediment of three sites on the Lebanese coast: identification of contamination sources and mobility. *Applied Geochemistry*, 24: 1990-1999.

Administration Centrale de la Statistique 2006. Compendium statistique national sur les statistiques de l'environnement au Liban 2006. Dar El-Kotob, 38p.

Al-Masri, M.S., Amin, Y., Ibrahim, S., Al-Bich, F. 2004. Distribution of some trace metals in Syrian phosphogypsum. *Applied Geochemistry,* 19: 747-753.

Al-Masri, M.S., Al-Kharfan, K., Al-Shamali, K. 2006. Speciation of Pb, Cu and Zn determined by sequential extraction for identification of air pollution sources in Syria. *Atmospheric Environment*, 40: 753-761.

Brigden, K., Stringer, R., Santillo, D. 2002. Heavy metal and radionuclide contamination of fertilizer products and phosphogypsum waste produced by the Lebanese Chemical Company, Lebanon, 2002. Greenpeace Reserach Laboratories, Department of Biological Sciences, University of Exeter, United Kindom, 16p.

Chaaban, F.B., Ayoub, G.M., Oulabi, M. 2001. A preliminary evaluation of selected transport related pollutants in the ambient atmosphere of the city of Beirut, Lebanon. *Water, Air, and Soil pollution*, 126: 53-62.

Chow, J.C., Watson, J.G., Lu, Z., Lowenthal, D.H., Frazier, C.A., Solomon, P.A., Thuillier, R.H. and Magliano, K. 1996. Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX. *Atmospheric Environment*, 30: 2079-2112.

Dayan, U. 1986. Climatology of back trajectories from Israel based on synoptic analysis. *Journal of Climate and Applied Meteorology,* 25: 591-595.

Dayan, U., Heffter, J., Miller, J., Gutman, G. 1991. Dust intrusion events into the Mediterranean basin. *Journal of Applied Meteorology*, 30: 1185-1199.

Dordević, D., Mihajlidi-Zelić, A., Relić, D. 2005. Differentiation of the contribution of local resuspension from that of regional and remote sources on trace elements content in the atmospheric aerosol in the Mediterranean area. *Atmospheric Environment*, 39: 6271-6281.

Draxler, R., Stunder, B., Rolph, G., Stein, A., Taylor, A. 2009. HYSPLIT 4 user's guide, NOAA ARL HYSPLIT Model.

El-Fadel, M., Bou-Zeid, E. 1999. Transportation GHG emissions in developing countries. The case of Lebanon. *Transportation Research Part D*, 4: 251-264.

El-Fadel, M., Bou-Zeid, E. 2000. Transportation emissions in Lebanon: extent and mitigation. *International Conference on Urban Transport No 5,* Wessex Institute of Technology Press, Southampton, Royaume-Uni, pp. 149-158.

El-Fadel, M., Zeinati, M., Ghaddar, N., Mezher, T. 2001. Uncertainty in estimating and mitigating industrial related GHG emissions. *Energy Policy,* 29: 1031-1043.

Erduran, S.M., Tuncel, G.S. 2001. Gaseous and particulate air pollutants in the Northeastern Mediterranean coast. *The Science of the Total Environment,* 281: 205-215.

Glavas, D.S., Nikolakis, P., Ambatzoglu, D., Mihalopoulos, N. 2008. Factors affecting the seasonal variation of mass and ionic composition of $PM_{2.5}$ at a central Mediterranean coastal site. *Atmospheric Environment*, 42: 5365-5373.

Goudie, A.S., Middleton, N.J. 2001. Saharian dust storms: nature and consequences. *Earth-Science Reviews*, 56: 179-204.

Güllü, H.G., Olmez, I., Tuncel, G. 2000. Temporal variability of atmospheric trace element concentrations over the eastern Mediterranean Sea. *Spectrochimica Acta* B, 55: 1135-1150.

Hashisho, S., El-Fadel, M. 2004. Impacts of traffic-induced lead emissions on air, soil and blood lead levels in Beirut. *Environmental Monitoring and Assessement,* 93: 185-202.

Karam, G., Tabbara, M. 2004. Air quality management and estimated health impact of pollutants in urban and industrial areas. Chekka and Koura region. *Lebanese American University,* 78p.

Kfoury, A., Ledoux, F., El Khoury, B., El-Nakat, H., Nouali, H., Cazier, F., Courcot, D., Abi-Aad, E., Aboukaïs, A. 2009. A Study of the inorganic chemical composition of atmospheric particulate matter in the region of Chekka, North Lebanon. *Lebanese Science Journal,* 10(2): 3-16.

Kobrossi, R.L. 2000. Health effects of air pollution in the regions of Koura, Batroun, and Jbeil. Master thesis, *American University of Beirut,* 155p.

Koçak, M., Mihalopoulos, N., Kubilay, N. 2007. Chemical composition of the fine and coarse fraction of aerosols in the Northeastern Mediterranean. *Atmospheric Environment,* 41: 7351-7368.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Makela,T., Hillamo, R., Mihalopoulos, N. 2008. Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean. *Atmospheric Environmen,* 42: 6542-6550.

Kouyoumdjian, H., Saliba, N.A. 2006. Mass concentration and ion composition of coarse and fine particles in an urban area in Beirut: effect of calcium carbonate on the absorption of nitric and sulfuric acids and the depletion of chloride. *Atmospheric Chemistry and Physics,* 6: 1865-1877.

Kubilay, N., Nickovic, S., Moulin, C., Dulac, F. 2000. An illustration of the transport and deposition of mineral dust onto the Eastern Mediterranean. *Atmospheric Environment,* 34: 1293-1303.

Ledoux, F., Courcot, L., Courcot, D., Aboukaïs, A., Puskaric, E. 2006. A summer and winter apportionment at urban and rural areas in northern France. *Atmospheric Research*, 82: 633-642.

Mamane, Y., Perrino, C., Yossef, O., Cartambone, M. 2008. Source characterization of fine and coarse particles at the East Mediterranean coast. *Atmospheric Environment,* 42: 6114-6130.

Martin, J.E., García-Tenorio, R., Respaldiza, M.A., Ontalba, M.A., Bolívar, J.P., da Silva, M.F. 1999. TTPIXE analysis of phosphate rocks and phosphogypsum. *Applied Radiation and Isotopes,* 50: 445-449.

Ministry of the Environment 2001. *Lebanon state of the environment report*. Lebanese Ministry of the Evironment. 246 p.

Moussa, S.G., El-Fadel, M., Saliba, N.A. 2006. Seasonal, diurnal and nocturnal behaviors of lower carbonyl compounds in the urban environment of Beirut, Lebanon. *Atmospheric Environment*, 40: 2459-2468.

Mourad, N.M., Sharshar, T., Elnimr, T., Mousa, M.A. 2009. Radioactivity and fluoride contamination derived from a phosphate fertilizer plant in Egypt. *Applied Radiation and Isotopes,* 67: 1259-1268.

Nakhlé, K. 2003. *Le mercure, le cadmium et le plomb dans les eaux littorales libanaises: apports et suivi au moyen de bioindicateurs quantitatifs (éponges, bivalves et gastéropodes*). These de Doctorat, Université Paris 7, 255 p.

Okuda, T., Nakao, S., Katsuno, M., Tanaka, S. 2007. Source identification of Nickel in TSP and PM2.5 in Tokyo, Japan. *Atmospheric Environment*, 41: 7642-7648.

Pantelica, A.I., Salagean, M.N., Georgescu, I.I., Pincovschi, E.T. 1997. INAA of some phosphates used in fertilizer industries. *Journal of Radioanalytical and Nuclear Chemistry,* 216 (2): 261-264.

Prodi, F., Belosi, F., Contini, D., Santachiara, G., Di Matteo, L., Gambaro, A., Donateo, A., Cesari, D. 2009. Aerosol fine fraction in the Venice lagoon: particle composition and sources. *Atmospheric Research,* 92: 141-150.

Querol, X., Pey, J., Pandolfi, M., Alastuey, A., Cusack, M., Pérez, N., Moreno, T., Viana, M., Mihalopoulos, N., Kallos, Kelanthous, S. 2009. African dust contributions to mean ambient PM_{10} mass-levels across the Mediterranean basin. *Atmospheric Environment,* 43: 4266-4277.

Sabiha-Javied, Waheed, S., Siddique N., Tufail, M., Chaudhry, M.M., Irfan, N. 2008. Elemental analysis of phosphate rocks: For sustainable agriculture in Pakistan. *Journal of Radioanalytical and Nuclear Chemistry,* 278 (1), 17-24.

Sabiha-Javied, Mehmood, T., Chaudhry M.M., Tufail M., Irfan N. 2009. Heavy metal pollution from phosphate rock used for the production of fertilizer in Pakistan. *Microchemical Journal,* 91: 94-99.

Saliba, N.A., Moussa, S., Salameh, H., El-Fadel, M. 2006. Variation of selected air quality indicators over the city of Beirut, Lebanon: assessment of emission sources. *Atmospheric Environment,* 40: 3263-3268.

Saliba, N.A., Kouyoumdjian, H., Roumie, M. 2007. Effect of local and long-range transport emissions on the elemental composition of $PM_{10-2.5}$ and $PM_{2.5}$ in Beirut. *Atmospheric Environment,* 41: 6497-6509.

Saliba, N.A., Atallah, M., Al-Kadamany, G. 2009. Levels and indoor-outdoor relationships of PM10 and soluble inorganic ions in Beirut, Lebanon. *Atmospheric Research*, 92: 131-137.

Sanchez de la Campa, A.-M., De la Rosa, J., Querol, X., Alastuey, A., Mantilla, E. 2007. Geochemistry and origin of PM_{10} in the Huelva region, Southwestern Spain. *Environmental Research,* 103: 305-316.

Sbayti, H., El-Fadel, M., Kaysi, I. 2002. Effect of roadway network aggregation levels on modeling of traffic-induced emission inventories in Beirut. *Transportation Research Part D*, 7: 163-173.

Shaka', H., Saliba, N.A. 2004. Concentration measurments and chemical composition of $PM_{10-2.5}$ and $PM_{2.5}$ at a coastal site in Beirut, Lebanon. *Atmospheric Environment,* 38: 523-531.

USEPA 1995. *Compilation of air pollutant emission factors – volume I: stationary point and area sources.* United States Environmental Protection Agency, AP 42, fifth edition, chapter 8, section 8.5, 64 p., http://www.epa.gov/ttn/chief/ap42/ch08/index.html.

USEPA 2009. *Technical support document for the phosphoric acid production sector: proposed rule for mandatory reporting of greenhouse gases*. United States Envrironmental Protection Agency, Office of Air and Radiation, 13 p., http://www.epa.gov/climatechange/emissions/downloads/tsd/TSD%20Phosphoric%20-%20_EPA%202-18-09.pdf.

Wedepohl, K.H. 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta,* 7: 1217-1232.