A STUDY OF THE INORGANIC CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICULATE MATTER IN THE REGION OF CHEKKA, NORTH LEBANON

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ABSTRACT

In North Lebanon, the region of Chekka represents a group of villages scattered around an industrial complex of cement factories and a chemical fertilizer industry. In order to understand the nature of atmospheric aerosols in this region, 20 samples of atmospheric total suspended particles were collected next to the region of industrial activities. The analysis of inorganic water soluble ions and metal composition of the sampled particles was achieved using ion chromatography (I.C.) and inductively coupled plasma-mass spectrometer (ICP-MS). Higher global particle concentrations and NO_3^- *concentrations were identified in the sites near the cement factories. However, this nitrate concentration was attributed to long range transport and accumulation phenomenon happening in the region. Peaks in potassium concentrations were confirmed in some samples and most probably emitted by a secondary source of emissions, possibly from local biomass combustion. On the other hand, low levels of calcium were identified in the samples, despite the presence of cement quarries next to the sampling sites, because of the dominant low wind activity during the sampling period.*

Keywords: total suspended particles, inorganic chemical composition, ion chromatography, ICP-MS, Lebanon

INTRODUCTION

The Lebanese air quality has being studied since the 90's with most of the research focusing on transport emissions in urban areas (Beirut). Thus, transport related emissions were studied intensively by El-Fadel & Bou-Zeid (1999; 2000); Chaaban *et al.* (2001); Sbayti *et al.* (2002); Moussa *et al.* (2006); and the Administration Centrale de la Statistique (2006). Most of them focused on the emissions of green house gases (GHG) such as NO_x, SO_x, CO_2, and CO that are emitted by vehicles, but also on atmospheric lead (Pb_{atm}) that is linked to the use of lead enriched gasoline.

Industrial GHG emissions were also studied by El-Fadel et *al*. (2001). The result indicates that the industrial sector is the second most important GHG emitter after the energy sector in Lebanon. Moreover, the study showed that the cement, asphalt and iron factories were responsible of more than 98% of these industrial related emissions.

On the other hand, atmospheric particulate matter was studied mostly in the capital Beirut. These studies were often coupled with the analysis of transport and residential related emissions. In 2004, Shaka' and Saliba measured average concentrations of $PM_{10-2.5}$ (76 $\mu g/m^3$) and $PM_{2.5}$ (40 $\mu g/m^3$). They also found higher concentrations of SO_4^{2-}, NO_3^-, SiO_4^{2-}, CO_3^- and NH_4^+ in the $PM_{2.5}$ size fraction, and that dust storms are heavily enriched with SiO_4^{2-} and $CaCO_3$. In 2006, Saliba *et al*. followed the fluctuations of CO, SO_2, O_3, and PM_{10} concentrations to identify major sources of such emissions. Their results show that average monthly concentrations of CO, SO_2 and O_3 are lower than the American standards except for PM_{10}. They also proved that transport vehicles and indoor heating systems were the major sources of CO and SO_2 respectively. In the same year, Kouyoumdjian and Saliba (2006) studied the mass and the chemical composition of PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ over the city of Beirut. Annual averages of PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ were 84±27, 53±20 and 31±9 $\mu g/m^3$, respectively. Cl^- was found in high concentration in coarse particles and was attributed to waste mass burning in addition to sea-salt aerosols. Calcium carbonate originated from local crustal sources, whereas silicates were concentrated in dust transported from Africa.

Local versus long distance contribution in the composition of $PM_{10-2.5}$ and $PM_{2.5}$ was investigated by Saliba *et al.* (2007). Their results showed that crustal elements (Si, Ca, K, Ti, Mn and Fe) were abundant in the $PM_{10-2.5}$ fraction, and that anthropogenic elements (S, Cu, Zn and Pb) dominated in the $PM_{2.5}$. In the same study, sulfate origins were attributed to local, marine and long range transport (East Europe). The authors also found that high Cu and Zn concentrations were linked to the use of vehicles' braking systems during rush hours, and that high lead concentrations were originated in Israel and/or Egypt.

The relationship between indoor and outdoor PM_{10} concentrations and soluble inorganic ions in the city of Beirut was studied by Saliba *et al.* (2009). Higher PM_{10} concentrations were linked to traffic (outdoor), smoking activities (indoor), and with the degree of ventilation inside the studied houses. In the same study, water soluble sulfates and nitrates concentrations were almost identical between indoor and outdoor of houses without smokers. Whereas inside the houses with smokers, the level of nitrates was found much lower due to their reaction with tobacco smoke to produce nitrosamines.

In North Lebanon, the region of Chekka was the subject of few researches about atmospheric aerosols and their relative health impacts. Between these studies, Kobrossi (2000) worked on the effect of atmospheric pollution on kid's health, especially those living in cities scattered around the industrial complex, in the region of Chekka and Batroun. Kobrossi uncovered a correlation between the proximity to the industrial complex, the exposure to atmospheric pollutants, and the risk of getting respiratory diseases (chronic bronchitis, asthma, wheeze, *etc*…). In 2001, the Lebanese Ministry of the Environment published some of the results of the air quality monitoring program in the Chekka region, in which a minimum of 1.28 mg/m^3 and a maximum of 2 mg/m^3 were found for SO_2, as well as a minimum of 13.14 mg/m^3 and a maximum of 20.76 mg/m^3 for NO_2 (Ministry of the Environment, 2001). These values cross the Lebanese limit values for ambient air quality.

Finally, Karam and Tabbara (2004) used a dispersion model to estimate the dispersion and concentration of atmospheric pollutants that are emitted from the cement factories and their corresponding quarries in Chekka. They found that NO_2, SO_2 and PM_{10} concentrations exceeded United States Environmental Protection Agency (USEPA) standards, and that the secondary sources of emissions (quarries) and electric generators of the cement factories account for 80 to 90% of atmospheric particles emitted in that region. The aim of this study is to define the inorganic chemical composition of total suspended particles (TSP), with emphasis on the concentration of major ions and metals, to be able to detect possible factors that are altering the air quality in the region of Chekka.

MATERIALS & METHODS

Study area

Lebanon is a country of 10452 km^2, surrounded from the North and the East by Syria, and from the South by Palestine, and from the West by the Mediterranean Sea. The position of the country on the eastern coast of the Levantine Basin, with a topography that includes two mountain chains, Mount-Lebanon to the west and Anti-Lebanon to the east, gives the country two distinctive climatic regimes (Administration Centrale de la Statistique, 2006): Mediterranean to the west (winter with rain and hot dry summer) and dry to the east (from the Arab peninsula).

In spring time, Lebanon is affected by airborne dust coming from Africa, which passes over the country for a couple of days. These air masses are loaded with crustal particles and have a relatively high temperature.

Sampling sites and methodology

The sampling zone is located 50 km to the North of the capital Beirut. It is affected by many sources: direct canalized emissions coming from the cement factories (Holcim & Cimenterie Nationale), the quarries of each cement factory, a phosphate fertilizer industry (Lebanese Chemical Company) located in the south-west, the sea-spray, transport and other human activities, and finally from long range transport mechanisms (secondary aerosols). The sampling covered 10 points distributed along two circles surrounding the cement factories and quarries. The first circle assembles the following sites: Anfeh, Bdaibhoun, Chekka, Bednayel, Hamat, whereas the second circle regroups Deir Alnatour, Fiaa, Kfarhazir, Kelbata, and Mseilha (Figure 1). Each site has been sampled twice during two different days using a mobile sampling truck provided by the University of Balamand, covering the period from August 5th 2008 to October 30th 2008.

A high volume Staplex® TFIA-2 sampling pump was used to collect atmospheric particles on pre-cleaned cellulose filters (Whatman 41®) for 4 hours at each site, from 9 am till 1 pm, using a 68 m^3/h air flow rate. Each sample was collected under similar wind conditions: low speed West-North West winds. After sampling, the filters were placed in a previously washed Petri dish and sealed with a piece of Parafilm® and conserved in a freezer at -20°C before analysis.

Figure 1. Satellite photo showing the Chekka region and the position of the sampling sites (Red dots = emissions site; Yellow dots = sampling site).

Filters preparation

Unwashed Whatman® 41 cellulose filters used for bulk filtration, present varying trace metals contents and especially for Fe, up to 5µg per filter. So these kinds of filters need to be washed before sampling and they were treated as described by (Ledoux *et al.*, 2006) for Fe analysis. Filters are dived into 0.5M HCl and 0. M HNO_3 during 24h, then rinsed with ultrapure water (MilliQ®, Millipore; resistivity=18.2MΩ.cm). Filters are then dried under a laminar flow hood (Class 100, US Federal Standard 209a), and finally hermetically kept in cleaned Petri dishes and stored in a freezer (-20°C). Such a treatment lowers the Fe contamination under 0.1µg per filter, and contents of all other metals are lower than limit detection.

Chemical Analysis

Two analytical techniques were used to quantify the concentrations of different water soluble ions and metals in the sampled particles. Simultaneous analysis of water soluble anions (F^-, Cl^-, NO_3^-, PO_4^{3-} et SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+} et Ca^{2+}) was realized using ion chromatography (IC), after samples leaching, using a Dionex DX 100® coupled to a Dionex ICS 900®, an electrochemical suppressor and a conductivity meter. Standard solution used for calibration covered a concentration range of 0.5 – 100 mg/L. Water soluble anions and cations were extracted from the filters by leaching, using a 15-min ultrasonic treatment, repeat three times with 3 to 4 mL of fresh ultrapure water (MilliQ®, Millipore;

resistivity=18.2MΩ.cm). For each sample, the leachate was filtered in a polyethylene flask and the final volume adjusted up to 20 mL by adding ultrapure water.

Na, Mg, Al, K, Ca, Fe, Ti, V, Cr, Mn, Ni, Cu, Zn, Pb, and Cd concentrations were obtained using a Varian® 820-MS inductively coupled plasma-mass spectrometer (ICP-MS) coupled with a collision reaction cell to minimize polyatomic interferences during the measurements. Metal analysis was done after acid digestion in a high temperature environment. A part of each exposed cellulose filter was placed 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. The acids were then evaporated at 170°C for 4h using a hot plate, then ultrapure water was added to the residue and heated at 110°C for 1h. Finally, the cooled solution was diluted with MilliQ® water up to 10 mL acidified up to 0.2% using nitric acid and filtered on PTFE membrane (0.45µm) prior to analysis. Standard solutions for the ICP-MS analysis were prepared from a multi-element stock solution and covered a concentration range from 0.2 to 100 µg/L. Blank filters analysis showed negligible amounts of metals.

To validate the quantification methodology, a certified aerosol sample from American NIST (Standard Reference Material, n° 1648) was analyzed, and average concentrations of three replicates with their corresponding standard deviation (σ) were illustrated in Table 1. A maximum deviation of 8% was found between certified and obtained values. Therefore, we considered that the analytical procedure used herein is reliable.

TABLE 1

Results of the SRM 1648 Sample Analysis Compared with Certified Values (SD: Standard Deviation)

	Analysis results			Certified values			Recovery
	%	±	SD	%	±	SD	%
Al	3.437	±	0.127	3.42	±	0.11	101
Ca	5.956	±	0.190	-	±	-	-
Cu	0.059	±	0.001	0.061	±	-	97
Fe	3.894	±	0.030	3.91	±	0.01	100
K	1.032	±	0.002	1.05	±	0.01	98
Mg	0.781	±	0.023	0.800	±	0.014	98
Mn	0.081	±	0.003	0.079	±	-	103
Na	0.406	±	0.014	0.425	±	0.002	96
Ti	0.392	±	0.006	0.400	±	-	98
Zn	0.436	±	0.006	0.476	±	0.014	92
Pb	0.692	±	0.007	0.655	±	0.008	106

RESULTS AND DISCUSSION

Mean elemental concentrations

The mean elemental concentration is defined here as the average concentration of an analyzed element in all the samples. Between the analyzed metals (Table 2), K has the highest mean concentration (4370 ng/m^3) accounting for 20% of the analyzed species total concentration, followed by Ca (2134 ng/m^3, 10%) and Na (1079 ng/m^3, 5%). On the other hand, Al and Fe show moderate concentrations of 522 (2%) and 386 ng/m^3 (2%) respectively. As for metals other than Fe and Al, they represent 0.4% of the analyzed species total concentration. Between these elements, Ti and Zn had average concentrations of 37 ng/m^3 and 26 ng/m^3 respectively.

Among water soluble ions (Table 3), NO_3^- has the highest mean concentration (6182 ng/m^3), followed by SO_4^{2-} (4048 ng/m^3), Ca^{2+} (1854 ng/m^3), NH_4^+ (1726 ng/m^3), and Cl^- (1278 ng/m^3). Nitrates, sulfates and chloride represent 52% of the analyzed species total concentration, when ammonium contribution was 8%. The comparison between total Na and total Ca analyzed by ICP-MS and water soluble Na^+ and Ca^{2+} show little differences. Therefore, these elements are mainly present in their soluble form in the sampled particles. On the other hand, K is mainly present in a non-soluble form since 4370 ng/m^3 for total K versus 113 ng/m^3 for water soluble K^+ was found.

Comparison with other studies

Elemental mean concentrations

In this study, the metals analyzed by ICP-MS were divided into two groups. The ones usually found in high concentrations (Na, Mg, Al, K, Ca, and Fe) were assembled under "major metals". The remaining metals were named "minor metals" and include Ti, V, Cr, Mn, Cd, Ni, Cu, Zn, and Pb.

Mean element concentrations retrieved from Chekka samples are compared with those found in other sites in Table 2. Na mean concentration in Chekka appears to be the second highest behind that of Antalya, Turkey. The similarity in sodium concentration between these studies can be linked to the fact that both regions are coastal areas, and therefore might be affected by sea spray containing sodium. On the other hand, Mg concentration is found to be very close to the values found in close sites like Antalya (365 ng/m^3) and Ashdod, Israel (523 ng/m^3). Al level in Chekka (522 ng/m^3) is found close to the ones of Antalya (540 ng/m^3) and lower than that of Ashdod (776 ng/m^3).

Also, Ca concentration is found higher in Chekka than in all the other comparison sites except Beirut (6612 ng/m^3) and Ashdod (4655 ng/m^3). In fact, the Ca concentrations in Beirut and Ashdod correlated with dust storms, which was absent during the sampling campaign of this study. However, Ca average concentration in Chekka was still lower than the one found in Beirut during days that were not affected by dust storms, despite the presence of the cement factories and their quarries in Chekka. This can be caused by the fact that wind velocity was not sufficient enough to carry calcium carbonate loaded dust into the atmosphere. In the same time, Fe mean concentration in Chekka is the second lowest after

TABLE 2

Mean Metals Concentrations in the Chekka Region Compared to other Studies (Values Are in ng/m^3; SD: Standard Deviation)

	Present Study		Saliba *et al*., 2007	Sanchez de la Campa, 2007	Koulouri *et al*., 2008	Koçak *et al*., 2007	Mamane *et al*., 2008	Güllü *et al*., 2000
	(Chekka-Lebanon)		(Beirut-Lebanon)	(Huelva– Spain)	(Crete- Greece)	(Erdemli-Turkey)	(Ashdod-Israel)	(Antalya-Turkey)
	Mean	SD						
Na	1079	*376*	-	1000	-	-	692	1900
Mg	343	*115*	-	300	-	-	523.2	365
Al	522	*234*	-	-	-	-	776	540
K	4370	*4051*	533	600	-	360	630	365
Ca	2134	*675*	6612	1400	1548	1888	4655	2100
Fe	386	*175*	2157	700	598	351.3	1210	390
Ti	37	*14*	-	55	43	27.1	113	40
V	5	*2*	-	7	8	8.7	38.5	2.56
Cr	5	*1*	-	3	9	5.7	21.8	3.75
Mn	10	*4*	-	12	12	7.6	38	8.93
Cd	0	*0*	-	0.6	0	-	-	-
Ni	7	*1*	-	4	4	3.7	14.5	2.5
Cu	3	*1*	-	50	3	-	14.2	-
Zn	26	*5*	174	30	29	9.7	165	20.8
Pb	6	*2*	-	-	9	-	49	21

TABLE 3

Mean Water Soluble Ions Concentrations in the Chekka Region Compared to other Studies (Values Are in ng/m^3; SD: Standard Deviation)

	Present study		Prodi *et al.,* 2009	Koulouri *et al*., 2008	Galvas *et al.,* 2008	Koçak *et al*., 2007	Erduran & Tuncel, 2001	Güllü *et al*., 2000
	(Chekka - Lebanon)		(Venice - Italy)	(Crete - Greece)	(Patras-Greece)	(Erdemli - Turkey)	(Antalya - Turkey)	(Antalya-Turkey)
	Mean	SD						
Na^+	894	*424*	111	1375	-	3434	-	-
NH_4^+	1726	*317*	2567	1617	1600	850	2190	1400
K^+	113	*26*	54	189	-	203	-	-
Mg^{2+}	148	*45*	6	186	-	489	-	-
Ca^{2+}	1854	*621*	6	1298	330	1560	-	-
Cl^-	1278	*877*	167	1509	120	5492	4300	-
NO_3^-	6182	*1721*	3503	1731	400	1857	2280	1180
SO_4^{2-}	4048	*1045*	4423	5478	3200	4953	2350	5540

Erdemli, Turkey. This observation is not surprising considering that the Chekka region is not directly affected by any metallurgic emissions.

On the other hand, total K mean concentration is found higher in Chekka (4370 ng/m^3) when compared to the other selected studies, where K levels ranged from 500 to 600 ng/m^3. The majority of the K has been identified as non soluble potassium because soluble K^+ detected by I.C. was much lower than total K measured by ICP-MS. Therefore, the source of potassium can be associated with a crustal source or an anthropogenic one. Since elements that characterize crustal sources were not detected in high concentrations in this study, the crustal origin is discarded. This observation highlights the anthropogenic source as an origin of K, like combustion processes for example (Seinfeld & Pandis, 2006).

The comparison of minor metals mean concentrations shows that the values found in Chekka are most of the time lower than those of other studies with the exception of Ni (7 ng/m^3), which was found second highest after Ashdod (14.5 ng/m^3). Nickel can be originated by heavy oil combustion or from metal abrasion/erosion of metallic surfaces. In the first case, Ni concentrations correlated with V, when in the case of abrasion, they were found in correlation with Cr (Okuda *et al.*, 2007). In this study, Ni concentrations did not correlate neither with Cr nor with V, which leads us to assume that it might be generated by a different source. The Zn levels found in urbanized areas like Beirut (174 ng/m^3) and Ashdod (165 ng/m^3) was higher than the one found in Chekka (26 ng/m^3). This is not surprising since these two sites represent cities that have a relatively larger population than that of Chekka, and the source of these elements can be associated with transport vehicles emissions, since it is well known that elements like Ni, Zn V, Pb, Cu can be linked to this sector (Seinfeld & Pandis, 2006).

Water soluble ions mean concentrations

Table 3 compares the mean concentrations of water soluble ions found in Chekka with those of other studies. Na^+ concentration (894 ng/m^3) is relatively low compared to other coastal sites like Erdemli (3434 ng/m^3) and Crete Island (1375 ng/m^3) despite the proximity of the sea. This can be explained by the fact that wind speed was not high enough (wind velocity under 10 km/h) to carry sea salt aerosols.

Ammonium concentration in Chekka is found to be lower than in Venice, but also higher than in Erdemli, Patras and Crete Island, which are closer to the studied area. There are no obvious sources of ammonium in the region of Chekka; therefore ammonium concentration might be present in the atmosphere in a secondary aerosol form, and associated with long range transport mechanisms. As for soluble K^+ and Mg^{2+}, their concentrations in Chekka are lower than those of Crete Island and Erdemli, except for Venice. The opposite is found for soluble Ca^{2+} concentration, which is the highest in Chekka when compared to the other studies. On the other hand, Cl^- concentration in Chekka is found lower than the corresponding Turkish sites and Crete Island values.

The average concentration of NO_3^- in Chekka (6182 ng/m^3) is found to be almost two times higher than the highest concentration observed between the other studies (Venice: 3503 ng/m^3). This relatively high NO_3^- concentration found in this area is not surprising since it goes in the same direction as the results found in the state of the environment report

(Ministry of the Environment, 2001). In the latter, a maximum of 20.76 mg/m^3 NO_2 concentrations, which is a precursor of NO_3^- formation, was found in the Chekka region. In fact, cement factories emit NO_2 which is unstable in gaseous form and might react with sea salts and/or other gases like SO_2 (gas-particle conversion reactions) to transform to NO_3^- ions (Seinfeld and Pandis, 2006). However, this conversion occurs in a relatively high humidity media, which was absent during the sampling period and hence this possibility was discarded. The most probable explanation for this high level of atmospheric nitrate can be in the presence of secondary atmospheric aerosols, carried within air masses by long range transport mechanisms and accumulating in the regional atmosphere.

As for SO_4^{2-}, its concentration is comparable to all the other sites, with the exception of Patras, and Antalya (2001) in which the average SO_4^{2-} concentration was found lower.

Relationship between mean concentrations and distance from the cement factories

To be able to estimate the influence of the industrial activities such as cement factories and their quarries, sampling sites were assembled into two circles. The first one regroups the sites that are close to the cement factories and includes Anfeh, Bdaibhoun, Chekka, Bednayel, and Hamat. The second circle includes the remaining sites that are relatively distant from the industrial zone: Deir Alnatour, Fiaa, Kfarhazir, Kelbata, and Mseilha.

Table 4 compares the mean chemical species concentrations and the mean global load for each of the 1st and 2nd circle. The mean global load corresponds to the sum of the mean element concentrations in each circle.

The mean global load for the 1st circle appears significantly higher than that of the 2nd circle indicating that the mass of sampled particles rises as we move closer to the industrial zone (cement factories and quarries). On the other hand, this difference between the charge in the 1st and 2nd circle can be mainly explained by the difference in the average concentration of total potassium (K). In fact, when the average global load increases from 18215 to 26610 ng/m^3, K average concentration increases from 1278 ng/m^3 (2nd circle) to 7847 ng/m^3 (1st circle), explaining 78% of the difference in the global load between the two circles. Moreover, the average proportion of total potassium in the 1st circle represents about 29.5 %, compared to 7 % in the 2nd circle which indicates that the anthropogenic source of potassium affects mainly the sampling sites located in the 1st circle.

Chloride and nitrates mean concentrations vary in function of the proximity to the cement factories and quarries. The mean concentration of Cl^- is 1900 ng/m^3 in the 1st circle, three times higher than in the 2nd one (725 ng/m^3). Further calculations showed that this difference in Cl^- concentrations is not related to sea salt aerosols Cl^- depletion. On the other hand, NO_3^- concentration decreases slightly from 6892 ng/m^3 (1st circle) to 5551 ng/m^3 (2nd circle). Ca mean concentrations were practically the same between the 1st and the 2nd circle, which means that in this study, the influence of secondary industrial activities (mostly quarries) on calcium concentrations was not revealed. One explanation can be given to this case, which is that the sampling campaign occurred during a low wind speed period (below 3 m/s) and in this case, wind speed is not sufficient enough to carry dust from ground level.

TABLE 4

Element Mean Concentrations and Distribution Observed in the Nearest Sites (First Circle) and in the Distant Sites (2nd Circle) (Minor Metals = Ti, V, Cr, Cd, Mn, Zn, Cu, Ni and Pb)

Position	*1st circle*		*2nd circle*	
Number of samples	8		9	
Mean concentrations	μ_A (ng/m^3)	%	μ_A (ng/m^3)	%
Na	1271.8	4.8	906.9	5.0
Mg	360.2	1.4	327.8	1.8
Al	471.4	1.8	566.6	3.1
K	7847.4	29.5	1278.3	7.0
Ca	2135.2	8.0	2132.8	11.7
Fe	353.0	1.3	414.9	2.3
Minor metals	102.9	0.4	95.1	0.5
Cl^-	1899.6	7.1	725.3	4.0
NH_4^+	1717.5	6.5	1733.7	9.5
NO_3^-	6892.2	25.9	5550.6	30.5
SO_4^{2-}	3558.5	13.4	4483.3	24.6
Mean global load (ng/m^3)	26609.6	100	18215.3	100

Temporal and inter-site variability

Chronological and geographical variations have been studied by calculating the global load and the species distribution in each sample (Figure 2). On the one hand, these parameters differ geographically from one site to the other. On the other hand, the global load and the species distribution can also vary chronologically within a same site from one day to the other, like in the case of Bdaibhoun 1 and 2 (45 000 against 16 000 ng/m^3), Bednayel 1 and 2 (41 000 against 26 000 ng/m^3, Chekka 1 et 2 (27 000 against 20 000 ng/m^3), Fiaa 1 and 2 (17 000 against 10 000 ng/m^3). However, if we consider the species contribution to the global load, we notice that for a given site, when the global load is relatively constant in time, elements repartition is also constant (see Mseilha, Deir Alnatour, and Kelbata). In these cases, total potassium contribution is found low. On the other hand, when the global load varies in time, the species contribution to the global charge also changes (see Bdaibhoun, Bednayel, Chekka, and Fiaa). Moreover, a major K contribution to the global charge in these samples is also revealed.

For the purpose of uncovering the importance of this K contribution, another representation in which K was separated from the global charge for each sample is given in Figure 3. When K is excluded from the global load, the latter appears relatively constant in time for a same site, proving that K is probably linked to a chemical species that was not detected by neither IC nor ICP-MS. Furthermore, high K contribution is not specifically linked to a geographical position or to a certain period. In fact, K contribution can be observed as well in the first circle sites as in the second. Moreover for a given site, a high K contribution can be present in one sample and disappears in the other. For these reasons, we can conclude that K is emitted in an occasional manner. Koulouri *et al.* (2008) proved that a correlation between K and oxalate can be associated to biomass combustion emissions. This probably explains the source of K in Chekka, especially because it is emitted in an occasional non point source manner and is linked to a chemical species not identified in this study.

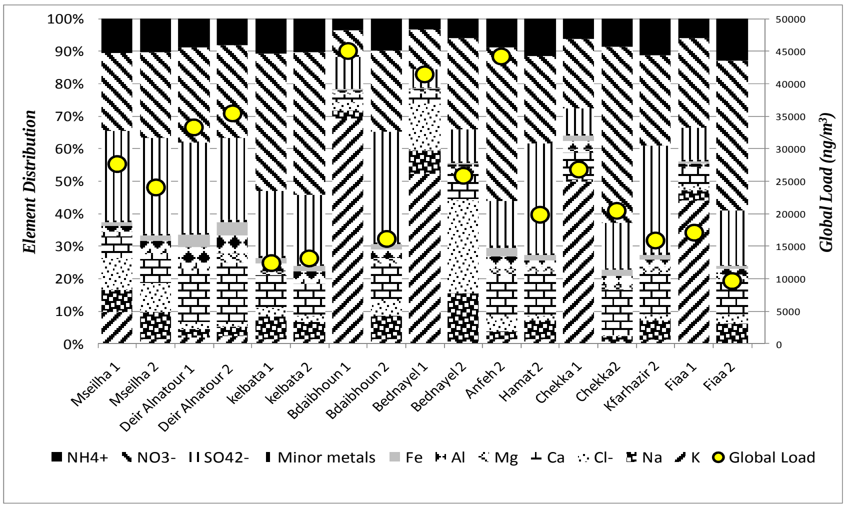

Figure 2. Global load (ng/m^3) and element distribution for each sample.

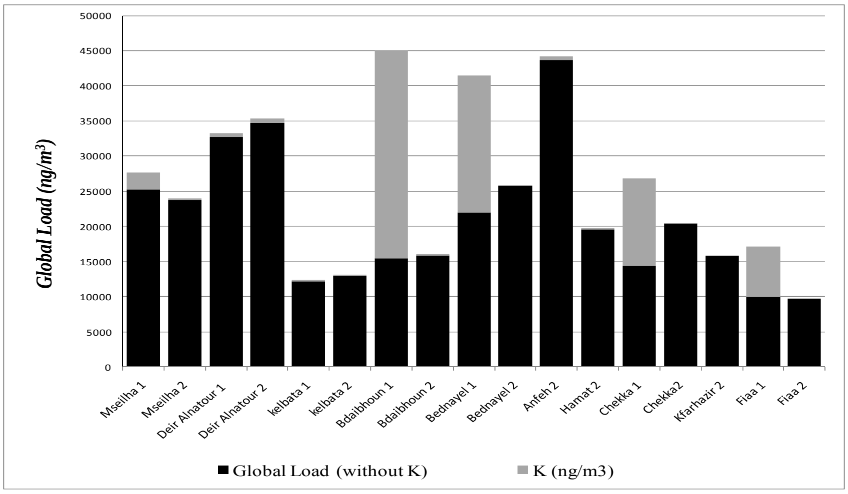

Figure 3. Global load variations (ng/m^3) with total K contribution.

CONCLUSION

This study concentrated on the chemical characterization of atmospheric aerosols as a first step in knowing and understanding the air quality in the Region of Chekka. The methodology used aimed to uncover the contribution of the cement factories and the quarries to the atmospheric particles composition. The results, in particular Ca concentrations, did not reveal the influence of such activities probably because of low wind activities. In fact, Ca average concentration appears in the same order of magnitude than that recorded in other sites located in the Mediterranean Basin, and in the same time Ca concentrations was independent from the distance to the cement factories and quarries. Similar results were also found for other elements and species average concentrations, except for K. The global load found in the sites that are located in the vicinity of the cement factories and quarries was higher than that found in distant sites. This increase can be explained mainly by potassium peaks occurring occasionally in several sites at different dates proving that K is not emitted by a point source. These K peaks were therefore associated to biomass combustion processes. High nitrate levels were probably caused by long range transport and accumulation mechanisms.

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