

# 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

H. Kouyoumdjian and N. A. Saliba

Department of Chemistry, American University of Beirut, Beirut, Lebanon

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**Abstract.** Levels of coarse (PM<sub>10-2.5</sub>) and fine (PM<sub>2.5</sub>) particles were determined between February 2004 and January 2005 in the city of Beirut, Lebanon. While low PM mass concentrations were measured in the rainy season, elevated levels were detected during sand storms originating from Arabian desert and/or Africa. Using ATR-FTIR and IC, it was shown that nitrate, sulfate, carbonate and chloride were the main anionic constituents of the coarse particles, whereas sulfate was mostly predominant in the fine particles in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Ammonium nitrate was not expected to be important because the medium was defined as ammonium poor. In parallel, the cations Ca<sup>2+</sup> and Na<sup>+</sup> dominated in the coarse, and NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> in the fine particles. Coarse nitrate and sulfate ions resulted from the respective reactions of nitric and sulfuric acid with a relatively high amount of calcium carbonate. Both CaCO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> crystals identified by ATR-FTIR in the coarse particles were found to be resistant to soaking in water for 24 h but became water soluble when they were formed in the fine particles suggesting, thereby, different growth and adsorption phenomena. The seasonal variational study showed that nitrate and sulfate ion concentrations increased in the summer due to the enhancement of photochemical reactions which facilitated the conversion of NO<sub>2</sub> and SO<sub>2</sub> gases into NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, respectively. While nitrate was mainly due to local heavy traffic, sulfates were due to local and long-range transport phenomena. Using the air mass trajectory HYSPLIT model, it was found that the increase in the sulfate concentration correlated with wind vectors coming from Eastern and Central Europe. Chloride levels, on the other hand, were high when wind originated from the sea and low during sand storms. In addition to sea salt, elevated levels of chloride were also attributed to waste mass burning in proximity to the site. In comparison to other neighboring Mediter-

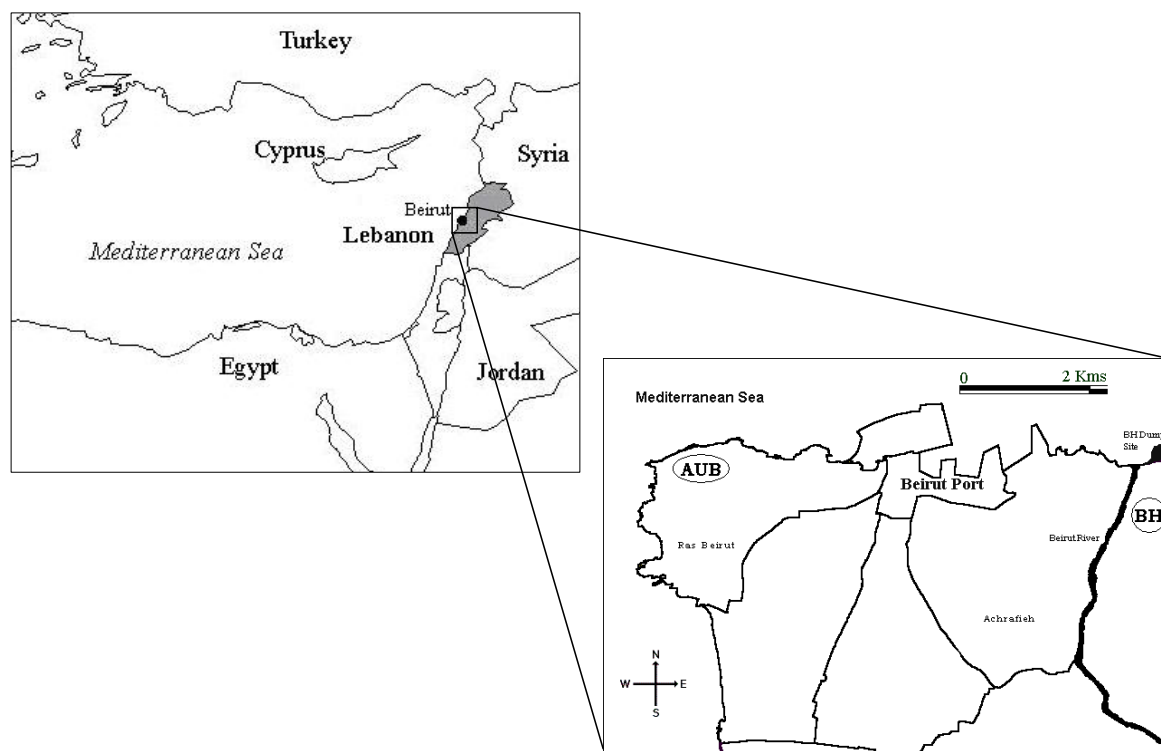
ranean countries, relatively higher concentrations of calcium in Beirut were good indication of calcitic crustal abundance. Considering the importance of the health and climate impacts of aerosols locally and regionally, this study constitutes a point of reference for eastern Mediterranean transport modeling studies and local regulatory and policy makers.

## 1 Introduction

Being an enclosed area, the Mediterranean region has experienced elevated aerosol concentrations and major acid deposition problems (Matvev et al., 2002; Graham et al., 2004). Stagnant winds originating from Eastern Europe, large-scale industrialization, high population density, high traffic areas, and the intense solar radiation contribute to photochemical reactions and thus the formation of high levels of secondary pollutants (Lelieveld et al., 2002) and other reactive species (Kouvarakis et al., 2000). While the assessment of pollutant emissions has been well defined in the western Mediterranean region due to several field investigations and modeling studies, (Khatami et al., 1998; Guerzoni et al., 1999; Ridame et al., 1999; Gangoiti et al., 2001; Masmoudi et al., 2002), fewer studies restricted to Greece, Turkey and Israel in addition to some reports from the Arab countries (North Africa and West Asia) (Momani et al., 2000; Borai and Soliman, 2001; Jaradat et al., 2004) are available in the eastern Mediterranean region. A constraining factor in studying air pollution in these countries is associated with the lack of standards, rules, regulations and support to control air pollution problems.

Eastern Mediterranean region is subject to several inputs of natural and anthropogenic pollutants that are generated from several regional and local sources. Seasonal dust storms coming from the Arabian (SE) and Saharan deserts (S/SW) constitute the major source of mineral elements in the region (Kubilay et al., 2000). The Saharan dust storms generally

Correspondence to: N. Saliba  
(ns30@aub.edu.lb)



**Fig. 1.** View of the Middle East region, Lebanon and the position of the Bourj-Hamoud sampling site in Beirut.

occur in spring and are commonly associated with the passage of a low pressure system towards the east (Goudie and Middleton, 2001), whereas, Arabian dust storms occur in autumn. (Dayan, 1986; Alpert et al., 1990; Kubilay et al., 2000). First, sandy storms cause a significant increase in PM levels and influence the chemical composition of aerosols in the region (Dayan et al., 1991; Kubilay et al., 2000; Goudie and Middleton, 2001). Second, long-range transport of pollutants from central Europe have been the cause of high  $\text{SO}_2$  levels as determined in Israel and Greece (Luria et al., 1996; Ganor et al., 2000; Zerefos et al., 2000; Sciare et al., 2003; Tsitouridou et al., 2003), and third, marine aerosols (sea spray), which are considered a major contributor to the eastern Mediterranean aerosols. Local sources are also major contributors to high levels of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  which are derivatives of oxides of nitrogen, sulfur dioxide and ammonia, respectively (Danalatos and Glavas, 1999; Kassomenos et al., 1999; Erduran and Tuncel, 2001).

This study reports the levels of particulate matters (PM<sub>10-2.5</sub> (coarse) and PM<sub>2.5</sub> (fine)) in a populated site of Beirut; Bourj Hammoud and the formation and adsorption phenomena of different inorganic ions in two particulate modes. Seasonal variability is also discussed and long- and short-range sources are assessed based on the interrelation among the different inorganic ions in the coarse and fine particles.

## 2 Experimental

### 2.1 Sampling

The sampling was done in one of the busiest areas of Beirut; Bourj Hammoud (BH) ( $33^\circ 53' \text{N}$ ,  $35^\circ 32' \text{E}$ ); a highly populated area with several commercial and industrial facilities (Fig. 1). This site experiences high traffic density, sea spray, Beirut harbor operations, and some waste-mass burning activities. It is considered a good representation of urban Beirut. Sampling was performed at 3 m above the ground on the municipality building overlooking a busy street with heavy traffic. The sampling site is located one kilometer away from the Mediterranean coast at an elevation less than 10 m above sea-level.

Random sampling (every sixth day) was conducted between February 2004 and January 2005 for the BH site. Particulate matter (PM<sub>10-2.5</sub> and PM<sub>2.5</sub>) was drawn from the air stream by the use of a dichotomous sampler (Sierra-Anderson Dichotomous Model SA246B) (Shaka' and Saliba, 2004). The filters (Osmonics<sup>®</sup>: TefSep, Teflon, 47 mm, Laminated  $0.45 \mu\text{m}$  for the coarse particles and  $0.22 \mu\text{m}$  for the fine particles) were desiccated for 24 h at constant temperature ( $21.6^\circ\text{C}$ ) and relative humidity (9.6% RH) before and after sampling, and weighed using a Metler-Toledo microgram balance (model UMX2) housed in an isolated compartment. The sampling was done over a 24 h period with

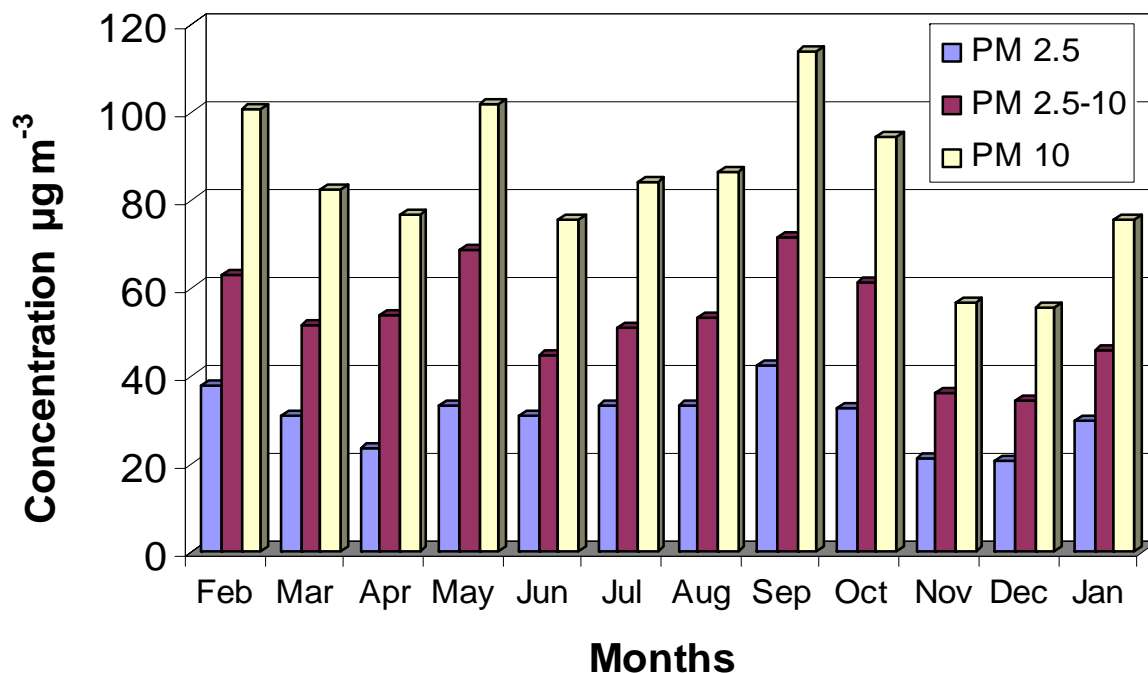


Fig. 2. Annual fine and coarse particle concentrations at the Bourj Hammoud site measured between February 2004 and January 2005.

a total flow rate of  $11.0 \text{ L min}^{-1}$ . Pressure, temperature and relative humidities of the sampling days that were used for the ionic concentration measurements are shown in Table 1. The samples were stored in Petri dishes and preserved in a refrigerator.

## 2.2 Chemical analysis

### 2.2.1 Ion analysis

Collected filters and blanks were extracted ultrasonically with 20 ml of deionized water ( $18 \text{ M}\Omega\text{cm}^{-1}$ ) for 40 min and filtered through a  $0.22 \mu\text{m}$  pore size Nylon filters. One coarse and one fine filter per month, which were collected on the same day, were dedicated for the analysis of the anion ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) concentrations and another similar set of filters for the cation ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ) concentrations. Ion concentrations were determined by Ion Chromatography (IC, model AllTech,) which consisted of an HPLC-AllTech pump model 262, a separation anionic column (Novosep A-1 anion,  $150 \text{ mm} \times 4.6 \text{ mm}$ ) and a cationic column (Universal cation,  $100 \text{ mm} \times 4.6 \text{ mm}$ ), a self-regenerating suppressor model DS-PLUS<sup>®</sup> and a conductivity detector model 650. A carbonic buffer of  $1.7 \text{ mM NaHCO}_3/1.8 \text{ mM Na}_2\text{CO}_3$  was used as a mobile phase for the anions, and for the cations a  $3 \text{ mM}$  methane sulfonic acid mobile phase was used. Concentrations of ions were determined in relative to calibration curves with a regression range ( $r^2$ ) of 0.993 and 0.999. The relative standard deviation for each ion was less than 0.71 and the sensitivity of the detector was  $0.01 \mu\text{S}$ .

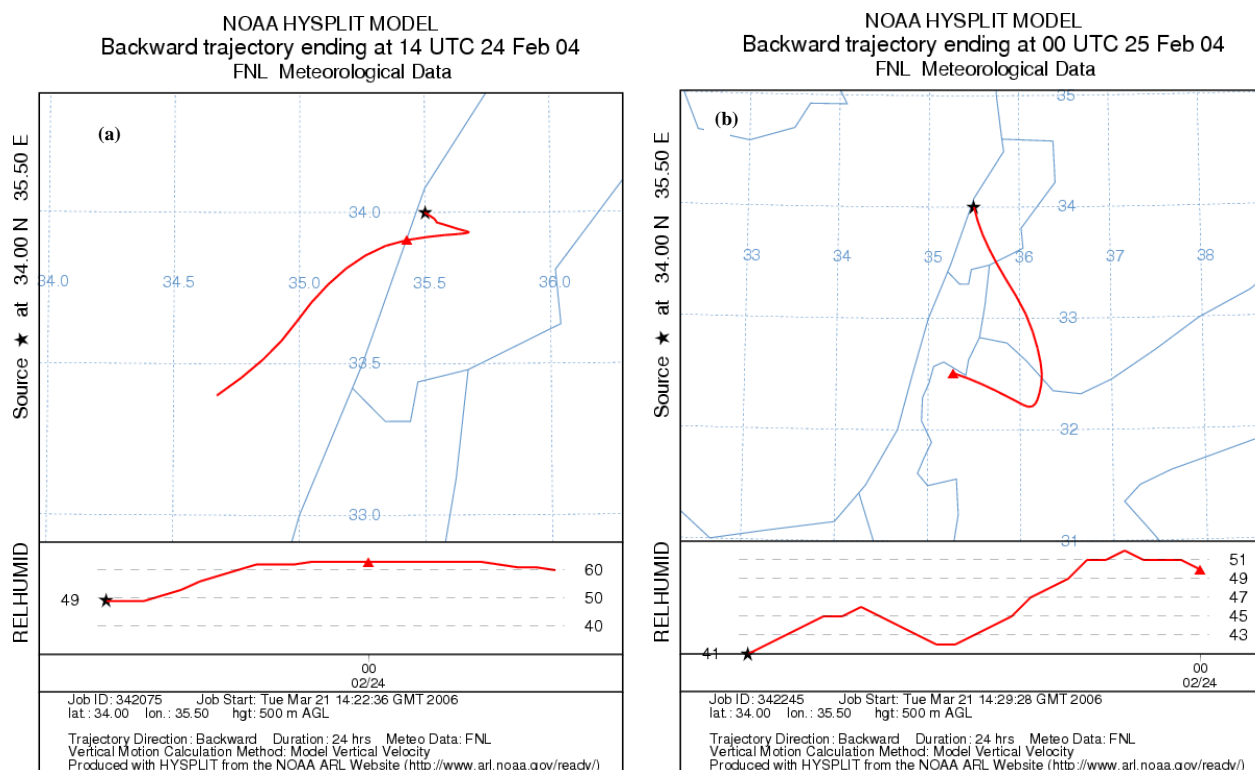
### 2.2.2 ATR-FTIR analysis

Field samples of PM10-2.5 and PM2.5 collected on Teflon filters were analyzed using a Nicolet AVATR Multibounce HATR 360 FTIR spectrometer equipped with a DTGS-detector and ZnSe horizontal crystals ( $45^\circ$  angle of incidence). Teflon filters were gently pressed against the ZnSe crystal using a regulated pressure exerted by a Teflon coated plate to ensure even and repeatable readings. Spectra were collected by averaging 1250 co-added scans at wavenumbers ranging from  $750$  to  $4000 \text{ cm}^{-1}$  at a resolution of  $1 \text{ cm}^{-1}$ . All spectra were ratioed against the spectrum of an empty cell. ATR spectra show peaks that are more intense at lower wavenumbers. As a result, the relative peak intensities for ATR and transmission spectra for the same sample are different; however, the absorption frequencies remain unchanged.

## 3 Results and discussions

### 3.1 Total PM10, PM10-2.5 and PM2.5 mass concentrations

Annual averages of PM10, PM10-2.5 and PM2.5 concentrations at BH were  $84 \pm 27$ ,  $53 \pm 20$  and  $31 \pm 9 \mu\text{g m}^{-3}$ , respectively. Figure 2 shows the variation of the monthly averages of coarse and fine particles during the whole year. Lower PM concentrations were recorded in the rainy season (November–January), whereas highest PM concentrations were determined during dust storms episodes where an

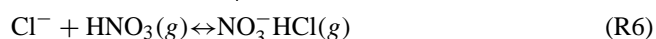
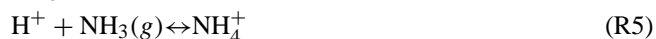
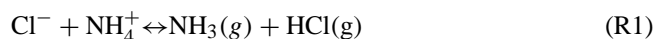


**Fig. 3.** Air mass backward trajectory HYSPLIT model for the sampling days on 24 February 2004 (a) and 25 February 2004 (b).

increase by 170% was recorded during the month of February. This increase was correlated with wind vectors originating from Egypt as deduced by the air mass trajectory HYSPLIT model on the dust-storms days (i.e. February 24th and 25th of 2004) shown in Fig. 3. Increases in PM<sub>10</sub> concentrations during dust storms have been reported in other coastal Mediterranean regions Dayan et al., 1991; Gullu et al., 2000; Kubilay et al., 2000; Goudie and Middleton, 2001; Rodriguez et al., 2002).

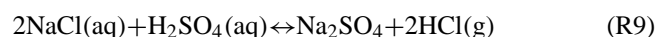
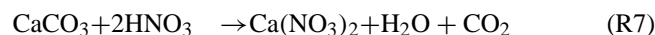
### 3.2 Sampling artifacts

As it is well known, the nitrate, sulfate, chloride and ammonium concentrations in aerosols vary due to the change in the meteorological conditions, the inter-particle and the gas-particle interactions.

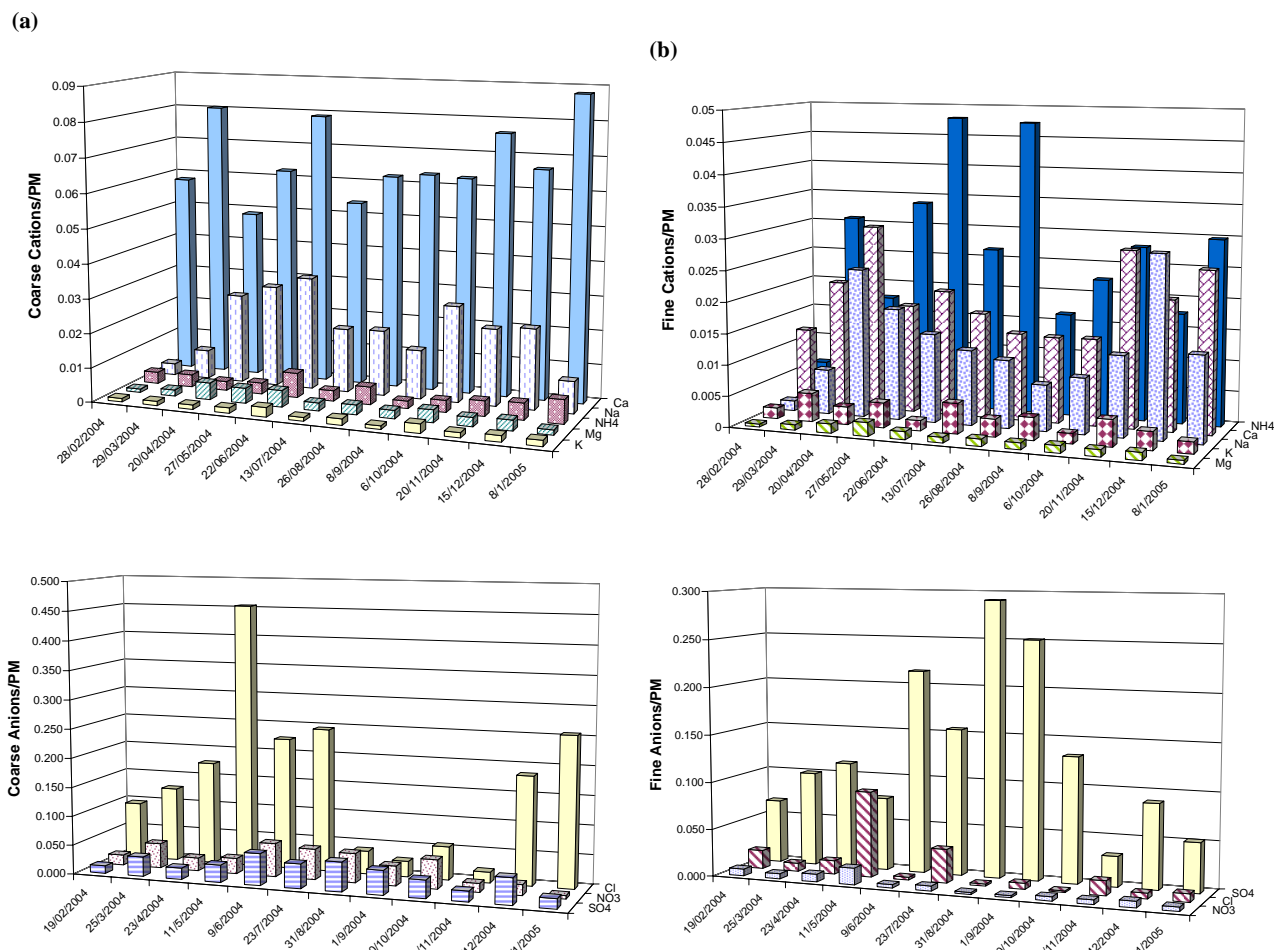


During sampling, reactions (R1–R6) may take place leading to sampling artifacts (Pathak et al., 2004). Sampling arti-

facts in sulfate, nitrate, chloride and ammonium concentrations have been shown to relate with the ambient particulate concentration ratio of  $\text{NH}_4^+/\text{SO}_4^{2-}$ . Being less than 1.5, the  $\text{NH}_4^+/\text{SO}_4^{2-}$  ratio indicated an ammonium poor ambient atmosphere, which prevents the formation and consequently the evaporation of  $\text{NH}_4\text{NO}_3$  from filters (Trebs et al., 2005). Hence sampling artifacts in sulfate and ammonium concentrations determined for the ammonium poor medium will be applied (Pathak and Chan, 2005). In this study, the positive errors of sulfate due to the  $\text{SO}_2$  absorption by the collected Teflon filters are considered negligible for both the coarse and fine modes, especially that the ambient concentration of  $\text{SO}_2$  is low (A six-monthly average of  $25\mu\text{g}/\text{m}^3$ ) (Saliba et al., 2006). Also, the ammonium percentage errors of ammonium in the same conditions are considered small and are neglected for the coarse and fine particles. However, the negative nitrate and chloride losses due to  $\text{HNO}_3$  and  $\text{HCl}$  evaporation, respectively, is not usually neglected in the ammonium poor media and are assumed to be 55% for the nitrates and 68% for the chlorides (Pathak and Chan, 2005).



These percent losses were not considered in this study due to the predominance of the reaction of  $\text{CaCO}_3$  with  $\text{HNO}_3$



**Fig. 4.** Normalized cationic and anionic concentrations over the total mass of the coarse (a) and fine (b) fraction of the particulate matter.

(R7), over the reaction of NaCl with HNO<sub>3</sub> (R8) and H<sub>2</sub>SO<sub>4</sub> (R9) which lead to the evaporation of HCl to the gas phase. The enhancement of (R7–R9) was supported by the AIM2 model that showed that the measured cations and anions were done at relative humidities above the deliquescence relative humidity (DRH) of calcium and sodium nitrates and so all nitrates and sulfates are taken in the aqueous phase and limited evaporation of HNO<sub>3</sub> was considered.

### 3.3 Ion composition and speciation of PM10-2.5 and PM2.5

Figure 4 represents the cationic and anionic normalized concentrations with respect to the mass concentration of the coarse and fine particles calculated for the same sampling day. The main coarse, water-soluble cations were mainly Na<sup>+</sup> and Ca<sup>2+</sup> ions and the water soluble anions included Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> (Fig. 4a). The fine particles were formed of water soluble NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Na<sup>+</sup> cations and SO<sub>4</sub><sup>2-</sup> as the main predominant anion (Fig. 4b). In both par-

ticles low amounts of K<sup>+</sup> and Mg<sup>2+</sup> were detected. The concentration ratio of ammonium to sulfate (NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup>) was found to be less than 1.5; a critical value indicating an ammonium poor ambient atmosphere (Pathak and Chan, 2005).

#### 3.3.1 PM10-2.5 coarse particles

In the coarse mode (Fig. 4a), almost constant high levels of calcium were determined due to the calcitic nature of the rocks in Lebanon (Abdel-Rahman and Nader, 2002). Sodium was also predominant and showed a constant variation during these sampled days between April and December. In February, March, and January, Na<sup>+</sup> exhibited lower concentrations with the lowest value being measured on 28 February 2004. The variation in the Na<sup>+</sup> concentration was directly dependent on the wind direction and rain since Na<sup>+</sup> originates mainly from sea-salt aerosols and its main sink is wet deposition. The air mass trajectory HYSPLIT model (Fig. 5) for the sampling dates on 28 February, 29 March 2004 and 8 January 2005 showed that wind originated over dry lands, hence, the low Na<sup>+</sup> concentration. Potassium, magnesium

**Table 1.** Meteorological conditions of the sampling days that were used for cation and anion concentration measurements.

Cations	Date	Day	Temp (°C)	% RH	Pressure (Pa)	Wind direction	Wind Spd (m s <sup>-1</sup> )
February	28 February 2004	Sat	–	–	–	–	–
Mar	29 March 2004	Mon	20.5	58.8	103 598	128.8	1.8327
Apr	20 April 2004	Tue	17.5	68.3	102 921	135.3	1.2516
May	27 May 2004	Thu	22.2	69.0	102 582	83.6	1.5198
Jun	22 June 2004	Tue	28.5	62.7	103 259	186.2	1.8327
Jul	13 July 2004	Tue	29.8	69.1	103 259	77.9	1.6539
Aug	26 August 2004	Thu	30.1	65.4	103 259	119.5	0.7599
Sep	8 September 2004	Wed	29.3	58.7	103 598	222.7	3.576
Oct	6 October 2004	Wed	27.1	57.6	103 598	176.7	1.6986
Nov	20 November 2004	Sat	19.5	53.3	104 275	160.1	1.0281
Dec	15 December 2004	Wed	–	–	–	–	–
Jan	8 January 2005	Sat	–	–	–	–	–

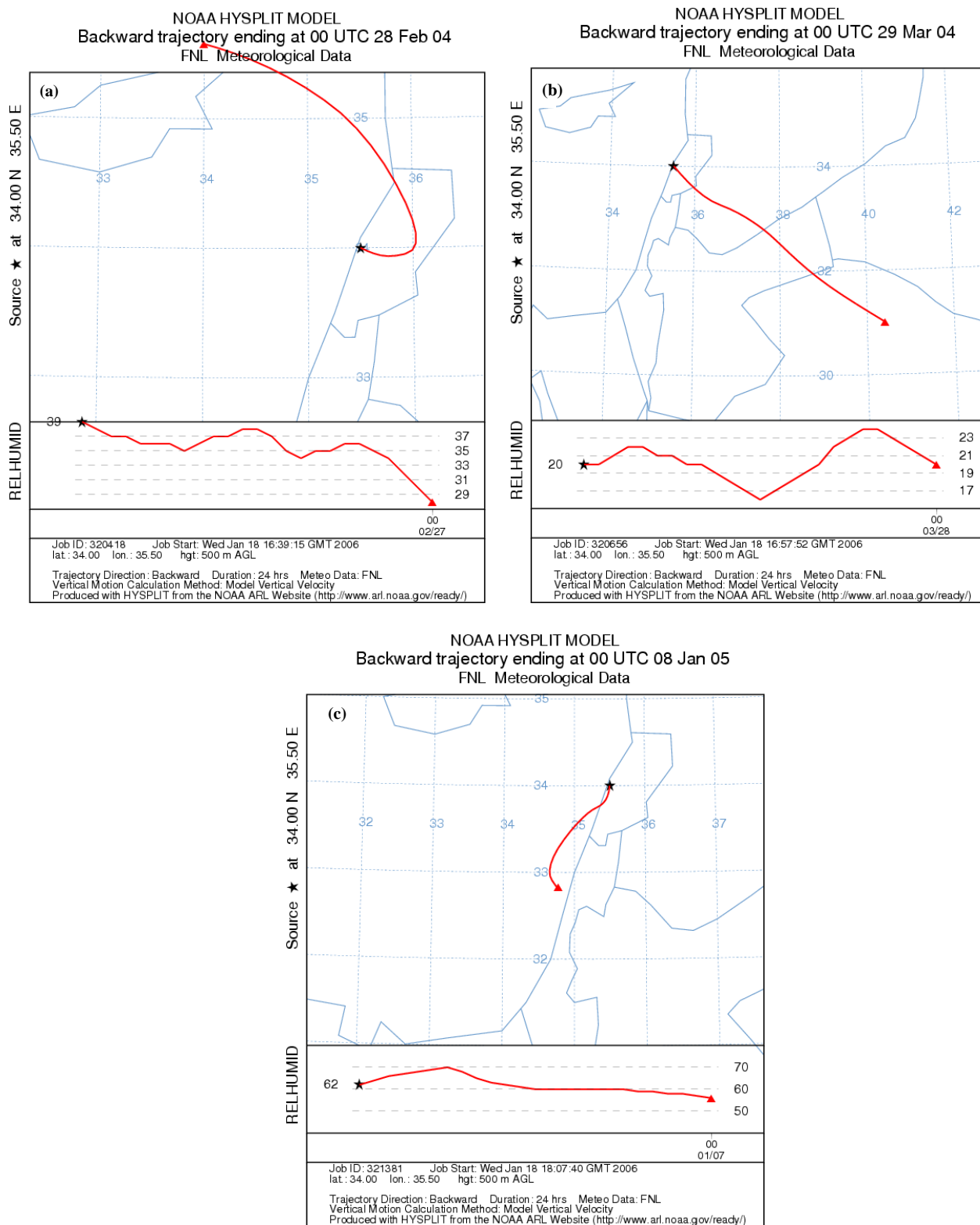
Anions	Date	Day	Temp (°C)	% RH	Pressure (Pa)	Wind direction	Wind Spd (m s <sup>-1</sup> )
Feb	19 February 2004	Thu	–	–	–	–	–
Mar	25 March 2004	Thu	14.8	69.3	103 936	110.3	1.4304
Apr	23 April 2004	Fri	17.4	56.4	102 921	138.5	1.0728
May	11 May 2004	Tue	20.0	65.2	103 598	83.6	2.1456
Jun	9 June 2004	Wed	24.0	62.5	103 598	131.0	1.2069
Jul	23 July 2004	Fri	29.6	63.8	103 259	127.9	1.2516
Aug	31 August 2004	Tue	28.6	57.2	103 598	147.8	0.894
Sep	1 September 2004	Wed	29.4	58.1	103 598	104.7	0.9387
Oct	20 October 2004	Wed	25.7	59.2	103 598	170.0	1.1175
Nov	29 November 2004	Mon	14.3	39.1	104 952	218.3	1.1175
Dec	8 December 2004	Wed	–	–	–	–	–
Jan	5 January 2005	Wed	–	–	–	–	–

**Table 2.** The ( $r^2$ ) correlation between different inorganic ions in coarse and fine particulate matters.

	Coarse									Fine									
	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	nss-SO <sub>4</sub> <sup>2-</sup>	
NO <sub>3</sub> <sup>-</sup>	1.00									1.00									
SO <sub>4</sub> <sup>2-</sup>	0.44	1.00								0.14	1.00								
Na <sup>+</sup>	0.27	0.59	1.00							0.00	0.13	1.00							
NH <sub>4</sub> <sup>+</sup>	0.12	0.62	0.19	1.00						0.13	0.97	0.08	1.00						
K <sup>+</sup>	0.12	0.60	0.60	0.50	1.00					0.09	0.10	0.00	0.07	1.00					
Mg <sup>2+</sup>	0.33	0.54	0.90	0.14	0.47	1.00				0.03	0.39	0.33	0.28	0.13	1.00				
Ca <sup>2+</sup>	0.59	0.59	0.20	0.30	0.33	0.21	1.00			0.11	0.13	0.20	0.08	0.03	0.09	1.00			
Cl <sup>-</sup>	0.30	0.12	0.82	0.18	0.61	0.82	0.27	1.00		0.00	0.11	0.65	0.08	0.05	0.17	0.27	1.00		
nss-SO <sub>4</sub> <sup>2-</sup>	0.48	0.49	0.19	0.27	0.28	0.16	0.87	0.24	1.00	0.29	0.35	0.00	0.35	0.17	0.15	0.01	0.00	1.00	

and ammonium were at much lower concentration throughout the year. The chloride concentration originating from sea salt is defined as 1.174 the concentration of Na<sup>+</sup> and this

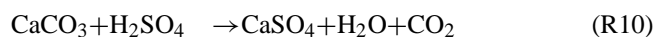
constituted only a small percentage of the total concentration of chloride in the coarse particles. The high Cl<sup>-</sup> concentration indicated that limited losses of chloride occurred via



**Fig. 5.** Air mass backward trajectory HYSPLIT model for the sampling days on 28 February 2004 (a), 29 March 2004 (b) and 8 January 2005 (c).



the reaction with acids to lead to nitrate and sulfate followed by the evaporation of HCl to the gas phase ((R8) and (R9)) (Kerminen et al., 1997; Zhuang et al., 1999; Kocak et al., 2004; Pathak et al., 2004; Niemi et al., 2005). The highest level of  $\text{Cl}^-$  was determined on May 11, 2004, where a westerly wind vector with a relatively higher average wind speed was measured (Table 1). An approximately 40% drop in the concentration was observed in the sampled days during the months of February, March, April, July, August, December and January. Much lower values were measured between August and November accompanied by relatively higher levels of nitrate and sulfate in the coarse mode attributed to reactions of NaCl and/or  $\text{CaCO}_3$  with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  ((R7)-(R10)) in the aqueous phases to form coarse mode nitrate and sulfate salts.



The reactions of NaCl and  $\text{CaCO}_3$  with  $\text{HNO}_3$  are both considered rapid with the latter being several orders of magnitude higher than the former (Evans et al., 2004). Consequently, in the presence of relatively higher levels of mineral dust, the reaction of  $\text{CaCO}_3$  with  $\text{HNO}_3$  leading to the formation of  $\text{Ca}(\text{NO}_3)_2$  is expected to predominate (Laskin et al., 2005). In fact, reactivity studies of individual mineral dust particles with nitric acid has shown that the calcium nitrate formed from (R7) is very hygroscopic and undergoes deliquescence at approximately 10% RH so it becomes capable of retaining water droplets and allowing for the continuous reactivity of the carbonate particle with unrestricted transport of  $\text{HNO}_3$  (Krueger et al., 2004). Calcium sulfate was also shown to be the product of  $\text{CaCO}_3$  and  $\text{H}_2\text{SO}_4$  reaction in aerosols (Davis and Jixiang, 2000; Xie et al., 2005). The lowest value of chloride observed in November was assigned to sea-salt chloride with  $[\text{Cl}^-]$  being equal to 1.174.  $[\text{Na}^+]$ . Higher values determined during the other sampling days, were attributed to the emission of HCl from the waste mass burning activities located at 450 m away from the sampling site. Elevated levels of chloride have also been reported in Kanto Plain, Japan (Kaneyasu et al., 1999). On the other hand, strong correlation ( $r^2 > 0.82$ ) (Table 2) between the overall average concentrations of  $\text{Na}^+$  and  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  and  $\text{nss-SO}_4^{2-}$  emphasized the fact that salts like NaCl,  $\text{MgCl}_2$  and  $\text{CaSO}_4$  are predominant. Also, the good correlations ( $0.59 < r^2 < 0.62$ ) identified between  $\text{NO}_3^-$  and  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , and  $\text{K}^+$  and  $\text{Cl}^-$  suggested that salts like  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and KCl, were present. Both  $\text{CaSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$  are the products of (R7) and (R10).

The abundance of  $\text{CaCO}_3$  and crystal nitrate in the coarse particles have been confirmed by the ATR-FTIR measurements of the PM coarse filters collected after 11 consecutive sampling days. As shown in Fig. 6a, absorption bands at 873 and  $712\text{ cm}^{-1}$  that are characteristic of carbonates and nitrates, respectively, were identified (Blanco and McIntyre, 1972; Grassian, 2002). Carbonate ions are also distinguished

by a peak at  $1413\text{ cm}^{-1}$  (Al-Abadleh and Grassian, 2000) on surfaces; and/or  $1390\text{ cm}^{-1}$  in aqueous media (Villalobos et al., 2001). Peaks at 1401 and  $1480\text{ cm}^{-1}$  were assigned to vibrational modes of dissolved carbonate ions and adsorbed species, respectively (Arihara et al., 2001). In Fig. 6a, a broad peak between 1300 and  $1560\text{ cm}^{-1}$  is detected, and assigned to the presence of carbonate, nitrate and ammonium ions which were reported to absorb in the 1320–60 and  $1400\text{ cm}^{-1}$  range, respectively (Cunningham et al., 1974; Marley et al., 1993; Allen et al., 1994; Yang et al., 2001; Rivera-Figueroa et al., 2003). In addition, a sharp vibrational band at  $712\text{ cm}^{-1}$  has been shown to be characteristic to solid nitrate (Toops et al., 2005). The O-Si-O asymmetrical stretch of the silicate ion ( $\text{SiO}_4^{4-}$ ) at  $1033\text{ cm}^{-1}$  is clearly visible in all spectra and confirms what has been stated in the literature (Cunningham et al., 1974; Allen et al., 1994; Martinez et al., 1998; Muroya, 1999). Blanco and McIntyre (1972) identified quartz ( $\text{SiO}_2$ ) and kaolinite to be the major species in coarse atmospheric aerosol samples. Quartz absorbs most strongly around 1090 and  $730\text{ cm}^{-1}$ , (Martinez et al., 1998) whereas kaolinite absorbs around  $1010\text{ cm}^{-1}$  (Allen et al., 1994). The peak in Fig. 6a which was observed at  $1010\text{ cm}^{-1}$  may be attributed to kaolinite which is known to be extracted by the wind from the African continent and carried to the Mediterranean region. After soaking the coarse filter in water for 24 h, peaks assigned to solid carbonates, nitrates and silicates remained, hence the confirmation of their assignments (Béléké et al., 2003; Toops et al., 2005).

### 3.3.2 PM2.5 fine particles

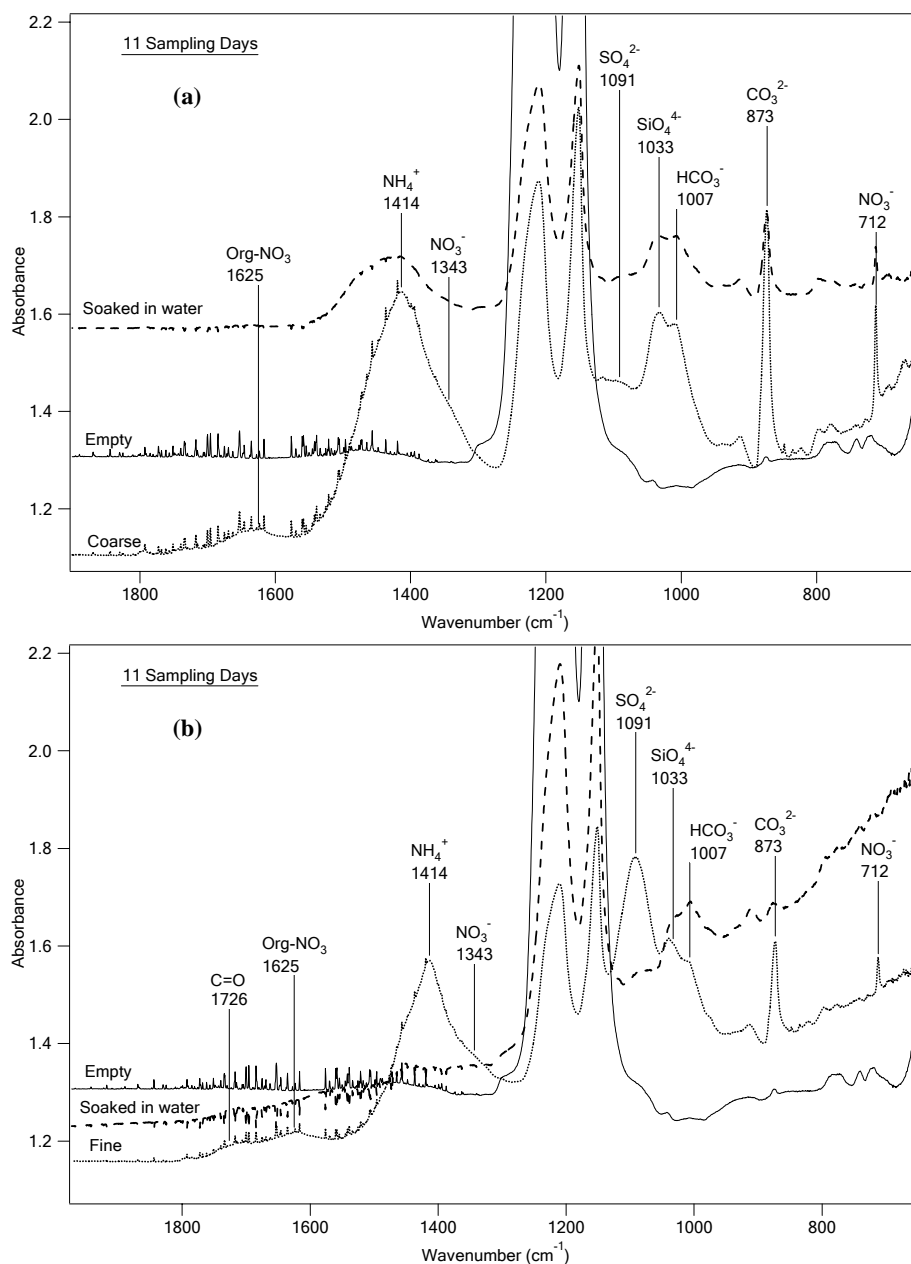
In the fine mode, almost constant levels of  $\text{Ca}^{2+}$  were detected (Fig. 4b) throughout the year.  $\text{Na}^+$  also showed constant levels with lower values correlated with an easterly wind direction originated over the dry land as it is the case in February, March, September and November. The ammonium concentration which exhibited the highest % concentration in the fine particles showed relatively higher levels in the summer. The variation in the ammonium concentration correlated well with the variation in the sulfate concentration. Sulfate increased in summer due to the enhancement of the photooxidation rate of  $\text{SO}_2$ .



The  $r^2$  values of the different water soluble ions (Table 2) in the fine particles, showed a strong correlation ( $r^2 > 0.97$ ) between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  via (R11) indicating that the predominant salt present in the fine particles is  $(\text{NH}_4)_2\text{SO}_4$ . Also, the high correlation ( $r^2 = 0.65$ ) identified between  $\text{Cl}^-$  and  $\text{Na}^+$  suggested the presence of NaCl.

The identification of  $(\text{NH}_4)_2\text{SO}_4$  was supported by the ATR spectrum shown in Fig. 6b where peaks at 1091 and  $1414\text{ cm}^{-1}$  were assigned to  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , respectively. These peaks were completely dissolved after soaking the PM2.5 filter in water for 24 h. In comparison to the coarse





**Fig. 6.** ATR-FTIR Spectra showing the inorganic ion bands of particles collected on Teflon filters during 11 consecutive sampling days. (a) shows the coarse particulate matters before and after soaking the filters in water and (b) shows fine particulate matters before and after soaking the filters in water for 24 h.

filter, the relative increase of the assigned  $\text{SO}_4^{2-}$  peak and the complete water dissolution of the two absorption bands assigned to crystals  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$ , at 873 and 712  $\text{cm}^{-1}$ , respectively, indicated that chemical reactions and carbonate and nitrate crystal growth mechanisms occurring in the fine filters were different from the coarse filters. Except for the silicate and bicarbonate ions, which seemed to be more resistant to water, most ions present in the fine particles were in the form of water soluble salts.

The sum of the micro-equivalent anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) in the fine particles was found to be highly correlated to the sum of all the micro-equivalent cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ). In addition, the median cation/anion ratio was 0.98 suggesting that an ammonium poor medium was prevalent in some cases and in some others anions were balanced by their counter ions to give neutrality to the aerosols. In the case where an ammonium poor medium was detected, it was expected that hydronium ions will compensate for the charge balance (Trebs et al., 2005).

### 3.3.3 Total PM<sub>10</sub> particles

The PM<sub>10</sub> ionic nitrate concentrations ( $1.92 \mu\text{g m}^{-3}$ ) are lower than the levels reported in Finokalia, Greece ( $2.75 \mu\text{g m}^{-3}$ ) (Bardouki et al., 2003), but higher than the concentration listed for Antalya, Turkey ( $1.18 \mu\text{g m}^{-3}$ ) (Gullu et al., 2000) and coastal Israel ( $1.14 \mu\text{g m}^{-3}$ ) (Ganor et al., 2000). Even though the level of  $\text{SO}_4^{2-}$  ( $5.98 \mu\text{g m}^{-3}$ ) was comparable to levels reported in Greece ( $6.87 \mu\text{g m}^{-3}$ ) and Turkey ( $5.54 \mu\text{g m}^{-3}$ ), but it was lower by 151% than the one reported in Israel ( $14.99 \mu\text{g m}^{-3}$ ) due to the lower effect of the sulfate loaded soil-dust originating from the Tibesti Mountains-Sinai desert trajectory (Falkovich et al., 2001; Levin et al., 2003; Falkovich et al., 2004), and the lack of local industrial emission. Relative to other eastern Mediterranean cities, the lowest concentration of ammonium concentrations reported in this study reflects the absence of agricultural activities near the sampling site. The average calcium ion concentration in the PM<sub>10</sub> was found to be  $3.49 \mu\text{g m}^{-3}$ , which is a high value with regard to the levels obtained in some eastern Mediterranean cities like, 1.54 and  $1.39 \mu\text{g m}^{-3}$  in Finokalia (Bardouki et al., 2003), and Thessaloniki (Tsitouridou et al., 2003), Greece, respectively. However, similar concentrations of  $4 \mu\text{g m}^{-3}$  were reported in Tel Aviv, Israel (Graham et al., 2004).

## 4 Seasonal variation of PM

The monthly variations of the cation and anion concentrations revealed that the concentration of nitrate ions, in the coarse mode particles, was the highest during the sampling days of the summer, and dropped by half during the winter sampling days due to lower photochemical oxidation rates of organics to produce OH; a radical responsible for the formation of  $\text{HNO}_3$  via (R12) (Vrekoussis et al., 2004).



The sulfate ion concentrations in the coarse mode followed a pattern similar to the one observed for nitrate ions in both the coarse and fine particles. The photochemical oxidation of  $\text{SO}_2$  becomes active under summer conditions (high solar radiation and temperatures) to produce  $\text{SO}_4^{2-}$  (Luria et al., 1996; Mihalopoulos et al., 1997; Danalatos and Glavas, 1999). Relatively lower values of sea-salt components ( $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{Mg}^{2+}$ ) correlated well with southerly wind vectors as deduced from the meteorological conditions listed in Table 1 and the air mass trajectory HYSPLIT models (Fig. 5). Soil and mineral dust factors are highly linked to the concentration of  $\text{Ca}^{2+}$  in the coarse particles. Ammonium, displayed a maximum concentration during the sampling days of June and August due to high temperature and dry soil; a favoring medium for ammonia evaporation into the atmosphere. Ammonium seasonal cycles, in the fine particles, followed a pattern similar to that observed for sulfate ions with

a minimum in winter and a maximum in summer (Danalatos and Glavas, 1999).

## 5 Source of PM particles

The coarse particles being highly loaded with  $\text{Cl}^-$  were most representatives of waste mass burning in addition to sea-salt particles (Kaneyasu et al., 1999).  $\text{CaCO}_3$  originated from crustal rocks (Abdel-Rahman and Nader, 2002), whereas silicate and kaolinite ions identified by ATR are typical of continental dust coming from Africa (Alastuey et al., 2005; Fiol et al., 2005). Sulfate and nitrate ions are the result of secondary reactions of crustal dust particles with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Sulfate is the result of high levels of  $\text{SO}_2$  originating from long range transport; i.e. Eastern and Central Europe in winter (Falkovich et al., 2001; Levin et al., 2003; Sciare et al., 2003; Falkovich et al., 2004) as supported by the air mass trajectories during the same sampling days, and to local exhaust emissions such as residential heating, diesel operating busses and ship emission from the harbor that is located at approximately 3 km away from the sampling site. As for the source of particulate nitrates, vehicle emission generating  $\text{NO}_2$  seemed to be the precursor of  $\text{HNO}_3$ . The emission from local mass burning activities was supported by the good correlation that was determined between  $\text{K}^+$  and  $\text{SO}_4^{2-}$  as a result of the conversion of  $\text{KCl}$  to  $\text{K}_2\text{SO}_4$  during smoke formation (Liu et al., 2000).

## 6 Summary and conclusions

The annual averages of PM<sub>10</sub>, PM<sub>10-2.5</sub> and PM<sub>2.5</sub> concentrations at BH were higher than the U.S. Environmental Protection Agency (EPA) limits, with higher values recorded during sand storms coming from Arabian desert and/or Africa. The main water-soluble ions in the coarse particles were  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , and in the fine particles  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  were determined. The concentration ratio  $\text{NH}_4^+/\text{SO}_4^{2-}$  being less than 1.5 characterized the ambient atmosphere as an ammonium poor medium preventing the formation of  $\text{NH}_4\text{NO}_3$ . In addition, calcium carbonate was shown to be abundant in the coarse particles by means of ATR-FTIR. This led to the enhancement of the reaction of calcium carbonate with nitric and sulfuric acids and the increase in the concentration of calcium nitrate and sulfate salts over the calcium and sodium chloride. This behavior eliminated the losses of chloride from the filters by the  $\text{Cl}^-$  depletion processes and the absorbance of higher amounts of nitric acid by the coarse particles.  $\text{CaCO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  crystals identified in the coarse particles did not dissolve in water after soaking the coarse filter in water for 24 h but were found to be water soluble when the same procedure was applied to fine particles indicating different growth and adsorption phenomena. In the fine particles, the

ammonium concentration exhibited the highest percent concentration with relatively higher levels in the summer. A strong correlation with  $\text{SO}_4^{2-}$  indicated that  $(\text{NH}_4)_2\text{SO}_4$  predominated. The air mass trajectory HYSPLIT model showed that wind originated over the dry lands was accompanied by a drop in the sodium and the chloride concentrations with the latter remaining higher than other Mediterranean countries and this has been attributed to the emission of chloride from local waste mass burning sources. Nitrate and sulfate ion concentrations in the coarse mode followed similar pattern variations with an increase in the concentration during summer due to the enhancement of photochemical reactions. The increase in the concentration of these ions correlated with wind vectors coming from Eastern and Central Europe.  $\text{CaCO}_3$ , on the other hand, originated mainly from the calcitic rocks abundant in Lebanon. Hence, local and long-range transported phenomena contributed to the diverse composition of coarse and fine particles in Bourj-Hammoud.

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