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Ion concentrations of $PM_{10-2.5}$ and $PM_{2.5}$ aerosols over the eastern Mediterranean region: seasonal variation and source identification

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Abstract

The annual averages of particulate matters (PM_{10}, $PM_{10-2.5}$ (coarse) and $PM_{2.5}$ (fine)) in a densely populated area of Beirut were measured and found to be 84±27, 53±20 and 31±9 $\mu g\,m^{-3}$, respectively. Ion Chromatography (IC) analysis of the collected PM Teflon filters showed that NaCl, $CaSO_4$ and $Ca(NO_3)_2$ were predominant in the coarse particles, while $(NH_4)_2SO_4$ was the main salt in the fine particles. Using the non destructive Fourier Transform Infra Red-Attenuated Total Reflection (FTIR-ATR) technique, $CaCO_3$ was determined in the coarse filter. In addition, ATR measurements showed that inorganic salts present in the coarse particles are mostly water insoluble while salts found in fine particles are soluble. Concentrations of nitrates and calcium higher than the ones reported in neighboring Mediterranean countries were good indication of high traffic density and crustal dust abundance in Beirut, respectively. The study of the seasonal variation showed that long-range transport of SO_2 from Eastern and Central Europe, sandy storms coming from Africa and marine aerosols are considered major sources of the determined inorganic ions. 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 West-

ACPD

5, 13053–13073, 2005

ern 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; Sellergi 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) 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, 2000). The Saharan dust storms generally 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, African 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 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 HNO_3, H_2SO_4 and 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_{10}, $PM_{10-2.5}$ (coarse) and $PM_{2.5}$ (fine)) in a populated site of Beirut; Bourj Hammoud. The seasonal variability is discussed and long- and short-range sources are assessed based on the interrelation among the different inorganic ions in the coarse and fine particles.

ACPD
5, 13053–13073, 2005

2. Experimental

2.1. Sampling

Random sampling (every sixth day) was conducted between February 2004 and January 2005 for the Bourj Hammoud (BH) site. Particulate matters ($PM_{10-2.5}$ and $PM_{2.5}$) were removed from the air stream by the use of a dichotomous sampler (Sierra-Anderson Dichotomous Model SA246B) (Shaka' and Saliba, 2004). The filters were desiccated for 24 h before and after sampling and weighed using a Metler-Toledo microgram balance model UMX2. The sampling was done over a 24 h period with a total flow rate of 11.0 L min^{-1}. The samples were put in Petri dishes and preserved in a refrigerator.

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

2.2. Chemical analysis

2.2.1. Ion analysis

Collected filters and blanks were extracted ultrasonically with 20 ml of deionized water (18 MΩ cm^{-1}) for 40 min and filtered through a 0.22 μm pore size Nylon filters. One filter per month was dedicated for the analysis of the anion (SO_4^{2-}, NO_3^-, Cl^-) concentrations and another filter for the cation (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) concentrations. Ion concentrations were determined by Ion Chromatography (IC, model AllTech,) which

ACPD
5, 13053–13073, 2005

consisted of an HPLC pump model 262, a separation anionic column (Novosep A-1 anion, 150 mm×4.6 mm) and a cationic column (Universal cation, 100 mm×4.6 mm), a self-regenerating suppressor model DS-PLUS® and a conductivity detector model 650. A carbonic buffer of 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3 was used as a mobile phase for the anions and for the cations a 3 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 lowest detection limit was around 0.01 $\mu g\,m^{-3}$.

2.2.2. FTIR-ATR analysis

Field samples of $PM_{10-2.5}$ and $PM_{2.5}$ 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° angle of incidence). Spectra were collected by averaging 1250 co-added scans at wavenumbers ranging from 750 to 4000 cm^{-1} at a resolution of 1 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 PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ mass concentrations

Annual averages of PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ concentrations at BH were 84±27, 53±20 and 31±9 $\mu g\,m^{-3}$, respectively. Figure 1 shows the variation of the monthly averages of coarse and fine particles during the whole year. A lower PM concentrations were recorded in the rainy season (November–January), whereas highest PM concentrations were determined during dust storms episodes. Similar increase in PM_{10}

ACPD
5, 13053–13073, 2005

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; Rodríguez et al., 2002).

3.2. Ion composition and speciation of $PM_{10-2.5}$ and $PM_{2.5}$

As shown in Figs. 2a and 2b, 44 and 33% of the total $PM_{10-2.5}$ and $PM_{2.5}$, respectively, are constituted of water soluble ions. Concentrations of different compounds are represented in Table 1. The coarse, water-soluble particles included Cl^-, SO_4^{2-}, NO_3^-, Na^+ and Ca^{2+} ions (Fig. 2a), whereas the fine particles are mostly formed of SO_4^{2-}, Cl^-, Na^+, NH_4^+ and Ca^{2+} ions (Fig. 2b). In both particles low amounts of K^+ and Mg^{2+} were detected.

3.2.1. $PM_{10-2.5}$ coarse particles

While the high amount of Cl^- in the coarse particles is usually due to sea-salt aerosols, the high values of SO_4^{2-} and NO_3^-, are attributed to secondary products that are formed from the reaction of sea-salt particles with nitric (HNO_3) and sulfuric (H_2SO_4) acids in urban maritime environments (Savoie and Prospero, 1982; Harrison and Pio, 1983; Wall et al., 1988; Harrison et al., 1994; Wu and Okada, 1994; Pakkanen, 1996; Kerminen et al., 1997; Zhuang et al., 1999; Satsangi et al., 2002; Lestaria et al., 2003; Xiaoxiu et al., 2003; Huang et al., 2004; Kocak et al., 2004; Pathaka et al., 2004; Hueglina et al., 2005; Nakamuraa et al., 2005; Niemi et al., 2005; Takeuchia et al., 2005). In this study, the coarse particles showed a strong correlation (r^2>0.82) (Table 2) between Na^+ and Mg^{2+}, Na^+ and Cl^-, Mg^{2+} and Cl^- and Ca^{2+} and nss-SO_4^{2-} implying that salts like NaCl, $MgCl_2$ and $CaSO_4$ might be predominant. Hence, Reaction (R1) between $CaCO_3$ and H_2SO_4 to produce $CaSO_4$ seemed to be more favored than Reaction (R2) between NaCl and H_2SO_4 to produce Na_2SO_4. Also, the good correlations (0.59<r^2<0.62) identified between NO_3^- and Ca^{2+}; SO_4^{2-} and Na^+, NH_4^+,

K^+ and Ca^{2+}; and K^+ and Cl^- suggested that salts like $Ca(NO_3)_2$, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, and KCl, were present. The driving reaction that led to the formation of secondary nitrates in the coarse particles is not the depletion of sea-salt particles from Cl^- by HNO_3 (low correlation between Na^+ and NO_3^-) but rather it is the neutralization reaction of $CaCO_3$ with HNO_3 to form $Ca(NO_3)_2$ as shown in Reaction (R3) (Wolff, 1984; Mamane and Gottlieb, 1992; Zhuang et al., 1999; Laskin et al., 2005). As indicated by the $PM_{2.5}/PM_{10-2.5}$ nitrate ratios of 0.03 in the summer and 0.51 in the winter, a higher nitrate concentration in the coarse fraction is due to the high concentration of $CaCO_3$ and the faster rate of Reaction (R3) over (R4) (Chow et al., 1996).

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad \text{(R1)}$$

$$NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl \quad \text{(R2)}$$

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad \text{(R3)}$$

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl \quad \text{(R4)}$$

The average calcium ion concentration in the PM_{10} was found to be 3.49 $\mu g\,m^{-3}$, which is a high value with regard to the levels obtained in eastern Mediterranean cities like, 1.54, 1.39 and 0.40 $\mu g\,m^{-3}$ in Finokalia (Bardouki et al., 2003), Thessaloniki (Tsitouridou et al., 2003), Greece, and Mount Meron, Israel (Levin et al., 2003), respectively. The abundance of $CaCO_3$ and $Ca(NO_3)_2$ 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. 3a, absorption bands at 873 and 712 cm^{-1} that are characteristic of CO_3^{2-} and NO_3^-, respectively, were identified. These peaks remained even after soaking the PM coarse filter in water for 24 h, and so the attribution to $CaCO_3$ that reacted with H_2SO_4 and HNO_3. Other sulfate, silicate and bicarbonate peaks were determined at 1091, 1030 and 1007 cm^{-1}, respectively, (Shaka' and Saliba, 2004). These peaks were all insoluble in water since no dissolution of the peaks was observed after soaking the coarse filter in water for 24 h.

ACPD
5, 13053–13073, 2005

3.2.2. $PM_{2.5}$ fine particles

Being 1.03 in the winter and 3.61 in the summer, the $PM_{2.5}/PM_{10-2.5}$ sulfate ratio shows that sulfates remain the main component of the fine particles with higher concentrations during the increase in the photooxidation rate of SO_2 in the summer. In addition, r^2 values of the different water soluble ions (Table 2) in the fine particles, showed a strong correlation (r^2>0.97) between NH_4^+ and SO_4^{2-} (R5) indicating that the predominant salt present in the fine particles is $(NH_4)_2SO_4$. Also, the high correlation (r^2=0.65) identified between Cl^- and Na^+ suggested the presence of NaCl.

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \quad \text{(R5)}$$

The identification of $(NH_4)_2SO_4$ was confirmed by the ATR spectrum shown in Fig. 3b where a peak at 1091 cm^{-1} was assigned to SO_4^{2-}. This peak was completely dissolved after soaking the $PM_{2.5}$ filter in water for 24 h. Ions such as NH_4^+, SiO_4^{4-}, HCO_3^-, CO_3^{2-} and NO_3^- were also identified at 1414, 1033, 1007, 873 and 712 cm^{-1}, respectively, (Shaka' and Saliba, 2004). Figure 3b also shows that ammonium, sulfate, carbonate and nitrate ions present in the fine particles were water soluble salts while silicate and bicarbonate were not since the peaks attributed to the former ions were strongly reduced after soaking the fine filter in water for 24 h. As compared to ionic levels determined in Finokalia, Greece (Bardouki et al., 2003), Antalya, Turkey (Gullu et al., 2000) and costal Israel (Ganor et al., 2000), nitrate concentrations (1.92 $\mu g\,m^{-3}$) are lower than the levels reported in Greece (2.75 $\mu g\,m^{-3}$) but higher than the concentration listed for Turkey (1.18 $\mu g\,m^{-3}$) and Israel (1.04 $\mu g\,m^{-3}$). The level of SO_4^{2-} (5.98 $\mu g\,m^{-3}$) was comparable to levels reported in Greece (6.87 $\mu g\,m^{-3}$) and Turkey (5.54 $\mu g\,m^{-3}$) but lower by 61% than the one reported in Israel (9.74 $\mu g\,m^{-3}$) due to high levels of SO_2 originated from long-range transport as well as from local sources. Relative to other Eastern Mediterranean cities, the lowest concentration of ammonium concentrations reported in this study reflects the absence of agricultural activity near the sampling site.

ACPD
5, 13053–13073, 2005

3.3. Seasonal variation of PM

The monthly variations of the cation and anion concentrations including sulfate and nitrate ions are represented in Fig. 4. It is apparent that the concentration of nitrate ions remained almost constant between May and October and dropped by 22% during the rainy season in the coarse mode particles due to wet deposition processes. The sulfate ion concentrations mostly predominant in the fine mode increased in the summer between June and October by 342% due to the increase in the photochemical oxidation of SO_2 which becomes active under summer conditions (high solar radiation and temperatures) to produce SO_4^{2-} (Luria et al., 1996; Mihalopoulos et al., 1997; Danalatos and Glavas, 1999). Sea-salt components (Cl^-, Na^+, and Mg^{2+}) demonstrated relatively lower values during dust storms. Variability of these components during winter is due to the local meteorological factors. Soil and mineral dust factors are highly linked to the concentration of Ca^{2+} in the coarse particles. Ammonium, displayed a maximum concentration in 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).

3.4. Source of PM particles

The coarse particles being highly loaded with Cl^- with smaller quantities of SO_4^{2-}, NO_3^-, and Ca^{2+} ions were most representatives of sea-salt particles. In addition, $CaCO_3$ originated from crustal rocks, whereas silicate ions identified by ATR during sand storms are typical of continental dust coming from Africa. Sulfate and nitrate ions are the result of secondary reactions of sea-salt and crustal dust particles with HNO_3 and H_2SO_4. Sulfuric acid which is shown to be more abundant than nitric acid in particles is the result of high levels of SO_2 originating from long range transport; i.e. Eastern and Central Europe in winter (Sciare et al., 2003), and to a smaller extent from local exhaust

ACPD
5, 13053–13073, 2005

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 NO_2 seems to be the main precursor of HNO_3. On another hand, emission from local mass burning activities was deduced from the good correlation that was determined between K^+ and SO_4^{2-} and K^+ and Cl^- (r^2~0.6) as a result of the rapid substitution of KCl by K_2SO_4 during smoke formation (Liu et al., 2000).

4. Conclusion

The variations of meteorological and climatic conditions, seasonal pollution episodes, and local anthropogenic factors from one region to another affect the PM levels, chemical composition and aerosol behavior in local environments. Hence, extrapolation of studies conducted in other eastern Mediterranean cities like, Finokalia, Thessaloniki, Antalya, and Tel Aviv could not have given a clear description of levels and chemical variation of particulate matters in BH. For example, the chemical composition in BH showed levels of SO_2 lower than the ones observed in Israel and Turkey because of the absence of local industrial facilities. In addition, higher levels of nitrates and calcium were good indication of high traffic density and crustal dust abundance in Beirut, respectively. 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.

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ACPD
5, 13053–13073, 2005

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ACPD
5, 13053–13073, 2005

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Table 1. Annual PM and ion concentrations in $\mu g\,m^{-3}$ measured at the Bourj Hammoud site between February 2004 and January 2005.

	Coarse (PM and ions in $\mu g/m^3$)									Fine (PM and ions in $\mu g/m^3$)								
Month	PM	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	PM	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}
Concentration	44.47	1.72	1.74	8.50	0.91	0.07	0.18	0.14	2.98	26.18	4.27	0.18	0.55	0.34	0.08	0.77	0.03	0.52
s.d.	13.42	0.77	0.96	8.18	0.49	0.03	0.07	0.07	0.68	8.41	3.17	0.14	0.83	0.15	0.04	0.44	0.01	0.09

ACPD

5, 13053–13073, 2005

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

Coarse										Fine								
	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	nss-SO_4^{2-}	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	nss-SO_4^{2-}
NO_3^-	1.00									1.00								
SO_4^{2-}	0.44	1.00								0.14	1.00							
Na^+	0.27	**0.59**	1.00							0.00	0.13	1.00						
NH_4^+	0.12	**0.62**	0.19	1.00						0.13	**0.97**	0.08	1.00					
K^+	0.12	**0.60**	**0.60**	0.50	1.00					0.09	0.10	0.00	0.07	1.00				
Mg^{2+}	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^{2+}	**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^-	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_4^{2-}	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

ACPD
5, 13053–13073, 2005

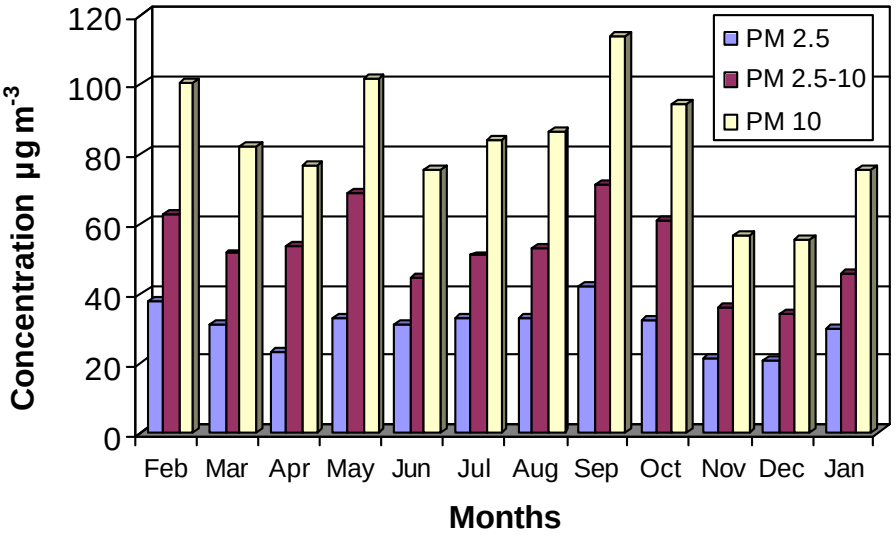

Fig. 1. Annual fine and coarse particle concentrations at the Bourj Hammoud site measured between February 2004 and January 2005.

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5, 13053–13073, 2005

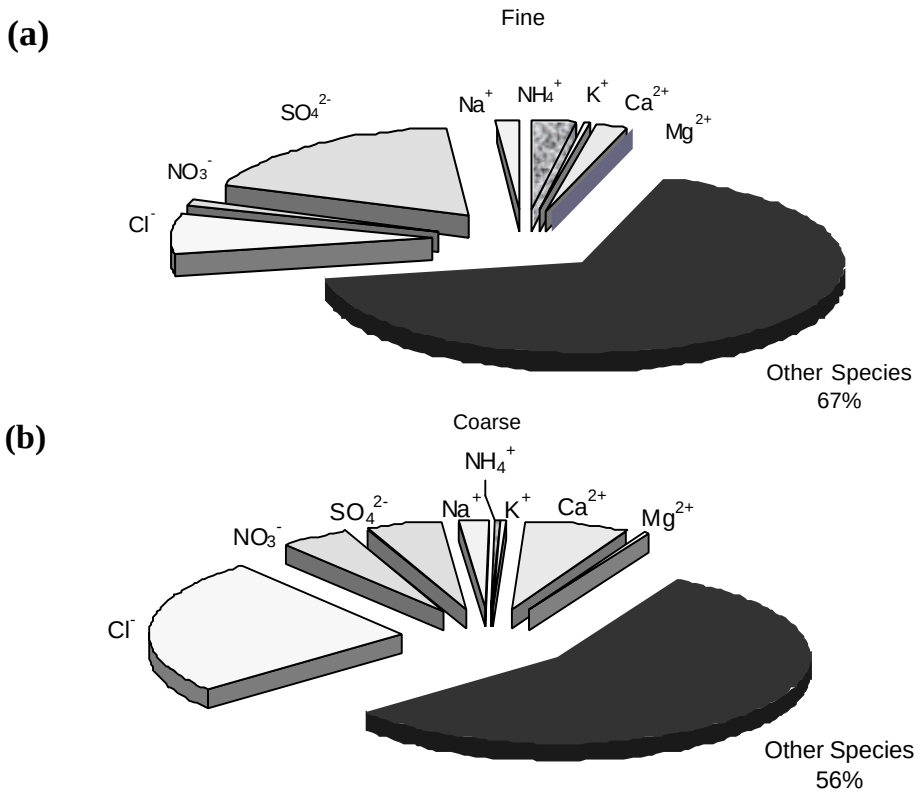

Fig. 2. Pie charts representing the ionic contribution to the total mass of the coarse **(a)** and fine **(b)** particulate matters.

ACPD
5, 13053–13073, 2005

Sources and contents of coarse and fine particulate matters

H. Kouyoumdjian and N. A. Saliba

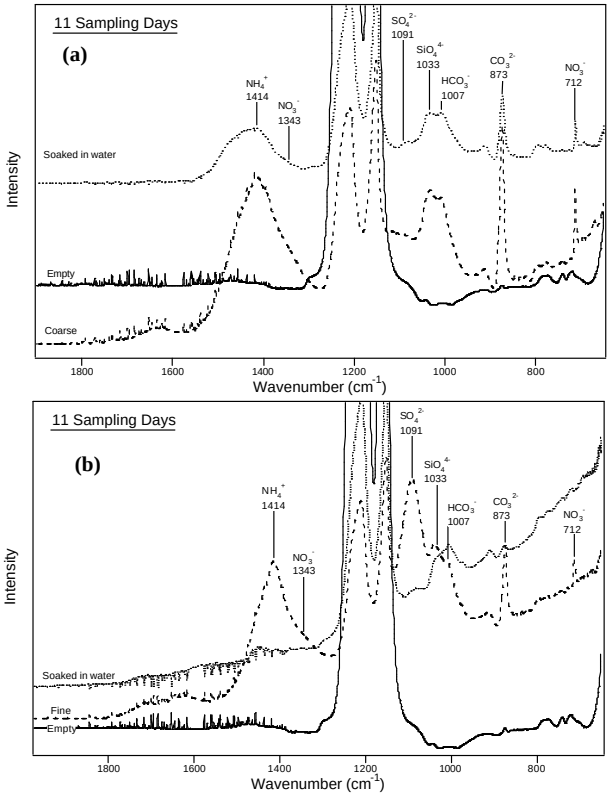

Fig. 3. FTIR-ATR spectra showing the inorganic ion bands for particles collected on Teflon filters during 11 consecutive sampling days. **(a)** shows the coarse particulate matters before and after soaking the filters in water and **(b)** shows fine particulate matters before and after soaking the filters in water for 24 h.

ACPD
5, 13053–13073, 2005

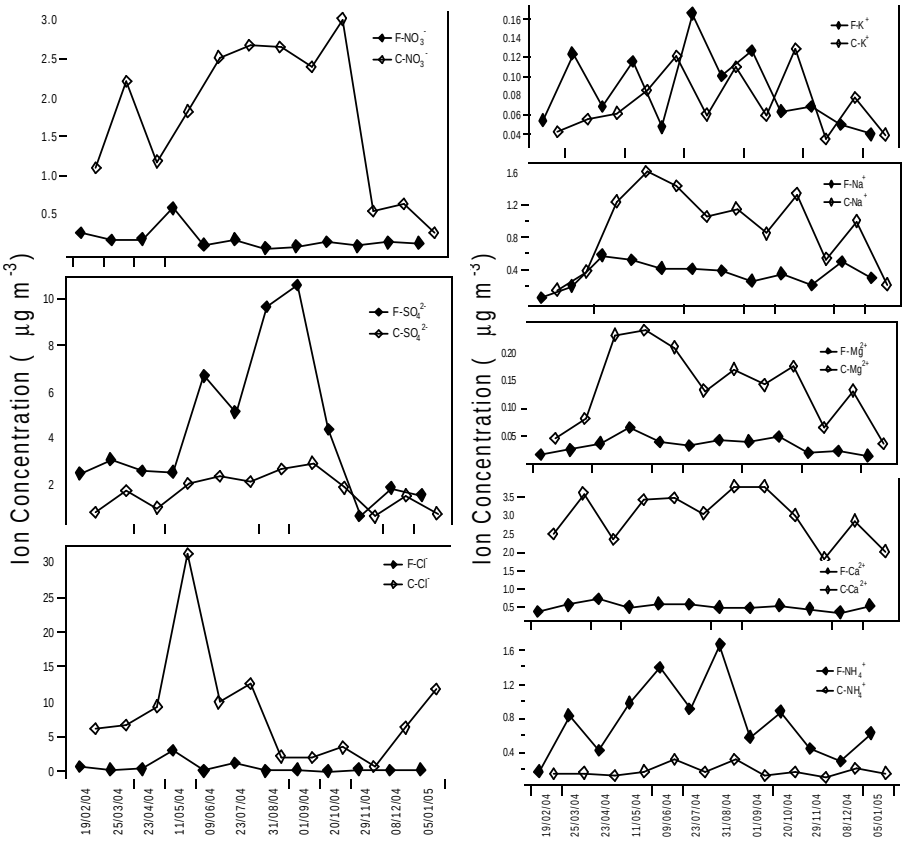

Fig. 4. Seasonal variations of NO_3^-, SO_4^{2-}, Cl^-, K^+, Na^+, Mg^{2+}, Ca^{2+}, and NH_4^+ concentrations determined in the coarse (◇) and fine (◆) particulate matters.

ACPD
5, 13053–13073, 2005