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Atmospheric
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Discussions

Interactive comment on "Ion concentrations of PM$_{10-2.5}$ and PM$_{2.5}$ aerosols over the eastern Mediterranean region: seasonal variation and source identification" *by* H. Kouyoumdjian and N. A. Saliba

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1. Source identification: As mentioned above, the title of the article speaks of PM source identification. However, this promise is not fulfilled. Rather, in some instances long range SO2 transport from East Europe is invoked, without explanation (Abstract line 14; pg. 13060, line 24; pg. 13061, line 25). If the authors have some evidence that high SO2 levels arise from long range transport from East Europe, they must present them. Else, if this is a hypothesis, the authors should explain how they arrived at it, and add heddging phrases, such as "possibly", "perhaps" and so on to the text.

The HYSPLIT model along with the meteorological data that were measured during sampling were added to the discussion of the results as suggested by the referee. Please refer to "Results and Discussions" shown below for a detailed explanation.

2. The discussion of CaCO3 transformation into Ca(NO3)2 and CaSO4: The reviewer believes that this is an important and valuable discussion. Moreover, the method of FTIR measurements before and after water dissolution is an innovative and interesting way for determining salt associations, which is not trivial to deduce from mere IC results, which give only ionic composition, without assigning the ions with salts. For this reason, the reviewer has regretted to see that this otherwise valuable and intriguing discussion was not carried out to its full scope, and again, in a less rigorous fashion. And more speicifically: This method has been introduced in a separate manuscript (Atmospheric Environment 2004, volume 38, p 523) as referenced, but more details will also be added in here to clarify the technique.

Page 13058 lines 22-24: It is suggested that reaction R1 is favored over reaction R2, however, this hypothesis is not explained nor are the possible sources for CaCO3 and H2SO4 in Beirut's atmosphere and why it is likely to react. The authors are therefore requested to explain why R1 is favorable to R2 (acid-base, entropy), where do CaCO3 and H2SO4 supposedly come from, and why should they react to begin with The preference of one of the reactions over the second was explained in detail and backed up with references. Please refer to the paragraph PM10-2.5 Coarse particles, shown below

Page 13059, lines 4-9: This sentence is a bit of a mystery to the reviewer. The sentence states, in other words, that since there is more nitrate in the coarse fraction in summer (than in winter) it arises that high coarse nitrate concentrations are due to high coarse CaCO3 concentrations and the favoring of reaction R3 over R4. This connection is not a trivial one. If the authors had meant that since HNO3 is a photochemical gas phase product, and therefore its higher concentration in particulate matter under light intensive conditions is due to reaction absorption from the gas-phase, they should state it clearly, and again with proper hedging, since this is a hypothesis and not a fact. Further more to make their point, the authors use the absolute nitrate concentration values, but these values are of little significance. What the author should really refer to is nitrate/PM values, since high absolute nitrate values can also indicate high PM concentrations, unless normalized to PM values. Based on the referee's recommendations, the normalized nitrate and sulfate concentration have been reported and shown in Figure 3. The discussion has been changed to fit the newly calculated concentration. Please refer to the Results and Discussion section shown below..

Page 13059, lines 2-7: Although the hypothesis stated in this sentence is rather reasonable, it is still requested that the authors add some kind of hedging work, such as "apparently", "it is suggested that" or the like As suggested hedging on the sources of particulate matter was added

Page 13059, lines 20-23: It is suggested that since CO32- and NO3- lines detected in the FTIR spectrum were resistant to water soaking of sample filters, Ca(NO3)2 and CaSO4 were produced by a reaction of CaCO3 with H2SO4 and HNO3. Firstly, is a conclusion concerning the sulfate salt is to be drawn, then the observation of water insoluble sulfate FTIR line should be added before the conclusion and not after it. Second, this si also not a straightforward conclusion, and the authors are requested to better explain how they arrived at it, and again hedge it (with words such as perhaps, apparently, etc.) to let the reader know it is a suggestion and not a fact The ATR-FTIR data was explained in more details. Please refer to the paragraph in question

3. Page 13056, line6: What kind of filters were used (material, pore size, manufacturer). Are there any sampling artifacts associated with these filters, especially over 24-h sampling periods? Details on filter specifications were added: The filters (TefSep, Teflon, Laminated 0.22 and 0.45 μm, 47mm), purchased from Osmonics61650;, were desiccated a "sampling artifact" paragraph has been added to the manuscript

4. Page 13057, line 1: who is the HPLC manufacturer? HPLC-AllTech and the para-

graph was corrected to read: 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, 150mm Œ 4.6mm) and a cationic column (Universal cation, 100mm Œ 4.6mm), a self-regenerating suppressor model DS-PLUSő and a conductivity detector model 650.

5. Page 13057, lines 7-8: was the relative standard deviation determined for standards or samples? Was it 0.71 (=71It is 71

6. page 13058, line 5: if all the calcium salts later discussed (nitrate, carbonate and sulfate) are water insoluble, they must be subtracted from the water soluble ion count, which means the water soluble species will be less than 44The authors agree with the referee's suggestion and since the cationic and anionic measurements were done on two different filters, we opted not to report a percentage ionic composition of coarse and fine particles. This also is in agreement of our findings of the presence of water insoluble salts.

7. page 13059, lines 14-20: It is indeed important to compare one's results to other values measured in the same area. However, at least the calcium particulate concentration value cites for Israel is not a good or relevant example, since in this particular work, Levine et al. reported concentration over Mount Meiron, as site distant from the coast, under cloudy to rainy conditions in the winter, in a time and location where one can expect minimal concentrations of coarse particulate calcium. In works more pertinent to this one, Falkovich et al. (2004) report coarse calcium concentrations as high as 11.75 μg/m3 during spring dust storms, and Graham et al. (2004) report up to 4 μg/m3 particulate calcium concentrations in winter, both in Tel-Aviv, a highly polluted urban maritime area, much resembling Beirut. It is therefore requested that the authors be more investigative in the regional comparison they perform, perhaps add some more values, and in any case be more careful about the pertinence of the results cited to the present case. Corrected and amended as suggested

Technical comments Abstract, line 1, pg. 13056, line 2: please replace “matters” by “matter” Replaced

Pg. 13056, line 5: please replace “were” by “was” Replaced

Pg. 13057, line 20: Please define BH BH was defined in the experimental section

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 84ś27, 53ś20 and 31ś9 μg 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 increase by 170

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. Cl- + NH4+ 8594; NH3(g) + HCl(g) (R1) NO3-+ NH4+ 8594; NH3(g) + HNO3(g) (R2) Cl-+ H+ 8594; HCl(g) (R3) NO3-+ H+ 8594; HNO3(g) (R4) H+ + NH3(g) 8594; NH4+ (R5) Cl- + HNO3(g) 8594; NO3- + HCl(g) (R6) During sampling, reactions (R1)-(R6) may take place leading to sampling artifacts (Pathak, et al., 2004). Sampling artifacts in sulfate, nitrate, chloride and ammonium concentrations have been shown to relate with the ambient particulate concentration ratio of NH4+/SO42-. Being less than 1.5, the NH4+/SO42- ratio indicated an ammonium poor ambient atmosphere, and 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 SO2 absorption by the collected Teflon filters are considered negligible for both the coarse and fine modes, especially that the ambient concentration of SO2 is low (A six-monthly average of 25μg/m3) (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 HNO3 and HCl evaporation, respectively, is not usually neglected in the ammonium poor media and are assumed to be 55CaCO3 + 2HNO3 8594; Ca(NO3)2 + H2O + CO2 (R7) NaCl(aq) + HNO3(aq) 8594; NaNO3(aq, s)+ HCl(g) (R8) 2NaCl(aq) + H2SO4(aq) 8594; Na2SO4 + 2HCl(g) (R9) These percentages were not considered in this study due to: i) the reactions of CaCO3 with HNO3 (R7), which will be shown to predominate over reaction of NaCl with HNO3 (R8) and H2SO4 (R9) leading to the evaporation of HCl to the gas phase, and ii) the relatively higher sodium and calcium concentrations in particles leading to a higher nitrogen flux. 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 HNO3 was considered.

3.3. Ion composition and speciation of PM10-2.5 and PM2.5 Figure 3 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+ and Ca2+ ions and the water soluble anions included Cl-, SO42-and NO3- (Figure 3A). The fine particles were formed of water soluble NH4+, Ca2+ and Na+ cations and SO42- as the main predominant anion (Figure 3B). In both particles low amounts of K+ and Mg2+ were detected. The concentration ratio of ammonium to sulfate (NH4+/SO42-) 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 (Figure 3A), 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+ exhibited lower concentrations with the lowest value being measured on February 02, 2004. The variation in the Na+ concentration was directly dependent on the wind direction and rain since Na+ originates mainly from sea-salt aerosols and its main sink is wet deposition. The air mass trajectory HYSPLIT model for the sampling dates on February 28, March 29, 2004 and January 8, 2005 showed that wind originated over dry lands, hence, the low Na+ concentration. Potassium, magnesium 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+ and this constituted only a small percentage of the total concentration of chloride in the coarse particles. The high Cl- concentration indicated that limited losses of chloride occurred via 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 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 40CaCO3 + H2SO4 8594; CaSO4 + H2O + CO2 (R10) The reactions of NaCl and CaCO3 with HNO3 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 CaCO3 with HNO3 leading to the formation of Ca(NO3)2 is expected to predominate. 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 10The abundance of CaCO3 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 Figure 4A, absorption bands at 873 and 712 cm-1 that are characteristic of carbonates and nitrates, respectively, were identified (Blanco and McIntyre, 1972; Grassian, 2002). Carbonate (CO32-) ions are also distinguished by a peak at 1413 cm-1 (Al-Abadleh and Grassian, 2000) on surfaces; and/or 1390 cm-1 in aqueous media (Villalobos, et al., 2001). (Arihara, et al., 2001) assigned peaks at 1401 and 1480 to vibrational modes of dissolved carbonate ions and adsorbed species, re-

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spectively. In Figure 4A, a broad peak between 1300 and 1560 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 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 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 (SiO44-) at 1033 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 (SiO2) and kaolinite to be the major species in coarse atmospheric aerosol samples. Quartz absorbs most strongly around 1090 and 730 cm-1, (Martinez, et al., 1998) whereas kaolinite absorbs around 1010 cm-1 (Allen, et al., 1994). The peak in Figure 4A which was observed at 1010 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 hours, 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 Ca2+ were detected (Figure 3B) throughout the year. 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 H2SO4 + 2NH3 8594; (NH4)2SO4 (R11) The r2 values of the different water soluble ions (Table 2) in the fine particles, showed a strong correlation (r2 > 0.97) between NH4+ and SO42- via (R11) indicating that the predominant salt present in the fine particles is (NH4)2SO4. Also, the high correlation (r2 = 0.65) identified between Cl- and Na+ suggested the presence of NaCl. The identification of (NH4)2SO4 was supported by the ATR spectrum shown in Figure 4B where peaks at 1091 and 1414 cm-1 were assigned to SO42- and NH4+, respectively. These peaks were completely dissolved after soaking the PM2.5 filter in water for 24 hours.

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In comparison to the coarse filter, the relative increase of the assigned SO42- peak and the complete water dissolution of the two absorption bands assigned to crystals CO32- and NO3-, at 873 and 712 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 anions (Cl-, NO3-, and SO42-) in the fine particles was found to be more than 50

3.3.3. Total PM10 Particles The PM10 ionic nitrate concentrations (1.92 μg m-3) are lower than the levels reported in Finokalia, Greece (2.75 μg m-3) (Bardouki, et al., 2003), but higher than the concentration listed for Antalya, Turkey (1.18 μg m-3) (Gullu, et al., 2000) and coastal Israel (1.14 μg.m3) (Ganor, et al., 2000). Even though the level of SO42- (5.98 μg m-3) was comparable to levels reported in Greece (6.87 μg m-3) and Turkey (5.54 μg m-3), but it was lower by 151

3.4 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 HNO3 via (R12) (Vrekoussis, et al., 2004). NO2 + OH 8594; HNO3 (g) (R12) 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 SO2 becomes active under summer conditions (high solar radiation and temperatures) to produce SO42- (Luria, et al., 1996; Mihalopoulos, et al., 1997; Danalatos and Glavas, 1999). Relatively lower values of sea-salt components (Cl-, Na+, and Mg2+) correlated well with southerly wind vectors as deduced from the meteorological conditions listed in Table 1 and the air mass trajectory HYSPLIT models. Soil and mineral dust factors are highly linked to the concentration of Ca2+ in the coarse particles. Ammonium, displayed a maximum

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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).

3.5. Source of PM particles The coarse particles being highly loaded with Cl- with smaller quantities of SO42- and NO3- ions were most representatives of waste mass burning in addition to sea-salt particles. Also, CaCO3 originated from crustal rocks, whereas silicate and kaolinite ions identified by ATR are typical of continental dust coming from Africa. Sulfate and nitrate ions are the result of secondary reactions of crustal dust particles with HNO3 and H2SO4. Sulfate is the result of high levels of SO2 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 NO2 seemed to be the precursor of HNO3. On another hand, emission from local mass burning activities was supported by the good correlation that was determined between K+ and SO42- and K+ and Cl- (r2 0.6) as a result of the rapid substitution of KCl by K2SO4 during smoke formation (Liu, et al., 2000).

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