Atmos. Chem. Phys. Discuss., 5, S5667–S5678, 2005
www.atmos-chem-phys.org/acpd/5/S5667/
European Geosciences Union

Atmospheric Chemistry and Physics 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

H. Kouyoumdjian and N. A. Saliba

Received and published: 27 February 2006

1. My main concern is the application of a 24 hours filter sampling method for the determination of the chemical aerosol composition. Although these methods have been applied for a long time in atmospheric sampling, scientists know for more than 25 years that gaseous NH3 and HNO3 form the semi-volatile aerosol component NH4NO3 via reversible phase equilibria that are strongly dependent on temperature and relative humidity (RH) [e.g. Stelson et al., 1979; Spicer et al., 1979]. As a result, the determination of their ambient concentration subject to measurement artifacts [e.g., Slanina

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

et al. 2001]. Although new artifact-free on line methods have been developed, it is obvious that they cannot be employed everywhere on the globe. There are also more reliable off-line methods, such as denuder-filter packs which may be used to measure the inorganic aerosol composition. In any case, I expect from the authors a more thorough evaluation of the data in terms of sampling artifacts. Which influence do relative humidity and temperature have on the condensation of NH3 and HNO3 or evaporation of NH4NO3 from the filter substrates during a period of 24 hours? What is the estimated error of the measured concentrations? A “Sampling artifacts” paragraph has been added in the manuscript. The paragraph accounted for the variation in relative humidity and temperature and consequently the condensation and evaporation of NH3, HNO3 and NH4NO3. Please refer to the Results and Discussion section shown below.

2. Although the data set is new, the interpretation of the results is poor. The authors refer to several sea-salt displacement reactions and the transport of carbonate aerosols during dust storms coming from Africa. For this purpose, air mass trajectories should be calculated (HYSPLIT model). Such results can be used to elucidate whether aerosols originate from a nearby urban location, a Mediterranean region or dust storms. There is no evaluation of any meteorological data that proof the presence of different wind directions/air mass sources, temperatures and relative humidities. Therefore, the interpretation is rather speculative than based on scientifically sound results. The HYSPLIT model along with the meteorological data that was measured during sampling have been added to the discussion of the results as suggested by the referee. Please refer to “Results and Discussions”shown below for a detailed explanation.

3. To my knowledge, the weighting procedure of filter substrates should be carried out under controlled laboratory conditions (temperature and relative humidity). This is crucial for a correct determination of the total PM collected on the substrates. Please describe this procedure in detail. The conditions of the weighing procedure and the weighing room have been added to the experimental section. The paragraph now reads: The filters were desiccated for 24 hours at constant temperature (21.6 žC) and

relative humidity (9.6

4. Besides an interpretation of results using meteorological data and trajectories, I would like to encourage the authors to perform a detailed analysis of the ionic charge balance [see e.g. Trebs et al. 2005]. Additionally, it should be stated in the text how much of the total PM was chemically specified for coarse and fine mode aerosols. A hint could be given which chemical compounds are expected to represent the missing aerosol mass. The ionic charge balance was applied to the fine particles and the following paragraph was added to the ms: The sum of the anions (Cl-, NO3-, and SO42-) in the fine particles was found to be more than 50

5. The title of the paper: “Ion concentrations of PM10-2.5 and PM2.5 aerosols over the Eastern Mediterranean region: seasonal variation and source identification” is definitely overdimensioned. Aerosols were collected at 3m height at a busy road in Beirut, which is not a measure for the entire eastern Mediterranean region (as the authors also stated themselves in the manuscript). The title needs to be changed accordingly. The title of the paper is changed to reflect the chemistry observed in the area and it reads: 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

Detailed comments: 1. Page 13055, line 2+3: please make reference to some studies of the MINOS (Mediterranean intensive oxidant study) campaign Reference was added

2. page 13055, line3+4: :Ěfewer studies restricted to Greece, Turkey and Israel in addition to some reports from the Arab countries (North Africa and West Asia) are availableĚ” Please state which studies (give reference here) References were added as suggested “Ě. fewer studies restricted to Greece, Turkey and Israel in addition to some reports from the Arab countries (North Africa and West Asia) (Borai and Soliman, 2001; Momani K.A. 2000; Jaradat, 2004) are available in the eastern Mediterranean region.”

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

3. page 13056, sampling: It would be beneficial to have a map of the location of the sampling site which also shows that location of the Mediterranean seas towards the site A map of the site and the Mediterranean sea has been added

4. page 13056, line 9: “Ě total flow rate of 11 L/minĚ” please state for which temperature and Pressure. Temperature, Pressure and RH was added in Table 1.

5. page 13056, line 11-18: please move this paragraph upwards. Before describing the sampling technique the site should be described Corrected as suggested

6. page 13056, line 23+24L “One filter per month” was analyzed? What happened to the other samples that were collected every six days. The other samples were used for PIXE, XRD and ATR-FTIR analysis; data that is still under analysis

7. page 13057, line 8: How was the detection limit determined? The standard would be three times the baseline noise (361555;). The detection limit of each ion will vary from one ion to the second and so we prefer to report the sensitivity of the detector in 61549;S. In all our measurements, we used sensitivity levels (1 and 561549;S) that are a minimum of 100 times higher than the minimum sensitivity of the detector.

8. page 13057, FTIR-ATR analysis: It is not clear how these analysis were performed, please give more details. How exactly were the particles subjected to a light source? Please give a reference of the method if available. 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. The paragraph has been changed to read: Nicolet AVATR Multibounce HATR 360 FTIR spectrometer equipped with a DTGS-detector and ZnSe horizontal crystals (4561616; 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 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.

9. page 13058, line 13: high nitrate values in the coarse aerosol fraction may be a result of absorption of HNO_3 by filter substrates please comment on that. A detailed explanation of the high nitrate values in the coarse mode has been added to the Results and Discussion section of the manuscript.

10. page 13058, line 20-25: Please give reaction R1-R4 before discussing the results The reaction order in the manuscript has been changed but reactions are now given before discussing the results as suggested.

11. page 13059, line 7: high nitrate in summer can also be a result of typically higher HNO_3 concentrations during the summer, which may be retained by the filter material. Could $Ca(NO_3)_2$ be formed on the filter material due to topological reactions? Discussion of the matter was included in the PM10-2.5 Coarse particles

12. page 13059, line 19-25: Why are there large absorption band of aerosol ammonium in the coarse aerosol fraction? What are the origins and what is the corresponding anion? Why does the ammonium band remain after soaking the filter in water? This paragraph is misleading, please reformulate. The large absorption band of aerosol ammonium is due to many overlapping band in the region mainly organic nitrates. Please refer to the manuscript as I have added a detailed explanation of all possible overlapping bands.

13. page 13060, line 9: Please move R5 upwards before discussing it. H_2SO_4 is only fully neutralized if enough NH_3 is available, otherwise HSO_4^- is formed. Please comment on that. Acidic filter material may lead to uptake of NH_3 which might be misinterpreted to be aerosol $(NH_4)_2SO_4$. A discussion about that should be added here. 14. page 13060, line 10-15: same question as before: why are there large absorption bands of aerosol ammonium in the coarse aerosol fraction? 15. page 13061, line 13-15: It would be worthwhile to see the effect of temperature and general meteorological conditions on the concentrations of aerosol ammonium Points 13, 14

and 15 were addressed in the PM2.5 Fine particles paragraph

16. page 13062, line 2+3: NO from vehicles is certainly the main precursor for aerosol nitrate. This could be described more in detail, i.e. the oxidation to NO2 and HNO3 and the corresponding timescales (i.e., fresh or aged air masses) More discussion about the subject was added

17. page 13062, line 9: “The variations of meteorological and climatic conditions, seasonal pollution episodes, and local anthropogenic factors from one region to another affect the PM levels. “ Exactly this detailed interpretation is missing in the paper More discussion about the subject was added in the Source of particulate matter paragraph

18. page 13062, line 10-15: That statement is self-evident and does not need to be explicitly mentioned here The sentence has been omitted as suggested

Technical Corrections Page 13056, line 17: replace “a” by “one” Replaced Page 13058, line 15-20: delete some references Deleted Page 13059, line 25: “dissolution of the peaks” is probably not the right expression Changed The font size of all Tables should be increased Corrected Figure 2 should be in color Changed Figure 3: There should be a scale added to the y-axis (intensity, even if it is just arbitrary units. Font size and figure size must be increased substantially Figure 3 was changed accordingly Figure 4: Please use different colors for the lines and increase the font size Figure 4 was changed accordingly

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

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

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, respectively. 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. 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

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

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 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).

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 13053, 2005.