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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

Anonymous Referee #2

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1. General comments:

This paper presents the inorganic composition of aerosols collected in Beirut (Lebanon) at a busy street with heavy traffic using a Dichotomous filter sampler and subsequent analysis. The paper is written in a simple, clear style and the gathered data set is novel. The authors compare their results to other studies from the eastern Mediterranean and

the data are definitely valuable for use in modeling studies. Although, the topic is relevant for publication in ACP, I have serious doubts about the scientific quality of that manuscript. The authors must consider the following issues before the paper can meet the standards of ACP:

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 NH_3 and HNO_3 form the semi-volatile aerosol component NH_4NO_3 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 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 NH_3 and HNO_3 or evaporation of NH_4NO_3 from the filter substrates during a period of 24 hours? What is the estimated error of the measured concentrations?

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 (HYSLPIT 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, tempera-

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tures and relative humidities. Therefore, the interpretation is rather speculative than based on scientifically sound results.

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.

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.

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 3 m 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.

2. Detailed comments:

Page 13054, line 4 + 5: "...analysis of the collected PM Teflon filters showed..." the Teflon filters were not analyzed, but the particles collected on the substrates, please change this accordingly.

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

Page 13055, line 3 + 4: "...fewer studies restricted to Greece, Turkey and Israel in addition to some reports from the Arab countries (North Africa and West Asia) are available..." Please state which studies (give references here).

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.

Page 13056, line 9: "...total flow rate of 11 L/min..." please state for which temperature and pressure (STP?)

Page 13056, line 11 - 18: Please move this paragraph upwards. Before describing the sampling technique the site should be described.

Page 13056, line 23 + 24: "One filter per month" was analyzed? What happened to the other samples that were collected every six days?

Page 13057, line 8: How was the detection limit determined? The standard would be three times the baseline noise (3σ).

Page 13057, FTIR-ATR analysis: It is not clear how these analyses 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.

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.

Page 13058, line 20-25: Please give reaction R1-R4 before discussing the results.

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?

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Interactive Comment

Page 13059, line 19 - 25: Why are there large absorption bands 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.

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.

Page 13060, line 10-15: same question as before: Why are there large absorption bands of aerosol ammonium in the coarse aerosol fraction?

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.

Page 13061, 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 NO_2 and HNO_3 and the corresponding timescales (i.e., fresh or aged air masses).

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.

Page 13062, line 10-15: That statement is self-evident and does not need to be explicitly mentioned here.

3. Technical corrections:

Page 13056, line 17: replace "a" by "one"

Page 13058, line 9: replace "both particles" by "both fractions"

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Page 13058, line 15-20: Please delete some of the references.

Page 13059, line 25: "...dissolution of the peaks..." is probably not the right expression, maybe better use disappearance.

The font size of all tables should be increased.

Table 1: why is "month"there?

Figure 2 should be in color.

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 4: Please use different colors for the lines and increase the font size.

4. References:

Slanina, J., H.M. ten Brink, R.P. Otjes, A. Even, P. Jongejan, A. Khlystov, A. Waijers-Ijpelaan, and M. Hu (2001), The continuous analysis of nitrate and ammonium in aerosols by the steam jet aerosol collector (SJAC): extension and validation of the methodology, Atmospheric Environment, 35 (13), 2319-2330.

Spicer, C.W., and P.M. Schumacher (1979), Particulate Nitrate - Laboratory and Field Studies of Major Sampling Interferences, Atmospheric Environment, 13 (4), 543-552.

Stelson, A.W., S.K. Friedlander, and J.H. Seinfeld (1979), Note on the Equilibrium Relationship between Ammonia and Nitric-Acid and Particulate Ammonium-Nitrate, Atmospheric Environment, 13 (3), 369-371.

Trebs, I., S. Metzger, F.X. Meixner, G. Helas, A. Hoffer, Y. Rudich, A. Falkovich, M.A.L. Moura, R.J. Da Silva, P. Artaxo, J. Slanina, and M.O. Andreae (2005), The NH_4^+-NO_3^--Cl^--SO_4^{2-}-H_2O system and its gas phase precursors at a pasture site in the

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Amazon Basin: How relevant are mineral cations and soluble organic acids?, Journal of Geophysical Research-Atmospheres, 110 (D07303), doi:10.1029/2004JD005478.

National Oceanic and Atmospheric Administration (NOAA). (2005) Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT model) back trajectories, available at http://www.arl.noaa.gov/ready/hysplit4.html

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