Atmos. Chem. Phys. Discuss., 5, S4931–S4935, 2005
www.atmos-chem-phys.org/acpd/5/S4931/
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

Anonymous Referee #3

Received and published: 9 January 2006

General Comments:

The paper presents concentration changes during one year of particulate matter and chemical species for a heavily polluted area in Beirut, Lebanon. The data itself and the methods used to obtain it are innovative, interesting and of significance, especially for such an under characterized area. However, the discussion of the results is not as rigorous or well explained as could be expected of an ACP paper. The reviewer's two main concerns are the claim (appearing even in the title) of source identification,

which is not fulfilled in the article, other then in way of mentioning possible sources without explanation nor hedging; and the somewhat careless and lacking treatment of the otherwise intriguing discussion of the transformation of CaCO3 to Ca(NO3)2 and CaSO4. The reviewer would therefore recommend to accept this paper only after the presentation of methods, results and discussion is revised in such a way as to make it more rigorous and well explained, especially regarding the above concerns, and more specifically according to the following specific comments.

Specific comments:

1. Source identification: As mentioned above, the title of the article speaks of PM source identification. However, this promise is not fulfilled. Rather, in the 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 hedging phrases, such as “possibly”, “perhaps” and so on to the text.

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 very 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 then rigorous fashion. And more specifically:

Pg. 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 they react. The authors are therefore

ACPD

5, S4931–S4935, 2005

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.

Pg. 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 reactive absorption from the gas-phase, they should state it clearly, and again with proper hedging, since this is a hypothesis and not a fact. Furthermore, to make their point, the authors use the absolute nitrate concentration values, but these values are of little significance. What the authors should really refer to is nitrate/PM values, since high absolute nitrate values can also indicate high PM concentrations, unless normalized to PM values.

Pg. 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 word, such as “apparently”, “it is suggested that” or the like.

Pg. 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 is 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 readers know it is a suggestion and not a fact.

3. Pg. 13056, line 6: What kind of filters were used (material, pore size, manufacturer). Are there any sampling artifacts associated with these filters, especially over

ACPD

5, S4931–S4935, 2005

24h sampling periods?

4. Pg. 13057, line 1: who is the HPLC manufacturer?

5. Pg. 13057, lines 7-8: was the relative standard deviation determined for standards or samples? Was it 0.71 (=71%) or rather 0.71% ?

6. Pg. 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 then 44% and 33% of the coarse and fine PM respectively. Please make the required change.

7. Pg. 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 report concentration over Mount Meiron, a 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 ug/m3 during spring dust storms, and Graham et al. (2004) report up to 4 ug/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.

Technical comments:

Abstract, line 1, Pg. 13056, line 2: please replace "matters" by "matter".

Pg. 13056, line 5: please replace "were" by "was"

Pg. 13057, line 20: Please define BH.

ACPD

5, S4931–S4935, 2005

Pg. 13058, line 21: Please define nss.

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