Atmos. Chem. Phys. Discuss., 6, S6730–S6734, 2007
www.atmos-chem-phys-discuss.net/6/S6730/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical characterization of the inorganic fraction of aerosols and mechanisms of the neutralization of atmospheric acidity in Athens, Greece" *by* E. T. Karageorgos et al.

Anonymous Referee #1

Received and published: 9 February 2007

This manuscript presents a series of results for the chemical composition of coarse (PM10-PM2.5) and fine (PM2.5) aerosol fractions at two sites in Athens Greece. Such results can be very useful for the scientific community and the material provided by this work could certainly contribute to this end. However, there are several problems in this manuscript with the measurements and interpretation of the results. The authors could use the comments given below, reconsider the way they present their results and use parts of this material to resubmit the paper. This manuscript in my opinion cannot contribute towards elucidating the "mechanisms of the neutralization of atmo-

spheric acidity" General Comments Experimental There is a cloud of uncertainty on the sampling methodology employed by the authors, which in turn casts a doubt on their results. The Dichotomous Stack Filter Unit (DSFU) is in general an acceptable sampler and two-fraction aerosol classifier. However, for the device used here the description is given in a (not readily available) project report (Luhana et al., 2001). There is no description of the way the flow rate or sampled volume was monitored, recorded, or calibrated against an independent method. The precision of the flow readings between the two devices may well be high, with their accuracy being not necessarily high. The authors go into excessive detail about problems they had with overloaded filters where it is certain that the samplers did not function within specifications, while they do not state whether they remove these samples from their dataset. The analytical part is given very well. Results and Discussion The authors devote a large part of the manuscript discussing the PM10 concentration levels with respect to the E.U. limit guidelines. This is all very useful but not improving our knowledge towards the chemical characterization of the inorganic fraction of aerosols and mechanisms of the neutralization of atmospheric acidity The investigation of the difference in concentrations measured at 1.5, 5 and 25 m height is a useful exercise. However, the authors use for the height of 5m data from two different techniques. Gravimetric and beta attenuation PM10 measurements are found to display a ratio between 0.8 and 1.6 due to a number of reasons which are not well quantified (R. Gehrig, et al., 2005). Finally, the authors despite the fact that they seem to have a good knowledge of atmospheric chemistry, attempt to derive conclusions for the mechanisms of the neutralization of atmospheric acidity from data, which are clearly not adequate to provide such information. The shortcomings are several. In order to derive such information in a robust way, measurements of the inorganic aerosol anions and cations and the gaseous species in equilibrium are required by means of a denuder/filter pack system (Danalatos, D. and Glavas, 1999) Allegrini et al., 1994 or at least multiple filter pack sampler (Harrison et al., 1989) One can attempt to account for all possible artefacts involved and reach some conclusions for particular cases when the atmospheric conditions (RH, T) are

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also known. An example of this sort of approach can be seen in the work of H. Kouyoumdjian and N. A. Saliba, (2006) The authors attempt to derive conclusions only from mean concentration values for the various anions and cations with relative standard deviation between 50 and 100% . In my opinion the concentrations observed are to a lesser or greater extent modified by reactions of trace gases on the collected aerosol.

Detailed comments

1) The authors mention the use of OPCs and DMPS during their campaign but no data from these measurements are presented. These data have to be added or the description removed. 2) Introduction, line 25 the authors report data about the vehicle fleet in Athens, a reference should be added. Page 12392 line 5 there are a number of studies that report inorganic and/or organic species in Athens aerosol that could be mentioned

3) Sampling: the results were obtained from two different periods: 10 days in August 2003 and 10 days in March 2004. What is the collection efficiency of membrane filters with 12μm pore size for coarse particles? The flow rate of the DSFU samplers or the total sampled air is not reported. Was the flow constant during the 12h or 24h sampling?

4) Elemental analysis: ISO 17025 standard refers to the general requirements for the competence of calibration and testing laboratories. If the laboratory is accredited for the specific analytical method (determination of elements in ambient particles by PIXE) it should be mentioned. 5) Results and discussion: page 12398, line 25: the authors state that Cu has demonstrated an increase compared to the study of Scheff and Valiozis, (1990) but from the values given in Table 5b this could not be concluded. In August 2003 and March 2004 (1.5m above ground) Cu was found equal to 113 and 19.9 ng/m3 respectively, while during 1987 (27 m above ground) was 51 ng/m3. In the same paragraph S and Cu are attributed to traffic. A reference should support this conclusion. Furthermore fossil fuel combustion is known to be an important source of

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particulate sulphur but this is not mentioned as an explanation for S high values. Page 12399, line 10: No increase is observed for Cr according to the data shown in Table 5a. Page 12400, line 3-10: The conclusion that PM10 concentrations are significantly lower at 5m above ground can not be established due to the small sample size (10 daily samples) and the different measuring methods (DSFU and BAPA). Page 12401, line 5-20: How does the agreement with previous PM10 measurements at 25 m above ground support the fact that the concentrations in Athens are higher in the breathing zone? Page 12403 line 24: Since Ca is predominantly found in coarse particles has a unimodal distribution. Page 12406: all these details should be omitted. The authors could give approximately the percent of the analysed inorganic versus total particulate mass Page 12407, line 10-20: the whole paragraph is in complete disagreement with the next page: The fact that NH4 ion is found in fine particles could not lead to the conclusion that ammonia concentrations are low and insufficient to neutralize atmospheric acidity. In the next page Ca and NH4 are indicated as important neutralizing agents. The Cl/Na ratio from tables 3 and 4 does not agree with the value given it is below 1 which mean that chloride depletion occurs In fine particles if Line 21: The formation of NH4NO3 is rapid compared to the formation of (NH4)2SO4 Page 12408, line 24: the possible influence of the construction activity to Ca concentrations is not highlighted. Page 12408-9, line 26: The authors had previously stated that PM10 concentrations in Athina St. (at the breathing zone) were significantly higher than those in AEDA (25m height) as a result of the higher traffic influence at 1.5m above ground. However in this section it is stated that traffic related elements have higher concentrations in AEDA because traffic has higher influence in this site.

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