**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Night-time enhanced atmospheric ion concentrations in the marine boundary layer" *by* N. Kalivitis et al.

N. Kalivitis et al.

mihalo@chemistry.uoc.gr

Received and published: 31 October 2011

The authors would like to thank the reviewers for their constructive comments and helpful suggestions. All of the reviewer's comments have been taken into account and we respond point by point to all of them below.

Abstract Line 6 ": : :vary strongly with: : :" or ": : :depend strongly on: : :"

The sentence was corrected to "vary with".

Line 7 The sentence about new particle formation does not fit with the rest of the abstract about ions. Delete or expand.

The sentence about new particle formation has been expanded in the introduction, so

that it links charged particles' formation to total particle formation.

Line 9 What does enhanced mean? Above average? Greater than one standard deviation above average? This should be explained quantitatively here or in the body of the manuscript. A partial explanation is given in section 3.3, first sentence. Please expand this and present earlier in manuscript.

It is now explained in more detail in the text that an event was defined as an increase of ion concentration in the size range 1.25-1.66 nm over 50cm-3 and over one standard deviation from the day's median concentration, to provide that preexisting concentrations remained low. We are keeping the explanation of an event in section 3.3, since that is the section were enhanced ion concentrations observations are described and except of the introduction there is no earlier reference in the text.

Introduction Define ions to agree with abstract, charged molecular clusters or particles from 0.8 to 42 nm. Also it would be good to define new particle formation events in similar, practical, observable terms, e.g., an increase in particle concentration by some factor above the average within a specified time limit in a given particle size range.

The ion definition in the introduction has now been changed so that it fits to the abstract, clusters and particles in the size range 0.8 – 42 nm. In order to identify a new particle formation event, the event should have been apparent in SMPS data and fulfill the criteria given by Birmili et al., (2003) so that plateau concentration of N[8;20] was greater than 1000 cm−3 (criterion adjusted to detection limit of the SMPS we used), time for N[8;20] to increase was less than 4 hours , time for N[8;20] to decline was less than 7 hours and N[8;20]/Ntot was greater than 0.15. In those cases that no concurrent SMPS data were available, criteria by Hirsikko at al., 2007 were used so that the formation event continued for several hours, the growth of new particles was evident in the size distribution data and the particles grew from cluster sizes up to the upper detection limit of AIS (42nm).

Page 11811 Line 5. : : : atmospheric ions concentration: : :. Is ions possessive?

Then ..ion: : : Sentence reads better as: : : : study of atmospheric ion concentration is especially important for calculating cluster size.

We have changed to "atmospheric ion concentration". The sentence has been rephrased.

Line 6. Sentence is not clear. If the new particle formation events were suppressed, did they not occur or were they of lesser magnitude than expected? If they did not occur how did the ion spectrometer detect them? If they were of lesser magnitude than expected, what was the basis for the expectation in terms of measured actinic flux, gas and particle phase composition?

The events were of less magnitude, either because of high coagulation and condensation sinks or because of limited availability of condensable species. Therefore, the newly formed particles never grew to diameters larger than the detection limit of DMPS.

Line 7. The stated detection limit should be expressed as a concentration and diameter. I don't understand the value of 83nm.

The smaller particle diameters that the DMPS could detect was 3 nm and not 83 nm.

Page 11813 Line 1. Give the number counting threshold and accuracy as well as the size range and time resolution.

The instrument's number counting threshold is below 1 cm-3. The size range of the measurements was 0.8-42 nm. The uncertainty of the AIS data is ±10% for negative and positive ion concentrations and ±0.2 nm in size based on the laboratory calibrations (Asmi et al. 2009). Time resolution of measurements was 5 min. These instrument operation details are now added in the text.

Line 6. Quantify the "good" performance in this summary.

The AIS is calibrated during the calibration workshop in Helsinki at 2008 prior (Asmi et al. ACP 2009) and after the EUCAARI field measurements (Gagné et al. AMT

C11188

2011). Accoording to Asmi et al. (ACP 2009), the median of the average negative ion concentration ratios for all ion spectrometers obtained from different calibration set-ups were 1.5±0.2, 1.1±0.1, and 1.0±0.1, for standards (1-2.5 nm), high-resolution DMA (1-6 nm), and HAUKE DMA (4-40 nm), respectively. Same numbers for positive ion concentration ratios were 0.9±0.2, 1.0±0.1, and 1.0±0.2.

Line 24. Are particle and ion losses in the inlet and tubing to the AIS and SMPS significant? Quantify them as appropriate.

The diffusional losses inside the inlet tubing even for the smallest ions are minor. The diameter of the inlet tube is 35 mm and the sample flow rate is 60 lpm. The losses in the AIS sampling lines have been taken into account in the data inversion. The above have been added in the manuscript.

Page 11814 Line 15. Given the large standard deviations, is the + vs. − ion difference significant? Are the secondary maxima in − ions significant? I assume the value is the std. deviation of the monthly mean. What are the uncertainties in the AIS data?

Yes, the concentration difference between the polarities is significant since most of the ions are in cluster ion size range (1-2 nm) and the both polarities detect concentrations with similar accuracy (with ratio ~1.0±0.2). Yes, the second maximum in negative ions in Fig. 1 is significant especially during June when the concentration difference between the average negative and positive ions is significant (negative ion 584.56 cm-3, positive ion 235.92 cm-3). The uncertainty of the AIS data is ±10% for negative and positive ion concentrations and ±0.2 nm in size based on the laboratory calibrations (Asmi et al. 2009).

Line 25. The four plots in figure 3 do not present the data adequately. Most of the data is in the region where the dots are heavily overplotted and the anti-correlations are not at all clear to me. The line of maximum occurrence could, in fact, be constant with windspeed within the black region. All that can be discerned is the domain subsets where ions were not observed or those where ions were observed infrequently.

C11189

The major data set is a black hole with no obvious information. I suggest presenting this data as a contour plot of the two dimensional probability distribution of number of occurrences vs. wind velocity vs. ion concentration. Then you will be able to see a possible relation within the domain of the majority of the data; it might be illuminating. What are the correlation coefficients and R values?

All the corresponding plots are now presented using probability distributions and the R values are displayed as well. Representation of the different data sets as contour plots are enlightening and give new information. The correlation coefficients and R values are displayed in Table 1. In general, weak correlations are found for all set of data. However, when looking in the mean diurnal variations of each parameter, better correlations can be achieved, especially with ion concentrations with BC.

Page 11815 Line 2. Considering the Earth's surface to be the source of Radon, it's both the advection wind speed and vertical mixing and boundary layer depth that affect its concentration in a simple box model. I note that this is presented more clearly on page 11818. Paragraph 2. The primary sink of ions should be to the Aitken and accumulation mode effective surface area. Thus, it would make sense to first compare ion concentration to surface area derived from the SMPS data. Secondarily, BC may have an effect due to its chemistry and physical, fractal dimensionality, if recently emitted.

All discussion related to Radon was removed from the manuscript. We have calculated condensation and coagulation sinks (CS and CoagS respectively) in order to examine the effect of preexisting aerosols on cluster ion concentrations. Diurnal patterns of both sinks are quite similar to daily variability of atmospheric ions concentrations and since no additional data of radon exist to support our hypothesis we have chosen to examine our observations in terms of the fate of ions and not in terms of sources. Indeed, ion concentrations especially for cluster sizes have been found to be anti-correlated to CS and CoagS exponentially.

My comments regarding figure 3 apply to figure 4 as well.

For Figure 4 contour plots have been created.

Page 11816 Figure 5 and related discussion. It would be useful for the SMPS to AIS comparison if the diameter scales were the same. Why are the number integrals of the AIS (sum of + and − ions and particles less than that of the SMPS? Given the theoretical charge distribution is this reasonable?

We agree with the reviewer that the scale had to be changed. The AIS measures only atmospheric naturally charged particles. As only part of the total particles are charged, the sum on negative and positive ions measured with the AIS is smaller compared to the total particle concentration measured with the SMPS. According to other fields measurements ions seem to be overcharged compared to equilibrium charge distribution (Gagné et al. 2008 and reference therein). Page 11817 Line 8. Define phenomenal quantitatively.

For the analysis performed we did not use any quantitative criteria to evaluate growth. Since these events were quite weak and the growth was about 1 nm, just a hump over the preexisting ion pool, there was no classification according to growth.

Page 11818 Regarding figures 8 and 9, see comment about figure 3.

For Figure 8 and 9 contour plots have been created and R values are displayed.

Page 11819 Line 1. It would be very useful to quantify and plot the results of the coagulation model calculations.

The calculations for CS and CoagS have been plotted and will be included in the manuscript. The manuscript will be modified accordingly.

Line 10. What is the height of the boundary layer, daytime and nighttime, at Finokalia cf. the 1000m HYSPLIT trajectory data set?

We have computed air mass back trajectories at an altitude of 1000m because it has been shown in the past that this altitude is the most representative for Finokalia site

to represent boundary layer (Mihalopoulos et al 1997) . Due to the presence of high mountains in the region, calculation of trajectories for lower altitudes would be affected and would not be representative of the regional conditions. Additionally, earlier Lidar studies have shown that no significant variations of MBL are observed at Finokalia between day and night.

Line 13. The pie chart figure 11 does not need to be three dimensional; a simple planar chart would be adequate. Present the percentage of each sector in the plot.

The plot has been changed according to the suggestions of the reviewers.

Line 20. Do you mean local wind direction or air mass trajectory direction at the origination point or at the end of the trajectory?

The original analysis of the manuscript referred to the end of the trajectory. However, a closer look at the trajectories, taking into account and the origination point of the trajectory, showed that the actual sector that was dominant was the wide W/SW by 77%.

Line 21. Regarding figures 12, see comment about figure 3 and overplotting of dots

Figure 12 is now presented as a contour plot to avoid the overplotting of the data points.

References

Hirsikko, A., Bergman, T., Laakso, L., Dal Maso, M., Riipinen, I., Hõrrak, U., and Kulmala, M.: Identification and classification of the formation of intermediate ions measured in boreal forest, Atmospheric Chemistry and Physics, 7, 201–210, 2007.

Birmili, W., H. Berresheim, C. Plass-Dülmer, T. Elste, S. Gilge, A. Wiedensohler, and U. Uhrner: The Hohenpeissenberg aerosol formation experiment (HAFEX): a long-term study including size-resolved aerosol, H2SO4, OH, and monoterpenes measurements, Atmos. Chem. Phys., 3, 361-376, 2003

Asmi, E., M. Sipilä, H. E. Manninen, J. Vanhanen, K. Lehtipalo, S. Gagné, K. Neitola,

C11192

A. Mirme, S. Mirme, E. Tamm, J. Uin, K. Komsaare, M. Attoui, and M. Kulmala Atmos. Chem. Phys., 9, 141-154, 2009

Gagné, S., Lehtipalo, K., Manninen, H. E., Nieminen, T., Schobesberger, S., Franchin, A., Yli-Juuti, T., Boulon, J., Sonntag, A., Mirme, S., Mirme, A., Hõrrak, U., Petäjä, T., Asmi, E., and Kulmala, M.: Intercomparison of air ion spectrometers: an evaluation of results in varying conditions, Atmos. Meas. Tech., 4, 805-822, doi:10.5194/amt-4-805-2011, 2011.

Gagné, S., Laakso, L., Petäjä, T., Kerminen, V.-M. and Kulmala, M. : Analysis of one year of Ion-DMPS data from the SMEAR II station, Finland, Tellus, 60B, 318-329, 2008.

Mihalopoulos N., Stephanou E., Pilitsidis S., Kanakidou M., Bousquet P., Atmospheric aerosol composition above the Eastern Mediterranean region, Tellus, 49B, 314-326, 1997.

—————————————————

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 11809, 2011.