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Atmospheric Chemistry and Physics Discussions

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

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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.

-The authors explain the diurnal cycle of minimum ion concentrations during the day and maximum concentrations during the night by dilution through thermal mixing in the boundary layer after sunrise. If this is the case, I would expect to find decreasing ion concentrations after sunrise. Fig. 2 shows that concentrations start to decrease between 3 AM and 4 AM in the morning. Is this in fact consistent with the abovementioned explanation?

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After the suggestions of the reviewers we performed coagulation (CoagS)and condensation (CS) sinks calculations. After these calculations, the assumption about dilution is now removed and instead explanation of the observations was made based on sinks. Diurnal circle of both CS and CoagS indicate that minimum and maximum values of ion concentration follow closely the ones observed for CS and CoagS.

-What is the authors' definition of enhanced ion concentrations? For example, in the discussion of Fig. 3 (p.11814/11815), the authors use the qualitative statement of enhanced ion concentrations instead of a quantitative criterion, e.g. 1000 cm-3.

At first identification of an event was done through visual inspection of AIS measurements contour plots. We observed in total 39 nights throughout the measuring period that there was a kind of burst in the 0.8 to 2 nm diameter preexisting ion pool. After that we specified the size range of 1.25-1.66 nm as the size range in which the phenomenon is taking place. We thereafter calculated the median of the ion concentration in this size range during the whole two days in which the phenomenon occurs. If the ion concentration reached over 50cm-3 the increase of the concentration during the burst versus the median concentration during the rest of the days was greater than one standard deviation we characterized the event as an enhanced ion concentrations event.

-In Fig. 4, the authors compare air ion concentrations, ozone mixing ratios and BC mass concentrations to "explore the dependence of air ions ... on atmospheric composition". I have a hard time following the authors' discussion. They find ion concentrations to be highly anti-correlated with BC, and give as a possible explanation that high BC concentrations suggest the abundance of accumulation mode particles. It would be more convincing to calculate the coagulation sink and condensation sink, e.g. from the SMPS measurements, than to speculate on the abundance of accumulation mode particles based on BC. With respect to ozone: Is there a causal relationship between low ion concentrations and high ozone mixing ratios, or is this just an apparent correlation due to the fact that ozone mixing ratios are highest during the summer when ion

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concentrations are lowest?

We have calculated CS and CoagS. Ion concentrations are anti-correlated with both parameters. In order to investigate whether there is a connection between the abundance of accumulation mode particles resulting to high sinks and high BC concentrations, we performed linear regression for the BC concentration vs. the CS calculated from the SMPS data for their average diurnal variation and the correlation was quite good (R2=0.58). The anti-correlation observed with ozone was found to be not connected to summer values but it was a trend observed throughout the year.

-On p. 11817, the authors state that 28 % of the night-time events were followed by a day-time nucleation event, and 18 % of the night-time events were preceded by a day-time nucleation event. I can understand that a day-time nucleation event may be connected to a preceding ion concentration event but what is the connection of a daytime nucleation event followed by enhanced ion concentrations in the following night?

There are 7 events during which a night-time enhancement comes after a day-time nucleation event. These events are scattered through the whole measuring period thus implying that there is no seasonality. The possible link would be that the general conditions favoring a day event could still prevail the following night and lead to enhancement of ion concentrations.

-The observations presented in Fig. 7 show that there are no high concentration events in the summer months from July to September even though radon concentrations are high during the summer months, and radon decay is considered to be a major source of atmospheric ions. The authors give no explanation for this contradictory result. If the anti-correlation with wind velocity, BC concentrations and ambient temperatures (p. 11818, l. 5/6) causes low atmospheric ion concentrations, what is the process that causes this anti-correlation?

After the calculations of CS and CoagS we have explained our observations according

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to their variability.

-The discussion of Fig. 9 is highly speculative, and in my opinion, the data do not support the conclusion that atmospheric ion concentrations are extremely sensitive to the presence of anthropogenic pollutants. If high BC and ozone concentrations imply effective scavenging by accumulation mode particles, it would be more convincing to compare directly with the accumulation mode particle concentration, e.g. the particle surface concentration from the SMPS measurements. Also, the authors should present the coagulation sink calculations mentioned on p. 11819, l.1/2.

The sentence about the presence of anthropogenic pollutants has been removed, and the discussion about dependence on ozone is now restricted to referring a weak anti-correlation. The discussion is now focused on the effect of the coagulation and condensation processes, that can explain the observations more effectively.

-Backward trajectory analysis was used to assess the air mass history at Finokalia. In Fig. 11 the authors show that almost 75 % of the observed events are associated with the W sector. What is the main wind direction at Finokalia, and is there a significant difference in the distribution of air mass origin if the back trajectories are evaluated for non-event days? Furthermore, the authors found an "intrusion of air masses from higher altitudes for the majority of the events" but continue to conclude that "the contact of air masses with the soil was the major source of atmospheric ions". Please explain these contradictory statements.

The prevailing winds at Finokalia are N/NE. Air mass back trajectory analysis showed that the majority of the “ion” events (77%) was associated with the wide W/SW sector and not to the W as mistakenly was referred initially. This mistake was reproduced because the last day trajectory was analyzed and not the route during 5 days as stated in the text. Air masses coming from higher altitudes are less polluted and have lower concentrations of aerosol particles are therefore having lower CS and CoagS. After their descend, passing over land where the stronger sources of ions exist (Tunved et

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al., 2006) ion production and ion enhanced concentrations may occur more efficiently.

Minor comments: p. 11811, l.7/8: Please specify "high sink by pre-existing aerosol particles": condensation sink, coagulation sink, etc.

When referring to high sink both coagulation and condensation sinks processes are meant. This is now stated in the text.

p. 11811, l.8: The detection limit of the DMPS system in Hirsikko et al. (2007) was 3 nm rather than 83 nm.

The detection limit has been corrected to 3 nm.

p. 11814, l.13-15: The statement "Throughout the measurement period negative ions had slightly higher values..." contradicts Fig. 1, where positive ion concentrations are higher than negative ion concentrations in January, February, July, August, September, and December.

This statement is with regard to average values throughout the measuring period. The slightly higher values of negative ion concentrations can be better observed at Fig. 2 at the median diurnal circles. However, the fact that for average monthly values, positive ion concentrations are higher in January, February, July, August, September, and December is now added in the text.

p. 11816, l.2: What is the detection limit of the BC measurement? Are you confident that the BC concentrations smaller than 100 nm m-3 are accurate?

The detection limit of the Aethalometer is indeed 0.1 μg m-3. However we have selected not to remove values less than 0.1 μg m-3 since they are indicative of clean air masses and what we wanted to demonstrate with these data is that ion concentrations strongly vary with BC concentrations in an inversely proportional way. The Finokalia site is a relatively clean environment and especially after rain events and during winter, BC concentration can reach values well below 0.1 μg m-3 (Koulouri et al., 2008).

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p. 11816, l.13/14: In the discussion of Fig. 5, you state that nucleation is more pronounced for negatively charged ions than for positive ions. However, in Fig. 5, the positive ion concentration is as high or even higher compared to the negative ion concentration.

Although nucleation is general is more pronounced for negative than for positive ions, in the day (29/01/2009) presented this is not the case. Therefore we have chosen to present another day when this tendency is more obvious. Nevertheless, the statement that “nucleation is more pronounced for negatively charged ions than for positive ions” is a general remark and refers to how evident the nucleation events were in contour plots. p. 11817, l.8: What do you mean by "phenomenal growth"?

With the expression phenomenal growth, an apparent growth of cluster ions to somewhat larger diameters than the upper limit of the preexisting ion pool is meant. The identification of such growth was made with the visual inspection of AIS contour plots.

p. 11817, Fig. 7: The presented event to non-event day ratio is somewhat cumbersome. I would prefer a figure showing the relative fraction of event days (in percent).

The number of events is now presented as relative fraction.

p. 11818, l.16: I cannot follow the discussion of the relationship between rH and ion concentrations. While there are some high concentration events at rH = 100 % which could be connected to rain, I don’t see anything special at rH = 60 %.

We have removed the comment about 60% RH from the manuscript.

p. 11819, Fig. 10: What happens with temperature, relative humidity, and wind speed/direction when air ion concentrations are high and BC concentrations are low?

We restricted our analysis to BC concentration below 200 ng m-3, however we did not find any significant correlations.

p. 11819, l.25/26: In my opinion, neither the presented observational data nor the

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backward trajectories provide sufficient evidence to conclude that "radon contained in soil could be the dominating source of atmospheric ions".

We have removed the references about radon to explain the observations.

p. 11820, l.3-5: What do you mean by the statement: "Therefore, the limited growth observed for the atmospheric ions can be attributed to the condensation of the oxidation products of biogenic volatile organic compounds"?

In order to identify an enhanced ion concentration event some phenomenal growth had to be observed besides the increase in cluster ion concentration. Given the lack of photochemical processes during the night, sulfuric acid concentrations remain low and some other species have to condense on newly formed ions in order for them to grow to larger diameters of the preexisting ion pool. BVOC's could account for this growth.

p. 11820, l.16/17: I do not agree with the statement that "high ozone values restrict the abundance of ion clusters." A correlation does not necessarily imply a causal relationship.

The mentioned statement has now been rephrased so that it implies just the weak anti-correlation as an observation and not any causal relationship.

p. 11821, l.7/8: What are the "very effective removal processes" causing the low ion concentrations in summer?

High coagulation and condensation sinks because of the dominance of accumulation mode particles in summer (Gerasopoulos et al., 2007) result to lower concentrations of atmospheric ions.

Technical corrections:

p. 11810, l.24: add "the" between "a small fraction of" and "ambient particle population".

The word “between” has been added.

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p. 11811, l.1: "Virkkula et al., 2007b" should be changed to "Virkkula et al., 2007a" both in the text in the list of references. At the same time, "Virkkula et al., 2007a" on p. 11813, l.22 and in the list of references should be changed to "Virkkula et al., 2007b".

The appropriate changes have been made.

p. 11813, l.3: remove "had been calibrated and intercompared. The instrument".

This sentence has been removed.

p. 11814, l.28: remove "limited".

This word “limited” has been removed.

p. 11816, l.24/25: Rephrase the sentence "During some cases, enough growth was observed: : :".

The sentence has been rephrased to “In some cases subsequent growth to larger diameters took place”

p. 11817, l.26: replace "June" by "July".

The month was corrected to “July”.

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