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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.

**Anonymous Referee #2**

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The authors present a full year of atmospheric ion mobility distribution measurements at Finokalia, Crete, and compare air ion concentrations with meteorological parameters and air pollutant concentrations. In particular, they compare enhanced air ion concentration events during day and night with non-event situations. While such measurements are interesting and extremely useful to better understand atmospheric new particle formation, the manuscript lacks adequate interpretation and discussion of the experimental observations in the present form. Therefore, the authors should expand on their conclusions and add some deductive reasoning in order to clarify what can be learned from the presented data. Overall, the presented analysis needs to be more rigorous and quantitative, and additional data (e.g. accumulation mode particle concentrations) should be included in a revised manuscript before publication can be recommended. I have several specific comments, some minor comments, and a

few technical corrections:

Specific comments:

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 above-mentioned explanation?

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.

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 concentrations are lowest?

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 day-time nucleation event followed by enhanced ion concentrations in the following night?



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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?

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.

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.

Minor comments:

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

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



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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.

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?

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.

p. 11817, l.8: What do you mean by "phenomenal growth"?

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).

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 %.

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?

p. 11819, l.25/26: In my opinion, neither the presented observational data nor the backward trajectories provide sufficient evidence to conclude that "radon contained in soil could be the dominating source of atmospheric ions".

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"?

p. 11820, l.16/17: I do not agree with the statement that "high ozone values restrict the



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abundance of ion clusters." A correlation does not necessarily imply a causal relationship.

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

Technical corrections:

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

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".

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

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

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

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

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