

Interactive comment on “Fog composition at Baengnyeong Island in the Eastern Yellow Sea: detecting markers of aqueous atmospheric oxidations” by A. J. Boris et al.

Anonymous Referee #1

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General Comments:

Boris et al. describe measurements conducted at Baengnyeong Island (BYI) off the coast of the Korean Peninsula. The aim of the study is to characterize regional fog water and evaluate the fate of regional pollution sources. The authors invoke tracers for aqueous processing to demonstrate the likelihood of aqueous phase oxidation of samples advected by long-range transport. The authors compare the composition of fog collected at BYI with that of fog collected to the west of the Yellow Sea at Mount Tai where anthropogenic sources are generally closer to the sampling site (Shen et al. 2012). The authors demonstrate that sulfur primarily exists as sulfate and per-

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oxides are generally low, suggesting enhanced oxidation in samples collected at BYI relative to Mount Tai. Further investigation of organic species demonstrates that oxidation products of anthropogenic and biogenic precursors tend to follow functionalization pathways consistent with an aqueous OH mechanism. These results are supported by the observation of highly oxidized species such as sulfate and oxalate.

The results from this study are important when assessing the processes affecting aerosol, cloud, and fog composition in the western Yellow Sea. In addition, the manuscript is easy to follow and the figures are generally very clear. However, in its current state, the manuscript would benefit from additional analysis and discussion. The authors have a rich data set; yet, at present, interpretations are made based on the measurements as a whole without consideration of the potential differences between samples (excluding the brief discussion in the supplementary information). Based on Fig. 2, fog events have back trajectories originating from regions with marine, continental anthropogenic, and continental biogenic influence. Previous studies in the region have observed differences in cloud water composition depending on air mass history. For example, Guo et al. (2012) observed that cloud water originating from the southeast of Mt. Tai exhibited the lowest pH and highest concentration of nitrate, suggesting anthropogenic contributions of nitric acid. Samples originating from the northwest exhibit the highest concentrations of Ca, which was attributed to the dust from arid and semi-arid regions.

Questions that I have include the following: Do some fog events exhibit enhancements in oxidized biogenic species relative to others? What other species, other than nitrogen-containing organics and K⁺, are enhanced during fog events impacted by biomass burning? Are some samples enriched in crustal minerals (e.g. nss-Ca) that might suggest influence from dust? If there are no differences between samples, does that suggest that there is a homogeneous mixture of anthropogenic and biogenic sources upwind of BYI, or would this be an indication that AAOP reactions are strong enough to smear our differences between samples? Furthermore, nearly all of the

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back trajectories run through major shipping lanes, yet there is no discussion about the contribution from “marine anthropogenic” sources. What impact do ship emissions of primary sulfate have on the interpretation of the measurements?

Below are comments and suggestions related to the concerns described above. In my opinion, the manuscript would be greatly strengthened if the authors discuss the differences between samples and draw source-dependent observations. After addressing these comments and providing additional discussion, I recommend the manuscript for publication.

Specific Comments:

Section 1, Paragraph 2. This discussion is important to show that laboratory measurements alone are not sufficient to understand AAOP; however, a more detailed discussion of what previous field measurements have shown would be very useful for readers and more pertinent to the discussion. For example, on pg. 24875, line 2, it is stated “these chemical measurements helped determine whether AAOP reactions occur at BYI. . .” What measurements are you referring to? What other studies have used such markers to understand AAOP (e.g. Sorooshian et al. 2007, Ervens et al. 2011,2014)? A broader discussion about previous field measurements is needed.

Page 24880, Line 5. What sources contribute to nss-Ca in this region? Enriched Ca may be an indication of transported mineral dust (e.g. Straub et al. 2007, Benedict et al. 2012) or possibly an enriched layer at the sea surface due to biological activity. Are similar mechanisms expected in this region?

Section 3.2. This section focuses on measurements of inorganic ions (which largely originate from marine sources). Were measurements of other inorganic ions made? For example, Guo et al. (2012) discuss iron measurements conducted at Mt. Tai. Iron is known to play a role in OH production via the Fenton and photo-Fenton reactions and is potentially a major sink of dicarboxylic acids, such as oxalate and malonate, and hydrogen peroxide (Daumit et al. 2014, Deguillaume et al. 2005, Faust and Zepp

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1993, Johnson and Meskhidze 2013, Nguyen et al. 2013, Weller et al. 2014). If such measurements are available, then perhaps some amount of peroxide loss can be attributed to Fenton chemistry.

Sections 3.2 and 3.3. There is little discussion about the potential contribution from shipping emissions. Major shipping lanes and ports lie to the south and east of BYI (Streets et al. 2000) and Korean cities near BYI are thought to have pollution impacts from shipping ports (e.g. Kang et al. 2006, Mutlu et al. 2012). Aerosol and cloud measurements conducted in regions impacted by shipping lanes have demonstrated that ships contribute significant quantities of primary sulfate down wind of the ship stack (e.g. Murphy et al. 2009, Coggon et al. 2012, Prabhakar et al. 2014). Since a comparison is made with measurements conducted at Mount Tai, I believe it is important to discuss that additional anthropogenic sources of sulfate may contribute to the observed measurements conducted at BYI.

Page 24882, Line 25. Where do these anthropogenic and biogenic sources originate? Are there major forests upwind of BYI that could contribute to monoterpene oxidation products? The observation of organosulfates in Section 3.8 is compelling evidence for the aqueous-phase processing of biogenic material, however it would be useful for future studies to know where these biogenic sources originate. Do some fog samples exhibit stronger biogenic signatures than others? From what direction were these samples transported?

Page 24883, Line 1. Do the series correspond to the distribution of a single fog water sample, or are these a scattering of compounds measured in all samples? I’m interpreting this analysis as demonstrating the oxidation pathway of all samples collected at BYI; however, I normally think of this analysis as applied to a single air mass. Please clarify.

Page 24884, Lines 10-17. Here, a time-series trend or figure comparing biomass-burning impacted periods vs. non-biomass burning impacted periods would help to

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distinguish what effect biomass burning has on the measurements conducted at BYI. Are there other species (aside from nitrogen-containing compounds) that exhibit enhanced signal?

Figure 2. It would be useful to have some geographic markers, including country borders, major cities, and the location of the atmospheric research center. Since a comparison is made to Shen et al. (2012), it would be helpful to have a marker demonstrating the location of Mount Tai.

Minor Comments

Page 24877, line 10. I am unfamiliar with the term “massed.” Do you mean that the samples were weighed?

Page 24882, line 6. Please define how liquid concentrations are converted to air-equivalent units.

Figure 6. The term “series” is described in the text, but not in the caption. Please indicate what each “series” corresponds to. It would also be helpful to include sloped lines indicating functionalization pathways to quickly help guide readers.

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