Atmos. Chem. Phys. Discuss., 15, C10151–C10179, 2015
www.atmos-chem-phys-discuss.net/15/C10151/2015/

Atmospheric Chemistry and Physics
Open Access
Discussions

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.

A. J. Boris et al.

collett@atmos.colostate.edu

Received and published: 5 December 2015

Dear Referee,

Thank you for your insightful, relevant suggestions for our research and manuscript. Please find below our responses to your comments and questions (in italics). In many cases, the limited number of fog samples collected during this particular field campaign makes the results of further data analyses uncertain. We appreciate the importance of the questions raised and

agree that further analysis would be interesting. We hope that this study will be preliminary to future work involving fog chemical analysis at Baengnyeong Island over a more extended period of time. Several of your comments have been responded to by altering or adding figures; these relevant figures are attached at the end of this response.

General Comments from the Referee

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 peroxides 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 highlighted 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. 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 (Guo et al., 2012.)

In response to your suggestion that chemical analysis with respect to air mass upwind histories would be interesting, we have added two figures (one in the supplemental information) and a paragraph discussing the difference between the samples from the N, E, S, and W "sectors" (based on back trajectory analyses; Figs. 4 and SI-4). We have found that, due mostly to the sampling period on 2 July 2014, the concentrations of fog water constituents were highest (for almost all species) when the air mass traveled from the west. The sample with a back trajectory originating to the east (only one was collected with sufficient liquid volume for chemical analyses) was lowest in concentration for nearly all species. These trends make apparent sense with respect to pollutant source regions; however, because a small number of samples were analyzed, the certainty of these results is low. Our field campaign was limited in duration and we hope that future campaigns at this site will allow more thorough characterization of pollutant sources and processes leading to fog constituent concentrations. The following sentence reflecting these findings has been added to the manuscript at line 351:

"Concentrations of nearly all species were highest in samples with westerly back trajectories (Fig. 4). Anthropogenic influence was likely greatest from this sector because of the large number of urban areas and major industry in Shandong Province and surrounding regions (Cao et al., 2006). The lowest concentrations of most species originated from the east (note that only one sample included in the analyses originated from the east). The only exception was Na^+, which was most abundant from the south, and least abundant from the north."

Questions that I have include the following:

Do some fog events exhibit enhancements in oxidized biogenic species relative to others?

Yes, there is variation in the concentration of the quantified biogenic hydrocarbon pinic acid. However, its concentration appears to be independent of changes in air mass (back trajectory upwind direction). There is also variation in the peak areas of other identified oxidized biogenic species between fog samples; this variation is summarized in a figure in the supplemental information (Fig. SI-5). Species considered were tentatively identified as an isoprene oxidation product ($C_7H_{10}O_5$) and monoterpene oxidation products ($C_8H_{12}O_5$, diaterpenylic acid, $C_9H_{14}O_5$, Methyl-butane-tricarboxylic acid, $C_{10}H_{17}NO_7S$, and $C_{10}H_{17}NO_8S$). The peak area variations of tentatively identified anthropogenic species (benzenedicarboxylic acid and an oxidation product of 1,3,5-trimethylbenzene) were also included. The result of this analysis is the finding that samples impacted by air from the east (n=1) and from the west (n=7) contained the greatest quantities of the biogenic species, while the anthropogenic species were found in greatest quantities from the west (n=7). This is a qualitative analysis for trends, and no conclusions with regards to the total quantities of these compounds within samples should be drawn (no standards for calibration were available for these species, and the sensitivity of the electrospray ionization mass spectrometer used in our analyses is highly variable with chemical structure). The following sentence has been added to the manuscript at line 511:

"Based on a qualitative analysis of the abundances of mass spectral peak areas, westerly air masses brought the greatest quantities of anthropogenic species to BYI fog water, while the greatest biogenic species quantities were contributed by air masses from the west and east (depending on the constituent; note that only one sample with an easterly back trajectory was available; see Fig. SI-5)."

What other species, other than nitrogen-containing organics and K^+, are enhanced during fog events impacted by biomass burning?

Due to the limited number of samples and the qualitative nature of our biomass burning influence determination, a figure addressing this issue was originally omitted from the article. However, we have provided new diagrams in the supplemental information (Figs. SI-6 and SI-7) contrasting several chemical constituents of the fog samples between periods that were influenced by biomass burning, and periods that were not. This analysis demonstrated that during periods when fire was detected (via back trajectory colocation with MODIS fire detection), mean concentrations of most species were elevated. However, some fire periods likely also coincided with the arrival of air masses from more polluted source regions (e.g., the samples collected on 2 July). A larger sample set might allow a more conclusive determination of the regional fire impact on fog chemistry at BYI. Levoglucosan concentrations, which are discussed in the manuscript, were low throughout the study in contrast to even background concentrations in aerosol samples, but one fire-impacted sample did contain substantially higher concentrations of levoglucosan than other samples. The following discussion in the manuscript has been changed to better describe possible biomass burning impacts (line 556):

"These nitrogen-containing organic species may have originated from biomass burning and/or wildfires in Southeast Asia and Eastern Russia during the fog study period. For the three events with quantified fog nitrophenol concentrations above detection limits, large-scale fires were detected in upwind source regions (MODIS data). Levoglucosan (a biomass burning marker) concentrations measured within fog samples from BYI were below background concentrations measured in aerosol samples (Weber et al., 2007) however, those concentrations measured within the fog from 2 July were high relative to other fog samples (Fig. SI-7), and thus may have been impacted by biomass burning emissions. Aqueous solubility of levoglucosan as well as oxidation processes may have affected the concentrations measured in BYI fog samples. Concentrations of the biomass burning marker K^+ were additionally above the study mean on dates when regional fires were detected (Fig. SI-6) and a correlation of r^2=0.93 (n=11, $p \leq 0.001$) was observed between nss-K^+ and total quantified nitrophenols as air equivalent

concentrations (nmol m^{-3})."

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?

Mineral dust is the predominant source of nss-Ca^{+2} in East Asia (Arimoto et al., 2004; Kawamura et al., 2004). For example, according to the latter study, marine aerosol collected at Jeju Island off the south coast of Korea contained Ca^{+2} mainly associated with dust. Although some anthropogenic sources of Ca^{+2} might be anticipated, Arimoto et al. (2004) discuss the insolubility of the Ca^{+2} from combustion sources found in precipitation collected in Korea (as measured by Mattigod et al., 1990). Despite the likelihood that dust is an important constituent of fog nuclei at BYI, we observed low variation in nss-Ca^{+2} and Ca^{+2} concentrations, with higher variation within fog events than between events. The finding that no obvious dust influence was observed is now discussed at the end of Section 3.1 (line 344):

"The concentrations of Ca^{+2} (mean 77 μM) were within the range of previous studies in other, remote parts of the world (Benedict et al., 2012; Munger et al., 1989), indicating that inputs to fog water chemistry by mineral dust were likely unimportant during the study period (Arimoto et al., 2004; Kawamura et al., 2004; Mattigod et al., 1990)."

During our quadrant analysis to elucidate chemical source regions (as suggested; see Fig. 4), the concentrations of Ca^{+2}, Mg^{+2}, K^+, and others were found to be greatest in air masses from the west on average (mainly due to the samples on 2 July). Non-sea salt concentrations of Ca^{+2} and K^+ showed similar trends. This suggests that the most substantial differences between samples are a result of variation in sources of fog constituents. Although it is possible that AAOP reactions could result in somewhat homogeneous organic composition between fog samples, it likely that mixing with inorganic particulate matter would be more affected by microphysical effects due to aerosol particle hydration, such as partitioning of semi-volatile organic species onto hydrated particles with mostly inorganic composition. Organic speciation, as we will discuss below, does show variation between samples, suggesting that the extent of AAOP reactions was not sufficient to remove chemical distinction between samples.

Furthermore, nearly all of the 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?

The articles cited in your suggestions regarding shipping provide compelling evidence for a large relative shipping contribution to atmospheric pollutant concentrations to atmospheric samples at BYI. We have included a section describing this possible contribution to inorganic sulfur concentrations measured in BYI fog (within Section 3.3). All fog samples had traveled to some extent over the Yellow Sea, where major shipping lanes exist; it is therefore likely that all samples were impacted to some extent by this source of SO_2, SO_4^{-2}, *and other species. However, other molecular tracers for shipping emissions such as vanadium or black carbon were not measured in our campaign, so the influence of shipping emissions on our collected fog water samples is uncertain for this sample set. The following sentence has been added to the manuscript (line 414):*

"International shipping lanes could also contribute to the measured SO_4^{-2} *concentrations in BYI fog: some of the world's largest shipping ports are located in the Yellow Sea (Streets et al., 2000). The contribution of fine particle (≤2.5 µm diameter)* SO_4^{-2} *has been estimated at ≤15% from ship oil combustion in this region (Lauer et al., 2007), and shipping routes in the Yellow Sea have been identified as major* SO_2 *source regions (Kang et al., 2006). Shipping emissions have also been associated with elevated concentrations of other atmospheric constituents, including* NO_3^- *(Prabhakar et al., 2014)."*

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.

We have added a paragraph to improve the background information provided to our readers. This includes findings from the authors you suggested regarding AAOP reaction observations in the real atmosphere. We have additionally attempted to clarify the particular chemical species important for our analysis of possible AAOP reactions at BYI (line 92).

"Unequivocal evidence of AAOP reactions within the real atmosphere is challenging to show because no specific molecular or physical tracers for AAOP have been identified. Known products of aqueous oxidation reactions including oxalic acid and SO_4^{-2} *are frequently used as non-specific molecular tracers. Successful approaches toward identifying the location and timing of AAOP reactions have included the use of coincident non-specific molecular tracers such as organic acids (Sorooshian et al., 2006, 2013), the predominance of oxalic acid and* SO_4^{-2} *in a size mode generated from aqueous processes (the droplet size mode, Crahan et*

al., 2004), and high carbon oxidation states (Chen et al., 2015). Additional observations of AAOP evidence have been summarized by Blando and Turpin (2000) and Ervens et al. (2011). Although oxalic acid in particular has been used as a molecular tracer for AAOP reactions (Sorooshian et al., 2006; Wonaschuetz et al., 2012; Yu et al., 2005), other sources for oxalic acid in the atmosphere have been proposed: gas-phase oxidation of aromatic and anthropogenic molecules(Borrás et al., 2012; Edney et al., 2000; Kalberer et al., 2000a; Kamens et al., 2011; and Kleindienst et al., 1999), diesel exhaust emissions (Kawamura Kaplan, 1987), and forest fire emissions (Narukawa Kawamura, 1999; Yamasoe et al., 2000)."

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?

Please see discussion of nss-Ca^{+2} *in response to a question above.*

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 et al., 1993; Johnson et al., 2013b; 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.

Measurements of other metals such as iron, copper, and manganese were not made in this study. We understand that these species are important to consider in organic acids and peroxides analysis and certainly recommend them for future studies of BYI fog.

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 quantifies 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.

Please see discussion of shipping emissions in response to your suggestion above (now discussed within Section 3.3).

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?

Please see discussion of additional qualitative biogenic analysis in response to your suggestion above (also Fig SI-5 and line 511).

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.

We have added clarifying information to the discussion of the van Krevelen figure to our *paper and the figure (now Fig. 7) caption. The "series" correspond to species that were identified in one or more of the fog water samples; this figure represents a composite of the compounds identified within the samples. This analysis was intended to illustrate the organic composition of the fog water in a concise way, and also point out the similarities of the composition to other atmospheric samples. The series do not necessarily reflect oxidation mechanisms, since the constituents of most series differ from one another by groupings of* CH_2 *rather than oxygen-containing moieties such as OH groups. The new language used in the manuscript reflects this distinction by using the term "family" rather than "series". Below is the revised text of the section discussing organic compound analysis via mass spectrometry.*

"Polar organic components of the fog water with C_4 *were tentatively identified using HPLC-(-)-ESI-HR-ToF-MS. These compounds were biogenic and anthropogenic in origin, including pinic acid and monoterpene-derived organosulfates, and phthalic acid (Table 2). Di-carboxylic and hydroxy-di-carboxylic acids are a prominent group of compounds identified within the polar organic matter of the BYI fog samples. A van Krevelen diagram (Chen et al., 2015; Heald et al., 2010; Mazzoleni et al., 2010a; Noziere et al., 2015) was used to illustrate the distribution of organic species identified within all fog water samples (CHO, CHNO, CHOS, CHNOS; Fig. 7), with the objectives of showing groupings of like species within the fog samples, and comparing the fog composition to previously analyzed atmospheric samples. Molecules differing by specific, oxygen-containing elemental combinations can be identified in van Krevelen space by slope: i.e., addition of carbonyl (-2H, +1O; slope = -2); carboxylic acid (-2H, +2O; slope = -1); alcohol (or oxidation of an aldehyde to a carboxylic acid group; slope = 0); or water (slope = +2). In BYI fog samples, families of species differing by methylene* (CH_2) *are visible: (1) saturated di-acids* (C_5-C_7*; slope = -0.5); (2) hydroxy-di-acids* (C_5-C_7*; slope = -0.7); (3) hydroxy-mono-unsaturated di-acids* (C_7-C_9*; slope = -0.8); (4) mono-unsaturated di-acids* (C_4-C_9*; slope = -1); (5) nitrophenols (di-methyl-nitrophenol, methyl-nitrophenol, and nitrophenol; slope = -2.3); and (6) organosulfates* ($C_9H_{16}O_7S$ *through* $C_6H_{10}O_7S$*; slope = -0.3). The slopes between points in these families vary because the O content remains constant while the C and H contents differ. A family of phthalate*

derivatives (7) with differing oxygen contents ($C_8H_6O_3$ *through* $C_8H_6O_5$*; slope = 0) is also visible. Several CHO species were additionally identified as both biogenic and anthropogenic secondary organic species; for example, 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) was tentatively identified* (m/z^- *203.078 and formula* $C_8H_{12}O_6$*), as was diaterpenylic acid* m/z^- *189.078;* $C_8H_{14}O_5$*), which are gas-phase oxidation products of* α*-pinene (**??**). Based on a qualitative analysis of the abundances of mass spectral peak areas, westerly air masses brought the greatest quantities of anthropogenic species to BYI fog water, while the greatest biogenic species quantities were contributed by air masses from the west and east (depending on the constituent; note that only one sample with an easterly back trajectory was available; see Fig. SI-5). Mean O/C and H/C of ambient aerosol samples (mass-normalized, from aerosol mass spectrometry; (Chen et al., 2015; Heald et al., 2010; Ng et al., 2011) typically fall on a line within van Krevelen space at a slope of -1 and y-intercept of 2 for samples with fresh emissions and a slope of -0.5 for rural/remote samples. Within the molecular level analysis employed here, the slopes between -1 and -0.5 appear to correspond to families of organic acids differing by a* CH_2 *group, with differing levels of unsaturation and/or number of hydroxyl groups. The space within the van Krevelen diagram occupied by these identified families indicates they are chemically similar to aged aerosol from previous studies (Chen et al., 2015) and may be analogous to ring-opened and oxygenated species present within the fragmentation scheme of the atmospheric aging process (Kroll et al., 2009)."*

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 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?

Please see additional biomass burning analysis in response to your suggestion above (also in Figs. SI-6 and SI-7, as well as line 556).

Figure 2. It would be useful to have some geographic markers, including country bor-

ders, 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.

We have added several landmarks to this figure, as well as country borders (Fig. 2).

Minor Comments

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

We have changed this sentence for clarification (line 273):

"Samples were each weighed, divided into aliquots for analyses, and remaining fog water was stored frozen in Nalgene wide-mouth HDPE plastic bottles (also used for collection)."

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

We have added an equation defining this conversion (line 265):

$$\frac{nmol\ i}{m^3\ air} = \frac{\mu mol\ i}{L\ sample} \times \frac{L}{1000\ mL} \times \frac{mL}{1.00\ g} \times mass\ sampled\ (g) \times \frac{hr}{m^3\ air} \times \frac{1}{time\ sampled\ (hr)} \times \frac{1000\ nmol\ i}{\mu mol\ i}$$

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.

We have attempted to clarify our discussion of the van Krevelen diagram by changing our term "series" to "family", and have added a clarifying sentence to the caption. A sentence has additionally been added to the discussion to clarify the intention of the figure (Fig. 7). The slopes are included to allow a connection between the studies of Chen et al., 2015 and others because the species identified in the BYI fog samples occupy a similar van Krevelen space as those identified in previous studies. Since functionalization pathways typically observed using van Krevelen diagrams do not correspond to the majority of identified chemical families in BYI fog water (e.g., OH addition), additional slopes of functionalization pathway labels have been avoided. The caption of Fig. 7 now reads as follows:

"Polar organic compounds identified within fog samples using HPLC-(-)-ESI-HR-ToF-MS detection illustrated via a van Krevelen diagram. Colors of points distinguish compound elemental composition; solid lines show families differing by methylene groups of di-acids (blue, families 1-4), nitrophenols (green, family 5), and organosulfates (black, family 6); aromatic oxygenated species differing by an O atom are also shown (blue; family 7). Dashed lines show slopes typical of samples in previous studies (Chen et al., 2015) of -0.5 for remote/rural (top) and -1 for urban (bottom); organic acid families fit within the space of these previously analyzed atmospheric samples."

References

Arimoto, R., Zhang, X. Y., Huebert, B. J., Kang, C. H., Savoie, D. L., Prospero, J. M., Sage, S. K., Schloesslin, C. A., Khaing, H. M., and Oh, S. N. (2004). Chemical composition of atmospheric aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia. Journal of Geophysical Research, 109(D19):D19S04.

Benedict, K. B., Lee, T., and Collett, J. L. (2012). Cloud water composition over the southeastern Pacific Ocean during the VOCALS regional experiment. Atmospheric Environment, 46:104–114. Blando, J. and Turpin, B. (2000). Secondary organic aerosol formation in cloud and fog droplets: A literature evaluation of plausibility. Atmospheric Environment, 34:1623–1632.

Borrás, E. and Tortajada-Genaro, L. A. (2012). Secondary organic aerosol formation from the photo- oxidation of benzene. Atmospheric Environment, 47:154–163.

Cao, G., Zhang, X., and Zheng, F. (2006). Inventory of black carbon and organic carbon emissions from China. Atmospheric Environment, 40(34):6516–6527.

Chen, Q., Heald, C. L., Jimenez, J. L., Canagaratna, M. R., He, L.-Y., Huang, X.-F., Campuzano-Jost, P., Palm, B. B., Poulain, L., Kuwata, M., Martin, S. T., Abbatt, J. P. D., Lee, A. K. Y., and Liggio, J. (2015). Elemental Composition of Organic Aerosol: The Gap Between Ambient and Laboratory Measurements. Geophysical Research Letters, 42:1–8.

Coggon, M. M., Sorooshian, A., Wang, Z., Metcalf, A. R., Frossard, A. A., Lin, J. J., Craven, J. S., Nenes, A., Jonsson, H. H., Russell, L. M., Flagan, R. C., and Seinfeld, J. H. (2012). Ship impacts on the marine atmosphere: insights into the contribution of shipping emissions to the properties of marine aerosol and clouds. Atmospheric Chemistry and Physics, 12(18):8439–8458.

Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H. (2004). An exploration of aqueous oxalic acid production in the coastal marine atmosphere. Atmospheric Environment, 38(23):3757–3764.

Daumit, K. E., Carrasquillo, A. J., Hunter, J. F., and Kroll, J. H. (2014). Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution. Atmospheric Chemistry and Physics, 14(19):10773–10784.

Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., and Chaumerliac, N. (2005). Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters. Chemical Reviews, 105:3388–3431.

Edney, E. O., Driscoll, D. J., Speer, R. E., Weathers, W. S., Kleindienst, T. E., Li, W., and Smith, D. F. (2000). Impact of aerosol liquid water on secondary organic aerosol yields of irradiated toluene/propylene/NOx/(NH4)2SO4/air mixtures. Atmospheric Environment, 34:3907–3919.

Ervens, B., Renard, P., Ravier, S., Clément, J.-L., and Monod, A. (2014). Aqueous phase oligomerization of methyl vinyl ketone through photooxidation Part 2: Development of the chemical mechanism and atmospheric implications. Atmospheric Chemistry and Physics Discussions, 14(15):21565–21609.

Ervens, B., Turpin, B., and Weber, R. (2011). Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): A review of laboratory, field and model studies. Atmospheric Chemistry and Physics, 11:11069–11102.

Faust, B. C., Anastasio, C., Allen, J. M., and Arakaki, T. (1993). Aqueous-phase photochemical formation of peroxides in authentic cloud and fog waters. Science (New York, N.Y.), 260(5104):73-75.

Guo, J., Wang, Y., Shen, X., Wang, Z., Lee, T., Wang, X., Li, P., Sun, M., Collett, J. L., Wang, W., and Wang, T. (2012). Characterization of cloud water chemistry at Mount Tai, China: Seasonal variation, anthropogenic impact, and cloud processing. Atmospheric Environment, 60:467–476.

Heald, C. L., Kroll, J. H., Jimenez, J. L., Docherty, K. S., DeCarlo, P. F., Aiken, A. C., Chen, Q., Martin, S. T., and Farmer, D. K. (2010). A simplified description of the evolution of organic aerosol composition in the atmosphere. Geophysical Research Letters, 37(L08803).

Johnson, M. S. and Meskhidze, N. (2013). Atmospheric dissolved iron deposition to the global oceans: effects of oxalate-promoted Fe dissolution, photochemical redox cycling, and dust mineralogy. Geoscientific Model Development Discussions, 6(1):1901–1947.

Kalberer, M., Yu, J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H. (2000). Aerosol Formation in the Cyclohexene-Ozone System. Environmental Science Technology, 34(23):4894–4901.

Kamens, R. M., Zhang, H., Chen, E. H., Zhou, Y., Parikh, H. M., Wilson, R. L., Galloway, K. E., and Rosen, E. P. (2011). Secondary organic aerosol formation from toluene in an atmospheric hydrocarbon mixture: Water and particle seed effects. Atmospheric Environment, 45:2324–2334.

Kang, C.-M., Kang, B.-W., and Lee, H. S. (2006). Source identification and trends in concentrations of gaseous and fine particulate principal species in Seoul, South Korea. Journal of the Air Waste Management Association (1995), 56(7):911–921.

Kawamura, K. and Kaplan, I. (1987). Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air. Environmental Science Technology, 21(1):105–110.

Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M. (2004). Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition. In Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan, pages 243–265. The Geochemical Society, Amsterdam, The Netherlands, first edition.

Kleindienst, T. E., Smith, D. F., Li, W., Edney, E. O., Driscoll, D. J., Speer, R. E., and Weathers, W. S. (1999). Secondary organic aerosol formation from the oxidation of aromatic hydrocarbons in the presence of dry submicron ammonium sulfate aerosol. Atmospheric Environment, 33:3669–3681.

Kroll, J. H., Smith, J. D., Dung, L. C., Kessler, S. H., Worsnop, D. R., and Wilson, K. R. (2009). Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol. Physical Chemistry Chemical Physics, 11:8005–8014.

Mattigod, S., Rai, D., Eary, L., and Ainsworth, C. (1990). Geochemical factors controlling the mo- bilisation of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. Journal of Environmental Quality, 19:188–201.

Mazzoleni, L. R., Ehrmann, B. M., Shen, X., Marshall, A. G., and Collett, J. L. (2010). Water-soluble atmospheric organic matter in fog: Exact masses and chemical formula identification by ultrahigh- resolution fourier transform ion cyclotron resonance mass spectrometry. Environmental Science Technology, 44(10):3690–3697.

Munger, J., Collett, J., Daube, B., and Hoffmann, M. (1989). Carboxylic acids and carbonyl com- pounds in southern California clouds and fogs. Tellus B, 41B:230–242.

Mutlu, A., Lee, B. K., Park, G. H., Yu, B. G., and Lee, C. H. (2012). Long-term concentrations of airborne cadmium in metropolitan cities in Korea and potential health risks. Atmospheric Environment, 47:164–173.

Narukawa, M. and Kawamura, K. (1999). Distribution of dicarboxylic acids and carbon isotopic com- positions in aerosols from 1997 Indonesian forest fires. Geophysical Research Letters, 26(20):3101– 3104.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R. (2011). Changes in organic aerosol composition with aging inferred from aerosol mass spectra. Atmospheric Chemistry and Physics, 11(13):6465–6474.

Nguyen, T. B., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H. (2013). Reactive uptake and photo- fenton oxidation of glycolaldehyde in aerosol liquid water. Environmental science technology, 47(9):4307–16.

Noziere, B., Kalberer, M., Claeys, M., Allan, J., Anna, B. D., Decesari, S., Finessi, E., Glasius, M., Grgic, I., Hamilton, J. F., Ho, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., and Wisthaler, A. (2015). The molecular identification of organic compounds in the atmosphere: State of the art and challenges. Chemical Reviews, 115(10):3919–3983.

Prabhakar, G., Ervens, B., Wang, Z., Maudlin, L., Coggon, M., Jonsson, H., Seinfeld, J., and Sorooshian, A. (2014). Sources of nitrate in stratocumulus cloud water: Airborne measurements during the 2011 E-PEACE and 2013 NiCE studies. Atmospheric Environment, 97:166–173.

Shen, X., Lee, T., Guo, J., Wang, X., Li, P., Xu, P., Wang, Y., Ren, Y., Wang, W., Wang, T., Li, Y., Carn, S. A., and Collett, J. L. (2012). Aqueous phase sulfate production in clouds in eastern China. Atmospheric Environment, 62:502–511.

Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and Seinfeld, J. H. (2007). On the source of organic acid aerosol layers above clouds. Environmental science technology, 41(13):4647–54.

Sorooshian, A. and Varutbangkul, V. (2006). Oxalic acid in clear and cloudy atmospheres:

Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004. Journal of Geophysical Research, 111(D23):1–10.

Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B. (2013). Observations of Sharp Oxalate Reductions in Stratocumulus Clouds at Variable Altitudes: Organic Acid and Metal Measurements During the 2011 E-PEACE Campaign. Environmental Science Technology, 47:7747–7756.

Straub, D. J., Lee, T., and Collett, J. L. (2007). Chemical composition of marine stratocumulus clouds over the eastern Pacific Ocean. Journal of Geophysical Research, 112(D4):D04307.

Streets, D. G., Guttikunda, S. K., and Carmichael, G. R. (2000). The growing contribution of sulfur emissions from ships in Asian waters, 1988-1995. Atmospheric Environment, 34:4425–4439.

Szmigielski, R., Surratt, J. D., Gömez-Gonzälez, Y., van der Veken, P., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Edney, E. O., Seinfeld, J. H., Maenhaut, W., and Claeys, M. (2007). 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol. Geophysical Research Letters, 34(24):2-7.

Weber, R. J., Sullivan, A. P., Peltier, R. E., Russell, A., Yan, B., Zheng, M., de Gouw, J., Warneke, C., Brock, C., Holloway, J. S., Atlas, E. L., and Edgerton, E. (2007). A study of secondary organic aerosol formation in the anthropogenic-influenced southeastern United States. Journal of Geophysical Research: Atmospheres, 112(D13).

Weller, C., Tilgner, A., Braüer, P., and Herrmann, H. (2014). Modelling the impact of iron-carboxylate photochemistry on radical budget and carboxylate degradation in cloud droplets and particles. Environmental Science Technology, page 140328152101005.

Wonaschuetz, A., Sorooshian, A., Ervens, B., Chuang, P. Y., Feingold, G., Murphy, S. M., de Gouw, J., Warneke, C., and Jonsson, H. H. (2012). Aerosol and gas re-distribution by shallow cumulus clouds: An investigation using airborne measurements. Journal of Geophysical Research, 117(D17):D17202.

Yamasoe, M., Artaxo, P., Miguel, A., and Allen, A. (2000). Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. Atmospheric Environment, 34:1641–1653.

Yasmeen, F., Vermeylen, R., Szmigielski, R., Iinuma, Y., Böge, O., Herrmann, H., Maenhaut, W., and Claeys, M. (2010). Terpenylic acid and related compounds: precursors for dimers in secondary organic aerosol from the ozonolysis of α- and β-pinene. Atmospheric Chemistry and Physics, 10(19):9383-9392.

Yu, L., Shulman, M., Kopperud, R., and Hildemann, L. (2005). Fine organic aerosols collected in a humid, rural location (Great Smoky Mountains, Tennessee, USA): Chemical and temporal characteristics. Atmospheric Environment, 39(33):6037–6050.

Relevant Figures

Figure Captions:

Figure 2: Map Back Trajectories. Back trajectories of air masses intercepted during fog events (72 hours at one hour time resolution; HySPLIT). Locations labeled on plot include Mount Tai, where previous atmospheric water chemical measurements were made, and the highest throughput shipping ports in the region pictured. The BYI ARC is shown as a gold diamond. Sectors were defined to determine whether particular source regions existed for

chemical constituents of the fog: northerly (30 June and 1 July); westerly (2, 14, and 15 July); southerly (18 and 20 July); and easterly (5 July). Each trajectory was initiated at the approximate beginning of a fog event. Imagery from NASA Blue Marble; plot generated using Python Matplotlib Toolkit BaseMap.

Figure 4. Sector Concentrations. Sector analysis of most abundant inorganic fog water components, as well as selected organic acids. Highest concentrations of most species originated from the west. For Na$^+$ and Cl$^-$, high concentrations were also observed from the south. Ca^{+2} concentrations were also heightened within samples with northerly trajectories, which may suggest a continental dust source. In agreement with high measured NH$_4^+$ concentrations, pH as highest from the west. Note that samples were low in volume in some cases so that pH analyses were not performed. For inorganic species except pH, n=1 easterly, n=3 northerly, n=4 southerly, and n=5 for westerly trajectories. For organic species and pH, n=0 easterly, n=2 northerly, n=3 southerly, n=4 westerly.

Figure 7. van Krevelen. Polar organic compounds identified within fog samples using HPLC-(-)-ESI-HR-ToF-MS detection illustrated via a van Krevelen diagram. Colors of points distinguish compound elemental composition; solid lines show families differing by methylene groups of di-acids (blue, families 1-4), nitrophenols (green, family 5), and organosulfates (black, family 6); aromatic oxygenated species differing by an O atom are also shown (blue; family 7). Dashed lines show slopes typical of samples in previous studies (Chen et al., 2015) of -0.5 for remote/rural (top) and -1 for urban (bottom); organic acid families fit within the space of these previously analyzed atmospheric samples.

Figure SI-5. Peak Areas Anthropogenic Biogenic. Peak areas of tentatively identified anthropogenic (two categories on left) and biogenic (two categories on right) species in BYI fog water (see Table 2). Samples with westerly back trajectories contained the greatest quantities of the anthropogenic species, while the samples collected with westerly trajectories and an easterly trajectory (n=1) contained the greatest quantities of the biogenic species.

Samples with southerly back trajectories (from over the sea) contained the smallest quantities of most species. Note that sensitivities of the mass spectrometer to these species are highly variable, and no calibration has been made for these compounds.

Figure SI-6. Biomass Burning Constituents. Contrast of most abundant species in fog samples between days with fire impact (based on qualitative observation of fires in MODIS fire product outputs, co-located with back trajectories). Note that fire periods included the samples from 07/02/14, which typically contained the greatest concentrations of most abundant species; this is likely due to sources other than fires. A larger sample set might allow a more conclusive determination of the regional fire impact on fog chemistry at BYI.

Figure SI-7. Biomass Burning Correlation. Correlation of levoglucosan (triangles) and total nitrophenol (circles) concentrations with those of non-sea salt K$^+$ (nss-K$^+$). Air equivalent concentrations were used to remove the impact of liquid water content between fog samples. Levoglucosan concentrations were only analyzed in six fog samples, representative of most fog events (the fog samples from the event on 18 June were not analyzed due to contamination by CASCC cleaning solution; four samples were analyzed from days when fire was detected; two from days when no fire was detected). The overall correlation of nitrophenols with nss-K$^+$ was r^2=0.93 (n=11, p ≤0.001).

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 24871, 2015.

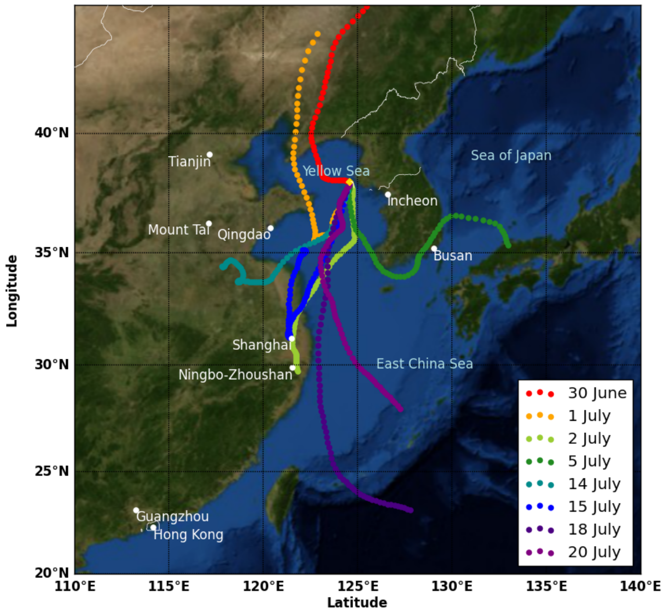

Fig. 1. Figure 2 Map Back Trajectories

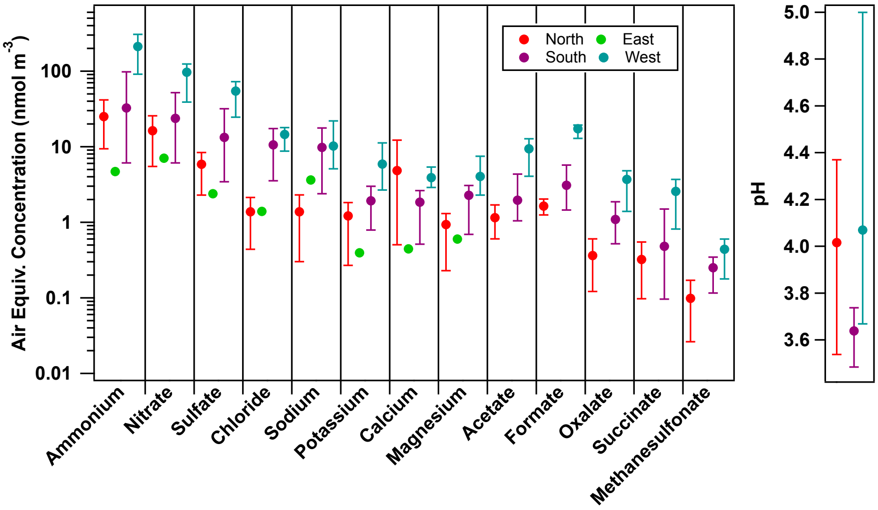

Fig. 2. Figure 4 Sector Concentrations

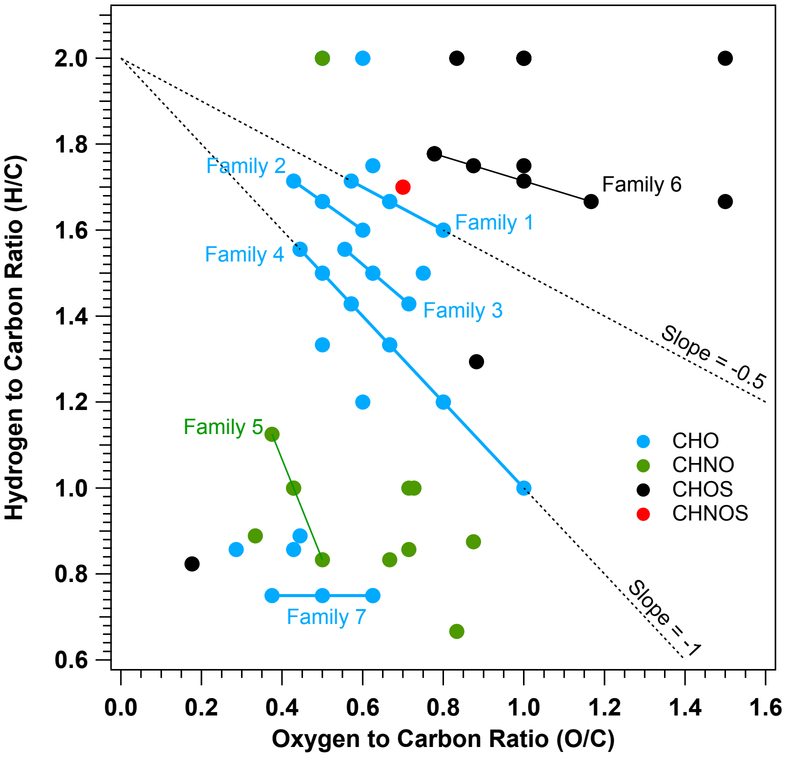

Fig. 3. Figure 7 van Krevelen

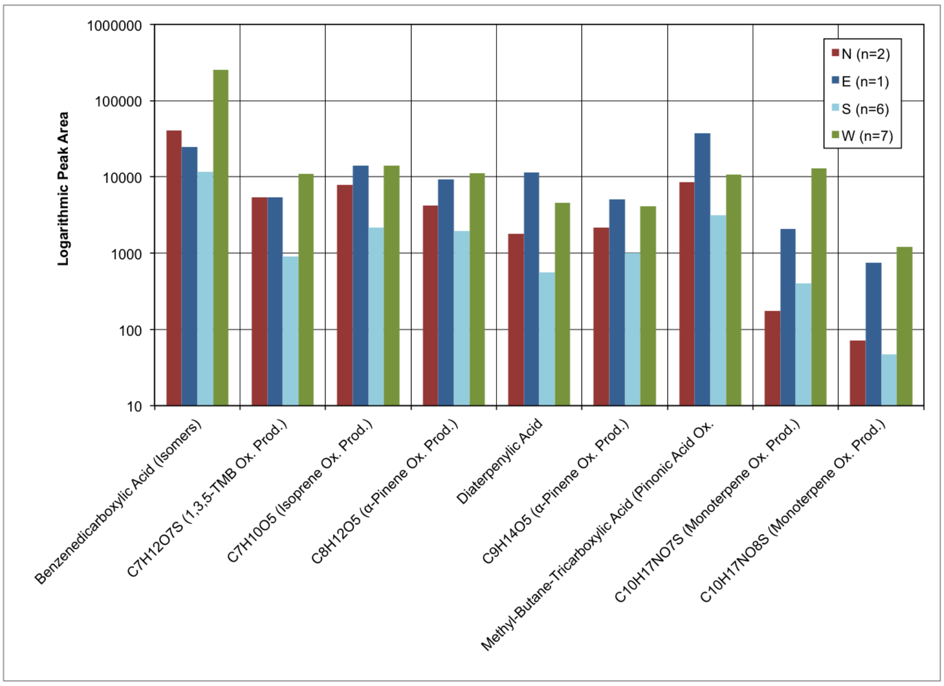

Fig. 4. Figure SI 5 Peak Areas Anthropogenic Biogenic

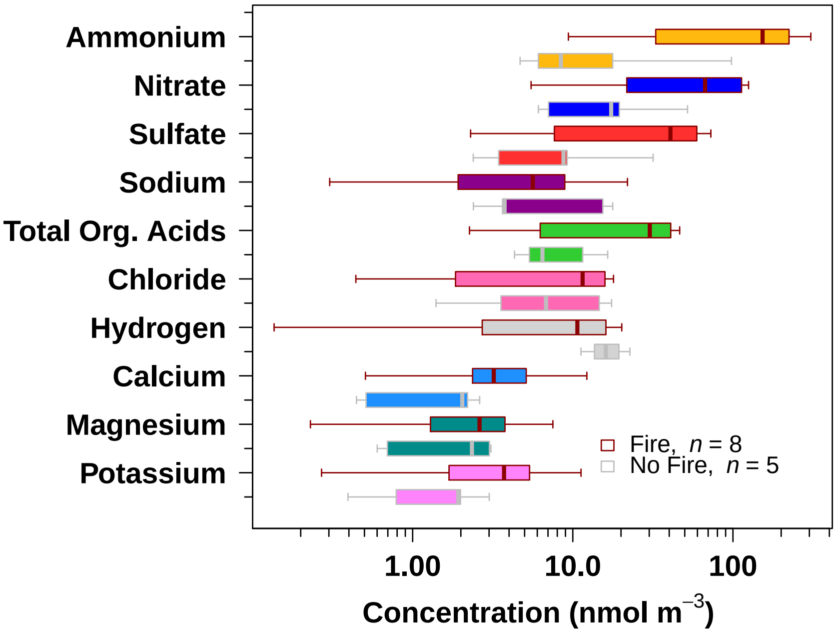

Fig. 5. Figure SI 6 Biomass Burning Constituents

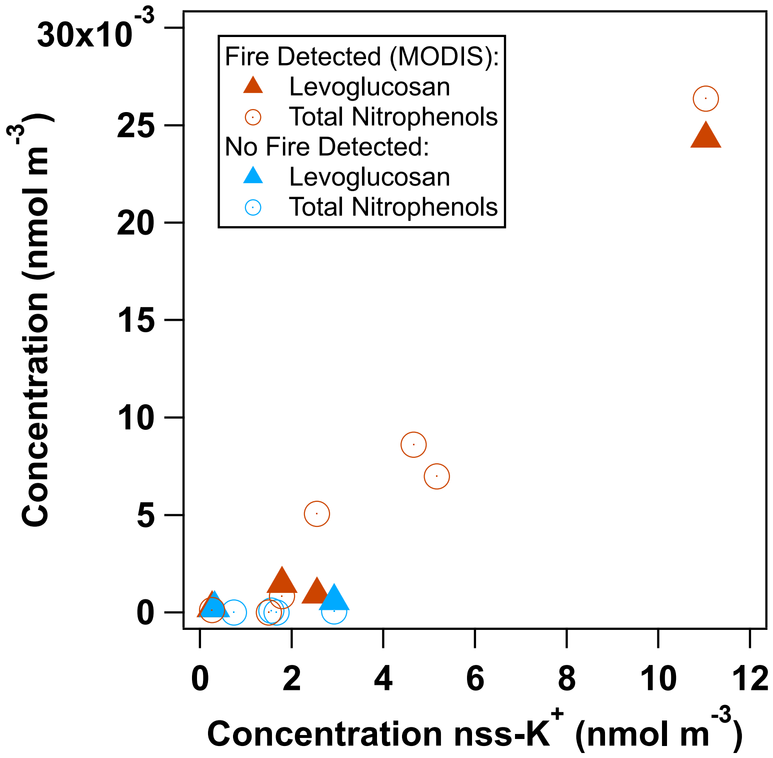

Fig. 6. Figure SI 7 Biomass Burning Correlation