Author response to Referee 1 comment on "Fog composition at Baengnyeong Island in the Eastern Yellow Sea: detecting markers of aqueous atmospheric oxidations" by A. J. Boris et al.

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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 blue; your comments are in black). 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 ? 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 ($\leq$2.5 μm diameter) SO_4^{-2} has been estimated at $\leq$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 SO4-2 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 and Varutbangkul (2006); Sorooshian et al. (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 and Varutbangkul (2006); ?); ?, other sources for oxalic acid in the atmosphere have been proposed: gas-phase oxidation of aromatic and anthropogenic molecules Borrás and Tortajada-Genaro (2012); Edney et al. (2000); Kalberer et al. (2000); Kamens et al. (2011); Kleindienst et al. (1999), diesel exhaust emissions Kawamura and Kaplan (1987), and forest fire emissions Narukawa and Kawamura (1999); ?.”*

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 and Meskhidze, 2013; Nguyen et al., 2013; ?). 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., 2010; 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 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.

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):

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

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.”

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Relevant Figures

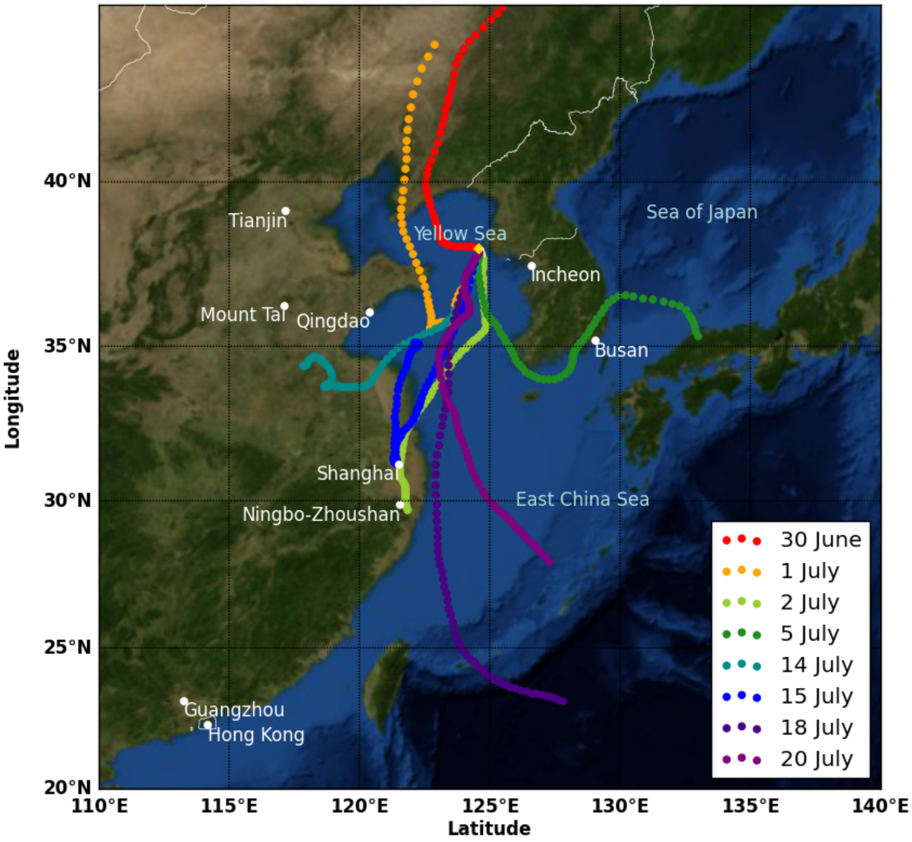

Figure 2: Back trajectories of air masses intercepted during fog events (72 hours at one hour time resolution; HySPLIT). Locations labeled on plot include Mount Tai, where previous atmospheric water chemical measurements were made, and the highest throughput shipping ports in the region pictured. The 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.

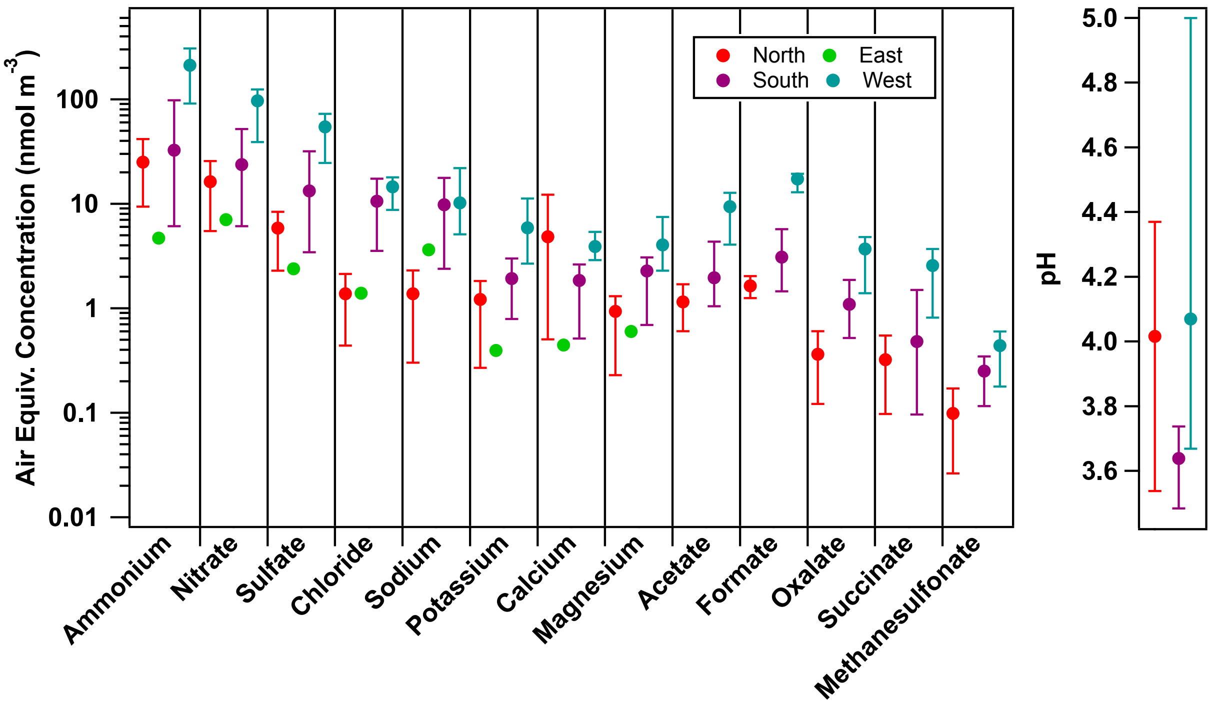

Figure 4: Sector analysis of most abundant inorganic fog water components, as well as selected organic acids. Highest concentrations of most species originated from the west. For Na^+ and Cl^-, high concentrations were also observed from the south. Ca^{+2} concentrations were also heightened within samples 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.

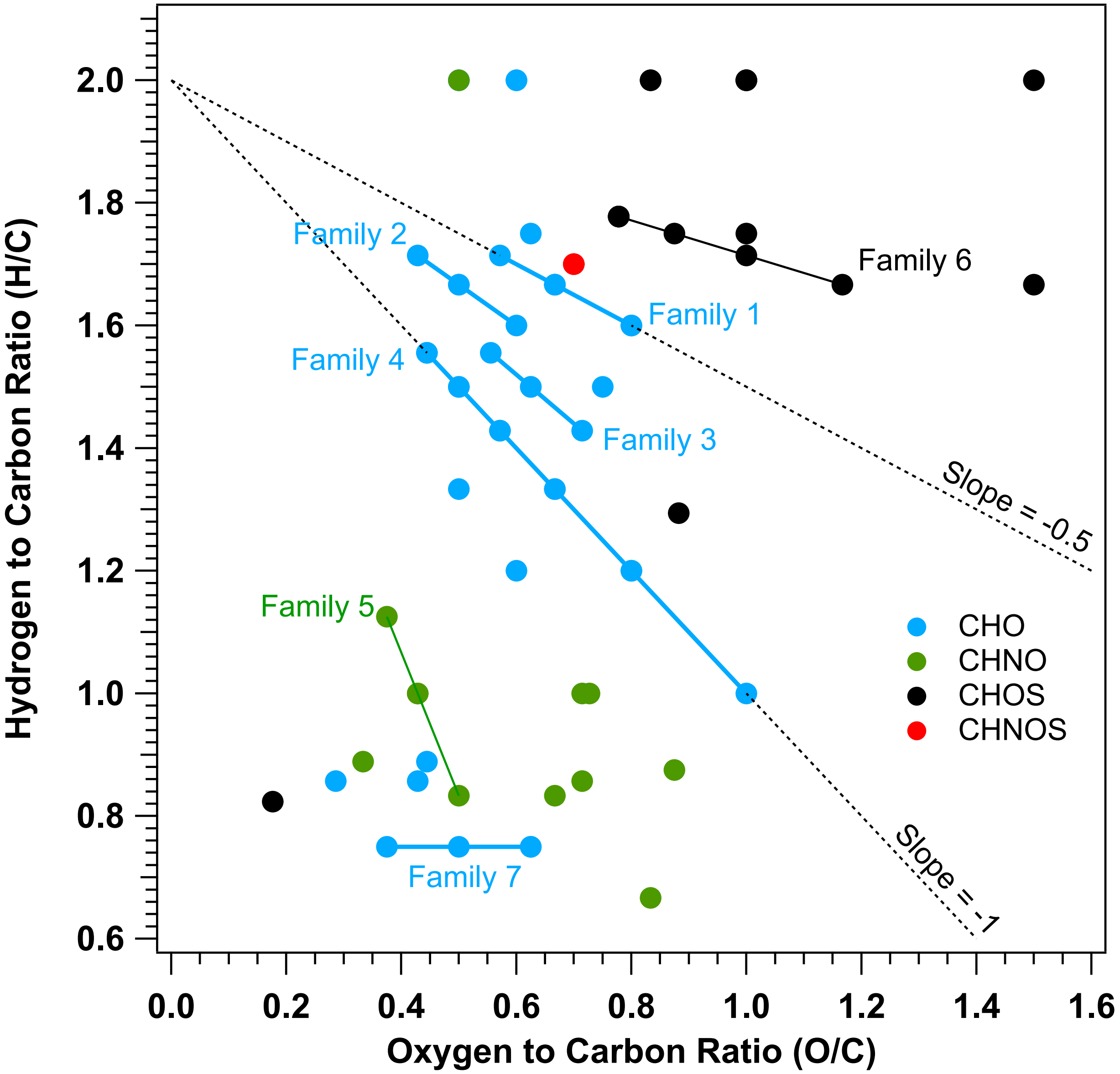

Figure 7: Polar organic compounds identified within fog samples using HPLC-(-)-ESI-HR-ToF-MS detection illustrated via a van Krevelen diagram. Colors of points distinguish compound elemental composition; solid lines show families differing by methylene groups of di-acids (blue, families 1-4), nitrophenols (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.

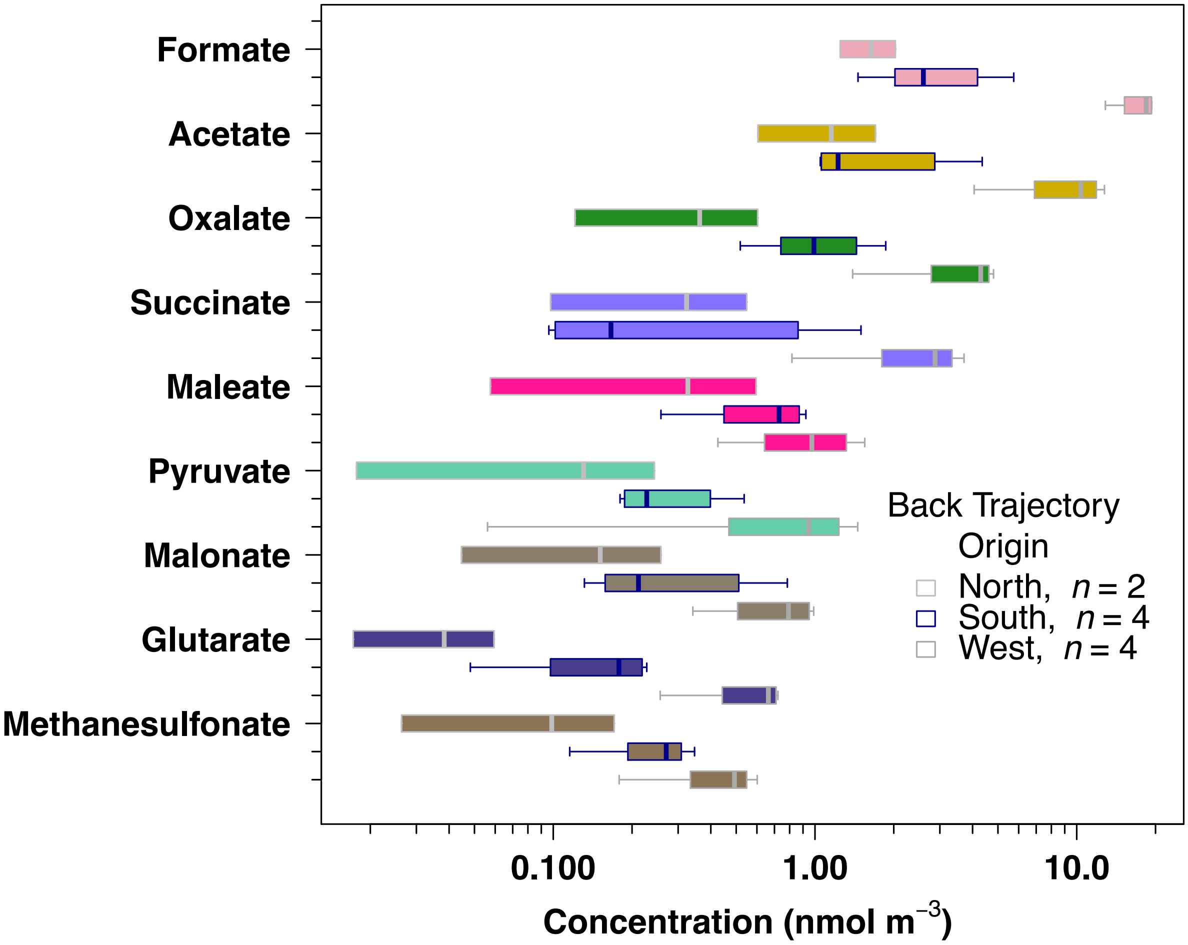

Figure SI-4: Sector analysis of most abundant organic acids, demonstrating that highest concentrations of organic acids originated from the west. Note that samples from the east were low in volume so that organic acids analyses were not performed (samples collected on 5 and 6 June 2014).

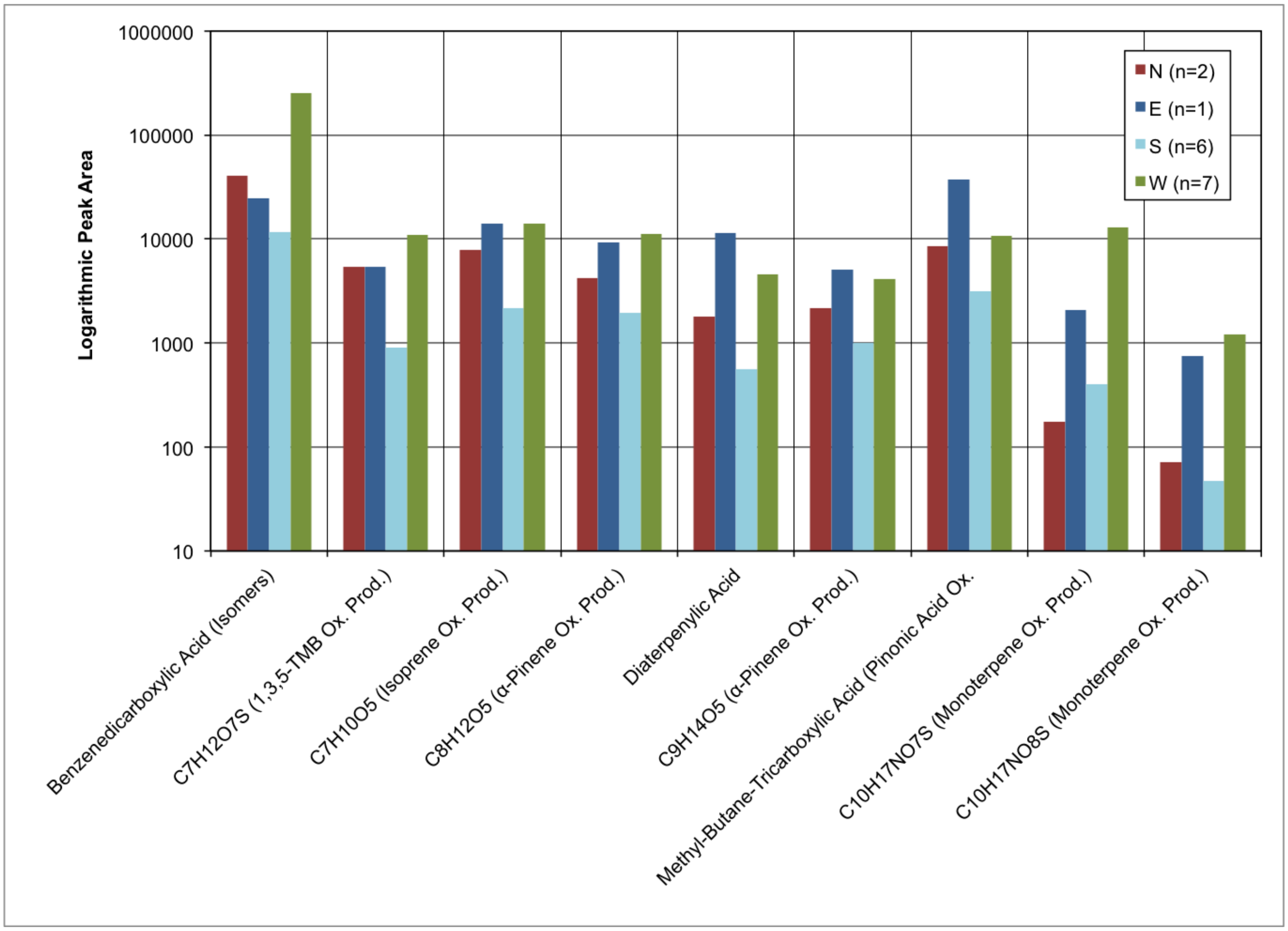

Figure SI-5: Peak areas of tentatively identified anthropogenic (two categories on left) and biogenic (two categories on right) species in BYI fog water (see Table 2). Samples with westerly back trajectories contained the greatest quantities of the anthropogenic species, while the samples collected with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

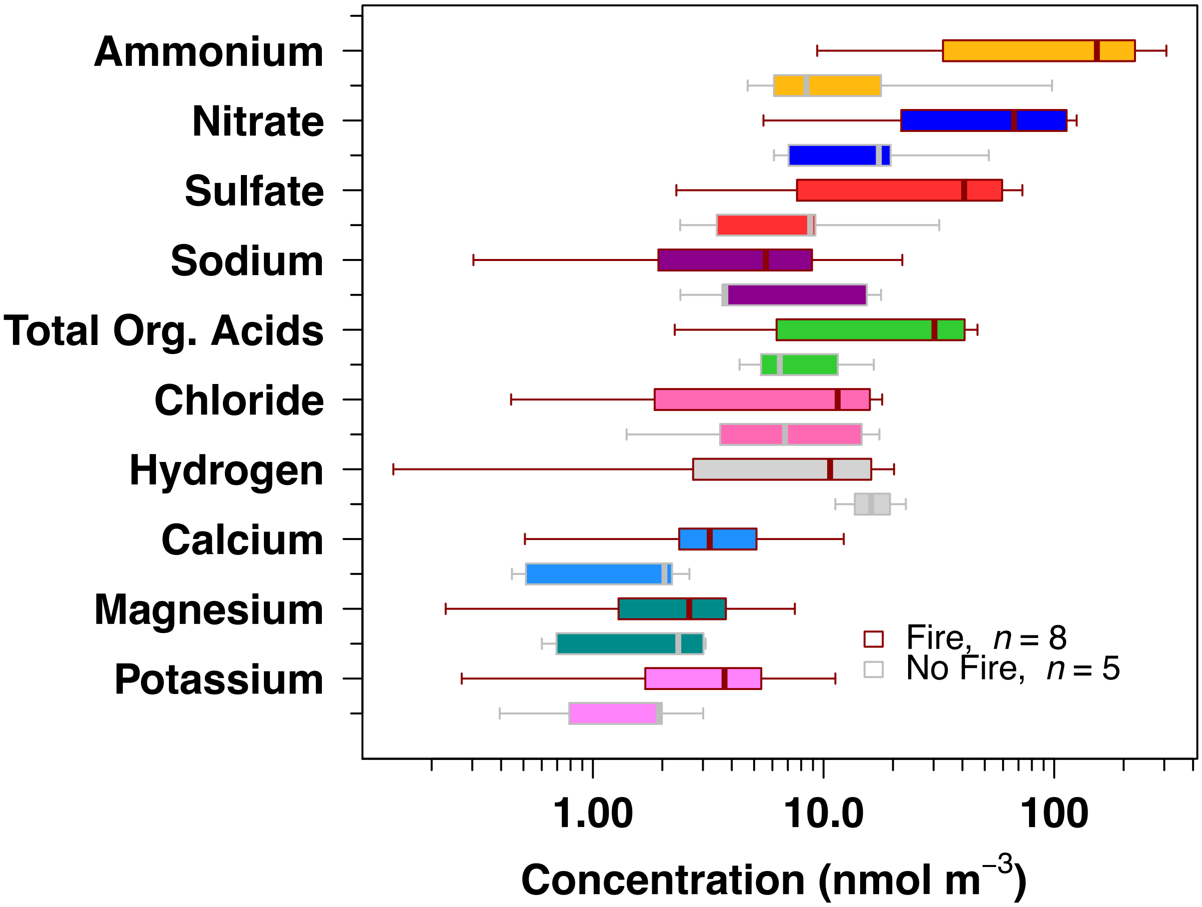

Figure SI-6: Contrast of most abundant species in fog samples between days with fire impact (based on qualitative observation of fires in MODIS fire product outputs, co-located with back trajectories). Note that fire periods included the samples from 07/02/14, which typically contained the greatest concentrations 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.

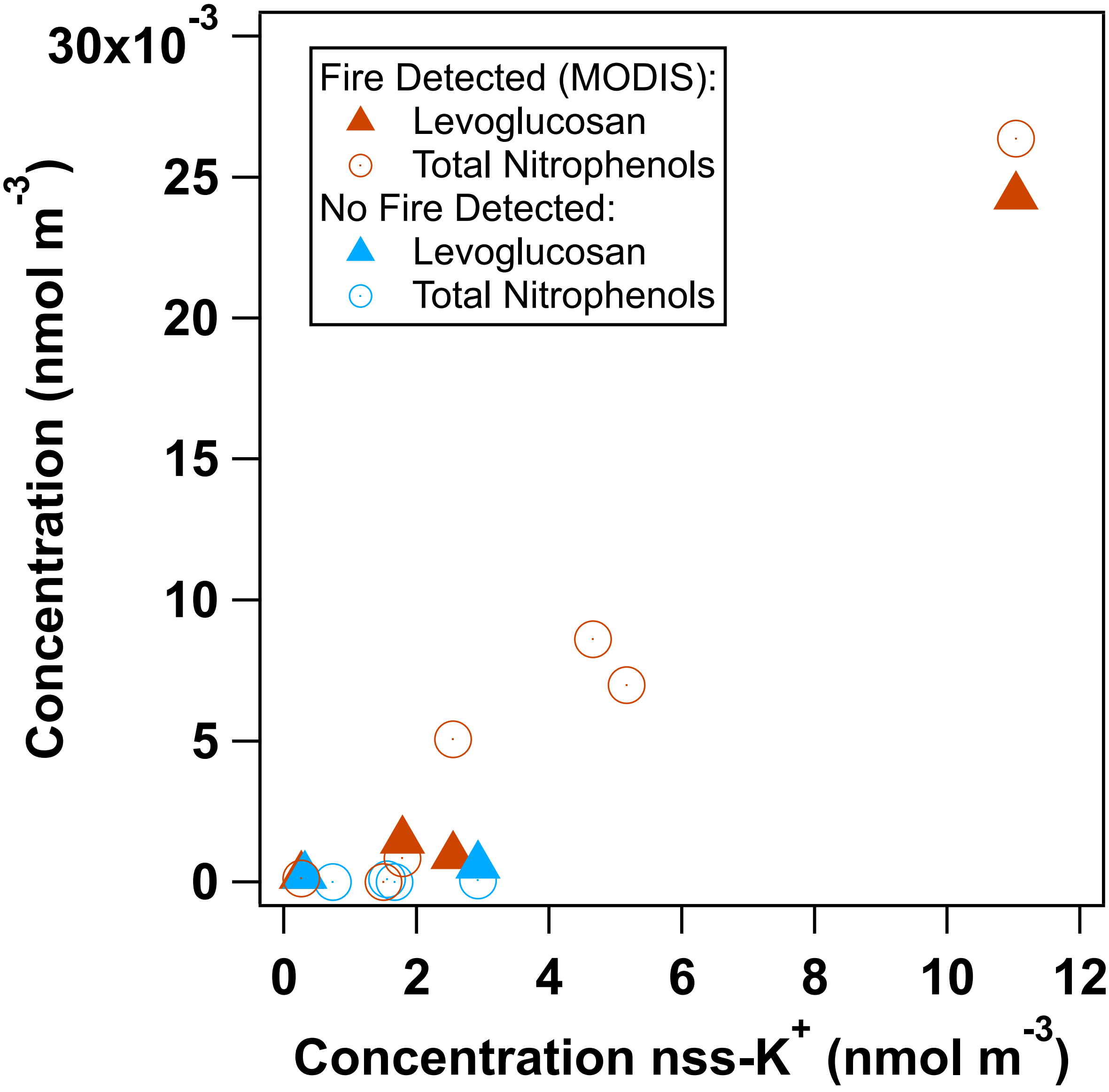

Figure SI-7: Correlation of levoglucosan (triangles) and total nitrophenol (circles) concentrations with those of non-sea salt K^+ (nss-K^+). Air equivalent concentrations were used to remove the impact of liquid water content between fog samples. Levoglucosan concentrations were only analyzed in six 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 \leq$0.001).

Author response to Referee 2 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; T. Lee; T. Park; J. Choi; S. J. Seo; J. L. Collett, Jr.

Response written by Alexandra J. Boris
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December 4, 2015

Dear Referee,

Thank you for your comments. Please see below for responses to your specific questions and suggestions (in blue; your comments are in black). 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

"This manuscript reports measurements of chemical composition of fog water at Baengnyeong Island in the Yellow Sea. It provides a very rich set of measurements of fog water chemical composition in a region where fewer field measurements are available. The paper shows evidence that strongly suggest aqueous phase oxidation of organics upwind of the island, thereby, providing insight into the atmospheric chemical processing in this specific region. The chemical components of the fog water measured in this study indicate that the samples were influenced by emissions from anthropogenic activities, marine background and forest fires. The most dominant chemical species measured, ammonium, showed no correlation to wind direction at the measurement site, indicating long-range transport. The concentration of S(IV) was low relative to SO_4^{2-}, which suggests that oxidation may have occurred upwind of BYI. I think this article is written clearly with easy to interpret plots. I recommend this manuscript for publications, although I suggest a few minor revisions."

Specific Comments:

1. Page 24881, Line 7: Could include more recent measurements of cloud water composition over the Eastern Pacific in the references here - Z. Wang, A. Sorooshian, G. Prabhakar, M. M. Coggon and H. H. Jonsson (2014): Impact of emissions from shipping, land, and the ocean on stratocumulus cloud water elemental composition during the 2011 E-PEACE Field Campaign, Atmospheric Environment, doi:10.1016/j.atmosenv.2014.01.020

We have added the E-PEACE campaign results to our discussion of field campaigns during which aqueous atmospheric organic processing evidence has been detected. Unfortunately, the measurements did not include, to our knowledge, measurement of peroxides or S(IV).

The following sentence has been added to the manuscript with regards to recent measurements of atmospheric constituents made during the E-PEACE campaign:

"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 and Varutbangkul, 2006; Sorooshian et al., 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)."

The following sentence has also been added to the manuscript with regards to shipping emissions impacts (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 ($\leq$2.5 μm diameter) SO_4^{-2} has been estimated at $\leq$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)."

2. Page 24884, Line 20: Are the r-squares reported here (and elsewhere in the paper) statistically significant?

Statistical significance (p-values) has been added to the text. Specifically, the following section describing organic acids contributions has been changed (line 455):

"Concentrations of low molecular mass organic acids were strongly correlated with one another (air equivalent concentrations): r^2=0.83 on average, with probability p $\leq$0.01 of random correlation, ranging from 0.47 to 0.99 (p $\leq$0.001 to 0.2) for C_1 -C_6 mono and di-acids. The predominance of succinate suggests a major anthropogenic source of organic acids at BYI (Kawamura and Usukura, 1993). While substantial contributions of oxalate to TOC suggest that AAOP reactions took place, they are not unequivocal evidence of it, since other atmospheric sources for oxalate have been documented (e.g., Kawamura and Kaplan, 1987; Yamasoe et al., 2000). The presence of MSA in the observed samples and its correlation with other measured organic acids (r^2 $\leq$0.7 and p $\leq$0.02 with all low molecular mass organic acids, r^2=0.88 and p $\leq$0.001 with oxalate) additionally supports the occurrence of AAOP upwind of fog water collection."

3. References Missing: Page 24874, Line 24-25: Kim et al., 2011 Page 24875, Line 13: Yoo et al., 2010

These references have been added to the manuscript reference section.

4. Figure 2: Interpretation of the map would be easier if it included more labels.

This figure has been re-made, and now includes regional labels, including many high-throughput shipping ports (Fig. 2).

Technical Corrections:

Page 2, Line 10: There should be a comma before the word gradient for clarity. Page 24877, Line 24: Please explain the abbreviation CSU

These corrections have been made.

References

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.

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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.

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.

Relevant Figures

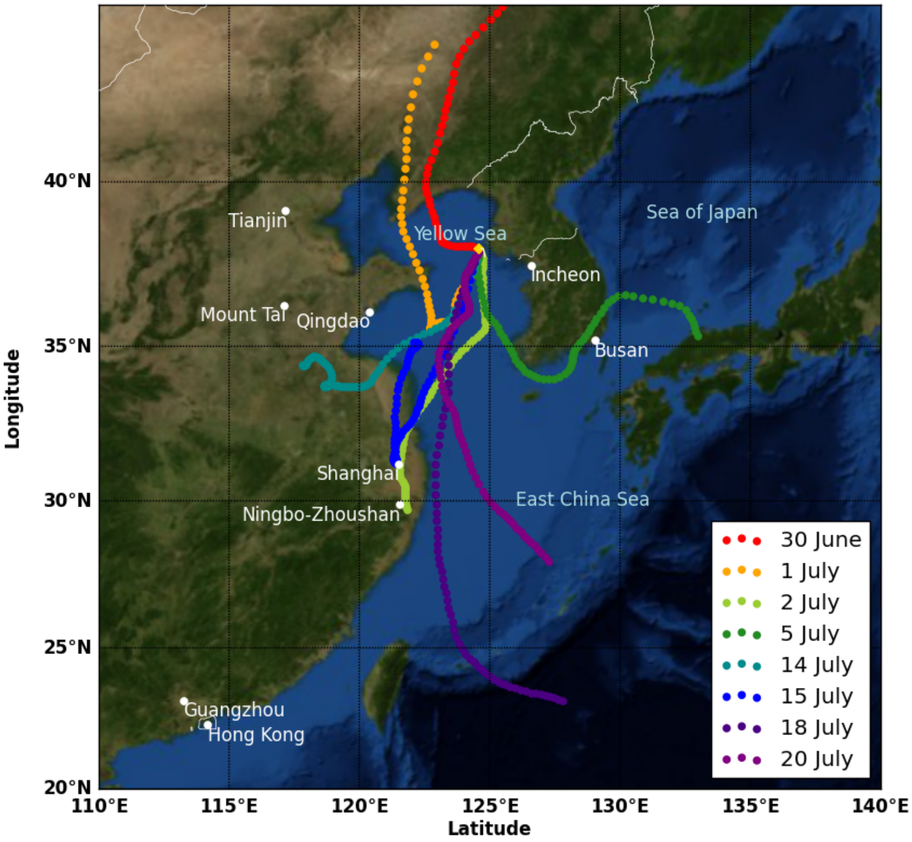

Figure 2: Back trajectories of air masses intercepted during fog events (72 hours at one hour time resolution; HySPLIT). Locations labeled on plot include Mount Tai, where previous atmospheric water chemical measurements were made, and the highest throughput shipping ports in the region pictured. The 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.

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Fog composition at Baengnyeong Island in the Eastern Yellow Sea: Detecting markers of aqueous atmospheric oxidations

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Abstract. Samples of fog water were collected at Baengnyeong Island (BYI) in the Yellow Sea during the summer of 2014. The most abundant chemical species in the fog water were NH_4^+ (mean of 2220 µM), NO_3^- (1260 µM), SO_4^{-2} (730 µM), and Na^+ (551 µM), with substantial contributions from other ions consistent with marine and biomass burning influence on some dates. The pH of the samples ranged between 3.48 and 5.00, with a mean of 3.94, intermediate within pH values of fog/cloud water reported previously in Southeast Asia. Back trajectories (72 hrs) showed that high relative humidity (>80%) was encountered upwind of the sampling site by all but one of the sampled air masses, and that the fog composition at BYI can be impacted by several different source regions, including the Sea of Japan, Southeastern China, Northeastern China, and the East China Sea. Sulfur in the collected fog was highly oxidized: low S(IV) concentrations were measured (mean of 2.36 µM) in contrast to SO_4^{-2} and in contrast to fog/cloud S(IV) concentrations from pollutant source regions; organosulfate species were also observed and were most likely formed through aging of mainly biogenic volatile organic compounds. Low molecular mass organic acids were major contributors to total organic carbon (TOC; 36-69%), comprising a fraction of TOC at the upper end of that seen in fogs and clouds in other polluted environments. Large contributions were observed from not only acetic and formic acids, but also oxalic, succinic, maleic, and other organic acids that can be produced in aqueous atmospheric organic processing (AAOP) reactions. These samples of East Asian fog water containing highly oxidized components represent fog downwind of pollutant sources and can provide new insight into the fate of regional emissions. In particular, these samples demonstrate the result of extensive photochemical aging during multiday transport, including oxidation within wet aerosols and fogs.

Added

1 Introduction

The chemistry of the atmosphere occurs within multiple phases, one of which is the aqueous phase. Atmospheric water includes fog droplets, cloud droplets, and wet aerosol particles, all of which can act as miniature aqueous reaction vessels. Distinct chemical phenomena occur within the atmospheric aqueous phase: formation of organic hydrates and protonation/deprotonation occur frequently, time spent by reactants in proximity to one another increases, and interactions involving metals such as the Fenton reactions and iron-oxalate complexes are possible (Lelieveld and Crutzen, 1991; Zuo and Hoigné, 1994). The study of carbonaceous species is particularly pertinent to understanding particle, gas, and aqueous phase atmospheric processes because the composition and formation of organics are complex. Particle phase organics in particular cannot yet be modeled well by laboratory or computer experiments (Aiken et al., 2008; Chen et al., 2015; Heald et al., 2005, 2010) and can account for a large fraction of aerosol mass (Fu et al., 2008; Lin et al., 2014; Liu et al., 2012). Uptake of organic components into atmospheric water represents a pathway for their removal from the atmosphere, via deposition and/or chemical degradation (Collett et al., 2008). Aqueous atmospheric organic processing (AAOP) can yield low molecular mass products with typically increased volatilities, effectively reducing pollutant concentrations in an air mass via chemical water treatment (Brinkmann et al., 2003; Zhang et al., 2003). Some reactions of organic material within atmospheric water form aqueous secondary organic aerosol (aqSOA) by oxidation of dissolved organic precursors to form lower volatility products that remain in the particle phase as fog drops evaporate (Ervens et al., 2011).

The most common approach to studying AAOP reactions in the lab is to introduce $^{\bullet}$OH oxidant into a bulk solution of a standard carbonaceous ”precursor” molecule such as glyoxal and monitor the reaction as it proceeds (Lim et al., 2010). Some assumptions of this common type of simulation can also be studied within a lab: for example, real cloud water constituents have been shown to cause an effective kinetic slowing, via oxidant competition, of a given organic chemical reaction (Boris et al., 2014). However, while these commonly applied lab simulations are useful for studying specific AAOP reactions, more accurate representations of fogs and clouds are needed to validate simulation results and elucidate more complex phenomena. Daumit et al. (2014) demonstrated that microphysical dynamics of in-droplet diffusion and bidirectional air-water mass transfer are inaccurate in simple ”bulk reactions”: carrying out a reaction within a photoreactor does not allow species, including oxidants, to continuously partition into and out of solution, as in the real atmosphere (Ervens et al., 2003). Bulk photoreactions also do not correctly simulate differences in chemical constituents between droplets within a cloud (Bator and Collett, 1997; Collett et al., 1994), gradients inside individual droplets (Ervens et al., 2014), or physical processes of fogs and clouds such as evaporation and deposition (Collett et al., 2008; Herckes et al., 2002b; Pandis et al., 1990).

Added

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 and Varutbangkul, 2006; Sorooshian et al., 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 and Varutbangkul, 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 (Edney et al., 2000; Kamens et al., 2011; Kleindienst et al., 1999; Borrás and Tortajada-Genaro, 2012; Kalberer et al., 2000), diesel exhaust emissions (Kawamura and Kaplan, 1987), and forest fire emissions (Narukawa and Kawamura, 1999; Yamasoe et al., 2000).

High aerosol concentrations near major cities in China have been attributed in large part to secondary aerosol formation processes from various sources of carbonaceous emissions (Bian et al., 2014; Zheng et al., 2005). Cloud water collected on Mount Tai in Shandong Province (west of the Yellow Sea) contained some of the highest total organic carbon (TOC) concentrations measured in the world (Herckes et al., 2013; Shen et al., 2012; Wang et al., 2011), consistent with strong regional organic pollutant sources, including agricultural burning (Desyaterik et al., 2013). AAOP reactions could produce measurable quantities of aqSOA and low molecular mass organic acids during atmospheric transport of chemicals, especially at high concentrations and within humid environments as observed in Southeast Asia. Anthropogenic emissions from mainland China and Korea frequently impact remote sites around the Yellow Sea (Kim et al., 2011). Oxygenated organic species observed within atmospheric water and aerosol samples at coastal sites in South Korea (Decesari et al., 2005; Lee et al., 2015) are evidence for AAOP reactions occurring in this part of the world.

Fog water was collected at BYI to characterize the composition of fog formed in aged air masses intercepted in the Eastern Yellow Sea. Frequent sea fog events are observed at BYI, particularly during the late spring and early summer (Cho et al., 2000; Zhang et al., 2009). In addition to gathering new information about the composition of fogs in this little-studied region, chemical measurements discussed herein helped to determine whether AAOP reactions occurred at BYI, either within the fog or upwind of the sampling site within cloud droplets/wet aerosol particles. Specifically, it was hypothesized that highly oxidized sulfur and oxidized organics (e.g., low molecular mass organic acids such as oxalic acid) would be measured within the fog water, indicating that AAOP reactions had occurred.

2 Methods

2.1 Study overview

Fog water was collected from 29 June through 21 July 2014 on BYI at an established atmospheric research center (ARC) run by the Korean National Institute for Environmental Research (NIER; 37°58’0”N, 124°37’4”E). The collection site was approximately 100 m above sea level (Yoo et al., 2010; Zhang et al., 2009) and was collocated with a meteorological station and an international Interagency Monitoring of Protected Visual Environments (IMPROVE) network site. Meteorological data were accessed online (http://rp5.ru/Weather_archive_on_Baengnyeong_Island). The ARC is on the northwest corner of the island; to the east and south are local agricultural sources of emissions and small towns that are home to approximately 4,000 total permanent residents. Regular transport of air masses from Eastern China and mainland South Korea were expected to provide a high loading of pollutants to the island (Kim et al., 2006), and frequent haze events were indeed encountered during the study. Three day (72 hr) back trajecto-

Added “,” and changed from “h” to “hr”

Changed for clarity

ries generated using the NOAA HySPLIT model (online version: http://ready.arl.noaa.gov/HYSPLIT.php; 0.5 degree global GDAS archived meteorological data) were used to determine the upwind histories of air masses sampled during fog events. The model was initiated using the coordinates of the research station, a height of 100 m, an the approximate beginning time of each fog event. Latitude, longitude, and air mass relative humidity (RH) as estimated by the model were outputted at each one-hour interval. Periods during which large-scale fires may have impacted fog samples were detected using MODIS archive graphics retrieved from the Naval Research Lab 7 SEA Data Repository (http://www.nrlmry.navy.mil/aerosol-bin 7seas/view_7seas_by_date_t.cgi) and NASA FIRMS (produced by the University of Maryland and provided by NAS FIRMS operated by NASA/GSFC/ESDIS; https://earthdata nasa.gov/active-fire-data-tab-content-6).

2.2 Fog collection and handling

A size-fractionating Caltech Active Strand Cloudwater Collector (sf-CASCC; Demoz et al., 1996) was used to collec small and large fog droplets (diameters predominantly 4-1 μm, and <16 μm, respectively). The sf-CASCC is a polycarbonate structure outfitted with a fan at the rear to pull droplet laden air into the body of the collector (at 19 $\mathrm{m^3\,min^{-1}}$) Droplets were impacted onto rows of forward-tilted Teflo rods and strands and pulled by gravity and aerodynamic dra into Teflon sampling troughs at the bottom of the collecto Fog water was collected for durations of one to three hours four events (1, 2, 5, and 18 July) were long enough for collection of multiple fog samples. A Gerber Particulate Volume Monitor (PVM-100; Gerber, 1991) was used to determine the liquid water content (LWC) of the atmosphere during the study; an approximate threshold of 30 $\mathrm{mg\,m^{-3}}$ wa used to initiate fog sampling. When fog was not present, th sf-CASCC inlet and outlet were covered to prevent collectio of contaminants onto the inner surfaces of the collector. Th sf-CASCC was cleaned after each fog event: a high powe sprayer was used to rinse deionized water (approx. 2-3 L through the collector body. Field blanks were collected after each cleaning, and were stored and analyzed in the sam manner as samples. Limits of detection (LODs) were calculated using these blanks and are tabulated in Table 1. Dee cleanings were also performed periodically by removing th Teflon strands, rods, and troughs from the body of the sf CASCC and scrubbing all surfaces with Triton X-100 detergent, then thoroughly rinsing all surfaces with deionize water. Collected fog water was refrigerated for a short perio of time (<3 hrs) prior to separation into aliquots for specifi chemical analyses.

Changed from “h”

Contamination from Triton X-100 detergent in the fog water samples between 14 and 19 July and (seven samples was discovered by positive ionization HR-ToF-MS analysis TOC concentrations are not reported for the affected samples; however, duplicate analyses of standards of inorganic ions and organic acids containing Triton X-100 were not different from uncontaminated standards. Peroxides, formaldehyde, and S(IV) were also assumed to be unaffected by the contamination. Deionized water used in analyses and sample collection at BYI was obtained from a distillation and ion exchange/UV light purification system at the ARC. The calculated charge balance and sample volume were used to determine whether measurements made from a given fog sample were accurate and should be included in results (most samples not containing balanced ionic charges consisted of small liquid volumes). If charge balance, which included all organic and inorganic ionic species, was not within 1.0 ± 0.3 (positive/negative charge), that sample was not included (four of 17 samples were excluded). Directly after sample collection, liquid water from samples with only small collected volumes were dispensed to aliquots according to volume needed and importance of analysis to the study purpose; therefore, in some cases, only some analyses could be carried out for a given sample. For those samples with insufficient volumes (<2 mL) of the small droplet fraction due to a predominance of large droplets in the sampled fog, the large droplet fraction was assumed to be representative of the entire fog water sample in data analyses. Chemical and physical interactions differ between droplet sizes, and the collection of different sizes of droplets helps preserve real differences in drop composition as compared to bulk fog sampling (Hoag et al., 1999; Moore et al., 2004a, b; Reilly et al., 2001). Mean fog constituent concentrations were calculated from the two droplet fractions (e.g., [(small drop sample volume × small sample concentration) + (large drop volume × large drop concentration)] / total sample volume); mean, median, maximum, and minimum values calculated over the size fraction weighted values of all samples were used in further discussion of the fog chemical composition. Air equivalent concentrations (also referred to as loadings) were calculated from molar concentrations in water to establish trends in fog water constituents independent (or less dependent) of the amount of liquid water present during a given fog event. Equation (1) was used, where *i* represents a given chemical constituent of interest.

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

The collection rate of the sf-CASCC was assumed to be 19.0 $\mathrm{m^3\ air\ min^{-1}}$ (Demoz et al., 1996) and the density of water was assumed to be 1.00 $\mathrm{g\,mL^{-1}}$.

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Arrows less dense, more defined, plot color improved

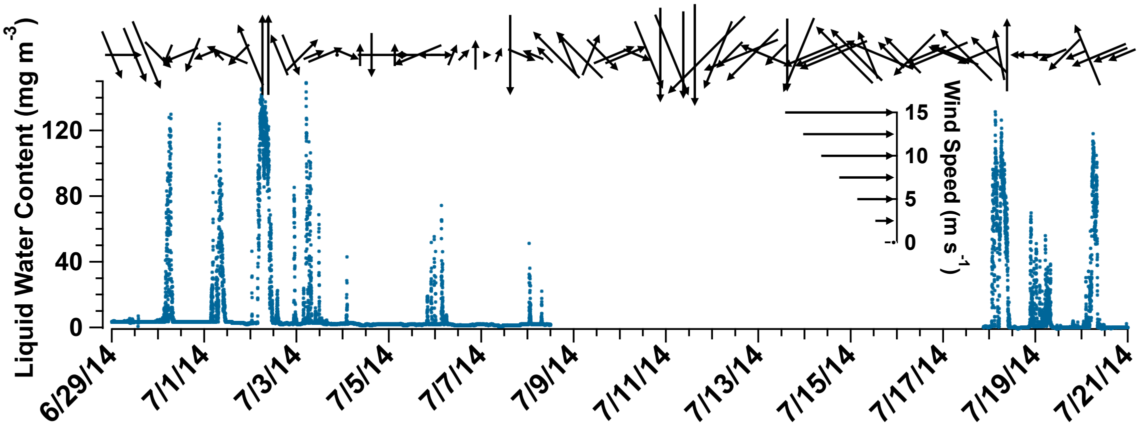

Figure 1. Wind speed and direction during fog sampling period, shown as vector arrows (top): speed is displayed as the length of each arrow and direction is displayed as tilt, pointing away from wind origin. LWC measured during the entire study period is shown in blue along the bottom of the plot. Fog was not collected in mid-July during the monsoonal period.

2.3 Fog water analysis

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). Measurement of fog water pH was carried out at the BYI ARC using a Cole-Parmer microelectrode and pH meter, calibrated with pH 4 and 7 buffers. The mean of three replicate measurements was recorded for each sample. Preservation of other aliquots for chemical analyses (as performed previously; e.g., Benedict et al., 2012) was as follows: peroxides were preserved with *para*-hydroxy-phenyl-acetic acid (POPHA) and ethylenediaminetetraacetic acid (EDTA); S(IV) was stabilized using formaldehyde, *trans*-1,2-cyclohexylenedinitrilotetraacetic acid (CDTA) and bovine catalase enzyme was added to eliminate hydrogen peroxide; formaldehyde was preserved with Na_2SO_3 and CDTA; samples for analysis of major ionic species (Cl^-, NO_2^-, NO_3^-, SO_4^{-2}, Na^+, NH_4^+, K^+, Mg^{+2}, Ca^{+2}) were aliquotted without added reagents; and microbial activity was eliminated for the storage of organic acids and other organic components by addition of chloroform. Aliquots for TOC and carbohydrates (including levoglucosan) analysis were taken from thawed samples after arrival at Colorado State University (CSU). Additional organic molecules were identified and/or quantified via high performance liquid chromatography (HPLC) followed by negative electrospray ionization high-resolution time-of-flight mass spectrometry ((-)-ESI-HR-ToF-MS) from the aliquot preserved for organic acids analysis. Levoglucosan and other carbohydrates were measured using high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) as described previously (Sullivan et al., 2008) from frozen remaining fog water samples; only some samples were analyzed for carbohydrates.

Added

3 Results and discussion

Fog water was collected during nine fog events (17 total samples) at the BYI ARC during July 2014; seven events and 13 samples were included in mean chemical concentrations calculated over the duration of the sampling campaign and will be discussed here (Fig. 1). Events on 2 and 18 July persisted for several hours, allowing collection of up to five samples per event. Air masses sampled during the seven fog events traveled either from the south over the Yellow Sea as documented in Zhang et al. (2009), from the west over Eastern China, from the east over the Sea of Japan, or from the north over Northeastern China (Fig. 2).

Added

Changed figure: added labels, topographical coloring

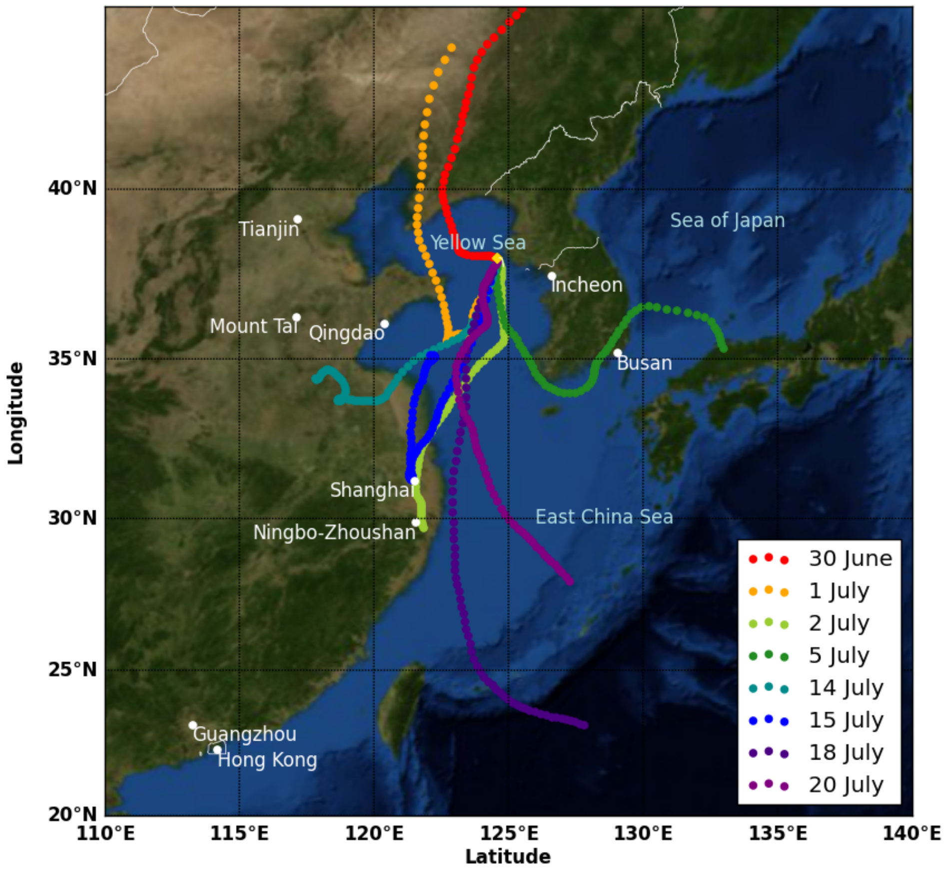

Figure 2. Back trajectories of air masses intercepted during fog events (72 hours at one hour time resolution; HySPLIT). Locations labeled on plot include Mount Tai, where previous atmospheric water chemical measurements were made, and the highest throughput shipping ports in the region pictured. The 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.

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3.1 Fog characteristics and major contributing species

A moderately acidic pH was observed (study mean 3.94, ranging between 3.48 and 5.00). This value is intermediate between values measured in fog and cloud samples from Southeast Asia (Mount Tai: pH 3.68, Wang et al., 2011; Jeju Island, Korea: pH 5.2, Kim et al., 2006; Daekwanreung, Korea: pH 4.7, Kim et al., 2006; and Shanghai, China: pH 5.97, Li et al., 2011a). Major inorganic species contributing to the measured acidity of the fog water at BYI (Table 1; Fig. 3) were NH_4^+ (mean concentration of 2220 µM), followed by NO_3^- (1260 µM), and SO_4^{-2} (730 µM); these concentrations were elevated compared to fog and cloud samples collected globally (e.g., Collett et al., 2002; Raja et al., 2008; Wang et al., 2011). Sea salt was also an abundant constituent of the fog water (mean concentrations of 551 µM Na^+ and 253 µM Cl^-), as was organic matter (mean 276 µM, estimated using a molecular mass of 100 $\mathrm{g\,mol^{-1}}$ and OM/OC=1.8 Zhang et al., 2005). The mean NH_4^+ concentration measured at BYI was within the upper range of measured NH_4^+ in fog and cloud samples (similar to e.g., the Po Valley, Italy, Fuzzi et al., 1992; and Baton Rouge, Louisiana, Raja et al., 2008). Although agriculture was a main land use on BYI, no correlation between wind direction and fog NH_4^+ concentrations was observed (Fig. SI-1), suggesting long-range transport of fine particle NH_4^+ as an important source. The concentrations

Added text regarding dust/Ca

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; Mattigod et al., 1990; Kawamura et al., 2004).

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.

Added discussion on sector analysis

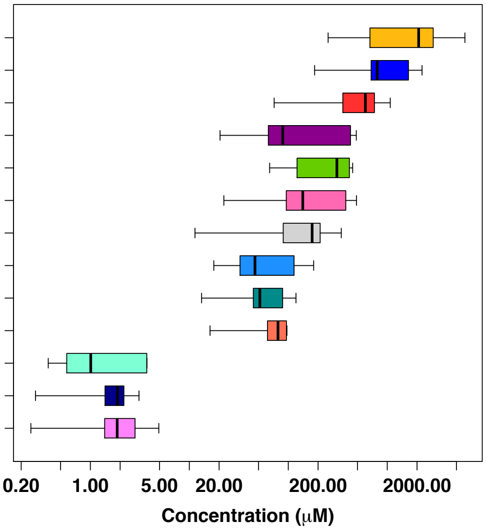

Figure 3. Concentrations of major components quantified in BYI fog samples. Boxes show 25th and 75th percentiles with the median bar in the center, and whiskers show outliers. Total organic matter was calculated from measured TOC using a ratio of 1.8 g/1.0 g OM/OC (Zhang et al., 2005) and an estimated mean molecular mass of 100 g mol^{-1}. Note that for most ions, n=13, for pH, S(IV) and peroxides, n=11, for formaldehyde, n=10, and for total organic matter, n=8.

Un-capitalized N, whiskers are now outliers

3.2 Marine source contribution

Evidence of a marine contribution to fog composition was clear. Upwind trajectories of all air masses sampled included some duration over the Yellow Sea, and in some cases the Sea of Japan (Fig. 2). Measured Ca^{+2} was contributed in part by sea salt particle scavenging: 21% was attributed to sea salt (Fig. SI-2) using an observed ratio in seawater of 0.022 mol Ca^{+2}/mol Na^+ (Lee, 2007; Radojevic and Bashkin, 2006). Depletion of particle phase Cl^- appears to have occurred in some scavenged sea salt particles, likely due to displacement of HCl to the gas phase by NO_3^- and SO_4^{-2} (Mouri and Okada, 1993) or organic acids (Wang et al., 2015). Measured Cl^-/Na^+ molar ratios ranged as low as 0.08, with a mean value of 1.20; this mean value is within measurement error (Table 1) of the typical sea salt ratio of 1.16 (Radojevic and Bashkin, 2006). In some samples, the Cl^- concentration was in excess of the sea salt ratio, indicating possible contributions from other sources such as incineration or coal combustion (McCulloch et al., 1999). Small contributions of K^+ (study mean concentration 82.5 µM) and SO_4^{-2} were estimated to derive from scavenged sea salt particles: only 12% of the measured K^+ and 6% of the SO_4^{-2} were attributed to a marine source on average. This estimate of nss-SO_4^{-2} does not account for SO_4^{-2} formed via oxidation of biogenic, marine dimethylsulfide, which could be as much as 12% (Yang et al., 2009). Elevated concentrations of cations including K^+ in aerosol have also been associated with the influence of biomass burning activities (Andreae, 1983; Lee et al., 2010), mineral dust from arid regions (Zhang et al., 1993), and/or construction in urban areas (Li et al., 2011b).

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3.3 Inorganic sulfur

Aqueous sulfur oxidation in the pH range measured in this study (3.48-5.00) is expected to be dominated by reaction with H_2O_2 (Rao and Collett, 1995). The mean concentrations of total peroxides and S(IV) (7.8 µM and 2.36 µM, respectively; Table 1) were low compared to the mean S(IV) and peroxides concentrations measured during summer 2007 and 2008 field campaigns at Mount Tai, China (Shen et al., 2012), consistent with a low potential for additional S(IV) oxidation within the BYI fog samples (Fig. 5). Since Mount Tai is located west across the Yellow Sea from BYI and is influenced by the abundant SO_2 sources in Shandong Province including large numbers of coal-fired power plants, these observations are consistent with extensive aging of S(IV) during transport to the BYI fog collection site. In contrast to BYI measurements, cloud samples from remote areas contain high concentrations of peroxides and low concentrations of S(IV) (1.9-610 µM peroxides, <0.91-3.7 µM S(IV), Straub et al., 2007; Benedict et al., 2012). Measured SO_4^{-2} was abundant within BYI samples, demonstrating that sources of atmospheric sulfur existed upwind, and that oxidation of sulfur occurred prior to arrival at BYI. Between 98.9% and 99.8% of sulfur measured (as the sum of SO_4^{-2} and S(IV)) was in the form of SO_4^{-2}. 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 (<1 µm diameter) SO_4^{-2} has been estimated at ≤15% from ship oil combustion in this region (Lauer et al., 2007),

Figure added

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Added discussion of shipping impact

Added figure on sector analysis

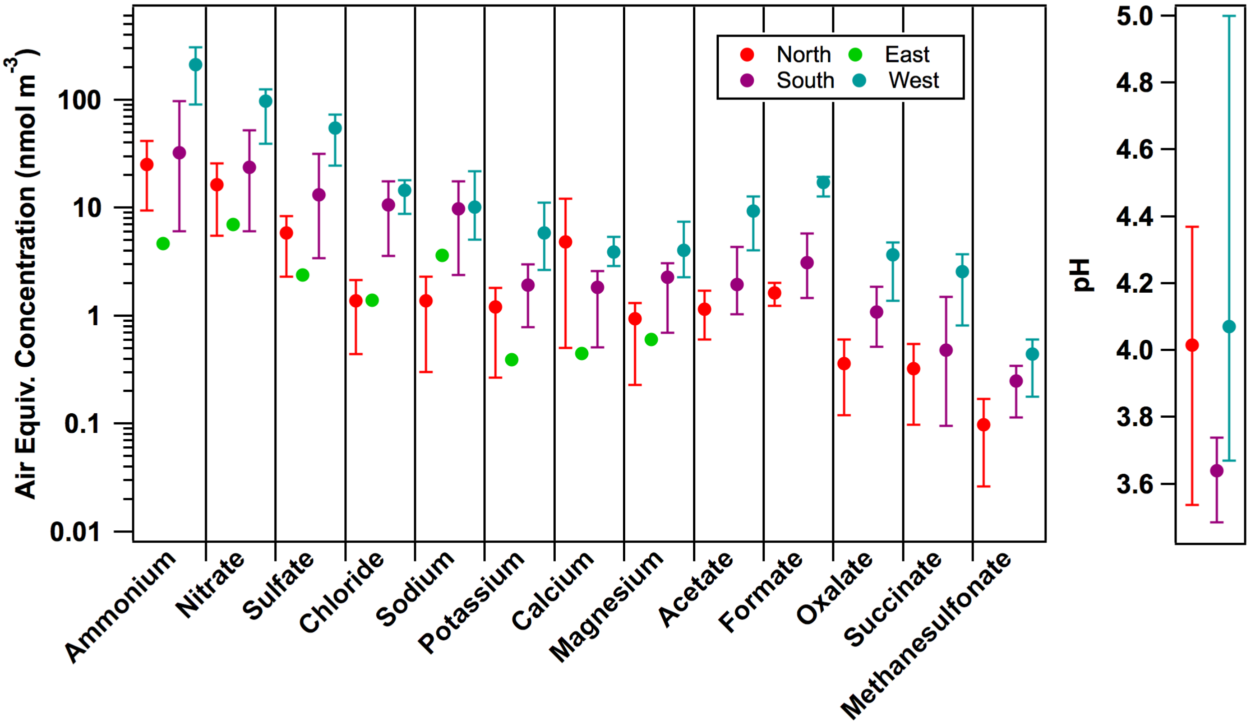

Figure 4. Sector analysis of most abundant inorganic fog water components, as well as selected organic acids. Highest concentrations of most species originated from the west. For Na^+ and Cl^-, high concentrations were also observed from the south. Ca^{+2} concentrations were also heightened within samples 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.

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). Further findings regarding aerosol sources at BYI will be elucidated from the aerosol composition data collected simultaneously with fog water (Lee et al., in preparation). Methanesulfonic acid (MSA) was also observed within all fog samples collected at BYI, indicating that oxidation of marine emissions via either $^\bullet$OH or $^\bullet NO_3$ reaction occurred upwind of fog collection at BYI (Seinfeld and Pandis, 2006; Kukui et al., 2003; Scaduto, 1995).

Moved references, discussion on MSA oxidation

3.4 Total organic carbon

Concentrations of fog water TOC measured at BYI were 3.60-24.8 $\mathrm{mg\,C\,L^{-1}}$, with a mean of 15.3 $\mathrm{mg\,C\,L^{-1}}$, comparable to concentrations measured in polluted environments globally (Herckes et al., 2013). Although the mean BYI TOC was also similar to that measured in cloud water from Mount Tai during the summer of 2008 (15.8 $\mathrm{mg\,C\,L^{-1}}$), several samples impacted by agricultural burning were collected during the latter campaign ranging between 100 and 200 $\mathrm{mg\,C\,L^{-1}}$ (Shen, 2011).

3.5 Organic acids

The products of AAOP reactions commonly include C_2-C_4 (two to four carbon) oxo- and di-carboxylic acid molecules (Lim et al., 2010). The percent BYI fog TOC accounted for by organic acids was 36-69% (mean 52% by mole; n=8), which is at the upper end of values typical for fog samples (e.g., 16% at Davis, CA, Herckes et al., 2002a; 18% at Angiola, CA, Ervens et al., 2003; 43% at Fresno, CA, Collett et al., 2008; 44% at Baton Rouge, LA, and 51% at Houston, TX, Raja et al., 2008). Among the organic acids quantified, major contributions to TOC came not only from acetate and formate, but also succinate, maleate and oxalate, with

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Table 1. Mean, minimum, and maximum concentrations of organic and inorganic species quantified in fog samples collected at BYI. Values below the LOD are shown in italics.

Chemical	Unit	No. Samples	Aqueous Concentration Mean	Min	Max	LOD	Uncertainty (95% CI)	Air Equivalent Concentration Mean	Unit
pH	–	11	3.94	3.48	5.00	–	–	11.8	$\mathrm{nmol\,m^{-3}}$
NH_4^+	µM	13	2220	253	6090	7.41	4	97.8	$\mathrm{nmol\,m^{-3}}$
NO_3^-	µM	13	1260	185	4900	0.34	10	49.0	$\mathrm{nmol\,m^{-3}}$
SO_4^{-2}	µM	13	730	72.0	2270	7.16	0.4	26.6	$\mathrm{nmol\,m^{-3}}$
Na^+	µM	13	551	24	2920	2.06	2	7.55	$\mathrm{nmol\,m^{-3}}$
Cl^-	µM	13	253	22	900	0.76	3	9.29	$\mathrm{nmol\,m^{-3}}$
K^+	µM	13	83	16	172	0.70	2	3.17	$\mathrm{nmol\,m^{-3}}$
Ca^{+2}	µM	13	77	12	217	0.22	1	3.23	$\mathrm{nmol\,m^{-3}}$
Mg^{+2}	µM	13	73	13	276	0.54	1	2.53	$\mathrm{nmol\,m^{-3}}$
Peroxides	µM	11	7.8	0.4	58.9	0.17	0.2	0.45	$\mathrm{nmol\,m^{-3}}$
S(IV)	µM	11	2.36	0.25	6.27	0.18	0.001	0.12	$\mathrm{nmol\,m^{-3}}$
NO_2^-	µM	13	2.1	0.3	5.6	0.05	0.9	0.18	$\mathrm{nmol\,m^{-3}}$
TOC	$\mathrm{mg\,C\,L^{-1}}$	8	15.3	3.60	24.8	0.26	0.03	0.95	$\mathrm{ng\,C\,m^{-3}}$
Acetate	µM	11	138	19.3	640	2.36	0.007	4.77	$\mathrm{nmol\,m^{-3}}$
Formate	µM	11	120	1.77	532	1.47	0.05	8.47	$\mathrm{nmol\,m^{-3}}$
Oxalate	µM	11	41.5	5.86	110	1.47	0.03	1.99	$\mathrm{nmol\,m^{-3}}$
Succinate	µM	11	22.9	3.31	52.6	0.74	0.002	1.29	$\mathrm{nmol\,m^{-3}}$
Maleate	µM	11	21.1	3.04	58.8	0.29	0.02	0.72	$\mathrm{nmol\,m^{-3}}$
Malonate	µM	11	10.7	1.48	24.8	0.45	0.002	0.46	$\mathrm{nmol\,m^{-3}}$
Pyruvate	µM	11	9.19	0.79	38.8	0.23	0.02	0.48	$\mathrm{nmol\,m^{-3}}$
Methanesulfonate	µM	11	7.75	1.77	18.6	0.18	0.009	0.30	$\mathrm{nmol\,m^{-3}}$
HCHO	µM	10	7	3	21	4.81	2	0.65	$\mathrm{nmol\,m^{-3}}$
Glutarate	µM	11	6.5	0.92	18.3	0.66	0.02	0.30	$\mathrm{nmol\,m^{-3}}$
Valerate	µM	11	1.03	0.21	3.78	0.06	0.004	0.11	$\mathrm{nmol\,m^{-3}}$
Propionate	µM	11	0.88	0.35	1.36	0.06	0.004	0.11	$\mathrm{nmol\,m^{-3}}$
Adipate	µM	11	0.09	<LOD	0.24	0.006	0.04	0.01	$\mathrm{nmol\,m^{-3}}$
Salicylate	µM	11	0.06	0.001	0.15	0.0003	0.04	0.006	$\mathrm{nmol\,m^{-3}}$
Benzoate	µM	11	0.06	<LOD	0.15	0.002	0.02	0.005	$\mathrm{nmol\,m^{-3}}$
Pinate	µM	11	0.009	<LOD	0.03	0.001	0.01	0.0005	$\mathrm{nmol\,m^{-3}}$
Azelate	µM	11	0.02	<LOD	0.09	0.001	0.03	0.0009	$\mathrm{nmol\,m^{-3}}$
All Organic Acids	µM	11	379	138	1000	–	–	19.0	$\mathrm{nmol\,m^{-3}}$

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Value was not accurate

lesser but substantial contributions from other acids (Fig. 6). Concentrations of low molecular mass organic acids were strongly correlated with one another (air equivalent concentrations): r^2=0.83 on average, with probability $p \leq 0.01$ of random correlation, ranging from 0.47 to 0.99 ($p \leq 0.001$ to 0.2) for C_1-C_6 mono and di-acids. The predominance of succinate suggests a major anthropogenic source of organic acids at BYI (Kawamura and Ikushima, 1993). While substantial contributions of oxalate to TOC suggest that AAOP reactions took place, they are not unequivocal evidence of it, since other atmospheric sources for oxalate have been documented (e.g., Kawamura and Kaplan, 1987; Yamasoe et al., 2000). The presence of MSA in the observed samples and its correlation with other measured organic acids ($r^2 \leq 0.7$ and $p \leq 0.02$ with all low molecular mass organic acids, r^2=0.88 and $p \leq 0.001$ with oxalate) additionally supports the occurrence of AAOP upwind of fog water collection.

Added p-values

Summarized (redundant)

3.6 Mass spectral analysis

Polar organic components of the fog water with $\geq C_4$ 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., 2010; 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.

Added for consistency

Added for clarity

Table 2. Chemical formulae and possible structures of organic components identified via HPLC-(-)-ESI-HR-ToF-MS within BYI fog water samples. Formulae with multiple isomers (different retention times) are marked with an asterisk (*). Multiple plausible formulae were identified for species prefixed with 'e.g.'. Only species with mass spectral abundances ≥500 abundance units were included.

Removed "differences", "Abundances" columns, added "O/C" and "H/C"

Removed extra digits

m/z^{-}	Molecular Formula	t_R (min)	O/C	H/C	Possible Identification and References
85.0311	C4H6O2	3.182	0.5	0.67	Methacrylic acid
105.034		9.32			
113.027	C5H6O3	3.67	0.6	1.2	Oxo-pentenoic acid
117.057	C5H10O3	4.54	0.6	2	Hydroxy-pentanoic acid*
117.057	C5H10O3	3.43	0.6	2	Hydroxy-pentanoic acid*
121.031	C7H6O2	9.82	0.29	0.86	ydroxy-benzaldehyde
127.042	C6H8O3	5.79	0.5	1.3	Oxo-hexeneoic acid
129.022	C5H6O4	3.67	0.8	1.2	Pentenedioic acid*
129.021	C5H6O4	3.18	0.8	1.2	Pentenedioic acid*
129.057	C6H10O3	5.96	0.5	1.7	Methyl-oxo-pentanoic acid*
129.057	C6H10O3	7.00	0.5	1.7	Methyl-oxo-pentanoic acid*
131.036	C5H8O4	3.18	0.8	1.6	Methyl-succinic acid
131.036	C5H8O4	4.34	0.8	1.6	Glutaric acid
131.073	C6H12O3	9.82	0.5	2	Hydroxy-Hexanoic acid*
131.073	C6H12O3	7.95	0.5	2	Hydroxy-Hexanoic acid*
137.026	C7H6O3	16.17	0.43	0.86	Salicylic acid
138.021	C6H5NO3	13.18	0.5	0.83	4-Nitrophenol
143.036	C6H8O4	3.18	0.67	1.7	Hexenedioic acid*
143.037	C6H8O4	6.86	0.67	1.7	Hexenedioic acid*
143.073	C7H12O3	11.43	0.43	1.7	Methyl-pentenedioic acid
145.051	C6H10O4	8.93	0.67	1.7	Methyl-glutaric acid*
145.052	C6H10O4	7.10	0.67	1.7	Adipic acid
145.052	C6H10O4	9.52	0.67	1.7	Methyl-glutaric acid*
149.026	C8H6O3	9.32	0.38	0.75	Formyl-benzoic acid
152.036	C7H7NO3	17.85	0.43	1	Methyl-nitrophenol
152.037	C7H7NO3	19.33	0.43	1	2-Methyl-4-nitrophenol
154.016	C6H5NO4	10.46	0.67	0.83	Nitroguaiacol
157.052	C7H10O4	6.32	0.57	1.4	Heptenedioic acid*
157.053	C7H10O4	5.22	0.57	1.4	Heptenedioic acid*
159.068	C7H12O4	10.79	0.57	1.7	Pimelic acid
163.042	C9H8O3	12.63	0.33	0.89	Previously identified (Desyaterik et al., 2013)
165.021	C8H6O4	10.13	0.5	0.75	Phthalic acid
165.021	C8H6O4	12.06	0.5	0.75	Benzenedicarboxylic acid
166.053	C8H9NO3	23.61	0.38	1.1	Dimethyl-nitrophenol
171.067	C8H12O4	8.33	0.5	1.5	Octenedioic acid*
171.068	C8H12O4	6.95	0.5	1.5	Octenedioic acid*
171.983		19.712			
173.047	C7H10O5	4.22	0.71	1.4	Isoprene photooxidation product (Nguyen et al., 2011)
179.037	C9H8O4	15.23	0.44	0.89	Phthalic acid, methyl ester
181.016	C8H6O5	5.65	0.63	0.75	Hydroxy-benzene-dicarboxylic acid*
181.016	C8H6O5	8.81	0.63	0.75	Hydroxy-benzene-dicarboxylic acid*
181.019	C5H10O5S	2.82	1	2	Previously identified (Nguyen et al., 2014a)

Table 2. Continued

m/z^-	Molecular Formula	t_{R} (min)	O/C	H/C	Possible Identification and References
182.012	C7H5NO5	18.75	0.71	1	Carboxy-nitrophenol
182.999	C4H8O6S	1.92	1.5	2	
183.007	C6H4N2O5	15.08	0.83	0.67	2,4-Dinitrophenol
185.083	C9H14O4	13.54	0.44	1.6	Pinic acid*
185.084	C9H14O4	9.70	0.44	1.6	Nonenedioic acid*
187.063	C8H12O5	5.10	0.63	1.5	Alpha-pinene oxidation product (Claeys et al., 2009)*
187.064	C8H12O5	7.76	0.63	1.5	Alpha-pinene oxidation product*
189.078	C8H14O5	6.54	0.63	1.8	Diaterpenylic acid; known oxidation product of alpha-pinene (Yasmeen et al., 2010)
195.034	C6H12O5S	6.17	0.83	2	
195.035	C6H12O5S	6.0	0.83	2	
197.022	C7H6N2O5	21.23	0.71	0.86	Methyl-dinitrophenol
201.079	C9H14O5	10.74	0.56	1.6	Alpha-pinene oxidation product (Kahnt et al., 2013)
203.058	C8H12O6	8.75	0.75	1.5	Methyl-butane-tricarboxylic acid (MBTCA); gas-phase pinonic acid oxidation product (Szmigielski et al., 2007)
211.031	C6H12O6S	7.40	1	2	
211.031	C6H12O6S	6.86	1	2	
211.031	C6H12O6S	9.40	1	2	
225.009	C6H10O7S	2.50	1.2	1.2	Methylglyoxal oxidation product (Sareen et al., 2010)
228.021	C8H7NO7	12.97	0.88	0.88	Oxygenated nitrophenol
239.025	C7H12O7S	4.10	1	1.7	1,3,5-trimethylbenzene oxidation product (Praplan et al., 2014)
239.048		21.56	0.5	2	
241.005	C6H10O8S	2.18	1.5	1.7	
253.042	C8H14O7S	7.59	0.88	1.8	Limonene oxidation product (Mazzoleni et al., 2010; Surratt et al., 2008)*
267.057	C9H16O7S	10.55	0.78	1.8	Limonene oxidation product (Mazzoleni et al., 2010; Nguyen et al., 2014)*
267.058	C9H16O7S	10.85	0.78	1.8	Limonene oxidation product(Mazzoleni et al., 2010; Nguyen et al., 2014)*
267.058	C9H16O7S	9.92	0.78	1.8	Limonene oxidation product (Mazzoleni et al., 2010; Nguyen et al., 2014)*
267.058	C9H16O7S	11.00	0.78	1.8	Limonene oxidation product (Mazzoleni et al., 2010; Nguyen et al., 2014)*
269.036	C8H14O8S	7.44	1	1.8	
284.047	C11H11NO8	14.96	0.72	1	
294.068	C10H17NO7S	24.87	0.7	1.7	Monoterpene oxidation product (Surratt et al., 2008)*
294.068	C10H17NO7S	26.71	0.7	1.7	Monoterpene oxidation product*
297.060	e.g., C17H14O3S	8.87			
310.063	C10H17NO8S	19.56	0.8	1.7	Monoterpene oxidation product (Mazzoleni et al., 2010; Surratt et al., 2008)*
333.021	C14H10N2O6S	20.65	0.43	0.71	
361.165	C15H26N2O8	12.32	0.53	1.7	
497.333	C23H50N2O7S	16.74	0.3	2.2	
514.322	C22H49N3O8S	16.74	0.36	2.2	
635.351	e.g., C26H56N2O13S	18.46			

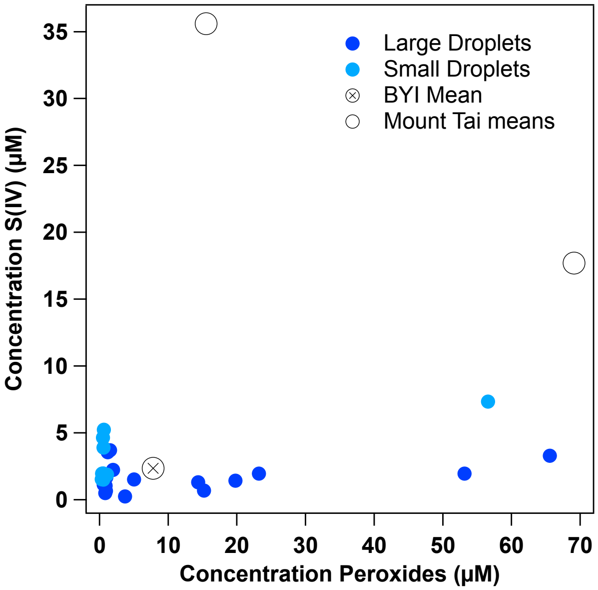

Figure 5. Droplet size-segregated concentrations of S(IV) and peroxides quantified in BYI fog samples. S(IV) concentrations were low in BYI fog as compared to those measured at Mount Tai (summer 2007 and 2008; Shen et al., 2012). For both species, *n*=11.

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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^- 203.058 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 (Szmigielski et al., 2007; Yasmeen et al., 2010). Based on a qualitative analysis 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; Heald et al., 2010; Ng et al., 2011; Chen et al., 2015) 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).

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3.7 Nitrophenols

Four identified nitrophenols were quantified via HPLC-(-)-ESI-HR-ToF-MS (Table SI-4): 4-nitrophenol (36.4±1.8 nM; max 297 nM), 2-methyl-4-nitrophenol (3.8±0.5 nM; max 42.7 nM), 2,4-dinitrophenol (20.7±0.1 nM; max 74.8 nM), and 2-methyl-4,6-dinitrophenol (0.7±0.1 nM; max 5.1 nM). Concentrations detected in most previous fog and cloud water field studies were 1-300 nM (Harrison et al., 2005), in the same range as identified in this study. However, the concentrations of 4-nitrophenol measured within cloud water from Mount Tai were as high as 15 µM (Desyaterik et al., 2013). The lower concentrations measured at BYI versus at Mount Tai likely reflect the strong influence of aged biomass burning emissions in the Mount Tai region, and may also be a result of aqueous aging in the samples collected at BYI, since species such as 4-nitrophenol are oxidized by $^{\bullet}OH$ in the aqueous phase (Zhang et al., 2003). Other nitrate-containing species (tentatively identified; Table 2) included a second methyl-nitrophenol isomer (m/z^- 152.04, $C_7H_7NO_3$), a hydroxy-nitrophenol (also called a nitrocatechol; m/z^- 154.02, $C_6H_5NO_4$), a dimethyl-nitrophenol (m/z^- 166.05, $C_8H_9NO_3$), and three other oxygenated nitrophenols (m/z^- 228.02, $C_8H_7NO_7$; m/z^- 284.05, $C_{11}H_{11}NO_8$; and m/z^- 361.16, $C_{15}H_{26}N_2O_8$). 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

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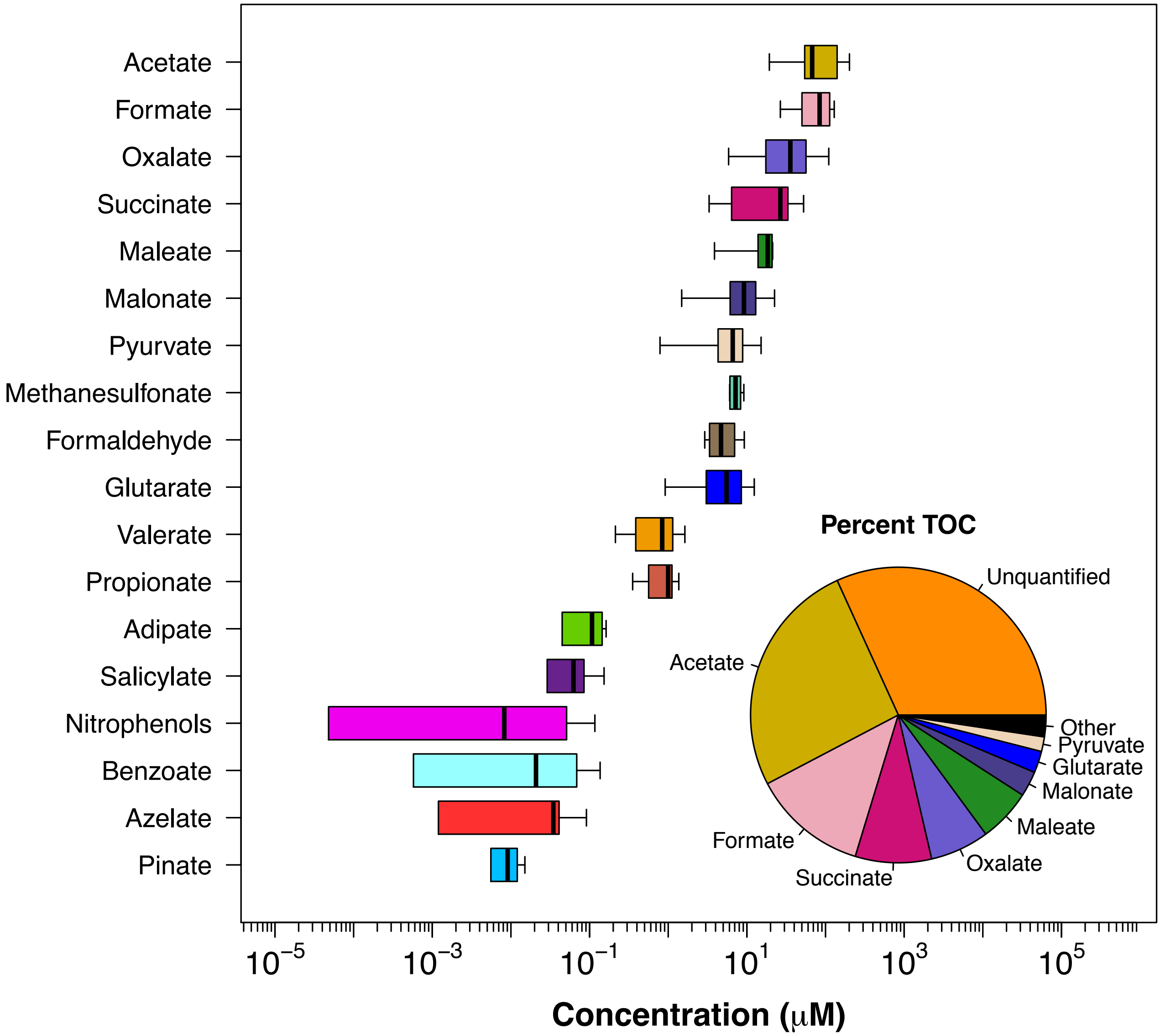

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Figure 6. Concentrations of major carbonaceous components quantified in BYI fog samples. Box-and-whisker plot shows 25th and 75th percentiles with the median bar in the center, and whiskers at the min and max. Note that for C_1-C_5 organic acids, $n = 11$, for formaldehyde, n=10, and for components with C_6 or greater, n=11. Pie chart (inset) shows carbonaceous composition as a percentage of TOC (only those samples with results from all organic analyses included, n=7).

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 ($\mathrm{nmol\,m^{-3}}$).

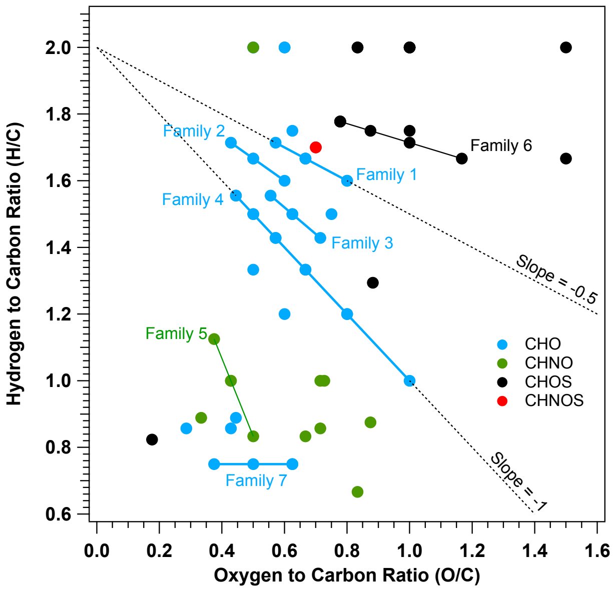

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Figure 7. Polar organic compounds identified within fog samples using HPLC-(-)-ESI-HR-ToF-MS detection illustrated via a van Krevelen diagram. Colors of points distinguish compound elemental composition; solid lines show families differing by methylene 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.

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3.8 Organosulfates

Organic sulfur (CHOS) species were identified within BYI fog samples (Table 2), some of which have also been found within rainwater (samples collected in urban and rural New Jersey; Altieri et al., 2009). Most organosulfates identified were likely from oxidation and sulfonation of biogenic emissions, including m/z^- 225.01, 253.04, and 267.06 corresponding to $C_6H_{10}O_7S$, $C_8H_{14}O_7S$ and $C_9H_{16}O_7S$, respectively; however, no isoprene-derived organosulfates were detected in the BYI samples (Surratt et al., 2008). Nguyen and coworkers (2014) observed a compound with the formula $C_8H_{14}O_7S$ in aerosol samples, and Surratt and coworkers (2008) showed that the source may have been esterification of a *d*-limonene oxidation product with SO_4^{-2}. An observed compound at m/z^- 239.02 with a formula of $C_7H_{12}O_7S$ was previously identified by Praplan et al. (2014) as an oxidation product of the anthropogenic species 1,3,5-trimethylbenzene. Several pairs of organosulfates appear to have originated from loss of a hydroxyl group: for example, m/z^- 195.03 and 211.03, corresponding to $C_6H_{12}O_5S$ and $C_6H_{12}O_6S$; the latter species was noted to possibly be formed from the sulfonation of a fatty acid (Surratt et al., 2008). CHONS species were also found in the fog samples from BYI, two of which were identified previously as monoterpene oxidation products (Surratt et al., 2008): m/z^- 294.07 with formula $C_{10}H_{17}NO_7S$ and m/z^- 310.06 with formula $C_{10}H_{17}NO_8S$. A compound with the formula $C_{10}H_{17}NO_7S$ was also identified within Fresno fog samples (Mazzoleni et al., 2010).

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3.9 Atmospheric aqueous organic processing

Many features of the fog water at BYI, including the organic composition and the humid conditions encountered prior to arrival at the collection site, suggest that components in the fog were oxidized in the atmospheric aqueous phase. The oxidation may have occurred in the fogs themselves or during upwind transport of wet aerosol later scavenged by the fog. The RH upwind of fog-producing air masses as they traveled to BYI was high, with only a few time periods at $<$50%, and mean 65-91% (Fig. SI-7). Only the air mass intercepted during the fog event on 30 June did not encounter RH $>$80% within 72 hr of fog formation at BYI. Mixtures of organic and inorganic components can easily take up water (growth factors $\leq$1.71 at 85% RH for several organic acids, Wise et al., 2003; and $\leq$1.16 at 85% RH for chamber-generated secondary organic aerosol, Varutbangkul et al., 2006). It is therefore likely that the aerosol LWC was sufficient to allow radical or even non-radical aqueous reactions to occur upwind of the BYI fog collection site (Lim et al., 2010, 2013). The high abundance and large diversity of organic acids, oxidized sulfur, lack of peroxides, and organosulfates identified within fog samples also support the hypothesis that AAOP reactions took place within wetted aerosol particles, in-cloud/fog during transit of the intercepted air masses to BYI, or within the fog at BYI (Lim et al., 2005; McNeill, 2015).

Added for clarity

3.10 Size and microphysical considerations

Changes in LWC, species concentrations, and enrichments of species within large or small droplets can be indicative of many simultaneous microphysical processes: coalescence or condensational growth, evaporation, deposition, and collisions between droplets and interstitial particles (Degefie et al., 2015; Fahey et al., 2005; Seinfeld and Pandis, 2006). Fig. 8 shows differences in large and small droplet concentrations of abundant chemical constituents in the BYI fog samples collected on the two stages of the sf-CASCC. Much higher volumes of liquid water were typically collected into the large droplet fraction (>16 µm) than the small droplet fraction (4-16 µm) at BYI; on average, the small fraction comprised only 10% of the total liquid water volume, indicating relatively large fog droplets made up most of the LWC. All species shown are enriched in the small droplet (4-16 µm) size fraction, with the exception of peroxides; similar observations have previously been reported in many clouds and

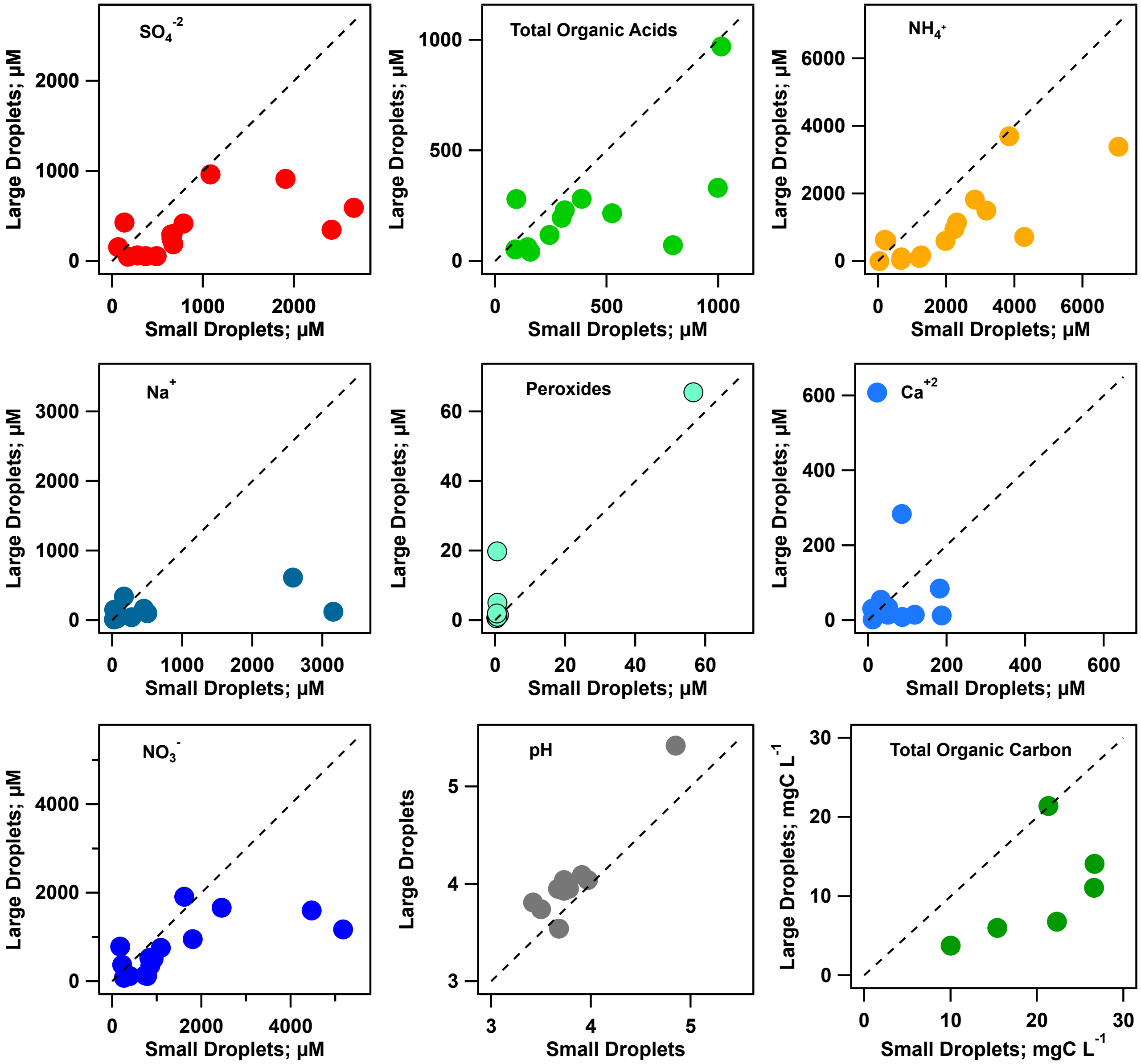

Figure 8. Scatter plots showing size distribution of major species in BYI fog water samples. All species shown, with the exception of peroxides, were enriched in small droplets.

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fogs, especially for species typically associated with submicron aerosol, including SO_4^{-2}, NO_3^-, NH_4^+, and TOC (Bator and Collett, 1997; Herckes et al., 2007; Munger et al., 1989). As in most of these prior observations, the pH in large BYI fog droplets was also typically higher than in small droplets. Differences in pH among cloud drops can give rise to differences in the rates of pH-dependent chemical reaction rates, including the aqueous oxidation of S(IV) to SO_4^{-2} by ozone or by oxygen in the presence of trace metal catalysts (Collett et al., 1994; Hegg and Larson, 1990; Rao and Collett, 1998). Enrichment of solutes in large or small fog drops can also affect rates of removal by fog drop deposition (e.g., Fahey et al., 2005; Herckes et al., 2007; Hoag et al., 1999).

4 Conclusions

The fogs at BYI were on average slightly acidic, and the chemical composition was dominated by NH_4NO_3 from long-range transport, with contributions from anthropogenic nss-SO_4^{-2}, marine NaCl, and a variety of organic compounds. Biomass burning activities throughout Eastern Russia and Southeast Asia appear to have contributed K^+ and organic species, including nitrophenols, in some periods. Organosulfate species deriving from oxidation products of monoterpenes (e.g., Surratt et al., 2008; Nguyen et al., 2014) were observed, several of which have been identified in aqueous atmospheric samples in the past (Altieri et al., 2009; Mazzoleni et al., 2010). Low concentrations of S(IV), high concentrations of SO_4^{-2}, and generally low concentrations of peroxides suggest that chemical components of the fog water were highly oxidized during upwind transport and/or within the local fog. Low molecular mass organic acids accounted for 36-69% of TOC, a higher fraction than observed in fogs from other environments, with acetate, formate, succinate, oxalate, and maleate each contributing >5% of TOC on average. Further analysis of the fog organic matter via HPLC-(-)-ESI-HR-ToF-MS revealed homologous families of dicarboxylic acids and nitrophenols. The position within van Krevelen space occupied by identified organics matches well with the fragmentation aging regime (at high oxidation state) shown by Kroll and coworkers (2009).

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Future studies of fog or cloud water composition in the region should include the characterization of carbonyl species which have been cited as important AAOP reactants (Ervens, 2015) and are direct oxidation precursors of organic acids. Additional studies to analyze the evolution of gaseous, particulate, and aqueous phase organics during fog events as well as the advancement of laboratory simulated reactions will be essential in more fully characterizing AAOP reactions and aqSOA formation.

Data Availability

Processed data are available in the supplement to this article. Raw data are archived at the Colorado State University Atmospheric Science Department and are available on request.

Added

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