

Supplement of Atmos. Chem. Phys., 16, 437–453, 2016  
<http://www.atmos-chem-phys.net/16/437/2016/>  
doi:10.5194/acp-16-437-2016-supplement  
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Atmospheric  
Chemistry  
and Physics  
Open Access  
EGU

*Supplement of*

## **Fog composition at Baengnyeong Island in the eastern Yellow Sea: detecting markers of aqueous atmospheric oxidations**

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## 1 **Supplementary Material**

### 2 **Methods: Chemicals**

3 Chemical standards and solvents were purchased as follows: malonic acid (99%), 4-nitrophenol  
4 (98%), and 2,4-dinitrophenol (98%) were purchased from Acros organics. Glutaric acid (99%),  
5 oxalic acid (99.999%), benzoic acid (99%), succinic acid (99+%), pyruvic acid (98%), propionic  
6 acid (99+%), 2-methyl-4-nitrophenol (97%), maleic acid (99%), *cis*-pinonic acid (98%), and 2,4-  
7 pentanedione (99+%) were purchased from Aldrich. Inorganic salt standards (Six Cation-II and  
8 Seven Anion Standards) were purchased from Dionex and diluted. Formaldehyde (37%  
9 aqueous/methanol), sodium hydroxide pellets, potassium iodide (KI; 99.6%), iodine (100.0%),  
10 potassium hydrogen phthalate (99.95%), sodium carbonate (HPLC grade), and sodium  
11 bicarbonate (certified ACS) were purchased from Fischer. Ammonium acetate ( $\geq 99.0\%$ ), *para*-  
12 hydroxy-phenylacetic acid (POPHA;  $\geq 98.0\%$ ),  $\text{Na}_4\text{EDTA}\cdot 4\text{H}_2\text{O}$  ( $\geq 99\%$ ), CDTA ( $\geq 98\%$ ),  
13 parafuchsin (containing pararosaniline), methanesulfonic acid (MSA;  $\geq 99.0\%$ ), acetic acid (99%),  
14 formic acid ( $\sim 98\%$ ), adipic acid ( $\geq 99\%$ ), *n*-valeric acid ( $\geq 99\%$ ), azelaic acid (98%), and 4,6-  
15 dinitro-*o*-cresol (2-methyl-4,6-dinitrophenol;  $\geq 98\%$ ) were purchased from Fluka. Salicylic acid  
16 ( $\geq 99.0\%$ ), monobasic potassium phosphate (99.99%), and catalase enzyme from bovine liver  
17 were purchased from Sigma. Buffers for pH measurement (pH 4, 7), hydrogen peroxide (30%  
18 w/w aqueous solution), and Triton X-100 non-ionic detergent were obtained from Sigma-Aldrich.  
19 Pinic acid was obtained from the Sigma-Aldrich Library of Rare Chemicals (no purity  
20 characterization was carried out). Horseradish peroxidase (Type VI, 250-330 units/mg solid using  
21 pyrogallol) was purchased from both Fisher Scientific and Sigma. Anhydrous sodium sulfite was  
22 purchased from Chempure Lab Chemicals (99.9%). Methanol and acetonitrile (LCMS grade)  
23 were purchased from Honeywell.

24 Stock standards of organic acids (100 mM) were prepared in water, with the exception of valeric  
25 and succinic acids, which were prepared using  $\sim 2\%$  methanol in water. Stock standards of

26 nitrophenols (4 and 10 mM) were prepared using up to 40% methanol and/or 4% acetonitrile in  
27 water.

## 28 **Methods: Chemical Analysis**

29 All chemical analyses were carried out without prior filtration of the collected fog water. Most  
30 analyses were carried out using procedures previously employed for fog and cloud samples (e.g.,  
31 Collett et al., 1999; Benedict et al., 2012). Information about purchased chemicals can be found in  
32 the Supporting Information. S(IV), which includes dissolved sulfur dioxide, bisulfite, sulfite, and  
33 hydroxymethanesulfonate (HMS), was measured after reaction with 4,4'-[(4-Imino-2,5-  
34 cyclohexadien-1-ylidene)methylene]dianiline (pararosaniline) via UV/visible absorption  
35 spectrometry (Shimadzu UV-1800 spectrophotometer) at 580 nm according to a modified  
36 procedure introduced by Dasgupta et al. (1980; 1981). Formaldehyde was reacted with 2,4-  
37 pentanedione and ammonia to form diacetyldihydrolutidine (DDL), which can be measured via  
38 fluorescence spectrometry at an excitation wavelength of 412 nm and an emission wavelength of  
39 510 nm (BioTek Synergy H1 fluorescence plate reader, Peqlab PeqStar 96 Universal Gradient  
40 Heating Unit, and Ultra-Fast skirted 96-well polypropylene polymerase chain reaction plates)  
41 following a procedure published by Dong and Dasgupta (1987). Formaldehyde naturally  
42 complexed in the form of HMS is included in the quantified formaldehyde using this method.  
43 The mean of three replicate formaldehyde measurements was used for each sample. Total  
44 peroxides (organic peroxides and hydrogen peroxide) were reacted with *para*-hydroxy-phenyl-  
45 acetic acid (POPHA) to form a fluorescent dimer in the presence of horseradish peroxidase (412  
46 nm excitation, 510 nm emission; Biotek fluorescence plate reader; Lazrus et al., 1986). A solution  
47 of triiodide ( $I_3^-$  from  $KI/I_2$ ) was used to calibrate the stock solution of hydrogen peroxide. The  
48 mean of three replicate peroxides measurements was used for each sample. TOC was measured  
49 using a Sievers Model 800 Turbo TOC Analyzer in Turbo mode (via digestion of carbonaceous  
50 material to  $CO_2$  followed by conductivity detection). Major inorganic ions were quantified using

51 a Dionex DX-500 ion chromatography (IC) system with conductivity detection; cations were  
52 separated along a Dionex CS12A analytical column with an installed CG12 guard column and  
53 CSRS ULTRA II suppressor using MSA as eluent; anions were separated along a Dionex AS14A  
54 analytical column with an installed AG14A guard column and ASRS ULTRA II suppressor using  
55  $\text{CO}_3^{2-}/\text{HCO}_3^-$  eluent. Organic acids were analyzed using a gradient Dionex IC system with a  
56 Dionex AS11-HC analytical column, AG11 guard column, and ASRS ULTRA II suppressor  
57 using NaOH eluent and a conductivity detector. A small number of samples were also analyzed  
58 after separation using (-)-ESI-HR-ToF-MS to confirm the identifications of eluted organic acids.  
59 Additional organic molecules were identified via HPLC(-)-ESI-HR-ToF-MS: a Kinetex 2.6  $\mu\text{m}$   
60 particle size XB-C18 column designed for polar organic species separation with 100 Å pore size  
61 and 3.00 mm internal diameter was used to separate organic species (higher molecular mass  
62 organic acids, phenols and organosulfates) via a 0.1% formic acid/methanol gradient elution. The  
63 HPLC(-)-ESI-HR-ToF-MS system consisted of an Agilent 1100 Series LC with Agilent  
64 MSD/ToF detector. Agilent EI-TOF tuning mix was used to perform external mass calibration  
65 prior to analyses, initially giving  $\pm 1$  ppm mass accuracy. Mass accuracies during analysis are  
66 tabulated in Table 2, and are typically  $< 15$  ppm. External calibrations performed on the HPLC(-)  
67 )-ESI-HR-ToF-MS were linear ( $r^2 > 0.90$ ). Mass spectral results were filtered so that only species  
68 with abundances  $\geq 500$  abundance units (a.u.) were included. A mass range of 100 to 300 Da was  
69 chosen for inclusion in the analyses of these species to exclude organic species identified via IC  
70 (organic acids) and compounds with uncertain formula assignments at higher masses.

#### 71 **Methods: Statistical Calculations**

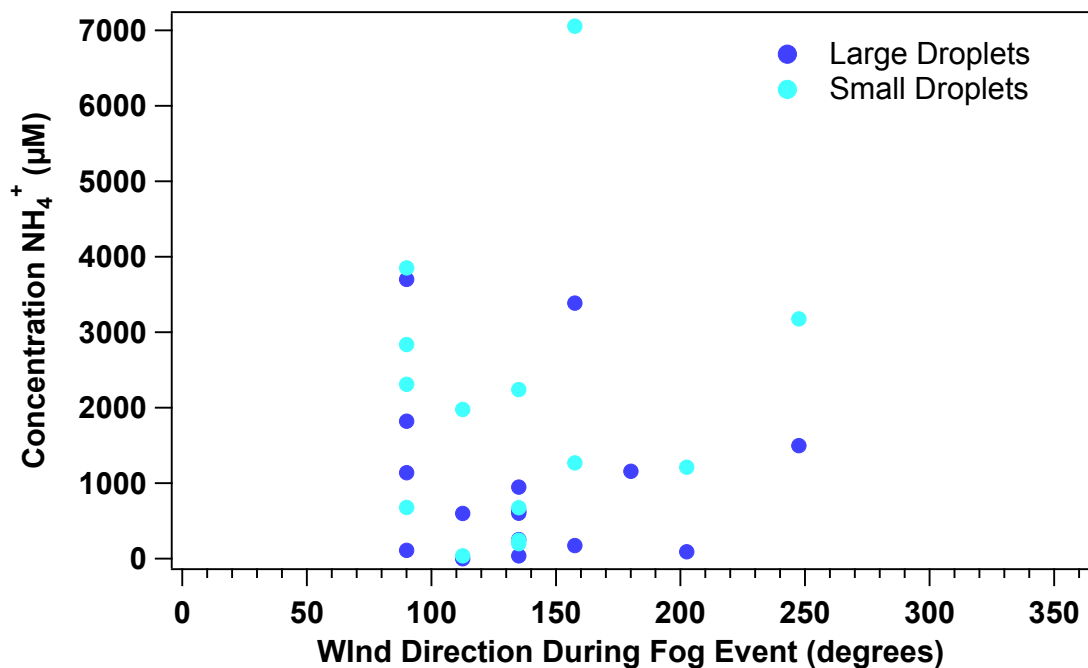
72 Limits of detection (LODs) were estimated from blanks collected after each event during the  
73 sampling campaign, and calculated as  $t s \sqrt{((N_s + N_{\text{blk}})/(N_s * N_{\text{blk}}))}$  where  $N_{\text{blk}}$  is the number of  
74 replicate blanks,  $N_s$  is the number of replicate samples,  $t$  is the Student's t-statistic value for the  
75 given  $N_{\text{blk}}$  at the one-tailed 95% confidence level, and  $s$  is the standard deviation of the replicate

76 blanks. Uncertainties were calculated as  $ts/\sqrt{N}$ , for replicate standard solutions at a median  
77 concentration from each calibration curve, where  $N$  is the number of standard replicates ( $\geq 3$ ),  $t$  is  
78 the Student's t-statistic value for the given  $N$  at the two-tailed 95% confidence level, and  $s$  is the  
79 standard deviation of the standard replicates.

## 80 **Results: Changes in Composition during Fog Events**

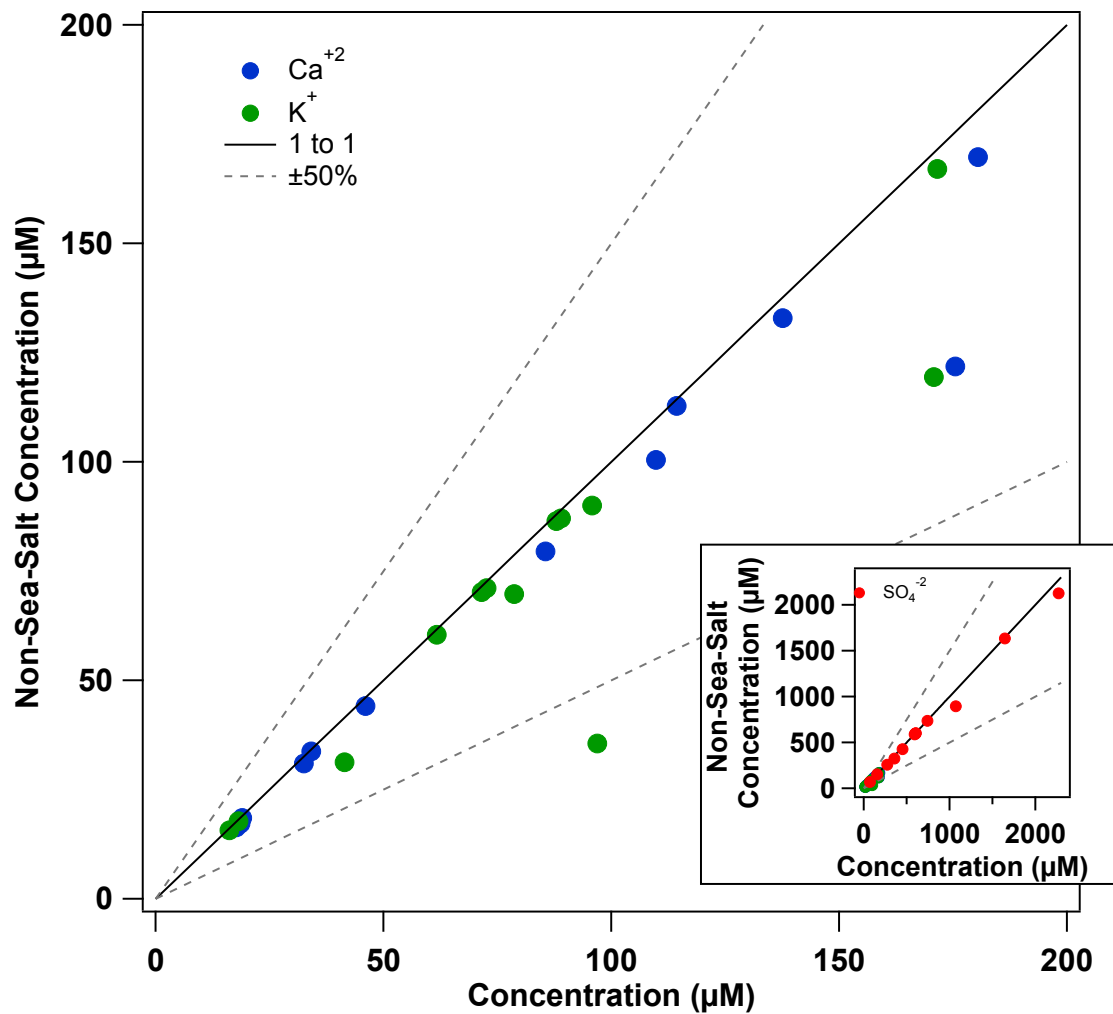
81 Constraining the processes leading to composition changes during a fog event is difficult. Trends  
82 in concentrations of major ions are shown in Fig. SI-4 for two fog events through which multiple  
83 fog water samples were collected (2 and 18 July). Although clearly demonstrating that AAOP  
84 reactions occurred during these events is not possible, there are changes during the fog events that  
85 are apparent within the measured chemical and physical parameters. During the dissipation stage  
86 of fogs observed on 2 and 18 July, the LWC decreased and concentrations of all species measured  
87 increased. While LWC and constituent concentrations have a generally inverse relationship  
88 during the events, the LWC explains 25% or less of concentration variation ( $r^2 \leq 0.25$ ) in samples  
89 overall for small and large samples. On 18 July (Fig. SI-4, right), the decrease in the magnitude  
90 of concentrations at 7:30 am agrees with previously observed depositional velocities for  
91 individual inorganic species (Herckes et al., 2007). Throughout the two fog events, changes in  
92 total low molecular mass organic acid concentrations, which might reflect oxidation of organic  
93 species within the fog water, are either low or follow trends of other inorganic species, consistent  
94 with a dominance of physical processes. The lack of clear evidence for supporting or negating  
95 aqueous organic reactions within these specific fog events emphasizes the utility of laboratory  
96 studies in which many chemical and physical variables can be controlled.

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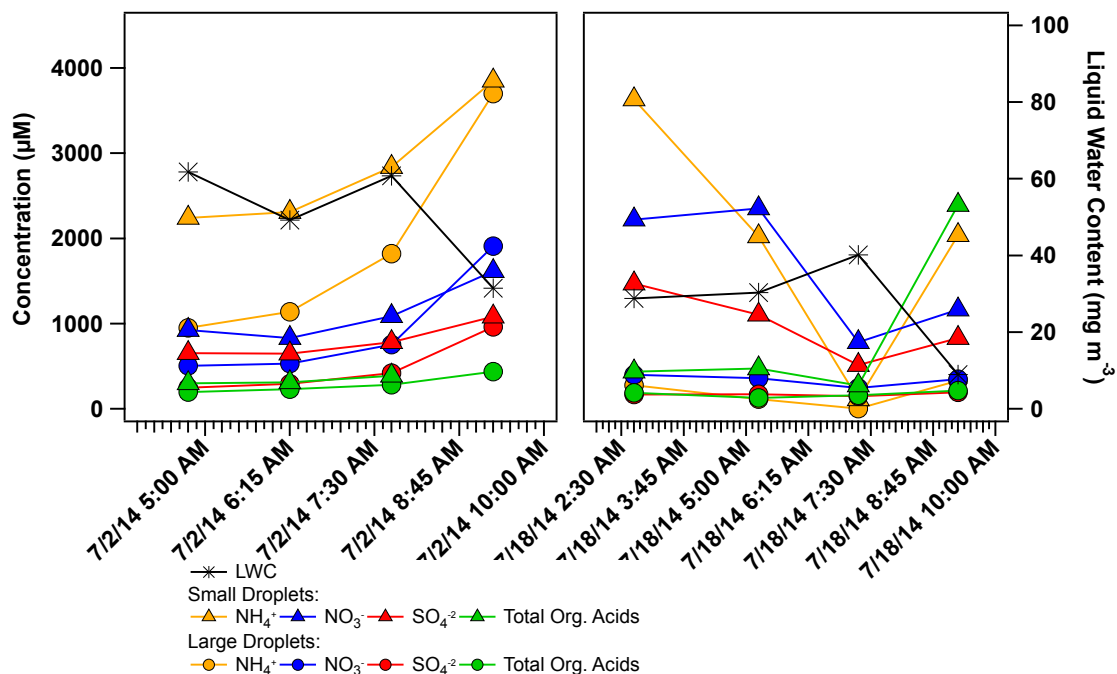
98

99 **Figure SI-1.** Ammonium concentrations during fog events as a function of wind directions  
 100 measured at co-located meteorological station. No correlation can be observed between  $\text{NH}_4^+$  and  
 101 wind, showing that the source of this species was likely long-rang transport as  $\text{NH}_4\text{NO}_3$ .



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103 **Figure SI-2.** nss components of several ionic species, calculated using molar ratios of species and  
 104 Na<sup>+</sup> in sea salt. Area between solid line denoting 100% nss contribution and dashed line denoting  
 105 50% below includes most data points. Inset shows nss-SO<sub>4</sub><sup>2-</sup> contribution. nss-Cl<sup>-</sup> concentrations  
 106 are sometimes well below zero (due to Cl<sup>-</sup> depletion) and are therefore not shown.

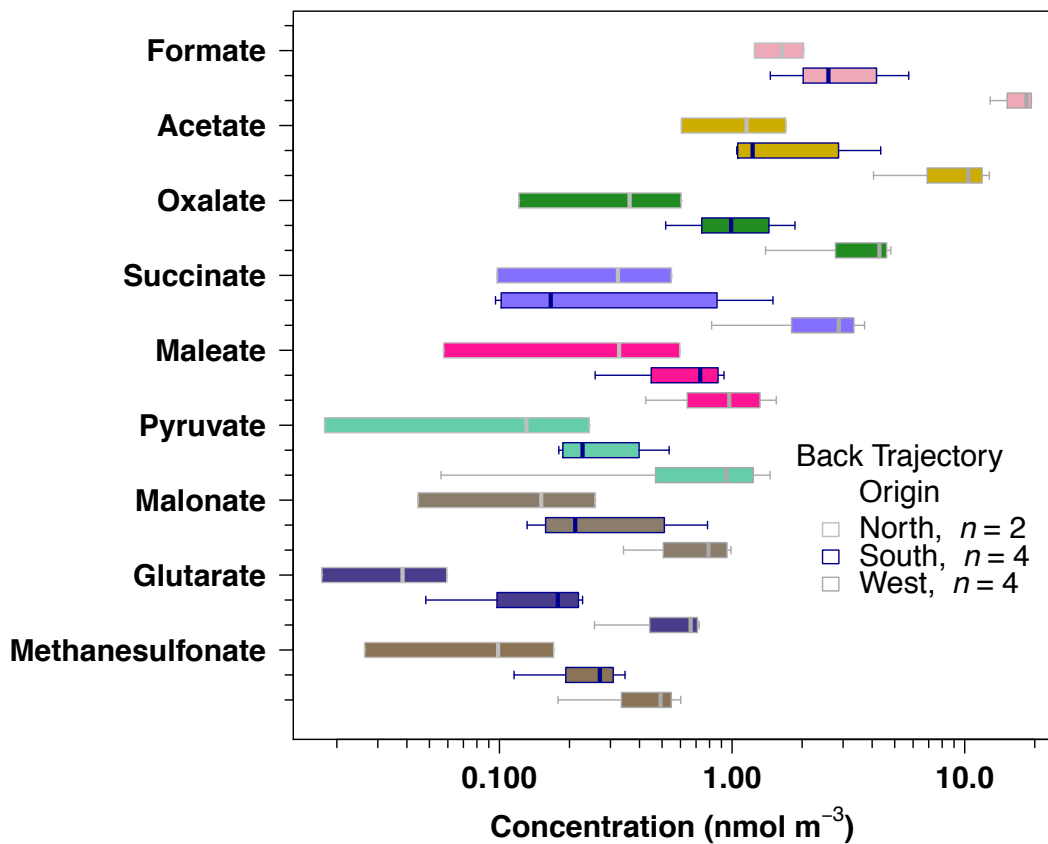


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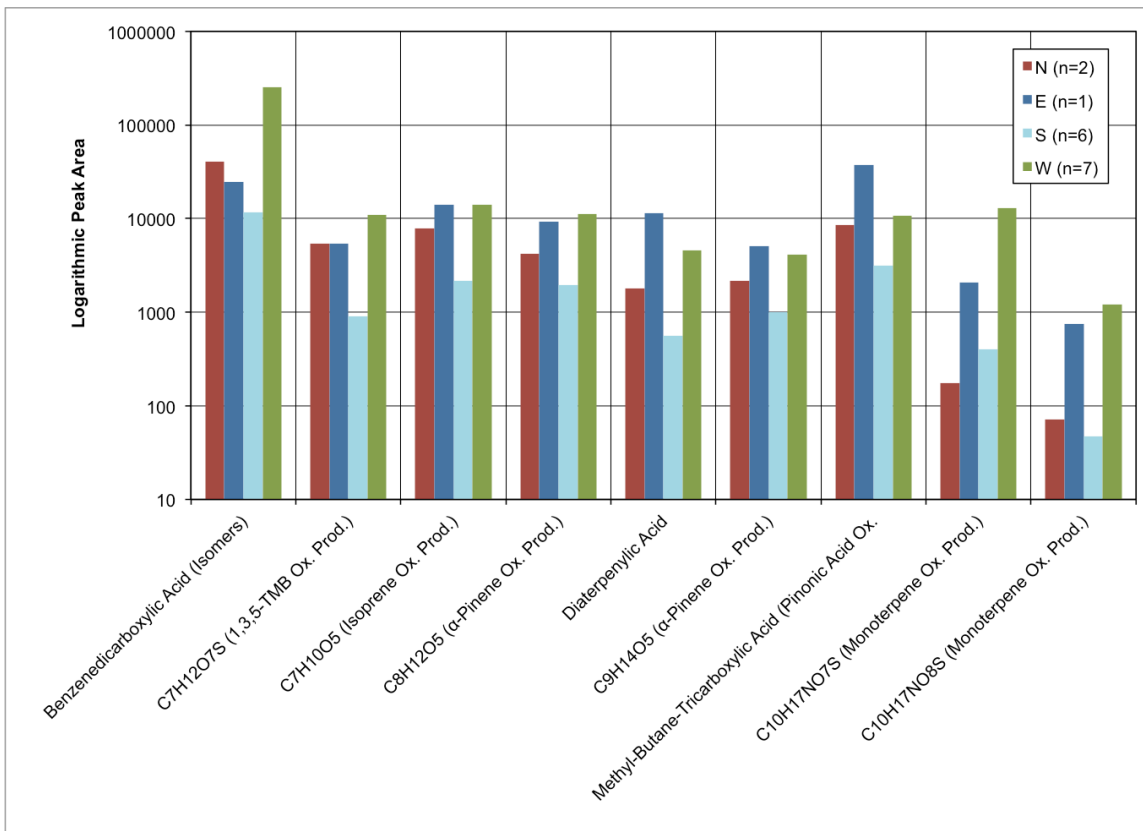
**Figure SI-3.** Chemical trends with time for two fog events during which multiple fog water samples were collected (on the mornings of 2 and 18 July 2014). LWC was calculated as the mean value measured by the PVM through the duration of each fog sample (times along the bottom of the plot are at the start of each sampling period).

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



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**Figure SI-5.** Peak areas of tentatively identified anthropogenic (two categories on left) and

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biogenic (two categories on right) species in BYI fog water (see Table 2). Samples with westerly

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back trajectories contained the greatest quantities of the anthropogenic species, while the samples

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collected with westerly trajectories and an easterly trajectory ( $n=1$ ) contained the greatest

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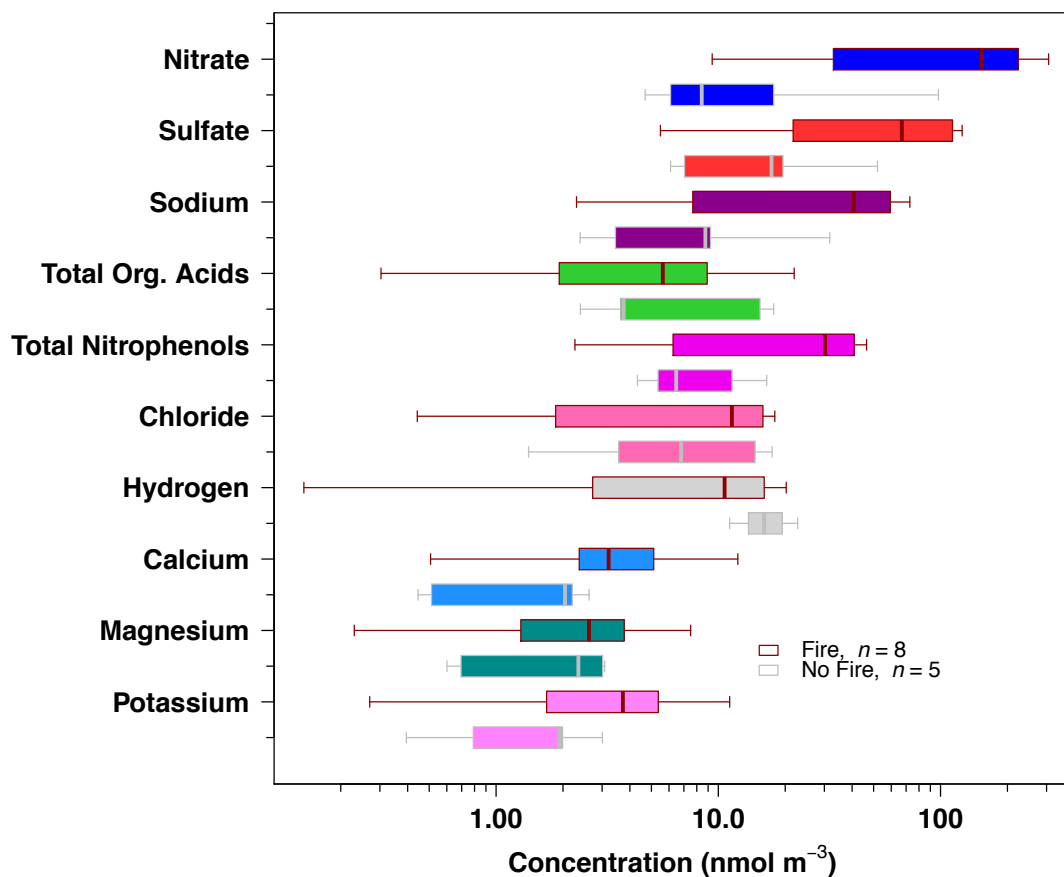
quantities of the biogenic species. Samples with southerly back trajectories (from over the sea)

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contained the smallest quantities of most species. Note that sensitivities of the mass spectrometer

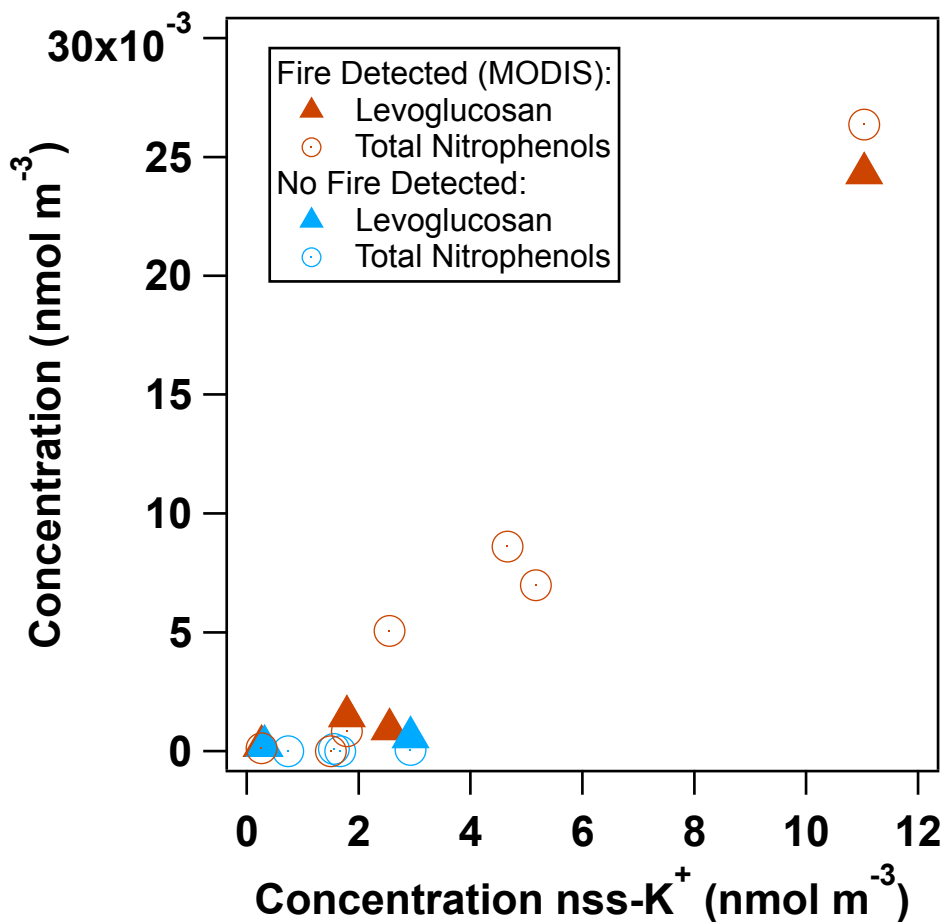
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to these species are highly variable, and no calibration has been made for these compounds.



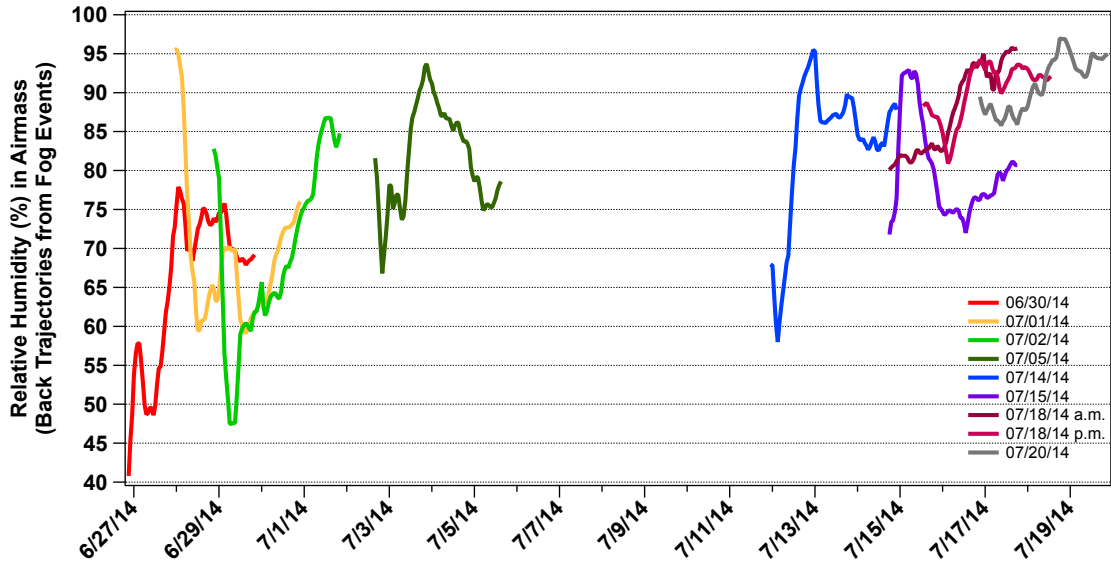
125  
 126 **Figure SI-6.** Contrast of most abundant species in fog samples between days with fire impact  
 127 (based on qualitative observation of fires in MODIS fire product outputs, co-located with back  
 128 trajectories). Note that fire periods included the samples from 07/02/14, which typically  
 129 contained the greatest concentrations of most abundant species; this is likely due to sources other  
 130 than fires. A larger sample set might allow a more conclusive determination of the regional fire  
 131 impact on fog chemistry at BYI.

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134 **Figure SI-7.** Correlation of levoglucosan (triangles) and total nitrophenol (circles) concentrations  
 135 with those of non-sea salt K<sup>+</sup> (nss-K<sup>+</sup>). Air equivalent concentrations were used to remove the  
 136 impact of liquid water content between fog samples. Levoglucosan concentrations were only  
 137 analyzed in six fog samples, representative of most fog events (the fog samples from the event on  
 138 18 June were not analyzed due to contamination by CASC cleaning solution; four samples were  
 139 analyzed from days when fire was detected; two from days when no fire was detected). The  
 140 overall correlation of nitrophenols with nss-K<sup>+</sup> was  $r^2=0.93$  ( $n=11$ ,  $p<0.001$ ).



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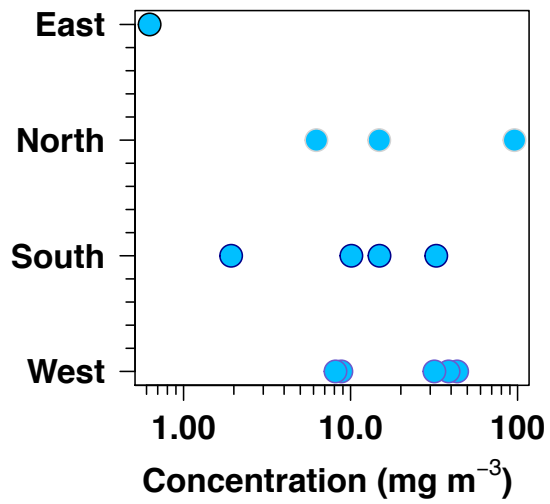
142 **Figure SI-8.** Relative humidity outputted from HySPLIT back trajectories initialized at the

143 beginning of each fog event sampled in this study. All samples with the exception of that

144 collected on 30 June were impacted by air masses that had been at high RH (>80%) for a portion

145 of the previous 72 hours.

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148 **Figure SI-9.** Liquid water contents ( $\text{mg m}^{-3}$ ) measured during fog water events at BYI,  
 149 categorized by direction of back trajectory. The category “East” contains only one sample, but  
 150 this sample was collected during the lowest LWC of the field campaign. No other apparent  
 151 dependence of LWC on air mass origin direction can be observed.

152 **Table SI-1.** Meteorological and sample variables recorded during fog events. Sample masses are volume-weighted means.

<b>Date and Time</b>	<b>End Time</b>	<b>Duration (min)</b>	<b>Temperature (°C)</b>	<b>Wind Dir. (Deg)</b>	<b>Sample Mass (g)</b>
6/30/14 5:02	8:00	175	20.4	247.5	20.76
7/1/14 7:21	9:16	116	21.4	135	211.23
7/1/14 9:16	12:05	169	19.9	135	47.67
7/2/14 4:45	6:15	90	20.4	135	74.34
7/2/14 6:15	7:45	90	19.1	90	66.05
7/2/14 7:45	9:15	90	19.1	90	54.31
7/2/14 9:14	11:30	135	20.1	90	22.59
7/6/14 3:16	6:40	205	21.1	0	2.44
7/14/14 20:45	22:45	120	24.3	157.5	18.52
7/18/14 2:46	4:45	120	23.2	202.5	33.96
7/18/14 5:15	7:15	120	21.5	135	23.06
7/18/14 9:14	10:15	60	21.9	90	2.20
7/20/14 6:15	8:15	120	22.3	112.5	74.32

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156 **Table SI-2.** Concentrations of measured inorganic species during fog events. Unless specified, units of chemical species are  $\mu\text{M}$ , with the  
 157 exception of that for pH (unitless).

Date and Time	pH	$\text{NH}_4^+$	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{Cl}^-$	$\text{Ca}^{+2}$	$\text{Na}^+$	$\text{Mg}^{+2}$	$\text{K}^+$	S(IV)	Charge Balance (+/-)
6/30/14 5:02	3.54	2914	606.2	1674	1.6	111	114	70	56	88	2.17	1.14
7/1/14 7:21	4.14	253	72.0	185	0.3	22	19	24	13	16	0.250	1.02
7/1/14 9:16	4.37	632	155.0	370	2.2	30	34	20	15	18	0.684	1.08
7/2/14 4:45	3.77	2076	601.8	873	1.9	90	33	71	48	73	1.40	1.10
7/2/14 6:15	3.93	2153	601.3	792	1.7	118	19	63	44	72	1.39	1.14
7/2/14 7:45	3.98	2723	742.2	1050	1.9	140	46	88	50	89	1.87	1.16
7/2/14 9:14	3.67	3840	1072	1638	3.1	219	34	2921	53	97	1.89	1.76
7/6/14 3:16	n.m.	4044	2272	4897	4.1	900	175	2445	276	171	n.m.	0.73
7/14/14 20:45	5.00	6088	1645	2247	5.6	381	138	213	120	172	6.27	1.18
7/18/14 2:46	3.69	1113	451.6	687	0.3	418	110	425	91	79	4.92	1.00
7/18/14 5:15	3.74	650	355.7	758	1.4	489	180	487	88	41	1.67	0.87
7/18/14 9:14	n.m.	668	273.2	383	2.1	279	86	275	40	96	n.m.	1.07
7/20/14 6:15	3.48	1750	592.3	772	1.2	95	18	59	52	62	3.49	0.98

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161 **Table SI-3.** Concentrations of measured TOC and low molecular mass organic acids during fog events. Units of organic acids are  $\mu\text{M}$ .

Date and Time	TOC (ppmC)	Acetate	Propionate	Formate	MSA	Pyruvate	Valerate	Succinate	Malonate	Maleate	Oxalate	Glutarate	Total Organic Acids
6/30/14 5:02	24.7	121	0.929	115	18.6	15.2	0.943	47.6	24.8	58.8	69.4	3.30	476
7/1/14 7:21	n.m.	160	1.07	101	1.79	0.79	0.245	3.31	1.48	3.04	5.86	0.92	280
7/1/14 9:16	4.66	40.8	0.998	84.1	1.77	1.19	0.676	6.58	3.00	3.87	8.16	1.16	152
7/2/14 4:45	14.2	66.9	1.06	81.0	9.15	6.86	1.27	29.7	11.0	15.3	54.8	8.42	286
7/2/14 6:15	20.2	67.6	1.16	110	7.50	6.61	0.838	26.6	9.19	12.5	49.5	8.58	301
7/2/14 7:45	24.8	91.2	1.20	129	7.50	10.7	1.63	36.8	11.2	16.2	58.2	12.4	376
7/2/14 9:14	21.3	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
7/6/14 3:16	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
7/14/14 20:45	n.m.	202	1.36	532	12.9	5.02	3.78	52.6	22.5	42.2	110	18.3	1002
7/18/14 2:46	n.m.	19.3	0.418	35.8	7.18	3.58	0.213	9.15	7.45	19.6	29.7	5.59	138
7/18/14 5:15	n.m.	59.0	0.353	26.6	6.05	5.35	0.337	6.21	6.21	21.3	18.6	2.78	153
7/18/14 9:14	n.m.	640	0.528	42.7	6.71	38.8	0.436	6.19	6.05	20.6	16.2	4.61	783
7/20/14 6:15	8.97	49.7	0.600	57.6	6.12	7.03	1.01	26.8	14.7	18.4	35.7	5.51	223

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165 **Table SI-4.** Concentrations of measured organic species during fog events. Unless specified, units of chemical species are  $\mu\text{M}$ . Pinonate was also  
 166 quantified, but no measurable values were found within fog samples. Grey, italicized values: Not significantly different from 0 because value was  
 167 less than LOD or less than uncertainty (95% CI).

Date and Time	Peroxides	Formaldehyde	2-Methyl-4,6-Dinitrophenol	4-Nitrophenol	2,4-Dinitrophenol	2-Methyl-4-Nitrophenol	Benzoate	Salicylate	Adipate	Pinate	Azelaate
6/30/14 5:02	1.1	21	0	0.04	0.02	<i>0.00007</i>	0.03	0.11	0.15	0.01	0.04
7/1/14 7:21	3.7	6	0	0	0	0	0	0	0	0	0
7/1/14 9:16	15.2	3	0	0	<i>0.008</i>	0	0.02	<i>0.07</i>	0.04	<i>0.009</i>	<i>0.002</i>
7/2/14 4:45	0.6	4	<i>0.00002</i>	0	0.024	0	0.06	<i>0.06</i>	0.10	<i>0.006</i>	0.03
7/2/14 6:15	0.4	4	<i>0.0004</i>	0	0.04	0	0.08	<i>0.06</i>	0.11	<i>0.007</i>	0.04
7/2/14 7:45	0.6	6	<i>0.0012</i>	0.05	0.06	<i>0.00004</i>	0.11	0.10	0.14	0.01	0.04
7/2/14 9:14	0.4	7	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
7/6/14 3:16	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
7/14/14 20:45	58.9	9	<i>0.004</i>	0.14	0.07	0.04	0.14	0.15	0.14	<i>0.009</i>	0.04
7/18/14 2:46	1.0	3	0	0	<i>0.0001</i>	0	<i>0.001</i>	<i>0.03</i>	0.15	0.02	0.03
7/18/14 5:15	0.6	n.m.	0	0	0	0	<i>0.000003</i>	<i>0.03</i>	0.16	<i>0.005</i>	0.09
7/18/14 9:14	n.m.	n.m.	0	0	0	0	<i>0.00008</i>	<i>0.02</i>	0.02	<i>0.00003</i>	0
7/20/14 6:15	3.7	3	0	0	<i>0.0001</i>	0	0.02	<i>0.06</i>	0.05	0.03	0