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# **RESEARCH ARTICLE**

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# **Special Section:**

Nitrogen, Aerosol Composition and Halogens Over a Tall Tower (NACHTT1)

#### **Key Points:**

- Coarse-fraction sodium chloride aerosols are prevalent in winter in Colorado
- Marine sources may contribute to NaCl aerosols at this midcontinental site
- Saline soil sources may also contribute to the observed NaCl aerosols

## Supporting Information:

- Readme
- Figures S1–S6
- Tables S1–S8

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# Origins of aerosol chlorine during winter over north central Colorado, USA

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Abstract The Nitrogen, Aerosol Composition, and Halogens on a Tall Tower campaign (February–March 2011) near Boulder, Colorado, investigated nighttime CINO<sub>2</sub> production and processing. Virtually all particulate CI was in the form of ionic  $CI^-$ . The size distributions of  $CI^-$  and  $Na^+$  were similar, with most of the mass in the supermicrometer size fraction, suggesting primary sources for both. Median Cl<sup>-</sup> concentrations were about half those of Na<sup>+</sup> and Ca<sup>2+</sup> for particle diameters centered at 1.4 and 2.5  $\mu$ m. To investigate potential sources of Na<sup>+</sup> and Cl<sup>-</sup>, four cases were studied that featured the prevalence of Na<sup>+</sup> and Cl<sup>-</sup> and different transport pathways based on FLEXible PARTicle dispersion model (FLEXPART) retroplumes. Estimates of supermicrometer Na<sup>+</sup> particle lifetime against deposition indicate that long-range transport of marine aerosols could account for the observed Na<sup>+</sup>. However, measured molar ratios of Ca<sup>2+</sup> to Na<sup>+</sup> (0.143–0.588) compared to seawater (0.022) indicate significant contributions from crustal sources to the supermicrometer aerosol composition during these four case studies. Further, low molar ratios of Mg<sup>2+</sup> to Na<sup>+</sup> (0.007–0.098) relative to seawater (0.114) suggest that some of the Na<sup>+</sup>, and presumably associated Cl<sup>-</sup>, originated from non-sea-salt sources. The heterogeneous chemical composition of saline soils throughout the western U.S., along with the nonlinearity of wind-driven soil deflation as a function of various surface soil properties, precludes a quantitative apportionment of soil, marine, and anthropogenic sources to the observed coarse-fraction aerosol. Nonetheless, results suggest that deflation of saline soils was a potentially important source of particulate CI<sup>-</sup> that sustained atmospheric CINO<sub>2</sub> production and associated impacts on oxidation processes over northern Colorado.

# 1. Introduction

The potentially important role of halogen chemistry in the troposphere was first suggested 40 years ago [e.g., *Schroeder and Urone*, 1974; *Zafiriou*, 1974]. As summarized recently by *Saiz-Lopez and von Glasow* [2012], reactive halogen species destroy tropospheric ozone through efficient catalytic cycles analogous to those in the stratosphere. Chlorine also enhances ozone production in polluted air by affecting the partitioning of HO<sub>x</sub> and NO<sub>x</sub> as well as the oxidation of volatile organic compounds. Chemical processes involving tropospheric bromine oxidize elemental mercury (Hg<sup>0</sup>  $\rightarrow$  Hg<sup>2+</sup>) [*Steffen et al.*, 2008; *Moore et al.*, 2013] and dimethyl sulfide [*Toumi*, 1994; *von Glasow and Crutzen*, 2004]. lodine compounds also participate in new particle formation under some conditions [*O'Dowd et al.*, 2002].

The dominant source of chlorine-containing gases in the troposphere is volatilization of inorganic Cl species from primary marine aerosol, although sources associated with human activities are also important over land [e.g., *Keene et al.*, 1999]. Several Cl-containing molecules are released. Absorption and acidification of the aerosol primarily by nitric and sulfuric acids leads to HCl volatilization (e.g., *Eriksson* [1959] among many others):

$$HNO_{3}(g) + NaCI (p) \rightarrow HCI(g) + NaNO_{3}(p)$$
(R1)

$$\label{eq:H2SO4} \begin{array}{ll} \mathsf{H_2SO}_4(g) + 2 \ \ \mathsf{NaCl} \ \ (p) {\rightarrow} 2 \ \ \mathsf{HCl}(g) + \mathsf{Na}_2\mathsf{SO}_4(p) \end{array} \tag{R2}$$

Some organic acids such as oxalic acid may also contribute to aerosol acidification and associated dechlorination [e.g., *Laskin et al.*, 2012]. However, oxalate (and other organic anions) in the particulate phase are typically present at much lower concentrations relative to nitrate and sulfate indicating that mineral acids are the major drivers of dechlorination via acid displacement under most conditions. Multiphase reactions involving N-containing gases

other than HNO<sub>3</sub> also occur. These include NO<sub>2</sub> [*Altshuler*, 1958; *Schroeder and Urone*, 1974], CINO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> [*Finlayson-Pitts et al.*, 1989]:

$$2 NO_2(g) + NaCI(p) \rightarrow NOCI(g) + NaNO_3(p)$$
(R3)

$$CINO_{3}(g) + NaCI(p) \rightarrow CI_{2}(g) + NaNO_{3}(p)$$
(R4)

$$N_2O_5(g) + NaCl(p) \rightarrow CINO_2(g) + NaNO_3(p)$$
(R5a)

NOCl,  $Cl_2$ , and  $ClNO_2$  all photolyze readily to yield atomic Cl (Cl-). Cl- reacts rapidly with  $CH_4$ , which may account for a small but significant fraction of the global atmospheric  $CH_4$  sink [e.g., *Allan et al.*, 2007; *Lawler et al.*, 2011]. Cl- also oxidizes other hydrocarbons primarily via hydrogen abstraction yielding HCl and, in the presence of sufficient  $NO_x$ , organic radicals that enhance net ozone production [e.g., *Keene et al.*, 1990].

According to Brown and Stutz [2012], the analog to reaction (R5a)

$$N_2O_5(g) + HCI(aq) \rightarrow CINO_2(g) + HNO_3(aq)$$
(R5b)

was first suggested by *Cantrell et al.* [1987] and confirmed in the laboratory by *Tolbert et al.* [1988], who reacted  $N_2O_5$  on HCl/ice films and observed the ClNO<sub>2</sub> product at low temperature. *Finlayson-Pitts et al.* [1989] subsequently reacted  $N_2O_5$  on bulk NaCl at room temperature and detected the ClNO<sub>2</sub> product by infrared spectroscopy. This group later defined the yield of ClNO<sub>2</sub> from uptake of  $N_2O_5$  to dry NaCl to be unity and suggested that the process should lead to nmol mol<sup>-1</sup> levels of ClNO<sub>2</sub> in the polluted marine boundary layer at dawn [*Livingston and Finlayson-Pitts*, 1991]. Not until 15 years later was this suggestion confirmed by the first ambient measurements of ClNO<sub>2</sub> by *Osthoff et al.* [2008], who found nmol mol<sup>-1</sup> levels in polluted coastal Gulf of Mexico air. *Riedel et al.* [2012] recently reported ClNO<sub>2</sub> mixing ratios up to 2.1 nmol mol<sup>-1</sup> in air flowing offshore from the Los Angeles, California, basin at night.

It had been assumed that reactions (R5a) and (R5b) would be inconsequential far inland, where a marine source for particulate  $CI^-$  would be negligible. Thus, it was a surprise when *Thornton et al.* [2010] measured  $CINO_2$  at mixing ratios approaching 1 nmol mol<sup>-1</sup> at times in Boulder, Colorado, during winter. The nearest seacoast (northern Gulf of California) is more than 1200 km distant, the Pacific coast is of order 1500 km away, and lying in between are the Rocky Mountains. Measurements of nonrefractory  $CI^-$  associated with submicrometer diameter aerosol indicated that, without replenishment and/or significant concentrations of unmeasured  $CI^-$  (i.e., associated with either refractory compounds or supermicrometer size fractions), amounts were insufficient to sustain the inferred  $CINO_2$  production. This led *Thornton et al.* [2010] to hypothesize that the particulate  $CI^-$  consumed in the production of  $CINO_2$  at night was replenished via condensation of HCl vapor. However, HCl was not measured during their study.

Only three other measurements of CINO<sub>2</sub> mixing ratios at inland sites have been reported to date. Levels similar to those in and near Boulder were observed in Calgary, Alberta, Canada, in April by *Mielke et al.* [2011]. In this case neither HCl nor aerosol composition was measured. Like Boulder, Calgary is far inland and leeward of the Rocky Mountains. Urban/industrial sources of Cl were assumed to sustain CINO<sub>2</sub> production. Measurements atop Kleiner Feldberg near Frankfurt, Germany, during August and September also showed similar CINO<sub>2</sub> mixing ratios (up to ~800 pmol mol<sup>-1</sup>) [*Phillips et al.*, 2012]. Again, neither HCl nor aerosol composition was measured. However, this site is only ~400 km from the North Sea coast and there are no major mountain ranges in between. Aerosol optical depth and trajectory analysis were used to argue reasonably for a sea-salt source for precursor aerosol Cl<sup>-</sup>.

During February–March 2011, the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) campaign (http://www.esrl.noaa.gov/csd/tropchem/2011NACHTT) was conducted near Boulder, Colorado, to resolve the nature of CINO<sub>2</sub> production during winter nights in continental regions [*Brown et al.*, 2013]. *Riedel et al.* [2013] measured an average of 0.27 nmol mol<sup>-1</sup> and maximum of 1.3 nmol mol<sup>-1</sup> CINO<sub>2</sub> during NACHTT. Concurrent measurements of HCl and size-resolved aerosol composition revealed that multiphase recycling of Cl via HCl condensation to particles, refractory Cl<sup>-</sup> in the form of NaCl, and Cl<sup>-</sup> associated with supermicrometer diameter size fractions were all important in sustaining CINO<sub>2</sub> production [*Young et al.*, 2013]. Surprisingly, the soluble ionic composition suggested that much of the aerosol Cl<sup>-</sup> during NACHTT



**Figure 1.** Site of Boulder Atmospheric Observatory (BAO) mapped along with surface soils classified as moderately and strongly saline in the Natural Resources Conservation Service (NRCS) Soil Survey Geographic Database (SSURGO).

was in the form of NaCl associated with relatively short-lived supermicrometer size fraction. In this paper, we report additional details of aerosol composition measured during NACHTT and interpret these data in conjunction with air mass history to evaluate primary sources for the precursor Cl required to drive this chemical pathway.

## 2. Methods

#### 2.1. Field Site

A comprehensive suite of airborne chemical species and associated physical conditions were measured at the National Oceanic and Atmospheric Administration (NOAA) Boulder Atmospheric Observatory (BAO) tower near Erie, Colorado (40.05°N, 105.01°W, and 1584 m elevation; see Figure 1) during the NACHTT campaign, on 18 February to 12 March 2011 (see *Brown et al.* [2013] and *Young et al.* [2013] for details). The size-resolved and bulk aerosols reported here were sampled from a platform on the BAO tower at 22 m above ground level.

#### 2.2. Aerosol Sampling and Chemical Analysis

The aerosol sampling methodology has been described in detail in a companion paper to this study [Young et al., 2013]. In brief, bulk high-volume aerosol was sampled on cellulose filters (here denoted Bulk<sub>HV</sub>) and size-segregated aerosols were sampled with a cascade impactor (denoted "impactor"). Impactor and Bulk<sub>HV</sub> samples were analyzed via ion chromatography (the latter denoted Bulk<sub>HV,IC</sub>) for SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and several organic ions including (COO)<sub>2</sub><sup>2-</sup> [Keene et al., 2009]. The impactor 50% aerodynamic diameter cut sizes were 0.25, 0.44, 0.80, 1.4, 2.5, 10, and 20 µm.

Aerosols were also sampled in bulk using a filter pack (FP) technique, with the methodology described in detail by *Sander et al.* [2013]. Samples and field blanks were collected on 47 mm diameter Whatman 41 cellulose filters mounted in 47 mm diameter Nuclepore polycarbonate cassettes. Eight samples were collected each day with sample changes keyed to sunrise and sunset and other change times adjusted such that sampling intervals were approximately equal (~3 h). Field blanks were obtained once per day at different times. Exposed filters were stored frozen at the University of New Hampshire (UNH) prior to preparation for neutron activation analysis (NAA) at the Rhode Island Nuclear Science Center (RINSC).

Bulk<sub>HV</sub> and FP samples were analyzed by NAA (Bulk<sub>HV,NAA</sub> and Bulk<sub>FP</sub> respectively) using a procedure similar to that described by *Uematsu et al.* [1983]. For Bulk<sub>FP</sub> samples and blanks the entire filter was analyzed. For Bulk<sub>HV,NAA</sub> samples and blanks a 47 mm diameter circle was punched from exposed areas of each filter using



**Figure 2.** Wind Erodibility Indices (WEI) of moderately and strongly saline soils shown with locations of meteorological stations for which there is wind speed data for each of the case studies shown in Figure 3.

a stainless steel cutting die. Details of the storage, preparation, and analytical methodology employed for the NAA analysis are identical to those provided in *Sander et al.* [2013]. Data were obtained for seven elements: Na, Mg, Al, Cl, Mn, V, and Br.

Further information on the analyses and data quality may be found in the supporting information with this manuscript.

# 2.3. Ancillary Data 2.3.1. Meteorological Information

Hourly surface meteorological conditions measured at stations upwind of the study site were downloaded from NOAA's National Climate Data Center archive at http://www.ncdc.noaa.gov/ oa/ncdc.html. The locations of the stations from which wind speed data were available within the FLEXPART retroplume footprints of the case studies (described below) are shown in Figure 2 and listed in Tables S5-S8 in the supporting information. All stations active during the NACHTT campaign are shown in Figure 3 (small white dots, in addition to the larger white squares identifying stations in the retroplume footprints).

#### 2.3.2. Land Surface Data

Surface soil salinity and wind erodibility indices were drawn from the U.S. Department of Agriculture, Natural Resource Conservation Service (NRCS) Soil Survey Geographic Database (SSURGO), available online at http://websoilsurvey.nrcs.usda.gov/, [Soil Survey Staff, 2014]. Here the objective is to identify potential source regions of saline soils readily erodible by wind; hence, only surface soil (depth = 0 cm) attributes were queried.

Electrical conductivity (EC) is used to identify saline soils. Only moderately (8.1 mS/cm  $\leq$  EC  $\leq$  16 mS/cm) and strongly (EC > 16 mS/cm) saline soils are mapped in Figure 1, and the wind erodibility indices (WEI) for these soils are mapped in Figure 2. WEI are discrete values used to indicate the mass of soil eroded by wind in tons/acre/yr. For details on these indices, see the supporting information with this manuscript.

#### 2.3.3. Road Deicer Information

Repeated requests to the Colorado Department of Transportation (CDOT) for information regarding dates, types, and amounts of deicer applied to highways near the BAO tower during the campaign yielded no response. The CDOT website (http://www.coloradodot.info/travel/winter-driving/faqs.html) suggests that the deicing agent used most often is Mg rather than Na based. However, a study commissioned by CDOT indicates that in 2007 a variety of deicing agents was in use statewide, including several that contain Na, K, Ca, and Mg in different combinations [*Shi et al.*, 2009].

#### 2.4. FLEXPART

The FLEXPART Lagrangian particle dispersion model (version 8.2) [*Stohl et al.*, 2005] was used to simulate the transport histories of the air masses arriving at the BAO tower during NACHTT. The model was driven by global National Centers for Environmental Prediction Global Forecast System wind fields with a temporal resolution of 3 h (analyses at 0000, 0600, 1200, and 1800 UTC; 3 h forecasts at 0300, 0900, 1500, and 2100 UTC), horizontal resolution of  $0.5^{\circ} \times 0.5^{\circ}$ , and 26 vertical levels. The air arriving at the BAO tower is represented



**Figure 3.** FLEXPART retroplume footprints for four case studies: (a) case 1 (19–20 February), (b) case 2 (25–26 February), (c) case 3 (5 March), and (d) case 4 (8–9 March). Small white dots indicate meteorological stations active during February and March 2011. Large white squares highlight meteorological stations within the densest portion of each footprint for which there are wind speed data. Black circles indicate major urban areas, scaled to population. Black triangles mark the locations of ocean buoys with meteorological data available for case 2.

by thousands of hypothetical back trajectory particles, proportional to the mass of an air parcel at the base of the tower. Particles are transported by both the resolved winds and parameterized subgrid motions, including a vertical deep convection scheme.

A retroplume was calculated every 30 min (see *Cooper et al.* [2005] for a detailed description of the method); each consisted of 40,000 particles released from the latitude and longitude of the BAO tower between 0 and 50 m above ground level and advected backward in time over an 8 day period. Results indicate both likely transport pathways and associated emission source regions for the species measured at the tower. The so-called footprint layer, which is the 300 m deep layer adjacent to the Earth's surface, is particularly useful in characterizing upwind surface source regions for atmospheric constituents.

# 3. Results

Ratios and size distributions of chemical constituents in the particulate phase provide insight regarding the nature of the parent material from which the constituents originated [Keene et al., 1986; Arimoto et al., 1995; Savoie et al., 2002; Sander et al., 2003].

#### 3.1. Comparisons of NAA and IC Results

Paired measurements of ionic and elemental Na, Mg, Cl, and Br in bulk high-volume samples (Bulk<sub>HV,IC</sub> and Bulk<sub>HV,NAA</sub>, respectively) are summarized in Table S3 and Figure S1. A reduced major axis (RMA) regression of Cl<sup>-</sup> versus total Cl yielded a slope statistically indistinguishable from 1.0 and an  $r^2$  of 0.98 indicating that



**Figure 4.** Time series of (a) total AI, (b) total Na, and (c) total CI measured in Bulk<sub>FP</sub> samples. Vertical gray bars indicate nighttime. Case study periods denoted by the numbers at the top of Figure 4b, cases 1, 2, and 4 were overnight ~1800–0600, while case 3 was daytime ~0600–1800 Mountain Standard Time (MST).

virtually all particulate Cl was in the form of ionic Cl<sup>-</sup> (Figure S1a). Na<sup>+</sup>, Mg<sup>2+</sup>, and Br<sup>-</sup> concentrations were also significantly correlated (p < 0.05) with corresponding total element concentrations ( $r^2 = 0.62$ , 0.35, and 0.62, respectively) but with RMA regression slopes less than 1, indicating significant contributions of water-insoluble forms. On average, only ~7% of Mg was soluble. Br was approximately 50% soluble, although it should be noted that Br<sup>-</sup> was present above the detection limit in only 14 of the 45 samples. Because the major chemical constituents of sea water are present as dissolved ions [*Wilson*, 1975], these results imply that significant amounts of elemental Na, Mg, and Br associated with particles sampled during the campaign originated from non-sea-salt sources.

#### 3.2. Trace Element Time Series

Time series of elemental Al, Na, Cl, and Br sampled with the filter packs are shown in Figures 4 and S3. Virtually all particulate Al in the atmosphere originates from crustal sources [e.g., *Arimoto et al.*, 1995, 1997]; Mg, Mn, and V (not shown) were highly correlated with Al ( $r^2 = 0.92$ , 0.98, and 0.97, respectively) suggesting that these elements were also associated primarily with mineral aerosol. The Na time series (Figure 4b) is similar to that of crustal Al during some periods but not during others. For example, both Na and Al concentrations peaked near sunset on 19 February and on 2 March. In contrast, Na peaked near sunset on 20 and 21 February and near sunrise on 23 February and 9 March, whereas Al did not. These time series relationships are consistent with the hypothesis that Na originated from both crustal and noncrustal sources. Chlorine (Figure 4c) follows Na quite closely through 6 March and moderately well thereafter indicating association with the same aerosol component. The Br time series (Figure S3) is quite distinct from all of the others suggesting that either sources for particulate Br differ from those of chemically conservative aerosol constituents such as Al and Na or multiphase chemical processing leads to divergence in concentrations of particulate Br relative to conservative aerosol constituents [e.g., *Sander et al.*, 2003].

#### 3.3. Variations of Ionic Composition With Particle Size

Particle size distributions of the major ionic species are summarized in Figure 5. Na<sup>+</sup> and Ca<sup>2+</sup> were mainly associated with supermicrometer sizes suggesting that these chemically conservative species originated from primary sources such as sea salt, soils, road salt, etc. Most  $CI^-$  was also associated with supermicrometer sizes, but  $CI^-$  is not chemically conservative (e.g., reactions (R1)–(R5a), and the gas-aerosol phase partitioning



**Figure 5.** Size distributions (particle aerodynamic diameters,  $D_{ae}$ , in micrometers) of (left) NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> and (right) Ca<sup>2+</sup>, Cl<sup>-</sup>, and Na<sup>+</sup>. Larger symbols joined by lines depict median values and smaller symbols depict individual data. Note that the vertical scales differ between the panels.

HCl is a function of solution pH [Young et al., 2013]. Consequently, the size distribution of Cl<sup>-</sup> may vary in response to both chemical processing and source.  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  were predominantly associated with submicrometer sizes suggesting production primarily via secondary pathways involving gas phase precursors. The median concentrations of the submicrometer size fractions indicate that  $NH_4^+$  and  $NO_3^-$  were the dominant ionic components of aerosol mass, consistent with previous measurements in areas influenced by Denver regional emissions (summarized by *Brown et al.* [2013]) and with observations over much of the western U.S. generally [e.g., *Seinfeld and Pandis*, 1998].

Median concentrations for Na<sup>+</sup> and Ca<sup>2+</sup> were similar in each size fraction, whereas median Cl<sup>-</sup> concentrations were about half those of Na<sup>+</sup> and Ca<sup>2+</sup> for particle diameters centered at 1.4 and 2.5  $\mu$ m (Figure 5). However, the size distributions of these three ions for each impactor sample [see *Young*, 2012, Appendix] reveal distinct variability. In the coarse fraction, Ca<sup>2+</sup> is the dominant ion on a molar basis in 15 samples (i.e., Ca<sup>2+</sup> concentration exceeds all other ions by at least 50% in at least one coarse-fraction stage of these 15 impactor samples). Na<sup>+</sup> and Cl<sup>-</sup> are the dominant ions on a molar basis in eight samples (each exceeding all other ions by at least 50% in at least one coarse-fraction grave fraction stage of these eight impactor samples). The remaining 20 impactor samples exhibit comparable coarse-fraction molar concentrations of Ca<sup>2+</sup> and Na<sup>+</sup>, with Cl<sup>-</sup> coarse-fraction concentrations sometimes comparable to both of those ions. It is evident from the above that relative influences of different types of source and atmospheric processes on the composition of coarse-fraction aerosols varied temporally during the campaign.

Molar ratios of  $Ca^{2+}$  relative to  $Na^+$  that are significantly higher than that in surface seawater (0.022) indicate nonmarine and presumably crustal origins for  $Ca^{2+}$  [*Keene et al.*, 1986; *Arimoto et al.*, 1995]. As noted above, the presence of significant insoluble Na (Figure S1 and Table S3) also implies a non-sea-salt and presumably crustal source for both the insoluble component and possibly some of the corresponding  $Na^+$ , along with other ionic species (including  $Cl^-$ ) that are emitted to the atmosphere in association with surface soils [*Graedel and Keene*, 1996].

#### 3.4. Case Studies to Probe Aerosol Na and Cl Sources

We investigated potential marine and terrestrial sources of Na<sup>+</sup> and Cl<sup>-</sup> based on four case studies for which Na<sup>+</sup> and Cl<sup>-</sup> dominated the molar composition of supermicrometer size fractions (Figure 6). Composites of the retroplume footprints were created for these periods with the resulting transport pathways found to be different for all four cases (Figure 3). These cases are noted in the time series plots of major ionic aerosol constituents in Figure S4. Meteorological stations within the FLEXPART retroplume footprints (Figure 3) provide wind speed data (Figures S5 and 7) that are interpreted in the context of typical threshold speeds (described below) needed to loft soil dust particles. Where the wind speeds exceed these thresholds in the vicinity of saline soils (Figure 2), crustal sources may contribute to aerosol NaCl observed at BAO.



Figure 6. Size distributions (particle geometric mean diameters, GMD, in micrometers) of major ionic constituents for (a) case 1, (b) case 2, (c) case 3, and (d) case 4.

Case 1 (19 to 20 February, 1757–0647 Mountain Standard Time, MST) had a dominant footprint region nearly due south of the site that extended to the Gulf of California. The most distant meteorological station along the retroplume footprint was ~1600 km from BAO with a transport time over this distance for this case of ~24 h (Figure 3a). The footprint for case 2 (25 to 26 February, 1818–0638 MST) extended southwest of BAO to the north coast of the Gulf of California and beyond with a northerly branch that continued up along the California coast line (Figure 3b). The distance from the offshore meteorological sites along the southern California coast to BAO is ~1500 km. Transport from the mid-California coast near the end of the FLEXPART back trajectory was ~24 h for this case. Case 3 (5 March, 0637–1756 MST) had a more westerly footprint that extended both to the north and south but not to the coast (Figure 3c). Transport from the most distant meteorological stations in Utah along the retroplume footprint for this case was < 24 h over a distance of ~650 km. Finally, the case 4 (8 to 9 March, 1813–0621 MST) footprint extended northwesterly to the Pacific coast (Figure 3d). Transport for this case was ~48 h from the Oregon coast, >1600 km, and ~24 h from the most distant meteorological station along the retroplume footprint in Idaho, ~1000 km.

White dots in Figure 3 indicate the locations of meteorological stations in the vicinity of the case study FLEXPART footprints that were active during February and March 2011. Larger white squares highlight the stations in the peak regions of each FLEXPART footprint that reported wind speeds during the period of each case study. Available wind speed data for all of the stations for each case study are shown in Figure S5. For reference, two threshold wind speeds of  $8 \text{ m s}^{-1}$  and  $14 \text{ m s}^{-1}$  are depicted (Figure S5) as dashed and solid black lines, respectively, indicating potential wind-driven lofting of crustal material. The choice of those particular thresholds is explained in the discussion section below. To place these meteorological data in context of the saline soil erodibility, markers indicating each of the stations with meteorological data (large white squares, Figure 3) for each case study are shown in Figure 2. A subset of the wind speed data illustrating key features of each of the case studies is provided in Figure 7.

In the description of each case that follows, the wind speed thresholds of  $8 \text{ m s}^{-1}$  and  $14 \text{ m s}^{-1}$  (based on *Boyer* [2003], which may be conservative as discussed below) are used to assess the plausibility of saline crustal contributions from the retroplume footprint regions to the aerosol observations at BAO. Once initiated, deflation can continue after the wind speeds drop below the threshold speed [*Boyer*, 2003].

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**Figure 7.** Wind speeds at three meteorological stations for each case study ((top left) case 1, (top right) case 2, (bottom left) case 3, and (bottom right) case 4). All plots start 48 h before sampling commenced at BAO for each case. The 24 h point before sampling started is indicated in all plots with a black vertical line. The sampling period is highlighted in the gray section of each panel. Two threshold wind speeds are indicated in all panels by horizontal lines (dashed line, 8 m s<sup>-1</sup>, and solid line, 14 m s<sup>-1</sup>). Note that the *y* axes differ for each case. Wind speed data (SPD) are shown in blue, wind gust data (GUS), where available, are shown in black. Individual meteorological station IDs (two- to four-letter codes in legends) may be found in Tables 55–58 in the supporting information. The panels for each case are arranged such that the top panel in each set is for the station nearest BAO and the bottom panel is for the station farthest from BAO. Wind speed data for the four case studies from all meteorological stations shown with large white squares in Figure 3 are provided in Figure 55 in the supporting information.

**Table 1.** Measured Coarse-Fraction Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> Concentrations (nmol m<sup>-3</sup>) at BAO, Along With the Molar Ratios of Coarse-Fraction Ca<sup>2+</sup> and Mg<sup>2+</sup> to Na<sup>+</sup> at BAO for the Four Case Studies<sup>a</sup>

|        | UTC Midpoint<br>(m-dd-yyyy hhmm) | Supermicrometer Na <sup>+</sup><br>(nmol/m <sup>3</sup> ) | Supermicrometer Cl <sup>-</sup><br>(nmol/m <sup>3</sup> ) | Supermicrometer Ca <sup>2+</sup><br>(nmol/m <sup>3</sup> ) | Supermicrometer Mg <sup>2+</sup><br>(nmol/m <sup>3</sup> ) | Ca <sup>2+</sup> :Na <sup>+</sup><br>(Molar Ratio) | Mg <sup>2+</sup> :Na <sup>+</sup><br>(Molar Ratio) |
|--------|----------------------------------|---|---|--|--|--|--|
| Case 1 | 2-20-2011 0722                   | 15.81   | 16.34   | 2.26   | 1.15   | 0.143  | 0.073  |
| Case 2 | 2-26-2011 0728                   | 12.82   | 10.76   | 4.83   | 0.84   | 0.377  | 0.066  |
| Case 3 | 3-05-2011 1916                   | 4.78  | 4.63  | 2.81   | 0.59   | 0.588  | 0.123  |
| Case 4 | 3-09-2011 0717                   | 5.63  | 5.40  | 1.45   | 0.55   | 0.258  | 0.098  |

<sup>a</sup>For comparison, the expected seawater ratios for  $Ca^{2+}:Na^+$  and  $Mg^{2+}:Na^+$  are provided. Seawater molar ratios:  $Ca^{2+}/Na^+ = 0.022$ ;  $Mg^{2+}/Na^+ = 0.114$  [*Wilson*, 1975].

#### 3.4.1. Case 1

The FLEXPART footprint for case 1 (Figure 3) shows transport to BAO from nearly due south to southwest extending to the Gulf of California and Baja California. SSURGO does not include soil data outside of the U.S., so the maps here include no salinity or WEI information for the four meteorological stations in the footprint in Mexico. Further, the wind speed data from those stations during NACHTT is extremely limited (Figure S5b). In the 24 h prior to observations at BAO, the wind speed does not exceed 8 m s<sup>-1</sup> at the four Mexican meteorological stations, although the few gust data at one site (HI, Table S5) are  $\geq 10 \text{ m s}^{-1}$ .

Data for the New Mexico stations all exhibit higher wind speeds and more frequent gusts (Figures S5a and S5b). Of particular note here, all five stations in New Mexico lie along a line of moderately saline soils (Figures 1 and 2). With wind gusts at all five stations exceeding  $15 \text{ m s}^{-1}$ , these saline soils may contribute to particulate Na<sup>+</sup> and Cl<sup>-</sup> at BAO. Data from the Albuquerque International and Alexander Municipal stations (Figure 7 and Table S5) are characteristic of the wind speeds at all of the New Mexico stations.

For the most part, the Colorado meteorological stations (Table S5) for this case are either not near saline soils or are in regions where there is no SSURGO data, with the exception of the Alamosa Municipal station which is in a region of moderately saline soils in the south central part of the state (Figure 2). Here wind gusts  $>20 \text{ m s}^{-1}$  (Figure 7) occurred in the 24 h prior to sampling at BAO, potentially contributing to the observed atmospheric saline aerosols.

Among the four cases, the highest wind speeds occurred during case 1 (Figure 7), which may have contributed to the higher Na<sup>+</sup> and Cl<sup>-</sup> coarse-fraction concentrations (15.81 and 16.34 nmol m<sup>-3</sup>, respectively) relative to the other cases (Table 1 and Figure 6) via more efficient production and transport to the site of both marine and crustal aerosol. For this case, supermicrometer aerosol concentrations for Ca<sup>2+</sup> and Mg<sup>2+</sup> were 2.26 and 1.15 nmol m<sup>-3</sup>, respectively, resulting in ratios of 0.143 (well in excess of the 0.022 molar sea-salt ratio) for Ca<sup>2+</sup>:Na<sup>+</sup> and 0.073 (smaller than the 0.114 molar sea-salt ratio) for Mg<sup>2+</sup>:Na<sup>+</sup> (Table 1). This suggests not only the presence of crustal Ca<sup>2+</sup> but crustal Na<sup>+</sup> as well.

#### 3.4.2. Case 2

The meteorological data for this case are particularly sparse with no wind speed data available during NACHTT along most of the FLEXPART footprint from southwestern Colorado across Arizona (Figures 2 and 3). Further, along most of this pathway there are few saline soil sources, although the four Arizona sites (two at Yuma, Table S6a, appear as one dot in Figures 2 and 3) are collocated with regions where there are no SSURGO data. The few sites near moderately and strongly saline soils (Figures 1 and 2) are along the northern branch of the California footprint. The Madera site, northernmost in California and nearest the saline soils, has wind speeds >10 m s<sup>-1</sup>, with gusts up to ~18 m s<sup>-1</sup> in the 24 h prior to sampling at BAO (Figure 7).

With so much of the footprint along the southern California coast, marine aerosols may be more likely than crustal dust as a source for the observed coarse-fraction Na<sup>+</sup> and Cl<sup>-</sup>. Indeed, National Data Buoy Center data (http://www.ndbc.noaa.gov) for buoys active during the NACHTT campaign indicate that surface wind speeds over open water off the southern California coast were 4 m s<sup>-1</sup> or greater (Figure S6) for the 48 h prior to the case 2 sampling interval at BAO, sufficient for sea-salt aerosol generation. Such wind speeds are consistent with those from island sites such as San Nicolas Island (Figure 7; westernmost station off the coast of California, Figure 2) ~5 m s<sup>-1</sup>.

In addition, although the H A Clark Memorial Field site in Arizona (Table S6a and Figure 2) is in a SSURGO data gap, wind speed data (Figure 7) would indicate that deflation of soil material might have occurred at this

station. The high coarse-fraction concentration of  $Ca^{2+}$  (4.83 nmol m<sup>-3</sup>, the largest concentration observed among the four cases and well in excess of the median of ~2.50 nmol m<sup>-3</sup>, Table 1) clearly indicates the presence of significant crustal material in this sample at BAO. As was observed for case 1, the molar ratio of supermicrometer  $Ca^{2+}:Na^+$  for this case, 0.377, far exceeds the molar sea-salt ratio (0.022), while that for Mg<sup>2+</sup>:Na<sup>+</sup>, 0.066, again is smaller than that of seawater, 0.114, suggesting crustal contributions to both coarse-fraction  $Ca^{2+}$  and Na<sup>+</sup> for this case at BAO (Table 1).

#### 3.4.3. Case 3

Case 3 was associated with the smallest FLEXPART footprint of the four case studies (Figure 3), the fewest meteorological stations (Figure 2), and the slowest wind speeds (Figures 7 and S5f). Coarse-fraction concentrations of Na<sup>+</sup> and Cl<sup>-</sup> (4.78 and 4.63 nmol m<sup>-3</sup>, respectively) observed at BAO (Table 1 and Figure 6) were significantly lower than those for the first two cases. The coarse Ca<sup>2+</sup> concentration (2.81 nmol m<sup>-3</sup>) was substantially lower than case 2 but still higher than case 1 and the median during NACHTT, suggesting a crustal component to the coarse aerosols at BAO.

The northern branch to the FLEXPART footprint extends into northern Utah, with the remainder of the footprint extending west southwest of BAO into south central Utah (Figures 2 and 3). All of the Utah meteorological stations are near strongly and moderately saline soil sources (Figures 1 and 2), but the wind speeds observed are all  $<8 \text{ m s}^{-1}$  (Figures 7 and S5f). Similarly, the wind speeds (Figure 7) at the westernmost Colorado site (GJW, Table S7), collocated with moderately saline soils, are also  $<8 \text{ m s}^{-1}$ , but there are a couple of gusts recorded ~10 m s<sup>-1</sup>. The highest wind speeds in the 24 h prior to sampling at BAO are found at Montrose Regional (MR, Table S7 and Figures 2 and 7) with wind speeds exceeding 8 m s<sup>-1</sup> and gusts over 10 m s<sup>-1</sup>. However, this site is in a SSURGO data gap, so the availability of erodible saline soils is unknown.

Here supermicrometer  $Ca^{2+}:Na^+$  is 0.588, the highest ratio of the four cases, while  $Mg^{2+}:Na^+$  is 0.123 (Table 1) not only the highest of the four cases but the only one that exceeds the sea-salt ratio of 0.114. These ratios suggest that crustal sources are important here (for both  $Ca^{2+}$  and  $Mg^{2+}$ ), yet the low winds speeds within the FLEXPART footprint, along with the gaps in the available soil and meteorological data, make it difficult to definitively ascribe the observed aerosol properties at BAO for this case to recent upwind soil deflation along the retroplume footprint.

#### 3.4.4. Case 4

Case 4 has the broadest FLEXPART footprint, extending west northwest into Idaho and northeastern Oregon and beyond to the Pacific coast (Figure 3). Saline soils are near a few meteorological stations from which we have wind speed data for this case (Figure 2). Wind speeds are generally  $< 8 \text{ m s}^{-1}$  for all but four of the stations in Idaho (Figures S5g and S5h). Jerome County (JC, Table S8 and Figure 2) is the southernmost station in Idaho and nearest the saline soils to its west. If the wind speeds are typical of those in the region of the saline soils, then the wind gusts up to  $15 \text{ m s}^{-1}$  may have lofted saline soils into the atmosphere (Figure 7) during this period.

Saline soils in Wyoming are sparse, with large regions of limited data. One meteorological station in the region without SSURGO data (Rock Springs Sweetwater, Table S8 and Figure 2) reported wind speeds  $> 14 \text{ m s}^{-1}$  (Figures 7 and S5g) potentially sufficient to loft dust, but whether there are suitably erodible saline soils nearby is unknown. Saline soils are near the meteorological stations in Utah (Figure 2 and Table S8), but the wind speeds are  $< 8 \text{ m s}^{-1}$ , with only a few gusts (e.g., at Ogden-Hinckley Municipal site, Figure 7) above that threshold. The remaining sites in Colorado either have low wind speeds (e.g., Dinosaur, Dnsr, Figure S5g) or lack saline soils (Figure 2 and Table S8).

As with case 3, the coarse-fraction Na<sup>+</sup> and Cl<sup>-</sup> concentrations for this case are not large (5.63 and 5.40 nmol m<sup>-3</sup>, respectively, Table 1 and Figure 6). Coarse-fraction Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations are 1.45 and 0.55 nmol m<sup>-3</sup>, the smallest observed at BAO for the four cases, resulting in ratios to Na<sup>+</sup> of 0.258 and 0.098, respectively. The former indicates crustal Ca<sup>2+</sup> sources, while the latter is close to the ratio found in seawater.

### 4. Discussion

The four cases selected for further investigation due to the prevalence of  $Na^+$  and  $Cl^-$  in the coarse-fraction aerosols do not exhibit retroplume footprints emanating from one source region. Further, not all of the retroplumes indicate likely marine sources. In addition to deflation of playa deposits and other chloride-rich soil types, other possible non-sea-salt sources for particulate Na and Cl during NACHTT include deicing salts applied to roads, biomass burning, and fossil fuel combustion and other industrial processes. Although fossil fuel combustion and other industrial processes emit HCl [*McCulloch et al.*, 1999], some of which would subsequently condense and contribute to particulate Cl<sup>-</sup>, these are not important sources for particulate Na.

Prior studies in the Denver area in January (e.g., 1979 [*Dzubay et al.*, 1981] and 1982 [*Lewis et al.*, 1986]) have attributed coarse-fraction Cl<sup>-</sup> to road salt. However, there were no significant snowfall events near the site throughout the duration of the campaign [*Brown et al.*, 2013]. Hence, road salt was not applied to the local roadways, limiting any coarse-aerosol generation from active road salting in the vicinity of the site. We did not have access to information on the application or composition of road salt applied over more distant upwind regions during the period of the campaign and, consequently, could not explicitly evaluate potential contributions to particulate Cl<sup>-</sup> from this source. However, given the limited areal extent of such applications over the western U.S., it seems unlikely that emissions from road salting and the subsequent long-distance transport from distant locations would have contributed significantly to supermicrometer Cl<sup>-</sup> at BAO during NACHTT.

All biomass contains Cl, most of which is emitted to the atmosphere during combustion in the form of volatile inorganic Cl (including HCl) and particulate Cl [*Lobert et al.*, 1999; *Keene et al.*, 2006]. HCl emitted directly or produced from reactions involving other inorganic Cl gases emitted during combustion will subsequently partition with particles based on thermodynamic properties of the system. Although most Na associated with biomass is also emitted during combustion, the Na content of biomass is typically low relative to Cl [*Keene et al.*, 2006], and, consequently, ratios of total Cl to Na emitted during biomass burning are generally greater than those associated with marine aerosol, playa deposits, or road salts.

Acetonitrile, a tracer of biomass burning emissions [*Holzinger et al.*, 1999], was measured during NACHTT by *Swarthout et al.* [2013]. Although several range fires occurred in the region during the period of the campaign, the relatively low acetonitrile mixing ratios (median of 113 pptv and range of 36 to 503 pptv) indicated that plumes from those burns were not sampled directly. *Swarthout et al.* [2013] suggested that emissions from these fires probably contributed to the measured levels of acetonitrile in the region. Emissions from biofuel burned for domestic space heating would have also contributed. However, the strong correlations with propane in flow from the northeast, south, and west wind sectors suggested that significant amounts of the measured acetonitrile were emitted in association with natural gas production, which implies that the relatively low mixing ratios of acetonitrile during the campaign represent upper limits for contributions from biomass burning.

Based on the above, we infer that emissions from industrial sources, road salts, and biomass burning were relatively minor to negligible sources of particulate Na and CI measured during NACHTT. Available evidence suggests that the long-distance transport of marine aerosol from the North Pacific and deflation of surface soils were the primary sources for these species.

Long-Range Transport of Marine Aerosols. It has been recognized for many years that the long-distance transport of marine aerosols may influence geochemical cycles in continental regions far inland from coasts [e.g., *Stallard and Edmond*, 1981]. Most estimates of marine aerosol lifetimes against deposition based on in situ observations and model calculations range from 0.5 to 2 days [e.g., *Graedel and Keene*, 1995; *Gong et al.*, 1997; *Erickson et al.*, 1999; *Williams et al.*, 2002; *Jaeglé et al.*, 2011; *Long et al.*, 2014]. These residence times can be applied to the observed supermicrometer concentrations of Na<sup>+</sup> at BAO, to provide constraints for the initial Na<sup>+</sup> concentrations at the coast that would be required to account for Na<sup>+</sup> at the study site. Such estimates are based on the assumptions that (1) all Na<sup>+</sup> at BAO originated from marine aerosol production (an upper limit) and (2) deposition rates of marine aerosol populations do not vary during transport over land. We recognize that this latter assumption is problematic.

The largest, shortest-lived size fractions dominate the dry deposition fluxes of marine aerosols to the surface ocean [e.g., *Hummelshøj et al.*, 1992]. As these larger size fractions rapidly dry deposit but are not replaced during transport over land, size distributions of marine aerosol populations shift toward smaller-sized, longer-lived particles. Via this process marine aerosol lifetimes against deposition would increase when transported over land, everything else being the same. However, topography and vegetation increase near-surface turbulence over land relative to the ocean thereby increasing dry deposition fluxes to land surfaces and decreasing marine aerosol lifetimes against dry deposition, which would tend to counteract the influence of longer lifetimes due to decreasing particles sizes.

**Table 2.** Estimate of Sea-Salt Na<sup>+</sup> Concentrations at the Coast Required to Sustain Supermicrometer Na<sup>+</sup> Measured at BAO Based on a Transport Time of 24 h and Aerosol Removal as a Function of *e*-Folding Time and Assumed Lifetimes Against Deposition of 0.5 and 2 Days<sup>a</sup>

|        |                                |   | Estimated Supermicrometer $Na^+$ at the Coast          |  |  |
|--------|--------------------------------|---|--|--|--|
|        | UTC Midpoint<br>m-dd-yyyy hhmm | Measured BAO<br>Supermicrometer Na <sup>+</sup> | Residence Time: 0.5 Day<br>(2 <i>e</i> -Folding Times) | Residence Time: 2.0 Days<br>(1/2 <i>e</i> -Folding Time) |  |
| Case 1 | 2-20-2011 0722                 | 15.81   | 116.82   | 26.07  |  |
| Case 2 | 2-26-2011 0728                 | 12.82   | 94.73  | 21.14  |  |
| Case 3 | 3-05-2011 1916                 | 4.78  | 35.32  | 7.88   |  |
| Case 4 | 3-09-2011 0717                 | 5.63  | 41.60  | 9.28   |  |
| 2      | 2                              |   |  |  |  |

<sup>a</sup>All units nmol m<sup>-3</sup>.

Assuming that the above influences are of roughly comparable magnitude but in opposite direction and that other potentially important factors (e.g., variability in removal via wet versus dry deposition or variability in wind velocity and associated dry deposition velocities) are inconsequential, we applied the published estimates of marine aerosol lifetimes to constrain the initial concentrations at the coast that would be required to account for Na<sup>+</sup> at the study site (Table 2). The required initial concentrations are well within the range for typical mean Na<sup>+</sup> concentrations observed over the open ocean (e.g., 150 to 250 nmol Na<sup>+</sup> m<sup>-3</sup>) [*Galloway et al.*, 1993; *Gong et al.*, 1997; *Jaeglé et al.*, 2011] and in coastal regions (e.g., 85 nmol Na<sup>+</sup> m<sup>-3</sup>) [*Jordan et al.*, 2000]. These results suggest that long-range transport of marine aerosol can account for the observed Na<sup>+</sup> and Cl<sup>-</sup> at BAO during these four cases.

However, in all four cases, molar ratios of  $Ca^{2+}$  to  $Na^+$  associated with supermicrometer size fractions (ranging from 0.143 to 0.588, Table 1) were much greater than that for surface seawater 0.022 [*Wilson*, 1975] indicating significant contributions from crustal sources. In addition, for cases 1, 2, and 4, molar ratios of  $Mg^{2+}$  to  $Na^+$  associated with supermicrometer size fractions (0.073, 0.066, and 0.098, respectively, Table 1) were somewhat less than that in surface seawater (0.114) [*Wilson*, 1975] indicating that some of the  $Na^+$  originated from non-sea-salt sources [*Keene et al.*, 1986]. If some of this non-sea-salt  $Na^+$  was emitted in the form of NaCl (for example from evaporite deposits), the associated  $Cl^-$  would have also originated from non-sea-salt sources [*Graedel and Keene*, 1996]. Crustal NaCl sources are certainly plausible in this region, due to the prevalence of saline soils in the western United States (Figure 1), with strongly saline soils particularly concentrated in Nevada, Utah, and southeastern Oregon.

Saline Soils. Playas (dry lake beds composed of saline soils) are known dust sources [e.g., *Prospero et al.*, 2002; *Boyer*, 2003; *Mahowald et al.*, 2003; *Pratt et al.*, 2010] that are prevalent throughout the western U.S. and northern Mexico. Additionally, former ocean sediments (e.g., in Baja California), alluvial flats, and other landforms that contain saline soils can be readily eroded by wind representing a terrestrial crustal source of Na<sup>+</sup> and Cl<sup>-</sup>. *Pratt et al.* [2010] noted the presence of playa sources as distinct from marine sources (distinguished in part on the presence of negative organic nitrogen ion markers in aerosol mass spectra) in orographic clouds over Wyoming when back trajectories indicated the precursor air mass had passed over regions of playa soils.

Dust storms arise from relatively localized regions due to the fact that aerosol production via deflation of soils depends not just on wind speed but on surface soil characteristics that include soil texture (i.e., sand, silt, and clay content), the presence/absence of vegetation, soil moisture, soil particle grain sizes, the presence of a surface crust and aggregate materials, including rocks. These characteristics are extremely inhomogeneous, and their interactions are such that aerosol dust generation is highly nonlinear, exhibiting a particular sensitivity to thresholds [*Webb and McGowan*, 2009, and references therein].

Crusts can form on dry playas limiting their susceptibility to wind erosion. However, wet playas (those subject to precipitation or wetting via groundwater fluctuations) have salt crystals reform on the surface as the moisture evaporates leaving behind a "fluffy" easily erodible surface [*Pratt et al.*, 2010, and references therein]. *Reynolds et al.* [2007] argued that only wet playas offer a significant source of aeolian dust. This intermittent role of water can lead to seasonal variability that complicates the identification of a threshold wind velocity required to loft soil particles into the air.

Additionally, field studies [*Ishizuka et al.*, 2012] in the Gobi Desert of Mongolia found that in late winter/early spring at the start of the annual Asian dust storm season, the threshold wind speed was ~14.0 m s<sup>-1</sup>. After a few weeks, however, there was a significant decrease to ~8.8 m s<sup>-1</sup>, attributed to the breakdown of the thin fragile surface crust by saltation of large particles during the early storms. A field study at a playa site in the Mojave Desert, California, found a threshold wind speed of ~6 m s<sup>-1</sup> [*Ravi and D'Odorico*, 2005] that varied somewhat (from 5.7 to 6.4 m s<sup>-1</sup>) with atmospheric relative humidity (that influences soil moisture in such arid regions). Anthropogenic activities can also affect soil surface properties. For example, off-road vehicles disturb the natural surface, which may either promote or suppress wind erosion, depending on the soil characteristics [*Goossens and Buck*, 2009].

It is important to note that wind speed thresholds identified in the literature for dust storms are relevant to lofting large soil grains that lead to visible atmospheric dust. Such grains range in size on the order of 100–1000  $\mu$ m diameter for sand, tens of micrometers diameter for silt, and <10  $\mu$ m for clay [e.g., *Goossens and Buck*, 2009]. A laboratory study in a wind tunnel using soil samples from four sites at Owens Lake (a dry lake), California, found that particulate matter  $\leq$  10  $\mu$ m in diameter (PM<sub>10</sub>) wind speed thresholds were 50%–75% of those traditionally identified for visible dust erosion [*Roney and White*, 2004]. In this particular case soils from three sites exhibited a PM<sub>10</sub> wind speed threshold of 4 m s<sup>-1</sup>, and one site had a threshold of 6 m s<sup>-1</sup>, compared to a visible dust wind speed threshold of 8 m s<sup>-1</sup> [*Roney and White*, 2004]. This last finding has important implications for the possibility of subvisible dust deflation relevant to atmospheric PM<sub>10</sub>.

In addition to the heterogeneities associated with wind-driven soil deflation described above, the nature of closed playa basins and the minerals and salts within them vary spatially [*Eugster*, 1980]. This variability precludes unequivocal characterization of contributions from playa dusts to aerosol composition based on chemically conservative crustal tracers such as Al and non-sea-salt Ca<sup>2+</sup>. For example, *Pratt et al.* [2010] list 14 evaporite minerals commonly found in playas, of which five contain Cl, and each of those contains Cl in different proportions to the base cations Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Ca<sup>2+</sup>. Depending on the relative amount of minerals in each basin, a different proportionality will be found among ionic and elemental constituents. This is in stark contrast to marine aerosols for which the relative proportions of inorganic constituents are indistinguishable from those in seawater over most of Earth's surface. Halite (NaCl) has been reported to constitute  $\geq$ 95% by mass of minerals in some deposits in California, while in others the proportion was much smaller [*Ver Planck*, 1958]. Deposits near the Great Salt Lake in Utah were reported to contain only 3% to 7% halite [*Güven and Kerr*, 1966], illustrating the range of variability that may be encountered. Nonetheless, broadly speaking, playa evaporites are typically enriched in Ca<sup>2+</sup> and K<sup>+</sup> relative to Na<sup>+</sup> in seawater [*Pratt et al.*, 2010].

#### 5. Conclusions

For all of the reasons above, we cannot precisely differentiate relative contributions from marine versus crustal sources, or even adequately account for potential contributions from anthropogenic road salt, although available evidence suggests that this source is probably minor to negligible. Nonetheless, using maps of soil characteristics and wind speeds within FLEXPART retroplume footprints coupled with crustal tracers, it is possible to broadly characterize potential contributions of saline soils to aerosol composition measured during the campaign.

The four case studies examined here, selected solely on the basis of the dominance of  $Na^+$  and  $Cl^-$  in the supermicrometer aerosol mass, revealed that these ions do not arrive at BAO from a limited region under specific meteorological and transport regimes but rather arrive from large geographically diverse source regions surrounding the site to the south, west, and northwest. Maps indicate that saline soils are prevalent throughout these source regions. Here we show that these soils in the western U.S. and Mexico are likely important sources of particulate  $Na^+$  and  $Cl^-$  in the middle of North America, although long-distance transport of marine aerosol from the western North Pacific Ocean probably also contributes significantly to ambient concentrations.

Although the variability of inorganic crustal components precludes the identification of unique ratios that can be used as source tracers in the same way sea-salt ratios may be used, the ability to distinguish marine versus crustal sources of NaCl via negative organic nitrogen ion markers in mass spectra [*Pratt et al.*, 2010]

promises to be a useful technique to further constrain inland coarse-aerosol CI sources in the future. No matter the source, the evidence obtained during NACHTT clearly indicates that significant concentrations of supermicrometer  $Na^+$  and  $Cl^-$  are not confined to coastal regions.

*Pratt et al.* [2010] reported evidence that playa dust aerosols contributed cloud condensation nuclei to orographic clouds over Wyoming. They suggested that future studies are needed to quantify the influence of playa salts on cloud formation and climate particularly in light of anticipated climate and land use changes that may lead to increased frequency and intensity of dust storms. The NACHTT data set suggests that these dust sources may also play an important role in oxidative tropospheric chemical processes and air quality, supporting the need for greater understanding of the various atmospheric processes in which these soil salts may play a role.

## References

Allan, W., H. Struthers, and D. C. Lowe (2007), Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements, *J. Geophys. Res.*, 112, D04306, doi:10.1029/2006JD007369.
Altshuler, A. P. (1958), Natural sources of gaseous pollutants in the atmosphere, *Tellus*, 10, 479–492.

Arimoto, R., R. A. Duce, B. J. Ray, W. G. Ellis Jr., J. D. Cullen, and J. T. Merrill (1995), Trace elements in the atmosphere over the North Atlantic, J. Geophys. Res., 100, 1199–1213, doi:10.1029/94JD02618.

Arimoto, R., B. J. Ray, N. F. Lewis, U. Tomza, and R. A. Duce (1997), Mass-particle size distributions of atmospheric dust and the dry deposition of dust to the remote ocean, J. Geophys. Res., 102, 15,867–15,874, doi:10.1029/97JD00796.

Boyer, J. (2003), Forecasting dust storms. [Available at http://www.nrlmry.navy.mil/aerosol\_web/Docs/comet/mesoprim/dust/print.htm.] Brown, S. S., and J. Stutz (2012), Nighttime radical observations and chemistry, *Chem. Soc. Rev.*, 41, 6405–6447.

Brown, S. S., et al. (2013), Nitrogen, Aerosol Composition and Halogens on a Tall Tower (NACHTT): Overview of a wintertime air chemistry field study in the Front Range urban corridor of Colorado, J. Geophys. Res. Atmos., 118, 8067–8085, doi:10.1002/jgrd.50537.

Cantrell, C. A., J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert (1987), Reactions of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> with molecular-species of possible atmospheric interest, *J. Phys. Chem.*, *91*, 6017–6021.

Cooper, O. R., et al. (2005), A springtime comparison of tropospheric ozone and transport pathways on the east and west coasts of the United States, J. Geophys. Res., 110, D05590, doi:10.1029/2004JD005183.

Dzubay, T. G., R. K. Stevens, W. J. Courtney, and E. A. Drane (1981), *Electron Microscopy and X-Ray Applications to Environmental and Occupational Health Analysis*, vol. 2, edited by P. A. Russell, pp. 23–42, Ann Arbor Sci., Ann Arbor, Mich.

- Erickson, D. J., C. Seuzaret, W. C. Keene, and S.-L. Gong (1999), A GCM-based model of HCl and CINO<sub>2</sub> production from sea-salt dechlorination: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8347–8372, doi:10.1029/98JD01384.
- Eriksson, E. (1959), The yearly circulation of chlorine and sulfur in nature: Meteorological, geochemical and pedologica1implications, 1, *Tellus*, 11, 375–403.

Eugster, H. P. (1980), Geochemistry of evaporitic lacustrine deposits, Annu. Rev. Earth Planet. Sci., 8, 35-63.

Finlayson-Pitts, B. J., M. J. Ezell, and J. N. Pitts (1989), Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>, *Nature*, 337, 241–244.

Galloway, J. N., D. L. Savoie, W. C. Keene, and J. M. Prospero (1993), The temporal and spatial variability of scavenging ratios for NSS sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean, Atmos. Environ., 27A, 235–250.

Gong, S. L., L. A. Barrie, J. M. Prospero, D. L. Savoie, G. P. Ayers, J.-P. Blanchett, and L. Spacek (1997), Modeling sea-salt aerosols in the atmosphere: 2. Atmospheric concentrations and fluxes, J. Geophys. Res., 102, 3819–3830, doi:10.1029/96JD03401.

Goossens, D., and B. Buck (2009), Dust dynamics in off-road vehicle trails: Measurements on 16 arid soil types, Nevada, USA, J. Environ. Manage., 90, 3458–3469.

Graedel, T. E., and W. C. Keene (1995), The tropospheric budget of reactive chlorine, *Global Biogeochem. Cycles*, *9*, 47–78, doi:10.1029/94GB03103. Graedel, T. E., and W. C. Keene (1996), The budget and cycle of Earth's natural chlorine, *Pure Appl. Chem.*, *68*, 1689–1697.

Güven, N., and P. F. Kerr (1966), Weathering effects on the structures of mica-type clay minerals, Am. Mineral., 51, 858-874.

- Holzinger, R., C. Warneke, A. Hansel, A. Jordan, W. Lindinger, D. H. Scharffe, G. Schade, and P. J. Crutzen (1999), Biomass burning as a source of formaldehyde, acetaldehyde, methanol, acetone, acetonitrile, and hydrogen cyanide, *Geophys. Res. Lett.*, 26, 1161–1164, doi:10.1029/ 1999GL900156.
- Hummelshøj, P., N. O. Jensen, and S. E. Larsen (1992), Particle dry deposition to a sea surface, in *Precipitation Scavenging and Atmosphere-Surface Exchange*, edited by S. E. Schwartz and W. G. N. Slinn, pp. 829–840, Hemisphere Corp., Wash.
- Ishizuka, M., M. Mikami, Y. Yamada, R. Kimura, Y. Kurosaki, D. Jugder, B. Gantsetseg, Y. Cheng, and M. Shinoda (2012), Does ground surface soil aggregation affect transition of the wind speed threshold for saltation and dust emission?, SOLA, 8, 129–132, doi:10.2151/ sola.2012-032.

Jaeglé, L., P. K. Quinn, T. S. Bates, B. Alexander, and J.-T. Lin (2011), Global distribution of sea salt aerosols: New constraints from in situ and remote sensing observations, *Atmos. Chem. Phys.*, *11*, 3137–3157.

Jordan, C. E., R. W. Talbot, and B. D. Keim (2000), Water-soluble nitrogen at the New Hampshire sea coast: HNO<sub>3</sub>, aerosols, precipitation, and fog, J. Geophys. Res., 105, 26,403–26,431, doi:10.1029/2000JD900298.

Keene, W. C., A. A. P. Pszenny, J. N. Galloway, and M. E. Hawley (1986), Sea-salt corrections and interpretation of constituent ratios in marine precipitation, J. Geophys. Res., 91, 6647–6658, doi:10.1029/JD091iD06p06647.

Keene, W. C., A. A. P. Pszenny, D. J. Jacob, R. A. Duce, J. N. Galloway, J. J. Schultz-Tokos Jr., H. Sievering, and J. F. Boatman (1990), The geochemical cycling of reactive chlorine through the marine troposphere, *Global Biogeochem. Cycles*, *4*, 407–430, doi:10.1029/GB004i004p00407.

Keene, W. C., et al. (1999), Composite global emissions of reactive chlorine from natural and anthropogenic sources: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8429–8440, doi:10.1029/1998JD100084.

Keene, W. C., J. M. Lobert, P. J. Crutzen, J. R. Maben, D. H. Scharffe, T. Landmann, C. Hély, and C. Brain (2006), Emissions of major gaseous and particulate species during experimental burns of southern African biomass, J. Geophys. Res., 111, D04301, doi:10.1029/ 2005JD006319.

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Keene, W. C., M. S. Long, A. A. P. Pszenny, R. Sander, J. R. Maben, A. J. Wall, T. L. O'Halloran, A. Kerkweg, E. V. Fischer, and O. Schrems (2009), Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans, Atmos. Chem. Phys., 9, 7361–7385.

Laskin, A., R. C. Moffet, M. K. Gilles, J. D. Fast, R. A. Zaveri, B. Wang, P. Nigge, and J. Shutthanandan (2012), Tropospheric chemistry of internally mixed sea salt and organic particles: Surprising reactivity of NaCl with weak organic acids, J. Geophys. Res., 117, D15302, doi:10.1029/ 2012JD017743.

Lawler, M. J., R. Sander, L. J. Carpenter, J. D. Lee, R. von Glasow, R. Sommariva, and E. S. Saltzman (2011), HOCl and Cl<sub>2</sub> observations in marine air, Atmos. Chem. Phys., 11, 7617–7628, doi:10.5194/acp-11-7617-2011.

Lewis, C. W., R. H. Baumgardner, R. K. Stevens, and G. M. Russwurm (1986), Receptor modeling study of Denver winter haze, *Environ. Sci. Technol.*, 20, 1126–1136.

Livingston, F. E., and B. J. Finlayson-Pitts (1991), The reaction of gaseous N<sub>2</sub>O<sub>5</sub> with solid NaCl at 298 K: Estimated lower limit to the reaction probability and its potential role in tropospheric and stratospheric chemistry, *Geophys. Res. Lett.*, *18*, 17–20, doi:10.1029/90GL02595.

Lobert, J., W. C. Keene, J. A. Logan, and R. Yevich (1999), Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8373–8389, doi:10.1029/1998JD100077.

Long, M. S., W. C. Keene, R. Easter, R. Sander, X. Liu, A. Kerkweg, and D. J. Erickson (2014), Sensitivity of tropospheric chemical composition to halogen-radical chemistry using a fully coupled size-resolved multiphase chemistry/global climate system: Halogen distributions, aerosol composition, and sensitivity of climate-relevant gases, Atmos. Chem. Phys., 14, 3397–3425.

Mahowald, N. M., R. G. Bryant, J. del Corral, and L. Steinberger (2003), Ephemeral lakes and desert dust sources, *Geophys. Res. Lett.*, 30(2), 1074, doi:10.1029/2002GL016041.

McCulloch, A., M. L. Aucott, C. M. Benkovitz, T. E. Graedel, G. Kleiman, P. M. Midgley, and Y.-F. Li (1999), Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory, J. Geophys. Res., 104, 8391–8403, doi:10.1029/1999JD900025.

Mielke, L. H., A. Furgeson, and H. D. Osthoff (2011), Observation of CINO<sub>2</sub> in a mid-continental urban environment, *Environ. Sci. Technol.*, 45, 8889–8896.

Moore, C. W., D. Obrist, and M. Luria (2013), Atmospheric mercury depletion events at the Dead Sea: Spatial and temporal aspects, Atmos. Environ., 69, 231–239.

O'Dowd, C. D., J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hameri, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffman (2002), Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632–636.

Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, *1*, 324–328, doi:10.1038/ngeo177.

Phillips, G. J., M. Tang, J. Thieser, B. Brickwedde, G. Schuster, B. Bohn, J. Lelieveld, and J. N. Crowley (2012), Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophys. Res. Lett.*, 39, L10811, doi:10.1029/2012GL051912.

Pratt, K. A., et al. (2010), Observation of playa salts as nuclei in orographic wave clouds, J. Geophys. Res., 115, D15301, doi:10.1029/ 2009JD013606.

Prospero, J. M., P. Ginoux, O. Torres, S. E. Nicholson, and T. E. Gill (2002), Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product, *Rev. Geophys.*, 40(1), 1002, doi:10.1029/2000RG000095.

- Ravi, S., and P. D'Odorico (2005), A field-scale analysis of the dependence of wind erosion threshold velocity on air humidity, *Geophys. Res. Lett.*, 32, L21404, doi:10.1029/2005GL023675.
- Reynolds, R. L., J. C. Yount, M. Reheis, H. Goldstein, P. Chavez Jr., R. Fulton, J. Whitney, C. Fuller, and R. M. Forester (2007), Dust emission from wet and dry playas in the Mojave Desert, USA, *Earth Surf. Processes Landforms*, *32*, 1811–1827, doi:10.1002/esp.1515.

Riedel, T. P., et al. (2012), Nitryl chloride and molecular chlorine in the coastal marine boundary layer, *Environ. Sci. Technol.*, 46, 10,463–10,470, doi:10.1021/es204632r.

Riedel, T. P., et al. (2013), Chlorine activation within urban or power plant plumes: Vertically resolved CINO<sub>2</sub> and Cl<sub>2</sub> measurements from a tall tower in a polluted continental setting, J. Geophys. Res. Atmos., 118, 8702–8715, doi:10.1002/jgrd.50637.

Roney, J. A., and B. R. White (2004), Definition and measurement of dust aeolian thresholds, J. Geophys. Res., 109, F01013, doi:10.1029/2003JF000061.

Saiz-Lopez, A., and R. von Glasow (2012), Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41, 6448–6472.

Sander, R., et al. (2003), Inorganic bromine in the marine boundary layer: A critical review, Atmos. Chem. Phys., 3, 1301–1336.

Sander, R., A. A. P. Pszenny, W. C. Keene, E. Crete, B. Deegan, M. S. Long, J. R. Maben, and A. H. Young (2013), Gas phase acid, ammonia and aerosol ionic and trace element concentrations at Cape Verde during the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) 2007 intensive sampling period, *Earth Syst. Sci. Data*, *5*, 385–392.

Savoie, D. L., R. Arimoto, W. C. Keene, J. M. Prospero, R. A. Duce, and J. N. Galloway (2002), Marine biogenic and anthropogenic contributions to non-sea-salt sulfate in the marine boundary layer over the North Atlantic Ocean, J. Geophys. Res., 107(D18), 4356, doi:10.1029/2001JD000970.

Schroeder, W. H., and P. Urone (1974), Formation of nitrosy1 chloride from sea particles in air, *Environ. Sci. Technol.*, 8, 756–758. Seinfeld, J. H., and S. N. Pandis (1998), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley, New York.

Shi, X., et al. (2009), Evaluation of alternative Anti-icing and deicing compounds using sodium chloride and magnesium chloride as baseline deicers—Phase I, *Rep. No. CDOT-2009-1*.

Soil Survey Staff (2014), Web Soil Survey, Natural Resources Conservation Service, United States Department of Agriculture. [Available at http://websoilsurvey.nrcs.usda.gov/, Accessed March and April of 2014.]

Stallard, R. F., and J. M. Edmond (1981), Geochemistry of the Amazon: 1. Precipitation chemistry and the marine contribution to the dissolved load at the time of peak discharge, J. Geophys. Res., 86, 9844–9858, doi:10.1029/JC086iC10p09844.

Steffen, A., et al. (2008), A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow, *Atmos. Chem. Phys.*, 8, 1445–1482.

Stohl, A., C. Forster, A. Frank, P. Seibert, and G. Wotowa (2005), Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2, Atmos. Chem. Phys., 5, 2461–2474.

Swarthout, R. F., R. S. Russo, Y. Zhou, A. H. Hart, and B. C. Sive (2013), Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources, J. Geophys. Res. Atmos., 118, 10,614–10,637, doi:10.1002/jgrd.50722.

Thornton, J. A., et al. (2010), A large atomic chlorine source inferred from mid-continental reaction nitrogen chemistry, *Nature*, 464, 271–274, doi:10.1038/nature08905.

Tolbert, M. A., M. J. Rossi, and D. M. Golden (1988), Antarctic ozone depletion chemistry: Reactions of N<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O and HCl on ice surfaces, *Science*, *240*, 1018–1021.

Toumi, R. (1994), BrO as a sink for dimethylsulfide in the marine atmosphere, *Geophys. Res. Lett.*, *21*, 117–120, doi:10.1029/93GL03536. Uematsu, M., R. A. Duce, J. M. Prospero, L. Chen, J. T. Merrill, and R. L. McDonald (1983), Transport of mineral aerosol from Asia over the North Pacific Ocean, *J. Geophys. Res.*, *88*, 5343–5352, doi:10.1029/JC088iC09p05343.

Ver Planck, W. L. (1958), Salt in California, 178 pp., Calif. Div. Mines Bull, San Francisco, Calif.

von Glasow, R., and P. J. Crutzen (2004), Model study of multiphase DMS oxidation with a focus on halogens, *Atmos. Chem. Phys.*, *4*, 589–608. Webb, N. P., and H. A. McGowan (2009), Approaches to modeling land erodibility by wind, *Prog. Phys. Geogr.*, *33*, 587–613.

Williams, J., M. de Reus, R. Krejci, H. Fischer, and J. Ström (2002), Application of the variability-size relationship to atmospheric aerosol studies: Estimating aerosol lifetimes and ages, Atmos. Chem. Phys., 2, 133–145.

Wilson, T. R. S. (1975), Salinity and the major elements of seawater, in *Chemical Oceanography*, vol. 1, 2nd ed., edited by J. P. Riley and G. Skirrow, chap. 6, Academic Press, London.

Young, A. H. (2012), Phase Partitioning of Soluble Trace Gases With Size-Resolved Aerosols in Near-Surface Continental Air Over Northern Colorado, USA During Winter, MS thesis, pp. 365–413, Univ. of New Hampshire, ProQuest, UMI Dissertations, Durham, N. H.

Young, A. H., W. C. Keene, A. A. P. Pszenny, R. Sander, J. A. Thornton, T. P. Riedel, and J. R. Maben (2013), Phase partitioning of soluble trace gases with size-resolved aerosols in near-surface continental air over northern Colorado, USA during winter, J. Geophys. Res. Atmos., 118, 9414–9427, doi:10.1002/jgrd.50655.

Zafiriou, O. C. (1974), Photochemistry of halogens in the marine atmosphere, J. Geophys. Res., 79, 2730–2732, doi:10.1029/JC079i018p02730.