Response to Reviewer #2

> **We thank the reviewer for their helpful comments and suggestions. We provide below the original comments, shown in gray, and our responses, with specific revisions noted, in bold font. Line numbers refer to the non-tracked changes version of the manuscript. The tracked changes manuscript is included.**

The detailed particle analyses given in this paper offers important information about the nature of the Arctic aerosol during winter. Both the presence of sea salt associated with many particles and the demonstration of a potential Prudhoe Bay influence (Fig. 5) are interesting. The paper is well presented. Improvements can be made with some relatively simple additions/changes. Please consider the following comments.

1) January and February are winter months. There are no spring measurements given in the paper, and the title needs to be changed appropriately. There are other places in the paper where this work is mistakenly referred to as winter-spring.

> **We defined the seasons based on the timing of polar sunrise. The January samples were collected the week of polar sunrise. Since the literature is not consistent with the naming of the seasons, we changed "winter-spring" to "winter" in the title and elsewhere when appropriate. We also added text in the abstract and introduction (Pg 1, Line 18 and Pg 3, Line 22) to clarify the definition of winter-spring transition as before and shortly after polar sunrise.**

2) While the authors have done a good job of representing previous work, there are a few references that should be added. Particularly relevant to your paper is the recent work of Köllner et al. (https://doi.org/10.5194/acp-17-13747-2017) that discusses single particle measurements in the Arctic, including the distribution of sea salt particles relative to other components. In support of the discussion of aerosol influences on longwave radiation on page 2, you should include some reference to work by Tim Garrett (U. Utah).

> **We added references to Köllner et al. (2017) on Pg 2, Line 21 and to Garrett and Zhao (2006) on Pg 2, Line 26.**

3) In the abstract, please mention that there are seven days of sampling. As it stands now, the abstract implies there are two months of sampling. Also in the abstract, please add that the results are based on 24,847 particles analyzed by CCSEM-EDX, 300 by Raman microspectroscopy and 290 by STXM-NEXAFS.

> **This information was added to the abstract on Pg 1, Lines 20-24.**

4) On page 5, lines 23-24 you note that 290 particles from the Feb 26 night sample (0.10-0.18 um) were analysed by STXM-NEXAFS. Is that meant to indicate you analysed 290 particles in the 100-180 nm size range? In Fig. 4 you show an example of the STXM-NEXAFS analysis from that sample, which shows the analysis of particles much larger than 180 nm. Please clarify.

STXM-NEXAFS was conducted for particles collected on the MOUDI stage with an 0.10 – 0.18 µm aerodynamic diameter size range. The scale bar in Fig. 4 is indicative of projected area diameter, measured by STXM-NEXAFS, which is characteristically larger than aerodynamic diameter (Pg 6, Lines 5-7). The text on Pg 6, Line 3 was updated to clarify aerodynamic diameter size range for the stage analyzed with STXM-NEXAFS, consistent with the stated aerodynamic diameter size ranges for stages analyzed by CCSEM-EDX (Pg 4, Lines 12-13) and Raman (Pg 5, Line 14).

5) You state that 50-60% of the 0.1-0.5 um particles contain sea salt. Since a substantial fraction of the winter-spring Arctic aerosol number concentration resides in that size fraction, your result would indicate that about 50% of the winter Arctic number concentration is due to primary emissions of sea salt. As the other reviewer notes, that has strong implications for the modelling of the winter Arctic aerosol, and thus we need to know if your various analyses have the same efficiency for smaller particles as they do for larger particles. Are smaller particles more difficult to analyse, or is the fraction of analysed particles to sampled particles in the 200 nm size bin (bins as shown in Fig. 2) the same as the fraction of analysed to sampled particles in the 1000 nm size bin? I would like to see a plot of the number size distribution of analysed particles added to the paper or supplement.

These percentages correspond to the fractions for the size bins shown in Figure 2, rather than the fraction of analyzed particles in this size range, which would be biased by the analysis. While smaller particles (< 200 nm) are more difficult to analyze with CCSEM-EDX, 57 % of the analyzed particles were smaller than 0.56 µm due to spreading upon impaction. As also noted on Pg 6, Lines 5-7, the measured projected area diameter is an upper bound and often larger than the particle diameter in the atmosphere. We added a number size distribution of analyzed particles to the supplement and indicated this addition in the main text on Pg 5, Lines 1-2.

6) On page 9, line 12 and elsewhere, you refer to “inorganic (sulfate) components”. Does ‘inorganic’ include sea salt? Please clarify.

STXM-NEXAFS distinguishes between three major components: organic carbon, elemental carbon, and all inorganic species. “Inorganic”, as defined by STXM-NEXAFS, can include sea salt (NaCl). However, we used the CCSEM-EDX and Raman results to determine that this inorganic component is sulfate, when observed to be mixed with primarily organic carbon particles. We clarified the wording on Pg 9, Line 23 and Pg 10, Line 9 to indicate the inorganic component detected by STXM-NEXAFS is likely sulfate.

7) How fresh is the “fresh SSA” in this case? You based the term ‘fresh’ on chemical transformation, but in the dark winter boundary layer of the Arctic, chemical transformations may be substantially reduced compared with such processes at lower latitudes (e.g. sulphuric acid and nitric acid production). In Fig. 5, you limit your trajectories to two days, which is relatively short compared to the lifetime of an aerosol particle in the Arctic (e.g. see Stohl, JGR, 2006). What were the sea ice conditions under the trajectories shown in Fig. 5 c and d? Were there any large areas of open water in the region during the sampling times? Do you think all the SSA was from leads (on page 6, you mention leads as a possible source)? Could there have been a contribution from frost flowers, as in Shaw et al. (2010)? Could the fresh SSA component have been an accumulation of the transport over much greater distances, while remaining less chemically processed? A paragraph added to your discussion is needed to provide some context for the potential origins of the SSA.

> **The reviewer is correct to note that what the manuscript refers to as fresh SSA is with respect to its similarity in composition to seawater (Table 1), with Cl/Na ratios very close to the seawater ratio of 1.16. We clarified our definition of fresh SSA on Pg 6, Lines 23 – 26. Only ~ 15 % of analyzed fresh SSA particles contained N or S (beyond natural S), indicating little chemical transformation took place following emission. The point that fresh SSA could exist after transport from the emission point due to low sulfuric or nitric acid, is well taken, and text has been added on Pg 7, Lines 13 – 16 to reflect this. It should be noted that partially aged SSA particles with greatly reduced Cl/Na ratios, and elevated S and N, were also observed (Table 1), so chemical transformations during transport were observed for many partially aged SSA particles. Longer backward air mass trajectories (5 days) were also analyzed, but no difference in trends of air mass sources locations were observed, so 48 h trajectories are shown in the manuscript for simplicity. Even for the longer trajectories, the air masses remained within the boundary layer (below the mixed layer depth) for less than 48 h, for all samples (Pg 10, Lines 25 – 26). The source of fresh SSA (e.g. potentially from open leads near the sampling site) is not a central focus of this paper and is the focus of follow-up analyses, with a manuscript currently in preparation.**

8) A follow-on to comment 7 - What were the wind speeds during the sampling? At the beginning of section 3.4, you mention there was no correlation of certain chemical ratios with wind speed, but sampling at some distance or time from marine sources will make wind speeds difficult to correlate with chemistry. If your sampling was done during times of particularly high sea salt influence due to regional winds, then your results may be skewed to the north coast of Alaska; although sea salt is prevalent in other areas of the winter Arctic that are more distant from open water (e.g. Alert, Leaitch et al., ACPD, 2017). If your source is purely regional, then that point needs to be made clear.

> **Text was added to Pg 10, Lines 18 and 21 to note average wind speeds of 5 – 12 m/s and prevailing wind from the north over the Beaufort Sea to the sampling site. While there are unique regional aerosol sources due to Prudhoe Bay influence (Sec. 3.4) and sea ice conditions in the Alaskan Arctic, SSA has also been observed in winter at other Arctic sites (Svalbard and Utqiaġvik), as stated on Pg 7, Lines 17 - 20.**

References:

Garrett, T. J., and Zhao, C.: Increased Arctic cloud longwave emissivity associated with pollution from mid-latitudes, Natur, 440, 787, 10.1038/nature04636, 2006.

Köllner, F., Schneider, J., Willis, M. D., Klimach, T., Helleis, F., Bozem, H., Kunkel, D., Hoor, P., Burkart, J., Leaitch, W. R., Aliabadi, A. A., Abbatt, J. P. D., Herber, A. B., and Borrmann, S.: Particulate trimethylamine in the summertime Canadian high Arctic lower troposphere, Atmos. Chem. Phys., 17, 13747-13766, 10.5194/acp-17-13747-2017, 2017.

Secondary Sulfate is Internally Mixed with Sea Spray Aerosol and Organic Aerosol in the Winter~~ Spring~~ Arctic

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Abstract. Few measurements of aerosol chemical composition have been made during the winter-spring transition (following polar sunrise) to constrain Arctic aerosol-cloud-climate feedbacks. Herein, we report the first measurements of individual particle chemical composition near Utqiaġvik (Barrow), Alaska in winter~~-spring (January and February 2014).~~ (seven sample days in January and February 2014). Individual particles were analyzed by computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy (CCSEM-EDX, 24,847 particles), Raman microspectroscopy (300 particles), and scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure spectroscopy (STXM-NEXAFS, 290 particles). Sea spray aerosol (SSA) was observed in all samples, with fresh and aged SSA comprising 99 %, by number, of 2.5-~~10~~7.5 μm diameter particles, 65-95 % from 0.5-2.5 μm, and 50-60 % from 0.1-0.5 μm, indicating SSA is the dominant contributor to accumulation and coarse mode aerosol during the winter~~-spring transition.~~. The aged SSA particles were characterized by reduced chlorine content with 94 %, by number, internally mixed with secondary sulfate (39 %, by number, internally mixed with both nitrate and sulfate), indicative of multiphase aging reactions during

transport. There was a large number fraction (40 % of 1.0 – 4.0 µm diameter particles) of aged SSA during periods when particles were transported from near Prudhoe Bay, consistent with pollutant emissions from the oil fields participating in atmospheric processing of aerosol particles. Organic carbon and sulfate particles were observed in all samples and comprised 40-50 %, by number, of 0.1-0.4 µm diameter particles, indicative of Arctic haze influence. Soot was internally mixed with organic and sulfate components. All sulfate was mixed with organic carbon or SSA particles. Therefore, aerosol sources in the Alaskan Arctic and resulting aerosol chemical mixing states need to be considered when predicting aerosol climate effects, particularly cloud formation, in the winter~~-spring~~ Arctic.

1 Introduction

The Arctic region is experiencing warming at a greater rate than elsewhere on Earth (Pachauri et al., 2014) and undergoing substantial transformations, including rapid loss of sea ice (Overland and Wang, 2013). This is leading to increased aerosol emissions, resulting in changes to atmospheric aerosol budgets and associated climate feedbacks (Struthers et al., 2011). Characterizing the chemical composition and morphology of individual Arctic aerosol particles is important for understanding the influence of local and transported aerosols on climate (Leck et al., 2002; Leck and Svensson, 2015), which remains one of the largest uncertainties in radiative forcing (Boucher et al., 2013). Aerosol mixing state, the distribution of chemical species across an aerosol population and within each individual particle, determines particle reactivity, hygroscopicity/cloud activation efficiency, and optical properties (Prather et al., 2008; Ault and Axson, 2017). However, the few studies that have used single particle analysis techniques to characterize the chemical mixing state of the Arctic aerosol population have been limited to ~~the Norwegian and central Arctic~~Svalbard ~~(Weinbruch et al., 2012; Hara et al., 2003; Geng et al., 2010; Hara et al., 2002c; Chi et al., 2015; Sierau et al., 2014)~~(Weinbruch et al., 2012; Hara et al., 2003; Hara et al., 2002c; Geng et al., 2010; Chi et al., 2015), Canadian archipelago (Köllner et al., 2017), and central Arctic (Sierau et al., 2014). Evaluating aerosol impacts on climate across the Arctic region is of particular importance given rapid changes in aerosol sources. Therefore, there is an urgent need to study the chemical composition of individual Arctic aerosol particles.

Aerosol influences on cloud formation and cloud-climate feedbacks in the Arctic are highly uncertain during winter~~-spring~~, when there is little direct solar radiation and longwave radiative forcing dominates ~~(Holland and Bitz, 2003; Letterly et al., 2016; Pithan and Mauritsen, 2014)~~(Holland and Bitz, 2003; Letterly et al., 2016; Pithan and Mauritsen, 2014; Garrett and Zhao, 2006). Few studies have characterized Arctic aerosols, particularly those that may act as cloud condensation nuclei (CCN) and ice nucleating particles (INP), during this period. Most studies in the winter-spring have focused on the components of Arctic haze, long-range transported pollution from the mid-latitudes present in the Arctic after polar sunrise, including non-sea salt sulfate, soot, organics, and metals (e.g., Sturges and Barrie, 1988; Norman et al., 1999; Sirois and Barrie, 1999; Quinn et al., 2002; Polissar et al., 1999; Hara et al., 2002b; Fisher et al., 2011). Notably, particulate sulfate concentrations in the Alaskan Arctic during haze season are 0.1-0.4 µg m^{-3} on average, and much higher than average nitrate concentrations of 0.01-0.03 µg m^{-3} (Quinn et al., 2007). SSA has also been identified as a significant contributor to the winter-spring aerosol budget by mass (10-30 %) in the Canadian Arctic (Sirois and Barrie, 1999; Norman et al., 1999; Quinn et al., 2002) and by number (55-85 %) in the Norwegian Arctic (Weinbruch et al., 2012). SSA are efficient CCN (Collins et al., 2013; Quinn et al., 2014) and can act as INP (DeMott et al., 2016), resulting in complex sea ice-aerosol-cloud interactions in the Arctic (Browse et al., 2014). Gaseous sulfuric acid or sulfur dioxide associated with Arctic haze has been shown to react with SSA, resulting in sulfate formation and internally mixed SSA-sulfate particles (Hara et al., 2002a; Hara et al., 2003). While less commonly observed in the Arctic, reactions between gaseous HNO_3 or N_2O_5 and SSA can also form mixed SSA-nitrate particles (Hara et al., 1999). These multiphase reactions result in chlorine (HCl, $ClNO_2$, Cl_2) liberation from SSA, contributing to atmospheric halogen chemistry (Sturges and Barrie, 1988; Barrie and Barrie, 1990; Hara et al., 2002c; Hara et al., 2002a). Given changing marine emissions coupled with transported pollution, it is important to understand aerosol chemical composition and heterogeneous processing to determine impacts on climate in the winter~~-spring~~ Arctic.

To improve our understanding of Arctic aerosol chemical mixing state under the changing radiation and sea ice conditions during the winter-spring transition~~,~~ (following polar sunrise), atmospheric particles were collected near Utqiaġvik (Barrow), Alaska during January and February 2014. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), Raman microspectroscopy, and scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure spectroscopy (STXM-NEXAFS) were utilized to characterize individual particle chemical composition and mixing state. To our knowledge, these are the first measurements of individual particle chemical composition in the Alaskan Arctic during winter. The relative contributions of regional Arctic haze and SSA on the aerosol budget during this winter-spring transition were examined, and the mixing states of individual aerosol particles were evaluated to examine atmospheric aging by multiphase reactions forming sulfate and nitrate.

2 Methods

Atmospheric particle sampling was conducted from January 23-28 and February 24-28, 2014 near Utqiaġvik (Barrow), Alaska at a tundra field site (71.28° N, 156.64° W) located ~5 km inland from the Arctic Ocean. Ozone concentrations and meteorological data, including wind speed, wind direction, and solar radiation, were obtained from the NOAA Barrow Observatory (71.32° N, 156.61° W), located 5 km to the northeast of the sampling site and separated only by flat tundra. Atmospheric particles were collected using a rotating micro-orifice uniform deposition impactor (MOUDI, MSP Corp., model 110) sampling at 30 LPM through a 10 µm cut-point cyclone (URG-2000-30EA) located ~2 m above the snow surface. 50 % particle collection efficiency size cuts for the six MOUDI stages used were 3.2, 1.8, 1.0, 0.56, 0.32, and 0.18 µm aerodynamic diameter (D_a). Particles were impacted on transmission electron microscopy grids (Carbon Type-B film copper grids, Ted Pella, Inc.) and silicon substrates (Ted Pella, Inc.) for SEM analysis, and quartz substrates (Ted Pella, Inc.) for Raman microspectroscopy analysis. Particle samples were stored frozen prior to analysis to keep near the ambient temperature at collection. Samples selected for analysis were collected for ~24 h on January 24-25 (10:15-10:00 AKST) and January 27-28 (11:00-10:30 AKST), ~18 h on January 26 (11:00-17:15 AKST), ~12 h on February 26 day (9:00-19:30 AKST), February 26 night (19:45-8:30 AKST), February 27 day (9:00-19:30 AKST), and February 27 night (20:00-7:30 AKST). These time periods were characterized by wind directions of 75-225° such that the town of Utqiaġvik was not upwind during sampling. Polar sunrise occurred at Utqiaġvik on January 22, 2014.

Computer-controlled SEM (CCSEM) analysis of individual atmospheric particles was completed using a FEI Quanta environmental SEM with a field emission gun operating at 20 keV with a high angle annular dark field (HAADF) detector (Laskin et al., 2006; Laskin et al., 2012). An EDX spectrometer (EDAX, Inc.) collected X-ray spectra from elements with atomic numbers higher than Be (Z=4). 24,847 individual particles, typically ~1000 per sample, were analyzed by CCSEM-EDX. A size distribution showing the number of particles analyzed by CCSEM-EDX is shown in Fig. S1. Morphological data, including projected area diameter (D_{pa}) and perimeter, were collected for each particle, in addition to the relative abundance of the following elements quantified from the EDX spectra: C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe. Individual particle data were analyzed using K-means clustering of the EDX spectra (Ault et al., 2012; Shen et al., 2016; Axson et al., 2016). K-means cluster analysis resulted in 50 clusters, which were then grouped into five particle classes (fresh SSA, partially aged SSA, organic+sulfate aerosol, fly ash aerosol, and mineral dust aerosol), based on comparisons of cluster EDX spectra with particle classes identified in previous studies. Prior ambient aerosol CCSEM-EDX studies have established EDX spectral signatures for fresh and aged SSA (Ault et al., 2013a; Hara et al., 2002c; Hara et al., 2003), organic+sulfate aerosol (Moffet et al., 2010b; Laskin et al., 2006; Allen et al., 2015), fly ash (Ault et al., 2012), and mineral dust (Coz et al., 2009; Sobanska et al., 2003; Axson et al., 2016; Creamean et al., 2016).

Individual particles from two MOUDI stages (1.0 – 1.8 and 0.56 – 1.0 µm aerodynamic diameter size ranges) for each of the seven samples were also analyzed by Raman microspectroscopy using a Horiba Scientific Labram HR Evolution spectrometer coupled with a confocal optical microscope (100x Olympus objective, 0.9 Numerical Aperture) equipped with a Nd:YAG laser source (50 mW, 532 nm) and CCD detector. A 600 groove/mm diffraction grating was used, yielding spectral resolution of 1.8 cm^{-1}. The laser power was adjusted between 25 – 100 % by varying a neutral density filter to prevent damage to the sample. Raman spectra were obtained over the 500-4000 cm^{-1} range for ~300 particles. Spectra were compared with prior Raman studies of nascent and reacted sea spray aerosol (Ault et al., 2013c; Ault et al., 2014).

Beamline 5.3.2 on the Advanced Light Source at Lawrence Berkeley National Laboratory (Berkeley, CA) was used for STXM-NEXAFS analysis over the carbon k-edge (280-320 eV), as previously described by Moffet et al. (2010a). Briefly, X-rays from the synchrotron were energy-selected using a monochromator, focused on the sample, and raster scanned across a selected area. The sample was rescanned at closely spaced X-ray energies to complete a spectral image stack. After the X-ray spectra were converted to optical density using the Beer-Lambert law, STXM-NEXAFS maps were generated to show the distribution of organic carbon, soot, and inorganic components in individual aerosol particles, based on the X-ray absorptions at 288.5 eV, 285.4 eV, and 283 eV, respectively. 290 particles from the February 26 night sample (0.10 - 0.18 μm D_a) were analyzed for detection of organic carbon. D_{pa} was measured by CCSEM-EDX, Raman, and STXM-NEXAFS; therefore, is the parameter reported for all data herein. D_{pa} is often larger than geometric diameter due to particle deformation upon impaction (Sobanska et al., 2014; Hinds, 2012; O'Brien et al., 2014), indicating that particle size reported here is an upper bound and could represent smaller diameter in the atmosphere.

3 Results and Discussion

3.1 Chemical Composition and Size Distribution of Observed Particle Types

Five individual particle classes, including fresh sea spray aerosol (SSA), partially aged SSA, organic+sulfate particles, fly ash, and mineral dust particles, were identified from the CCSEM-EDX data (Fig. 1). SSA (both fresh and partially aged) and organic (with and without sulfate) particles were the most commonly observed types, indicating that mixing of sulfate with SSA and organic aerosol may be significant in the winter~~-spring~~ Arctic. Fresh and partially aged SSA comprised 99 %, by number, of the observed supermicron particles (1.0-~~10~~7.5 μm D_{pa}) (Fig. 2). Across the submicron size range (0.1-1.0 μm D_{pa}), the majority of particles were also SSA (50-75 %, by number) (Fig. 2). The prevalence of SSA particles, even in the winter~~-spring transition~~, may be a result of changing conditions in the Arctic, with previous work showing local SSA influence in Utqiaġvik, AK from nearby sea ice leads, even during winter (May et al., 2016). Organic particles (with and without sulfate) were also a significant fraction (25 – 50 %, by number) of submicron particles. Only a limited fraction of particles (~ 1 % by number across the entire size range) were classified as fly ash or mineral dust, characterized by silicon and oxygen, with trace amounts of aluminum, sodium, and iron (Coz et al., 2009; Sobanska et al., 2003).

Field Code Changed

Particles classified as fresh SSA, based on grouping by chemical composition by K-means analysis, contained sodium, magnesium, sulfur, and chlorine in similar mole ratios (Table 1) to those found in seawater (Cl/Na = 1.2, Mg/Na = 0.11, S/Na = 0.06) (Quinn et al., 2015; Pilson, 2013), indicating these particles had not undergone chemical aging processes during atmospheric transport. Some SSA particles were observed with a sodium chloride core and magnesium chloride outer coating (Fig. 1), which is likely due to the particle undergoing efflorescence after collection (Ault et al., 2013b); this morphology has been previously observed for Arctic SSA particles (Chi et al., 2015). The partially aged SSA particles contained sulfur and/or nitrogen and were characterized by Cl/(Na+0.5Mg) ratios of less than 1 (Laskin et al., 2012). This indicates that multi-phase reactions had occurred releasing chlorine-containing trace gases, primarily hydrochloric acid (Laskin et al., 2002; Laskin et al., 2003; Gard et al., 1998), resulting in the formation of sulfate and nitrate in the particles. SSA chemical mixing state information is further discussed in Sec. 3.2. SSA aging was observed for few 1.0-~~10~~7.5 µm particles (7 %, by number, aged SSA and 90 % fresh SSA), with a greater fraction of submicron 0.1-1.0 µm SSA particles having undergone aging (18 %, by number, aged SSA and 42 % fresh SSA) (Fig. 2). Compared to supermicron particles, submicron particles have longer atmospheric lifetimes, a smaller Cl reservoir, and greater surface area to volume ratios, which are conducive to increased atmospheric processing (Hara et al., 2002a; Leck et al., 2002; Williams et al., 2002; Ault et al., 2014). While concentrations of sulfur- and nitrogen-containing gases are lower in the Arctic winter compared to the peak of spring haze season, allowing for SSA particles to remain chemically fresh further from the emission point, aged SSA particles have also been observed during winter at Svalbard (Hara et al., 1999; Hara et al., 2002a). Overall, fresh and aged SSA were significant contributors to the winter~~-spring~~ Arctic aerosol budget (Fig. 2 and ~~S1~~S2). This observation is consistent with studies of annual Arctic aerosol trends that have shown a large influence of SSA in the winter by mass: constituting up to 40 % of supermicron mass at Barrow (Quinn et al., 2002) and 60-90 % of 0.5-10 µm particles, by number, for winter samples at Svalbard (Weinbruch et al., 2012).

Organic particles, classified by K-means analysis, were characterized by spherical morphology and carbon and oxygen in the single particle EDX spectra. Since there is background C and O EDX signal from the TEM grid substrate film, the contribution of C and O to this particle class was confirmed by

CCSEM-EDX analysis of 110 particles that had been collected simultaneously on silicon substrates that do not have these interferences. Figure 1 shows the representative EDX spectra of organic particles analyzed on TEM grids and silicon substrates for comparison. Sulfur was present in 47 %, by number, of organic particles, at levels of at least 2% atomic content in the EDX spectrum; therefore, these organic particles will be discussed together as an organic+sulfate particle class (Laskin et al., 2006; Moffet et al., 2010b). Example organic+sulfate particles are shown in Fig. 1c and d. Organic+sulfate particles were primarily observed in the submicron size range (Fig. 2). Overall, 40-50 % of the particles 0.1 - 0.5 μm in diameter and 15 - 25 % of the particles 0.5 – 1.0 μm, by number, were classified as organic+sulfate (Fig. 2). The detailed chemical mixing states of these organic+sulfate particles will be discussed in Sect. 3.3. The presence of a large number fraction of submicron organic+sulfate particles is consistent with previous winter-spring Arctic studies, which have observed organic particles contributing up to 30 % of submicron aerosol by mass and greater than 80 %, by number, at Barrow (Shaw et al., 2010; Hiranuma et al., 2013) and greater than 80 %, by number, of 0.1-0.5 μm (aerodynamic diameter) particles at Svalbard (Weinbruch et al., 2012). Internal mixing of organic and sulfate aerosol has previously been observed in the Arctic winter-spring at Svalbard, with most 0.2-2.0 μm (aerodynamic diameter) organic particles containing sulfate (Hara et al., 2002b). Internally mixed organic+sulfate aerosol is now being observed across the Arctic during the winter~~-spring~~, highlighting the importance of considering sulfate mixing states during this period.

3.2 Internal Mixing of SSA with Sulfate and Nitrate

Raman microspectroscopic analysis of individual aged SSA particles confirmed that the sulfur and nitrogen detected by EDX in SSA were in the forms of sulfate and nitrate, respectively, based on the presence of sharp peaks corresponding to characteristic symmetric stretches at ~1000 cm^{-1} for $\nu_s(SO_4^{2-})$ and ~1050 cm^{-1} for $\nu_s(NO_3^-)$ (Fig. 3) (Ault et al., 2014; Deng et al., 2014; Eom et al., 2016). In addition, these particles were characterized by broad peaks in the 3000-3500 cm^{-1} range (Fig. 3), corresponding to O–H stretching, likely due to particle-phase water (Ault et al., 2014), confirmed by the frequency of the $\nu_s(NO_3^-)_{(aq)}$ mode at ~1050 cm^{-1}. Raman C-H stretching peaks in the 2800-3000 cm^{-1} range indicated that organic compounds were present in both fresh and aged SSA (Ault et al., 2013c; Baustian et al., 2012; Eom et al., 2016); the organic functional groups present will be discussed further in a future publication.

Based on the CCSEM-EDX analysis, SSA aging by sulfur species (e.g. sulfuric acid) was more prevalent than aging by nitrogen species (e.g. nitric acid) in the submicron size range consistent with previous measurements of SSA during Arctic haze periods in the Norwegian Arctic (Hara et al., 2002c). 73 % of partially aged SSA, by number, in the 0.1-1.0 μm size range contained secondary sulfate. This was determined by a S/Na ratio at least 25 % greater than the seawater molar ratio 0.06 (Pilson, 2013), with these particles having an average S/Na ratio of 1.07 (Table 1). In comparison, only 22 % of 0.1-1.0 μm particles contained nitrate (Table 1). The diffusion limited uptake of SO_2 in submicron particles is favored over the thermodynamically controlled uptake of HNO_3, resulting in a preference for sulfate in submicron aged SSA (Liu et al., 2007; Zhuang et al., 1999; Kerminen et al., 1998). However, sulfate was also more prevalent than nitrate in supermicron SSA (Table 1), where kinetically favorable uptake of HNO_3 would be expected to dominate, suggesting higher concentrations of H_2SO_4, compared to HNO_3, influenced particle aging. The prevalence of SSA aging by sulfur species near Utqiaġvik is consistent with the appearance of springtime Arctic haze, as 30 % of submicron particle mass corresponds to sulfate during haze season (January to May) (Quinn et al., 2007; Quinn et al., 2002). Sulfate mass concentrations peak in winter-spring near Utqiaġvik, while methanesulfonic acid mass is greatest in the summer and has not been observed during winter months (Quinn et al., 2007). Therefore, the prevalence of mixed SSA-sulfate suggests that reactions with sulfuric acid from Arctic haze are an important source of SSA sulfate (Hara et al., 2002a; Barrie and Barrie, 1990). SSA aging through sulfate addition was likely also due to influence from Prudhoe Bay SO_2 emissions (Peters et al., 2011; Gunsch et al., 2017), discussed further in Sec. 3.4.2.

3.3 Organic Particle Mixing States

Organic particles and internally mixed organic+sulfate particles ~~comprised~~composed a significant number fraction of submicron particles, which is consistent with the presence of organic aerosol, sulfuric acid, and ammonium sulfate in Arctic haze (Hara et al., 2002b; Hirdman et al., 2010). STXM-NEXAFS indicated the presence of organic carbon in these particles, based on X-ray absorption at 288.5 eV, characteristic of carboxylic acids (Moffet et al., 2010a). Additionally, STXM-NEXAFS analysis confirmed that organic and inorganic (likely sulfate, based on sulfur detected during CCSEM-EDX analyses) components were internally mixed within individual particles (Fig. 4), with particles showing an internal mix of both inorganic dominant (> 50 %) and organic dominant regions. The pre-post edge ratio of inorganic to organic components also indicated that most analyzed particles contained both inorganic and organic species (Fig. 4b). Raman analysis confirmed sulfur was present in the form of sulfate. Nitrogen (nitrate, according to Raman analysis) was also present in 15 % of 0.1 – 1.0 µm organic+sulfate particles, by number.

Chemical mixing state analysis determined that a small fraction of particles classified as organic+sulfate (7 % of this particle class, by number) by CCSEM-EDX were primarily carbon-containing particles with less than 5 % oxygen and sulfur. For the February 26 night sample analyzed by STXM-NEXAFS, elevated levels of sp^2 carbon, indicative of soot, were observed in some particles (Fig. 4) (Moffet et al., 2010a). These small soot particles observed by STXM-NEXAFS were likely members of the "primarily carbon" group identified by CCSEM-EDX and were internally mixed with organic carbon and inorganic species (~~sulfate).~~likely sulfate, based on sulfur detected during CCSEM-EDX analyses). Therefore, these particles were included in the organic+sulfate class. Externally mixed soot particles, comprised solely of elemental carbon with no organic or sulfate component, were not observed in any sample, indicating that all soot was internally mixed with organic+sulfate particles. Soot present in Arctic haze (Quinn et al., 2007; Law and Stohl, 2007) has previously been observed to be internally mixed with sulfate for winter-spring Arctic aerosol, with soot-sulfate particles contributing ~ 10-20 % of observed particles sampled (<2.0 µm), by number, at Svalbard (Hara et al., 2003).

3.4 Influence of Marine- and Prudhoe Bay-Influenced Air Masses on Particle Composition

There was no clear dependence or trend with wind speed or month (Jan. vs. Feb.) for SSA S/Na or Cl/Na ratios, with average wind speeds ranging from 5 – 12 m/s for the selected sampling periods, but some variability in particle composition between samples could be attributed to the influence of different air masses. Though all samples experienced some degree of Arctic Ocean air mass influence due to the sampling location and prevailing wind ~~directions~~direction from the north over the Beaufort Sea to the sampling site, using NOAA HYSPLIT 48 h backward air mass trajectory analysis two main air mass source regions (Arctic Ocean and Prudhoe Bay influence) were determined for the seven analyzed sample periods. Most notably, the February 26 day sample was influenced by air from the north and east over the Arctic Ocean within the boundary layer for the 6-7 h prior to arrival at the sampling site, whereas the January 27 sample had prolonged surface influence (18 h) along the air mass trajectory from the east/southeast, during which the air mass passed over Prudhoe Bay, the third largest oilfield in North America (U.S. Energy Information Administration, 2015) (Fig. 5). Prudhoe Bay influence was determined by HYSPLIT trajectories that passed within 1 degree (~50 km) of the Prudhoe Bay emissions box, described in Kolesar et al. (2017) as the area significantly influenced by combustion emissions from the oilfields. The air mass trajectories for the remaining samples (January 24, January 26 day, February 26 night, February 27 day, February 27 night) fell in between the two regions (Arctic Ocean and Prudhoe Bay influence).

Comparison of particle type contributions as a function of size for the representative Arctic Ocean influenced (February 26 day) and Prudhoe Bay influenced (January 27) samples are shown in Fig. 5 (with results of additional samples shown in Fig. ~~S1~~S2). The Arctic Ocean influenced sample was characterized by a large fraction (95 %) of fresh SSA in the 1.0 – ~~10.0~~7.5 µm size range. In comparison, the Prudhoe Bay influenced sample was characterized by 55 % fresh SSA and 40 - 45 % partially aged SSA, by number, in the supermicron range. This is indicative of multiphase reactions between SSA and gaseous emissions from combustion at the oilfields (e.g. SO_2, NO_x) (Jaffe et al., 1991; Peters et al., 2011; Gunsch et al., 2017), contributing to a greater number fraction of aged SSA during Prudhoe Bay influenced periods. The Prudhoe Bay influenced sample also had a greater number fraction of organic+sulfate particles in the 0.1-0.5 µm range (60 - 70 %) compared to the Arctic Ocean influenced sample (40 – 50 %). Given that organic+sulfate particles were a significant fraction of submicron particles in all samples, including ocean-influenced periods, these samples were likely influenced by long-range transported pollution from the mid latitudes, consistent with regional background haze (Quinn et al., 2007). However, it is likely that gas-particle partitioning of oxidation products from Prudhoe Bay oilfield combustion emissions, including volatile organic compounds and SO_2 (Peters et al., 2011; Jaffe et al., 1991; Gunsch et al., 2017), also results in the formation of organic+sulfate particles, including particles internally mixed with soot (Sect. 3.3), contributing to the increased number fraction of organic+sulfate particles observed during Prudhoe Bay influenced periods.

4 Conclusions

For atmospheric particles collected in January and February 2014 near Utqiaġvik, Alaska, SSA was observed to be the most prevalent particle type, ~~comprising~~composing 50-75 % and 99 %, by number, of particles in the 0.1-1.0 µm and 1.0-~~10~~7.5 µm projected area diameter ranges, respectively. Internal mixing of sulfate and nitrate with SSA particles was observed in all samples, regardless of air mass influence, suggesting prevalent regional pollution, such as Arctic haze influence, for secondary inorganic aerosol formation. Prudhoe Bay influenced air masses were characterized by higher number fractions of partially aged SSA, however, suggesting that oilfield emissions also contribute significantly to multiphase reactions with SSA. Most global and regional climate models assume that Arctic haze components (sulfate, organic aerosol, black carbon) and natural aerosols are externally mixed and do not predict climate impacts of internally mixed species (Eckhardt et al., 2015; Alterskjaer et al., 2010; Korhonen et al., 2008). However, no externally mixed sulfate or sulfuric acid particles were observed during January or February sampling in Utqiaġvik, Alaska; all sulfate was internally mixed with organic aerosol particles or with SSA. Internal mixing of SSA and sulfate reduces CCN efficiencies compared to externally mixed sulfate aerosol or SSA, as sodium sulfate is less hygroscopic than sodium chloride or sulfuric acid (Gong and Barrie, 2003; Petters and Kreidenweis, 2007). The prevalence of SSA internally mixed with sulfate should be considered in the interpretation of elevated sulfate concentrations in the winter-spring Arctic atmosphere (Sturges and Barrie, 1988; Sirois and Barrie, 1999; Hara et al., 2002a).

While SSA comprised 50-60 % of 0.1 – 0.5 µm particles, by number, organic+sulfate particles made up 40-50 %, by number, in this particle diameter range and were present in similar number fractions in all samples, suggesting the importance of Arctic haze as a source of submicron particles in January and February in Utqiaġvik, Alaska. Internal mixing of sulfate and nitrate with organic aerosol is consistent with previous single particle measurements at Svalbard, where organic aerosol mixed with sulfate and nitrate was observed to be the dominant particle type in the submicron size range in the winter and spring

(Weinbruch et al., 2012). Weinbruch et al. (2012) also observed soot particles internally mixed with organics, sulfate, and nitrate, consistent with the small fraction of internally mixed organic+sulfate and soot particles (~2 – 3 % of total observed particles, by number) observed in this study. The internal mixing of sulfate with organic aerosol is important to consider in climate predictions, as the CCN activity of internally mixed organic+sulfate aerosol is reduced relative to externally mixed sulfate, due to the lower hygroscopicity of the organic fraction (Wang et al., 2015; Petters and Petters, 2016). Continuing oil and gas development in the Arctic region will influence both SSA and organic aerosol composition (Peters et al., 2011), as well as mixing state, due to secondary inorganic aerosol formation.

Competing Interests. The authors declare that they have no competing financial interests.

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Table 1: Size resolved number fractions of individual fresh SSA, partially aged SSA, and organic+sulfate particles containing Cl, S, and N, in addition to average atomic (mole) ratios of Cl/Na, S/Na, and N/Na for individual fresh and partially aged SSA.

Particle class and size range	Number fraction containing Cl	Number fraction containing S	Number fraction containing N	Average Cl/Na	Average S/Na	Average N/Na
Fresh SSA (0.1 – 1.0 µm)	1.0	0.15	0.15	0.98	0.05	0.04
Fresh SSA (1.0 – 10 µm)	1.0	0.18	0.10	1.26	0.05	0.04
Partially aged SSA (0.1 – 1.0 µm)	0.07	0.73	0.22	0.04	1.07	0.25
Partially aged SSA (1.0 – 10 µm)	0.38	0.81	0.52	0.24	1.53	0.95
Organic+sulfate (0.1 – 1.0 µm)	---	0.46	0.13	---	---	---
Organic+sulfate (1.0 – 10 µm)	---	0.87	0.60	---	---	---

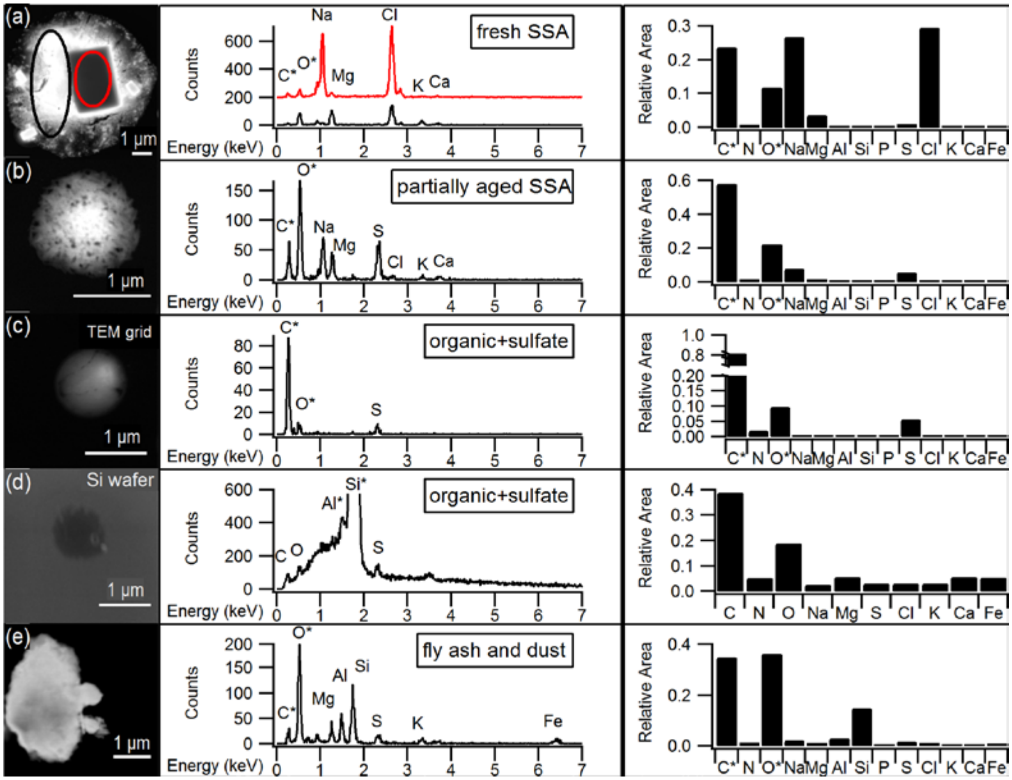

Figure 1: Representative SEM images and EDX spectra of individual particles corresponding to the main particle types observed by CCSEM-EDX, and the average EDX spectrum for each particle type. Average spectra show the relative peak areas of all elements analyzed by CCSEM-EDX. (a) Fresh SSA particle comprised of sodium chloride core (red) and magnesium chloride shell (black). The spectrum for the core is offset for clarity. (b) Partially aged SSA particle containing sodium and more sulfur than chlorine. (c) Organic+sulfate particle. (d) Organic+sulfate particle on silicon substrate. (e) Aluminum- and silicon- containing dust particle. *Carbon and oxygen peaks include some signal from TEM grid substrate background for particles a, b, c, and e. Aluminum and silicon peaks are due to sample holder and silicon substrate background, respectively, for particle d.

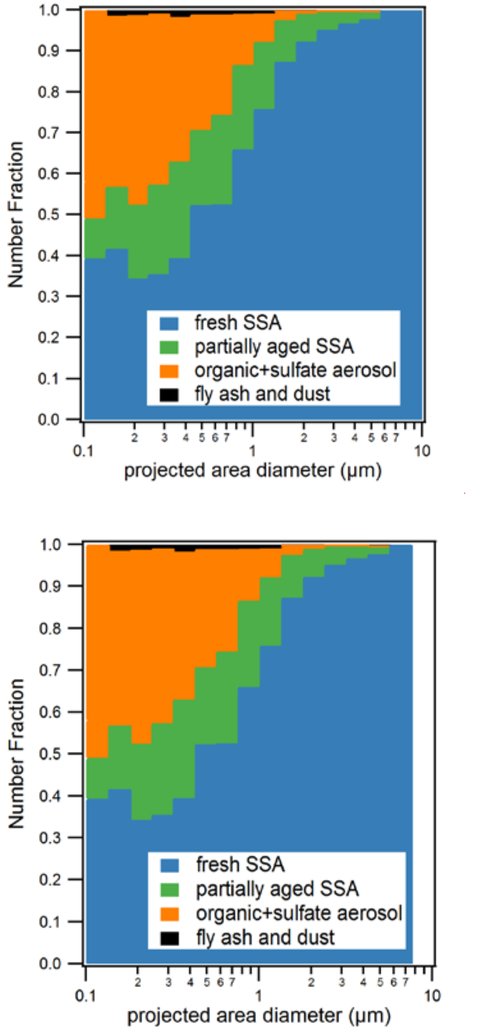

Figure 2: Size-resolved CCSEM-EDX number fraction distributions of observed particle types for all samples. Particles were sorted into 16 bins (logarithmic) from 0.1 to 10.0 µm projected area diameter (8 bins per decade). Organic+sulfate class includes a small fraction of internally mixed soot.

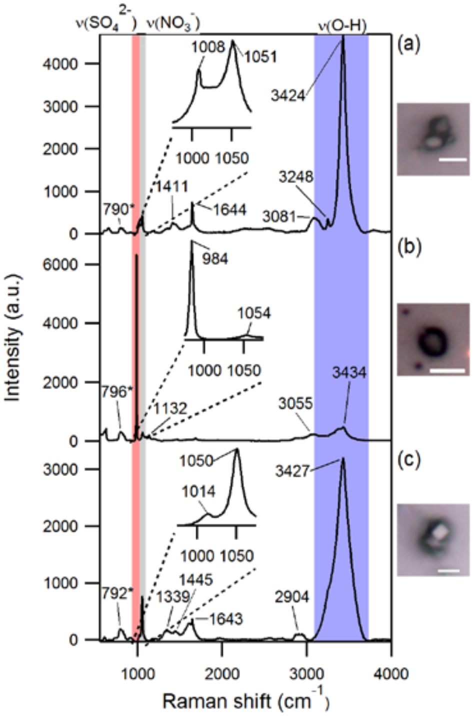

Figure 3: Optical images and Raman spectra of three representative SSA particles containing nitrate and/or sulfate and hydroxyl groups. A total of ~300 individual particles were analyzed by Raman microspectroscopy. *790-796 cm^{-1} peak is due to quartz substrate background. Scale bar for all images is 5 μm.

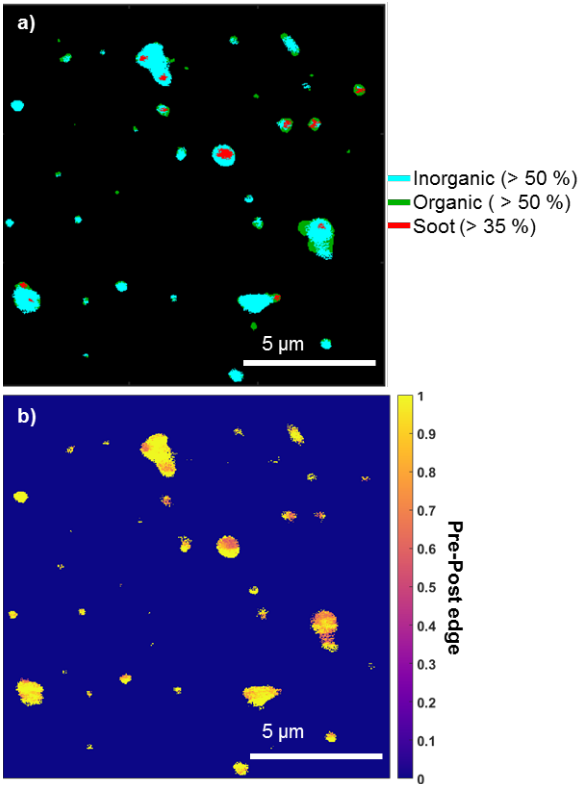

Figure 4: Representative STXM/NEXAFS map from February 26 night showing a) the distributions of inorganic dominant (blue, > 50 % by mass), organic carbon dominant (green, > 50 % by mass), and soot (red, sp^2 > 35 %) and b) the ratio of inorganic (pre-) and organic (post-edge) components between populations of individual particles sampled during a period with a high fraction of organic+sulfate particles.

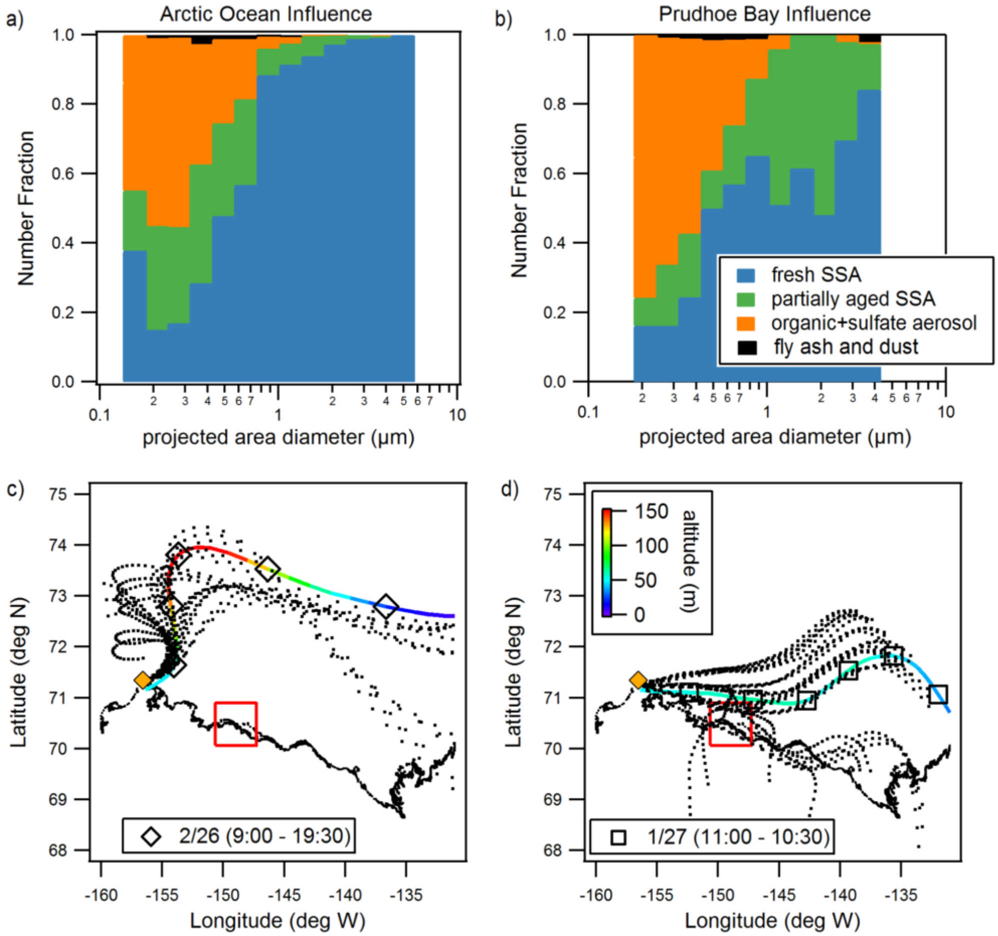

Figure 5: Size-resolved number fractions of observed particle types (CCSEM-EDX) for example a) Arctic Ocean (February 26 day, 4490 particles) and b) Prudhoe Bay (January 27, 1475 particles) influenced sample periods. Air mass influence is shown for c) February 26 day and d) January 27 as determined by NOAA HYSPLIT 48 h
5 backward air mass trajectories. Both ensemble (dotted line) and single representative trajectories are shown. Color scale indicates air mass altitude, and markers are placed at 6 h intervals. Red line shows extent of Prudhoe Bay emissions influence box (Kolesar et al., 2017). Yellow diamond indicates sampling site near Utqiaġvik.

Field Code Changed

Secondary Sulfate is Internally Mixed with Sea Spray Aerosol and Organic Aerosol in the Winter~~-Spring~~ Arctic

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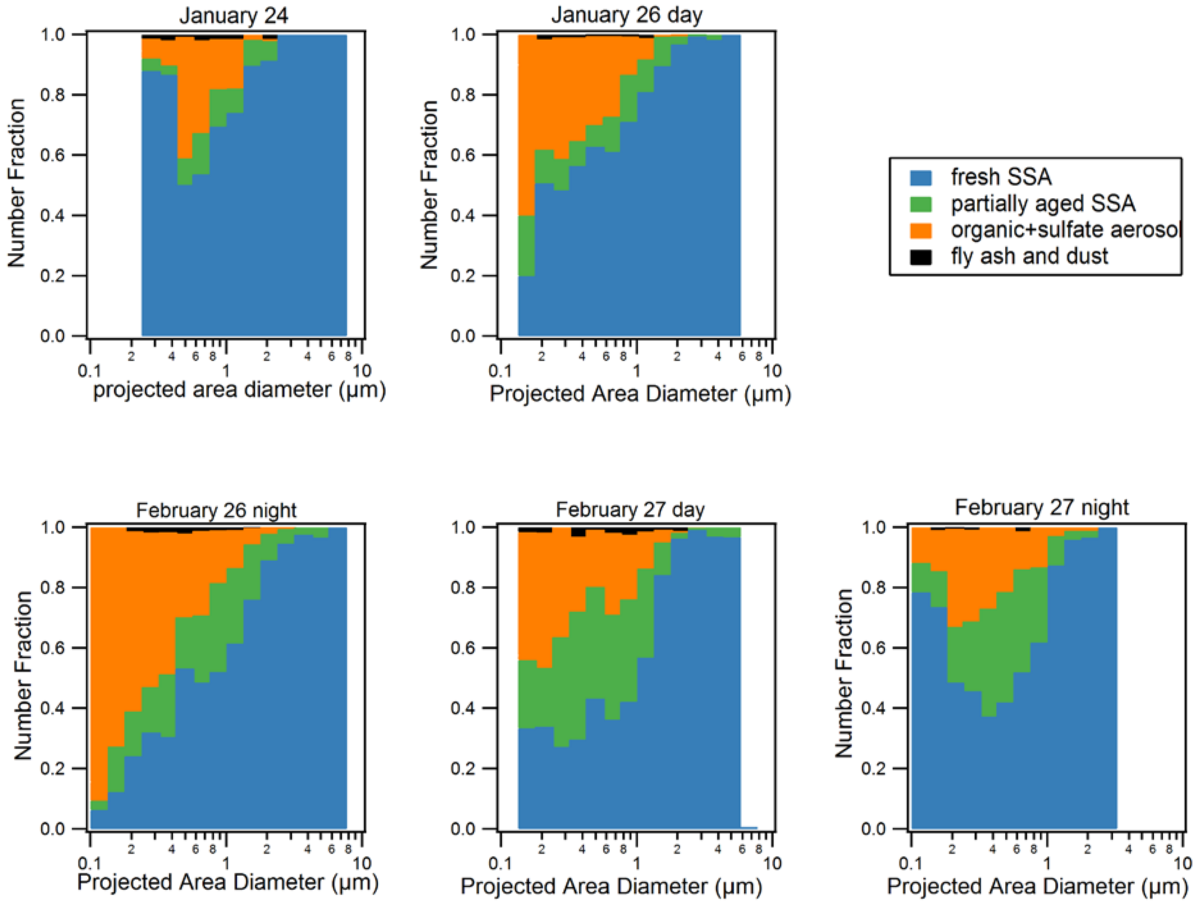
January 24
January 26 day
February 26 night
February 27 day
February 27 night
Number Fraction
0.0
0.2
0.4
0.6
0.8
1.0
0.1
2
4
6
8
1
2
4
6
8
10
projected area diameter (µm)
Projected Area Diameter (µm)
fresh SSA
partially aged SSA
organic+sulfate aerosol
fly ash and dust

~~**Figure S1**~~

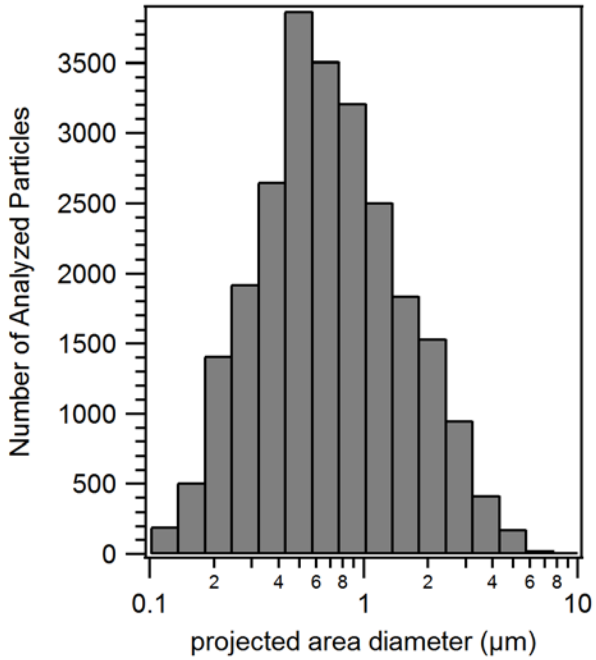

Figure S1: The number of individual particles analyzed by CCSEM-EDX for each of 16 log size bins.

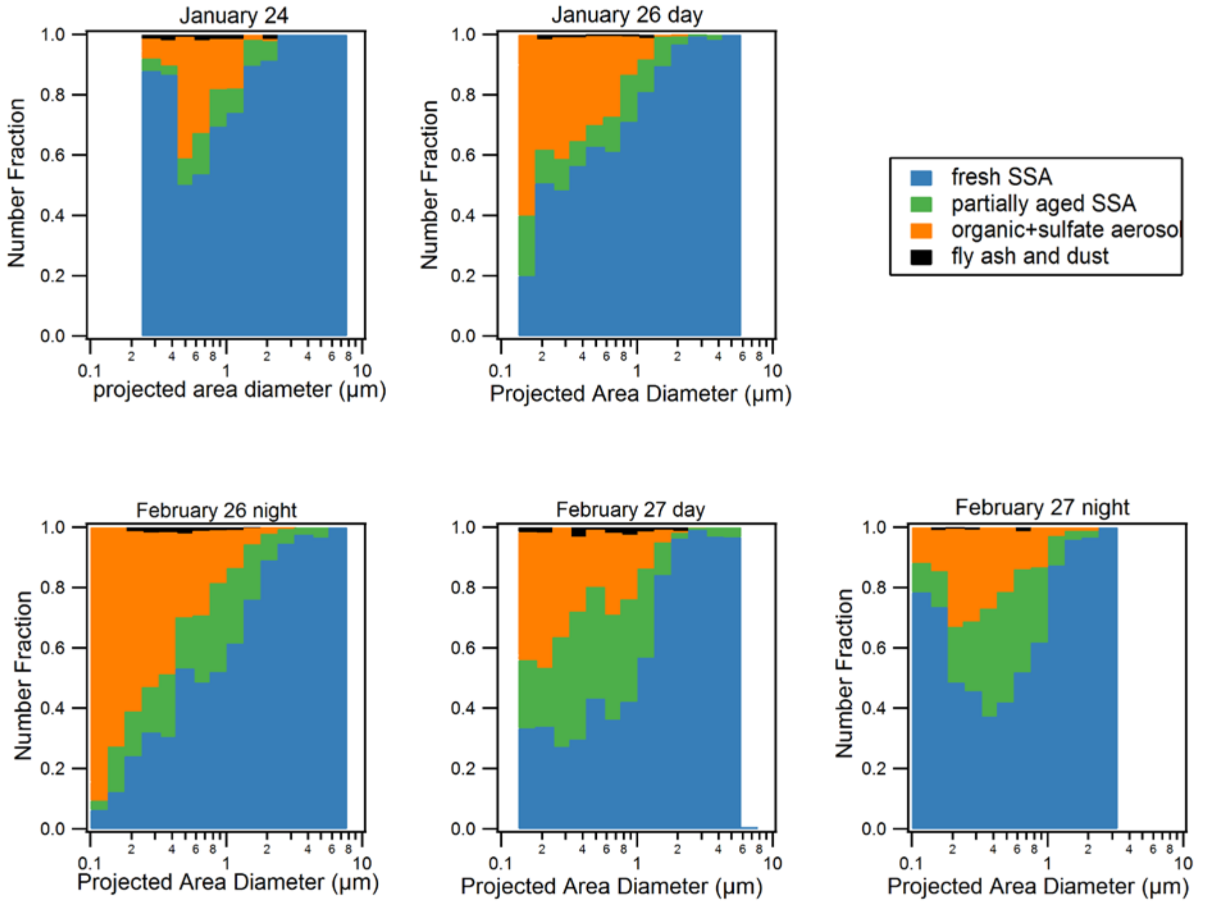

Figure S2: Size-resolved number fractions of particle types for additional sample periods not shown in Figure 7. Particles were sorted into 16 log size bins.