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Emerging investigator series: influence of marine emissions and atmospheric processing on individual particle composition of summertime Arctic aerosol over the Bering Strait and Chukchi Sea†

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The Arctic is rapidly transforming due to sea ice loss, increasing shipping activity, and oil and gas development. Associated marine and combustion emissions influence atmospheric aerosol composition, impacting complex aerosol–cloud–climate feedbacks. To improve understanding of the sources and processes determining Arctic aerosol composition, atmospheric particles were collected aboard the Korean icebreaker R/V *Araon* cruising within the Bering Strait and Chukchi Sea during August 2016. Offline analyses of individual particles by microspectroscopic techniques, including scanning electron microscopy with energy dispersive X-ray spectroscopy and atomic force microscopy with infrared spectroscopy, provided information on particle size, morphology, and chemical composition. The most commonly observed particle types were sea spray aerosol (SSA), comprising ∼60–90%, by number, of supermicron particles, and organic aerosol (OA), comprising ∼50–90%, by number, of submicron particles. Sulfate and nitrate were internally mixed within both SSA and OA particles, consistent with particle multiphase reactions during atmospheric transport. Within the Bering Strait, SSA and OA particles were more aged, with greater number fractions of particles containing sulfate and/or nitrate, compared to particles collected over the Chukchi Sea. This is indicative of greater pollution influence within the Bering Strait from coastal and inland sources, while the Chukchi Sea is primarily influenced by marine sources.

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Environmental significance

As the Alaskan Arctic is rapidly changing due to sea ice loss, there is also increasing shipping activity and oil and gas development in the region. These changing sources of atmospheric particles and trace gases impact atmospheric chemistry in the Bering Strait and Chukchi Sea in the Alaskan Arctic. However, there have been few measurements of individual atmospheric particle size and composition, which drive particle impacts on climate. We observed marine biogenic, terrestrial, and anthropogenic sources to influence summertime atmospheric particle composition.

Introduction

The Arctic region is currently warming at twice the rate of the global average.[1,2] In the Arctic summertime, atmospheric particles directly affect climate by scattering or absorbing incoming solar radiation, both in the atmosphere and when deposited on snow and ice-covered surfaces,[3–9] contributing to the Arctic amplification of temperature changes compared to the global average.[1,2] Additionally, atmospheric particles impact the Arctic climate by altering cloud formation and properties, including cloud brightness and lifetime.[9–11] Particle composition is influenced by condensation of lower volatility species and multiphase reactions in the atmosphere with both natural

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marine and anthropogenic trace gases.[12–15] The resulting complex and evolving aerosol mixture affects subsequent climate-relevant properties, including cloud condensation nuclei (CCN) and ice nucleating particle (INP) propensities.[16–18]

The summertime Arctic is primarily influenced by local and regional aerosol sources,[4,8,14] which are changing as a result of Arctic warming and melting of the sea ice.[19,20] The ice loss is particularly extreme in coastal regions, including the Bering and Chukchi Seas in the Alaskan Arctic and the Greenland Sea.[21] With declining sea ice, production of primary sea spray aerosol (SSA) and secondary aerosol precursors, including the trace gases dimethyl sulfide (DMS) and biogenic volatile organic compounds (VOCs), are expected to be increasing.[22–24] Increasing development, including oil and gas extraction in the Alaskan, Russian, and Norwegian Arctic, is also contributing to local anthropogenic aerosol and precursor emissions.[25–27] Decreasing sea ice is also resulting in increased shipping activity and associated emissions, particularly in the Alaskan Arctic,[25–27] since the Bering Strait is a critical point of entry to the Arctic and the Northern Sea route.[28] Projected increases in ship traffic (by more than 50% by 2050) and continued oil and gas exploration and drilling will contribute to combustion emissions, including soot,[29–31] and secondary aerosol precursors, including trace gases NO_x, SO_2, and VOCs.[14,25,26,32–35]

Aerosol mixing state describes the distribution of chemical species across a population of particles and within each individual particle.[36] The direction and magnitude of aerosol impacts on radiative forcing depends on individual particle composition and mixing state, as well as particle size and morphology.[36] For example, soot absorbs radiation, resulting in warming, and sulfate scatters radiation, resulting in cooling.[36] Mixing state also controls particle properties that influence aerosol indirect effects; for example, the hygroscopicity of sea salt can be reduced by an organic coating, thereby decreasing particle CCN efficiency.[4] Aerosol composition and mixing state are determined by emission sources and subsequent atmospheric processing through reactions and condensation of secondary materials.[37,38] Single particle techniques are well-suited to determine aerosol mixing state, by measuring the distribution of chemical species within individual particles.[37–39] However, few single particle studies have been conducted in the Arctic,[4] and significant gaps remain in understanding Arctic aerosol mixing state.

Ship-based studies in the Bering Strait and Chukchi Sea have observed influences of both natural and anthropogenic sources on aerosol composition based on bulk measurements assessing contributions of sea salt, mineral dust, metals, organic compounds, and soot.[40–45] Despite the climate implications of this complex aerosol chemistry in the summertime Arctic, there have been few single particle measurements in the Bering Strait or Chukchi Sea.[40,46,47] In this study, atmospheric particles were collected during the icebreaker (IBR/V) *Araon* 2016 Arctic research cruise in August, 2016 within the Bering Strait and eastern Chukchi Sea. Subsequent measurements of individual particle chemical composition and morphology were conducted to determine the influences of marine and anthropogenic sources on atmospheric composition and mixing state in the Alaskan Arctic.

Methods

Atmospheric particles were collected during the IBR/V *Araon* research cruise from August 1–August 20, 2016 in the Alaskan Arctic. Particles were collected using a microanalysis particle sampler (MPS-3, California Measurements) with aluminum foil substrates (MPS Corp.) on stage 2 (0.40–2.8 μm aerodynamic diameter, d_a) and transmission electron microscopy (TEM) grid substrates (carbon Type-B Formvar film copper grids, Ted Pella Inc.) on stage 3 (0.07–0.40 μm d_a). Samples were collected at ambient relative humidity and temperature (Table 1) and then sealed and stored in the dark at room temperature (~20 °C) until analysis.[48] Samples were collected for 12 h durations during clean periods, which were determined by establishing a clean sector void of ship emissions, defined by the relative wind direction to the bow of the ship.[49] This study focuses on eight sampling periods during the cruise in the Bering Strait and Chukchi Sea; these periods were selected based on clean sector sampling within regions of interest, without active precipitation, and representing a range of meteorological conditions (*i.e.* temperature and wind speed) (Table 1 and Fig. S1†). NOAA HYSPLIT 48 h backward air mass trajectories[50,51] were calculated for the midpoint of each sampling period, using the ship position at that time as the trajectory start. The August 02 sample was collected during a port stop at Nome, Alaska, during stagnant air (wind speeds < 2 m s^{-1}). For these samples, less than 1% of measured particles, by number, were soot, indicating that the particle samples were not influenced by the ship's emissions.

Table 1 Summary of atmospheric particle samples collected aboard the IBR/V *Araon* during August, 2016. The number of particles analyzed refers to CCSEM-EDX. Wind speed data were not available for all samples

Sample	Sample time (UTC)	Start location	Average wind speed	Average temperature	Weather	Number of particles analyzed
August 01 (morning)	0418–1624	61.67° N, 171.79° W		11 °C	Clear	2165
August 01 (evening)	1639–0443	62.97° N, 167.42° W	Stagnant	11 °C	Foggy, cloudy	1710
August 02	0449–1625	64.48° N, 165.32° W	Stagnant	10 °C	Cloudy	2113
August 06	0412–1603	65.15° N, 168.65° W	5.5 m s^{-1}	10 °C	Foggy, cloudy	3777
August 10	1845–0416	75.12° N, 175.26° W	13 m s^{-1}	−4 °C	Cloudy	1651
August 12	1952–0618	77.01° N, 176.62° W		−4 °C	Cloudy, foggy	1938
August 14	0623–1903	77.99° N, 177.00 °W		−3 °C	Foggy, cloudy	2006
August 20	0615–1840	76.01° N, 162.30° W	5.5 m s^{-1}	−1 °C	Cloudy	1868

Computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy (CCSEM-EDX) was performed to analyze ∼1000 particles per sample, for a total of 17 228 particles (Table 1). Samples on stage 3 TEM grid substrates were analyzed using a FEI Quanta environmental SEM with a field emission gun (FEG) operating at 20 keV accelerating voltage with a scanning transmission electron microscopy high angle annular dark field detector to collect SEM images, providing morphological information. An EDX spectrometer (EDAX, Inc.) measured individual particle X-ray spectra and provided the relative atomic abundance of elements C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Fe, Ni, and Zn. Additional CCSEM-EDX analysis of stage 2 samples on aluminum foil were conducted using a FEI Helios SEM/FIB with FEG operating at 20 keV with a secondary electron Everhart-Thornley detector to collect SEM images. An EDX spectrometer (EDAX, Inc.) measured X-ray spectra and provided the relative atomic abundance of elements C, N, O, Na, Mg, P, S, Cl, K, Ca, Ti, V, Fe, Ni, and Zn. Al and Si were omitted from stage 2 EDX measurements due to significant background from the substrate and detector, respectively.[14]

Following the method described by Ault *et al.*,[52] *k*-means clustering of the individual particle EDX spectra resulted in 50 clusters each for all stage 2 particle data and stage 3 particle data. The optimal number of clusters (50) applied to the data in this study was selected by determining the number of clusters when cluster error began to plateau and spectra with minimal differences began to split into separate clusters.[52] The 50 clusters were then grouped into six broader particle classes primarily separated by sources (fresh SSA, aged SSA, mineral dust, ammonium sulfate, organic aerosol (OA), and soot), based on comparisons of the EDX spectra to particle classes reported in previous studies.[14,52,53] Prior CCSEM-EDX studies have established EDX spectral signatures for fresh SSA,[15,54] aged SSA,[14,15] mineral dust,[15,55,56] ammonium sulfate,[57] OA,[14,15,57] and soot.[14,58] These particle types have been previously observed in the Arctic environment.[14,15,59,60] EDX can be less sensitive to lighter elements including C, N, and O; therefore, the values presented herein represent lower limits.[61] While a small number of particles with morphology indicative of primary biological aerosol were observed during manual SEM imaging, no biological particle cluster (characterized by particles containing P and K)[62] was identified by *k*-means clustering. These particles were likely included in the OA class based on similarity of chemical composition[57] and the low abundance of biological particles.

Individual particle morphology, phase, and infrared spectra were measured by atomic force microscopy with photothermal infrared spectroscopy (AFM-PTIR) using a nanoIR2 instrument (Anasys Instruments), following a method previously established for atmospheric particles.[63–65] August 2 (12 particles) and August 12 (15 particles) stage 3 samples (0.07–0.40 μm d_a) were analyzed by AFM-PTIR. AFM images were collected in contact mode at a 1.0 Hz scan rate over a 5 μm × 5 μm area on the copper grid bar of the TEM grid substrates. IR spectra were collected over the 900–3600 cm^{-1} range at 4 cm^{-1} resolution.

Results and discussion

Observed particle types

For the atmospheric particles collected within the Bering Strait and Chukchi Sea and presented here, six individual particle

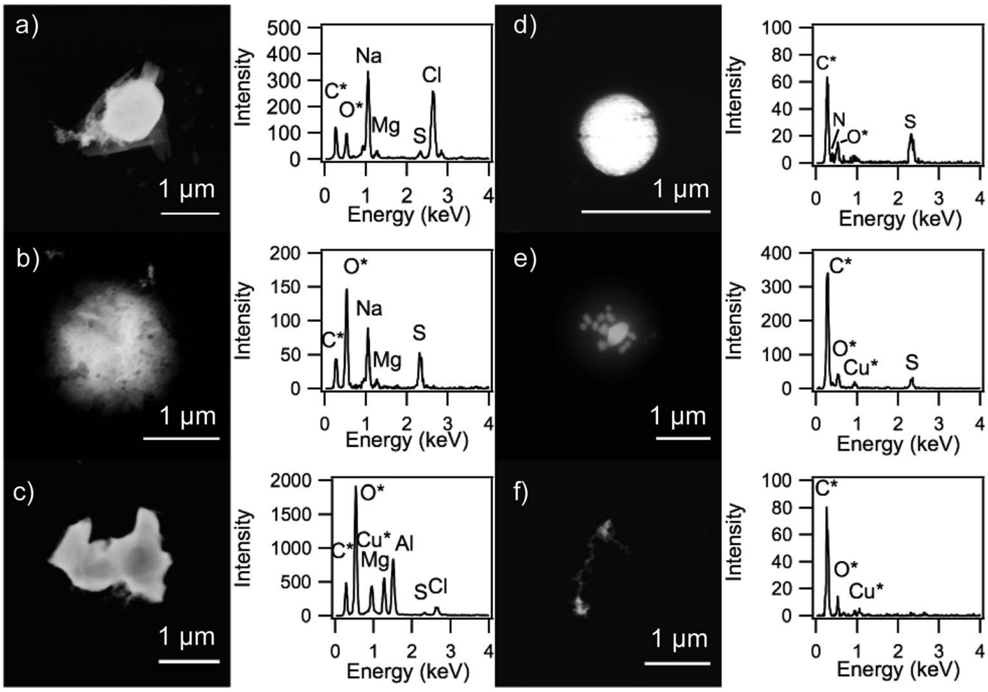

Fig. 1 Representative SEM images and EDX spectra of individual particles corresponding to the six types, identified by CCSEM-EDX: (a) fresh SSA, characterized by Na and Cl, (b) aged SSA, characterized by Na and S, (c) aluminum and magnesium dust particle, (d) ammonium sulfate particle, (e) OA particle with sulfur, and (f) soot. *Copper, carbon, and oxygen peaks include some signal from the TEM grid and substrate background.

classes were identified by CCSEM-EDX analysis: fresh SSA, aged SSA, OA, ammonium sulfate, dust, and soot (Fig. 1). Fresh SSA particles were characterized by Na and Cl with mole ratios (average $\text{Cl/Na} = 0.98 \pm 0.01$, 95% confidence interval) similar to seawater (1.16),[66] indicative of local production.[15,67] Aged SSA particles exhibited partial or full Cl depletion (average $\text{Cl/Na} = 0.2 \pm 0.4$), with quantitative replacement by sulfate and/or nitrate (identified by S and/or N in the EDX spectra) (Fig. S2†).[14,15,68,69] SSA aging is a result of multiphase reactions during atmospheric transport between sodium chloride and nitrogen- and sulfur-containing gases, resulting in the formation of sodium nitrate and sodium sulfate in the particle phase, with Cl liberation typically in the form of gaseous HCl.[70–73] Additional Cl depletion beyond replacement by sulfate or nitrate (Fig. S2†) may be explained by atmospheric reactions with organic acids.[73] SSA particles (both fresh and aged) can also contain organic material in the form of an organic coating;[74] SSA composition is discussed further below.

Ammonium sulfate particles were identified based on the predominance of N and S in the EDX spectra,[57] in addition to their distinct morphology determined by CCSEM-EDX images and behavior during SEM imaging, as these particles are semivolatile and sensitive to the electron beam.[75,76] Since EDX is not particularly sensitive to detection of N,[61] the detection of these N and S dominant particles is indicative of an ammonium sulfate rich particle type, formed by the reaction of ammonia with sulfuric acid.[57,76,77] The ammonium sulfate particles likely also contained some organic material. OA particles were characterized by primarily containing C and O, with a fraction of the particles, by number, also containing S and/or N, showing internal mixing of organic compounds with sulfate and/or nitrate.[14,15] Greater number fractions of supermicron OA particles contained sulfate and nitrate compared to submicron particles, possibly due to challenges in detecting S and N by EDX in the submicron particles.[61] Internal mixing of organics and sulfate in submicron OA particles was confirmed by AFM-IR analysis (Fig. S3†), with IR peaks corresponding to sulfate, ν(C–H), ν(C=O), and ∂(C–H).[63–65] Based on their morphology, these OA particles are likely secondary aerosol formed from the condensation of semivolatile anthropogenic or biogenic trace gases.

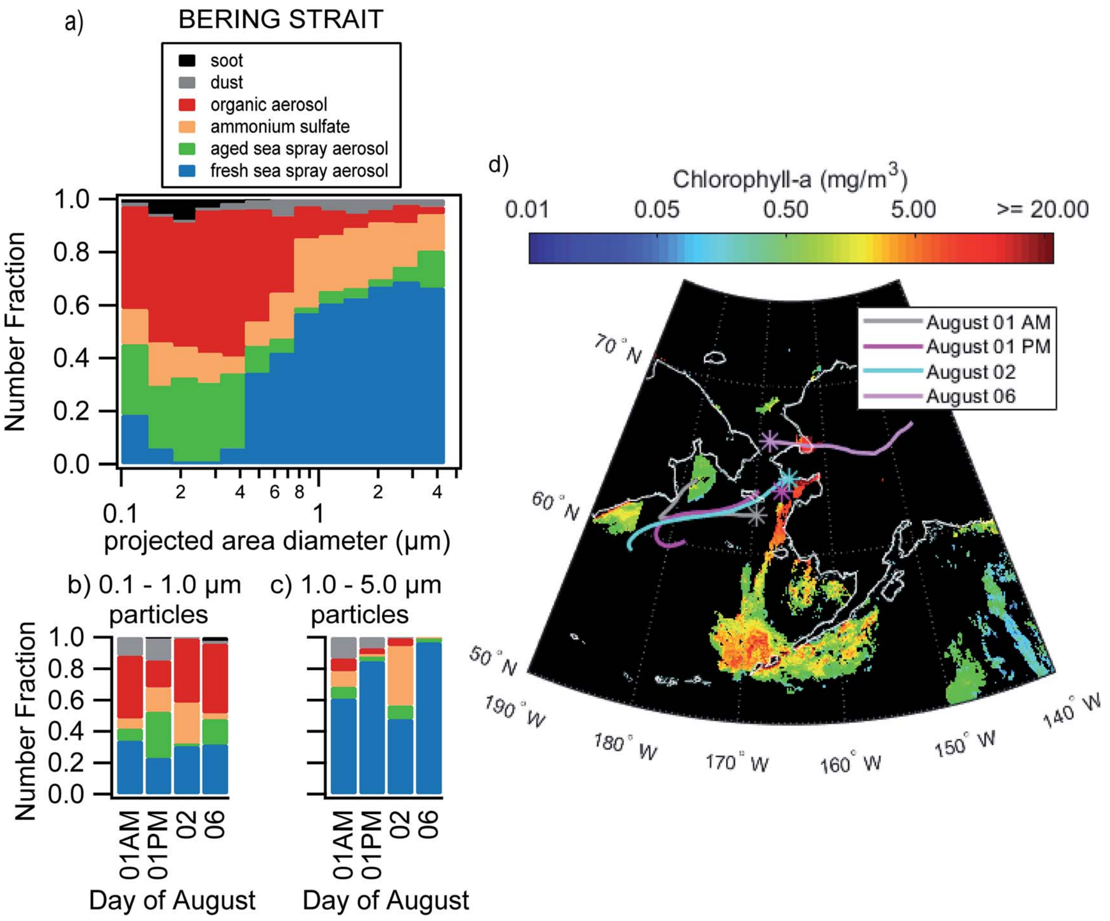

Fig. 2 (a) Average size-resolved CCSEM-EDX number fraction distributions of observed particle types from 0.1 to 5.0 µm projected area diameter for all Bering Strait samples. Number fractions of particle types observed for each Bering Strait sample in the (b) submicron and (c) supermicron size ranges. August 01 AM and August 01 PM correspond to morning and evening samples (Table 1). (d) Air mass influence of each Bering Strait sample as determined by NOAA HYPSLIT 48 h backward air mass trajectories. Stars denote particle sampling locations. MODIS ocean chlorophyll-a concentrations (NASA Worldview) across the sampling region on August 1, 2016, representative of the study period, are shown. Chlorophyll-a concentrations < 0.01 mg m^{-3} are shown in black.

Minor particle types (in total < 5% of the particle number) included dust and soot. Dust particles contained mostly Ca, Al, and/or Si; a fraction of particles also contained trace metals including Mg and Zn, suggesting influence from both terrestrial and industrial sources.[15,55,56,78] Dust particles were overall a small fraction of the observed aerosol number (<3%), but were present in all samples, likely transported from regional sources in Alaska or from long range transport from the Asian continent.[79] A small fraction of observed particles were also identified as soot, characterized by C-rich EDX spectra and distinct morphology (Fig. 1f).[14,58,78] Soot was a small fraction of the observed particles (<2%, by number, from 0.1–1.0 μm), indicating that these samples were not contaminated by direct emissions from the ship itself. Some soot may have been present internally mixed with OA and/or sulfate as a result of atmospheric aging during transport from pollution sources, and these particles would be classified as part of the OA type.[14,15]

Air mass influences and particle sources

Distinct differences in the size-resolved number fractions of the particle classes were observed for particles collected in the Bering Strait compared to the Chukchi Sea, indicative of different air mass and source influences (Fig. 2 and 3). No sea ice was present in the Bering Strait during August, 2016, but the region is biologically productive,[80,81] as indicated by high chlorophyll-a concentrations inferred from satellite imaging (Fig. 2d). There was also minimal sea ice present in the Chukchi Sea during this period, with samples collected above open water and near the ice edge in the marginal ice zone (Fig. 3d). With this great extent of open water, marine influences were present in the Bering Strait and Chukchi Sea. However, the Bering Strait also experienced terrestrial dust influence from Alaska and eastern Russia, and anthropogenic influence from oil and gas exploration and shipping activity.

Bering Strait samples included August 01 morning and evening, August 02, and August 06. Backward air mass trajectories showed influence of marine coastal regions within the Bering Strait for August 01 morning and evening and August 02, and terrestrial influence from inland Alaska on August 06 (Fig. 2). All Bering Strait samples showed coastal marine and anthropogenic influence. Fresh SSA was the dominant particle type in the supermicron range (55–65% of particles, by number), and was present in the submicron range as well (20–30%). Aged SSA comprised only ~20% of particles in the submicron size range (0.1–1.0 μm projected area diameter (d_{pa}), as measured by CCSEM-EDX)[69] (Fig. 2). Consistent with this observation, previous bulk aerosol studies have observed influence of sodium and chloride on atmospheric particle composition in the Bering Strait.[40,42,44]

Dust was also present in all Bering Strait samples (~1–5%, by number, from 0.5–5.0 μm), from terrestrial and industrial sources.[14,42,45,78] Increased number fractions of dust were present in both the sub- and supermicron ranges on August 01 (Fig. 2), with air masses from eastern Russia. These August 01 dust particles contained aluminum and zinc, likely from Russian industrial sources,[82] while calcium-containing dust,

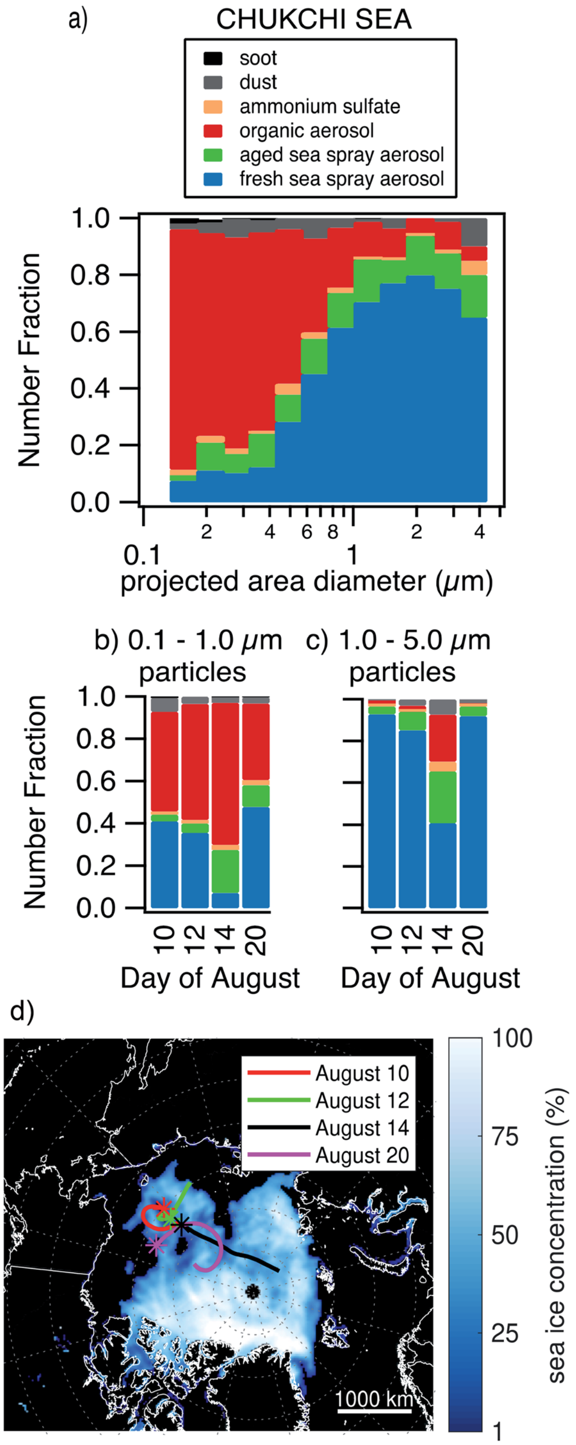

Fig. 3 (a) Average size-resolved CCSEM-EDX number fraction distributions of observed particle types from 0.1 to 5.0 μm projected area diameter for all Chukchi Sea samples. Number fractions of particle types observed for each Chukchi Sea sample in the (b) submicron and (c) supermicron size ranges. (d) Air mass influence of each Chukchi Sea sample as determined by NOAA HYPSLIT 48 h backward air mass trajectories. Stars denote particle sampling locations. Nimbus-7 SMMR and SSM/I-SSMIS sea ice concentration map (NASA Worldview) of the sampling region on August 14, 2016 is shown.

likely from crustal weathering dust,[42,55,79] was present in all samples at number fractions of less than 5%.

In all Bering Strait samples, OA particles dominated the submicron size range (number fraction: 40–50%) (Fig. 2). Previous studies have attributed OA observed in the Bering Strait to marine biogenic SOA,[40,83] wildfires,[84] and anthropogenic sources (*e.g.* shipping emissions).[40,46] Vanadium, a tracer for shipping emissions, was present in 7% of the Bering Strait OA particles, with similar number fractions of vanadium-containing particles observed in all samples. Overall, a greater number fraction of Bering Strait OA particles contained nitrate and/or sulfate and nitrate (Fig. S4†), compared to Chukchi Sea OA, likely due to greater anthropogenic influence. Previous summertime studies have measured non-sea salt sulfate within the north Bering Sea, with higher concentrations observed with more pollution influence.[85] The Bering Strait is a busy shipping lane, providing NO_x and SO_2 combustion emissions for nitrate and sulfate formation.[25,27,32,34] In addition, in the summer, a fraction of the OA particulate sulfate likely originates from marine DMS oxidation.[86–89] Elevated DMS levels have been observed in the Bering and Chukchi Seas and correlated with phytoplankton blooms,[90–93] with elevated chlorophyll levels observed in the region during this study (Fig. 2), suggesting both marine and anthropogenic sources influenced the OA mixing state.

In addition to OA, ammonium sulfate (likely also containing organics) contributed a significant fraction to the aerosol number (~15–25%) in both the submicron (0.1–1.0 μm d_{pa}) and supermicron (1.0–5.0 μm d_{pa}) size ranges (Fig. 2). Arctic sources of ammonia, a precursor to ammonium sulfate aerosol, include wildfire emissions, microbial oxidation of marine dissolved organic nitrogen, and seabirds.[77,94–97] On August 01 and 02, there were wildfires present upwind in eastern Russia (Fig. S5†). There are also large seabird colonies present in the Bering Strait during summer,[96,97] likely a large contributor to atmospheric ammonia and subsequent ammonium sulfate formation.[96–100] The August 02 sample had a greater number fraction of ammonium sulfate particles in both the submicron (0.1–1.0 μm d_{pa}, 25%) and supermicron (1.0–5.0 μm d_{pa}, 65%) size ranges, compared to the other samples (Fig. 2). It was also characterized by an increased number fraction of supermicron aged SSA (10%) (Fig. 2), indicative of more polluted air mass influence, including local sources at Nome. Only a small fraction of fresh soot was observed in the Bering Strait samples (<5%, by number, from 0.1–0.5 μm). No significant soot fraction was observed on August 02 (<1%) during the stop at Nome, consistent with other samples. Low background levels of soot, averaging 1.0 ng m^{-3}, have been previously observed in this region.[41] Local combustion emissions from Nome are expected to be below the measured size range (<0.1 μm d_{pa}).[101] The August 06 sample showed an increased fraction of submicron (0.1–1.0 d_{pa}) soot, likely from inland pollution sources,[14,41,102] consistent with aging timescales for soot in remote environments (Fig. 2).[103,104]

In contrast to the Bering Strait samples showing influence of anthropogenic pollution and terrestrial emissions, the Chukchi Sea samples, collected on August 10, 12, 14, and 20, showed primarily marine influence. These samples were all influenced by air mass trajectories coming from within the Chukchi Sea and across the Arctic Ocean, through the marginal ice zone and pack ice (Fig. 3). Consistent with this marine influence, supermicron (1.0–5.0 μm d_{pa}) particles were mainly fresh SSA (60–80%, by number), and submicron particles were mainly OA (50% from 0.5–1.0 μm and 85% from 0.1–0.5 μm) (Fig. 3). Previous studies in the Chukchi Sea have identified sea spray aerosol and marine biogenic aerosol (OA) as major sources.[40,42,45,47,105] Aged SSA comprised only ~10% of the particle number across both the sub- and supermicron size ranges (Fig. 3), consistent with limited pollution influence. Ammonium sulfate and dust particles each contributed less than ~5% of the overall particle number, and soot was negligible, suggesting minor influence of anthropogenic and terrestrial sources. All Chukchi Sea samples, like the Bering Strait samples, contained a small fraction (<1%) of calcium-containing dust. However, silicon-containing dust was observed only in the Chukchi Sea samples, and the aluminum- or zinc-containing dust was unique to the Bering Strait samples. Silicon-containing dust is likely from soil or coastal beach sand sources, indicating a small amount of terrestrial influence.[14,42]

Chukchi Sea particle samples had relatively smaller number fractions of OA particles containing nitrate compared to Bering Strait samples (Fig. S4†). Given the sampling locations and limited nitrate contributions, these are likely secondary marine-derived OA particles (externally mixed from SSA) with sulfate from DMS oxidation, rather than anthropogenic SO_2 oxidation.[40,106,107] Elevated levels of MSA (average 12 ng m^{-3}) have been previously observed during summer near the ice edge in the Chukchi Sea.[105] Additionally, marine VOCs have recently been observed to be involved in Arctic secondary OA formation.[24,100,108]

Notably, the August 14 Chukchi Sea sample was influenced by an air mass that had traveled from across the pack ice in the central Arctic Ocean (Fig. 3). Compared to the other Chukchi Sea samples, this sample had increased number fractions of aged SSA (~25% of submicron and ~20% of supermicron particles) and OA (~70% of submicron and ~20% of supermicron particles) (Fig. 3). This sample also had a smaller number fraction of fresh SSA (40%) compared to the other Chukchi Sea samples (85–95%), indicative of longer atmospheric transport over the pack ice. Additionally, a greater number fraction of the OA particles observed on August 14 contained sulfate (48% of supermicron OA particles and 88% of submicron OA particles), compared to the other Chukchi Sea samples (15% of supermicron OA particles and 45% of submicron OA particles) (Fig. 3). The increased fraction of aerosol containing secondary sulfate is consistent with an aged air mass transported further from aerosol sources over a region with greater ice concentration in the central Arctic Ocean.[15,109,110]

Sea spray aerosol composition

To further investigate the degree of atmospheric aging of the observed SSA, average individual particle sulfate (S/Na), nitrate (N/Na), and chloride (Cl/Na) mole ratios were determined for the SSA (fresh and aged) for the Bering Strait and Chukchi Sea samples (Fig. 4 and S2†). For the Bering Strait SSA particles, individual particle Cl/Na mole ratios were depleted relative to seawater (1.16),[66] with greater depletion observed for submicron SSA (Cl/Na of 0.40 ± 0.02, 95% confidence interval) than supermicron SSA (0.98 ± 0.04) (Fig. 4), consistent with the greater fraction of submicron aged SSA (Fig. 2). A greater fraction of aged SSA is typically observed in the submicron size range due to the longer atmospheric lifetimes, smaller Cl reservoir, and greater surface area to volume ratios of submicron particles, which are conducive to greater atmospheric processing.[111–114] Additionally, S/Na (0.165 ± 0.007 for submicron and 0.139 ± 0.006 for supermicron SSA) and N/Na mole ratios (0.035 ± 0.002 for submicron and 0.081 ± 0.004 for supermicron SSA) were enhanced relative to seawater (0.06 and 0.0002, respectively),[66] with greater N/Na enrichment observed for supermicron SSA (Fig. 4a). SSA aging by reactions with H_2SO_4, in addition to reactions with HNO_3, is commonly observed in the Arctic,[13–15,115] and is consistent with the anthropogenic air mass influences observed for the Bering Strait samples. In comparison, Chukchi Sea SSA particles were more similar in composition to seawater, indicative of fresh SSA,[14,15,67] with supermicron Cl/Na mole ratios (1.02 ± 0.05) close to the seawater ratio (1.16). Modest chloride depletion was observed for submicron Cl/Na (0.75 ± 0.04), with slight S/Na and N/Na enrichment for both sub- (0.154 ± 0.008 S/Na and 0.039 ± 0.002 N/Na) and supermicron particles (0.139 ± 0.007 S/Na and 0.070 ± 0.004 N/Na) (Fig. 4c), consistent with the small fraction of aged SSA observed in addition to fresh SSA (Fig. 3).

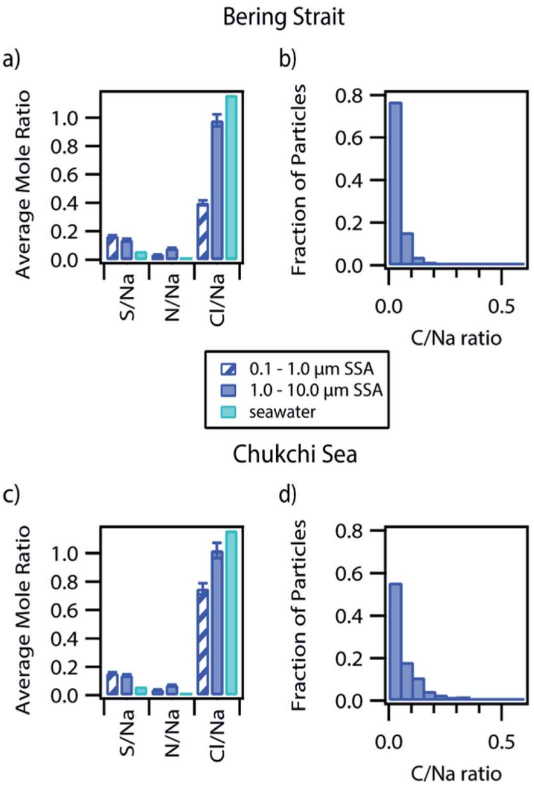

Fig. 4 Average S/Na, N/Na, and Cl/Na mole ratios for individual sea spray aerosol (SSA) particles for (a) Bering Strait (2029 particles) and (c) Chukchi Sea (1417 particles) samples, compared to standard seawater ratios (0.06, 0.0002, and 1.16, respectively).[66] Error bars denote 95% confidence intervals. Histograms of C/Na mole ratios for individual supermicron SSA particles on foil substrates for (b) Bering Strait and (d) Chukchi Sea samples.

The Bering Strait is a region of biologically productive water,[28,116] enriched in organic material that has been observed in the aerosol phase.[83,117] Enrichment of marine organics in Arctic SSA has been previously observed as organic coatings on the salt particles,[74,118] and previous observations in Antarctica have shown increased SSA C/Na mole ratios in more productive waters.[94] For supermicron SSA particles (collected on foil substrates), C/Na mole ratios were compared to seawater to determine carbon enrichment. For the Bering Strait samples, 39%, by number, of the SSA particles contained carbon, with C/Na mole ratios between 0.05 and 0.2 (Fig. 4b), compared to the seawater ratio of 0.01.[66] For the Chukchi Sea samples, 60% of the SSA particles from the Chukchi Sea samples contained carbon, with C/Na mole ratios between 0.05 and 0.5 (Fig. 4d). A higher number fraction of Chukchi Sea SSA particles had C/Na mole ratios greater than 0.1 (20%), compared to the Bering Strait SSA (5%). This may be indicative of increased algal mass near the ice edge in the Chukchi Sea,[81,119,120] providing additional organic material that is transferred to the aerosol phase. This is consistent with previous observations of SSA organic enrichment present as an organic coating on the inorganic salt core, which may alter CCN efficiency.[121–125]

Conclusions

Characterization of aerosol composition in the summertime Alaskan Arctic is important for determining particle CCN efficiency and INP activity, influence on surface albedo, and resulting climate effects in the region with declining sea ice. Previous studies in the region have observed influence of marine biogenic and anthropogenic sources on the aerosol composition,[40–45] but there have been few single particle studies to determine the aerosol mixing state.[40,46] Individual atmospheric particles collected in the summertime Alaskan Arctic within the Bering Strait and Chukchi Sea were comprised primarily of fresh and aged sea spray aerosol, organic aerosol, and ammonium sulfate particles. Chukchi Sea samples were primarily marine influenced, with fresh SSA and OA. In contrast, Bering Strait samples contained more aged SSA, ammonium sulfate, soot, and internally mixed sulfate with OA, indicating anthropogenic and terrestrial influence on the aerosol mixing state. In a changing Arctic with decreasing sea ice, increasing emissions of SSA are expected,[22] as well as greater anthropogenic influence from increasing shipping activity,[25–27] particularly in the Bering Strait.[28] These evolving aerosol and precursor gas sources will likely impact regional atmospheric chemistry and climate effects, including cloud formation and properties.[126,127]

Further studies are needed for improved predictions of atmospheric composition and climate impacts in the changing Arctic. Continued studies are needed to determine the impacts of sea ice loss on both natural and anthropogenic emissions, as increasing open water will result in greater marine aerosol and trace gas emissions, as well as increasing combustion emissions from development and shipping activity, as both natural and anthropogenic emissions have been identified as important sources of atmospheric aerosol herein. Additionally, a more detailed molecular characterization of OA composition is necessary to further investigate OA sources, formation mechanisms, and potential climate impacts, as this work has demonstrated that OA is a significant contributor to the submicron aerosol in both the Bering Strait and Chukchi Sea. Within the Bering Strait and Chukchi Sea, measurements across seasons are needed to characterize aerosol sources, concentrations, and mixing state with increasing sea ice loss, particularly during autumn freeze up and with springtime algal blooms. In order to determine aerosol-cloud-climate impacts in the Bering Strait and Chukchi Sea region, measurements of concurrent cloud and aerosol properties are needed, including CCN and INP measurements, to connect the observed particle composition to cloud nucleation efficiencies.[128] Observations of aerosol and cloud properties across seasons are necessary to understand the seasonality of aerosol-cloud impacts in the Alaskan Arctic, given rapidly changing sea ice conditions.

Author contributions

R. M. Kirpes and K. A. Pratt led data interpretation and prepared the manuscript. A. P. Ault assisted in data interpretation. B. Rodriguez collected the samples, with assistance from S. Kim, J. Jung, and K. Park. R. M. Kirpes conducted CCSEM-EDX analyses, with assistance from S. China and A. Laskin. R. M. Kirpes conducted AFM-IR analyses. All authors reviewed and commented on the paper.

Conflicts of interest

There are no conflicts to declare.

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