Response to Reviewer #1

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.

This manuscript describes single particle characterization (ATOFMS and CCSEM- EDX) of particulate matter attributed to Arctic oil extraction activities at Prudhoe Bay, Alaska, and contrasts this with particulate matter dominated by natural emissions from the nearby Arctic Ocean for ~1 month of measurements in late summer. This work con- tributes to the very few studies of local Arctic emissions of anthropogenic aerosol, and is therefore valuable in extending our understanding of local Arctic pollution sources in the context of the summertime Arctic natural background. The manuscript is overall well written and clear. It merits publication in ACP after the following comments have been addressed.

Major Comments:

In the introduction as well as in the discussion sections, the authors should make further efforts to ensure that proper, complete, and most importantly accurate, credit is given to prior related work. Specific instances are indicated in the minor comments.

We added and revised references used throughout, with specific instances requested by the reviewer addressed in the responses to the comments below.

Minor Comments:

Introduction: This introduction gives no context for the conditions expected in the unpolluted summer Arctic. The seasonal cycle in Arctic aerosol is very relevant to the context of these measurements, especially under the cleaner conditions of summer to autumn. Similarly, an acknowledgment of pollution influences in winter and spring is also relevant. The natural question here is how Prudhoe Bay emissions might compare to influences of long range transport in terms of aerosol loading and composition.

We added a statement to the introduction (P3 L9-13) addressing pollution contributions from oil and gas extraction in regards to the seasonal cycle, which states: "The Arctic aerosol population is characterized by a maximum mass loading in the winter, due to transported pollutants from the mid-latitudes, and a minimum in the summer, when local sources, including sea spray aerosol, dominate (Quinn et al., 2002; Quinn et al., 2007). However, there is limited knowledge of aerosols produced within the Arctic, particularly in the context of changing emissions from both natural and anthropogenic sources (Arnold et al., 2016)."

P3 L10-15: The discussion of BC and OC contributions from total Arctic oil and gas extraction, versus that from Prudhoe Bay is at present somewhat confusing. In addition, the methods used to arrive at BC and OC estimates might be relevant to this discussion, e.g., were in-situ measurements used to arrive at these estimates?

We revised this paragraph to reduce confusion about what is from the overall Arctic vs. Prudhoe Bay.

P3 L17: Are these US contributions from Prudhoe Bay alone or does this estimate represent expansion to other sites?

> **These particulate emissions represent contributions from all US Arctic oil and gas extraction sites. We clarified in this paragraph that Prudhoe Bay is the primary, but not only, contributor to the estimated US oil field emissions in the Arctic.**

P3 L20: It is not strictly true to suggest that emission of gas phase species would lead to solely new particle formation. If the intention is to highlight the role that the very low condensation sinks of the summer Arctic could play in this respect, then the authors should state this clearly.

> **We revised this to state "…drilling operations can emit aerosol precursors (NO_x, SO_2, and VOCs) and alter oxidant levels, which can lead to the formation of secondary aerosol, as well as contribute to new particle formation…".**

P3 L22: Flanner et al., 2013 does not indicate anything about the impact of BC on clouds. In abstract the authors state that the study has limitations owing to their lack of treatment of indirect effects.

> **This was not clearly worded, and we clarified this to now state: "BC is estimated to have a warming effect on the Arctic atmosphere (e.g. Bond et al., 2013; Flanner, 2013; Flanner et al., 2007; Sand et al., 2013; Sharma et al., 2013)."**

P3 L25: Citation of other relevant work, such as Flanner et al, 2007 (and others) is advisable here

> **References to Flanner et al. (2007), Sand et al. (2013), and Sharma et al. (2013) have been added to this paragraph.**

P3 L27: Is this result directly from Koch 2009, or is it elaborated by Bond 2013?

> **This is directly from Koch et al. (2009), and we updated the sentence to accurately reflect this.**

P3 L27-28: Did the modelling studies discussed here include local Arctic BC sources? This is worth discussing.

> **The following sentence was added on P4 L4-7 to discuss that these modeling inaccuracies may be improved by the inclusion of local Arctic BC sources. "Koch et al. (2009) suggest that Arctic BC concentrations are under-predicted by a variety of models by an average factor of 2.5, which may be improved by more accurately incorporating local BC sources (Flanner, 2013)."**

P4 L4: To do justice to the study of Barrett 2015 the authors should discuss the varying contribution of fossil fuels to Barrow EC over the winter period. Biomass burning is also an important source and can have local Arctic sources.

> **Following the reviewer's suggestion, we expanded the discussion of Barrett et al. (2015) (P4 L9-11) to now state: "…similar to the recent results of Barrett et al. (2015) at Utqiaġvik during December 2012 – March 2013 when transported particles from Russian oil fields were observed. Barrett et al. (2015) also measured regional Arctic BC from both fossil fuel combustion and biomass burning."**

P4 L9: Do the authors suggest that due to the focus on biomass burning, the results of this study are less relevant to their discussion? The measurements of Brock 2011 likely represent some of the few more complete chemical characterizations of Prudhoe Bay aerosol emissions.

> **We removed this statement; it was not our intention to appear to be overlooking the characterization efforts of Brock et al. (2011) in terms of the Prudhoe Bay aerosol.**

P4 L22: Cappa 2012 explicitly shows that absorption enhancement was not detectable, despite significant particle mixing, during their measurement campaign. This needs to be much more clearly stated, and the complexity of this issue need to be addressed. In particular, I do not agree with the statement that light absorption is enhanced the presence of sulfate or organic species in the same particles. Some studies have observed absorption enhancements (e.g., Knox 2009, Liu 2015) while others have not (e.g., Cappa 2012, Healy 2015). It is not clear whether this effect is significant in all ambient aerosol and this issue should not be stated as being entirely clear.

> **We acknowledge that this is a complex topic and updated P4 L26-28 accordingly: "It is currently not clear whether light absorption by a BC particle is enhanced by sulfate or organic coatings (e.g., Cappa et al., 2012; Chung and Seinfeld, 2005; Healy et al., 2015; Jacobson, 2001; Knox et al., 2009; Liu et al., 2015; Moffet and Prather, 2009)."**

P4 L26: Is such a binary definition relevant to ambient particles? It might be more accurate to state that ambient aerosol can be found with range of mixing states approaching external or internal mixing in different cases and with influence from different source types.

> **We clarified this on P5 L3-5, which now reads: "Ambient aerosol populations typically vary between internal mixtures, with multiple chemical species contained within a single particle, and external mixtures, with chemical species present as separate particles (Prather et al., 2008)."**

Method section: Please ensure that all manufacturer information is as complete as possible with relevant names, models and locations.

> **This information has been added.**

P5 L21: How do back trajectories compare for the two sites?

> **These sites are separated by 5.5 km, less than the resolution of HYSPLIT (1 degree, ~100 km), with only flat tundra located between them (P6 L1). Therefore, use of HYSPLIT to differentiate between the sites is not possible, and trajectories at the two sites are expected to be similar.**

P6 L23: Given the long sampling period and the acknowledgement of local vehicle emission contributing to particle measurements, how might fast-varying local emissions (such as vehicles or generators) influence the particle composition interpreted from these 8h measurements?

> **Short particle spikes due to local emissions would have been detected as brief increases in particle number concentrations by the SMPS, operated with 5 min resolution (Figure S2). These events were only observed during the Utqiagvik influence sampling periods (e.g. Sept 7, see Figure S2); these local contributions were not observed during the clean Arctic or Prudhoe Bay influenced periods (Figure S2).**

Section 2.3: How is statistical significance determined for these measurements? What is the minimum number of particles that must be analyzed in order to to have a representative sample?

> **Significance was determined using binomial statistics, which we have clarified on P8 L5-6. The minimum number of particles for a representative sample are between ~300 and 1,000. See Willis et al. (2002), Section 4.6.2.**

P8 L10: This is a remarkably small number of particle spectra to draw conclusions from. While I acknowledge the challenges of obtaining a large number of particle spectra in such a low concentration environment, the authors should acknowledge this limitation of the ATOFMS measurement in a more prominent manner (for example, Sierau 2014 acknowledges this challenge in their abstract). Related to this, what fraction of ATOFMS detected particles did not provide mass spectra? These limitations in no way contradict the main conclusions of the work, since the CCSEM-EDX analysis provides a complementary data set that provides similar conclusions; however, this limitation needs to be clearly stated.

> **We acknowledge the limitations of having a small number of particle spectra, which is why much of the in-depth analysis focuses on CCSEM-EDX data. However, the main difference is that the ATOFMS used by Sierau et al. (2014) was operating properly, to our knowledge, and that paper relied solely on the ATOFMS data obtained. In contrast, during our study, there was an instrumental issue with the time-of-flight mass analyzer, as described on P8 L25- P9 L1. This resulted in an extremely low fraction of particles producing mass spectra. The mass analyzer was fixed following the field campaign, and laboratory tests verified that the mass spectra produced during the field campaign were accurate, with just a much lower fraction of individual particle mass spectra collected. In our more recent Arctic deployment of the ATOFMS (after fixing the mass analyzer), over 33,000 particles were chemically analyzed over a similar time frame as the present study (unpublished work). To more clearly acknowledge the limitations of the ATOFMS results in the present study, we now state the**

total number of ATOFMS particles chemically analyzed in the Figure 5 caption, in addition to the statement in the methods section (P8 L23).

P9 up to L25: Emission of small, primary particles from Prudhoe Bay emissions is likely also associated with emission of oxidizable or condensible gas phase species. Why might the Prudhoe emissions have stayed relatively small during transport to your measurement site?

We reorganized this section (moved later paragraph discussing emissions of condensable gases up to P10 L13-20) and clarified the discussion. P10 L23-28 now reads "Kolesar et al. (2017) previously observed Prudhoe Bay air masses to preferentially exhibit particle growth, compared to Arctic Ocean air masses. However, particle growth was not observed to occur within all Prudhoe Bay air masses during the summer, and particle growth events were not observed in September in Utqiaġvik." Given the lack of measurements of trace gases both in Kolesar et al. (2017) and this study, it is not possible, unfortunately, to comment on the reason for the lack of observed particle growth. Note that Kolesar et al. (2017) did not observe any particle growth events in September in Utqiaġvik over multiple years.

P10 L8: Is comparison to Alert, Nunavut also possible?

We added a comparison to Alert on P11 L7. The full sentence now reads: "The median particle concentration within Arctic Ocean air masses is similar to the median particle number concentrations during August at Station Nord, Greenland (227 particles cm^{-3}, Nguyen et al., 2016) and Alert, Canada (~160 particles cm^{-3}; Croft et al., 2016), during September at Tiksi, Russia (222 particles cm^{-3}; Asmi et al., 2016), and within the range of observations onboard the Swedish icebreaker Oden from July – September during multiple central Arctic Ocean studies when the air masses were exposed to the open ocean (90-210 particles cm^{-3}; Heintzenberg et al., 2015).".

P10 L20: However, your measurements show that the chemical composition of particles >100nm is different between the two types of air masses, and I doubt that no influence on these particle sizes occurs.

While the aerosol size distributions above 100 nm were not statistically different between Prudhoe Bay and Arctic Ocean air masses, there were indeed chemical composition differences observed by ATOFMS and SEM-EDX (e.g. increased chloride depletion, coupled with nitrate and sulfate addition in sea spray aerosol). Since these differences in chemical composition are discussed in the later sections, this confusing sentence has been deleted.

P11 L1: This work is from Summit, Greenland, which is arguably quite different from other, lower altitude, regions of the Arctic for a few reasons. First, ascent over Greenland can cause deposition of transported species leading to quite clean air masses. Second, the lack of local sources (aside from snow pack photochemistry) compared to other Arctic regions which are directly subject to marine, coastal, and tundra influences. While some recent studies have suggested the presence of condensible material in the summer Arctic (e.g., Mungall 2017, Willis 2016), it would be very surprising if Prudhoe Bay did not also emit gas phase species. The authors might want to discuss what is known about gas phase emissions from oil and gas extraction. Some studies from lower latitudes (e.g., Liggio 2016) suggest these can be substantial.

> **We removed the reference to Ziemba et al. (2010) for work at Summit. These sentences (moved to P10 L17-23 in response to an earlier comment) now read: "Based on the simulations by Fierce et al. (2015), particle growth during transport for particles ~30-50 nm would take ~1-7 days, if coagulation-dominated due to limited condensable material. Particle growth was not observed during this study, suggesting that sufficient condensable material was not available for an observable change in particle diameter. Therefore, particles of this size could potentially be transported from Prudhoe Bay to Utqiaġvik during the average 21 ± 7 h transit time. Given the lack of primary ultrafine aerosol sources between Utqiaġvik and Prudhoe Bay, it is suggested that these particles were likely transported from Prudhoe Bay."**

P11 L5: A contradiction of your observations by those of Kolesar 2017 does not help to make your argument clearer here. If particle growth from Prudhoe Bay was observed previously what differences do we expect in late summer 2015? Was the time of year significant (Kolesar 2017 shows growth peaking in June to July)? What the meteorology different? This really needs further discussion.

> **Our results do not contradict those of Kolesar et al. (2017), as particle growth was not observed to occur within all air masses from Prudhoe Bay in the summer. As shown in Fig. 3 of Kolesar et al. (2017), particle growth events were not observed in September, with particle growth occurring only part of the time during August. We expanded on this discussion on P10 L23-27.**

P11 L20: Given that the ATOFMS misses sulfur-rich particles, which should be a reasonable contributor to Arctic Ocean air masses owing to DMS oxidation, how reliable are ATOFMS estimates of the fractional particle number contribution from various particle types? Is there some was to estimate the fraction of particles that are detected by the ATOFMS but not desorbed and ionized due to being sulfate rich? Table 1 would suggest a large fraction of particles contained sulfate. What fraction of particles scattered light in the ATOFMS, but did not produce mass spectra?

> **In order to further address this "missing" particle type, we added estimates of fractional particle number contributions based on the CCSEM-EDX observations of the sulfur-rich particles. The sentence on P12 L9-13 now states "Based on CCSEM-EDX analysis (Figure 6), these sulfur particles likely comprised ~10 – 30% of the 0.13 – 1 µm particle number fraction during Arctic Ocean air mass influence, and ~10 – 20% of the 0.13 – 0.3 µm particle number fraction during Prudhoe Bay air mass influence. Accounting for these sulfur**

particles would reduce the reported ATOFMS fractions by ~5 – 15% for Arctic Ocean air mass influence, and ~5 – 10% for Prudhoe Bay air mass influence.”

P11 L23: Would these sources not have been captured during the ’local’ or Utqiagvik influenced periods?

As shown in Figure 5 and now stated on P12 L19-20, the contributions from biomass burning and dust particles were greatest in the wind direction of Utqiaġvik influence.

P12 section 3.2.1: Besides trajectories and wind-sector analysis, what chemical characteristics do the authors have for the Arctic Ocean sector being representative of a clean marine background for the local region? The presence of BC-containing particles as well as aged SSA showing nitrate peaks (suggesting NOx chemistry), while I acknowledge that sulfate peaks could arise from interaction with DMS oxidation products, suggest a pollution influence (at least to some extent) on these air masses as well. Do these air masses, either at the measurement site or at the Barrow Observatory, conform the the thresholds in BC (or absorbing aerosol) usually associated with clean marine conditions (e.g., < 50 ng/m3 of BC (Gantt 2013))?

As noted in Sec. 3.2.1 (P12 L24 – P13 L3) and shown in Fig. 6, nearly all of the supermicron particles were sea spray aerosol (SSA). As shown in Table 1, during the Arctic Ocean influence, Cl/Na ratios of the observed submicron and supermicron SSA particles were 0.81 and 0.99, respectively, indicative of fresh SSA and supporting a clean marine background; corresponding SSA S/Na ratios were also close to the expected seawater ratio (Keene et al., 1986). Previous remote marine studies have also measured some anthropogenic influences (Pósfai et al., 1999; Shank et al., 2012). Also, as discussed in Section 3.1, average particle number concentrations during the Arctic Ocean influence were comparable to other Arctic background sites, further suggesting that our measurements are representative of background Arctic conditions.

P13 L10: Do these estimates still correspond to 2004, or rather a yearly average?

These estimates still correspond to 2004. The sentence has been clarified: “For air masses influenced by Prudhoe Bay emissions, increased number fractions of soot, OC, and partially aged SSA particles were measured, with increased soot and OC particles expected based on 2004 estimates of soot (1.9 kt) and OC (2.0 kt) emissions from US Arctic (primarily Prudhoe Bay) oil and gas extraction activities (Peters et al., 2011).”

P13 L17: Is this single fragment really an unambiguous indicator of SOA formation? If SOA formation was occurring on Prudhoe bay emissions, why did the particles remain quite small, or put another way why do the authors suggest earlier in the text that particle growth did not occur?

Previous ATOFMS studies (Qin et al., 2012) established *m/z* 43 ($C_2H_3O^+$) as a marker of oxidized organic compounds. However, since particle growth was not observed, we added the following sentence on P14 L12-13: “However, as particle growth was not observed during Prudhoe Bay air mass influence (Section 3.1), it is likely that SOA contributions to particle mass were minor.”

P13 L27: It is difficult to draw conclusions from these differences, especially when the number of detected particles is so small. Do long term aerosol absorption data from the Barrow Observatory help with these conclusions at all?

We incorporated data from a co-located aethalometer and revised the sentence now on P14 L21-24 as follows: "Soot was also identified by ATOFMS during Prudhoe Bay periods by C_n^+ clusters (C^+ [*m/z* 12], C_2^+ [*m/z* 24], C_3^+ [*m/z* 36], etc). Elevated black carbon mass concentrations (up to 0.27 $\mu g/m^3$) were also measured by the aethalometer during the Prudhoe Bay air mass on August 25 (Figure S5)." Unfortunately, aerosol absorption data from the Barrow Observatory are unavailable during the Prudhoe Bay influenced periods we chemically characterized in late September.

P14 L16: Why is the main sulfate peak used to identify sulfur specifc different here compared to line 20 on the previous page?

This is due to spectral interference between HSO_4^- and $NaCl_2^-$ in SSA. We have clarified this by adding the following sentence to P12 L3-5: "Sulfate is identified as SO_3^- (*m/z* -80) in SSA due to mass spectral interferences between HSO_4^- [*m/z* -97] and $NaCl_2^-$ [*m/z* -93,95,97] (Qin et al., 2012; Sultana et al., 2017)."

P14 L20: Does a peak at NO2- indicate nitrite or just fragmentation of nitrate?

Based on previous ATOFMS studies, this is likely a fragment of nitrate (e.g. Dall'Osto et al., 2009; Liu et al., 2003). The nitrite identification has been removed.

Figure 1: Average trajectories for the study period might be more meaningful that selected trajectories. Additionally, is the area North of Utqiagvik completely ice free during the measurement, as pictured?

As suggested, we replaced the representative trajectories with average trajectories. The area north of Utqiagvik, shown in the Figure, was completely ice free during the study, as pictured.

Figure 2: Percentiles to illustrate the range of the data might be more appropriate here

We added Figure S3, which shows the 25th, 50th and 75th percentiles for the Prudhoe Bay and Arctic Ocean particle number distributions. A note was also added to the Figure 2 caption referring to this new supplemental figure.

Figure 4: Were elemental carbon peaks observed in OC particles? And similarly, was OC present on the EC particles detected? Can carbon and oxygen peaks be quantified in the CCSEM-EDX spectra?

OC markers were not observed in the EC particle mass spectra. However, minor contributions from m/z 12 (C^+) were observed in the OC particle mass spectra (now noted in the Supplemental P1 L20); however, without evidence of many carbon cluster ions, this ion peak can also be attributed as an OC fragment ion. However, the EC peaks in the OC mass spectra were minor and therefore not labeled in Figure 4 due to space constraints.

Unfortunately, there are substrate interferences with carbon and oxygen peaks in the CCSEM-EDX spectra.

Figure 5: The number of detected particles should be noted in this figure caption

This is now noted.

Supplement: Is mention of the TMA containing particles warranted in the main body of the paper? It helps to show different source influences, since these were presumably detected during Arctic Ocean influence. Or, are there too few particle spectra with TMA peaks to draw conclusions?

Unfortunately, there were too few TMA-containing mass spectra measured to draw conclusions. We added a sentence to Supplemental P1 L26 indicating this.

Specific comments:

P3 L4: natural gas

We added this.

P3 L7: Which types of pollutants are relevant here? Maybe list the major ones we expect, that are then discussed in following paragraphs?

We now list PM, VOCs, SO_2, and NO_x here.

P4 L13: “primary aerosol can. . .”

We added this.

P4 L22: What is meant by “mostly” here?

We replaced “mostly” with “primarily”.

P9 L17: perhaps: “Arctic Ocean influenced periods”

We changed this to “Arctic Ocean influenced air masses”.

P9 L19: Prudhoe Bay air masses

We’ve changed this wording to Prudhoe Bay air masses.

P15 L26: respectively

We’ve corrected this word.

P16 L5: “may contribute to further decrease”

This has been added.

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Reviewer #2

General comments: In this study, the authors present observations of particle composition and size distributions from the Barrow Environmental Observatory. The authors compare and contrast observations of aerosol from air masses that originated over the Arctic Ocean with aerosol from air masses that originated from the direction of the Prudhoe Bay oil fields. I recommend the manuscript for publication, provided that my following points, and those of the first reviewer, are addressed. In order to reduce redundancy for the authors' response, I will restrict my points to those not covered by the first reviewer.

Specific comments:

P3 Lines 14-16: Stohl et al. (2013) makes no attribution of PM or OC from Prudhoe Bay.

> **We clarified this statement to now read: "The majority of PM emitted by US Arctic oil and gas extraction sources (turbine gas combustion, diesel emissions from generators and vehicles, and flaring (Stohl et al., 2013)) in 2004 corresponded to BC (1.9 kt) and OC (2.0 kt) (Peters et al., 2011)".**

P9 Lines 18-25: I think perhaps that the authors intend to exclude regional-scale nucleation events here, but not nucleation within emissions plumes from the Prudhoe Bay oil fields. The authors even suggest that the emissions from such drilling operations can contribute to new-particle formation on page 3, lines 19-21. Observations of particle growth would be expected for a regional-scale nucleation event, but not for continuous nucleation within an emitted plume of condensable gases, such as those observed by Brock et al. (2002) and Brock et al. (2003). If there was continuous new-particle formation occurring within a plume from the Prudhoe Bay oil field, under steady-state conditions (including constant wind speed and direction), no change in the size of observed aerosol would be observed unless the distance from the source changed. The age of the aerosol between nucleation in the plume and detection at the observation site would be constant with time, and therefore so would the size of the aerosol.

> **We clarified this on P10 L9-10: "However, regional new particle formation would typically be followed by particle growth (Kulmala et al., 2004), which was not observed (Figure S2)."**

Technical Corrections:
P11 Line 16: "(Sierau et al. (2014)" should be "(Sierau et al., 2014)"

> **We corrected this.**

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Contributions of Transported Prudhoe Bay ~~Oilfield~~Oil Field Emissions to the Aerosol Population in Utqiaġvik, Alaska

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Abstract. Loss of sea ice is opening the Arctic to increasing development involving oil and gas extraction and shipping. Given the significant impacts of absorbing aerosol and secondary aerosol precursors emitted within the rapidly warming Arctic region, there is a need to characterize local anthropogenic aerosol sources and compare to natural conditions. From August-September 2015 in Utqiaġvik, AK, the chemical composition of individual atmospheric particles was measured by computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy (0.13 - 4 µm projected area diameter) and real-time single particle mass spectrometry (0.2 – 1.5 µm aerodynamic diameter). During Arctic Ocean influenced periods (70% of the study), our results show that fresh sea spray aerosol contributed ~20%, by number, of particles between 0.13 – 0.4 µm, 40 – 70% between 0.4 – 1 µm, and 80 – 100% of 1 – 4 µm particles. In contrast, for periods influenced by emissions from Prudhoe Bay (10% of the study), the third largest ~~oilfield~~oil field in North America, there was a strong influence from submicron (0.13 – 1 µm) combustion derived particles (20 - 50% OC, by number, 5 – 10% soot by number). While sea spray aerosol still comprised a large fraction of particles (90% by number from 1 – 4 µm) detected under Prudhoe Bay influence, these particles were internally mixed with sulfate and nitrate indicative of aging processes during transport. In addition, the overall mode of the particle size number distribution shifted

from 76 nm during Arctic Ocean influence to 27 nm during Prudhoe Bay influence with particle concentrations increasing from 130 cm^{-3} to 920 cm^{-3} due to transported particle emissions from the oil fields. The increased contributions of carbonaceous combustion products and partially aged ~~SSA~~sea spray aerosol should be ~~taken into consideration for~~considered in future Arctic atmospheric composition and climate simulations.

1 Introduction

The Arctic is experiencing dramatic climate change with sea ice extent declining rapidly and complete summertime sea ice loss expected by 2050 (Wang and Overland, 2015; Overland and Wang, 2013). With 30% of the world's undiscovered natural gas and 13% of undiscovered oil thought to be located in the Arctic (Gautier et al., 2009), increasing open water makes previously inaccessible areas of the Arctic available for oil and gas development and shipping (Harsem et al., 2015; Allison and Bassett, 2015). These ~~developing~~ oil and gas extraction activities ~~will~~ add pollutants, including particulate matter (PM), volatile organic compounds (VOCs), SO_2, and NO_x, to the Arctic atmosphere (Peters et al., 2011), thereby influencing ~~Arctic~~ climate. The Arctic aerosol population is characterized by a maximum mass loading in the winter, due to transported pollutants from the mid-latitudes, and a minimum in the summer, when local sources, including sea spray aerosol, dominate (Quinn et al., 2002; Quinn et al., 2007). However, there is limited knowledge of aerosols produced within the Arctic, particularly in the context of changing emissions from both natural and anthropogenic sources (Arnold et al., 2016).

Modeling by Peters et al. (2011) estimates that Arctic ~~oil and gas extraction~~ during 2004 contributed 47 kilotons (kt) of ~~particulate matter (~~PM~~)~~ emissions, with ~~in the Arctic during 2004;~~ 15 kt correspond to black carbon (BC) and~~, with~~ 16 kt attributed to organic carbon (OC). The majority of e~~E~~missions ~~primarily~~ originated in western Russia (~41 kt in 2004 ~~a year~~); activities within the Alaskan Arctic, primarily the Prudhoe Bay oil fields, contributed ~~however, the United States (US) contributes an additional~~ 6 kt during 2004 ~~primarily from Prudhoe Bay~~ (Peters et al., 2011).~~,~~ Prudhoe Bay is the third largest oil field ~~in the US~~ and tenth largest gas field in the US by estimated production as of 2013 (EIA, 2015). The majority of ~~the~~ PM emitted by US Arctic oil and gas extraction sources (turbine gas combustion, diesel emissions from generators and vehicles, and flaring (Stohl et al., 2013)) in 2004 corresponded to ~~contributed to the Arctic in 2004 from Prudhoe Bay was~~ BC (1.9 kt) and OC (2.0 kt) (Peters et al., 2011).~~, attributed to gas combustion within turbines, diesel emissions from generators and vehicles, and flaring (Stohl et al., 2013).~~ With new drilling operations opening due to reduced sea ice coverage, Peters et al. (2011) estimate US contributions increasing up to 10 kt of primary PM (including 3.3 kt BC and 3.5 kt OC) by 2030 and 17 kt of PM (including 5.3 kt BC and 5.7 kt OC) by 2050. In addition to directly emitted PM, drilling operations can emit aerosol precursors ~~such as (~~NO_x, SO_2, and

VOCs), and alter oxidant levels, which can lead to the formation of secondary aerosol, as well as contribute to new particle formation (Peters et al., 2011; Volkamer et al., 2006; Roiger et al., 2015; Kolesar et al., 2017; Jaffe et al., 1995).~~, leading (Peters et al., 2011; Volkamer et al., 2006; Roiger et al., 2015; Kolesar et al., 2017).~~

BC is estimated to have a ~~has a strong~~ warming effect on the Arctic atmosphere (e.g. Flanner, 2013; Sand et al., 2013a; Sharma et al., 2013; Bond et al., 2013; Flanner et al., 2007). ~~due to amplification from cloud and sea ice feedbacks (Flanner, 2013), with BC shown to contribute to melting of sea ice by decreasing snow and sea ice albedo (Ramanathan and Carmichael, 2008).~~ Modeling predicts local Arctic BC emissions to cause as much as a factor of five greater increase in Arctic warming compared to BC transported from the lower latitudes (Sand et al., 2013). Koch et al. (2009) ~~In a recent review, Bond et al. (2013)~~ suggest that Arctic BC concentrations are under predicted by a variety of models ~~(Koch et al., 2009)~~ by an average factor of 2.5, which may be improved by more accurately incorporating local BC sources (Flanner, 2013). However, few studies have measured PM emitted from oil and gas extraction in the Arctic. Measurements of BC from 1977 – 1997 in Utqiaġvik showed contributions from Russian oil fields year round (Polissar et al., 1999; Polissar et al., 2001), similar to the recent results of Barrett et al. (2015) at Utqiaġvik during December 2012 – March 2013 when transported particles from Russian oil fields were observed. Barrett et al. (2015) also measured regional Arctic BC from both fossil fuel combustion and biomass burning. The Arctic Climate Change, Economy, and Society (ACCESS) aircraft field campaign recently investigated emissions from oil and gas extraction in the Norwegian Arctic and measured increased BC, among other pollutants, compared to the Arctic background while sampling within plumes from oil and gas extraction facilities (Roiger et al., 2015). Also, Brock et al. (2011) conducted aircraft measurements of Prudhoe Bay emissions and detected increased PM, including OC and BC~~; however, the study was more focused on biomass burning emissions~~. Stohl et al. (2013) modeled BC contributions from flaring due to Arctic oil and gas extraction and determined that it contributed 42% of the annual surface soot concentrations in the Arctic. With only these limited measurements available, further characterization of combustion emissions from oil and gas extraction activities are needed to further improve simulations.

During transport, primary aerosol can undergo chemical aging and accumulate secondary species, such as sulfate, nitrate, ammonium, oxidized organic carbon, and water, impacting both chemical composition and particle properties, such as light absorption and scattering, hygroscopicity, toxicity, and chemical reactivity (Moffet and Prather, 2009; Pöschl, 2005). Combustion particles in particular are co-emitted with ~~volatile organic compounds (~~VOCs~~)~~ and can rapidly undergo aging and accumulate these secondary organic species (Petzold et al., 2005). The distribution of these secondary species across the aerosol population determines ~~the~~aerosol climate impacts (Prather et al., 2008)~~. For example, modeling and field studies (e.g., Chung and Seinfeld, 2005; Jacobson, 2001; Moffet and Prather, 2009; Cappa et al., 2012) indicate that the~~. It is currently not clear whether light absorption by a ~~pure~~ BC particle is enhanced by ~~a~~ sulfate or organic ~~coating.~~coatings (e.g., Chung and Seinfeld, 2005; Jacobson, 2001; Moffet and Prather, 2009; Knox et al., 2009; Liu et al., 2015; Cappa et al., 2012; Healy et al., 2015). In contrast, pure sulfate particles (i.e., without BC (soot) inclusions) ~~mostly~~primarily scatter light (Haywood and Boucher, 2000). In addition, soot particles internally mixed with nitrate and sulfate have been shown to have increased CCN-activity (Bond et al., 2013). ~~Particles can either be internally mixed~~Ambient aerosol populations typically vary between internal mixtures, with multiple chemical species contained within a single particle, ~~or externally mixed~~and external mixtures, with multiple chemical species present as separate particles (Prather et al., 2008). Therefore, it is important to determine the influence of Prudhoe Bay emissions on downwind aerosol chemical composition and mixing state of the individual particles in order to better understand and predict the effects of oil and gas extraction activities on the Arctic aerosol population and climate.

To investigate particle chemical composition and sources in the coastal Alaskan Arctic, sampling was conducted at Utqiaġvik, Alaska, a location influenced by Prudhoe Bay (Jaffe et al., 1995) and the Arctic Ocean (Quinn et al., 2002) in August – September 2015. On-line aerosol time-of-flight mass spectrometry (ATOFMS) and off-line computer controlled scanning electron microscopy with energy dispersive X-ray spectroscopy (CCSEM-EDX) analyses provided size-resolved individual particle chemical composition. The impacts of transported Prudhoe Bay oil field emissions on aerosol size distributions, primary combustion particle contributions, and secondary aerosol formation are compared to the background Arctic aerosol ~~composition~~combustion.

2 Methods

Atmospheric aerosol sampling was conducted over a period of August 21 – September 30, 2015 at a field site (71°16’30"N, 156°38'26"W), on the Barrow Environmental Observatory, located 4 km southeast of the town of Utqiaġvik, AK. Aerosol sampling occurred 4.5 m above ground level through 1.4 cm ID copper tubing at a flow rate of 17 Lpm through a ~~PM$_{2.5}$~~PM$_{10}$ (PM less than 10 µm) teflon-coated aluminum cyclone (URG ~~Corporation~~ 2000-30ENB, URG Corp., Chapel Hill, NC). A stainless steel cylindrical manifold (ID 8.9 cm) split the flow to dedicated insulated sampling lines for each instrument. Meteorological data, including wind speed, wind direction, relative humidity, and temperature, were obtained from the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) long-term monitoring station (NOAA Barrow Observatory, 71° 19’ 40” N, 156° 38’ 20” W), located 5.5 km across flat tundra to the northeast of the aerosol sampling site. On-line measurements of aerosol absorption at seven wavelengths, including 880 nm, were completed using an aethalometer to obtain BC mass concentrations. BC concentrations were calculated, at 5-10 minute time resolution, using a portable aethalometer (Model AE42, Magee Scientific, Berkeley, CA). The aethalometer was outfitted with a seven wavelength source and PM$_{2.5}$ inlet. The sample is collected on a quartz fiber filter tape and the optical analysis (wavelengths ranging from 370 to 950 nm) is performed continuously.

2.1 Air Mass Classification

Backward air mass trajectories were calculated using the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Stein et al., 2015). A final height of 50 m AGL was used for arrival at the field site, and a new trajectory was calculated every 8 h and modeled the preceding 48 h. Trajectories originated from three major directions: north/northeast, southeast, and to the west (Figure 1). Based on these trajectories, air masses were classified into three areas of influence. Air masses that originated in the Beaufort Sea to the north/northeast of the site were classified as Arctic Ocean influenced periods. Air masses from the southeast that crossed over the Prudhoe Bay oil fields, were classified as Prudhoe Bay influenced air masses, based on a previous study of air mass transport from Prudhoe Bay to

Utqiaġvik (Kolesar et al., 2017). Air masses that originated from the west were primarily influenced by the town of Utqiaġvik and classified as local influence.

2.2 Particle Number Distributions

A scanning mobility particle sizer (SMPS, model 3082, TSI Inc~~.)~~., Shoreview, MN) was located at the field site from August 21 – September 20, 2015 for online measurements of size-resolved particle number concentrations from 13 - 746 nm (mobility diameter). Additionally, long-term measurements of particle number size distributions from the NOAA Barrow Observatory were collected with a TROPOS-type mobility particle size spectrometer (Wiedensohler et al., 2012) to determine daily average particle number concentrations and size distributions in August and September for the available years of 2008, 2009, 2013, and 2014. Time periods when the wind direction was between 170 and 330° were excluded from daily averages because of the influence from the town of Utqiaġvik. In addition, short (< 1 h) bursts of ultrafine particles during clean time periods were excluded due to the likely short-term influence from local vehicle emissions. For the long-term data, the daily averages were classified according to air mass source region using 48 h backward air mass trajectories and then averaged over a month-long period.

2.3 Computer-Controlled Scanning Electron Microscopy with Energy Dispersive X-Ray Spectroscopy

From August 21-September 30, 2015, 0.07 – 5.0 µm particles were collected during 8 h sampling periods (00:00 – 08:00, 08:00 – 16:00, 16:00 – 00:00 AKDT) on aluminum foil substrates (MSP Corp~~.)~~., Shoreview, MN) and transmission electron microscopy (TEM) grids (carbon Type-B Formvar film copper grids, Ted Pella Inc~~.)~~., Redding, CA) using a three-stage impactor (MPS-3, California Measurements, Sierra Madre, CA) with aerodynamic diameter size cuts of 0.07 – 0.4 µm, 0.4 –2.8 µm, and 2.8 – 5 µm, respectively. Individual particles were analyzed using computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy (CCSEM-EDX). A FEI Quanta environmental SEM with a field emission gun (FEG) operating at 20 keV with a high-angle annular dark field (HAADF) detector collected SEM images and morphological data (including diameter, perimeter, and projected area) of individual particles 0.13 – 4.0 µm projected area diameter (Laskin et al., 2006;

Laskin et al., 2012). The instrument is equipped with an EDX spectrometer (EDAX~~,~~ Inc~~.)~~., Mahwah, NJ) to measure X-ray spectra of elements with atomic numbers higher than Be, providing the relative atomic abundance of elements C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Fe, and Zn. Additional CCSEM-EDX analysis was conducted using the same method with an FEI Helios 650 Nanolab SEM/FIB (focused ion beam) with an FEG operating at 20 keV using HAADF and through-the-lens detectors with an EDX spectrometer.

K-means cluster analysis was conducted over EDX spectra from 13,972 individual particles analyzed by the Quanta instrument and 5,121 particles analyzed by the Helios instrument, resulting in 50 clusters from each data set. These clusters were then regrouped into seven main particle classes based on elemental composition, described in Section 3.2 and the supplemental information. For periods corresponding to Arctic Ocean air mass influence, SEM images and EDX spectra were obtained for 2,869 particles from four samples which coincided with ATOFMS sampling: September 8, 2015 (00:00 – 08:00 and 08:00 – 16:00 AKDT), September 9, 2015 00:00 – 08:00, and September 15, 2015 00:00 – 08:00. For periods of Prudhoe Bay air mass influence, 1,997 particles from two samples which coincide with ATOFMS sampling (September 23, 2015 00:00 – 08:00 and 08:00 – 16:00) were analyzed. Error resulting from number fraction for different particle types were calculated using binomial statistics, and the minimum number of particles for a representative sample are between ~300 - 1,000 (Willis et al., 2002).

2.4 Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)

An aerosol time-of-flight mass spectrometer (ATOFMS) measured the size and chemical composition of individual aerosol particles (0.2-1.5 µm) in real-time from September 8 – 30, 2015. The ATOFMS used in the current study is based on the design of Pratt et al. (2009) with modifications as described below. Briefly, particles are focused using an aerodynamic lens system, and particle velocity is measured by the transit time between two continuous wave lasers, 405 nm and 488 nm (OBIX LX, Coherent, Inc~~.),~~., Santa Clara, CA), spaced 6 cm apart. Vacuum aerodynamic particle diameter (d_{va}) is calculated based on particle velocity from polystyrene latex sphere standards of known diameter (90 nm – 1.5 µm) and density (1 g cm^{-3}). Particles enter a dual-polarity reflectron time-of-flight mass spectrometer (Tofwerk AG, Thun, Switzerland) and are desorbed and ionized by a Q-switched 100 Hz 266nm Nd:YAG laser (Centurion, Quantel~~, Inc~~ USA, Bozeman, MT) operated at 0.8 – 1.0 mJ, resulting in positive and negative ion mass spectra of laser-ablated individual particles. Mass spectral peak lists were created in custom software developed in LabVIEW and MATLAB. Prior to ATOFMS sampling, particles were dried in-line using two silica gel diffusion driers. Despite this, negative ion mass spectra were present for only 53% of the detected particles due to the accumulation of particulate water which suppresses negative ion formation (Neubauer et al., 1997), as commonly observed for marine environments (Spencer et al., 2008).

The ATOFMS collected dual-polarity mass spectra of 496 individual particles with aerodynamic diameters of 0.2 – 1.5 μm from September 8-30, 2016. In addition to low ambient particle concentrations impacting the data collection rate, an instrumental issue with the time-of-flight mass analyzer, which has since been fixed, led to ~~the~~a significantly reduced particle hit rate (fraction of mass spectra collected per number of particles sized within the instrument~~);~~) of less than 1%; however, laboratory tests showed that the quality of the mass spectra collected were not affected. Individual mass spectra were analyzed using YAADA, a custom software toolkit for MATLAB (Allen, 2004). Mass spectra were clustered based on the presence and intensity of ion peaks within individual mass spectra using an ART-2a algorithm, with a vigilance factor of 0.8 and a learning rate of 0.05 for 20 iterations (Song et al., 1999). Mass spectral peaks were identified based on the most probable *m/z* considering previous laboratory and field studies (Toner et al., 2008; Pratt et al., 2011; Ault et al., 2013; Qin et al., 2012; Rehbein et al., 2011). The resulting clusters were manually combined into five groups, each representing an individual particle type (Section 3.2 and supplemental information). Due to the small sample number of particles, 100% of the measured particles were clustered either by ART-2a or manually. Despite the low number of collected mass spectra, the observed particle types are consistent with previous Arctic surface-based ATOFMS measurements by Sierau et al. (2014), who also obtained a similar number of mass spectra in part due to low particle number concentrations in the summertime Arctic boundary layer. The errors associated with number fractions for different particle types were calculated using binomial statistics.

3 Results and Discussion

3.1 Air Masses from the Arctic Ocean and Prudhoe Bay Oil Fields

The prevailing wind direction at Utqiaġvik is from the northeast across the Beaufort Sea (Searby and Hunter, 1971). Based on backward air mass trajectories (Figure 1) and wind direction (Figure S1), 70% of the days between August 21 – September 30, 2015 were influenced by the Arctic Ocean (~6 km northeast), with 10% of days influenced by the Prudhoe Bay oil fields (~300 km southeast) and 20% influenced by the town of Utqiaġvik (~5 km northwest)**.** Prudhoe Bay air masses traveled along the coast and were therefore influenced by both tundra and the Beaufort Sea, in addition to the emissions from the Prudhoe Bay oil fields. Here we discuss the influences from the two main source regions of interest, the Arctic Ocean and Prudhoe Bay, on atmospheric particle number and chemical composition.

From August 21 to September 20, 2015, the average number concentration of 13 – 746 nm particles during Arctic Ocean influenced air masses (130 ± 1 particles cm^{-3} with standard error of the mean) was nearly five times less than the average number concentration of Prudhoe Bay influenced air masses (920 ± 4 particles cm^{-3} with standard error of the mean) (Figure 2). ~~The individual~~Aerosol number distributions for time periods classified as Arctic Ocean and Prudhoe Bay are shown in Figure S2; corresponding median and 25th and 75th percentile aerosol number distributions for both time periods are shown in Figure S3. Notably, the average particle mode diameter of 27 ± 4 nm during Prudhoe Bay influence was smaller than the average particle mode diameter of 76 ± 40 nm during Arctic Ocean influenced air masses, illustrating that the majority of the additional particles in the Prudhoe Bay air mass were less than 30 nm in diameter (Figure 2). ~~While these ultrafine particles in the Prudhoe Bay air mass were outside of the size range of our chemical characterization methods, particles~~ Particles smaller than ~50 nm are often associated with ~~oil field~~combustion emissions, either from primary particles or nucleated particles within the emission plume, but can also be indicative of regional new particle formation. However, regional new particle formation ~~is often~~would typically be followed by particle growth (Kulmala et al., 2004), which was not observed (Figure S2). ~~Also~~Rather, this ultrafine particle mode was sustained over multiple hours (Figure S2), which also eliminates the possibility that these ~~are~~were from local ~~bursts of particles such as local~~ vehicle emissions~~. Therefore, the increase in the number concentration of ultrafine particles is likely due to transported oil field emissions from Prudhoe Bay~~.

The condensation sink, a measure of how fast molecules will condense onto existing particles (Lehtinen et al., 2003), was calculated during the 2015 study Prudhoe Bay air mass periods using the method of Dal Maso et al. (2002). The average condensation sink was 6 x 10^{-4} s^{-1}, over an order of magnitude lower than typically observed at mid-latitude and boreal forest sites (e.g. Jung et al., 2013; Dal Maso et al., 2002; Kulmala et al., 2001). Based on the simulations by Fierce et al. (2015), particle growth during transport for particles ~30-50 nm would take ~1-7 days, if coagulation-dominated due to limited condensable material. Particle growth was not observed during this study, suggesting that sufficient condensable material was not available for an observable change in particle diameter. Therefore, particles of this size could potentially be transported from Prudhoe Bay to Utqiaġvik during the average 21 ± 7 h transit time. Given the lack of primary ultrafine aerosol sources between Utqiaġvik and Prudhoe Bay, it is suggested that these particles were likely transported from Prudhoe Bay. Kolesar et al. (2017) previously observed Prudhoe Bay air masses to preferentially exhibit particle growth, compared to Arctic Ocean air masses. However, particle growth was not observed to occur within all Prudhoe Bay air masses during the summer, and particle growth events were not observed in September in Utqiaġvik (Kolesar et al., 2017).

Multi-year measurements of particle number size distributions were also compared for Arctic Ocean and Prudhoe Bay influenced air masses for the months of August and September (Figure 3). Prudhoe Bay air masses had a significantly (95% confidence interval) higher median concentration (407 particles cm^{-3}) compared to Arctic Ocean air masses (294 particles cm^{-3}), similar to the trends observed during the 2015 study. The median particle concentration ~~from~~within Arctic Ocean air masses is similar to the median particle number ~~concentration~~concentrations during August at Station Nord, Greenland (227 particles cm^{-3}, Nguyen et al., 2016)~~, during September in~~ and Alert, Canada (~160 particles cm^{-3}; Croft et al., 2016), during September at Tiksi, Russia (222 particles cm^{-3}; Asmi et al., 2016), and within the range of observations onboard the Swedish icebreaker *Oden* ~~between~~from July – September during ~~multi-year (1991, 1996, 2001 and 2008)~~multiple central Arctic Ocean studies when the air masses were exposed to the open ocean (90-210 particles cm^{-3}; Heintzenberg et al., 2015). However, the median particle number concentration during August in Tiksi, Russia (383 particles cm^{-3}) is similar to the median concentration of Prudhoe Bay influenced air masses (407 particles cm^{-3}) even though the elevated number concentrations in Tiksi are due to biogenic influence leading to new particle formation and growth (Asmi et al., 2016).

For the multi-year measurements, the median Arctic Ocean influenced particle size distribution has three modes (10 nm, 35 nm, 118 nm), similar to observations during August at Alert, Canada (Croft et al., 2016), Station Nord, Greenland (Nguyen et al., 2016), and Ny-Ålesund, Svalbard (Tunved et al., 2013). The Prudhoe Bay air mass median size distribution also has a clear accumulation mode ~150 nm that is typical of summertime background Arctic aerosol seen in the previously mentioned studies. A two-sample Kolmogorov-Smirnov test on Prudhoe Bay and Arctic Ocean influenced distributions from both the multi-year and 2015 study concluded that the two distributions are not significantly different (p = 0.05) above 100 nm~~. This suggests that the Prudhoe Bay emissions do not significantly alter the size and number of greater than 100 nm particles, compared to the Arctic background particle distribution.~~, despite chemical differences described below.

~~The condensation sink, a measure of how fast molecules will condense onto existing particles (Lehtinen et al., 2003), was calculated during the 2015 study Prudhoe Bay air mass periods using the method of Dal Maso et al. (2002). The average condensation sink was 6 x 10^{-4} s^{-1}, over an order of magnitude lower than typically observed at mid-latitude and boreal forest sites (e.g. Jung et al., 2013; Dal Maso et al., 2002; Kulmala et al., 2001). Based on the simulations by Fierce et al. (2015), accumulation of secondary species during transport for particles ~30-50 nm would take ~1-7 days if it was coagulation-dominated, which is likely due to the low amount of condensable species in the clean Arctic environment (Ziemba et al., 2010). Therefore, particles of this size could be transported from Prudhoe Bay (average 21 ± 7 hour transit time to Utqiaġvik based on HYSPLIT backward air mass trajectories) without growing to larger diameters. Notably, Kolesar et al. (2017) previously observed Prudhoe Bay air masses preferentially exhibit particle growth, compared to Arctic Ocean air masses; therefore, it is clear the required precursors were not available for particle growth during the 2015 study.~~

3.2 Single Particle Chemical Characterization

Analysis of the individual particle (0.1 – 4.0 µm) ATOFMS and CCSEM-EDX spectra resulted in the identification of five major single-particle types: sea spray aerosol (SSA), soot, organic carbon (OC), biomass burning, and mineral dust (Figure 4). Detailed descriptions of particle-type mass spectra and classifications can be found in the supplemental information. SSA internally mixed with nitrate (NO_2^- [*m/z* -46] or NO_3^- [*m/z* -62] using ~~with~~ ATOFMS, N with EDX) and/or sulfate (SO_3^- [*m/z* -80] with ATOFMS, S with EDX) were sub-classified as partially aged SSA (Qin et al., 2012; Gard et al., 1998) and are discussed further in Sections 3.2.1 and 3.2.2. Sulfate is identified as SO_3^- [*m/z* -80] in SSA due to mass spectral interference between HSO_4^- [*m/z* -97] and $NaCl_2^-$ [*m/z* -93,95,97] (Qin et al., 2012; Sultana et al., 2017). CCSEM-EDX identified a unique sulfur-rich particle type not observed by ATOFMS; this is consistent with previous ATOFMS studies, including an Arctic summer ship-based study ~~(Sierau et al. (2014),~~(Sierau et al., 2014), that attributed a "missing" ATOFMS particle type to relatively pure ammonium sulfate particles that scatter visible radiation~~ (ATOFMS sized particles),~~, but are not ionized by 266 nm radiation (Wenzel et al., 2003; Spencer et al., 2008). Based on CCSEM-EDX analysis (Figure 6), these sulfur particles likely comprised ~10 – 30% of the 0.13 – 1 µm particle number fraction during Arctic Ocean air mass influence, and ~10 – 20% of the 0.13 – 0.3 µm particle number fraction during Prudhoe Bay air mass influence. Accounting for these sulfur particles would reduce the reported ATOFMS fractions by ~5 – 15% for Arctic Ocean air mass influence, and ~5 – 10% for Prudhoe Bay air mass influence. Minor contributions were observed from biomass burning and mineral dust particles for Arctic Ocean (14 ± 4% and 14 ± 3%, respectively, by number) and Prudhoe Bay (10 ± 11% and 4 ± 7%, respectively, by number) influenced air masses (Figure 5). Wildfire smoke from on-going central Alaskan wildfires did not influence the site during the study~~,~~, based on air mass origin; therefore, biomass burning particles were likely from local residential heating or beach bonfires commonly seen around Utqiaġvik. The dirt roads ~~around~~and beaches near the ~~town of Utqiaġvik~~field site are the likely source of the observed mineral dust. Both dust and biomass burning contributions were greatest when the wind was coming from Utqiaġvik.

3.2.1 Chemical Characterization of Aerosols during Arctic Ocean Air Mass Influence

Based on HYSPLIT backward air mass trajectories, periods of Arctic Ocean air mass influence occurred between September 8 – 12, 14 – 22 and 26 – 30. Fresh SSA contributed 80 – 100%, by number, to the measured 1 – 4 µm, as measured by CCSEM-EDX (Figure 6), consistent with previous Utqiaġvik measurements which demonstrated that SSA comprises approximately 70% of the summertime Arctic supermicron (1-10 µm) particle mass (Quinn et al., 2002). Approximately 20% of 0.13 – 0.4 µm and 40 – 70% of 0.4 – 1 µm particles, by number, were identified as fresh SSA, as determined by CCSEM-EDX, and in agreement with the measured ATOFMS number fraction of 63 ± 5% for 0.2 – 1.5 µm particles (Figure 5). Prominent chloride peaks, including Cl^- ~~(~~[*m/z* -35/37~~),~~], $NaCl_2^-$ ~~(~~[*m/z* -93/95~~)~~] and Na_2Cl^+ ~~(~~[*m/z* 81/83~~)~~] (Ault et al., 2014; Gard et al., 1998), were present in the ATOFMS SSA mass spectra. The majority of the identified supermicron SSA (>99%, by number) also showed little evidence of atmospheric processing through addition of nitrogen or sulfur, identified as nitrate and sulfate by ATOFMS (Figure 4), in part due to local SSA production. Minimal chloride depletion was observed for supermicron SSA particles during Arctic Ocean influence, with an average Cl/Na mole ratio of 0.99 for 1 – 4 µm (15% depletion) (Table 1 and Figure ~~S3~~S4), compared to the seawater Cl/Na ratio of 1.16 (Keene et al., 1986). Supermicron SSA particles also had low S/Na and N/Na mole ratios (0.15 and >0.1, respectively), indicating low contributions from sulfate and nitrate on the particles. In fact, the S/Na mole ratio of 0.15 for supermicron SSA is near the ratio expected of seawater (0.121) (Keene et al., 1986), indicating that very little atmospheric processing occurred, consistent with local SSA production. Comparatively, submicron (0.13 – 1 µm) SSA had a lower Cl/Na mole ratio (0.81, 30% depletion), as well as higher S/Na and N/Na mole ratios (0.36 and 0.27, respectively), indicating increased atmospheric processing (Williams et al., 2002; Gong et al., 2002; Laskin et al., 2002; Hopkins et al., 2008). As residence times for submicron particles are longer compared to supermicron particles, submicron SSA can be transported further, providing longer periods of atmospheric processing and leading to the observed increases in sulfate and nitrate, coincident with chloride depletion.

OC particles contributed 27%, by number, to 0.13 – 1 µm particles with minimal size dependence (Figure 6). OC contributed ~10%, by number, from 1 – 2 µm particles, with no OC particles measured between 2 and 4 µm. For the submicron OC particles, 94%, by number, were internally mixed with sulfur with an average atomic composition of 11% during Arctic Ocean influence (Table 1). Sulfur was identified as sulfate using ATOFMS spectral markers (Figure 4). The Arctic Ocean has previously been shown to be a significant source of biogenic sulfur in the form of dimethyl sulfide (DMS) (Ferek et al., 1995). DMS oxidizes in the atmosphere to form methanesulfonic acid (MSA), previously observed in Arctic aerosols (e.g. Sharma et al., 2012; Geng et al., 2010; Tjernström et al., 2014; Quinn et al., 2009; Quinn et al., 2007).

3.2.2 Chemical Characterization of Transported Prudhoe Bay Aerosols

For air masses influenced by Prudhoe Bay emissions, increased number fractions of soot, OC, and partially aged SSA particles were measured, with increased soot and OC expected ~~as an estimated 2.0 kilotons of OC and 1.9 kilotons~~based on previous estimates of soot ~~are emitted annually~~(1.9 kt) and OC (2.0 kt) emissions from 2004 US Arctic oil and gas extraction activities, primarily at Prudhoe Bay ~~(Peters et al., 2011)~~(Peters et al., 2011). ATOFMS analyses identified 32 ± 18%, by number, of 0.2 – 1.5 µm particles as OC (Figure 5). CCSEM-EDX identified OC particles to comprise 60%, by number, of 0.13 – 0.3 µm particles, with contributions decreasing to 10%, by number, for 0.8 – 1 µm particles and 5%, by number, for supermicron (1 – 2 µm) particles (Figure 6). ATOFMS identified hydrocarbon markers within the OC particles (e.g. C_2H_3~~$^+$[~~$^+$ [*m/z* 27], $C_3H_2^+$ [*m/z 37*], C_4H_2~~$^+$[~~$^+$ [*m/z* 50]), similar to those detected in previous studies of vehicle combustion (Toner et al., 2008). The presence of oxidized OC was also identified (~~$C_2H_3O^+$, ~~$C_2H_3O^+$[*m/z 43*~~)~~]) in these OC particles, suggesting secondary organic aerosol formation (Qin et al., 2012). ~~Ammonium signal (*m/z* 18, NH_4^+)~~. However, as particle growth was not observed during Prudhoe Bay air mass influence (Section 3.1), it is likely that SOA contributions to particle mass were minor. Ammonium signal (NH_4^+ [*m/z* 18]) was also detected in the OC particles. Sulfur and nitrogen were identified in 60% and 28%, by number, respectively, of OC particles between 0.13 – 1 µm, confirmed as sulfate (HSO_4~~$^-$[~~$^-$ [*m/z* -97]) and nitrate (NO_3~~$^-$[~~$^-$ [*m/z* -62]), respectively, by ATOFMS (Figure 4) (Pratt and Prather, 2009). Internally mixed sulfate and nitrate have been shown to increase the hygroscopicity of organic particles and therefore enhance their CCN activity (Petters and Kreidenweis, 2007; Wang et al., 2010).

Similar number fractions of fine mode soot particles were observed by CCSEM-EDX during both Prudhoe Bay and Arctic Ocean periods (5 – 10% and 5 – 20%, by number, across 0.13 – 1 µm, respectively) (Figure 6). ~~Though not statistically significant, ATOFMS~~ Soot was also identified ~~increased soot~~ by ~~number~~ATOFMS during Prudhoe Bay periods ~~(18 ± 14%) compared to Arctic Ocean periods (5~~

~~± 2%). Identified~~ by C_n^+ clusters (C^+ [*m/z* 12~~ [C^+],~~], C_2^+ [*m/z* 24~~ [C_2^+],~~], C_3^+ [*m/z* 36~~ [C_3^+],~~], etc~~) in ATOFMS spectra, soot~~). Elevated black carbon mass concentrations (up to 0.27 μg/m^3) were also measured by the aethalometer during the Prudhoe Bay air mass observed on August 25 (Figure S5). Soot particles are primarily emitted through diesel combustion from heavy duty vehicles (Spencer et al., 2006) and ships (Ault et al., 2009). ~~The~~However, the majority of soot ~~particles are~~is expected to be less than 100 nm in diameter and therefore not chemically characterized in this study. During the 2012 ACCESS campaign off the coast of Norway, Roiger et al. (2015) observed increased soot mass concentrations <~~80nm~~80 nm in diameter while sampling near oil and gas extraction facilities, consistent with the observed elevated ultrafine ~~particles~~particle number concentrations in the present study when under Prudhoe Bay air mass influence (Figure 2 and 3).

Since the air mass trajectory from Prudhoe Bay to Utqiaġvik crosses the Beaufort Sea, SSA particles were still a major contributor, making up over 90% of supermicron (1 – 4 μm) particles by number. However, unlike the Arctic Ocean air mass influence, ~60%, by number, of the supermicron SSA was classified as partially aged SSA. This is over three times the fraction compared to Arctic Ocean air masses (16%) due to atmospheric processing during 21 ± 7 hour transit over land before reaching Utqiaġvik. SSA shows 43% chloride depletion in the SSA EDX spectra (Cl/Na mole ratio of 0.66 compared to 1.16 in seawater (Keene et al., 1986)) (Table 1); ATOFMS chloride peak intensities ($NaCl_2^-$ [*m/z* -93/95], Cl^- [*m/z* -35/37]) are lower than during the Arctic Ocean influence for the SSA particles. Sulfur, identified as sulfate (SO_3^- [*m/z* -80]) in ATOFMS spectra (Pratt and Prather, 2009), was internally mixed with 86%, by number, of SSA (Table 1). For these particles, the S/Na mole ratio of the submicron (0.13 – 1 μm) SSA during Prudhoe Bay influence (0.53) is higher than expected from seawater (0.121), indicating contributions of secondary sulfate (Keene et al., 1986). Nitrogen, identified as ~~nitrite and~~ nitrate (NO_2^-[*m/z* -46] and NO_3^-[*m/z* -62] by ATOFMS (Liu et al., 2003)~~, respectively) by ATOFMS,~~ was observed in 40%, by number, of the SSA particles by CCSEM-EDX. Similar to S/Na mole ratios, submicron (0.13 – 1 μm) SSA N/Na ratios were substantially higher during Prudhoe Bay influence (0.54) compared to Arctic Ocean influenced SSA (0.27). In addition to longer atmospheric residence time for submicron particles leading to increased submicron atmospheric processing (Williams et al., 2002; Gong et al., 2002), models have found that secondary species such as sulfate and nitrate preferentially

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accumulate on submicron particles (Bassett and Seinfeld, 1984). These SSA particles were likely transported from the Arctic Ocean surrounding Prudhoe Bay, and underwent chloride displacement during transport due to multiphase reactions with N- and S- containing trace gases from precursor Prudhoe Bay combustion emissions (SO_2 and NO_x) leading to nitrate (Hara et al., 1999) and sulfate (Hara et al., 2003) formation. A previous ATOFMS study during the summertime in the high Arctic Ocean detected similar partially aged SSA particles containing nitrate and sulfate with low intensity chloride markers (Sierau et al., 2014).

4 Conclusions

The chemical composition of individual atmospheric particles transported to Utqiaġvik, Alaska from the Arctic Ocean and Prudhoe Bay were measured from August 21 to September 30, 2015. During periods of Arctic Ocean influence, fresh SSA was the major contributor to both submicron (~20%, by number, from 0.13 – 0.4 µm, 40 – 70% between 0.4 – 1 µm) and supermicron (80 – 100%, by number, from 1-4 µm) particles with only 30% chloride depletion (average Cl/Na mole ratio of 0.81) for all submicron SSA and 15% chloride depletion (average Cl/Na mole ratio of 0.99) for all supermicron SSA. Submicron OC particles contributed an average of 27%, by number, from 0.13 – 1 µm with a minimum of 10%, by number, from 0.13 – 0.2 µm and were likely from a marine biogenic source. With complete summertime sea ice loss expected by 2050 (Wang and Overland, 2015; Overland and Wang, 2013), increasing aerosol and trace gas emissions from the open Arctic Ocean are expected (Browse et al., 2013; Struthers et al., 2011).

Increased total particle number concentrations (920 ± 4 particles cm^{-3}) and a smaller particle size mode of 27 ± 4 nm were observed during periods of Prudhoe Bay air mass influence, in comparison to Arctic Ocean air masses (130 ± 1 particles cm^{-3}, 76 ± 40 nm, respectively), due to transportation of ultrafine combustion particles from the Prudhoe Bay oil fields. These transported particles have the potential to grow (Kolesar et al., 2017) and serve as CCN, which would have a large impact on the low CCN concentrations currently in the Arctic (Mauritsen et al., 2011). During these periods, increased number fractions of partially aged SSA (28 ± 1%, by number, of particles 0.13 – 4 µm) and OC (60%, by number, of 0.13 – 0.3 μm particles with a minimum of 10%, by number, of 0.8 – 1 μm particles) were observed by CCSEM-EDX, with evidence of sulfate and nitrate internally mixed with SSA and OC particles due to heterogeneous reactions and gas-particle partitioning, ~~respectfully~~respectively, during transport. Increased particle aging has been shown previously to increase the CCN activity of combustion particles (Furutani et al., 2008; Petzold et al., 2005). ~~An increase in these combustion products due to oil and gas extraction activities will likely contribute overall to further Arctic warming (Peters et al., 2011) and, with summertime ice extent already at an all-time low (Overland and Wang, 2013; Wang and Overland, 2015), may cause an even further decrease in ice extent~~. Therefore, increasing trace gas and aerosol emissions due to Arctic oil and gas extraction activities will contribute to further Arctic climate change (Law and Stohl, 2007).

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

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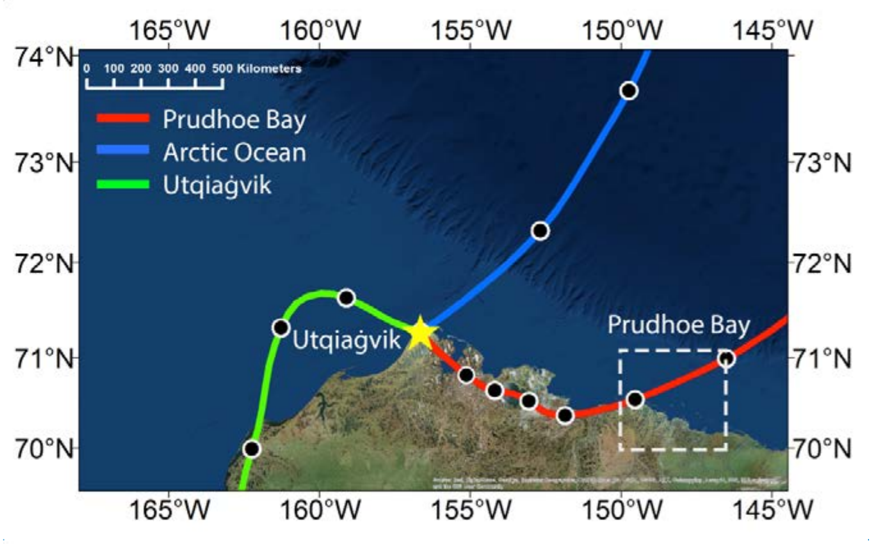
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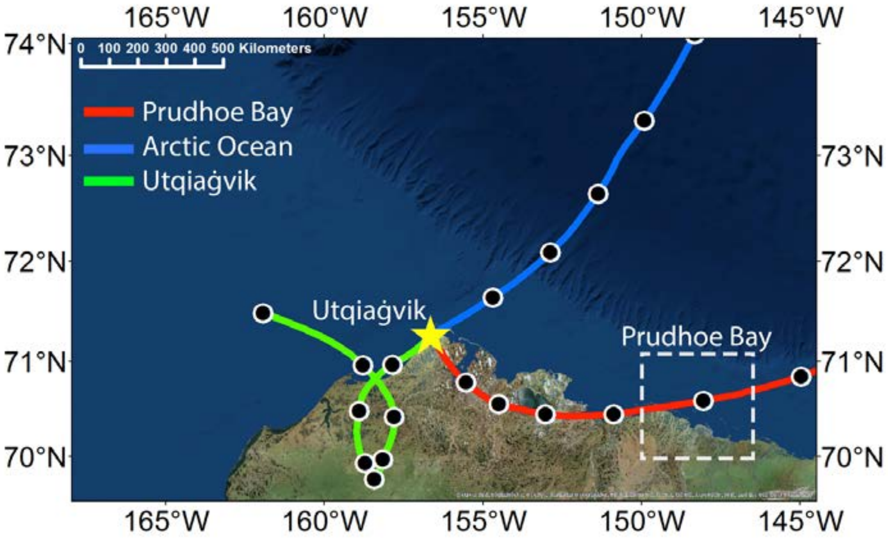

Figure 1. ~~Representative~~Average 48 h HYSPLIT backward air mass trajectories for three major areas of influence: Prudhoe Bay~~ (9/23/15 00:00 AKDT),~~, the ice-free Arctic Ocean~~ (9/9/15 16:00 AKDT),~~, and the town of Utqiaġvik~~ (9/25/15 08:00 AKDT).~~. 6 h time intervals are indicated by black circles. The Utqiaġvik, AK sampling site is indicated by the ~~orange~~yellow star, and the area of the greatest Prudhoe Bay emissions influence is indicated by the white dashed square as defined by ~~Kolesar et al. (2017)~~Kolesar et al. (2017). The map background was provided by ArcGIS 10.3.1 with the World Imagery basemap (Sources: Esri, DigitalGlobe, Earthstar Geographics, CNES/Airbus DS, GeoEye, USDA FSA, USGS, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community).

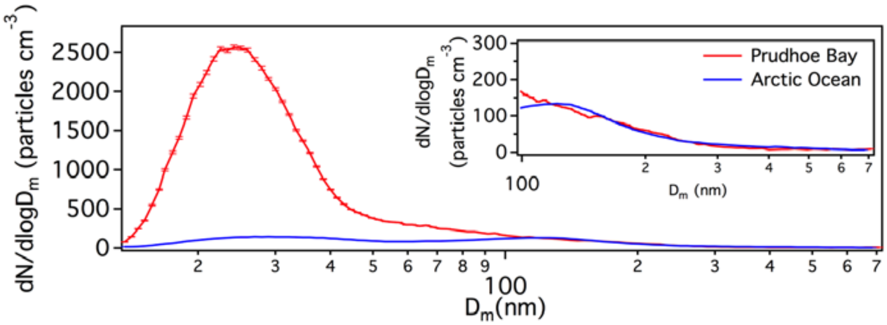

Figure 2. Average~~-~~, and standard error of the mean, particle number ~~weighted ~~size (mobility diameter ~~particle size ~~) distributions~~ and standard error of the mean~~ during Prudhoe Bay and Arctic Ocean influenced air masses from August 21–September 20, 2015, with the above 100 nm ~~distribution~~distributions inset. The full time series of the time-varying aerosol distribution ~~are~~is shown in Figure S2.

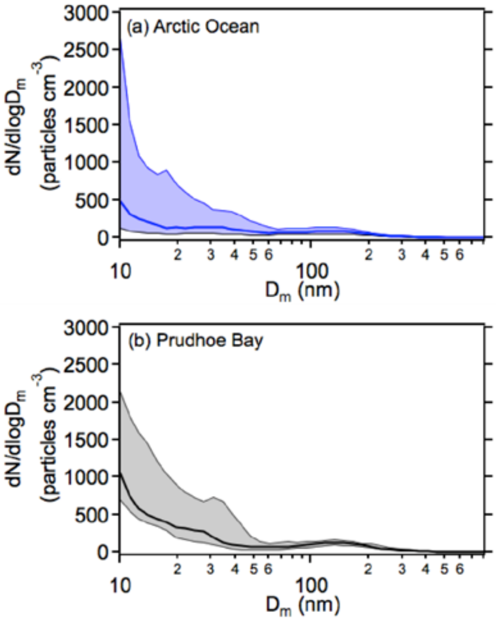

Figure 3. Particle number distribution for (a) Arctic Ocean and (b) Prudhoe Bay air masses observed for August-September 2008, 2009, 2013, and 2014 (median shown by the solid line, 25th and 75th percentiles shaded) at the NOAA Barrow Observatory.

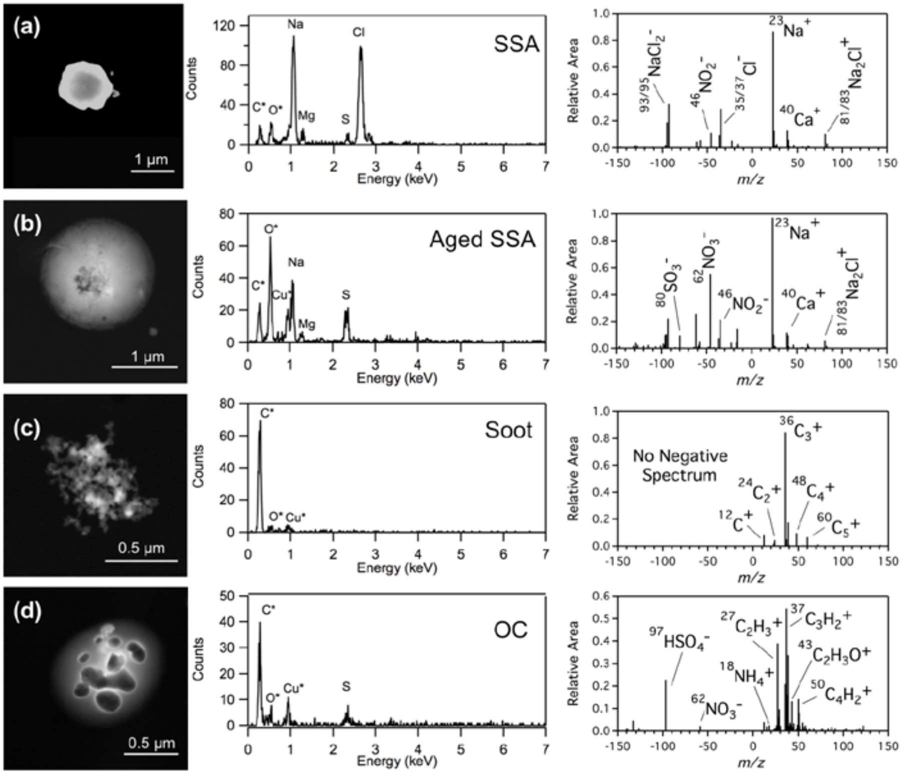

Figure 4. Representative SEM images (left) and EDX spectra (middle), as well as average ATOFMS mass spectra (right), for the major particle types observed: (a) Sea Spray Aerosol (SSA), (b) Partially Aged SSA, (c) Soot, (d) Organic Carbon (OC).

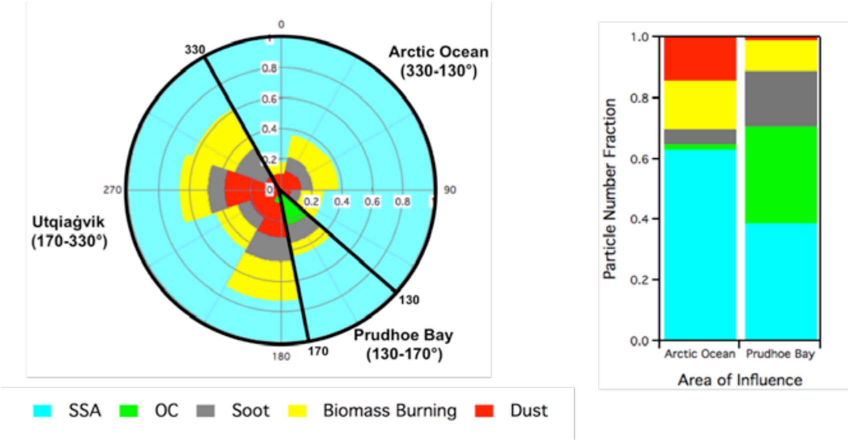

Figure 5. ATOFMS individual particle composition (0.2-1.5 µm) number fractions for 496 analyzed particles from September 8-20, 2015, based on wind direction (left) and air mass influence (right), determined by backward air mass trajectories. Data were binned every 40 degrees.

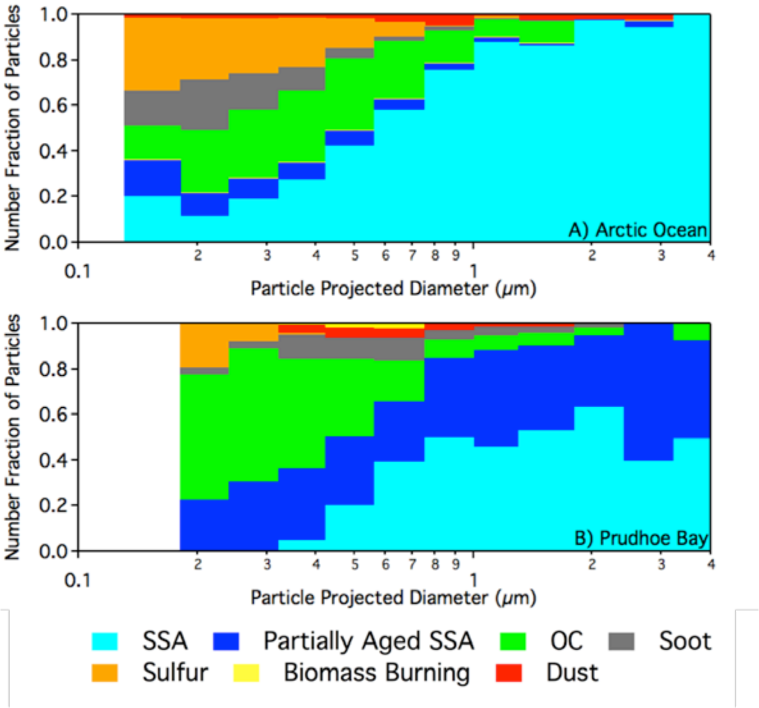

Figure 6. Size and chemical composition of individual particles measured by CCSEM-EDX during influence by (A) Arctic Ocean (2,869 particles analyzed) and (B) Prudhoe Bay (1,997 particles analyzed) air masses. For Arctic Ocean influenced periods, the following 8 h samples were analyzed: September 8, 2015 (00:00–08:00, 08:00 – 16:00), September 9, 2015 (00:00–08:00), September 15, 2015 (00:00–08:00). For Prudhoe Bay influenced periods, the following 8 h samples were analyzed: September 23, 2015 (00:00–08:00, 08:00–16:00). All times are in AKDT.

Table 1. Submicron and supermicron CCSEM-EDX number fractions and mole ratios for sulfate, nitrate, and chloride within individual SSA particles (SSA and partially aged SSA classes combined) during Arctic Ocean and Prudhoe Bay air masses. S, N and Cl were confirmed as sulfate, nitrate, and chloride by ATOFMS.

5

SSA Projected Area Diameter	Sulfate (Number Fraction)	Nitrate (Number Fraction)	Chloride (Number Fraction)	S/Na	N/Na	Cl/Na
Arctic Ocean						
0.13 – 1 µm	0.77	0.33	0.81	0.36	0.27	0.81
1 – 4 µm	0.97	0.22	0.99	0.15	<0.1	0.99
Prudhoe Bay						
0.13 – 1 µm	0.86	0.40	0.87	0.53	0.54	0.67
1 – 4 µm	0.90	0.43	0.87	0.32	0.76	0.55

Formatted Table

Supplement For Contributions of Transported Prudhoe Bay ~~Oilfield~~Oil Field Emissions to the Aerosol Population in Utqiaġvik, Alaska

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Particle Type Classification

SSA was characterized by an intense peak at *m/z* 23, corresponding to Na^+, and less intense peaks at *m/z* 39 (K^+), 81 (Na_2Cl^+), -35/37 (Cl^-) and -93/95 (Na_2Cl^-) (Ault et al., 2013). ~~Spectra~~Mass spectra that also contained intense markers for nitrate (*m/z* -46, -62) or sulfate (*m/z* -64, -80) ~~was~~were sub-classified as aged SSA. Organic carbon (OC) ~~was~~particles were characterized by intense peaks at *m/z* 37 (C_3H^+) and 27 ($C_2H_3^+$) and are attributed to combustion (Toner et al., 2008). ~~A sub-classification of OC~~OC particles also contained minor contributions from *m/z* 12 (C^+), identified as a potential OC fragment by Silva and Prather (2000). A sub-classification of OC particles was characterized by an intense peak at *m/z* 59 ($N(CH_3)_3^+$), which is characteristic of the presence of trimethylamine (TMA) (Rehbein et al., 2011) and has been detected previously in the Arctic (Willis et al., 2016). Rehbein et al. (2011) found that TMA was exclusively found during high relative humidity or fog events when gas phase TMA partitioned onto the particles or fog droplets. Relative humidity was high throughout the duration of the study (average of 91%), thus partitioning of TMA to the particle-phase is likely to occur. ~~Both~~Due to the small number of

TMA-containing particles measured, both OC particle types were grouped into a single OC class. Soot particles were characterized by elemental carbon C_n^+ fragment peaks, observed at *m/z* 12~~[~~ (C~~$^{+}$]~~,$^{+}$), 24~~[~~ (C$_2$~~$^{+}$]~~,$^{+}$), 36~~[~~ (C$_3$~~$^{+}$]~~,$^{+}$), 48~~[~~ (C$_4$~~$^{+}$]~~,$^{+}$), etc~~.~~., that are typical of incomplete combustion (Toner et al., 2008). Biomass burning (BB) particles were characterized by an intense peak at *m/z* 39 (K^+) and *m/z* -97 (HSO_4^-) with less intense peaks at *m/z* 43 ($C_3H_2O^+$), 27 ($C_2H_3^+$) and 12 (C^+) (Pratt et al., 2011). Dust was present in two different forms: calcium-rich and iron-rich. Calcium-rich dust (Ca-Dust) was characterized by an intense peak at *m/z* 40 (Ca^+) with less intense peaks at *m/z* 23 (Na^+), 24 (Mg^+) and 56/57 ($CaOH^+$/$CaOH_2^+$). Iron-rich dust (Fe-dust) was characterized by intense peaks at *m/z* 54/56 (Fe^+). All dust particle types were combined into a single cluster, as the majority likely originated from the nearby beaches, dirt roads and soil. Average spectra for each particle type are shown in Figure 2.

Particle types were identified based on observed morphology from SEM as well as composition and atomic percentages calculated from the EDX spectra. These classes are based on prior SEM-EDX studies, which established EDX spectra for fresh and aged SSA (Ault et al., 2013; Hara et al., 2003), organic carbon aerosol (Laskin et al., 2006; Moffet et al., 2010), soot (Jiang et al., 2011), biomass burning aerosol (Li et al., 2003; Pósfai et al., 2003), and mineral dust (Coz et al., 2009; Sobanska et al., 2003). Fresh SSA was characterized by large amounts Na and Cl, with Na/Mg and Na/Cl ratios close to those found in seawater. Aged SSA was characterized by Na and S and/or N > Cl, indicative of chlorine displacement by heterogeneous reactions (Laskin et al., 2003; Laskin et al., 2002). OC particles were round and contained large amounts of C and O with the majority also containing small fractions of S and/or N (Moffet et al., 2010). Soot was primarily carbon in composition and had a chain-like agglomerate morphology (Quennehen et al., 2012; Weinbruch et al., 2012). Dust particles were characterized by large fractions of Al and Si, in addition to trace metals such as Fe (Coz et al., 2009; Sobanska et al., 2003). Some fly ash particles, primarily aluminum and silicon oxides, may also be present in this class, but due to similarities in chemical composition between fly ash and dust accompanied by low abundance, fly ash and dust will be considered together. Minor contributions from BB were also identified, characterized by large amounts of K and Cl but little Na (Pósfai et al., 2003). A sulfur-rich particle type was identified by greater amounts of S as compared to C and O. This is likely the “missing” particle type unable to be characterized by the ATOFMS in this study, as well as the previous ATOFMS study by Sierau et al.

(2014). Wenzel et al. (2003) previously attributed scattered, but not ionized particles by ATOFMS, as relatively pure ammonium sulfate particles.

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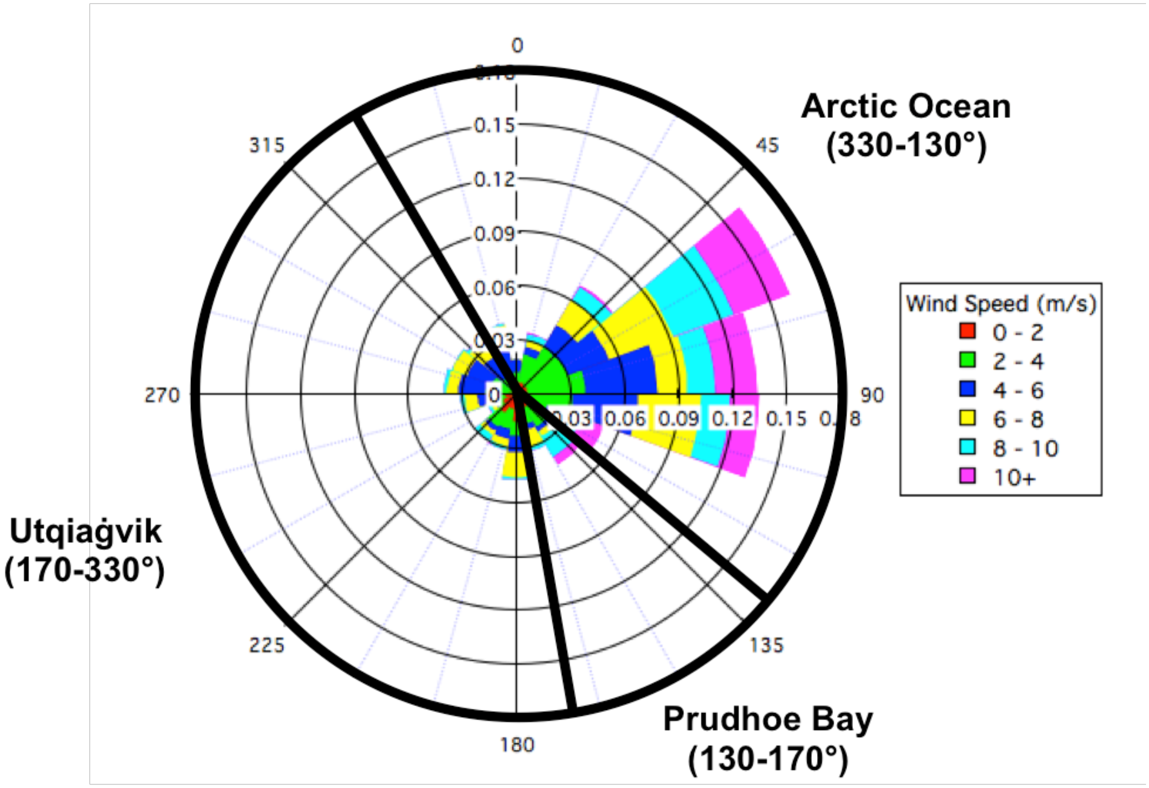


Figure S1. Wind rose from August 21–September 30, 2015 measured at the NOAA Barrow Observatory. Wind speed is binned by 2 m/s, and wind direction is binned by 20 degrees, with the radial axes representing the fraction of the study under those wind conditions.

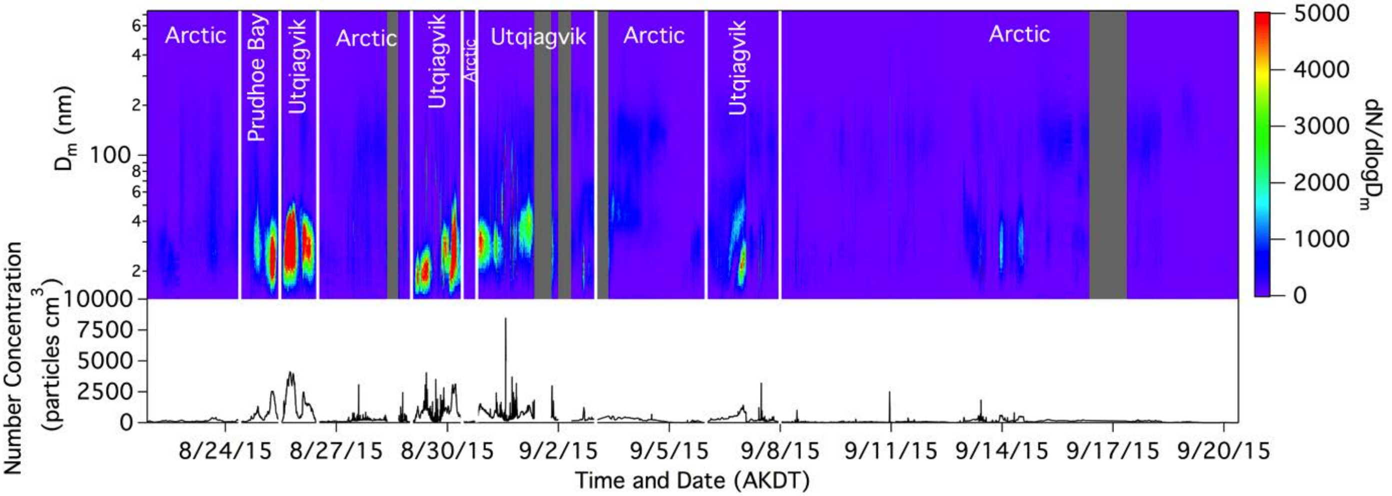
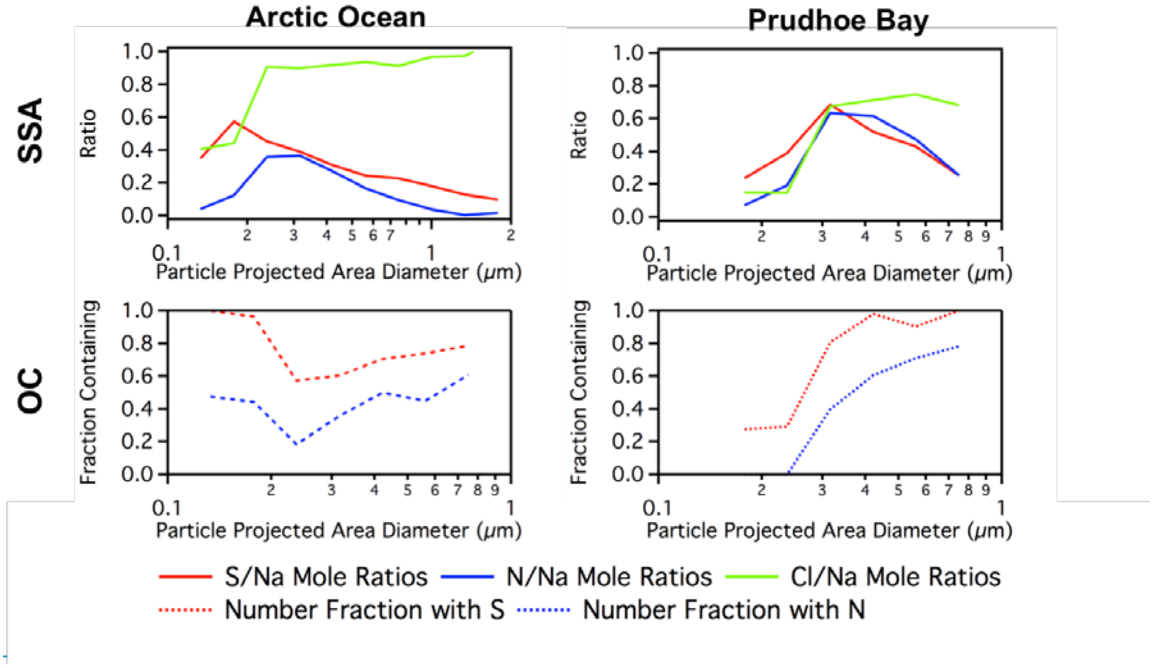


Figure S2. Aerosol size-resolved number concentrations (mobility diameter) measured by the SMPS from August 21-September 20, 2015. Identified air mass source regions, determined based on wind direction and backward air mass trajectories, are labeled and divided by white lines in the time series. Periods lacking data are indicated in gray. ~~The total~~Total particle (0.013 – 746 nm) ~~–~~number ~~concentration is~~concentrations are also shown.



~~**Figure S3.**~~

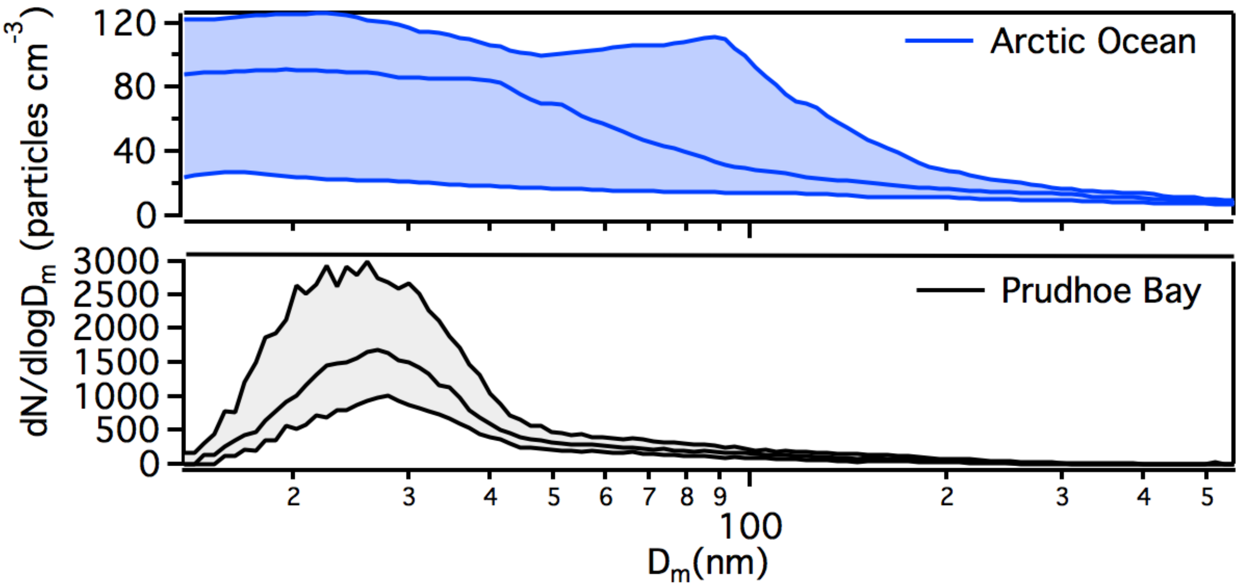


Figure S3. Median, as well as 25th and 75th percentile, particle size distributions, measured by SMPS, during Prudhoe Bay and Arctic Ocean influenced air masses from August 21–September 20, 2015.

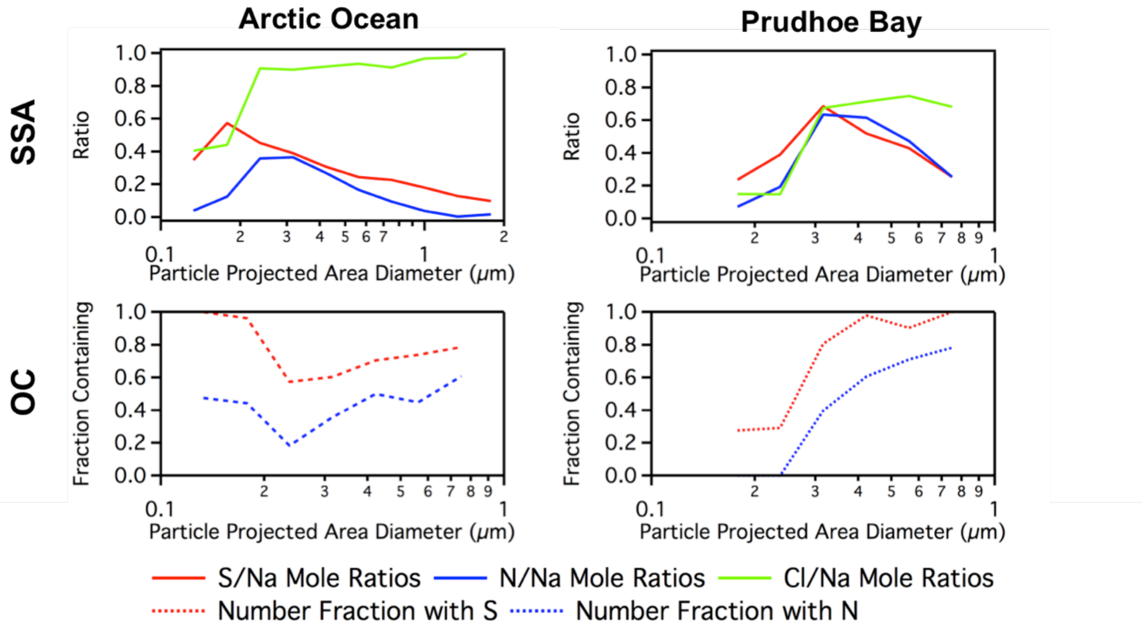


Figure S4. S/Na, N/Na, Cl/Na mole ratios of individual SSA (top) and fraction of OC particles (bottom) containing S, N, and/or Cl, measured by CCSEM-EDX for Arctic Ocean and Prudhoe Bay influenced air masses. Size bins with less than 25 particles are not displayed.

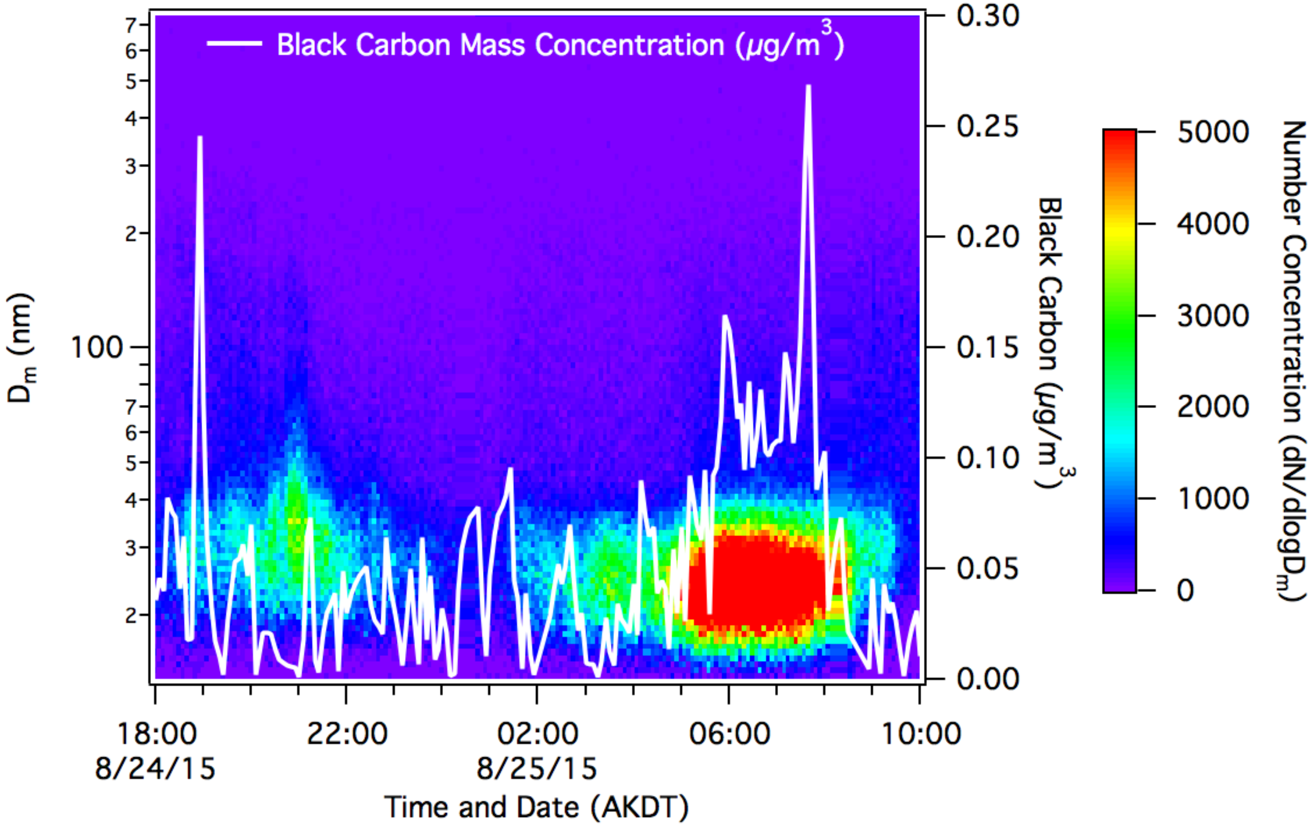


Figure S5. Aerosol size-resolved number concentrations (mobility diameter) measured by the SMPS during Prudhoe Bay air mass influence on August 24-25, 2015. Black carbon mass concentrations measured by the aethalometer are overlaid in white.