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High Summertime Aerosol Organic Functional Group Concentrations from Marine and Seabird Sources at Ross Island, Antarctica, during AWARE

Jun Liu[1], Jeramy Dedrick[1,2], Lynn M. Russell[1], Gunnar I. Senum[3], Janek Uin[3], Chongai Kuang[3],
5 Stephen R. Springston[3], W. Richard Leaitch[4], Allison C. Aiken[5] and Dan Lubin[1]

[1]Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093;
[2]Now at Texas A&M University, 400 Bizzell St, College Station, TX 77843
[3]Environmental & Climate Sciences Department, Brookhaven National Laboratory, Building 815-E, Upton, NY 11973-5000.
[4]Environment and Climate Change Canada (ECCC), Toronto, ON, Canada\
10 [5]Earth and Environmental Science, Earth Systems Observations, Los Alamos National Laboratory, Los Alamos, New Mexico, USA

Correspondence to: Lynn M. Russell (lmrussell@ucsd.edu)

Abstract.

15   From November 2015 to December 2016, the ARM West Antarctic Radiation Experiment (AWARE) measured submicron aerosol properties near McMurdo Station at the southern tip of the Ross Island. Submicron organic mass (OM), particle number, and cloud condensation nuclei concentrations were higher in summer than other seasons. The measurements included a range of compositions and concentrations that likely reflected both local anthropogenic emissions and natural background sources. We isolated the natural organic components by separating a natural factor and a local combustion
20   factor. The natural OM was 150 times higher in summer than in winter. The local anthropogenic emissions were not hygroscopic and had little contribution to the CCN concentrations. Natural sources that included marine sea spray and seabird emissions contributed 56 % of OM in the austral summer but only 3 % in the austral winter. The natural OM had high hydroxyl group fraction (55%), 6% alkane, and 6% amine group mass, consistent with marine organic composition. In addition, the Fourier transform infrared (FTIR) spectra showed the natural sources of organic aerosol were characterized by
25   amide group absorption, which may be from seabird populations. Carboxylic acid group contributions from natural sources were correlated to incoming solar radiation, indicating that some OM formed by secondary pathways.

1 Introduction

There are few places on Earth where measurements of ambient aerosol and cloud condensation nuclei (CCN) are as scarce as in Antarctica. Yet since West Antarctica is one of the most rapidly warming regions on Earth (Steig et al., 2009; Lambeck et
30   al., 2002; Bromwich et al., 2013) , these measurements may be crucial to understanding the changing climate – especially given the close connection between the Antarctic ice sheets and potential global sea level rise.

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In1966, electron micrographs of particles collected on a four-stage impactor provided some of the first aerosol measurements carried out at McMurdo Station (Cadle et al., 1968) . Filter samples were collected for elemental analysis in 1970-1971 (Ondov et al., 1973) . During the austral summers of 1969 and 1970, the Aitken nuclei concentration was reported to be ~1000 cm^{-3} (Warburton, 1973) . In another study, the number concentration was 50 to 150 cm^{-3} with continental winds and

5   ~300 cm^{-3} with maritime winds (Hogan, 1975) . Balloon measurements were conducted later for stratospheric aerosols, and long distance signals from volcanic sources in tropical areas were found in the stratosphere (Hofmann et al., 1986; Solomon et al., 1994) . Hansen et al. (2001) measured black carbon at McMurdo in austral summer in 1995-1996. Another study (Mazzera et al., 2001b) reported more detailed PM$_{10}$ elemental composition, elemental and organic carbon, and nitrate concentrations for 1995–1996 and 1996–1997 at McMurdo. Chemical Mass Balance (CMB) receptor modeling estimated

10   that soil dust, sea salt, combustion emissions, sulfates, methanesulfonate, and nitrates contributed 57%, 15%, 14%, 10%, 3%, and 1%, respectively, to the summertime PM$_{10}$ mass (Mazzera et al., 2001a) . Kalnajs et al. (2013) showed that ozone depletion is correlated to aerosol concentrations because halogen-containing aerosol consumed ozone. An aerosol mass spectrometer (AMS) at a site 20 km northeast from McMurdo Station during October 2014 to December 2014 and August to October 2015 (Giordano et al., 2017) found sulfate accounted for more than 50% of non-refractory composition.

15   The few hygroscopicity and CCN measurements reported near West Antarctica are also recent and sparse. DeFelice et al. (1997) conducted CCN measurements at Palmer Station on the Antarctic Peninsula in January and February 1994. They collected CCN for 27 days at 0.3% and 1% SS and found CCN concentration to be between 79 and 158 cm^{-3}. Asmi et al. (2010) found that, aerosol particles over the Southern Ocean are very hygroscopic with a growth factor of 1.75 at 90 nm. At King Sejong Station on King George Island, Kim et al. (2017) found that CCN concentrations are high in summer (~200 cm^{-3}

20   ) and low in winter (~50 cm^{-3}). Biological emissions from marine sulfate sources have been proposed to explain a large fraction of CCN in the Southern Ocean region (McCoy et al., 2015) .

The organic composition of particles in marine and Arctic regions have shown a high fraction of hydroxyl group as well as some alkane and amine groups, likely associated with sugars, carbohydrates, and amino sugars originated from biological materials in seawater (Hawkins and Russell, 2010; Modini et al., 2015; Russell et al., 2010; Frossard et al., 2013; Leaitch et

25   al., 2017; Shaw et al., 2010) . Organic nitrogen has also been identified as a component in aerosol particles in various studies in Antarctic (Schmale et al., 2013; Barbaro et al., 2015; Dall'Osto et al., 2017) and Arctic (Scalabrin et al., 2012; Dall'Osto et al., 2012) regions. Marine and polar amino acid measurements are summarized in Table S1 (Mace et al., 2003a; Kuznetsova et al., 2005; Scalabrin et al., 2012; Barbaro et al., 2015; Mace et al., 2003b; Wedyan and Preston, 2008; Shi et al., 2010; Matsumoto and Uematsu, 2005; Mandalakis et al., 2011; Violaki et al., 2010) .

30   The Ross Sea has a surprisingly high biological primary production rate in the summer, making it the most biologically active part of the southern polar region (Arrigo et al., 2008) . Seabird emissions were linked to new particle formation (Weber et al., 1998) and to particles containing CNH and CNHO fragments (Schmale et al., 2013) . The ammonia emissions from seabird colonies have also been shown to contribute substantially to atmospheric particle formation and cloud-albedo radiative effects in the Arctic (Croft et al., 2016) . Organic aerosol components were also associated with melt-water ponds

in continental Antarctica (Kyro et al., 2013) .

AWARE (ARM West Antarctic Radiation Experiment) provides the most thorough yearlong aerosol and radiative property measurements yet obtained from Antarctica, and the only four-season time series of weekly FTIR measurements of organic functional groups in Antarctica. To remove contributions from emissions associated with local McMurdo Station activities,

5   we used smoothing of condensation nuclei (CN) time series and factorization of organic composition. The organic functional groups were used to interpret the seasonal patterns of natural marine and coastal particle sources after separating the local emissions. Dust, sea salt, and non-sea salt sulfate mass concentrations were also measured by XRF to evaluate the seasonal contributions to inorganic particle components. Specific FTIR absorption features were also investigated as indicators of emissions from seabird populations.

10   2 Methods

The AWARE aerosol measurements were collected from 23 November 2015 to 29 December 2016 at the Cosray site on the eastern edge of McMurdo Station (77.85°S, 166.66°E), which is located on the southern tip of Ross Island in Antarctica. The details of the measurement system can be found online in the description of the second ARM Mobile Facility (AMF2, https://www.arm.gov/capabilities/observatories/amf) and Aerosol Observing System (AOS,

15   https://www.arm.gov/capabilities/instruments/aos). The station hosts more than 1000 scientists and support personnel during austral summer and consumes more than 2 million gallons of AN-8 diesel fuel (with a 0.3% sulfur content by weight) for station operations (Mazzera et al., 2001a) . Ambient aerosol particles were measured by CPC (Condensation Particle Counter, TSI model 3772), HTDMA (Hygroscopic Tandem Differential Mobility Analyser, Brechtel model 3002), and CCN Counter (Cloud Condensation Nuclei, DMT model CCN100) and were collected on filters for off-line FTIR and X-ray

20   fluorescence (XRF).

Submicron aerosol particle samples were collected on pre-scanned Teflon filters (Teflon, Pall Life Science Inc., 37 mm diameter, 1.0 μm pore size) behind a PM_1 sharp-cut cyclone (SCC2.229 PM_1, BGI Inc.). One sample filter and one background filter were collected each week. Samples were frozen and transported to the UCSD laboratory for FTIR spectroscopy. A Bruker Tensor 27 FTIR spectrometer with a deuterated triglycine sulfate (DTGS) detector (Bruker,

25   Waltham, MA) was used to scan the filters both before and after sampling. An automated algorithm was applied to quantify the mass of the organic functional groups (Takahama et al., 2013; Russell et al., 2009) . Four groups (alkane, amine, hydroxyl and carboxylic acid) were quantified by the area of absorption peaks and the sum of the mass of the five functional groups is used as the quantified OM (Maria et al., 2002) . Other groups (organonitrate, organosulfate and non-acid carbonyl) were fit but all samples were below detection limit. Pure (>99%) uric acid (Sigma-Aldrich) and urea (Fisher Scientific) were

30   dissolved in water, atomized and collected on triplicate Teflon filters to provide FTIR reference spectra for comparison of the amide group region.

Half of the filters (25) were selected for X-ray fluorescence (XRF) (Chester Labnet, OR) quantification of major elements above 23 amu. The elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Zr, Ag, Pb and Ba had mass above detection limit (3 times the uncertainty) for 95% of the samples and are used here. The mass of dust was calculated from XRF metal concentrations, assuming dust consists of $MgCO_3$, Al_2O_3, SiO_2, K_2O, $CaCO_3$, TiO_2, Fe_2O_3, MnO

5 and BaO (Usher et al., 2003) after excluding mass associated with sea salt. Sea salt particle mass components were calculated from XRF-measured Na and Cl concentration (Frossard et al., 2014b; Modini et al., 2015) .

The CPC measured particles with diameters larger than 10 nm and operated continuously, except from 29 March to 7 April 2016 when a malfunction occurred (Figure S1). The CCN Counter measured the particle concentration activated at supersaturations of 0.1%, 0.2%, 0.5%, 0.8%, and 1.0% during AWARE, with only short time periods of missing data (Figure

10 S1). HTDMA provided humidified aerosol size distributions for five dry particle sizes at specified relative humidity (RH = 90%) for two periods during the campaign: 23 November to 20 December 2015 and 16 to 31 January 2016. Aerosol particle growth factors (GF_i) from the HTDMA measurements were calculated as the ratio of humidified particle diameter of size i to the selected dry diameter. Mean growth factors (GF) and hygroscopicity parameters (κ) (Petters and Kreidenweis, 2007; Su et al., 2010) were calculated from Eq. (1) and Eq. (2):

15
$$\overline{GF} = \frac{\sum_i GF_i (\frac{dN}{dlogD_p})_i}{\sum_i (\frac{dN}{dlogD_p})_i} \tag{1}$$

$$\kappa = \frac{(\overline{GF}^3 - 1)(1 - a_w)}{a_w}, \tag{2}$$

where N is the measured number concentration and a_w is water activity (Rickards et al., 2013) .

Meteorological variables (temperature, humidity, wind speed and wind direction) were measured with a Vaisala model WXT-520 (Helsinki, Finland). The Surface Energy Balance System (SEBS) included upwelling and downwelling solar and

20 infrared radiometers at the measurement site at McMurdo Station from 4 February to 29 December 2016. Aerosol absorption was measured at three wavelengths (470, 522 and 660 nm) by a Particle Soot Absorption Photometer (PSAP; Radiance Research, Seattle, WA). The PSAP absorption at 660 nm was used as a proxy for black carbon (BC) because it is expected to have the least interference from brown carbon (Olson et al., 2015) .

3 CN, CCN, Hygroscopicity, and Inorganic Particle Measurements

25 To quantify seasonal differences, four seasons were defined as Summer (November through February), Fall (March through April), Winter (May through August) and Spring (September through October) (Figure 1). The four-month winter is characterized by irradiance of nearly zero and average temperature below -20 °C. The four-month summer had irradiance above 250 W m^{-2} and temperature higher than -10 °C. Spring and fall marked transitions between summer and winter. CN concentrations had frequent short-lived increases that typically had high concentrations (>1000 particles cm^{-3} for 10-min

30 average), which we attributed to short-term local contamination events (Figure S1). High CN concentrations (>1000 cm^{-3})

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occurred 48% of the time when the wind was from the west (Figure S2), which is the same direction as the McMurdo Station

central facilities. However, westerly winds only occurred 3% of the time, so emissions at McMurdo Station were unlikely to

account for most of the emissions. Spikes were separated using a "despike" algorithm (Goring and Nikora, 2002) (Beaton

and Tukey, 1974; Tukey, 1977; Velleman, 1977; Goring and Nikora, 2002) , with a running median length of 24 hr and

5   weighted by cosine bell running mean of 24 hr. The resulting SLCE accounted for 55% of the annual 1-Hz CN

concentrations and occurred 19 % of the time. The SLCE were characterized by an average duration of less than 1 hr (0.5

min$\pm$6 min), rapid changes in concentration (8520 ± 36780 cm^{-3} min^{-1}), and concentrations exceeding 1000 cm^{-3}. The

distribution of SLCE duration and timing (Figure S3) shows that SLCE events were approximately two times more frequent

during local daytime than nighttime. This short duration and largely daytime timing of SLCE suggests that site maintenance

10   and nearby road traffic are likely responsible for many of the high CN events. SLCE accounted for 55% of the measured CN

number concentration, leaving 45% of the CN to potentially be from natural sources. SLCE accounted for 46% of the CN in

summer and 72% of CN in winter. The CN concentration associated with natural sources was very low (~60 cm^{-3}) in winter

but could be as high as 2000 cm^{-3} in summer (Figure S1). Wind speed was not correlated (r=-0.32) to CN concentration.

SLCE had nearly no contribution to CCN, which is consistent with SLCE particles being extremely low hygroscopicity and

15   freshly emitted from fuel combustion (Wex et al., 2010) (Figure S1). The CCN concentration correlated moderately or

strongly to SLCE-removed CN (r=0.80, 0.83, 0.87 and 0.88 for 0.2%, 0.5%, 0.8% and 1% SS, respectively). CCN and CN

were 5 to 7 times higher during summer, but the ratio of CCN/CN changed less than 30% throughout the year (Table 1).

CCN/CN was largely constant at all five supersaturations during most of 2016, but from late September to early October the

ratio of CCN/CN decreased to 0.5 at 1% supersaturation (Figure S1). This decrease of CCN/CN ratio during the winter-

20   spring transition could be related to the decrease in particle diameter observed previously at a site 10 km from McMurdo

Station (Giordano et al., 2017) . The higher CCN/CN ratio in the summer (Table 1) is consistent with the slightly larger

diameter of the accumulation mode particles observed in previous summers (Kim et al., 2017) .

The growth factors and hygroscopicity parameters were both nearly constant during the two measurement periods (Figure

S4), with values of 1.5 ± 0.3 for growth factors and 0.4 ± 0.1 for hygroscopicity parameters. These numbers were constant

25   across the measured size range of 50 nm to 250 nm diameter and are comparable to other observations in the Antarctic

region (Wex et al., 2010; Asmi et al., 2010; Kim et al., 2017) . The PSAP absorption at 660 nm was correlated moderately to

the measured CN concentrations (R=0.53). The absorption is 1.7 times higher in summer than winter, which is consistent

with the higher CN and OM in summer than winter but with a much smaller change, likely because the summertime

increases are largely non-absorbing aerosol particles. The absorption also correlated moderately to the fraction of particles

30   that did not grow at increased relative humidity in the HTDMA (R=0.52, Figure 2 (a)). In addition, absorption correlated

moderately to the non-activated CN particles (1-CCN/CN) (R=0.34 for 1% supersaturation, Figure 2 (b)). The correlation of

more absorbing particles to those that did not take up water is consistent with the SLCE particles being freshly-emitted from

fuel combustion, as such particles have high BC (Peng et al., 2017; Vu et al., 2017) .

XRF measurements of elemental concentrations of S, P, K, Ca, Si, Mn, Al, Ag, Fe, and V were 2 to 15 times higher in

summer than in winter (Figure S5). Submicron dust mass concentration was 7 times higher in summer, consistent with the lack of exposed soil in winter (Figure 1). Sea salt particle mass concentration (Figure 1) was 3 times higher in winter than in summer, consistent with the higher circumpolar wind speed providing more sea spray in winter than summer (Bintanja et al., 2014) . The depletion of Na relative to Cl in winter is consistent with a contribution to the aerosol submicron mass from

5   wind-blown frost flowers (Alvarez‑Aviles et al., 2008; Thomas and Dieckmann, 2003; Stein and MacDonald, 2004; Papadimitriou et al., 2007; Giannelli et al., 2001; Belzile et al., 2002; Shaw et al., 2010).

4 Organic Mass and Composition

The measured organic functional group mass concentrations are shown in Figure 3(c). The average OM is 0.13 μg m^{-3} for AWARE, with hydroxyl groups having the highest mass fraction (41%), followed by alkane (39%), amine (13%) and

10   carboxylic acid (7%) groups.

Positive Matrix Factorization (PMF) was applied to the baselined FTIR spectra for the PM$_1$ samples collected in 2016 at McMurdo Station with the PMF2 V4.2 (Paatero and Tapper, 1994; Paatero, 1997) . Six-factor solution spaces (1~6) were considered. Fpeak values from -2 to 2 at 0.5 increments were considered. Seeds of 1, 10 and 100 were used at each Fpeak and factor number to examine the robustness of each solution. There was little change in solutions with rotations for all

15   solutions. Q/Qexpected decreases as factor number increases for all solutions (Table S2). The two-factor solution is considered robust because the spectra are almost identical for all rotations and seeding conditions (Figure S6). The solution leaves an average of 23% of the OM as residual. The two factors are not correlated in time and do not have similar spectra (Table S2). The new factor identified from the 3-factor solutions is either degenerate or very similar (cosine similarity =0.99) to one of the first two factors. Similarly for 4 or more factor solutions two or more degenerate or duplicate factors are found.

20   This makes the two-factor solution with Fpeak of 0 optimal for the AWARE data set. The low aerosol concentrations and limited personnel access at AWARE reduced the time resolution of FTIR samples to one week each for a total of 54 samples in one year, which is significantly longer than is possible in other regions (Russell et al., 2011) ,. The small number of samples and the low variability during the study is likely the reason that PMF is unable to separate more than two factors.

K-means clustering (Hartigan and Wong, 1979) was applied to the baselined FTIR spectra (Takahama et al., 2013).

25   Solutions with 1 to 10 clusters were explored and the 2-cluster solution was chosen because clusters with similar or redundant centroid spectra were present in solutions with 3 or more clusters.

The two clusters and two PMF factors (Figure 3 and Figure 4) were separated and identified as associated with Fossil Fuel Combustion (FFC) and Marine and Seabird (M&S) sources, as described below. The low time resolution (one week) of the samples in AWARE limited both the accuracy and the number of sources that could be separated. A measure of the

30   uncertainty of the PMF factors is provided by the ratio of the PMF residual to each factor. The ratio of the PMF residual to the FFC OM varies from 29% in winter to 63% in summer, but relative to M&S OM the PMF residual is only 33% in summer but almost 900% in winter (Table 1).

The FFC cluster and factor are similar to each other (cosine similarity=0.97) and are both named because of the similarity of the spectra to factors identified as FFC previously (Price et al., 2017; Guzman-Morales et al., 2014; Saliba et al., 2017) . The FFC Factor has two narrow peaks at 2865 and 2934 cm^{-1} that are characteristic of long-chain hydrocarbons and a cosine similiarity greater than 0.8 with factors identified as urban combustion emissions (Guzman-Morales et al., 2014) and fresh

5 ship engine emissions (Price et al., 2017) . The FFC factor has alkane and amine groups that account for 80% of OM (Figure 4), which is consistent with urban combustion emissions and vehicle engine tests (Guzman-Morales et al., 2014; Saliba et al., 2017) . The FFC factor was 73% of organic mass in winter but only 23% in summer (Figure 3 (a) and (b)). The FFC factor concentration is weakly or moderately correlated to Ca, P, Fe, Cu, Cr, Mn and Zn (r=0.3~0.5), which have been identified as tracers of vehicle emissions (Lin et al., 2015; Cheung et al., 2010) .

10 The M&S Factor is identified as "marine" because of its high hydroxyl group fraction, which is similar to past marine sea spray factors (Russell et al., 2010), and as "seabird" because of absorption from ammonium and an organic nitrogen peak that is likely associated with coastal penguin emissions. The high hydroxyl group that accounted for 55% of OM in the M&S factor makes this factor overall similar to the marine factors identified in measurements at Barrow and Alert (cosine similarity=0.53-0.57) (Shaw et al., 2010; Leaitch et al., 2017) (Figure 3 and Figure 4). The M&S hydroxyl group fraction is

15 lower than the Arctic marine factors that have 80% hydroxyl group (Shaw et al., 2010; Leaitch et al., 2017) . The M&S factor has higher alkane (38%) and amine (8%) group mass compared to two marine factors in Arctic regions that had only 6% alkane and 6% amine group mass (Shaw et al., 2010; Leaitch et al., 2017) . This factor contributed a substantial fraction of organic mass in summer (58%) but very little in winter (5%) (Figure 3b). The M&S organic mass concentration was only 0.001 μg m^{-3} during winter and was 0.15 μg m^{-3} during summer (Figure 3d). The low summer and high winter M&S OM

20 means that salt was not correlated to the M&S Factor organic mass, indicating the high summertime concentrations of natural OM could not be explained by primary marine aerosol contributions alone.

The FTIR spectra for summer samples show an absorption peak at 1680 cm^{-1} that is not present in winter (Figure 1). The location of the M&S factor FTIR absorption peak (Figure 5) was located at a wavenumber that was both too high (>1630 cm^{-1}) to be primary amine bending and too low (<1714 cm^{-1}) to be carbonyl bending (Figure 5) (Takahama et al., 2013) .

25 Seabirds excrete urea that degrades to uric acid, and the amide groups found in both urea and uric acid could explain the 1680 cm^{-1} peak in the summer FTIR spectra (Figure 5). The ammonium peaks (above and below 3100 cm^{-1} (Takahama et al., 2013)) associated with the M&S factor are also consistent with ammonia emissions from guano (Legrand et al., 1998) , which is neutralized to ammonium in the particle phase.

More than 155,000 breeding pairs reside in the ice-free areas on Ross Island (Attwood et al., 2014) from October to March

30 (Davis et al., 2001) . The three penguin habitats on Ross Island are all less than 50 miles from McMurdo Station (Figure S2) (Lyver et al., 2014) . Penguin activities have been linked previously to particle formation (Weber et al., 1998) , enriching aerosols with oxalate (Legrand et al., 2012) and containing CNHO fragments (Schmale et al., 2013) . Since McMurdo Station is most frequently downwind from Cape Crozier, its estimated ~300,000 penguins are a likely source of this organic and ammonium contribution to particles (Lyver et al., 2014) .

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This 1680 cm^{-1} peak was present in very small amounts in multi-year Arctic FTIR measurements (Shaw et al., 2010; Leaitch et al., 2017) (Figure 5), but their low concentrations did not support further investigation. The 1680 cm^{-1} peak has not been observed in open ocean marine factors (Russell et al., 2010; Frossard et al., 2014a) , suggesting that a coastal source is likely. An alternative explanation of the amide group is emissions from seasonal ice microbiota (Dall'Osto et al., 2017) . Given the

5   proximity and abundance of seabirds at McMurdo Station, seabirds are the more likely source than are sea ice algae or other phytoplankton during AWARE.

The carboxylic acid group mass concentration that was associated with the M&S factor was correlated moderately to downwelling shortwave irradiance (r=0.75, Figure 6), suggesting this carboxylic acid group mass was likely from photochemical reactions. Carboxylic acids have been identified as secondary based on their correlation to solar radiation in

10   urban conditions (Rogge et al., 1993; Kawamura and Ikushima, 1993) , and carboxylic acid group mass fractions were also identified as secondary photochemical products based on their correlation to solar radiation in clean, open-ocean conditions (Frossard et al., 2014a) . In contrast, the carboxylic acid group associated with the FFC factor had no correlation (r= 0.09) to downwelling shortwave irradiance. This may be because the local emissions from McMurdo Station facilities reached the Cosray site in a very short time and may not have had enough time for photochemical reactions to proceed. The correlation

15   of the M&S factor carboxylic acid group mass concentration to solar radiation here provides evidence that OM in Antarctica has contributions from condensation of secondary photochemical products. The source of the vapor-phase organic precursors for these products is not known, but given their substantial contribution to mass seems worthy of further investigation.

5 Conclusions

The first year-long organic functional group measurements in Antarctica show the seasonal trend of higher summer

20   concentrations in most of the aerosol measurements. Short-lived contamination events (SLCE) of typically less than 1 hr (Figure S3) from local sources were separated from the CN time series to investigate the more regionally-representative patterns. With SLCE removed, average CN concentrations were 65 cm^{-3} in winter but 400 cm^{-3} in summer.

The ratio of CCN to SLCE-removed CN was largely constant for most of the measured seasons. Growth factors (1.5±0.3) and hygroscopicity parameters κ (0.4±0.1) were measured in two one-month periods during the 2015-2016 summer and are

25   comparable to marine aerosols reported near Antarctica.

Both natural dust and biogenic as well as anthropogenic emission concentrations were more abundant in the summer months due to both the higher sunlight for productivity and the higher site accessibility. Summer OM was 0.27 μg m^{-3}, which was 7 times higher than winter OM. Hydroxyl and alkane groups were found to be the most abundant and accounted for 80% of OM. Two factors were identified by PMF: the M&S factor was associated with natural marine sea spray and coastal seabird

30   sources, and the FFC was associated with local combustion emissions. The M&S factor mass concentration was 150 times higher in summer than winter; the FFC factor had a higher concentration than M&S in winter but not in summer.

In addition to the primary amine peak present in past marine sea spray measurements, an FTIR absorption peak at 1680 cm^{-1} was associated with the M&S Factor in summer. The likely source of this peak as well as the coincident ammonium concentrations was seabird emissions from penguin colonies at Cape Crozier. The carboxylic acid group mass in the M&S factor was well correlated to downwelling shortwave irradiance (r=0.69) and was likely from secondary products of

5 photochemical reactions.

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Table 1. Mean concentrations and ratios with standard deviations during 2016 at McMurdo.

Season		Spring	Summer	Fall	Winter
CCN Number Concentration cm^{-3} (CCN/SLCE-Removed CN)	0.1 % SS	11.2±13.3 (0.07±0.06)	40.1±34.2 (0.08±0.06)	9.7±6.6 (0.06±0.05)	7.1±8.5 (0.1±0.09)
	0.2 % SS	37.9±36.4 (0.19±0.11)	131±80.2 (0.26±0.12)	48.2±29.3 (0.29±0.11)	18.6±20.5 (0.26±0.14)
	0.5 % SS	72.1±48.5 (0.37±0.20)	276.4±147.9 (0.56±0.24)	104±60.7 (0.63±0.20)	33.3±25.3 (0.49±0.26)
	0.8 % SS	99.7±73.9 (0.5±0.23)	348±203 (0.68±0.25)	124±72.3 (0.75±0.23)	42.9±39.6 (0.57±0.29)
	1 % SS	117±110 (0.55±0.24)	371±234 (0.73±0.26)	132±77.5 (0.8±0.23)	48.5±50.2 (0.6±0.30)
CN cm^{-3}	CN SLCE-Removed	161±94	400±228	141±88	65±77
	CN	376±571	740±693	241±187	237±502
Absorption mM^{-1}		0.2±0.47	0.34±0.66	0.16±0.66	0.2±0.50
Measured FTIR OM µg m^{-3}		0.06±0.04	0.27±0.16	0.07±0.06	0.04±0.02
PMF of FTIR OM	FFC OM µg m^{-3}	0.03±0.01	0.06±0.05	0.03±0.02	0.03±0.02
	M&S OM µg m^{-3}	0.018±0.028	0.155±0.121	0.026±0.046	0.001±0.001
	Residual/FFC	0.40±0.72	0.63±0.84	0.36±0.49	0.28±0.52
	Residual/M&S	1.12±097	0.33±0.46	1.03±0.63	9.22±7.74

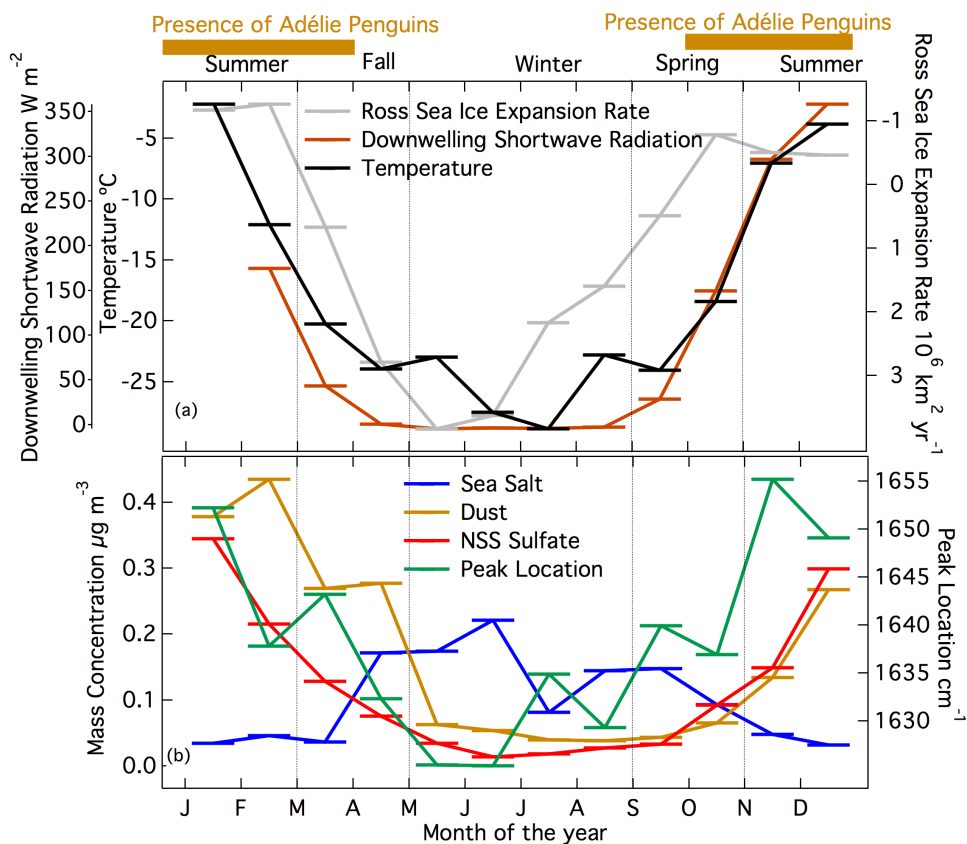Atmospheric
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Figure 1. Monthly average of (a) Temperature, shortwave downwelling irradiance measured in this study and sea ice expansion rate of the Ross Sea (Holland, 2014) ; (b) Sea salt, dust and non-sea salt sulfate concentration from XRF and FTIR peak location at 1500~1800 cm^{-1} wavenumber region.
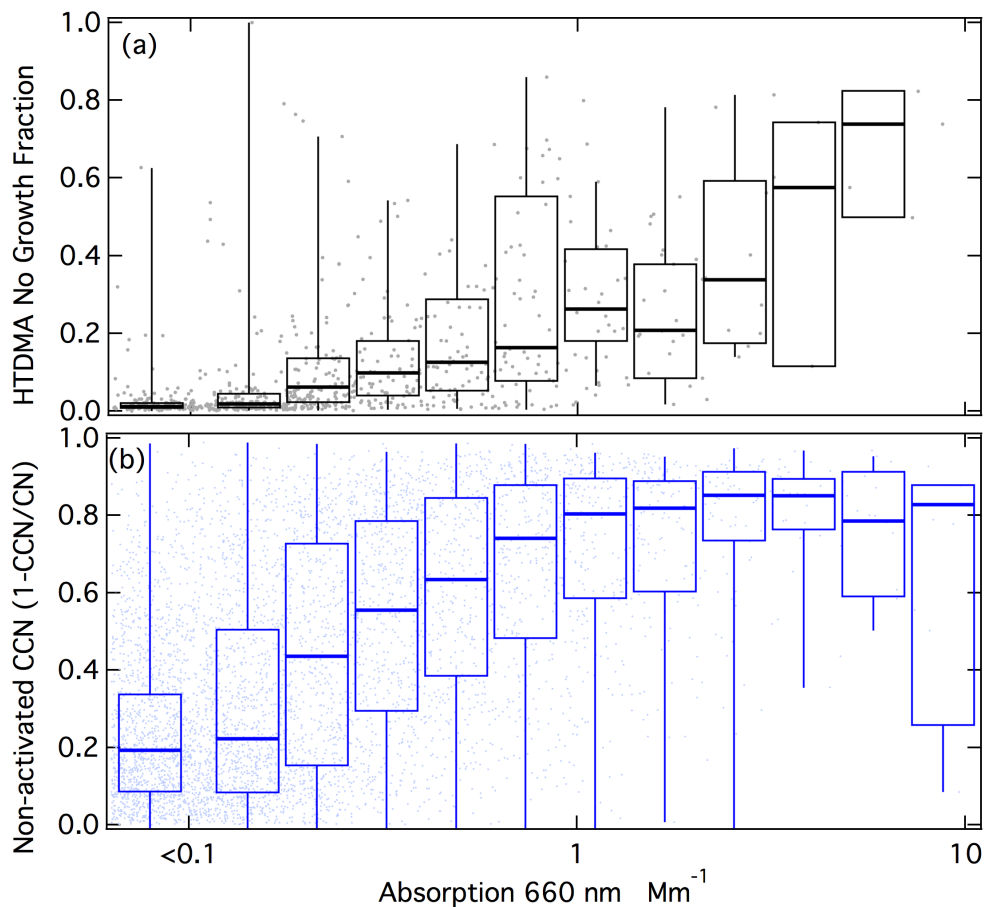
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Figure 2. Scatter and box-whisker plot of PSAP 660 nm absorption and: (a) HTDMA no growth fration (r=0.52); (b) Non-activated CCN fraction (1-CCN/SLCE-removed CN) for 1% supersatuartion (r=0.34). The boxes show the 25th, 50th and 75th percentile values; the Whiskers show the minimum and maximum values.
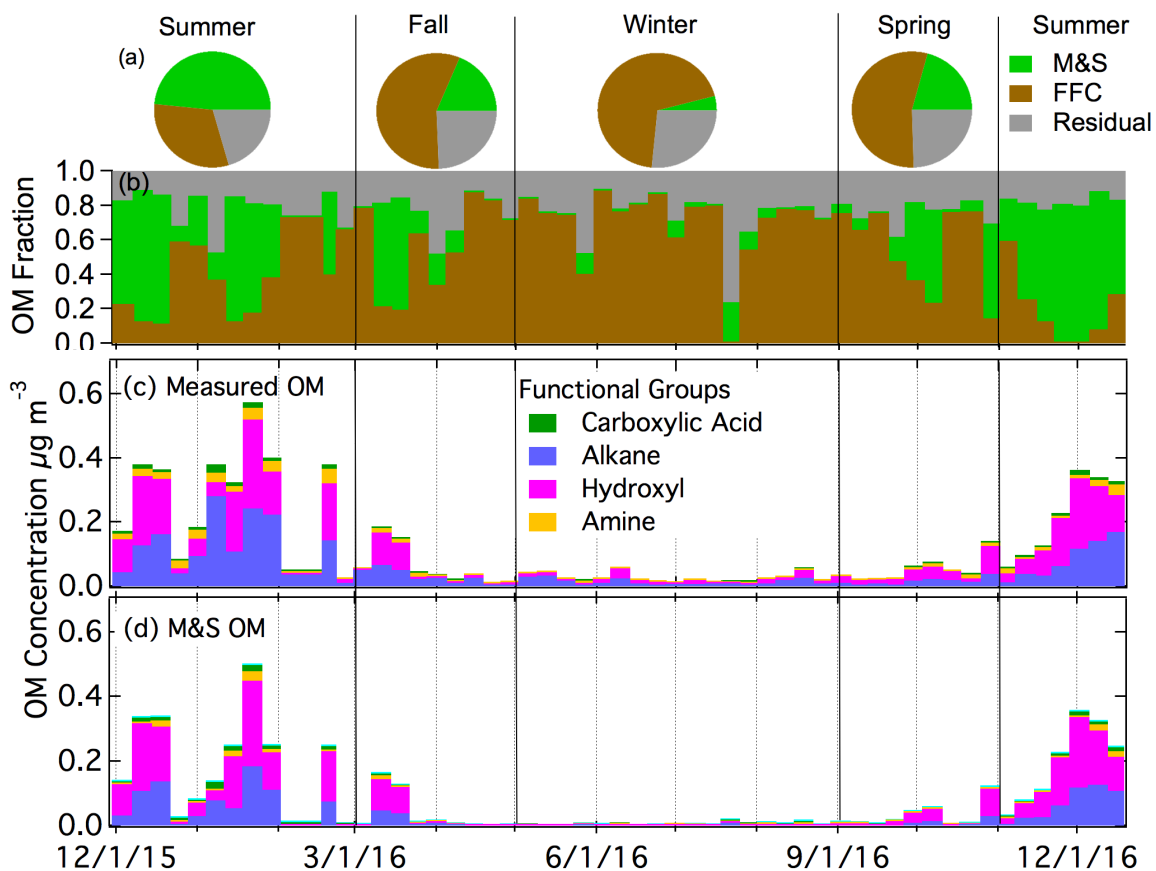
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Figure 3. (a) Mass fraction of PMF factors in four seasons. Time series of (b) PMF factor OM fractions, (c) OM concentration with functional groups and (d) M&S OM concentration with functional groups.

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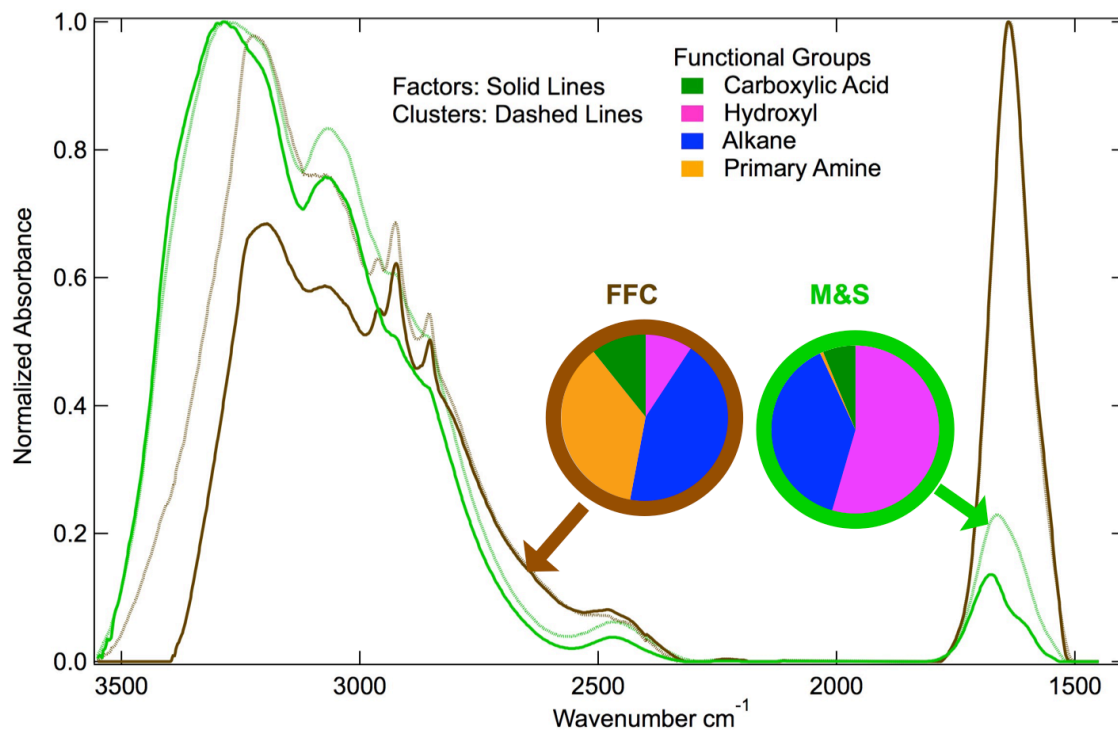Chemistry
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Figure 4. Normalized spectra from k-means clustering centroids and PMF factors. Functional group fractions of PMF factors are shown in the pie charts.
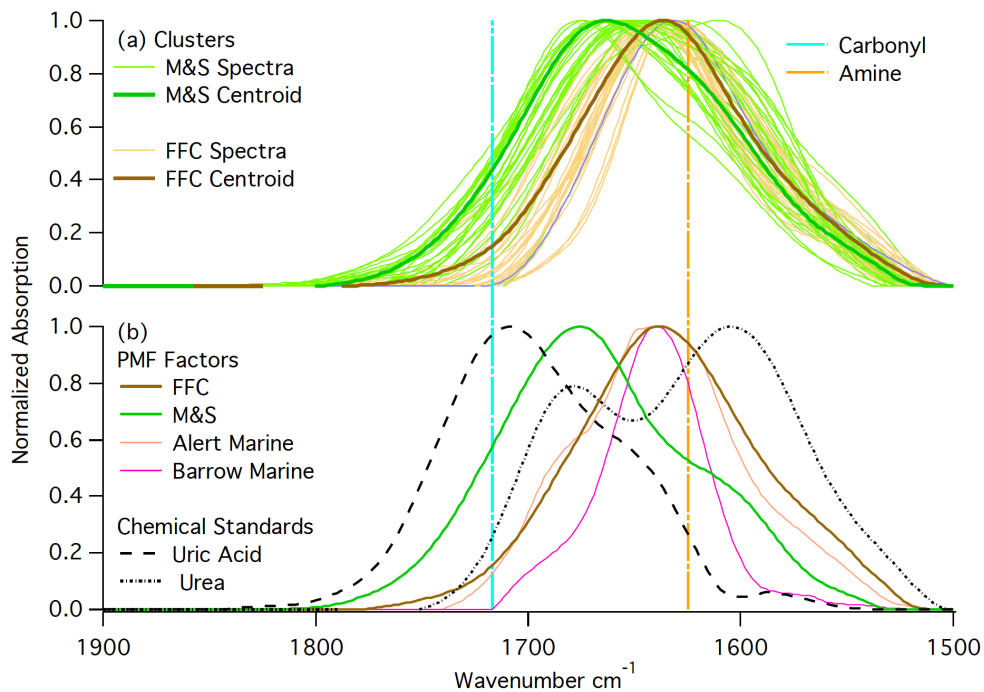
Figure 5. Normalized spectra at 1500 to 1800 cm^{-1} wavenumber region from (a) K-means clustering centroid and spectra in the clusters; (b) PMF factors from this study and two previous arctic studies, and chemical standards: urea and uric acid. Locations of primary amine and carbonyl group are marked on the figure.
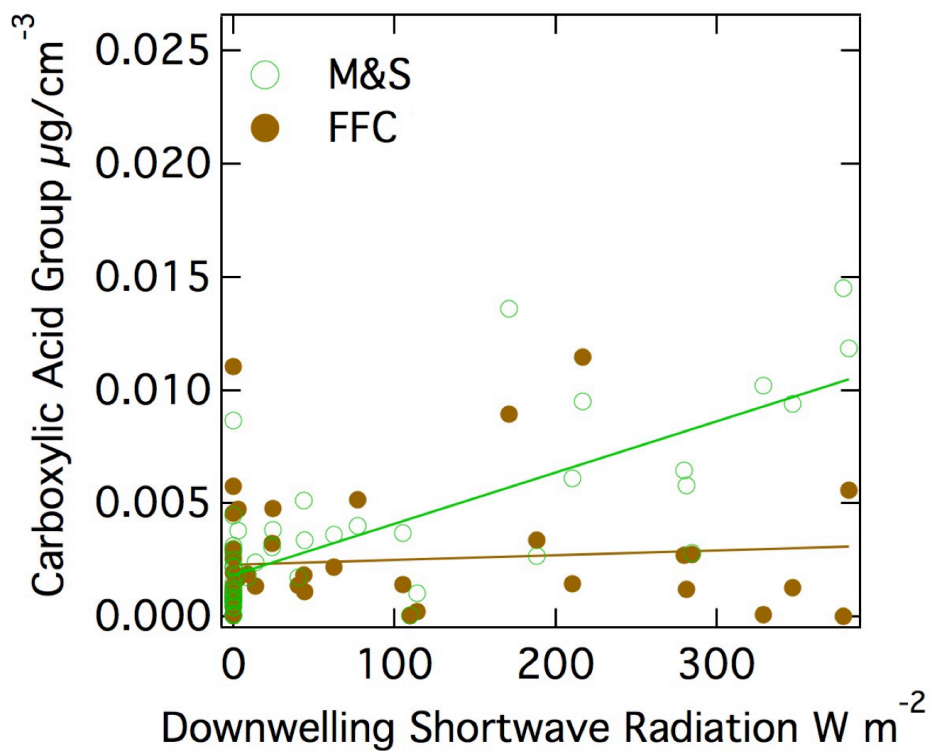
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Figure 6. Scatter plot of (a) M&S carboxylic acid group and shortwave downwelling radiation (r=0.75) and (b) carboxylic acid group in FFC and shortwave downwelling radiation (r=0.09)

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