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Key Points:

- Organic compounds make up only a small fraction of submicron sea spray particle mass over the remote oceans
- Regional seasonal cycles in sea spray organic mass fraction are mostly small in amplitude, indicating weak biological control
- Atmospheric aging can drive sea spray organic mass fractions significantly higher than in primary emitted sea spray

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:
M. J. Lawler,
michael.lawler@noaa.gov

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Author Contributions:
Conceptualization: Michael J. Lawler, Daniel M. Murphy
Formal analysis: Michael J. Lawler
Investigation: Michael J. Lawler, Gregory P. Schill, Charles A. Brock, Karl D. Froyd, Christina Williamson, Agnieszka Kupc, Daniel M. Murphy
Methodology: Michael J. Lawler, Gregory P. Schill, Charles A. Brock, Karl D. Froyd, Daniel M. Murphy
Project administration: Daniel M. Murphy
Software: Daniel M. Murphy
Supervision: Daniel M. Murphy

Sea Spray Aerosol Over the Remote Oceans Has Low Organic Content

Michael J. Lawler[1,2], **Gregory P. Schill**[1,2], **Charles A. Brock**[2], **Karl D. Froyd**[1,2], **Christina Williamson**[1,2,3,4], **Agnieszka Kupc**[1,2,5], **and Daniel M. Murphy**[2]

[1]University of Colorado, Boulder, Cooperative Institute for Environmental Science, Boulder, CO, USA, [2]NOAA Chemical Sciences Laboratory, Boulder, CO, USA, [3]Now at Finnish Meteorological Institute, Helsinki, Finland, [4]Now at University of Helsinki, Institute for Atmospheric and Earth System Research/Physics, Helsinki, Finland, [5]Now at University of Vienna, Aerosol Physics and Environmental Physics, Vienna, Austria

Abstract Biogenic organic compounds in the surface ocean may significantly alter the cloud-forming ability of sea spray aerosol and thereby affect the amount of solar radiation reaching the ocean surface. Estimates of the organic mass fraction of sea spray vary widely, and some results show a significant dependence on biological activity in the source seawater. We present airborne observations of the organic mass fraction of individual sea spray particles measured using the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument during the Atmospheric Tomography (ATom) mission, which sampled a wide range of latitudes and altitudes over the remote Atlantic and Pacific Oceans across four seasons, from the marine boundary layer to the upper troposphere. The measured sea spray particles of about 0.15–0.7 μm dry diameter showed higher average organic mass fractions at smaller sizes, but values were low overall, with regional integrated submicron means almost always <10%. Atmospheric aging adds organics to sea spray particles, leading to higher mean organic mass fractions (sometimes exceeding 50%) in the free troposphere than in the marine boundary layer. The average submicron sea spray organic mass fractions are on the low end of previously reported values and show weak seasonal variability for most regions. These results imply that recent biological activity in the surface ocean has only weak control over how much organic matter is in nascent submicron sea spray particles over the remote oceans, in contrast to findings from some observational studies and global numerical simulations.

Plain Language Summary The physical properties of particles found over the oceans are important to understand because marine particles interact with radiation both directly and by affecting the formation and lifetime of clouds. Both of these roles are important for the climate. Some studies show that biologically formed organic matter in the surface ocean can be a major component of sea spray particles formed at the ocean surface by wave breaking. If this is true broadly over the oceans, then biological cycles may control the climate-relevant properties of sea spray particles. However, measurements that can directly answer this question are limited. Here we report multi-season, size-dependent, ambient global-scale observations of particle composition in which only sea spray particles are considered. The results show that fresh sea spray particles over the remote oceans have relatively little organic matter, even in biologically productive seasons. This implies that surface ocean biology may have only a small role in governing the properties of fresh sea spray particles over most of the oceans.

1. Introduction: Organics in Sea Spray Aerosol

"Sea spray" aerosol refers to aerosol of any composition which was originally emitted to the atmosphere as primary droplets or particles from the ocean surface. Sea spray particles that are mainly NaCl have been traditionally referred to as "sea salt," and in previous literature the detection of inorganic sea salt ions in individual particles has been used operationally to classify the particles as sea salt (Bian et al., 2019; Murphy et al., 1998). "Organic" sea spray aerosol is discussed in the literature, but there exists some uncertainty about the precise meaning of the term. Recent results show that submicron sea spray particles considered "organic" in fact contain a significant amount of inorganic seawater cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.), sometimes showing enrichments in the divalent cations associated with marine gel particles (Ault et al., 2013; Chin et al., 1998; Gaston et al., 2011; Orellana & Leck, 2014). Such particles (or such organic inclusions on inorganic sea salt particles) lack sufficient Cl^- to form NaCl or other inorganic salt crystals and therefore do not exhibit angular

Visualization: Michael J. Lawler
Writing – original draft: Michael J. Lawler
Writing – review & editing: Gregory P. Schill, Charles A. Brock, Karl D. Froyd, Christina Williamson, Agnieszka Kupc, Daniel M. Murphy

sea salt morphology. A critical inference for the present study is that, given a single-particle composition measurement that has high sensitivity to saltwater cations, sea spray particles of any composition (even almost entirely organic) can be identified as sea spray particles and distinguished from aerosol particles from other sources. This means that "sea salt" as described in some previous single particle mass spectrometry work probably encompasses particles more accurately described as sea spray, that is, including "organic" sea spray. In this work, submicron particles containing sea salt cations will be referred to as sea spray, and further justification for this will be given in the text.

It has been known for decades that sea spray formed in wave breaking at the sea-air interface contains organic compounds as well as salt (Blanchard, 1964; Gantt & Meskhidze, 2013). The composition, physicochemical properties, atmospheric relevance, and controls on the presence of this material have been the subjects of many studies in the intervening time (Burrows et al., 2022; Collins et al., 2016; Prather et al., 2013; Quinn et al., 2014; Russell et al., 2023). Sea salt can be the dominant aerosol control on the radiative budget in the boundary layer in remote ocean regions (Murphy et al., 1998). Most of its direct effect is in supermicron particles, but submicron particles also play some role, and understanding their concentration and size is relevant for constraining their radiative forcing (Regayre et al., 2020).

The sea spray organic mass fraction (SSOMF), defined for a particle or collection of particles as the fraction of dry mass which consists of organic molecules, may in principle affect the cloud condensation nucleus (CCN) activity of fresh sea spray particles by modulating their diameter and/or hygroscopicity and thereby influence cloud radiative properties (O'Dowd et al., 2004). However, even relatively large changes in surface ocean biological activity appear to only modestly impact particle CCN activity (Mayer et al., 2020; Ovadnevaite, Ceburnis, et al., 2011). Surface ocean organics may actually have a greater effect on CCN concentrations by driving larger emission fluxes of sea spray (Alpert et al., 2015; Burrows et al., 2022; Christiansen et al., 2019; Dall'Osto et al., 2022; Sellegri et al., 2021). The factors controlling this process and also the number flux of CCN-relevant sub-0.5 μm diameter sea spray generally remain highly uncertain (Russell et al., 2023). Sparse measurements of SSOMF and of speciated sea spray organics further limit our understanding of these relationships.

The presence of even relatively small amounts of organic material on sea spray aerosol is also potentially important for oxidation chemistry over the oceans. Organics may be both a source and sink of radical species in aerosol, and hydrophobic compounds present in sea spray may in particular influence heterogeneous uptake and reactions involving gas phase molecules (Lawler et al., 2011; Stropoli et al., 2023; Wang et al., 2018; Zhou et al., 2008).

The organic content of ambient sea spray aerosol is difficult to quantify mainly because it is difficult to isolate primary (directly emitted) sea spray organics from other types of organic aerosol, especially ubiquitous secondary (atmosphere-formed) organics, which may be present on sea spray particles or as an externally mixed aerosol. Both primary marine organics and secondary organics are complex and incompletely understood (Ovadevaite, O'Dowd, et al., 2011; Rinaldi et al., 2010), and secondary organics can represent the majority of organic mass in marine air (Hoffman & Duce, 1977). Primary aerosol can be isolated by artificially generating sea spray using natural seawater, but it is hard to determine how representative such approaches are (Bates et al., 2020; Collins et al., 2014). Some analytical techniques with broad chemical sensitivity have some facility for separating out primary organics from ambient samples, but existing data sets either have very limited size-resolved information (Lewis et al., 2021; Russell et al., 2009) or use methods which have not been applied over wide swaths of the ocean (Facchini et al., 2008; Miyazaki et al., 2010), limiting our ability to draw broad conclusions.

Evidence regarding the importance of surface seawater biological activity on sea spray organic mass fraction can appear contradictory. Higher SSOMF has been linked to increased microbiological activity in the surface ocean or sample seawater (O'Dowd et al., 2004; Prather et al., 2013). But other studies have shown that high productivity and low productivity seawater yield similar SSOMFs in artificially generated sea spray aerosol (Quinn et al., 2014), and that a significant fraction of SSA organics are from a well-distributed pool of very old dissolved organic carbon (Beaupré et al., 2019). A multi-season survey of the North Atlantic (NAAMES mission) identified no clear seasonal dependence in major primary aerosol properties or the dominant primary sea spray organics (Bates et al., 2020), though one minor component (polysaccharides) did show a seasonal cycle (Lawler et al., 2020). Efforts to parameterize SSOMF range from relatively simple functions of surface seawater chlorophyll-a and sometimes wind (Gantt et al., 2011) to more recent global biogeochemical simulations that include ocean microphysical processes such as macromolecule formation and adsorption to entrained air bubbles (Burrows et al., 2022). The uncertainties on the controls of SSOMF lead to very different model parameterizations and results for CCN and radiative forcing (Zhao et al., 2021), and measurements to evaluate global-scale estimates are sparse.

Recent publications from our group explored the geographic distribution of sea spray aerosol in the MBL and in the free troposphere (Bian et al., 2019; Liu et al., 2021; Murphy et al., 2019). Here we report measured organic mass fractions of sea spray particles from the Atmospheric Tomography (ATom) mission, funded by the National Aeronautics and Space Administration (NASA) (Thompson et al., 2022), which vertically and latitudinally profiled the remote atmosphere over four seasons, from the marine boundary layer to the upper troposphere, using the same instrumentation and measurement platform. This data set avoids biases that arise from sampling in a specific location and in particular minimizes coastal sampling. These qualities make it a powerful data set to assess the global mean and seasonal characteristics of sea spray aerosol.

2. Materials and Methods

2.1. PALMS as Deployed During ATom

All particle composition data considered are from the Particle Analysis by Laser Mass Spectrometry (PALMS) single-particle instrument developed at NOAA (Murphy et al., 2006; Thomson et al., 2000). The instrument was rack-mounted in the main cabin of the NASA DC-8 aircraft and drew air from outside using the University of Hawaii aircraft inlet, as described in more detail elsewhere (Froyd et al., 2019). PALMS sampled ∼0.15–5 μm aerosol during the four ATom deployments: July-Aug 2016, Jan-Feb 2017, Sept-Oct 2017, and April-May 2018. Number fractions of particle types were reported, as were estimates of size-dependent atmospheric mass concentrations (Froyd et al., 2021). These results contributed to the development of size-dependent number concentrations of different aerosol types (Brock et al., 2021). In particular, size distributions from the NOAA ultra-high sensitivity aerosol spectrometer (UHSAS, Droplet Measurement Technologies) (Kupc et al., 2018), a Cloud, Aerosol and Precipitation Spectrometer (CAPS, Droplet Measurement Technologies) (Baumgardner et al., 2001), and a Laser Aerosol Spectrometer (LAS, TSI Inc., model 3340) (Brock et al., 2019) were combined with PALMS data to calculate sea spray number size distributions from about 0.15 to 10 μm diameter (termed "sea salt" in the archived data set). The aircraft performed vertical profiles from the marine boundary layer up to about 13 km altitude to sample the remote troposphere as broadly as possible. Further details of the ATom mission are available in the overview paper (Thompson et al., 2022).

2.2. Calibration of PALMS for Sea Spray Organic Mass Fractions

To calibrate the PALMS response to organics in sea spray aerosol, a series of calibration aerosols were sampled in the laboratory. For organic mass fraction quantification, an organic compound was mixed with artificial sea salt in ultrapure water and atomized using a medical nebulizer. The resulting aerosol was analyzed with PALMS, and the m/z 12 (C^+) and m/z 28 (CO^+) peaks were used for quantification because these showed the most consistent and strong signals across the different calibrants (see Text S1 and S2 in Supporting Information S1 for details). The calibrants were chosen to represent a range of molecular O:C and H:C ratios, to be soluble enough to generate aqueous solutions of practical concentrations, and to have low enough volatility that calibrant evaporation from the particles would be insignificant so that the sampled aerosol had the same organic:inorganic ratio as the bulk solutions. Having both high and low O:C ratio compounds is potentially important both because they may generate different characteristic ions and because they are likely to exhibit different phase separation behavior (You et al., 2013), which could affect the ionization process. The compounds used to develop the calibration include a compound with a short aliphatic chain (sodium hexanoate), an aromatic ring (phthalic acid), a non-gel-forming alginic acid analog (glucuronic acid), and a non-carboxylic acid (glucose). After developing the calibration curve, a calibration using azelaic acid was conducted because it is highly likely to phase separate from the inorganic salts (You et al., 2013). It showed consistent results, giving confidence that PALMS can efficiently sample organics that are mostly separated from the inorganic salts (e.g., on the particle surface like surfactants would be). A calibration with glycerol was also performed because it was used in the first PALMS paper to describe sea spray aerosol measurement in detail (Middlebrook et al., 1998), but we found that glycerol is too volatile to provide aerosol of known composition and we do not present results from it here. Results for precision and accuracy of the calibrations are presented in Figure S2 in Supporting Information S1.

Based on the calibrations, we found that PALMS has extremely high sensitivity to sea salt cations, such that sea spray particles which are as little as 1% sea salt and 99% organic compounds are identified as sea spray. This means it is very unlikely that highly organic sea spray particles are missed in the present analysis. As a further check on the possibility of misidentified "pure organic" sea spray particles, a simple statistical analysis was performed to show that there is no evidence for a source of such particles from the ATom data for the particle sizes detectable by PALMS (See Text S5 and Table S2 in Supporting Information S1).

We relied on positive ion mode for SSOMF quantification because the salt cations detected in positive mode provide definite identification of sea salt and, unlike chloride, they cannot be volatilized by atmospheric processing. We also found that the detection limit and precision are significantly better in positive ion mode. However, because the negative ion data may show different sensitivity to different types of ambient organic compounds or particle phase states, we calculated calibration curves based on combined results for glucose and sodium hexanoate standards and compared the distributions of ambient ATom results with those of the calibration particles. In negative ion mode for both calibration species, particles with SSOMF >25% were generally distinguishable from particles with <25% SSOMF. Therefore the ambient number fractions of those two groups of particles were compared with those in positive ion mode. No large or systematic differences were identified between the ion modes. In addition, the distribution of SSOMF values measured for calibration particles at each calibration SSOMF can be used to compare with the distribution of values measured in a given region or season. These comparisons showed that the central values of the ambient distributions in negative ion mode were similar to those quantified using the positive ion data.

2.3. Calculation of Aerosol Distribution Properties and Submicron Totals

The sampling efficiency of PALMS is a function of aerosol transmission through the sampling and focusing inlet, and of particle light scattering, meaning that different particle sizes have different sampling efficiencies (Froyd et al., 2019). To quantify ambient size-dependent concentrations and size-integrated concentrations, it is necessary to derive the size distribution of sea spray aerosol. This was done for ATom by size-binning the number fraction of PALMS sea spray particles and mapping these to ambient total size distributions (Brock et al., 2021). This product (termed "sea salt" aerosol size distribution in the archive) is fairly well-constrained at the large size range where sea spray dominates in the MBL and at the low end where secondary particles dominate. We applied a correction to improve the sea spray size distributions in the midrange (See Figure S8 in Supporting Information S1). This had only a minor impact on the derived integrated quantities. To calculate total submicron organic mass and SSOMF for different regions, the regional SSOMF versus diameter relationships were extrapolated to 1 μm diameter using fits to the data. This was done on the basis that SSOMF showed weak diameter dependence and that all previous studies we are aware of show a decrease in SSOMF with diameter in the diameter range examined here. Exponential fits were preferred, but sometimes linear fits to the data were used.

2.4. Marine Boundary Layer (MBL) Height Determination

The marine boundary layer (MBL) height was determined by a manual inspection of individual vertical profiles of atmospheric composition, temperature, and relative humidity and is the same as that used in previous ATom work (Brock et al., 2021).

2.5. Exclusion of Pollution Plumes

To reduce any possible influence of anthropogenic pollution plumes on the results, particles were excluded if sampled in air with carbon monoxide (CO) concentrations exceeding 170 parts per billion (ppb). CO was measured with two instruments, a commercial cavity ring down spectrometer (Picarro G2401) and a quantum cascade laser spectrometer (custom built, Harvard University). Both were used to avoid removing particles due to gaps in CO data. This criterion removed less than 1% of the data and does not change any qualitative patterns but slightly tightens the scatter for some SSOMF versus diameter plots.

Table 1
Statistical Overview of Sea Spray Particle Sampling

	All			<0.5 μm		
	N_{SS}	N_{quant}	F_{quant}	N_{SS}	N_{quant}	F_{quant}
ATom1	16,175	4,661	0.29	6,567	3,413	0.52
ATom2	44,980	4,991	0.11	7,691	4,314	0.56
ATom3	52,379	5,832	0.11	12,059	5,031	0.42
ATom4	34,217	14,965	0.44	16,094	9,701	0.60

Note. N_{SS} is the total number of sea spray particles identified and sized by PALMS. N_{quant} is the number of sea spray particles for which an organic mass fraction could be quantified with good precision, and F_{quant} is the fraction such particles represent of all sea spray particles, presented for all and for <0.5 μm dry diameter sea spray particles.

3. Results

3.1. Overview of Results

For each of the four ATom deployments of the highly instrumented NASA DC-8 aircraft, between 4,661 and 14,965 sea spray particles over remote ocean regions were quantified for their organic mass fraction (see Table 1). This represents about 9%–41% of the total sea spray particles detected using PALMS. The largest portion of the non-quantified sea spray particles are at large particle diameters, where total ion current begins to drop sharply with increasing diameter and the organic mass calibration no longer applies (see Text S1 and Figure S7 in Supporting Information S1). For most deployments at least half of the detected sub-0.5 μm dry diameter particles were quantified. Most of these particles were encountered in the marine boundary layer (MBL), though the flight time in the MBL was a small fraction of the total flight hours. Most of the unquantified sub-0.5 μm dry diameter particles were excluded because they generated a mass spectrum type with low dynamic range for organics (see Text S1 in Supporting Information S1). No systematic biases for location, altitude, or particle density could be identified between the quantified and non-quantified particles. The most likely explanation for the difference is insufficient laser intensity for the low-dynamic-range particles due to variability in the particle trajectories in the instrument (i.e., the particles missed the middle of the laser beam).

3.2. Sea Spray Organic Mass Fraction (SSOMF) Versus Particle Diameter

Over the range of analyzed 0.15–0.7 μm dry diameter sea spray particles, smaller particles had on average higher organic mass fractions than larger particles, consistent with theoretical expectations and previous results (Facchini et al., 2008; Oppo et al., 1999). This was broadly true across marine regions and seasons. The regional seasonal averages of SSOMF in marine boundary layer sea spray particles are plotted alongside the sampling locations (Figure 1). The results are separated into "fresh" particles for which secondary non-sea-salt (nss-)sulfate could not be detected (See Text S3), and all quantified particles, which includes particles which have clearly been modified ("aged") in the atmosphere by the addition of sulfate. This modification could have resulted from either naturally formed compounds (e.g., sulfate from dimethylsulfide oxidation), anthropogenic compounds, or a combination. For the Tropics and Extratropical South regions, many sub-regions with similar patterns were combined for clarity and improved statistics (see Table S1 and Figure S1 in Supporting Information S1). The size dependence of SSOMF was modest in most regions and seasons, and it was flattest in the tropics. Only two regions demonstrated a clear seasonal cycle: the Arctic and the Extratropical South. In both cases, the highest SSOMF values were during summer for that hemisphere, and the contribution of secondary organics was significant but not dominant. The summertime Arctic showed the highest SSOMF of any region in any season.

The size-dependent SSOMF distribution for the combined all-ATom data set is presented in Figure 2, again separated into fresh and all particles. The presented data include particles between 0.2 and 0.6 μm dry diameter. The range of quantified particles extends further, but the chosen range is well-represented by all four flight missions, is encompassed by the calibration aerosol diameters, and avoids biases associated with the smallest detectable sizes (See Text S4 in Supporting Information S1). The decrease in mean SSOMF with size is weak over this range for fresh particles. All sizes have mean SSOMF below 10%, with very few particles exceeding 80%. Median values were always less than 5% and sometimes at the detection limit (1%–2%). When particles with aging markers are included, the SSOMF distributions at the smaller sizes shift to larger values, and there is a mode of aged particles with SSOMF >80%. At diameters greater than 0.4 μm, this mode is less apparent, presumably due to the much greater secondary mass needed to alter the composition of larger particles. The mean fresh data were well-fit by an exponential function:

$$\mathrm{SSOMF} = 0.045 + 0.258e^{-8.55\bullet D} \tag{1}$$

where D is the dry particle diameter in μm. This represents our best single estimate of mean size-dependent sea spray emission organic mass fractions over the remote oceans. Extrapolating the relationship to 1 μm, this would correspond to an integrated submicron SSOMF of about 4.6% and sea spray organic mass concentration of

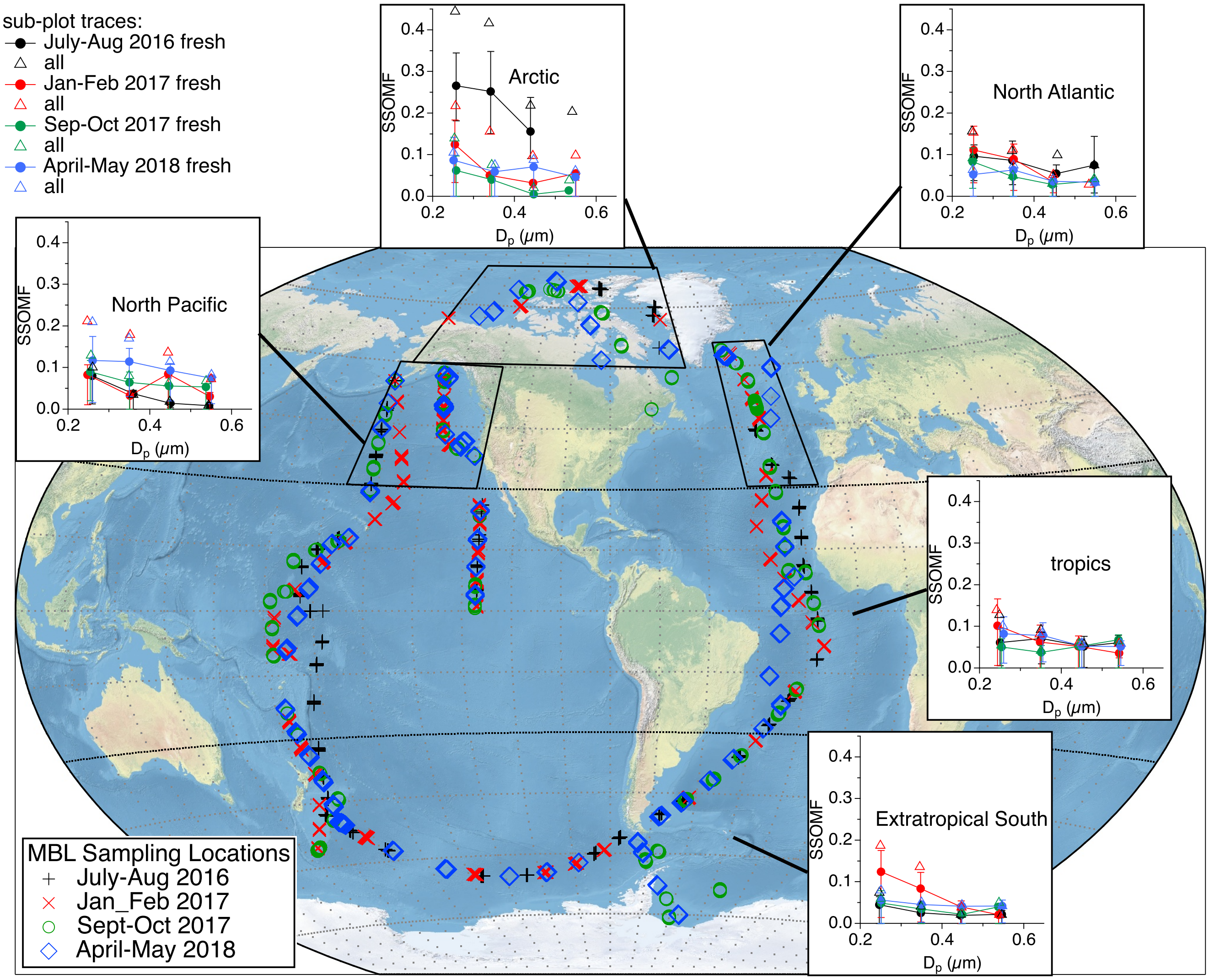

Figure 1. Sea spray organic mass fraction (SSOMF) versus dry diameter for sea spray particles in the marine boundary layer across the multi-season ATom missions. Particles are binned by size (0.1 μm width bins from 0.2 to 0.6 μm) and grouped into broad regions with similar SSOMF patterns. For fresh sea spray particles, regional means are plotted as solid circles with 75th and 25th quartiles as vertical bars. Means for all quantified sea spray particles (including aged) are plotted as open triangles. Colors indicate the mission dates per legend. Symbols plotted directly on the map represent the sampling locations in the MBL. MBL sampling periods depicted here were typically 7–10 min.

0.1 μg m^{-3} for ATom-mean MBL sea spray particle number size distributions. The seasonal and regional variability in these values is presented in Figures 3a and 3c. There is the potential that the SSOMF may increase significantly at smaller sizes. However, smaller particles are not very important for integrated or bulk (e.g., total submicron) measurements because they contribute an insignificant amount of mass under most conditions (see Figure S10 in Supporting Information S1).

3.3. Role of Aging

Atmospheric aging can drive large increases in the organic content of sea spray aerosol (Figures 2 and 3d). Sea spray particles with secondary sulfate are much more likely to have high organic mass fractions. This is true for particles in the MBL as well as in the free troposphere. Fresh sea spray particles with organic mass fractions above ~50% are exceedingly rare in this remote atmosphere data set, but among the population of aged sea spray, they are not uncommon. In the MBL about 5%–15% of the 0.2–0.6 μm sea spray particles are aged by our criterion, and in the free troposphere this value is closer to 30%–40%. As sea spray aerosol gains sulfate and nitrate from atmospheric aging, HCl is driven off from the particles (Keene et al., 1998). Note that no attempt has been made to

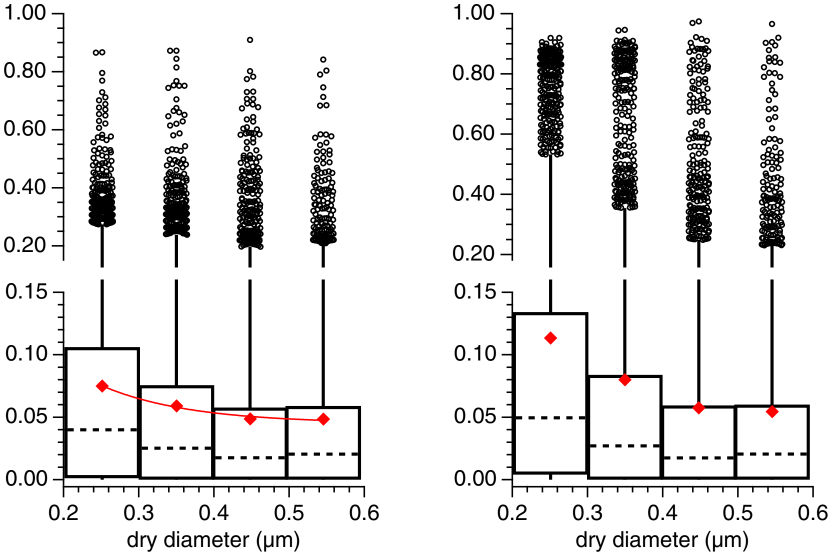

Figure 2. All-ATom mean sea spray organic mass fraction (SSOMF) as a function of dry particle diameter, for (a.) "fresh" sea spray (no detectable non-sea-salt sulfate) in the marine boundary layer (MBL) and for (b.) all MBL sea spray particles. Data are binned into 0.1 μm-wide bins from 0.2 to 0.6 μm, and each binned box plot represents at least 2500 particles. The median for each bin is plotted as a dashed line and the mean as a red diamond, with the box top and bottom representing the 75th and 25th percentiles. Medians and 25th percentiles are sometimes below the detection limit (<1% SSOMF). Whiskers encompass 95% of the data, and outliers beyond that are plotted as open circles. An exponential fit to the means for the fresh particles is included and its equation reported in the main text. Two linear scales are used for each plot to preserve features at small SSOMF values.

correct the organic mass fractions for the replacement of chloride by sulfate or nitrate during aging. This means that the SSOMF reported for aged particles may be overestimated. This has the benefit however that the reported values may be more directly compared to SSOMF inferred from ambient bulk measurements of organic matter and sodium mass.

It is important to establish that the higher SSOMF values observed in aged particles are mainly due to organics being added in the atmosphere and not simply a result of rapid aging of most fresh particles with high SSOMF. Several pieces of evidence support this. Mean SSOMF increases with altitude, consistent with more aging time causing more additional secondary organics on the sea spray particles (Figure 4). This is probably not caused by preferential loss of saltier particles to wet deposition, as fresh particles reach the free troposphere with almost the same SSOMF distribution as fresh particles in the MBL (Figure 3d). That the SSOMF distributions of fresh and aged particles look the same whether within the MBL or without suggests that sea spray does not always undergo significant aging on the timescale of escaping the MBL (Figure 3d). Finally, fresh high SSOMF and fresh low SSOMF particles are sampled from an almost identical size distribution (Figure S9a in Supporting Information S1), consistent with their formation via the same process (bubble bursting at the sea surface); aged high SSOMF particles come from a different distribution of particle sizes, one which we infer has been influenced by atmospheric aging (Figure S9b in Supporting Information S1). Cloud droplet collision-coalescence could contribute to the shape of the aged particle size distribution (Hoffmann & Feingold, 2023), and cloud processing likely adds significantly to the organics in aged marine particles (Ervens et al., 2018).

4. Discussion

4.1. Comparison With Previous Observations

For comparison with previous results from ambient observations and artificial sea spray generation, we focus on SSOMF. This intrinsic aerosol property is not directly proportional to the total ambient concentrations of sea spray aerosol. This makes it easier to compare with other measurements than for example, total primary organics concentrations, which can have high variability due to short-term variability in sea spray sources and sinks. For the ATom results, the integrated submicron SSOMF values do depend on the relative ambient concentrations of

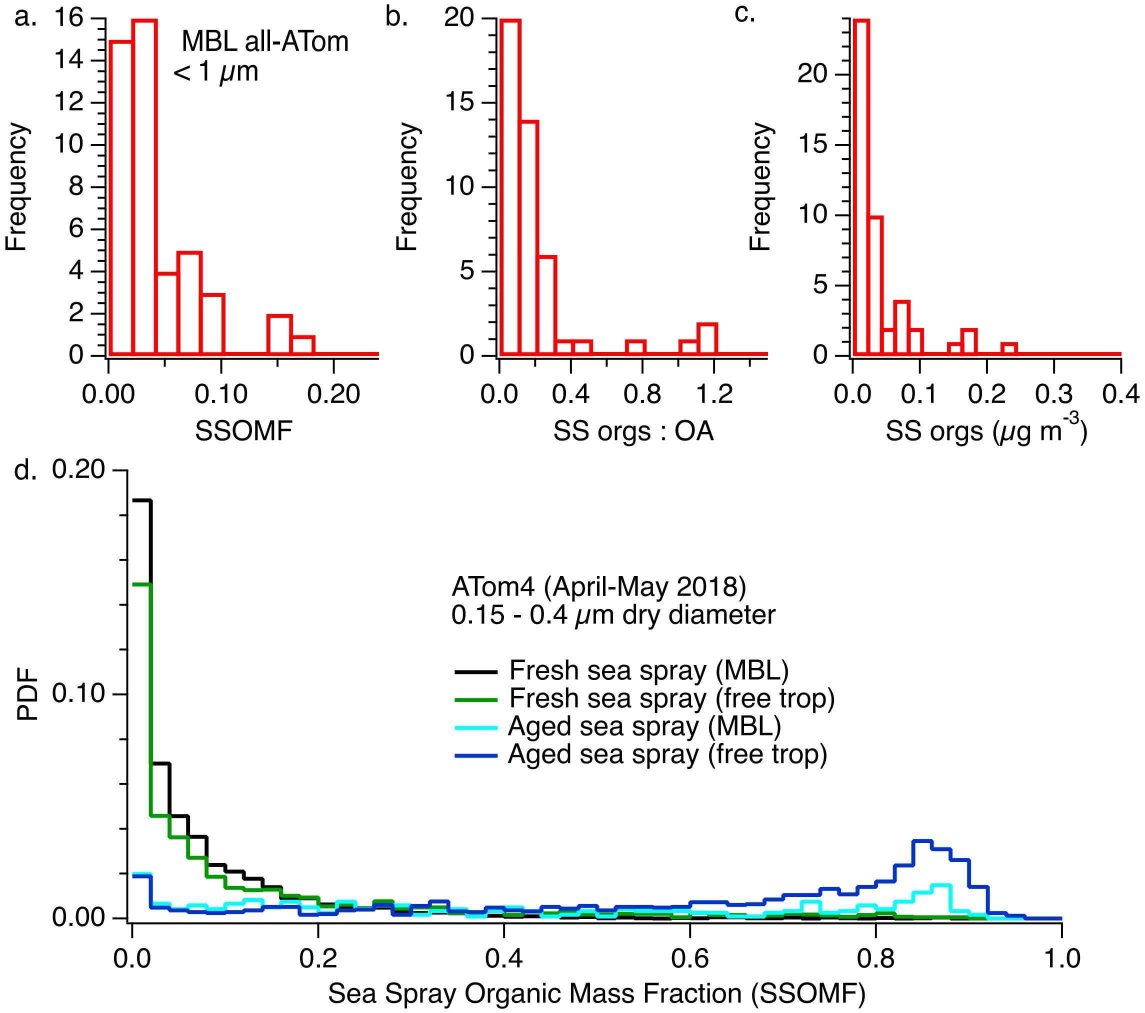

Figure 3. Frequency distributions of the abundance of sea spray organics. For a-c., Frequency distributions for all quantifiable sea spray particles measured in the marine boundary layer during ATom. The data are grouped into averages by sub-regions (see Figure S1 and Table S1 in Supporting Information S1) and seasons, and the measured SSOMF was extrapolated to 1 μm diameter and converted to mass using the average sea spray size distribution for that season and sub-region. (a) Sea spray organic mass fraction (SSOMF). (b) Ratio of organics present on sea spray particles to organic aerosol derived from PALMS sulfate-organic particles. (c) Sea spray organic mass concentrations in air. (d) Probability distribution functions for SSOMF during all ATom 4 flights (April-May 2018), separated by interception above and within the MBL, and for aged (nss-sulfate detected) and fresh particles.

different sizes of sea spray particles, but the shape of these size distributions is much less variable than their amplitude.

Figure 5 presents a comparison of the present results with previous reports of sea spray organic mass fractions from both ambient observations and artificially generated sea spray. The size-resolved results are segregated into two main bands, one with SSOMF >40% at 0.4 μm diameter and one with SSOMF <10% at that diameter. The ATom results fall within the lower SSOMF band. They are quite consistent with the “low biological activity” period average reported in O’Dowd et al. (2004) from ambient Mace Head observations, with the Barker and Zeitlin (1972) results from Hawaii, and with two wave channel mesocosm studies using coastal California water (Kaluarachchi et al., 2022; Lee et al., 2020). The “high biological activity” period from the O’Dowd paper is roughly at the 99.5th percentile of observed fresh MBL values from the present study. Similarly high values were reported from other waters in the North Atlantic near Ireland, from both artificial bubble bursting and ambient observations (Facchini et al., 2008). Such conditions may be representative of the sampled areas relatively near the Irish coast at some times, but they do not appear to be representative of the whole North Atlantic or of the

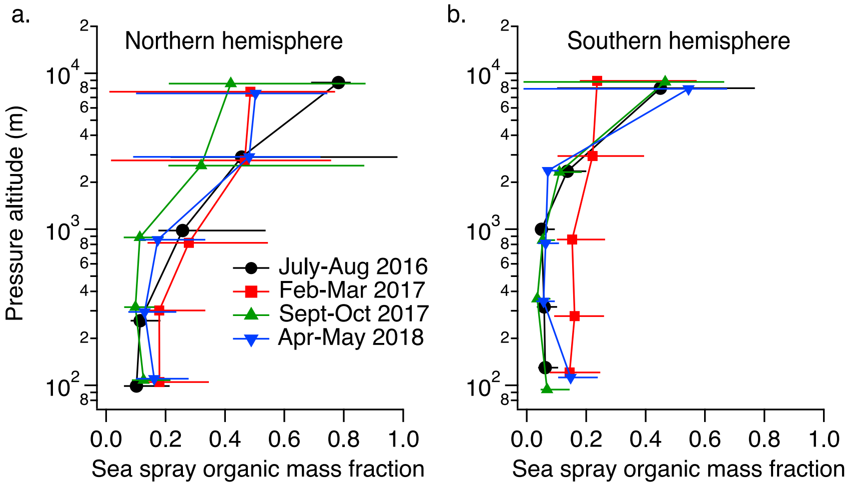

Figure 4. Vertical profiles of the organic mass fraction of 0.15–0.4 μm dry diameter sea spray particles over the northern hemisphere, binned by altitude. The means and 25%–75% quartiles are plotted for each seasonal mission. A logarithmic altitude scale was used to improve resolution in the lower atmosphere. (a) Northern hemisphere. (b) Southern hemisphere.

global oceans broadly. Bubbling of coastal Bermuda water showed similarly high results (Keene et al., 2007). However, later shipboard measurements using an improved version of the same technique showed SSOMF more in line with the lower SSOMF band (Keene et al., 2017). The authors note that bubble rafting in the older bubbler design and potentially coastal sources of surfactant organic matter may have contributed to the much higher SSOMF measured in the earlier study.

The in situ bubbling results from two ocean basins largely in coastal waters (Quinn et al., 2014) are about a factor of 3 greater than the global mean from the present integrated submicron results. This difference from the ATom results may at least partly be explained by the underproduction of larger, saltier sea spray by the in situ bubbling approach (Bates et al., 2020). This could lead to a factor of 2–3 overestimate of SSOMF (Figure S10 in Supporting Information S1). Finer size-resolved SSOMF measurements of the bubbling-generated particles could help resolve this question. The present results also have about a factor of 2 uncertainty at the low SSOMF values typically measured, based on the calibrations (Figure S2 in Supporting Information S1).

The seasonal pattern of the Extratropical South SSOMF for particles <0.4 μm (Figure 1) resembles that reported for water-insoluble organic carbon concentrations in bulk ambient aerosol at Amsterdam Island, where the values in austral summer were a factor of 3 or so greater than during the rest of the year (Sciare et al., 2009). Unfortunately sea salt concentrations were not reported in that study, so SSOMF cannot be calculated. Also, the Amsterdam Island sampling included particles up to 10 μm in diameter, meaning the seasonal variability reported may be controlled by supermicron particles, which were not quantified for SSOMF in this study. Data from Mace Head, Ireland, show a very strong seasonal cycle in water-insoluble organic matter (shown to be mainly primary sea spray organics at this site), with mean submicron SSOMF approaching 50% during the spring and summer, about five times higher than the lowest value measured in January (Meskhidze et al., 2011; Yoon et al., 2007; as represented in Zhao et al., 2021). In contrast, the present data set over the remote North Atlantic shows uniformly lower SSOMF (below about 10%, Figure 1). There is evidence for a modest summer maximum. This seasonal pattern is similar to the late summer maximum SSOMF observed for artificially generated sea spray during NAAMES (see Figure S11). However, the ambient marine primary organic aerosol concentrations during NAAMES did not show a summer maximum (Lewis et al., 2021). It is worth noting that NAAMES did not sample during the months of highest model-predicted SSOMF, as pointed out in Burrows et al. (2022). Amsterdam Island is volcanic in origin and lacks a continental margin, and it therefore has low influence from coastal biological activity, while Mace Head is situated next to a broad, biologically active continental shelf (Raine & McMahon, 1998). This could be a reason why Amsterdam Island would be more representative of patterns in the surrounding remote ocean. Researchers at Mace Head have taken pains to show that organic marine aerosol

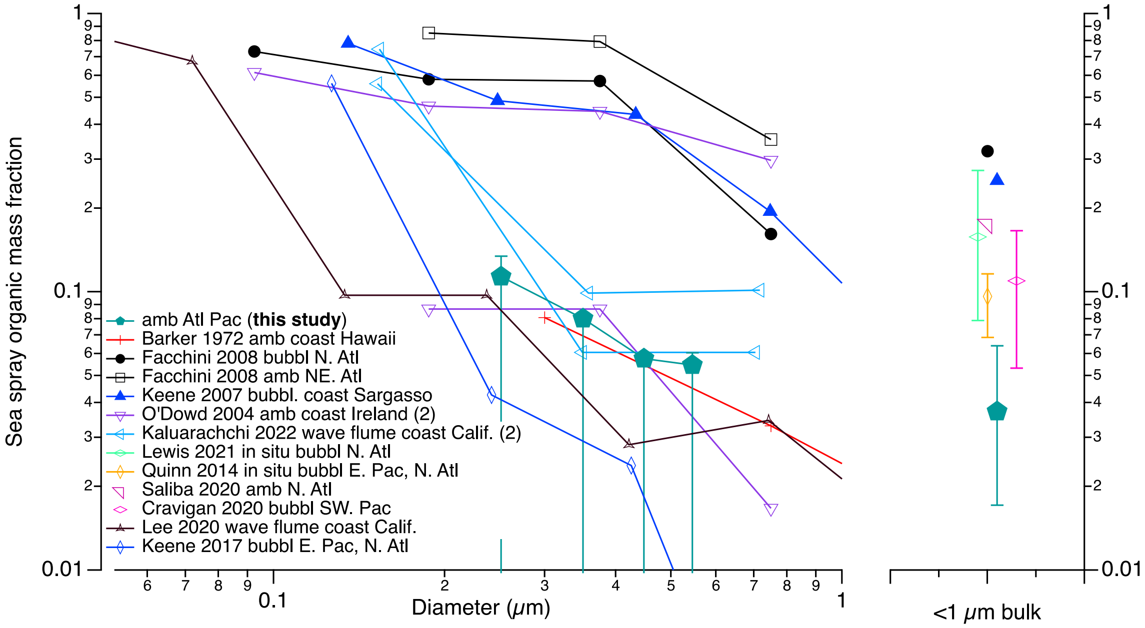

Figure 5. Comparison of the present sea spray organic mass fraction results with previous studies (Barker & Zeitlin, 1972; Facchini et al., 2008; Kaluarachchi et al., 2022; Keene et al., 2007, 2017; Lee et al., 2020; Lewis et al., 2021; CD O'Dowd et al., 2004; Quinn et al., 2014; Saliba et al., 2020; T. Cravigan et al., 2020). Studies with size-dependent data are plotted on the left axes, and integrated or bulk sub-1.0 or sub-1.1 μm data are plotted on the right axes. Solid markers are used for data sets which appear on both sets of axes. Error bars are omitted from most traces for clarity (and sometimes lack of reporting). There are two traces for O'Dowd et al. (2004), high and low periods, and for Kaluarachchi et al. (2022), pre- and peak-bloom, with below-detection points estimated as half the smallest detected values. The size-resolved Keene et al. (2017) data are an average of all bubbling measurements. For the bulk data, the Lewis et al. (2021) results are reported as mean of four seasonal averages with error bars showing the range of data within reported standard deviations. The Quinn et al. (2014) data are reported as the mean of 4 reported mean SSOMF values and error bars show the range of the means. Their reported organic carbon mass fractions were converted to organic mass assuming a 2:1 OM:OC ratio after Frossard et al. (2014). Ratios to Na^+ were converted to ratios to sea salt assuming Na^+:seasalt = 0.305 (Seinfeld & Pandis, 2016). For the present study, the mean and 25%–75% quartiles of the regionally and seasonally averaged MBL data are reported for bulk data, and the size-dependent points are means of all MBL data with 25%–75% quartiles (same as Figure 2b.). Particles with aging markers were not excluded. For ambient impactor-collected samples, only likely primary organics are included. The exception is Barker and Zeitlin (1972), which had no way to isolate primary organics. Based on the present results, we assumed conservatively that half the collected organic mass in that study was secondary. In the legend, ambient studies are marked "amb," artificial bubbling in a lab setting is marked "bubbl," in situ bubbling using Sea Sweep (Bates et al., 2012) is marked "in situ bubbl," and artificial wave breaking is marked "wave flume." Seawater source locations are also indicated.

measured there is not strictly a coastal feature (O'Dowd et al., 2014). Another possibility is that the strong Arctic air influence at Mace Head (Cavalli et al., 2004) contributes to very high SSOMF values in ambient aerosol.

4.2. The Relationship of Ocean Biological Cycles and Sea Spray Organics

Relatively little seasonal variability was observed in this data set, suggesting that seasonal changes in irradiation and biological productivity do not drive strong changes in primary sea spray organics in submicron aerosol over basin-scale ocean regions. The Arctic data are the greatest exception to that conclusion, as they show a significant summertime SSOMF maximum at all measured sizes. That the Arctic should show high SSOMF is somewhat expected based on our existing understanding of regional differences in organic sea spray generation (Burrows et al., 2022). However, this result could indicate one of two things: that the summertime Arctic is a rather unique marine region with significant biogenic primary organic production associated with sea ice algae, as has been suggested by previous results in the Arctic (Bigg & Leck, 2008; Kirpes et al., 2019; Leck & Bigg, 2005), or it may highlight how different near-coast observations can be from open ocean measurements. Given the limited summertime Arctic MBL sampling locations from ATom, all either in the Canadian Arctic or near Greenland (Figure 1), it is difficult to conclude which is the cause on these basis of these data. In any case the increase in open water and sunlight during the summer are likely important in driving this seasonal cycle. The Extratropical South also showed a clear summer maximum in the smallest measured sizes, but not at the larger >0.4 μm sizes that dominate the submicron mass. In both cases, aged sea spray aerosol had significantly higher SSOMF, suggesting the production of aerosol precursor gases was also significant in summer, consistent with biogenic and/or photochemical sources.

4.3. Relevance to Cloud Condensation Nucleus (CCN) Concentrations and Light Scattering

As discussed in the introduction, sea spray particles with a wide variety of organic mass fractions appear to activate efficiently into droplets, so any influences on CCN from surface ocean organics are expected to result from changes in the emission flux of sea spray. Unfortunately, most CCN have smaller diameters than PALMS can detect efficiently, making it difficult to directly constrain the impact of seasonal biological cycles on remote ocean CCN on the basis of this study. However, our results are more consistent with studies that show there is not a large seasonal impact on CCN from biogenic sea surface organics. The multi-season NAAMES study sought such a relationship in the North Atlantic and did not identify one (Bates et al., 2020). The submicron SSOMF measured for in situ bubbling generated sea spray in that study was reasonably similar to the present results (Figure 5). During the high biological activity period at Mace Head, when SSOMF of 0.25–0.5 μm aerosol was about 45% (assuming all water-insoluble organic carbon was primary marine), the authors estimated an increase in cloud droplet number concentration of 15%–29% relative to organics-free cases. Such high SSOMF values are outliers in the ATom data set (Figure 2). Global scale models also show modest impacts on CCN when SSOMF reaches higher levels (Zhao et al., 2021). However, while the current model formulations are able to approximate the seasonal cycle at Mace Head, they are at odds with the generally lower, less variable SSOMF observed from in situ bubbling-generated sea spray and from the ambient measurements presented here. In any case, there remains very large uncertainty about the controls on emission and composition of sea spray smaller than 0.2 μm diameter, which is of the greatest importance for CCN concentrations.

The relatively low SSOMF found in this study over the remote oceans implies a very small average impact of primary sea spray organics on light scattering by sea spray aerosol. Previous work shows relatively low hygroscopic growth factors of roughly 1.2 for sea spray organics (Forestieri et al., 2016; Ovadnevaite, Ceburnis, et al., 2011), but the roughly 5% SSOMF values reported here nonetheless correspond to only about a 2% decrease in aerosol scattering coefficient and optical depth due to reduced water uptake. Most light scattering by aerosol over the remote oceans is due to supermicron sea salt (Murphy et al., 1998), which can be expected to contain even lower fractions of organic matter. The presence of organics in particles which have not been activated into droplets can reduce water uptake, opening the possibility that very small amounts of surface-active organic matter could have a significant effect (Ovadnevaite, Ceburnis, et al., 2011). However, a recent study of internally mixed aerosol of sea salt, soluble organics, and surfactants showed that even with surfactants at 5% of the sea salt mass, the decrease of the growth factor is quite small (Bramblett & Frossard, 2022). The measured SSOMF of a few percent is unlikely to represent only very strong surfactants such as those considered in that study because the bulk of sea spray organics are fairly highly oxygenated with polar hydroxyl groups (Bates et al., 2012; Russell et al., 2010) and sea spray organics exhibit water uptake characteristics distinct from surfactants (Ovadevaite, O'Dowd, et al., 2011; Ovadnevaite, Ceburnis, et al., 2011). Therefore we think it is most likely that the average influence of primary sea spray organics on hygroscopic growth and the direct radiative effect over the remote oceans is small.

5. Conclusions

Sea spray particles in the size range of 0.15–0.7 μm dry diameter were analyzed for their organic mass fractions from observations that span essentially all latitudes over the Atlantic and Pacific Oceans, as well as the Arctic and Southern Oceans, from the marine boundary layer to about 10 km altitude. Submicron SSOMF in the MBL was less than 10% in most regions and seasons. While atmospherically aged particles smaller than 0.4 μm often have organic mass fractions greater than 50%, such high values are very rare for fresh sea spray particles that only contain primary organics. The results indicate that strong, biogenically driven seasonal cycles in the organic fraction of fresh sea spray particles are not typical of the remote oceans. Further work is needed to clarify the controls on sub-0.2 μm sea spray production, as well as to assess and improve the agreement between the submicron sea spray organic mass fractions measured in the remote MBL and those predicted by numerical models.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Combined aerosol size-dependent composition and properties data are reported in Brock et al. (2021). Single-particle type number fractions, mass concentrations, and all individual particle spectra are available in Froyd et al. (2021). Carbon monoxide data from the two instruments are found in McKain and Sweeney (2021) and Commane et al. (2021).

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