

Fig. 1. The study region and a schematic of the hypothesized OVOC formation and effects. (A) Polar projected map showing the Central Arctic Ocean, the Canadian Archipelago, and northern Greenland. The surface waters carrying terrestrial dissolved organic matter to Nares Strait are represented schematically in brown (40, 41). The land type data are taken from the Olson Land Map (https://lta.cr.usgs.gov/GLCC/globe_int) and the sea ice data from the NSIDC (<https://nsidc.org/data/NSIDC-0051>) for August 1, 2014. The yellow star highlights the location (Nares Strait) where we observed the maximum oceanic source of OVOCs. (B) A schematic of the proposed OVOC generation mechanisms (A, photochemical; B, heterogeneous oxidation by O_3 or OH, potentially followed by gas-phase OH oxidation) at the study site. (C) Representative FLEXPART potential emissions sensitivity (PES) plot (7-d backward run, released at 23:02 Coordinated Universal Time, August 6, 2014) showing the strong local marine influence with high residence times in Nares Strait and Baffin Bay.

Recent laboratory studies (17, 26–31) have uncovered novel mechanisms for the emission of OVOCs to the MBL involving chemistry at the interface between the ocean and atmosphere, where the sea surface microlayer (SML) can be enriched in organic matter. The thickness of the SML is typically about 50 μm (32), and substantial SML enrichments (relative to underlying bulk seawater) in surfactants, saccharides, and plankton exudates have been observed globally in both eutrophic and oligotrophic waters (e.g., ref. 33). Although SML chemical composition is complex and not fully understood, it contains both saturated and unsaturated fatty acids (32, 34, 35). Gas-phase production of smaller and more oxygenated molecules from these model SML constituents can occur via three different mechanisms: direct photooxidation (17, 26), photosensitized oxidation (27, 28, 31), or heterogeneous oxidation (29). Thus, OVOCs can be produced from the SML in the presence of light with or without the action of photosensitizers, or in the presence of gas-phase oxidants such as ozone or the hydroxyl radical. Given the widespread global coverage of organic matter enrichment in the SML (33) and the apparent ease of OVOC production from individual SML components, this mechanism is a likely candidate for the missing source of marine OVOCs. These laboratory studies agree with earlier field work that found enrichment of OVOCs in the SML (36) or suggested that bulk water OVOC concentrations could not explain measured atmospheric mixing ratios (37) or fluxes (15).

Here, we present high time-resolution OVOC measurements collected in the Canadian Arctic aboard a research icebreaker in July and August 2014. These measurements offer an unparalleled view into the previously unexplored gas-phase organic composition of the climatically important summer Arctic atmosphere and provide indications from the ambient atmosphere for the production of OVOCs from the SML.

Results

The study region is shown in Fig. 1 together with a schematic depicting the production of OVOCs at the SML and their possible subsequent transformation to SOA. The time series of key variables measured along the ship track appear in Fig. 2 and *SI Appendix, Figs. S1 and S4*.

The OVOC measurements were made by an on-line high-resolution time-of-flight chemical ionization mass spectrometer with acetate ionization (Aerodyne acetate HR-ToF-CIMS). The acetate ionization method preferentially detects organic acids via

abstraction of acidic protons and detection of the anion. A mass spectrum of the ambient air from 3 to 500 mass to charge ratio (m/z) was collected every 10 s. This yielded time series of mass spectral peaks that could be used as input to a positive matrix factorization (PMF) algorithm (*SI Appendix*). PMF is a statistical source apportionment tool that provides weighted profiles of measured species (factors) along with their variation in time. The implicit assumption is that each factor represents signals with a common source (38). PMF analysis yielded a factor (referred to herein as the Ocean Factor) whose time series showed the highest signal when the ship was located within Nares Strait (a narrow water body between Ellesmere Island, CA and Greenland, indicated by a star in Fig. 1A), the most northerly and remote region visited by the CCGS *Amundsen* in 2014 (Fig. 1A). Fig. 2D shows the strength of this factor as a function of time, and *SI Appendix, Fig. S14* shows its mass spectral profile. A few of the individual molecules that contributed most strongly to the Ocean Factor were formic acid, isocyanic acid, and a five-carbon oxo-acid (such as levulinic acid), but the less intense signals were equally well described by the Ocean Factor (apportioned to the Ocean Factor with little residual). The mass spectra and time series for all of the PMF factors and an explanation of how the four-factor PMF solution was chosen are presented in *SI Appendix*. The other factors include fluorinated compounds identified as contaminants from the inlet line (Line Contaminants Factor), a combustion source arising from the influence of the ship's engine and long range transport (Combustion Factor), and heavily oxygenated C_2 compounds often associated with cloudwater chemistry (Small Oxygenates Factor).

The Ocean Factor is composed of high levels of formic acid (up to 4 parts per billion by volume) and moderate levels [tens of parts per trillion by volume (pptv)] of isocyanic acid (Fig. 3), as well as several other compounds tentatively identified as oxo-acids, for example levulinic acid and oxo-2-butenic acid (mass spectrum shown in *SI Appendix, Fig. S14*). Peaks corresponding to the C_4 – C_{11} oxo-acids were identified in the mass spectrum but those larger than C_5 proved too difficult to calibrate and were not quantified. That the Ocean Factor is robust with respect to the inclusion of these organic acids was shown by obtaining the same factor when PMF analysis was performed with the two most intense components of the Ocean Factor, formic and isocyanic acids, removed from the dataset (*SI Appendix, Figs. S23 and S24*). The discussion that follows focuses on the source of these molecules and thus of the Ocean Factor. A given molecule's mixing ratio is

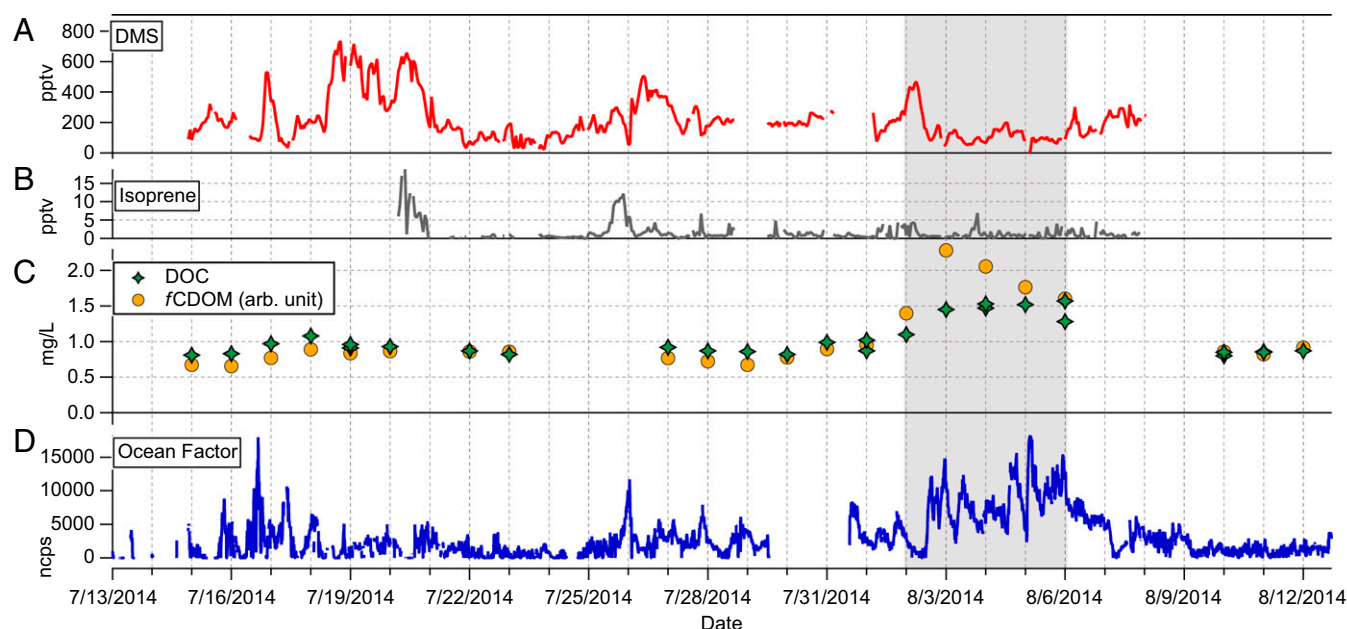


Fig. 2. Time series of shipboard observations. (A) DMS and (B) isoprene atmospheric mixing ratios. (C) DOC and fCDOM (arbitrary units) in surface seawater. (D) PMF Ocean Factor (discussed in the text). Gray shading highlights the time the ship spent in Nares Strait.

determined not only by its sources but also by its sinks. We do not believe that common sinks are driving the factors in the present analysis for two reasons. First, the lifetimes against OH oxidation of the compounds comprising the Ocean Factor vary enormously, suggesting that OH oxidation is not the common factor. Second, deposition rates are expected to be similar for compounds with similar Henry's law coefficients, and our PMF analysis yields two distinctly different factors both composed largely of molecules with large Henry's law coefficients (the Ocean Factor and the Small Oxygenates Factor). This suggests that it is the sources that are driving the variability we observe in the signals of the measured compounds, and that the Ocean Factor represents a group of molecules with a common source.

Discussion

Evidence for a Microlayer Source. The Ocean Factor shows robust correlations with measurements of dissolved organic carbon (DOC) and fluorescent chromophoric dissolved organic matter (fCDOM; $R^2 = 0.82$ and 0.72 , respectively) in the surface waters along the ship track (Fig. 4 and *SI Appendix*, Fig. S4). The DOC values measured here are typical of surface seawaters globally (39). Fig. 4 shows the strong spatial relationship between the Ocean Factor, DOC, and fCDOM, as well as the correlation between the diurnal cycle of the Ocean Factor and the incoming shortwave solar flux. These are the critical ingredients for direct emission of oxygenated products formed via photochemical reactions at the SML (26–28) and for generation of gas-phase OH that might be involved in heterogeneous oxidation.

As discussed below in *Atmospheric Implications*, when total particle volume as measured by a scanning mobility particle sizer (SMPS) for the period July 22–August 12 is time-averaged to daily resolution it shows a correlation with the Ocean Factor (Fig. 4D and *SI Appendix*).

The largest values of the Ocean Factor, DOC, and fCDOM occurred in Nares Strait, consistent with ocean circulation patterns in the region that bring organic matter-laden river waters from around the Arctic Basin into this area via the Trans-Polar Drift (40, 41). The path of such surface waters is shown schematically in Fig. 1.

The SML was consistently enriched in DOC during the cruise, as demonstrated by enrichment factors (defined as the ratio of DOC in

the SML to DOC in the bulk surface water) between 0.6–30 with values between 7 and 30 in Nares Strait. An example of the glassy sea state associated with this enrichment and low wind speeds is shown in *SI Appendix*, Fig. S8. We use the bulk DOC measurements for correlations, because many more DOC measurements in the bulk than in the microlayer were available. Because the organic matter producing SML enrichment must originate from the bulk seawater organic matter, DOC can be used as a proxy for SML DOC, at least under these conditions, wherein all of the samples in Nares Strait were enriched. SML enrichment can begin to break down at wind speeds above 5 m/s (42), although other studies have found that enrichments can be maintained at wind speeds up to 10 or 12 m/s (33). Consistent with a breakdown of SML enrichment, the highest values of the Ocean Factor occur at wind speeds below 5 m/s and the lowest values at high wind speeds (*SI Appendix*, Fig. S9).

Retroplume analysis using FLEXPART-WRF indicates that when the ship was in Nares Strait the local air masses were slow-moving and had spent most of the previous few days over Baffin Bay and Nares Strait (example shown in Fig. 1C). Taken together with fairly low wind speeds over this period (mean 4.8 m/s) and the ship's extreme northerly location at the time, this analysis makes biomass burning emissions from further south (e.g., the Northwest Territories) an unlikely source for the OVOCs. Using a chemical transport model (GEOS-Chem), a study from the same cruise similarly concluded that the contribution of biomass burning emissions to measured ammonia

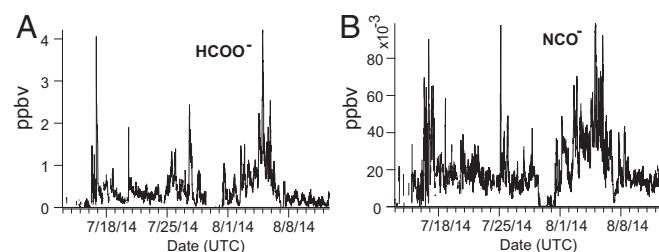


Fig. 3. (A) Mixing ratio of formic acid. (B) Mixing ratio of isocyanic acid.

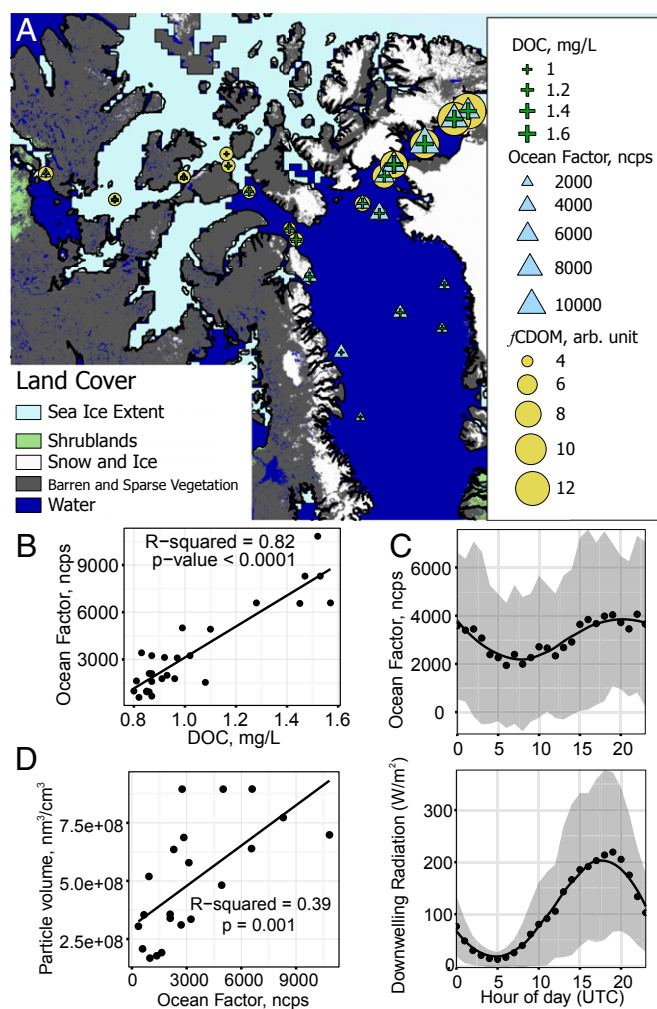


Fig. 4. Relationship between the PMF Ocean Factor, fCDOM, and DOC. (A) Shown spatially. (B) Linear regression of the Ocean Factor on DOC. (C) Diurnal profiles of the Ocean Factor and incoming shortwave solar radiation. Points show the mean hourly values, shaded areas show one SD, and lines are a LOESS smooth meant to guide the eye. (D) Linear regression of total particle volume on the Ocean Factor (daily averaged values).

mixing ratios was <5% in Nares Strait (43). Isocyanic acid, which displayed high mixing ratios in Nares Strait (Fig. 3), is sometimes considered a tracer for biomass burning. However, in this remote marine setting oxidation of reduced nitrogen compounds in the SML seems the most likely explanation for the observed isocyanic acid. The majority of the compounds comprising the Ocean Factor are expected to have tropospheric lifetimes on the order of days due to the combined effects of deposition and oxidation. Because the largest values of the Ocean Factor occur during times affected by local air masses [as opposed to times of rapid transport from lower latitudes (44)], it is unlikely that long-range transport plays a major role in determining its strength.

Having established the absence of significant long-range transport at this time, possible sources are restricted to those present in the high Arctic: the snowpack, the terrestrial vegetation, and the ocean. Photochemistry in the snowpack can produce small OVOCs (e.g., ref. 45). However, snowpack chemistry is more important in the spring, when the sun rises and photochemistry begins to act on chemicals accumulated from Arctic haze deposition, and by mid to late summer most of the ground-level snow has melted. Although vegetation is extremely sparse at these latitudes (Fig. 1), a source of precursor VOCs from high

Arctic vegetation cannot be excluded because some plants have been shown to be sources (46). The oxidation of these precursor VOCs could then give rise to the OVOCs we observe. Nor can we exclude soils as a source of the observed OVOCs. A soil source for formic acid in particular has recently been suggested to be quite important (47). However, instead, retroplume analysis indicates a marine origin for the Ocean Factor. We calculated the FLEXPART-WRF predicted residence times of air over land and open water (defined as a sea ice concentration of <50%) before arriving at the ship. A weak negative correlation is seen between the Ocean Factor and the residence time over land, and a corresponding weak positive correlation is seen with residence time over open water (*SI Appendix, Fig. S11*). The combination of retroplume evidence for a marine source, the correlation of the Ocean Factor with DOC, and the lack of other likely sources lends support to our hypothesis of a marine source.

In addition to work with small OVOCs, many studies of marine contributions to atmospheric VOCs have focused on wind-driven fluxes of dimethyl sulfide (DMS) and compounds such as isoprene and the monoterpenes. Measured mixing ratios of DMS, isoprene, and the sum of the monoterpenes are not correlated with the Ocean Factor (Fig. 2 and *SI Appendix, Fig. S12*, $R^2_{\text{DMS,OF}} = 0.1$, $R^2_{\text{Isoprene,OF}} = 0.002$). Additionally, very low mixing ratios were observed: The mean mixing ratio of isoprene was 1.6 pptv, and that of the sum of monoterpenes was less than 5 pptv (Fig. 2 and *SI Appendix, Fig. S13*). Noncorrelation and even in some cases anticorrelation of OVOCs with DMS in marine settings has been observed before, most notably, a mesocosm flux study found a decoupling of fluxes of DMS and methanol and acetaldehyde (6, 48). Decouplings might arise from different production mechanisms (a biological explanation) or emission mechanisms (a chemical explanation). That the correlation between the Ocean Factor and chlorophyll-*a* is weak (*SI Appendix, Fig. S4*, $R^2 = 0.15$) is consistent with a nonbiogenic production mechanism for the Ocean Factor. In any case, the lack of correlation with DMS, which is known to be emitted via wind-driven fluxes [on this cruise, mixing ratios were reproduced fairly well using a chemical transport model and wind-driven fluxes (44)], supports our hypothesis of a different mechanism for OVOC emission.

Such low levels of terpenoid precursors could not have given rise to the high measured formic acid mixing ratios via gas-phase chemistry (shown using box model calculations; see *SI Appendix* for details). However, laboratory work involving OH heterogeneous oxidation of a variety of organic substrates has indicated that the most dominant OVOC product released is consistently formic acid, although many other acids and carbonyls are also volatilized (49). The detailed molecular mechanism by which acids are formed is not clear (50).

Finally, we note that the presence, and often the enrichment, of carboxylic acids in the SML has been demonstrated repeatedly (35, 36). Due to the experimental difficulty of probing such a thin layer of material, the chemical environment of the SML remains poorly understood but may be sufficiently different from bulk seawater to radically change the partitioning characteristics of organic acids (36). We also point to the work of Singh et al. (37) showing that the reservoir of some small OVOC compounds in bulk seawater would have to be enormous to sustain measured mixing ratios of OVOCs in the atmosphere and that the available evidence does not support such a large reservoir. Notably, measured glyoxal fluxes also require an SML source due to glyoxal's extreme solubility in water (15). This earlier work supports our hypothesis that photochemistry or heterogeneous oxidation at the SML is the source of the OVOCs we observed.

In summary, the Ocean Factor displayed its highest levels in a local marine-influenced air mass in the presence of an organic-enriched SML. The Ocean Factor shows a robust correlation with oceanic DOC, and its diurnal cycle coincides with that of solar radiation. Gas-phase production from traditional precursors cannot explain the observed levels of organic acids described

by the Ocean Factor, and it is not correlated with mixing ratios of DMS, a compound known to be emitted by wind-driven fluxes. All available evidence is thus consistent with a photochemical or heterogeneous oxidation source from the SML.

Atmospheric Implications. Evidence is mounting that organics drive aerosol growth in the summer Arctic boundary layer. Condensation of organics during a particle nucleation and growth event was directly measured in a more southerly marine location in the Canadian Arctic (25). These recent observations are consistent with earlier work that demonstrated that Aitken mode particles in the central Arctic summertime can contain a large organic component (51).

The volatilities of the OVOCs in the Ocean Factor, and thus their likelihood of participating in SOA formation, can be estimated by using the number of carbon and oxygen atoms each molecule contains as proxies for chemical structure (52). Many of the compounds measured (e.g., butyric acid and levulinic acid and, in general, oxo-acids with fewer than eight carbon atoms) fall into the category of intermediate volatility organic compounds (IVOCs), whereas the oxo-acids with more than eight carbon atoms are classified as semi-volatile organic compounds (SVOCs) (53). Our sampling methodology was optimized for small organic acids and not for larger molecules, but it is likely that larger, lower-volatility species were coemitted with the species that we measured. The contribution of SVOCs and IVOCs to SOA formation is crucial in some contexts (54), suggesting that the Ocean Factor organic acids may participate in SOA formation. A link between the Ocean Factor and aerosol particle volume is suggested by the positive correlation between these measurements on the timescale of a day (Fig. 4D, $R^2 = 0.39$). However, without quantifying condensable vapors or measuring the chemical composition of the aerosol particles it is not possible to mechanistically connect these two quantities.

Another means for the smaller measured organic acids to contribute to SOA formation was provided by the high relative humidity and frequent fog observed both during the cruise and in the summer Arctic MBL more generally (20, 55). Small organic acids have been shown to form oligomers in the aqueous phase, such that smaller molecules may contribute to SOA (56). Beyond SOA, the presence of elevated levels of small gas-phase acids, such as formic acid, may indicate one component of a missing OVOC source that has previously been identified (18).

Overall, quantifying the amount of organic material that DOC-rich water might eject to the gas phase is important because it represents an unconstrained source of VOCs. Inputs of DOC and CDOM to Arctic waters are increasing as the North warms and the permafrost melts (57). The production of OVOCs at the SML may be increasingly important as the world transitions to a warmer climate, particularly in the Arctic as DOC increases and sea ice retreats (4).

Conclusion

Shipboard measurements of a suite of OVOCs were made in the summer Arctic MBL. These measurements demonstrate that high mixing ratios of certain OVOCs such as formic acid are present above waters with high dissolved organic carbon content. Factor analysis of the mass spectra isolates a factor that correlates in a robust manner with the levels of DOC and fCDOM throughout the cruise. Comparison of this factor with measurements of DOC, fCDOM, and solar radiation made aboard the ship, coupled with retroplume analysis and wind speed considerations, indicates that the source of this factor was likely photochemistry or heterogeneous oxidation occurring at the sea SML.

The high-latitude location of highest OVOCs we measured has riverine inputs of DOC and is far removed from most conventional sources of VOCs common to lower latitude settings. This unique situation provides a natural laboratory with fewer variables to account for than most field locations. This relatively simple environment allowed us to detect OVOCs that were emitted not by

wind-driven fluxes or gas-phase chemistry but by chemistry at the air–sea interface. Our field observations combined with previous laboratory experiments (17, 26–29) provide a compelling reason to consider this chemistry as a source of OVOCs in the MBL globally.

Finally, this work highlights the potential for the sea to be a nontraditional source of VOCs, and we suggest that the VOCs driving the formation of marine SOA may be very different from those that drive SOA formation in terrestrial settings. Understanding the composition and sources of marine SOA will require simultaneous measurements of condensable vapors and the chemical composition of small aerosol particles.

Materials and Methods

The data presented in this work were collected aboard the CCGS *Amundsen* during the NETCARE cruise in the Canadian Arctic Archipelago and Baffin Bay in July and August 2014. One of the goals was to draw upon both atmospheric and oceanic measurements to better understand Arctic tropospheric chemistry. To this end, online atmospheric sampling occurred concurrently with oceanographic sampling.

VOOCs were detected using an HR-ToF-CIMS (Aerodyne) and the acetate reagent ion. This reagent ion deprotonates organic acids in the gas phase (58), so it is expected that many of the mass spectral signals arise from organic acids. The acetate CIMS was located in a trailer behind the ship's bridge and sampled from the bridge (details in [SI Appendix](#)). DMS, isoprene, and the sum of monoterpenes were detected using a second HR-ToF-CIMS that used the benzene reagent ion (59) (see [SI Appendix](#) and ref. 44). The benzene CIMS was located in a container on the foredeck and sampled from a tower at the bow. The two mass spectrometers could not be colocated due to space restrictions. An SMPS (TSI) sampled through a separate inlet on the starboard foredeck. The inlet consisted of 1/4-inch (o.d.; 0.18-inch i.d.) stainless steel tubing, positioned 7 m above the sea surface and 5 m aft of the bow of the ship. The inlet was protected from rain using an inverted metal bowl.

Water samples for DOC determination were collected from 2- to 5-m depth with a rosette sampler (General Oceanics) equipped with 12-L Niskin-type bottles (OceanTest Equipment). Microlayer samples were collected using the glass plate method (60) from a rigid-hull inflatable boat deployed from the *Amundsen*. DOC was determined on a high-temperature combustion Shimadzu TOC-VCN total organic carbon analyzer (61). The analyses were calibrated using potassium hydrogen phthalate and validated against Consensus Reference Materials provided by Dennis Hansell, University of Miami, Miami. Fluorescent CDOM signals were measured by a WetLabs ECO CDOM fluorometer mounted on the rosette.

Meteorological data details can be found in ref. 44. The incoming short-wave (SWa) flux was measured aboard the *Amundsen* by a pyranometer (0.285–2.8 μm , Eppley Precision Spectral Pyranometer) mounted <20 m above sea level. The radiation flux was measured at 1-s intervals and saved as 1-min averages (with SDs) making use of the programming environment of a Campbell Scientific datalogger (model CR23X).

FLEXPART-WRF (62) (<https://www.flexpart.eu/wiki/FpLimitedareaWrf>) was used to determine the influences (i.e., marine or terrestrial) on the air sampled by the ship during the time of highest Ocean Factor signal. FLEXPART-WRF is a Lagrangian particle dispersion model based on FLEXPART (63) that is driven by meteorology from the Weather Research and Forecasting (WRF) Model (64). Details concerning the use of FLEXPART-WRF for this study can be found in ref. 43.

PMF was performed on the OVOC measurements. The bilinear model was solved using the PMF2 algorithm in robust mode (38) and the final solution was selected using the PMF Evaluation Tool (PET) version 2.06 (65) (see [SI Appendix](#) for details). In this study, a four-factor solution was selected based on examination of the PMF quality of fit parameter (Q/Q_{expected}) as a function of the number of PMF factors up to 10 factors. Three and five factor solutions are shown in [SI Appendix, Figs. S17–S20](#). The four-factor solution was chosen because physical meaning could be assigned to each of the four factors, but the five-factor solution split one of those factors without providing any further meaning. The data presented herein may be found in [Dataset S1](#).

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