

Contribution of sea surface carbon pool to organic matter enrichment in sea spray aerosol

Patricia K. Quinn^{1*}, Timothy S. Bates¹, Kristen S. Schulz¹, D. J. Coffman¹, A. A. Frossard², L. M. Russell², W. C. Keene³ and D. J. Kieber⁴

Breaking waves on the ocean surface generate air bubbles that scavenge organic matter from the surrounding sea water. When injected into the atmosphere, these bubbles burst, yielding sea spray aerosols enriched in organic matter, relative to the sea water. Downwind of plankton blooms, the organic carbon content of sea spray aerosol is weakly correlated with satellite-derived measurements of chlorophyll *a* levels, a measure of phytoplankton biomass. This correlation has been used in large-scale models to calculate the organic enrichment in sea spray aerosol. Here, we assess the relationship between the organic carbon content of sea water and freshly emitted sea spray aerosol in the presence and absence of plankton blooms in the North Atlantic Ocean and the coastal waters of California. The organic carbon content of freshly emitted sea spray aerosol was similar in all regions sampled, despite significant differences in seawater chlorophyll *a* levels. The proportion of freshly emitted aerosols that served as cloud condensation nuclei at a given supersaturation was also similar across sampling sites. The large reservoir of organic carbon in surface sea water remained relatively constant across the regions sampled, and independent of variations in chlorophyll *a* concentrations. We suggest that this reservoir is responsible for the organic carbon enrichment of freshly emitted sea spray aerosol, overwhelming any influence of local biological activity as measured by chlorophyll *a* levels.

Chlorophyll *a* (Chl *a*) is attractive as a proxy for the organic fraction of sea spray aerosol (SSA) because it can be retrieved from satellite observations that offer global coverage of the world's oceans. Chl *a* is a measure of phytoplankton, or algal, biomass which contributes to the surface seawater pool of particulate organic carbon (POC). Sources of dissolved organic carbon (DOC), the much larger pool of carbon in ocean surface waters, include direct algal release, grazing-induced sloppy feeding of algal-derived POC by marine heterotrophs, bacterial and viral lysis, and cell senescence¹. In addition to multiple sources of DOC, the link between DOC and algal dynamics can be decoupled by the inertness of algal-derived DOC (refs 2,3) and physical forcings such as vertical mixing and advection⁴. Nevertheless, emission parametrizations of the organic fraction of SSA based on Chl *a* have been developed using data acquired at coastal and island sites downwind of ocean regions with seasonal plankton blooms, including the northeast Atlantic and the Southern Ocean^{5–7}. Correlations between upwind satellite-derived Chl *a* and the organic mass fraction of marine ambient aerosol measured at these sites result in r^2 values ranging from 0.3 to 0.5 (refs 6,8–10), indicating that Chl *a* is able to explain only a fraction of the variance of the organic content of ambient marine aerosol that is assumed to originate during SSA production. Much of this explained variance is due to seasonality in plankton blooms¹⁰.

Chlorophyll-based emission parametrizations have been extrapolated globally^{5,9,11} even though they have not been evaluated empirically over open-ocean regions. Also, the parametrizations are based on ambient marine aerosol even though it is known that the organic content of freshly emitted SSA is not conservative with respect to atmospheric processing. Primary organic matter reacts photochemically to form volatile products¹² whereas secondary organic reaction products, from the oxidation of precursor gases,

condense onto ambient marine aerosol¹³. As a result, emission parametrizations based on correlations with organic matter associated with ambient marine aerosol are not expected to be representative of the organic composition and enrichment of freshly emitted SSA.

The Western Atlantic Climate Study (WACS) was conducted in August 2012 to assess the use of Chl *a* as a proxy for the sources of the organic fraction of SSA as well as the degree of organic enrichment in SSA relative to sea water, EF_{OC} . An *in situ* particle generator (Sea Sweep)¹⁴ was deployed to sample nascent SSA particles before modification in the atmosphere by interactions with solar radiation and existing ambient gases and particles. Sampling was conducted in the high-chlorophyll, biologically productive region of Georges Bank (Station 1) and in the low-chlorophyll, oligotrophic Sargasso Sea (Station 2; Fig. 1). We also include results from the coastal waters offshore of California, obtained in May 2010 during CalNex¹⁴.

Surface seawater properties

Station 1, located on Georges Bank 170 nm east of Boston ($\sim 41.9^\circ$ N, 67.4° W), was occupied from 20 August to 23 August. Georges Bank is surrounded by deep, nutrient-rich waters. Vigorous tidal mixing leads to the upwelling of nutrients onto the bank making it one of the most productive shelf ecosystems in the world, with high concentrations of Chl *a* (ref. 15). Sea surface temperature (SST) and salinity during WACS averaged $18.0 \pm 0.2^\circ$ C and 32.45 ± 0.02 ppt, respectively, typical of summertime values¹⁵. Chl *a* concentrations measured *in situ* from the ship's seawater system (nominal 5 m depth) ranged from 4 to $14 \mu\text{g l}^{-1}$ and averaged $7.1 \pm 2.2 \mu\text{g l}^{-1}$.

Station 2, located in the Sargasso Sea ($\sim 36.3^\circ$ N, 64.7° W), was occupied from 24 August to 26 August. The Sargasso Sea lies

¹NOAA Pacific Marine Environmental Laboratory, 7600 Sand Point Way NE, Seattle, Washington 98115, USA, ²Scripps Institute of Oceanography, UC San Diego, La Jolla, California 92093, USA, ³Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia 22904, USA, ⁴SUNY, College of Environmental Science and Forestry, Syracuse, New York 13210, USA. *e-mail: patricia.k.quinn@noaa.gov

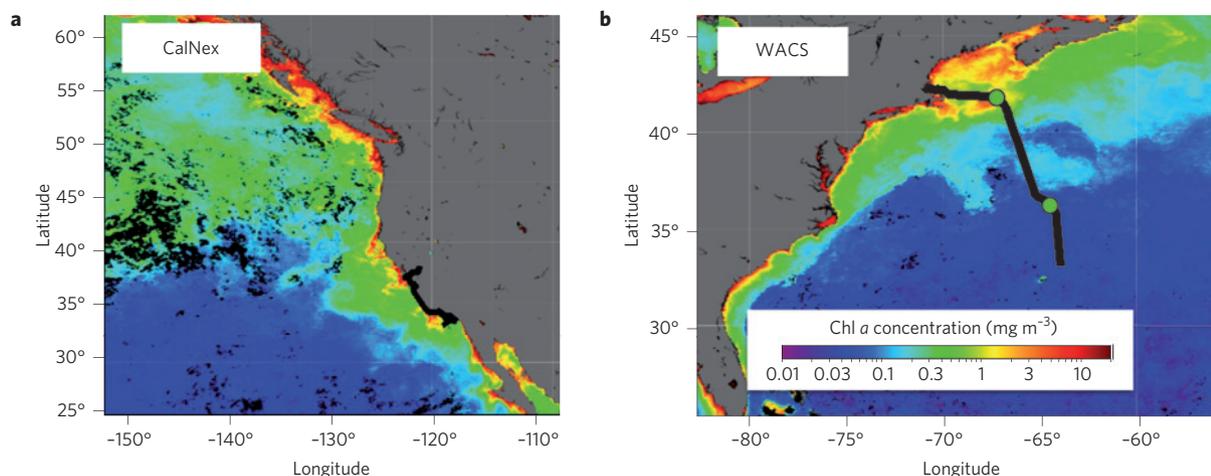


Figure 1 | CalNex and WACS cruise tracks superimposed on maps of satellite-derived Chl *a* concentration. Cruise tracks are shown in black for the CalNex cruise superimposed on a composite image of Chl *a* concentration retrieved from Aqua MODIS for the month of May 2010 (Source data credit: NASA/GSFC/OBPG, <http://oceancolor.gsfc.nasa.gov/cgi/13>) (a) and the WACS cruise superimposed on a composite image of Chl *a* concentration retrieved from Aqua MODIS for the month of August 2012, with locations of Sea Sweep stations 1 and 2 indicated by green circles (b).

within the Northern Atlantic Subtropical Gyre. It is characterized by high SST and salinity, with the upper 1,000 m separated from deeper waters by a permanent pycnocline. This density gradient prevents upwelling of nutrients from deeper waters and results in a region of very low biological productivity. SST and salinity averaged 28.5 ± 0.2 °C and 36.0 ± 0.1 ppt, respectively. Chl *a* concentrations were much lower than at Station 1, with an average (\pm s.d.) of 0.03 ± 0.06 $\mu\text{g l}^{-1}$.

Surface seawater POC, operationally defined here as organic matter large enough in size to be retained on a quartz fibre filter, is a mixture of living planktonic organisms and organic detritus. Concentrations measured at Station 1 averaged 19 ± 4 $\mu\text{M C}$, consistent with high Chl *a* concentrations and with previous measurements that found an increase in POC concentration from 11.7 to 52.5 $\mu\text{M C}$ over the course of a winter-spring (January–June) bloom on Georges Bank¹⁶. POC concentrations were an order of magnitude lower at Station 2 (2.3 ± 0.3 $\mu\text{M C}$), reflecting low Chl *a* concentrations in the Sargasso Sea. Measurements offshore of California found variable seawater Chl *a* concentrations due to areas of coastal upwelling with values ranging from near detection limit to 30 $\mu\text{g l}^{-1}$ (ref. 14). POC concentrations also were variable and generally higher than open-ocean WACS values, with an average of 29 ± 28 $\mu\text{M C}$.

Concentrations of seawater DOC, defined here as organic matter small enough in size to pass through a 0.2 μm Polycap filter and containing particulate matter including viruses and colloids, were 89 ± 3 and 72 ± 3 $\mu\text{M C}$ at Stations 1 and 2, respectively. DOC dominated the total organic carbon ($\text{TOC} = \text{POC} + \text{DOC}$) pool in surface sea water at both Station 1 ($82 \pm 3\%$ of TOC) and Station 2 ($97 \pm 0.8\%$ of TOC). DOC concentrations in the coastal waters off California averaged 62 ± 4 $\mu\text{M C}$ and made up 46 \pm 45% of the TOC.

Concentrations of Chl *a* and surface seawater POC were highly correlated during both WACS ($r^2 = 0.90$) and CalNex ($r^2 = 0.96$) (Supplementary Fig. 1). DOC concentrations during all of WACS and CalNex were much less variable than POC concentrations. In general, DOC concentrations in the upper ocean vary over space and time within a relatively narrow range (40–80 $\mu\text{M C}$, ref. 3). This limited variability in DOC is often uncorrelated with Chl *a* or primary production because of the decoupling between DOC and algal dynamics⁴. Not surprisingly, no correlation was found between surface seawater DOC and Chl *a* at either WACS Station 1 or 2 or during CalNex (Supplementary Fig. 2).

Organic enrichment in nascent sea spray aerosol

Organic carbon enrichment factors, EF_{OC} , in nascent SSA relative to sea water were calculated from simultaneous measurements of organic carbon (as C) and Na^+ in both sea water and nascent SSA (see Methods for calculation details). EF_{OC} values for sub-1.0 μm SSA sampled at the WACS high- and low-Chl *a* stations averaged $1.5 \pm 0.46 \times 10^3$ and $2.6 \pm 0.9 \times 10^3$ respectively. Sub-0.18 μm EF_{OC} values for the high- and low-Chl *a* stations were $2.7 \pm 0.92 \times 10^4$ and $6.1 \pm 1.4 \times 10^4$, respectively, or about an order of magnitude larger, indicating an increasing degree of organic enrichment with decreasing particle size (Supplementary Table 1). No correlation was found between EF_{OC} and Chl *a* for either the sub-0.18 μm or the sub-1.1 μm size range during both WACS and CalNex (Supplementary Fig. 2). Furthermore, the large EF_{OC} observed in SSA emitted from the oligotrophic waters of the Sargasso Sea provide evidence for a pool of surface seawater organic matter that is not directly associated with Chl *a* and phytoplankton biomass, but is available for incorporation into nascent SSA.

Published EF_{OC} for size-resolved nascent SSA are few; values have been reported previously for the Sargasso Sea^{17,18} and the northeast Atlantic during a plankton bloom¹⁹. In all cases, including WACS and CalNex, the smallest particles measured (sub-0.18 μm) had the highest EF_{OC} , with values ranging from 10^4 to 10^5 relative to surface seawater TOC (Supplementary Fig. 3 and Table 1). Values for sub-1.1 μm nascent SSA were an order of magnitude lower, ranging from 10^3 to 10^4 . Even lower is a value reported for sub-20 μm SSA (74 ± 27), owing to inorganic seasalt constituents dominating bulk SSA mass¹⁷. During each of these experiments, seawater Chl *a* concentrations were measured *in situ*. A comparison of Chl *a* concentrations and EF_{OC} across the different regions, a range of surface seawater properties, and experiments revealed no coherent dependence of EF_{OC} on Chl *a* (Supplementary Fig. 1).

Chemical composition of nascent sea spray aerosol

The chemical composition of nascent SSA generated at the two WACS stations and during CalNex were compared to assess the impact of surface seawater properties represented by Chl *a* on SSA composition. Average mass fractions of SSA OC for both the sub-0.18 μm and sub-1.1 μm size ranges, were calculated as the concentration of OC in air ($\mu\text{g C m}^{-3}$) divided by the sum of the concentrations of OC and seasalt in air ($\mu\text{g C m}^{-3} + \mu\text{g seasalt m}^{-3}$). All other chemically analyzed species, including NH_4^+ , NO_3^- and

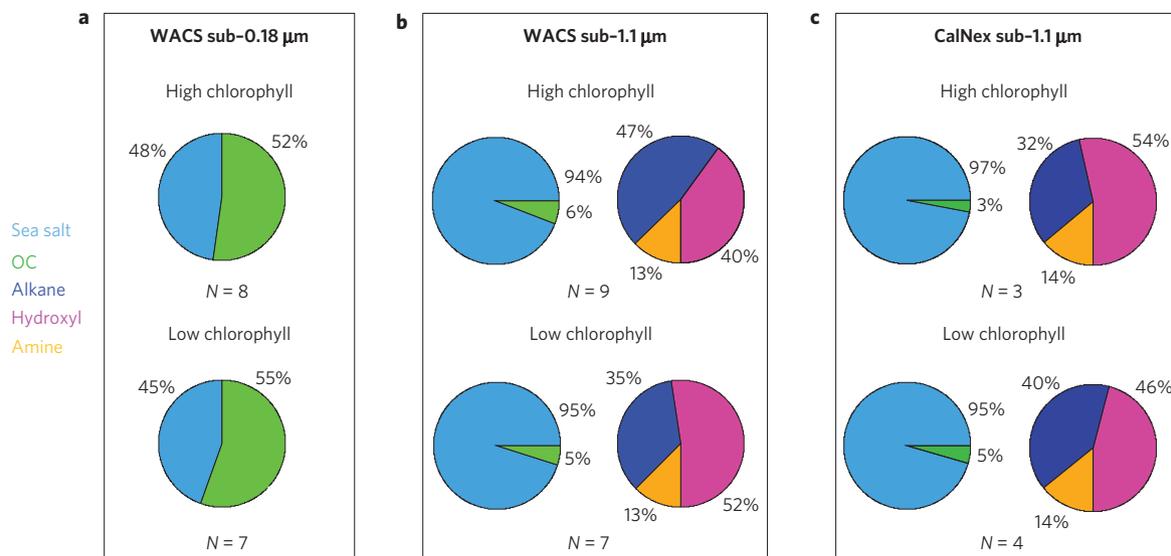


Figure 2 | Average mass fractions of organic carbon (OC) and sea salt in nascent sea spray aerosol generated by Sea Sweep. Mass fractions are shown for WACS sub-0.18 μm (a), WACS sub-1.1 μm (b) and CalNex sub-1.1 μm size fractions (c). The mass fraction is calculated as the concentration of OC ($\mu\text{g C m}^{-3}$) or sea salt ($\mu\text{g seasalt m}^{-3}$) in air divided by their sum. The mass of OC is shown in $\mu\text{g C}$. Also shown are average alkane, hydroxyl and amine functional group fractions of organic matter associated with the total OC mass. The number of samples, N , for each average value is indicated.

non-seasalt SO_4^- made up less than 0.1% of the SSA mass. Average mass fractions of OC and seasalt were similar for high- and low-Chl a waters (Fig. 2 and Supplementary Table 2). During WACS, OC accounted for about 50% and 5% of the non-water mass of sub-0.18 μm and sub-1.1 μm size fractions, respectively. Analysis of sub-1.1 μm SSA by Fourier transform infrared spectroscopy (FTIR) indicated only slight differences, on average, in functional group composition at the two WACS stations, with more alkane ($45 \pm 11\%$ versus $36 \pm 12\%$) and less hydroxyl for the high-Chl a waters than for the low-Chl a waters (Fig. 2 and Supplementary Table 2). Furthermore, regardless of seawater Chl a concentration, throughout both WACS and CalNex, the sub-0.18 μm nascent SSA exhibited relatively constant behaviour when heated to 230 °C. In all cases, the particle number concentration decreased by less than 15% upon heating, indicating that the majority of the organics in this size range were not semi-volatile (Supplementary Fig. 3).

Sea spray aerosol cloud condensation nuclei activity

During WACS Stations 1 and 2, the CCN activity of nascent SSA was measured as a function of particle size. Resulting CCN activation ratios, which indicate the fraction of total particles that activate to form CCN at a given supersaturation, were similar for both stations, indicating no difference between high- and low-Chl a waters (Fig. 3). For both stations, SSA particles with a dry diameter of 100 nm were slightly less CCN active than the NaCl calibration aerosol. With decreasing particle size, SSA became less like NaCl owing to an increasing volume fraction of OC with a lower CCN activity relative to NaCl. The volume fraction of OC as a function of particle size was estimated using the difference between the CCN activity of SSA and NaCl. This approach assumes that the CCN activity of the inorganic fraction of SSA is similar to that of pure NaCl and that the contribution of organic material to the hygroscopicity is additive^{20,21} (see Supplementary Information for details of the calculation). The estimated organic volume fraction was around 80% for 40 nm (dry diameter) SSA particles and decreased by a factor of 2 to 40% for 100 nm particles (Fig. 4).

An average organic volume fraction was also estimated from the mass concentrations of OC and seasalt measured in the sub-0.18 μm size fraction of nascent SSA and found to average 0.54 ± 0.06

(Supplementary Information for details of the calculation). The aerodynamic cut-off diameter of 0.18 μm at 60% relative humidity corresponds to a geometric dry diameter of 140 nm and, therefore, extends to larger sizes than considered in the CCN activation measurements. Because the organic volume fraction decreases with increasing diameter, it is reasonable that the mass composition derived value of 0.54 is on the lower end of values based on the CCN measurements. If the SSA OC were volatile, it would be possible to also calculate an organic volume fraction from the thermal denuder measurements. However, as discussed above, less than 15% of the OC volatilized at the measurement temperature of 230 °C (Supplementary Fig. 3).

Chlorophyll a as a proxy for sea spray aerosol organics

These results, the first reported for simultaneous measurements of surface sea water and nascent SSA properties, indicate that organic matter in surface sea water yields large EF_{OC} in nascent SSA even when Chl a concentrations are low. Moreover, freshly emitted SSA chemical composition and CCN activity, as measured here, are not significantly different for high- and low-chlorophyll waters. We conclude that there is a large reservoir of OC in surface sea water that results in the enrichment of organic matter in SSA and that this ocean source of OC is uncoupled from and overwhelms any influence of local biological activity as measured by Chl a over large ocean regions. As a result, although source functions based on Chl a may explain up to 50% of the variance in the organic fraction of ambient SSA downwind of plankton bloom regions, they do not apply to other regions. As reported previously²², linear source functions based on Chl a underpredict OC enrichments for nascent SSA produced from oligotrophic waters and overpredict OC enrichments for those produced from highly productive waters.

The results presented here indicate that the OC enrichment and CCN activity of nascent SSA are relatively constant over very different ocean regions. Further *in situ* measurements of surface sea water and nascent SSA properties are needed to confirm these results and to constrain and develop realistic parametrizations of the emission of the organic fraction of SSA to the atmosphere. In the absence of such a parametrization, the most accurate approach may be to calculate the size-dependent number flux of SSA as a

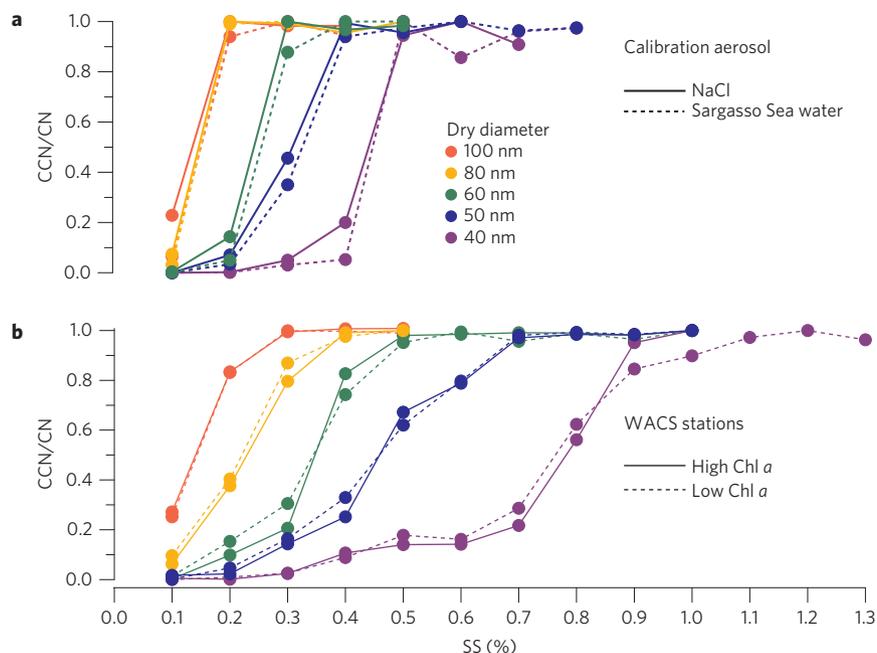


Figure 3 | CCN activity for the calibration aerosol and WACS Stations 1 and 2 for size-selected dry diameters (40, 50, 60, 80, and 100 nm). CCN activity is shown as the ratio of the number of particles that activated to become CCN to total particle number (CN) at a given supersaturation for a calibration aerosol consisting of either atomized NaCl or Sargasso Sea water (**a**) and for WACS high- and low-Chl *a* stations (**b**).

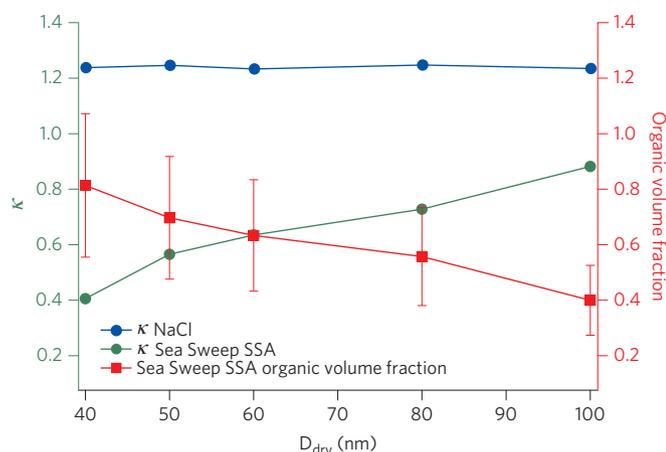


Figure 4 | Size-resolved Sea-Sweep-generated SSA organic volume fraction and hygroscopicity parameter (κ), derived from CCN activation curves. Error bars indicate the uncertainty in the estimated SSA organic volume fraction based on a quadratic sum of the measurement uncertainties. Also shown is κ for atomized NaCl.

function of wind speed and apply an average OC enrichment factor based on the data presented here and distributed as a function of particle size using previously published size distributions for nascent SSA (refs 18,19).

Methods

Sea Sweep. The Sea Sweep *in situ* SSA particle generator has been described previously in detail¹⁴. Sea Sweep sample air was drawn into the aerosol sampling mast 18 m above the ocean surface, where it is conditioned to be at a constant relative humidity of 60%²³. It is then distributed to aerosol sampling equipment. Sea Sweep was deployed off the port bow of the ship. Wind was kept off the starboard bow while the ship steamed slowly either forward or backward, depending on the direction of the current, to ensure a continual renewal of ocean surface water.

SSA measurements. Multi-jet cascade impactors²⁴ were used to collect nascent SSA generated from Sea Sweep for the quantification of inorganic ions and

organic carbon. The 50% aerodynamic cut-off diameters, $D_{50,aero}$, were 0.18 and 1.1 μm at 60% relative humidity. Concentrations of inorganic ions were determined by ion chromatography²⁵. Sea Sweep aerosol seasalt concentrations were calculated as:

$$\text{seasalt}(\mu\text{g m}^{-3}) = \text{Na}^+(\mu\text{g m}^{-3}) \times 3.26$$

where 3.26 is the seawater ratio of $(\text{Na}^+ + \text{Mg}^{+2} + \text{Ca}^{+2} + \text{K}^+ + \text{Cl}^- + \text{SO}_4^{-2} + \text{HCO}_3^-)/\text{Na}^+$ (ref. 26).

Pre-combusted quartz fibre filters were used to collect samples for the quantification of organic carbon (OC) concentrations²⁷. Charcoal diffusion denuders were deployed upstream of two single-stage impactors ($D_{50,aero}$ of 0.18 μm and $D_{50,aero}$ of 1.1 μm at 60% relative humidity) to remove gas phase organic species. OC concentrations were determined with a Sunset Laboratory thermal/optical analyser. Three temperature steps were used to evolve OC under O_2 -free conditions (230, 600, and 870 $^\circ\text{C}$). No correction was made for carbonate carbon, therefore OC includes both organic and carbonate carbon. All aerosol OC concentrations are reported as $\mu\text{g C}$.

Sub-1.1 μm particles were collected on Teflon filters and dehydrated²⁸ prior to organic functional group analysis²⁹. The filters used have been shown not to adsorb organic vapours. The FTIR spectra were analysed using an automated algorithm that includes baselining, peakfitting, and integrating at specific peak locations to quantify the organic functional group mass associated with major carbon bonds. The sampling configuration did not allow a separate analysis of the sub-0.18 μm size fraction.

SSA volatility at 230 $^\circ\text{C}$ was measured with a thermodenuder—twin Scanning Mobility Particle Sizer (SMPS) system downstream of an impactor with a $D_{50,aero}$ of 1.1 μm ¹⁴. As well as the twin SMPSs, TSI 3010 CN counters were used to sample the heated and unheated total particle number concentration. The twin systems were intercompared daily using an unheated flow and found to agree in total number to within 10%. Tests with $(\text{NH}_4)_2\text{SO}_4$ showed a complete removal of aerosol particle number in the thermodenuder.

A Droplet Measurement Technologies (DMT) CCN Counter³⁰ was used to determine CCN concentrations of 40, 50, 60, 80 and 100 nm particles (dry diameter) at supersaturations ranging from 0.1 to 1.3%. An SMPS was used to size-select particles of a given diameter, which were then sampled in parallel by the CCN counter and a TSI 3010 particle counter. The CCN counter was calibrated before and after the experiment using the methods detailed in ref. 31. The uncertainty associated with the CCN number concentrations is estimated to be less than 10% and, for the conditions used here, less than 1% for the instrumental supersaturation³¹.

Seawater measurements. Sea water was collected from the ship's continuous, uncontaminated sampling line, located at the bow of the ship, 5.3 m below the

water line. Sea surface temperature (SST) and salinity were measured with the ship's thermosalinograph. Chl *a* concentrations were determined from measurements of continuous fluorescence and a post-cruise calibration using discrete samples collected during the cruise and a commercial Chl *a* standard¹⁴. Throughout the cruise, seawater samples were collected from this same inlet and filtered through combusted quartz fibre filters. The filters were analysed for particulate organic carbon (POC) with a Sunset Laboratory thermal/optical analyser and the same temperature program that was used for the Sea Sweep aerosol samples. Seawater samples also were collected at a depth of 6 m from Niskin bottles secured to a conductivity–temperature–depth instrument. These samples were filtered directly from the Niskin bottles through pre-cleaned 0.2 µm Whatman POLYCAP 75 AS filter capsules. The filtrate was analysed with a Shimadzu TOC-V catalytic oxidation/NDIR analyser for dissolved organic carbon (DOC). Seawater total organic carbon (TOC) was derived from the sum of POC and DOC. POC, DOC and TOC concentrations are reported as µM C.

Organic carbon enrichment factors in nascent SSA. The organic enrichment factor for nascent SSA relative to sea water is defined here as:

$$EF_{OC} = [(OC \text{ as } \mu\text{g C})/Na^+]_{ssa} / [(TOC \text{ as } \mu\text{g C})/Na^+]_{seawater}$$

EF_{OC} calculated for WACS, CalNex and bulk Sargasso Sea¹⁷ SSA are based on total organic carbon measured by thermal/optical analysis. EF_{OC} for the sub-0.18 and sub-1.0 m Sargasso Sea data reported by ref. 18 are based on measurements of water-extractable OC. EF_{OC} for the North Atlantic SSA reported by ref. 19 are based on measurements of water insoluble organic carbon.

Received 08 August 2014; accepted 14 January 2014;
published online 27 February 2014

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Acknowledgements

This work was supported in part by the NOAA Atmospheric Composition and Climate Program and the National Science Foundation Chemical Oceanography Program (1129896 to DJK, 1129836 to WCK and 1129580 to LMR) and Atmospheric Dynamics Program (1013423 to LMR). We thank D. Hamilton, J. Johnson, I. Tyssebotn, J. Kinsey and M. Haserodt for their assistance in sample collection and analysis; V. Trainer for the loan and calibration of the fluorometer; the captain and crew of the NOAA R/V *Ronald H. Brown* for support at sea; M. Rinaldi and C. Facchini for MAP data and helpful comments; and S. Gasso for discussions on satellite images of Chl *a*. This is PMEL contribution 4046.

Author contributions

All authors contributed extensively to the work presented in this paper. P.K.Q., T.S.B., W.C.K., D.J.K., L.M.R., and A.A.F. designed and performed the experiments, analysed data and wrote the paper. D.J.C. and K.S.S. performed the experiments and analysed data.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to P. K. Q.

Competing financial interests

The authors declare no competing financial interests.