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The Atlantic Ocean surface microlayer from 50°N to 50°S is ubiquitously enriched in surfactants at wind speeds up to 13 m s^{-1}

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Key Points:
- First measurements of surfactant activity (SA) in the sea surface microlayer (SML) and in subsurface waters at the ocean basin scale
- The Atlantic Ocean SML is ubiquitously enriched in SA relative to underlying water between 50°N and 50°S and up to wind speeds ~13 m s^{-1}
- The high-latitude ocean contribution to air-sea gas exchange globally may be lower than previously assumed and should be reexamined

Supporting Information:
- Supporting Information S1

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Abstract We report the first measurements of surfactant activity (SA) in the sea surface microlayer (SML) and in subsurface waters (SSW) at the ocean basin scale, for two Atlantic Meridional Transect from cruises 50°N to 50°S during 2014 and 2015. Northern Hemisphere (NH) SA was significantly higher than Southern Hemisphere (SH) SA in the SML and in the SSW. SA enrichment factors ($EF = SA_{SML}/SA_{SSW}$) were also higher in the NH, for wind speeds up to ~13 m s^{-1}, questioning a prior assertion that Atlantic Ocean wind speeds >12 m s^{-1} poleward of 30°N and 30°S would preclude high EFs and showing the SML to be self-sustaining with respect to SA. Our results imply that surfactants exert a control on air-sea CO_2 exchange across the whole North Atlantic CO_2 sink region and that the contribution made by high wind, high latitude oceans to air-sea gas exchange globally should be reexamined.

1. Introduction

The physics and biogeochemistry of the sea surface microlayer (SML) afford it a unique role in global element cycling and in the production and removal of climate active gases [*Upstill-Goddard et al.*, 2003; *Cunliffe et al.*, 2013; *Carpenter and Nightingale*, 2015]. Open ocean surfactants include polysaccharides, lipids and proteins [*Allan et al.*, 1972; *Myklestad*, 1974; *Sakugawa and Handa*, 1985], transparent exopolymer particles [*Wurl and Holmes*, 2008], and chromophoric dissolved organic matter [*Tilstone et al.*, 2010]. They are mainly biologically derived, from phytoplankton [*Ẑutić et al.*, 1981], via zooplankton grazing [*Kujawinski et al.*, 2002] and from bacteria [*Kurata et al.*, 2016], with additional small components of terrestrial [*Frew et al.*, 2002] origin and from the in situ photochemical reworking of preexisting organics [*Tilstone et al.*, 2010]. Surfactants accumulate in the SML through bubble scavenging from subsurface water (SSW) [*Tseng et al.*, 1992], generating marine boundary layer aerosols [*Leck and Bigg*, 1999; *Ovadnevaite et al.*, 2011] and lowering the air-sea gas transfer velocity (k_w) of CO_2 and other climate-active gases [*Nightingale*, 2009]. Surfactant suppression of k_w by up to 50% may be typical [*Bock et al.*, 1999; *Frew*, 2005; *Salter et al.*, 2011]. While strong spatiotemporal gradients in SML surfactant, and hence in k_w, have been reported for some coastal waters [*Frew et al.*, 1990; *Schneider-Zapp et al.*, 2014; *Pereira et al.*, 2016], surfactant distributions at the ocean basin scale are currently estimates derived from proxies [*Wurl et al.*, 2011]. Here we present the first comprehensive measurements of total surfactant activity (SA) in the SML and SSW across large spatial scales and up to high wind speeds, from two Atlantic Meridional Transect (AMT) cruises between 50°N and 50°S: AMT 24 (2014) and AMT 25 (2015).

2. Study Site and Sampling

The annual AMT cruises target distinct “biogeographical ocean provinces”, as defined by the regulation of phytoplankton distributions by hydrographic properties [*Longhurst*, 1995; *Reygondeau et al.*, 2013], between ~50°N and ~50°S. AMT 24 (21 September to 6 November 2014) and AMT 25 (11 September to 4 November 2015) both ran from Immingham (UK), to Punta Arenas (Chile) and Port Stanley (Falkland Islands), respectively (Figure 1).

The SML was sampled twice daily, during predawn and solar noon hydrocasts when the ship (RRS *James Clark Ross*: JCR) was on-station. Although collecting SML samples from a moving ship or from its stern disrupts SML integrity [*Wurl and Soloviev*, 2014], the SML can be successfully sampled from the bow of a large vessel while on-station. We achieved this by aligning JCR head to wind to minimize ship-derived contamination. Doing this, we found that even under high-wind conditions surface water was continually advected toward the

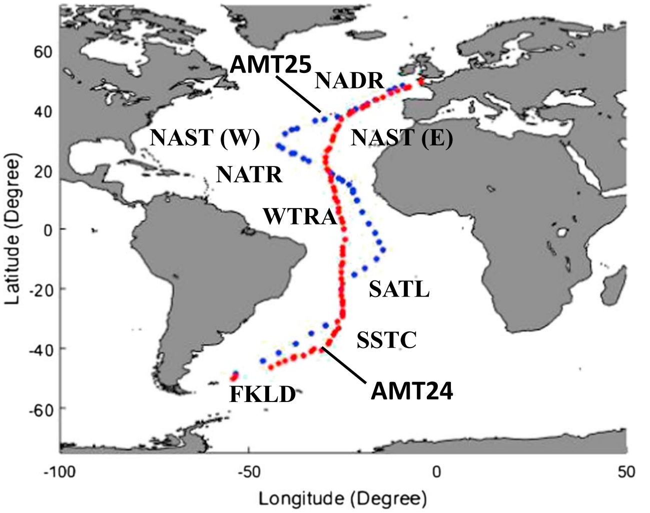

Figure 1. Sampling locations on AMT 24 (red circles, $n = 66$) and AMT 25 (blue circles, $n = 47$) and corresponding biogeographical provinces [*Reygondeau et al*., 2013]. NADR, North Atlantic Drift Region; NAST (E), North-East Atlantic Subtropical gyre; NAST (W), North-West Atlantic Subtropical gyre; NATR, North Atlantic Tropical gyre; WTRA, Western Tropical Atlantic; SATL, South Atlantic Subtropical gyre; SSTC, South Subtropical Convergence; FKLD, Southwest Atlantic Continental shelf.

bow and the protrusion of the foredeck ~3 m ahead of the waterline ensured that sampling was always well away from JCR's hull. With such conditions satisfied we previously sampled the SML for surfactants from the bow of a large research vessel [*Salter et al*., 2011], and in another study *Kurata et al*. [2016] similarly sampled SML bacteria. Observing these protocols we collected SML samples by using a Garrett Screen [*Garrett*, 1965] (mesh: 16, wire diameter: 0.36 mm, and effective surface area: 2025 cm^2), as in our previous work [*Salter et al*., 2011].

Deployment and recovery of the Garrett Screen followed standard procedures described in *Gašparović et al*. [2014], which also discusses appropriate procedures for cleaning and for optimizing sampling efficiency. Each deployment typically collected 15–16 cm^3 of the SML, and each sample comprised water from three repeat deployments (40–50 cm^3) to provide a sufficient volume for analysis. SSW samples were collected simultaneously via a hull-mounted "nontoxic" seawater inlet at 7 m.

3. Analytical Methods

Samples were left unfiltered to retain particulate surfactants [*Ćosović and Vojvodić*, 1987; *Wurl et al*., 2011; *Pereira et al*., 2016] and stored in clean, high-density polyethylene bottles prerinsed with analytical grade water (18.2 ohm Milli-Q, Millipore System Inc., USA) followed by excess sample. SA was measured immediately in triplicate by phase sensitive AC voltammetry (797VA Computrace, Metrohm, Switzerland) using a hanging mercury drop electrode [*Ćosović and Vojvodić*, 1987]. Calibration was against a nonionic soluble surfactant (Triton T-X-100 (Sigma-Aldrich, UK); data reported in mg L^{-1} T-X-100 equivalents) in a 0.55 mol L^{-1} NaCl matrix. Samples were adjusted to the same ionic strength as the standards by adding of 3 mol L^{-1} NaCl solution typically up to a maximum of 50 μL. Analytical precision was always better than ±10% and was frequently better than ±4%. Wind speeds from the ship's anemometer were corrected to U_{10n}, the value at 10 m height and neutral stability, as in *Nightingale et al*. [2000]. Total chlorophyll (Chl *a–c*) and total pigments were measured according to *Zapata et al*. [2000], and total primary productivity and size-fractioned phytoplankton productivity were determined according to *Serret et al*. [2001]; these data are currently available for AMT 24 only.

4. Results

Latitudinal SA distributions on AMT 24 and AMT 25 were rather similar (Figure 2), both in the SML and in the SSW. Given that the two transects differed by up to 13° of longitude between ~40°N and 20°S, AMT25 proceeding further into the North Atlantic Gyre between 20°N and 40°N and somewhat more easterly between the equator and 20°S (Figure 1), it appears that longitudinal SA gradients are comparatively small across a substantial part of the Atlantic Ocean and that surfactant distributions remain relatively constant between consecutive years. The most notable features of the data, common to both transects and in both the SML and the SSW, were distinct SA maxima centered on ~40°N, in North Atlantic Drift Region (NADR) (AMT 24, SML 1.00 ± 0.28 mg L^{-1} T-X-100, SSW 0.36 ± 0.15 mg L^{-1} T-X-100; AMT 25, SML 1.76 ± 0.1 mg L^{-1} T-X-100, SSW 0.58 ± 0.16 mg L^{-1} T-X-100; Figure 2). On AMT 24 there were also two small SA maxima that were

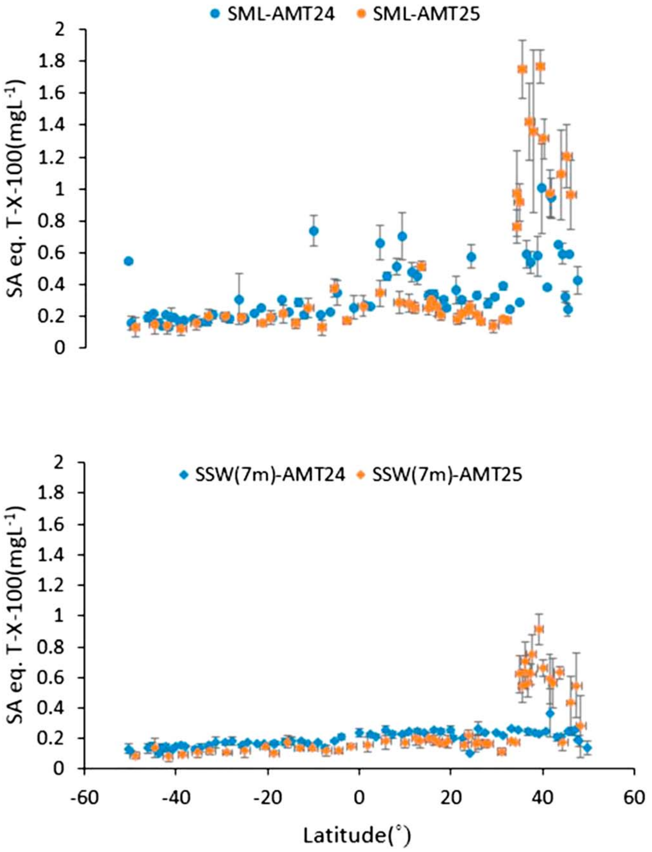

Figure 2. Surfactant activity (SA) during AMT 24 and AMT 25 in the Atlantic Ocean. Latitudinal distribution of SA (top) in the SML and (bottom) in the SSW (7 m depth). The error bars represent the standard deviation of the mean for each sample.

exclusive to the SML, between ~36°N and ~26°N (North-East/West Atlantic Subtropical gyre (NAST)) and at ~10°N (Western Tropical Atlantic (WTRA)).

During AMT 24 the ranges in U_{10} between 36°N and 26°N and between 12°N and 9°N ($6.69 \pm 1.33\ \mathrm{m\,s^{-1}}$; $3.91 \pm 0.71\ \mathrm{m\,s^{-1}}$) were somewhat higher than on AMT25 ($4.77 \pm 1.14\ \mathrm{m\,s^{-1}}$; $1.26 \pm 0.35\ \mathrm{m\,s^{-1}}$), consistent with the possibility that these SML maxima are a consequence of enhanced bubble scavenging under the somewhat more turbulent conditions experienced during AMT 24. An alternative explanation is that these maxima reflect more intense and/or more frequent local precipitation on AMT 24 than during AMT 25. Elevated SML surfactant following rainfall has been ascribed to an enhanced rate of delivery of particulate organics to the SML [*Wurl et al.*, 2011], but in the absence of precipitation data for either cruise we are unable to substantiate or otherwise, this possibility.

Additional high SA at ~50°S (Southwest Atlantic Continental shelf (FKLD)) ($0.54 \pm 0.01\ \mathrm{mg\,L^{-1}}$ T-X-100, $n = 3$) during AMT 24 may indicate high local productivity, terrestrially derived surfactants on the Falklands shelf, or an aggregate of both. During AMT 25 this feature was much less evident (Figure 2). While indices of terrestrially derived surfactant are detectable offshore in other regions [*Cuscov and Muller*, 2015; *Pereira et al.*, 2016], they were not measured here and primary productivity, total chlorophyll, and total pigments are unavailable for 50°S. We additionally did not detect any measurable difference in salinity that might indicate a freshwater input signal at this location. The precise origin of this SA maximum thus remains unknown.

These important details of the SA distributions aside, on both transects SA was significantly higher overall (*t* test, $p < 0.05$) in the Northern Hemisphere than in the Southern Hemisphere, both in the SML and in the SSW (Table S1 in the supporting information). Excluding the SA maxima, there were small but discernible trends of progressively decreasing SA from north to south on both transects, both in the SML and in the SSW (Figure 2). SA was enriched in the SML (enrichment factor, $\mathrm{EF} = \mathrm{SA_{SML}}/\mathrm{SA_{SSW}}$) at 64 of 66 and 45 of 47 locations ($\mathrm{EF} > 1$) during AMT 24 and AMT 25, respectively (maximum $\mathrm{EF} = 4.5$; Figure 3 and Table S1); the remaining four EF values being equal to unity within the analytical error (Table S1). Evidently, the SML is typically enriched in SA at all values of U_{10n} up to the highest recorded ($12.9\ \mathrm{m\,s^{-1}}$; Figure 4). In agreement with this observation *Wurl et al.* [2011] consistently found $\mathrm{EF} > 1$ in 44 oceanic samples (>20 km from land) from the North Pacific (mean 2.7 ± 1.3; range = 1.1–5.6). On this evidence surfactant enrichment of the SML could be a ubiquitous feature of the open ocean. In contrast, of 18 SML samples collected during seasonal transects up to 20 km from the North Sea coast, two had $\mathrm{EF} < 1$ and values overall (mean EF 1.2 ± 0.3; range = 0.8–1.5) were comparatively low [*Pereira et al.*, 2016]. *Wurl et al.* [2011] also found $\mathrm{EFs} < 1$, in 21% of low wind speed ($0\text{–}2\ \mathrm{m\,s^{-1}}$) and in 9% of moderate wind speed ($2\text{–}5\ \mathrm{m\,s^{-1}}$) samples from coastal and offshore sites

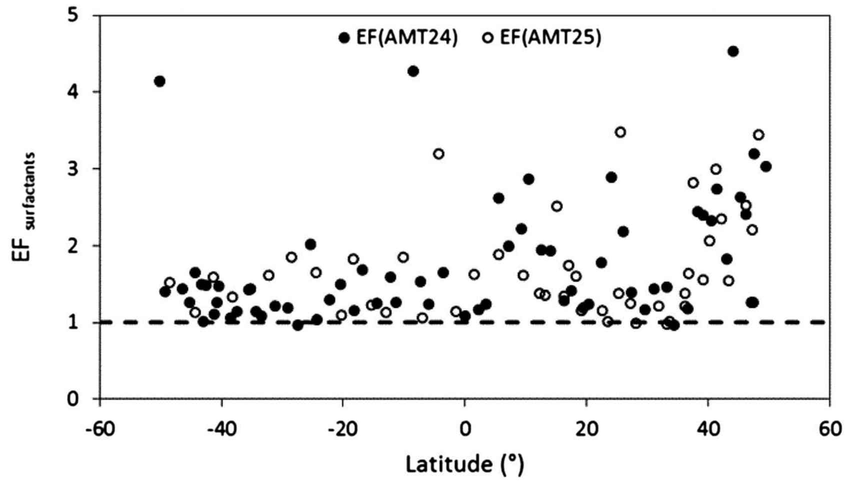

Figure 3. Latitudinal distribution of SA enrichment factors (EFs) in the SML.

(<20 km from land) in the North Pacific Ocean, Beaufort and Labrador Seas, and Baffin Bay. The persistent, high EFs during AMT 24 and AMT 25 are mirrored in high surface enrichments in dissolved organic carbon and amino acids in the subtropical Atlantic and western Mediterranean Sea at wind speeds approaching 10 m s^{-1} [*Reinthaler et al.*, 2008]. Mean EFs for the complete data set and for the Northern and Southern Hemispheres individually were statistically identical for both transects (*t* test, $p > 0.05$; Table S1). As observed for SA, mean Northern Hemisphere EF was higher than mean Southern Hemisphere EF, although the difference was only significant during AMT 24 (*t* test, $p < 0.05$) (Table S1). For both transects high EFs were mostly observed when SSW SA was <0.4 mg L^{-1} T-X-100. For SSW SA > 0.4 mg L^{-1} T-X-100, EF was always <2.6 (Figure 4).

We found no clear relationships between SA in the SML and either total chlorophyll or total pigments, for either the whole data set or on an individual province basis (Figure S1 in the supporting information), and we similarly found no relationships with either total or size-fractionated primary production (Figure S2). Although this is consistent with our finding no clear relationship between SA and chlorophyll *a* in the coastal North Sea [*Pereira et al.*, 2016], it contrasts with earlier work showing mean SA in the SML to increase linearly with "trophic state," as defined by using estimates of primary production, which implies at least a broad relationship between SML SA and primary production [*Wurl et al.*, 2011].

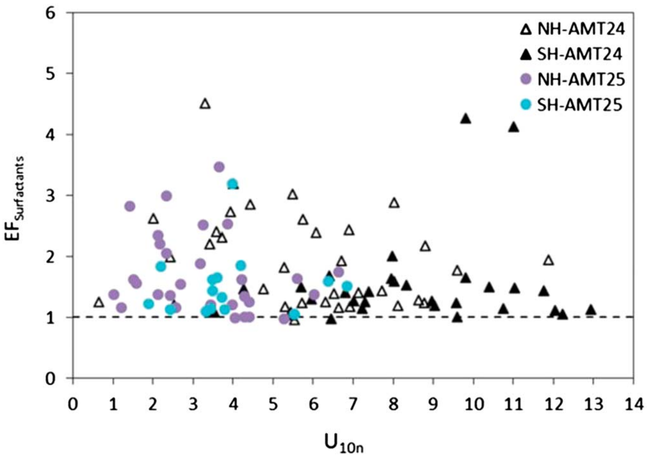

Figure 4. EF versus U_{10n} in the Northern Hemisphere (NH) and the Southern Hemisphere (SH). The dashed line represents EF = 1.

5. Discussion

The SA values we observed in the SML between 50°N and 50°S in the Atlantic Ocean (Figure 3) constitute the first direct test of an earlier prediction of SA distributions at the ocean basin scale derived from global maps of primary productivity and wind speed [*Wurl et al.*, 2011]. These authors reported SA values of 0.49 ± 0.4 mg L^{-1} T-X-100 in the SML (range: 0.1–1.57 mg L^{-1} T-X-100) for several oligotrophic regions including the North Pacific, the subtropical North Pacific, and the Arctic. Our ranges in SA and EF (Table S1) were within those given by *Wurl et al.* [2011], but our failure to observe any relationships between SA and either total chlorophyll (Figure S1), total primary production (Figure S2), or size-fractionated primary production (Figure S2) must challenge the validity of using either estimates of total primary production or indices thereof in a predictive capacity for SA. Even so, we do not find this surprising given the variability in surfactant production rates among individual species of phytoplankton [*Žutić et al.*, 1981], by bacteria [*Kurata et al.*, 2016], and following phytoplankton grazing by zooplankton [*Kujawinski et al.*, 2002]. While an additional possibility is that any relationships between surfactant and indices of primary productivity could be masked, at least in part, by the bacterial degradation of surfactant, the evidence for surfactant degradation by bacteria is rather limited, being restricted to coastal locations [*Nguyen and Sigoillot*, 1990; *Sigoillot and Nguyen*, 1996].

At ocean basin scales with diverse biogeochemical regimes, variability in the pathways of bacterial surfactant production will likely be maximal, involving temporal signals and additional effects from advection and mixing. Even so, our observations suggest a rather small interannual variability in Atlantic Ocean surfactant distributions, with major latitudinal contrasts being maintained (Figure 2).

Wurl et al. [2011] also predicted that high EFs for SA, and presumably for some other SML components, poleward of both 30°N and 30°S in the Atlantic Ocean, would be precluded by high ambient wind speeds ($>12\,\mathrm{m\,s^{-1}}$). On the contrary, our data clearly show high EFs (up to ~4.5) both north of 30°N and south of 30°S (Figure 4) and up to the maximum wind speed we observed ($U_{10n} = 12.9\,\mathrm{m\,s^{-1}}$; Figure 4). We contend that high EFs at such wind speeds should not be unexpected because it has long been known that the SML reforms rapidly following physical disruption [*Dragcevic and Pravdic*, 1981], something we later confirmed experimentally with respect to SA [*Cunliffe et al.*, 2013]. It is now well established that rapid SML recovery occurs because SML organics dispersed by breaking waves readily reabsorb to the surfaces of rising bubbles generated by the same breaking waves [*Stefan and Szeri*, 1999; *Woolf*, 2005], to be released back to the SML and or ejected to air via bubble bursting at the air-sea interface. Consequently, our data strongly support the notion of an essentially self-sustaining SML and we have no reason to suspect that this mechanism would cease to operate either at or beyond the maximum wind speeds we observed. The high level of agreement in SA distributions in the SML between AMT 24 and AMT 25 therefore likely indicates a dynamic equilibrium, whereby increased SML disruption at higher sea states is at least largely compensated by concomitantly increased bubble fluxes that act to continuously restore surfactant material to the SML. In other words, the greater is the SML disruption, the greater is the bubble flux acting to restore the status quo.

An important outcome of our reasoning is that SA enrichment of the SML should be essentially decoupled from ambient wind speed, a conclusion that was also reached by *Wurl et al.* [2011] for dissolved surfactant and by *Carlson* [1983] for surface dissolved organic carbon. Indeed, SA EFs are evidently more closely correlated with SSW SA. Our consistent observation of low EF coincident with high SSW SA (EF always <2.6 for SSW SA values $>0.4\,\mathrm{mg\,L^{-1}}$ T-X-100 is also supported by *Wurl et al.* [2011], who reported EF values <2.7 for SSW SA values $>0.6\,\mathrm{mg\,L^{-1}}$ T-X-100 in waters ranging from nearshore to oceanic. We believe the most plausible explanation for these observations is that for any given wind speed, bubble scavenging is proportionally greater in low SA waters than in high SA waters. This is a result of there being a finite limit to the amount of surfactant that can be supplied by any individual bubble to the SML. Consequently, SML enrichment is limited by the total number/surface area of bubbles and so in SSW of comparatively low SA a proportionately larger fraction of the available surfactant pool is available for bubble scavenging (leading to high EF) than in SSW of comparatively high SA (leading to low EF). An inverse relationship between EF and SSW SA is therefore inevitable.

6. Implications and Conclusions

A better understanding of the spatial and temporal variabilities of SML surfactants [*Frew*, 2005; *Schneider-Zapp et al.*, 2014; *Pereira et al.*, 2016] will be critical to improving future estimates of air-sea gas exchange rates. Ultimately, such understanding will enhance our ability to predict the variability in regional- to global-scale trace gas fluxes and feedback. For CO_2 the lack of direct measurements of SA, both in the SML and in the SSW, constitutes a large proportion of the current uncertainty surrounding the inherent spatiotemporal variability of k_w. Even correcting for such errors in k_w as may arise from methodological differences [*Asher*, 2009], this uncertainty is much larger than the spatiotemporal uncertainty in surface ΔpCO_2 [*Takahashi et al.*, 2009]. Two aspects of our SA data from AMT are especially relevant. First, the elevated SA values we observed in the NADR between 38°N and 48°N strongly imply that surfactant control of the air-sea exchange of CO_2 may be important over at least a substantial fraction of the North Atlantic, an ocean region that not only is a major CO_2 sink [*Watson et al.*, 1995; *Takahashi et al.*, 2009], but which shows a high variability in respect of its CO_2 uptake rate on subdecadal time scales that remains incompletely understood [*Schuster and Watson*, 2007; *Schuster et al.*, 2009; *Watson et al.*, 2009]. Second, our observations strongly imply that high-wind, high-latitude oceans may make a smaller contribution to air-sea gas exchange globally than is currently perceived. High SA in the SML at high latitudes suggests that air-sea trace gas fluxes might be lower than predicted from wind speed parameterizations alone, a conclusion that is supported by our earlier work in which a deliberate surfactant release in the North Atlantic resulted in up to 55% reduction in k_w relative to adjacent waters that were surfactant unamended, at a mean wind speed of 11 m s^{-1} [*Salter et al.*, 2011]. For coastal North Sea waters we also found evidence for strong k_w control, due not only to variability in SA but evidently also reflecting variability in the chemical composition of the surfactant pool that still remains largely unresolved [*Pereira et al.*, 2016].

To conclude, there is a clear need for continued measurements of SA in the SML and SSW at ocean basin scales, at contrasting times of year and over the full range of environmental wind speeds. Moreover, the mechanisms of surfactant production and consumption and the chemical composition of the surfactant pool need to be much better characterized in order to further advance our understanding of one of the most important environmental controls of k_w, and ultimately of the global budgets of a suite of climate-active gases.

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