

Impact of an artificial surfactant release on air-sea gas fluxes during Deep Ocean Gas Exchange Experiment II

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[1] During the 2007 UK SOLAS Deep Ocean Gas Exchange Experiment in the northeast Atlantic Ocean, we conducted the first ever study of the effect of a deliberately released surfactant (oleyl alcohol) on gas transfer velocities (k_w) in the open ocean. Exchange rates were estimated with the $^3\text{He}/\text{SF}_6$ dual tracer technique and from measured sea-to-air DMS fluxes and surface water concentrations. A total of seven k_w estimates derived from $^3\text{He}/\text{SF}_6$ were made, two of which were deemed to be influenced by the surfactant. These exhibited suppression from ~5% to 55% at intermediate wind speeds (U_{10}) in the range 7.2–10.7 m s⁻¹. Similarly, k_w determined from DMS data (k_{DMS}) was also depressed by the surfactant; suppression ranged from ~39% at 5.0 m s⁻¹ to ~24% at 10.8 m s⁻¹. Surfactant thus has the potential to measurably suppress gas exchange rates even at moderate to high wind speeds.

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1. Introduction

[2] Improved parameterization of air-sea gas exchange would substantially advance the science of ocean-atmosphere interaction. An exchange flux is the product of an air-sea gas concentration difference, ΔC , and a gas transfer velocity, k_w . The latter cannot be directly measured and is largely controlled by wind-driven near-surface turbulence. Estimating a dependence on wind speed at 10 m (U_{10}) is practical but has led to several divergent, highly nonlinear k_w vs U_{10} relations [e.g., *Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Nightingale et al.*, 2000a]. Uncertainty in k_w is now considered one of the greatest challenges to quantifying net global air-sea CO₂ exchange [*Takahashi et al.*, 2009] and is also important to the air-sea exchange of climate-active gases such as dimethyl sulfide (DMS). The data scatter within and between the various k_w vs U_{10} relations highlights the importance of additional geophysical controls of k_w such as atmospheric stability, sea state, wave breaking, white capping and bubble bursting, sea surface temperature, rain, wind stress, and the presence of surfactants

and organics [e.g., *Woolf*, 2005; *Ho et al.*, 2000; *Frew et al.*, 2004].

[3] Sea surface surfactants influence gas exchange in two fundamental ways, as a monolayer physical barrier and through modification of sea surface hydrodynamics and hence turbulent energy transfer. Owing to film disruption by winds and breaking waves, static “barrier” effects can largely be ignored [*Liss*, 1983].

[4] *Brockmann et al.* [1982] inferred ~30% reduction in coastal water CO₂ exchange following a deliberate release of oleyl alcohol (CH₃(CH₂)₇-CH = CH-(CH₂)₈OH). As far as we are aware, this is the only in situ study of surfactant control of gas exchange, most data being laboratory derived [*Goldman et al.*, 1988; *Frew et al.*, 1990; *Frew*, 1997; *Bock et al.*, 1999].

[5] During the UKSOLAS Deep Ocean Gas Exchange Experiment (DOGEE) II [*Brooks et al.*, 2009] we examined in situ modification of k_w by oleyl alcohol. This was the first deliberate release of an artificial surfactant in the open ocean (N.E. Atlantic) and was made in conjunction with a release of SF₆ and ^3He in order to estimate k_w on timescales of hours-days [*Watson et al.*, 1991] as follows:

$$k_{^3\text{He}} = h \frac{\delta}{\delta t} \left(\ln(^3\text{He}/\text{SF}_6) / \left(1 - (\text{Sc}_{\text{SF}_6} / \text{Sc}_{^3\text{He}})^{1/2} \right) \right) \quad (1)$$

where h is the tracer mixed layer depth and SF₆ and ^3He are the measured SF₆ and excess ^3He concentrations in the mixed layer, respectively. We also made independent estimates of k_w for dimethyl sulfide (DMS) from measured DMS

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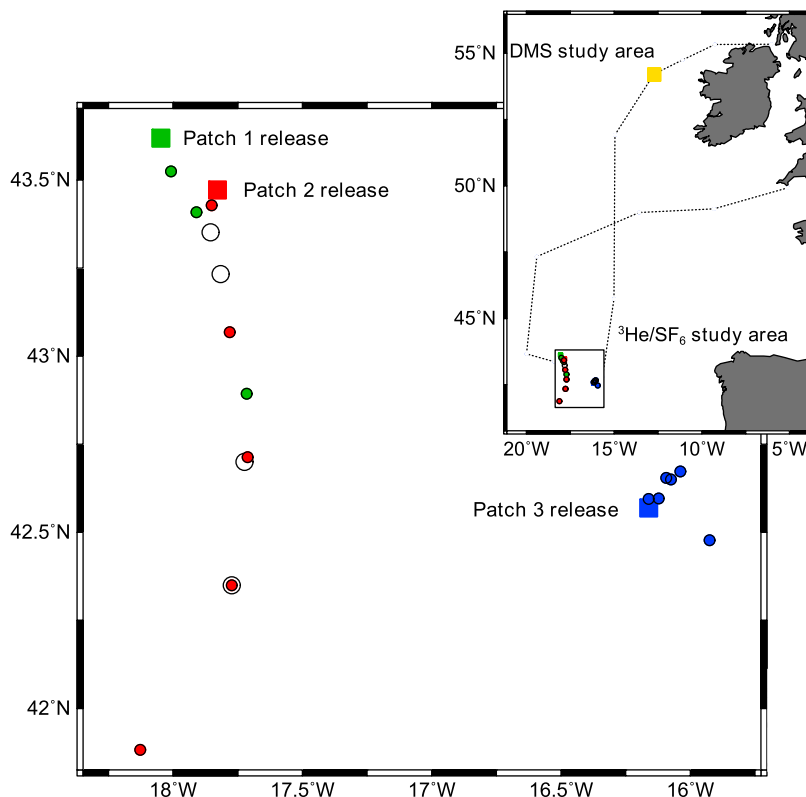


Figure 1. Map of the Deep Ocean Gas Exchange Experiment (DOGEE II) cruise study area, with the ship track (dots); locations of $^3\text{He}/\text{SF}_6$ tracer patches 1 (green square), 2 (red square) and 3 (blue square); stations where $^3\text{He}/\text{SF}_6$ samples were taken to calculate $k(660)$ (green, red, and blue circles); stations where surface film samples containing oleyl alcohol were identified (open circles); and the k_{DMS} surfactant release (yellow square).

fluxes and surface water DMS concentrations [Huebert *et al.*, 2010].

2. Methods

[6] The requirement to establish a large continuous surfactant film that would persist for several days without the need for reinjection dictated our surfactant choice. Although both soluble and insoluble surfactants occur in nature, surface slicks of insoluble surfactant that may form under calm conditions are thought to break down in moderate winds and hence only soluble surfactants effectively suppress k_w over a wide environmental range [Goldman *et al.*, 1988; Frew *et al.*, 1990; Bock *et al.*, 1999]. Nevertheless, the use of soluble surfactants in this work was precluded by the large quantities required. For an initial 1 km^2 surface patch of mixed layer depth $\sim 30 \text{ m}$ and with similar soluble surfactant concentrations used in laboratory experiments (i.e., $\sim 0.1 \mu\text{M}$ Triton-X-100 [Bock *et al.*, 1999], $\sim 1 \text{ ppm}$ Polyethylene oxide (PEO) [Frew, 1997]), $\sim 2000 \text{ kg}$ Triton-X-100 or $\sim 30,000 \text{ kg}$ PEO would be required. We therefore chose insoluble oleyl alcohol, recognizing that the timescale of the release might be limited by wind driven dispersal. Oleyl alcohol was used previously by Brockmann *et al.* [1982] in a coastal North Sea release and is well-characterized physicochemically (<http://www.chemicaland21.com>). Although oleyl alcohol readily forms a monomolecular surface film simulating natural surfactant [Hühnerfuss *et al.*, 1994;

Wismann *et al.*, 1998], it does not form condensed films. Static effects deriving from the intrinsic transfer resistance of monolayers are thus precluded and its effect on gas exchange is dynamic (viscoelastic) only [Takata *et al.*, 2002].

[7] During cruise D320 (DOGEE II) of RRS *Discovery* in the northeast Atlantic Ocean (06.16–07.17; 2007), we released three $\text{SF}_6/{}^3\text{He}$ dual tracer patches [Upstill-Goddard *et al.*, 1991], each at $\sim 10 \text{ m}$ depth and with initial dimensions $\sim 1 \times 1 \text{ km}$, in the vicinity of $\sim 43^\circ\text{N}$, 17°W (patches 1–3, Figure 1) to estimate k_w [Watson *et al.*, 1991].

[8] Preliminary hydrographic surveys revealed a sufficiently uniform hydrography around the selected release sites and this was confirmed postrelease using thermistor chain data obtained at the patch centers (Figure 2). We chose to define mixed layer depths (MLDs) by identifying the deepest sample in which we detected SF_6 above background in each case. These were always 15 to 30 m (Figure 3), on average $\sim 4 \text{ m}$ deeper than the MLD defined according to density criteria (i.e., $10 \text{ m density} + 0.03 \text{ kg m}^{-3}$) or thermistor chain data (Figure 2). Our chosen definition of MLD thus more accurately represents the depth of the water column actively exchanging gas with the overlying air. Patches were optimally spaced so as to minimize the possibility of subsequent coalescence while exposing them as far as practically possible to the same wind distribution. Patch 2 (Figure 1) was subsequently overlain by oleyl alcohol deployed as a stream of fine droplets $\sim 30 \text{ cm}$ above the sea surface. Deployment

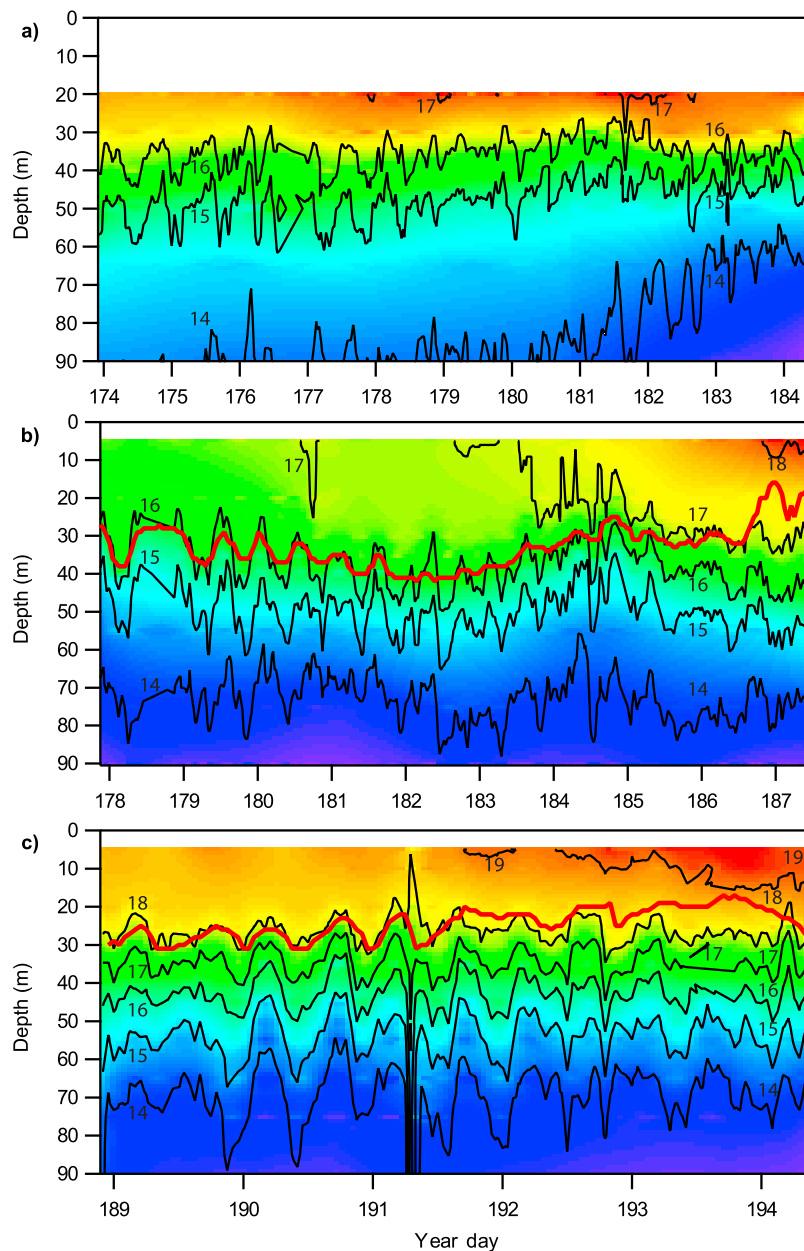


Figure 2. Contour plot of thermistor chain temperature data ($^{\circ}\text{C}$) from dual tracer patches (a) 1, (b) 2, and (c) 3. Note that the thermistor chains were repositioned at relevant patch centers in patches 1 and 2 and so time periods cannot be plotted: patch 1 year day (YD) 176.583–176.917 and YD 179.500–179.792; patch 2 YD 178.500–178.833. Mixed layer depths (MLDs) are those computed from the thermistor chain data using linear interpolation and based on the temperature criteria of *Kara et al.* [2000]. These are indicated by the solid red line in patches 2 and 3. Such analysis was not possible in patch 1 due to data logger failures.

was via a rotary hand pump and a hose attached to a sampling fish carefully located to avoid surfactant scavenging by the ship's propeller [Salter, 2010]. This produced a 2.5×2.5 km grid comprising two sets of parallel lines ~ 125 m apart intersecting at 90 degrees [Brooks et al., 2009; Salter, 2010] and centered on the maximal SF_6 concentration determined in continuous underway surveys [Upstill-Goddard et al., 1991]. On the basis of our observed low concentrations of chlorophyll-a ($1.5 \pm 1.0 \mu\text{g l}^{-1}$) we conclude the concentrations of natural, phytoplankton-derived surfactant

[Zutić et al., 1981] at the release site to have also been very low. For a 12 day period following the release we routinely sampled the patch centers with Niskin bottles at ~ 48 h intervals to generate duplicate or triplicate mixed layer profiles of SF_6 and ^3He [Law et al., 1994; Ludin et al., 1998] for multiple estimates of k_w [Watson et al., 1991]. Figure 3 shows the first four such mixed layer profiles obtained from patch 2; these profiles may be considered typical of the entire sampling period. Around $52^{\circ}\text{N } 15^{\circ}\text{W}$ to the west of Ireland (Figure 1) we made a smaller oleyl alcohol release ($\sim 1 \text{ km}^2$)

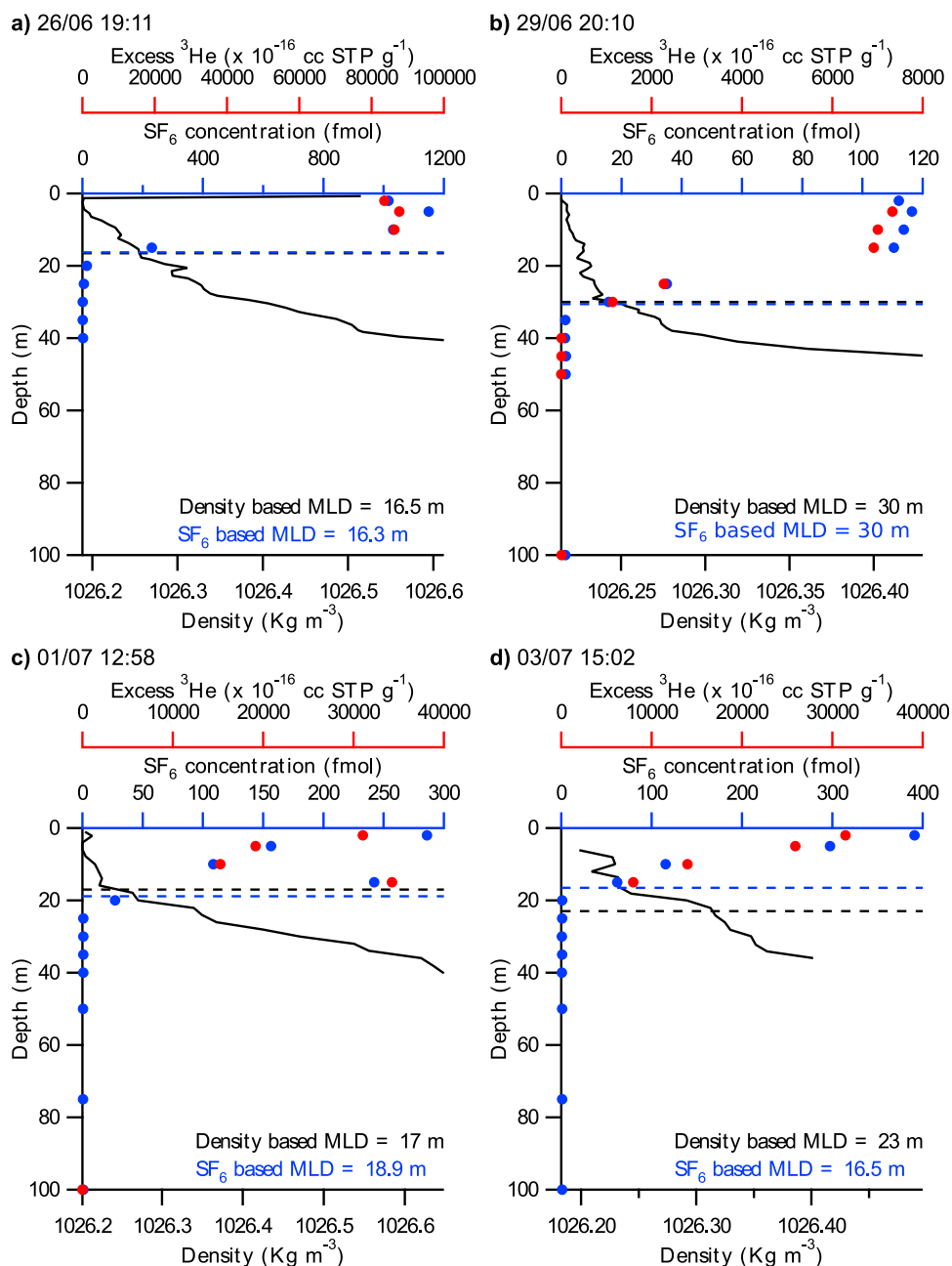


Figure 3. Depth profiles of SF₆ (blue circles; blue axis), ³He (red circles; red axis), and density (black line; black axis) for the first four stations in dual tracer patch 2 seeded with the surfactant (oleyl alcohol). The dashed black line represents the MLD calculated from 10 m density +0.03 kg m³ and the dashed blue line represents the MLD estimated from the deepest SF₆ measurement above background. Note the different concentration axis scales.

in high winds ($U_{10N} \sim 10 \text{ m s}^{-1}$) but without SF₆/³He. We estimated sea-to-air fluxes of DMS from eddy covariance [Huebert *et al.*, 2004, 2010] and surface water DMS measurements, thereby deriving independent k_w estimates for DMS (k_{DMS}) inside and outside the patches.

[9] DMS flux estimates were quality controlled following the protocols described by Huebert *et al.* [2010] with the added proviso for values “inside the patch” that the estimated flux footprint was always within the region influenced by the surfactant, as determined by surfactant analysis of corresponding surface microlayer samples [Salter, 2010].

All k_w estimates were normalized to a Schmidt number of 660, k_{660} , by multiplying by $(660/Sc)^{-0.5}$, where Sc is the temperature and salinity adjusted Schmidt number for SF₆ [King *et al.*, 1995], ³He (adjusted to account for a mass fractionation of 12.8% of ³He to ⁴He [Wanninkhof *et al.*, 1993]) or DMS [Saltzman *et al.*, 1993].

[10] We collected surface microlayer samples with a 275 × 275 mm stainless steel Garrett Screen (GS) (mesh size 16: 1.25 mm; wire diameter 0.36 mm) deployed from a small boat or directly from the ship’s bow and dark stored samples unfiltered at −80°C for subsequent oleyl alcohol analysis

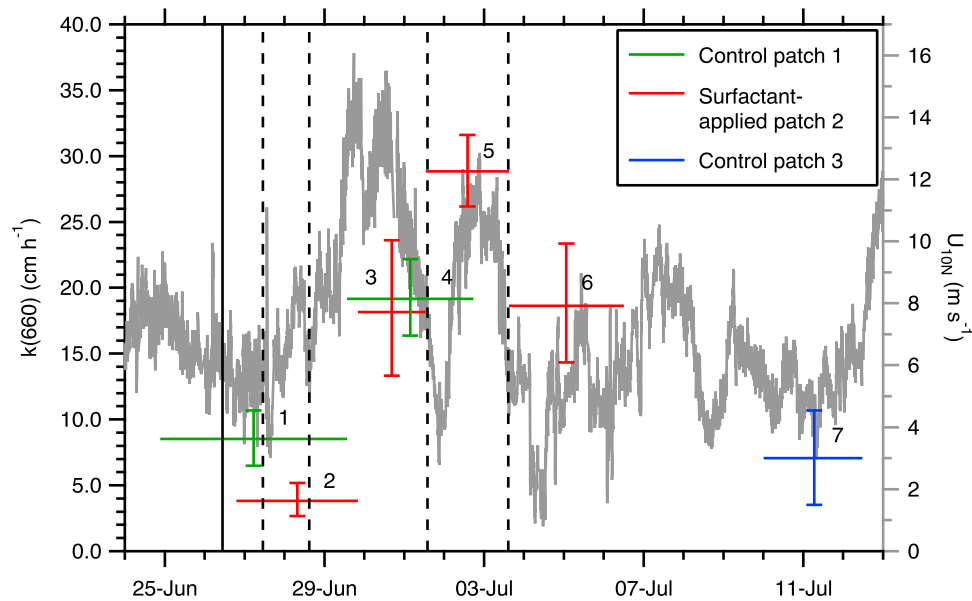


Figure 4. Air-sea gas transfer velocity estimates during DOGEE II. Estimates of k_{660} (the width of the solid horizontal lines indicates the time period over which the estimate was made) in control dual tracer patches 1 (green) and 3 (blue), and experiment dual tracer patch 2 with applied surfactant (red) are plotted with ship-derived U_{10N} (filled grey line). The filled black line indicates when the surfactant was released in dual tracer patch 2 and dashed lines indicate stations where the surfactant was identified in surface samples.

postcruise by phase-sensitive AC voltammetry [Salter, 2010]. The GS routinely samples the top 400 μm of the water column [Cunliffe *et al.*, 2009] and we found no measurable contamination of over-bow samples [Salter, 2010]. Wind speeds (5 min. averages) were derived from the ship's standard meteorological package located 18.5 m above the sea surface and corrected to 10 m adjusted for atmospheric stability (U_{10}) [Large and Pond, 1981] and flow distortion by the ship's superstructure (U_{10N}) [Yelland *et al.*, 2002].

3. Results

[11] Dual tracer-derived estimates of k_{660} were positively correlated with U_{10N} (Figure 4) and ranged from 7.1 to 19.2 cm h^{-1} in patches 1 and 3 (oleyl alcohol free) and 3.8

to 28.8 cm h^{-1} in patch 2 (oleyl alcohol applied) (Table 1). The estimates from patches 1 and 2 were obtained in close temporal proximity and their similar mean values of U_{10N} imply significant surfactant-induced suppression of k_{660} . For example, comparing the first two sampling points in each of patches 1 and 2 (mean U_{10N} 6.9 and 7.6 m s^{-1} respectively) implies a suppression of k_{660} by the surfactant $\sim 55\%$ (Figure 4). Although the enhancement of gas exchange caused by the variability in wind speed is slightly higher in the surfactant influenced estimate (by a factor of 1.12 compared to 1.05 (Table 1)), the ratio of these values is significantly smaller than the ratio of the k_{660} estimates. Therefore wind variability is unlikely to have been responsible for the differences in the k_{660} estimates. To examine the implied k_w suppression more robustly, we modeled the decrease in \ln

Table 1. Summary of Wind and Dual Tracer-Derived $k(660)$ Obtained During DOGEE II

Patch	Date/Time of Station (LT)	U_{10N} (m s^{-1})		$\overline{\Sigma u^2 u_{av}^{-2}}$	$\overline{\Sigma u^3 u_{av}^{-3}}$	$k(660)$		k_{inst,u^2}^a (cm h^{-1})	k_{inst,u^3}^a (cm h^{-1})	${}^3\text{He}/\text{SF}_6$ Suppression ^b
		Mean	SD			Mean	SE			
1	24 Jun 21:22									
	29 Jun 13:40	6.85	1.58	1.05	1.17	8.1	2.0	7.7	6.9	0.98
	2 Jul 17:36	10.11	3.04	1.09	1.26	18.3	2.8	16.8	14.5	0.86
2	26 Jun 19:11									
	29 Jun 20:10	7.63	2.64	1.12	1.40	3.6	1.2	3.2	2.6	1.21
	1 Jul 12:58	11.36	2.02	1.03	1.09	17.3	4.9	16.8	15.9	1.29
	3 Jul 15:02	8.49	2.51	1.09	1.25	27.5	2.6	25.2	22.2	1.09
3 ^c	6 Jul 12:03	4.95	1.54	1.10	1.27	17.8	4.3	16.2	14.0	0.48
	10 Jul 01:47									
	12 Jul 11:23	5.35	0.86	1.03	1.08	6.7	3.4	6.5	6.2	0.96

^aHere $k(660)$ is the average gas transfer velocity over the time period while k_{inst,u^2} and k_{inst,u^3} are the inferred steady or instantaneous gas transfer velocities at the mean wind speed based on the wind speed distribution over the time interval using a square law or cubic dependence, respectively.

^bThe ${}^3\text{He}/\text{SF}_6$ suppression is the measured ${}^3\text{He}/\text{SF}_6$ compared to the expected ${}^3\text{He}/\text{SF}_6$ derived using the commonly applied relation of Liss and Merlivat [1986] following the procedures of Kuss *et al.* [2004].

^cAll CTD stations in patch 3 were used to derive a single $k(660)$ value by averaging time and ${}^3\text{He}/\text{SF}_6$ ratios.

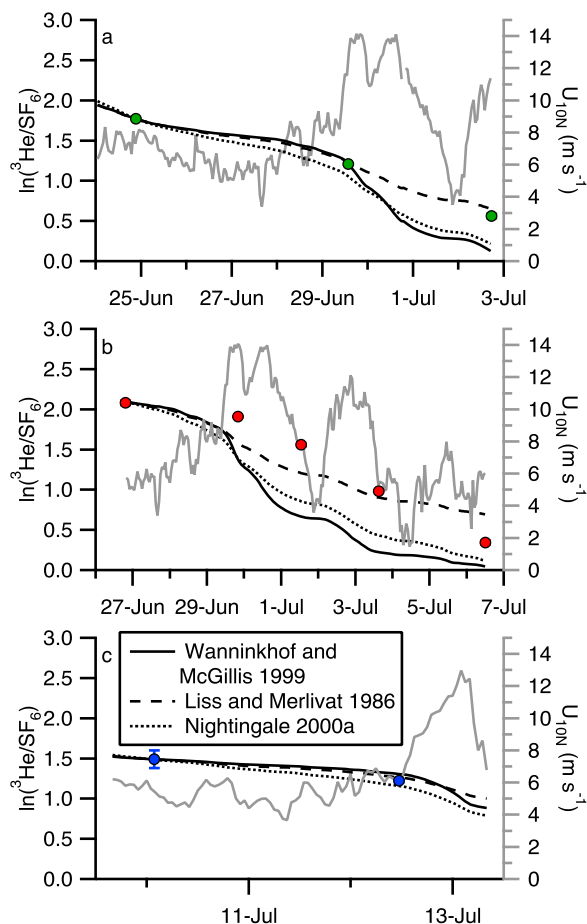


Figure 5. Observed and modeled changes in $\ln(^3\text{He}/\text{SF}_6)$ ratios over time in (a) control patch 1, (b) surfactant-applied patch 2, and (c) control patch 3, using three well-established wind speed–based dependencies of gas exchange; *Liss and Merlivat* [1986] (dashed line), *Wanninkhof and McGillis* [1999] (solid line), and *Nightingale et al.* [2000a] (dotted line). Error bars refer to standard errors in the mixed layer values of $\ln(^3\text{He}/\text{SF}_6)$ which typically were 2.0, 2.3, and 4.0% in patches 1, 2, and 3, respectively.

$(^3\text{He}/\text{SF}_6)$ with time for each of the three dual tracer patches and compared it with $\ln(^3\text{He}/\text{SF}_6)$ determined in situ (i.e., those values used to estimate k_w through equation (1)), according to the procedures of *Kuss et al.* [2004]. We applied the analysis to three commonly used k_w vs U_{10N} relations [*Liss and Merlivat*, 1986; *Wanninkhof and McGillis*, 1999; *Nightingale et al.*, 2000a] and plotted the results versus 5 min averaged values of U_{10N} , with the initial modeled value of $\ln(^3\text{He}/\text{SF}_6)$ adjusted to be numerically equal to the first in situ estimate of $\ln(^3\text{He}/\text{SF}_6)$ in each patch (Figure 5). In patches 1 and 3, modeled $\ln(^3\text{He}/\text{SF}_6)$ closely followed in situ $\ln(^3\text{He}/\text{SF}_6)$ for 5 days after patch release with the ratios derived according to the *Liss and Merlivat* [1986] dependency showing closest agreement. Root mean square (rms) analysis of the first 5 days in each case gave the following errors: *Liss and Merlivat* [1986] 3%; *Wanninkhof and McGillis* [1999] 4%; *Nightingale et al.* [2000a] 8%. By contrast, in oleyl alcohol patch 2, modeled $\ln(^3\text{He}/\text{SF}_6)$ was substantially lower than in situ $\ln(^3\text{He}/\text{SF}_6)$ for the 5 days

following patch release although the discrepancy decreased with time, presumably as a result of progressive oleyl alcohol dispersal. This difference is highlighted further upon evaluation of the difference between the observed $^3\text{He}/\text{SF}_6$ values and those modeled using the *Liss and Merlivat* [1986] relation, chosen due to its observed similarity with the data in patches 1 and 2. The $^3\text{He}/\text{SF}_6$ suppression values in Table 1 are a relative value using (measured $^3\text{He}/\text{SF}_6$)/(*Liss and Merlivat* [1986] modeled $^3\text{He}/\text{SF}_6$) such that values greater than 1 indicate suppression. The values in patch 2 emphasize the apparent suppression of gas exchange by the released surfactant during the first 5 days following release. Corresponding RMS errors to those in patches 1 and 3 were *Liss and Merlivat* [1986] 15%; *Wanninkhof and McGillis* [1999] 58%; *Nightingale et al.* [2000a] 37%. Our analysis unequivocally demonstrates a significant reduction of $\ln(^3\text{He}/\text{SF}_6)$ and hence k_w , in surfactant influenced water.

[12] Figure 6 shows all of our DMS-based estimates of k_{660} versus U_{10N} from DOGEE II. Those estimates made outside the surfactant affected region have been presented previously [*Huebert et al.*, 2010] but those from within the oleyl alcohol patch are here presented for the first time. Analysis of the linear regressions fitted to the oleyl alcohol and oleyl alcohol-free estimates of k_{660} (students t-test) show oleyl alcohol influenced estimates of k_{660} to be significantly lower than those for oleyl alcohol-free waters ($t = 2.87$, $\nu = 75$; since $t_{0.05(2)75} = 1.99$, [$P = 0.003$]). From our estimates of k_{660} , derived both with $\text{SF}_6/^3\text{He}$ and from DMS fluxes and concentrations, it seems to us an inescapable conclusion that the application of an artificial surfactant consistently resulted in significant suppression of k_{660} during DOGEE II, even at higher wind speeds; using DMS-based estimates k_{660} suppression ranged from 39% at 5.0 m s^{-1} to 24% at 10.8 m s^{-1} and using $\text{SF}_6/^3\text{He}$ -derived estimates k_{660} suppression ranged from 55% at 7.2 m s^{-1} to 5% at 10.7 m s^{-1} .

4. Discussion

[13] Suppression of k_w by both synthetic and natural surfactants is now clearly established in the laboratory and in the field (Table 2). Comparing our initial $\text{SF}_6/^3\text{He}$ estimates of k_{660} in patches 1 and 2 gives ~55% suppression of k_{660} for U_{10N} : ~7.2 m s^{-1} ; however comparing the second dual tracer estimates of k_{660} in patches 1 and 2 the suppression is only ~5% which is of the same order as the error inherent in $\text{SF}_6/^3\text{He}$ -derived estimates of k_w . It should however be noted that the second estimate incorporates a period of higher U_{10N} values ~10.7 m s^{-1} some 5 days postrelease and therefore must reflect substantial dispersal of the oleyl alcohol and dual tracer patches. Our estimate of an initial 55% suppression of k_{660} is similar to those for laboratory experiments with added synthetic soluble surfactants (maximum of 60–90% reduction in O_2 exchange) [*Frew*, 1997; *Bock et al.*, 1999] and somewhat higher than those for natural oceanic/coastal waters and phytoplankton exudates (5–50% reduction in O_2 exchange) [*Goldman et al.*, 1988; *Frew et al.*, 1990]. Considering that the oleyl alcohol used during this experiment is likely more physicochemically similar to the synthetic surfactants used previously than to natural surfactants such as phytoplankton exudates, this is perhaps unsurprising. Indeed oleyl alcohol

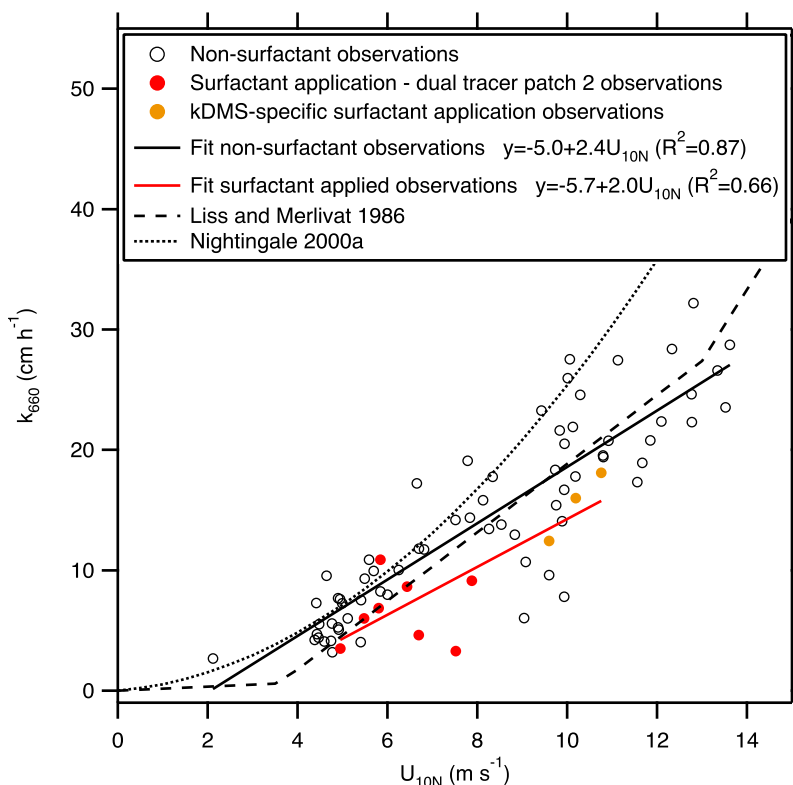


Figure 6. DMS-based estimates of k_{660} versus wind speed. Open circles represent estimates unaffected by the released surfactant, red and gold circles are estimates influenced by the surfactant from dual tracer patch 2 and the k_{DMS} -surfactant experiment patch, respectively. The black solid line is a linear fit to estimates unaffected by the surfactant and the red solid line is a linear fit to estimates influenced by the surfactant. The relationships proposed by *Liss and Merlivat* [1986] (dashed line) and *Nightingale et al.* [2000a] (dotted line) are added for reference.

and other synthetic surfactants such as Triton-X-100 have different adsorption/desorption kinetics to natural surfactants; for example both Triton-X-100 and oleyl alcohol are much more strongly adsorbed than is polysaccharide xanthan, which represents a significant fraction of the phytoplankton-derived surfactant pool [Passow *et al.*, 1994].

[14] As far as we are aware there has only been one prior field study in which the impact of added surfactant on air-sea gas exchange was evaluated in situ and this showed 30% suppression of CO_2 exchange in an oleyl alcohol patch relative to adjacent, comparatively low-surfactant waters [Brockmann *et al.*, 1982]. However these estimates were for relatively low wind speeds $\sim 1.5\text{--}3.0\text{ m s}^{-1}$, as compared to

$\sim 7\text{--}10\text{ m s}^{-1}$ during DOGEE II and because the experiment was conducted in coastal North Seawaters, natural background surfactant concentrations were likely much higher than during DOGEE II. Indeed, Brockmann *et al.* [1982] noted a decrease in the fatty acid content of sea surface microlayer samples following oleyl alcohol release which they attributed to the displacement of natural surfactant during the oleyl alcohol addition.

[15] Our DOGEE II data importantly show a strong suppression of k_w by surfactant, even at moderate-high wind speeds ($U_{10} > 10\text{ m s}^{-1}$) and a strong wind speed dependence (39% suppression at $U_{10} = 5.0\text{ m s}^{-1}$; 24% suppression at $U_{10} = 10.8\text{ m s}^{-1}$). This has also been observed in

Table 2. Studies Conducted to Evaluate the Suppression of Air-Sea Gas Exchange by Surfactants

Type of Study	k_w Suppression Observed	Reference
	<i>Laboratory Studies</i>	
Oceanic waters	$\sim 10\%$ reduction in O_2 exchange	Goldman <i>et al.</i> [1988]
Coastal waters	$\sim 50\%$ reduction in O_2 exchange	Goldman <i>et al.</i> [1988]
Phytoplankton exudates	$\sim 5\text{--}50\%$ reduction in O_2 exchange	Frew <i>et al.</i> [1990]
Addition of soluble surfactant	Up to 90% reduction in O_2 exchange	Frew [1997]
Addition of soluble surfactant ($0.1\ \mu\text{M}$ T-X-100)	Maximum of 60% reduction in O_2 exchange	Bock <i>et al.</i> [1999]
California Bight surface water samples	Power law dependence of k_w on surface active organic matter	Frew <i>et al.</i> [2002]
	<i>Field Studies</i>	
Artificial slick of oleyl alcohol	$\sim 30\%$ reduction in diffusion rate of CO_2	Brockmann <i>et al.</i> [1982]
Artificial slick of oleyl alcohol	$\sim 55\%$ reduction in SF_6/He -derived k_{660}	This study
Artificial slick of oleyl alcohol	$\sim 24\text{--}39\%$ reduction in DMS-derived k_{660}	This study

laboratory experiments with water-soluble surfactants, many of which found bilinearity of the U_{10N} versus k_w relation [Liss and Merlivat, 1986; Jähne et al., 1987; Wanninkhof, 1992; Frew, 1997]. This bilinearity is attributable to capillary waves which first occur at a critical wind speed dependent on the type and quantity of surfactants present [Saylor and Handler, 1997]. Both Frew et al. [1990] and Goldman et al. [1988] found reductions in CO_2 exchange rate $\sim 50\text{--}60\%$ at high levels of turbulence. Jähne et al. [1987] and Frew [1997] showed that even above the critical wind speed, k_w values for a surfactant influenced surface still fall well below the clean U_{10N} vs k_w relation. These findings, along with our observation of suppression at moderate wind speeds may be attributed to the high spreading pressure of the chosen surfactant. Garrett and Barger [1970] noted that materials with high spreading pressures not only spread rapidly but will move against and resist wind to a greater degree than low-pressure films. Therefore it is possible that short waves may have been damped even in the presence of larger breaking waves.

[16] Our observation that surfactants may suppress gas exchange at higher wind speeds with breaking waves is potentially important because it could to some degree offset the expected abrupt increase in k_w due to wave breaking [Asher et al., 1996].

5. Conclusions

[17] DOGEE II was the first attempt to directly investigate the role of surfactants in open ocean gas exchange in the field. Independent estimates of k_{660} from dual tracers (SF_6 / ^3He) and DMS fluxes and surface water concentrations unequivocally demonstrated significant k_w suppression in the presence of added oleyl alcohol surfactant. A measurable effect for values of U_{10N} as high as $\sim 10\text{ m s}^{-1}$ highlights the potential for surfactant reabsorption at the sea surface and perhaps provides a mechanism to offset the expected abrupt increase in gas exchange due to wave breaking.

[18] The extent to which variations in surfactant activity affect air-sea gas exchange at ocean basin scales from coastal waters to oligotrophic gyres remains unknown. Although 30-fold increases in chlorophyll-a during earlier SF_6 / ^3He estimates of k_w in the open ocean did not yield a detectable surfactant effect [Nightingale et al., 2000b], the available estuarine and coastal data imply large spatial and temporal gradients in surfactant activity that broadly relate to productivity proxies such as chlorophyll-a and other biogeochemical variables [Salter, 2010]. Future experiments of the type described here but also examining the gas exchange effects of natural gradients in surfactant should help elucidate further the role of surfactants in air-sea interaction.

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References

- Asher, W. E., L. M. Karle, B. J. Higgins, P. J. Farley, E. C. Monahan, and I. S. Leifer (1996), The influence of bubble plumes on air-seawater gas transfer velocities, *J. Geophys. Res.*, *101*, 12,027–12,041.
- Bock, E. J., T. Hara, N. M. Frew, and W. R. McGillis (1999), Relationship between air-sea gas transfer and short wind waves, *J. Geophys. Res.*, *104*, 25,821–25,831, doi:10.1029/1999JC900200.
- Brockmann, U. H., H. Hühnerfuss, G. Kattner, H. C. Broecker, and G. Hentzchel (1982), Artificial surface films in the sea area near Sylt, *Limnol. Oceanogr.*, *27*(6), 1050–1058.
- Brooks, I. M., et al. (2009), Physical exchanges at the air-sea interface: UK-SOLAS field measurements, *Bull. Am. Meteorol. Soc.*, *90*(5), 629–644, doi:10.1175/2008BAMS2578.1.
- Cunliffe, M., M. Salter, P. J. Mann, A. S. Whiteley, R. C. Upstill-Goddard, and J. C. Murrell (2009), Dissolved organic carbon and bacterial populations in the gelatinous surface microlayer of a Norwegian fjord mesocosm, *FEMS Microbiol. Lett.*, *299*, 248–254.
- Frew, N. M. (1997), The role of organic films in air-sea exchange, in *The Sea Surface and Global Change*, edited by P. S. Liss and R. A. Duce, pp. 121–172, Cambridge Univ. Press, New York.
- Frew, N. M., J. C. Goldman, M. R. Dennett, and A. S. Johnson (1990), Impact of phytoplankton-generated surfactants on air-sea gas exchange, *J. Geophys. Res.*, *95*, 3337–3352.
- Frew, N. M., R. K. Nelson, W. R. McGillis, J. B. Edson, E. J. Bock, and T. Hara (2002), Spatial variations in surface microlayer surfactants and their role in modulating air-sea exchange, in *Gas Transfer at Water Surfaces*, edited by M. Donelan et al., pp. 153–159, AGU, Washington, D. C.
- Frew, N. M., et al. (2004), Air-sea gas transfer: Its dependence on wind stress, small-scale roughness, and surface films, *J. Geophys. Res.*, *109*, C08S17, doi:10.1029/2003JC002131.
- Garrett, W. D., and W. R. Barger (1970), Factors affecting the use of monomolecular surface films to control oil pollution on water, *Environ. Sci. Technol.*, *4*, 123–127, doi:10.1021/es60037a006.
- Goldman, J. C., M. R. Dennett, and N. M. Frew (1988), Surfactant effects on air-sea gas exchange under turbulent conditions, *Deep Sea Res.*, *35*(12), 1953–1970, doi:10.1016/0198-0149(88)90119-7.
- Ho, D. T., W. E. Asher, L. F. Bliven, P. Schlosser, and E. L. Gordan (2000), On mechanisms of rain-induced air-water gas exchange, *J. Geophys. Res.*, *105*, 24,045–24,057, doi:10.1029/1999JC000280.
- Huebert, B., B. Blomquist, J. Hare, C. Fairall, J. Johnson, and T. Bates (2004), Measurement of the sea-air DMS flux and transfer velocity using eddy correlation, *Geophys. Res. Lett.*, *31*, L23113, doi:10.1029/2004GL021567.
- Huebert, B. J., B. W. Blomquist, M. X. Yang, S. D. Archer, P. D. Nightingale, M. J. Yelland, J. Stephens, R. W. Pascal, and B. I. Moat (2010), Linearity of DMS transfer coefficient with both friction velocity and wind speed in the moderate wind speed range, *Geophys. Res. Lett.*, *37*, L01605, doi:10.1029/2009GL041203.
- Hühnerfuss, H., A. Gericke, W. Alpers, R. Theis, V. Wismann, and P. A. Lange (1994), Classification of sea slicks by multifrequency radar techniques: New chemical insights and their geophysical implications, *J. Geophys. Res.*, *99*, 9835–9845, doi:10.1029/93JC03308.
- Jähne, B., K. O. Münnich, R. Bosinger, A. Dutzi, W. Huber, and P. Libner (1987), On the parameters influencing air-water gas exchange, *J. Geophys. Res.*, *92*, 1937–1949.
- Kara, A. B., P. A. Rochford, and H. E. Hurlburt (2000), An optimal definition for ocean mixed layer depth, *J. Geophys. Res.*, *105*, 16,803–16,821, doi:10.1029/2000JC900072.
- King, D. B., W. J. de Bryun, M. Zheng, and E. S. Saltzman (1995), Uncertainties in the molecular diffusion coefficient of gases in water for use in estimation of air-sea exchange, in *Air-Water Gas Transfer*, edited by B. Jähne and E. C. Monahan, pp. 13–23, AEON, Hanau, Germany.
- Kuss, J., K. Nagel, and B. Schneider (2004), Evidence from the Baltic Sea for enhanced CO_2 air-sea transfer velocity, *Tellus*, *56*, 175–182.
- Large, W. G., and S. Pond (1981), Open ocean momentum flux measurements in moderate to strong winds, *J. Phys. Oceanogr.*, *10*, 709–726.
- Law, C. S., A. J. Watson, and M. I. Liddicoat (1994), Automated vacuum analysis of sulphur hexafluoride in seawater: Derivation of the atmospheric trend (1970–1993) and potential as a transient tracer, *Mar. Chem.*, *48*(1), 57–69, doi:10.1016/0304-4203(94)90062-0.
- Liss, P. S. (1983), Gas transfer: Experiments and geochemical implications, in *Air-Sea Exchange of Gases and Particles*, edited by G. L. Hoffmann et al., pp. 241–298, D. Reidel, Dordrecht, Netherlands.
- Liss, P. S., and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113–129, D. Reidel, Dordrecht, Netherlands.

- Ludin, A., R. Weppernig, G. Bonisch, and P. Schlosser (1998), Mass spectrometric measurement of helium isotopes and tritium in water samples, technical report, Lamont-Doherty Earth Obs., Palisades, N. Y.
- Nightingale, P., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000a), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, *14*, 373–387, doi:10.1029/1999GB900091.
- Nightingale, P. D., P. S. Liss, and P. Schlosser (2000b), Measurements of air-sea gas transfer during an open ocean algal bloom, *Geophys. Res. Lett.*, *27*, 2117–2120, doi:10.1029/2000GL011541.
- Passow, U., B. E. Logan, and A. Alldredge (1994), The role of particulate carbohydrate exudates in the flocculation of diatom blooms, *Deep Sea Res.*, *41*, 335–357, doi:10.1016/0967-0637(94)90007-8.
- Salter, M. E. (2010), A role for natural surfactants in air-sea gas exchange?, Ph.D. thesis, Sch. of Mar. Sci. and Technol., Newcastle Univ., Newcastle upon Tyne, U. K.
- Saltzman, E. S., D. B. King, K. Holmen, and C. Leck (1993), Experimental determination of the diffusion coefficient of dimethylsulfide in water, *J. Geophys. Res.*, *98*, 16,481–16,486, doi:10.1029/93JC01858.
- Saylor, J. R., and R. A. Handler (1997), Gas transport across an air/water interface populated with capillary waves, *Phys. Fluids*, *9*, 2529–2541.
- Takahashi, T., et al. (2009), Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans, *Deep Sea Res. Part II*, *56*(8–10), 554–577, doi:10.1016/j.dsr2.2008.12.009.
- Takata, Y., R. Murakami, J. Taura, T. Maki, K. Mitsutake, M. Suzuki, T. Takiue, and M. Aratono (2002), Thermodynamic study on the adsorption of oleyl alcohol at oil/water interface, *Langmuir*, *18*(20), 7544–7548, doi:10.1021/la020269r.
- Upstill-Goddard, R. C., A. J. Watson, J. Wood, and M. I. Liddicoat (1991), Sulphur hexafluoride and helium-3 as sea-water tracers: Deployment techniques and continuous underway analysis for sulphur hexafluoride, *Anal. Chim. Acta*, *249*, 555–562.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382, doi:10.1029/92JC00188.
- Wanninkhof, R., and W. R. McGillis (1999), A cubic relationship between air-sea CO₂ exchange and wind speed, *Geophys. Res. Lett.*, *26*, 1889–1892.
- Wanninkhof, R., W. Asher, R. Weppernig, H. Chen, P. Schlosser, C. Langdon, and R. Sambrotto (1993), Gas transfer experiment on Georges Bank using two volatile deliberate tracers, *J. Geophys. Res.*, *98*, 20,237–20,248.
- Watson, A. J., R. C. Upstill-Goddard, and P. S. Liss (1991), Air-sea gas exchange in rough and stormy seas measured by a dual tracer technique, *Nature*, *349*, 145–147.
- Wismann, V., M. Gade, W. Alpers, and H. Hühnerfuss (1998), Radar signatures of marine mineral oil spills measured by an airborne multi-frequency radar, *Int. J. Remote Sens.*, *19*(18), 3607–3623, doi:10.1080/014311698213849.
- Woolf, D. K. (2005), Parameterization of gas transfer velocities and sea-state-dependent wave breaking, *Tellus Ser. B*, *57*(2), 87–94, doi:10.1111/j.1600-0889.2005.00139.x.
- Yelland, M. J., B. I. Moat, R. W. Pascal, and D. I. Berry (2002), CFD model estimates of the airflow distortion over research ships and the impact on momentum flux measurements, *J. Atmos. Oceanic Technol.*, *19*(10), 1477–1499.
- Zutić, V. B., E. Cosović, E. Marčenko, and N. Bihari (1981), Surfactant production by marine phytoplankton, *Mar. Chem.*, *10*, 505–520, doi:10.1016/0304-4203(81)90004-9.

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