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Formation and distribution of sea-surface microlayers

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BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Results from a study of surfactants in the sea-surface microlayer (SML) in different regions of the ocean (subtropical, temperate, polar) suggest that this interfacial layer between the ocean and atmosphere covers the ocean's surface to a significant extent.

5 Threshold values at which primary production acts as a significant source of natural surfactants have been derived from the enrichment of surfactants in the SML relative to underlying water and local primary production. Similarly, we have also derived a wind speed threshold at which the SML is disrupted. The results suggest that surfactant enrichment in the SML is typically greater in oligotrophic regions of the ocean than
10 in more productive waters. Furthermore, the enrichment of surfactants persisted at wind speeds of up to 10 m s^{-1} without any observed depletion above 5 m s^{-1} . This suggests that the SML is stable enough to exist even at the global average wind speed of 6.6 m s^{-1} . Global maps of primary production and wind speed are used to estimate the ocean's SML coverage. The maps indicate that wide regions of the Pacific and
15 Atlantic Oceans between 30° N and 30° S are more significantly affected by the SML than northern of 30° N and southern of 30° S due to higher productivity (spring/summer blooms) and wind speeds exceeding 12 m s^{-1} respectively.

1 Introduction

The sea-surface microlayer (SML) represents the boundary interface between the atmosphere and ocean, covering about 70% of the Earth's surface. Despite the thinness of the SML, ranging typically between 30 to $250 \mu\text{m}$, this interface may play a significant role in biogeochemical processes on a global scale, including air-sea gas and heat exchange (Liss and Duce, 1997), particle cycling (Wheeler, 1975; Wurl and Holmes, 2008), and microbial loops (Reinthal et al., 2008).

25 The SML is known to concentrate, to varying degrees, many chemical compounds, in particular those that are surface-active (surfactants). The enrichment of naturally

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

occurring organic compounds, such as carbohydrates, proteins, and lipids, modifies the chemical and physical properties of the sea surface. The primary sources of natural surfactants are phytoplankton exudates (Žutic et al., 1981), which are transported to the surface via rising bubbles and diffusion. Carbohydrates represent a high fraction of the exudates and are potentially surface-active. At the ocean surface, the surfactants form thin films, which have been found to significantly dampen air-sea gas exchange (Broecker, et al., 1978; Goldman et al., 1988; Frew et al., 2002). Thus, such surfactant films have the potential to cause significant biases in estimates of air-sea gas exchange rates of greenhouse gases (CO₂, CH₄, N₂O, DMS) affecting the Earth's radiation budget.

Asher (1997) and Tasi and Lui (2003) assessed the effect of the SML on global air-sea CO₂ fluxes using global ocean primary productivity maps and suggested that the annual net flux is reduced by at least 20%. However, the authors chose somewhat arbitrary threshold values of local primary production as an indicator for the presence of surfactant films.

Liss (1975) recognized early that rising air bubbles coated with surface-active organic matter are a major transport vector of these substances from the bulk water to the ocean surface. Bubbles bursting at the ocean's surface eject only a small fraction of the organic matter to the atmosphere as aerosols, and the remaining fraction is available for the formation of surfactant films (Liss, 1975).

Wurl et al. (2009) have observed enrichment of surface-active substances in the SML, relative to bulk water, by a factor of up to 2 at wind speeds exceeding the average global wind speed over the ocean of 6.6 m s⁻¹ (Archer and Jacobson, 2005). Earlier reports in the literature (Sieburth et al., 1976; Williams et al., 1986; Reinthaler et al., 2008) have already indicated that surfactant enrichment in the SML can exist at typical open ocean conditions. Therefore, wind conditions need to be considered when assessing the distribution and formation of surface surfactant films.

This study presents a first estimate of the ocean's coverage with SML based on experimental data using primary productivity and wind speed as indicators for the

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

5 withdrawn gently at a speed of $5\text{--}6\text{ cm s}^{-1}$ despite a higher withdrawal rate of 20 cm s^{-1} originally suggested by Harvey and Burzell (1972). The SML thickness collected by a withdrawal rate of $5\text{--}6\text{ cm s}^{-1}$ (as consistently as conditions allowed) is about $50\text{ }\mu\text{m}$ (Carlson, 1982) and consistent with experimentally determined SML thicknesses of $50 \pm 10\text{ }\mu\text{m}$ using pH microelectrodes (Zhang et al., 2003). At higher wind speeds above 6 m s^{-1} , i.e. in the presence of larger breaking waves, we dipped the glass plate between two breaking waves. Under such conditions, we had to collect the SML samples at a faster withdrawal rate ($8\text{--}10\text{ cm s}^{-1}$), about half the rate originally suggested by Harvey and Burzell (1972) to ensure integrity of SML samples adhering to the glass plate, resulting in thicker samples ($\approx 80\text{--}120\text{ }\mu\text{m}$). Glass plate dips affected by splashing water were rejected. Each adhering SML sample was scrapped off with a neoprene blade and collected in aged and acid-washed HDPE bottles free of leachable organic matter. Volumes of $50\text{--}150\text{-mL}$ were collected for each SML sample, requiring $30\text{--}90$ dips.

15 During the cruises, we conducted the sampling at a distance of 500 m upwind from the mother ship to avoid potential contamination. A total of nine samples were collected under partly ice-covered conditions at sampling area AC-2 (Fig. 1) from an ice cage lowered by a crane on the bow of the ship. The ship was positioned so that the surface water flowed from open waters towards the sampling point to minimize the contamination risk. Subsurface samples from 1 m were collected with a 12-volt DC Teflon gear pump and polypropylene tubing. Separate subsurface samples from 1 and 8 m were filtered onto GF/F filters (47 mm diameter; $500\text{--}2000\text{ mL}$) for chlorophyll-*a* (Chl-*a*) analysis. All samples were stored cool during sampling operations. All sampling equipment was washed with 10% HCl and rinsed with ultra-pure water prior to use.

25 In the land-based laboratory (for sampling in Saanich Inlet) or the ship's laboratory, sub-samples for total dissolved carbohydrates (TDC) were filtered over $0.2\text{ }\mu\text{m}$ polycarbonate filters pre-washed in 10% HCl. Filtrates were stored in pre-combusted ($450\text{ }^\circ\text{C}$ for 5 h) screw-cap test tubes. Sub-samples for TDC and GF/F filters for Chl-*a* analysis were stored at $-20\text{ }^\circ\text{C}$. Unfiltered sub-samples for surfactant analysis were analyzed on

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the day of collection, except for the CA and HI cruises (Table 1). On those cruises, unfiltered sub-samples were preserved with 1% formalin (final concentration) and stored at 4 °C until analysis in the home laboratory. This preservation technique stabilizes unfiltered samples for surfactant analysis for a period of at least two months (Wurl et al., 2009).

At the time we collected each SML sample, we also measured instant wind speed and air temperature using a hand-held weather station (instant wind speed). Wind speeds prevailing prior to sampling events were recorded by weather stations deployed on a buoy at Saanich Inlet or on the ships.

2.3 Chemical analysis

Surfactants were analyzed by phase-sensitive alternating current voltammetry with a hanging mercury drop electrode in unfiltered samples according to Ćosović and Vojvodić (1998). The total concentration of surfactants is expressed as the equivalent concentration of the non-ionic surfactant Triton X-100 (Teq), which mimics effects similar to natural surfactants. To eliminate matrix effects, the concentrations were determined using the standard addition method. The precision for triplicate samples was typically less than 10%.

The concentrations of TDC were determined spectrophotometrically using 2,4,6-tripyridyl-s-triazine (TPTZ) as a complexing reagent (Myklestad et al., 1997). Prior to analysis, the samples were subjected to hydrolysis with 0.85 M H₂SO₄ (final concentration) at 100 °C for 24 h to convert polysaccharides to monosaccharides (Borch and Kirchman, 1997). The procedure typically has a precision of less than 7%.

For Chl-*a* determination, filters were extracted into 10 mL of acetone for 24 h at 4 °C, with sonication for the first 5 min. Spectrophotometric analysis was conducted according to Strickland and Parsons (1972), substituting the equation from Jeffrey and Humphrey (1975).

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2.4 Estimation of primary production rates

We assessed primary production (PP), both locally and globally, using the Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski, 1997). The VGPM has been developed to estimate PP on a global scale based on satellite-derived Chl-*a* concentration, temperature, and photosynthetically active radiation (PAR). To estimate local PP similar to Holm-Hansen (2004), we applied the VGPM according to Eq. 1:

$$PP = 0.66125 \cdot P_{opt}^B \cdot \frac{E_0}{E_0 + 4.1} \cdot Z_{EU} \cdot C_{Chl} \cdot D_{irr} \quad (1)$$

with C_{Chl} being the measured surface concentrations of Chl-*a* ($\mu\text{g L}^{-1}$), D_{irr} the photoperiod (in hours) calculated as a function of latitude and time of day, and E_0 (mol quanta m^{-2}) the water surface PAR. We measured E_0 a few centimetres below the water surface with an SQ-110 sensor (Apogee Instruments Inc.) mounted on a small float. We estimated the depth of euphotic the zone (Z_{EU} in m) from the measured Secchi depth according to Preisendorfer (1986). P_{opt}^B can generally be described as a function of the water surface temperature according to Eq. 2 (Behrenfeld and Falkowski, 1997):

$$P_{opt}^B = 1.2956 + 0.2479 T + 0.0617 T^2 - 0.0205 T^3 + 0.002462 T^4 - 1.348 \times 10^{-4} T^5 + 3.4132 \times 10^{-6} T^6 - 3.27 \times 10^{-8} T^7 \quad (2)$$

with T ($^{\circ}\text{C}$) being the measured water surface temperature.

We have used similar approaches to assess both local and global PP to minimize uncertainties when extrapolating our results to the global scale.

Primary production rates were in good agreement with earlier ^{14}C measurements in the study areas (Table 1), except during the winter in Saanich Inlet. However, the primary production rate in Saanich Inlet can be highly variable, and in November and December 2008, we frequently observed elevated Chl-*a* concentrations above $5 \mu\text{g L}^{-1}$ at the sampling site.

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.5 Data analysis

Statistical analyses were performed using Graphpad PRISM Version 5.1. Differences, null hypothesis testing, and correlation were considered to be significant when $p < 0.05$, e.g. using 95% confidence interval. We tested hypotheses with parametric or nonparametric tests, as stated. If required for parametric and ANOVA tests the data were log transformed. Unless otherwise indicated, results are presented as means \pm 1 standard deviation. Enrichment factors (EF) were calculated as the ratio of concentrations in the SML sample to that of the corresponding subsurface bulk water sample.

For statistical data analysis, the enrichments of surfactants have been categorized at different wind states (states 0 to 4), based on the Pierson-Moskowitz sea spectrum (Pierson and Moskowitz, 1964). These wind states have been further merged into: low (state 0, $0-2 \text{ m s}^{-1}$), moderate (state 1-2, $2-5 \text{ m s}^{-1}$), and higher wind regimes (state ≥ 2.5 , $5-10 \text{ m s}^{-1}$).

Similarly, enrichments have been categorized in three trophic states based on Antoine et al. (1996): trophic state 1 represents oligotrophic waters with $\text{PP} < 0.4 \text{ g C m}^{-2} \text{ day}^{-1}$; state 2 represents mesotrophic waters with PP ranging from 0.4 to $1.2 \text{ g C m}^{-2} \text{ day}^{-1}$; and state 3 represents eutrophic waters with PP above $1.2 \text{ g C m}^{-2} \text{ day}^{-1}$.

3 Results

Statistical data on surfactants and TDC enrichments at different trophic levels and wind regimes are presented in Table 2. Statistical data of surfactant enrichment in the different study areas are summarized in Table 3.

3.1 Slick versus non-slick samples

We observed that the mean enrichment of surfactants in the SML during slick conditions (3.6 ± 3.4) was not significantly higher (t-test, $p < 0.05$) than during non-slick

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



conditions (1.9 ± 1.0) in Saanich Inlet. When the concentration of surfactants exceeds some presently unknown threshold value, microlayers become visible as smooth grey spots or stripes due to capillary wave-damping. Slick samples were not consistently enriched in the presence of elevated surfactant concentrations in the bulk water during bloom conditions. Highest observed surfactant enrichment was about 16 and occurred after rainfall events, when wet deposition provided elevated levels of particulate loads to the SML. In the subsequent analysis we excluded the slick samples as these may be less representative considering the objective of this study to map SML-influenced ocean surfaces on a global scale.

3.2 Enrichment versus wind speed

We found that the SML is consistently enriched in surfactants, relative to subsurface water, at wind speeds above 5 m s^{-1} (Fig. 2). At low ($0\text{--}2 \text{ m s}^{-1}$) and moderate wind speeds ($2\text{--}5.1 \text{ m s}^{-1}$) 21% and 9% of the observations showed a depletion of surfactants in the SML respectively, i.e. EF less than unity.

Occasionally, in oceanic SML we observed concentrations of surfactants above $1000 \mu\text{g Teq L}^{-1}$, which is more typical for coastal waters. These observations were in the presence of breaking waves at wind speeds above 5 m s^{-1} . The mean enrichments between the three wind regimes are not significantly different using wind data recorded during sampling (OneWay ANOVA, $p = 0.1410$). However, we observe a significant difference (OneWay ANOVA, $p = 0.0027$) using average wind speeds recorded for six hours prior to sampling, indicating that the wind history affects enrichment processes. Based on the six hour wind record, the mean enrichments at the low, moderate and high wind regimes were 1.7 ± 1.1 , 2.3 ± 1.4 and 2.1 ± 1.1 respectively; significantly lower for the low wind regime than for the moderate and higher wind regimes (Tukey multiple comparison test).

In contrast to surfactants, total dissolved carbohydrates (TDC) were depleted under the higher wind regime (Table 2). Within each wind regime about 25% of the observations indicated a depletion of TDC; major exudates of phytoplankton metabolism and

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



potentially surface-active. The mean enrichments among the wind regimes are not significantly different ($p > 0.05$) for either the instant or the six hour back-averaged wind records but are significantly smaller (<0.0001) than the corresponding mean surfactant enrichments.

Although the mean enrichments between the wind regimes are not significantly different, a fundamental observation from this study remains that surfactants were always enriched under the higher wind regimes we were able to sample (i.e. 5–10 m s⁻¹).

3.3 Enrichment versus PP

Our observations show that the mean enrichment of surfactants in the SML diminish with increasing primary productivity. We categorized the log-transformed enrichment data into the three trophic states (Fig. 3) and found that the mean enrichment in oligotrophic waters differ very significantly from meso- and eutrophic waters (one way ANOVA and Tukey's multiple comparison test). A significant difference ($p = 0.0251$) still remains if only enrichments obtained during the low wind regimes are considered for the ANOVA test to minimize effect of wind speed in the enrichment. Furthermore, the surfactant enrichment in the oligotrophic Labrador Fjords (AC5, Fig. 1) ($EF = 4.1 \pm 1.0$, $n = 4$) was significantly higher ($p = 0.0107$) than for the eutrophic fjord Saanich Inlet (SI, Fig. 1) ($EF = 2.3 \pm 1.1$, $n = 17$) during the same season (November) and under similar wind conditions.

During the summer season (June to Sept), the surfactant enrichment in the SML was greater in the oceanic regions (LineP and HI, Fig. 1) than at the near-shore site (Saanich Inlet, SI), with mean enrichments of 2.5 ± 1.3 and 1.9 ± 0.6 , respectively ($p = 0.0351$, t-test). Furthermore, surfactant enrichments at the oceanic study sites were consistently above unity (Fig. 4). In addition, we found no high surfactant enrichments in the SML (i.e. $EF > 2.7$) at bulk water concentrations exceeding 600 $\mu\text{g Teq. L}^{-1}$ (Fig. 5). Bulk water surfactant concentrations exceeding this level are typical during blooms that means under eutrophic conditions.

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

5 A seasonal trend in the enrichment of phytoplankton-exudated TDC has been observed in Saanich Inlet (Fig. 6). No similar trend was found for surfactants, which includes increased terrestrial runoff and enhanced atmospheric deposition during the winter months. As shown in Fig. 6, when PP was at its highest, the mean TDC enrichment was low (EF=0.9, Aug 2008) but increased during the less-productive bloom in the fall (EF=1.8, Nov 2008). The highest mean enrichment of TDC (EF=2.3) was observed during the period of low PP (Jan 2009), but decreased again to EF=0.7 with the onset and development of the spring bloom (Feb 2009 to May 2009). The differences in the monthly mean enrichments of TDC were very significant (One-way ANOVA, $p < 0.0001$).

10 Overall, we made the general observation that low productivity and moderate to high wind speeds lead to higher enrichments and consequently to enhanced formation of the SML.

3.4 Global Mapping

15 Global mapping are based on satellite-derived PP and wind speed maps and experimentally-derived threshold values obtained from mean enrichments of surfactants at each trophic state and wind regime. Seasonal ocean coverage of surfactant-enriched microlayers is illustrated in Fig. 7. Similar approaches have been used by Asher (1999) and Tsai and Lui (2003), but with somewhat arbitrarily set threshold values and no consideration of wind speeds.

20 We choose the concentration of surfactants as primary parameter, as it includes both dissolved and particulate fractions and therefore represent the total surface activity of the SML. Due to the fact that phytoplankton produces the majority of natural surfactants and therefore affects the local enrichment, we use the mean enrichments of each trophic state and compare those with threshold enrichment values describing the intensity of SML formation. The chosen threshold values of 1.0, 1.5 and 2.0 are used to describe weakly, moderately and strongly SML-influenced ocean surfaces, respectively, and were obtained from the observed range of enrichment values.

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The comparison of the mean enrichments of each trophic state with the chosen threshold enrichment values is illustrated in Fig. 3. The t-value for the comparison test is computed according to: $t = \frac{\text{Sample Mean} - \text{Threshold Mean}}{\text{Standard Error}}$ Eq. 2 (Motulsky, 2003)

If the result of the comparison showed a significant positive difference ($p < 0.05$), the regions on PP satellite-derived maps corresponding to the PP range of the trophic state are indicated with the intensity of influence described by the chosen threshold enrichment value. We use global ocean primary production maps estimated from SeaWiFS images using the VGPM model (Behrenfeld and Falkowski, 1997). The maps were provided by the Ocean Productivity Group at the Oregon State University (<http://www.science.oregonstate.edu/ocean.productivity>).

Because we found little relationship between wind speed and microlayer surfactant enrichment under our sampling conditions, we used wind only to set an upper limit for the presence of significant microlayer enrichment. Broecker et al. (1978) reported that an artificial surface film began to tear at a wind speed of 13 m s^{-1} during experiments in a linear wind-wave tunnel. Therefore, as a conservative estimate we considered all regions having a monthly average wind speed above 10 m s^{-1} as free of SML. We obtained monthly wind speed distributions from NCEP/NCAR Reanalysis Project (www.esrl.noaa.gov) (Kalnay et al., 1996). Those wind data are derived from various satellite measurements, but not including scatterometer data. Scatterometer measurements are based on sea-surface roughness, and accumulation of surfactants can cause wave-damping and therefore affect scatterometer-derived wind data (Kalnay et al., 1996).

4 Discussions

Our results suggest that the ocean's surface microlayer is more strongly enriched in surfactants in oceanic regions with low productivity than in more productive coastal regions (except some slicks), despite earlier assumptions that surfactant films increase with primary production (Asher, 1999; Tsai and Liu, 2003). For example, Tsai and Liu

identified wide regions between 30° N and 30° S as largely surfactant-free, whereas our field observations suggest that SML surfactant enrichments may actually be quite strong in those oligotrophic regions.

4.1 Evidence of microlayer enrichment at higher wind speeds

5 We made the fundamental observation that the enrichment of surfactants in the SML can persist up to wind speeds of 9.5 m s^{-1} , exceeding the average global wind speed over the ocean of 6.6 m s^{-1} (Acher and Jacobson, 2005). Reinthaler et al. (2008) reported enrichment of DOC and amino acids at all 17 sampling sites within the sub-tropical Atlantic gyre (Table 4), and at 8 of those stations, the wind speeds exceeded
10 7.5 m s^{-1} . Indeed, the second highest enrichments of DOC (EF=2.1) and dissolved free amino acids (EF=206) were observed at the site with the highest wind speed (i.e. 9.7 m s^{-1}). Kuznetsova et al. (2004) and Carlson (1983) detected enrichment of both amino acids and DOC at wind speeds of up to about 8 m s^{-1} .

For obvious reasons, the SML is temporally disrupted in the presence of breaking
15 waves, dispersing SML material into the bulk water. MacIntyre (1974) pointed out that 3–4% of the ocean's surface is covered by breaking waves at any particular time. We suggest that reformation can occur within seconds after disruption, as observed for artificial films during laboratory experiments (Dragóević and Pravdić, 1981) and natural films during field experiments (Williams et al., 1986). In the presence of breaking
20 waves, dispersed SML materials adsorb rapidly to the surface of the rising air bubbles, and therefore, bubble plumes may be the most important transport vector for surface-active material to the SML (Liss, 1975; Stefan and Szeri, 1999). When the bubble bursts at the sea-surface, only a fraction of attached organic matter is ejected into the air as aerosols, whereas the remainder is adsorbed on the surface to reform the SML
25 (Liss, 1975). The foamy patches frequently observed after waves breaking are a consequence of surfactant scavenging by rising air bubbles. Along those lines, we also note that wind-speed history is more important than instantaneous winds to microlayer enrichment, similarly as also reported by Obernosterer et al. (2008). Breaking waves

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



start to appear at wind speeds of 2.5 to 3.5 m s⁻¹ (Hwang and Sletten, 2008) and therefore are not present in our “low” wind regime. This further supports our observation that breaking waves can facilitate the formation of the SML through rising bubble plumes returning dispersed surfactants to the surface.

Besides acting as transport vector, it is reasonable to assume that bubbles can affect the composition of materials accumulating in the SML. Johnson and Cooke (1980) pointed out that the adsorption of surface-active compounds is selective, and compounds with higher surface activity have the highest potential to be scavenged and brought to the surface. Because even clean bubbles quickly become covered with surfactant while rising (Stefan and Szeri, 1999), globules of material may drop off the bottom of the bubbles, which could fractionate the material, leaving the most surface-active substances on the bubbles (GESAMP, 1995). Obernosterer et al. (2008) also pointed out that wind-induced physical mixing may affect the characteristics of particulate matter being enriched in the SML.

Furthermore, Carlson (1993) provided evidence that constant compression and dilation of the SML can facilitate particle aggregation and condensation of high molecular weight materials. Those processes may be more significant in oceanic regions through more intense compression and dilation driven by wave actions.

We found no evidence of significant relationships between surfactant enrichment and wind speed. Similarly, Carlson (1983) reported no relationship between DOC enrichment and wind state. Lui and Dickhut (1998) found an exponential relationship between wind speed and excess concentration of suspended particles in the SML of river estuaries. Obernosterer et al. (2008) reported a negative linear relationship of the enrichment of particulate organic carbon (POC) and nitrogen (PON) with the six hour wind speed records from the South Atlantic, but only for a narrow wind range of 0.5 to 2.5 m s⁻¹. At higher wind speeds, bubbling and turbulence may lead to more complex enrichment processes, confounding any simple relationship between enrichment and wind speed. Furthermore, our measurements include total surfactants (e.g. dissolved and particulate fraction), which could have affected the finding of similar relationships

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



found between wind measurement and the enrichment of particulate matter only. It should be also noted that the thickness of SML collected using the glass plate technique is affected by wind states (Carlson, 1982). Obernosterer (2008) used a screen sampler, which collects thicker layers of more consistent thickness (200–400 μm), independent of wind speeds. The visit of various sampling sites with different conditions and characteristics (nearshore, offshore and oceanic) during Carlson's and our study is likely to contribute for not finding a significant correlation between enrichment and wind speed.

However, one concrete observation remains from our study: enrichment always occurs at wind speeds higher than 5 m s^{-1} .

4.2 Microlayer at different trophic states

We found that the enrichment of surfactants in the SML is higher in oligotrophic waters than in mesotrophic and eutrophic waters. The absolute difference in those enrichments between regions with low and moderate/high primary productivity is low (EF=2.8 vs. EF=1.8), but statistically significant ($p = 0.01$). The observation is supported by the seasonal variations in the enrichment of carbohydrates, metabolic exudates by phytoplankton, in Saanich Inlet, with highest enrichments during seasons of low productivity and vice versa (Fig. 6).

Carlson (1983) found two patterns in DOC enrichments ($n = 251$), which our data confirmed: higher enrichments in oceanic samples (Table 3) and lower enrichments in coastal waters diminishing with increasing bulk water concentrations (Fig. 4). Carlson suggested that different accumulation and removal processes between oceanic (oligotrophic) waters and coastal (meso- and eutrophic) waters may exist. We observed that wind speeds at oceanic sites were typically 2–4 times higher than at offshore and near shore sites contributing to higher accumulation of surface-active material to oceanic SML as discussed in the earlier section. For example we found higher concentrations of surfactants (e.g. $>1000 \mu\text{g Teq L}^{-1}$) in both oceanic and coastal SMLs (Fig. 5), despite the differences in the trophic states and therefore in the production of natural

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



surfactants by phytoplankton communities. However, comparison of the mean SAS enrichments between oligotrophic and mesotrophic/eutrophic conditions under the low wind regime revealed that the trophic state alone has an effect on the enrichment.

Similar to our observations, Kostrzewska-Szlakowska (2005) found higher enrichments of organic matter, nutrients, and bacteria in oligotrophic lakes than in eutrophic lakes. In a mesocom study in a Norwegian Fjord mean DOC enrichment in a nutrient-amended mesocom 1.14, compared to 1.44 in the control (with a phytoplankton abundance three times lower; Cunliffe et al., 2009a). These studies support our finding that enrichment of organic materials in the SML is higher at lower trophic states, even at similar wind conditions. Williams et al. (1986) did not observe any differences in DOC enrichment between SML samples from oligotrophic and eutrophic waters, but their study was based on a limited number of observations ($n = 20$).

Wurl and Holmes (2008) showed that oceanic SMLs are significantly enriched in transparent exopolymer particles (TEPs), but that estuarine samples are not. TEPs are the most ubiquitous and abundant gel particles in the oceans; formed through coagulation of dissolved polysaccharides. Bubbling seawater significantly enhances the coagulation process, probably leading to higher enrichments in oceanic SML (Zhou et al., 1998).

The SML is an environment that is exposed to high levels of solar radiation potentially producing refractory material from the accumulated DOM pool. However the effect of UV exposure on DOM in the SML is widely unknown, and in bulk waters the interactions between UV radiation and DOM are complex, producing both labile and refractory products as reviewed by Carlson (2002). It suggests that the specific chemical composition of the DOM dictates whether photo-transformation produces labile or stable products. Further studies on the SML DOM pool and its transformation through enhanced level of solar radiation are therefore necessary.

Wurl and Holmes (2008) have also shown that TEPs residing in the SML contain a higher fraction (~75–85%) of sulphate-ester groups (relative to weaker-binding carboxyl-ester groups) than TEPs collected from the bulk water (~40–78%). Sulfate

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



content is known to influence the intrinsic viscosity of polymers coagulated from exopolymer polysaccharides (Nichols et al., 2005), which have also been shown to be more insoluble and nonhydrolyzable (Kok et al., 2000). Therefore, the SML, particularly in oceanic regions, may contain more refractory organic matter than the bulk water.

Sulzberger and Durisch-Kaiser (2009, and references therein) pointed out that terrigenous bulk DOM in coastal waters exhibits a greater re-mineralization potential through UV-induced transformations than autochthonous DOM (i.e. oceanic DOM). Such transformations of terrigenous bulk DOM usually increase bioavailability and therefore microbial respiration. Therefore, terrigenous DOM in coastal SML may undergo rapid remineralization compared to more resistant autochthonous DOM in oceanic SML. As discussed in the previous section, rising air bubbles may not only act as a transport vector but may also affect the composition of DOM in the SML (Johnson and Cooke, 1980; GESAMP, 1995), which could lead to differences in DOM composition between oceanic and coastal SML through higher frequency of breaking waves in oceanic regions.

Furthermore, Miller and Moran (1997) observed enhanced bulk DOM decomposition due to photochemical reactions and enhanced microbial decomposition. The SML of coastal and oceanic environments have been reported to be enriched in viable heterotrophic nanoflagellates and bacteria, with EFs of 2 and up to 5000 (Joux et al. 2006; Fehon and Oliver, 1979; Reinthaler et al., 2008; Obernosterer et al., 2005), respectively. Other studies suggested no significant enrichment in heterotrophic activities (Stolle et al., 2009, Obernosterer et al., 2008), but assessing the enrichment of microbiological parameters in the SML is difficult and often depends on the sampling technique being used (Cunliffe et al., 2009b). Cunliffe et al. reported that sampling with polycarbonate membranes yielded significant differences between bacterial cell abundances in the SML and underlying bulk water, and confirmed the high enrichments reported by Fehon and Oliver (1979). In general, sampling with glass plates and mesh screens, used during the other cited studies, collects a layer too thick to differentiate

Formation and distribution of sea-surface microlayers

O. Wurl et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

and yield lower enrichments of cell abundances (Cunliffe et al., 2009b). During SML collection, Reinthaler et al. (2008) drained the glass plate for 20 s after withdrawal to remove excess water before collection. This procedure leads to thinner collected layers, which may have allowed them to observed the enhancement in bacterial respiration in the SML. For that reason microbial decomposition may be enhanced within coastal SML approaching the air-water interface leading to lower enrichments of DOM including surfactants. However, oceanic blooms, as typically observed in the North Atlantic, provide a food source for heterotrophic organisms by producing low molecular weight compounds. The SML is likely to become enriched in those bio-available substrates, enhancing microbial growth, which eventually leads to lower enrichments through decomposition. The SML during non-bloom conditions is likely to be enriched of refractory high molecular compounds, thereby leading to higher enrichments.

Overall, we suggest that higher enrichments in oceanic SMLs originate from more resistant DOM and lower bacterial respiration compared to coastal SML.

4.3 Global maps

Global maps of SML surfactant enrichment, as derived in Sect. 3.4 above, are presented in Fig. 7. The maps represent the enrichment of surfactant, determined as the ratio of the surfactant concentration in the SML to that in the corresponding subsurface water, and not the absolute SML concentration. The maps indicate that the North Atlantic (north of 30° N) is not strongly influenced by SML surfactant enrichment, due to the large spring and summer phytoplankton blooms with PP rates that can exceed 1 g C m⁻² day⁻¹ (Siegel et al., 2002). Strong winds exceeding 11-12 m s⁻¹ are likely to disrupt the SML in the North Atlantic during seasons of lower productivity (Chl-*a* Northern Hemisphere fall and winter). Similar patterns can be seen in the North Pacific, although weaker enrichments are only observed along the southern coastline of Alaska, and most of the region still has moderate enrichments during spring and summer, consistent with the mesotrophic conditions reported by Harrison et al. (1999). Tsai and Lui (2003) derived substantial areas of surfactant enrichments for the North

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Atlantic and North Pacific during fall, but they did not account for the high winds during that period.

The maps indicate that regions within 30° N–30° S have stronger SML enrichments, except in the coastal upwelling areas off South America and West Africa. In particular, the moderate enrichments within the NW African upwelling system persist throughout the year, which is consistent with the observations from Tsai and Liu (2003). Although upwelling is generally restricted to a narrow coastal band, the upwelled water can be transported up to 450 km offshore in the form of large filaments and eddies (Zonnefeld et al., 2010), extending the areas of moderate enrichment. In contrast, we derived stronger enrichments during January to March along the central and SW African coast, which indicates lower productivity.

The Indian Ocean is widely affected by stronger enrichments, with lower enrichments along coastal areas. During the southwest monsoon (July to Sept), high winds disrupt SML formation in the central Indian Ocean and offshore Saudi Arabia.

The Southern Ocean is mainly free of SML surfactant enrichment due to high winds. Surfactant enrichment in the SML during the local summer season (January to March) was likely overestimated by Tsai and Lui (2003), as they did not consider the wind effect in their study. Circumpolar narrow areas of enrichment just north of 30° S are the result of diminishing winds

4.4 Implications for air-sea gas exchange

In this study, we have shown that the ocean's surface microlayer is likely wider enriched with surfactants than earlier studies suggested (Asher, 1997; Tsai and Lui, 2003). This discovery has implications for the assessment of air-sea exchange of greenhouse gases affecting the Earth's radiation budget.

Generally, the concentrations of surface-active compounds are low for typical oceanic waters, although we did measure some high concentrations (Fig. 5). However, this may not be an accurate reflection on their impact on air-sea gas exchange, since natural surfactants such as TEP and carbohydrates can exhibit substantial dynamic

BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



elasticities, a relevant quantity in controlling dynamical exchange processes at the air-water interface (Liss and Duce, 1997). Tsai and Liu (2003) reported that surfactant films can reduce the global annual net flux of CO_2 by 20 to 50%, using primary production rates of 0.5 and $0.8 \text{ g-C m}^{-2} \text{ day}^{-1}$ as the postulated thresholds for two scenarios of the ocean's coverage with surfactant films. As discussed in the previous section, those threshold values were based on an assumption that surfactant enrichment in the SML increases with primary productivity, but our experimental data showed an opposite effect, implying higher surfactant enrichments in regions with low primary productivity. The difference in those enrichments between regions with low and moderate/high primary productivity is low, but significant and it requires further studies to investigate the effect of this difference on air-sea gas exchange processes.

Our data also suggest that bubble-mediated upward transport of surfactants re-form the SML rapidly, and Asher (1996) demonstrated through experiments in a whitecap simulation tank that soluble surfactants (i.e. carbohydrates) inhibit gas transfer even when waves break. Asher (1996) showed that the presence of soluble surfactant reduced k_L , the liquid-phase transfer velocities. Such reduction has been observed for soluble (CO_2) and insoluble (He) gases even at the highest fractional area bubble coverage (i.e. area bubble plume/surface area tank in %)

Furthermore, Reinthaler et al. (2008) showed high bacterial respiration in the SML and suggested a biological control of CO_2 fluxes across the SML. Upstill-Goddard et al. (2003) highlight the potential significance of bacterioneuston in air-sea gas exchange of CH_4 and CO. Therefore we conclude that the SML have possibly a significant effect on air-sea gas exchange rates on a global scale.

5 Conclusions

Our study suggests that the ocean surface microlayer may be enriched with surfactants, relative to the underlying waters, to a much larger extent than previously realized. The SML surfactant enrichment appears to be generally greater in low-productivity regions

of the ocean (i.e. under oligotrophic conditions) than in productive coastal waters. The differences in enrichment may originate from the nature of organic material being enriched, especially in regards to resistance to degradation by UV radiation and enhanced microbial activities in the SML.

Furthermore the enrichment of surfactants persists at moderately wind speeds, up to nearly 10 m s^{-1} . This supports the known effect of bubble-mediating upward transport of surfactants within the water column, which facilitates rapid re-formation of the SML in the presence of breaking waves. Our study indicates that the impact of the SML on air-sea gas exchange and marine carbon cycle is likely of global significance.

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Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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BGD

7, 5719–5755, 2010

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Details of sampling events and local primary production (PP).

Sampling region	Cruise	Sampling period	# samples ^a		Mean \pm SD of PP in [$\text{gC m}^{-2} \text{day}^{-1}$]	
					this study	literature
Saanich Inlet (SI)	once or twice a week	June 2008– May 2009	235	Coastal (nearshore)	1.81 \pm 1.18 (year)	1.58 \pm 1.50 (year) ^b
					2.60 \pm 1.31 (summer)	3.13 \pm 0.25 (summer) ^b
					0.11 \pm 0.05 (winter) ^b	0.82 \pm 0.51 (winter)
Santa Barbara Channel, California (CA)	RaDyO	09 Sept 2008– 22 Sept 2008	26	Coastal (offshore)	1.07 \pm 0.12	1.24 ^c
Vancouver Island (VI)	LaPerouse	27 May 2009– 06 June 2009	12	Coastal (near-and offshore)	1.68 \pm 0.85	
North Pacific (NP)	Line P	7 June 2009– 20 June 2009	19	open ocean	0.49 \pm 0.25	0.70 \pm 0.30 ^d
North Pacific, tropical, Hawaii (HI)	RaDyO	27 Aug 2009– 13 Sept 2009	26	coastal (offshore)	1.05 \pm 0.21	
Arctic (AC)	ArcticNet	14 Oct 2009–	19	coastal (nearshore)	0.55 \pm 0.11	0.47 \pm 0.13 ^e
		13 Nov 2009		open ocean	0.056 \pm 0.035	0.062–0.076 ^f

^a number of non-slick samples

^b Timothy and Soon (2001)

^c Shipe and Brzezinski (2003), no SD reported, mean value for time period April to August

^d Welschmeyer et al. (1993)

^e Karl et al. (1998)

^f Lavoie et al. (2009)

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 2. Statistical data on surfactant enrichment factors (EF) of surfactants in the microlayer at different wind regimes and trophic states.

	Wind Regimes					
	Low		Moderate		Higher	
	EF SAS	EF TDC	EF SAS	EF TDC	EF SAS	EF TDC
n ^a	151	116	91	74	32	25
Min	0,5	0,3	0,6	0,4	1,1	0,6
Max	6,8	4,7	5,6	5,3	4,9	2,2
mean ± sd	2.0 ± 1.2	1.4 ± 0.7	2.1 ± 1.0	1.4 ± 0.8	2.2 ± 1.1	1.2 ± 0.4
Lower 95% CI of mean	1,8	1,3	1,8	1,2	1,8	1,0
Upper 95% CI of mean	2,2	1,5	2,3	1,6	2,6	1,3
Median 25	1,1	1,0	1,4	1,0	1,5	1,1
Median 50	1,7	1,2	1,8	1,3	1,8	1,1
Median 75	2,5	1,6	2,4	1,5	2,4	1,3

	Trophic States					
	Oligotrophic		Mesotrophic		Eutrophic	
	EF SAS	EF TDC	EF SAS	EF TDC	EF SAS	EF TDC
n ^a	38	17	93	69	144	124
Min	1,3	0,4	0,5	0,5	0,5	0,3
Max	5,6	2,5	4,6	4,2	4,0	5,3
mean ± sd	2.7 ± 1.3	1.2 ± 0.6	2.0 ± 1.0	1.4 ± 0.6	1.7 ± 0.8	1.4 ± 0.8
Lower 95% CI	2,3	0,9	1,8	1,3	1,7	1,2
Upper 95% CI	3,1	1,5	2,2	1,6	2,0	1,5
Median 25	1,7	0,8	1,2	1,0	1,1	1,0
Median 50	2,3	1,1	1,8	1,3	1,6	1,2
Median 75	3,6	1,5	2,5	1,6	2,2	1,5

Number of observations (n), minimum (Min), maximum (Max), standard deviation (SD).

^a non-slick samples only

Formation and distribution of sea-surface microlayers

O. Wurl et al.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Table 3. Statistical data on enrichment factors (EF) of surfactants in the microlayer at different study areas.

	Saanich Inlet (SI)	Vancouver Island (VI)		California (CA)	North Pacific (LineP)		subtrop. NorthPacific (HI)	
	Nearshore	Nearshore	Offshore	Offshore	Offshore	Oceanic	Offshore	Oceanic
n ^a	167	5	7	21	5	24	12	11
Min	0,5	0,7	0,6	0,6	1,0	1,1	0,6	1,4
Max	5,6	4,5	3,5	5,0	2,5	5,3	4,4	5,6
mean ± sd	1.9 ± 1.0	2.5 ± 1.3	1.8 ± 0.9	1.8 ± 1.1	1.7 ± 0.6	2.9 ± 1.3	1.7 ± 1.1	2.3 ± 1.2
Lower 95% CI ^b	1,7	0,8	0,9	1,3	0,9	2,4	1,0	1,5
Upper 95% CI ^b	2,0	4,2	2,6	2,3	2,5	3,4	2,4	3,2
Median 25	1,1	1,5	1,1	1,0	1,1	1,9	1,0	1,5
Median 50	1,6	2,5	1,7	1,7	1,9	2,5	1,3	1,9
Median 75	2,3	3,5	2,1	2,3	2,2	3,9	2,2	2,6

	Arctic (AC)			All data		
	Nearshore	Offshore	Oceanic	Nearshore	Offshore	Oceanic
n ^a	4	9	9	176	54	44
Min	1,4	3,2	1,5	0,5	0,6	1,1
Max	5,6	5,9	2,6	5,9	5,0	5,6
mean ± sd	4.8 ± 1.1	2.0 ± 0.4	2.7 ± 1.3	1.9 ± 1.1	1.8 ± 0.9	2.7 ± 1.3
Lower 95% CI ^b	1,7	3,0	1,7	1,8	1,6	2,3
Upper 95% CI ^b	3,8	6,6	2,3	2,1	2,1	3,1
Median 25	1,7	3,6	1,5	1,1	1,1	1,8
Median 50	2,3	5,0	2,2	1,6	1,7	2,3
Median 75	3,4	5,7	2,4	2,4	2,3	3,6

Number of observations (n), minimum (Min), maximum (Max), standard deviation (SD).

Nearshore: within 2 km to coast; Offshore: 2–20 km from coast; Oceanic: further than 20 km off the coast

^a non-slick samples only

^b Confidence interval of the mean

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 4. Literature values of oceanic enrichments of organic material in the microlayer.

Reference	Parameter	Enrichment	Location	
Sieburth et al. (1976)	DOC	1.6 ± 0.3	Atlantic Ocean	oceanic
	TDC	2.0 ± 0.9		
Williams et al. (1986)	DOC	1.4 ± 0.1	North Pacific	oceanic
	TDC	1.6 ± 0.2		
	POC	3.7 ± 1.6		
Frew et al. (2002)	CDOM	1.7 and 1.5 1.0 and 1.3	Atlantic Ocean	oceanic offshore
Calace et al. (2004)	Fulvic acids	4.8 ± 1.9	Gerlache Strait	offshore
Reinthaler et al. (2008)	DOC	1.5 ± 0.3	Atlantic Ocean	oceanic
		1.8 ± 0.3	Mediterranean Sea	oceanic

**Formation and
distribution of
sea-surface
microlayers**

O. Wurl et al.

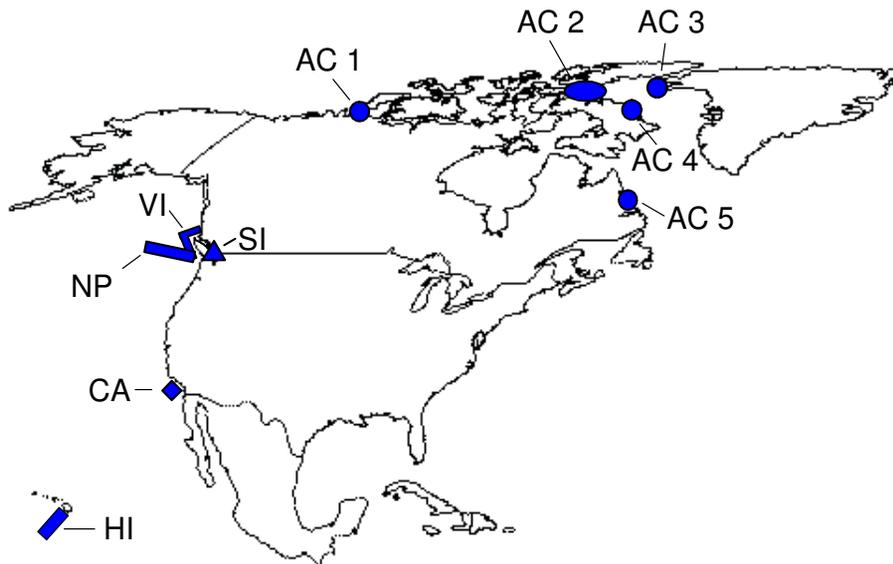


Fig. 1. Sampling stations. AC: Arctic; CA: California, Santa Barbara Channel; HI: Hawaii; LineP: North Pacific; SI: Saanich Inlet; VI: Vancouver Island, West Coast.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

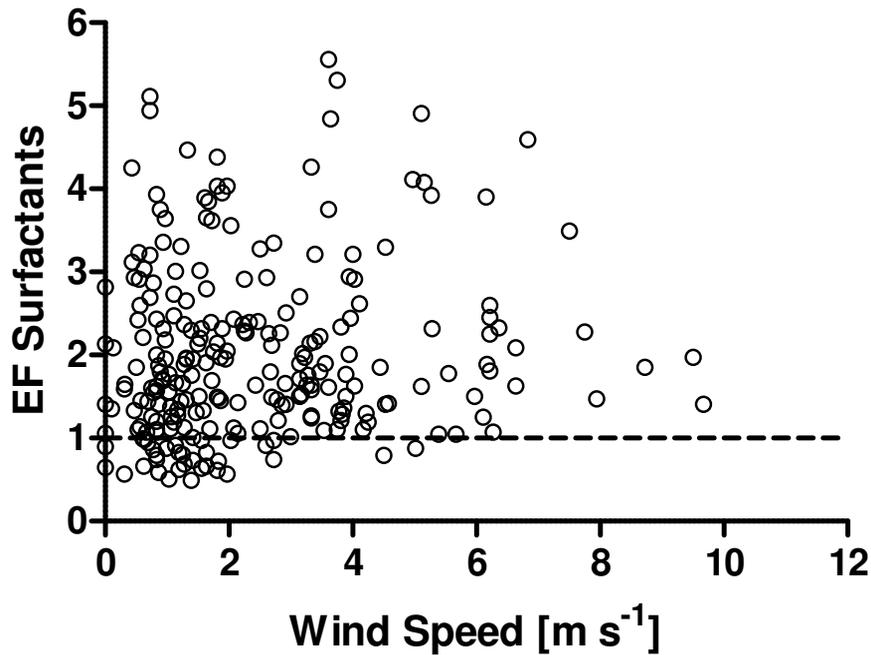


Fig. 2. Scatter plot of surfactant enrichment factor (EF) against observed wind speeds. Dashed line represent EF=1.

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

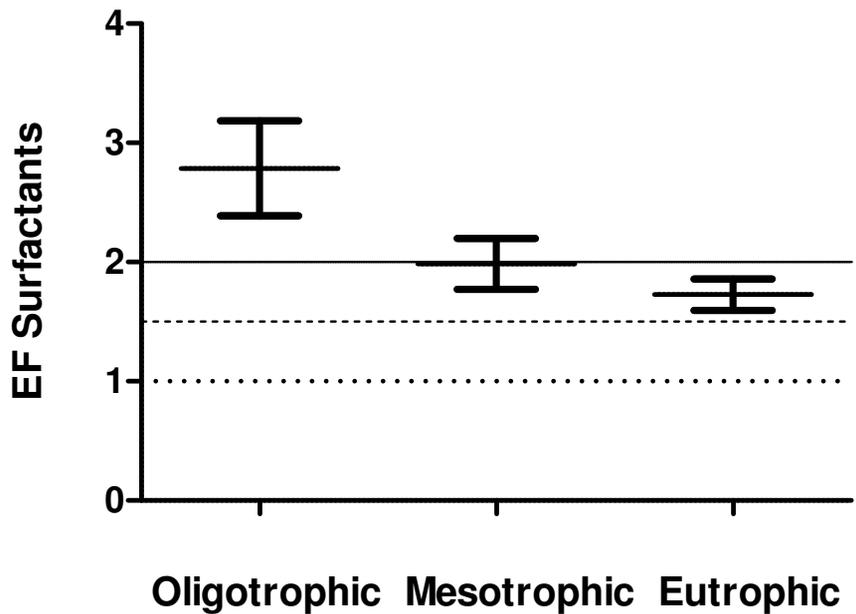


Fig. 3. Mean enrichment factor (EF) of surfactants at the three trophic states. The bars representing the 95% confidence interval of the mean. The chosen threshold enrichment values are indicated as lines: weak influence (....., EF=1.0); moderate influence (---, EF=1.5); and stronger influence (—, EF=2.0).

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



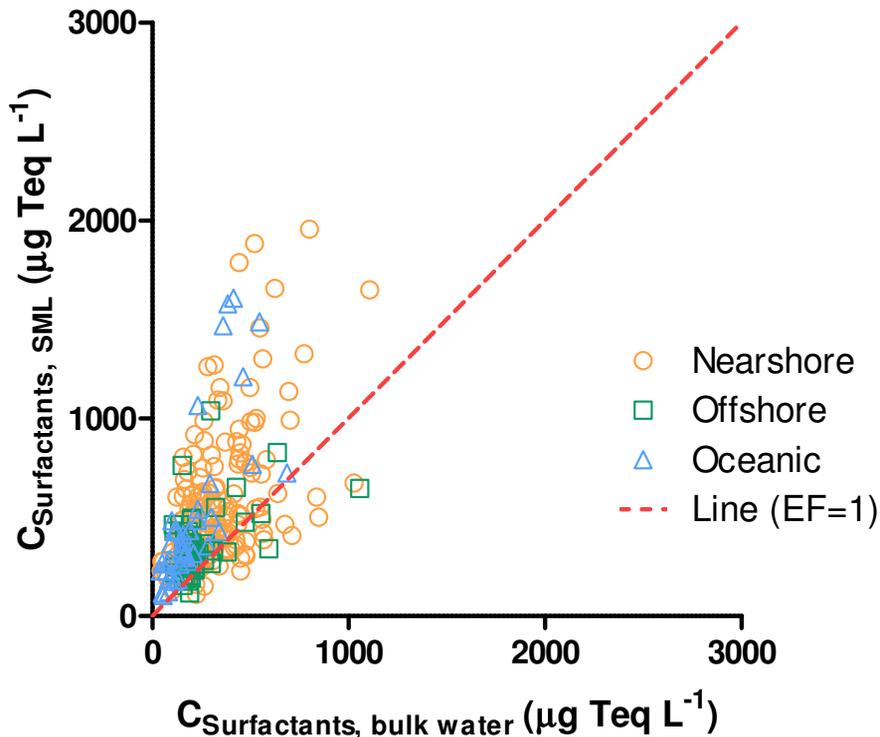


Fig. 4. SML concentration versus bulk water concentrations of surfactants in nearshore (within 2 km from coast), (2–20 km from coast) and open ocean (further than 20 km off the coast). Broken line indicates equal concentrations in SML and bulk water (EF=1).

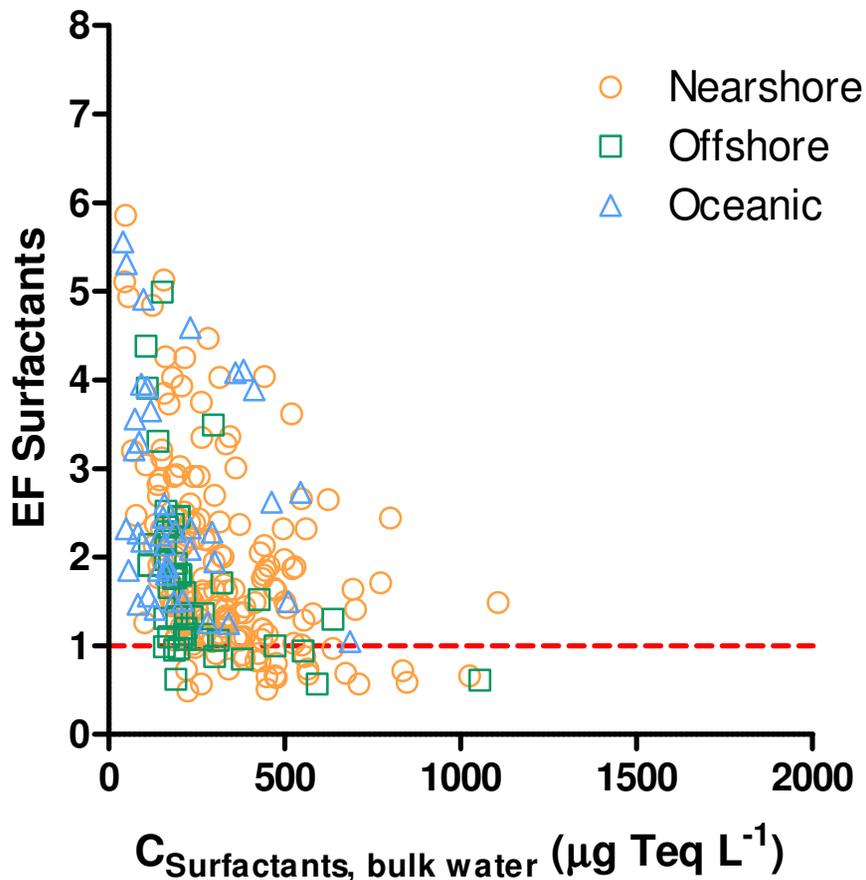


Fig. 5. Diminishing surfactant enrichment factors (EFs) with increasing bulk water concentration in nearshore (within 2 km of coast), offshore (2–20 km from the coast), and open ocean (further than 20 km from the coast).

Formation and distribution of sea-surface microlayers

O. Wurl et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Formation and distribution of sea-surface microlayers

O. Wurl et al.

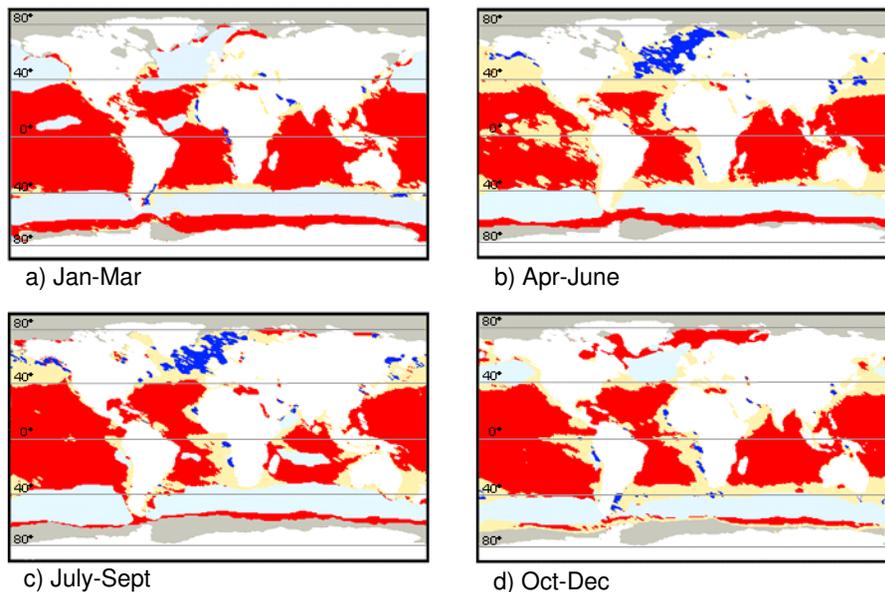


Fig. 7. Global maps of SML-coverage for **(a)** Jan–Mar, **(b)** Apr–Jun, **(c)** Jul–Sept and **(d)** Oct–Dec. **■** $EF > 2$; **■** $2 > EF > 1.5$; **■** $1.5 > EF > 1.0$; **■** no enrichment. Please note that maps represent enrichment factors (EF) and not absolute SML concentration.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion