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# The distribution and fate of surface-active substances in the sea-surface microlayer and water column

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ABSTRACT

Results from a study of surface-active substances (SAS) in the sea-surface microlayer (SML) of the Santa Barbara Channel suggest that the SML is stable enough to exist at typical oceanic wind conditions and that stratification plays an important role in SML formation through accumulation of surface-active organic matter above the pycnocline. We measured surface-active substances, total dissolved carbohydrates (TDC), chromophoric dissolved organic matter (CDOM) and transparent exopolymer particles (TEPs) in the SML and the underlying bulk water. While the enrichment factors of those compounds, defined as the ratio of the concentration in the SML to that in the corresponding underlying water, were generally less than 3, significant enrichment in the microlayer persisted at wind speeds greater than 6 m $s^{-1}$ (up to 9.6 m $s^{-1}$, the highest winds observed), which is close to the average global wind speed over the ocean. Additional measurements from three water column profiles indicated that stratification of the water column led to an accumulation of surface-active organic matter above the pycnocline. Carbohydrate-rich TEP correlated significantly with the density of the water column indicating an upward flux of these gel-like particles towards the SML.



## 1. Introduction

Surface-active substances (SAS) are an important subgroup of the dissolved organic matter pool present in seawater. Typical features of SAS are structural groups with both hydrophilic and hydrophobic character, and therefore, SAS tend to accumulate through adsorption processes at water phase boundaries, such as those with the atmosphere, particles, bubbles, and sediments. The primary sources of SAS are exudates from phytoplankton, either through direct release (Žutic et al., 1981) or zooplankton grazing (Kujawinski et al., 2002). The composition of released SAS varies between phytoplankton communities, yet carbohydrates comprise the major fraction, with proteins and lipids as minor fractions (Myklestad, 1995; Penna et al., 1999). It is known that SAS influence energy and mass transfer between the boundary layers and thus play an important role in biogeochemical cycles (Croot et al., 2007), distribution and fate of pollutants (Shine and Wallace, 1996), and air–sea gas exchange processes (Frew et al., 2002).

The boundary layer between the ocean and the atmosphere is the sea-surface microlayer (SML), operationally defined as roughly the uppermost 50–100 μm of the ocean surface. The SML in coastal and oceanic waters is known to concentrate SAS, such as carbohydrates, proteins, lipids and humic substances (Sieburth et al., 1976; Williams et al., 1986; Calace et al., 2007; Gašparović et al., 2007). The enrichment process forms complex thin surfactant films on the ocean surface, which strongly impact transport processes between the ocean and atmosphere (Liss and Duce, 1997), including retarding air–sea gas exchange (Goldman et al., 1988; Frew et al., 2002; Zhang et al., 2006). However, the formation and distribution of the SML under typical oceanic conditions, e.g. moderate wind speeds and presence of breaking waves, is not well known. Sieburth (1983) hypothesized that the SML is a hydrated gelatinous layer formed by a complex structure of carbohydrates, proteins and lipids, a suggestion that recently has been supported by the report that transparent exopolymer particles (TEPs) accumulate in the SML (Wurl and Holmes, 2008).

TEPs are the most ubiquitous and abundant gel particles in the ocean, possessing strong surface-active properties (Passow, 2002), and mainly formed by coagulation of dissolved carbohydrates (Zhou et al., 1998; Passow, 2000). Due to their surface-active properties, or "stickiness," TEPs play an active role in the formation of aggregate microhabitats (Passow and Alldredge, 1994; Mari and Kirboe, 1996), in biogeochemical cycling of elements (Passow, 2002), and in carbon export to the deep ocean by forming sinking aggregates known as marine snow. However, Azetsu-Scott and Passow (2004) pointed out that high TEP content in diatom aggregates can lead to an upward flux through positive buoyancy and can act as a vehicle in transporting particle-reactive chemicals towards the surface of the ocean. Such upward fluxes may play an important role in the formation of the SML. Croot et al. (2007) reported that SAS levels appeared to be highest in the regions with density discontinuities. It means that water column stratification leads to an accumulation of SAS in surface waters, which can be transported to the SML through adsorption on rising air bubbles or upward TEP fluxes.

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The objective of this study was to investigate the distribution and fate of SAS (as a sum parameter), including total dissolved carbohydrates (TDC) and TEP, in the water column and the SML. We have investigated the role of water column stratification and TEP accumulation in the formation of the SML, as well the existence of the SML at wind speeds close to the global average value over the ocean.

## 2. Experimental

### 2.1. Characteristics of the study site

Samples were collected during the second Radiance in a Dynamic Ocean (RaDyO) field experiment (9–22 Sept., 2008) in the Santa Barbara Channel on the RV *Kilo Moana*. The sampling location (34 13.2N, 119 37.2W; Fig. 1) is characterized by high chlorophyll-*a* concentrations in surface waters resulting from wind-forcing and circulation patterns that bring the pycnocline and nutricline to the surface (Hayward and Venrick, 1998). Venrick (1998) found that blooms in the Santa Barbara Channel were typically dominated by the phytoplankton *Chaetoceros* sp. (2238 cells $mL^{-1}$), *Pseudo-nitzschia* spp. (179 cells $mL^{-1}$) and *Skeletonema costatum* (139 cells $mL^{-1}$).

### 2.2. Sample collection

We collected 26 paired samples from the SML and subsurface water (1 m depth) over a 13-day period. Sea state parameters for each sampling event are listed in Table 1. Additional samples were collected from the water column (173 m depth) on September 9th (profile 1), 15th (profile 2) and 21st, 2008 (profile 3) using Niskin bottles. Samples from the SML were collected using the glass plate technique (Harvey and Burzell, 1972) and stored in aged polypropylene bottles free of leachable organics. The thickness of the SML collected by this technique is consistent with the most recently reported SML thickness of $50 \pm 10$ μm (Zhang et al., 2003) based on pH measurements using a microelectrode. The SML samples were collected under calm to moderate sea conditions (wind speeds from 1.1 to 9.6 m $s^{-1}$) from a small boat at a distance of 500 m from the mother ship. Sample collection required approximately 15 min for each sample. A 200-mL sample of the subsurface water was collected with a 12-volt DC Teflon gear pump and polypropylene tubing. Samples were stored on ice during the small boat sampling period. All sampling equipment was washed with 10% HCl and de-ionized water prior to use.

In the ship's laboratory, sub-samples for TDC were gently filtered over 0.4 μm polycarbonate filters pre-washed in 10% HCl. Filtrates for TDC analysis were stored in precombusted (450 °C for 5 h) and sealed glass tubes at −20 °C. Sub-samples for TEP analysis were filtered and stained onboard (see Section 2.3) and the stained filters were stored at 4 °C until analysis in the land-based laboratory. Unfiltered sub-samples for SAS analysis were preserved with 1% formalin and stored at 4 °C until analysis (see Section 2.3) in the land-based laboratory (within 6 weeks). The preservation technique was tested before the cruise, and stabilized unfiltered samples for SAS analysis were stored more than 2 months without any significant changes in the concentration (unpublished data). Enrichment factors (EF) were calculated as the ratio of the concentration in an SML sample to that in the corresponding subsurface water sample. Ship-based CTD profiles included measurements of fluorescence, beam attenuation, oxygen and photosynthetically active radiation (PAR). In-situ surface chlorophyll-*a* (depth 8 m) was measured with a fluorometer. Meteorological data, including wind speed and direction, and air temperature, were collected by the ship.

### 2.3. Chemical analyses

Total SAS measurements were conducted by phase-sensitive alternating current voltammetry with a hanging mercury drop electrode in unfiltered samples (for example, Ćosović and Vojvodić 1982, 1998; Gašparović et al., 2007). Teflon cups were used as electrochemical cells for the analysis to eliminate adsorption effects observed using glass cups. The concentrations of SAS in natural water samples are expressed as the equivalent concentration of the nonionic surfactant Triton X-100 (Teq), which produces effects similar to natural surfactants in the sample. The concentrations of SAS were calculated using the standard addition method according to Sander and Henze (2005) to eliminate matrix effects, such as different particulate concentration and composition and variations in sample conductivity. Final additions were still below the adsorption saturation level on the mercury drop, and the standard addition curves were

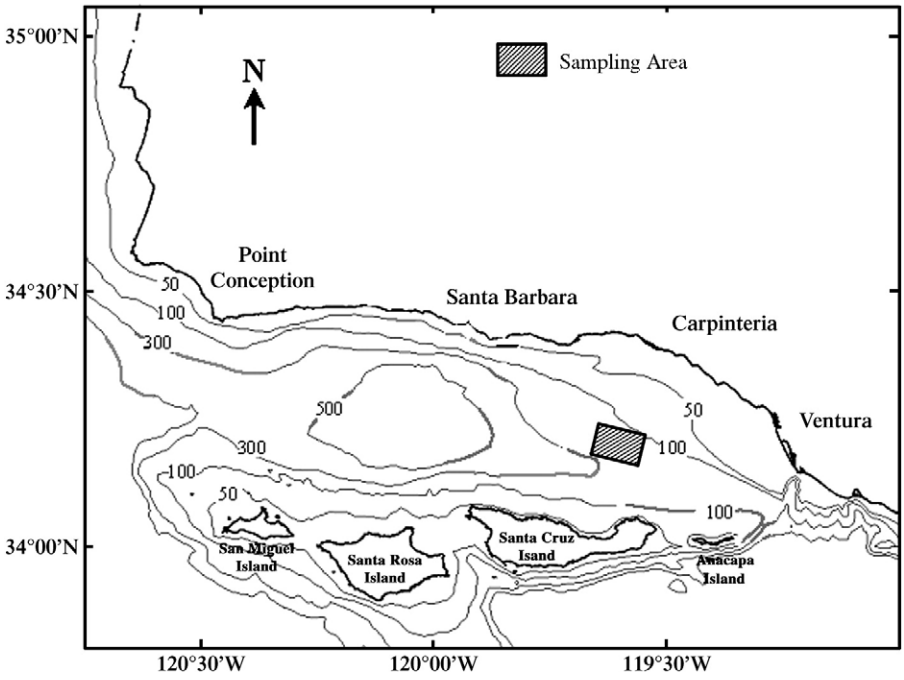


**Fig. 1.** Sampling station in the Santa Barbara Channel, California (depth contours in meters).