8.7 VARIABILITY OF SURFACE FILM DISTRIBUTIONS IN A COASTAL OCEAN REGIME

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1. INTRODUCTION

Surface-active compounds produced by marine biota are preferentially adsorbed at the air-sea interface, forming surface films that impart a finite viscoelastic modulus to the interface. In low and moderate winds, these surfactant films play a significant role in modulating physical transfer processes (mass, momentum and heat) across the air-sea interface. An improved knowledge of surface film distributions under different forcing conditions, their chemical composition, and their rheological properties is needed to understand and model the growth and dissipation of small-scale waves, wind stress-drag relationships, turbulent surface renewal, air-sea exchange of gases and heat, and microwave scattering processes and remote imagery.

Surfactant film distributions were surveyed during the ONR-sponsored Coupled Boundary Layers and Air-Sea Transfer (CBLAST) Low Wind experiments at the Martha's Vineyard Coastal Observatory (MVCO) site, a typical N. Atlantic coastal regime. Measurements of the sea surface microlayer and subsurface chromophoric dissolved organic matter (CDOM) fluorescence and of surface tension were carried out under different wind stress conditions in order to estimate sea-surface chemical enrichments, to determine the patchiness of surface film distributions on small scales (10m - 5km), and to estimate the deviation of surface tension and elasticity from mean values.

2. METHODS

We deployed a new survey tool, SCIMS (Slick Chemical Identification and Measurement System, www.whoi.edu/science/MCG/people/nfrew/Chemical_Mapping.htm) at the MVCO site. SCIMS, a semi-autonomous mobile instrument platform, detects the presence of surface microlayer films and allows mapping of their spatial and temporal distributions. SCIMS includes a surface microlayer skimmer coupled to a fluorometry package and an automated surfactant extraction interface. It is used in conjunction with innovative ion trap mass spectrometry technology to study microlayer film accumulations and their specific composition. In addition, SCIMS carries a flux measurement system consisting of a 2-D sonic anemometer and relative humidity and temperature probes mounted on a 3-meter mast, along with subsurface temperature and conductivity probes. Here we report results from the fluorometry observations.

2.1 Microlayer sampling

The sea surface was continuously sampled with a surface microlayer skimmer (SMS) designed by *Carlson et al.* [1988]. The SMS consisted of a partially submerged, rotating glass cylinder supported by a small catamaran. The rotating cylinder collected a thin layer of water (40-60 μm thickness) by viscous retention. The theoretical basis for the sampling mechanism has been described by *Levich* (1962) and experimentally verified by *Cinbis* (1992). Collection efficiencies of the glass cylinder are comparable to those obtained with a glass plate (*Carlson, et al.*, 1988; *Carlson*, 1982; *Harvey and Burzell*, 1972). The sampler produced a 100 ml min^{-1} flow of microlayer water; a second sampling line supplied subsurface water from a nominal depth of 10 cm. Both flow streams were routed to the SCIMS fluorometry package.

2.2 CDOM fluorescence and surface enrichment

Colored dissolved organic matter (CDOM) was used as a limited proxy for surfactants in seawater. CDOM fluorescence has been shown to correlate strongly with surfactants in seawater (*Frew et al.*, 2002), although it does not measure nonchromophoric, insoluble surfactants. CDOM fluorescence was measured using a Turner Designs 10-AU field fluorometer equipped with a 25 mm pathlength, continuous flow quartz cell. The excitation wavelength was 355 nm; the emission wavelength was 450 nm. The fluorometer alternately measured surface microlayer and subsurface fluorescence over 8 and 2 minute intervals respectively. Microlayer CDOM fluorescence was normalized to the fluorescence of quinine sulfate (q.s.) standards (*Vodacek et al.*, 1997) and compared with bulk CDOM fluorescence. A spline fit of the subsurface fluorescence was subtracted from the microlayer fluorescence to yield surface enrichment estimates as ΔCDOM (see example in Figure 1).

2.3 Surface tension and static elasticity

Point measurements of surface tension were made along the survey tracks using a series of calibrated spreading oils (*Garrett and Duce, 1980*; *Peltzer et al.*, 1992). Surface tension resolution using the spreading oil method is ~0.15 mN m^{-1} at surface tensions near that of clean seawater (~73.5 mN m^{-1} at 20°C) and decreases to ~2 mN m^{-1} at very low surface tensions (~50 mN m^{-1}). Film surface pressures were estimated from the ambient surface tension, salinity, and temperature data. Gibbs static elasticities (ε_0) were computed from surface pressure-elasticity relationships determined in a film balance using extracted film materials.

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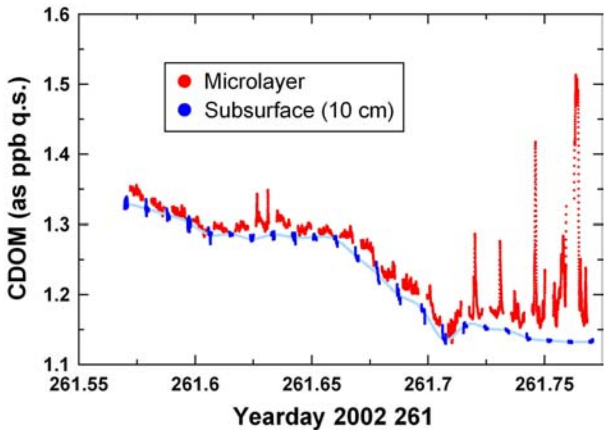

Figure 1. Microlayer and subsurface CDOM concentrations measured along a 5 hour, 11 km transect near the MVCO Air-Sea Interaction Tower on Yearday 261, 2002. The spline fit of the subsurface CDOM used to estimate microlayer enrichment is also plotted.

3. RESULTS

Analysis of the data from the SCIMS deployments at MVCO shows that this coastal environment was significantly impacted by surface films over the full range of wind stress conditions under which SCIMS can operate (U_{10} < 7 m/s). This was evident from observed surface excess CDOM distributions and depressed levels of surface tension. Film surface pressures were generally in the range of 1-2 mN m^{-1} but reached levels as high as 25 mN m^{-1} in regions of highest ΔCDOM. Near-surface CDOM concentrations (10 cm depth) generally were within the range of 0.75-1.5 ppb q.s. over the early summer and fall seasons. Surface chemical enrichments, represented by differences in surface microlayer and subsurface concentrations of CDOM (ΔCDOM), were observed in nearly all of the deployments and were extremely variable, ranging from 2-200% of bulk CDOM concentration. The CBLAST deployments focused on the response of the microlayer to changes in atmospheric forcing. Figure 2 shows the ΔCDOM records for individual SCIMS deployments at four different wind speeds. Histograms of ΔCDOM for these same four deployments are shown in Figure 3, arranged in order of increasing wind speed. The histograms illustrate the general tendency for ΔCDOM to adjust to the steady state wind stress. In very low winds, ΔCDOM distributions were very broad; films became highly patchy with slick features varying in scale from tens to hundreds of meters. Surface enrichments generally were not correlated with variations in subsurface CDOM. Thus, other processes, perhaps subsurface flows or buoyant overturning tended to dominate at low wind speeds and contribute to the enhanced inhomogeneity in surface coverage. As winds increased to moderate levels, the sea surface exhibited lower, more uniform surfactant film coverage and narrower ΔCDOM distributions. Several processes may contribute to the erosion of films as winds increase, including desorption into the bulk with increased surface straining, film disruption and downmixing by breaking of waves, and increasing lateral advection due to the surface drift velocity. These processes can erode films fairly rapidly. However, the response of the microlayer to a decrease in wind stress appears to be slow in the absence of organized subsurface flows that form zones of convergence.

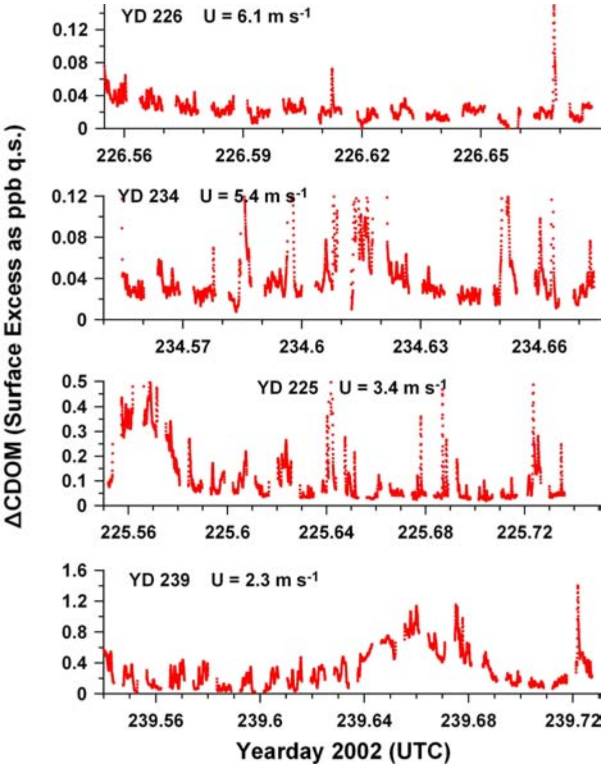

Figure 2. ΔCDOM traces recorded on four separate SCIMS transects at different average wind speeds during the 2002 CBLAST Intensive Operating Period.

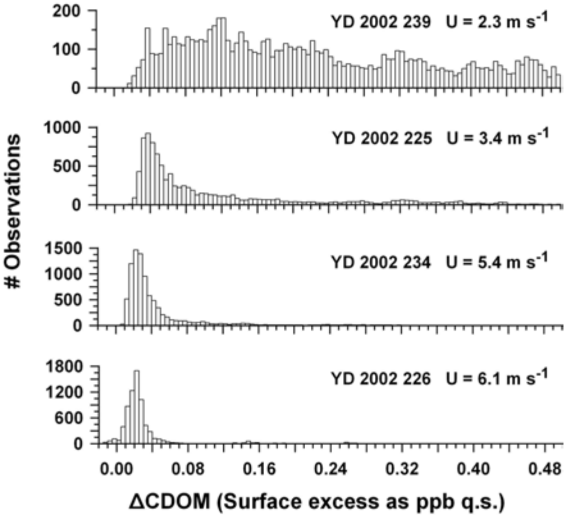

Figure 3. Histograms of ΔCDOM for the SCIMS transects shown in Figure 2. Distributions are typically broad with high mean ΔCDOM at low winds (U_{10} = 2 m s^{-1}) and become increasingly narrow with lower means as winds increase (U_{10} = 6 m s^{-1}).

Figure 4 summarizes the observations for 2002 and 2003 as histograms of ΔCDOM and static surface elasticity. Elasticities were estimated using an empirical relationship for the elasticity dependence on film surface pressure. Both the surface excess CDOM and elasticity variations observed at low winds imply large changes in ripple damping, with expected reductions in degree of saturation, $B(k)$, of 1-2 orders of magnitude at wavenumber k = 400 rad m^{-1} (Hara *et al.*, 1998). The wave number slope, $S(k)$, of ripples with wave numbers k > 200 declines for ΔCDOM levels as low as 0.02-0.04 ppb q.s. at winds up to 6 m s^{-1} (Frew *et al.*, 2002; 2004). These reductions in turn imply strong effects on momentum and mass transfer during low wind episodes.

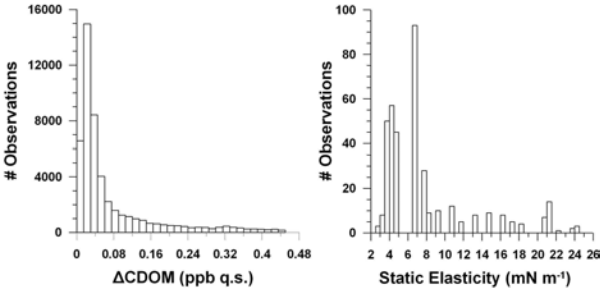

Figure 4. Histograms summarizing the distribution of surface excess colored dissolved organic matter (ΔCDOM) (left panel) and static elasticity ($\boldsymbol{\varepsilon_0}$) (right panel) for all SCIMS deployments at MVCO during 2002-03, over the wind speed range of 1-7 m s^{-1}. CDOM fluorescence is calibrated against quinine sulfate (q.s.) standards such that one CDOM fluorescence unit = 1 ppb q.s.

Figure 5. Photo taken from the Air-Sea Interaction Tower at MVCO of the SCIMS catamaran accompanied by R/V Asterias during a southeasterly survey transect on Yearday 227 2003. Numerous banded surface film features (light areas) evident in the field of view were also recorded in the CDOM fluorescence record. Photo by M. McElroy, WHOI.

At low winds, subsurface flows often appear to be the dominant process controlling surface film distributions. Figure 5 shows an interesting case observed during the 2003 CBLAST-Low Winds Main Experiment, in which an extended series of linear features roughly aligned to the coastline was observed. These linear features were most likely the surface expression of internal waves propagating onto the shelf. Similar features have been observed in infrared imagery taken by C. Zappa and A. Jessup (Zappa, 2002) during aircraft overflights of this site.

The 1 Hz record of CDOM fluorescence during this transect is shown in Figure 6 as ΔCDOM vs. decimal yearday. The record shows strong surfactant banding on different spatial scales. The fine scale features are estimated to be ~15-20 m wide, while major bands are up to 200 m in width. Wind speed and near-surface water temperature (15 cm depth) are also plotted in Figure 6. Many of the prominent features in the ΔCDOM record correspond to surface temperature anomalies rather than variations in wind speed. We plan to compare the surface film record with airborne IR imagery, as well as with the fan beam ADCP and temperature data from the buoy array deployed by the WHOI UOP group during CBLAST-LOW.

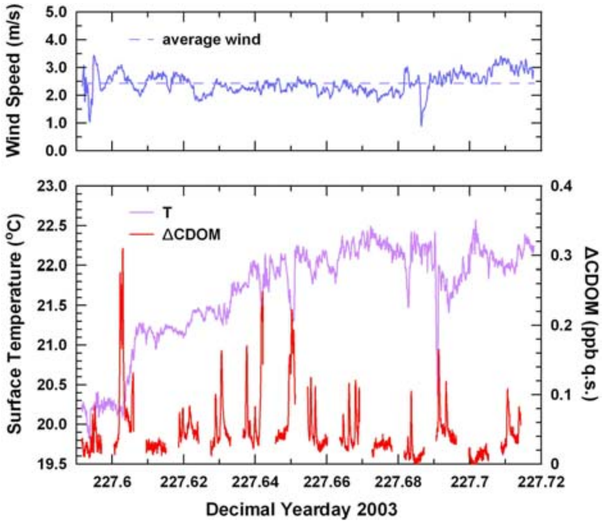

Figure 6. Lower panel: ΔCDOM and surface temperature records for Yearday 227, 2003 showing frequent correspondence between surface temperature anomalies and surface chemical enrichments. Upper panel: Wind speed for the same transect.

4. SUMMARY

SCIMS was deployed during CBLAST-Low to survey variations in surface chemical enrichments at the Martha's Vineyard Coastal Observatory (MVCO) site, a typical coastal regime. The MVCO site was significantly impacted by surface films for winds up to 6 m s^{-1}. Film distributions were patchy with features as small as a few tens of meters in scale, but with trends on kilometer scales. CDOM enrichments ranged from 2-200% of bulk CDOM concentration. Surface tension was typically 1-2 mn m^{-1} below that of pure seawater, but ranged as much as 25 mN m^{-1} below nominal in heavily filmed areas. Distributions were controlled by both water-side and atmospheric forcing. Banded features were frequently associated with near-surface temperature anomalies. Film distributions adjusted rapidly to increasing wind stress (erosion processes), but relatively slowly to decreasing wind stress (diffusion and readsorption). Observed CDOM and elasticity variations imply large variability in ripple damping and are consistent with reductions in the degree of saturation B(k) of 1-2 orders of magnitude for small-scale waves. These reductions in turn imply strong effects on momentum and mass transfer during low wind episodes.

5. ACKNOWLEDGMENTS

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