# Chemical Mapping of the Marine Microlayer: A System for Measurement of Spatial and Temporal Variations in Composition

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## LONG-TERM GOALS

The viscoelastic behavior of the air-sea interface, a key parameter affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew *et al.*, 2002). The long-term goals of this work are to understand the relationship between the composition of surface-active organic matter in the marine microlayer and the viscoelasticity of the sea surface and to delineate the role of microlayer films in modulating roughness and near-surface turbulence.

## OBJECTIVES

The occurrence, spatial distribution, concentration and composition of sea surface films are not well known. In order to understand and model the impact of the surface microlayer on air-sea exchange processes, it is useful to have detailed information about the following:

- film formation rates and persistence as a function of wind stress;
- patchiness of film distributions over a range of spatial scales (10m – 1 km);
- surface tension and elasticity variations on these spatial scales;
- film composition as a function of film pressure, wind stress, and seasonal factors.

In order to develop such information, this project focuses on designing and deploying systems to detect and measure organic analytes in the marine microlayer in near-real time. Responding to a broad range of organic compounds, such systems can provide specific information on the composition and structure of surface-active materials and estimates of surface enrichments of specific surfactants that control the viscoelasticity of the sea surface.

## APPROACH

A new survey tool, SCIMS (Slick Chemical Identification and Measurement System), which detects the presence of surface microlayer films and allows mapping their spatial and temporal distributions, is being deployed for seasonally distributed observations at the Martha's Vineyard Coastal Observatory (MVCO) off Cape Cod (see http://www.whoi.edu/science/MCG/people/nfrew/SCIMS_New_1.html). SCIMS consists of a surface microlayer skimmer that is coupled to a fluorometry package and an

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automated extraction interface. It is used in conjunction with innovative ion trap mass spectrometry technology to study microlayer film accumulations and their specific composition. Deployed on a remotely piloted catamaran, SCIMS processes the skimmer flow stream, carrying out cyclical, microscale solid-phase extraction, concentration, desalting, and elution of microlayer surface-active organics for short-term archiving in an autosampler-compatible vial array. The time-series 'snapshots' of the extracted microlayer are then processed by a shipboard or laboratory ion trap mass spectrometer (ITMS) to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of about ten minutes. The mass spectral information can be further used with elasticity data to develop correlative relationships between film composition and elasticity. SCIMS also provides real-time 1 Hz measurements of microlayer and subsurface colored dissolved organic matter (CDOM) fluorescence, which is normalized to the fluorescence of quinine sulfate (q.s.) standards (Vodacek *et al.*, 1997)

## WORK COMPLETED

During FY2003, we continued a series of deployments of SCIMS at the Martha's Vineyard Coastal Observatory (MVCO) site. Several of these coincided with the August 2003 CBLAST-LOW Main Experiment. SCIMS logged ~ 30 hrs of microlayer/subsurface CDOM fluorescence at the MVCO site and collected ~75 microlayer and subsurface surfactant samples. The fluorescence data from these deployments have been processed to provide estimates of microlayer surface excess CDOM. Film surface pressures have been estimated from the ambient surface tension, salinity and temperature data. Gibbs static elasticities ($\varepsilon_0$) have been computed from surface pressure-elasticity data. Roughly half the SCIMS extracts have been screened using electrospray mass spectrometry.

## RESULTS

As in last year's series, these deployments focused on the response of the microlayer to changes in atmospheric forcing. The results were similar to last year's observations showing that this coastal environment is significantly impacted by surface films over a wide range of wind stress conditions. This was evident from high levels of surface excess CDOM and depressed levels of surface tension. Near-surface bulk CDOM concentrations (0.75-1.1 ppb q.s.), were in close agreement with the previous measurements. Surface chemical enrichments, as represented by differences in surface microlayer and subsurface concentrations of CDOM (ΔCDOM), were observed in nearly all of the deployments and were extremely variable. Surface excess CDOM ranged from 2-35% of bulk CDOM concentration. Film surface pressures were generally in the range of 1-3 mN $m^{-1}$ but exceeded 25 mN $m^{-1}$ in regions of highest ΔCDOM. For winds speed > 6 m $s^{-1}$, the sea surface exhibited low, relatively uniform surfactant film coverage and narrow ΔCDOM distributions. At lower wind speeds, ΔCDOM distributions became increasing broad and film distributions were 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. Figure 1 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 (Hara *et al.*, 1998). The wave number slope, $S(k)$, of ripples with wavenumbers $k$ > 200 declines for ΔCDOM levels as low as 0.02-0.04 ppb q.s. at winds up to 6 m/s (Frew *et al.*, 2002; 2003). These reductions in turn imply strong effects on momentum and mass transfer during low wind episodes.

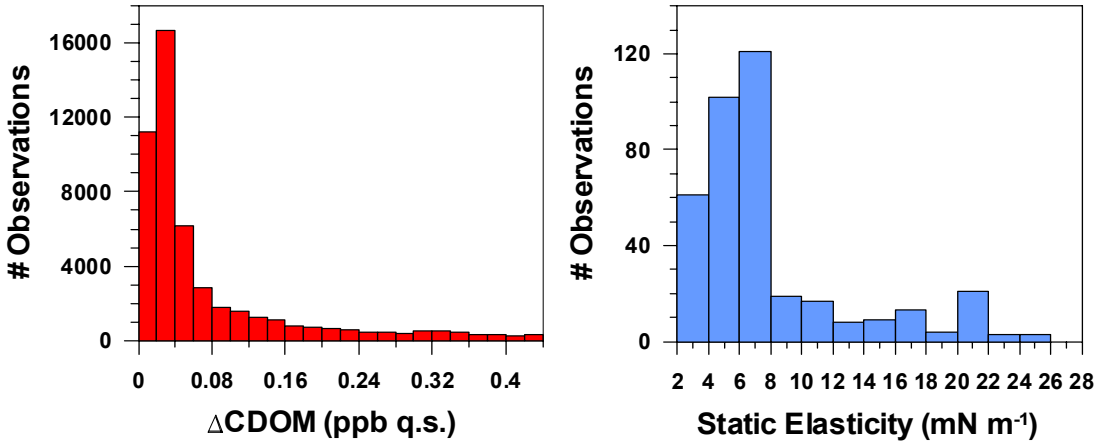


***Figure 1: Histograms summarizing the distribution of surface excess colored dissolved organic matter (ΔCDOM) (left panel) and static elasticity (ε0) (right panel) for all SCIMS deployments at MVCO during 2002-03, over the wind speed range of 1-7 m s-1. CDOM fluorescence is calibrated against quinine sulfate (q.s.) standards such that one CDOM fluorescence unit = 1 ppb q.s.***

At low winds, subsurface flows often appear to be the dominant process controlling surface film distributions. Figure 2 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.

***Figure 2. 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.***

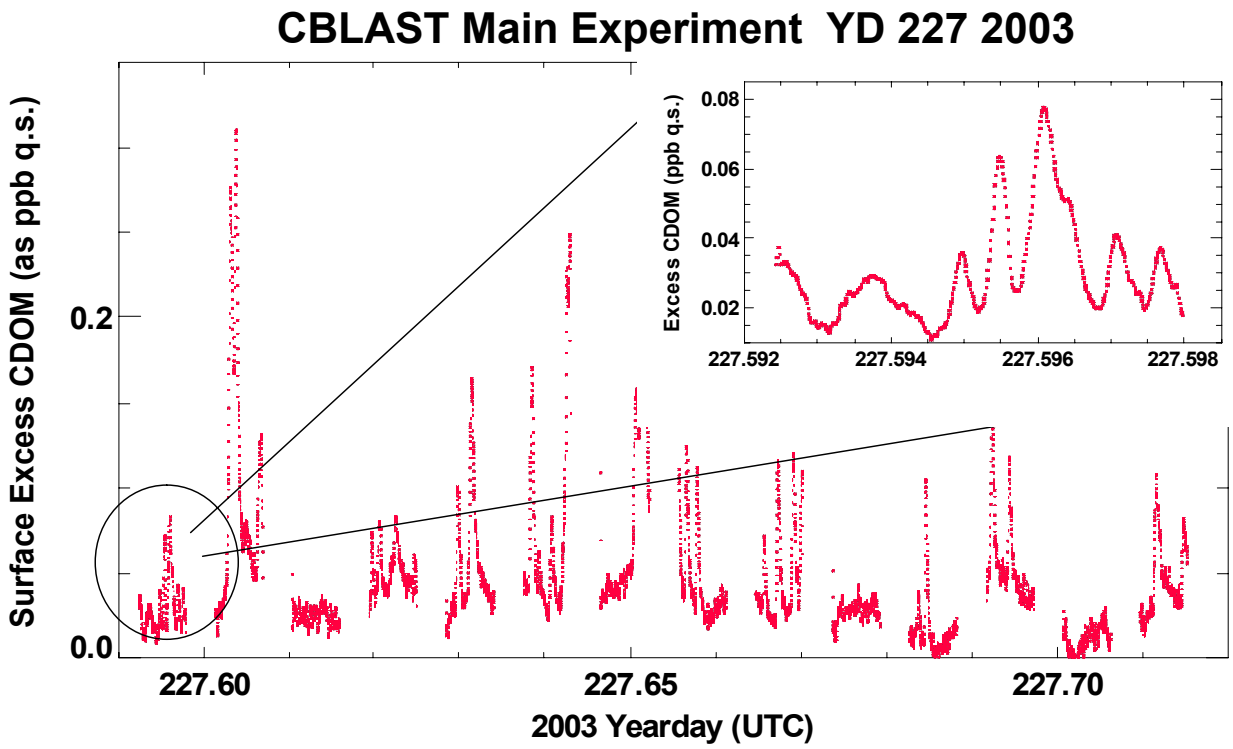


***Figure 3. Surface excess CDOM (ΔCDOM) record for the SCIMS transect surveyed on YD 227 2003 showing highly banded surface features seen in Figure 1. Gaps in record are intervals when fluorometer was switched to monitor subsurface CDOM levels.***

The 1 Hz record of CDOM fluorescence during this transect is shown in Figure 3 as ΔCDOM, the difference between the CDOM fluorescence in the microlayer and at 10 cm depth. The record shows strong surfactant banding on different spatial scales. The inset shows the initial portion of the record on an expanded time scale. Given a SCIMS catamaran forward speed of 0.5 m/s, the fine scale features are estimated to be ~15-20 m wide, while major bands are up to 200 m in width. We plan to compare the surface film record with airborne IR imagery, as well as with the fanbeam ADCP and temperature data from the buoy array deployed by the WHOI UOP group during CBLAST-LOW.

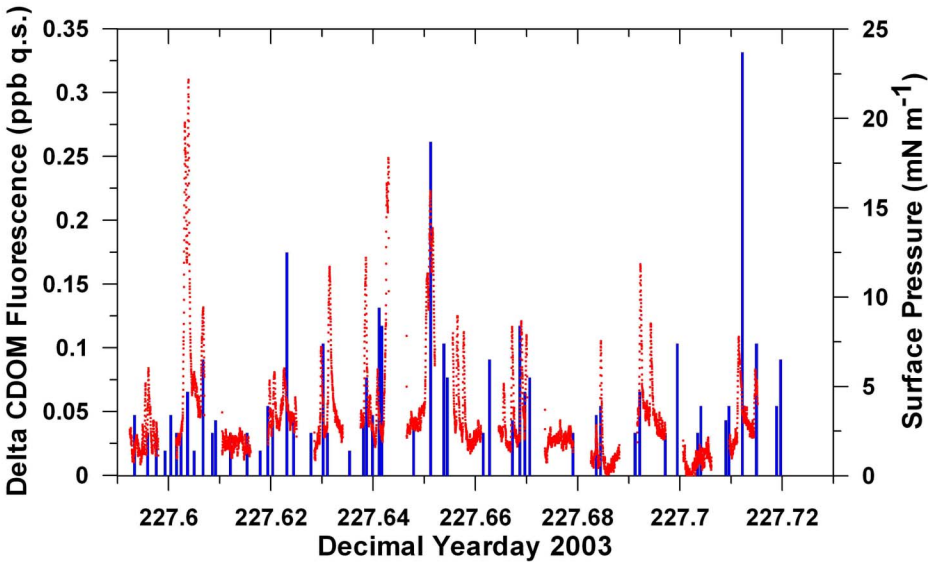


***Figure 4: Film surface pressure (blue) vs. decimal yearday for Yearday 227 2003, derived from discrete measurements of surface tension using calibrated spreading oils. The ΔCDOM record (red) is also plotted on the same time scale.***

Figure 4 shows a plot of surface film pressures calculated from discrete surface tension measurements made along the transect. These measurements were made from R/V Asterias and thus were not exactly co-located with the SCIMS sampler. There is a general correspondence between elevated film pressures and peaks in the ΔCDOM record (shown as an overlay). However, there are clearly several instances where the two parameters do not agree well, which suggests that surfactant composition was not uniform. The SCIMS microlayer extracts from this deployment are being analyzed using a variety of mass spectrometric techniques. The electrospray ionization (ESI) mass spectra are complex and show (1) a broad envelope of ions in the scan range of 200-2000 amu, (2) a maximum abundance in the molecular weight range of 500-1000 amu, and (3) sample to sample variations in the averaged spectra. At this stage of the analysis, we haven't determined whether compositional differences in these high molecular weight components are related to differences in fluorometer response relative to surface tension variations. Another possibility is that the differences are related to film compression and selective enhancement of low molecular weight lipid components. In addition to the ESI-MS, we plan to analyze the samples using pyrolysis electron impact ionization to look for enhanced lipid signatures.

## IMPACT/APPLICATIONS

SCIMS is providing new information on the surface microlayer, including film abundance and distributions in relation to physical forcing, the molecular identity and concentrations of organic compounds in the sea surface microlayer and better estimates of surface elasticity. The availability of such information during field studies will allow more detailed investigations of air-sea interactions and improved ground truth of microwave remote imagery. More rapid information acquisition will allow process studies of links between biology, surfactant production and film distributions, the role of hydrodynamic processes in film formation and dispersal, photochemical degradation processes in the microlayer, and the relative importance of insoluble lipid and soluble biopolymeric surfactants in determining sea surface viscoelasticity. Expected major applications include studies of the role of the

marine microlayer in modulating small-scale waves and microwave scattering, microwave signatures of internal waves, wind stress-drag relationships, and turbulent surface renewal and air-sea gas exchange.

## RELATED PROJECTS

This project is closely related to my NOAA-funded effort to understand the role of wind stress, small scale waves, near-surface turbulence, and surface films in modulating air-sea gas exchange (with T. Hara, (URI), U. Schimpf, and B. Jähne (U. Heidelberg)) and to my NASA-funded effort to develop algorithms to quantify air-sea gas exchange using remotely-sensed surface roughness (with D. Glover, WHOI). Collaboration with investigators involved in the CBLAST-LOW initiative to model boundary layer fluxes is also ongoing.

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