

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, which is an important factor affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew and Nelson, 1998). My goals 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, and the implications for interpreting both active and passive microwave imagery of the sea surface.

OBJECTIVES

The occurrence, spatial distribution, concentration and composition of sea surface films are not well known. In order to understand the impact of the microlayer on air-sea interactions, it is advantageous to make real-time or near real-time measurements of microlayer concentration and composition using a detection system that responds to a broad range of organic compounds and that also provides specific structural information. This new project focuses on developing an analytical system for detection and measurement of organic analytes in the marine microlayer in near real-time. The system will detect the presence of surface microlayer films, map their spatial distributions, and monitor their temporal variability. It will 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 rotating cylinder microlayer skimmer (Carlson *et al.*, 1988) will be coupled with innovative ion trap mass spectrometry technology to map spatial and temporal variations in microlayer film accumulations and their specific composition. An automated sampling interface, intended for deployment on the air-sea interaction catamaran LADAS (Bock *et al.*, 1998) will process 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 will then be processed by a shipboard ion trap mass spectrometer to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of a few minutes.

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WORK COMPLETED

During the startup phase of this project we have done an initial feasibility study of the solid phase microtrap extraction cycle, assessed the capabilities of the LCQ ion trap mass spectrometer in processing unseparated surfactant mixtures, designed the control hardware for the automated sampling interface, and developed a software graphical control interface.

RESULTS

One of the critical steps in developing the automated sampling system is to optimize the recovery of surface-active organics from the seawater flow stream. We have begun to evaluate various solid phase extraction media and formats for suitability to this task and to test the feasibility of making small volume extractions; the latter aspect is important in that the sample volume defines the ultimate temporal (and therefore spatial) resolution of the system. We have targeted on a 10 ml sample volume and a 3 min cycle time for sequential snapshots of microlayer composition. Initial results obtained using a Michrom BioResources (M-B) reverse phase microtrap validate the micro-extraction concept. The M-B microtrap allows sample loading rates up to 5 ml min^{-1} , but has a very small bed volume ($50 \mu\text{l}$). A sample can be eluted from the trap in as little as $100 \mu\text{l}$ of solvent, thus minimizing analyte dilution and maximizing sensitivity. Thus far we have tested the M-B 'peptide' reverse phase microtrap which uses a polystyrene-divinylbenzene resin as the sorption medium. Electrospray ionization mass spectra (ESI-MS) of surface-active organics isolated on M-B microtraps from Vineyard Sound surface waters indicated a wide molecular weight distribution. A broad envelope of ions was observed up to m/z 2000, with an intensity maximum near m/z 800. Intense ions indicative of the presence of lipid and polyoxy surfactants typically found in marine surface waters were observed. We were able to demonstrate quantitative response of the LCQ ion trap mass spectrometer to these compounds in unseparated flow-injected mixtures isolated from seawater, using electrospray ionization and MS-MS monitoring of specific reaction pathways. Experiments involving sequential flow injections of microextracts of increasing volumes of Vineyard Sound surface water demonstrated a linear ESI response for both total ion current and specific ion fragmentation pathways for model analytes. We also showed that the targeted 10 ml sample volume for the proposed extraction cycle is realistic, providing adequate sensitivity within the linear response range of the protocol and requiring only a 2 minute loading interval. Currently, the most important limitation is the microtrap blank level, which is sensitive to the sequence and composition of conditioning and elution solvents. The specifics of the extraction protocol, including optimum pH, buffer composition, and volumes for loading, desalting, elution as well as the ESI-MS analysis conditions, will need to be further investigated.

In addition to the preliminary work on the solid phase extraction cycle at the heart of the proposed system, work is progressing on a general hardware concept and development of a software interface for control of the instrumentation. The hardware design is based on positive displacement fluid delivery using syringe pumps, rather than timed flow delivery. The availability of 'smart' syringe pump modules with serial interfaces make this approach attractive. The syringe pumps will provide better control of delivery rates and more precise volumes than are possible with timed flow schemes, which are subject to variations in microtrap back pressure. The software interface is being developed in a Visual C++ programming environment to run under Windows NT. Typically the system will be operated remotely (from the ship) using wireless LAN communication with the LADAS platform. The user interface allows interactive control of all sampling and extraction operations as well as data acquisition functions

and status displays for all subcomponents of the system. Controls for a previously developed microlayer CDOM fluorometry package have been incorporated to provide a real time display of microlayer and subsurface CDOM fluorescence.

IMPACT/APPLICATION

Deployment of the combined sampling package and ion trap mass spectrometer at sea will provide the capability to determine the molecular identity and relative concentrations of organic compounds in the sea surface microlayer. The rapid availability of such information during field experiments will allow more detailed studies of microlayer film occurrence and dynamics and improve our ability to relate sea surface viscoelasticity to dynamic exchange processes at the air-sea interface. 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. I expect major applications to include the role of the marine microlayer in modulating small scale waves and microwave scattering, wind stress-drag relationships, and turbulent surface renewal and air-sea gas exchange.

TRANSITIONS

None as yet, although I anticipate strong interest in application of the system being developed from ONR-sponsored investigators working on mechanisms of radar scattering by small-scale waves (D. Trizna, P. Hwang), the effects of microscale wave breaking on emissivity and sea surface temperature (A. Jessup), high-resolution optical measurements of small scale waves (B. Jähne, J. Klinke) and the role of stress/wave interactions in modifying momentum flux in the wave boundary layer (J. Edson).

RELATED PROJECTS

This project is closely related to a NSF Coastal Ocean Processes effort to understand the role of wind stress, small scale waves, near-surface turbulence, and surface films in modulating air-sea gas exchange (with E. Bock, J. Edson, W. McGillis and T. Hara).

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