

Functional groups in the sea surface microlayer: Implications for air-sea transfer during a phytoplankton bloom

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Abstract

The impact of ocean microbiological activity on the chemical species present in the sea surface microlayer (SSML) was investigated using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy. We observe clear chemical differences in organic functionality before and during the peak of an induced phytoplankton bloom.

Introduction

The oceans cover 71% of Earth's surface. Therefore the SSML, as the air-sea interface, strongly influences the transfer of material between the ocean and atmosphere via sea spray production (1). Understanding the dynamic changes in SSML chemistry due to microbiological activity is a critical step to unraveling the link between ocean chemistry and climate. Here we used ATR-FTIR to identify changes in the organic species present in the SSML as microbiological activity alters seawater chemistry.

Experimental Conditions

SSML samples were collected daily using the glass plate method (1) during a large-scale mesocosm experiment (2) and stored at -80 °C until analysis. After thawing, organics were isolated via solid phase extraction (Bond Elut PPL, Agilent Technologies) into methanol (3), deposited onto an 80 x 10 x 2 mm ZnSe multiple reflection ATR trough plate for use with the HATR accessory from PIKE Technologies (Madison, WI) and dried under nitrogen for 24 hours. Spectra were acquired at 4 cm⁻¹ resolution (200 scans) after 30 minutes of instrument purging with nitrogen.

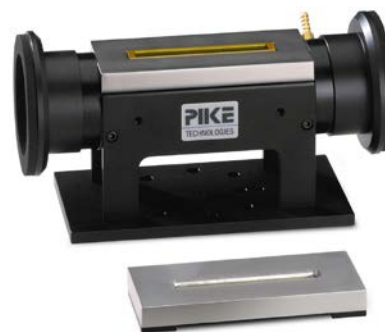


Figure 1. PIKE HATR multiple reflection ATR accessory.

Results

The sensitivity of the ATR measurements was enhanced by using a multiple reflection ATR plate with 20 reflections contacting the sample, and 40 total reflections. Absorbance values were amplified roughly by a factor of 20 relative to expected results from a single reflection ATR.

ATR-FTIR SSML spectra obtained before and at the bloom peak are shown in Figure 2. The pre-bloom spectrum contains peaks in the C-H, O-H and N-H stretching regions near 2900 and 3300 cm⁻¹, respectively. These peaks suggest the presence of aliphatic C-H groups due to fatty acids and lipids as well as the presence of alcohols, sugars, and amino acids.

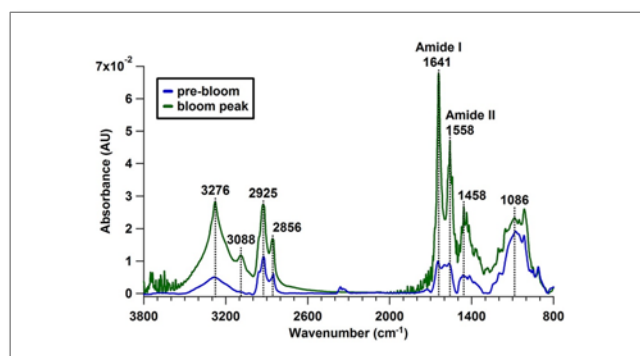


Figure 2. ATR-FTIR spectra for the SSML before (blue) and at the peak (green) of a phytoplankton bloom.

A peak in phytoplankton concentrations corresponds to an increase in organic functional group signal intensities. In addition, several peaks are more prominent and new peaks appear. Specifically, sharp peaks at 1641 and 1558 cm⁻¹ are

associated with amide I and amide II bonds, respectively (4). A new peak at 3088 cm^{-1} is due to the C-H stretch associated with unsaturated hydrocarbons.

The amide I and II bonds are particularly noteworthy and suggest that proteins, likely from microbial cell fragments, are abundant in the SSML during periods of high biological activity. Biological particles are known to have profound impacts on cloud properties and precipitation (5). Therefore SSML enrichment of proteins and cell fragments may lead to enhanced transfer to the atmosphere via sea spray and play a crucial role in affecting marine clouds and climate.

Conclusion

Using a highly sensitive multiple reflection ATR accessory, we identified changes in SSML chemistry resulting from microbiological activity. Results suggest that proteins are abundant in the SSML during a phytoplankton bloom. This enrichment likely alters sea spray chemistry, which has subsequent implications for atmospheric chemistry, clouds, and climate.

References

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