

# **MEASUREMENTS OF DISSOLVED ORGANIC MATTER AT THE CONTINENT-OCEAN BOUNDARY: EXAMINING REMINERALIZATION WITH THE ZAPS PROBE**

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## **LONG TERM GOALS**

We use innovative experimental approaches to measure biogeochemical interaction driven by the input of terrestrial organic carbon to the coastal oceans. The evolution of organic carbon from continents to oceans is not well understood. Remineralization of this carbon plays an unknown but apparently important role in stimulating productivity. This process and associated phenomena also affect ocean color, turbidity, and elemental recycling. Our long range goal is to quantify these processes in space and time.

## **OBJECTIVES**

Quantification of biogeochemical change at the land-ocean boundary requires that we gain better insights into fundamental relationships between dissolved organic carbon and other parameters, such as total suspended particulate matter and dissolved metals. Several interrelated objectives link the processes affecting organic carbon to our ability to measure physical and chemical gradients in the water column.

- development of technology to make it possible to collect high resolution data sets of trace substances in situ and in real time
- delineation of mixing trends for particles, dissolved organic carbon, and metals to ground truth sensors and to identify the most labile parts of the system
- quantification of remineralization rates by detailed sampling and controlled in situ experiments
- extrapolation of observations to a representative group of oceanic settings.

These objectives provide a framework for developing new technology and using these innovations to follow the evolution of terrestrial carbon from rivers, through estuaries, and into the coastal ocean.

# Report Documentation Page

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## **APPROACH**

Our objectives require technology that allows us to measure several optical and chemical properties at the same place and time. In the early stages of our project we developed a system of instruments capable of recording critical parameters associated with the cycling of metals and dissolved organic carbon -the ZAPS instrument package. This package produces high-resolution distributions of several parameters including chlorophyll, dissolved terrestrial humic material, marine proteins, dissolved manganese and suspended particulate matter, as well as temperature, depth, and conductivity. The centerpiece of this package is the ZAPS (zero angle photon spectrometer) fiber optic spectrometer (Klinkhammer, 1994). ZAPS allows us to examine the behavior of terrestrial organic carbon as it mixes into the coastal ocean by following the fluorescence signature of dissolved humic material (Klinkhammer et al., 1996).

In our recent work we have expanded our fluorescence studies to include another family of compounds. Following the lead of Mopper and Schultz (1993) we now measure fluorescent dissolved organic matter from proteinaceous material (FDOM-P) as well as from humic material (FDOM-H). Our approach has been to use the ZAPS package to explore the Columbia River estuary and its plume that extends for considerable distance along the Oregon or Washington coasts, depending on the time of year.

## **WORK COMPLETED**

Last year we carried out a series of tows in the Columbia River plume jet. Before we did this work we redesigned the flash lamp assembly in ZAPS and incorporated a new flash lamp and socket. These changes resulted in a better signal-noise ratio that allowed us to examine trends in DOM in greater detail—they essentially lowered the detection limit of ZAPS for natural fluorescence by more than a factor of three. With the old system we were able to reproduce fluorescent signals from dissolved humics at the 5% level (Klinkhammer et al, 1996), this precision is now at the 1-2% level. This advance is important to our work because of the small changes in DOM expected during remineralization. DOM makes up most of the organic carbon pool, even in productive coastal waters. Remineralization of 10% of the DOM could double new production if most of this material were recycled as marine organic matter. It thus becomes crucial to measure DOM precisely if we want to look at potentially important shifts in the organic carbon pool.

## **RESULTS**

Our transects in Dec. 1996 started just seaward of the marker buoy at the mouth of the Columbia and cut westward across the plume. From our previous work in the estuary and plume we knew that FDOM-H in this area has a terrestrial origin (Klinkhammer, 1997). The primary goal of this cruise was to look for evidence of remineralization as Columbia River Plume Water (CRPW) mixed across the shelf. As an adjunct to this study we planned to develop a companion data set for FDOM-P. We assume that FDOM-P corresponds to primarily marine proteinaceous material, based on the results of Mopper and Schultz (1993).

Shown in Fig. 1 are typical FDOM profiles from the 1996 cruise with accompanying salinity data. In these figures we distinguish between data collected as the package went down through the water column and data collected during the return to the surface. Assuming that the downcast and upcast traces should be identical, we estimate that these measurements are reproducible at the  $\pm 2\%$  level. This is a liberal estimate as some of this variability is certainly real, as indicated by differences in salinity between the up and down traces. Based on these results, it seems clear that FDOM parameters reproduce well enough and are distinct enough to be useful water mass tracers.

Fig. 2 is a plot of FDOM-H against salt for the 1996 study. This figure documents the dramatic shift that occurs in the salt-humic relationship between river and ocean waters. The elbow in this plot occurs exactly at the base of CRPW (40m). In the broadest sense this distinct distribution is produced by mixing of river water, coastal surface water, and coastal water masses. The reversal in the FDOM-salt relationship below the influence of Columbia River water results from the dichotomous behavior of organic carbon in the oceans. It illustrates the non-conservative nature of dissolved organic carbon on the time scale of vertical mixing. Looking at Fig. 2 in detail we can see that deviations from conservative behavior occur in both limbs of this relationship. These underlying trends are consistent with removal of DOM from plume water, and input of DOM into bottom water. Taken as a whole these observations support the view of Opsahl and Benner (1997) that terrigenous DOM undergoes rapid cycling and thus has the potential of fertilizing the coastal ocean.

The idea that remineralization of terrestrial DOM can have a dominant influence on productivity is gaining strength in the recent literature (Bacastow and Maier-Paier 1991; Lefèvre et al., 1996, Opsahl and Benner, 1997). The ZAPS package gives us a tool to detect this process directly as changes in the DOM pool.

## **IMPACT**

This work demonstrates that fiber optic spectrometers can resolve the fluorescent signature of DOM at the 1-2% level. Such data can distinguish coastal water masses and indicate where carbon compounds are produced and degraded. These high resolution data sets make it possible to sample more efficiently, experiment more effectively, and extrapolate more confidently. From a Navy perspective such information might be used for chemical sensing of littoral water types (nonacoustic guidance) and pollution monitoring.

## **TRANSITIONS**

Fiber optic spectrometers are patented technology (US patent no. 5,304,492). Wheaton Associates (London, UK) hold a license from Oregon State University to develop this technology for ocean-related applications. ORETEC Inc. (Corvallis, OR) have a license pending to develop ZAPS technology into the area of groundwater monitoring.

## **RELATED PROJECTS**

For the last three years our group has been funded to develop instrumentation for use on Navy submarines through SCICEX. This program has given us the opportunity to mount a ZAPS instrument on a nuclear submarine during patrols in the Arctic Ocean. We just completed our second successful operation.

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