

Carbon and Manganese Transformations at the Continent-Ocean Margin Quantified with the ZAPS Instrument Package

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LONG TERM GOAL

We use innovative experimental approaches to measure the extent of 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 and applying technology to follow the evolution of terrestrial carbon from rivers, through estuaries, and into the coastal ocean.

APPROACH

Our objectives require technology to measure 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. This package produces high-resolution distributions of several parameters including light level, chlorophyll, dissolved terrestrial humic material, dissolved marine proteins, dissolved manganese and suspended particulate matter, as well as temperature, depth, and conductivity. We call this package the ZAPS

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instrument package. The centerpiece of this package is the ZAPS (zero angle photon spectrometer) fiber optic spectrometer (Klinkhammer, 1994). ZAPS makes it possible 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., 1997).

The ZAPS package is a flexible system that allows us to incorporate special instrumentation for specific experiments or develop new technology. The large database produced by the ZAPS package helps to ground truth new measurements and sort out artifacts.

WORK COMPLETED

In 1996 we used fluorescence from humic material to trace the evolution of organic carbon in the coastal plume from the Columbia River. We found that fluorescent DOM was depleted by about 7% from what we would expect from mixing of coastal water and river water. It was unclear from this work whether the anomaly we observed resulted from an in situ process or was advected from the estuary.

In 1997 and 1998 we carried out a series of operations in the Columbia estuary. Our 1997 results indicate that there is substantial removal of fluorescent material within the estuary. In 1998 we did more work on the behavior of humic material in the estuary. These data confirmed the 1997 results. We also developed an UV-absorption technique for measuring NO_3^- with ZAPS and applied this technique during a series of transects.

In 1997 we calibrated ZAPS output against DOC (Guay et al., 1998). This work was done in the Arctic as part of the SCICEX Program. We found a linear correlation ($r^2=0.86$) between DOC as measured by high-temperature combustion (HTC done in the laboratory of R. Benner at the University of Texas Marine Science Institute) and output from the ZAPS instrument. As part of this same study we sent a subset of frozen samples to P. Coble (University of South Florida) who performed a full spectrum analysis using a scanning fluorometer. We compared integrated fluorescent output (330 through 700 nm) with ZAPS output at 420 nm and obtained a correlation coefficient (r^2) of 0.997.

The strong correlation between HTC-DOC and ZAPS-DOC allows us to make some empirical statements about optical DOC measurements made with this instrument. (i) The SCICEX correlation belies the notion that ZAPS fluorescence (or the efficiency of fluorescence) is a non-congruent property and thus decoupled from DOC concentration. (ii) While the fluorescence of natural organic matter sometimes increases with decreasing temperature (Willey and Atkinson, 1982), the effect of this artifact on ZAPS data must be relatively small. During the Arctic work we encountered T excursions of $>5^\circ\text{C}$ but these changes did not affect ZAPS response in a way that could be directly attributed to temperature. Our results from the Columbia support this conclusion. (iii) During the Arctic patrol we encountered water containing terrestrial DOC from multiple riverine sources draining dramatically different watersheds. There was no evidence that the DOC from these sources created a different ZAPS response. This observation implies that fluorescence induced by this instrument is independent of relatively subtle differences in the composition of humic material that we assume must exist in waters from such a variety of fluvial sources. Rather optical DOC appears to be a bulk property of terrestrial humic-like material that has little spatial variability. We refer to this material as h(humic)DOC. Our working hypothesis is that hDOC is of mainly terrestrial origin. Results from the Columbia system support this idea.

RESULTS

When we applied the Arctic calibration to fluorescence data from the Columbia we found good agreement between HTC measurements from the Columbia (OSU data) and optical DOC results (Fig. 1). There are several ways to interpret the results shown in this figure. We prefer to think of this distribution as representing the sum of two distinct trends: dilution of humic-rich river water and removal of dissolved humics at higher salinities. By extending the riverine trend we estimate that 40 $\mu\text{mol C L}^{-1}$ are removed within the estuary. Given a residence time in the lower Columbia of approximately one day (Baptista et al., 1998), this anomaly translates to a degradation rate of 1.7 $\mu\text{mol C L}^{-1} \text{ hr}^{-1}$. This rate is similar to those measured in bottle incubation experiments, for example Amon and Benner (1996) measured a rate of 4.0 $\mu\text{mol C hr}^{-1}$ in the Amazon River system. The maximum productivity in the Columbia is about 2.5 $\mu\text{mol C L}^{-1} \text{ hr}^{-1}$ (Lara-Lara et al., 1990) making remineralization of terrestrial carbon a significant factor in the organic carbon cycle of the lower Columbia.

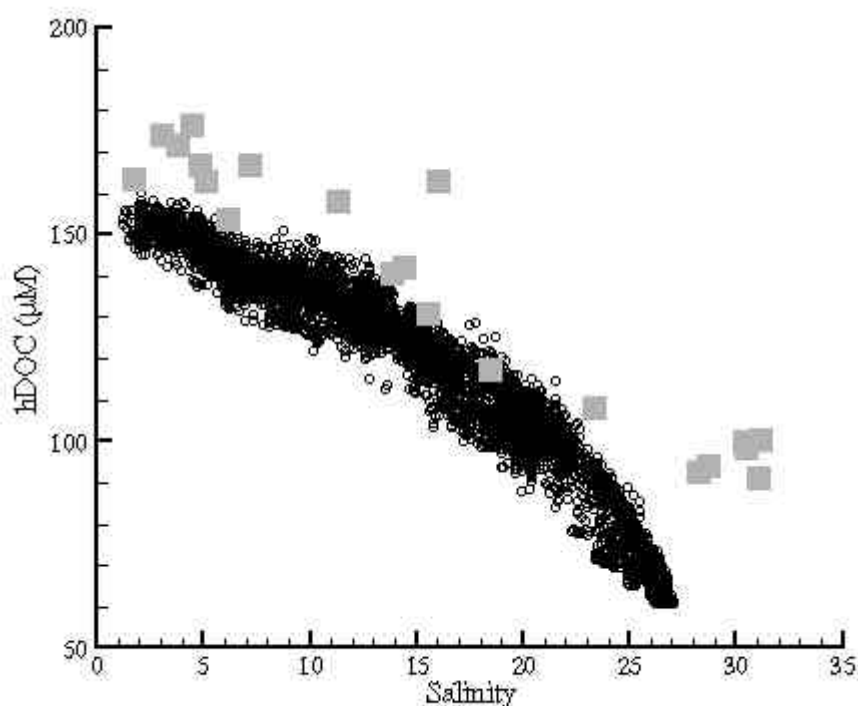


Figure 1. This figure shows the distribution of DOC in the Columbia River estuary in Nov. 1997. Black circles are optical humic DOC data, squares are DOC concentrations determined by high temperature combustion of filtered samples. Previously reported levels of DOC in the Columbia (salinity=0) range between 140 and 190 $\mu\text{mol C L}^{-1}$ (Damn et al., 1981; Bristow et al., 1985; Prahl et al., 1998). The distribution of hDOC is consistent with removal of some 30% of the riverine flux of DOC within the estuary. DOC is generally higher being a mixture of hDOC and marine carbonaceous material, although this dilution is attenuated by recycling.

We assume that this remineralization occurs by a combination of microbial degradation and photooxidation. Many workers have observed evidence of photooxidation (photobleaching) (Kramer 1979; Amador et al., 1989; Kieber et al., 1990; Mopper et al., 1991; Herndl et al., 1993; Miller and Zepp; 1995; Amon and Benner; 1996). More recently Twardowski (1998) has developed a high-

resolution data set similar to the one reported here but using light absorption measurements in embayments in the San Juan Islands. This study was able to show that the material being degraded is colored dissolved organic matter (CDOM). Twardowski found that about 20% of the CDOM was remineralized --comparable to the 30% that we find in the Columbia. Twardowski (1998) also observed new production associated with this degradation, similar to what we saw in the Columbia plume (Klinkhammer et al., 1997).

While it seems certain that photooxidation is responsible for some of the DOC remineralization that we observe, the evidence for significant microbial degradation is mounting. Microbial activity in the Columbia seems to be centered on the estuary turbidity maximum (ETM). The ETM is a transient maximum in suspended material that is common to many estuaries (Berner and Berner, 1996). The ETM of the Columbia contains >50 mg of suspended particulate matter (SPM) per liter (Gelfenbaum, 1983; Prahl et al., 1997).

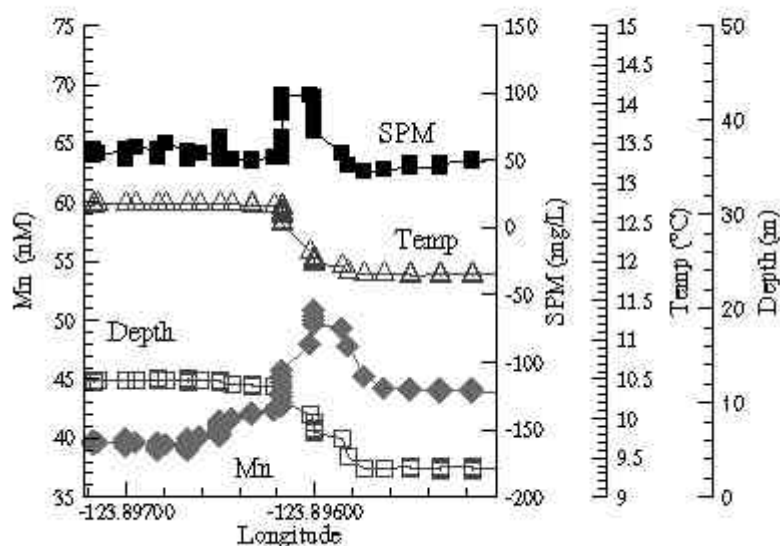


Figure 2. Suspended particulate matter (SPM), temperature, depth, and dissolved manganese in the Columbia River estuary. The maximum in SPM is commonly referred to as the ETM. These results illustrate the rapid response of the ZAPS chemical-analyzer. The presence of increased levels of dissolved Mn in the ETM is consistent with microbial degradation of humic material (Klinkhammer et al., 1996).

Previous workers have shown that the ETM is enriched in bacteria (Baross et al., 1994) and contains Mn-rich particles (Prahl et al, 1997). Two years ago we found that the ETM is characterized by reduced DOM fluorescence (Klinkhammer et al., 1996). Last year we discovered that the ETM has anomalously high levels of dissolved Mn (Fig. 2). Preliminary results from this year show that this feature also has anomalously low nitrate levels coincident with reduced amounts of humic DOC. (NO_3^- was also done with ZAPS using UV absorption.) Output from the PAR sensor (that we had on our package for the first time this year) shows that the minimum depth of the ETM is associated with the base of the photic zone suggesting that the ETM may be related to a heterotrophic microbial loop. The

picture developing for the ETM is a classical picture of microbially mediated suboxic diagenesis:
—particle-rich, oxide-rich, and bacteria-rich layer associated with an aphotic environment
—degradation of humic-rich organic carbon —consumption of nitrate —production of dissolved Mn .
In other words our data point to the ETM as a source of remineralization and denitrification by facultative heterotrophic bacteria. Normally we associate this process with sediments (Froelich et al., 1979) or anoxic basins. Our work redefines the limits under which such processes can occur. High-resolution instrumental data is the best way we have to quantify the effects of such activity.

IMPACT / APPLICATION

Our optical hDOC measurements isolate the terrestrial component of the DOC pool. They reveal that much of the DOC coming into an estuary from the ocean is recycled terrestrial material. They also show that a large percentage (30%) of fresh riverine material is degraded in the estuary by a combination of photooxidation and microbial activity. There is every reason to think that such activity is a common feature of estuarine systems world-wide. Remineralization on this scale affects ocean color, turbidity, odor, and volatile content. It becomes an important process in partitioning anthropogenic waste. Moreover the products of remineralization act as a fertilizer to the coastal ocean stimulating ocean productivity. These processes determine the CDOM characteristics of the coastal ocean.

From a geochemical standpoint these results allow us to improve our estimate for the fluvial flux of DOC to the oceans. We are now able to say that a large fraction of the DOC flux from rivers is remineralized in estuaries. This affects how we view the organic carbon budget of the Earth. Furthermore, it seems reasonable to assume that the process of remineralization continues in the coastal ocean, albeit at a reduced rate. The terrestrial carbon that escapes degradation mixes into the oceans. Our preliminary results suggest that a significant amount (>50%) of the DOC pool of the oceans is refractory terrestrial material. This conclusion is at odds with lower estimates based on lignins (Opsahl and Benner, 1997). Nevertheless, when combined with a large amount of degradation (>66%), our estimate brings the fluvial flux more in line with the radiocarbon age of DOC in the oceans.

TRANSITIONS

We deployed the SAFIRE multi-wavelength light absorption spectrograph (WetLabs) as part of the ZAPS package this year. These data will allow us to cross calibrate our fluorescence results to CDOM. We upgraded our computer system so we have more reliable real-time processing of the data.

RELATED PROJECTS

ZAPS technology has found application in a wide range of projects. Besides our Columbia work this year we also participated in a joint US-German cruise to the Wadden Sea. Next year we will use our package in three projects: (1) to explore the Bransfield Strait, Antarctica for hydrothermal vent sites (NSF -Office of Polar Programs; OPP-9725872), (2) to investigate water column chemistry above an emerging hydrate site off the Oregon coast as part of the TECFLUX Program (NSF -Chem. Ocean.; OCE-9811471), and (3) to continue this study in the Columbia system.. We are also working with K. Falkner to develop additional methods so we can broaden the use of ZAPS as a chemical analyzer.

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