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Technical Progress Report, Year 2
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Origins and Fates of DOM along the New England Continental Margin

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Summary

In year two, we have analyzed DOM (dissolved organic matter) samples from the Atlantic and Pacific Oceans, performed preliminary experiments concerning the decomposition of DOM, and continued methodological development work for measuring DOM isotopic contents. Our year three plans are to finish the methods development, and use samples from two upcoming cruises to characterize the cycling of dissolved organic matter along the eastern U.S. seaboard. A brief summary of our year two activities follows.

1. DOC analysis.

We have developed a reference, high temperature sealed tube method for DOC analysis, and have joined several intercalibration exercises designed to show how to and how not to analyze DOC (dissolved organic carbon). With Ed Peltzer, we have analyzed an annual set of DOC samples from Woods Hole Harbor. The results agree very well (within 1%), and show no marked seasonal pattern (Fig. 1). A second intercalibration exercise involved samples collected from an offshore depth profile at Bermuda. Results from this intercalibration were recently published in Limnology and Oceanography; our results are generally similar to analysts who used persulfate and rapid-injection high temperature methods (Fig. 2). A third ongoing intercalibration involves samples collected

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from the Equatorial Pacific. There our values are slightly higher in deep waters but slightly lower in surface waters than those obtained from shipboard analyses by Ed Peltzer. We will be working with Peltzer this spring, analyzing common standards and blanks, to resolve reasons for these minor discrepancies.

The overall conclusion of this community-wide analytical effort seems to be that the older, low temperature wet chemistry techniques for analyzing DOC (including persulfate and uv digestions), were largely adequate. The new high temperature techniques are, however, more rapid and, in the hands of experienced investigators, more precise.

2. Georges Bank

We joined Dan Repeta and Tim Eglinton of WHOI in May 1993 for a short 5-day cruise to Georges Bank. The spring bloom was underway, but DOC analyses did not show any marked changes across the Bank, in spite of large changes in algal biomass (Fig. 3). Mesocosm experiments and previous survey work on Georges suggest that phytoplankton excrete DOC at the end of blooms; we had apparently arrived too early, in mid rather than late bloom, to observe an increase in DOC. We will revisit Georges Bank this April and later in July 1994 to check for higher DOC levels.

We also collected water from Georges Bank to check how fast DOM might decay. Overall, rates of decay were very slow, not detectable over 6 months in samples from deep 700m waters, and on the order of 5-15 μ M C loss over this same long interval for samples from more productive surface waters. Samples that had been enriched with porewater DOM from the Mud Patch region southwest of Georges Bank also showed slow, but detectable 15-20% declines in DOM concentration over six months.

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In the upcoming spring and summer cruises, we will be searching for more labile DOC that we expect at the end of phytoplankton blooms. If we can find this end-of-bloom water, we expect to see much larger 20-50 μM C changes in our decomposition experiment, as labile carbon built up in a bloom is rapidly degraded over a few days.

Overall, the results of these first field efforts show little evidence for rapid dynamics of DOC production and decay. We plan further long-term decomposition work to estimate decay rate constants for high-concentration surface water DOM that probably persists at the time scales of water export from continental shelves.

3. Isotope methods development work.

We have expended much of our effort developing routine, reliable methods for analyzing carbon and nitrogen isotopes in DOM. Our methods for $\delta^{13}\text{C}$ are well-advanced, although we still suffer contamination problems as we dry samples over several days prior to combustion. After using both freeze driers and ovens, we are now experimenting with blowing samples dry using highly filtered air to overcome these last low-level contamination problems. This procedure will be used for analysis of natural levels of ^{14}C in DOM as well, using large samples of 500-1000ml. We have carried several ^{14}C samples through our procedures, but are striving to eliminate the last traces of contamination before moving to routine ^{14}C analyses.

Efforts to analyze ^{15}N in DON have not yet been successful, in spite of many determined efforts. Because no one has ever reported DO^{15}N measurements for seawater, we have identified this as a top priority goal for our project. Fry is attempting to combust dried sea salts at high temperature to obtain N_2 gas for analysis; the major problem seems to be that salts are very effective

in taking up N_2 from air, resulting in a large blank. Altabet is mounting an independent effort based on low-temperature oxidation of DON to nitrate, followed by $\delta^{15}N$ analysis of nitrate by well-established conventional methods. Hopkinson is helping in our DON effort by leading a community-wide intercalibration exercise to show which high and low-temperature methods are best for DON analysis.

4. Year 3 Plans.

Our year three plans revolve around two cruises, one in April and one in late July 1994. The first cruise is from Georges Bank to Cape Hatteras, conducted as part of a shelf-wide survey led by Dan Repeta, and will examine DOC distributions during the spring bloom period across the mid-Atlantic Bight. The second cruise in late July is to Georges Bank, where we will follow recently upwelled water to see if DOC levels rise as nutrients are depleted and phytoplankton begin to senesce. We will spend the 1994-1995 fall-winter-spring period analyzing samples from these cruises, as well as completing work on methods for analyzing carbon and nitrogen isotopes in DOM.

Papers in progress:

1. Norrman, B., U.L. Zweifel, C.S. Hopkinson, and B. Fry. Turnover of ^{13}C -labeled carbon during an experimental diatom bloom.
2. Fry, B., L. Redmond, and E. Peltzer. Dissolved organic carbon in Woods Hole Harbor.
3. Peltzer, E., B. Fry, P. Doering and B. Norrman. Comparison of four different methods for DOC analysis.
4. Hopkinson, C.H. and others. Intercomparison of methods for analysis of dissolved organic nitrogen.
5. Chen, R., B. Fry, C.H. Hopkinson and others. Dissolved organic carbon dynamics on Georges Bank, May 1993.

Figure Legends.

Figure 1. DOC concentrations and $\delta^{13}C$ values over an annual cycle in Woods Hole Harbor.

Figure 2. Left: DOC concentrations at Bermuda analyzed with persulfate (o) and three high temperature techniques (Shimadzu data are closed squares).

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Right: DOC concentrations using sealed tube combustions; error are standard deviations.

Figure 3. DOC concentrations in surface waters of the Georges Bank area, with one deep water value from 700m also indicated. Data are from a May 1993 cruise.

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Figure 1

Fig. 2. Concentration of DOC in samples from five depth at the Bermuda BATS station measured by four methods. Samples were analyzed with HTC instruments (Shimadzu—■, Ionics—□, Dohrmann—●) and by the modified persulfate oxidation ampoule method (○).

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Figure 3

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