Technical Progress Report, Year 1

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Origins and Fates of DOM along the New England Continental Margin

Brian Fry and Charles Hopkinson

The Ecosystems Center

Marine Biological Laboratory

Woods Hole, MA 02543

Mark Altabet

Woods Hole Oceanographic Institution

Woods Hole, MA 02543

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In year one, we have focused on methods development and completed an initial survey of DOM concentration and isotopic composition during the 1994 spring bloom on Georges Bank. The methods development phase assures that high quality measurements will be made in years 2 and 3, and emphasizes developing two independent methods for DON determination. The survey work on Georges Bank will be extended in years 2 and 3 to determine seasonal and spatial changes in DOM concentrations and isotopic compositions along the eastern U.S. continental margin, from Georges Bank to Cape Hatteras.

DOM Methods Development

To meet our goal of using multiple tracers in studies of DOM cycling in ocean margin systems, we need to be able to measure concentrations and isotopic compositions of both

DOC and DON accurately, quickly and with relative ease. This requires some attention to methods development and to methodological advances made elsewhere, since DOM analysis is a difficult area. In this regard, we have been actively developing DOM methods since 1988, collaborating with Ionics Corporation of Boston and Dr. Ed Peltzer of the Woods Hole Oceanographic Institute (WHOI).

A. DOC Progress

Sealed Tube Analysis of DOC: We have made excellent progress in the development of a sealed tube technique for highly accurate and precise DOC measurements, as evidenced by the acceptance of our sealed tube technique as the standard to which HTCO DOC analyses are compared. Since the initiation of this project, we have made 2 important modifications to our published technique (Fry et al. 1992). We are now using a large volume pan evaporation step in place of our previous low volume tube lyophilization. This modification improves isotopic accuracy and speeds sample throughput. The second change has been to add a second sealed tube combustion step. This important modification removes SO_2 gas formed during the initial combustion resulting in increased accuracy in our quantification of total C.

Intercalibration: An outcome of the Seattle workshop on DOM was the realization that there was no accepted standard by which to compare the results of the new HTCO analyses and that there was a potential problem with blank corrections, or lack thereof. It was recommended at the workshop that a sealed tube technique be used as a reference technique for HTCO analyses. Since that workshop we have refined our sealed tube technique to the point that it is now an accepted standard. Over the past half year, we have been participating in four intercalibration exercises: 1) a comparison of HTCO, modified persulfate and sealed tube techniques in a variety of fresh and marine waters (with Ed Peltzer, U. Zweifel and Peter Doering), 2) an NSF-sponsored (Jon Sharp - leader) blank and seawater assessment and intercalibration between our sealed tube technique and Ed

Peltzer and Craig Carlson running HTCO instruments (working with Hugh Ducklow), 3) an intercalibration between two sealed tube techniques (ours and that of M. Alperin) using water samples collected from the May 1992 Bermuda intercalibration (another NSF-sponsored intercalibration led by Jon Sharp with participation from R. Benner, C. Carlson, L. Bennett, R. Dow, M. Alperin and S. Fitzwater), and 4) an intercalibration between Ed Peltzer's HTCO technique and our sealed tube technique on EQPAC samples collected during several cruises in 1992.

Very good agreement was reached between the various techniques compared in the first intercomparison. Of particular importance was the preparation, by Peltzer, and certification, with the sealed tube technique, of a "DOC-free" deionized water sample which could be used to establish an instrument blank in HTCO instruments. With proper accounting of instrument blanks there was generally fairly good agreement between the four methods. This observation supported a conclusion of the Seattle workshop concerning the potential importance of HTCO instrument blanks. Although the Shimadzu and persulfate techniques occasionally appeared to underestimate DOC concentration, Peltzer's HTCO results agreed within 5% of our sealed tube results (Table 1).

Our sealed tube technique was called upon as the reference standard in the initial NSF-sponsored intercalibration launched in order to establish a common protocol for the 1992 JGOFS EQPAC cruises (Intercalibration exercise 2, above). We established DOC concentrations in blank water, standards and seawater samples which were later used to intercalibrate Peltzer's and Carlson's HTCO instruments.

Samples are still being analyzed for our third and fourth intercalibration efforts.

HTCO: The large-scale synoptic surveys and intensive experimental procedures we intend to make in years 2 and 3 require an HTCO technique that is fast, accurate and precise. We will be making far more determinations than possible with the time-consuming and laborious sealed tube technique (< 15 samples per week). While we were initially quite happy with the results of our modified Ionics HTCO instrument, once we

were able to secure a "DOC-free" water sample, we have learned that the Ionics instrument suffers from a large instrument blank and poor precision (about 15%). This is not a problem unique to the Ionics. Initial unpublished results from the Bermuda intercomparison (which are not yet available to the public) demonstrate that all the commercially available HTCO instruments including Shimadzu, Ionics and Dohrman suffer from poor precision. In fact, analyses of the same water with the same instrument from morning to afternoon and day to day vary by up to 21%! Thus these instruments are incapable of resolving the difference between a $75\mu\text{M}$ sample and a $94\mu\text{M}$ sample. To solve this problem it will be necessary to fabricate our own HTCO instrument along the lines of Peltzer. Peltzer routinely has a sample precision better than 5% and up to 1%. This is the level of precision we will later need for mass balance accounts of C during seawater incubation experiments. Peltzer's instrument achieves this level of precision through a well planned 2-stage combustion oven, a solid state LiCor infrared gas analyzer that operates on a different principle from the Luft cell of old IRGAs and highly accurate and precise computer controlled chromatographic software for peak quantification.

B. DON Progress

We have been working on DON measurements since the summer of 1990, collaborating with Ionics Corporation until mid-1992. Initial work was supported by NSF. With the initiation of this DOE-funded project, we have begun investigating in earnest sealed tube combustions for DON isotopic as well as concentration measurements. We are making substantial progress in this field and have great confidence that we can bring the DON methods development to a timely conclusion.

Sealed Tube Analysis of DON: We are confident that we have eliminated large blank and combustion gas mixture problems that plagued our initial sealed tube analyses of DON. We were initially freeze-drying water and our combustions yielded a mixture of N_2 and NO in about an 80/20 mix. We are now using pan evaporation of larger water volumes

(similar to our DOC technique), combusting at a higher temperature ($>650^{\circ}\text{C}$) in quartz ampoules, and adding combustion reagents (CuO , Cu^{++}) to the neck of ampoules where they are not poisoned by direct contact with dried salts. Blanks are now under control as evidenced by low argon values and accurate $\delta^{15}\text{N}$ readings of the N_2 combustion gas.

HTCO: We have chosen to drop any further DON developmental work with Ionics Corporation. We found that we did not always obtain 100% nitrogen yields, even when carbon combustion efficiencies were high. We suspect various side reactions were responsible for the incomplete nitrogen yields. For example, N_2 or N_2O_4 could potentially be formed during combustion, and these gases would not be detected with NO_x detectors. Even more likely, we suspect that NO_2 reacted with the large amounts of water downstream of the hot combustion column, forming nitrite or nitrate, which was not detected. The major cause of these side reactions turned out to be an impurity in the so-called 100% Pt catalyst Ionics uses. The impurity is a key catalyst used to convert NO to NO_2 and vice versa, the equilibrium of which is strongly controlled by temperature. Compounds such as NH_4^+ have a high tendency to go towards NO_2 at certain temperatures, thus our relatively low recovery of NH_2 -compounds.

We plan to circumvent these problems in two ways: organizing a DON intercalibration exercise and coupling our NO detector with Ed Peltzer's HTCO DOC analyzer. We have distributed six DON samples to 14 laboratories in an intercalibration exercise aimed at identifying the most convenient yet accurate method for rapid DON concentration measurement (see letter, attached). Results have come back from a third of the laboratories at this time (mid-May 1993), and considerable differences are evident with the various methods employed. Hopkinson will be summarizing this intercalibration exercise at the 1993 June ASLO meeting in Edmonton, Canada.

For our own part we have made an agreement with Ed Peltzer of WHOI to couple an NO analyzer available to us with his HTCO C analyzer to evaluate its suitability for simultaneous measurements of C and N. This work is underway. This is a highly favorable

approach for 2 reasons: 1) Peltzer's HTCO is proving to be the most accurate and precise HTCO analyzer in the community and 2) we ultimately want to perform coupled DOC and DON measurements from the same injection.

DIN Removal and Sample Storage: Removal of DIN (dissolved inorganic nitrogen: nitrate plus nitrite and ammonium) and evaluation of DON sample storage are two concerns we will address in the next six months of our YEAR 1 methods development phase. For most samples in the ocean margin area, DON and nitrate are the dominant components of total dissolved nitrogen (Suzuki et al. 1985). Although our first goal is to find a good method for analyzing total dissolved nitrogen, determining nitrate separately and then DON as Total minus Nitrate, we are also interested in removing nitrate for subsequent direct determination of DON.

To remove nitrate, we have tried adding base and Devarda's alloy to samples, then heating to 80°C while sparging with helium. This treatment converts most nitrate (plus any ammonium and nitrite) to ammonia gas that can be removed by sparging; preliminary tests show that prolonged heating at 80°C does not break down simple organic nitrogen compounds such as glucosamine (C. Hopkinson, personal observation).

C. DO¹⁴C Progress

We have begun scaling up of DOC analyses to the large 1-4 liter sample sizes for ¹⁴C-age determination of DOC. We have prepared two sets of samples in Year 1 that are being analyzed at the National Ocean Sciences AMS Facility in Woods Hole. Our first result, an age of 3240 ± 200 yr BP ($\sim 300 \Delta^{14}\text{C}$) for a sample of Woods Hole surface water, is in reasonable agreement with age-estimates based on UV and HTC oxidation methods.

Field Studies

We joined DOE-funded chemists from Woods Hole Oceanographic Institution (Dan Repeta, Tim Eglington) in an April 1993 cruise to sample mud and water from the Georges

Bank area. We collected 50+ samples for DOM analyses at 10 stations, and will compare results to those obtained in a year-long study of monthly changes in DOC concentration and $\delta^{13}\text{C}$ in waters of Woods Hole Harbor. Initial Woods Hole harbor results show DOC concentrations are 100-150 $\mu\text{M C}$ year-round, with $\delta^{13}\text{C}$ values near $-22.5^\circ/\text{‰}$.

Fry, B., S. Saupe, M. Hullar and B. J. Peterson. 1993. Platinum-catalyzed combustion of DOC in sealed tubes for stable isotopic analysis. *Marine Chemistry* 41:187-193.

Suzuki, Y., Y. Sugimura and T. Itoh. 1985. A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. *Mar. Chem.* 16:83-97

TABLE 1. ESTIMATES OF DOC BY VARIOUS METHODS. ALL VALUES, IN $\mu\text{M C}$, ARE AVERAGES OF 2-10 DETERMINATIONS

STATION	METHOD			
	Sealed Tubes ¹	Suzuki clone ²	HTCO Shimadzu 5000 ³	Modified Persulfate ⁴
Deionized Water ("DOC-free")	0	0		0
North Atlantic Deepwater, 1000m Aged 2.5 yr	54	47		47
Aged Woods Hole Seawater	102	103	93	108
Fresh Woods Hole Seawater	110			112
Narragansett Bay		159		152
Bothnian Sea Water (4‰)	321	334	285	330
Paquatuck River, RI		462		427
Parker River Freshwater:				
Stn. P2	844	811	786	748
Stn. P3	865	814	789	762

NOTES: Individuals responsible for measurements - ¹B. Fry, ²E. Peltzer, ³U. L. Zweifel, ⁴P. Doering

MARINE BIOLOGICAL LABORATORY

WOODS HOLE · MASSACHUSETTS · 02543 · (508) 548-3705

THE ECOSYSTEMS CENTER

March 29, 1993

DON USERS:

Find enclosed 12 water samples for DON analysis. Included are 4 samples made up with distilled/deionized water and 2 made up with seawater. Some have been amended with either KNO_3 , $(\text{NH}_4)_2\text{SO}_4$, or nicotinic acid. The highest amendments are less than plus $50 \mu\text{M}$. Samples have not been preserved in any manner, i.e., no acid or poison added. Seawater samples were filtered through a GF/F filter. The samples were shipped frozen on Monday 29 March. Please note the time and condition of samples when they arrive in your lab.

The following individuals/labs/companies have agreed to run samples:

- Antek Instruments
- Jim Bauer
- Luis Cifuentes
- Dohrman Analyzers
- Steve Fitzwater
- Brian Fry
- Dennis Hansell
- Dave Karl
- Ron Jones
- Mitsubishi analyzers
- Ed Peltzer/Hopkinson
- Jon Sharp
- David Walgast
- Ted Walsh

This group has experience ranging from high temperature without catalyst, high temperature with catalyst, UV oxidation, persulfate oxidation, and sealed tube. Ted Walsh and Steve Fitzwater have agreed to run the inorganic N analyses on these samples.

Hopefully this will be a learning and beneficial experience for all analysts involved. To facilitate this process I ask that when the sample results are returned that everyone briefly describe the plumbing and operating conditions of their instrument. For instance, describe the carrier gas, carrier gas flow rates, plumbing configuration, type(s) of moisture removal, sites of moisture removal, other contaminant removal procedures, detector type, whether you are measuring NO or NO_x , method of peak integration, etc.

Instrument calibration and standardization procedures are another aspect about which we must compare notes. Everyone should indicate how they are standardizing their instrument and how instrument blanks are being dealt with. We would like to know your source of low or zero N water. One of the pair of samples (all unlabeled) that you are

being supplied with was obtained from the WHOI AMS facility. This water has proven to have a consistently low level of DOC in previous intercalibrations that Jon Sharp and/or Ed Peltzer have participated in. How this water will fare for TDN is not known. For this reason I am sure we are all interested in learning whether any of you have a better or more reliable source of N free water. Along these lines, I know that at least a few of you have been trying to compare total instrument recovery through comparisons with gaseous NO injections into the sample stream. Please share these results with us if used as part of this intercalibration.

Let's get the results returned to me by the end of April, sooner if possible! I will tabulate results, statistically analyze results and search for common weaknesses and strengths. By mid-May I would like to get a copy of all results and comparisons to everyone who has participated.

I think it would be wise to try to publish a short note describing the results. My only concern at this time is whether or not to specifically identify the results of each analyst. I query your opinion on this matter. My suggestion would be that we at least identify our results to each other, but if necessary (due to fear of failing) report only instrument configurations/types in the publishable note (I think most of us agree that more details on instrument types/blank procedures for the Seattle intercalibration would have been desirable). The most important objective of this exercise is for everyone to benefit. We all want to be able to measure TDN routinely and to get beyond the controversial stage. It is my hope that from this exercise we learn which configurations work and which don't. For the ones that don't, I hope that we will learn what aspect of the configuration causes the problem and how to remedy it.

Sincerely,

Charles S. Hopkinson, Jr.

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