Dissolved Organic Matter– Carlson's Group UCSB

A10 Cruise Report for DOM Biogeochemistry

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Cruise Participants:

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Support:
NSF

Project Goals.

The goal of the DOM project is to evaluate dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) concentrations over Along the A10 Atlantic line. During the A10 cruise, casts were specifically targeted in order to overlap with the TCO_2 sampling program.

Dissolved Organic Carbon and Total Dissolved Nitrogen (DOC/TDN)
DOC profiles were taken at approximately every other station (~1400 samples). Depending on the station depth, 12 – 36 Niskin bottles were sampled following directly behind the TCO_2 sample draw. DOC samples were passed through an inline filter holding a combusted GF/F filter attached directly to the Niskin for samples in the top 250 m of each cast. This was done to eliminated particles > than 0.7 μm from the sample. Samples from deeper depths were not filtered. Previous work has demonstrated that there is no resolvable difference between filtered and unfiltered sample in waters below the upper 200 m at the μmol kg^{-1} resolution. High density polyethylene 60 ml sample bottles were 10% HCl cleaned and Mili-Q water rinsed. Filters were combusted at 450°C overnight to remove organic carbon. Filter holders were 10% HCl cleaned and Mili-Q water rinsed between sampling. Samples were introduced into the sample bottles via pre-cleaned silicone tubing. Bottles were rinsed with sample 3 times before filling. A volume of 40-50 ml of was collected for each sample. Samples were kept frozen at -20C in the ship's freezer. Frozen samples will be shipped back by express shipping to UC Santa Barbara for analysis. All samples will be analyzed via the high temperature combustion technique on a Shimadzu TOC-V analyzer. TDN samples were analyzed for the surface 200 m from the same DOC sample bottle.

Standard Operating Procedure for DOC analyses- Carlson Lab UCSB

DOC samples are analyzed via high temperature combustion using a Shimadzu TOC-V in shore based laboratory at the University of California, Santa Barbara. The operating conditions of the Shimadzu TOC-V have been slightly modified from the manufacturer's model system. The condensation coil has been removed and the headspace of an internal

water trap was reduced to minimize the system's dead space. The combustion tube contains 0.5 cm Pt pillows placed on top of Pt alumina beads to improve peak shape and to reduce alteration of combustion matrix throughout the run. CO_2 free carrier gas is produced with a Whatman® gas generator (Carlson et al. 2004). Sample are drawn into 5 ml injection syringe and acidified with 2M HCL (1.5%) and sparged for 1.5 minutes with CO_2 free gas. Three to five replicate 100 µl of sample are injected into combustion tube heated to 680° C. The resulting gas stream is passed though several water and halide traps, including an added magnesium perchlorate trap. The CO_2 in the carrier gas is analyzed with a non-dispersive infrared detector and the resulting peak area is integrated with Shimadzu chromatographic software. Injections continued until the at least three injection meet the specified range of a SD of 0.1 area counts, CV ≤2% or best 3 of 5 injections.

Extensive conditioning of the combustion tube with repeated injections of low carbon water (LCW) and deep seawater is essential to minimize the machine blanks. After conditioning, the system blank is assessed with UV oxidized low carbon water. The system response is standardized daily with a four-point calibration curve of potassium hydrogen phthalate solution in LCW. All samples are systematically referenced against low carbon water and deep Sargasso Sea reference waters (2600 m) and surface Sargasso Sea water every 6 – 8 analyses (Hansell and Carlson 1998). The standard deviation of the deep and surface references analyzed throughout a run generally have a coefficient of variation ranging between 1-3% over the 3-7 independent analyses (number of references depends on size of the run).
Daily reference waters were calibrated with DOC CRM provided by D. Hansell (University of Miami; Hansell 2005).

DOC calculation

µMC = (average sample area – average machine blank area) / (slope of std curve)

Carlson, C.A., S.J. Giovannoni, D.A. Hansell, S.J. Goldberg, R. Parsons, and K. Vergin. 2004. Interactions between DOC, microbial processes, and community structure in the mesopelagic zone of the northwestern Sargasso Sea. *Limnology and Oceanography* 49: 1073-1083.

Hansell, D.A. and C.A. Carlson 1998. Deep ocean gradients in the concentration of dissolved organic carbon. *Nature,* 395: 263-266.

Hansell, D.A. 2005 Dissolved Organic Carbon Reference Material Program. EOS, 35:318-319.

Standard Operating Procedure for TN analyses- Carlson Lab UCSB

TN samples were analyzed via high temperature combustion using a Shimadzu TOC-V with attached Shimadzu TNM1 unit at an in-shore based laboratory at the University of California, Santa Barbara. The operating conditions of the Shimadzu TOC-V were slightly modified from the manufacturer's model system. The condensation coil was

removed and the headspace of an internal water trap was reduced to minimize the system's dead space. The combustion tube contained 0.5 cm Pt pillows placed on top of Pt alumina beads to improve peak shape and to reduce alteration of combustion matrix throughout the run. Carrier gas was produced with a Whatman® gas generator (Carlson et al. 2004) and ozone was generated by the TNM1 unit at 0.5L/min flow rate. Three to five replicate 100 µl of sample were injected at 130mL/min flow rate into the combustion tube heated to 680° C, where the TN in the sample was converted to nitric oxide (NO). The resulting gas stream was passed through an electronic dehumidifier. The dried NO gas then reacted with ozone producing an excited chemiluminescence NO_2 species (Walsh 1989) and the fluorescence signal was detected with a Shimadzu TNMI chemiluminescence detector. The resulting peak area was integrated with Shimadzu chromatographic software. Injections continued until at least three injections meet the specified range of a SD of 0.1 area counts, CV ≤2% or best 3 of 5 injections.

Extensive conditioning of the combustion tube with repeated injections of low nitrogen water and deep seawater was essential to minimize the machine blanks. After conditioning, the system blank was assessed with UV oxidized low nitrogen water. The system response was standardized daily with a four-point calibration curve of potassium nitrate solution in blank water. All samples were systematically referenced against low nitrogen water and deep Sargasso Sea reference waters (2600 m) and surface Sargasso Sea water every 6 – 8 analyses (Hansell and Carlson 1998). Daily reference waters were calibrated with deep CRM provided by D. Hansell (University of Miami; Hansell 2005).

TN calculation

µMN = (average sample area – average machine blank area) / (slope of std curve)

Carlson, C.A., S.J. Giovannoni, D.A. Hansell, S.J. Goldberg, R. Parsons, and K. Vergin. 2004. Interactions between DOC, microbial processes, and community structure in the mesopelagic zone of the northwestern Sargasso Sea. *Limnology and Oceanography* 49: 1073-1083.

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Hansell, D.A. 2005 Dissolved Organic Carbon Reference Material Program. EOS, 35:318-319.

Walsh, T.W., 1989. Total dissolved nitrogen in seawater: a new high-temperature combustion method and a comparison with photo-oxidation. Mar. Chem., 26:295-311.