

## **Dissolved Organic Carbon and Total Dissolved Nitrogen— Carlson's Group UCSB**

### **P06 Leg 1 and 2 Cruise Report for DOM Biogeochemistry**

**PI:** Craig Carlson, University of California, Santa Barbara

**Cruise Technician:** Chance English

**Analysts:** Elisa Halewood, Keri Opalk

**Support:**

NSF

### **Project Goals.**

The goal of the DOM project is to evaluate dissolved organic carbon (DOC) (full water column) and total dissolved nitrogen (TDN) (surface 250 m) concentrations along the P06 zonal transect. The cruise was split into two legs. P06 Leg 1 (Sydney to Tahiti along ~30- 32.5°S; July 3 – Aug 17, 2017) and Leg 2 (Tahiti – Valparaiso along 32.5° S Aug 20 – Sept 20, 2017). Casts were specifically targeted in order to overlap with the TCO<sub>2</sub> sampling program.

### **Dissolved Organic Carbon and Total Dissolved Nitrogen (DOC/TDN )**

DOC profiles were taken at approximately every other station from 26 of 36 Niskin bottles ranging the full depth of the water column (125 stations; ~3200 DOC and 1375 TDN samples. DOC and TDN samples were passed through an inline filter holding a combusted GF/F filter attached directly to the Niskin for samples in the top 500 m of each cast. This was done to eliminate 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 500 m at the μmol kg<sup>-1</sup> resolution. All samples were rinsed 3 times with about 5 mL of seawater, collected into combusted 40 mL glass EPA, 50 μL of 4N Hydrochloric acid were added to preserve samples vials and stored at 4°C on board. Samples were shipped back to UCSB for analysis via high temperature combustion on Shimadzu TOC-V or TOC L analyzers.

Sample Vials were prepared for this cruise by soaking in 10% Hydrochloric acid, followed by a 3 times rinse with DI water. The vials were then combusted at 450C for 4 hours to remove any organic matter. Vial caps were cleaned by soaking in DI water overnight, followed by a 3 times rinse with DI water and left out to dry.

Sampling goals for this cruise were to continue high resolution, long term monitoring of DOC distribution throughout the water column, in order to help better understand biogeochemical cycling in global oceans.

### **Standard Operating Procedure for DOC analyses- Carlson Lab UCSB**

DOC samples will be analyzed via high temperature combustion using a Shimadzu TOC-V or Shimadzu TOC-L 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<sub>2</sub> free carrier gas is produced with a Whatman® gas generator (Carlson et al. 2010). Sample are drawn into 5 ml injection syringe and acidified with 2M HCL (1.5%) and sparged for 1.5 minutes with CO<sub>2</sub> 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 through several water and halide traps, including an added magnesium perchlorate trap. The CO<sub>2</sub> 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 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 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 (2600 m) or Santa Barbara Channel (400 m) reference waters and surface Sargasso Sea or Santa Barbara Channel 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

$$\mu\text{MC} = (\text{average sample area} - \text{average machine blank area}) / (\text{slope of std curve})$$

Carlson, C. A., D. A. Hansell, N. B. Nelson, D. A. Siegel, W. M. Smethie, S. Khatiwala, M. M. Meyers and E. Halewood 2010. Dissolved organic carbon export and subsequent remineralization in the mesopelagic and bathypelagic realms of the North Atlantic basin. *Deep Sea Research II*, **57**: 1433-1445.

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 TDN analyses- Carlson Lab UCSB**

TDN 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. 2010) 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<sub>2</sub> 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).

Dissolved organic nitrogen (DON) concentrations are calculated as the difference between TDN and DIN. Samples with less than 10 µmol/kg DIN are most reliable estimates of DON.

**TDN calculation**

$$\mu\text{MN} = (\text{average sample area} - \text{average machine blank area}) / (\text{slope of std curve})$$

Carlson, C.A., S.J. Giovannoni, D.A. Hansell, S.J. Goldberg, R. Parsons, and K. Vergin. 2004. Interactions Carlson, C.A., D.A. Hansell, N.B. Nelson, D.A. Siegel, W.M. Smethie, S. Khatiwala, M.M. Meyers, and E. Halewood. "Dissolved Organic Carbon Export and Subsequent Remineralization in the Mesopelagic and Bathypelagic Realms of the North Atlantic Basin." *Deep Sea Research II* 57 (2010): 1433-45.

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.

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.