Dissolved organic matter in the Cariaco Basin, Venezuela

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Abstract

Measurements of **dissolved organic carbon (DOC)** and **dissolved organic nitrogen (DON)** were made at the CARIACO time-series station (10°30' N, 64°40' W) as part of the **CARIACO time-series program**. There was a marked **seasonal variability in DOC concentrations, with lower values (~70 µMC) during the upwelling season (December-May)**, due to the injection of cold, DOC-depleted Subtropical Underwater (SUW) near the coast. **During the rainy season** (June-November) waters were stratified and **DOC accumulated in the upper 100m of the water column, increasing to ~85 µMC**. DOC concentrations decreased with depth, from a yearly average of ~77 µMC at the surface to ~56 µMC at 1310m. DON concentrations also decrease with depth, from a yearly average of 5.8 at surface to 4.3 below 350 m. **Consistent DON increase and decrease were observed near the oxic/anoxic interface, attributed to bacterial production and consumption, respectively**. DON concentrations remained relatively unchanged with season. DOC:DON ratios did not vary significantly below 350m (~13.2 mol C mol N^{-1}), supporting the idea that not all deep DOC is refractory. Deep (>350m) DOC in the Cariaco Basin is estimated to be 80% refractory, with 20% of semilabile material not utilized because of the lack of oxygen. Horizontal DOC advection is thought to be the principal mode of **carbon export out of the basin**, with an **estimated 20.18 GMCy^{-1}** transported out of the basin and into the Caribbean Sea. This export is comparable to the flux of POC to depth measured at the CARIACO time-series station. This is the first information available on DOM in the Cariaco Basin, an important upwelling site in the Caribbean Sea.

Background and Methods

Adequate quantification and cycling of the marine DOM pools is essential to understand how the oceans will respond to the increasing concentrations of carbon dioxide and climate change. (Hopkinson and Valino, 2005). Ocean margins are important sites of primary production and enhanced nutrient and organic matter fluxes, contributing to an estimated 40% of the carbon sequestration in the ocean (Muller-Karger et al., 2005).

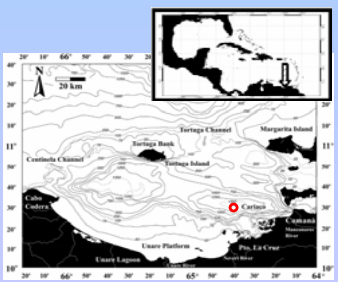

Figure 1: The Cariaco Basin, bathymetry and location of the CARIACO time-series station

However, DOM in continental margins is not well constrained. Here we present the first data on DOM in the Cariaco Basin, Venezuela (Figure 1).

- The Cariaco Basin is a 1400m deep depression on the continental margin off Venezuela with water circulation restricted to the upper 130-150m.
- It experiences strong upwelling during the first half of the year (December-May). It is permanently anoxic below ~250m.
- During the second half of the year (June-November, rainy season) the upper waters are stratified.
- The CARIACO (Carbon Retention In A Colored Ocean) time-series project (Muller-Karger et al., 2007) provides high resolution chemical, physical, biological and geological data on a regular basis at the CARIACO station (10°30'N; 64°40'W).
- DOC/TOC, DON and DIC were obtained as part of the CARIACO time-series project between March 2005-2007 (see Table I and II for depths).
- DOC concentrations (Table I) determined using a Shimadzu TOC-5000 HTC instrument (Hansell and Carlson, 2001).
- DON was sampled at 19 depths (Table II) and estimated by difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN) (Gordon et al., 1993).

Table I: Summary of DOC concentrations and DOC:DON ratios measured in the Cariaco Basin between 2005 – 2007. All concentrations are in µM.

Depth	Mean DOC	SD	Mean DOC:DON	DOC ♦	SD	DOC ▼	SD
1	77.16	5.46	13.31	71.92	6.44	84.13	8.40
35	69.77	6.26	12.04	66.16	6.73	73.97	9.27
75	64.93	6.08	12.37	61.31	3.27	68.78	3.54
130	63.23	6.28	13.37	59.91	4.69	66.26	7.66
200	61.26	10.13	14.26	58.12	3.10	65.98	13.22
269	59.87	7.01	13.26	56.95	9.00	57.72	9.30
350	58.79	9.18	12.97	54.85	3.72	65.98	1.22
1310	57.71	4.49	13.32	58.92	4.03	56.44	2.82

♦ Upwelling period, defined as the period between December-May
▼ Rainy period, defined as the period between June-November
SD = standard deviation

Table II: Summary of DON (µM) concentrations measured in the Cariaco Basin between 2005 – 2007.

Depth	DON	SD
1	5.80	0.73
7	6.13	1.17
16	6.03	1.00
25	5.94	1.03
35	5.79	1.41
65	5.26	1.08
75	5.26	0.69
100	4.89	1.17
130	4.73	1.11
160	4.33	0.76
200	4.29	1.02
250	4.78	1.08
280	4.62	1.17
300	4.76	1.38
350	4.45	1.45
400	4.38	1.40
600	4.37	0.65
760	4.34	1.06
1310	4.27	1.11

SD = standard deviation

Seasonal Variability

DOC experienced marked seasonal changes - upper water (1-130m) **DOC concentrations were low during the upwelling season (71.92 µMC ±6.44, N = 12), increasing during the rainy season by over 10 µMC (84.13 µMC, ±8.40, N = 10;** Table I, Figure 2). **Deep concentrations remained relatively unchanged** throughout the study period at **~57 µMC**. The variation in DOC concentrations was controlled by physical, biological and chemical variables, mainly upwelling, stratification and NO_3 depletion in the upper water column. **DON did not show seasonal variations. C:N ratios did not change significantly with depth** (average of 13.12 (±0.67, N = 19)).

Carbon partitioning and export

During the upwelling season winds intensify and SUW is injected into surface waters. Subtropical Underwater (SUW) has an average DOC concentration of ~57 µMC (CLIVAR-Repeat Hydrography). **The mixing of SUW and Cariaco Waters, and subsequent outflow into the open Caribbean Sea** (seen in Figure 3 as the plume of cold sea surface temperature) **results in a net export of organic carbon estimated to be around 20.18 Giga-moles of carbon per year (GMC yr^{-1})**, comparable to the vertical POC flux measured in the Basin (16 GMC yr^{-1}, Muller-Karger et al., 2007). DOC and DON showed the classical decrease in concentration with increasing depth (Figure 2). **DOM values measured in the Cariaco Basin agree well with those measured at similar locations.**

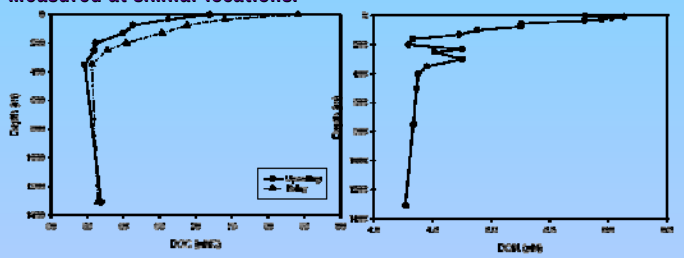

Figure 2: Vertical profiles of DOC and DON. Standard deviations are indicated in Tables I and II

Deep (>350m) DOC concentrations were higher than average deep open ocean values by ~10 µMC (~46 µMC, Hansell and Carlson, 1998). The higher DOC in CARIACO is thought to be the result of accumulation due to the lack of circulation (Virmani and Weisberg, 2007), active particle degradation (Thunell et al., 2000) and low efficiency of bacterial consumption (Taylor, pers. Comm). Assuming classical concentrations of deep refractory DOC, **the semilabile DOC below 350m in CARIACO is estimated to be ~20% of the total deep DOC**. The existence of a semilabile pool of DOC in the deep basin is further supported by low DOC:DON ratios below 350m (Hopkinson and Valino, 2005). The increase and decrease in the DON profile between 200-300m (Figure 2) were attributed to **bacterial generation and consumption of DON in the oxic-anoxic interfase**.

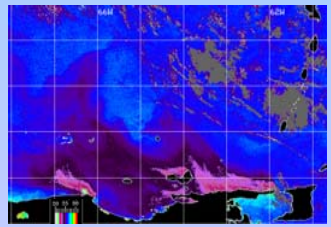

Figure 3: Satellite sea surface temperature (SST) during the upwelling season in Eastern Venezuela.

Summary and future research

We presented the first data on dissolved organic matter (DOM) in the Cariaco Basin, providing an important contribution to the growing worldwide DOM data pool. **DOM profiles showed the classical decrease in concentration with increasing depth**. However, DOC accumulates in the deep (>350m) basin by a combination of physical, biological and chemical factors. At these depths, **approximately 80% of the DOC present is refractory**. The seasonal accumulation of DOC in the upper water column gives rise to an **estimated carbon export of ~20.18 GMC per year**. However, DOC flux to the Caribbean Sea is complex and more observations on DOC distribution around the Basin are necessary to make a more accurate assessment.

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