

This discussion paper is/has been under review for the journal Biogeosciences (BG).
Please refer to the corresponding final paper in BG if available.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin, Venezuela

**E. Montes¹, M. A. Altabet², F. E. Muller-Karger¹, M. I. Scranton³, R. C. Thunell⁴,
C. Benitez-Nelson⁴, L. Lorenzoni¹, and Y. M. Astor⁵**

¹College of Marine Science, University of South Florida, St. Petersburg, Florida, USA

²School of Marine Science and Technology, University of Massachusetts Dartmouth, New Bedford, Massachusetts, USA

³School of Marine and Atmospheric Science, Stony Brook University, Stony Brook, New York, USA

⁴Marine Science Program & Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA

⁵Estación de Investigaciones Marinas de Margarita, Fundación La Salle de Ciencias Naturales, Apartado 144, Porlamar, Estado Nueva Esparta, Venezuela

Received: 16 July 2012 – Accepted: 19 July 2012 – Published: 8 August 2012

Correspondence to: E. Montes (emontesh@mail.usf.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

Abstract

Excess nitrogen gas (excess N_2) was measured in samples collected at six locations in the eastern and western sub-basins of the Cariaco Basin, Venezuela, in September 2008 (non-upwelling conditions) and March 2009 (upwelling conditions). During both sampling periods, excess N_2 concentrations were below detection in surface waters, increasing to $\sim 22 \mu\text{mol N kg}^{-1}$ at the oxic-anoxic interface ($[O_2] < \sim 4 \mu\text{mol kg}^{-1}$, ~ 250 m). Below the oxic-anoxic interface (300–400 m), the average concentration of excess N_2 was $24.7 \pm 1.9 \mu\text{mol N kg}^{-1}$ in September 2008 and $27.5 \pm 2.0 \mu\text{mol N kg}^{-1}$ in March 2009, i.e., excess N_2 concentrations within this depth interval were $\sim 3 \mu\text{mol N kg}^{-1}$ higher ($p < 0.001$) during the upwelling season compared to the non-upwelling period. These results suggest that N-loss in the Cariaco Basin may vary seasonally in response to changes in the flux of sinking particulate organic matter. We attribute the increase in excess N_2 concentrations, or N-loss, observed during upwelling to: (1) higher availability of fixed nitrogen derived from suspended and sinking particles at the oxic-anoxic interface and/or (2) enhanced ventilation at the oxic-anoxic interface during upwelling.

1 Introduction

Dissolved inorganic nitrogen (DIN or “fixed” nitrogen), includes nitrate, nitrite, and ammonium. This nutrient often limits primary production in marine systems (Codispoti, 1989; Smith, 1984) and thus plays a role in the modulation of climate (Altabet et al., 2002; Falkowski, 1997; Ganeshram et al., 2000; Gruber, 2004). In the ocean, new DIN is primarily derived from nitrogen fixation ($N_2 \rightarrow NH_4^+$) by microbial diazotrophs. The microbial processes that result in the conversion of DIN back to dinitrogen gas (N-loss) are the primary oceanic sinks for fixed nitrogen (Chang et al., 2010; Codispoti, 2007; Devol et al., 2006). These include water column and sedimentary denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$), and anammox (anaerobic ammonium oxidation;

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$\text{NO}_2^- + \text{NH}_4^+ \rightarrow \text{N}_2$). Large-scale water column N-loss in the global ocean occurs mainly in the three major oceanic oxygen minimum zones (Eastern Tropical North Pacific, Eastern Tropical South Pacific, and the Arabian Sea; Codispoti et al., 2001; Gruber and Sarmiento, 1997).

Recent studies suggest that today's rate of ocean N-loss exceeds the rate of nitrogen fixation by over 200 Tg yr^{-1} (Brandes and Devol, 2002; Codispoti, 2007). Whether this imbalance in the nitrogen inventory is due to an underestimation of nitrogen fixation or an overestimation of N-loss, is a topic of current debate (Capone and Knapp, 2007; Codispoti, 2007; Deutsch et al., 2007). This estimate assumes that nitrate is the sole source for biogenic N_2 and that its removal is equivalent to nitrate deficits based on deviation from the Redfield N : P ratio (N' ; Gruber and Sarmiento, 1997). Rates can also be estimated from the accumulation of nitrate deficit as a function of the residence time of oxygen-depleted water masses (Gruber, 2004; Gruber and Sarmiento, 1997, 2002). Although nitrate is the most abundant form of fixed nitrogen in the ocean, the use of other DIN species (and potentially organic nitrogen) by microbes other than denitrifiers could account for the gap between previous and recent denitrification rates estimates (Codispoti et al., 2001; Dalsgaard et al., 2003; Kuypers et al., 2003; Thamdrup et al., 2006). A prime example is the anammox reaction, which combines NO_2^- and NH_4^+ to form N_2 .

The removal of fixed nitrogen can also be estimated by measuring excess N_2 (with respect atmospheric equilibrium) as has been done by Devol et al. (2006) and Chang et al. (2010) in the Arabian Sea and the Eastern Tropical South Pacific. An objective of these studies was to overcome uncertainties associated with regional variations in N : P ratios and the complexities of DIN conversion pathways. Excess N_2 was also measured in anoxic waters of the Black Sea by Fuchsman et al. (2008), who attributed interannual variations in excess N_2 to changes in the downward flux of organic matter from phytoplankton blooms. Löffler et al. (2011) also measured excess N_2 in the Baltic Sea with the aim of determining water column N-loss rates in this region. Despite these

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

efforts many questions remain regarding the role of organic matter as a source of nitrogen for fueling water column N-loss.

The Cariaco Basin offers an opportunity to examine the linkage between surface productivity and the loss of fixed nitrogen at depth. This basin exhibits water column N-loss, and seasonal phytoplankton production and high vertical flux of particulate organic matter ($\sim 700\text{--}2300$ and $\sim 40\text{--}100\text{ mg C m}^{-2}\text{ d}^{-1}$, respectively; Muller-Karger et al., 2001; Scranton et al., 2006; Thunell et al., 2007; Zhang and Millero, 1993). One of the first measurements of marine “excess N_2 ” was conducted in the anoxic waters of the Cariaco Basin by Richards and Benson (1961) using N_2/Ar radiometry. In this manuscript we build on Richards and Benson’s work, and report new estimates of N_2 gas production at several locations within the Cariaco Basin during the upwelling and non-upwelling seasons. We tested the hypothesis that the biogenic production of N_2 varies both spatially and temporally within the anoxic waters of the basin in response to changes in the flux of organic matter. We also compared DIN deficits in the water column with excess N_2 measurements to understand whether the removal of fixed nitrogen by denitrification was balanced by the biogenic production of N_2 . We assumed that heterotrophic (canonical water column denitrification) and chemoautotrophic (anammox) consumption of DIN were the only sources of biogenic N_2 (Chang et al., 2010; Devol et al., 2006).

2 Study area

The Cariaco Basin is a 1400 m deep, tectonically-derived depression on the continental shelf of Venezuela (Schubert, 1982; Fig. 1). Its sill (~ 100 m) has two deeper channels, La Tortuga (135 m) and Centinela (145 m; Lidz et al., 1969; Richards, 1975). The exchange of water between the Cariaco Basin and the Caribbean Sea/Atlantic Ocean is limited. Cariaco waters > 150 m deep are poorly ventilated; waters at the oxic-anoxic interface (~ 250 m) have residence times of months to years, while bottom waters have residence times of years to decades (Holmén and Rooth, 1990; Zhang and Millero,

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1993). The basin is subject to seasonal changes in the wind intensity along the coast related to the meridional migration of the intertropical convergence zone (ITCZ), which drives alternating upwelling (January–May) and thermally stratified conditions (August–November) (Astor et al., 2003).

5 During upwelling, primary production (PP) and particulate organic matter (POM) vertical fluxes are high; the 14-yr PP and sediment trap particulate organic carbon (POC) flux (225 m) averages are 1871 ± 394 and $80 \pm 20 \text{ mg C m}^{-2} \text{ d}^{-1}$, respectively (Muller-Karger et al., 2001, 2010). During the non-upwelling period primary production averages $874 \pm 136 \text{ mg C m}^{-2} \text{ d}^{-1}$ and settling POC flux $60 \pm 20 \text{ mg C m}^{-2} \text{ d}^{-1}$.

10 The decomposition of the sinking POC contributes to present-day anoxic and sulfidic conditions below ~ 250 m (Scranton et al., 2001; Zhang and Millero, 1993).

3 Methods

3.1 Sample collection

15 Samples were collected from the R/V *Hermano Ginés* during two cruises to Cariaco Basin (1–6 September 2008 and 9–13 March 2009). A total of 36 stations were occupied for general oceanographic observations during each cruise, while dissolved N_2 samples were collected at six stations: three in the eastern sub-basin (stations 10, 11 and 13) and three in the western sub-basin (stations 21, 29 and 32) (Table 1, Fig. 1). These six stations all have water depths exceeding 300 m and included the oxic-anoxic interface. Hydrographic data were obtained using a Seabird™ SBE-25 Conductivity-Temperature-Depth (CTD) device equipped with an Eco chlorophyll fluorometer (Wet-

20 labs), an SBE43 dissolved oxygen sensor, and a rosette with 12 Teflon-coated 8 l Niskin bottles.

25 Stations 10 and 21 featured the deepest (> 1300 m) profiles of anoxic waters. Station 10 is the location of the CARIACO Ocean Time-Series Station (10.5° N , 64.6° W) sampled monthly since November 1995. Combined with stations 11 and 13, these three

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco BasinE. Montes et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

5 sites were chosen to help assess spatial changes in the Eastern Cariaco Basin. Station 29 was sampled to look for possible riverine influences on local hydrographic conditions, as it was closer to the mouth of the Tuy River, the largest river discharging into the Cariaco Basin. Finally, station 32 was selected to evaluate the effect of the influx of Caribbean waters through Centinela Channel (Fig. 1).

Chlorophyll *a* and nutrient samples were collected at the 36 stations during each cruise, from the surface to 100 m (1, 20, 30, 50, 100 m); below this depth chlorophyll concentrations are typically below the detection limit of $0.01 \mu\text{g l}^{-1}$. Chlorophyll *a* determinations were carried out using methanol extractions (see Muller-Karger et al., 2001) a Turner Designs model 10 fluorometer as described by Falkowski and Kiefer (1985) and Holm-Hansen et al. (1965).

DIN and soluble reactive phosphorus (SRP) samples were collected at 1, 20, 50 and 100 m at stations 10, 11, 13 and 29, and at the surface at stations 21 and 32. Nutrient determinations were conducted at the University of South Florida following the protocols of Gordon et al. (2000) and Strickland and Parsons (1972).

Water for the dissolved N_2 analyses was collected using Niskin bottles at 1, 50, 100, 200, 275, 300, and 400 m at the six stations selected for this study. At stations 10 and 21, additional samples were collected at 500, 750, and 1300 m. Samples were collected using 60 ml biological oxygen demand (BOD) bottles using the filling procedure for Winkler O_2 determinations. A $100 \mu\text{l}$ aliquot of saturated HgCl_2 were added to each sample for preservation. Bottles were sealed with glass stoppers; standing seawater was left around the exterior of the glass stopper at the mouth of the bottle to inhibit gas exchange with the atmosphere. The mouth of the BOD bottle, including the stopper and standing water were sealed with a plastic cap to avoid spilling of the standing seawater, and samples were kept in a cooler or refrigerator at $\sim 4^\circ\text{C}$ until analyzed.

3.2 Gas analyses

High-precision estimates of nitrogen gas were conducted at the School of Marine Science and Technology, University of Massachusetts Dartmouth using isotope ratio mass

spectrometry (IRMS). Dissolved gasses were extracted from each sample by pumping an aliquot at 10 ml min^{-1} through a chambered microfiber-microporous gas extractor coupled to a continuous flow of He carrier gas. The extracted gas was then passed through water, CO_2 , and O_2 traps before transferring to a GV IsoPrime IRMS for simultaneous measurements of N_2 (mass 28) and Ar (mass 40). Gas ratios from samples were compared against calibrated references of artificial compressed gas mixtures of N_2 and Ar covering the expected dissolved gas ratios. Further calibration also included comparing gas measurements in distilled water equilibrated with air at controlled temperatures of 10 and 20°C ($\pm 0.01^\circ\text{C}$) to theoretical determinations based on the solubility of these gases. The analytical precision of N_2/Ar measurements was better than 0.3‰, and thus the limit of detection of N_2 was $\sim 0.3 \mu\text{M}$. Finally, excess N_2 was derived from deviations of the sample N_2/Ar ratio from equilibrium values expected from in situ measurements of potential temperature and salinity (Hamme and Emerson, 2004).

4 Results

4.1 Hydrographic data

Average profiles of dissolved oxygen (O_2) concentration and density (σ_θ) were calculated at the six stations sampled for gas analyses during September 2008 and March 2009 (Fig. 2). For both seasons, oxygen concentrations decreased from $\sim 185 \pm 12 \mu\text{mol kg}^{-1}$ at the surface to below detection at 300 m. There was higher $[\text{O}_2]$ at the $\sim 25\text{--}26$ isopycnal surface ($\sim 0\text{--}120$ m) in March 2009 likely as a result of increased vertical mixing and ventilation; the $[\text{O}_2]$ at 25 isopycnal was $\sim 35 \mu\text{mol kg}^{-1}$ higher in March 2009 than in September 2008.

A plot of salinity (S) versus potential temperature (θ) for the six stations selected for excess N_2 measurements during the two cruises indicates that water masses below ~ 150 m in the Cariaco Basin during the two sampling periods were similar (Fig. 3). During September 2008, stations in the western sub-basin (stations 21, 29 and 32)

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

showed lower salinities near the surface than those in the eastern sub-basin (stations 10, 11 and 13). This surface water is derived from the western tropical North Atlantic and the Caribbean Sea. The salinity maximum, which is associated with subtropical underwater (SUW), shows a slight warming during the upwelling season, when this water mass is close to the surface and therefore exposed to sunlight.

4.2 Nutrients and chlorophyll *a*

Nutrient concentrations at the surface were nearly undetectable during both seasons due to biological uptake. They were slightly higher in the upper 50 m at the six stations sampled for gas determinations (Fig. 4) in March 2009 as a result of upwelling compared to September 2008. Nitrite and SRP concentrations in the top 100 m were below 1 μM in both seasons. A peak in $[\text{NO}_3^-]$ of 10–12 μM was observed around 200 m, and $[\text{NO}_3^-]$ declined to $< 0.5 \mu\text{M}$ at 300 m. $[\text{NH}_4^+]$ was low but variable near the surface ($< 0.5 \mu\text{M}$), with slightly higher concentrations in the upper 50 m during March 2009 compared to September 2008. Ammonium concentrations showed a minimum at 200 m in both seasons. From 250 m to the bottom, $[\text{NH}_4^+]$ increased at a rate of $\sim 0.04 \mu\text{M m}^{-1}$ reaching values as high as $\sim 23 \mu\text{M}$ at 1300 m (stations 10 and 21; data not shown).

A deep chlorophyll maximum (DCM) was observed at 50–65 m in September 2008 ($0.48 \pm 0.12 \mu\text{g l}^{-1}$; Table 1), and at 20–50 m in March 2009 ($1.04 \pm 0.60 \mu\text{g l}^{-1}$). This shoaling of the DCM is characteristic of the upwelling season (Astor et al., 2003). Chlorophyll *a* concentrations at the DCM in the eastern sub-basin were in the order of $0.60 \mu\text{g l}^{-1}$, while in the western sub-basin concentrations ranged 1.15–2.10 $\mu\text{g l}^{-1}$.

4.3 N_2/Ar ratios

The N_2 gas concentration measured in Cariaco samples was normalized to the concentration of the noble gas argon (i.e., N_2/Ar ratios). This largely eliminates artifacts related to changes in gas concentration caused by physical effects due to variations in temperature and salinity on the dissolution of N_2 . N_2/Ar ratios were, in turn, normalized

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to ratios at atmospheric equilibrium ($N_2 : Ar_{\text{sample}} / N_2 : Ar_{\text{atm.equilibrium}}$) to detect departures of N_2 concentrations from expected equilibrium values due to biogenic N_2 production. Excess N_2 can also arise physically from air injection in the water mass formation region (Craig and Weiss, 1971). Negative anomalies in N_2 can be produced by in situ heating. Vertical distributions of N_2/Ar ratios at each station during both cruises are shown in Fig. 5a. For both sampling periods, normalized N_2/Ar ratios in the upper 100 m were close to equilibrium (~ 0.995 – 1.005) at all stations, but reached maxima of between ~ 1.015 and ~ 1.033 near the oxic-anoxic interface (250–300 m). Below this depth, N_2/Ar ratios decreased slightly and remained fairly constant below ~ 400 m.

4.4 Excess [N_2]

Profiles of excess N_2 concentration ($[N_2]_{\text{XS}}$) are shown in Fig. 5b. In September 2008 waters in the upper 100 m were stratified and up to 4°C warmer than in March 2009, resulting in dissolved N_2 undersaturation by as much as $\sim 8 \mu\text{mol N kg}^{-1}$. In contrast, in March 2009 N_2 gas in surface waters was in equilibrium with the atmosphere. Waters ≥ 200 m were supersaturated with dissolved N_2 at all stations during both cruises. Below the upper 150 m, $[N_2]_{\text{XS}}$ rapidly increased at all stations to peak concentrations near the oxic-anoxic interface (250–300 m). Excess N_2 decreased by 1 – $3 \mu\text{mol N kg}^{-1}$ from these maximal values at depths below 400 m. In addition, samples collected between 300–400 m at four stations during the upwelling period (March 2009) had significantly higher $[N_2]_{\text{XS}}$ (2.7 – $6.1 \mu\text{mol N kg}^{-1}$, $p < 0.001$) than those at the same stations during the relaxation period (September 2008) (Fig. 6). This was not observed at stations 10 (in the center of the eastern basin) and 29 (in the western Basin near the Tuy River).

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

5 Discussion

5.1 N₂/Ar ratios and excess N₂

Surface waters of the Cariaco Basin were undersaturated in dissolved N₂ with respect to the atmosphere during September 2008 (Non-upwelling period; Fig. 5a and b). Two mechanisms can cause this: nitrogen fixation and/or in situ near-surface water heating without gas reequilibration. Nitrogen fixation by diazotrophic organisms removes N₂ gas. Although rare, higher *Trichodesmium* spp. abundances have been observed during the summer-fall stratification period within Cariaco waters (Montes et al., 2012a), suggesting that higher nitrogen fixation rates may occur in the Caribbean and the tropical Atlantic during this time period as also inferred by Capone et al. (2005) and Montoya et al. (2002). In general, however, the biological removal of dissolved N₂ is negligible compared to physical processes such as air-sea gas exchange and bubble injection. For example, rates of N₂ consumption by diazotrophs measured at the Hawaiian Ocean Time-series (HOT) are nearly two orders of magnitude lower than the net fluxes of nitrogen gas between the ocean and the atmosphere (5×10^{-4} versus $100\text{--}200 \times 10^{-4} \text{ mol N m}^{-2} \text{ d}^{-1}$, respectively; Emerson et al., 2002). Therefore, in situ heating is the most likely cause for the apparent undersaturation observed in September 2008 when sea surface temperatures (SST) reached values $> 29^\circ\text{C}$. Increasing SST reduces the equilibrium concentration of N₂ to a lesser degree than Ar thereby increasing equilibrium N₂/Ar. If actual N₂ and Ar concentrations have little to no change due to low air-sea gas exchange then the observed N₂/Ar is less than the equilibrium value and a negative excess N₂ results. Calculations show that the magnitude of observed negative excess N₂ is consistent with the seasonal temperature increase assuming in situ heating with little gas exchange.

Excess N₂ concentrations were relatively constant with depth in the upper 100 m during both sampling periods but increase below 200 m, as dissolved oxygen decreased and N-loss began. The [NO₃⁻] profile shows the consumption of nitrate by denitrification between ~ 200 m and 300–400 m (Fig. 4). In most stations, the highest [N₂]_{xs}

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



($\sim 12\text{--}30 \mu\text{mol N kg}^{-1}$; average = $23.8 \pm 4.3 \mu\text{mol N kg}^{-1}$) was measured at 250–300 m (Fig. 5). Excess N_2 might be expected to continue to increase below this depth since waters below the sill have accumulated N_2 from denitrification supported by nitrate-rich sill-depth Caribbean Sea waters that filled the basin (Richards and Benson, 1961). In contrast, however, excess N_2 concentrations decreased by $1\text{--}3 \mu\text{mol N kg}^{-1}$ below this depth and remained around $\sim 24 \mu\text{mol N kg}^{-1}$ below 400. This suggests that the $[\text{N}_2]_{\text{XS}}$ maximum detected at the oxic-anoxic interface may reflect the combined effects of denitrification of nitrate coming from the Caribbean Sea through ventilation events (Astor et al., 2003), and N-loss generated by the decomposition of sinking organic matter, as will be discussed later on. A possible additional source to the excess N_2 inventory in the redoxcline is the contribution from denitrification in sediments exposed to sub-oxic conditions ($[\text{O}_2] < 4\text{--}2 \mu\text{mol N kg}^{-1}$ at $\sim 250\text{--}300$ m) from the surrounding shelf and slope.

Our profiles of N_2/Ar ratios and $[\text{N}_2]_{\text{XS}}$ are similar in shape to the earlier profiles measured by Richards and Benson (1961) in the Cariaco Basin. They found an average $[\text{N}_2]_{\text{XS}}$ of $20.7 \pm 2.1 \mu\text{mol N kg}^{-1}$ at $\sim 400\text{--}1200$ m, or $\sim 25\%$ lower than our average $[\text{N}_2]_{\text{XS}}$ of $25.0 \pm 1.8 \mu\text{mol N kg}^{-1}$ in the same depth range in the eastern sub-basin (stations 10, 11 and 13). To our knowledge, these are the only two observations of $[\text{N}_2]_{\text{XS}}$ that have been conducted in the Cariaco Basin. The difference may suggest that excess N_2 has been accumulating in the basin at a rate of $\sim 0.08 \mu\text{mol N kg}^{-1} \text{ yr}^{-1}$ (from 1957 to 2009) within this depth interval ($\sim 400\text{--}1200$ m). We see a concurrent increase in SRP, ammonium and silicate concentrations ($0.035\text{--}0.037$, $0.28\text{--}0.62$ and $0.85\text{--}1.3 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$, respectively, consistent with previous reports by Scranton et al., 2006 and Zhang and Millero, 1993). The increase in SRP better matches Redfield stoichiometry ($15\text{--}16 : 1 \text{ N} : \text{P}$) when both the accumulation rate of excess N_2 ($0.08 \mu\text{mol N kg}^{-1} \text{ yr}^{-1}$) and ammonium ($0.45 \mu\text{mol N kg}^{-1} \text{ yr}^{-1}$; average based on values reported above) are accounted for. The DIN/SRP ratio of the accumulation is 14.7 ($[0.08 + 0.45] : 0.036$) if excess N_2 is included and 12.5 when it is not.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

5.2 Biogenic N₂ production and upwelling

The higher concentrations of excess N₂ ($p < 0.001$) measured immediately below the oxic-anoxic interface at 300–400 m in March 2009 (upwelling) compared to September 2008 (non-upwelling; Fig. 6) suggest that the N-loss and thus the production of biogenic N₂ are stimulated during upwelling in the Cariaco Basin. The upwelling period usually is associated with higher fluxes of settling particulate organic matter (Montes et al., 2012b; Thunell et al., 2007). Enhanced vertical transport of particulate organic matter can be an important mode of supply of fixed nitrogen to the oxic-anoxic interface, where degradation of the flux releases ammonium and organic carbon that can be utilized by microbes. This is consistent with findings by Fuchsman et al (2008) in the Black Sea, who observed higher production of biogenic N₂ in years that had large phytoplankton blooms compared to those in which phytoplankton abundances were lower. We did not observe a difference in the average nutrient concentrations at the oxic-anoxic interface (~250 m) between the two sampling periods. However, nutrient and suspended organic particles measurements from the CARIACO Time-Series program show that DIN, POC and particulate organic nitrogen (PON) at the oxic-anoxic interface were higher in March 2009 than in September 2008 (5.18 vs. 1.02 $\mu\text{mol N kg}^{-1}$, 65.12 vs. 46.04 $\mu\text{g C kg}^{-1}$ and 11.16 vs. 8.05 $\mu\text{g N kg}^{-1}$, respectively). Furthermore, particulate settling flux records from CARIACO show that the median POC and PON fluxes (1997–2010) at > 400 m are higher in March than in September months (Fig. 7); CARIACO median POC and PON fluxes were used since settling flux data were not available for 2009 because of a mooring malfunction. These observations show that more inorganic and organic forms of dissolved nitrogen are generally available during upwelling compared to non-upwelling periods, stimulating stronger N-loss processes during upwelling.

Ammonium produced by the decay of sinking organic matter, in particular, is likely an important DIN source for N-loss. It can be incorporated into non-canonical nitrogen pathways such as coupled nitrification-denitrification in which nitrifiers exploit the newly

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

generated ammonium at the oxic-anoxic interface, producing nitrite and nitrate that can in turn be utilized by heterotrophic denitrifiers. Another plausible utilization pathway of NH_4^+ is anammox. Although we do not have nitrite measurements at or near the oxic-anoxic interface for our two sampling periods, historical nutrient records from the CARIACO Time-Series program indicate that NO_2^- is often present at the redoxcline in high enough concentrations to fuel the anammox reaction (Scranton et al., 2006).

From the observations reported in this study, however, we cannot determine what specific pathways (denitrification or anammox) dominate the conversion of DIN to biogenic N_2 within Cariaco's sub-oxic layer. Nonetheless, from a general perspective our results can shed light on the microbially-mediated biogeochemical processes that impact the production of biogenic N_2 in the basin on a seasonal basis. Here we propose a model explaining the response of the N-loss to the upwelling cycle of Cariaco (Fig. 8). The rain of organic matter is an important source of carbon and nitrogen for autotrophs and heterotrophs at the oxic-anoxic interface. Previous work has shown that seasonal changes in bacterial respiration rates within this layer can be associated with changes in the upwelling conditions in the basin (Taylor et al., 2006, 2009). Our hypothesis is that enhanced settling flux of organic matter during the upwelling period stimulates both heterotrophic and autotrophic metabolism at the oxic-anoxic interface. Though in a different setting, Lomas et al. (2010) found that Sargasso Sea's mesopelagic export production (300 m) has remained constant since the late 90's while epipelagic export (~ 150 m) has increased. They suggested that the decrease in the POC transfer efficiency (POC flux at 300 m : POC flux at 150 m) is the result of enhanced microbial respiration rates. In other words, heterotrophy responds proportionally to the increase in the POC flux below the euphotic zone. Enhanced microbial metabolism, such as denitrification and anammox, within the oxic-anoxic layer in Cariaco can thus result in higher biogenic N_2 production during the upwelling period. During the relaxation period, however, when the flux of organic matter escaping the base of the euphotic zone is lower (Montes et al., 2012b), a decrease of the microbial activity can be expected, which would lead to lower production of biogenic N_2 .

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



An alternative explanation for the increase in biogenic N_2 is water mass intrusions at intermediate depths (Fig. 8). Episodic intrusions of oxygen and nutrient-rich water masses from the Caribbean Sea deepen the oxic-anoxic interface in the Cariaco Basin. These alter the vertical distribution of redox sensitive species such as hydrogen sulfide, iron and manganese oxides, and ammonium, among others (Percy et al., 2008; Scranton et al., 2001, 2006). Dissolved oxygen concentrations were higher between ~ 25 and ~ 26 isopycnal surfaces in March 2009 compared to September 2008 (Fig. 2). The increase in dissolved O_2 during the upwelling season results from enhanced vertical mixing and ventilation of cold (~ 21 – 22°C) subsurface waters. Higher $[O_2]$ in the upper ~ 120 m in March 2009 suggests that an intrusion of water from the Caribbean Sea could have occurred during the upwelling period. The supply of oxygen to the redoxcline would stimulate nitrification, and enhance the abundance of NO_x available for denitrifiers. Also, the intrusion of nitrate-rich waters from the Caribbean would enhance denitrification at the oxic-anoxic interface.

5.3 DIN deficit and excess nitrogen gas

We estimate the DIN deficit (N_{def}) in the basin as the amount of fixed nitrogen that has been removed by the N-loss (Chang et al., 2010; Devol et al., 2006). The N_{def} is calculated by subtracting the observed DIN (N_{obs}) from the total expected fixed nitrogen ($N_{\text{exp}} = [NO_3^-] + [NO_2^-] + [NH_4^+]$) based on in situ SRP concentrations and Redfield stoichiometry. The expected DIN abundance is typically obtained by plotting DIN versus SRP concentrations measured in waters with dissolved $O_2 > 65 \mu\text{M}$ (Devol et al., 2006). For our work we used nutrient data collected at the CARIACO and BATS stations during 2008 and 2009 using the same criteria as Devol et al. (Fig. 9). Data from the BATS program was used in this analysis since waters entering into the Cariaco Basin originated in the sub-tropical North Atlantic. N_{exp} is then calculated by linear regression:

$$N_{\text{exp}} = 14.5(P_{\text{obs}}) - 0.7$$

where P_{obs} corresponds to in situ SRP concentrations. The negative Y-intercept indicates the DIN deficit when the SRP concentration is zero. A slope and intercept of 14.5 and 0.7, respectively, are the result of averaging the corresponding values from the DIN : SRP relationships from the CARIACO (13.8, 0.5) and BATS (15.1, 0.9) time series. These N : P relationships are similar to those reported from the Eastern Tropical South Pacific (15.8) and the Arabian Sea (14.9) (Chang et al., 2010; Codispoti et al., 2001, respectively). The DIN deficit is then:

$$N_{\text{def}} = (N_{\text{exp}} - N_{\text{obs}}) \cdot 0.86$$

where 0.86 is a factor that removes the effect of SRP production from organic matter remineralization during denitrification (Gruber and Sarmiento, 1997).

We based N_{def} estimates on monthly observations at the CARIACO Station (station 10 in this study) for 2008–2009 since no nitrite or SRP measurements were made at depths below 100 m during our cruises. We believe that these are representative for the basin because the vertical nutrient profiles within each season were similar among all stations during the regional cruises at the oxic-anoxic interface (Fig. 4).

DIN deficits in September 2008 and March 2009 were calculated by averaging the N_{def} for the CARIACO observations between August and October 2008, and between February and April 2009, respectively. Combined N_{def} in the upper ~ 120 m were below detection during both seasons, as expected, but increased in waters with low oxygen (≥ 200 m). Measurements of $[N_2]_{\text{xs}}$ were similar to N_{def} (least squares linear correlation, $R^2 = 0.95$, $p < 0.001$; Fig. 10), showing that biogenic N_2 production reflects the amount of fixed nitrogen removed by the N-loss process in Cariaco.

These observations support the conclusion of Chang et al. (2010) that measurements of excess N_2 provide a useful means for estimating N-loss rates in oxygen minimum zones, and that excess N_2 concentrations can be used to validate N-loss rates in marine systems where DIN deficits or N^* estimates are affected by non-Redfield N : P ratios. Some potential problems of using DIN deficits calculated from SRP include variable N : P ratios, the scavenging of SRP by redox species such as iron and manganese

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



oxides, or (specifically for Cariaco) the accumulation of SRP and ammonium below the oxic-anoxic interface (Scranton et al., 2006; Zhang and Millero, 1993). Although we did not determine background or absolute concentrations of excess N_2 , which would provide information about the contribution from physical processes (i.e., supersaturation due to bubble injection) to the excess N_2 inventory (Chang et al., 2010; Devol et al., 2006), the excellent agreement with DIN deficits supports our assertion that excess N_2 in the Cariaco Basin is mainly of biological origin (Fig. 10).

6 Conclusions

In this study we evaluated changes in excess N_2 concentrations in the Cariaco Basin under contrasting seasonal conditions (upwelling versus non-upwelling conditions). Excess N_2 concentrations ($[N_2]_{xs}$) were below detection at the surface, and increased to a mean value of $\sim 22 \mu\text{mol N kg}^{-1}$ at the oxic-anoxic interface (250–300 m) and deeper. Our $[N_2]_{xs}$ estimates are $\sim 25\%$ larger than those from Richards and Benson (1961), suggesting that biogenic N_2 has been accumulating in the basin at a rate of $\sim 0.08 \mu\text{mol N kg}^{-1} \text{ yr}^{-1}$.

$[N_2]_{xs}$ was higher by $\sim 3\text{--}6 \mu\text{mol N kg}^{-1}$ at 300–400 m during the upwelling period (March 2009) than when the basin was thermally stratified (September 2008). Higher biogenic N_2 production can be the result of enhanced DIN availability in Cariaco's oxic-anoxic interface during the upwelling period due to higher vertical transport of organic matter.

N-loss at the oxic-anoxic interface of the Cariaco Basin appears to be stimulated during the upwelling period. We attribute this observation to two mechanisms: (1) increased supply of sinking organic nitrogen and/or (2) ventilation of the oxic-anoxic interface by intermediate oxygenated and nitrate-rich Caribbean waters (see Fig. 8).

DIN deficits based on nutrient Redfield stoichiometry are similar to our estimates of excess N_2 concentrations at the oxic-anoxic interface (250–300 m). This suggests

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

that excess N₂ in Cariaco is generated mainly by biological processes associated with oceanic N-loss.

Our observations show that measuring excess N₂ is a robust method for quantifying the sink of fixed nitrogen in Cariaco and in low oxygen environments in general.

We conclude that biogenic N₂ determinations are a useful tool for complementing information provided by the N* parameter, and should be considered in future studies addressing questions regarding the state of the contemporary global nitrogen cycle.

References

Altabet, M. A., Higginson, M. J., and Murray, D. W.: The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO₂, *Nature*, 415, 159–162, 2002.

Astor, Y., Muller-Karger, F., and Scranton, M. I.: Seasonal and interannual variation in the hydrography of the Cariaco Basin: implications for basin ventilation, *Cont. Shelf Res.*, 23, 125–144, 2003.

Brandes, J. A. and Devol, A. H.: A global marine-fixed nitrogen isotopic budget: implications for Holocene nitrogen cycling, *Global Biogeochem. Cy.*, 16, 1120, doi:10.1029/2001GB001856, 2002.

Capone, D. G. and Knapp, A. N.: Oceanography: a marine nitrogen cycle fix?, *Nature*, 445, 159–160, 2007.

Capone, D. G., Burns, J. A., Montoya, J. P., Subramaniam, A., Mahaffey, C., Gunderson, T., Michaels, A. F., and Carpenter, E. J.: Nitrogen fixation by *Trichodesmium* spp.: an important source of new nitrogen to the tropical and subtropical North Atlantic Ocean, *Global Biogeochem. Cy.*, 19, GB2024, doi:10.1029/2004GB002331, 2005.

Chang, B. X., Devol, A. H., and Emerson, S. R.: Denitrification and the nitrogen gas excess in the Eastern Tropical South Pacific oxygen deficient zone, *Deep-Sea Res. Pt. I*, 57, 1092–1101, 2010.

Codispoti, L. A.: Phosphorus vs. nitrogen limitation of new and export production, in: *Productivity of the Ocean: Present and Past*, edited by: Berger, W. H., Smetacek, V. S., and Wefer, G., John Wiley & Sons Limited, New York, 377–394, 1989.

BGD

9, 10551–10582, 2012

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Codispoti, L. A.: An oceanic fixed nitrogen sink exceeding 400 Tg Na^{-1} vs the concept of homeostasis in the fixed-nitrogen inventory, *Biogeosciences*, 4, 233–253, doi:10.5194/bg-4-233-2007, 2007.

Codispoti, L. A., Brandes, J. A., Christensen, J. P., Devol, A. H., Naqvi, S. W. A., Paerl, H. W., and Yoshinari, T.: The oceanic fixed nitrogen and nitrous oxide budgets: moving targets as we enter the anthropocene?, *Sci. Mar.*, 65, 85–105, 2001.

Craig, H. and Weiss, R. F.: Dissolved gas saturation anomalies and excess helium in the ocean, *Earth Planet. Sc. Lett.*, 10, 289–296, 1971.

Dalsgaard, T., Canfield, D. E., Petersen, J., Thamdrup, B., and Acuna-Gonzalez, J.: N_2 production by the anammox reaction in the anoxic water column of Golfo Dulce, Costa Rica, *Nature*, 422, 606–608, 2003.

Dalsgaard, T., Thamdrup, B., and Canfield, D. E.: Anaerobic ammonium oxidation (anammox) in the marine environment, *Res. Microbiol.*, 156, 457–464, 2005.

Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N., and Dunne, J. P.: Spatial coupling of nitrogen inputs and losses in the ocean, *Nature*, 445, 163–167, 2007.

Devol, A., Uhlenhopp, A., Naqvi, S., Brandes, J., Jayakumar, D., Naik, H., Gaurin, S., Codispoti, L., and Yoshinari, T.: Denitrification rates and excess nitrogen gas concentrations in the Arabian Sea oxygen deficient zone, *Deep-Sea Res. Pt. I*, 53, 1533–1547, 2006.

Emerson, S., Stump, C., Johnson, B., and Karl, D. M.: In situ determination of oxygen and nitrogen dynamics in the upper ocean, *Deep-Sea Res. Pt. I*, 49, 941–952, 2002.

Falkowski, P. G.: Evolution of the nitrogen cycle and its influence on the biological sequestration of CO_2 in the ocean, *Nature*, 387, 272–275, 1997.

Falkowski, P. and Kiefer, D. A.: Chlorophyll *a* fluorescence in phytoplankton: relationship to photosynthesis and biomass, *J. Plankton Res.* 7, 715–731, 1985.

Fuchsman, C. A., Murray, J. W., and Konovalov, S. K.: Concentration and natural stable isotope profiles of nitrogen species in the Black Sea, *Mar. Chem.*, 111, 90–105, 2008.

Ganeshram, R. S., Pedersen, T. F., Calvert, S. E., McNeill, G. W., and Fontugne, M. R.: Glacial-interglacial variability in denitrification in the World's oceans: causes and consequences, *Paleoceanography*, 15, 361–376, 2000.

Gordon, L. I., Jennings, J. C., Ross, A. A., and Krest, J. M.: Suggested protocol for continuous flow automated analysis of seawater nutrients, WOCE Operation Manual, WHP Office Rept 90–1, WOCE Rept 77 No 68/91, 1–52, 2000.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Gruber, N.: The dynamics of the marine nitrogen cycle and its influence on atmospheric CO₂, in: The Ocean Carbon Cycle and Climate, edited by: Follows, M. and Oguz, T., Kluwer Academic Publishers, Dordrecht, Netherlands, 97–148, 2004.
- Gruber, N. and Sarmiento, J. L.: Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cy.*, 11, 235–266, 1997.
- Gruber, N. and Sarmiento, J. L.: Biogeochemical/physical interactions in elemental cycles, in: THE SEA: Biological-Physical Interactions in the Oceans, edited by: Robinson, A. R., McCarthy, J. J., and Rothschild, B. J., John Wiley and Sons, New York, 337–399, 2002.
- Hamme, R. and Emerson, S.: The solubility of neon, nitrogen and argon in distilled water and seawater, *Deep-Sea Res. Pt. I*, 51, 1517–1528, 2004.
- Holm-Hansen, O., Lorenzen, C. J., Holmes, R. W., and Strickland, J. D. H.: Fluorometric determination of chlorophyll, *J. Conseil*, 30, 3–15, 1965.
- Holmén, K. J. and Rooth, C. G. H.: Ventilation of the Cariaco Trench, a case of multiple source competition?, *Deep-Sea Res. Pt. I*, 37, 203–225, 1990.
- Jetten, M. S. M., Sliemers, O., Kuypers, M., Dalsgaard, T., Niftrik, L., Cirpus, I., Paschoonen, K., Lavik, G., Thamdrup, B., Paslier, D., Camp, H. J. M., Hulth, S., Nielsen, L. P., Abma, W., Third, K., Engström, P., Kuenen, J. G., Jørgensen, B. B., Canfield, D. E., Sinninghe Damsté, J. S., Revsbech, N. P., Fuerst, J., Weissenbach, J., Wagner, M., Schmidt, I., Schmid, M., and Strous, M.: Anaerobic ammonium oxidation by marine and freshwater planctomycete-like bacteria, *Appl. Microbiol. Biot.*, 63, 107–114, 2003.
- Kuypers, M. M. M., Sliemers, A. O., Lavik, G., Schmid, M., Jørgensen, B. B., Kuenen, J. G., Sinninghe Damsté, J. S., Strous, M., and Jetten, M. S. M.: Anaerobic ammonium oxidation by anammox bacteria in the Black Sea, *Nature*, 422, 608–611, 2003.
- Lidz, L., Charm, W. B., Ball, M. M., and Valdes, S.: Marine Basins off the coast of Venezuela, *B. Mar Sci.*, 19, 1–17, 1969.
- Löffler, A., Schneider, B., Schmidt, M., and Nausch, G.: Estimation of denitrification in Baltic Sea deep water from gas tension measurements, *Mar. Chem.*, 125, 91–100, 2011.
- Lomas, M. W., Steinberg, D. K., Dickey, T., Carlson, C. A., Nelson, N. B., Condon, R. H., and Bates, N. R.: Increased ocean carbon export in the Sargasso Sea linked to climate variability is countered by its enhanced mesopelagic attenuation, *Biogeosciences*, 7, 57–70, doi:10.5194/bg-7-57-2010, 2010.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Montes, E., Thunell, R., Muller-Karger, F. E., Tappa, E., Lorenzoni, L., Troccoli, L., Astor, Y., and Varela, R.: Sources of ^{15}N variability in sinking particulate nitrogen in the Cariaco Basin, Venezuela, *Deep-Sea Res. Pt. II*, submitted, 2012a.

Montes, E., Muller-Karger, F., Thunell, R., Hollander, D., Astor, Y., Varela, R., Soto, I., and Lorenzoni, L.: Vertical fluxes of particulate biogenic material through the euphotic and twilight zones in the Cariaco Basin, Venezuela, *Deep-Sea Res. Pt. I.*, 2012b.

Montoya, J. P., Carpenter, E. J., and Capone, D. G.: Nitrogen fixation and nitrogen isotope abundances in zooplankton of the oligotrophic North Atlantic, *Limnol. Oceanogr.*, 47, 1617–1628, 2002.

Muller-Karger, F., Varela, R., Thunell, R., Scranton, M., Bohrer, R., Taylor, G., Capelo, J., Astor, Y., Tappa, E., Ho, T.-Y., and Walsh, J. J.: Annual cycle of primary production in the Cariaco Basin: response to upwelling and implications for vertical export, *J. Geophys. Res.*, 106, 4527–4542, 2001.

Muller-Karger, F. E., Varela, R., Thunell, R. C., Scranton, M. I., Taylor, G. T., Astor, Y., Benitez-Nelson, C. R., Lorenzoni, L., Tappa, E., Goñi, M. A., Rueda, D., and Hu, C.: The CARIACO oceanographic time series, in: *Carbon and Nutrient Fluxes in Continental Margins: a Global Synthesis*, JGOFS Continental Margins Task Team (CMTT), edited by: Liu, K.-K., Atkinson, L., Quinones, R., and Talaue-McManus, L., Springer-Verlag, Berlin Heidelberg, 454, 2010.

Percy, D., Li, X., Taylor, G. T., Astor, Y., and Scranton, M. I.: Controls on iron, manganese and intermediate oxidation state sulfur compounds in the Cariaco Basin, *Mar. Chem.*, 111, 47–62, 2008.

Richards, F. A.: The Cariaco Basin (Trench), *Oceanogr. Mar. Biol.*, 13, 11–67, 1975.

Richards, F. A. and Benson, B. B.: Nitrogen/argon and nitrogen isotope ratios in two anaerobic environments, the Cariaco Trench in the Caribbean Sea and Dramsfjord, Norway, *Deep-Sea Res.*, 7, 254–264, 1961.

Schubert, C.: Origin of Cariaco Basin, Southern Caribbean Sea, *Mar. Geol.*, 47, 345–360, 1982.

Scranton, M. I., Astor, Y., Bohrer, R., Ho, T.-Y., and Muller-Karger, F.: Controls on temporal variability of the geochemistry of the deep Cariaco Basin, *Deep-Sea Res. Pt. I*, 7, 1605–1625, 2001.

Scranton, M. I., McIntyre, M., Astor, Y., Taylor, G. T., Müller-Karger, F., and Fanning, K.: Temporal variability in the nutrient chemistry of the Cariaco Basin, in: *Past and Present Water Column Anoxia*, edited by: Neretin, L. N., Springer Netherlands, 139–160, 2006.

**Biogenic nitrogen
gas production at the
oxic-anoxic interface
in the Cariaco Basin**

E. Montes et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Smith, S. V.: Phosphorus versus nitrogen limitation in the marine environment, *Limnol. Oceanogr.*, 29, 1149–1160, 1984.
- Strickland, J. D. H. and Parsons, T. R.: *A Practical Handbook of Seawater Analysis*, Fisheries Research Board of Canada, Ottawa, Ontario, 1972.
- 5 Taylor, G. T., Labichella-Armas, M., Varela, R., Müller-Karger, F., Lin, X., and Scranton, M. I.: Microbial ecology of the Cariaco Basin's oxic-anoxic interface: the US–Venezuela CARIACO times series program, in: *Past and Present Water Column Anoxia*, edited by: Neretin, L. N., NATO Science Series, Springer, Netherlands, 473–499, 2006.
- 10 Taylor, G. T., Thunell, R., Varela, R., Benitez-Nelson, C., and Scranton, M. I.: Hydrolytic ectoenzyme activity associated with suspended and sinking organic particles within the anoxic Cariaco Basin, *Deep-Sea Res. Pt. I*, 56, 1266–1283, doi:10.1016/j.dsr.2009.02.006, 2009.
- Thamdrup, B., Dalsgaard, T., Jensen, M. M., Ulloa, O., Farías, L., and Escribano, R.: Anaerobic ammonium oxidation in the oxygen-deficient waters off Northern Chile, *Limnol. Oceanogr.*, 51, 2145–2156, 2006.
- 15 Thunell, R., Benitez-Nelson, C., Varela, R., Astor, Y., and Muller-Karger, F.: Particulate organic carbon fluxes along upwelling-dominated continental margins: rates and mechanisms, *Global Biogeochem. Cy.*, 21, GB1022, doi:10.1029/2006GB002793, 2007.
- Zhang, J.-Z. and Millero, F. J.: The chemistry of the anoxic waters in the Cariaco Trench, *Deep-Sea Res. Pt. I*, 40, 1023–1041, 1993.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Table 1. Location, profile depth, and chlorophyll *a* concentration at the depth of chlorophyll maximum (DCM) at stations sampled for excess N₂ during September 2008 and March 2009 in the Cariaco Basin.

Station #	Latitude (° N)	Longitude (° W)	Profile depth (m)	September 2008		March 2009	
				[Chl <i>a</i>] (µg l ⁻¹)	DCM (m)	[Chl <i>a</i>] (µg l ⁻¹)	DCM (m)
10	10.5	64.7	1300	0.31	50	0.60	20
11	10.7	64.7	400	0.61	57	0.60	33
13	10.5	65.0	400	0.63	61	0.54	42
21	10.7	65.7	1300	0.42	50	1.25	43
29	10.7	65.9	400	0.42	65	1.15	38
32	10.8	65.7	400	0.52	50	2.10	50

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Biogenic nitrogen
gas production at the
oxic-anoxic interface
in the Cariaco Basin**

E. Montes et al.

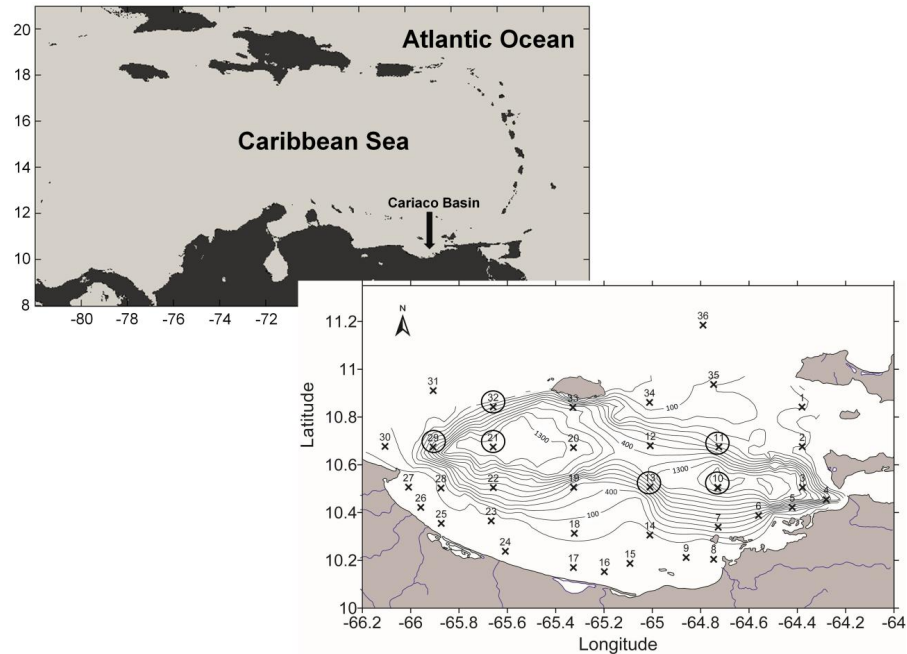


Fig. 1. Location of the Cariaco Basin and stations sampled for excess N_2 (circles) in September 2008 and March 2008. Station 10 corresponds to the CARIACO Ocean Time-Series station (10.5° N, 64.7° W). Broken lines trace the bathymetry of the basin.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

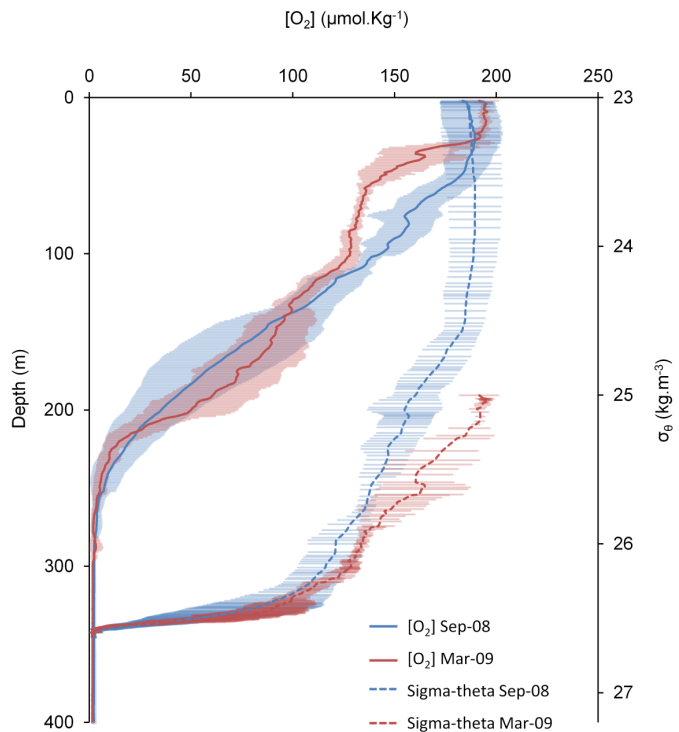


Fig. 2. Average oxygen and density (σ_θ) profiles in the upper 400 m of the Cariaco Basin constructed from all six stations sampled during September 2008 and March 2009 for excess N_2 determinations.

Biogenic nitrogen gas production at the oxitic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



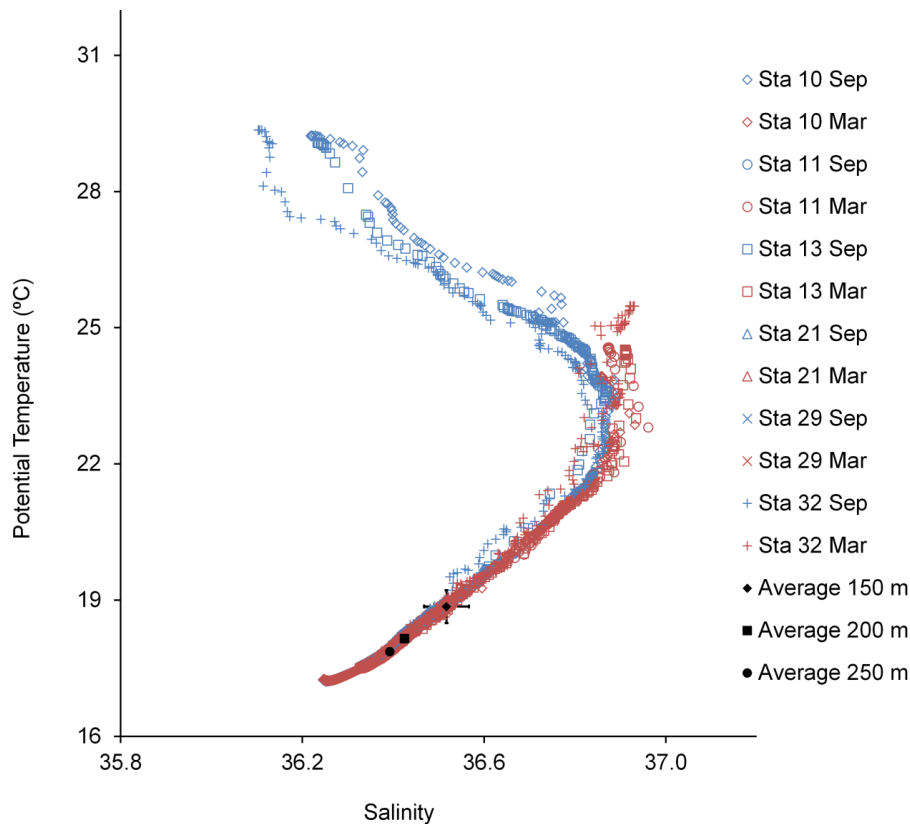


Fig. 3. Salinity versus potential temperature (θ) in the Cariaco Basin at stations sampled for excess N_2 measurements during September 2008 and March 2009. Black symbols represent the average potential temperature and salinity from all six stations and sampling periods at 150 (diamond), 200 (square) and 250 (circle) m.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogenic nitrogen gas production at the oxidic-anoxic interface in the Cariaco Basin

E. Montes et al.

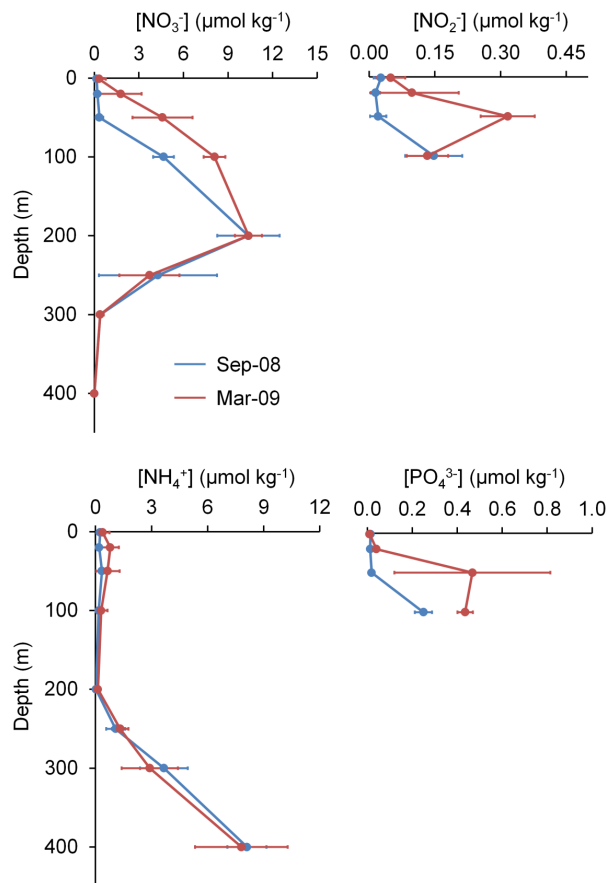


Fig. 4. Average nutrient profiles in the Cariaco Basin from stations sampled for excess N_2 during September 2008 and March 2009.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

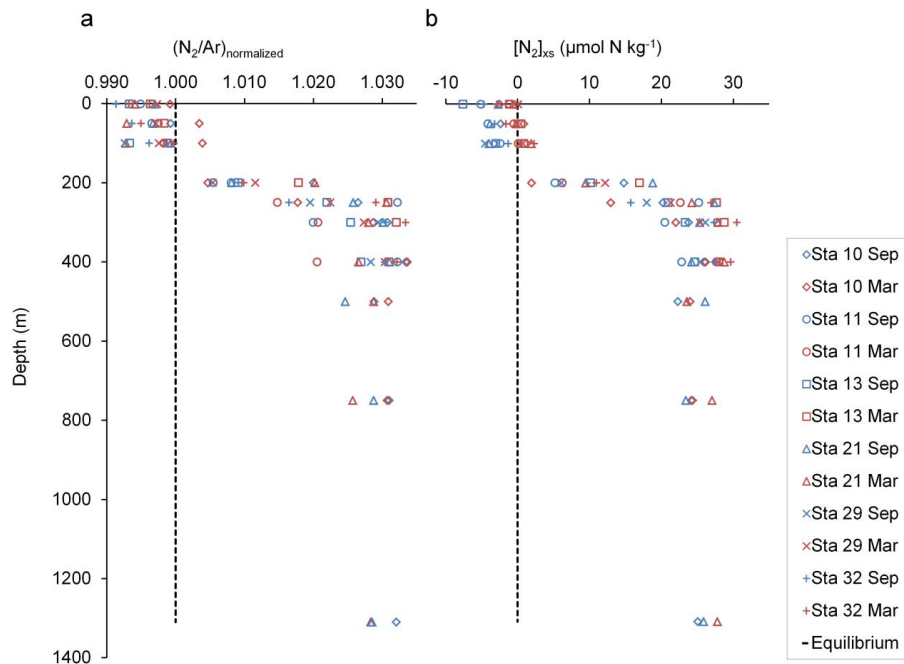


Fig. 5. Profiles of N_2/Ar ratios (**a**) and excess N_2 concentrations (**b**) in the Cariaco Basin normalized to values at atmospheric equilibrium (blue symbols: September 2008; red: March 2009). Vertical dotted line indicates the theoretical value at atmospheric equilibrium. Error bars in plots (**a** and **b**) are smaller than symbols and were thus omitted.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



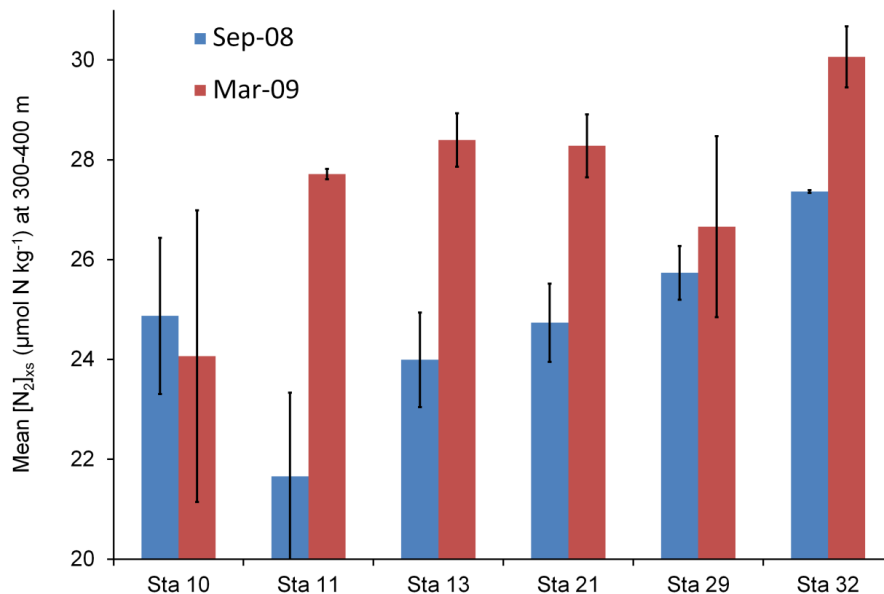


Fig. 6. Mean excess N_2 concentration at 300–400 m in the Cariaco Basin eastern (stations 10, 11 and 13) and western (stations 21, 29 and 32) sub-basins during September 2008 and March 2009.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



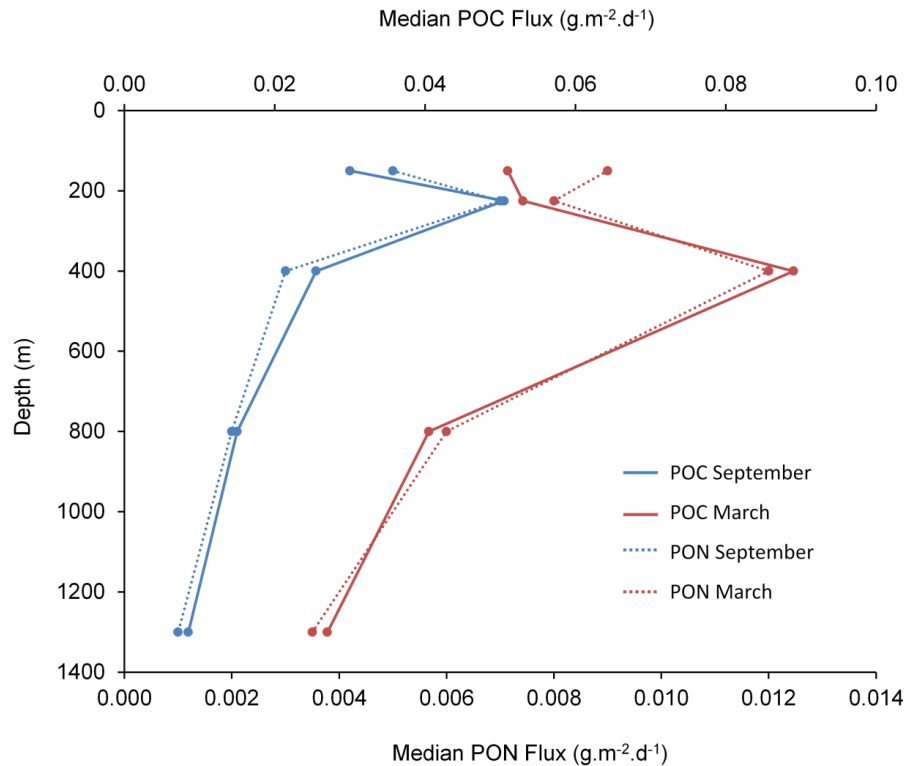


Fig. 7. Median vertical flux of POC and PON during September (non-upwelling) and March (upwelling) months from the CARIACO time-series program between 1997 and 2010.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

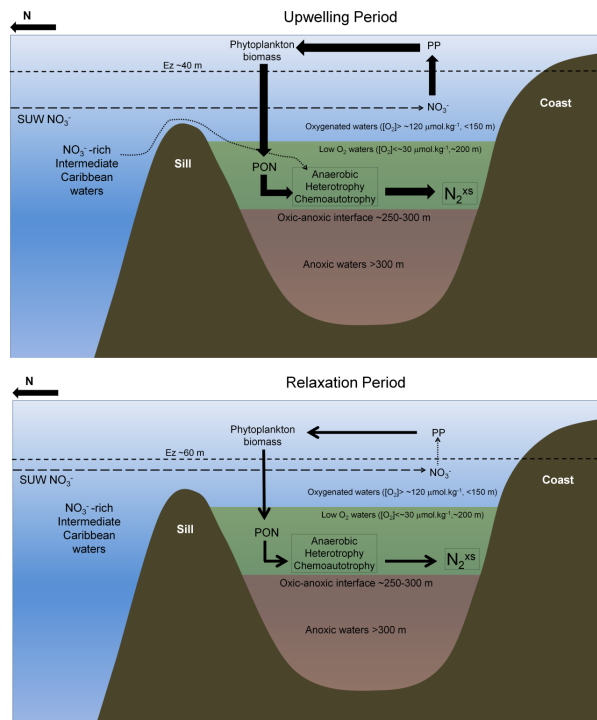


Fig. 8. Cartoon depicting the primary mechanisms modulating the production of biogenic N₂ during upwelling (upper panel) and relaxation (lower panel) in the Cariaco Basin. The width of the arrows is proportional to the magnitude of the processes described. Intrusions from the Caribbean are indicated by the dotted line in the lower panel. The thickness of the oxic, suboxic and anoxic layers is only schematic and is not drawn to scale.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

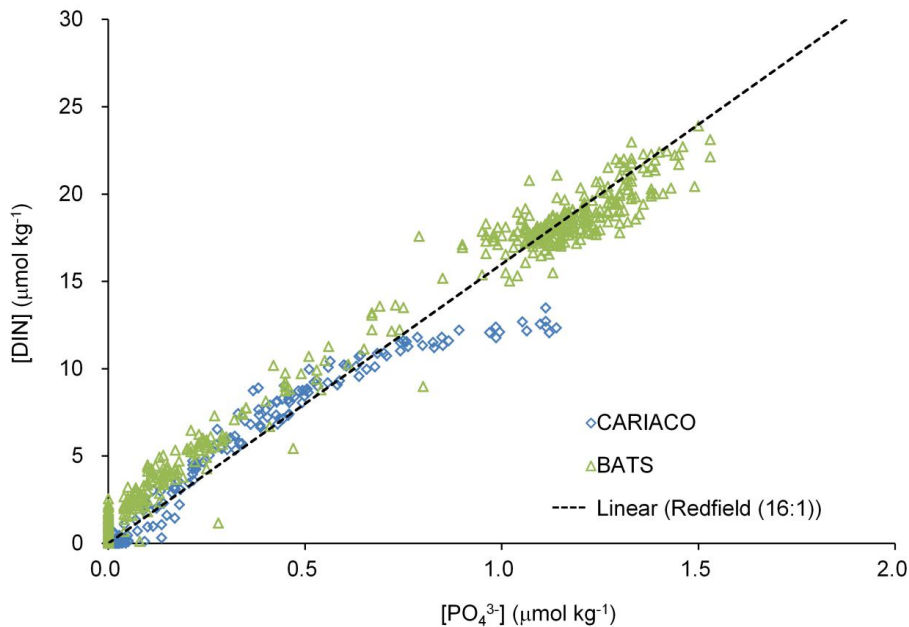


Fig. 9. Phosphate (SRP) versus DIN concentrations in waters with dissolved O_2 concentrations above $\sim 65 \mu\text{mol kg}^{-1}$ from the CARIACO and BATS time-series stations during 2008 and 2009.

Biogenic nitrogen gas production at the oxic-anoxic interface in the Cariaco Basin

E. Montes et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



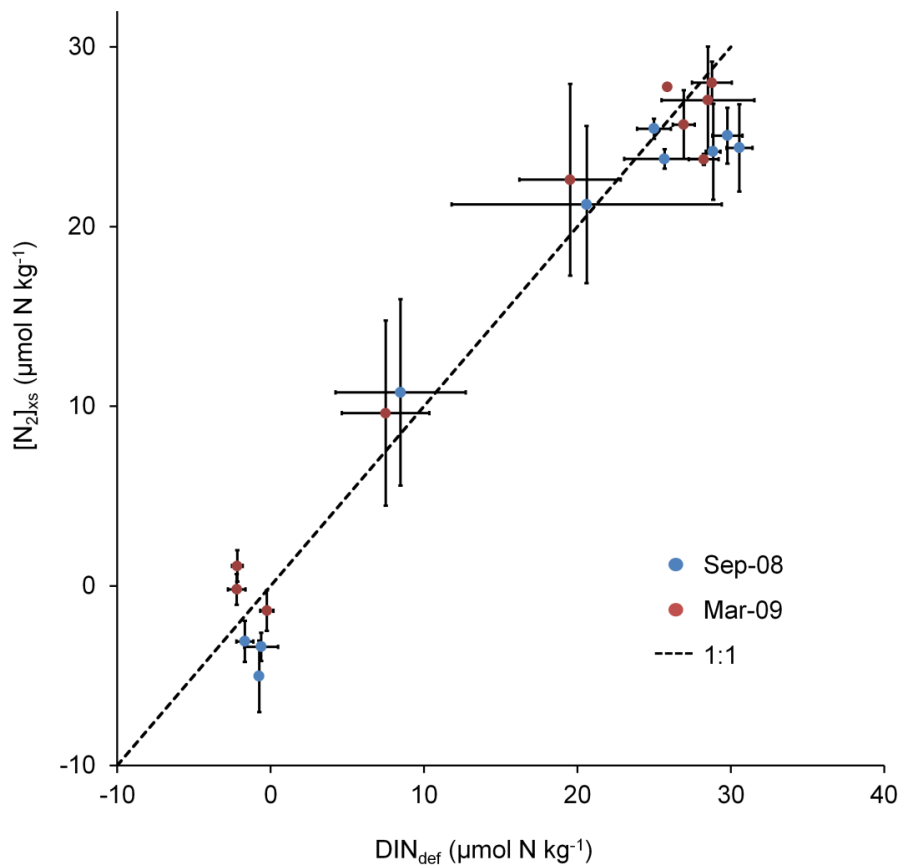


Fig. 10. Average DIN deficits (DIN_{def}) versus biogenic nitrogen gas concentrations ($[N_2]_{xs}$) in the Cariaco Basin. The dashed line shows the theoretical 1 : 1 relationship.