



HAL
open science

Organic nutrients and excess nitrogen in the North Atlantic subtropical gyre

A. Landolfi, A. Oschlies, R. Sanders

► **To cite this version:**

A. Landolfi, A. Oschlies, R. Sanders. Organic nutrients and excess nitrogen in the North Atlantic subtropical gyre. *Biogeosciences Discussions*, 2008, 5 (1), pp.685-724. hal-00297972

HAL Id: hal-00297972

<https://hal.science/hal-00297972>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Biogeosciences Discussions is the access reviewed discussion forum of *Biogeosciences*

**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Organic nutrients and excess nitrogen in the North Atlantic subtropical gyre

A. Landolfi¹, A. Oschlies¹, and R. Sanders²

¹IFM-GEOMAR, Leibniz-Institut für Meereswissenschaften, Dusternbrooker Weg 20, 24105
Kiel, Germany

²National Oceanography Centre, Southampton University, European way, SO14 3ZH,
Southampton, UK

Received: 11 December 2007 – Accepted: 24 December 2007 – Published: 14 February 2008

Correspondence to: A. Landolfi (alandolfi@ifm-geomar.de)

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

To enable an accurate estimate of total excess nitrogen (N) in the North Atlantic a new tracer, TNxs, is defined which includes the contribution of organic nutrients to the assessment of N:P stoichiometric anomalies. We estimate the spatial distribution of TNxs within the North Atlantic using data from a trans-Atlantic section across 24.5° N conducted in 2004. We then employ three different approaches to infer rates of total excess nitrogen accumulation using pCFC-12 derived ventilation ages (a TNxs vertical integration, a one end-member and a two-end member mixing model). Despite some variability among the different methods the dissolved organic nutrient fraction always contributes to about half of the TNxs accumulation, which is in the order of $9.38 \pm 4.18 \times 10^{11} \text{ mol N y}^{-1}$. Here we suggest that neglecting organic nutrients in stoichiometric balances of the marine N and P inventories can lead to systematic errors when estimating a nitrogen excess or deficit relative to the Redfield ratio in the oceans. For the North Atlantic the inclusion of the organic fraction leads to an upward revision of the N supply by N_2 fixation to $10.2 \pm 6.9 \times 10^{11} \text{ mol N y}^{-1}$. This enhanced estimate of nitrogen fixation reconciles the geochemical estimates of N_2 fixation derived from excess nitrate and the direct estimates from N_2 fixation measurements.

1 Introduction

The oceans contain the largest pool of carbon on the planet accessible on time scales shorter than millennia and are implicated in the regulation of atmospheric CO_2 through the temperature dependent solubility of CO_2 in seawater (the solubility pump) and the sinking of organic matter from the productive surface layers to the deep ocean (the biological pump). The strength of the biological carbon pump is strongly controlled by the bioavailability of nutrients, principally fixed nitrogen (N) and phosphorus (P) in the sunlit surface ocean. Hence, quantifying the processes that control the fluxes of N and P into the oceans and to surface waters, where they sustain phytoplankton growth, is

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**A. Landolfi et al.

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

important in assessing the role of marine biology in the global carbon cycle. One critical area where such efforts are required is the subtropical gyres. These extensive areas are estimated to account for half the global export of organic carbon from the surface to the deep ocean (Emerson et al., 2001). For the North Atlantic gyre recent efforts have determined rates of nutrients delivery by means of atmospheric deposition, physical processes (Jenkins, 1988; Jenkins and Goldman, 1985; McGillicuddy et al., 1998; Dietze et al., 2004) and nitrogen fixation (Capone et al., 2005; Gruber and Sarmiento, 1997; Hansell and Carlson, 2001).

Large uncertainties exist in estimates of N_2 fixation with a significant offset between direct measurements and indirect geochemical estimates which have been attributed to the different spatial and temporal scales of the two methodologies. Recent direct observations of N_2 fixation rates are more consistent with geochemical ones (Capone et al., 2005); however, it is unclear whether this discrepancy has been fully resolved. Geochemical estimates of the large scale distribution and rate of N_2 fixation have been based upon NO_3^- to PO_4^{3-} ratio anomalies (Gruber and Sarmiento, 1997; Hansell et al., 2004; Michaels et al., 1996; Deutsch et al., 2001)(hereafter referred to as M96, GS97, D01 and H04) as compared to the Redfield stoichiometry (16:1) (Redfield et al., 1963) which is assumed to reflect the average N and P demand and composition of marine phytoplankton.

M96 first introduced the concept of the quasi-conservative geochemical tracer $N^* = [NO_3^-] - 16 * [PO_4^{3-}] + 2.7 \mu mol kg^{-1}$, which traces the production or consumption of nitrate, with a N:P stoichiometry different from the canonical 16:1. The definition of N^* has undergone minor modifications by other authors (GS97, D01) and evolved into the concept of excess nitrate ($DINxs = [NO_3^-] - 16 * [PO_4^{3-}]$; H04). Despite the various parameterizations, N^* and $DINxs$ represent the deviation from the 16:1 nutrient ratio and reflect the net impact of processes that add or remove NO_3^- or PO_4^{3-} with a N:P stoichiometry different from 16:1. Previous geochemical estimates assumed N_2 fixation and denitrification to be the only relevant processes able to alter the Redfield stoichiometry; corrections accounting for the small contribution of atmospheric deposition have

**Total nitrogen excess
in the North Atlantic**A. Landolfi et al.

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

been applied a-posteriori (GS97). Using this technique, an excess of nitrate over phosphate has been reported for the North Atlantic thermocline waters and N_2 fixation has been invoked to explain such stoichiometric anomalies, based on the assumption that N_2 fixing organisms have a non-Redfield stoichiometry of $N:P=125$ (Karl et al., 1992).
5 However, GS97 and Karl et al. (2002) both suggested that the lack of knowledge of the dissolved organic N (DON) and P (DOP) pools limit the accurate determination of the stoichiometric ratios of N and P. For example, processes such as any preferential remineralization of DON, or the selective uptake of PO_4^{3-} w.r.t. NO_3^- may cause positive $NO_3^-:PO_4^{3-}$ anomalies and could lead to erroneous N_2 fixation estimates. Similarly, re-
10 cently fixed N by diazotrophs may enter the dissolved organic nutrient pool and hence may not be accounted for in the local N^* signal. A major fraction of the nutrient pool of the surface oceans consists of DON and DOP (Jackson and Williams, 1985) and up to half of the recently fixed nitrogen has been observed to be released as DON (Glibert and Bronk, 1994; Mulholland et al., 2004; Capone et al., 1994). Thus neglecting the
15 organic nutrient pools in the stoichiometric balances may adversely affect our interpretation of the oceanic processes that involve N and P cycling. In this paper we include the organic nutrient pools in an analysis of excess nitrogen stocks in the upper waters of the north Atlantic subtropical gyre and use them in combination with pCFC-12 derived ventilation ages to estimate the production rate of total nitrogen excess and infer
20 N_2 fixation estimates in this region.

1.1 Two new variables: TONxs and TNxs

Building on the concepts of N^* and DINxs, two new variables, TONxs and TNxs, are defined as: $TONxs=[TON]-16[TOP]$; $TNxs=DINxs+TONxs=[TN]-16[TP]$

25 The interpretation of TONxs and TNxs is similar to N^* (GS97) or DINxs (H04) with the advantage of including the organic nutrient pools and being independent from differential nutrient remineralization/utilization. TONxs and TNxs represent the distance of a TON and TOP or a TN and TP pair from the mean oceanic trend line of 16:1. In the

**Total nitrogen excess
in the North Atlantic**A. Landolfi et al.

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

simple case of an ocean in hypothetical Redfield equilibrium, where terrestrial inputs of N and P are in steady state, preformed TNxs would be zero. Note that even when TNxs=0 a positive or negative DINxs and TONxs could occur however they would need to balance. The development of a positive (or negative) TNxs values simply imply an excess (or a deficit) of N with respect to P relative to a Redfield ocean. For these deviations to occur, only the net input or removal of N and P matter. Organic-inorganic nutrient transformations that would affect DINxs and TONxs development with opposite sign do not affect TNxs. TNxs is insensitive to differential remineralization and accumulation of dissolved refractory material; therefore it unambiguously reflects only the net non-Redfieldian sources and sinks of the marine N and P inventories. For example, a positive TNxs anomaly would reflect a net excess of N over P due to N₂ fixation, atmospheric deposition or excess P loss. Similarly negative TNxs anomaly would indicate losses of fixed nitrogen by denitrification and anammox or export of organic matter deviating from Redfield stoichiometry. We now calculate TNxs and TONxs for the N Atlantic subtropical gyre and use these data in combination with transient tracer data to estimate the rate of excess total nitrogen accumulation and infer rates of nitrogen fixation in the North Atlantic subtropical gyre.

2 Methods

The North Atlantic subtropical gyre was surveyed along the nominal latitude of 24.5° N in April–May 2004 on board RRS Discovery on cruise D279 (Fig. 1). During D279, 125 full depth CTD stations were occupied. At each station up to 24 water samples were collected in Niskin bottles for the analysis of oxygen, salinity, nitrate, silicate, phosphate and total organic nutrients (TON and TOP).

Unfiltered samples for inorganic nutrients (NO₃⁻+NO₂⁻ hereafter nitrate, PO₄³⁻ hereafter phosphate, and Si(OH)₄ hereafter silicate) were collected from all bottles on all the CTD casts. Inorganic nutrient concentrations were measured immediately on board using a Skalar San Plus autoanalyser according to standard colorimetric techniques

(Kirkwood et al., 1996). The analytical precision, based on the coefficient of variation (CV) of replicate analysis of a single sample, was 1.1% for nitrate and 0.9% for phosphate. The detection limit of the analyses, calculated as three times the noise of the baseline, was 0.1 μM for nitrate and 0.01 μM for phosphate.

5 Samples for TON and TOP analysis were carefully collected directly from Niskin bottles into 60-ml sterile high-density polythene bottles. Sample bottles were rinsed with three times their own volume of sample and immediately frozen. Total nitrogen (TN) and (TP) phosphorus were UV oxidized in duplicate replicates to nitrate and soluble reactive phosphorus (hereafter phosphate) using high intensity ultraviolet light at a wavelength below 250 nm in a Metrohm UV705 digester according to the method used by Sanders and Jickells (2000). Samples were subsequently analyzed for nitrate and phosphate according to the standard colorimetric techniques using a Skalar San Plus autoanalyser (Kirkwood et al., 1996). The UV lamp oxidation efficiency was checked at every oxidation using a organic compound (adenosin-5monophosphatemonohydrate AMP). The recovery of the AMP compound was 94% for P and 60% for N. Duplicate samples coefficient of variation (CV) was for nitrate, 2% and for phosphate, 7%. Given the low oxidation efficiency of organic nitrogen using the UV method, replicate samples were re-analyzed for TN using the High Temperature Catalytic Oxidation (HTCO). This method is known to have the highest oxidation efficiency for the most refractory compounds (Bronk et al., 2000). HTCO was performed with a Shimadzu 5000A DOC analyser connected in series with an Antek 705E chemiluminescent nitrogen specific detector (Alvarez-Salgado and Miller, 1998). The instruments system and analytical blanks were $<1 \mu\text{MN}$ with a CV of 4%. The instrument detection limit, estimated as three times the SD of the blank (Bronk et al., 2000), was typically 0.12 μMN . The oxidation efficiency was monitored using caffeine standard solutions and varied from 96% to 100%. Sample concentrations were not corrected for these recovery estimates. The CV of 4 replicate injections of the samples was typically 2% for N. The accuracy of the HTCO method has been determined by the use of consensus reference (CRM) materials distributed by Dr. Hansell's laboratory, University of Miami. The accuracy of

**Total nitrogen excess
in the North Atlantic**A. Landolfi et al.

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

N measurements are within 5% of the CRM concentrations.

The organic concentration, TON and TOP, are calculated by subtracting the inorganic concentration (nitrate and nitrite or phosphate) from the total (TN and TP): As each of the measurements has an associated analytical error, TON concentration estimates have an error given by the combined uncertainty of the two analyses TN and DIN:

$$SD_{TON} = \sqrt{(SD_{TDN}^2 + SD_{DIN}^2)}.$$

3 Results

As expected, nitrate and phosphate concentrations increased with depth as the remineralization of organic matter occurs during particle settling (Fig. 2). Nutrient rich waters were closer to the surface on the eastern side of the subtropical gyre, generally following the sloping isopycnals. The highest concentrations of both NO_3^- and PO_4^{3-} were associated with low oxygen waters at around 1000 m (data not shown). Dissolved organic nutrient concentrations decreased with depth suggesting a surface ocean TON and TOP source (Fig. 3). A zonal gradient of upper-ocean TON concentrations occurs with the highest concentrations found in the western basin. TOP showed a more complex spatial variability. Low surface concentrations possibly indicate TOP utilization, a suggestion corroborated by observed high alkaline phosphatase activities (Landolfi, 2005). Figure 4 shows average vertical profiles of dissolved inorganic and organic N and P. Nitrate and phosphate concentrations increased from the surface to 1000 m where the maximum concentrations reached $25.6 \pm 5.8 \text{ mmol m}^{-3} \text{ NO}_3^-$ and $1.60 \pm 0.52 \text{ mmol m}^{-3} \text{ PO}_4^{3-}$ respectively. Below 1000 m, concentrations became rather constant, both for nitrate ($21.0 \pm 0.4 \text{ mmol m}^{-3}$) and phosphate ($1.43 \pm 0.08 \text{ mmol m}^{-3}$). Average TON concentrations decreased from surface values of $4.6 \pm 1.8 \text{ mmol m}^{-3}$ to $1.7 \pm 0.1 \text{ mmol m}^{-3}$ at 1000 m and did not vary much below this depth. TOP decreased similarly from $0.11 \pm 0.11 \text{ mmol m}^{-3}$ near the surface to almost undetectable concentrations ($0.03 \pm 0.01 \text{ mmol m}^{-3}$) below 1000 m.

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Existence of excess N

Positive DINxs anomalies occur across the entire gyre in a limited portion of the water column comprised between 150 and 400 m on the $\sigma_{\theta}=26\text{--}27.5$ isopycnals (Fig. 5a). TON was always in excess with respect to TOP relative to the Redfield ratio throughout the water column due in part to its refractory nature (Fig. 5b). A total positive N excess anomaly, TNxs, occurred in the top 1000 m of the entire transect (Fig. 5c).

From the excess nitrogen profiles (Fig. 6) the vertical contribution of DINxs and TONxs to TNxs development can be resolved. In the top 150 m DINxs exhibited a negative anomaly likely due to the preferential remineralization of TOP. TON exceeded $16\times\text{TOP}$ on average by $2.7\pm 0.3\text{ mmol m}^{-3}$. TONxs decreased to $1.9\pm 0.3\text{ mmol m}^{-3}$ from 150 m to 700 m, possibly contributing about 70–80% to the concomitant increase in DINxs. Below 1000 m, the mean TONxs was $1.4\pm 0.2\text{ mmol m}^{-3}\text{ N}$, which closely balances the deep DINxs deficit ($-1.4\pm 0.3\text{ mmol m}^{-3}$). Thus below 1000 m, it is likely that the TONxs positive anomaly and the DINxs negative anomaly result from the residual (refractory) TON pool left by TOP preferential remineralization. Therefore, the water column can be crudely divided into the upper 1000 m characterised by an N excess (TN positive anomaly) of $2.6\pm 0.6\text{ mmol m}^{-3}$ and the lower 1000 m where TN and TP are approximately in balance ($0.0\pm 0.4\text{ mmol N m}^{-3}$) w.r.t. the Redfield ratio.

4.1 Processes contributing to DINxs and TONxs development – origin of TN excess

The distributions of DINxs, TONxs and TNxs can be rationalized using a conceptual model representing the partitioning between the organic and the inorganic pools in the area studied (Fig. 7). The relative sizes of the inorganic and organic N and P pools will depend on whether organic matter production or remineralization is more efficient. However, the transformations and redistribution of N and P within the organic and inorganic fractions do not alter the concentrations of the total inventories (TN and TP) and thus TNxs. The following processes govern N:P shifts in the organic and inorganic fractions:

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Negative DINex anomalies can result from

- The preferential remineralization of TOP to phosphate compared to the remineralisation of TON to nitrate
- The preferential uptake of NO_3^- relative to the uptake of phosphate
- The remineralization of P rich organic matter
- Denitrification

Positive DINxs anomalies can result from

- The remineralization of N rich organic matter (including that derived from N_2 fixation).
- The preferential remineralization of TON to nitrate relative to the mineralization of TOP to phosphate.
- The preferential uptake of PO_4^{3-} relative to nitrate
- The deposition of low phosphate, high $\text{NO}_x + \text{NH}_3$ material from the atmosphere

Positive TONex anomalies can result from

- The preferential remineralisation of TOP to phosphate relative to TON to nitrate
- The production of TON rich organic material (including that derived from nitrogen fixation)
- The deposition of material rich in TON relative to TOP from the atmosphere.

Positive TNxs anomalies result from:

- The deposition of nitrogen rich material from the atmosphere

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- The production of N rich organic material (including material derived from nitrogen fixation)

Preferential remineralization and uptake only redistribute N and P between the inorganic and the organic pools, they cannot alter their absolute and relative amounts. The processes that are of interest in terms of regulating TNxs are the ones that have an effect on the absolute amount of nutrients (net input or removal of N and P) which alter the TN:TP ratio. As long as the fraction of sinking particles that undergo differential remineralization and fall out of the area of interest (0–1000 m) is small, the ratio between the N and P inventories in the ocean can be unambiguously diagnosed by TNxs. Any net excess or deficit of nitrogen relative to the expected concentration of phosphorus derived using the Redfield Ratio will be reflected in the development of TNxs.

4.2 Rates of accumulation of total nitrogen excess

Here we attempt to estimate TNxs accumulation using several techniques.

4.2.1 One end-member mixing model – vertical integration

Firstly, we use the distribution of N excess in combination with the pCFC-12 transient tracer distribution at each data point to infer the water-column-integrated TNex development rate. The pCFC-12 data collected during D279 has been kindly provided by Dr. Rana Fine at RSMAS/MAC, University of Miami.

We first assume a one end member mixing model where the end member age represents the time since the water mass has been ventilated. The accumulation rate of TNxs since the water particle has left the surface is:

$$\frac{\Delta \text{TNxs}}{\Delta t} = \frac{\text{TNxs}_t - \text{TNxs}_o}{t_t - t_o} \quad (1)$$

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and the water column integrated accumulation rate is:

$$\int_0^z \frac{\Delta \text{TNxs}}{\Delta t} dz \quad (2)$$

TNxs₀ represents the preformed end member TNxs value and t_0 is the time at which the water mass is in contact with the atmosphere and is set to zero.

TNxs and pCFC-12 age were measured at different casts and different depths. To improve the match up between TNxs and pCFC-12 age data a linear interpolation of pCFC-12 age and TNxs along a constant depth grid was carried out. Shallow ($\sigma_\theta \lesssim 26$) pCFC-12 age data are characterized by a larger uncertainty relative to the deep thermocline, due to the decrease of atmospheric pCFC-12 after the year 2000. Also, pCFC age represents a model age for air-sea exchange processes and is not ideal for organic matter production as it is zeroed at the surface whereas organic matter, due to its biological origin, will possibly exhibit a seasonal cycle in surface waters. Therefore, for near surface waters (pCFC-12 age < 1 yr) the development of TNxs has been conservatively been considered to occur on an annual timescale. As no seasonal TNxs data is available any temporal variability of TNxs shorter than a year is difficult to constrain. No TON and TOP concentrations data are available in winter in the North Atlantic where near-surface and thermocline waters ventilation occurs. Therefore, the values measured in spring (Torres-Valdes, personal communication) were taken as preformed values in the regions where the 25, 26, 26.5 and 27 isopycnal outcrop (Table 1).

The 1000 m depth-integrated TNxs development (Fig. 8) indicates a large spatial variability along 24° N ranging from -0.0013 to $0.43 \text{ mol m}^{-2} \text{ y}^{-1}$ with the lowest accumulation rates at the gyre margins and in the central region ($\sim 40^\circ \text{ W}$). This spatial pattern appears anti-correlated with the natural ^{15}N isotopic abundance of particulate organic nitrogen collected on the same cruise (Reynolds et al., 2007). On average the TNxs accumulation rate was $0.16 \pm 0.12 \text{ mol m}^{-2} \text{ y}^{-1}$. DINxs accumulation rates ranged from -0.074 (the negative sign indicates a decrease of DINxs from the original water mass) to $0.05 \text{ mol m}^{-2} \text{ y}^{-1}$. The largest contribution to the development of

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



TNxs comes from the development of TONxs which occurs with an average rate of $0.13 \pm 0.10 \text{ mol m}^{-2} \text{ y}^{-1}$. If the total nitrogen accumulation rate is representative of the region extending from 15° N to 25° N and 25° W to 75° W ($6.83 \times 10^{12} \text{ m}^2$) then the areal accumulation rate would be of the order of $1.09 \pm 0.81 \times 10^{12} \text{ mol y}^{-1}$ where the large range derives from the observed large spatial variability.

It could be argued that the farfield lateral advection of N rich organic matter from the tropics to the subtropical gyre is not accounted for in the preformed TNxs calculation. The lateral Ekman advection of inorganic nutrients and organic matter from the tropics into the North Atlantic subtropical gyre has been diagnosed to provide $0.047 \text{ mol m}^{-2} \text{ y}^{-1}$ and $0.92 \text{ mmol m}^{-2} \text{ y}^{-1}$ for TON and TOP (Mahaffey et al., 2004) and $0.005 \text{ mol m}^{-2} \text{ y}^{-1}$ and $0.14 \text{ mmol m}^{-2} \text{ y}^{-1}$ for nitrate and phosphate, respectively. These fluxes would cause positive TONxs and DINxs anomalies of $0.032 \text{ mol m}^{-2} \text{ y}^{-1}$ and $0.0028 \text{ mol m}^{-2} \text{ y}^{-1}$, respectively. Subtracting these “advective” positive anomalies in the upper 100m reduces the estimate of TNxs development by $\sim 20\%$ to $0.13 \pm 0.12 \text{ mol m}^{-2} \text{ y}^{-1}$ and the areal estimate to $8.72 \pm 8.11 \times 10^{11} \text{ mol y}^{-1}$.

4.2.2 One-end member mixing model – ventilation rates

To gain confidence in the above areal estimate and bypass our inability to accurately determine the TONxs turnover in the near-surface waters (pCFC-12 age < 1 yrs) where pCFC age measurements are associated with a large uncertainties, the total nitrogen accumulation rate has also been estimated from the independently estimated ventilation rates of the North Atlantic water masses. A similar approach has recently been used by Hansell et al. (2007) to investigate the excess inorganic nitrogen accumulation (DINxs). For each datapoint, TNxs values (DINxs + TONxs) have been corrected for their preformed concentrations and multiplied by the ventilation rate of the corresponding density class taken from Qiu and Huang (1995) (Table 2).

If TNxs passively accumulates along the gyre circulation on each isopycnal surface one would expect maximum concentrations to occur near the western boundary with increased ageing of the water as shown in the cartoon Fig. 9. This can be observed

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for DINxs, on the density range $26 < \sigma_\theta < 26.6$, (Figs. 10, 11) and only on isopycnals $\sigma_\theta < 26.6$ for TONxs (Fig. 11). On isopycnals $\sigma_\theta > 26.6$ mixing with low preformed DINxs of southern Atlantic water masses can possibly explain DINxs patterns west of 60° W. On the intermediate and surface layers TONxs accumulation is also affected by “local” processes which have time scales shorter than the gyre circulation (Figs. 10, 11).

The annual accumulation of N in the study area has been estimated from the concentration range of TNxs at the ventilation site and the site at the end of the gyre circulation pattern (as in Fig. 9) (maximum) value in Table 2, section average values are shown for comparison. However, we acknowledge that mixing with other water masses with different preformed TNxs values can lead to deviations in the TNxs gradient, therefore more than one end-member could improve the estimates of the mixing model (see below). Also, the variability due to shorter timescales (than the timescale of gyre circulation) is not resolved by this method.

Summing up the contribution of all isopycnals (Table 2), the annual accumulation of TNxs is $9.38 \pm 4.18 \times 10^{11} \text{ mol y}^{-1}$. At least 40% of this is due to organic nitrogen ($3.70 \pm 3.26 \times 10^{11} \text{ mol y}^{-1}$). Low surface ventilation rates limit the importance of TONxs development as compared to the estimate obtained by the vertical integration method. Overall, the two areal estimates (from the vertical integration and the one end-member mixing using literature ventilation rates) are in relatively good agreement. Despite the large uncertainties this gives us some confidence regarding the size of annual production of total excess nitrogen in the North Atlantic. This areal estimate is up to 1.6 times larger than the inorganic estimate reported by Hansell et al. (2007) and would lie at the lower end of their range ($6.1 - 8.3 \times 10^{11} \text{ mol y}^{-1}$) if only DINxs accumulation rate ($5.68 \pm 0.82 \times 10^{11} \text{ mol y}^{-1}$) was considered.

4.2.3 Two end member isopycnal mixing model

We now use an isopycnal two end-member mixing model, following H04 to estimate rates of development of DINex and TONex on specific isopycnal layers. The basic assumption is that transport occurs along isopycnal surfaces and that the mixing on any

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



isopycnal surface can be described by a two end-member mixing model. As a water parcel is transported away from its original location it loses its original properties (one end-member mixing model) and mixes with other water masses (two end-member mixing model). This mixing can be monitored and quantified using a conservative tracer.

5 The production or consumption of a non-conservative property can be quantified as the difference between the measured concentration and the value of the property expected if only linear mixing occurred (preformed value). This technique was used to calculate the non-conservative development of N^* (GS97) and DINxs (H04) on specific isopycnal surfaces, allowing for the effect of elevated N/P ratios of organic matter released by N_2 fixers.

10 In the North Atlantic the depths of maximum DINxs and N^* development coincide with the $\sigma_\theta=26.2\text{--}27.2\text{ kg m}^{-3}$ isopycnal surfaces (Fig. 5). These potential density surfaces represent the subtropical and subpolar mode waters respectively.

15 The distribution of potential temperature, pCFC-12 ages, DINxs and TONxs on three isopycnal surfaces is used to infer the rates of DINxs and TONxs production. The two end member water masses used for the calculation were the Northern Component (NC) and the Southern Component (SC) described in H04. The end member reference values for potential temperature, DINxs and pCFC-12 ages are indicated in Table 1. Waters entering these isopycnal surfaces from the north and from the south have low preformed values of N^* and DINxs (H04) (Table 1). The subtropical gyre imports low TONxs waters from the South Atlantic (Torres-Valdes, personal communication) and positive TONxs from the north where ventilation of the $\sigma_\theta=25\text{--}27$ isopycnals occur (Table 1).

25 Preformed values were calculated using potential temperature as a conservative tracer on the $\sigma_\theta=26, 26.5$ and $27\text{ (kgm}^{-3}\text{)}$ isopycnal layers following Takahashi et al. (1985):

$$fa = \frac{(\theta b - \theta m)}{(\theta b - \theta a)}; \quad fa + fb = 1 \quad (3)$$

where fa and fb are the fractions of the two end members, a and b , in the mixed water

region, θ_a and θ_b are the potential temperatures of the two end members and θ_m is the measured potential temperature. The preformed concentrations of DINxs were obtained for a two end member mixing model as follows:

$$\text{DINxs}_{\text{preformed}} = fa \bullet \text{DINxs}_a + fb \bullet \text{DINxs}_b \quad (4)$$

where DINxs_a and DINxs_b are the preformed values of the DINxs in the a and b components, respectively. The same approach has been used to obtain preformed TONxs concentrations. The difference between preformed DINxs and the measured value of DINxs accounts for the non-conservative development of DINxs.

Rates for DINxs and TONxs development were computed at the western and eastern extremes of the 24.5° N section (24.5° N, 65.4° W and 24.7° N, 22.8° W) to coincide with the beginning and the end of the gyre circulation; these sites also match the analyses made by H04. Results of the preformed values of DINxs and TONex are reported in Table 3. Measured DINxs and TONxs at the two locations are reported in Table 4. Rates of change of DINxs and TONxs were calculated from the differences between the respective preformed and measured values over the time since the water parcels left its end member location (pCFC-12 age difference) (Table 5).

On the eastern side of the gyre, the isopycnal surface $\sigma_\theta=26$ broadly coincided with the northern component so no measurable ageing occurred since the water mass left the end member location. The $\sigma_\theta=26$ surface was deep enough (163 m) to experience both DINxs and TONxs development on the western side. The accumulation rates of DINxs on the $\sigma_\theta=26.5$ surface in the two regions are comparable, indicating that a two end-member model is a good approximation of water mass mixing on this isopycnal. From this analysis TONxs appears to decrease on the $\sigma_\theta=26.5$ isopycnal possibly contributing about 60% to the observed DINxs build up. The accumulation rate of TONxs appears to be influenced by local processes (Fig. 10), which have time scales shorter than the gyre circulation. These events are not accounted for with this two end-member approach. On the deepest surface $\sigma_\theta=27$, the positive DINxs anomaly vanished at the western end but was still visible on the eastern side. This is consistent with the spatial

**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



extension of DINxs reported by H04. On the contrary, TONxs accumulation shows the largest rates on the western side.

The contribution of the organic N fraction to the total N excess is ~60% on the shallowest isopycnal, zero on the intermediate one and it ranges from 30–100% on the deepest isopycnal. The rates of maximum DINxs accumulation on the three isopycnals amount to $0.47 \pm 0.48 \text{ mmol m}^{-3} \text{ y}^{-1}$. If the contribution of the $\sigma_{\theta}=27$ isopycnal, with its relatively small DINxs accumulation and large age-associated errors is excluded then this estimate becomes $0.46 \pm 0.27 \text{ mmol m}^{-3} \text{ y}^{-1}$. This estimate is lower but consistent with those reported by H04 of, $0.56 \pm 0.40 \text{ mmol m}^{-3} \text{ y}^{-1}$. Adding the contribution of maximum TONxs accumulation increases to the total N excess accumulation to $0.93 \pm 0.46 \text{ mmol m}^{-3} \text{ y}^{-1}$ and implies an average contribution of TONxs to TNxs of ~50%.

It is possible to estimate the areal N excess from the three isopycnal volumes reported in H04 (Table 6). For the area extending from 15° N to 25° N and 25° W to 75° W , the net N excess (TNxs) amounts to $1.28 \pm 1.10 \times 10^{11} \text{ mol y}^{-1}$ while the inorganic nitrogen excess is $0.68 \pm 0.35 \times 10^{11} \text{ mol y}^{-1}$. In this estimate, given the large uncertainty of DINxs on $\sigma_{\theta}=27$ the contribution of the last isopycnal has been ignored (Table 6).

The large uncertainties are the outcome of the propagation of the uncertainties of the preformed and the measured DINxs, TONxs and the pCFC-age values. As in H04, this estimate can be extrapolated for all the isopycnals and can be compared with the other areal estimates reported by this study (Table 7). The two end-member mixing model yields the lowest areal rates of TNxs production of the three methods used. It should be noted however that, given the difficulty to constrain pCFC-12 age gradients, the potential density surfaces $\sigma_{\theta} < 25.75$ have been omitted from this analysis and the development of TONxs on shallow layers has not been accounted for in the two end-member model calculations. The usage of a two end-member mixing model has not improved the uncertainty estimate relative to the other two methods, which may be due to an inaccurate choice of the southern component end-member or to the necessity to use more than two end-members. Despite the large uncertainties and the

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



possibility of redefining the end member choice with more data, our data indicate that the total excess N accumulation, which includes the contribution of TONxs, is about ~50% larger than the corresponding estimate of DINxs accumulation rate (Table 7) irrespective of the method used. We now consider the likely source of this excess nitrogen and the implications of this result on the nitrogen budget of the subtropical North Atlantic.

4.3 Sources of excess nitrogen

Only non Redfieldian processes which alter the absolute amounts of N and P can affect TNxs. To produce the positive TNxs signal observed in the North Atlantic, these processes must selectively introduce N but not P.

Aerosol is known to contain much larger concentrations of nitrate than phosphate (Baker et al., 2003). Estimates of North Atlantic atmospheric deposition range from 0.017 to 0.021 mol Nm⁻² y⁻¹ (Prospero et al., 1996), with areal estimates south of 40° N amounting to 3×10¹¹ mol Ny⁻¹ (Duce et al., 1996). Given the high DIN:DIP (>1000) measured in the North Atlantic aerosol at similar latitudes (Baker et al., 2003) this deposition would likely induce a corresponding DINxs anomaly of 2.9×10¹¹ mol Ny⁻¹, i.e. 24 to 66% of the total N accumulation rate estimated in this study. These estimates do not include the organic nitrogen deposition, which has been reported to represent 35% of the total nitrogen atmospheric input (Cornell et al., 2003). However, the uncertainty in the atmospheric organic phosphorus deposition make a robust estimate of the contribution of atmospheric deposition to the observed build up of TONxs difficult. Here we acknowledge the possibility that it might be a non-trivial source.

The remaining TNxs signal must come from the selective production of N as PON, and/or DON and/or DIN. As processes that selectively introduce DIN, other than atmospheric deposition, are not known it is reasonable to think that the excess of N originates from the selective introduction of either PON or DON.

It has been suggested (Hansell et al., 2007) that *Synechococcus* and *Prochlorococcus*, which have an elevated N:P (Heldal et al., 2003) have the potential to contribute

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to the TNxs signal observed. Here we attempt to estimate the potential contribution of the most abundant of the two species, *Prochlorococcus*, to the accumulation of TNxs. From the reported estimates of cell abundance (10^5 cell ml⁻¹), doubling times (0.5 d⁻¹), N cell content (~ 9.4 fg N cell⁻¹) and N:P (21–33) (Heldal et al., 2003) the estimated excess N addition rate would range from 0.19 to 0.45×10^{11} mol N y⁻¹. This amount of excess N is, again, not trivial but is lower than the error reported in our areal estimates. If we assume that the contribution of *Synechococcus* is of the same order of magnitude as the contribution of *Prochlorococcus* to TNxs estimates then they can be excluded as major source of TNxs in the North Atlantic.

The other known candidate responsible for introducing PON and DON, is N₂ fixation. Newly fixed nitrogen enters the marine PON pool as diazotrophic biomass, with a high N:P (LaRoche and Breitbarth, 2005), and evidence supports the release of newly fixed N as DON (Capone et al., 1994; Glibert and Bronk, 1994). Contrary to these observations, the lack of seasonal variability of bulk DON and its stable and enriched isotopic composition measured in the North Atlantic (Knapp et al., 2005; Meador et al., 2007), suggest that DON derived from N₂ fixation does not accumulate in the bulk DON pool. This result has led to hypothesize that surface DON does not originate from N₂ fixers (Hansell et al., 2007). However, recent evidence of isotopically depleted proteins, high molecular weight (HMW) DON derived from *Trichodesmium* cultures and bacterial nucleic acids (Meador et al., 2007) supports the existence of a small and rapidly cycling HMW DON fraction derived from N₂ fixation. If this fraction of fresh DON is channelled through the microbial heterotrophic and autotrophic communities (size class $0.2 \mu\text{m}$ – $0.5 \mu\text{m}$) (Meador, 2007) it will not accumulate in surface waters. Instead, picoplankton grazers can provide a mechanism by which diazotrophic DON is channelled to higher trophic levels. Sloppy feeding and excretion could release isotopically enriched DON back into the water. Therefore, although this mechanistic pathway of diazotrophic DON transfer to higher trophic levels awaits testing, given the low TONxs waters imported from the South Atlantic, N₂ fixation seems the only possible explanation for the origin of the high TONxs observed in the North Atlantic. Subtracting the

**Total nitrogen excess
in the North Atlantic**A. Landolfi et al.

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

contribution of atmospheric deposition from the net TNxs accumulation estimated from the ventilation method and allowing for the diazotrophic N:P ratio of 40:1, we derive an areal N₂ fixation in the order of $10.2 \pm 6.9 \times 10^{11} \text{ mol N y}^{-1}$. This estimate is larger than the recent geochemical estimates of $4.3 \times 10^{11} \text{ mol N y}^{-1}$ by Hansell et al. (2007), but it is consistent with direct *Trichodesmium* N₂ fixation rates from the North Atlantic (16 × 10¹¹ mol N y⁻¹, Capone et al., 2005). The discrepancy with the recent Hansell et al. (2007) paper is not unexpected given the important contribution of TONxs accumulation to total N excess, which has been neglected previously.

5 Conclusions

The new geochemical tracer TNxs incorporates the contribution of organic nutrients to assess the stoichiometric anomalies of the marine N and P pools. This tracer indicates that the inclusion of organic nutrients significantly increases the estimate of excess nitrogen inputs into the North Atlantic subtropical gyre by about 50. Given that the waters from the South Atlantic transferred into the North Atlantic have low TNxs values, the build up of this TNxs signal must be occurring in the North Atlantic. The two most likely processes responsible for this signal are atmospheric deposition and N₂ fixation. The DINxs signal due to atmospheric deposition has been determined with reasonable accuracy; however the atmospheric organic nitrogen excess deposition to the ocean is unclear and it may be that the remainder of the TNxs signal is associated with this. Until the atmospheric deposition of the organic nutrient fraction TONxs is also defined more accurately, the best possible candidate to make up for the rest of the TNxs observed is N₂ fixation. Consequently an upward estimate of N₂ fixation emerges; this estimate can reconcile the recent geochemical and direct N₂ fixation estimates.

Acknowledgements. We thank R. A. Fine for providing CFC data and S. Torres-Valdes for making the nutrient AMT data available to us. Thanks to W. Koeve for his comments on the manuscript.

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

- Alvarez-Salgado, X. A. and Miller, A. E. J.: Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: Conditions for precise shipboard measurements, *Mar. Chem.*, 62, 325–333, 1998.
- 5 Baker, A. R., Kelly, S. D., Biswas, K. F., Witt, M., and Jickells, T. D.: Atmospheric deposition of nutrients to the atlantic ocean, *Geophys. Res. Lett.*, 30(24), 2296, doi:10.1029/2003GL018518, 2003.
- Bronk, D. A., Lomas, M. W., Glibert, P. M., Schukert, K. J., and Sanderson, M. P.: Total dissolved nitrogen analysis: Comparisons between the persulfate, uv and high temperature oxidation methods, *Mar. Chem.*, 69, 163–178, 2000.
- 10 Capone, D. G., Ferrier, M. D., and Carpenter, E. J.: Amino-acid cycling in colonies of the planktonic marine cyanobacterium *trichodesmium-thiebautii*, *Appl. Environ. Microb.*, 60, 3989–3995, 1994.
- 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:2010.1029/2004GB002331, 2005.
- 15 Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., and Duce, R. A.: Organic nitrogen deposition on land and coastal environments: A review of methods and data, *Atmos. Environ.*, 37, 2173–2191, 2003.
- 20 Deutsch, C., Gruber, N., Key, R. M., Sarmiento, J. L., and Ganachaud, A.: Denitrification and n_2 fixation in the pacific ocean, *Global Biogeochem. Cy.*, 15, 483–506, 2001.
- Dietze, H., Oschlies, A., and Kahler, P.: Internal-wave-induced and double-diffusive nutrient fluxes to the nutrient-consuming surface layer in the oligotrophic subtropical north atlantic, *Ocean Dynam.*, 54(1), doi:10.1007/510236-003-0060-9, 2004.
- 25 Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, L. L., Buat-Menard, P., Hicks, B. B., Miller, J. M., Prospero, J. M., Arimoto, R., Church, T. M., Ellis, W., Galloway, J. N., Hansen, L., Jickells, T. D., Knap, A. H., Reinhardt, K. H., Schneider, B., Soudine, A., Tokos, J. J., Tsunogai, S., Wollast, R., and Zhou, M.: The atmospheric input of trace species to the world ocean, *Global Biogeochem. Cy.*, 5, 193–259, 1991.
- 30 Emerson, S., Mecking, S., and Abell, J.: The biological pump in the subtropical north pacific ocean: Nutrient sources, redfield ratios, and recent changes, *Global Biogeochem. Cy.*, 15,

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



535–554, 2001.

Glibert, P. M. and Bronk, D. A.: Release of dissolved organic nitrogen by marine diazotrophic cyanobacteria, *trichodesmium* spp., *Appl. Environ. Microb.*, 60, 3996–4000, 1994.

Gruber, N. and Sarmiento, J. L.: Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cy.*, 11, 235–266, 1997.

Hansell, D. A., Bates, N. R., and Olson, D. B.: Excess nitrate and nitrogen fixation in the north atlantic ocean, *Mar. Chem.*, 84, 243–265, 2004.

Hansell, D. A. and Carlson, C. A.: Biogeochemistry of total organic carbon and nitrogen in the sargasso sea: Control by convective overturn, *Deep-Sea Res. Pt. II*, 48, 1649–1667, 2001.

Hansell, D. A., Olson, D. B., Denter, F., and Zamora, L. M.: Assessment of excess nitrate developmnet in the subtropical north atlantic, *Mar. Chem.*, 106, 562–579, doi:10.1016/j.marchem.20070605, 2007.

Heldal, M., Scanlan, D. J., Norland, S., Thingstad, F., and Mann, N. H.: Elemental composition of single cells of various strains of marine *prochlorococcus* and *synechococcus* using x-ray microanalysis, *Limnol. Oceanogr.*, 48, 1732–1743, 2003.

Jackson, G. A. and Williams, P. M.: Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling, *Deep-Sea Res.*, 32, 223–235, 1985.

Jenkins, W. J. and Goldman, J. C.: Seasonal oxygen cycling and primary production in the sargasso sea, *J. Mar. Res.*, 43, 465–491, 1985.

Jenkins, W. J.: Nitrate flux into the euphotic zone near bermuda, *Nature*, 331, 521–523, 1988.

Karl, D., Michaels, A., Bergman, B., Capone, D., Carpenter, E., Letelier, R., Lipschultz, F., Paerl, H., Sigman, D., and Stal, L.: Dinitrogen fixation in the world's oceans, *Biogeochemistry*, 57, 47–98, 2002.

Karl, D. M., Letelier, R., Hebel, D. V., Bird, D. F., and Winn, C. D.: *Trichodesmium* blooms and new production in the north pacific gyre, in: *Marine pelagic cyanobacteria: Trichodesmium and other diazotrophs*, edited by: Carpenter, E. J., Kluwer Academic Publishers, Dordrecht, 219–237, 1992.

Kirkwood, D. S., Aminot, A., and Carlberg, S. R.: The 1994 quasimeme laboratory performance study: Nutrients in seawater and standard solutions, *Mar. Pollut. Bull.*, 32, 640–645, 1996.

Knapp, A. N., Sigman, D. M., and Lipschultz, F.: N isotopic composition of dissolved organic nitrogen and nitrate at the bermuda atlantic time-series study site, *Global Biogeochem. Cy.*, 19, GB1018, doi:10.1029/2004GB002320, 2005.

Landolfi, A.: The importance of dissolved organic nutrients in the biogeochemistry of olig-

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



otrophic gyres, PhD thesis, National Oceanography Centre, University of Southampton, Southampton, 2005.

LaRoche, J. and Breitbarth, E.: Importance of the diazotrophs as a source of new nitrogen in the ocean, *J. Sea Res.*, 53, 67–91, 2005.

5 Mahaffey, C., Williams, R. G., Wolff, G. A., and Anderson, W. T.: Physical supply of nitrogen to phytoplankton in the atlantic ocean, *Global Biogeochem. Cy.*, 18, GB1034, doi:10.1029/200368002129, 2004.

McGillicuddy, D. J., Robinson, A. R., Siegel, D. A., Jannasch, H. W., Johnson, R., Dickeys, T., McNeil, J., Michaels, A. F., and Knap, A. H.: Influence of mesoscale eddies on new production in the sargasso sea, *Nature*, 394, 263–266, 1998.

10 Meador, T. B., Aluwihare L. I., and Mahaffey, C.: Isotopic heterogeneity and cycling of organic nitrogen in the oligotrophic ocean, *Limnol. Oceanogr.*, 52, 934–947, 2007.

Michaels, A. F., Olson, D., Sarmiento, J. L., Ammerman, J. W., Fanning, K., Jahnke, R., Knap, A. H., Lipschultz, F., and Prospero, J. M.: Inputs, losses and transformations of nitrogen and phosphorus in the pelagic north atlantic ocean, *Biogeochemistry*, 35, 181–226, 1996.

15 Mulholland, M. R., Bronk, D. A., and Capone, D. G.: Dinitrogen fixation and release of ammonium and dissolved organic nitrogen by trichodesmium ims101, *Aquat. Microb. Ecol.*, 37, 85–94, 2004.

Prospero, J. M., Barrett, K., Church, T., Dentener, F., Duce, R. A., Galloway, J. N., Levy, H., Moody, J., and Quinn, P.: Atmospheric deposition of nutrients to the north atlantic basin, *Biogeochemistry*, 35, 27–73, 1996.

20 Qiu, B. and Huang, R. X.: Ventilation of the north atlantic and north pacific: Subduction versus obduction, *J. Phys. Oceanogr.*, 25, 2374–2390, 1995.

Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the composition of sea water, in: *The sea*, edited by: Ed, M. N. H., 26–77, 1963.

25 Reynolds, S. E., Mather, R. L., Wolff, G. A., Williams, R. G., Landolfi, A., Sanders, R., and Woodward, E. M. S.: How widespread and important is n_2 fixation in the atlantic ocean?, *Global Biogeochem. Cycles*, 21, GB4015, doi:10.1029/2006GB002886, 2007.

Sanders, R. and Jickells, T.: Total organic nutrients in drake passage, *Deep-Sea Res. Pt I*, 47, 997–1014, 2000.

30 Takahashi, T., Broecker, W. S., and Langer, S.: Redfield ratio based on chemical data from isopycnal surfaces, *J. Geophys. Res.*, 90, 6907–6924, 1985.

BGD

5, 685–724, 2008

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 1. Northern and Southern Component (NC, SC) end-member values of potential temperature, CFC-12 age DINxs and TONxs on selected isopycnal surfaces. End-member values have been estimated from the Atlantic Meridional Transect (AMT) 14 cruise. (SC: average of data points deeper than 50 m from stations 0–10° S, 24.99° W; NC: $\sigma_{\theta}26=18.8^{\circ}$ N, 32.3° W at 50 m; $\sigma_{\theta}26.5=29.5^{\circ}$ N, 35.2° W at 130 m; $\sigma_{\theta}27=42^{\circ}$ N, 18.8° W at 70 m (Torres-Valdes, personal communication).

Density kg m ⁻³	Potential Temperature °C	pCFC-12 AGE (years)	DINxs mmol m ⁻³	TONxs mmol m ⁻³
NC				
26 (25.75–26.25)	21.4	1.3	–0.43	2.2
26.5(26.25–26.75)	18	2.7	–0.25	2.73
27 (26.75–27.25)	12.7	0.3	0.52	2.86
SC				
26 (25.75–26.25)	17.8	11.9	–0.43	–0.96
26.5(26.25–26.75)	14	13.9	–0.43	–1.24
27 (26.75–27.25)	8.7	30	1.17	–1.9

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 2. Average and maximum DINxs and TONxs development in the thermocline and in surface waters. Ventilation rates have been taken from Qiu and Huang (1995).

Density	Ventilation (Sv)	Mean DINxs $10^{11} \text{ mol Ny}^{-1}$	Max DINxs $10^{11} \text{ mol Ny}^{-1}$	Mean TONxs $10^{11} \text{ mol Ny}^{-1}$	Max TONxs $10^{11} \text{ mol Ny}^{-1}$
<26	1.5	0.02±0.013	0.15±0.16	0.88±0.56	0.87±0.55
26–26.2	2.2	0.43±0.28	0.77±0.10	0.97±0.61	1.09±0.68
26.2–26.4	4	1.66±0.59	1.94±0.35	1.51±0.96	1.98±1.27
26.4–26.6	3.1	1.30±0.46	1.59±0.10	0.50±1.05	0.77±0.24
26.6–26.8	2.3	-0.02±0.29	0.68±0.04	-0.05±0.08	-0.40±0.24
26.8–27	1.4	0.08±0.37	0.38±0.05	-0.05±0.06	-0.30±0.27
27–27.2	0.6	-0.03±0.22	0.13±0.01	-0.02±0.03	-0.30±0.01
Total		3.44±0.97	5.68±0.82	2.53±2.0	3.70±3.26

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 3. Fraction of SC (F.SO) and NC (F.NO) and preformed DINxs, TONxs and pCFC-12 ages (P.DINxs, P.TONxs and P.CFC-12) along selected isopycnals at western (W) and Eastern (E) locations of the Subtropical gyres.

ST	σ kgm ⁻³	F.SO	F.NO	P.DINxs mmol m ⁻³	P.TONxs mmol m ⁻³	P.CFC age
W	26.0	0.15	0.85±0.01	-0.43±0.0	1.20±0.08	2.8±0.88
W	26.5	0.07	0.93±0.01	-0.26±0.01	2.43±0.05	3.53±0.13
W	27.0	0.42	0.54±0.02	1.06±0.02	0.69±0.09	11.60±0.53
E	26.0	0.00	100±0.03	-0.43±0.0	2.21±0.22	–
E	26.5	0.22	0.78±0.02	-0.29±0.01	1.86±0.08	5.17±0.23
E	27.0	0.13	0.87±0.17	0.68±0.20	2.23±0.79	8.07±0.52

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 4. Measured DINxs and TONxs along selected isopycnal surfaces at station 50 (West) and 108 (East).

ST	$\sigma\theta$ kgm^{-3}	Depth (m)	M. CFC-12 age (y)	M.DINxs mmol m^{-3}	M.TONxs mmol m^{-3}
W	26.0	163	6.13±1.37	0.64±0.034	2.74±0.30
W	26.5	360	14.78±0.61	0.96±0.12	1.63±0.06
W	27.0	700	30.79±1.4	-0.80±0.068	3.62±0.49
E	26.0	20	-	-0.176±0.015	2.74±0.22
E	26.5	200	11.23±0.71	0.92±0.37	1.51±0.08
E	27.0	500	24.88±0.46	0.7±0.02	2.25±0.19

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 5. Estimated rates of Nitrogen accumulation on selected isopycnal layers after correction for mixing between end members. Uncertainties have been calculated with the standard equation of the error propagation of pCFC-age, preformed and measured DINxs and TONxs.

ST	σ kgm ⁻³	D. CFC age (y)	Prod.R DINxs mmol m ⁻³ y ⁻¹	Prod.R TONxs mmol m ⁻³ y ⁻¹	Prod R. TNxs mmol m ⁻³ y ⁻¹
W	26.0	3.25±0.81	0.33±0.25	0.47±0.32	0.80±0.41
W	26.5	11.25±0.31	0.11±0.11	-0.07±0.1	0.04±0.14
W	27.0	19.19±0.75	-0.10±0.16	0.15±0.18	0.06±0.18
E	26.0	–	–	–	–
E	26.5	6.055±0.37	0.13±0.1	-0.06±0.13	0.07±0.16
E	27.0	16.31±0.35	0.002±0.40	0.001±0.5	0.003±0.65

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 6. Volume of isopycnals as reported by H04 and associated TNxs and DINxs accumulation rate (mol N y^{-1}). DINxs accumulation rate from H04 are reported for comparison.

Isopycnal	Volume 10^{14} m^3	TNxs Areal Rate $10^{11} \text{ mol N y}^{-1}$	DINxs Areal rate $10^{11} \text{ mol N y}^{-1}$	H04 DINxs Areal rate $10^{11} \text{ mol N y}^{-1}$
26	1.0	0.82 ± 0.40	0.33 ± 0.25	0.43 ± 0.26
26.5	2.6	0.19 ± 0.34	0.34 ± 0.24	0.24 ± 0.30
27	5.1	0.28 ± 0.93	–	0.20 ± 0.13
Total		1.28 ± 1.08	0.68 ± 0.35	0.87 ± 0.42

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

Table 7. Estimates of TNxs and DINxs accumulation rate (mol N y^{-1}) using different methods within this study. Estimates of DINxs accumulation rate from H04 (^) and H07 (*) are reported for comparison.

Method	TNxs rate	TNxs Areal Rate $10^{11} \text{ mol N y}^{-1}$	DINxs Areal rate $10^{11} \text{ mol N y}^{-1}$	DINxs Areal rate $10^{11} \text{ mol N y}^{-1}$
Vertical Integration	$0.13 \pm 0.12 \text{ mol m}^{-2} \text{ y}^{-1}$	8.72 ± 8.11	0–3.4	–
Ventilation Rate	–	9.38 ± 4.18	5.68 ± 0.82	$6.1\text{--}8.3^*$
Two end-member mixing	$0.93 \pm 0.46 \text{ mmol m}^{-3} \text{ y}^{-1}$	4.40 ± 3.71	2.35 ± 1.21	$2.98 \pm 1.43^{\wedge}$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.

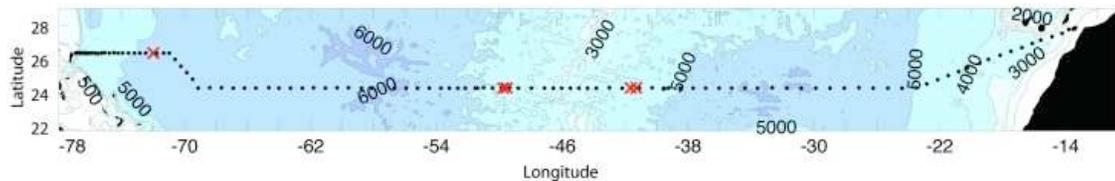


Fig. 1. Stations occupied during the cruise D279 in April–May 2004.

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

Total nitrogen excess
in the North Atlantic

A. Landolfi et al.

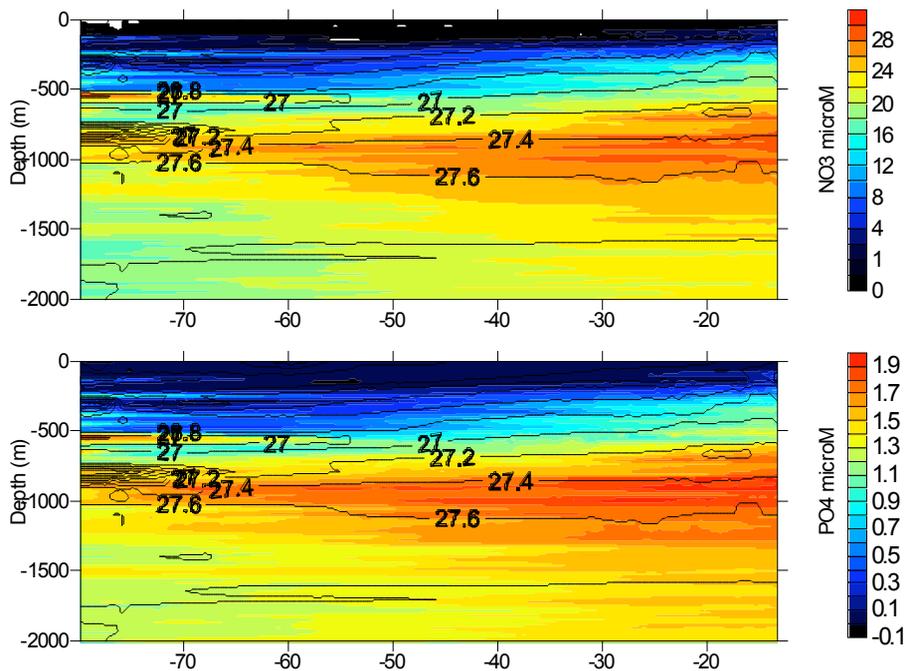


Fig. 2. Zonal (24.5° N) distribution of nitrate **(a)** and phosphate **(b)** concentrations (m mol m^{-3}) in the North Atlantic.

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

Total nitrogen excess in the North Atlantic

A. Landolfi et al.

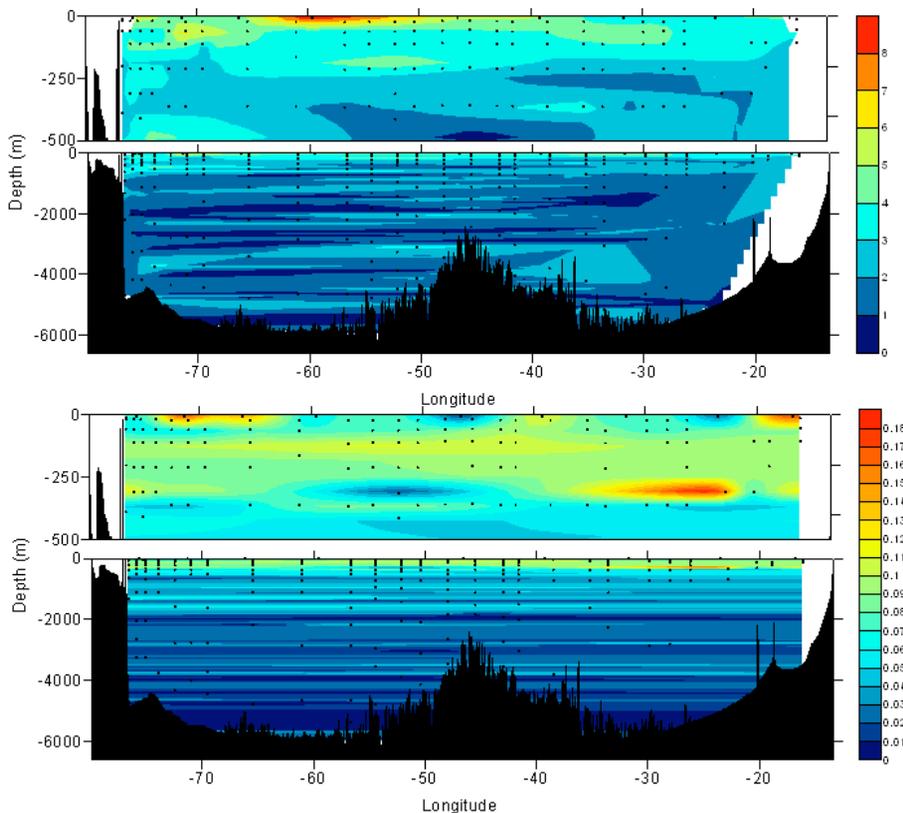


Fig. 3. Zonal (24.5° N) distribution of TON **(a)** and TOP **(b)** concentrations (mmol m^{-3}) in the North Atlantic.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

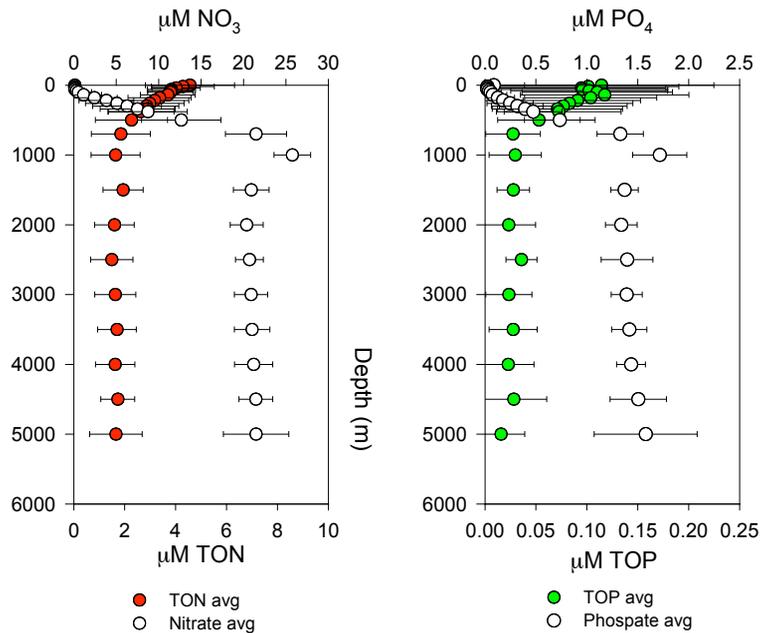


Fig. 4. Average vertical distribution of nitrate and TON (left) and phosphate and TOP (right) (mmol m^{-3}) in the North Atlantic at 24.5°N .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

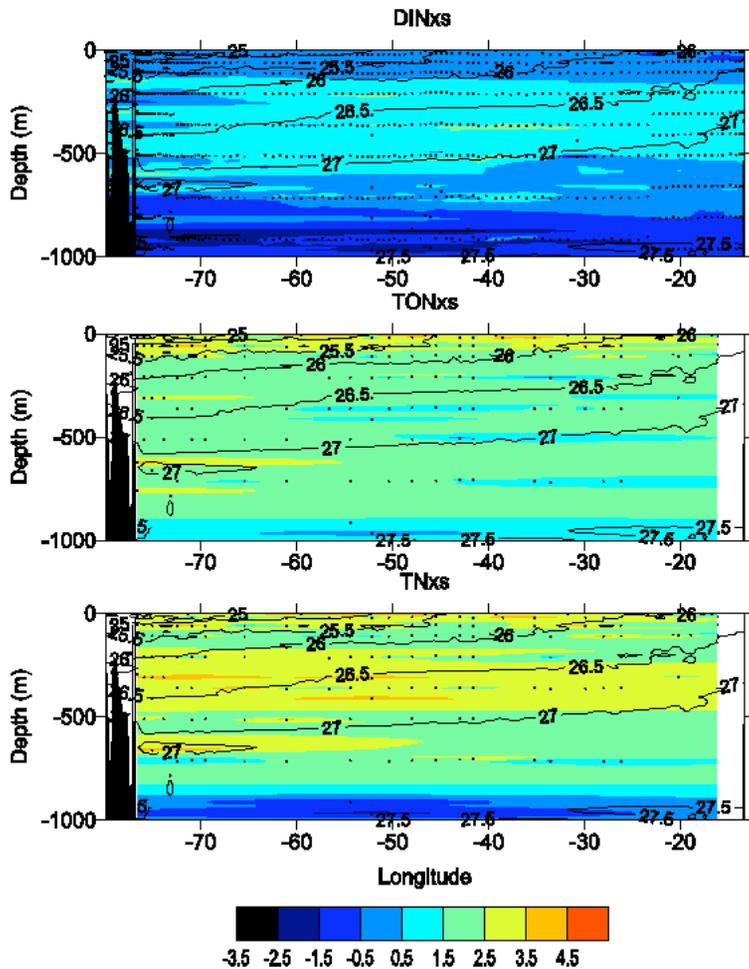


Fig. 5. Zonal (24.5° N) distribution of DINxs (a), TONxs (b) and TNxs (c) (m mol m^{-3}) in the North Atlantic.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

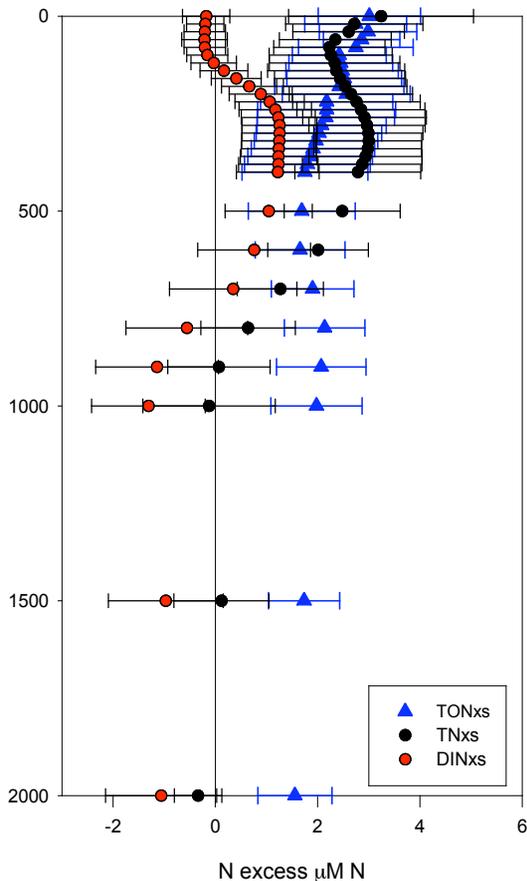


Fig. 6. Average vertical variation of DINxs, TONxs and TNxs (mmol m^{-3}) measured in the North Atlantic at 24.5°N . Error bars represent range bars.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

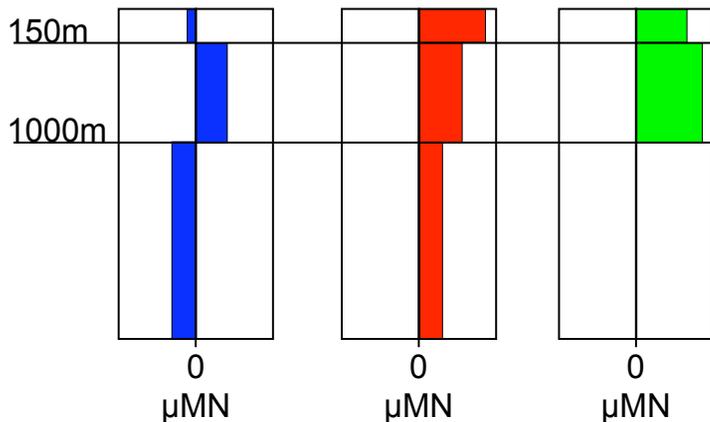
Printer-friendly Version

Interactive Discussion



**Total nitrogen excess
in the North Atlantic**

A. Landolfi et al.



- DINxs < 0:** Preferential TOP remineralization and NO₃ uptake
- DINxs > 0:** Preferential TON remineralization, PO₄ uptake, and N atmospheric deposition
- TONxs > 0:** Preferential TOP remineralization, TON production and TON atmospheric deposition
- TNxs > 0:** N excess (N₂ fixation, atmospheric deposition)
- TNxs = 0:** Redfield equilibrium between N and P

Fig. 7. Conceptual model of the partitioning and dynamics between the N and P pools.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

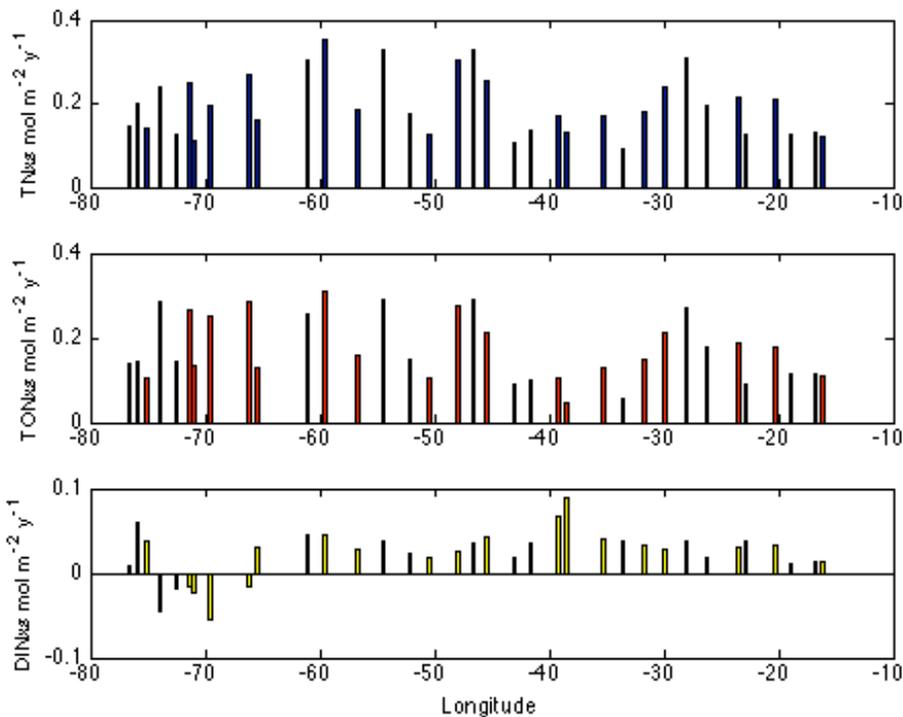


Fig. 8. Depth integrated (1000 m) development rates of TNxs, TONxs and DINxs ($\text{mol m}^{-2} \text{y}^{-1}$) across the North Atlantic at 24.5°N .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess
in the North Atlantic

A. Landolfi et al.

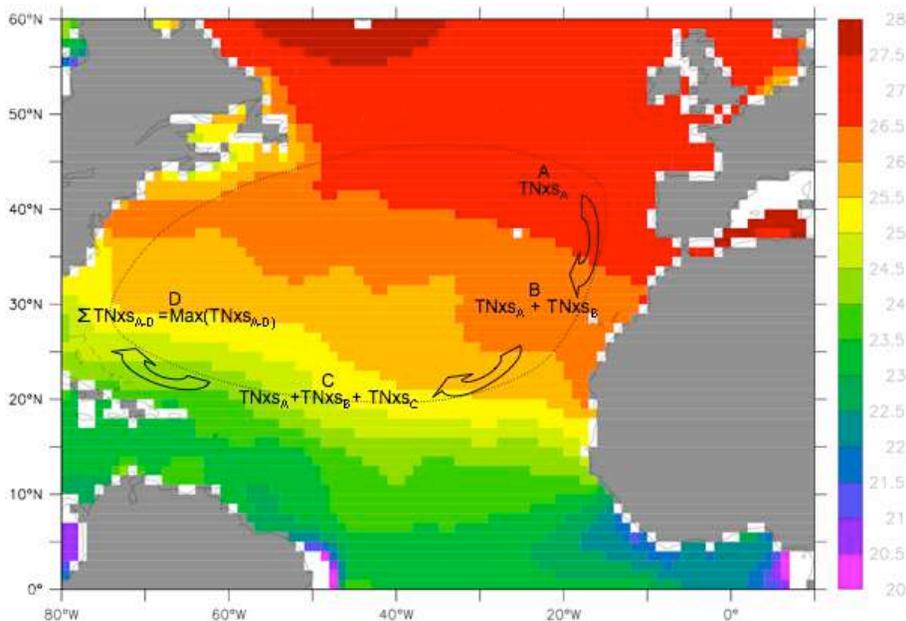


Fig. 9. Cartoon representing the built up of TNxs from the end member location following the gyre circulation pattern. Winter surface distribution of sigma theta from WOCE data is superimposed. Point A represents the end member location where the outcropping of $\sigma_\theta=26.5\text{--}27$ occurs and TNxs_A represents the end member preformed TNxs. At point B the TNxs will be given by the sum of the TNxs developed during the trajectory from point A to point B (TNxs_B) on that given isopycnal and the preformed TNxs_A . At the end of the gyre circulation pattern, point D, the accumulated TNxs corresponds to the sum of TNxs developed among each step (A, B, C, D) and equals the maximum TNxs developed on that isopycnal. This general scheme is valid for gyre circulation timescales but remains insensitive to short time scale built up and remineralization of TNxs.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess
in the North Atlantic

A. Landolfi et al.

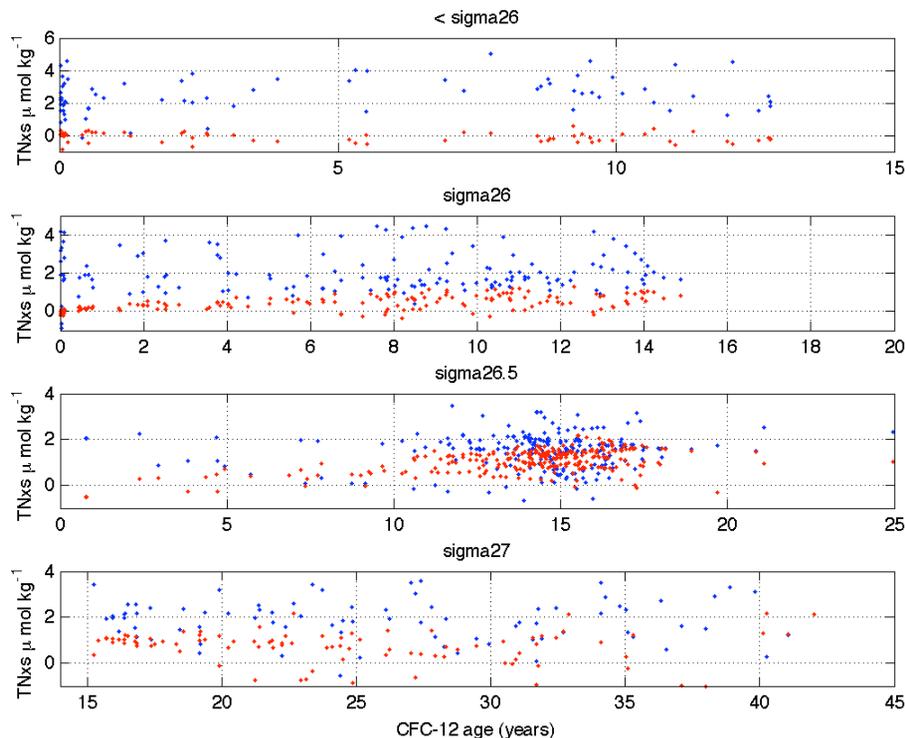


Fig. 10. Covariations of DINxs (blue), TONxs (red) and pCFC-12 on density intervals $\sigma_{\theta} < 26.75$ (a), $25.75 < \sigma_{\theta} < 26.25$ (b), $26.25 < \sigma_{\theta} < 26.75$ (c), $26.75 < \sigma_{\theta} < 27.25$ (d), from vertically interpolated data. Please note that DINxs, TONxs and TNxs have not been corrected for preformed concentrations and therefore Δ DINxs: Δ age, Δ TONxs: Δ age, and Δ TNxs: Δ age do not represent the real gradients.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I ◀

▶ I

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Total nitrogen excess in the North Atlantic

A. Landolfi et al.

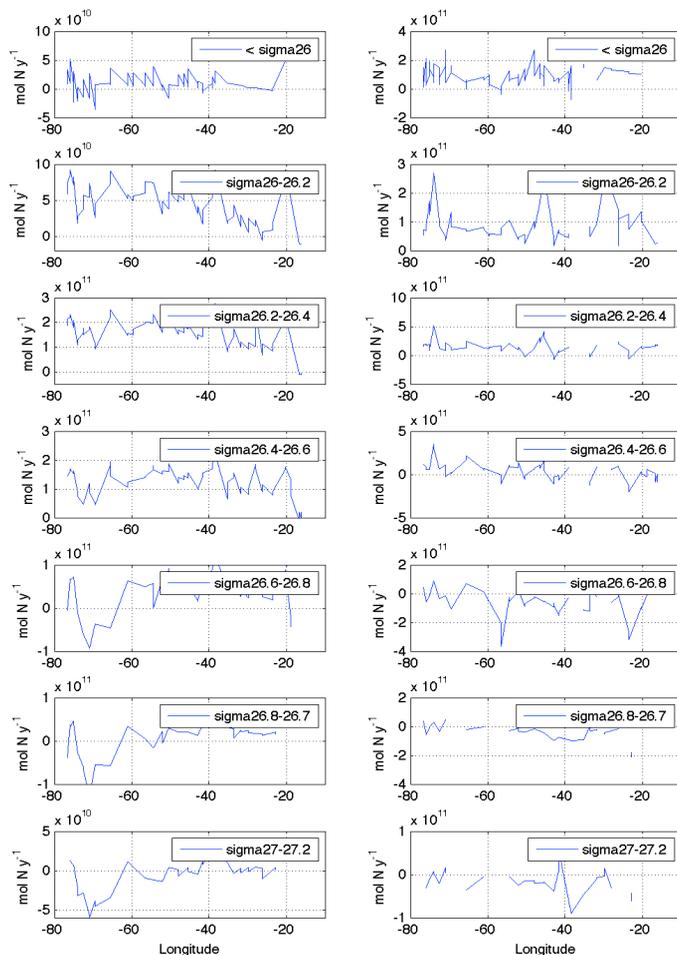


Fig. 11. Spatial variability of the areal annual DINxs (left) and TONxs (right) development (mol N y^{-1}) on specific isopycnal layers calculated using ventilation rates from Qiu and Huang (1995).

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