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Temporal variability of excess nitrate in the subtropical mode water of the North Atlantic Ocean

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Abstract

A dichotomy exists between rates of nitrogen fixation directly measured by biological techniques, and rates inferred from the geochemical distributions of excess nitrate within the thermocline of the North Atlantic Ocean. Part of the dichotomy relates to the temporal and spatial uncoupling between the event (i.e., nitrogen fixation by diazotrophs) and signal (i.e., excess nitrate (DIN_{xs}) in the thermocline), as well as the interannual variability of both. Here, temporal variability of excess nitrate in the subtropical mode water (STMW) of the North Atlantic Ocean is evaluated for the 1988–2001 period. The excess nitrate signal has a maximum in this water mass, and it is by far the largest volumetric component of thermocline waters in the subtropical gyre. DIN_{xs} variability and excess nitrate production rates in the STMW layer were well correlated with the North Atlantic Oscillation (NAO). For example, DIN_{xs} values (~ 1.5–2.8 μmol kg^{-1}) and excess nitrate production rates (~ 3.7 Tg N year^{-1}) were generally high during positive phases of the NAO (e.g., 1989–1994; 1997–2000) and coincident with periods of higher atmospheric mineral dust input to the ocean. When the NAO was in its negative phase and dust inputs lower (e.g., 1995–1996; 2001), DIN_{xs} values (~ 0–1.0 μmol kg^{-1}) and excess nitrate production rates were generally low (up to ~ 0.6 Tg N year^{-1}). The NAO potentially influences DIN_{xs} variability by modulating the extent and magnitude of STMW formation, thereby changing the fate of accumulated DIN_{xs} during circulation of STMW in the subtropical gyre, and the variability of nitrogen fixers through changes in dust inputs to the subtropical gyre.

Keywords: Temporal variability; Excess nitrate; North Atlantic Ocean

1. Introduction

Marine nitrogen fixation has been recognized as a source of new nitrogen supporting production in oligotrophic oceans for several decades (e.g., Menzel and Ryther, 1961; Dugdale and Goering, 1967; Lipschultz et al., 2002). More, recently, it has been viewed as quantitatively important for the global nitrogen cycle (Michaels et al., 1996; Gruber and Sarmiento, 1997, 2002) with global rates estimated at ~110±40 Tg N year^{-1} (Gruber and Sarmiento, 1997; Lee et al., 2002).

Geochemical (indirect) estimates of nitrogen fixation by marine diazotrophic organisms are based on quantification of nitrate in excess of that expected from thermocline N/P ratios (i.e., N/P of 16:1; Red-

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field et al., 1963; Takahashi et al., 1985; Anderson and Sarmiento, 1994). In the subtropical North Atlantic Ocean, annual rates of N_2 fixation have been estimated at 72–230 mmol N m^{-2} $year^{-1}$ (Michaels et al., 1996) or 14–30 Tg of fixed N (Michaels et al., 1996; Gruber and Sarmiento, 1997). However, these geochemically derived rates are inconsistent with the low rates (~ 0.25–34 mmol N m^{-2} $year^{-1}$) observed using biological (direct) measurement techniques for the dominant diazotroph, *Trichodesmium* spp. (Carpenter, 1983; Capone et al., 1997; Carpenter et al., 1999; Orcutt et al., 2001). The difference between geochemical and biological rate estimates is partly reconciled by lower geochemical estimates of N_2 fixation (Hansell et al., in press), but the quantitative importance of this source of new nitrogen to the upper ocean and to the global nitrogen cycle remains uncertain and highly debated (Gruber and Sarmiento, 2002; Lee et al., 2002).

Biologically derived estimates measure the local, short-term "event" (i.e., nitrogen fixation by *Trichodesmium* over a period of days), whereas geochemically derived estimates integrate the thermocline signal (i.e., excess N relative to P) over considerable time and space. Part of the dichotomy may relate to the temporal and spatial uncoupling between the event and the signal, and the interannual variability of both. For example, the geochemical rate estimates of Gruber and Sarmiento (1997) integrated excess nitrate data from hydrographic programs predominantly collected in 1972 (Geochemical Sections [GEOSECS] program) and 1981 (Transient Tracers in the Oceans [TTO] program), while Hansell et al. (in press) used World Ocean Circulation Experiment (WOCE) data, largely collected in the 1990s. Most direct biological measurements were made in the mid-1970s, 1980s (Carpenter, 1983; Capone et al., 1997), and mid-1990s (Orcutt et al., 2001). Thus, both geochemical and biological techniques for determining nitrogen fixation may be relevant to their particular time and space, but not directly comparable.

The goals of this paper are to evaluate the temporal variability of excess nitrate in the thermocline of the North Atlantic subtropical gyre for the period 1988–2001. Attention is focused on variability in nutrient stoichiometry in the subtropical mode water (STMW) of the North Atlantic Ocean (Hanawa and Talley, 2001). The excess nitrate signal has a maximum in this water mass, and it is the largest volumetric component of thermocline waters in the subtropical gyre. Evaluating interannual variability in the mass of excess nitrate in the STMW layer provides valuable context for comparing and reconciling geochemical and biologically derived estimates of nitrogen fixation. The temporal relationship between excess nitrate and climate variability associated with the North Atlantic Oscillation (NAO) is also evaluated. Several studies have demonstrated linkages between the NAO and interannual variability of hydrographic and biogeochemical properties (e.g., temperature, mixed layer depth, CO_2 and nutrient distributions) and rates (e.g., primary productivity) in the North Atlantic subtropical gyre (e.g., Bates, 2001; Oschlies, 2001; Bates et al., 2002; Gruber et al., 2002).

1.1. Subtropical Mode Water (STMW) in the North Atlantic and North Atlantic Oscillation (NAO) variability

The STMW of the North Atlantic Ocean is thought to form each winter by convection in an area of net ocean to atmosphere heat flux at the northern edges of the subtropical gyre south of the Gulf Stream (e.g., Hazeleger and Drijfhout, 1998; Joyce et al., 2000; Alfutis and Cornillon, 2001). STMW is the principal mode water of the Atlantic, characterized by low potential vorticity (i.e., minimum in the vertical gradient of potential density), temperatures ranging from 17.8 to 18.4 °C (Worthington, 1959; Ebbesmeyer and Lindstrom, 1986), salinity of ~ 36.5 ± 0.05, and density of ~ 26.45 (typical range of 26.40–26.55) (e.g., Talley and Raymer, 1982; Hazeleger and Drijfhout, 1998; Alfutis and Cornillon, 2001; Hanawa and Talley, 2001). A substantial bowl of low potential vorticity STMW is found at depths of 250–500 m primarily in the western basin of the Atlantic (e.g., ~ 45°–75°W; 20°–38°N; Worthington, 1959; Halliwell et al., 1994; Klein and Hogg, 1996). The STMW layer is found throughout the subtropical gyre, and its age increases following the mean geostrophic circulation from the site of STMW formation to the western boundary current (Jenkins, 1998).

The dominant mode of atmospheric variability in the North Atlantic region is the North Atlantic Oscillation (NAO; e.g., Hurrell, 1995; Jones et al., 1997; Hurrell and Van Loon, 1997; Osborn et al., 1999;

Hurrell et al., 2001), which is a measure of the dipole meridional oscillation in atmospheric pressure between the Iceland Low and Açores High (Hurrell, 1995; Jones et al., 1997; Osborn et al., 1999). The oscillation in NAO produces a myriad of climate change in the Northern Hemisphere (e.g., Visbeck et al., 2001), with pronounced impacts on the mid-latitude and subtropical Atlantic. The strength and geographic extent of STMW formation is highly variable interannually (Worthington, 1959; Jenkins, 1982; Klein and Hogg, 1996; Joyce and Robbins, 1996), being primarily correlated to NAO variability (e.g., Jenkins, 1982; Dickson et al., 1996; Klein and Hogg, 1996; Rodwell et al., 1999; Alfutis and Cornillon, 2001). When the NAO is in its negative phase, cyclonic storm tracks are thought to shift southward, cooling surface waters, enhancing STMW formation and deepening winter mixed layers (e.g., Rodwell et al., 1999). When the NAO is in its positive phase, westerlies that usually prevail in the region between Florida and Cape Hatteras (west of the Açores High) weaken. This leads to reduced wind stress and heat exchange that in turn leads to the development of warm temperature anomalies in the subtropical gyre (Bjerknes, 1964; Cayan, 1992a,b) between 0.2 and 0.5 °C (e.g., Davies et al., 1997; Kapala et al., 1998; Bates, 2001; Sutton et al., 2000; Bojariu and Reverdin, 2002), and reduced STMW formation (Alfutis and Cornillon, 2001).

2. Methods

2.1. Definition of excess nitrate (DIN$_{xs}$)

Anomalous N/P ratios in the North Atlantic subtropical gyre were first recognized and assigned to nitrogen fixation by Fanning (1987, 1992). Here, the tracer DIN$_{xs}$, as defined by Hansell et al. (in press), is used to quantify the excess nitrate concentration relative to phosphate concentration expected from thermocline elemental ratios of N/P (Redfield et al., 1963; Takahashi et al., 1985; Anderson and Sarmiento, 1994). The following equation is used:

$$\mathrm{DIN_{xs}} = N - 16P \tag{1}$$

where N is the concentration (μmol kg^{-1} N) of nitrate (plus nitrite where available) and P is the concentration of soluble reactive phosphate (μmol kg^{-1} P). The existing quasi-conservative tracer of excess nitrate, N^* (Gruber and Sarmiento, 1997, 2002) is defined as:

$$N^* = (N - 16P + 2.90) \times 0.87 \tag{2}$$

where the constant (2.90) and multiplier (0.87) are used to force the global mean N^* to zero. Deutsch et al. (2001) redefined Eq. (2) by removing the multiplier 0.87. DIN$_{xs}$ and N^* are related by a constant offset:

$$N^* = (\mathrm{DIN_{xs}} + 2.9) \tag{3}$$

DIN$_{xs}$ is used here rather than N^* as we focus on a single ocean basin.

2.2. Data sources

The temporal variability of DIN$_{xs}$ in the subtropical gyre was determined from nutrient data collected at the U.S. Joint Global Ocean Flux Study (JGOFS) Bermuda Atlantic Time-series Study (BATS) site (31°50′N, 64°10′W) near Bermuda. Each month since October 1988, nitrate+nitrite and phosphate were sampled at the site, along with other hydrographic and biogeochemical parameters (Michaels and Knap, 1996; Steinberg et al., 2001; http://www.bbsr.edu). Both nutrients were determined by standard spectrophotometric techniques using a Technicon auto-analyzer (Knap et al., 1993, 1997). The precision of the measurement was 0.02 μmol kg^{-1}.

Seawater reference standards for nutrients from Ocean Scientific have been used since 2000. Prior to that, batches of nutrient samples from 3000 m depth have been periodically frozen and analyzed as a set of secondary standards since 1997. In addition, routine quality control-quality assurance techniques (see Knap et al., 1993) have been used to identify individual samples or individual cruise data that fall outside the vertical data envelope profile, thus requiring repeat analyses. Two other approaches were used to assess the long-term accuracy of nitrate and phosphate. First, the observed variance of nutrient data at deep depth horizons (where natural variability is expected to be at a minimum) provides the upper bounds to the variability in nutrient data (both from analytical inaccuracy and natural variability). It is estimated that nitrate and phosphate within the core of the STMW have a potential inaccuracy of ~0.12 μmol kg^{-1} and ~>0.02 μmol kg^{-1}, respectively. This imparts a potential error of ~5–15% for the DIN_{xs} value. In a second approach, nitrate and phosphate values at different depth horizons (at 26 depths from 200 to 4200 m deep) from each cruise were compared to the mean nutrient value at each depth for the period 1988–2001. Time-series of nutrient anomalies (i.e., deviation from mean value) were then generated for each depth horizon. Since different water masses were sampled each cruise (e.g., STMW, Subtropical Underwater, Labrador Sea Water, North Atlantic Deep Water, Antarctic Bottom Water; Schmitz, 1996), nutrient anomalies should be variable at the different depth horizons. There were no cruise profiles for the 1988–2001 period that showed consistently higher or lower nutrient anomalies (greater than 1 standard deviation of the mean) at nearly all depth surfaces. This suggests that there were no significant offsets in the nutrient data (due to standardization or instrument problems, for example) for all of the cruises considered here.

The spatial distribution of DIN_{xs} across the subtropical gyre was evaluated using nutrient data from several meridional sections. DIN_{xs} for the core STMW layer was estimated using data from: (1) BATS "validation" cruises along the 64°W meridion; March 1995 (Validation 13), July 1995 (Validation 14), and October, 1995 (Validation 15); and (2) the WOCE A22 section in May 1997 along 66°W. Along the ~55°W meridion, data sources used were: (1) the WOCE A20 section in August 1997, and; (2) cruise in May 2001 aboard the R/V Oceanus. Nutrient and hydrographic data from the WOCE A22 and A20 sections were retrieved from the World Hydrographic Program Data Archive Center (http://www-ocean.tamu.edu/WOCE/Progress/data.html). Water mass ages were determined for this section with *p*CFC-12 data using standard solubility considerations (Warner and Weiss, 1985), time-series data of the atmospheric *p*CFC-12 transient (Walker et al., 2000), and an assumption that thermocline waters at the outcrop were in equilibrium with the present atmosphere.

In this analysis, the STMW layer is defined using a 17.8–18.4 °C temperature criterion. The results were independent of the criterion used to define the STMW layer (e.g., using a σ_Θ density criterion of 26.45+0.1 gives similar results). The volume of STMW between the permanent and seasonal thermocline in the North Atlantic is estimated using volume data computed for $0.1\sigma_\Theta$ density layers by Geoff Daniels and Don Olson (University of Miami), with density derived from the temperature and salinity climatology of the World Ocean Atlas (http://www.nodc.noaa.gov/OC5/data_woa.html). This calculation yields volumes of STMW in the North Atlantic of 1.14×10^{15}, 1.79×10^{15}, and 2.54×10^{15} m^3 for the 26.4–26.6, 26.4–26.7, and 26.4–$26.8\sigma_\Theta$ layers, respectively. The volume estimated for the 26.4–$26.6\sigma_\Theta$ density layer was somewhat smaller than previous estimates of the volume of STMW of 1.67×10^{15} m^3 (Worthington, 1959).

3. Results and discussion

3.1. Temporal and spatial variability of DIN_{xs} within the STMW layer

Across the subtropical North Atlantic, excess nitrate is typically located at depths between 150 and 600 m deep (Gruber and Sarmiento, 1997; Hansell et al., in press). At the BATS site, excess nitrate occurs within the density layers of ~26.2–$27.0\sigma_\Theta$ (Fig. 1a) at depths of 200–600 m (Fig. 1b). The DIN_{xs} maximum was typically located in the core STMW layer (~250–400 m deep; 26.4–$26.6\sigma_\Theta$ density layer; Figs. 1a and 2a), with occasional deepening of the maximum. Within the seasonal thermocline (0–~250 m deep; or waters with density<$26.2\sigma_\Theta$), DIN_{xs} values were<0 μmol kg^{-1}. Below the DIN_{xs} maximum in the STMW layer, excess nitrate decreased to the 26.8–$27.0\sigma_\Theta$ density surface (Fig. 2b), below which zero or negative DIN_{xs} values were observed (e.g., >27.0–$27.2\sigma_\Theta$ density layer; Figs. 1a and 2c).

Within the core of STMW (i.e., 26.4–$26.6\sigma_\Theta$ density layer; Fig. 2a), DIN_{xs} temporal variability of ~3 μmol kg^{-1} was observed during the 1988–2001 period. Distinct periods of high, medium and low DIN_{xs} values characterize the DIN_{xs} time-series record. For example, two extended periods of high DIN_{xs} values (~2.0–3.0 μmol kg^{-1}) were observed in 1989–1990, and in 2000. In contrast, extended periods of low DIN_{xs} values (~0–0.5 μmol kg^{-1}) were observed in 1995 and 2001, with brief low DIN_{xs} periods in 1992 and 1993. At other periods during the 1988–2001 time-

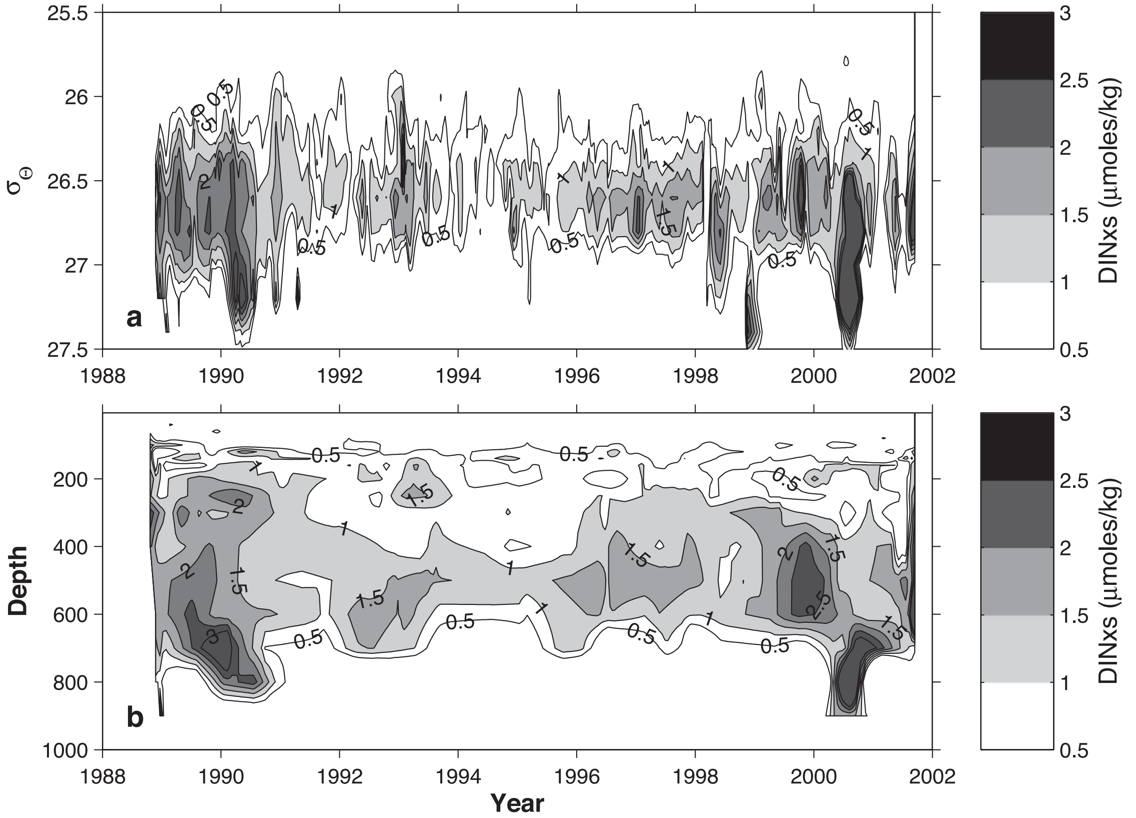

Fig. 1. Temporal variability of DIN_{xs} at the BATS site from 1988–2001. Upper panel is DIN_{xs} plotted against σ_Θ, while lower panel illustrates DIN_{xs} against depth.

series, DIN_{xs} values were mostly within the 1.0–1.5 μmol kg^{-1} range. Similar temporal patterns of DIN_{xs} variability were observed in deeper density layers. For example, in the 26.8–27.0σ_Θ density layer, DIN_{xs} values typically ranged between ~0 and 1.0 μmol kg^{-1}, with notably higher values in 1989–1990, and 2001 (Fig. 2b).

Considerable cruise-to-cruise variability in DIN_{xs} was observed, with the average difference in DIN_{xs} between cruises (i.e., between each individual cruise and the following cruise) of 0.48+0.40 μmol kg^{-1}. This short-term variability in DIN_{xs} was greater than the 5–15% (~0.05–0.15 μmol kg^{-1}) cruise-to-cruise uncertainty for DIN_{xs} estimated from analytical precision and accuracy. The temporal heterogeneity of DIN_{xs} likely reflects the physical variability in the STMW layer (i.e., age, composition) observed at the BATS site and, for example, the dynamic modulation of the hydrographic and inorganic nutrient distributions by mesoscale eddies and sub-mesoscale phenomena in the subtropical gyre (e.g., McGillicuddy et al., 1999).

How do the temporal patterns of DIN_{xs} recorded at BATS relate to DIN_{xs} distributions across the subtropical gyre? Although there are limited data to evaluate the spatiotemporal variability of DIN_{xs}, data from five occupations of meridional sections across the Sargasso Sea (1995 and 1997) suggests there is spatial homogeneity in DIN_{xs} with small meridional gradients of DIN_{xs} across the gyre. DIN_{xs} generally increases from the site of STMW formation ~37–39°N southward along both the ~64°W and ~55°W meridional sections (Fig. 3a and b). DIN_{xs} values for 1995 and 1997 ranged from ~0.5 to 1.2 μmol kg^{-1} across the gyre and the southward increase of DIN_{xs} was estimated at ~0.02 μmol kg^{-1} per degree of latitude. In contrast, in 2001, higher DIN_{xs} values (~1.0–2.0 μmol kg^{-1}) were observed along the 55°W meridion in the southern regions of the subtropical gyre (Fig.

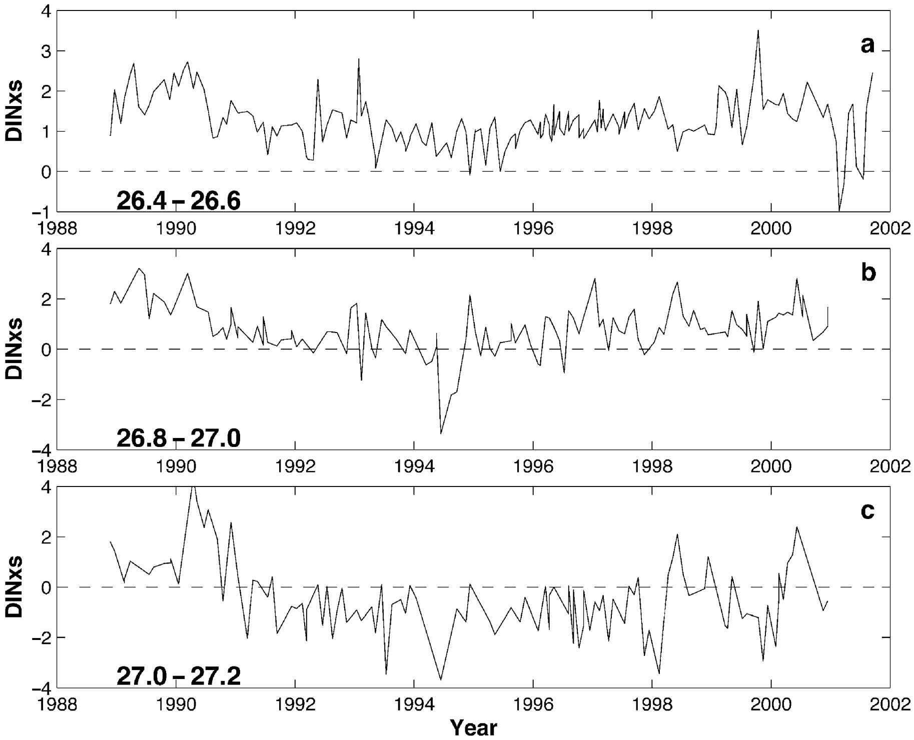

Fig. 2. Temporal variability of mean DIN_{xs} at the BATS site from 1988–2001 for specific density layers. (a) 26.4–26.6σ_Θ; (b) 26.8–27.0σ_Θ; and (c) 27.0–27.2σ_Θ. The DIN_{xs}=0 μmol kg^{-1} level is noted as a dashed line.

3b). The southward increase of DIN_{xs} was ~0.08 μmol kg^{-1} per degree of latitude. The potential causes for this change in DIN_{xs} are discussed later.

In the region of the wintertime outcrop of STMW south of the Gulf Stream (~37–39°N), DIN_{xs} values were ~0.5 μmol kg^{-1} (Fig. 3). The source water for STMW each winter is a composite of Gulf Stream and upper ocean subtropical gyre water (e.g., Speer and Tziperman, 1992). Thus the source water for STMW appears to have a preformed DIN_{xs} signal of ~+0.5 μmol kg^{-1}, presumably reflecting transport of excess nitrate via the Gulf Stream from the Caribbean and tropical Atlantic (where there is significant oceanic nitrogen fixation; e.g., Carpenter, 1983; Capone et al., 1997).

3.2. Estimates of the inventory and production rate of DIN_{XS} in the STMW layer

The inventory and production rates of excess nitrate are estimated here from empirical and model understanding of the physical structure and circulation of the STMW layer in the subtropical gyre, and a simple input–output steady-state budget. The annual rate of STMW formation has been estimated through empirical and model studies to range from 5 to 23 Sv (Sv=10^6 m^3 s^{-1})(Woods and Barkmann, 1986; Speer and Tziperman, 1992; Marsh and New, 1996; Hazeleger and Drijfhout, 1998). After formation of STMW in the northern regions of the subtropical gyre, the average time for a parcel of STMW to be transported from the site of formation to the western boundary current along the path of gyre recirculation has been reported to range from 6 to 14 years (e.g., Speer and Tziperman, 1992; Marsh and New, 1996; Hazeleger and Drijfhout, 1998) with an average of 10 years. STMW is then subducted to the ocean interior within the “cooling spiral” of circulation in the subtropical gyre (e.g., Behringer and Stommel, 1980; Luyten et al., 1983; Woods and Barkmann, 1986; Spall, 1992; Williams et al., 1995).

^{3}H/^{3}He tracer data indicate that the typical age of STMW observed near Bermuda is 3–4 years (Jenkins,

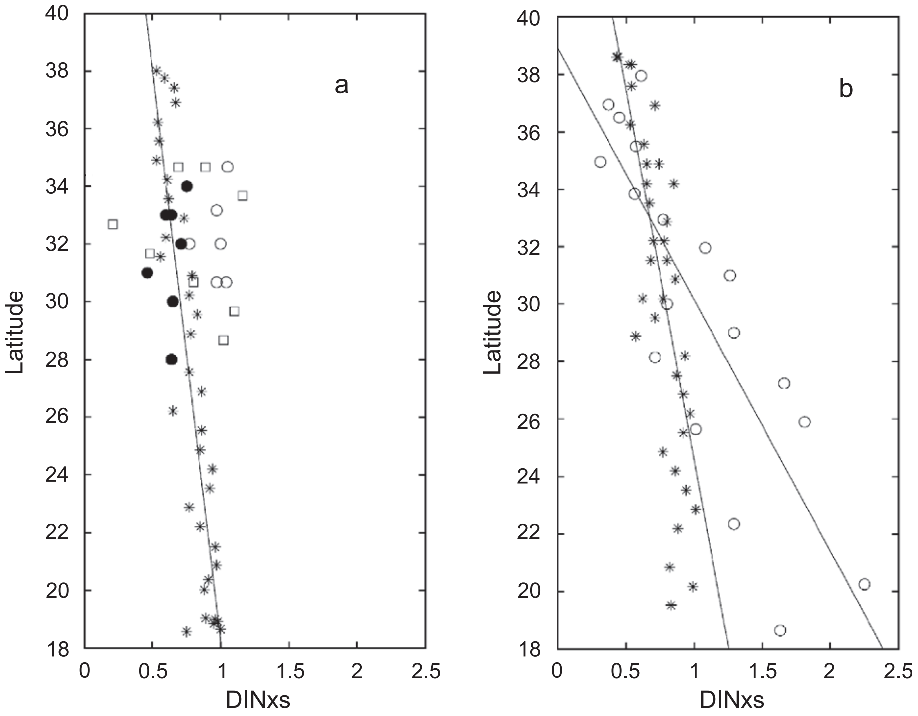

Fig. 3. Variability of DIN_{xs} in the STMW layer in the North Atlantic subtropical gyre along the ~64°W and ~55°W meridions. (a) Data from the ~64°W line for four cruises, including: (1) March 1995 (filled circles; ~0.002 $\mu mol\ kg^{-1}\ deg^{-1}$); (2) July 1995 (open square; ~0.02 $\mu mol\ kg^{-1}\ deg^{-1}$); (3) October 1995 (open circle; ~0.02 $\mu mol\ kg^{-1}\ deg^{-1}$); (4) WOCE A22 section on 66°W in May 1997 (asterisks). The regression statistics for the WOCE A22 line are $latitude = -39.4989DIN_{xs} + 57.7727$ ($r^2 = 0.7783$); and the slope was ~0.02 $\mu mol\ kg^{-1}\ deg^{-1}$. (b) Data from the ~55°W line for two cruises, including: (1) May 2001 (open circle); the regression statistics for the R/V Oceanus line are $latitude = -8.7592DIN_{xs} + 38.9017$ ($r^2 = 0.6992$); and the slope was ~0.085 $\mu mol\ kg^{-1}\ deg^{-1}$. (2) WOCE A20 section in May 1997 (asterisks). The regression statistics for the WOCE A20 line are $latitude = -25.7965DIN_{xs} + 50.3417$ ($r^2 = 0.4267$); and the slope was ~0.02 $\mu mol\ kg^{-1}\ deg^{-1}$.

1998), with the age of STMW increasing along the mean geostrophic circulation pathway from the site of STMW formation to the western boundary current (Woods and Barkmann, 1986; Spall, 1992). Water mass ages determined for the WOCE section A22 in 1997 using *p*CFC-12 data revealed ages of ~4–5 years for water at the latitude of BATS (~32°N; Fig. 4). It is possible for some portion of the STMW to be entrained into the surface mixed layer during deep winter mixing in subsequent winters after formation. However, this process does not appear to have occurred since 1987 (Bates et al., 2002).

3.2.1. Inventory of excess nitrate in the STMW layer

Temporal variability in the inventory of DIN_{xs} in the STMW layer in the subtropical gyre was determined using a mass balance approach. The total inventory of excess nitrate in the STMW layer (ΣDIN_{xs}) was estimated by multiplying the ΔDIN_{xs} value observed at BATS by the volume of STMW (V_{STMW}), such that:

$$\sum DIN_{xs} = \Delta DIN_{xs} V_{STMW} \tag{4}$$

where ΔDIN_{xs} was determined from the observed DIN_{xs} minus the source water value for the STMW layer. Estimated DIN_{xs} values and the inventory of excess nitrate were highly variable during the 1988–2001 period (Figs. 1 and 2). In order to illustrate changes in the inventory and production rate of excess nitrate in the STMW layer within the subtropical gyre, ΣDIN_{xs} values were estimated from observed DIN_{xs} values of 1.0 and 2.8 $\mu mol\ kg^{-1}$ (note: these DIN_{xs}

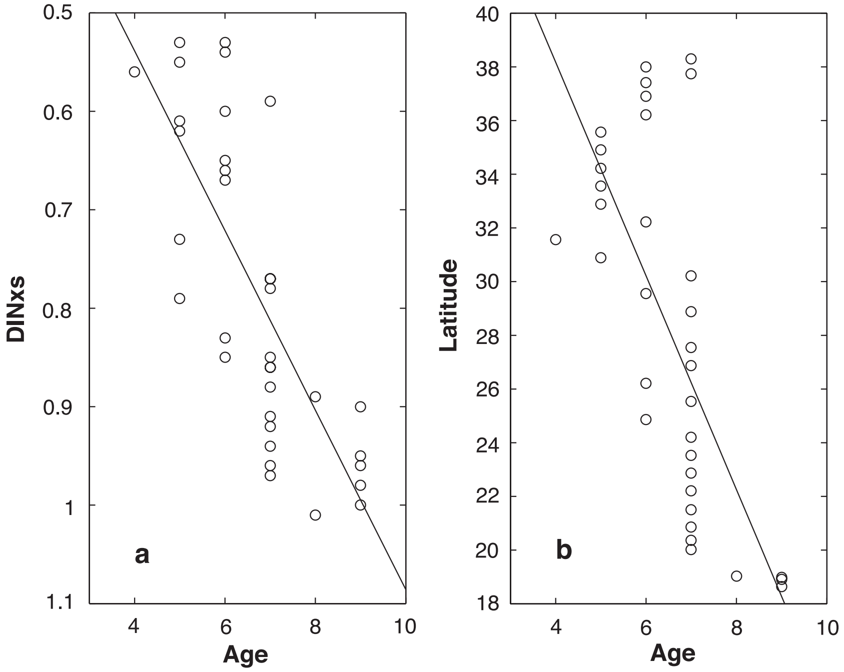

Fig. 4. Water mass age determined from *p*CFC-12 ages for the WOCE A22 section in May 1997 against DIN_{xs} for the 26.4–26.6σ_Θ density surface (a) and against latitude (b). Regression line for (a) was DIN_{xs}=0.0912age+0.1739 (r^2=0.5854). Regression line for (b) was latitude=−3.9791age+54.0882 (r^2=0.5621). Note that *p*CFC-12 ages are reported as whole numbers, hence the quantized appearance to their distributions.

values bound the range of *low* and *high* excess nitrate periods), using a DIN_{xs} value of 0.5 μmol kg^{-1} for the source waters of STMW. The inventory of excess nitrate was close to zero during periods when observed DIN_{xs} was ~0.5 μmol kg^{-1}.

ΣDIN_{xs} values (and production rates) were sensitive to the volume chosen as representative of the STMW layer. In the western basin of the North Atlantic (i.e., 35–75°W, 15–40°N), excess nitrate inventories for the 26.4–26.6 density layer were estimated at ~5.9–8.0 Tg N during periods of low observed DIN_{xs} (Table 1). Much higher excess nitrate inventories of 27.0–36.7 Tg N were determined for periods of higher observed DIN_{xs} (Table 1). If the entire subtropical gyre was considered, or the V_{STMW} of Worthington (1959) used (i.e., 1.67×10^{15} m^3), ΣDIN_{xs} values ranged from 8.0 to 59.2 Tg N (Table 1).

Several other assumptions and caveats apply to this simple mass balance approach to estimate excess nitrate inventories. Firstly, it was assumed that the DIN_{xs} value of the source waters for STMW did not change interannually. Secondly, it was assumed that the volume of the STMW layer remained constant on a multi-year timescale. The assumption of constancy to the volume of STMW implies that the input (STMW formation rate) equals output (subduction of STMW to deeper layers of the ocean). Most previous studies of STMW formation (e.g., Jenkins, 1982; Woods and Barkmann, 1986; Speer and Tziperman, 1992; Marsh and New, 1996; Hazeleger and Drijfhout, 1998) suggest that the typical formation rates of 5–10 Sv (~10% of STMW is renewed each year) are balanced by output to deeper layers and vertical entrainment at the margins of the subtropical gyre (e.g., Williams and Follows, 1998). It remains uncertain how interannual variability in the formation of STMW influences interannual variability of excess nitrate in the subtropical gyre.

Thirdly, it was assumed that the observed DIN_{xs} values at BATS were representative of the entire STMW layer in the North Atlantic. As shown earlier, DIN_{xs} accumulates in the STMW layer over time during the transit of STMW from the source region to the western boundary current (Fig. 3). Fortuitously, the BATS site is located approximately halfway along the transit pathway of STMW in the gyre. The 3–6 year age of STMW observed at the BATS site is about half that of the average 6–10 year residence time of STMW (τ_{STMW}) in the subtropical gyre. It is therefore assumed that DIN$_{xs}$ values at BATS provide a reasonable choice for a gyre-wide extrapolation. Finally, the counteracting influence of denitrification on N/P stoichiometry is assumed to be neglible in the oxygenated waters in the upper levels of the gyre.

Table 1
Inventory of excess nitrate (ΣDIN$_{xs}$) estimated from the volume of STMW (V_{STMW}), and ΔDIN$_{xs}$ value (e.g., Eq. (4))

Density layer	Region	V_{STMW} (10^{15} m^3)	ΣDIN$_{xs}$ values (Tg N or 10^{12} g N)	
			Low DIN$_{xs}$ (1.0 μmol kg^{-1})	*High* DIN$_{xs}$ (2.8 μmol kg^{-1})
26.4–26.6	35–75°W, 15–40°N	0.84	5.9	27.0
26.4–26.6	Entire N. Atlantic	1.14	8.0	36.7
26.4–26.6	Entire N. Atlantic	1.67	12.8[a]	59.2[a]

The ΔDIN$_{xs}$ values for observed DIN$_{xs}$ values of 0.5, 1.0 and 2.8 μmol kg^{-1} were 0, 0.5 and 2.3 μmol kg^{-1}, respectively. The major volumetric component of the STMW layer (e.g., for the 26.4–26.6 density layer) resides in the western part (i.e., 35–75°W, 15–40°N) of the North Atlantic subtropical gyre. The entirety of the subtropical North Atlantic considered here is 10–75°W, 10–40°N.

[a] These inventories were determined using the high V_{STMW} (i.e., 1.67×10^{15} m^3) of Worthington (1959).

3.2.2. Production rate of excess nitrate

The production rate of DIN$_{xs}$ in the subtropical gyre is estimated using two approaches. Firstly, the DIN$_{xs}$ production rate was determined from spatial gradients of DIN$_{xs}$ and water mass ages. This is done using *p*CFC-12 data computed for the WOCE A22 section collected in 1997 (for the 26.4–26.6σ_θ density layer) with the assumption that horizontal mixing is not substantial. These data indicate a DIN$_{xs}$ production rate of ~0.09 μmol kg^{-1} year^{-1} (slope in Fig. 4a), which is identical to rates estimated by Hansell et al. (in press) for the 26.5σ_Θ density surface across a greater extent of the subtropical gyre. The differences in volume of STMW (e.g., western basin, entire subtropical gyre or Worthington, 1959 volume estimate) yields a range of DIN$_{xs}$ production rate from ~1.1 to 2.1 Tg N year^{-1} (Table 2).

Secondly, excess nitrate production rates were computed from inventory (i.e., ΣDIN$_{xs}$) and STMW replacement considerations (i.e., mean residence time, τ). Assuming a mean residence time (τ) of 10 years for water in the STMW layer, this yields excess nitrate production rates of ~0.6 to 3.7 Tg N year^{-1}, for DIN$_{xs}$ values of 1.0 and 2.8 μmol kg^{-1}, respectively (Table 2). During periods of low DIN$_{xs}$ (~0.5 μmol kg^{-1}), minimal local production of excess nitrate occurs in this part of the subtropical gyre. These estimates of excess nitrate production bracket the other estimate (i.e., 1.1–2.1 Tg N year^{-1}) and are dependent on the residence time chosen for the calculation. For example, for DIN$_{xs}$ values of 1.0 μmol kg^{-1} and considering only the western basin of the subtropical gyre, the production rate of excess

Table 2
Estimates of excess nitrate production rates (Tg N year^{-1})

Density layer	Region	V_{STMW} (10^{15} m^3)	Excess nitrate production rate (Tg N year^{-1} or 10^{12} g N year^{-1})
CFC age constraints			
26.4–26.6	35–75°W, 15–40°N	0.84	1.1
26.4–26.6	Entire N. Atlantic	1.14	1.4
26.4–26.6	Entire N. Atlantic	1.67	2.1[a]
Mass balance considerations			
26.4–26.6	35–75°W, 15–40°N	0.84	0.6 (low DIN$_{xs}$; 1.0 μmol kg^{-1})
26.4–26.6	35–75°W, 15–40°N	0.84	2.3 (high DIN$_{xs}$; 2.8 μmol kg^{-1})
26.4–26.6	Entire N. Atlantic	1.14	0.9 (low DIN$_{xs}$; 1.0 μmol kg^{-1})
26.4–26.6	Entire N. Atlantic	1.14	3.7 (high DIN$_{xs}$; 2.8 μmol kg^{-1})

In a first approach (CFC age constraints), the rates were determined as the slope of a linear regression between DIN$_{xs}$ and water mass age of STMW from the WOCE A22 section (collected in 1997). In a second approach (mass balance considerations), the rates were estimated from DIN$_{xs}$ inventory (ΣDIN$_{xs}$), residence time (τ_{STMW} of 10) for the STMW layer, and a DIN$_{xs}$ value of 0.5 μmol kg^{-1} for the source water of the STMW layer.

[a] This inventory was determined using the high V_{STMW} (i.e., 1.67×10^{15} m^3) of Worthington (1959).

nitrate would be 1.0 Tg N $year^{-1}$ for a shorter residence time (i.e., 6 years), 0.6 Tg N $year^{-1}$ for the average τ of 10 years, or 0.4 Tg N $year^{-1}$ for a longer residence time (i.e., 14 years).

3.3. Comparisons to regional rates of excess nitrate production

The presence of excess nitrate in the thermocline of the North Atlantic subtropical gyre has been attributed to nitrogen fixation in the surface layer and subsequent remineralization of N rich sinking particulate matter at depth (Michaels et al., 1996; Gruber and Sarmiento, 1997). Gruber and Sarmiento (1997) estimated nitrogen fixation rates of ~28 Tg N $year^{-1}$ (2.0×10^{12} mol N $year^{-1}$) for the entire North Atlantic. Michaels et al. (1996) estimated nitrogen fixation rates of ~14–30 Tg N $year^{-1}$ ($1.06–2.45\times10^{12}$ mol N $year^{-1}$) within the 26.4–26.6σ_{Θ} density layer of the subtropical gyre (Table 3). More recently, Hansell et al. (in press) calculated nitrogen fixation rate using end-member mixing scenarios to account for source water variability of preformed DIN_{xs}. For the area 15° to 45°N by 25° to 75°W, they estimated an N_2 fixation rate of 4.3 ± 2.1 Tg N $year^{-1}$. Analyses in this paper yields time varying production rates of excess nitrate within the STMW layer of ~0–3.7 Tg N $year^{-1}$ (Table 2). In order to compare rates directly with Michaels et al. (1996) and Gruber and Sarmiento (1997), rates of excess nitrate production are divided by a factor of 0.76 (Eq. (14); Gruber and Sarmiento, 1997) to yield nitrogen fixation rates of ~<0.8–4.7 Tg N $year^{-1}$ (Table 3). However, during most of the 1988–2001 period (when DIN_{xs} was<1–1.5 μmol kg^{-1}), excess nitrate production was relatively low (~<0.8–2.7 Tg N $year^{-1}$) and in better agreement with Hansell et al. (in press).

Table 3
Comparative estimates of N_2 fixation rates in the North Atlantic (Tg N $year^{-1}$)

N_2 fixation (Tg N $year^{-1}$)	Year of nutrient sampling and survey program	Reference
28[a]	1977–1982	Gruber and Sarmiento, 1997
~14–30	1989–1992	Michaels et al., 1996
~4.3	1992–1998	Hansell et al., in press
~<0.8–4.7	1988–2001	This study

[a] This value includes excess nitrate in the Gulf of Mexico.

These four studies (e.g., Michaels et al., 1996; Gruber and Sarmiento, 1997; Hansell et al., in press; this study) have yielded a wide range of nitrogen fixation rates (~<0.8–2.7 Tg N $year^{-1}$) for the North Atlantic subtropical gyre (Table 3). The various methods and data sets used to determine the fixation rates may partly explain the large differences, but part of the dichotomy may also relate to the observed interannual variability of DIN_{xs}. For example, Michaels et al. (1996) used N^* values equivalent to a DIN_{xs} of ~2.6–4.0 μmol kg^{-1} in the 26.4–26.6σ_{θ} layer to estimate a *high* regional production rate of ~14–30 Tg N $year^{-1}$ in the STMW layer (this was estimated from the 26.4–26.6σ_{θ} layer in Table 5 of Michaels et al., 1996). Nutrient data for the Michaels et al. (1996) analysis was collected at BATS during the 1989–1992 period when high DIN_{xs} values (~2.0–2.8 μmol kg^{-1}) were observed (Figs. 1 and 2a). In contrast, Hansell et al. (in press) used WOCE sections, predominantly collected between 1992 and 1997, to estimate a *low* regional excess nitrate production rate of ~4.3 Tg N $year^{-1}$. During the period of 1992–1997, relatively low DIN_{xs} values (~0.5–1.5 μmol kg^{-1}) were observed at the BATS site (Figs. 1 and 2a). Thus interannual variability of DIN_{xs} appears to be an important determinant and context for estimating and interpreting excess nitrate production rates in the subtropical gyre of the North Atlantic.

3.4. Possible mechanisms for explaining variability of excess nitrate in the STMW layer

The large interannual variability of DIN_{xs} observed at the BATS site requires interannual variability in the biological and physical processes responsible for producing excess nitrate. Biological mechanisms invoked have included regeneration of sinking N rich particles resulting from nitrogen fixation by diazotrophic organisms (e.g., Michaels et al., 1996; Gruber and Sarmiento, 1997) and regeneration of dissolved organic nitrogen (DON) during horizontal recirculation (e.g., Rintoul and Wunsch, 1991; Martel and Wunsch, 1993; Williams and Follows, 1998). If nitrogen fixation is indeed the cause for excess nitrate in the thermocline, it remains difficult to reconcile the "event" (i.e., nitrogen fixation) with the "signal" in the thermocline (i.e., DIN_{xs} or N^*)(Lipschultz et al., 2002). For example, directly measured mean rates of nitrogen fixation by *Trichodesmium* colonies and free trichomes (Orcutt et al., 2001) in the northern subtropical gyre are much lower (~0.015 mol N m^{-2} $year^{-1}$) than the geochemical estimates from excess nitrate (~0.07–0.23 mol N m^{-2} $year^{-1}$; Michaels et al. 1996; Gruber and Sarmiento, 1997). There are also difficulties reconciling the seasonal characteristics of nitrogen fixation (e.g., *Trichodesmium* biomass and N_2 fixation rate maxima occur during seasonal water column stratification in summer and fall; Orcutt et al., 2001) with the multi-year integration and smoothing of the excess nitrate signal in the thermocline. N_2 fixation in the surface ocean should also result in a dissolved organic nitrogen (DON) signal (Bronk and Glibert, 1993) in the surface layer. But, Hansell and Carlson (2001) have only observed minor variability (~0.1–0.2 μM) in DON at the BATS site for the 1994–1999 period.

The differences between biological and geochemical estimates of nitrogen fixation may be partly reconciled by interpreting these estimates within the context of interannual variability of DIN_{xs}. In a recent modelling paper, Hood et al. (2001) suggested that nitrogen fixation in the subtropical gyre by diazotrophs such as *Trichodesmium* is coupled to variability of winter mixing and rates of primary production. For the period 1989–1996, they proposed that during the summer stratified period following deep winter mixing, low *Trichodesmium* biomass and N_2 fixation rates were expected due to their slow growth rate (e.g., 1995 and 1996). In contrast, higher *Trichodesmium* biomass and N_2 fixation rates were expected during summers following weak wintertime mixing (e.g., 1989–1994). During a period of relatively low DIN_{xs} at the BATS site (see Fig. 2a), Orcutt et al. (2001) directly measured nitrogen fixation rates for *Trichodesmium* colonies of 0.001, 0.005, and 0.035 mol N m^{-2} $year^{-1}$ in 1995, 1996 and 1997, respectively. If these rates are scaled up to include free trichomes (following Orcutt et al., 2001), the range of nitrogen fixation for the 1995–1997 period was 0.004–0.020 mol N m^{-2} $year^{-1}$. If N-rich sinking organic material is subsequently remineralized primarily in the 100–350 m depth range, N_2 fixation rates should contribute to an excess nitrate of ~0.016–0.08 μmol kg^{-1} $year^{-1}$ in the STMW layer. This is comparable to the excess nitrate production rates estimated earlier (0.09 μmol kg^{-1} $year^{-1}$).

3.5. DIN_{xs} signal and NAO variability

There is other evidence to suggest that complex linkages exist between excess nitrate variability, STMW renewal and dilution of the DIN_{xs} signal in STMW, atmospheric dust and climate (i.e., NAO) variability, and variability of nitrogen fixers in the surface ocean of the subtropical gyre. As stated earlier, the dominant mode of atmospheric variability in the North Atlantic region is the NAO (e.g., Hurrell, 1995; Jones et al., 1997; Hurrell and Van Loon, 1997; Osborn et al., 1999; Hurrell et al., 2001). At the BATS site, a significant component of DIN_{xs} variance was correlated with the summertime NAO index (Figs. 5a and 6). The mean summertime NAO and DIN_{xs} values for the May to October period (which coincides with seasonal stratification) were significantly correlated (r^2=0.531; Fig. 6). For example, when the NAO is in its positive phase (e.g., 1989–1994; 1997–2000), DIN_{xs} values were generally high (~>1.5 μmol kg^{-1}). Positive NAO periods tend to enhance stratification in the subtropical gyre, conditions conducive for nitrogen fixers such as *Trichodesmium*. At other times, when the NAO was in its negative phase (e.g., 1995–1996; 2001), DIN_{xs} values were generally low (~<1.0 μmol kg^{-1}). From 1996 to 2001, associated with a shift from negative summertime NAO to neutral conditions, DIN_{xs} increased from ~0.5 to >1.5 μmol kg^{-1} (Fig. 5a). The accumulation of DIN_{xs} can be observed, particularly in the southern region of the subtropical gyre) along the 55°W meridion between the WOCE A20 (August 1997) and Oceanus (May 2001) sampling (Fig. 3b).

3.6. STMW formation, DIN_{Xs} and NAO variability

If variability in DIN_{xs} is primarily caused by variations in nitrogen fixation, variability in the observed excess nitrate signal in the thermocline (i.e., STMW layer) may also be reinforced or suppressed by variability in STMW formation and its linkage to NAO variability. During negative phases in *wintertime* NAO, extensive STMW formation occurs across the northern regions of the subtropical gyre (Rodwell et al., 1999; Alfutis and Cornillon, 2001). Wintertime NAO indices are compared here since this influences STMW formation in the winter, while summertime NAO conditions primarily influence summer-

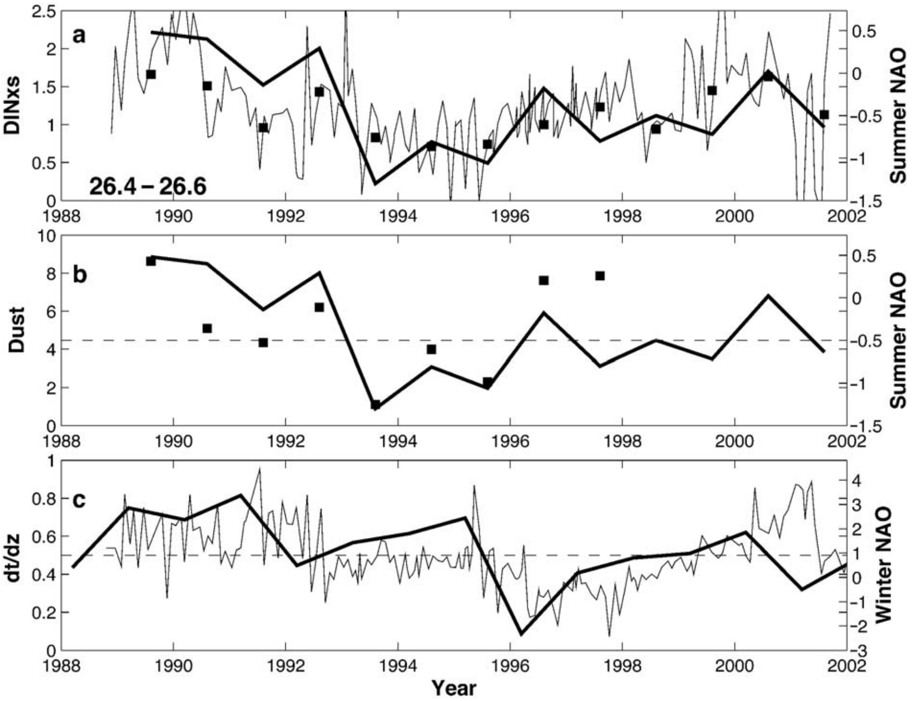

Fig. 5. Variability of atmospheric and ocean properties for the 1988–2001 period. (a) $\mathrm{DIN_{xs}}$ variability (expressed in μmol $\mathrm{kg^{-1}}$) in the STMW layer (i.e., 26.4–26.6σ_{Θ}, layer) (thin line) versus the summertime NAO index (bold line). The mean $\mathrm{DIN_{xs}}$ for the May–October period each year is shown in the plot as closed square. Climate indices for NAO were compiled by the Climate and Global Dynamics (CGD) division at National Centre for Atmospheric Research (NCAR; http://www.cgd.ucar.edu/cas/climind/). Summertime (May through October) NAO indices were based on sea level pressure (SLP) differences between Lisbon, Portugal and Stykkisholmur, Iceland (Hurrell, 1995; Osborn et al., 1999). (b) The mean atmospheric dust concentration (μg $\mathrm{m^3}$ $\mathrm{month^{-1}}$) (closed square) sampled at the AEROCE tower, Bermuda (data courtesy of Rick Arimoto and Joe Prospero) versus the summertime NAO index (bold line). The mean atmospheric dust deposition is for the May to October period each year (where data exist). (c) Vertical temperature gradients within the STMW layer (i.e., $\delta T/\delta z_{\mathrm{STMW}}$), expressed in °C 100 $\mathrm{m^{-1}}$ (thin line), using the methodology of Alfutis and Cornillon (2001), versus wintertime NAO index (bold line). $\delta T/\delta z_{\mathrm{STMW}}$ values at BATS were relatively high at ~0.2–>0.8 °C 100 $\mathrm{m^{-1}}$ for the 1988–2001 period indicating that STMW was not ventilated or formed near Bermuda during the winter. $\delta T/\delta z$ values<0.2 °C 100 $\mathrm{m^{-1}}$ are indicative of recent STMW renewal (Alfutis and Cornillon, 2001). Wintertime (December through March) NAO indices were based on sea level pressure (SLP) differences between Lisbon, Portugal and Stykkisholmur, Iceland (Hurrell, 1995; Osborn et al., 1999).

time stratification and atmospheric circulation. Recent analyses indicate that the last extensive formation of STMW occurred in 1987, during a negative wintertime NAO phase (Alfutis and Cornillon, 2001). Since 1988, the wintertime NAO phase has predominantly been positive, with brief negative excursions in 1996 and 2001 (Fig. 5c) when presumably larger amounts of STMW were formed. At the BATS site, winter mixed layer depths were well correlated with NAO, with deeper mixed layers in 1995–1996 (Bates, 2001) and 2001 (N.R. Bates, unpublished data).

The vertical temperature gradients within STMW (i.e., $\delta T/\delta z_{\mathrm{STMW}}$) are useful indicators of ventilation history of the STMW layer. For example, $\delta T/\delta z$ values of less than 0.2 °C/100 m within the STMW layer are indicative of recent STMW renewal (<1–2 years; Alfutis and Cornillon, 2001), while higher values are in a broad sense indicative of older, less recently ventilated water (e.g., in 1995, *p*CFC-12 data from the WOCE section indicates that the STMW layer near BATS was ~4–5 years old). $\delta T/\delta z_{\mathrm{STMW}}$ values at the BATS site were relatively high at ~0.2–>0.8 °C per 100 m during the 1988–2001 period indicating that the STMW layer was not ventilated or formed near Bermuda (Fig. 5c). However, $\delta T/\delta z_{\mathrm{STMW}}$ minima should record periods when the STMW layer was

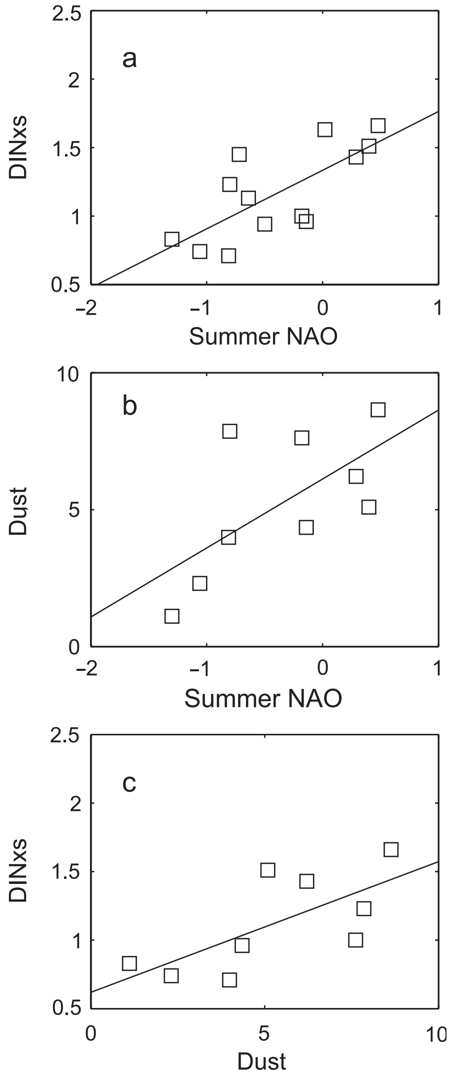

Fig. 6. Correlations of atmospheric and oceanic properties for the 1988–2001 period. (a) Mean summertime $\mathrm{DIN}_{\mathrm{xs}}$ (μmol kg^{-1}) versus summertime NAO (NAO computed as in Fig. 5). Regression line was $\mathrm{DIN}_{\mathrm{xs}}$=0.4286×summertime NAO+1.3343 (r^2=0.5311). (b) Mean summertime dust concentration (μg m^3 month^{-1}) versus summertime NAO. Regression line was dust=2.5172×summertime NAO+6.1149 (r^2=0.4246). (c) Mean summertime $\mathrm{DIN}_{\mathrm{xs}}$ (μmol kg^{-1}) versus mean summertime dust concentration (μg m^3 month^{-1}). Regression line was $\mathrm{DIN}_{\mathrm{xs}}$=0.0951×dust+0.6202 ($r^2$=0.4857).

younger and more recently ventilated. For example, $\delta T/\delta z_{\mathrm{STMW}}$ minima occur at the BATS site in 1998 and late 2001, ~2 years after the brief negative wintertime NAO phases in 1995–1996 and 2001. The ~2 years lag between the "event" (i.e., wintertime negative NAO phase and increased STMW formation) and "signal" (i.e., $\delta T/\delta z_{\mathrm{STMW}}$ minima at BATS) is expected.

The subduction and dispersion of STMW within the subtropical gyre is a complex and poorly understood process that involves isopycnal mixing and lateral eddy fluxes (e.g., Gent and McWilliams, 1990; Visbeck et al., 1997) that lead to an interleaving and blending of younger and older STMW (e.g., Alfutis and Cornillon, 2001). It can be posited though that during negative wintertime NAO phases, larger volumes of STMW would be expected to form during winter. If the $\mathrm{DIN}_{\mathrm{xs}}$ of the source water remains constant, $\mathrm{DIN}_{\mathrm{xs}}$ in the thermocline (i.e., STMW layer) could be diluted by a higher proportion of newly formed STMW water mixing into the pre-existing STMW layer. During positive NAO phases, the opposite might be expected to occur with resultant higher excess nitrate signals in the STMW layer. The $\delta T/\delta z_{\mathrm{STMW}}$ and CFC-12 age data suggest that there is a lag of several years observed at the BATS site. Thus, the negative wintertime NAO event that occurred in 1996 appears as a $\delta T/\delta z_{\mathrm{STMW}}$ minimum signal at the BATS site in 1998. Although the lowest $\mathrm{DIN}_{\mathrm{xs}}$ values occurred in 1994–1995 (<1 μmol kg^{-1}), $\mathrm{DIN}_{\mathrm{xs}}$ values in the STMW layer were lower (~1 μmol kg^{-1}) in 1998, compared to other years (1996–1997 and 1999–2000; $\mathrm{DIN}_{\mathrm{xs}}$ of >1–2 μmol kg^{-1}). These periods of high $\mathrm{DIN}_{\mathrm{xs}}$ values (e.g., 1996–1997 and 1999–2000) may result in part from the longer accumulation time for excess nitrate in older STMW water, undiluted by newly formed STMW water.

3.7. Variability of atmospheric dust, NAO and nitrogen fixers?

Recent studies suggest that *Trichodesmium* biomass and nitrogen fixation can be limited by availability of iron (e.g., Rueter et al., 1992; Falkowski, 1997; Wu et al., 2003) or phosphorus (Sãnudo-Wilhemy et al., 2001). The case for iron limitation is supported by high iron growth requirements (Raven, 1988), and higher *Trichodesmium* biomass where there is high iron input through dust deposition (Michaels et al., 1996). Is there any evidence linking atmospheric variability, nitrogen fixers and STMW excess nitrate variability?

The magnitude and interannual variability in the atmospheric transport of mineral dust to the tropical and subtropical Atlantic has been linked to NAO and El Niño-Southern Oscillation (ENSO) variability (e.g., Prospero, 1999). Recent analysis of dust and climate variability indicates that dust inputs to the subtropical Atlantic Ocean are correlated with NAO. For example, when the NAO is in its negative phase, increased precipitation over the Sahel region of Africa tends to reduce the availability of dust and its transport to the Atlantic Ocean with the prevailing easterlies (Moulin et al., 1997). Similar features have been observed in the Barbados and Miami atmospheric mineral aerosol records (Prospero, 1999). Indeed, the record of atmospheric mineral dust collected off Bermuda from 1989–1998 indicates a period of low dust deposition for the 1993–1995 period when the summertime NAO was particularly negative (Fig. 5b). The summertime dust concentration is well correlated with summertime NAO (r^2=0.486; Fig. 6b). The summertime dust concentration is also well correlated with the observed DIN_{xs} signal in the STMW layer (r^2=0.425; Fig. 6c). Thus, in years with positive summertime NAO, dust concentration at the latitude of the BATS site and STMW DIN_{xs} values were higher (i.e., 1989–1992, 1996–1997). In contrast, years with negative summertime NAO coincided with reduced dust deposition and low STMW DIN_{xs} values (i.e., 1993–1995).

Although temporal correlations can be demonstrated between atmospheric dust concentration, NAO and excess nitrate in the STMW layer, evidence for linkages to variability of nitrogen fixation and iron availability is lacking. It is interesting to note that in 1996 and 1997, Orcutt et al. (2001) observed much higher *Trichodesmium* colony biomass and nitrogen fixation rates (0.005 and 0.035 mol N m^{-2} $year^{-1}$), compared to 1995 (0.001 mol N m^{-2} $year^{-1}$). The higher *Trichodesmium* colony biomass coincide with much higher summertime dust deposition occurring in 1996 and 1997 (Fig. 5b).

Demonstrating linkages between dust, Fe availability and *Trichodesmium* biomass, however, remains problematic, hindered by the lack of observational data. In the southern regions of the North Atlantic subtropical gyre (at 10–15°N), Sãnudo-Wilhemy et al. (2001) have reported that *Trichodesmium* was limited by phosphorus rather than Fe availability. In this region, *Trichodesmium* biomass is high, atmospheric mineral dust concentration is plentiful and dissolved Fe concentrations were in the ~0.5–1.0 nM range. Recently, Wu et al. (2003) reported low concentrations of dissolved iron (~0.2–0.3 nM) in the South China Sea surface water, a region of low *Trichodesmium* biomass (putatively Fe limited) but a high rate of atmospheric dust concentration and deposition. Similarly, in the northern regions of the North Atlantic subtropical gyre (at 32°N), a region of low *Trichodesmium* biomass (Orcutt et al., 2001), Wu and Boyle (2002) have reported low dissolved Fe concentrations (~0.2 nM) in the surface ocean near the BATS site in the summer of 1998.

Relaxation of iron limitation for nitrogen fixers by atmospheric dust inputs of iron has been put forward as explanation of the geochemical signal of nitrogen fixation (i.e., excess nitrate) in the North Atlantic Ocean (Michaels et al., 1996; Gruber and Sarmiento, 1997). It may be that the enhancement of dust transport to the northern regions of the subtropical gyre during positive NAO phases may relax iron limitation of *Trichodesmium* biomass which in turn enhances nitrogen fixation and a remineralization signature (i.e., excess nitrate) from sinking N-rich organic material imparted upon the thermocline (e.g., STMW layer). However, observational and experimental data is required to confirm this hypothetical coupling between atmospheric dust deposition, Fe availability, diazotroph biomass, nitrogen fixation, and thermocline excess nitrate signal in the northern regions of the North Atlantic subtropical gyre.

4. Conclusions

DIN_{xs} within the STMW of the subtropical gyre was highly variable over the 1988–2001 period, with two extended periods of high DIN_{xs} values (~2.0–3.0 μmol kg^{-1}) in 1989–1990 and in 2000. In contrast, extended periods of low DIN_{xs} values (~0–0.5 μmol kg^{-1}) were observed in 1995 and 2001, with brief low DIN_{xs} periods in 1992 and 1993. However, for most of the 1988–2001 period DIN_{xs} values were largely within the 1.0–1.5 μmol kg^{-1} range, and production rates of excess nitrate for most of the 1988–2001 period were low (~0.5–3.7 Tg N $year^{-1}$).

The interannual variability of DIN_{xs} and the rate of excess nitrate production appears coupled to summertime NAO variability (and perhaps variability of atmospheric dust inputs to the surface ocean). For example, DIN_{xs} values (~ 1.5–2.8 μmol kg^{-1}) and rates of excess nitrate production (~ 2.7–3.7 Tg N $year^{-1}$) were generally high during positive phases of the NAO (e.g., 1989–1992; 1996–2000), and periods of higher atmospheric mineral dust input to the ocean. When the NAO was in its negative phase and dust inputs lower (e.g., 1993–1995; 2001), DIN_{xs} values (~ 0–1.0 μmol kg^{-1}) and rates of excess nitrate production (~ 0–0.8 Tg N $year^{-1}$) were generally low.

A partial explanation for the differences between geochemical (indirect) and biological (direct) rates of nitrogen fixation in the subtropical North Atlantic may relate to the interannual variability of DIN_{xs}. The datasets used by Gruber and Sarmiento (1997) to determine excess nitrate in the North Atlantic (e.g., GEOSECS, 1972–1973; TTO NAS, 1981; Atlantis II cruise 1979, 1981; A16N, 1988; A21, 1990; A12, 1992) all occurred during strong positive winter NAO years. Similarly, Michaels et al. (1996) used BATS data primarily from a NAO positive period (1989–1992). Thus, excess nitrate production rates determined using these datasets should be biased towards higher values. In contrast, biological estimates of nitrogen fixation (i.e., Orcutt et al., 2001; measurements from the 1995–1997 period) and geochemical estimates of excess nitrate production (i.e., Hansell et al., in press; data from 1993–1997, and this study) were low during a predominantly negative NAO period. The coupling between excess nitrate and NAO suggests highly dynamical variability of nitrogen cycling and the fate of nitrogen in the subtropical gyre of the North Atlantic Ocean.

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