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Contrasting decadal trends of subsurface excess nitrate in the western and eastern North Atlantic Ocean

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Abstract

Temporal variations in excess nitrate (DIN_{xs}) relative to phosphate were evaluated using datasets derived from repeated measurements along meridional and zonal transects in the upper (200–600 m) North Atlantic (NAtl) between the 1980s and 2010s. The analysis revealed that the DIN_{xs} trend in the western NAtl differed from that in the eastern NAtl. In the western NAtl, which has been subject to atmospheric nitrogen deposition (AND) from the USA, the subsurface DIN_{xs} concentrations have increased over the last two decades. This increase was associated with the increase in AND measured along the US east coast, with a mean lag period of 15 years. This time lag was approximately equivalent to the time elapsed since the subsurface waters in the western NAtl were last in contact with the atmosphere (the ventilation age). Our finding provides an evidence that the DIN_{xs} dynamics in the western NAtl in recent years has been affected by anthropogenic nitrogen inputs, although this influence is weak relative to that in the North Pacific. In contrast, a decreasing trend in subsurface DIN_{xs} was observed after the 2000s in the eastern NAtl, particularly in the high latitudes. This finding may be associated with a possible decline of tropical N_2 fixation and the weakening of the Atlantic meridional overturning circulation, although more time-resolved data on nutrients and meridional circulation are needed to assess this hypothesis. Our results highlight the importance of both anthropogenic and climate forcing in impacting the nutrient dynamics in the upper NAtl.

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1. Introduction

The supply of reactive inorganic nitrogen (Nr = NO_y + NH_x) to the surface ocean is limited in most of the oligotrophic marine environments (Fanning, 1989; Moore et al., 2013; Moore, 2016). The addition of Nr will lead to an increase in primary and export production, and eventually an enhancement of carbon sequestration in the ocean interior (Okin et al., 2011; Jickells and Moore, 2015). Anthropogenic nitrogen deposition (AND) to the contemporary ocean is comparable in magnitude to marine biological N_2 fixation, which has been thought to be the major external source of Nr to the oligotrophic ocean (Duce et al., 2008; Fowler et al., 2013; Jickells et al., 2017). In particular, AND has been found to enhance phytoplankton productivity in Nr-depleted tropical and subtropical oceans located downwind of continents that are sources of pollutant nitrogen (Kim et al., 2014b; St-Laurent et al., 2017). Any changes in this external source of Nr induced largely by human activities could cause a wide range of ecological and biogeochemical consequences (e.g., Doney et al., 2007; Yang et al., 2016).

The impact of AND on the dissolved inorganic nitrogen concentration (DIN) in seawater has recently been assessed in coastal and marginal seas (Kim et al., 2011; Moon et al., 2016), and in the remote open ocean (Kim et al., 2014a), using historical nutrient concentration datasets. The analysis of 30 years of data showed that the DIN has increased in marginal seas off the northeast Asian continent, whereas the dissolved inorganic phosphorus concentration (DIP) has remained relatively unchanged over this time period (Kim et al., 2011). For open-ocean areas, the temporal change in excess nitrate relative to DIP (DIN_{xs} = DIN – $R_{N:P}$ × DIP, where $R_{N:P}$ is the average DIN:DIP ratio of 15:1 for deep waters) was estimated using the relationship between DIN_{xs} in a particular water parcel and the chlorofluorocarbon (CFC)-12-derived ventilation age of that parcel (Kim et al., 2014a). An underlying assumption in this analysis is that ocean

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biological processes (i.e., production and microbial oxidation of organic matter) operate at a DIN:DIP ratio of 15:1 and thus do not change DIN_{xs}. Changes in seawater DIN_{xs} only occur when either N input (i.e., AND and N_2 fixation) or N loss (i.e., denitrification) occurs. The analysis using this method revealed that the DIN_{xs} has increased in the western North Pacific Ocean (NPO) since the 1970s (Kim et al., 2014a).

The addition of Nr to the North Atlantic Ocean (NAtl), which is located downwind from North America, has more than doubled since 1986 (Galloway et al., 1996). The increasing addition of Nr may lead to an increase in DIN_{xs} in the NAtl (Zamora et al., 2010). However, it has been argued that N_2 fixation is a more likely cause of the higher subsurface DIN_{xs} in the NAtl (Gruber and Sarmiento, 1997; Bates and Hansell, 2004). Differentiating the contributions of N_2 fixation and AND is not straightforward because both processes leave similar biogeochemical signals in seawater, including a high DIN:DIP ratio and low nitrogen isotope composition (Hastings et al., 2003; Knapp et al., 2010; Yang et al., 2014). In addition to these two processes, climate variations (commonly expressed as the North Atlantic Oscillation Index) can concurrently influence the nutrient dynamics in the NAtl (Bates and Hansell, 2004; Singh et al., 2013). As a result, the processes causing the change in the subsurface DIN_{xs} signal in the NAtl remain unresolved. This knowledge gap needs to be filled to improve understanding of the marine nitrogen cycle (Gruber, 2008).

The present study was designed to explore the occurrence and rate of decadal change in DIN_{xs} (ΔDIN_{xs} in μmol kg^{-1} decade^{-1}) in the subsurface NAtl, as well as the explanations for ΔDIN_{xs}, based on repeat measurements of nutrients and other oceanographic parameters made over the past three decades or longer.

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2. Materials and methods

2.1. Data

Historical data on temperature, salinity, and the concentrations of nitrate, nitrite, phosphate and oxygen used in this study have been collected as parts of the Transient Tracers in the Ocean (TTO), the World Ocean Circulation Experiment (WOCE), the Climate Variability CO_2 Repeat Hydrography (CLIVAR), and the Global Ocean Ship-Based Hydrographic Investigations (GO-SHIP) programs. Analysis of nutrient data was based only on concentrations greater than 0.1 μmol kg^{-1} for DIN and 0.01 μmol kg^{-1} for DIP. These concentration levels approximate the detection limits of DIN and DIP for the analytical methods used in the field observations (Zhang et al., 2001; Hydes et al., 2010). The data used in our analysis are available at https://www.nodc.noaa.gov/ocads/oceans/ (the Global Ocean Data Analysis Project Version 2, GLODAPv2 product and CLIVAR database).

Data analysis was primarily focused on three meridional (A22, A20, and A16N) transects in the NAtl (Fig. 1). A zonal transect (A05) was also included for comparison. All four transects used in the study are located downwind of the North American continent, which is a major source region of anthropogenic nitrogen (Fig. 1). Each of these transects was sampled 3 or 4 times during the past 30 years (Table S1). To extend temporal data coverage in the analysis, historical data obtained from locations adjacent to the four study transects were included in the analysis. Moreover, the repeat measurements along transect A22 occurred on slightly different tracks, particularly in the Caribbean Sea and in the northern end of the transect. We therefore excluded data for areas south of Puerto Rico (~18.5°N) and north of 36°N, where the distance between the location of repeat measurements exceeded 2° longitude. Data obtained south of 20°N along A16N and south of 15°N along A20 were also excluded from the analysis, because

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these regions are considerably influenced by the water masses originated from the equatorial upwelling region (Hansell et al., 2004), and any change in the intensity of upwelling could bias our analysis of changes in DIN_{xs}. To make datasets collected in different years consistent, an inverse analysis of repeated measurements made at the same locations was performed to estimate measurement biases. Any biases found were accounted for by applying adjustment factors to the original datasets. The adjusted datasets were reported in the GLODAPv2 product and CLIVAR database (Key et al., 2015; Olsen et al., 2016).

The datasets from the GLODAPv2 and CLIVAR did not have systematic biases (Table S1). To account for any small discrepancies that may exist among the various datasets collected on the 4 transects, we adjusted the DIN and DIP concentrations based on the assumption that the physical and chemical properties in deep waters of the tropical and subtropical NAtl (south of 50°N) did not change on decadal time scales (Figs. S1 and S2; see details in Text S1). The mean corrections were found to be 0.04 ± 0.03 μmol kg^{-1} for DIN and 0.006 ± 0.004 μmol kg^{-1} for DIP, corresponding to their adjustment factors mostly less than 1.5% (Table S2 and Fig. S3). These corrections fell within the detection limits for DIN and DIP, and were an order of magnitude smaller than the subsurface ΔDIN_{xs} signals (see section 3.1). The finding that the subsurface ΔDIN_{xs} signals were considerably greater than the detection limit of DIN is a strong indication that our data adjustments probably did not influence the temporal trend of DIN_{xs}. It also suggests that our method can extract the decadal trends of DIN_{xs} from less time-resolved datasets, as has successfully been used in previous studies (Zhang et al., 2000; Ríos et al., 2015; Woosley et al., 2016).

2.2. Relative abundance of DIN over DIP (DIN_{xs}) in water parcels

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We calculated the DIN surplus or deficit relative to DIP in each seawater sample (i.e. the deviation of the DIN:DIP ratio from that in deep water) by calculating DIN_{xs} (Fig. 2). This calculation was performed in the upper 1500 m; and the ΔDIN_{xs} signals between GO-SHIP and WOCE time periods were also evaluated using data obtained from the subsurface layer (200–600 m) because the majority of DIN_{xs} signals derive from this layer and hence any changes would be expected to be more marked (see the next section and the ΔDIN_{xs} signals at 1200–1500 m for reference in Fig. 2). In addition, the effect of seasonal variations on DIN_{xs} signals at this depth layer is generally insignificant, because seasonal variations are largely confined to waters shallower than the climatological winter mixed layer (down to 200 m depth). Based on analysis of data obtained from the BATS site, seasonal variations in subsurface (the target water depth range) mean DIN_{xs} values were < 0.1 μmol kg^{-1} (Note that nutrient data at BATS are available at http://batsftp.bios.edu/ BATS/bottle/bats_bottle.txt).

The values for ΔDIN_{xs} and nutrients in the water column could be biased because of mixing of water masses having different DIN_{xs} concentrations, and different nitrogen to phosphorus ratios associated with organic matter oxidation during various observation periods. To minimize biases caused by these natural processes, we examined changes in potential temperature θ, salinity and AOU along the potential density surfaces σ_θ (corresponding to 200–600 m where the DIN_{xs} signals are the largest) at 5°–15° latitude or longitude intervals representing average regional variations along each transect. We found that the θ and salinity of a water mass occupying any given density surface did not change between repeat occupations ($p > 0.05$, Student's t-test and ANOVA with Games-Howell test), except for slightly lower θ and salinity since 2000s in the subpolar region (north of 45°N) along A16N (Figs. S4 and S5). This finding is a strong indication that biases in ΔDIN_{xs} from the mixing of different water masses

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were negligible in the subtropical regions over the observation periods (approximately 30 years). In contrast, we found slight differences in ΔAOU among a few of selected reoccupations (not shown). To remove the contribution of DIN and DIP from oxidation of organic matter, adjustment of the nutrient concentrations was made by using the DIP:DIN:O_2 remineralization ratio of 1:15:(–160) derived from data along the σ_θ = 27.0 horizon in the NAtl (Takahashi et al., 1985; Anderson and Sarmiento, 1994). The estimated DIN:DIP ratio for remineralization of organic matter was in the range 15–18 (Takahashi et al., 1985; Anderson and Sarmiento, 1994). The chosen value of the DIN:DIP ratio for remineralization did not significantly change the patterns of ΔDIN_{xs}. Therefore, the ΔDIN_{xs} within the layer of the DIN_{xs} maxima along all transects examined were free from biases of either mixing of water masses or changes in oxidation of organic matter. For each subregion, DIN_{xs} (or DIP) anomalies indicated individual DIN_{xs} (or DIP) values minus the mean DIN_{xs} (or DIP) values from the GO-SHIP dataset (Figs. 3–5). Note that the positive anomalies indicate higher values than the GO-SHIP data.

3. Results and discussion

3.1. Decadal variations of DIN_{xs} in the upper North Atlantic Ocean

High DIN_{xs} values were broadly distributed in the subsurface waters (< 1000 m) in the NAtl. In particular, the maximum DIN_{xs} values were found between 200 and 600 m (Fig. 2), and were slightly higher in the western basin (an average value of 1.4 ± 0.3 μmol kg^{-1} was calculated for A22 in 2012) than those in the eastern basin (an average value of 0.8 ± 0.2 μmol kg^{-1} was calculated for A16N in 2013). Similarly, the west-east gradient in DIN_{xs} was apparent along the zonal transect A05 at 24.5°N latitude (Fig. S6).

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Based on multiple cruises along each transect, changes in DIN_{xs} were discernable over the decadal periods; these changes were most pronounced between 200 m and 600 m (Fig. 2). The rate of ΔDIN_{xs} in the NAtl differed among locations of transects between GO-SHIP and WOCE periods. Specifically, the ΔDIN_{xs} values were mostly positive in the western NAtl (A22 and A20), where they varied from 0.02 to 0.33 μmol kg^{-1} decade^{-1}, with the highest rate found at 31°N–36°N along A22. In contrast, the ΔDIN_{xs} values became negative in the eastern NAtl (20°N–60°N along A16N), where they ranged from –0.07 to –0.40 μmol kg^{-1} decade^{-1}; the greatest rate of DIN_{xs} decrease was in the subpolar region (north of 45°N). Moreover, the ΔDIN_{xs} values remained close to zero in the intermediate waters (1200–1500 m) in the western and eastern subtropical NAtl (Fig. 2). This observation confirms that the marked changes in DIN_{xs} largely occurred in the subsurface waters.

The ΔDIN_{xs} in the NAtl showed geographically distinct patterns after removing the influence of remineralization of organic matter (Fig. 3). We found that the ΔDIN_{xs} within the layer of the DIN_{xs} maximum decreased since 1997 (measurement year) along the transects near the source continent (i.e. the entire transect of A22, and 31°N–36°N along A20) (Figs. 3a and 3b), and its rates ranged from 0.19 to 0.33 μmol kg^{-1} decade^{-1} (Fig. 2). The trend in DIN_{xs} found at the BATS site is broadly comparable to that found between 31°N and 36°N along A22 (Fig. 3a). The rate of increase of DIN_{xs} at the BATS site since the late 1990s (0.40 μmol kg^{-1} decade^{-1}) was also similar to that observed in the latitude band 31°N–36°N along A22. Such agreement with time series data strengthens our finding derived from less time-resolved datasets.

The discernable increase in DIN_{xs} rapidly diminished in the central gyre of the NAtl (15°N–31°N for A20, 20°N–45°N for A16N and A05), where the ΔDIN_{xs} was statistically insignificant ($p > 0.05$, Student's t-test and ANOVA with Games-Howell test; Figs. 3 and S7).

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Furthermore, the level of DIN_{xs} appeared to decrease at high latitudes in the eastern NAtl (north of 45°N on A16N; Fig. 3c). The trend of decrease has been more pronounced since the 2000s in this region, and occurred concurrently with decreases in temperature and salinity ($p < 0.05$, Student's t-test and ANOVA with Games-Howell test; Figs. S4c and S5c). Our observations indicate that the mechanisms responsible for the ΔDIN_{xs} in the subtropical and subpolar NAtl are likely to differ.

3.2 AND influence on the ΔDIN_{xs} in the western North Atlantic Ocean

More pronounced increase in the subsurface DIN_{xs} has been observed in recent decades in the western mid-latitude NAtl (Fig. 3), which is subject to considerable AND input from the North American continent. Recent studies suggest that the reduced form of nitrogen entering the NAtl is primarily of marine autochthonous origin, rather than of anthropogenic origin (i.e. atmospheric deposition) (Altieri et al., 2014; Altieri et al., 2016). Thus, this autochthonous reduced nitrogen would not influence seawater DIN_{xs} values. Therefore, we only included the effect of NO_x emissions and deposition (mostly in the forms of NO_3^- and HNO_3; hereinafter NO_x is used to represent the major form of AND) on the ΔDIN_{xs} values (Figs. 1 and 5b). From the 1970s to the 2010s the NO_x emissions from the USA showed a three-phase temporal transition (EPA, 2000). The NO_x emissions from the USA increased from 1970 to the mid 1980s, and stayed at high levels for approximately 20 years, and then decreased gradually after the mid 2000s as a result of the regulation of air pollutant emissions throughout the North American continent (Fig. 5b). The anthropogenic nitrogen pollutants are mostly transported eastward and ultimately deposited in the western NAtl (Fig. 1).

Although there are limited data (time and space) on wet deposition of NO_x, the temporal pattern based on measurements on the US Atlantic coast is comparable to that for the NO_x

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emissions. For example, based on data obtained from the National Atmospheric Deposition Program (NADP; http://nadp.sws.uiuc.edu/), there was an increase from the 1980s to early 1990s, and the level remained high for approximately 15 years and then decreased (Fig. 5b). This trend of wet deposition of NO_x was commonly found at AND monitoring sites located along the US Atlantic coast (Table S3).

The AND signals can be transported to the subsurface waters of the mesopelagic western NAtl via two associated mechanisms. The first process involves production and bacterial oxidation of organic matter. In these biological processes, new anthropogenic nitrogen added by atmospheric deposition are removed from the surface via photosynthetic utilization by phytoplankton and gravitational sinking of the resulting organic matter with N:P ratio higher than 15:1 (Singh et al., 2013). These N-rich organic matters are subsequently remineralized by bacteria at depth (Antia, 2005). This process involving well-known biological processes would facilitate the transfer of high surface N:P signals to the subsurface waters. The second process involves the physical transport of surface waters with greater N:P signals, which is a plausible mechanism for generating the subsurface AND signals observed in the western NAtl. High inputs of NO_x by atmospheric deposition occur over the coastal areas of the NAtl and are mostly entrained in areas close to the northern edge of the western NAtl via the strong and persistent western boundary current (i.e. the Gulf Stream, Fig. 1). Both active winter mixing and the concurrent formation of mode water in this region would be expected to facilitate the transport of surface waters loaded with high DIN_{xs} (and anthropogenic CO_2 and CFCs) to the subsurface layer, and to spread these DIN_{xs}-loaded waters southward (Palter et al., 2005).

The substantial increase in subsurface DIN_{xs} after 1997 (approximately equal to the pCFC-12 ventilation year of 1982) at sites having greater inputs of AND (boxes 1–3 in Fig. 5a, and at

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the BATS site) appears to coincide with the increasing wet deposition of NO_x from the US continent, with a lag period of approximately 15 years. The time lag observed is approximately equal to the ventilation age of the target subsurface waters in this region, which was estimated to be 6–25 years based on the CFCs concentrations (Hansell et al., 2004; Hansell et al., 2007). The time lag suggests that the physical mechanism is important in transporting the AND signals to the subsurface waters, although the mismatch between the observed time lag and the ventilation age of water masses may be due, at least in part, to the biological processes.

The rates of DIN_{xs} increase (0.19–0.33 μmol kg^{-1} $decade^{-1}$; boxes 1–3 in Fig. 5a) measured in the western NAtl (reported in the preceding section) are equivalent to an increase of 78–135 mmol N m^{-2} $decade^{-1}$ in the subsurface N inventory (200–600 m) of the western NAtl. This is slightly higher than the increase in wet NO_x deposition (approximately 60 mmol N m^{-2} $decade^{-1}$) measured along the US east coast from the 1980s to the 2000s (Fig. 5b), but is broadly consistent with the total NO_x fluxes (approximately 90 mmol N m^{-2} $decade^{-1}$) if dry deposition is included in the modeled and observed results (Dentener et al., 2006; Baker et al., 2010). We thus suggest that anthropogenic nitrogen input is probably a main driver of DIN_{xs} increase in the western basin. An anthropogenic influence manifested in oceanic nutrient dynamics having a lag period of 15 years, has also been detected at 200–600 m in the Mediterranean Sea, where Moon et al., (2016) showed a three-phase temporal transition (a trend of increase–stability–decline) in DIN concentration between 1985 and 2014; this was probably associated with corresponding changes in anthropogenic nitrogen input.

The temporal trend of the nitrogen isotope record (CS-δ^{15}N) measured on the Bermuda coral skeleton is comparable to the trends of NO_x emission from the USA (Fig. S8), indicating that the AND signals have been embedded in the coral δ^{15}N record. The CS-δ^{15}N record on the

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Bermuda coral reflects the annual biological response to the local AND signals in the surface waters; hence, its trend may follow changes in anthropogenic NO_x input without a time lag. For the western NAtl, the rates of DIN_{xs} increase we found are in agreement with those from the earlier studies using different datasets and methodologies (Hansell et al., 2007; Landolfi et al., 2008; Singh et al., 2013), but are lower than those observed in the NPO (0.30–1.20 μmol kg^{-1} decade^{-1}, Kim et al., 2014a). The different rates of seawater DIN_{xs} increase found between the western NAtl and NPO appear to be consistent with the CS-δ^{15}N records in these two basins. During the 20th century, a small decline (–0.2‰) in CS-δ^{15}N was observed in corals from Bermuda (Wang et al., 2018), whereas a greater decrease (–0.7‰) in CS-δ^{15}N was detected from the South China Sea (Ren et al., 2017). The lower rates of seawater DIN_{xs} increase (or slower decline in CS-δ^{15}N) in the NAtl were likely due to the lower rate of nitrogen emissions (also indicating nitrogen deposition) from the North American continent (0.15 Tg N year^{-1} observed from 1970 to 2000; EPA, 2000) than from northeast Asia (0.40 Tg N year^{-1} observed from 1980 to 2010; Liu et al., 2013). In this case, the recent trend of decreasing emission in anthropogenic nitrogen from North America, as well as the decrease in wet nitrogen deposition observed along the US east coast, may reverse the pattern of the increase in subsurface DIN_{xs} in the western NAtl in the near future. Indeed, this reversed pattern appears to have emerged recently at the BATS site (Figs. 3a and 5b), based on more time-resolved observations. Together, our findings suggest that the AND has affected the nutrient dynamics in the western NAtl, although the magnitude of this effect is relatively small, and its influence would be expected to become less significant under a scenario of increased control of pollutant emissions.

3.3. Biogeochemical processes that may affect the ΔDIN_{xs} in the western North Atlantic Ocean

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Other biogeochemical processes may also affect the observed pattern of ΔDIN_{xs} in the western NAtl. Nitrogen fixation contributes considerably to the total export production (1.3–3.8 mol C m^{-2} $year^{-1}$; Lee, 2001) in oligotrophic gyres of the NAtl (Lee et al., 2002; Ko et al., 2018), which could therefore generate the positive signals of DIN_{xs} in subsurface waters (Hansell et al., 2004). The rate of N_2 fixation and the abundance of diazotrophs have been reported to be highest (Luo et al., 2012; Benavides and Voss, 2015) in the subtropical gyre of the western NAtl (see boxes 4–6 in Fig. 5a), however, the subsurface DIN_{xs} did not change significantly among the repeat occupations of transects (Figs. 3 and S7a). No direct evidence for increasing activity of diazotrophs in the NAtl is available (Mahaffey et al., 2005; Benavides and Voss, 2015). Contrary to our expectation, the increase in subsurface DIN_{xs} was only found upstream of the subduction zone (north of the hot spots for N_2 fixation; Figs. 3 and 5a). In this region (boxes 1–3) the observed rate of N_2 fixation was 4.2 mmol m^{-2} $year^{-1}$ (Luo et al., 2012), considerably lower than the atmospheric NO_x deposition (10–40 mmol m^{-2} $year^{-1}$; see Fig. 1). If N_2 fixation mainly drives the increase in subsurface DIN_{xs} in this region, its rate would have been expected to increase by 2 to 3-fold during recent decades. Such an increase in N_2 fixation activity is highly unlikely (Benavides and Voss, 2015). Moreover, if N_2 fixation activity had increased during the study period we would expect the DIP concentration decreases in the surface ocean and concurrently increases below (Kim et al., 2014a), but this was not observed (Fig. 4). Therefore, N_2 fixation has probably not been a major factor leading to the increase in DIN_{xs} in the western NAtl over the study period.

Remineralization of particulate and dissolved organic matters (POM and DOM) is another potential source of subsurface DIN_{xs} in the NAtl, as a result of the high N:P ratios of organic matters and the preferential remineralization of P from POM and DOM (Landolfi et al., 2008;

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Lomas et al., 2010). The DON concentration in the subsurface waters in the western NAtl (near the BATS site), however, remained unchanged during the period 1998–2011 (http://bats.bios.edu/). Moreover, the N:P ratios in DOM and suspended POM obtained at 0–100 m at the BATS site did not change between 2004 and 2012 (Singh et al., 2015). Likewise, we did not find any discernible interannual changes in the N:P ratio of sinking particles collected between 150 and 300 m at the BATS site (Fig. S9). Thus, the change in subsurface DIN_{xs} in the western NAtl was not primarily driven by variable N:P ratios of sinking POM. Taken together, these findings suggest that DOM and POM remineralization has not contributed to the ΔDIN_{xs} in the subsurface waters of the western NAtl during the periods in this study. Having excluded N_2 fixation and remineralization of organic matters as key drivers, we hypothesize that the addition of AND has been the major contributor to the recent increases in subsurface DIN_{xs} in the western NAtl.

3.4. Influences of climate variability on the ΔDIN_{xs} in the western North Atlantic Ocean

As a prevailing climate mode over the NAtl, the North Atlantic Oscillation (NAO) strongly influences the formation of the subtropical mode water (STMW) in the western NAtl, which in turn affects subsurface nutrient and DIN_{xs} concentrations in the downstream region (Bates and Hansell, 2004; Palter et al., 2005). The STMW is known to form in areas south of the Gulf Stream extension, and then primarily flows southward to the entire western basin; its intrusion to the eastern basin has been suggested to be minor (Palter et al., 2005; Palter et al., 2011). The formation of the STMW is generally enhanced when the NAO index becomes negative. During this negative phase of the NAO, an increased contribution of low-nutrient water to the STMW lowers the subsurface nutrient concentrations and DIN_{xs} in the subtropical gyre. In contrast, during the positive phase of the NAO, the STMW formation becomes weaker, and thus the subsurface nutrient concentrations and DIN_{xs} would increase downstream of the STMW

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formation region (Palter et al., 2005). The winter (December–March) NAO index has been mostly positive values since 1980, although its trend appeared to show an increase before the early 1990s and to decrease slightly thereafter (Fig. S10). Contrary to the trend in this atmospheric forcing, our nutrient data showed no evident changes in the subsurface DIP in the downstream region (e.g. A22 and A20; $p > 0.05$, Student's t-test and ANOVA with Games-Howell test; Figs. 4 and S7b) over the past 3 decades, irrespective of changes in the NAO index. These observations indicate that the basin-wide ΔDIN_{xs} are probably less likely controlled by a persistent positive phase of the NAO. Time-series data further strengthened the conclusion drawn from the basin-scale data. For example, the decline in the Bermuda CS-$\delta^{15}N$ value was accompanied by several superimposed decadal oscillations induced by the NAO (Wang et al., 2018). Similarly, such oscillations appear to be imprinted in the time-series measurements of subsurface DIN_{xs} at the BATS site (Fig. 5b). Nonetheless, the basin-wide ΔDIN_{xs} trends induced by anthropogenic inputs of nitrogen are still visible.

3.5. Subsurface ΔDIN_{xs} trend in the eastern North Atlantic Ocean

There was an apparent decrease in subsurface DIN_{xs} in the eastern NAtl (e.g. A16N), which is the opposite trend to that found in the western NAtl (Fig. 5a). The decreasing trend (–0.40 μmol kg^{-1} decade^{-1}) in the subsurface DIN_{xs} in the eastern subpolar NAtl (45°N–60°N along A16N) has been more evident since the 2000s (Fig. 3c). A similar decrease in the subsurface (300–500 m) DIN between 1998 and 2013 was also found at a site (68.0°N, 12.7°W) in the northern Iceland Sea, but little change in DIP was observed (Fig. S12). The remineralization of DOM may play an important role (Kähler et al., 2010); however, due to insufficient time-resolved data, we could not confirm whether there was any decrease in the rate of DOM remineralization in the eastern subpolar NAtl. From 1999 to 2009, NO_x emission from

Europe has decreased by 31%, mainly owing to change in energy consumption from fossil fuels to nuclear power (Vet et al., 2014). This decline in recent NO_x emission from Europe (the blue solid line in Fig. S11) is a viable explanation for the decrease in subsurface DIN_{xs} in the eastern subtropics. However, much of the NO_x derived from Europe is probably deposited to the European coasts, because the prevailing westerly winds carry it eastward to the eastern European continent (Fig. 1) (Baker et al., 2010). Moreover, the amounts of NO_x deposited onto the eastern subpolar basin (< 10 mmol N m^{-2} $year^{-1}$) were found to be small (Fig. 1). In the extreme scenario in which no such NO_x deposition occurred during the period of analysis, the lack of this NO_x deposition would only account for < 20% of the total decline in subsurface DIN_{xs} in the eastern subpolar NAtl (Fig. 2c). This suggests that the influence of European AND on seawater nutrient dynamics in the eastern subtropical NAtl is minimal (Hansell et al., 2007).

A recent study reported that most N_2 fixation occurs in the tropical NAtl (south of 24°N; Marconi et al., 2017). The upper loop of the Atlantic meridional overturning circulation (AMOC) acts as a passage through which nutrients are transported from the tropical regions to the subpolar gyre (Pelegrí and Csanady, 1991; Williams et al., 2006; Moore et al., 2009). Therefore, a decreasing rate of N_2 fixation is another likely explanation for the decreasing trend in subsurface DIN_{xs} in the eastern NAtl. Indeed, the supply of iron and phosphorus from Africa to the eastern tropical and subtropical NAtl has declined by approximately 10% per decade during the period 1980–2008 (Foltz and Mcphaden 2008; Ridley et al., 2014), and was likely accompanied by a reduction in the growth of diazotrophs in the eastern tropical NAtl (Mills et al., 2004; Benavides et al., 2013). On the other hand, the decrease in the subpolar subsurface DIN_{xs} occurred concurrently with decreases in temperature and salinity at the same water depth in the subpolar region (Figs. 3c, S4c and S5c). These observations of concurrent cooling and freshening were suggested to be associated with the fact that the strength of ocean circulation (as well as heat transport) in the NAtl is decreasing, as a result of weakening of the AMOC since 2005 (Srokosz and Bryden, 2015; Robson et al., 2016). Therefore, the observed weakening in the northward transport of tropical waters might in part contribute to a reduction in the DIN_{xs} signature in the subpolar gyres of the eastern NAtl, as seen north of 45°N on A16N (Fig. 5a). This result is consistent with a reduction in the subsurface DIN_{xs} observed in the north Iceland Sea since 2005 (Fig. S12d). If this mechanism plays a governing role, changes in nutrient supplies related to a reduction of the AMOC would have a large impact on biological export and the marine ecosystem (Schmittner, 2005). Although compelling, our observations are not a direct confirmation that decline in N_2 fixation rate and variations in the AMOC are the main cause of the decreasing trend in subsurface DIN_{xs} in the eastern subpolar region. Therefore, this finding remains a working hypothesis that needs confirmation using more time-resolved data in future studies.

4. Conclusions and implication

Our results support that AND has been a cause of the temporal variations in seawater DIN_{xs} in the subsurface waters of the western NAtl during the recent 3 decades. In the eastern subtropical NAtl, the decline in NO_x emission from Europe, and possibly a decrease in the N_2 fixation rate, are likely drivers of subsurface DIN_{xs} change. However, in the subpolar gyres of the eastern NAtl the subsurface DIN_{xs} has decreased since the 2000s, as a result of a possible decrease in N_2 fixation. Recent changes in ocean circulation (e.g., the AMOC) might also play a role. Ocean circulation did not directly influence the DIN_{xs} in the water column, but it rather redistributed the DIN_{xs} over the basin in the NAtl. This mechanism requires confirmation based

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on new data. Our study also shows that both human activities and climate variations together exert a discernable impact on the decadal variations of DIN_{xs} in the subsurface waters of the NAtl.

Human activities may have begun to influence the concentrations and stoichiometry of nutrients, at least in the western NAtl, and profound changes have been verified on the western NPO (Kim et al., 2014a) and Mediterranean Sea (Moon et al., 2016). These findings indicate global-scale changes in marine biogeochemistry, caused by human activities that are simultaneously influencing carbon sequestration and greenhouse gas emission (e.g., N_2O) (Duce et al., 2008). Continuing monitoring of changes in DIN_{xs} in the NAtl are needed to determine whether the levels have followed the recent decrease in AND, particularly in the USA. Such external perturbations could also alter the close homeostasis of the marine N cycle and its feedback to climate (Gruber and Deutsch, 2014).

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Supporting information

Detailed description of transects used in the analysis, and additional tables and figures.

Author contribution

JYTY and KL designed the present work and drafted the manuscript. JYTY and JYM did the data analysis. JZZ, ISH, JSL, and EL contributed to discussion and interpretation of the data.

Competing interests

We have no conflict of interest to declare.

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Figure captions

Figure 1. (a) Nutrient sampling locations (black dots) in the North Atlantic Ocean (NAtl). All datasets from the meridional (A22, A20 and A16N) and zonal (A05) cruises were collected in the GLODAPv2 product and CLIVAR database (see text). The red dashed line indicates the region of STMW formation, and the solid arrows indicates streamlines of high transport in the western NAtl (i.e., the Gulf Stream, modified from Palter et al., 2005). The color scale indicates the model-derived atmospheric NO_x deposition into the NAtl for 2000 (Dentener et al., 2006).

Figure 2. The vertical distributions of DIN_{xs} in the upper 1500 m for difference cruises along three meridional transects are shown in, (a) A22, (b) A20, and (c) A16N, respectively. The insets in (a−c) show the average rates (with 95% confidence limits) of ΔDIN_{xs} at 200−600 m and 1200–1500 m averaged for each 3°−8° latitude interval between GO-SHIP (2010s) and WOCE (late 1980s to 1990s) time periods along each transect (see Table S1).

Figure 3. Temporal trends of DIN_{xs} anomalies (dots) for the corresponding latitude interval for the subsurface potential density intervals σ_θ along the three meridional transects (a) A22, (b) A20, and (c) A16N in the NAtl. Data from A05 obtained in 2010 at three crossover sites are also shown (triangles). $mDIN_{xs}$ values in parentheses indicate the mean DIN_{xs} in GO-SHIP dataset. The selected σ_θ intervals are typically located at the depth intervals of 200−600 m with DIN_{xs} maximum along each transect. Note that the selected σ_θ interval (= 27.2–27.6) in the subpolar region along A16N (45°N−60°N) is different from that in the subtropical region, as σ_θ for 200−600 m depth becomes larger in the high-latitude region. Besides repeat cruises of these transects, the data sets from other cruises with similar tracks (Fig. 1) in the sub-regions were included for comparison. The DIN_{xs} values were corrected by the changes in AOU to remove the contribution from remineralization of organic matter (see text). The data points connected by the dashed lines indicate that the ΔDIN_{xs} were statistically

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significant in these regions ($p < 0.05$, Student's t-test and ANOVA with Games-Howell test). Otherwise, the data that were statistically unchanged are not connected by the dashed lines. The smoothed trend using the 5-year rLowess filter for DIN_{xs} anomalies of the STMW at the same depth ranges of the BATS site (near A22) is also shown (the gray shading in a). The gray dashed lines indicate DIN_{xs} anomaly equals to zero.

Figure 4. As for Figure 3, except for DIP anomalies. mDIP values in parentheses indicate the mean DIP in GO-SHIP dataset. The gray dashed lines indicate DIP anomaly equals to zero. Date from the BATS site are also included in (a).

Figure 5. (a) The rates of ΔDIN_{xs} in the subsurface waters (200−600 m) along the four transects between GO-SHIP and WOCE time periods (see Table S1). The study area is divided into 10 subregions of 10° longitude by 5°−15° latitude along the transects A22 (boxes 1–2), A20 (boxes 3–5), part of A05 (box 6) and A16N (boxes 7–10). The statistically significant changes (Student's t test and ANOVA with Games-Howell test, $p < 0.05$) are marked with the superscript "t" for the box numbers. (b) Temporal variations of DIN_{xs} anomalies (open dots and their fitting curve as black curve) in the western NAtl in which the subsurface DIN_{xs} increased significantly (boxes 1−3 in a). Trend in DIN_{xs} anomalies in the subsurface waters at the BATS site is shown in gray shading (the same as Fig. 3a). To ensure consistent comparisons between atmospheric N deposition rates and seawater DIN_{xs} anomalies, the seawater DIN_{xs} anomaly values were shifted by approximately 15 years. The 15-year shift corresponded to the mean time period that had elapsed since a given subsurface water mass had last been in contact with the atmosphere prior to subduction. The year that the subsurface water mass in the NAtl last had contacted the atmosphere was calculated using the CFCs contents in that subsurface water. The history of observed atmospheric wet deposition (WD) of NO_x from the US Atlantic coast. Orange curve and its shading show the 5-year moving average values and the range of the 95% confidence intervals, respectively (the

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monitoring sites are presented in Table S3). Blue curve indicates the NO_x emission from the USA. The NO_x emission strongly correlates with the WD of NO_x (r = 0.93, p < 0.01).

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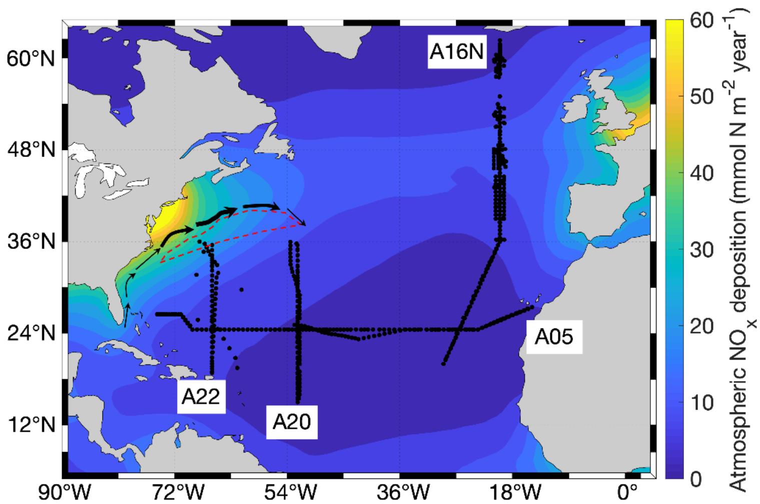
743 **Figure 1**



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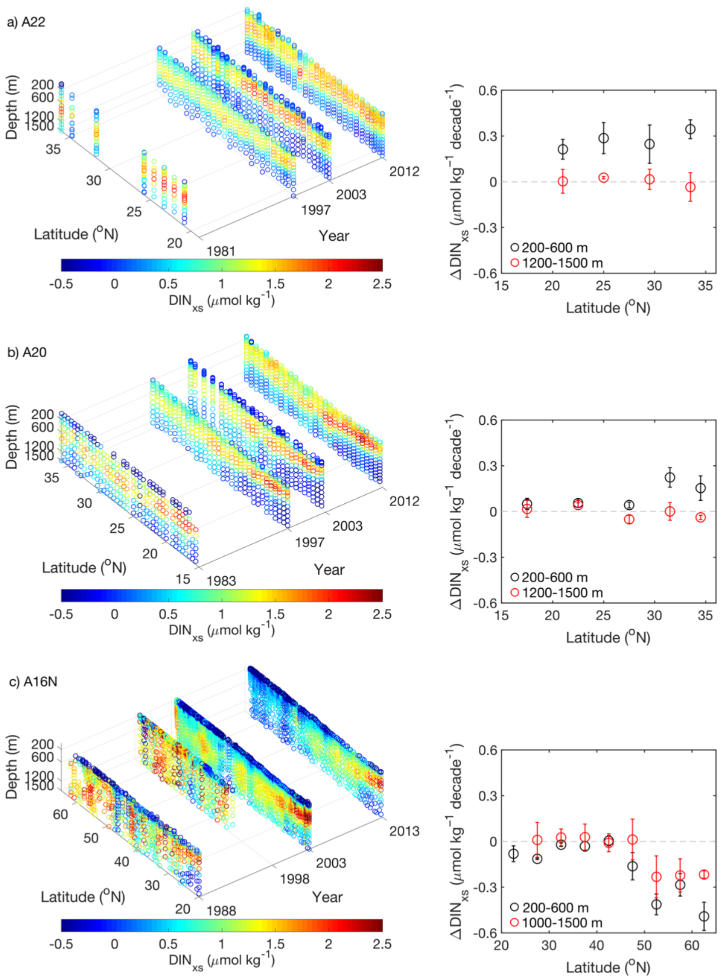
745 **Figure 2**



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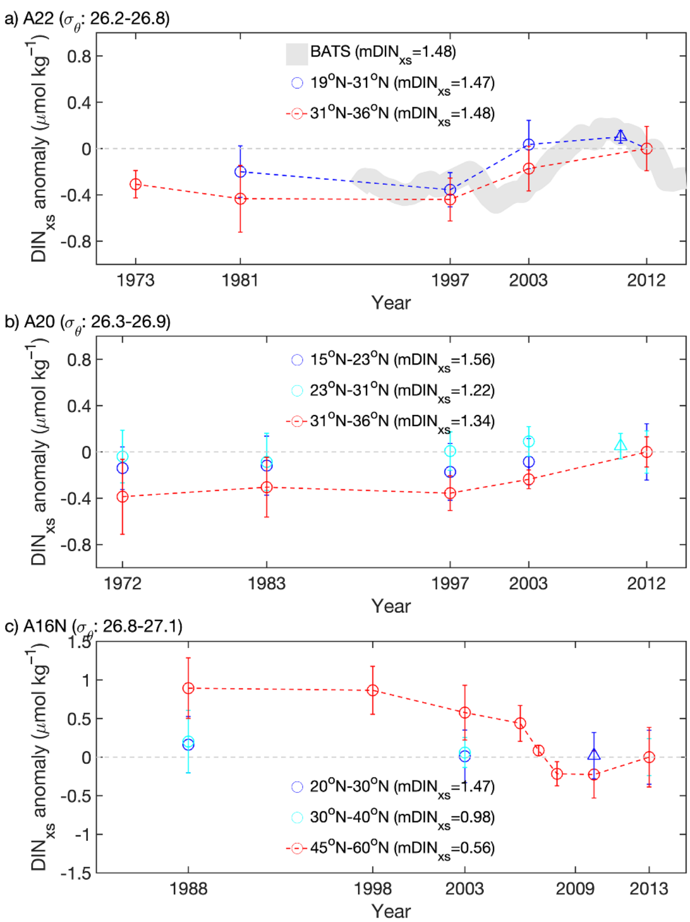
747 **Figure 3**



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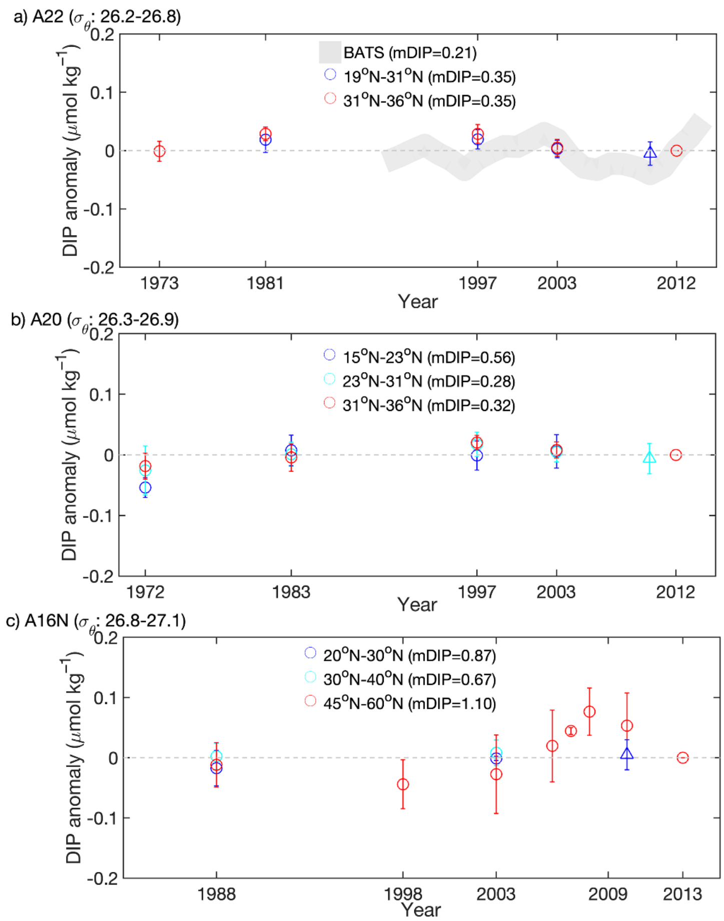
749 **Figure 4**



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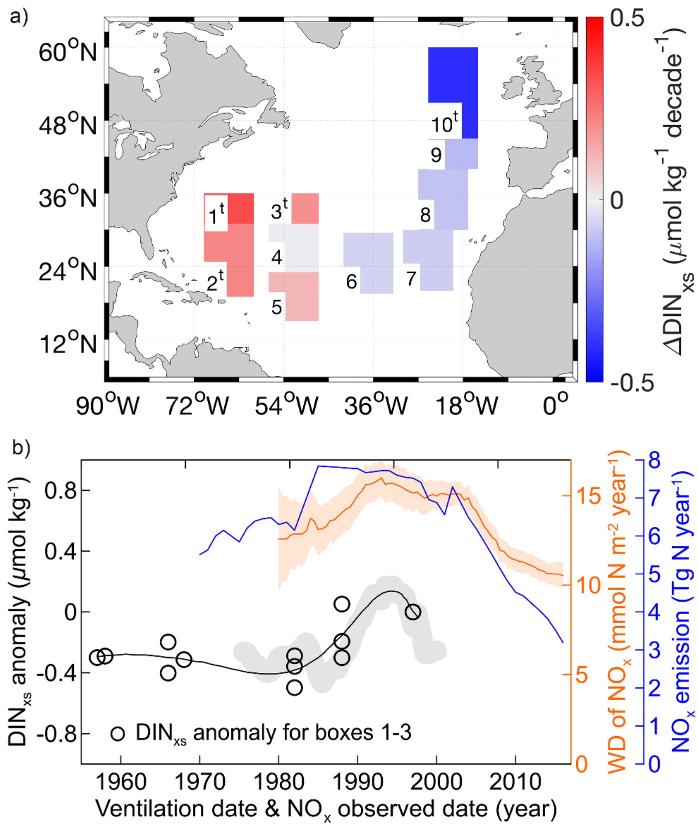
751 **Figure 5**



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