

# An oceanic fixed nitrogen sink exceeding $400 \text{ Tg N a}^{-1}$ vs the concept of homeostasis in the fixed-nitrogen inventory

L. A. Codispoti

University of Maryland Center for Environmental Science, Horn Point Lab., P.O. Box 775, Cambridge, MD 21613, USA

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**Abstract.** Measurements of the  $\text{N}_2$  produced by denitrification, a better understanding of non-canonical pathways for  $\text{N}_2$  production such as the anammox reaction, better appreciation of the multiple environments in which denitrification can occur (e.g. brine pockets in ice, within particles outside of suboxic water, etc.) suggest that it is unlikely that the oceanic denitrification rate is less than  $400 \text{ Tg N a}^{-1}$ . Because this sink term far exceeds present estimates for nitrogen fixation, the main source for oceanic fixed-N, there is a large apparent deficit ( $\sim 200 \text{ Tg N a}^{-1}$ ) in the oceanic fixed-N budget. The size of the deficit appears to conflict with apparent constraints of the atmospheric carbon dioxide and sedimentary  $\delta^{15}\text{N}$  records that suggest homeostasis during the Holocene. In addition, the oceanic nitrate/phosphate ratio tends to be close to the canonical Redfield biological uptake ratio of 16 (by N and P atoms) which can be interpreted to indicate the existence of a powerful feed-back mechanism that forces the system towards a balance. *The main point of this paper is that one cannot solve this conundrum by reducing the oceanic sink term.* To do so would violate an avalanche of recent data on oceanic denitrification.

A solution to this problem may be as simple as an upwards revision of the oceanic nitrogen fixation rate, and it is noted that most direct estimates for this term have concentrated on nitrogen fixation by autotrophs in the photic zone, even though nitrogen fixing genes are widespread. Another simple explanation may be that we are simply no longer in the Holocene and one might expect to see temporary imbalances in the oceanic fixed-N budget as we transition from the Holocene to the Anthropocene in line with an apparent denitrification maximum during the Glacial-Holocene transition. Other possible full or partial explanations involve plausible changes in the oceanic nitrate/phosphate and N/C ratios, an oceanic phosphorus budget that may also be in deficit, and

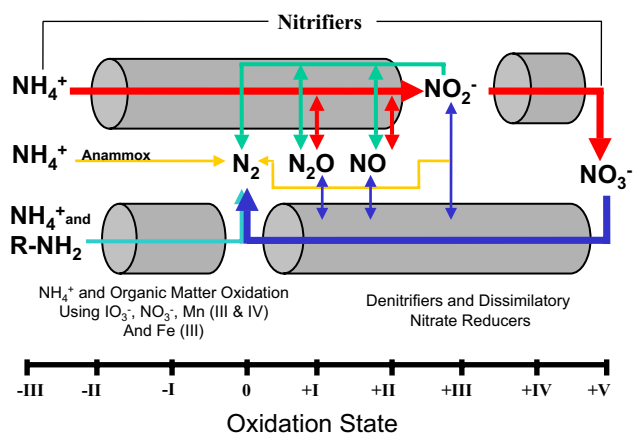
oscillations in the source and sink terms that are short enough to be averaged out in the atmospheric and geologic records, but which could, perhaps, last long enough to have significant impacts.

## 1 Introduction

Because of its relationship with the planetary nitrous oxide distribution, biological productivity (e.g. Redfield et al., 1963) and the ocean's ability to sequester atmospheric carbon dioxide (e.g. Codispoti et al., 2001; Falkowski, 1997), there is more than academic interest in the oceanic fixed-N budget. Moreover, there has been considerable debate over the state of the oceanic fixed-N budget in recent years (Gruber and Sarmiento, 1997; Codispoti et al., 2001; Gruber, 2004). This contribution originated as an invitation to provide a thought-provoking talk on the oceanic fixed-N budget at the SPOT-ON (Significant Processes, Observations, and Transformation in Oceanic Nitrogen) conference held in Warnemünde, Germany during June–July 2005. As a consequence, this paper has a point of view, and one of its goals is to excite interest in areas of research that might help to put our estimates on firmer ground.

Another major point of this paper is that attempts to bring the oceanic fixed-N budget more into balance by sufficiently reducing the total sink term have to confront an avalanche of results suggesting that these previous estimates of oceanic fixed-N removal (e.g. Codispoti et al., 2001) may, if anything, be too low! It will also suggest several possibilities for reconciling an oceanic sink for fixed-N of  $>400 \text{ Tg N a}^{-1}$  with constraints imposed by the atmospheric carbon dioxide record (Gruber and Sarmiento, 1997), the sedimentary nitrogen isotope record (Altabet, 2006; Deutsch et al., 2004) and by nitrate/phosphate relationships (Tyrell, 1999). With respect to nitrate/phosphate relationships, this paper will revisit the suggestion (Piper and Codispoti, 1975) that increases in

Correspondence to: L. A. Codispoti  
(codispot@hpl.umces.edu)



**Fig. 1.** This figure is re-drawn and updated from Codispoti et al. (2005). The suite of reactions supporting canonical denitrification are shown by the red (nitrification) and dark blue (canonical denitrification) arrows. The green arrows indicate a denitrification process that is associated with nitrification. This process produces  $\text{N}_2\text{O}$  and might also produce  $\text{N}_2$ . During these three processes, the intermediates,  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2^-$  can leave the cell and be changed between nitrifiers and denitrifiers. The  $\text{NO}_2^-$  produced can also support the anammox pathway (yellow arrows) in which  $\text{NH}_4^+$  is oxidized to  $\text{N}_2$  and  $\text{NO}_2^-$  is reduced to  $\text{N}_2$ . A review of the literature also suggests that oxidation of organic-N or  $\text{NH}_4^+$  by  $\text{NO}_3^-$ , iodate ( $\text{IO}_3^-$ ), oxidized metals such as Mn (III&IV), Fe (III) and various oxidized trace metals can also produce  $\text{N}_2$  (light blue arrow). Not shown is the possibility that the oxidation of Mn (II) by  $\text{NO}_3^-$  may also produce  $\text{N}_2$  (Luther et al., 1997). Intermediate chemicals involved in the anammox reaction (e.g. hydrazine) are omitted for simplicity.

denitrification are correlated with increased phosphate removal rates and review some data and concepts that relate to the constancy (or lack thereof) of the oceanic nitrate/phosphate ratio. A constant refrain in this paper can be encapsulated by the phrase, “The more we look, the more we find”, a comment made by A. H. Devol when he and the author of this paper were puzzling over ever-increasing estimates of oceanic denitrification years ago. Reconciliation of the data on the oceanic fixed-N sink with prevailing concepts and beguiling notions such as a Redfieldian and homeostatic oceanic N cycle will be attempted. This paper will also make a case for increasing both the denitrification sink and nitrogen fixation terms in the oceanic fixed-N budget. This analysis also will suggest that the lessons from the past may be an uncertain predictor of the near-term ( $\sim 100$  yrs) future as we transition from Milankovich to Anthropogenic climate forcing, and as the already massive anthropogenic impingement on the marine environment increases (e.g. Crutzen, 2002).

## 2 Scientific background

### 2.1 General

Although there are other sources and sinks for oceanic fixed-N, there is general agreement that the oceanic fixed-N budget is dominated by internal biological cycling: a nitrogen fixation source and a sink that arises from the biological processes that convert fixed-N to  $\text{N}_2$  (e.g. Table 1; Gruber and Sarmiento, 1997; Codispoti et al., 2005; Tyrell, 1999). There is also a consensus that the estimates for these source and sink terms made only a decade or two ago (e.g. Codispoti and Christensen, 1985; Capone, 1983; Carpenter, 1983) were far too low. With respect to nitrogen fixation, estimates of the global oceanic fixation rate have been revised upwards and may require further upwards revision (Davis and McGillicuddy, 2006; Montoya et al., 2004). Changes in our understanding of denitrification have perhaps been even more dramatic. We now better appreciate that in addition to “canonical denitrification” that is encapsulated in the following reaction sequence,  $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ , there are multiple biological pathways to  $\text{N}_2$  (Fig. 1; Codispoti et al., 2005). One of these pathways, the anammox reaction ( $\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ), may be more important than the canonical route to  $\text{N}_2$  under some circumstances (Kuypers et al., 2005 and 2006; Thamdrup et al., 2006) and has been demonstrated to occur in the water column, in sediments and in sea ice (Dalsgaard and Thamdrup, 2002; Dalsgaard et al., 2003; Kuypers et al., 2005 and 2006). In addition, recent evidence from the Arabian Sea suggests that the biological production of dinitrogen ( $\text{N}_2$ ) in the ocean exceeds estimates based on canonical stoichiometries for denitrification (Codispoti et al., 2001; Devol et al., 2006a, b; Naqvi et al., 2006). Note that in this paper, “denitrification” denotes the ensemble (Fig. 1) of biological processes that can convert fixed-N to dinitrogen ( $\text{N}_2$ ).

### 2.2 Water column denitrification

Denitrification becomes a prominent metabolic process when oxygen concentrations become vanishingly small. Three major quasi-permanent sites for water column denitrification exist within suboxic ( $\text{O}_2 < \sim 2\text{--}4 \mu\text{M}$ ) portions of the thermocline in the Arabian Sea, the Eastern Tropical North Pacific (ETNP) and the Eastern Tropical South Pacific (ETSP). Although estimates vary, it is agreed that globally significant denitrification occurs in these three major zones even though they comprise only  $\sim 0.1\%$  of the oceanic volume (e.g. Codispoti et al., 2005; Gruber, 2004). Smaller reasonably well-studied sites exist in enclosed basins such as the Baltic and Black seas, and denitrification is known to occur off Namibia (Calvert and Price, 1971; Kuypers et al., 2005 and 2006). Transient suboxia also occurs in the vicinity of, but outside the canonical boundaries of the quasi-permanent zones (e.g. Codispoti and Packard, 1980; Codispoti et al.,

**Table 1.** Simplified<sup>1</sup> pro-forma present-day oceanic fixed-N budgets [in Tg] and the unfractionated/fractionated ratio<sup>2</sup>.

<u>Process</u>	<u>G&amp;S 2002</u>	<u>G2004</u>	<u>C et al. 2001</u>	<u>C 2007</u>
Nitrogen Fixation	132 ± 41	135 ± 51	132	135+++
Benthic Denitrification	95 ± 20	180 ± 50	300	300+
UF/F Ratio	1.2	3.6	3.8	3.8
Water Column Denit.	80 ± 20	50 ± 20	150	150++
<b>Totals (all sources&amp;sinks)</b>	<b>+ 34 ± 53</b>	<b>5 ± 78</b>	<b>-188</b>	<b>-234</b>

<sup>1</sup> G&S 2002 = Gruber and Sarmiento (2002). G 2004 = Gruber (2004). C et al. (2001) = Codispoti et al. (2001), and C 2007 = this paper. Other significant sources (in Tg N a<sup>-1</sup>) include riverine inputs estimated by the above budgets as 76–80±14. Estimates for atmospheric inputs are as follows: G&S 2002 = 30±5, C et al. = 86, G 2004 = 50 & C 2007 = 30. Benthic nitrogen fixation was taken to be 15±10 in all of the above budgets, and is lumped with water column nitrogen fixation. Other sinks include burial which is 25±10 in all budgets, and N<sub>2</sub>O loss to the atmosphere taken as 4±2 in G&S 2002 and G 2004, and as 6 in C et al. (2001), and C 2007. Some budgets suggest a loss of ~1 Tg N a<sup>-1</sup> due to organic-N export from the ocean.

<sup>2</sup> The arrows and the value “57” indicate that with respect to isotopic fractionation of N, this paper assumes that 38% of total water column denitrification behaves like sedimentary denitrification. Unfractionated (sediments + water)/fractionated denitrification ratios (UF/F) are shown in blue.

1986), as well as transiently during outbreaks of suboxia in shallow coastal waters such as has been documented over the West Indian Shelf (e.g. Naqvi, et al., 2000). With increases in the outbreaks of coastal hypoxia/suboxia/anoxia that may arise from increasing additions of anthropogenic nutrients (e.g. Naqvi et al., 2000; Rabalais et al., 2000), it is possible that water column denitrification rates in the coastal ocean are on the increase. Globally significant increases in the denitrification rate in the ETSP appeared to have occurred between the early 1970’s and the mid-1980s (Codispoti et al., 1986) perhaps as “natural” consequences of a regime shift, and a la Niña event (Codispoti et al., 1986; Chavez et al., 2003), and/or anthropogenic disturbance (Codispoti and Packard, 1980). Evidence for variability in the oceanic water column denitrification rate on glacial-interglacial time scales has been demonstrated for the Eastern Tropical Pacific (Ganeshram et al., 2002). Altabet et al.’s. (2002) examination of cores from the Arabian Sea suggests significant variability on glacial-interglacial and ~ millennial time scales.

Codispoti et al. (2001) suggested that a *conservative* estimate of oceanic water column denitrification in the present-day ocean was ~150 Tg N a<sup>-1</sup>. We shall present and extend their reasoning later (Sect. 3.3).

### 2.3 Sedimentary denitrification

Middelburg et al. (1996) suggest an oceanic sedimentary denitrification rate (including continental shelves) between 230–285 Tg N a<sup>-1</sup>. Brandes and Devol (2002) sug-

gest that the oceanic nitrogen isotope budget requires a sedimentary denitrification rate during the Holocene of ~280 Tg N a<sup>-1</sup> based on a nitrogen isotope budget. Gruber (2004) suggests an oceanic sedimentary denitrification rate of 180±50 Tg N a<sup>-1</sup>. This paper (Sect. 3.4) will make the case for an oceanic sedimentary denitrification rate of 300 Tg N a<sup>-1</sup> or higher. Here it is useful to note that many past estimates of oceanic sedimentary denitrification neglected the importance of coupled nitrification-denitrification in sediments (see Codispoti and Christensen, 1985) and that most sedimentary estimates have not directly determined N<sub>2</sub> fluxes from the sediments. As a consequence, many estimates may not account for all of the pathways to N<sub>2</sub>.

### 2.4 Nitrogen fixation

Nitrogen fixing microbes convert N<sub>2</sub> to fixed-N and this process is the main source term in the oceanic fixed-N budget (Table 1). During the past decade or so there has been an accumulation of data to suggest that earlier estimates of oceanic nitrogen fixation require upwards revision. For example, estimates of upper water column nitrogen fixation based on canonical genera (*Trichodesmium* sp. and the diatom endosymbiont *Richelia intracellularis*) have been revised upwards (e.g. Capone, 2001) and may require further upwards revision (Davis and McGillicuddy, 2006). There are also recent data suggesting a substantial contribution by nitrogen fixation in smaller microbes (e.g. Montoya et al., 2004).

It is likely that estimates for marine nitrogen fixation will continue to increase. Existing estimates for the total oceanic nitrogen fixation rate (e.g. Codispoti et al., 2005; Deutsch et al., 2005 and 2007; Gruber, 2004), do not exceed 160 Tg N a<sup>-1</sup>, but this rate is based on observations and models concentrated on the photic zone and coastal sediments. There does not appear to have been a comprehensive study of heterotrophic and lithotrophic nitrogen fixation rates in sub-euphotic zone waters and deeper sediments, although the genome for nitrogen fixation appears to be widespread (Capone, 2001; Zehr et al., 1998 and 2006).

### 3 Discussion

#### 3.1 The oceanic fixed-N budget

Table 1 presents simplified “pro forma” oceanic fixed-N budgets. The totals include all known processes, but only the nitrogen fixation and denitrification rates are explicitly indicated because it is the apparent imbalance between these rates that is at the core of the problem addressed in this paper. The other terms are noted in the footnotes to Table 1. Note that our budgets (this paper, and Codispoti et al., 2001) include continental shelves and marginal seas such as the Mediterranean, Black and Baltic seas, but omit estuaries. It is obvious that there is considerable disagreement on the denitrification sink terms and whether or not the available information suggest a balanced or unbalanced budget. We will discuss this matter in some detail in the following sections. At the outset, we will note that as a result of discussions at the SPOT-ON, (Jickells, 2006) and also as a consequence of a recent study (Chuck et al., 2002) suggesting that the ocean is a source of alkyl nitrates, we now believe that the upwards revision in the atmospheric source term in the Codispoti et al. (2001) budget was in error and have reduced this term to bring it in line with the other budgets. The effect of this revision is to put the Codispoti et al. (2001) budget (Table 1) into an even greater deficit (~230 Tg N a<sup>-1</sup>). We also note, that our budget’s N<sub>2</sub>O loss term (6 Tg N a<sup>-1</sup>) is in accord with the work of Bange (2006) who estimates that a *conservative* estimate for the oceanic loss (including estuaries, in his case) would be 7±4 Tg N a<sup>-1</sup>. We will not discuss this term further because a change of 2–3 Tg N a<sup>-1</sup> from the canonical values while important for atmospheric chemistry has only a minor impact on the overall oceanic fixed-N budget. Finally, the “+” signs in Table 1 are included to suggest the author’s speculations about the likelihood of some of the terms increasing as we learn more, and, of course, “pro forma” means that most of the budget terms are highly uncertain.

#### 3.2 The problem

There is a consensus that traditional estimates of nitrogen fixation and denitrification were too low and that the oceanic turnover time for fixed-N is ~2500 years or less (Codispoti

et al., 2005; Gruber, 2004; Middelburg et al., 1996). There is also agreement that the terms in the budget are poorly constrained (e.g. Gruber and Sarmiento, 1997 and 2002; Gruber, 2004). The problem that this paper seeks to address is that the total sink terms posited by Codispoti et al. (2001), produce fixed-N deficits that would be unlikely to exist for more than several hundred years without violating apparent constraints imposed by the Holocene atmospheric carbon dioxide record (Gruber and Sarmiento, 1997) and the Holocene sedimentary <sup>15</sup>N record (Altabet, 2002 and 2006; Deutsch et al., 2004). In addition, there exists the traditional “geochemist’s” view that since the oceanic nitrate/phosphate ratio (~15 by N and P atoms; Falkowski, 2000) is quite similar to the canonical “Redfieldian” ratio of 16 in “plankton” (see Falkowski, 2000), and since the fixed-N budget is dominated by a biological source (nitrogen fixation) and sink (denitrification) there is a strong tendency for “homeostasis” (e.g. Gruber, 2004; Tyrell, 1999). The coupling of denitrification and nitrogen fixation over ocean circulation and shorter time-scales (Broecker and Peng, 1982; Codispoti, 1989) does provide negative feed-backs that favor homeostasis, but this paper will suggest that there are several possible factors that could weaken the influence of this mechanism, and that, to the extent that it does apply in today’s ocean, it must account for a fixed-N sink term of >400 Tg N a<sup>-1</sup>.

#### 3.3 A water column denitrification rate of more than 150 Tg N a<sup>-1</sup>?

##### 3.3.1 Denitrification within regions with the largest volumes of suboxic water

Several estimates of denitrification rates exist for the three regions that contain the largest volumes of suboxic water. These regions occur in the northern Arabian Sea, the Eastern Tropical North Pacific and the Eastern Tropical South Pacific (e.g. Deutsch et al., 2004). The canonical estimate for total denitrification in these regions is ~80 Tg N a<sup>-1</sup> (Bange et al., 2005; Codispoti and Christensen, 1985; Codispoti and Packard, 1980; Codispoti and Richards, 1976; Deutsch et al., 2001). Codispoti et al. (2001) suggested that this value was too low. Their assertion was based, in part, on a new nitrate deficit equation for the northern Arabian Sea and the determination of excess N<sub>2</sub> production in the Northern Arabian Sea from N<sub>2</sub>/Ar ratios. The shapes of the new nitrate deficits and the excess N<sub>2</sub> profiles vs depth were similar. Both had maxima that exceeded maximum estimates of the nitrate deficit in prior studies (e.g. Mantoura et al., 1993; Naqvi and Sen Gupta, 1985; Naqvi, 1994), and both suggested that the denitrification signal extended deeper (to >1500 m) into the water column than indicated by previous studies (Codispoti et al., 2001; Devol et al., 2006a and b). Data on the <sup>15</sup>N enrichment in nitrate, an expected consequence of water column denitrification, also had similarly shaped profiles (Devol et al., 2006a).

The new nitrate deficit method produced a total water column burden about twice as high as canonical estimates, and about four times as high as the nitrate deficit method employed by Howell et al. (1997) who estimated an Arabian Sea denitrification rate of  $21 \pm 7 \text{ Tg N a}^{-1}$ . The excess  $\text{N}_2$  values available to Codispoti et al. (2001) plus more recent data (A. H. Devol, personal communication) suggest that the excess  $\text{N}_2$  burden in the water column was  $\sim 75\%$  higher than predicated by *the new nitrate deficit*. Taking these results at face value would, therefore, suggest that previously estimated denitrification rates of  $30 \text{ Tg N a}^{-1}$  for the Arabian Sea (e.g. Bange et al., 2005) based on canonical nitrate deficits should be multiplied by up to 3.5 which would yield a rate of  $105 \text{ Tg N a}^{-1}$ . But because a significant fraction of the increases in nitrate deficits were at depths  $>1000 \text{ m}$  (Codispoti et al., 2001; Devol et al., 2006a and b) where residence times should be longer and rates of advection slower, it was thought reasonable to suggest a revised denitrification estimate of  $60 \text{ Tg N a}^{-1}$  for the quasi-permanent suboxic zone in the Arabian Sea based on residence times/transport of the excess  $\text{N}_2$ . As a check on this estimate we may consider denitrification rate estimates for the quasi-permanent suboxic zone in the Arabian Sea based on the activity of the respiratory electron transport system (ETS; Naqvi and Shailaja, 1993) and on  $^{15}\text{NO}_3^-$  incubations. These estimates assumed no oxidation of organic-N and ammonium to  $\text{N}_2$  (Devol et al., 2006b), and it is, therefore, reasonable to suggest that they should be multiplied by the excess  $\text{N}_2$ /nitrate deficit ratio of 1.75 on the assumption that the “extra” excess  $\text{N}_2$  comes from the suite of ammonium and organic-N oxidations discussed by Codispoti et al. (2001 and 2005). The average of these estimates is  $39 \text{ Tg N a}^{-1}$  which multiplied by 1.75 returns a value of  $69 \text{ Tg N a}^{-1}$ . Thus, this ensemble of data suggests that a denitrification rate estimate for the quasi-permanent suboxic water mass in the northern Arabian Sea of  $60 \text{ Tg N a}^{-1}$  is more reasonable than the canonical estimate of  $\sim 30 \text{ Tg N a}^{-1}$ .

Turning to the suboxic waters in the Eastern Tropical Pacific where the canonical estimate for denitrification was  $\sim 50 \text{ Tg N a}^{-1}$  (e.g. Deutsch et al., 2001), Codispoti et al. (2001) thought it reasonable to multiply this value by 1.5 based on the excess  $\text{N}_2$  data from the Arabian Sea, and on the new stoichiometric possibilities (Fig. 1 and Sect. 3.3.2), giving a water column rate for the Eastern Tropical Pacific of  $75 \text{ Tg N a}^{-1}$  and a total water column rate for the three regions with the largest volumes of suboxic water of  $135 \text{ Tg N a}^{-1}$ .

### 3.3.2 Interpreting excess $\text{N}_2$ data

Because they represent a challenge to conventional wisdom, it may be useful to discuss the excess  $\text{N}_2$  values further. Firstly, it is worth noting that the original observations reported in Codispoti et al. (2001) have been repeated on subsequent cruises, and that the *excess  $\text{N}_2$  values are*

*calculated from the differences between nitrogen/argon ratios found within the Arabian Sea's quasi-permanent suboxic water mass and Arabian Sea values found outside of the suboxic waters.* This approach leads to values that should be relatively free of complications such as bubble injection and supersaturations arising from mixing of water masses (see Devol et al., 2006a and b). Secondly, it is also unlikely that the “extra” excess  $\text{N}_2$  (i.e. the amount that exceeds that predicted by the nitrate deficit) in the Arabian Sea is strongly influenced by sedimentary denitrification (Gruber, 2004) for the following reasons. 1) Sedimentary denitrification is widespread, and the sediments underlying suboxic water masses comprise  $<3\%$  of the total oceanic sedimentary area (Menard and Smith, 1966). 2) Since the *excess  $\text{N}_2$*  estimates are based on differences between  $\text{N}_2/\text{Ar}$  ratios from just outside and within the suboxic waters, it is only *local* sedimentary denitrification that should impact these values. 3) Estimates of denitrification in sediments in contact with the three major suboxic denitrification zones are low relative to the water column rates, partially because of the small sedimentary areas in contact with these water masses. Codispoti and Packard (1980) suggest a rate of  $2 \text{ Tg N a}^{-1}$  for sediments in contact with the suboxic waters found in the Eastern Tropical South Pacific. Codispoti (1973a) points out the small area of sediment in contact with suboxic waters in the ETNP. Devol et al. (2006a) suggest a potential sedimentary denitrification rate in sediments in contact with the suboxic waters in the Arabian Sea of  $3.9 \text{ Tg N a}^{-1}$  and much of this would occur outside the depth range and horizontal extent of the quasi-permanent suboxic zone. 4) Maximum  $\text{N}_2$  excesses occur at the same depths as the  $^{15}\text{N}$ -nitrate maxima that are a signal of water column denitrification since fractionation of nitrate during sedimentary denitrification is minimal (Brandes and Devol, 2002; Sigman et al., 2003). 5) Although both approaches are probably underestimates because of inadequate accounting for the conversion of organic-N and ammonium to  $\text{N}_2$ , water column denitrification rates estimated from  $^{15}\text{N}$  incubations, and electron transport activities (ETS) as reported by Codispoti and Packard (1980); Codispoti and Richards (1976); Naqvi and Shailaja (1992); and Devol et al. (2006b) are in fair agreement with nitrate deficit residence time and transport based estimates (e.g. Bange et al., 2005; Codispoti and Richards, 1976). 6) maximum nitrite concentrations that are a signal of canonical denitrification in suboxic waters (Codispoti and Packard, 1980) often occur offshore, separated from the coast (e.g. Codispoti, 1973a and b; Naqvi, 1994). It is unlikely, therefore, that sedimentary denitrification contributes more than  $\sim 5\%$  to the *excess  $\text{N}_2$*  signal observed in the Arabian Sea.

Codispoti et al. (2001) and Devol et al. (2006a) discuss processes that might permit an excess  $\text{N}_2$ /nitrate deficit ratio  $>1$ . These processes, include the anammox reaction that would yield a ratio of 2, iodate oxidation of organic matter with  $\text{N}_2$  production, a preference of heterotrophic denitrifiers for N-rich organic matter (amino acids; Van Mooy et

al., 2002), a supply of high N/C organic matter due to local nitrogen fixation, etc. These authors also suggest that an ammonium flux from the sediments into suboxic waters might encourage the anammox process and might also help to explain the high excess N<sub>2</sub>/nitrate deficit. This can only be true, however, if the nitrate deficits and N\* do not record this signal. Gruber (2004) pointed out that the original suggestion by Codispoti et al. (2001) was flawed because they discussed an ammonium flux arising from the activities of lithotrophs that gain energy by oxidizing sulfide with nitrate that they obtain from suboxic water. These bacteria thrive at the interface between suboxic waters and sediments (Fossing et al., 1995; Jørgensen and Gallardo, 1999). Since the resulting ammonium arises from water column nitrate, the signal should be contained in stoichiometric parameters such as N\*. Nevertheless, there are reasons to speculate that ammonium fluxes from the sediments into the suboxic waters of the Arabian Sea coupled with anammox do contribute to the “extra” excess N<sub>2</sub> that is observed. For example, Schulz and Schulz (2005) have shown that the bacteria that oxidize sulfur with nitrate off southwest Africa (*T. namibiensis*) also sequester large amounts of phosphate which they suggest contributes importantly to phosphorite formation. Such a removal of phosphate from the water column would reduce the denitrification signal recorded by N\*. In addition, ammonium fluxes out of the sediments arise from the totality of suboxic/anoxic respiratory processes (Graco et al., 2005; Zitzmann and Brüchert, 2005), and suboxic sediments are known sites of enhanced phosphorite deposition (Piper and Codispoti, 1975; Ganeshram et al., 2002). Thus, it is possible that the ammonium flux from suboxic sediments produces some N<sub>2</sub> that is not recorded by N\* or the Codispoti et al. (2001) nitrate deficit.

### 3.3.3 Water column denitrification outside the boundaries of major suboxic water masses

The estimated denitrification rate for the water column of the Arabian Sea discussed does not include denitrification associated with seasonal hypoxia/suboxia/anoxia found over the West Indian Shelf. Naqvi et al. (2006a) estimate a denitrification rate for this region of 1.3–3.8 Tg N a<sup>-1</sup> based on nitrate consumption. Because the other pathways to N<sub>2</sub> that lead to the “extra” excess N<sub>2</sub> found in the deep Arabian Sea are not included, this estimate may be conservative. In addition, the estimates based on ETS and <sup>15</sup>N incubations for the Arabian Sea discussed in Sect. 3.3.1 do not include episodic occurrences of suboxic waters containing nitrite along the Omani Coast including the entrance to the Gulf of Oman (Morrison et al., 1998). They also exclude the possibility of water-column denitrification within the Gulf of Oman’s water column. Similarly, although Codispoti and Packard (1980) included sites outside of the main suboxic zone in the eastern tropical South Pacific, they did not consider the possibility of denitrification in waters south of ~25° S, but recent studies

suggest that seasonal/episodic suboxia can occur at least as far south as ~36° S (Farías et al., 2004).

Another known site of water column suboxia and denitrification occurs off the coast of Namibia. Kuypers et al. (2005), suggest an N<sub>2</sub> production rate of 1.4±1 Tg N a<sup>-1</sup> for this region. Kuypers et al. (2006) also suggest a rate of ~0.3 Tg N a<sup>-1</sup> for the suboxic transition waters that lie between the oxic and anoxic layers in the Black Sea. Some denitrification must occur in the suboxic transition zone of the Cariaco Basin (Scranton et al., 2006), although probably at a much smaller overall rate than in the Black Sea. Total denitrification in the Baltic is ~0.5–1 Tg N a<sup>-1</sup> (Voss et al., 2005) of which 10–20% may take place in suboxic portions of the water column and the rest in sediments (e.g. Shaffer and Rønner, 1984). Denitrification is also known to occur in the water columns overlying California Borderland Basins (Liu and Kaplan, 1989). In the Santa Barbara Basin most (~75%) of the denitrification appears to occur in the sediments, but the water column rate (per unit volume) is comparable to that found in the suboxic waters of the eastern tropical North Pacific (Sigman et al., 2003). Suboxic waters and denitrification also occur in the Gulf of California (Altabet et al., 1999). Water column denitrification is also likely to occur during seasonal and episodic low oxygen outbreaks in coastal waters such as the shelf adjacent to the delta of the Mississippi River (Rabalais et al., 2000; Rabalais and Turner, 2006), and the northwestern Black Sea Shelf (Zaitsev, 2006). With increasing eutrophication of coastal waters, such outbreaks may be on the increase. In addition, there are several regions of the ocean that contain water masses “on the verge” of suboxia such as the Bay of Bengal (Helly and Levin, 2004) where one might expect episodic water column denitrification. Small contributions are also likely in the suboxic transition zones between oxic waters and anoxic hot brines such as found in the Orca Deep (Van Cappellen et al., 1998) and Bannock basin (Daffonchio et al., 2006).

Then we have the contributions from denitrifying environments within the oceanic water column that have not yet been given much consideration. It is known, for example, that denitrification can proceed in the presence of dissolved oxygen (Codispoti et al., 2005; Zehr and Ward, 2002), and there are data that suggest that denitrification occurs within particles suspended in low oxygen (but not suboxic) waters (Wolgast, 1998; Kuypers et al., 2005). There are also some suggestions that this process can occur in well-oxygenated water (Michotey and Bonin, 1997; Li et al., 2006). Given that suboxic waters comprise only ~0.1–0.2% of the oceanic volume, denitrification, even at low rates, at higher oxygen concentrations has the potential to greatly increase the total rate of water column denitrification.

Low inorganic-N concentrations have been associated with hydrothermal vents and adjacent waters (Mehta et al., 2003), and a bacterium from a hydrothermal vent chimney has been shown to grow *via* nitrate respiration with the production of N<sub>2</sub> (Nakagawa et al., 2003). No estimate for the

overall denitrification rate in the hydrothermal circulations associated with mid-ocean ridges/flanks exists, but Schultz and Elderfield (1977) suggest that the annual hydrothermal flow associated with ridges and ridge-flanks is  $2.4 \times 10^{16}$  kg. If one assumes that complete denitrification occurs in this entire flow and that the original nitrate concentration is  $30 \mu\text{M}$ , a denitrification rate of  $\sim 10 \text{ Tg N a}^{-1}$  results. Is this a wild over-estimate? Maybe, but perhaps we should take a systematic look.

Denitrification has also been shown to occur in brine pockets in Arctic and Baltic sea ice (Rysgaard and Glud, 2004; Kaartokallio, 2001, 2005). Rysgaard and Glud suggest integrated rates ranging from 10 to  $45 \mu\text{M-N m}^{-2} \text{ d}^{-1}$ . With an average annual sea ice-extent of  $19\text{--}29 \times 10^6 \text{ km}^2$  (Gloersen et al., 1992) these values yield a denitrification rate of  $1\text{--}7 \text{ Tg N a}^{-1}$ .

Finally and importantly, some nitrogen fixation occurs in proximity to denitrification (Brandes et al., 1998; Deutsch et al., 2007), and to the extent that the signals overlap, denitrification rate estimates based on excess N<sub>2</sub> and nitrate deficit signals may underestimate the actual (gross) denitrification rate. *From the above discussion and data, it would seem that one can erect the hypothesis that oceanic water column denitrification is  $150 \text{ Tg N a}^{-1}$  or higher.*

### 3.4 A sedimentary denitrification of $300 \text{ Tg N a}^{-1}$ or more?

#### 3.4.1 Data-based sedimentary denitrification rate estimates

The history of estimates for oceanic sedimentary denitrification has evolved in steps: the original stasis was disrupted by the realization that coupled nitrification-denitrification (e.g. Codispoti and Christensen, 1985; Grundmanis and Murray, 1977) required an upward revision in rates, and this was followed by the recognition that direct estimates of N<sub>2</sub> production in sediments yielded rates much higher than existing literature values based on pore water profiles. Given the rapidly evolving understanding of the multiple microbially mediated pathways to N<sub>2</sub> (Fig. 1) that, in turn, lead to uncertainties in the stoichiometry of sedimentary denitrification, it seems wise to emphasize estimates based on direct determination of N<sub>2</sub> fluxes.

Devol (1991) suggested that direct measurements of N<sub>2</sub> fluxes from the eastern North Pacific shelf and upper slope were 4-5 times greater than those estimated by indirect methods prevailing at that time. His shelf values (<150 m) when scaled up to the world-wide shelf area (Menard and Smith, 1966) yield a shelf-sediment denitrification rate of  $\sim 500 \text{ Tg N a}^{-1}$ . A subsequent study with additional data (Devol and Christensen, 1993) suggested that the nitrate influx to the sediments accounted for only  $\sim 40\%$  of the total denitrification rate, and, scaled up to the world-wide shelf area, yielded a rate of  $>440 \text{ Tg N a}^{-1}$ . Similar sedimentary N<sub>2</sub> flux data from the Bering, Chukchi and Beaufort shelves taken in late summer and early spring (heavy

ice, pre-bloom) scale up to a world-wide shelf estimate of  $170 \text{ Tg N a}^{-1}$  (Devol et al., 1997), and sedimentary N<sub>2</sub> flux data from the mid-Atlantic Bight (Laursen and Seitzinger, 2002) scale up to a global shelf rate of  $\sim 235 \text{ Tg N a}^{-1}$ . Note that the 0–200 m (shelf) sedimentary area comprises only 7.5% of the total area of oceanic sediments (Menard and Smith, 1966)!

Devol and Christensen (1993) present N<sub>2</sub> flux values from depths between 200–635 m. When scaled up to the world-wide area of sediment between 200 and 1000 m their values give a rate of  $>100 \text{ Tg N a}^{-1}$ . This depth range comprises only 4.4% of the total oceanic area (Menard and Smith, 1966). Lehmann et al. (2005) suggest a minimum rate of  $1.3 \text{ Tg N a}^{-1}$  for the abyssal Bering Sea (>2000 m) *based on nitrate deficits*. Devol and Christensen's data suggest that it might be appropriate to multiply this rate by 2.5 which would yield a total rate of  $3 \text{ Tg N a}^{-1}$  for abyssal Bering Sea sediments. If we can scale abyssal denitrification as proportional to sedimentary oxygen consumption rates (Jahnke, 1996), one can find an abyssal area with rates similar to the Bering Sea that is  $\sim 10$  times as large (Jahnke, 1996; SCOR, 2003). This would give a rate of  $30 \text{ Tg N a}^{-1}$  for  $\sim 3\%$  of the ocean sediments at depths >2000 m. If we assume that rates in the remaining 97% of the abyss average 1/10 of the Bering Sea rate, we obtain a total abyssal rate of  $\sim 130 \text{ Tg N a}^{-1}$ .

Admittedly, most of these data come from productive regions, but this foray through the literature suggests that an estimate of  $300 \text{ Tg N a}^{-1}$  or more for the global oceanic sedimentary rate can be defended, particularly since the 1000–2000 m depth range has not even been included!

#### 3.4.2 Sedimentary denitrification rate estimates from the Middelburg et al. model

Codispoti et al. (2001) suggested an oceanic sedimentary denitrification rate of  $\sim 300 \text{ Tg N a}^{-1}$ . They used the model-based estimate of  $230\text{--}285 \text{ Tg N a}^{-1}$  suggested by Middelburg et al. (1996) as a starting point, but observed that this range of values was based on canonical stoichiometries that did not account for anammox or for trace metal mediated reactions that might produce N<sub>2</sub>. In their standard run in which nitrate was allowed to oxidize ammonium to N<sub>2</sub> (by increasing the N<sub>2</sub> production/C consumption ratio from 0.8 to 1.0) Middelburg et al. (1996) found a total oceanic sedimentary denitrification rate of  $318 \text{ Tg N a}^{-1}$ . We now have data that suggest that anammox occurs in sediments (Dalsgaard and Thamdrup, 2002; Thamdrup and Dalsgaard, 2002), and trace metal and iodate mediated denitrification may also occur (Codispoti et al., 2005; Farrenkopf and Luther, 2002; Luther et al., 1997), so allowing nitrate to oxidize ammonium to N<sub>2</sub> may be justified. Additionally, taking full account of changing knowledge about the stoichiometry of denitrification (Fig. 1, Van Mooy et al., 2002, etc.) might require a larger increase in the N<sub>2</sub> production to C consumption ratio than the value (1.0) selected by Middelburg et al. (1996) for



the  $318 \text{ Tg N a}^{-1}$  model run. In addition, the direct  $\text{N}_2$  contributions of *Thiomargarita*, *Thioploca*, *Beggiatoa* (Fossing et al., 1995; Schulz and Schulz, 2005; Zitsman and Brüchert, 2005) and other sedimentary bacteria that oxidize reduced sulfur compounds with nitrate have yet to be explicitly addressed vis a vis the oceanic sedimentary denitrification rate. Finally, the bacteria that use nitrate or nitrite to oxidize ammonium and sulfide, etc. are lithotrophs that may be net *producers* of organic matter within the sediments.

Middelburg et al. (1996) compared their data with experimental estimates and suggested that the “model-predicted denitrification rates are rather conservative estimates of the true rates” since the modeled rates were generally lower than reported rates. In addition, they noted that many of the reported rates were probably low because they were not based on direct determinations of  $\text{N}_2$  (Devol, 1991). Their model results also depended strongly on a labile C supply that decays exponentially with depth. While this is a reasonable assumption there are “short circuits” that lead to enhanced downwards C fluxes. For example, high abyssal denitrification rates in Bering Sea sediments are associated with downwards transport (Lehmann et al., 2005) that may enhance the supply of labile C to the abyss. Similarly, canyon dynamics and lateral transport may enhance the abyssal C supply near basin margins (e.g. Jahnke and Jahnke, 2000; Moran et al., 2005). In addition, the lithotrophic productivity associated with hydrothermal vents and cold seeps, would cause local violations of the exponential decrease in the labile C supply with depth, as would lithotrophy within sediments. Primary production remains as the single most important source of the downwards flux of labile C, and estimated rates of primary production have tended to increase with time. For example, recent observations in the Arctic reveal a previously under-appreciated “hotspot” for primary production in Barrow Canyon (Hill and Cota, 2005).

### 3.4.3 Additional sedimentary denitrification sites

Recent studies suggest that coarse (silty and sandy) nearshore sediments that were previously discounted as sites of enhanced respiration because of low organic carbon contents, may be sites of high respiration including denitrification (Jahnke, 2006; Middelburg et al., 2005; Rao and Jahnke, 2006). Seasonal oscillations in water exchange between aquifers and the coastal ocean (Michael et al., 2005) might, in effect, expand coastal denitrifying sediments landward. In addition, there has been considerable recent interest in microbial activities that can be found deep in marine sediments (Parkes et al., 2005). Suboxic electron acceptors can be found more than 100m below the surface in sedimentary columns presumably as a consequence of water circulating through the underlying basement rock (Hondt et al., 2004) that supplies oxygen and nitrate producing an “upside-down” redox profile (Law, 2004). There has yet, to be an attempt to assess the overall impact of these processes.

### 3.4.4 Implications of isotope budgets

Whole ocean N isotope budgets, have a time-scale similar to the  $\sim 10^3$  year turnover time for fixed-nitrogen. Because  $\sim$  century-scale human impingement has dramatically effected continental shelf ecosystems where much of the sedimentary denitrification occurs (e.g. Watling and Norse, 1998), applying ratios based on global-scale isotope budgets to *present-day* denitrification is problematic. Moreover, at the moment, we can only speculate on the fractionation that occurs during the oxidation of organic-N and ammonium to  $\text{N}_2$  and for some of the other pathways shown in Fig. 1. Brandes and Devol (2002) suggested a sedimentary denitrification rate of  $280 \text{ Tg N a}^{-1}$  for the Holocene based on a global oceanic isotope budget for fixed-N. Major factors in their analysis were the high fractionation of N associated with canonical water column denitrification, the very low fractionations associated with sedimentary denitrification and nitrogen fixation, and an estimate of  $75 \text{ Tg N a}^{-1}$  for canonical denitrification in the water column. While these results seem to suggest that a water column rate of  $150 \text{ Tg N a}^{-1}$  would lead to an impossibly high sedimentary denitrification rate, this is not necessarily the case. because a portion of water column  $\text{N}_2$  production arises from oxidation of labile organic-N and ammonium. These pools tend to be depleted, so little or no isotope fractionation should occur, and it may be reasonable to assume that this portion of water column denitrification behaves like sedimentary denitrification with respect to fractionation of nitrogen isotopes. Because of this, it may be useful to rename the Brandes and Devol (2002) ratio (3.7) for sedimentary to water column denitrification as the “unfractionated (sediments + water)/fractionated” denitrification ratio.

What fraction of water column denitrification may behave like sedimentary denitrification with respect to N-isotope fractionation? One way of obtaining an answer is to examine nitrate deficit and excess  $\text{N}_2$  values for the Arabian Sea. Since the Codispoti et al. (2001) nitrate deficit equation for the Arabian Sea should exclude organic-N and ammonium oxidation, it may represent that portion of the water column denitrification that enriches the nitrate pool with  $^{15}\text{N}$ . The excess  $\text{N}_2$  values, on the other hand, represent the local biological  $\text{N}_2$  additions from all sources. Taking our earlier values of a total rate for the quasi permanent suboxic zone of the Arabian Sea of  $60 \text{ Tg N a}^{-1}$ , and a ratio of excess  $\text{N}_2$  to nitrate deficit of 1.75, we arrive at a value of  $34 \text{ Tg N a}^{-1}$  for “fractionated” water column denitrification in this water mass. The remaining  $26 \text{ Tg N a}^{-1}$  may then arise from two sources “unfractionated” water column denitrification and  $\text{N}_2$  supplied by the sediments. In Sect. 3.3.2 it was suggested that total sedimentary denitrification in this region is unlikely to exceed  $4 \text{ Tg N a}^{-1}$ , and that much of this would occur outside the depth range of the quasi-permanent suboxic water mass. Given all of the other uncertainties, we will ignore this minor complication and assume that 43% (26/60) of the water column denitrification in this water mass arises from “un-



fractionated" denitrification. With Gruber and Sarmiento's (1997) and Van Mooy et al.'s stoichiometries for canonical denitrification the ratios are 0.13 and 0.21 respectively. During the anammox reaction in which nitrite oxidizes ammonium to  $\text{N}_2$  this ratio is 0.5, but the ammonium and nitrite presumably arise largely from heterotrophic activity including canonical denitrification. Taking the average of Gruber and Sarmiento's ratio and the ratio during anammox gives a ratio of 0.32. Much more research is needed before anything definitive may be said about this ratio, but, for now, we will assume that unfractionated/total water column denitrification ratio is 0.38  $((0.43+0.32)/2)$ . With a ratio of 0.38 and a total water column denitrification rate of  $150 \text{ Tg N a}^{-1}$  "unfractionated" water column denitrification is  $57 \text{ Tg N a}^{-1}$ , and fractionated water column denitrification is  $93 \text{ Tg N a}^{-1}$ .

Deutsch et al. (2004) suggest that Brandes and Devol's (2002) unfractionated(sediments+water)/fractionated denitrification ratio of 3.7 should be reduced to 2.7 due because of isotope dilution. Lehman et al. (2004), on the other hand, suggest that release of "heavy" ammonium from sediments might make Brandes and Devol's ratio an underestimate. Altabet (2006) suggests that the ratio in the Arabian Sea could be  $\sim 1$ , but when the water column denitrification that is unfractionated is taken into account his ratio is  $\sim 1.8$ . Inspection of the potential nitrate values that should exist before the onset of denitrification (Codispoti, 1973a and b; Codispoti and Richards, 1976), and relationships between nitrate deficits and ambient nitrogen concentrations in the Arabian Sea, suggest that Altabet and Deutsch et al.'s estimates of the impact of isotope dilution on reducing the Brandes and Devol ratio may be too large. Ultimately this will depend on details of the distributions of nitrate, nitrate deficits and denitrification rates that require additional study. Finally, to the extent that local nitrogen fixation is enhanced in the vicinity of suboxic waters (Deutsch et al., 2007), the resulting local supply of isotopically light nitrate, might cause underestimates in the fractionation that occurs during water column denitrification necessitating an increase in the unfractionated (sediments+water)/fractionated ratio (Naqvi, 2007). Thus, it might be reasonable to suggest that the true unfractionated (sediments + water)/fractionated denitrification ratio for the Holocene is probably between 2 and 4.

Taking unfractionated denitrification to be  $357 \text{ Tg N a}^{-1}$  ( $300 \text{ Tg N a}^{-1}$  in sediments and  $57 \text{ Tg N a}^{-1}$  in the water column), and fractionated water column denitrification to be  $93 \text{ Tg N a}^{-1}$  yields an unfractionated (water + sediments)/fractionated ratio of 3.8. Given all of the uncertainties, all that can be said is that the values selected in this paper for water column and sedimentary denitrification are not in gross conflict with present knowledge about the oceanic isotopic budget for fixed-N. Because the ratio of 3.8 is on the higher side of the estimates, one might speculate that anthropogenic impingement on the coastal ocean during the Holocene-Anthropocene transition has increased sedimentary denitrification faster than the corresponding increase in

water column denitrification.

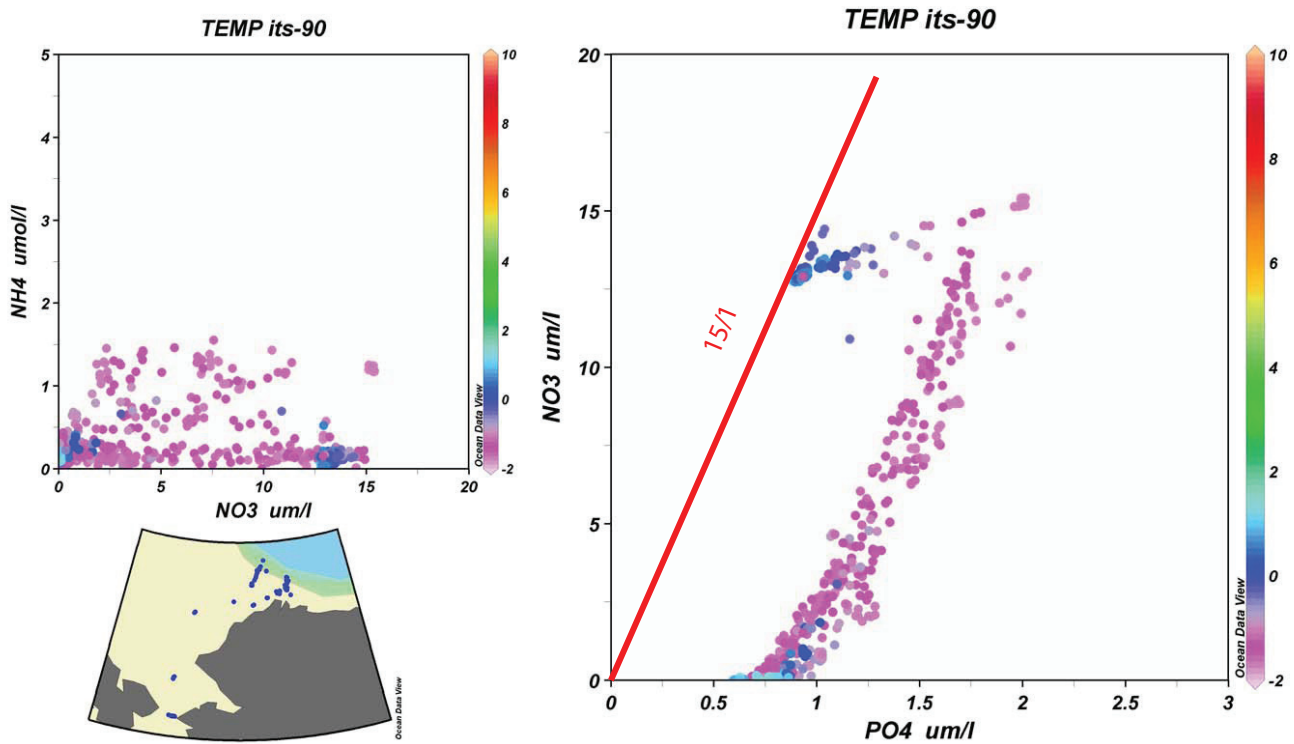
### 3.4.5 Sedimentary denitrification rates vs the oceanic fixed-N budget

To conclude this section, it seems reasonable to suggest that the weight of the evidence supports an oceanic sedimentary denitrification rate of  $>300 \text{ Tg N a}^{-1}$ . Even if the sedimentary rate was only  $200\text{--}250 \text{ Tg N a}^{-1}$ , however, it would not solve the problem of a deficit in the oceanic fixed-N budget (Table 1) that could not be maintained for more than a few hundred years without challenging current interpretations of the atmospheric  $\text{CO}_2$  record (Gruber and Sarmiento, 1997) and the  $^{15}\text{N}$  record in sediments (Altabet, 2002 and 2006; Deutsch et al., 2004). While the author favors an estimate of  $>300 \text{ Tg N a}^{-1}$  after a consideration of the history of estimates and his knowledge of ongoing research, there is clearly room for debate and for considerably more research on sedimentary denitrification, potentially the largest sink in the oceanic fixed-N budget.

## 3.5 Interpretation of the oceanic N/P ratio

### 3.5.1 N/P ratios and the Redfieldian case for homeostasis

Arguments for a "homeostatic" oceanic fixed-N budget that is balanced within the uncertainties often involve (in part) interpretation of oceanic N/P ratios and intercepts in N-P scatter diagrams (e.g. Gruber, 2004; Tyrell, 1999). In practice, the ratios employed for the water column are normally nitrate/phosphate ratios. Below the upper several hundred meters, ammonium and nitrite concentrations are usually low, and it is also reasonable to assume that most of the organic N is refractory (Aluwihare et al., 2005). Similarly, in nutrient-depleted surface waters it might be reasonable to assume that, when nitrate or phosphate are  $\sim 0$ , the other biologically available forms of these elements are also close to 0 (e.g. Codispoti et al., 2005; Thingstad et al., 2005; Krom et al., 2005; Fig. 2). The oceanic average for the nitrate/phosphate (by atoms of N&P) ratio at depths of 500 m and greater is  $\sim 14.7$  (Falkowski, 2000), vs nitrate and phosphate regeneration ratios of  $\sim 16$  (e.g. Redfield et al., 1963), and average planktonic N/P ratios of  $\sim 16$  (Hedges et al. 2002). Following Redfield, (1958), many investigators (e.g. Gruber, 2004; Tyrell, 1999) have used the near correspondence between the oceanic N/P ratio, regeneration ratios, and the average ratio in phytoplankton, to suggest that nitrogen fixation and denitrification interact in the Holocene ocean to produce a "homeostasis" that keeps the ocean fixed-N budget balanced within observational uncertainty. A hopefully not too unfair simplification of this view would be that the oceanic fixed-N inventory lags phosphate by only an amount small enough to "excite" sufficient nitrogen fixation to keep the inventories close to the canonical 16/1 Redfield ratio. Some have also looked at the oceanic zero intercepts of the phosphate-nitrate



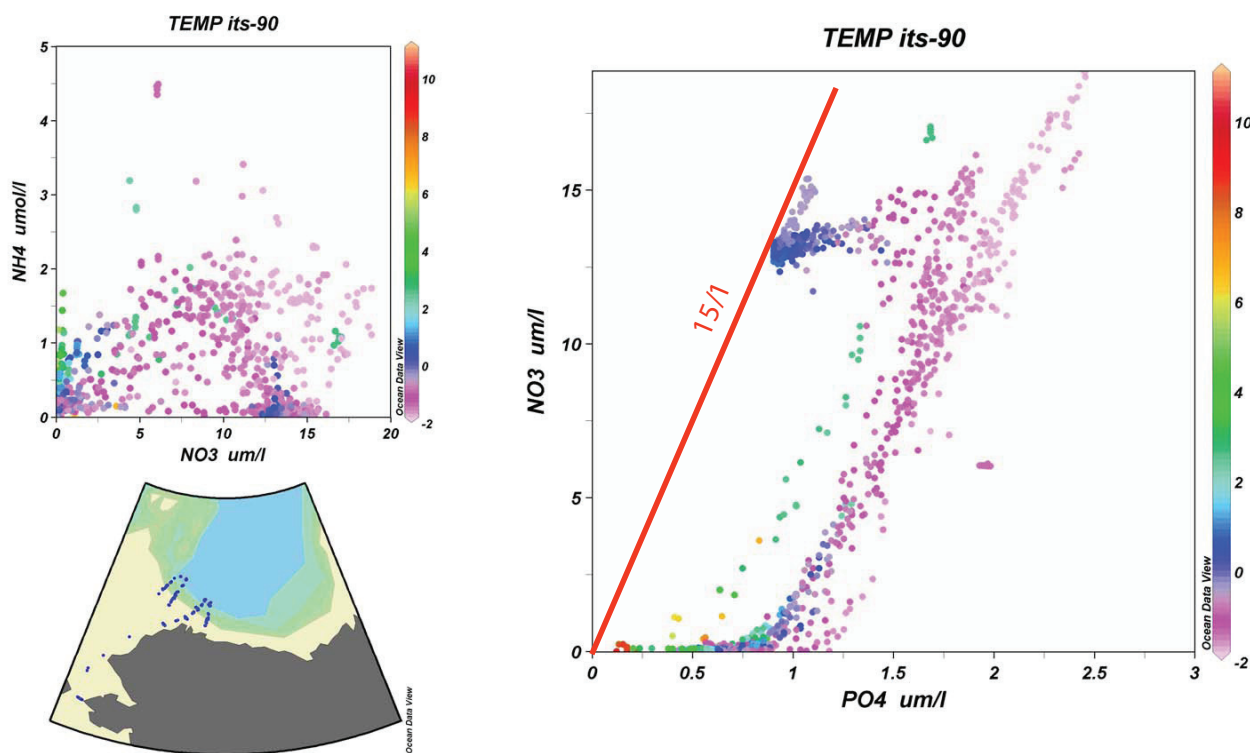
**Fig. 2a.** Nitrate-ammonium and nitrate-phosphate scatter diagrams (concentrations in  $\mu\text{M}$ ) from data collected in the Chukchi Sea during May-June 2004 (U.S.C.G.C. *Healy*, cruise HLY 04-02). Station locations are shown in the inset chart. Water temperature color scale is on the right.

scatter diagrams (e.g. Tyrell, 1999) to amplify this argument, since, on average, the phosphate intercept at 0 nitrate is only  $\sim 0.25 \mu\text{M}$ . With an atomic N/P ratio of 16 this corresponds to  $\sim 4.0 \mu\text{M}$  of fixed-N.

Whether or not an average nitrate deficit of  $\sim 4.0$  should be considered to be small relative to concentrations within 100 m of the photic zone is debatable. Nevertheless, Redfield's original idea has merit, and must help the ocean maintain a balance over some time-scale. Is the time scale dominated by biological processes acting in close proximity or must these processes be coupled, at least partially, by ocean circulation as suggested by the existence of ocean basins with significantly different N/P ratios (e.g. Fig. 2), and the studies of Broecker and Peng (1982), Coles and Hood (2006), Codispoti (1989), and Yamamoto-Kawai (2006)? Once, we admit that, on average, there is a time-lag in the coupling of denitrification and nitrogen fixation that requires some coupling via oceanic circulation a suite of questions arises including: How do regional differences in N/P ratios impact the quality of primary production and particle export from the surface ocean?, and how large a fixed-N deficit can develop before the system arrives at a new steady-state?

### 3.5.2 Multiple controls on nitrogen fixation

Several recent studies (e.g. Wu et al., 2000) suggest that iron limitation of nitrogen fixation, can retard the simple feedback mechanism originally proposed by Redfield (1958). In regions such as the North Atlantic where Saharan dust creates a relatively abundant iron supply, phosphate limitation (Sañudo-Wilhelmy et al., 2001) and co-limitation of nitrogen fixation by iron and phosphorus (Mills et al., 2004) may occur. In other regions such as the HOT site off Hawaii, iron is more likely to limit nitrogen fixation (e.g. Wu et al., 2000). Capone (2001) concluded that "Iron and phosphorus are the likely factors controlling oceanic nitrogen fixation and their relative influence may vary among ocean basins". Other trace metals such as zinc, a cofactor in many alkaline phosphatases (e.g. Mills et al., 2004), may also impact nitrogen fixation rates. In addition, nitrogen fixation is energy intensive, and the pelagic nitrogen fixation identified, so far, is restricted mainly to tropical and sub-tropical waters (Carpenter and Romans, 1991). Another complication vis a vis the traditional Redfieldian view is that nitrogen fixation proceeds in North Atlantic waters that reach the surface with  $>16/1$  nitrate/phosphate ratios (Wu et al., 2000) and that the organic material that is produced during nitrogen fixation has N/P ratios considerably higher than 16/1 (e.g.



**Fig. 2b.** Nitrate-ammonium and nitrate-phosphate scatter diagrams (concentrations in  $\mu\text{M}$ ) from data collected in the Chukchi Sea during July-August 2004 (U.S.C.G.C. *Healy*, cruise HLY 04-03). Station locations are shown in the inset chart. Water temperature color scale is on the right.

Gruber and Sarmiento, 1997; Karl et al., 1997). These facts suggest that nitrogen fixation does not respond to an excess of phosphate in a simple fashion and that nitrogen fixation may continue beyond the point at which the Redfield ratio of 16/1 is attained. Since the factors that govern phosphate, and iron concentrations, and water temperature differ, it is likely that the processes that permit nitrogen fixation to compensate for losses of fixed-N are complex and, may take longer than might be inferred from the original Redfield proposal.

### 3.5.3 Interpreting intercepts

There is considerable regional variability in the values of nitrate and phosphate intercepts in scatter diagrams of the two variables. We can find positive nitrate intercepts in the Mediterranean Sea and in portions of the North Atlantic (e.g. Wu et al., 2000), and we can find phosphate values at 0 inorganic-N much higher than  $0.25 \mu\text{M}$  in regions such as the Peruvian Upwelling and the Chukchi and East Siberian seas (Fig. 2; Codispoti et al., 1991). Positive nitrate intercepts at 0 P are often attributed to nitrogen fixation. High phosphate values at 0 inorganic-N can reasonably be attributed to the effects of far-field and local denitrification. In the Chukchi Sea, Pacific waters entering via Bering Strait are already deficient in inorganic-N as a consequence of external denitrifi-

cation, and additional denitrification occurs locally (Devol et al., 1997).

Early in the Chukchi Sea growing season (Fig. 2a) the phosphate value at 0 nitrate in these waters is  $\sim 0.7 \mu\text{M}$ , but we see a “march towards 0 phosphate” after the phytoplankton bloom in surface waters (Fig. 2b). This brings us to the next complication, “luxury consumption”. Redfield et al. (1963) suggested “luxury consumption” of phosphate to explain a phosphate-nitrate scatter diagram similar to Fig. 2b. Luxury consumption of inorganic-N can also occur when phosphate is depleted (Arrigo, 2005; Klausmeier and Litchman, 2004; Klausmeier et al., 2004; Krom et al., 2005). A similar situation exists with respect to carbon uptake after depletion of one or more nutrients (e.g. Sambrotto et al., 1994). Early growing season conditions in the Chukchi Sea were quite similar in 2002 (Codispoti et al., 2005) to the 2004 conditions shown in Fig. 2a suggesting that the system “re-sets” itself on an annual basis. This is in line with theoretical considerations (Peinert et al., 1989) that suggest that the unusual nutrient ratios associated with “luxury consumption” are transients that have little effect on the overall oceanic N/P ratio. The complication of “luxury consumption”, therefore, introduces uncertainty into the use of nitrate and phosphate intercepts *per se* as indicators of “homeostasis” in the oceanic N/P ratio, although the overall slopes of

the N/P ratio diagrams are not likely to change greatly if data near the intercepts were omitted.

### 3.5.4 Variability in N/P ratios?

Chukchi Sea/Canada Basin data (Fig. 2) provide an interesting juxtaposition of regional differences in N/P ratios because the Pacific waters that occupy the upper  $\sim 150 \text{ m}$  overlie deeper waters that change little with respect to their nutrient concentrations and ratios since entering the Arctic Ocean from the North Atlantic (Codispoti et al., 2005). Thus, we have waters in the upper  $\sim 150 \text{ m}$  that have ratios of nitrate/phosphate  $<10$  with a slope ( $\Delta\text{nitrate}/\Delta\text{phosphate}$ ) of  $<13$ , overlying Atlantic waters with ratios of  $\sim 15$ . In contrast to the low ratios in waters that contain a net denitrification signal such as the Chukchi Sea, several regions where nitrogen fixation is thought to be important have high ratios. For example, regeneration ratios ( $\Delta\text{nitrate}/\Delta\text{phosphate}$ ) in the Red Sea exceed 20 (Naqvi et al., 1986); N/P ratios in sinking particulate matter during a  $\sim$  decadal period of net nitrogen sequestration at the HOTS time-series station in the North Pacific subtropical gyre N/P were generally  $>16/1$  and at times  $>40$  (Karl et al., 2001); and nitrate/phosphate ratios in the Mediterranean Sea increase from  $\sim 22$  to 28 (Krom et al., 1991; Krom et al., 2004 and 2005) proceeding eastward from the Alboran Sea to the Cyprus Eddy. Finally, phosphate limitation is more prevalent in fresh water (including pristine fresh water lakes) than in the ocean (Howarth, 1988; Howarth and Marino, 2006; Falkowski, 2003). This raises the question of why the ocean is generally deficient in N and lakes deficient in P if one takes the view that a small excess of P is all that is required to maintain “Redfieldian” N/P ratios.

The above considerations raise the issue of the constancy of N/P ratios, and whether Redfield’s (1958) interpretation that the plankton control rather than respond to the oceanic nitrate/phosphate ratio (see Falkowski, 2000) is correct. The results that we have reviewed, so far, suggest that it is possible for nitrogen-fixers to produce organic material with N/P ratios higher than the Redfield ratio of 16/1. What about the rest of the phytoplankton? We have already noted the phenomenon of “luxury consumption”, but this process does not export large amounts of organic material, and therefore does not have large impact on observed subsurface regeneration ratios. After a literature review, Codispoti (1989) concluded that with possible exceptions in coastal waters, there was considerable evidence for an average oceanic phytoplankton uptake ratio and a regeneration ratio close to 16:1. Even if we examine the data from the Chukchi Sea where considerable excess phosphate seems to exist, the “low” regeneration ratio ( $<\sim 13:1$ ) can reasonably be attributed to the effects of sedimentary denitrification suggesting a ratio in the material exported from the photic zone during the growing season similar to 16:1. These observations contrast with an accumulation of data suggesting that phytoplankton groups can have uptake rates that stray far from the canonical Red-

field ratio. For example, empirical laboratory data suggest that phytoplankton can be divided into superfamilies (Quigg et al., 2003) with markedly different N:P and C:P ratios and smaller but still significant differences in C:N ratios. Laboratory studies also suggest differences in N:P ratios that may arise from physiological variables (e.g. Klausmeier and Litchman, 2003). Field studies can produce similar results. For example, Arrigo et al. (1999) found an overall disappearance ( $\sim$  uptake) ratio in nitrate and phosphate replete Antarctic waters close to the Redfield ratio, but when they broke down their data regionally, they found a *Phaeocystis* dominated community with a nitrate/phosphate disappearance ratio of  $\sim 19$  and a diatom dominated community with a ratio of  $\sim 10$ . This study was followed by that of Sweeney et al. (2000) who found similar results early in the growing season, but found that, as the growing season progressed, ratios in the diatom dominated community became more “Redfieldian”. These observations are in line with suggestions (Arrigo, 2005; Klausmeier et al., 2004) that nutrient ratios in phytoplankton can be affected by growth strategies and adjustment to environmental conditions in addition to the already noted “familial” differences. Arrigo (2005) suggested that “survivalists” have high N:P ratios, “bloomers” low N:P ratios, and “generalists” ratios close to the canonical Redfield ratio. Since diatoms in the Ross Sea early in the growing season should be in the “blooming” mode, their low N:P ratios could, in hindsight, be anticipated. Klausmeier et al.’s (2004) views are similar, but they also noted that P-limited environments favor slightly less P allocation to assembly than N-limited or light-limited environments. Their model predicted that optimal phytoplankton N:P ratios could vary from 8.2 to 45.0, and structural ratios from 7.1 to 43.3, with a median of 17.7, tantalizingly close to the canonical Redfield ratio. They suggest that “... the canonical Redfield N:P ratio of 16 is not a universal biochemical optimum, but instead represents an average of species-specific N:P ratios.” They also discuss the particularly high ratios in nitrogen-fixing species, noting an N:P range of 42–125 for *Trichodesmium* blooms. They also provide a mechanistic explanation for the high N:P and N:C ratios in nitrogen fixing phytoplankton that involves the need for more light-harvesting N rich machinery to power N fixation. They conclude that the Redfield ratio is not a universal value based on either empirical data or their model, that it is possible that N:P ratios in the ocean could vary over time and that Broecker and Henderson’s (1998) suggestion that the ratio could rise to 25 during glacial periods due to a higher iron supply is possible.

Here, we will take the position that the ocean-wide sinking flux of organic material in today’s ocean is close to 16:1, and that nutrient replete “communities” do tend to export organic material with an N:P ratio similar to the canonical Redfield ratio. Given the high N:P ratios associated with nitrogen-fixation, however, one can wonder if *an ocean in which nitrogen fixation was “easy” and/or in which denitrification is reduced might not have an N:P ratio close to 25*. Broecker

and Henderson (1998; see also, Wolff et al., 2006) suggest that such conditions could arise from stimulation of nitrogen fixation by an increased iron supply during glacial periods. Evidence from the present-day Eastern Mediterranean suggests that the high nitrate/phosphate ratio in the deep water (25–28) may arise from a high N/P ratio in inputs and limited denitrification (Krom et al., 2004 and 2005), and there is evidence to suggest that denitrification was reduced during glacial periods (e.g. Altabet et al., 2002; Christensen et al., 1987; Deustsch et al., 2004; Ganeshram et al., 2002). Thus, it is possible that the overall oceanic N:P ratio can fluctuate significantly. A reasonable range might be  $\sim 14$ – $25$ , values that can be found within large basins in today's ocean.

Accurate and comprehensive nitrate/phosphate ratios for the world ocean have only been available for the last  $\sim 50$ – $75$  yrs, a period of considerable global change. What if these ratios slowly change and could have been higher in the past? A Gedankenexperiment that has the nitrate/phosphate ratio decrease from 25 to 15, would decrease nitrate concentrations by  $20 \mu\text{M}$  ( $30/2=15$ ;  $50/2=25$ ) if we hold the mean phosphate concentration constant, take 15 as the average nitrate/phosphate ratio in today's ocean and employ an average oceanic nitrate concentration of  $\sim 30 \mu\text{M}$  (Gruber and Sarmiento, 1997). With an oceanic volume of  $1.35 \times 10^{18} \text{ m}^3$  (Menard and Smith, 1966) and recognizing that  $20 \mu\text{M}=20 \text{ millimoles m}^3=0.28 \text{ g N m}^3$ , we arrive at a total nitrate removal of  $400\,000 \text{ Tg N}$ , an amount that could sustain the imbalance in our "pro forma" budget (Table 1) for  $\sim 2000$  years!

### 3.5.5 Concurrent changes in P&N sinks may help stabilize N/P ratios

Piper and Codispoti (1975) suggested that increased denitrification might be associated with increased phosphate deposition in the form of phosphorite (mainly carbonate fluorapatite or CFA). Much has been learned about denitrification and about oceanic P deposition since the time of that paper, but the following quote is still worth considering. "Ultimately any impoverishment of combined nitrogen, caused by increased denitrification should cause marine nitrogen fixation rates to rise or should cause respiration rates at depth in the ocean to decrease because of reduced primary productivity, or both. Over geologic time, the nitrogen/phosphorus ratio may be maintained reasonably constant by such a feedback mechanism in the nitrogen cycle, *aided by the increased phosphorite precipitation which according to our proposal should accompany increased denitrification.*" (italics added). At that time, most of the identified denitrification in the ocean, was associated with suboxic waters, and Piper and Codispoti (1975) noted the association of such waters in the Eastern Tropical Pacific with phosphorite deposits. Phosphorus diagenesis is complex, and some experiments have been interpreted as suggesting an enhanced P flux from such sediments (e.g. Ingale and Jahnke, 1994). Such observations tend

to be at variance with other studies. For example, Compton et al. (2000) suggest that the Peru/Chile margin is the site of a "phosphorite giant" formation and that the present-day burial fluxes of P are high there and on the SW African Shelf, another site of water column denitrification (Kuypers et al., 2005 and 2006). Babu and Nath (2005) show that P is enriched in sediments within the depth range of the OMZ in the Arabian Sea, and Schulz and Schulz (2005) present exciting results from the Namibian shelf suggesting that the nitrate-reducing/sulfide-oxidizing bacterium *Thiomargarita namibiensis* can sequester large amounts of phosphate and enhance phosphorite deposition. They suggest that close relatives such as *Beggiatoa* spp. that is also abundant in Namibian sediments, and *Thioplaca* spp. that occur in the upwelling zone off Chile and Peru may have a similar enhancing effect. One can muse on the short-term effect of a "bottom lander" impact on bacterial mats that are rich in P. Confusion may also arise because anoxia and suboxia have quite different impacts on the oxidation state of iron. At the suboxic/anoxic interface in the Black Sea, for example, we see a phosphate minimum in the suboxic zone presumably from the uptake of P by particles formed via the oxidation by nitrate of reduced Fe and Mn that diffuses into the layer from the suboxic zone (Codispoti et al., 2005). Ganeshram et al.'s (2002) analysis of a core taken beneath suboxic waters in the Eastern Tropical North Pacific suggests that the heavy  $\delta^{15}\text{N}$  arising from water column denitrification occurs during interglacials and that P enriched layers in the sediments were also confined to the interglacials. They suggest similar conditions for the Arabian Sea and Peru margins. We believe that the weight of the evidence does suggest a positive correlation between water column denitrification and phosphorite deposition. Because the glacial-interglacial changes in phosphorite deposition that Ganeshram et al. (2002) estimated were relatively small (equivalent to  $\sim 3 \text{ Tg N a}^{-1}$  using a 16/1 N/P atomic ratio) compared to the sink and source terms in the oceanic fixed-N budget (Table 1), their view was that this process had only a small impact on the oceanic N/P ratio, and a major point of their paper was that phosphate limitation would limit postulated increases in glacial nitrogen fixation *assuming a constant Redfield ratio*. With respect to the oceanic N/P ratio and the suggestion of Piper and Codispoti (1975), this process would, indeed, help to maintain a constant ratio, but the effect would be small. One question worth investigating, however, is whether the estimates of the magnitude of the changes in phosphorite deposition in sediment underlying suboxic waters might need to be revised in light of the results of Schulz and Schulz (2005).

As is the case for upward increases in the fixed-N sink term, and in line with the "more we look, the more we find" theme of this paper, modern studies (Wheat et al., 1996) have shown that globally significant removals of P occur in association with mid-ocean ridge and flank hydrothermal processes. They produce an oceanic P budget that can be in deficit by  $\sim 4$ – $14 \times 10^{10} \text{ moles P a}^{-1}$  which (using

a Redfield atomic N/P ratio of 16) translates into a deficit  $9\text{--}31 \text{ Tg N a}^{-1}$ . They suggest, “This situation would require a transient oceanic or terrestrial source term that potentially dominated during glacial periods, but not during interglacials.”

To conclude, it is quite possible that increases in oceanic P removals may accompany increased denitrification and help to stabilize the oceanic N/P ratio, but whether the effect is minor or moderate will require further study.

### 3.6 The atmospheric carbon dioxide and sedimentary $^{15}\text{N}$ constraints

Gruber and Sarmiento (1997) suggested that deficits of  $\sim 100 \text{ Tg N a}^{-1}$  in the post-glacial oceanic combined nitrogen budget maintained for a thousand years would deplete the oceanic fixed-N inventory by  $\sim 30\%$  and change atmospheric  $\text{CO}_2$  by 50 ppm, an amount that exceeds the observed variability during the entire Holocene. This argument is worth considering, but there are some complications that they did not consider explicitly. For example, they did not account for compensating changes in terrestrial sequestration, or for the possibility that C/N uptake ratios can vary. As outlined above, photosynthetic nitrogen-fixers have N:P and N:C ratios that are high relative to “Redfieldian” plankton. If the ocean can oscillate between strong and weak nitrogen fixing phases such that the average N:P ratio can attain values of 20–25, during strong nitrogen fixation, the amount of C sequestered per N would decrease (see Sect. 3.5.4), and this would dampen the effect on the atmospheric carbon dioxide record.

Another potential constraint on the oceanic fixed-N budget of the ocean arises from the sedimentary  $\delta^{15}\text{N}$  record (Altabet, 2006). This record appears to undergo glacial-interglacial (orbital forcing) and  $\sim$  millenium scale variability during glacial Dansgaard-Oeschger events (Altabet et al., 2002). The  $\delta^{15}\text{N}$  record, during the Holocene, however, is more constant. Altabet (2006) suggests that to maintain constancy in the sedimentary  $\delta^{15}\text{N}$  signal in the face of significant changes in the oceanic fixed-N inventory requires the unlikely condition that the ratio of water column to sedimentary denitrification remains constant during such changes. Once again, the basic idea has merit, but there are a number of complications. As already noted, a substantial fraction of water column denitrification may behave like sedimentary denitrification (see Sect. 3.4.4.), and the distinction should be between those fixed-N sinks that have a large impact on  $^{15}\text{N}$  enrichments of the remaining fixed-N and those that have a small effect. In today’s ocean, we can occasionally find examples of complete denitrification in the water column (e.g. Codispoti et al., 1986; Naqvi et al., 2000), although the percentage contribution of this type of denitrification is small. What may be more important are the non-canonical water column pathways to  $\text{N}_2$  (see Sect. 3.4.4). To the extent that water column  $\text{N}_2$  production mimics sedimentary denitrifi-

cation there would be an alleviation of the sedimentary  $^{15}\text{N}$  record constraints. Moreover, the same processes that cause increases in water column denitrification (increased primary production, lower dissolved oxygen concentration) would, in many instances favor increased, sedimentary denitrification. In addition, the number of cores that have been analyzed in detail for  $\delta^{15}\text{N}$  are relatively few; there is some evidence for the occurrence of water column denitrification in the North Pacific during glaciations (Galbraith, 2006); there are diagenetic alterations of  $\delta^{15}\text{N}$  that are not well-understood (Galbraith, 2006); the estimates for the fractionation of  $\text{NO}_3^-$  during canonical denitrification vary a bit (Brandes et al., 1998; Altabet, 2006); and given the newly appreciated pathways for conversion of fixed-N to  $\text{N}_2$  (Fig. 1) much needs to be done with regard to determining appropriate fractionation factors. In addition, Naqvi (2007) points out that although the denitrification term is larger, nitrogen fixation and denitrification both occur at significant rates in the water column of the Arabian Sea such that the  $\delta^{15}\text{N}$  of local sediments is controlled partially by the *ratio between water column denitrification and nitrogen fixation*. Thus, while the sedimentary  $^{15}\text{N}$  record is sufficient to erect the hypothesis that the oceanic fixed-N inventory has been  $\sim$  constant during the Holocene, it would probably be unwise to fully accept this hypothesis without further substantiation, and it may not apply during the Holocene-Anthropocene transition for reasons that have already been stated.

## 4 Reconciliation

### 4.1 The Conundrum

Given the relatively stable climate during the Holocene, Gruber and Sarmiento (1997), Gruber (2004), and Altabet (2006), may well be correct in asserting that the oceanic fixed-N budget is  $\sim$  balanced throughout the Holocene and that if any large changes occur, they must be of a duration short enough to be averaged out in the atmospheric  $\text{CO}_2$  and sedimentary N records. The data reviewed herein, however, suggest a fixed-N sink, much larger than suggested in Gruber and Sarmiento’s (1997) and Gruber’s (2004) budgets. The following factors may permit reconciliation of these apparently divergent views:

### 4.2 Increasing the estimate of the oceanic nitrogen fixation rate

If the estimates of nitrogen fixation were raised significantly, the views of an approximate fixed-N inventory balance during the Holocene and of an oceanic fixed-N sink of  $>400 \text{ Tg N a}^{-1}$  could both be accommodated, and oceanic nitrogen fixation rate estimates have increased in recent years. More than a decade ago, Codispoti (1989) suggested that an increase in the oceanic nitrogen fixation rate would be needed to balance the fixed-N budget. Since that time,

the consensus estimate has increased by a factor of 4–5. Recently, an approximate doubling of the incubation based estimates has been suggested in order to account for previously neglected contributions of smaller sized nitrogen fixers (Montoya et al., 2004), and Davis and McGillicuddy (2006) suggest that the abundance of the larger canonical nitrogen fixer *Trichodesmium* has been underestimated. In addition, significant nitrogen fixation may occur in close proximity to zones of water column denitrification (Deutsch et al., 2007; Naqvi, 2007) but be difficult to detect with bulk parameters because the signal is swamped by denitrification. A signal does appear in some models (Deutsch et al., 2007) and in vertical  $\delta^{15}\text{N-NO}_3^-$  distributions in the Arabian Sea where “light”  $\text{NO}_3^-$  overlies “heavy”  $\delta^{15}\text{N NO}_3^-$  (Brandes et al., 1998; Naqvi, 2007; Devol et al., 2006). Brandes et al. (1998) suggest that nitrogen fixation in the Arabian Sea is  $\sim 6 \text{ Tg N a}^{-1}$  or about 20% of the water column rate for canonical denitrification. Interestingly, because of the high N:P and N:C ratios during nitrogen fixation, Devol et al. (2006a) suggest that the decomposition of the biogenic material produced by this nitrogen fixation could account for  $\sim 50\%$  of the “extra excess  $\text{N}_2$ ” found in the Arabian Sea. Finally, Coles and Hood (2006) suggest that some models of nitrogen fixation based on  $\text{N}^*$  will actually yield net rates of nitrogen fixation and not the gross rates employed in our budgets (Table 1), because of denitrification within the model domain (e.g. sedimentary denitrification in the North Atlantic).

Most direct estimates of nitrogen fixation rates in the ocean have been confined to the photic zone, yet genetic studies suggest that the capability for nitrogen fixation is widespread throughout the water column. Zehr et al. (1998), for example, have shown that the genes that support nitrogen fixation can be found within zooplankton and that these genes differ significantly from those found in free-living nitrogen fixers. Earlier experiments with shipworms showed that they were analogous to termites insofar as their symbiotic flora fixed-N when they were fed a diet of wood (Carpenter and Culliney, 1975). Two quotes from Zehr et al. (1998) are worth considering: (1) “This report shows that there are far more diverse nitrogen-fixing populations and diverse habitats which can support nitrogen fixation in the open ocean than previously documented.” and (2) “The intriguing finding that nitrogen fixation in the open ocean may occur in marine invertebrate guts is analogous to nitrogen fixation in guts of terrestrial insects and marine shipworms. Sequences of this cluster are not found in the bulk water samples, indicating that the organisms from which these sequences were derived may be permanent residents of the zooplankton gut and may even be symbiotic with zooplankton.”

Deep nitrogen fixation occurs in association with vent processes. For example, Mehta et al. (2003) suggest that some hydrothermal fluids have low nitrate and ammonium concentrations, and contain nitrogen-fixing (*nifH* genes). More recently, Mehta and Baross (2006) demonstrated that nitro-

gen fixation can occur in low fixed-N, high temperature fluids associated with hydrothermal vents. In addition, we do not know enough about the microbial environments of crustacean guts to assert that N-fixation does not occur in the presence of significant quantities of nitrate in the ambient water. Zehr et al. (1998) point out that reduced oxygen concentrations and high Fe concentrations should make conditions more favorable for N-fixation in copepod guts than it would be in ambient water. Zehr et al. (2006) suggest that it is clear that nitrogen fixation activity is suppressed by ammonium, but a strong case for suppression by nitrate cannot be made with available data, and they further point out the higher energetic cost of assimilating nitrate vs ammonium. Ammonium concentrations are quite low in most of the sub-100 m ocean, but we do not know, at this moment, whether high nitrate concentrations in the deep ocean would suppress fixation in crustacean guts. Another possibility is the occurrence of nitrogen-fixation in zooplankton in oligotrophic water. One might ask, for example, what happens when copepods are grazing on re-cycled post-bloom low N/C ratio organic matter ?

While conventional wisdom suggests that oceanic water column nitrogen fixation is concentrated in tropical and subtropical waters, nitrogen fixation has been found in the water/aggregate patches found in an Antarctic Dry Valley Lakes (Paerl and Priscu, 1998). To date, most oceanic studies of nitrogen fixation have been focused on the photic zone, on autotrophs, on subtropical and tropical waters, and to a lesser extent on shelf sediments. The question arises, therefore, *whether expanding the horizons of studies of oceanic nitrogen fixation from photic zone hotspots, to the remaining 97% of the oceanic volume might not lead to greatly increased estimates of oceanic nitrogen fixation.*

#### 4.3 The Holocene to Anthropocene transition

As already mentioned, Altabet et al. (2002) suggest that the  $\delta^{15}\text{N}$  record in cores from the Arabian Sea suggest some sharp ( $\sim$  millennial scale) changes during the last glaciation. Thus, relatively rapid changes in the oceanic fixed-N inventory may be possible. The question then arises, of how to compare the sedimentary Holocene record with relevant observations from the present-day ocean. Here it is worthwhile noting that a widely adopted and reasonably accurate nitrate method did not become available until the 1960s and oceanographic dissolved oxygen methods were not rationalized until that time as well (Carritt and Carpenter, 1967). Thus, our oceanographic observations are restricted to the last  $\sim 50$  years, a period when human impacts on the planet have become ever ( $\sim$  exponentially) more important, the Holocene-Anthropocene transition (Crutzen, 2002; Crutzen and Ramanathan, 2000). As one example of a process that may impact ocean ecosystems, bottom trawling sweeps an area equal to  $\sim 25\%$  of the global continental shelf every year (Watling and Norse, 1998), and yet there are no studies that directly



address how this process might effect sedimentary denitrification. Anthropogenic additions of nutrients to the coastal ocean must also have some effect, and Naqvi et al. (2000) suggest that such inputs may have increased denitrification and led to extremely high nitrous oxide production rates over the West Indian Shelf, etc. *Thus, it is not clear how applicable paleo records are to an ocean that is experiencing significant and unprecedented anthropogenic forcing.*

## 5 Conclusions

A review of the literature suggests that the oceanic denitrification rate may exceed 400 Tg N a<sup>-1</sup>. The three most likely factors that could reconcile this rate with paleo records are as follows:

1. Oceanic nitrogen fixation has been significantly underestimated.
2. There is a significant mis-match between the sedimentary record and ocean observations with the former largely confined to the Holocene and earlier, and the latter confined to the Anthropocene: *today's ocean may be in a transient state.*
3. Century scale and shorter oscillations occur and are averaged out in the paleo record (Altabet, 2006; Gruber and Sarmiento, 1997).

In addition, plausible changes in oceanic N/P and N/C ratios could mute the effects that imbalances in the oceanic fixed-N budget would have upon the sedimentary and atmospheric record, and the co-occurrence of water column nitrogen fixation and denitrification may complicate interpretation of the sedimentary record.

It is difficult to review the recent literature on denitrification and nitrogen fixation and not suspect that the phrase “the more we look, the more we find” will continue to apply at least for the next few decades. Given these exciting discoveries, the need for expanding our geographic and intellectual horizons seems evident. To paraphrase a famous quote, the nitrogen cycle is more complicated than we imagined a few years ago, and perhaps more complicated than it is possible for us to imagine! More research is required to provide data and model outputs that will help our beleaguered imaginations!

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