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The oceanic fixed nitrogen and nitrous oxide budgets: Moving targets as we enter the anthropocene?*

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SUMMARY: New data force us to raise previous estimates of oceanic denitrification. Our revised estimate of ~ 450 Tg N yr^{-1} (Tg = 10^{12} g) produces an oceanic fixed N budget with a large deficit (~ 200 Tg N yr^{-1}) that can be explained only by positing an ocean that has deviated far from a steady-state, the need for a major upwards revision of fixed N inputs, particularly nitrogen fixation, or both. Oceanic denitrification can be significantly altered by small re-distributions of carbon and dissolved oxygen. Since fixed N is a limiting nutrient, uncompensated changes in denitrification affect the ocean's ability to sequester atmospheric CO_2 via the "biological pump". We have also had to modify our concepts of the oceanic N_2O regime to take better account of the extremely high N_2O saturations that can arise in productive, low oxygen waters. Recent results from the western Indian Shelf during a period when hypoxic, suboxic and anoxic waters were present produced a maximum surface N_2O saturation of > 8000%, a likely consequence of "stop and go" denitrification. The sensitivity of N_2O production and consumption to small changes in the oceanic dissolved oxygen distribution and to the "spin-up" phase of denitrification suggests that the oceanic source term for N_2O could change rapidly.

Key words: Arabian Sea, denitrification, global change, Indian Shelf, nitrogen budget, nitrogen cycle, nitrogen fixation, nitrous oxide, suboxia.

INTRODUCTION

The senior author (LAC) was educated in an era when his geological oceanography instructor felt obliged to teach both the pros and **cons** of continental drift and when El Niño was described as an essentially Peruvian-scale phenomenon. At that time (the 1960s), limited observations and the principle of parsimony encouraged many to

assume an ocean that was in steady-state. Thus, when LAC's Ph.D. work (Codispoti, 1973; Codispoti and Richards, 1976) in combination with other studies (e.g. Cline, 1973; Devol, 1975) found enough denitrification to bring the oceanic fixed N budget, as it was then understood, into balance, the result was nothing more than expected. After all, many studies assumed a steady-state ocean, and even though we dutifully note our assumptions, their frequent use tends to color our view of how the real world works. A disturbing, present-day

manifestation of this is the tendency to call mathematical model outputs, "data".

The development of our view of the oceanic N system, to some extent, parallels the journey of the climate change community. When LAC began his career, most students of climate felt that change was slow enough to permit oceanographers to assume a steady-state for the present-day ocean without being ridiculous. Now, we know from studies of ice-cores (e.g. Alley, 1995) that there are modes of significant global climate change that take place over a few years, and that ocean basins have significant ~ annual to decadal variability, driven by El Niño/La Niña cycles, the North Atlantic Oscillation, the Arctic Oscillation (Thompson and Wallace, 1998), the Pacific Decadal Oscillation (Mantua *et al.,*1997; Stott *et al.*, 2000), etc.

If this paper simply documented our "path to enlightenment" it would have little value. It is our opinion, however, that we cannot neglect the oceanic N cycle when we attempt to understand global change. In particular, we hope to show that the following hypotheses are worth testing:

1. Some of the terms in the oceanic N regime are much larger than thought just a few years ago, and this has implications for the ability of the oceanic N cycle to impact atmospheric CO_2 and N_2O on the sub-1000 year time scale.

2. Key portions of the oceanic N cycle respond dramatically to relatively small environmental changes, including anthropogenic changes.

3. The oceanic fixed N budget is either considerably out of balance or present-day estimates of oceanic nitrogen fixation are much too low, or both.

4. Increasing inputs of nutrients into coastal waters from the atmosphere, groundwater, and runoff, encourage the development of suboxia and anoxia which lead to significant increases in oceanic denitrification and N_2O emissions, and

5. Denitrification may make the ocean more Fe limited.

Magnuson (1990) describes how short-term environmental observations are embedded in the "invisible present" and cannot be properly interpreted without addressing longer-term change (in his case driven by El Niño/La Niña cycles). With respect to the oceanic fixed N budget and N_2O turnover there is an additional and perhaps more significant issue: most studies have occurred during the last ~ 50 years, a time in which human impingements on the environment have become massive enough to cause some authors to coin a new term for the present era, *the Anthropocene* (e.g. Falkowski *et al.*, 2000; Crutzen

and Ramanathan, 2000). Thus, re-casting our results into periodic variations such as El Niño cycles and the North Atlantic Oscillation may be insufficient, as we move out of the relatively constrained climate realm that is described by ice-core data for the last 420,000 years (Falkowski *et al.,* 2000). One thing is certain, we have already intervened massively in the global N_2 cycle (Hellemans, 1998; Smil, 1997; Vitousek *et al.*, 1997a and 1997b). For example, anthropogenic nitrogen fixation is now on the order of 140 Tg N yr^{-1} *vs* a "natural" biotic terrestrial rate of 90-130 Tg N yr^{-1} (Galloway *et al.*, 1995), and human activities have caused major increases in the fixed N content of runoff, groundwater and the atmosphere (Capone and Bautista, 1985; Howarth *et al.*, 1996; Krest *et al.*, 2000; Paerl, 1997; Paerl *et al.*, 2000; Spalding and Exner, 1993).

METHODS

The methods used to collect most of our data are already described (Codispoti *et al.*, 1991; Friederich *et al.*, 1990; Morrison *et al.*, 1998; Morrison *et al.*, 1999). In addition, the data collected from the R/V *T.G. Thompson*, during US JGOFS Arabian Sea Cruises (Morrison *et al.*, 1998) are available on the U.S. JGOFS web site (http://www1.whoi.edu).

We employ a new method, for estimating local NO_3^- removals in the Arabian Sea. This method is based on ratios of inorganic N ($NO_3^- + NO_2^- + NH_3$) to PO_4^{3-} (reactive phosphorus) in waters of the Arabian Sea. Conceptually, this method differs little from the N* concept of Gruber and Sarmiento (1997). We reverse signs for convenience, and our lower N/P ratio and higher residual P value accounts for non-local denitrification signals advected into the Arabian Sea. Partly because of the necessity for highly precise PO_4^{3-} data, previous methods for estimating denitrification mediated nitrate removals in the Arabian Sea generally relied on nitrogen, temperature and oxygen (NTO) relationships. These methods give unrealistic values in the surface layers because of atmospheric exchange and phytoplankton processes, and they appear to underestimate the NO_3^- removals due to denitrification. Our new method is described more fully elsewhere (Uhlenhopp *et al.*, in prep.). Briefly, it is based on Type II linear regressions of PO_4^{3-} *vs* inorganic N ($NO_3^- + NO_2^- + NH_3$) on samples from the *Thompson* Arabian Sea cruises from depths of 100-1500 db, with oxygen concentrations > 65 μM. The resulting equation is:

$$N_{deficit} = (14.89(P\text{-}0.28)\text{-}N) \ \mu M \times 0.86, \qquad (1)$$

where, $N_{deficit}$ is the estimate of the inorganic N ($NO_3^- + NO_2^- + NH_3$) removed from a water parcel by denitrification, $14.89 = \Delta N/\Delta P$ (by atoms) as determined by the Type II regression, P = reactive phosphorus (PO_4^{3-}), 0.28 is the PO_4^{3-} intercept at 0 inorganic N, and 0.86 accounts for the reactive P released by the organic material re-mineralized by denitrification assuming that N/P in local organic matter is 14.89, and that consumption of 94.4 NO_3^- by denitrification releases one PO_4^{3-} (Richards, 1965; equation 3). We also present some excess N_2 values arising from denitrification in the Arabian Sea (total excess N_2 minus excess N_2 produced elsewhere). These were calculated from N/Ar ratios determined by mass spectroscopy, and are more fully described in Uhlenhopp *et al.* (in prep.) and in Emerson *et al.* (1999).

Please note the following nomenclature: We use PO_4^{3-} to denote reactive phosphorus as determined by our autoanalyzer method (SCOR, 1996); for convenience, in writing stoichiometric equations, etc. we use NH_3 to represent the sum of $NH_3 + NH_4^+$, and we use HS^- to represent the sum of H_2S, HS^- and S^{2-}. Also note that all forms of nitrogen other than elemental N_2 are referred to as fixed nitrogen (fixed N), and that we refer to the Eastern Tropical North Pacific and the Eastern Tropical South Pacific as the ETNP and ETSP, respectively.

SCIENTIFIC BACKGROUND

Oceanic nitrogen cycle

A simplified view of the oceanic N cycle is shown in Figure 1. This figure shows:

1. assimilatory uptake and reduction of nitrate during photosynthesis and heterotrophic bacterial growth (green arrows),

2. recycling of –III oxidation state N in the upper layers (purple arrows),

3. oxidation back to nitrate via nitrification (magenta arrows),

4. conversion of nitrate to N_2 by denitrification (orange arrows), and

5. conversion of N_2 to –III oxidation state N by nitrogen fixation (yellow arrow).

In the ocean and atmosphere, N_2 at the 0 oxidation state is most abundant, followed by nitrate at the +5 state, and then various forms of N at –III (NH_3,
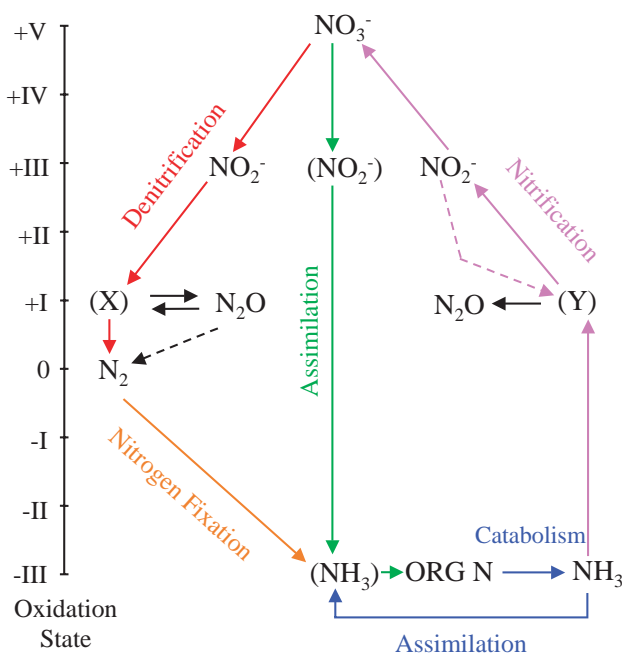

FIG. 1. – A simplified diagram of the oceanic nitrogen cycle based on an original figure presented by Liu (1979).

organic N). Nitrite (NO_2^-) builds up to concentrations that can rival –III and +V N under suboxic conditions (Fig. 2). Although present in trace quantities, the N_2O produced in the ocean has an important influence on atmospheric chemistry. Figure 1 leaves out some potentially important components about which we know little. These include, two labile components, hydroxylamine (NH_2OH) and nitric oxide (NO) at the –I and + II oxidation states. These compounds have received some attention (e.g. Butler and Gordon, 1996; Ward and Zafiriou; 1988), but we lack sufficient data to draw useful conclusions about the relationship of these components to global change.

Figure 1 also describes processes that produce and consume N_2O, mainly:

1. the first step of nitrification (the –III to +III change) where N_2O can be produced either by the break-down of an intermediate during NH_3 oxidation to NO_2^- or through reduction of NO_2^-, a process that appears to be enhanced at low O_2 and high NO_2^- concentrations (Capone, 1991; Poth and Focht, 1985; Ritchie and Nicholas, 1972; Ostrom *et al.*, 2000), and

2. during denitrification where, depending on conditions, there may be net production or net consumption of N_2O.

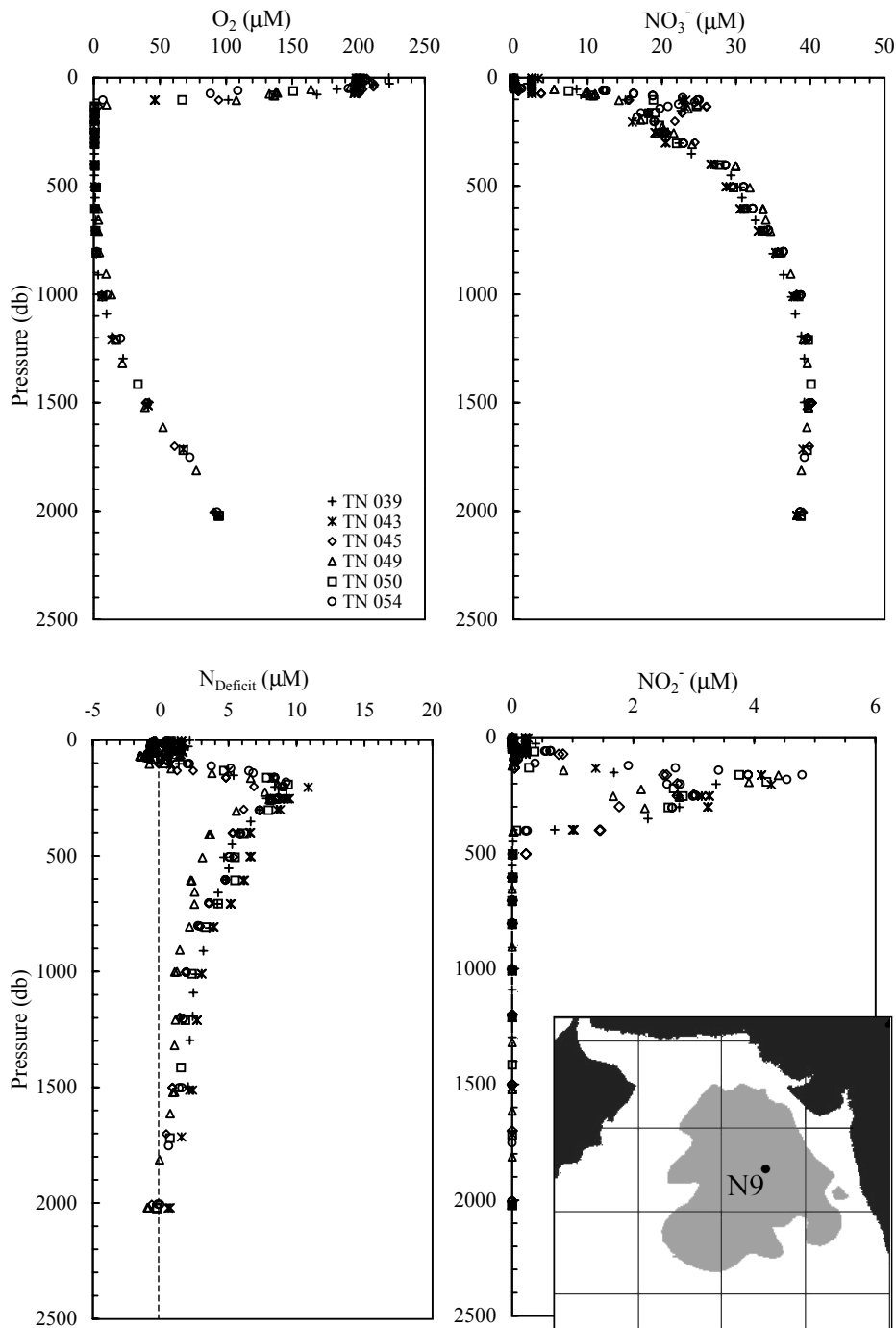There may be some uptake of N_2O during nitrogen fixation (dashed black arrow in Fig. 1) when N_2O

FIG. 2. – Data from station N9 located in the portion of the Arabian Sea that contains suboxic water at depths between ~100-1000 db. Cruises, TN039, 43, 45, 49, 50 and 54 comprise the U.S. Joint Global Ocean Flux Process Study of the Arabian Sea and they cover a complete annual cycle beginning in September 1994 and ending in December 1995. A nitrate (NO_3^-) minimum and nitrite (NO_2^-) maximum within the suboxic zone ($O_2 < 5$ μM) signal the presence of enhanced denitrification. The parameter, $N_{deficit}$ estimates the conversion of NO_3^- to N_2 by denitrification. The shaded area indicates the extent of the regions where, on average, the maximum concentration of nitrite (NO_2^-) in the oxygen minimum zone (the secondary nitrite maximum) exceeds 1 μM as described by Naqvi (1991). All concentrations are in μM.

may be reduced to –III N along with N_2 (Yamazaki *et al.*, 1987). This effect is probably small because of the high N_2/N_2O ratio in seawater. Vertical profiles of N_2O taken in N "starved" phytoplankton populations suggest no uptake in the absence of nitrogen fixation (Mantoura *et al.*, 1993). Additional sources of N_2O have been suggested, including production during assimilatory and dissimilatory reduction of NO_3^- to NH_3 (e.g. Oudot *et al.,* 1990; Tiedje, 1988), but based on existing knowledge, it seems reasonable to assume

that these sources are not important to the topics that we will discuss. In addition to denitrification, loss to the atmosphere is the other major sink for oceanic N_2O. Studies of the isotopic composition of N_2O (Dore *et al.*, 1998; Kim and Craig, 1993; Yoshinari *et al.*, 1997; Naqvi *et al.*, 1998) present some conundrums suggesting that we still have more to learn about the pathways and intermediates involved in the production of oceanic N_2O under varying environmental conditions.

While providing a useful overview, Figure 1 is greatly simplified. It omits, for example, direct reactions between reduced S and NO_3^- that involve dissimilatory reduction of NO_3^- to NH_3 (Einsle *et al.*, 1999). Lately, there has been heightened interest in bacteria (*Thioploca, Beggiatoa, Thiomargarita namibiensis*) that can store and transport NO_3^- from overlying waters to sulfide-bearing sediments (e.g. Fossing *et al.,* 1995; Schulz *et al.*, 1999). These bacteria contain giant vacuoles that can store NO_3^- at concentrations of several hundred **mM** (Jørgensen and Gallardo, 1999; Fossing *et al.,* 1995; Otte *et al.,* 1999), with a high of ~ 800 **mM** reported for *Thiomargarita namibiensis* (Schulz *et al.*, 1999). The vacuoles have been described as "anaerobic lungs" (Jørgensen and Gallardo, 1999), and they enable the bacteria to support chemotrophic growth (Otte *et al.,* 1999) through dissimilatory nitrate reduction or denitrification linked to the oxidation of hydrogen sulfide (HS⁻). Most of the NO_3^- appears to be converted to NH_3 during this reduction (Jørgensen and Gallardo, 1999; Otte *et al.*, 1999), but the possibility of some N_2 production has not been totally excluded. In addition, there are thiosulfate ($S_2O_3^{2-}$) oxidizing bacteria that are known to produce N_2 (e.g. *Thiobacillus denitrificans;* Stouthamer, 1988).

The following important interactions are also not described by Figure 1:

Dependence on dissolved O_2 concentrations: Nitrogen fixation, denitrification, and production of N_2O during nitrification either require or are enhanced by low oxygen concentrations. Specifically, the enzyme system required for nitrogen fixation (*nitrogenase*) is poisoned by O_2 (e.g. Falkowski, 1997; Paerl and Zehr, 2000), denitrification is inhibited at oxygen concentrations >5 μM (see below), and net production of N_2O during nitrification increases markedly at low oxygen concentrations (Codispoti *et al.,* 1992; Goreau *et al.,* 1980; Suntharalingam *et al.*, 2000).

Interactions with Fe: By removing fixed N from the ocean, denitrification creates a need for additional nitrogen fixation in order to maintain oceanic primary production. Since nitrogen fixation has an Fe requirement ~60 times greater than uptake of NO_3^- by phytoplankton (e.g. Falkowski, 1997; Raven, 1988), *denitrification may make the ocean more Fe limited.* While it is true that oxygen minimum zone (OMZ) waters in the Arabian Sea contain Fe concentrations a few nM higher than surrounding waters (Saagar *et al.*, 1989; Witter *et al.,* 2000), the stoichiometries involved (Bruland *et al.*, 1991) suggest that ~20 nM of Fe are required to support enough nitrogen fixation to account for each μM of fixed N removed by denitrification, and fixed N removals in the suboxic portion of the Arabian Sea water column can exceed 20 μM, thereby imposing an Fe requirement of several hundred nM. Indeed, it is not clear whether elevated Fe concentrations seen in suboxic zones are related to the suboxia/denitrification *per se,* or to other factors such as advection of Fe from anoxic zones. It is clear that Fe concentrations of >100 nM tend to be associated with anoxia not suboxia, and it is possible that NO_3^- can oxidize Fe II to less soluble Fe III (Murray *et al.*, 1995).

Differential C/N ratios: During phytoplankton growth the atomic ratio of N/C uptake is ~ 6.6 (Redfield *et al.*, 1963), but during denitrification (see equations 2-6, below), the ratio (by atoms) of N_2 production to C oxidation is <1 (Codispoti *et al.*, 1989; equations 3-5). Therefore, once enough organic material has been oxidized to produce suboxic conditions, *it would take only an additional < 1/6 of the C fixed by phytoplankton growth to fuel sufficient denitrification to consume all of the fixed N that supported that growth.*

Control of atmospheric O_2: At chemical equilibrium, virtually all of the oxygen in the atmosphere and ocean would be combined with N in the +V oxidation state (Lewis and Randall, 1923). Hutchinson (1975) suggests that were it not for the conversion of fixed N to N_2 by denitrification, the sea would be an anoxic weak solution of nitric acid with a pH of ~ 2. The basic idea is that the fixed N produced by nitrogen fixation, lightning discharges and combustion would eventually get oxidized to the +5 state (NO_3^-) and deplete O_2. The turnover times for O_2 and N_2 in the atmosphere under present-day conditions are, however, in the millions of years. Thus, this problem falls outside the scope of this paper.

Effect on the oceanic biological C pump: Fixed N and Fe limitation constrain primary production in most of the ocean (e.g. Falkowski, 1997) and thus limit the oceanic biological pump's ability to

sequester atmospheric CO_2. During periods when denitrification is removing fixed N from the ocean, the pump can be reversed and ocean biology can add rather than subtract CO_2 to the atmosphere (e.g. Codispoti et al., 1989). Conversely, the pump would be enhanced when nitrogen fixation exceeds denitrification (Broecker and Henderson, 1998).

Constraints on oceanic nitrogen fixation: We have already mentioned the constraints that the presence of dissolved oxygen and Fe limitation can impose on nitrogen fixation. Paerl and Zehr (2000) list several others including turbulence which can interfere with the mechanisms for protecting against oxygen, a high-energy requirement, and, in some cases, limitation by PO_4^{3-}.

Oceanic fixed N budget

Unlike the oceanic budgets for Fe, P, and Si that are dominated by riverine or atmospheric inputs and sedimentary sinks, the oceanic fixed N budget is heavily influenced by biological processes. Although there is a wide variation in estimates for each term (Gruber and Sarmiento, 1997; Table 1), it is clear that denitrification is the dominant sink. Nitrogen fixation is the most important source, at least for the pre-industrial period (e.g. Gruber and Sarmiento, 1997), but recent estimates (Table 1) suggest that it does not dominate the source terms,

TABLE 1. – Gruber and Sarmiento's fixed N budget for the present-day ocean and the changes suggested in this paper.

Process	Gruber and Sarmiento (1997)	This paper's updated values
Sources		
Pelagic N_2 fixation	110 ± 40	
Benthic N_2 fixation	15 ± 10	
River input (DN)	34 ± 10	
River input (PON)	42 ± 10	
Atmospheric deposition (Net)	30 ± 5	
Atmospheric deposition (DON)		56[a]
Total Sources	231 ± 44	287
Sinks		
Organic N export		1[b]
Benthic denitrification	95 ± 20	300
Water column denitrification	80 ± 20	150
Sedimentation	25 ± 10	
N_2O loss	4 ± 2	6
Total Sinks	204 ± 30	482

[a] Average atmospheric organic N (mostly anthropogenic) deposition value suggested by Cornell et al. (1995).
[b] Accounts for losses due to fishing and guano deposition (Söderlund and Svensson, 1976; Codispoti and Christensen, 1985)

in the present-day ocean, to the same degree that denitrification dominates the sinks. For example, Cornell et al. (1995) suggest that, at present, there may be a large unaccounted for source of anthropogenic atmospheric dissolved organic N (DON) to the ocean ranging from 28-84 Tg N yr^{-1}. More generally, we know that anthropogenic activities have ~ doubled the riverine and atmospheric inputs of fixed N, and that groundwater inputs have increased and may be underestimated (Capone and Bautista, 1985; Galloway et al., 1995; Duce et al., 1991; Howarth et al., 1996; Moore, 1996; Paerl, 1997). On the other hand, the riverine estimates in Table 1 may be too high because some of the studies on which they are based may not account for removal in estuaries and our focus is on the continental shelf and open ocean. The work of Nixon et al. (1996) suggests that a considerable fraction of the riverine input is removed by sedimentation or denitrification in estuaries. Moreover, some Type II (negative) estuaries (Smith et al., 1989) represent sinks for oceanic fixed N, because inflowing ocean waters have some of their fixed N removed by sedimentation and denitrification. Since we have a very poor idea of the ground-water inputs of fixed N to the open ocean, we will retain the total value of ~ 160 Tg N yr^{-1} for riverine, atmospheric and groundwater fixed N inputs to the present-day ocean. Since this value exceeds most existing estimates for oceanic nitrogen fixation (Table 1), it might be fair to assert that only the sink-term for oceanic fixed N in today's ocean is dominated by internal biological processes. Major points of this paper are, however, that:

1. Recent advances in our understanding require a significant upwards revision of the oceanic denitrification rate, which, in turn, requires,

2. a major increase in estimates of oceanic nitrogen fixation to achieve a balance, or

3. a drastic change in our concepts of how to interpret existing data.

Thus, it is entirely possible that oceanic nitrogen fixation is the major source of marine fixed N.

Until recently, a common assumption amongst geochemists was that denitrification/nitrogen fixation represented a well-coupled negative feed-back mechanism. Although there were exceptions (McElroy, 1983), most geochemists blithely dismissed the importance of fixed N as a limiting nutrient with respect to problems such as the ability of the oceanic biological pump to sequester atmospheric CO_2 (e.g. Bolin et al., 1983). As noted earlier, assuming that a budget is in a steady-state has its attractions.

Moreover, models of global change could be simplified, if the (on average) slight excess of P *vs* fixed N availability to phytoplankton existed only because you need a slight excess of P over fixed N to "drive" nitrogen fixation. In a weakened state, this view continues to the present-day (Tyrell, 1999). There is increasing recognition, however, that imbalances in the oceanic fixed N budget can be large enough and last long enough to have a significant influence on atmospheric CO_2 (e.g. Codispoti, 1989; Falkowski, 1997; Lenton and Watson, 2000). This is partially because *the sites of enhanced nitrogen fixation and denitrification are often separated.* Denitrification is enhanced in suboxic subsurface waters and sediments, whereas it follows from the constraints on nitrogen fixation that the main open-ocean sites of nitrogen fixation are warm, stratified surface waters (e.g. Capone *et al.*, 1997; Carpenter and Romans, 1991) with an abundant Fe supply (Falkowski, 1997) supplemented by fixation in some shallow benthic communities where nitrogen fixation and denitrification may co-occur (Paerl and Zehr, 2000). Thus, a fixed N deficiency relative to P is not a sufficient condition for nitrogen fixation (Codispoti, 1989).

Ultimately, imbalances in the fixed N source and sink terms are coupled through ocean circulation (Broecker and Peng, 1982; Codispoti, 1989). For example, if denitrification exceeds nitrogen fixation for a period, oceanic primary production should be reduced due to the draw down of fixed N. Eventually, this should reduce primary production leading to a decrease in the downward flux of organic matter, a decrease in subsurface respiration, and finally a reduction in the volume of suboxic environments where denitrification is enhanced. Of course, exactly what happens would depend on the details of circulation, flux and productivity patterns, but the point is that fixed N in the ocean cannot be drawn down continuously before the overall decrease in fixed N would depress denitrification rates. The time scale for this circulation-based feedback is probably in the range of several hundred to ~1000 years, again depending on the details. So the question becomes, how out of balance could the system become? Gruber and Sarmiento (1997) suggest that imbalances of 70 Tg N yr^{-1} could not persist for more than ~ 300 years without causing changes that would exceed the range of atmospheric CO_2 concentrations over the last millenium (280 ±10 ppm) suggesting that oceanic nitrogen budget imbalances have not exceeded this during this relatively quiet climatic period. Falkowski (1997) points out that only small imbalances, of the order of 3 Tg N yr^{-1}, would be sufficient to account for a major fraction of the variability in atmospheric CO_2 over the ~10,000 year period during which atmospheric CO_2 concentrations fell from ~ 290 to ~ 190 ppm as we entered the last glaciation. In this work, we are taking a more prospective view and ask:

Are we in a transition state as we enter the Anthropocene in which the deficit in the oceanic fixed N budget exceeds ~200 Tg N yr^{-1}, or are we significantly underestimating oceanic nitrogen fixation, or both?

The denitrification sink

The main identified sites of denitrification in the ocean are shelf and hemipelagic sediments (Christensen *et al.*, 1987; Devol, 1991) and suboxic ($O_2 < ~ 5$ μM) portions of the oxygen minimum zone (OMZ). The traditional view has been that shallow sediments dominate over abyssal sediments (Christensen *et al.*, 1987; Devol *et al.*, 1997) despite their relatively small area because of their high organic material supply. A model study of benthic denitrification by Middleburg *et al.* (1996), however, suggests that denitrification in slope and abyssal sediments exceeds benthic denitrification in shelf sediments. These authors note that estimates of denitrification in deep sediments are few, and are often based on flawed methods that, for example, only considered NO_3^- fluxes into the sediments, neglecting the frequently more important influence of coupled nitrification-denitrification (e.g. Codispoti and Christensen, 1985; Seitzinger *et al.*, 1993). Middleburg *et al.* suggest that at depths between ~ 500-3000 m the relative contribution of denitrification in sedimentary organic matter mineralization exceeds 10% with a maximum near 2000 m.

The major identified sites of water column denitrification occur in the ETNP (e.g. Cline and Richards, 1972; Codispoti and Richards, 1976), the ETSP (e.g. Codispoti and Packard, 1980), and the Arabian Sea (Bange *et al.*, 2000; Mantoura *et al.*, 1993; Naqvi, 1987; Naqvi and Sen-Gupta, 1985). Smaller, and more transient sites occur near the boundaries of the three major identified sites (e.g. Codispoti and Packard, 1980; Codispoti *et al.*, 1986). There also appears to be a significant body of suboxic water off SW Africa (Calvert and Price, 1971), but we can find no estimates of denitrification rates for this region.
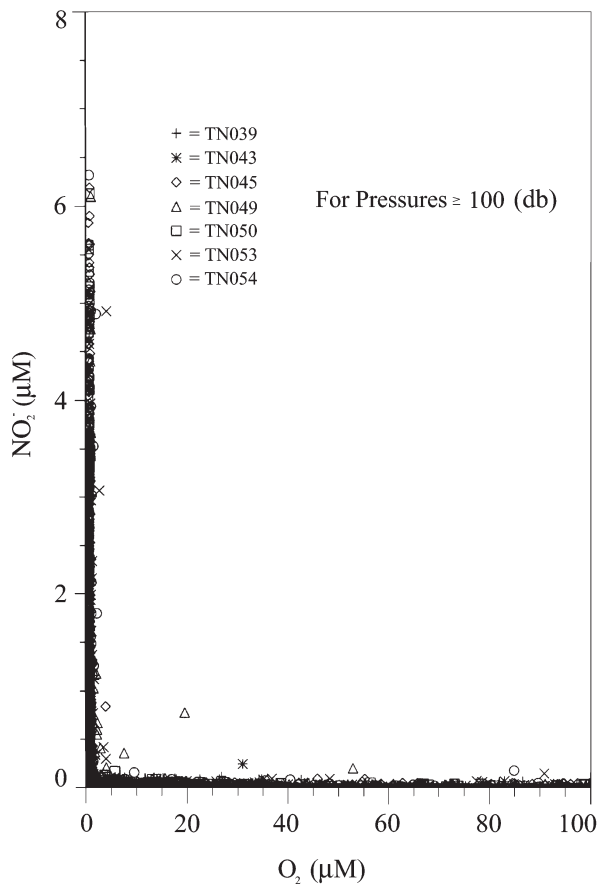
FIG. 3. – Nitrite (NO$_2^-$) concentrations (μM) versus oxygen concentrations (μM) from depths ≥ 100 db, observed during a seasonal cycle in the Arabian Sea (see Fig. 2). The bulk of the elevated nitrite (NO$_2^-$) concentrations occur at oxygen concentrations of < 2.5 μM (from Morrison *et al.*, 1998).
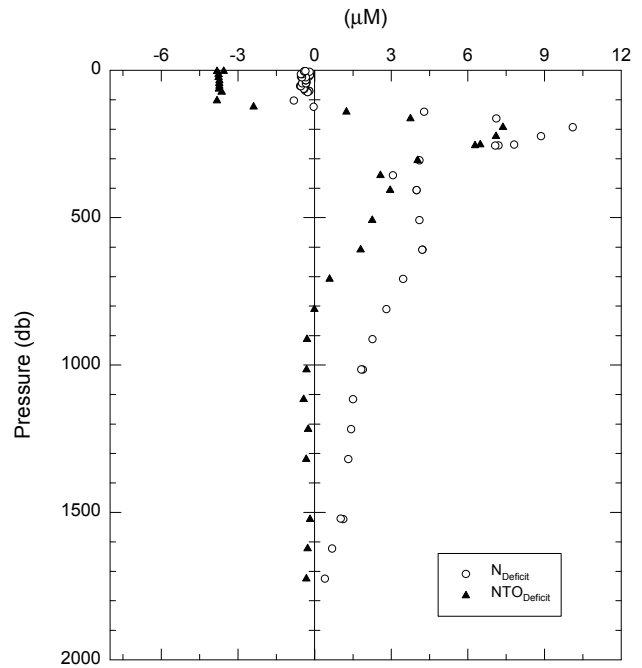

FIG. 4. – A comparison of nitrate deficits in the Arabian Sea computed by a frequently used method based on relationships between inorganic N, dissolved oxygen and temperature (NTO$_{deficit}$) and described in Naqvi (1994), with the phosphate based method (N$_{deficit}$) described herein. These results are from U.S. JGOFS Arabian Sea cruise TN049, station M1 (14.9°N, 66.9°E) Concentrations are in μM of NO$_3^-$ removed.

Anthropogenic impacts have led to increasing coastal hypoxia/suboxia/anoxia leading to water column denitrification over the Indian Shelf (Naqvi *et al.,* 2000a), in the Baltic Sea (Shaffer and Rönner, 1984), and probably off the mouth of the Mississippi River (Rabalais *et al.,* 2000). We also know that denitrification occurs in suboxic layers sandwiched between the oxic and anoxic layers in the Black Sea (e.g. Codispoti *et al.*, 1991, Fig. 4) and the Cariaco Trench (Scranton *et al*, 1987; Richards, 1975; Richards and Benson, 1960), and in California Borderland basins (Stott *et al.,* 2000; Liu, 1979; Codispoti, 1973). Given the expansion of low oxygen conditions in coastal waters (Malakoff, 1998) and the paucity of data, there may be several additional sites of water column suboxia and enhanced denitrification. For example, dissolved oxygen data from the Scorpio Expedition (Reid, 1973) suggest the presence of suboxic water in the S. Pacific, in regions that have never been closely examined.

Data from the Arabian Sea suboxic zone (Figs. 2-7) display the conditions under which water column denitrification is favored. The co-occurrence of low O$_2$ and high NO$_2^-$ in the suboxic zone signals an environment with high denitrification rates. These nitrite concentrations tend to build-up only when oxygen concentrations are < ~ 2.5 μM (Fig. 3), so our suggestion that suboxia begins at O$_2$ concentrations less than 5 μM may be generous. Although there appears to be a correlation between denitrification rates and NO$_2^-$ concentrations (Codispoti and Packard, 1980), this does not mean that denitrification does not occur in suboxic waters with low NO$_2^-$. For example, in the northern Arabian Sea and in the bottom portion of the suboxic zone, we sometimes see appreciable nitrate deficits (Figs. 5 and 6) even though NO$_2^-$ is low, suggesting that denitrification may continue to occur, albeit at presumably lower rates. In the past, we (LAC and SWAN) have only included suboxic waters with appreciable NO$_2^-$ (>0.2 to >0.5 μM depending on the region) when using respiration estimates based on the activity of the electron transport system (ETS) to calculate denitrification rates. This helped to account for the possibility of NO$_2^-$ diffusing out of the denitrification
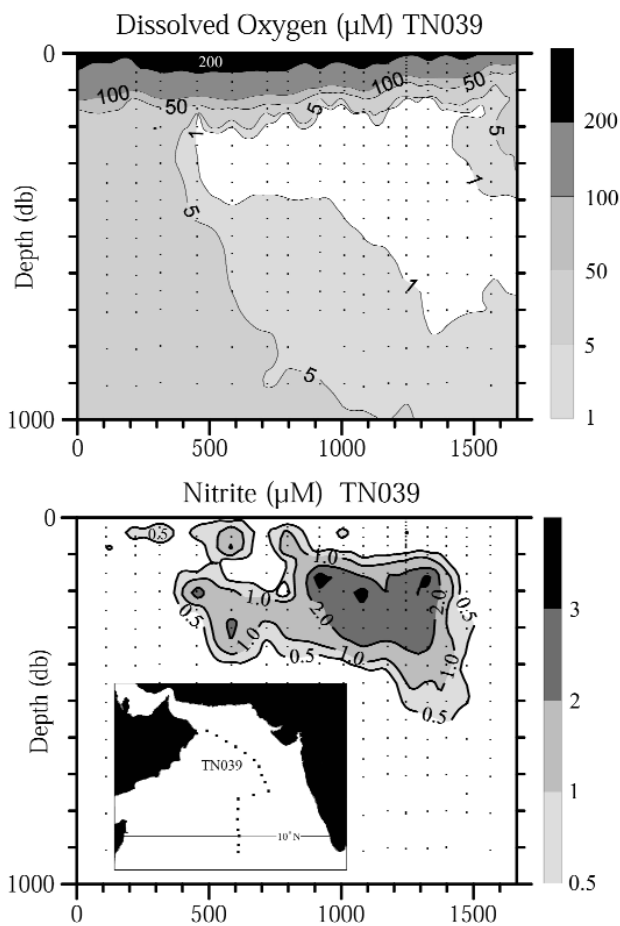
FIG. 5. – Dissolved oxygen and nitrite sections taken in the Arabian Sea during the first U.S. JGOFS Arabian Sea cruise (TN039, Sept.-Oct. 1994). Oxygen concentrations were determined by automated Winkler titration and compared with the low-concentration colorimetric method of Broenkow and Cline (1969). Concentrations are in μM.
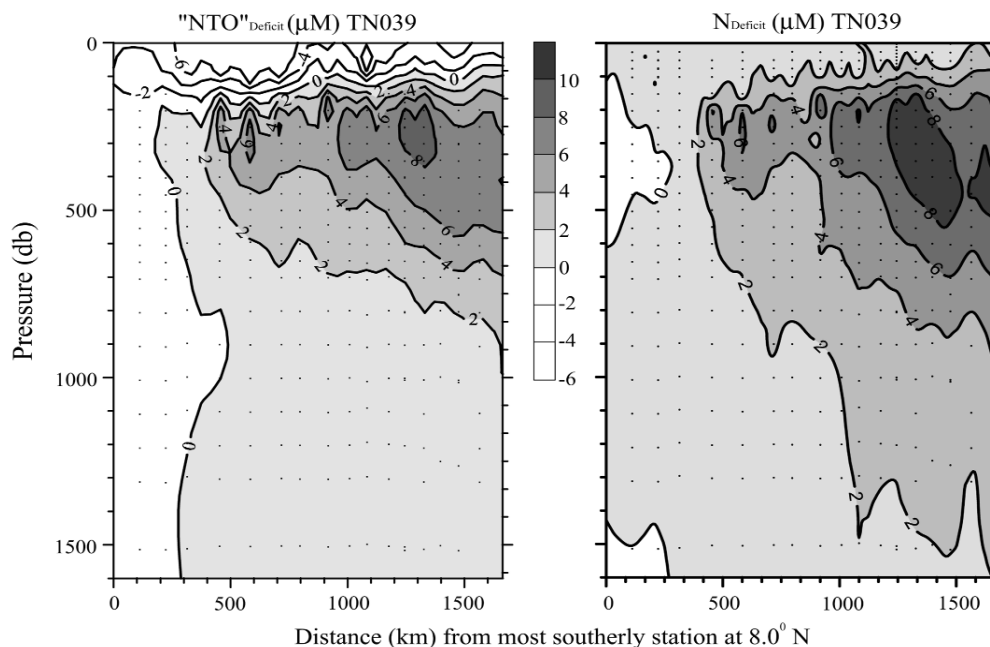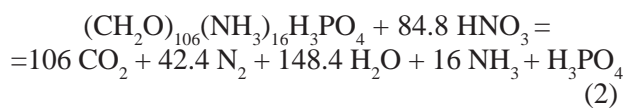
zone and escaping further reduction (Anderson *et al.*, 1982; Codispoti and Christensen, 1985), but may be too restrictive for the lower portion of the suboxic zone where suboxia and high $N_{deficits}$ extend to considerable depths even though NO_2^- is low (Figs. 5 and 6). Thus, the deep $N_{deficits}$ may arise from a combination of local denitrification as well as from the transport of deficits produced elsewhere.
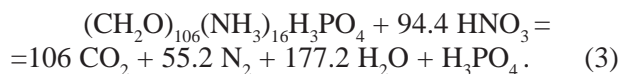
Note that *the known suboxic zones in today's ocean comprise only ~0.1% of the total oceanic volume.* We know (Table 1) that globally significant denitrification occurs within this volume. *It follows, therefore, that small changes in dissolved oxygen distributions and carbon fluxes can have globally significant effects on water column denitrification.* Calculations suggest that an additional 5% of primary production added to the suboxic waters in the ETSP could double the denitrification rate, and this calculation was based on old primary productivity data that might be too low (Codispoti, 1989). In addition, Codispoti and Packard (1980) and Codispoti *et al.* (1986) have described what appear to be globally significant accelerations in denitrification in the ETSP. One of these followed the collapse of the Peruvian anchoveta fishery, and the other was associated with the 1985 La Niña (Codispoti *et al.*, 1986; Codispoti *et al.*, 1988). The sedimentary record provides evidence for globally significant changes in oceanic denitrification over much longer time intervals (Altabet *et al.*, 1995; Ganeshram *et al.*, 1995). *We conclude that not only is the oceanic*

FIG. 6. – Distributions of NTO$_{deficit}$ and N$_{deficit}$ in the same section shown in Figure 5. Concentrations are in μM.

denitrification regime sensitive to change, but that it does undergo significant change over a wide range of time scales.

Based on the traditional concepts of denitrification and the concept of "Redfield ratios", Richards (1965) suggested the following two possible stoichiometric equations for oceanic denitrification:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\ HNO_3 =$$
$$= 106\ CO_2 + 42.4\ N_2 + 148.4\ H_2O + 16\ NH_3 + H_3PO_4 \tag{2}$$

and

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 94.4\ HNO_3 =$$
$$= 106\ CO_2 + 55.2\ N_2 + 177.2\ H_2O + H_3PO_4. \tag{3}$$

The major difference between the two equations involves the fate of organic N. In Equation (3), total N_2 production, exceeds NO_3^- consumption by 17%. Gruber and Sarmiento (1997) present an updated version of Equation (3) based on the elementary composition of surface ocean plankton (upper 400m) suggested by Anderson (1995) in which total N_2 production exceeds NO_3^- consumption by 15%. As we shall show, even Equation (3) appears to greatly underestimate the ratio of N_2 produced to NO_3^- consumed during denitrification, as do updated versions of Richards' equations presented by Codispoti and Christensen (1985). This is important when estimating denitrification rates based on parameters such as $N_{deficit}$. In the past, estimates of denitrification have assumed that none or only a fraction of the organic N was converted to N_2 (e.g. Codispoti and Richards, 1976). Direct estimates of the excess N_2 present in suboxic waters of the Arabian Sea (Fig. 7), however, suggest that the actual production of N_2 is much higher as do some preliminary excess N_2 estimates from the eastern tropical North Pacific (Brandes, 1996). Although $N_{deficit}$ gives integrated water column estimates of the nitrate removed by denitrification that are about twice as high as older methods (Fig. 6), integrated water column values of $N_{deficit}$ are only about half as large as the estimates of excess N_2. Therefore, integrated excess N_2 may exceed the older Arabian Sea nitrate deficits by a factor of ~ 4.

Equation (3) and its more recent analogues can explain about 15% of the difference between $N_{deficit}$ and excess N_2, but where does the rest of the N_2 come from? One explanation is that denitrification does not follow the traditional stoichiometries that vary only a little between authors (Richards, 1965; Codispoti and Christensen, 1985; Gruber and Sarmiento, 1997). In support of this notion, Van
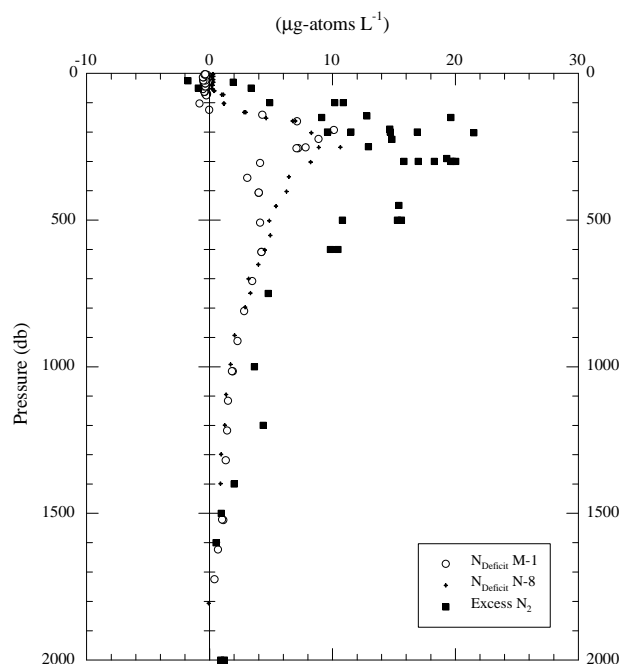

FIG. 7. – A comparison of nitrate deficits ($N_{deficit}$) at stations N8 (TN043, 18.25ºN, 67.6ºE) and M1, TN049 (see Fig. 4) with our ensemble of excess N_2 concentrations in the Arabian Sea. Concentrations are in µg-atoms of N L^{-1} (for $N_{deficit}$, µM = µg-atoms of N L^{-1}).

Mooy *et al's.* (in press) results suggest that denitrifying bacteria in the suboxic portion of the ETNP preferentially attack amino acids with a C/N ratio of about 4 (by atoms) *vs* the ratio of ~6.6 for "Redfieldian" organic matter. Starting with Gruber and Sarmiento's (1997) stoichiometric equation for denitrification:

$$C_{106}H_{175}O_{42}N_{16}P + 104NO_3^- =$$
$$= 4CO_2 + 102HCO_3^- + 60N_2 + 36H_2O + HPO_4^{2-} \tag{4}$$
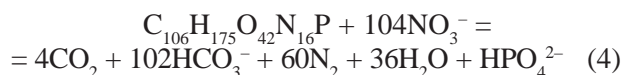
Van Mooy *et al.* assumed that the organic carbon oxidized by denitrifiers consists of an ideal protein (Anderson, 1995), and they produced the following equation for denitrification:

$$C_{61}H_{97}O_{20}N_{16} + 60.2NO_3^- =$$
$$= 38.1N_2 + 60.2HCO_3^- + 0.8CO_2 + 18.4H_2O. \tag{5}$$
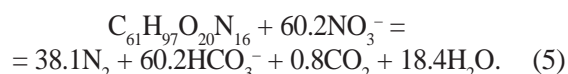
In Equation (5) the total yield of N_2 exceeds NO_3^- depletion by ~27%. In addition, to the extent that this equation is correct in suggesting that there is no accompanying release of PO_4^{3-}, $N_{deficit}$ would underestimate N_2 production by another ~15%. Thus, with no release of PO_4^{3-} we could now account for ~42% of the "extra excess N_2", but we doubt that no PO_4^{3-} is released. Instead, we will assume that, with preferential use of amino acids by denitrifiers, we can

account for ~35% of the "extra excess N_2". Codispoti and Christensen (1985) suggest that high rates of N_2O production during microaerophilic nitrification at the boundaries of suboxic zones could be coupled with reduction to N_2 by denitrifiers. This could increase the $N_{2produced}/NO_3^-$ consumed by another ~3%. In addition, the Arabian Sea, at times, has high nitrogen fixation rates. N/P ratios (by atoms) during nitrogen fixation range from ~57-140 (Gruber and Sarmiento, 1997; Karl *et al.*, 1992) and community N/P ratios under these conditions may be >20 (Naqvi *et al.*, 1986; Karl *et al.*, 1995) *vs* the canonical Redfield ratio of 16/1 (by atoms). Thus, if a significant portion of the organic matter supplied to the suboxic zone is supported by nitrogen fixation we could account for an additional fraction of the excess N_2. Overall, it is plausible to suggest that these revisions to the stoichiometry could yield a contribution of N_2 from the oxidation of organic N that is equivalent to ~40% of the contribution from NO_3^-, but how do we account for the rest?

If sediments contribute N_2 or precursors of N_2 to the water column without a corresponding contribution of PO_4^{3-}, a further portion of the discrepancy between $N_{deficit}$ and the excess N_2 values might be explained. Sedimentary denitrification rate estimates for the Arabian Sea range from ~6-20% of the pelagic rate (Bange *et al.*; 2000; Uhlenhopp *et al.*, in prep.). A large fraction of this probably occurs in shallow sediments that are in contact with water that can exchange excess N_2 with the atmosphere. In addition, although phosphorite deposits are found in margin sediments in contact with low oxygen waters (e.g. Piper and Codispoti, 1975), suggesting that N_2 might be released without proportionate P, we (AHD and JAB) have observed anomalously high (and puzzling) releases of P from sediment underlying suboxic waters. For these reasons, we speculate that, at most, only a few % of the "extra excess N_2" (not accounted for by $N_{deficit}$) is likely to come from sedimentary denitrification *via* the "canonical pathway" that involves coupled nitrification-denitrification (e.g. Seitzinger *et al.,* 1993).

There may be an important additional source of excess N_2 that arises from the interactions between the S and N cycles described earlier. We have already mentioned that *Thioploca*, *Beggiatoa,* and *Thiomargarita* can transport NO_3^- into HS^- bearing environments and gain energy by using the NO_3^- to oxidize HS^-. NH_3 is the most likely nitrogeneous end-product, but some N_2 may be produced, as noted earlier (e.g. during thiosulfate oxidation by

Thiobacillus denitrificans). One should expect high N/PO_4^{3-} export ratios from such sediments because these bacteria are using energy from NO_3^- oxidation of HS^- compounds to fuel growth instead of the oxidation of P containing "Redfieldian" organic matter. High rates of NH_3 export have been observed from sediments with *Thioploca* mats off Chile (Farias, 1998), and *Thioplaca* mats have been observed in the northwest Arabian Sea (Jørgensen and Gallardo, 1999; Levin *et al.*, 1997).

If this NH_3 is released into suboxic waters, it may be oxidized to N_2. We have already mentioned the possibility of microaerophilic production of N_2O from this NH_3 *via* nitrification followed by denitrification as suggested by Codispoti and Christensen (1985). Other possibilities are suggested by data from the Black Sea (Fig. 8). Examination of fixed N-gradients in the suboxic zone of the Black Sea (Fig. 8) shows that there is an apparent downwards flux of NO_3^- into the suboxic zone and an upwards flux of NH_3. Thus, the major observed forms of fixed-N enter this zone and appear to disappear! To explain this, it has been hypothesized (Codispoti *et al.*, 1991; Murray *et al.,* 1995) that all forms of inorganic N are converted to N_2 in this region. Two possible pathways for these transformations are the "annamox" reaction and reactions facilitated by Mn redox cycling. In the "annamox" reaction, NO_2^- (produced from NO_3^-, in our case) oxidizes NH_3 with both species being converted to N_2. A bacterium that can carry out the "annamox" reaction has recently been isolated from a biofilm (Strous *et al.*, 1999). Several authors have suggested that oxidation of NH_3 by NO_3^- is thermodynamically possible (e.g. Richards, 1965). In the cycle facilitated by Mn redox processes, Mn (II) is oxidized to Mn (III, IV) by NO_3^- which is reduced to N_2, and oxidation of NH_3 by Mn (III, IV) also produces N_2 (Luther *et al*., 1997).

Vertical PO_4^{3-} and HS^- profiles from the Black Sea (Fig. 8) provide support for this Mn redox cycle. The complex PO_4^{3-} profiles can be explained as follows:

1. a dissolved Fe (II) and Mn (II) flux from the anoxic zone to the suboxic zone,

2. oxidation to Fe (III) and Mn (III, IV) by NO_2^- and NO_3^- in the suboxic zone,

3. formation of Fe (III) and Mn (III, IV) containing precipitates that scavenge PO_4^{3-} creating the PO_4^{3-} minimum in the suboxic zone, and

4. formation of the PO_4^{3-} maximum in the upper part of the sulfide zone where the precipitates dissolve (Codispoti *et al.*, 1991a; Murray *et al.*, 1995; Spencer and Brewer, 1971;).
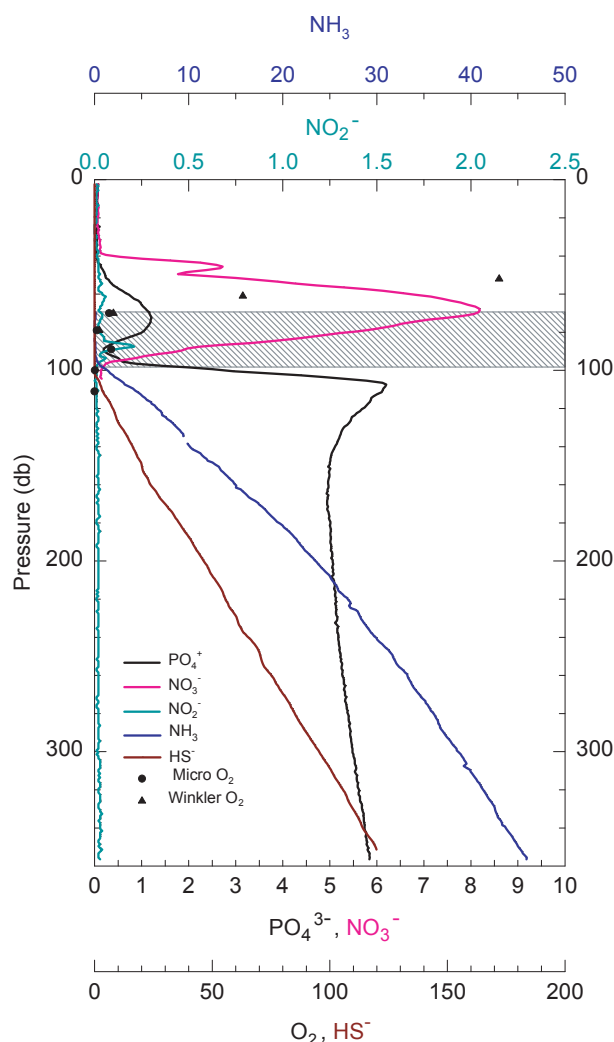
$$5NH_3 + 3HNO_3 \rightarrow 4N_2 + 9H_2O \qquad (6)$$

FIG. 8. – Continuous vertical profiles of NO_3^-, NO_2^-, NH_3, PO_4^{3-} and sulfide ($H_2S + HS^- + S^{2-}$) in a pump profile that sampled oxic, suboxic and anoxic portions of the Black Sea's water column. Discrete Winkler and colorimetric dissolved oxygen concentrations taken with the low-concentration method of Broenkow and Cline (1969) are also included. The shaded area denotes the suboxic zone. Sulfide is essentially zero in this zone, and oxygen concentrations are generally less than 5 μM, although in these data there is one depth within the zone were dissolved oxygen concentrations were ~ 7 μM. The low nitrite (NO_2^-) concentrations (~0.01-0.02 μM) in the anoxic zone are probably artifacts, The nitrite peak near the bottom of the suboxic zone was often more pronounced than in this pump profile (Codispoti et al., 1991a). These data are from (Friederich et al., 1990). Concentrations are in μM.

Luther et al. (1997) performed laboratory experiments, compared nitrogen cycling in Mn rich and Mn poor sediments, and provided thermodynamic calculations suggesting that such a N_2 producing Mn redox cycle is possible. Since it is likely that both Mn (II) and NH_3 are released from sediments underlying suboxic waters, we have another mechanism for producing excess N_2. Because Mn can be re-cycled it functions like a catalyst. Thus, we can write the same stoichiometric equation for both the annamox reaction and the Mn-NH_3-NO_3^- redox cycle:

For this reaction, the total N_2 produced exceeds the N_2 contributed by NO_3^- by 167%. Clearly, to the extent that there are fluxes of NH_3 that are coupled to energy production from the NO_3^- - HS^- couple and not to remineralization of P-containing organic matter, we have the potential for a reaction that could contribute powerfully to the pool of "extra excess N_2" (Fig. 7). We should also note that Luther et al. (1997) point out that oxidation of organic matter by MnO_2 produces N_2 and that this under-appreciated pathway for N_2 production may enhance sedimentary denitrification rates in Mn rich sediments. Lewis and Luther (2000) found elevated Mn concentrations at mid-depths in the Arabian Sea's suboxic waters suggesting that the catalytic Mn redox cycle may occur there as well. Maximum values were ~8 nM, so the quantitative significance of this process away from the sediments may be small even though the Mn can be recycled. Moreoever, the yield of "extra excess N_2" will be smaller than suggested in Equation 6 because, at mid-depths, the cycle is likely to be fueled largely by organic matter, not NH_3.

Farrenkopf et al. (1997a, b) have shown that bacteria can use IO_3^- to oxidize organic matter and gain a similar amount of free energy as gained from the use of NO_3^-. This is another process that could produce N_2 (from organic N) without consuming NO_3^-. The bacteria convert IO_3^- to I^-, and Farrenkopf et al. found that maximum I^- concentrations in the suboxic waters of the Arabian Sea approach 1 μM. Based on Equation (5) and an oxidation state change from +V to –I, it is possible that IO_3^- reduction could produce ~ 0.3 μg-atoms of N_2, about 3% of the maximum "extra excess N_2" values (Fig. 7). Of course, for this process or the water column Mn redox cycle to account for N_2 production not already included in $N_{deficit}$, PO_4^{3-} releases would have to be low.

Overall, there are several processes that could contribute to the "extra excess N_2". *We believe that these data imply that existing estimates of water column denitrification are too low.*

The oceanic N_2O regime

In addition to its importance as an intermediate in the nitrogen cycle, N_2O is an important trace gas that is increasing in the atmosphere. Depending on the chosen time frame, N_2O (per molecule) has a global warming potential 170 to 310 times greater than CO_2 (Manne and Richels, 2001). It adds several percent

to the greenhouse effect under present-day conditions and plays a role in the destruction of stratospheric ozone (Andreae and Crutzen, 1997; Nevison and Holland, 1997). The ocean is a net source of N_2O to the atmosphere but there is a wide range in the estimates. A widely accepted value is Nevinson *et al.'s* (1995) estimate of ~ 4 Tg N yr^{-1} (Table 1) with a range of 1.2-6.8 Tg N yr^{-1}. Bange *et al.* (1996) suggest that some estimates did not sufficiently account for high N_2O concentrations found in coastal and upwelling regions and estimate the oceanic source, excluding estuaries, as 4.5-7.4 Tg N yr^{-1}. A biologically constrained approach yielded an estimate of ~10.5 Tg N yr^{-1} for the open ocean and coastal regions (Capone, 1991).

Because N_2O production and consumption are enhanced at low oxygen concentrations (Codispoti and Christensen, 1985; Codispoti *et al.*, 1992; Goreau *et al.,* 1980; Suntharalingam *et al.*, 2000), the distribution of N_2O in the ocean is highly non-uniform. Indeed, the highest and lowest concentrations, can often be found in close proximity with the lowest values occurring in the core of suboxic zones or in anoxic zones and the highest values occurring at the boundaries of suboxic zones (Codispoti *et al.,* 1986; Law and Owens, 1990; Naqvi and Noronha, 1991; Naqvi *et al.*, 2000, Pierotti and Rasmussen, 1980; Yoshinari *et al.*, 1997). Results from the ETSP (Codispoti *et al.*, 1992) and the Arabian Sea (Naqvi *et al.*, 2000) where such conditions exist suggest that N_2O saturations in excess of 1000% can be found at the sea surface. Bange *et al.* (2000), Law and Owens (1990) and Naqvi and Noronha (1991) suggest that this situation leads to globally significant transport of N_2O from the Arabian Sea to the atmosphere, despite this region's small area (~2% of the oceanic total). Recently, Naqvi *et al.* (2000a) have reported record high N_2O concentrations during seasonal development of upwelling and low oxygen conditions over the western Indian shelf. Maximum values were > 500 nM, and the maximum surface value was 436 nM, or 8,250% saturation. Given that open ocean surface N_2O saturation values are generally less than 105%, the high surface values observed off Peru and India demonstrate the highly non-linear distribution of oceanic N_2O.

Although nitrification at low oxygen concentrations could contribute to the high values on the western Indian shelf, Naqvi *et al.* (2000a) suggest that the major contributor is "stop and go" denitrification. Laboratory experiments, suggest that *nitrous oxide reductase* is slow to be induced relative to the other enzymes involved in denitrification, and some stud-

ies suggest that it is relatively susceptible to oxygen inhibition (Dendooven and Anderson, 1994; Firestone and Tiedje, 1979). Thus, a portion of the high N_2O values found at the boundaries of suboxic zones probably arises from denitrification that is in the "spin-up" phase (Codispoti *et al.,* 1992). In the shallow waters studied by Naqvi *et al.* (2000a), there were strong gradients, with conditions varying from oxic to anoxic. In addition, meteorological events should have a strong influence on these shallow waters. Thus, the conditions are ripe for "stop and go" denitrification. Naqvi *et al.* (2000a) suggest that the N_2O flux to the atmosphere arising from these conditions is 0.04-0.25 Tg N yr^{-1}. Bange *et al.* (2000) suggest an average value for the Arabian Sea of 0.4 Tg N yr^{-1} not including the high N_2O values observed by Naqvi *et al.* (2000a). Considering the wide range of estimates, and as yet undiscovered N_2O "hotspots" that may occur during upwelling off Oman, one can speculate that the ~2% of the global oceanic area represented by the Arabian Sea might provide ~ 1 Tg N yr^{-1} of N_2O to the atmosphere under present-day conditions, a significant fraction of the global oceanic total (Table 1). To our knowledge, observations of other seasonal low oxygen zones that develop over other shelves such as the "dead zone" off the mouth of the Mississippi River (Rabalais *et al.*, 2000) have not been examined for their potential impact on oceanic N_2O emissions.

DISCUSSION

Perspective

The major goal of this paper is not to provide definitive answers *vis a vis* the oceanic fixed N budget and N_2O cyling, but to suggest that prior studies (including some of our own!) suffer from a rigidity imposed by a tendency to prefer budgets that balance and systems that are in a steady-state. So far, we have suggested that many traditional estimates of the oceanic water-column denitrification rate (including our own) are too low and that prevailing estimates of N_2O emissions from the ocean (Table 1) may also be low. We think that our upwards revisions are conservative, but given the present state of knowledge, our revised estimates are speculative. We use them not to provide a rigorous budget, but to show that prevailing budgets (e.g. Codispoti and Christensen, 1985; Table 1) may be misleading and that we might not be asking the right questions.

An oceanic denitrification rate of > 400 Tg N yr⁻¹?

Our data suggest that $N_{deficit}$ underestimates the excess N_2 burden in the water column by a factor of ~2 (Fig. 7), and that some prior nitrate deficit and denitrification rate estimates based on NTO relationships underestimate the excess N_2 burden by a factor of ~4 (Compare Figs. 4 and 7). Similarly, estimates of denitrification based on ETS activities (Codispoti and Packard, 1980; Codispoti *et al.*, 1986; Naqvi and Shailaja, 1993) did not account for the higher ratios of N_2 production to NO_3^- consumption during denitrification suggested by our Arabian Sea data (Fig. 7). In addition, they may have been applied to volumes that were too small due to the assumption that denitrification was important only in suboxic waters with NO_2^- concentrations > 0.2 -0.5 μM.

Although there is a wide range in recent denitrification rate estimates for the Arabian Sea water column (10-44 Tg N yr⁻¹, Uhlenhopp *et al.*, in prep.), for a variety of reasons we believe that a value of ~30 Tg N yr⁻¹ is reasonable for the NO_3^- consumption portion of the denitrification rate, in agreement with the recent results of Bange *et al.* (2000). Since water column burdens of excess N_2 exceed traditional NTO based nitrate deficit estimates by a factor of 4 (Fig. 7), it might seem reasonable to quadruple the existing estimate of ~ 30 Tg N yr⁻¹ in order to account for the additional sources of N_2 that we have discussed. A significant portion of the "extra excess N_2", however, occurs in the deeper portion of the water column where water residence times are likely to be longer. Therefore, for the purposes of this discussion, we will assume that a reasonable estimate for water column denitrification in the Arabian Sea's "permanently" suboxic portion of the OMZ is twice the "traditional" estimate, or 60 Tg N yr⁻¹.

Our prior estimates for the denitrification rate in the suboxic portions of the OMZ in the ETNP and ETSP total ~50 Tg N yr⁻¹ (Codispoti, 1989). The estimate for the ETSP included some transient sites on the margin of the "permanent" suboxic zone (Codispoti and Packard, 1980). Assuming that the methods used to estimate nitrate deficits in the Pacific adequately accounted for NO_3^- removals, we might expect water column burdens of excess N_2 to exceed nitrate deficits by a factor of ~2, a conclusion that is supported by some preliminary excess N_2 data from the ETNP (Brandes *et al.*, 1996). We will assume, therefore, that it is conservative to increase our previous estimates of water column denitrification in this region by 50% and to suggest that the true value in today's ocean is closer to 75 Tg N yr⁻¹. Thus, we arrive at a total rate for the three largest suboxic portions of the oceanic water column of 135 Tg N yr⁻¹ (60 + 75 Tg N yr⁻¹).

We must also account for the contributions of the smaller/more transient sites of water column denitrification mentioned earlier. Based on the data in Naqvi *et al.* (2000a), Naqvi *et al.* (2000b) have estimated a denitrification rate for the seasonal hypoxic/suboxic/anoxic zones over the western Indian Shelf to be ~ 5 Tg N yr⁻¹. Estimates for similar sites such as one that develops off the mouth of the Mississippi River (Rabalais *et al.*, 2000) are not available, but given the increase in such sites (Malakoff, 1998) in recent decades, it might be conservative to suggest a total denitrification rate of >5 Tg N yr⁻¹, for all such regions. An examination of the size of the suboxic zone off SW Africa (Calvert and Price, 1971) suggests that this region could also contribute several Tg N yr⁻¹ to the overall oceanic water column denitrification rate. Existing water column denitrification estimates for the Baltic Sea, Cariaco Trench and Black Seas total no more than 0.5 Tg N yr⁻¹, (Cline, 1973; Goering *et al.*, 1973; Rönner, 1983) but they must be adjusted upwards for the same reasons that we have adjusted the Pacific and Arabian Sea estimates upwards. In addition, anthropogenic impacts have increased maximum NO_3^- concentrations in the Black Sea in recent decades and the thickness of the suboxic zone may have increased (Codispoti *et al.*, 1991a; Murray *et al.,* 1989), so the older estimates for the Black Sea could be massive underestimates. All in all, we think it reasonable to suggest that a conservative estimate for the additional sites of oceanic suboxic water column denitrification would be ~10 Tg N yr⁻¹.

There is another potential contributor to the oceanic water column denitrification rate about which we know next to nothing, *the possibility of denitrification in oxygenated waters and within microenvironments in oxygenated waters* (Tsunogai, 1971; Yoshinari and Koike, 1994). Some studies suggest the presence of denitrification in microenvironments (Alldredge and Cohen, 1987; Wolgast *et al.*, 1998), but they do not allow us to scale up to a global rate for oxygenated waters. Remember, however, that the identified water column sites of denitrification comprise only ~0.1% of the total oceanic volume. Thus, an extremely small rate of N_2 production in oxygenated waters by any of the processes that we have mentioned could add significantly to the total oceanic water column rate. Laboratory

experiments (Lloyd, *et al.*, 1987) suggest that N_2 production by denitrifiers can persist in the presence of oxygen in excess of 100 μM. In addition, the energetics of oxidation of organic matter under oxic conditions by Mn (IV) compares favorably with direct oxidation, and the organic N oxidized by Mn (IV) may be converted to N_2 (Froelich *et al.*, 1979; Luther *et al.*, 1998). Overall, it seems that we can *conservatively* estimate a water column denitrification rate in the present-day ocean of ~150 Tg N yr^{-1}.

Middleburg *et al.* (1996) suggest an oceanic sedimentary denitrification rate between 230-285 Tg N yr^{-1} based on canonical stoichiometries similar to those that underestimate water column production of N_2. This estimate could, therefore, be conservative, particularly, since the potential importance of Mn redox processes to sedimentary production of N_2 has not received sufficient attention as noted by Luther *et al.* (1997). In addition, consideration of the isotopic composition of oceanic NO_3^- suggests that the sedimentary rate, on average, should exceed the water column production of N_2 from NO_3^- by several times (Brandes, 1996). This argument needs refinement due to the changing nature of our understanding of sources, sinks and pathways, but the essentials are as follows. Oceanic NO_3^- has a $\delta^{15}N$ of ~ +5 ‰ (Sigman et al., 1999), and this value arises from a balance of the inputs and losses. Neglecting the minor terms, the major input is nitrogen fixation, which produces fixed nitrogen with a $\delta^{15}N$ of ~ 0‰ (Hoering and Ford, 1960; Minagawa and Wada, 1986), and the major losses are water column and sedimentary denitrification. Water column denitrification, which in most suboxic zones occurs with only partial depletion of the NO_3^- pool, removes NO_3^- with a $\delta^{15}N$ of ~ -20‰ (Brandes *et al.*, 1998). In contrast, the isotopic fractionation during sedimentary denitrification is small and removes fixed N with a $\delta^{15}N$ of ~ 3‰. We will assume that the processes that produce the "extra excess N_2" observed in suboxic waters also removes fixed N with a $\delta^{15}N$ +3‰. Therefore, for the isotopic composition of the overall denitrification loss to match that of the nitrogen fixation input (~0 ‰), the overall denitrification rate would need to be about 8 times larger than the water column rate of nitrate removal by denitrification (i.e. {6.7x(+3)} + (-20) = 0). One eighth is, of course accounted for by water column conversion of NO_3^- to N_2. Another 1/8 would also come from water column processes since the water column burden of excess N_2 values in the suboxic portions of the Arabian Sea (Fig. 7) is about

twice the $N_{deficit}$ burden, indicating that processes other than NO_3^- reduction produce about 1/2 the excess N_2. The remaining 3/4 would come from sedimentary denitrification and would amount to 6 x 75 or 450 Tg N yr^{-1}. In addition to the preliminary nature of the isotopic argument, a possible weakness is that it is true only for periods long enough for us to assume a steady-state budget with respect to the $\delta^{15}N$ of oceanic NO_3^-. This may not be the case as we enter the Anthropocene. We employ the isotopic data, at this point, only to demonstrate that they do not contradict the assertion that our selected rate of 300 Tg N yr^{-1} for sedimentary denitrification (Table 1) could be conservative.

How can we reconcile our total denitrification rate for continental shelves and the open ocean of ~ 450 Tg N yr^{-1} with the other budget terms (Table 1)? Perhaps the simplest explanation is that the present-day oceanic N budget is more or less in balance, but we have underestimated the source terms. We have already adjusted the anthropogenic source terms upwards (Table 1) and noted that the atmospheric anthropogenic DON term and groundwater inputs (e.g. Krest *et al.*, 2000) are poorly documented. Reasonable increases in atmospheric, runoff and groundwater inputs appear, however, to be unlikely to completely balance the budget. If the budget is to be balanced, the oceanic nitrogen fixation term will have to be increased. A conundrum is that even Gruber and Sarmiento's (1997) estimate for oceanic nitrogen fixation of 125 Tg N yr^{-1} (Table 1) is high in relation to the results of direct incubations (e.g. Lipshultz and Owens, 1996). Studies of primary production rates in the Arctic are, however, instructive with regard to this type of a discrepancy between rates estimated from incubations and rates estimated from water mass properties. Traditional incubation-based estimates for Arctic primary production are lower than many estimates based on water mass properties (Codispoti *et al.*, 1991b). In the case of the Arctic, the discrepancy arose, in part, because many incubation studies were conducted in the post-bloom period when ice conditions were most favorable to navigation. Since primary productivity events in the Arctic tend to be localized, it is also easy to miss peak events. Water mass properties integrate over time and space and are not as subject to these problems. In addition, most studies of oceanic nitrogen fixation have concentrated on *Trichodesmium*, yet there are many other species that may have the ability to fix N. Finally, the incubations employed to obtain nitrogen fixation rates are

highly subject to experimental artifacts (Paerl, 1990; Paerl and Zehr, 2000). *We suggest that it is possible that the oceanic nitrogen fixation rate is considerably higher than present estimates.*

The large deficit (~200 Tg N yr⁻¹) in our revised oceanic fixed-N budget (Table 1) could also arise because all studies bearing on this subject have been made during the climatic transition from the Holocene to the Anthropocene. Thus, our observations were taken from a "moving target". How do we combine observations taken over several decades if we are in a period of rapid change? In addition, large imbalances are certainly possible during rapid transition. Firstly, there would be effects due to changes in circulation and stratification that are related to climate change, *per se.* For example, anthropogenic activities may be increasing the frequency of major El Niño/La Niña cycles, and we have already noted that an acceleration of the denitrification rate in the ETSP was noted during the 1985 Niña (Codispoti *et al.*, 1986). Recently, a combination of development and increased hurricane frequency have led to large pulses of fixed N to the North Carolina coastline (Paerl *et al.*, 2000, 2001). We have already mentioned increases in coastal hypoxia/anoxia, and the increase in maximum NO_3^- concentrations in the Black Sea. In mentioning, the two accelerations of denitrification off Peru, we noted that one followed the collapse of the Peruvian anchoveta fishery (Codispoti and Packard, 1980). We know of no other studies that have attempted to relate fishing pressure to oceanic denitrification rates, but we do know that fishing pressure has massively influenced oceanic ecosystems. Margalef (1974) and Watling and Norse (1998) have, for example, commented on major ecosystem changes arising from bottom trawling. Overall, *we believe that more attention must be given to how climate change and more direct anthropogenic impacts alter the oceanic fixed N regime.*

Our revised budget (Table 1) and a similar budget by Middleburg *et al.* (1996) produce a much shorter turnover time for oceanic fixed N (Table 2) and a significant reduction in the oceanic biological pump's ability to sequester atmospheric CO_2 because of decreases in fixed N. Multiplying the deficit in our budget by a Redfield C/N ratio of 6.6 (by atoms) gives a ~1.3 10^{15} g of C yr⁻¹ potential reduction in oceanic new primary production. Given the present state of knowledge, the fixed N deficit in our budget could be much smaller or much larger. It is also likely that these values are changing. *Until we better understand how far out of balance anthro-*

TABLE 2. – An unauthorized history of minimum turnover time estimates for oceanic fixed-N (Inventory/Total Sink Term)

Author(s)	Years
Brandt (1899)	2
1930 estimate quoted by Harvey (1960)	10,000
Emery, Orr and Rittenburg (1955)	10,000
Eriksson (1959)	10,000
Tsunogai & Ikeuchi (1968)	4,000
Tsunogai (1971)	26,000
Codispoti (1973)	8,000
Liu (1979)	8,000
Codispoti & Christensen (1985)	5,000
Capone (1991)	3,500
Codispoti (1995)	3,000
Middleburg *et al.* (1996)	1,700 – 2,300
Gruber and Sarmiento (1997)	3,500
This paper	1,500
And going lower???	

pogenic activities might drive the oceanic fixed N budget, we cannot neglect its potential influence on atmospheric CO_2 concentrations.

Potential for change in the oceanic nitrous oxide source term

On a per molecule basis, N_2O is ~ 200-300 times more powerful than CO_2 (Manne and Richels, 2001) as a greenhouse gas, and increases in N_2O contribute to the destruction of stratospheric ozone (Nevison and Holland, 1997). Thus, trying to understand how the oceanic source term for N_2O may change as we enter the Anthropocene is of more than casual interest. We have revised the prevailing oceanic N_2O source term upwards by 2 Tg N yr⁻¹ in our oceanic fixed N budget (Table 1) to account for the expansion of low oxygen conditions in coastal regions (e.g. Naqvi *et al.*, 2000a). Once again, at the present state of knowledge we could argue about whether this revision should be larger or smaller, but to do so misses the more important question of how this term might change. We know that the highest N_2O concentrations are found near the boundaries of suboxic waters (Codispoti *et al.*, 1992) and that in the "stop and go" denitrification regime found off the western Indian shelf surface concentrations can achieve saturations in excess of 8,000% (Naqvi *et al.*, 2000a). We also know that, with some exceptions such as the California Borderland Basins (Stott *et al.*, 2000), suboxia in coastal regions is on the increase and that only small changes in carbon and nutrient fluxes, and circulation (e.g. Codispoti, 1989) could cause significant increases in oceanic suboxia and N_2O cycling (Codispoti and Chris-

tensen, 1985). Finally, we note that the time scale for change in the oceanic N_2O regime is relatively short. The oceanic inventory of N_2O is ~ 1000 Tg N (Suntharalingam *et al.*, 2000) and dividing by our source term of 6 Tg N yr^{-1} (Table 1) gives a turnover time of < 200 years. Most of this turnover probably occurs in the upper 1000m of the water column, so it might be fair to say that the inherent time scale for change is closer to 50 years.

Ice core observations (Flückiger *et al.*, 1999; Leuenberger and Siegenthaler, 1992) suggest that variations in atmospheric N_2O during the last Glacial - Holocene moved roughly in concert with CH_4 and that each gas contributed about 15% to greenhouse forcing during the Glacial – Postglacial transition. Although the concentrations of CO_2, CH_4 and N_2O were all lower during the Glacial, there are significant departures in the trends for each gas. Present-day N_2O concentrations are unprecedented in the last 45 kyr. Of perhaps greater interest, are some spikes in the record that have not yet been fully explained. *Given a time-scale of ~50 yrs, the potency of N_2O as a greenhouse gas, and the expansion of coastal suboxia, can we be in for some surprises vs the oceanic N_2O source as we enter the Anthropocene?*

Some cautionary riddles

As we enter the Anthropocene, we are likely to hear more and more schemes advanced to engineer global climate, including Fe fertilization of the ocean. Some of the potential downside effects of Fe fertilization on the oceanic N cycle have already been described (e.g. Fuhrman and Capone, 1991). Here are three "cautionary riddles" that the reader can solve based on the information already presented:

1. If you want to make the ocean more Fe limited, add Fe in the wrong place.

2. If you want to make the ocean more N limited add fixed N in the wrong place.

3. If you want to increase greenhouse forcing try to decrease it by adding Fe to the ocean in the wrong place.

NOTE ADDED IN PROOF

Recently, Sañudo-Wilhelmy *et al.* (2001) have suggested that the Fe requirement for nitrogen fixation may have been considerably overestimated in prior studies. Thus, the ~60 times greater Fe requirement for nitrogen fixation in comparison to NO_3^-

uptake that we have employed when asserting that denitrification may make the ocean more Fe limited may be too high. A close reading of Sañudo-Wilhelmy *et al.* (2001) together with information provided by Brand (1991) and Raven (1988), still suggests to us that the Fe requirement for NO_3^- uptake by open ocean eukaryotic phytoplankton will prove to be significantly less than for nitrogen fixation, so we still believe that it is reasonable to assert that denitrification may make the ocean more Fe limited, although the Sañudo-Wilhelmy *et al.* (2001) paper weakens our argument a bit. These authors studied a relatively Fe rich portion of the Atlantic and found that nitrogen fixation was highly correlated to the P content of *Trichodesmium* and was enhanced at higher irradiance. This is in line with previous studies summarized in the main body of our text that suggest that PO_4^{3-} may limit nitrogen fixation in some cases and that the energy requirements for nitrogen fixation are high. Finally, please note that the data for station N-8 in Figure 7 were calculated using a preliminary data set and are too low by about 1.5 micromolar.

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