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Inputs, losses and transformations of nitrogen and phosphorus in the pelagic North Atlantic Ocean

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Abstract. The North Atlantic Ocean receives the largest allochthonous supplies of nitrogen of any ocean basin because of the close proximity of industrialized nations. In this paper, we describe the major standing stocks, fluxes and transformations of nitrogen (N) and phosphorus (P) in the pelagic regions of the North Atlantic, as one part of a larger effort to understand the entire N and P budgets in the North Atlantic Ocean, its watersheds and overlying atmosphere. The primary focus is on nitrogen, however, we consider both nitrogen and phosphorus because of the close inter-relationship between the N and P cycles in the ocean. The oceanic standing stocks of N and P are orders of magnitude larger than the annual amount transported off continents or deposited from the atmosphere. Atmospheric deposition can have an impact on oceanic nitrogen cycling at locations near the coasts where atmospheric sources are large, or in the centers of the highly stratified gyres where little nitrate is supplied to the surface by vertical mixing of the ocean. All of the reactive nitrogen transported to the coasts in rivers is denitrified or buried in the estuaries or on the continental shelves and an oceanic source of nitrate of 0.7–0.95 × 10^{12} moles NO_3^- y^{-1} is required to supply the remainder of the shelf denitrification (Nixon et al., this volume). The horizontal fluxes of nitrate caused by the ocean circulation are both large and uncertain. Even the sign of the transport across the equator is uncertain and this precludes a conclusion on whether the North Atlantic Ocean as a whole is a net source or sink of nitrate. We identify a source of nitrate of 3.7–6.4 × 10^{12} moles NO_3^- y^{-1} within the main thermocline of the Sargasso Sea that we infer is caused by nitrogen fixation. This nitrate source may explain the nitrate divergence observed by Rintoul & Wunsch (1991) in the mid-latitude gyre. The magnitude of nitrogen fixation inferred from this nitrate source would exceed previous estimates of global nitrogen fixation. Nitrogen fixation requires substantial quantities of iron as a micro-nutrient and the calculated iron requirement is comparable to the rates supplied by the deposition of iron associated with Saharan dust. Interannual variability in dust inputs is large and could cause comparable signals in the nitrogen fixation rate. The balance of the fluxes across the basin boundaries suggest that the total stocks of nitrate and phosphate in the North Atlantic may be increasing on time-scales of centuries. Some of the imbalance is related to the inferred nitrogen fixation in the gyre and the atmospheric deposition of nitrogen, both of which may be influenced by human activities. However, the fluxes of dissolved organic nutrients are almost completely unknown and they have the potential to alter our perception of the overall mass balance of the North Atlantic Ocean.

Introduction

The North Atlantic Ocean is one of the smallest of the ocean basins and it is surrounded by some of the most heavily industrialized countries in the world. Human activities at the boundaries of the North Atlantic modify the nitrogen (N) and phosphorus (P) dynamics of the ocean, watersheds and atmosphere. It is also one of the most heavily studied ocean basins and may be most amenable to a synthesis. In May 1994, a meeting was held on Block Island, R.I. (Galloway et al., this volume) to evaluate our understanding of the N and P cycles in the North Atlantic Ocean, its surrounding watersheds and overlying atmosphere. This question was addressed from four perspectives, the atmosphere (Prospero et al., this volume), watersheds (Howarth et al., this volume), coastal zone (Nixon et al., this volume) and open oceans (this paper). From the perspective of the open oceans group, the goal was stated succinctly in the question: "What are the current sources and sinks of nitrogen and phosphorus within the North Atlantic Ocean, what are the exchanges across its boundaries and how do the magnitudes of these exchanges, sources and sinks compare with recent changes from natural background levels as a result of human activity?" To address this question required specific information about both N and P in the oceanic realm: 1) The standing stocks of each form of each element, 2) the fluxes of N and P into and out of the ocean, and 3) the fluxes and transformations of N and P within the ocean and between important sub-sections of the ocean, particularly in areas where the biological transformations of N have resulted in depletion of reactive N with respect to the normal requirements of N and P for plant growth. This paper draws heavily on the estimates from the atmosphere and coastal groups for data on boundary exchanges. Prospero et al. (this volume) provided the N, P and Fe atmospheric deposition estimates (Prospero et al., this volume) and we relied on an analysis by Quinn et al. (this volume) to discuss the ammonia flux out of the North Atlantic. The net exchanges of N and P with neritic coastal waters were estimated by Nixon et al. (this volume).

We begin with assessments of the standing stocks of each form of N and P and a discussion of the vertical and horizontal flux processes that affect each stock. We then focus on two topics which we feel are important for understanding the whole-basin elemental cycles in the North Atlantic. Both topics involve the overall mass balance of nitrate and a comparison of nitrate fluxes with phosphate fluxes. 1) We evaluate a variety of estimates of the meridional fluxes of nitrate and phosphate at latitudes from 8° N to 65° N, across the Straits of Gibralter and the exchange with the Caribbean Sea. These analyses can be used to bound the likely sources and sinks of nitrate and phosphate within different subregions of the North Atlantic. 2) We reconsider the previously described anomalies in the ratios of nitrate to phosphate in the upper 1000 m of the Sargasso Sea (Fanning 1989, 1992; Michaels et al. 1994) and estimate a net nitrate creation rate for the gyre of 3.7–6.4 × 10^{12} moles y^{-1} that we infer is caused by nitrogen fixation. Finally, we discuss the overall balance of N and P in the pelagic North Atlantic.

Standing stocks and fluxes of nitrogen and phosphorus

A. *The boundaries of the North Atlantic Ocean*

Our choice for the horizontal boundaries of the Atlantic was determined primarily by the availability of data. For the southern extent of the Atlantic, we chose the Equator; however, for the meridional transport estimates at the southern boundary, we used data from 12° N as a proxy. We assumed that the outflow from the Amazon River, which lies directly on the equator, is part of the North Atlantic system because most of the offshore transport is to the north. We ignored the Panama Canal. We chose a boundary at the straits of Gibraltar and characterized all of the coastal and riverine inputs into the Mediterranean by the net flow through the straits. In the north, we chose boundaries at 60° N and 65° N, again based on the available zonal sections. Within the Atlantic, we further subdivided the basin at 24° N and 36° N, in part because of the earlier meridional flux estimates at these latitudes (Rintoul & Wunsch 1991; Martel & Wunsch 1993). The boundary with the coastal zone was chosen operationally as the 200 m bathymetric contour. In practice, the coastal group (Nixon et al., this volume) determined the net N and P fluxes into the shelf sediments. For nitrogen, there was frequently a nitrate deficit, and the required amount was supplied from the main thermocline of the adjacent ocean. For phosphate, net river outflow exceeded the estimates of burial and the residual was supplied to the oceans (Nixon et al., this volume).

B. *Standing stocks of nitrogen and phosphorus in the North Atlantic Ocean*

There are six major forms of nitrogen and three forms of phosphorus (some operationally defined) that are common in the ocean. Some of the trace nitrogen gases may also be useful as tracers of process, even if they do not contribute to the total nitrogen balance. The forms of nitrogen are nitrogen gas, nitrate, nitrite, ammonium (and ammonia), dissolved and particulate organic nitrogen (Table 1). Nitrogen gas is biologically unavailable to all but a few specialized organisms. The other species of nitrogen, which are readily converted by biological and chemical processes, can be called "reactive" nitrogen species. The principle forms of phosphorus are inorganic phosphate and dissolved and particulate organic phosphorous (Table 1). For each of these forms of N and P, we estimate the total standing stock for the basin and, for most, we compare these estimates with the fluxes of N and P in and out the basin. These fluxes are then discussed in further detail in the next section.

Nitrogen gas (N_2) is the most prevalent form of nitrogen in the ocean (Table 1), present at concentrations of approximately 450–600 μmoles kg^{-1} (Weiss 1970). It is generally biologically inert except for its utilization by nitrogen-fixing organisms and its production in denitrification. Although both of those transformations may affect the concentration of dinitrogen, the effects are likely to be local and must be small compared to the size of the standing stocks. The factor with the largest effect on N_2 concentration is the temperature dependence of N_2 solubility coupled to air-sea exchange.

Nitrate (NO_3^-) is the second most abundant form of nitrogen in the ocean and the most abundant form of reactive nitrogen. Concentrations below 1000 m are typically near 15–25 μmoles kg^{-1} in the North Atlantic. Concentrations near the surface are usually below the standard analytical detection limits (0.05 μmoles kg^{-1}) with seasonal exceptions that are very important for the biology of the upper ocean. In the permanent thermocline, there is a regular transition between these two extremes, determined both by mixing and remineralization. The spatial distribution of nitrate, particularly at 500–2000 m depth is strongly affected by midwater circulation. South Atlantic thermocline and Antarctic Intermediate water, with elevated nitrate concentrations, intrude into the North Atlantic from the south and create a zone of elevated nitrate at the base of the main thermocline.

We estimate the total standing stock of nitrate in the North Atlantic (Table 1) using mean nitrate concentrations from the TTO and GEOSECS datasets and the areal extent of different subregions of the North Atlantic (Platt et al. 1991). We estimate that there are 2,800 × 10^{12} moles NO_3^- in the North Atlantic, of which only 0.01% is on the continental shelves. Thus, the nitrate pool in the North Atlantic is 3–4 orders of magnitude larger than the nitrogen stocks described for the adjoining coastal areas, atmosphere and watersheds (Howarth et al., this volume; Nixon et al., this volume; Prospero et al., this volume). Even trivial uncertainties in the total standing stock of nitrate in the North Atlantic will preclude any attempt to infer boundary exchanges or the overall mass balance from sequential observations of the total nitrate standing stock. For example, if we naively assume that the accuracy of our estimate of the total nitrate standing stock is similar to the analytical accuracy of the measurement (as good as 0.5%) instead of the larger uncertainties inherent in the sparse data coverage, we would estimate an uncertainty in the total standing stock of 14 × 10^{12} moles NO_3^- (Table 1). This is larger than the annual nitrogen exchanged at the boundaries (Table 2), such as the 0.7–0.95 × 10^{12} moles N y^{-1} estimate of oceanic nitrate supply onto the shelves to

Table 1. Significant forms of nitrogen and phosphorus in the North Atlantic Ocean. Uncertainties for nitrogen are minimal values estimated from analytical accuracy and do not take into account the uncertainties that may arise when the sampling is inadequate to estimate the total stock. Uncertainties for the phosphorus species estimates are assumed to be the same as the corresponding nitrogen species. * In the case of dissolved organic N and P, the number of measurements is very small and very local, thus these estimates are actually much more uncertain than indicated in the table.

	Concentrations (μmoles/kg)	Stock in North Atlantic (× 10^{12} moles)	Uncertainty (%)	Uncertainty (× 10^{12} moles)
Nitrogen				
Dinitrogen gas (N_2)	450–600	112,000		
Nitrate (NO_3^-)	0–25	2,800	0.5	14
Nitrite (NO_2^-)	~0.01–0.2	2	1.0	<0.1
Ammonium (NH_4^+)	~0.01–0.5	5	1.0	<0.1
Dissolved Organic N (DON)	3–5	300–500	>5.0	>15–25
Particulate Organic N (PON)	0.02–1.0	13	>1.0	0.1
Phosphorus				
Phosphate (PO_4^{3-})	0.01–1.5	180	0.5	0.9
Dissolved Organic Phosphorus (DOP)	~0.2	37	>5.0	>1.9
Particulate Phosphorus (PP)	0.01–0.05	1	>1.0	<0.1

support denitrification and burial (Nixon et al., this volume), the 0.5–1.0 × 10^{12} moles N y^{-1} for atmospheric deposition of all reactive nitrogen species (Prospero et al., this volume) and the 0.9 × 10^{12} moles N y^{-1} for riverine fluxes of nitrogen to the coasts (Howarth et al., this volume).

Nitrite (NO_2^-) is generally present in low concentrations with the exception of a primary nitrite maximum that is present at the base of the euphotic zone in many areas (Herbland & Voituriez 1979; Olson 1981; Lipschultz et al., in press). Nitrite is an intermediate in the nitrification and denitrification pathways. Its standing stocks are likely unimportant in the overall budget of nitrogen (Table 1), but it can be an important marker for transformation processes. Nitrous oxide (N_2O) is a trace compound and is not a significant standing stock of nitrogen in the oceans. It is produced as a byproduct during nitrification and can be consumed during denitrification.

Ammonium (NH_4^+) and ammonia (NH_3) are trace nitrogen species in most areas. They are biologically very labile and are intermediates in many biologically-mediated transformations. As with NO_2^- and N_2O, ammonia/ammonium do not constitute a major standing stock of nitrogen. However, efflux of ammonia gas may be a significant source of nitrogen into the atmosphere, particularly in comparison to some of the atmospheric deposition fluxes (Quinn et al. 1988, 1990). Quinn et al. (this volume) compile the existing ammonia/ammonium data to attempt to estimate the air-sea flux of ammonia for the North Atlantic. The data are sparse, show both air-to-sea and sea-to-air fluxes of up to 100 μmoles m^{-2} d^{-1} and no conclusion was possible about the average flux (Quinn et al., this volume). If the mean net flux was only 1 μmole m^{-2} d^{-1} it would account for 16 × 10^9 moles y^{-1}, a small flux compared to the North Atlantic nitrogen budget, but large compared to some of the riverine and air-sea fluxes.

Dissolved organic nitrogen (DON) is a significant standing stock of nitrogen (Table 1) and likely the second largest pool of reactive nitrogen. However, there are very few measurements in the Atlantic Ocean. Typical concentrations are thought to be in the range of 3–5 μmoles kg^{-1} with only small variations with depth (Sharp 1983; Dennis Hansell, unpublished data). At these concentrations, the total standing stock of nitrogen in DON would be on the order of 300–500 × 10^{12} moles. There has been a great deal of controversy in recent years about the measurement of DON (Suzuki et al. 1985; Walsh 1989; Hansell 1993; Hopkinson et al. 1993), with suggestions in the early paper by Suzuki et al., that a new technique yielded higher concentrations and larger surface-deep sea gradients (Suzuki et al. 1985). However, these reports of higher concentrations have not been supported by subsequent research (Walsh 1989). It now appears that the traditional concentrations are reasonable and that vertical gradients are relatively small. Urea is

Table 2. Summary of nutrient fluxes across the boundaries of the North Atlantic Ocean. All fluxes are in units of 10^{12} moles y^{-1}.

Process and location	N	P
Atmospheric deposition		
0–10° N	0.13–0.26*	0.003
10–40° N	0.22–0.44*	0.003
40–70° N	0.18–0.36*	~0
Total atmospheric deposition	0.5–1.0	0.006
Ammonia air-sea exchange	?	–
Exchange with continental shelves **		
Western boundary, 0–10° N (Amazon)	0.11	0.014
Western boundary, 10–40° N	−0.26	0.004
Western boundary, 40–70° N	−0.41	0.003
Eastern boundary, 0–10° N	−0.15	0.003
Eastern boundary, 10–40° N	−0.03	0.002
Eastern boundary, 40–70° N	−0.18	0.004
Total exchange with shelves	−0.92	0.03
Burial in sediments	0.05	0.002
Nitrogen fixation		
0–10° N	?	–
10–40° N	3.7 to 6.4	–
Total nitrogen fixation	>3.7 to 6.4	–
Physical transport (negative is southward or westward)		
Equator***	−1.4 to 4.6	−0.07 to 0.31
Arctic Sea****	−0.3 to −2.8	−0.16 to −0.3
Mediterranean*****	−0.05 to −0.2	−0.003 to −0.005
Total North Atlantic Ocean	1.9–13.8	0.13–0.65

* The lower value in each range is the $NO_y + NH_x$ flux as calculated by Prospero et al. (this volume). These estimates exclude the potential contribution of DON which Prospero et al. estimate would approximately double the flux. Thus, the upper bound is estimated as twice the $NO_y + NH_x$ flux.

** The fluxes of nitrate and phosphate from the ocean onto the shelves are derived from the estimates of Nixon et al. (this volume) at the 200 m isobath. The partitioning of the nitrate fluxes by coastline is derived from the net balance of atmospheric deposition, riverine input and denitrification for each coastal region (Table 14 in Nixon et al., this volume). Nixon et al. also modify the total nitrate flux estimates by the inclusion of burial in shelf sediments and a loss to fisheries. This increases the net nitrogen deficit by approximately 16%. We modify each of the regional fluxes in their Table 14 upwards by 16% to approximate the small modifications from burial and fisheries. For phosphate, the regional data are restricted to riverflow and estuarian flux estimates (Table 12 in Nixon et al., this volume). Atmospheric fluxes, shelf burial and fisheries losses are small and ignored.

*** From Table 4. Range of estimate by Martel & Wunsch (1993) for 12 ° N

**** From Table 4. Full range of estimates by Martel & Wunsch (1993) for 60° N and of Anderson & Dyrssen (1981, 1983).

***** From Table 3. Range of estimates excluding the case where an inflow is calculated.

a biologically labile form of dissolved organic nitrogen and has been studied separately in many cases (Antia et al. 1991). The uncertainties in the size of the total DON pool are also large compared to the annual amount of nitrogen exchanged at the boundaries of the North Atlantic. The accuracy of the historical estimates is a combination of the 5–10% analytical uncertainty and the very small number of measurements. Even at 5%, the total DON pool is uncertain by 15–25 $\times$ 10^{12} moles (Table 1) and the true uncertainty is much higher.

Particulate organic nitrogen (PON) is an important standing stock of nitrogen, even though the total standing stock is only a fraction that of nitrate or DON. Concentrations range from 0.5–10 μmoles kg^{-1} in the surface waters and are generally less than 0.1 μmoles kg^{-1} in the deep water (e.g. Sharp 1983; Martin et al. 1993; Michaels et al. 1994b). In the upper water column, PON is comprised of phytoplankton, bacteria, zooplankton and detritus and it is these organisms that are responsible for the transformation of most other forms of nitrogen. In the water column, autotrophic and heterotrophic bacteria likely account for a significant fraction of the total PON (order 10–80%). Phytoplankton (some of which are prokaryotes) are a highly variable fraction, they can dominate during blooms and in oligotrophic environments are 10–30% of the PON. Detritus is usually calculated as the difference between the total standing stock and the living standing stocks and has been determined as anywhere from 10–90% of the PON.

Inorganic phosphorus in aerobic marine ecosystems is almost entirely orthophosphate. Dissolved phosphate is often called soluble reactive phosphate (SRP). Molybdate complexation techniques are most commonly used to measure phosphate concentrations in seawater, and these techniques measure both the dissolved phosphate and any phosphate that is released from organic compounds in the acidic conditions of the analysis (the term phosphate will be used to denote SRP throughout this paper). Phosphate is typically present in deep waters at concentrations of 1.0–1.5 μmoles kg^{-1}. At the surface, concentrations are low (order 0.1–0.2 μmoles kg^{-1}), although usually measurable with colorometric techniques. In the center of the Sargasso Sea, phosphate concentrations are almost always below 0.03 μmoles kg^{-1}.

We estimate a total standing stock of phosphate in the North Atlantic of 181 $\times$ 10^{12} moles PO_4^{3-} using the same approach as for nitrate. Similarly, the annual boundary exchanges of phosphate are small compared to the total standing stock (Table 2). The boundary exchange estimates are 18–30 $\times$ 10^9 moles P y^{-1} net input to the ocean from the shelves (Nixon et al., this volume), 6 $\times$ 10^9 moles P y^{-1} for atmospheric deposition of phosphate (Prospero et al., this volume) and 7 $\times$ 10^{10} moles P y^{-1} for riverine fluxes of phosphate to the coasts (Howarth et al., this volume).

The vertical and horizontal patterns of phosphate typically mirror those of nitrate with a tight covariance near the Redfield ratio of 16 moles NO_3^- : 1 mole PO_4^{3-}. The major exception to this pattern is an excess of nitrate or depletion of phosphate in the upper 1000 m of the western Sargasso Sea which results in NO_3^-:PO_4^{3-} ratios of between 20 and 50 moles NO_3^-:1 mole PO_4^{3-}. This local deviation from Redfield stoichiometry indicates that other processes are influencing the behavior of nitrate and/or phosphate in this area compared to the rest of the North Atlantic. Proposed processes include nitrogen fixation, nitrogen pollution or unique phosphate dynamics (Fanning 1989; Michaels et al. 1994a; Michaels et al. 1994b). We return to this topic later in the paper.

The fluxes of nitrate and phosphate in and out of the North Atlantic Ocean are also not at Redfield ratios. Riverine supplies of nutrients to the coasts occur at a ratio of 13 moles NO_3^-:1 mole PO_4^{3-} (Howarth et al., this volume). However in the estuaries and shelves, denitrification removes nitrate. Consequently, the shelves are a net sink for oceanic nitrate, while they provide a small source of phosphate to the open ocean (Nixon et al., this volume). Rates of atmospheric deposition are very low for phosphate compared to nitrate, with a basin average deposition ratio of 80–150 moles reactive N:1 mole PO_4^{3-} (Prospero et al., this volume).

Dissolved organic phosphorus (DOP) pools are typically on the order of 0.2 μmoles kg^{-1} (Ammerman et al. 1994), exceeding the inorganic phosphate concentration in many surface waters, but lower than phosphate concentrations below the surface. DOP is a severely under-sampled pool of P, even though its dynamics may influence the cycling of P in many oceanic ecosystems. Data from near Bermuda (Ammerman et al. 1994) suggest that dissolved DNA in the Sargasso Sea is only a small fraction of the DOP. Dissolved nucleic acids in general appear to be a small fraction of the DOP unless the concentration of dissolved RNA is very high (Karl & Bailiff 1989). Particulate organic phosphorus is usually present at relatively low concentrations, typically 10–20 nanomoles kg^{-1} in oligotrophic environments (Ammerman et al. 1994) and 1–2 orders of magnitude higher in productive zones. As with DOP, POP is under sampled and more poorly understood than particulate nitrogen. Ammerman's results suggest that much of the POP in Bermuda is bacterial DNA.

C. *Transformation and transport processes*

We divide the fluxes of N and P into vertical and horizontal fluxes and distinguish between physical and biogeochemical flux processes. We concentrated on estimating a subset of the relevant fluxes as they may be relevant to calculating the overall mass balance of N and P in the North Atlantic (Table 2). Horizontal and vertical fluxes of N and P from rivers and the atmosphere are subdivided geographically by reference to the appropriate companion papers (Nixon et al., this volume; Prospero et al., this volume).

The physical environment determines most of the patterns of N and P in the ocean. Large-scale transport creates the major oceanic provinces such as the subtropical gyre called the Sargasso Sea and provides the dominant mechanism for horizontal transport of nutrients. Mixing at many scales acts to smooth the strong vertical and horizontal gradients created by biogeochemical processes. The vertical gradients are greatest near the surface where biological activity causes a near-complete depletion of nutrients; here mixing becomes the major regulatory force that determines the resupply of nutrients to the surface and, thus, controls many of the subsequent biogeochemical transformation rates. At the surface, both gas exchange and atmospheric deposition can also change the concentrations of N and P species.

Biological and chemical processes transform nutrient elements from one species to another and transport them from one water mass to another. The biogenic transformation of nitrogen and phosphorus species is usually associated with the creation or destruction of the organic species (e.g. assimilation, remineralization) and with the energy yielding reactions that fuel microbial metabolism (e.g. nitrification and denitrification). Biological transport processes are restricted to the active movements of large organisms (such as vertical migration of zooplankton and nekton) and the passive settling of particles (primarily detritus, fecal wastes or recently moribund organisms). Transformations of nutrient elements within a parcel of water modify the gradients in the concentration of a particular form of the element, but cannot modify the total standing stock of N or P in that parcel. For example, the conversion of nitrate into organic nitrogen at the surface produces gradients in both nitrate (an increased concentration with depth) and PON (a decreased concentration with depth). However, the total standing stock of N at the surface (NO_3^-+PON) will remain unchanged in the absence of a transport process. Biological transport (e.g. the sinking of PON for the example above) can change both the total standing stock of a nutrient element (decrease the surface NO_3^-+PON) and the gradient of one particular form of the element (e.g. remove the surface PON maximum).

Vertical transport processes

The primary vertical pattern in the ocean is the surface depletion of inorganic nutrients by biological utilization in illuminated surface waters and the subsequent transport of the organic matter to depth. Vertical mixing within the ocean acts to homogenize these gradients and results in a net flux of nutrient to the surface. Where there are surface accumulations of organic matter (e.g.

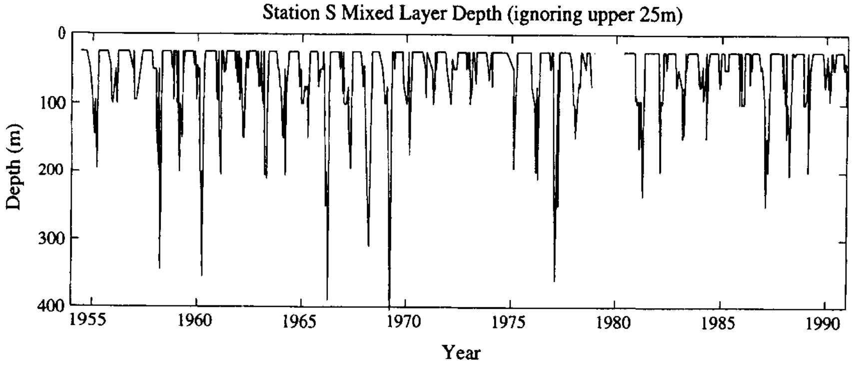

Figure 1. Time-series of mixed-layer depth at Hydrostation S (32.2° N 64.5° W) from 1954 to 1992. Modified from (Michaels et al. 1994b)

a plankton bloom or surface maximum in dissolved organic matter), this same mixing will act to transport the organic material to depth (Toggweiler 1989; Carlson et al. 1994). The balance between the processes that remove nitrate and phosphate from surface waters and the mixing that returns nutrients to the surface regulates both the surface concentrations and, for many ecosystems, the overall productivity. Thus, the near-surface nitrate or phosphate concentration provides an indication of the areas where uptake processes are inefficient or where vertical transport of nutrients by mixing or upwelling exceeds the biological uptake rate, at least over a part of the year. For example, upwelling off West Africa and the deep winter convection of the North Atlantic Ocean both cause elevated nutrient concentrations at the surface for part of the year.

Estimates of the actual vertical velocities or the net vertical mixing rates in a few regions have been determined by measurements of the microscale physical structure (Lewis et al. 1986; Gregg 1989), tracer release experiments (Ledwell et al. 1993), or models of the physical processes in an area (e.g. Sarmiento 1986). North of approximately 30° N latitude, there are strong seasonal patterns in the near-surface mixing. Cooling of the surface waters in the fall and winter causes a convectively driven mixing of the upper ocean. The magnitude of winter mixing increases with increasing latitude (Siegel et al. 1990) and there is significant interannual variability in this wintertime overturn (Figure 1).

The spatial patterns in vertical transport from wind-driven or eddy-driven upwelling, downwelling and wind or convection driven mixing, can be deduced from coupled circulation/biogeochemistry models (e.g. see Sarmiento et al. 1993) and from remote sensing. Direct estimates of wind-driven upwelling and downwelling velocities from satellite data show the upwelling centers off Western Africa and the downwelling of the central gyres (McClain & Firestone 1993). The circulation models give detailed maps of nitrate fluxes to the surface which, when coupled to a biological model, allow inferences of the biological uptake rates of nitrate (e.g Figure 2c). These types of models also illustrate the ventilation of mode water, the path of the Gulf Stream, the upwellings in the equator and off of the west coast of Africa, and the nitrate supply to the surface in the North Atlantic that causes the spring bloom at higher latitudes. These models have limitations in terms of the actual magnitude of the fluxes, due to uncertainties that are usually related to assumptions in the physical models. For instance, in Sarmiento et al. (1993), nitrate supply in the middle of the gyre is much lower than many of the direct measurements for these types of habitats.However, the models provide a good relative standard for comparison with the spatial patterns of other processes.

Nitrogen is added to or removed from the surface of the ocean by two processes, atmospheric deposition (both wet and dry) and gas exchange (for ammonia and N_2). Phosphorus lacks a significant gas phase and thus the air-sea exchange of P is only through deposition. Prospero et al. (this volume) have compiled and validated a set of measurements and model results on the spatial patterns and magnitude of atmospheric N and P deposition into the North Atlantic. They conclude that the total N deposition to the basin is approximately 1×10^{12} moles N yr^{-1}. About half of this deposition is due to a flux of dissolved organic nitrogen that is very uncertain (Prospero et al., this volume). The other half of the N deposition is approximately evenly divided between NO_y and NH_x species. We partition the total deposition of N into the three latitude bands (Table 2) using the deposition patterns for the sum of NO_y and NH_x. Approximately 25% of the atmospheric deposition of NO_y + NH_x occurs between 0 and 10° N and 33% occurs north of 40° N (Table 2). Atmospheric deposition of phosphate is approximately 6×10^9 moles N yr^{-1} and largely occurs south of 40° N (Prospero et al., this volume). This atmospheric transport of phosphate is largely associated with dust.

The atmospheric reactive nitrogen is produced by natural and human activities on the continents and much of this nitrogen is redeposited onto the surface after being transported relatively short distances. There is strong seasonality to most atmospheric deposition (Prospero et al., this volume). The patterns of deposition show strong maxima near the continental sources of North America, Europe and, to a lesser extent, Africa (Figure 2). Ammonia and nitrate wet deposition have very similar magnitudes and spatial patterns (Figures 2a and 2b). Much of the production of atmospheric reactive nitrogen is from human activity. The rates of deposition are certainly higher than before

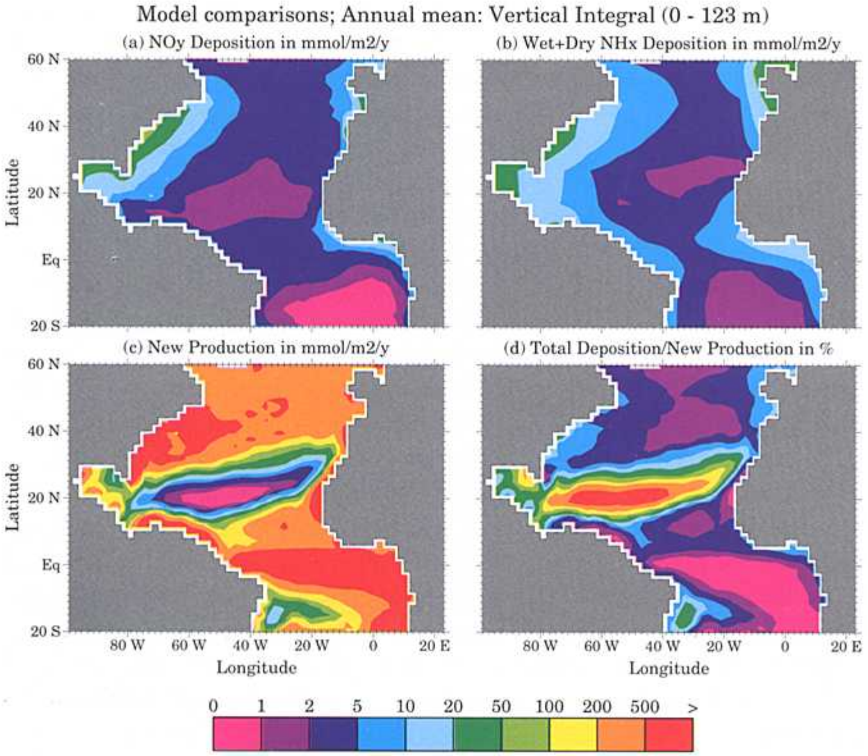

Figure 2. Comparisons of atmospheric deposition (courtesy of Chip Levy, see Prospero et al., this volume) of (a) NO_y and (b) NH_x and (c) new production from the Sarmiento et al. (1993) model. In (d) these are expressed as the sum of NO_y and NH_x as a percent of new production.

the industrial revolution and will likely continue to increase (Galloway et al. 1995; Prospero et al., this volume).

To assess the potential impacts of the current supply of reactive nitrogen by atmospheric deposition on marine ecosystem productivity, the deposition rates can be compared to the nitrate supplied to the surface by mixing as estimated with the Sarmiento et al. (1993) model. Since nitrate is usually completely depleted at the surface, the annual amount of nitrate used by phytoplankton will be approximately equal to the nitrate supplied by mixing (Figure 2c, keeping the caveats about the absolute magnitude of those fluxes in mind). Atmospheric deposition is a large source of N compared to the nitrate supply very near the coasts, where the deposition is high, and in the very center of the Sargasso Sea where the model predicts an extremely low nitrate utilization (Figure 2d). In intermediate locations, such as Bermuda, the combination of a modest nitrate supply and diminished atmospheric deposition make the atmospheric source unimportant (Knap et al. 1986; Michaels et al. 1993). Atmospheric deposition can be an important source of N in coastal waters (Paerl 1985). Few direct measurements of deposition or nitrate supply exist for the middle of the gyre (Knap et al. 1986; Owens et al. 1992; Michaels et al. 1993). Also, nitrate utilization in the the Sargasso Sea is certainly higher than these model estimates, perhaps as high as 0.2–0.7 moles N m^{-2} y^{-1} (Jenkins 1982; Jenkins & Goldman 1985; Sarmiento et al. 1990). Consequently, even though the deposition is very low this far from the sources, the low new production expected for these regions may make atmospheric deposition an important nitrogen source (Owens et al. 1992).

The atmospheric deposition of nitrogen in the open ocean is both seasonal and very episodic. During short periods of high deposition, it may be the dominant source of reactive N to the near-surface phytoplankton (Glover et al. 1988; Owens et al. 1992; Michaels et al. 1993). In the highly stratified waters that characterize the central gyre, most nitrate uptake occurs in the lower part of the euphotic zone (Goldman 1988). Thus, for the surface populations of phytoplankton, these atmospheric sources may be an important local nutrient source and in these stratified ecosystems, future changes in the anthropogenic production of atmospheric reactive nitrogen may have their largest effects. Furthermore, the stimulation of surface plankton blooms could cause a pigment signature that would be visible from ocean color satellites (Michaels et al. 1993).

The biological transport processes include the passive sinking of large particles (McCave 1975), the downward mixing of suspended particles and dissolved organic matter (Toggweiler 1989) and the vertical migration of zooplankton (Longhurst & Harrison 1988). The passive sinking of large particles has long been considered the major mechanism for the downward transport of organic material in the ocean (McCave 1975). Particle fluxes are highest near the surface and decline rapidly with depth (Martin et al. 1987; Bishop 1989) because of the remineralization or degradation of most sinking particles in the upper thermocline. Particulate fluxes near the sea floor are usually only a few percent of the fluxes leaving the euphotic zone. Recent measurements near Bermuda call into question our overall understanding of vertical flux processes. A comparison of all vertical fluxes with the changes in the standing stocks of carbon over a number of years indicates threefold discrepancies that can only be resolved if some of the vertical fluxes have been measured incorrectly, or if many of the observed patterns are due to horizontal advection (Michaels et al. 1994a). Further, seasonal measurements of dissolved organic carbon indicate that the downward mixing of dissolved organic matter may be an important transport process, at least for carbon (Carlson et al. 1994). Dissolved organic nitrogen and phosphorus dynamics are rarely measured, but have the potential to be important components of the large-scale N and P cycles (Najjar et al. 1992).

Burial of nitrogen and phosphorus in sediments is the ultimate link to elemental cycling on geological time-scales. However, even on the time-scales of anthropogenic production of reduced nitrogen, burial can be an important process. Jahnke & Jackson (1992) compare estimates of sediment accumulation rates of carbon with benthic respiration measurements. Using this dataset, and a C:N ratio of 10 for sediment organic matter (Nixon et al., this volume) we calculate a net burial of 1.1–1.7 × 10^{10} moles N y^{-1} on the deep sea floor. Berner (1982) estimated that approximately 2.3 times as much organic carbon is buried in sediments under upwelling regions than in the deep sea for the world's oceans. This is exclusive of shallow carbonate, shelf and delta sediments (treated by Nixon et al., this volume). Assuming that a ratio of 2.3 applies to the North Atlantic, we estimate that 2.5–3.9 × 10^{10} moles N y^{-1} are buried in slope sediments using the pelagic burial rates above. Similarly, we estimate a total phosphate burial of 2–3 × 10^9 moles P y^{-1} from the same data (Jahnke & Jackson 1992) using a C:P ratio of 200 (Table 2). These estimates are sensitive to both the accuracy of the carbon burial term and the C:N and C:P conversion factors. However, the fluxes are very small compared to other processes.

Nutrient transformation and cycling processes

The biological cycling of nitrogen in the upper ocean is usually interpreted in the context of the New Production Hypothesis (Dugdale & Goering 1967; Eppley & Peterson 1979). This hypothesis describes the nitrogen flows into and out of the euphotic zone. The euphotic zone is defined as the surface layer of the ocean which has adequate light for the growth of phytoplankton. It is usually delimited by the depth where the *in situ* irradiance is 1% of surface irradiance (typically depths of 30–120 m in different parts of the North Atlantic). New production is defined as phytoplankton growth on nutrients exogenous to the euphotic zone, primarily nitrate mixed into this layer from below. There are additional contributions from *in situ* nitrogen fixation and atmospheric deposition of various nitrogen species. Regenerated production is based on internal recycling within the euphotic zone and the total production is the sum of new and regenerated. The convenient division of nutrient species by their source (nitrate is largely an exogenous nutrient and ammonia is largely derived from regeneration) allows a partitioning of the total production based on the relative uptake of nitrate and ammonia (Dugdale & Goering 1967). When nitrogen fixation or atmospheric deposition are significant, the production of amines or deposition of ammonia will confound this simple distinction.

Nitrogen fixation and denitrification both occur in the water column of the North Atlantic. Nitrogen fixation is the process through which N_2 is converted to reactive nitrogen for use in the creation of organic nitrogen. This process is mediated by specialized bacteria and cyanobacteria, both free-living and symbiotic. The rates of N_2 fixation have traditionally been thought to be very low (although see below) and it has usually been ignored as a source of reactive N to the oceans (Carpenter 1983; Galloway et al. 1995). Denitrification is the bacterially-mediated conversion of nitrate to N_2 gas. It is largely confined to anoxic waters or microzones and is probably the major loss mechanism for reactive nitrogen; global estimates of marine denitrification are of the order $11–13 \times 10^{12}$ moles N y^{-1}, approximately evenly divided between the water column (primarily in the equatorial Pacific and the Indian Ocean) and the sediments (Galloway et al. 1995). Water column denitrification is largely restricted to areas with strong sub-surface oxygen minimum zones and anoxic basins. In the Atlantic, these conditions only occur in marginal seas (e.g. the Cariaco Trench), suggesting that water column denitrification is low in the rest of this basin. Sediment denitrification is predominantly found on continental shelves and the basin-wide rates have been estimated by Seitzinger and Giblin (Seitzinger & Giblin, in press) and summarized by Nixon et al. (this volume).

Phosphate uptake can also be conceptually separated into autochthonous and allochthonous sources, however, the lack of a unique P species associated with new versus regenerated production makes distinguishing the source of the production technically more difficult. There is also no analog of nitrogen fixation for phosphate; therefore, the ocean inventory of phosphate is tied to the combination of sedimentation and the hydrologic cycle. Atmospheric deposition rates for phosphate are small (Prospero et al., this volume). The dominant allochthonous source of phosphate to the phytoplankton communities in oceanic regimes will be the subsurface nutrient stocks.

Typically, organic biomass in the ocean has an N:P ratio of approximately 16:1 (the Redfield ratio; Redfield et al. 1963) and the concentrations of the two nutrients covary closely. Deep-ocean remineralization rates inferred by nutrient changes along neutral density surfaces are also at this ratio (Anderson & Sarmiento 1994). However, deviations do occur (Fanning 1989, 1992) and, when present, they are probably due to anomalies in the cycling of nitrogen, not phosphate. Denitrification removes nitrate and reduces the apparent ratio. Nitrogen fixation will add reactive nitrogen and should skew the ratio in a positive direction. The differential remineralization of DON compared to DOP will also affect the nutrient ratios. We take advantage of the non-Redfield nutrient stoichiometry later in this paper to infer a nitrogen fixation rate in the Sargasso Sea.

Horizontal nitrogen/phosphorus transport

The goal of this section is to consider broad scale nutrient transport, the problems in estimating it and the consequences of transport estimates for the nutrient balance in the North Atlantic basin. We address the flux of nutrients across the boundaries of the North Atlantic (i.e. the cross equatorial, Mediterranean and Arctic inflows) and the exchanges with the continental shelves. The flux divergence between different latitude bands based on recent calculations such as those found in Rintoul & Wunsch (1991) or Martel & Wunsch (1993) is considered in relationship to nutrient dynamics within the ocean. We assess the methods by which estimates of fluxes are calculated. These vary from very crude estimates of fluxes based on cross-sections of properties and educated guesses of transport such as the rates available from the Arctic, to nutrient balance arguments for basins such as the Mediterranean or Gulf of Mexico and Caribbean Sea, to sophisticated estimates of fluxes across trans-ocean sections using inverse techniques. The latter two methods are more rigorous, but both make heavy demands on data and assumptions. This is not meant to degrade the importance of the more ad hoc estimates such as those available for the Arctic. These often end up being approximately correct even though they involve intuition and a host of assumptions. For our estimates of nutrient exchange between the open ocean and the continental shelves, it proved easier to define the net balance on the shelves and then assume that any nutrient deficit was supplied from the ocean and any residual nutrient tranported offshore.

The large-scale currents in the North Atlantic Ocean cause horizontal transports of the dominant species of N and P. Surface currents are extremely pronounced, particularly the northerly flow of the Gulf Stream in the Western Atlantic. Thermohaline circulation at both intermediate and deeper depths also plays an important role in the meridional transport of nutrients with a net southerly flow in North Atlantic Deep Water and net northerly transport in Antarctic Bottom Water and Intermediate Water. Unfortunately, for making estimates of the appropriate meridional fluxes, we are constrained by the nature of the historical measurements. Zonal sections of nitrate and phosphate exist at a number of latitudes, but measurements of dissolved organic nitrogen and phosphorus are nearly non-existent. Nitrate and phosphate standing stocks are nearly an order of magnitude larger than the dissolved organic pools (Table 1) and the vertical patterns of the inorganic and organic species differ. Thus, the N and P flux by transport of DON and DOP is likely both smaller in magnitude and different in latitudinal pattern than the nitrate or phosphate fluxes. In the absense of any zonal sections of DON and DOP, this flux remains unknown. The unfortunate conclusion for a North Atlantic basin budget of N and P is that the uncertainties in the transport estimates are still very large and, in most cases, the ocean meridional transport uncertainties are larger than the total of riverine and atmospheric inputs to the North Atlantic basin.

Shelf boundary exchanges

The net loss of nitrate from the oceans required to satisfy the balance of nitrogen sources and sinks on the shelves is estimated as 0.7–0.95 × 10^{12} moles NO_3^- y^{-1} (Nixon et al., this volume; Table 2). This estimate arises from a detailed consideration of the riverine fluxes, atmospheric deposition, shelf denitrification, burial on shelves, deltas and estuaries and the losses through fish harvests in the coastal zone and continental shelves out to the 200 m isobath (Nixon et al., this volume). Shelf denitrification removes approximately 1.4 × 10^{12} moles NO_3^- y^{-1} from the overlying and *in situ* waters (Nixon et al., this volume). Denitrification and burial exceed the supply of nitrogen from the atmosphere and rivers; thus the remainder of the nitrate must come from water-column reactive nitrogen, ultimately nitrate. The shelf-ocean exchange is rapid and we assume that all of the net nitrate requirements of the shelves are met by a supply from the ocean.

We can partition the on-shelf nitrate flux geographically using the data in Nixon et al. (this volume, their Table 14). Losses of nitrate to the shelves are predominantly in the higher latitudes and in mid-latitude North America (Table 2). The Amazon provides a net source of nitrate to the open sea. The same dataset indicates a net flux of phosphate to the open ocean of 18–30 × 10^9 moles PO_4^{3-} y^{-1}, again dominated by the Amazon flux (Nixon et al., this volume). This combination of net sediment denitrification and phosphate transport should result in low water column $NO_3^-:PO_4^{3-}$ ratios. For the water column N:P to remain near Redfield or higher, there must be a complimentary rate of nitrogen fixation in the water column or the oxidation of dissolved organic matter at very high N:P ratios (see below).

Ocean transport calculations – approaches

There are basically two approaches that can be used to estimate element or nutrient budgets in an ocean basin; (1) estimates of the flux divergence for a basin and (2) direct computations of a flux using velocity and concentration estimates for the element of interest. In the first approach, one estimates the flux divergence over the bounding surface area of a basin and then uses this in combination with available vertical fluxes and an assumption of steady state to estimate the lateral fluxes. This approach has been used to estimate heat fluxes in the Atlantic and world oceans (Vonder Haar & Ort 1973; Trenburth & Soloman 1994). A good example of this approach applied to a biogeochemical budget is the analysis of nutrient and dissolved oxygen budgets in the Mediterranean by Sarmiento et al. (1988). The second approach is to directly compute the fluxes by determining the horizontal velocity and the concentration of the desired element or property. This direct approach is thought to provide the best estimates of meridional heat flux (Hall & Bryden 1982; Rintoul & Wunsch 1991). Direct calculations have typically given lower heat fluxes than the basin-scale flux divergence estimates (although the most recent measurements of the latter are converging with the direct calculations; Trenburth & Soloman 1994). A direct approach using inverse models has been used to estimate nutrient fluxes in the Atlantic (Rintoul & Wunsch 1991; Martel & Wunsch 1993). Below, we summarize these results and also compute nutrient fluxes associated with the overturning cell, i.e. the zonally averaged circulation, for various inverse calculations of transports found in the literature. Since the actual completion of a full inverse with nitrate and phosphate included is beyond the scope of this paper, the contribution of the horizontal circulation to these meridional fluxes cannot be assessed fully. The degree to which these estimates are inadequate, however, can be addressed by comparing these calculations with the full inverses in Rintoul & Wunsch (1991).

Before going into the details of actually estimating the transport fluxes of nitrate and phosphate in the North Atlantic, we consider a conceptual steady-state framework for interpreting these fluxes. Sarmiento et al. (1988) divide basins into what they term "desert" basins and "nutrient trap" basins, building upon an earlier conceptual system described by Berger (1970). Desert basins have a combination of inputs and losses that result in low nutrient concentrations while nutrient trap basin dynamics result in high nutrient concentrations. The North Atlantic as a whole is a desert basin with low nutrients as compared to the nutrient trap basins in the Indian and Pacific. On a regional scale the Mediterranean is a desert basin (Sarmiento et al. 1988) while the Caribbean is a nutrient trap basin. The Arctic Sea is more complicated and seems to be a nutrient trap basin even though it exports deep water into the North Atlantic proper. The reason for this is a combination of inputs of nutrient rich waters from the Atlantic thermocline and the contribution made from the Pacific through the Bering Straits. Although there is no strict reason that these basin types would be constrained to import or export nitrate, it appears that desert basins export nutrients with their deep waters and "nutrient trap" basins accumulate nutrients brought in by deep flows. The basic difference in the two types of basins is that the desert basins are very efficient in removing nutrients through the formation of deep waters. Nutrient trap basins may also be more likely to lose nutrients to the sediments as the high nutrient concentrations would promote productivity and export to the sediments and the low oxygen concentrations would enhance burial.

The distribution of nitrate in the North Atlantic can be interpreted as a modification of nutrient contents in water masses as they proceed through the basin with the far North Atlantic being the most nutrient impoverished. It is not, however, possible to interpret this change directly in terms of fluxes or more correctly flux divergences of nutrients. While the property profiles suggest an overall pumping of nutrients out of the Atlantic, it is not possible to sort out the importance of recirculation and mixing from net advective fluxes. For example, much of the high nitrate water in the lower latitudes of the North Atlantic may simply be caught up in a northerly flow of Antarctic Intermediate Water, much or all of which circulates back to the south without contributing to any net flux. The only means of estimating the net intra-basin flux is to complete a calculation that explicitly conserves mass across some bounding surface. In other words, the observed property distributions say nothing about rates although they may be used to infer the sign of the fluxes under a steady state assumption. In order to demonstrate these methods and explore their capabilities the Mediterranean situation is considered in some detail.

Nutrient fluxes between the Mediterranean and Atlantic

The nutrient balance for the entire Mediterranean can be calculated using both the flux divergence method (see Sarmiento et al. 1988 for details) and the direct calculation method using a combination of outflow estimates (Baringer 1993; Price et al. 1993) and historical nutrient versus density relationships. Sarmiento et al. (1988) assume the sign of the fluxes based on the nature of the nutrient relations in the basin and they calculate a balance using the inputs from riverine and atmospheric deposition, sediment deposition and a two layer (surface and deep water) depiction of the fluxes across the sills into the basins. Their analysis assumes steady state and makes use of a closed salinity budget. The Sarmiento et al. (1988) water transport estimate for the Gibraltar outflow is 0.69×10^6 m^3 s^{-1} to the west (out of the Mediterranean). This is lower but comparable to the recent estimate of 0.79×10^6 m^3 s^{-1} by Bryden et al. (1989). Sarmiento et al. (1988) estimate the PO_4^{3-} balance to give an outward flux of phosphate of 2.96×10^9 moles y^{-1}. Using the canonical Redfield ratio of 16 moles NO_3^-:1 mole PO_4^{3-}, we can estimate a westward NO_3^- flux of 4.74×10^{10} moles y^{-1}. The Sarmiento et al. (1988) analysis is based on property end points for the inflowing and outgoing waters at Gibraltar (indicated by the S symbol in Figure 3). As shown these fit on the

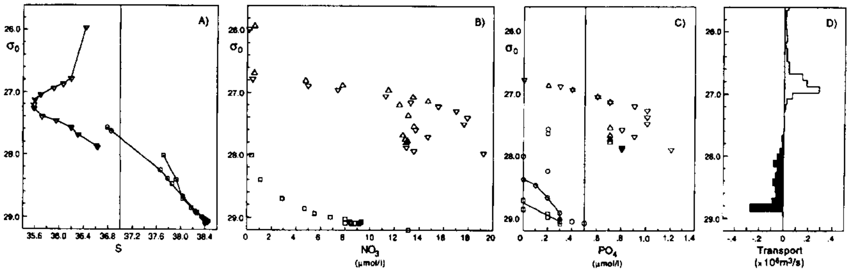

Figure 3. Properties for the flow through Gibralter as a function of potential density. Curves are based on historical station data from the Reid and Mantyla (per. comm.) data set (a.-c.) and Baringer's (1993) transport estimates. a) Salinity from either side of strait. Triangles indicate the Atlantic side while squares and circles are from the deep layers in the Mediterranean. Straight line indicates the salinity at the interface in the strait. b) Nitrate from outside (triangles) and inside the Mediterranean (squares and circles). c) Same but for phosphate. d) Transport estimates from the Atlantic side of the Straits.

mixing curves for the regions on either side of the sill and are in this sense reasonable.

The Mediterranean outflow nutrient fluxes can also be calculated using the property end points (Figure 3) and direct estimates of water transport at the sill (Bryden et al. 1989) or calculated transport rates just to the west of the Gibraltar sill (Baringer 1993; Price et al. 1993). As a first comparison, the westward salinity flux of 1.61×10^3 m^3 s^{-1} estimated by Bryden et al. (1989) is in good agreement with the salinity flux of 1.74×10^3 m^3 s^{-1} calculated using Sarmiento et al. (1988) end points and the Bryden et al. (1989) transport. Since Sarmiento et al. (1988) use a lower transport rate, they must be using larger differences in salinities. This makes sense given the high mixing rates over the sill region where the Bryden et al. calculation was made; i.e. mixing in the straits will reduce the contrast between the surface and deep layers.

Keeping the distinctions in end point values in mind, we can calculate westward fluxes of 21.8×10^{10} moles NO_3^- y^{-1} and 5.1×10^9 moles PO_4^{3-} y^{-1} using the Sarmiento et al. (1988) end points and the Bryden et al. (1989) transport. This estimate of the nitrate flux is greater than the estimate based on the Sarmiento et al. (1988) phosphate flux and the Redfield ratio. The nitrate:phosphate ratio of these fluxes is 42.5 and high nitrate:phosphate ratios are typical of certain parts of the Mediterranean (Krom et al. 1991). Clearly these calculations are sensitive to assumptions about the mixing curves in Figure 3 and nitrate:phosphate ratios. This sensitivity is obvious when the nutrient fluxes are calculated using historical profiles of nutrients from either side of the sill with the transport estimates made just to the west of the sill (Baringer 1993; Price et al. 1993; Figure 3d). With this combination, the calculated nutrient fluxes are in the opposite direction, eastward into the

Table 3. Estimates of the transport of nitrate and phosphate into or out of the Mediterranean through the Straits of Gibralter. Negative fluxes indicate a transport westward, out of the Mediterranean. All estimates are in units of 10^{10} moles y^{-1}.

Calculation approach	NO_3^-	PO_4^{3-}
Sarmiento et al. (1988)	−4.74	−0.30
Direct Baringer (1993) transports with historical end members.	9.59	0.19
Sarmiento end points with Bryden et al. (1989) transports	−21.78	−0.51
Sarmiento end points with Bryden et al. (1989) transports and accounting for changes in nutrient ratios	−10.4	−0.51

Mediterranean (Table 3), even though the salinity fluxes are in agreement with the other estimates. We can obtain yet another estimate of the flux of both NO_3^- and PO_4^{3-} using the Sarmiento et al. (1988) PO_4^{3-} end point, the Bryden et al. (1989) transport and by taking into account the differences in Redfield ratio between the incoming and outflowing waters. This calculation gives westward fluxes of 5.1×10^9 moles PO_4^{3-} y^{-1} (as above) and 10.4×10^{10} moles NO_3^- y^{-1}.

The diverse outcomes of these different methods for calculating nutrient fluxes for the Mediterranean illustrate several issues of general importance to the problem of estimating the nutrient fluxes caused by the ocean circulation. The results are sensitive to the shape of the property curves (e.g. Figure 3). The agreement between the salinity fluxes calculated by the different methods is due to the nearly linear salinity relationship in Figure 3. Thus the results from the direct estimates of Bryden et al. (1989) fall on basically the same portion of the mixing line as that assumed by Sarmiento et al. (1988). However, the nutrient curves (Figure 3b,c) are better approximated by a nonlinear S-shaped curve. The pronounced nutrient maximum associated with the Atlantic thermocline falls near the salinity of the interface between the upper and lower layers in the strait (discussed by Bryden et al. 1989, Figure 3a, vertical line) and therefore the zero in the transport versus density curve (Figure 3d). While the observations suggest that Sarmiento et al. (1988) are correct about the sign of the flux, the error bars on this estimate are likely to be large. It is hard to quantify the overall uncertainty in these calculations, given all of the assumptions, but with the uncertainties in the choice of end points and transports the variation is at least a factor of two. All of the methods could be improved with better observational data, primarily the concurrent measurement of transport and nutrients.

Finally these calculations all assume steady state conditions. Sarmiento et al. (1988) concluded that steady-state assumptions were reasonable in the Mediterranean, but they also pointed out that there have been major perturbations in the regional nutrient fluxes because of increased atmospheric and riverine fluxes of nutrients and the influence of dams on the Nile. These recent influences are expected to change the salt and nutrient property distributions in the Mediterranean and thus they could effect the exchange with the Atlantic since the fluxes across the sill are very sensitive to the property contrasts (Bryden & Kinder 1991). Secular trends in nutrient concentrations in the Mediterranean are not clear, but there have been changes in deep water salinity over the past few decades (Leaman 1994). Changes in nutrient concentrations and fluxes in the relatively small volume of the Mediterranean are proportionately greater than possible changes in the deep ocean and, for this reason, are easier to measure.

Nutrient fluxes in the Arctic, Caribbean and Gulf of Mexico

Estimation of net nutrient fluxes in the two other marginal sea complexes is even more difficult than in the Mediterranean. The Arctic, like the Mediterranean, is a basin that is dominated by deep-water formation. This occurs in the southern limb of the Arctic in the Greenland Sea. Deep-water formation would suggest that the Arctic is a desert basin (sensu Sarmiento et al. 1988) and possibly exports nutrients into the Atlantic Ocean. Indeed, based on the volume transports and nutrient concentrations in Anderson and Dyrssen (Anderson & Dyrssen 1981; Anderson et al. 1983) one obtains a southward flux of 30.0×10^{10} moles NO_3^- y^{-1} and 16.0×10^{10} moles PO_4^{3-} y^{-1}. These estimates have the same types of uncertainties as documented for the Mediterranean and the additional complexities associated with the various paths for water to enter and exit the basin.

Estimates of the nutrient fluxes through Caribbean Sea and Gulf of Mexico pose significant problems because of a very large volume flux and very small changes in nutrient concentrations (Figure 4). The flows in the Caribbean and Gulf of Mexico are dominated by the large volume transport of the southern limb of the North Atlantic subtropical gyre. There are also significant inputs of southern hemisphere waters (approximately 15×10^6 m^3 s^{-1}; Schmitz & Richardson 1991) and the input of two major rivers, the Orinoco and the Mississippi. These basins should be nutrient traps, consistent with the nutrient loading of the deep waters beneath the sill depth of the Caribbean passages. The calculations of Walsh et al. (1989) for the Gulf of Mexico suggest there is a net flux of NO_3^- into the Atlantic through the Florida Straits of 2.14 ×

10^{10} moles y^{-1}. They suggest that an equal amount of nitrogen is exported as particulate organic nitrogen (PON) under current conditions. This estimate includes an increase of 0.71 × 10^{10} moles y^{-1} from anthropogenic influences, primarily changes in the Mississippi nitrogen flux. The PO_4^{3-} flux calculated by using the Walsh et al. (1989) computation and Redfield stoichiometry is an export of 1.34 × 10^9 moles PO_4^{3-} y^{-1} to the Atlantic Ocean. These estimates are based on a very coarse vertical resolution of the flow through the bounding straits (Yucatan and Florida, respectively). The nutrient cross sections seem to have considerable structure both in the horizontal and vertical and there are some questions about whether the data are accurate in time (Walsh et al. 1989).

The Walsh et al. (1989) physical transport estimates for the net nutrient balance in the Caribbean and Gulf of Mexico are quite different than the nutrient budgets implied by the estimates of riverine flows and shelf denitrification and burial (Nixon et al., this volume). Nixon et al. (this volume) estimate that denitrification exceeds the sum of atmospheric deposition and riverine flux for both basins. This net denitrification may be required if these basins are to stay nutrient traps as the large horizontal flows through a small basin could result in dramatically elevated deep nutrient concentrations in the absense of denitrification.

We attempted to estimate the flux of NO_3^- and PO_4^{3-} through the Caribean and Gulf of Mexico using the inverse calculation of water transport made by Roemmich (1981). This inverse calculation is well constrained and has reasonable resolution (five layers in the region of interest; Roemmich 1981). However, when combined with existing nutrient data, it is inadequate for computing the desired nutrient fluxes because of the large gradients in nutrient concentrations along the isopycnal surfaces used in the calculation of the water transport. Any brute force calculation that averages the data within layers, independent of position across the Caribbean or the Straits of Florida, would lead to a net inflow of both nitrate and phosphate into the basins. This arises because NO_3^- and PO_4^{3-} concentrations are actually higher on isopycnals in the central and southern Caribbean than they are in the Straits (Figure 4). The data are also sparse regionally. The northern Caribbean is under-represented and the Windward Passage had no nutrient data of sufficient quality.

One conclusion that can be drawn from the Roemich (1981) flows, as well as from those of other authors (Leaman et al. 1989) is that there is a net deposition of NO_3^- in the basin. The transports of waters with high NO_3^- and PO_4^{3-} into the Caribbean and the lower concentrations on the same isopycnal surface across the Florida Straits requires a net convergence throughout most of the thermocline in the Caribbean and Gulf of Mexico (Figure 4). This conclusion is at odds with that of Walsh et al. (1989) for the Gulf of Mexico.

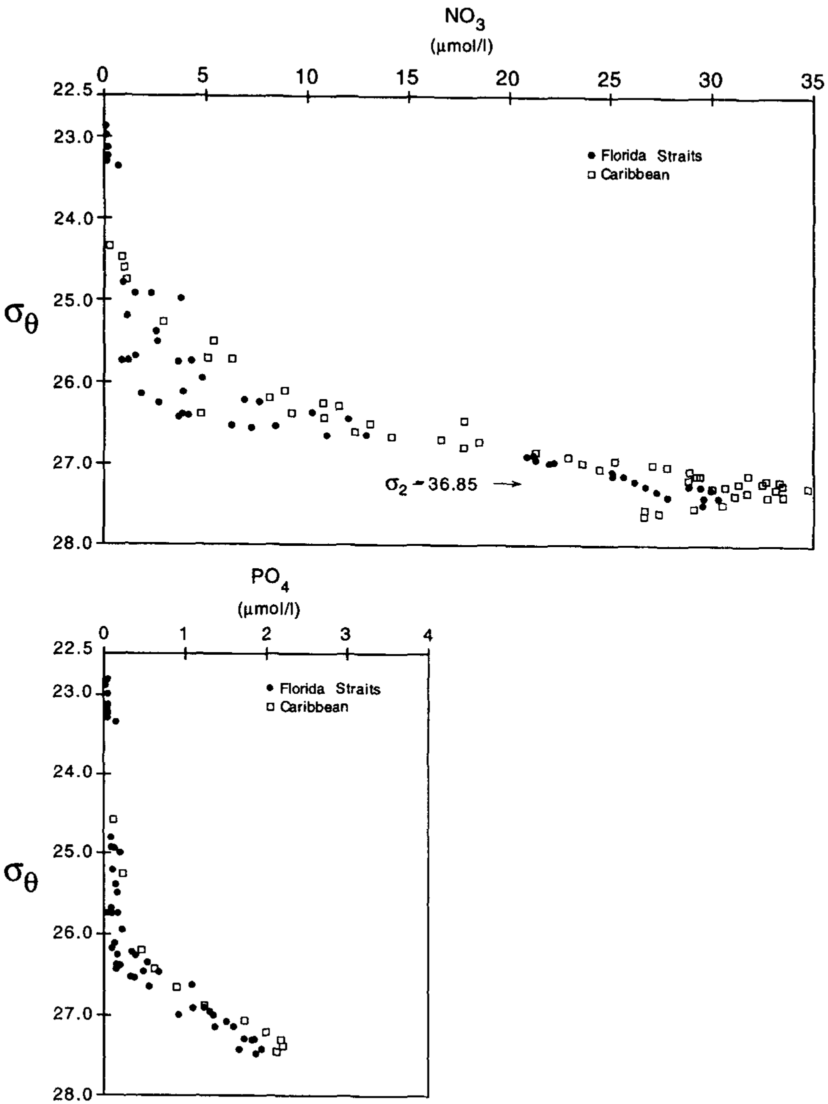

Figure 4. Nitrate and phosphate as a function of potential density in the Caribbean and Florida Straits. Notice that Florida Straits nutrients are lower on isopycnal surfaces suggesting a decline in nutrient levels in the upper pycnocline as the fluid traverses the basins.

The flow in the basins and the nutrient distributions (Figure 4) suggest that their treatment of the large scale oceanic transport is too coarse to define the oceanic flux. The current conclusion agrees with that of Nixon et al. (this issue) that overall, the Caribbean Sea and Gulf of Mexico complex should be a net sink for nitrate.

Meridional transport in the Atlantic Ocean

The north-south flux of nutrients within the North Atlantic can be estimated from either of the approaches outlined above. The Atlantic as a whole acts like a desert basin (sensu Sarmiento et al. 1988); it is depleted in nutrients at depth as compared to the other oceans. This depletion is marked by a strong north to south increase in NO_3^- and PO_4^{3-} at most depths in the Atlantic. If one assumes steady state conditions, there must be a balance between inputs into each latitudinal band and exports. Thus, the residual northward or southward flux in each latitudinal band must equal the balance between sources of reactive nitrogen (nitrogen fixation, riverine fluxes and atmospheric deposition) compared to the losses in that band (sedimentation and denitrification). Completing this balance using the flux convergence approach described for the Mediterranean is difficult because of the uncertainties in and relatively small size of many of the boundary exchanges (e.g. Nixon et al., this volume; Prospero et al., this volume). Thus most of the attempts to calculate meridional transport have come through direct calculations of volume fluxes and nutrient fluxes using oceanographic data.

We summarize three studies that apply inverse methods to oceanographic hydrographic station data in order to estimate nitrate and phosphate fluxes from meridional transects (Schlitzer 1988; Rintoul & Wunsch 1991; Martel & Wunsch 1993). We also discuss the earlier inverse estimates of meridional transports by Roemmich (1983) in an attempt to interpret the fluxes through the tropics into the North Atlantic. Of the four studies Schlitzer's (1988) calculations are based on highly smoothed historical data, those of Roemmich (1983) and Rintoul & Wunsch (1991) are based on cross-basin sections taken on single cruises and those of Martel & Wunsch (1993) are based on a set of data collected in the central Atlantic during the early 1980's. Martel & Wunsch (1993) make use of a rather coarse gridding of their data base and therefore their study is somewhat similar in resolution in space to that of Schlitzer (1988). All of these studies make use of mass, heat, salt and nutrients to estimate nutrient transport. While there are differences in the approaches used in these studies they are not faced with the uncertainties from the almost arbitrary choices of property values or transports for particular density strata as affected the previous calculations. Finally, these methods are capable of producing error estimates as an integral part of the calculation based on the statistics of the data used.

The results of the inverse estimates with the exception of Schlitzer's (Schlitzer 1988, 1989) are shown in Table 4. Schlitzer (1988, 1989) suggests that there is no flux of NO_3^- across lines of latitude in the Atlantic. The estimates by Martel & Wunsch (1993) contain Schlitzer's conclusion within their estimated uncertainty. Both of these studies utilize highly smoothed datasets either in terms of the actual data or in terms of the gridding of the data set for the finite difference analysis in Martel & Wunsch (1993). The Rintoul & Wunsch (1991) estimate makes use of data that resolve the eddy field along their sections. They find a significant northward flux of nitrate across 36° N and they argue that this becomes evident because they resolve the eddy field. Again, these estimates fall within the error bars and agree in sign with the estimates of Martel & Wunsch (1993). Unfortunately, the inverse methods, while quantitative, do little to constrain the nutrient budget for the North Atlantic because of the large uncertainty associated with each flux estimate.

In the absence of tightly constrained estimates of meridional fluxes, it is still useful to ask how the fluxes take place and what they imply about nutrient cycling in the Atlantic. One might question the relative role in nutrient fluxes of thermohaline circulation versus the locally semi-closed wind gyres. This distinction between a buoyancy driven vertical circulation (a zonally-averaged meridional and vertical circulation) and the horizontal gyre flows (with both meridional and zonal features) can be estimated by comparing the averaged fluxes from inverse computations (e.g. Roemmich 1983) with the full estimates.

The flux calculation for a substance carried in the meridional circulation has been worked out in detail by investigators interested in the oceanic heat flux (Bryan 1962, 1987; Hall & Bryden 1982). The basic computation involves decomposing the flux into zonally average contributions and correlations between the anomalies from this average. The flux of some quanity C is then

$$\overline{[F_c]} = \overline{[V]'[C]'} + \overline{[\bar{V}^*\bar{C}^*]} + \overline{[V^{*\prime}C^{*\prime}]}$$

where the brackets ([]) denote a zonal average, the asterix (*) the deviation from the zonal mean, the overbar a depth average, and the primes (′) the deviation from the depth average. The three terms on the right are the vertical overturning contribution, the depth averaged contribution of anomalies in the transport and concentrations in the horizontal, and the contribution due to deviations from both the zonal and depth averages. The full inverse calculations of Rintoul & Wunsch (1991) include the entire flux. Their published results, however, only give [V]'. Therefore the computations here only include the second term. This overturning contribution is typically thought of as a thermohaline contribution since there is no wind-driven contribution to this term.

To get meridional nutrient fluxes, the meridional overturning estimates from Roemmich's (1983) inversions are combined with historical mean nutrient profiles at these latitudes. The product of the average nutrient concentration for each density layer and Roemmich's transport estimate gives fluxes

Table 4. Nutrient fluxes in the North Atlantic. Unless otherwise noted fluxes are across lines of latitude with northward being positive. For a description of the estimation techniques and sources see text. The Arctic and Gulf of Mexico fluxes use the same nomenclature. The Mediterranean flux is negative denoting a flux out to the west. All estimates are in units of 10^{10} moles y^{-1}.

Latitude	NO_3^- flux	PO_4^{3-} flux
Martel & Wunsch (1993)		
12 N	160 ± 300	12 ± 19
24 N	−100 ± 250	−10 ± 16
36 N	50 ± 250	2 ± 16
43 N	−90 ± 275	−10 ± 19
48 N	−60 ± 175	−3 ± 10
55 N	−10 ± 150	−3 ± 10
60 N	−180 ± 100	−23 ± 7
Rintoul & Wunsch (1991)		
24 N	−25 ± 123	–
36 N	375 ± 119	–
Roemmich (1983) with historical nutrient profiles (see text)		
8 N	−665 to 610	−31 to 34
24 N	−805 to −400	−380 to −2
Mediterranean		
36 N	−5 to −22	−3 to −5
Arctic (Anderson & Dyrssen 1981, 1983)		
65 N	−30	−16
Gulf of Mexico (Walsh et al. 1989)		
25 N	2	–

at 8° and 24° N that can be compared to the full calculations of Rintoul & Wunsch (1991) and Martel & Wunsch (1993). This approach assumes that the Roemmich-mean nutrient profile calculation is indicative of the thermohaline overturning cell and the difference between this estimate and the full inversion is the flux in the horizontal or the along-isopycnal flux of nutrients. At 8° N, the flux has a very large uncertainty (Table 4, the range of values is discussed in Roemmich 1983). At 24° N both calculations indicate a southward flux of NO_3^- and PO_4^{3-}. A similar calculation done crudely from the figure for zonally averaged transport from Rintoul & Wunsch (1991) matches the result using Roemmich (1983) for 24° N and suggests a southward transport at 36° N by the thermohaline cell. Furthermore the range of nutrient estimates from the calculation using Roemmich (1983) transports falls below the error bars for both Rintoul & Wunsch (1991) and Martel & Wunsch (1993). If these crude computations are valid, they imply that the thermohaline cell may indeed be pumping nutrients southward, out of the North Atlantic. However, this is partially reversed in the subtropical gyre by the horizontal circulation. This conclusion is consistent with that of Rintoul & Wunsch (1991). The reversal in flux and the flux divergence between 24° N and 36° N calculated by Rintoul & Wunsch (1991) poses further questions concerning the nutrient budget in the central North Atlantic Ocean. We concur with the conclusion of Rintoul & Wunsch (1991) that the horizontal circulation in the gyres has a major impact on the flux of nutrients and that resolution in space is important in these calculations.

Rintoul & Wunsch (1991), in their interpretation of the analysis of hydrographic sections at 24° N and 36° N, invoke an unmeasured flux of dissolved organic nitrogen (DON) to the south at 36° N to balance the northward flux of nitrate. At 36° N, they estimate a net northward flux of $3.75 \pm 1.19 \times 10^{12}$ moles NO_3^- y^{-1} (119 ± 35 kmoles NO_3^- s^{-1}), causing a divergence between 24° and 36° N and a convergence north of 36° N. They suggest that there is a net southward transport of DON to balance this northward flow of nitrate, an amount equal to about 1/3 of the nitrate carried in the Gulf Stream. They then use these estimates to calculate a new production rate for the zone between 36° and 60° of 2.1 moles C m^{-2} y^{-1} over an area of 1.2×10^{13} m^2. Since there are no data on DON on these sections, their hypothesis cannot currently be tested. However with an appropriate section of DON data, this mechanism for balancing the apparent flux divergence of nitrate in the Sargasso Sea can be assessed. The estimates of excess nitrate creation in the Sargasso Sea described below are relevant to this question as the fluxes are similar to the northward nitrate flux across 36° N and they further constrain the source of the excess nitrate to be the center of the gyre. These constraints may indicate that nitrogen fixation is another logical (and unmeasured) source of the nitrate transported north across 36° N.

Excess nitrate and nitrogen fixation in the Sargasso Sea

The Sargasso Sea has elevated ratios of nitrate to phosphate in the main thermocline compared with surrounding waters and with other oceans (Fanning 1989, 1992; Michaels et al. 1994b). Nitrogen fixation and atmospheric deposition have previously been suggested to account for this feature

(Fanning 1989; Michaels et al. 1994b). The waters of the main thermocline (above 1000 m) where this nutrient ratio anomaly is most pronounced are ventilated on time-scales of decades or less (Jenkins 1980, 1988; Sarmiento 1983; Sarmiento et al. 1990). In the areas where these isopycnal surfaces outcrop, the concentrations of both nitrate and phosphate are often near zero. Thus nutrients that are present on these isopycnal surfaces in regions away from the ventillation areas come from remineralization of organic matter that has been transported from the overlying surface waters. If the organisms that comprise the bulk of the organic biomass in sinking material have N:P elemental concentrations near the Redfield ratio of 16, the remineralization of this biomass will lead to the production of 16 moles of nitrate for every mole of phosphate produced. If organisms such as nitrogen-fixing cyanobacteria create biomass that is richer in nitrogen (more correctly, phosphate-poor) this could yield the remineralization of more than 16 moles of nitrate for every mole of phosphate. Conversely, denitrification would remove nitrate with respect to phosphate and decrease the *in situ* elemental ratio. We may be able to use the changes in nutrient ratios on density surfaces along with some assumptions to estimate the annual supply of excess nitrate that would be required to maintain the observed patterns under the Sargasso Sea.

We define a parameter N* as the concentration of nitrate in excess (or deficit) of that expected from the remineralization of phosphate at Redfield stoichiometries:

$$N* = [NO_3^-] - 16 * [PO_4^{3-}] + 2.72$$

$[NO_3^-]$ and $[PO_4^{3-}]$ are the concentrations of nitrate and phosphate respectively. We have arbitrarily added 2.72 to the nominal ($[NO_3^-] - 16*[PO_4^{3-}]$) quantity so that the global average N* as estimated from the GEOSECS dataset is zero (Gruber and Sarmiento in preparation). This implies that for the global ocean, denitrification exceeds nitrogen fixation. The addition of 2.72 will have no effect on the first-order flux estimates below as the 2.72 cancels out in the calculation of the gradient on a density surface.

In a mean profile of N* at the Bermuda Atlantic Time-series Study (BATS) site, N* is elevated throughout the upper 800 m and becomes less than 2.72 below this depth (Figure 5). A similar profile is observed at the TTO stations occupied in 1981 in the central Sargasso Sea, although the values are slightly lower than the BATS composite. GEOSECS nutrient profiles in this same area are similar to the BATS data. If we compare N* at BATS or the TTO stations with N* from the regions where each density surface outcrops during the winter ventilation, we can determine an N* gradient. This gradient can be compared to the ventilation time-scale of each isopycnal surface to calculate the rate of supply of excess nitrate that would be required to maintain the

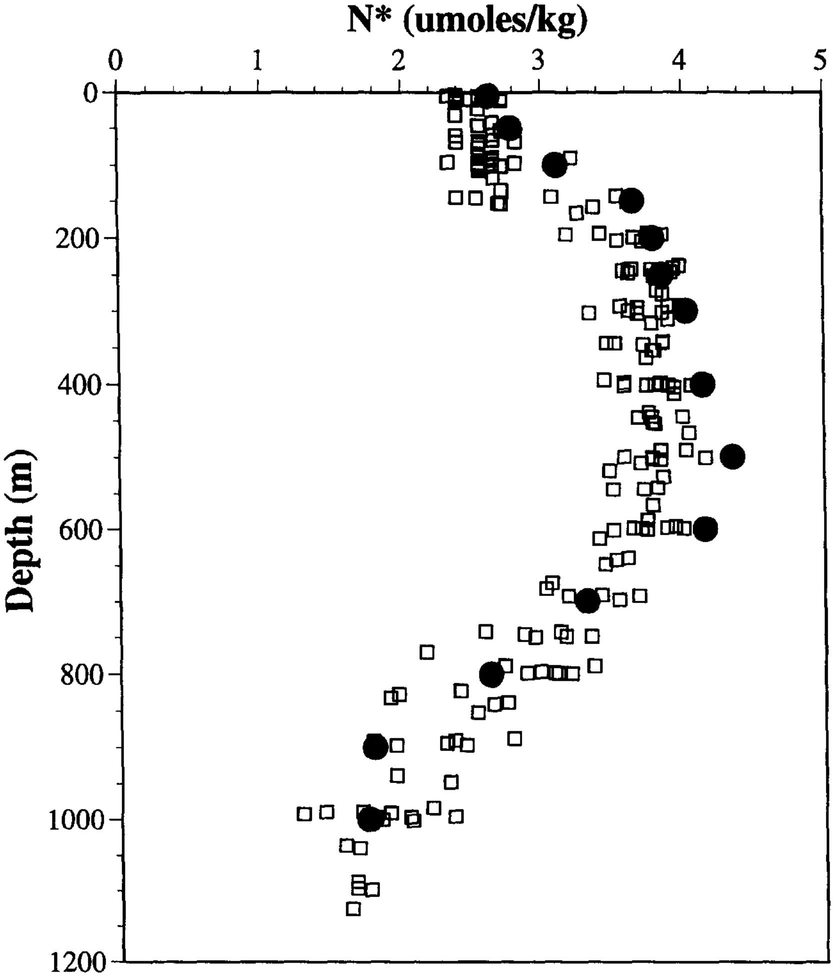

Figure 5. Mean profile of excess nitrate at BATS (solid circles) and at various TTO stations in the central Sargasso Sea (open squares).

gradient (using techniques described by Sarmiento 1983). This calculation is similar to the approach commonly used to estimate oxygen utilization rates (OUR) in the same region (Sarmiento et al. 1990). The outcrop N* (N*(O)) is estimated from the TTO stations near the outcrop regions (Sarmiento 1983; Table 5).

From these calculations, we estimate that 3.4–6.1 × 10^{12} moles of "excess" nitrate are created in the Sargasso Sea each year (Table 5). The range in the estimates is largely a function of the different residence time estimates for each density surface and less a function of the uncertainty in the magnitude of

Table 5. N* and excess nitrate creation-rate calculations. N* in units of μmoles kg^{-1}, volume in 10^{15} m^3, residence times τ in years with $\tau_{(J)}$ from Jenkins 1980 and $\tau_{(S)}$ from Sarmiento 1983. $N_{(J)}$ and $N_{(S)}$ are the rate of nitrate formation in 10^{11} moles y^{-1} estimated using $\tau_{(J)}$ and $\tau_{(S)}$ respectively. N* (B) data were collected at BATS and N*(O) data for outcrop regions from TTO. Data in parentheses are estimates made for this analysis that are not in the cited references. Density surfaces less than 26.2 ventillate near Bermuda every year, but do not ventillate just to the south. Exclusion of the data from the 26.0 and 26.1 isopycnals reduces the nitrate creation estimates by approximately 10%.

Density (sigma-theta)	N*(B)	N*(O)	ΔN*	Volume	$\tau_{(J)}$	$N_{(J)}$	$\tau_{(S)}$	$N_{(S)}$
26.0	3.06	2.22	0.84	(0.3)	(0.75)	3.38	(1)	2.53
26.1	3.31	2.20	1.11	(0.3)	(0.75)	4.44	(4)	0.83
26.2	3.69	2.24	1.41	0.36	(0.75)	6.95	7.2	0.72
26.3	3.80	2.22	1.58	0.48	(0.75)	10.08	7.3	1.04
26.4	3.99	1.42	2.57	0.64	1	16.46	7.5	2.19
26.5	4.14	1.45	2.70	0.98	7.4	3.57	8.2	3.22
26.6	4.30	0.26	4.04	1.2	10.8	4.49	9.3	5.22
26.7	4.26	0.94	3.32	1.1	11.5	3.18	11	3.32
26.8	4.06	1.06	3.00	1.2	16.5	2.18	12	3.00
26.9	3.56	0.64	2.92	1.3	21	1.81	14	2.71
27.0	3.16	0.56	2.60	1.6	28	1.49	15	2.78
27.1	2.84	0.69	2.15	1.9	39	1.05	16	2.56
27.2	2.50	0.48	2.02	2.2	49	0.91	19	2.34
27.3	2.08	0.98	1.10	2.4	61	0.43	29	0.91
27.4	1.78	0.91	0.87	2.6	71	0.32	39	0.58
Sum of nitrate creation rates from sigma-theta = 26.0–27.4:						60.72		33.95

the horizontal N* gradient. This rate is likely an underestimate of the gross rate of excess nitrate creation as other boundary exchanges could further modify the nitrate and phosphate concentrations in the upper layers of the Sargasso Sea. Nixon et al. (this volume) estimate that the continental shelves require 0.7–0.95 × 10^{12} moles NO_3^- y^{-1} from the open ocean to supply the excess of denitrification rates over riverine and atmospheric nitrogen supplies. At the same time, they calculate a net supply of phosphate to the open ocean of 1.8–3.0 × 10^{10} moles PO_4^{3-} y^{-1}. Some fraction of these fluxes would exchange with the density layers used to calculate the excess nitrate gradients and should act to lower N*. Thus the gross rate of excess nitrate production would have to be higher than the net rate to compensate for these and other sources and sinks. Most of the phosphate flux comes from the Amazon River (Nixon et al., this volume) and it is difficult to determine if it would exchange with the upper

Sargasso Sea isopycnal surfaces. We estimate that approximately one third of the net nitrate loss to the shelves may exchange with these surfaces (based on a comparison of the net nitrogen balance for each shelf section in Table 13 of Nixon et al., this volume), potentially enhancing the excess nitrate production rate by 0.3×10^{12} moles NO_3^- y^{-1}. This results in an estimate of total excess nitrate production of $3.7\text{–}6.4 \times 10^{12}$ moles y^{-1} for the subtropical regions. There are two possible sources of the nitrate excess in the main thermocline, nitrogen fixation and/or differential fluxes or lability in dissolved organic nitrogen compared to dissolved organic phosphate. Unfortunately, neither process is well constrained by measurements.

Nitrogen fixation

Marine nitrogen fixation usually occurs in the nitrate and phosphate-depleted, illuminated waters near the surface. The link between diazotrophy at the surface and excess nitrate production in the mesopelagic requires that nitrogen-fixing organisms create biomass with a high N:P ratio (Karl 1992; Karl et al. 1995), either sink or become incorporated into large sinking particles and then that the organic matter be remineralized to nitrate and phosphate in the main thermocline. In oligotrophic ecosystems, most of the organic biomass is dominated by small particles and rapid recycling. Larger organisms play a disproportionate role in export processes dominated by sinking particles (Michaels & Silver 1988) and, thus, it seems likely that diazotrophs that could mediate the excess nitrate signal would have to be relatively large. In addition, these organisms would have to acquire an appropriate supply of phosphate in a part of the ocean that has been strongly depleted in phosphate to depths of 100–200 m.

The most conspicuous large diazotroph in the Sargasso Sea is the colonial cyanobacterium, *Trichodesmium sp.* . This organism has a number of attractive properties that may both mediate the transport of nitrogen to the mesopelagic and allow it access to the phosphate in the main thermocline (Karl 1992). It is capable of active bouyancy regulation (Villareal & Carpenter 1990) and can have vertical migration rates of up to 150 m d^{-1} through both buoyancy and sinking. It can store phosphate as polyphosphate when it is at depth (nitrogen storage is much less efficient compared to the growth requirements, although some organisms may also migrate to gain access to nitrogen). It uses a carbohydrate ballast to control buoyancy (Romans et al. 1994); the respiration of this ballast at depth would result in a net downward transfer of CO_2 in excess of its nominal biomass C:N ratio.

Carpenter (1983) estimated a global nitrogen fixation rate for *Trichodesmium sp.* of approximately 7.5×10^{11} moles N y^{-1}. Both specific growth rates and abundance tend to be low, and the areally weighted nitrogen fixation rates are usually very small compared to other parts of the nitrogen cycle (Lipschultz & Owens, this volume). Carpenter & Romans (1991) concluded that the rate of nitrogen fixation might be much higher than previously estimated for the Caribbean Sea. They found N fixation rates of 2.1 mmoles m^{-2} d^{-1}, comparable to total new production from other sources. This higher rate comes from a combination of using the higher estimates of the specific growth rates of *Trichodesmium sp.* , and from higher abundance estimates from a recent series of cruises in the area (Carpenter & Romans 1991). Interestingly, these new estimates completely change the global estimates of new production. At the estimated fixation rate of 2.1 mmoles m^{-2} d^{-1}, the approximately 7–19 × 10^{12} m^2 area in the Caribbean and Sargasso Seas, where one could logically extrapolate the measurements, would account for 5–14 × 10^{12} moles N y^{-1} of nitrogen fixation, 8–20 times the earlier estimates for the entire globe (Carpenter 1983). Thus, combining the higher rates with moderately higher abundance estimates indicates that nitrogen fixation could be significant in many parts of the Sargasso Sea. Lipschultz & Owens (this volume) summarize the existing literature on nitrogen fixation by *Trichodesmium sp.* They discount some assumptions in the calculations of high nitrogen fixation rates and estimate that *Trichodesmium sp.* could only account for about 1.1 × 10^{12} moles N y^{-1} in the Sargasso Sea. This is only a fraction of the excess nitrate signal. It remains possible that other, less well studied diazotrophs may play a role.

Dissolved organic nitrogen

The potential role of dissolved organic nitrogen (DON) in the creation of excess nitrate is more difficult to constrain, largely because DON is rarely measured. The net production of organic nitrogen must occur near the surface. DON can invade the thermocline by mixing along isopycnal surfaces or by horizontal transport into the Sargasso Sea at the surface, where it would then have to be used by surface biota and transferred into the thermocline by sinking particles. In both cases, the source of the putative DON would be the spring blooms in the outcrop zones at northern latitudes. Such a southward transport of DON was suggested to explain the measured northward transport of nitrate across 36° N latitude (Rintoul & Wunsch 1991). Both scenarios require a pool of DON that is very refractory for the first few years after creation, but quite labile on time-scales of a decade (it must create the N* maximum in the main thermocline at the center of the Sargasso Sea). If the remineralization time-scale of the DON was short, the N* signal would be strongest near the outcrop. If it was similar to the ventillation time scale of these layers, there would be no gradient as nitrate would be created relatively evenly over the density surface. Thus, the isopycnal mixing of DON would require an unlikely change in lability as it passed under the Sargasso Sea to produce the observed mid-gyre maximum. A surface transport of DON from the North would also require a similar change in lability after the water had moved south of 36° N.

As both the total concentration of nutrients and the excess nitrate increase towards the center of the gyre, a horizontal DON source would also require a DOP pool that has similar characteristics and a slightly higher lability on all time-scales. DOP pools are low (200 nmoles kg^{-1}) and fairly constant in the surface waters of the Sargasso Sea (Ammerman et al. 1994). Thus any uptake process that uses DON in the surface waters would face the phosphate limitations described earlier. It seems unlikely that DON and DOP with these characteristics could exist and not result in higher rates of remineralization at the source region than in the center of the gyre. Thus nitrogen fixation seems to be the most likely source of the elevated N* in the Sargasso Sea. However, until adequate surveys of DON and DOP are performed, a dissolved organic source cannot be ruled out.

Midwater particle fluxes

We can attempt to further bound the mass balances in the main thermocline of the Sargasso Sea by examining the vertical transport of N and P within this layer. We estimate a particulate nitrogen flux across the 27.0 sigma-theta surface of 0.1–0.3 mmoles N m^{-2} d^{-1} (the mean depth of this surface is 430 m in the midst of the region of elevated NO_3^-:PO_4^{3-} ratios; Sarmiento 1983). This flux is comparable to the fluxes measured with sediment traps at these depths at the Bermuda Atlantic Time-series Study (BATS) site (0.05–0.3 at 31.7° N, 64.2° W; Lohrenz et al. 1992; Michaels & Knap 1996) and springtime fluxes at the North Atlantic Bloom Experiment site (0.3–0.6 at 42° N, 20° W; Martin et al. 1993). In addition, extrapolating the basin-wide benthic oxygen respiration rate (Jahnke 1992) to 430 m using the flux profile algorithm of Berger et al. (1987) yields a rate of 0.27 mmoles N m^{-2} d^{-1} at 430 m. The oceanic region between 10° N and 40° N encompasses approximately 27×10^{12} m^2 and the total vertical flux out of this region would be $1–3 \times 10^{12}$ moles y^{-1}. This estimate is likely to be uncertain by at least a factor of two because of the recognized uncertainties in the accuracy of sediment traps (Buesseler 1992; Michaels et al. 1994) and the limited number of measurements.

The downward flux of nitrogen is balanced by an upward mixing of nitrate. We can estimate this flux by taking the product of a gradient at 500 m of 0.03–0.04 mmols NO_3^- m^{-4} (calculated from the BATS and TTO datasets) and diapycnal eddy diffusivities of $1–4 \times 10^{-5}$ m^2 s^{-1}. Typical thermocline values of eddy diffusivity are thought to range between 10^{-5} and 10^{-4} (Munk 1966; Gregg 1989). A vertical diffusivity of 4×10^{-5} m^2 s^{-1} is calculated from the typical density profile following the parameterization suggested by Gargett (1984). This agrees well with estimates of 3.7×10^{-5} m^2 s^{-1} from microstructure measurements (Lewis et al. 1986). A more recent study using a tracer release found lower diapycnal diffusivities of 1×10^{-5} m^2 s^{-1}.(Ledwell et al. 1993) Using this range of parameters, we estimate an upward mixing of nitrate of 0.03–0.16 mmoles NO_3^- m^{-2} d^{-1} and 0.3–1.6 × 10^{12} moles NO_3^- y^{-1}. Thus the downward flux of nitrogen on particles appears to be larger than the upward nitrate flux, but the ranges in the two estimates overlap. A similar comparison is not possible for phosphate as there are no measurements of the flux of P on sinking particles. The phosphate gradients are 0.002–0.003 mmols PO_4^{3-} m^{-4}, indicating an upward flux of 2–12 × 10^{10} moles PO_4^{3-} y^{-1}.

Carbon cycle implications

Nitrogen fixation as a source of the excess nitrate could also help resolve some unanswered questions about the measured carbon imbalance in the Sargasso Sea. Each year, between April and December, approximately 3 moles m^{-2} of carbon disappear from the surface waters at BATS (Michaels et al. 1994a). This disappearance is a conundrum because it occurs in the absence of a supply of nitrate and because only 1 mole C m^{-2} can be accounted for in the balance of all of the vertical processes that modify the surface concentration of dissolved inorganic and organic carbon (DIC+DOC+POC). The imbalance is likely caused by one of two issues, either some of the measurements of vertical processes are in error or there is a summer/fall advection of low DIC waters into the region. Sediment traps seem to underestimate the sinking particle flux in this region and this error is probably responsible for at least part of the discrepancy between the observed disappearance and the flux measurements. Since latitudinal gradients in DIC are small relative to the seasonal signal, advection may just require that the anomalous carbon uptake occur elsewhere. This anomalous carbon uptake has a strong effect on the air-sea gas flux of CO_2 in this region (Bates et al. 1996); using a Redfield DIC:NO_3^- stoichiometry for the surface DIC balance would raise summer pCO_2 values by 60 μatm and turn the area at BATS from a weak sink into a strong source of CO_2 with respect to the atmosphere.

Nitrogen fixation would require the uptake of dissolved CO_2 as the new reduced nitrogen is converted into biomass. This may occur at the typical Redfield ratio of 6.6 moles C:1 mole N, or likely at a much higher ratio as the most conspicuous diazotroph, *Trichodesmium sp.* uses a carbohydrate ballasting process to regulate buoyancy . Using C:N ratios of both 6.6 and 15, we estimate the total carbon uptake in the surface waters overlying the Sargasso Sea as 24–96 × 10^{12} moles C y^{-1} (0.3–1.2 × 10^{15} g C y^{-1}). In the seasonal environment of BATS, this would likely be confined to the summer/fall period where oligotrophy is conducive to nitrogen fixation, but could occur year-round to the south. Approximately 50–80% of this carbon

Table 6. Wet and Dry deposition of iron to the Sargasso Sea. Calculated as 3.5% of the total dust deposition by weight. Each value is the total deposition of iron to a 10° × 10° square centered on each latitude and longitude in 10^9 moles Fe y^{-1}. Data modified from Prospero (this volume).

		Longitude								
		95° W	85° W	75° W	65° W	55° W	45° W	35° W	25° W	15° W
	35° N			0.60	0.99	0.54	0.16	0.15	0.29	0.91
Lat.	25° N	0.56	0.95	1.41	0.96	0.57	0.38	0.59	1.09	
	15° N		1.79	1.52	2.51	2.52	2.17	2.64	4.34	

would be sequestered for multi-year timescales, but little for time-scales of longer than a decade (Table 5). The area over which this nitrogen fixation likely occurs is approximately 20×10^{12} m^2 which gives an annual carbon fixation rate of 1.2–4.8 moles C m^{-2} y^{-1}. This rate is very similar to the observed summertime carbon drawdown at the BATS site (Michaels et al. 1994a).

Atmospheric deposition of iron

Nitrogen fixation requires a great deal of iron, approximately 100–1000 fold higher intracellular concentrations than required by organisms that utilize nitrate (Hutchins 1989; Rueter et al. 1992; Elardo 1994). The iron supply to the Sargasso Sea is primarily through the deposition of Saharan dust (Prospero et al., this volume). Model estimates of total dust deposition to the Sargasso Sea between 10 and 40° N latitude (excluding the areas near the African coast) are approximately 44×10^{12} g dry wt. y^{-1} (Prospero et al., this volume). Assuming 3.5% iron by weight, dust would supply 2.8×10^{10} moles Fe y^{-1} (Table 6). *Trichodesmium sp.* typically has an N:Fe ratio of the order 1000 moles N:1 mole Fe (range = 200–3000; Hutchins 1989; Rueter et al. 1992; Elardo 1994). The export of particulate biomass produced by nitrogen fixing organisms would likely transport the intracellular iron to depth as well. Thus, the total iron deposition could support an annual excess nitrate production rate from N_2 fixation of as much as 28×10^{12} moles N y^{-1}. Much of the atmospheric iron is insoluble and thus unavailable to nitrogen-fixing phytoplankton. The iron supply would support the estimated excess nitrate production if *Trichodesmium sp.* was able to utilize about 13–23% of the iron supply. Interestingly, the relatively close match between the nitrogen fixation rate and the rate supportable by the iron deposition may indicate that Fe supply limits the total amount of nitrogen fixation that can occur.

There is a large interannual variation in dust deposition (Figure 4 in Prospero et al., this volume). The Barbados record shows the typical annual pattern (summer maximum), the large interannual variability and a distinct trend towards higher rates of deposition over the past 3 decades. This long-term increase is the result of the large expansion of the Sahara in the early 1970s. A combination of the onset of the drought, perhaps coupled with changes in land use caused the area of the Sahara to expand four-fold. Prior to the 1970s, dust deposition to the Atlantic would have been approximately one third of today's rates and the levels of nitrogen fixation may have been correspondingly reduced. Thus the current nutrient anomalies in the Sargasso Sea may be the result of a recent change in iron supply. The N* at BATS is slightly higher than the N* from the TTO composite of a decade earlier, however, the few GEOSEC profiles in this area are similar to BATS profiles. If dust supply controls this process, we may even expect annual and decadal fluctuations in nitrogen fixation that could drive 0.3–1.2 Gt C y^{-1} fluctuations in the northern hemisphere atmospheric CO_2 stocks. However, the main thermocline ventillates on time-scales of 7–30 years. Thus, nitrogen fixation in the Sargasso Sea cannot result in the sequestration of large amounts of CO_2 on the longer time-scales associated with the anthropogenic signal in the atmosphere.

Mass balances in the pelagic North Atlantic Ocean

The estimates of the fluxes of nitrogen and phosphorus across the boundaries of the North Atlantic Ocean that we present here suggest that this basin is accumulating nitrogen. The range of possible accumulation rates from all of our estimates is $1.9–13.8 \times 10^{12}$ moles N y^{-1} and $0.13–0.65 \times 10^{12}$ moles P y^{-1} (Table 2). These net annual rates are approximately 0.06–0.4% of the stock of the nutrient in the basin and would suggest that the nutrients would increase by 10% on time-scales of 23–170 years. The relative similarity of nutrient profiles collected during the GEOSECS program in the early 1970s with the profiles in recent years suggests that the most rapid of these accumulation rates must be incorrect, however the uncertainties in the stocks and fluxes are large and they preclude a strong conclusion about the slower rates of accumulation. To further evaluate the inferred basin-wide balances, we look at the mass balances within various subsets of the basin. Just two processes account for the majority of the imbalance, the meridional transport estimates and the nitrogen fixation rate inferred from the excess nitrate calculation. We concentrate on these two processes and discuss three issues related to the observed patterns. 1. The predicted accumulation may be an artifact of errors in some of the estimated fluxes. 2. The basins are accumulating nutrients. 3. The nutrient fluxes are not constant on decade to century time-scales.

The range of meridional transport estimates in Table 2 is a reflection of the uncertainties in the transport estimates by each method. These transports only involve the inorganic nutrients and the inclusion of organic nitrogen or phosphorus could provide counter-balancing fluxes as the vertical profiles of organic matter are very different than those of nutrients. The flux across the equator as inferred from the 12° N section has a very wide range from -1.4 to 4.6×10^{12} moles NO_3^- y^{-1} and from -0.07 to 0.31×10^{12} moles PO_4^3 y^{-1}. The net accumulation from all other fluxes into the basin (i.e. ignoring the flux at 12° N) is still very large compared to the uncertainty in the equatorial flux: 3.3 to 9.2×10^{12} moles N y^{-1} and 0.2 to 0.34×10^{12} moles P y^{-1}. It would require a southward equatorial flux that was 2–6 times the estimate for the northward flux just to bring the basin into balance.

If we calculate the balance of fluxes for the North Atlantic north of 24° N we find that this subset of the basin has an estimated net accumulation rate that ranges from 0.6 to 7.0×10^{12} moles N y^{-1} (using the Rintoul and Wunsch fluxes) or from -1.4 to 7.5×10^{12} moles N y^{-1} (using the Martel and Wunsch fluxes, Table 7). The phosphate stock in this subregion could be in balance. The calaculation for the basin north of 36° N becomes less balanced as we include the large northward transport inferred by Rintoul and Wunsch (1991, Table 8), despite the lack of a nitrogen fixation signal. North of 43° N the atmospheric deposition, shelf losses and nitrogen fixation are all small and the various transport terms (Table 4) indicate similar southward transports. The divergence between the fluxes at 24° N and 36° N of 4×10^{12} moles NO_3^- y^{-1} and the divergence of 5.4×10^{12} moles NO_3^- y^{-1} between the fluxes at 12° N and 36° N is similar to the nitrogen fixation source of 3.7–6.4×10^{12} moles NO_3^- y^{-1} estimated from the excess nitrate. Thus, the nitrogen balance in the North Atlantic seems to be most sensitive to the transport terms in the subtropical gyre and across the equator and to the large nitrogen fixation estimate. The fluxes are internally consistent with a source of nitrate in the mid-latitudes. However, there may still have to be an unmeasured southward flux of dissolved organic nitrogen at 36° N as inferred by Rintoul & Wunsch (1991).

On the time-scale of the observations that are used to estimate these fluxes, we must also consider the likelihood that the North Atlantic Ocean is not in steady state. This can either imply that there are changes in the concentrations of nitrogen and phosphorus stocks or that the fluxes themselves change with time. The dust deposition record already indicates that the putative nitrogen fixation rate may have been as much as 4 fold lower before 1970, a change that may have been exacerbated by human activity. Atmospheric deposition of reactive nitrogen was also lower before the industrial revolution. Removing the source of excess nitrate and the nitrogen deposition bring the entire

Table 7. Mass balances of N and P in the North Atlantic Ocean north of 24° N. Data are abstracted from Tables 2 and 4. All fluxes are in units of 10^{12} moles y^{-1}.

North of 24° N latitude	N	P
Atmospheric deposition		
24–40° N	0.22*	0.003
40–70° N	0.36	~0
Total atmospheric deposition	0.58	0.003
Exchange with continental shelves		
Western boundary, 24–70° N	−0.54	0.005
Eastern boundary, 24–70° N	−0.21	0.005
Total exchange with shelves	−0.75	0.01
Nitrogen fixation		
10–40° N*	1.9 to 3.2	–
Total nitrogen fixation	1.9 to 3.2	–
Physical Transport (negative is southward or westward)		
24° N (Rintoul & Wunsch 1991)	−1.48 to 0.98	–
24° N (Martel & Wunsch 1993)	−3.5 to 1.5	−0.26 to 0.06
Arctic Sea	−0.3 to −2.8	−0.16 to −0.3
Mediterranean	−0.05 to −0.2	−0.003 to −0.005
Estimated imbalance	0.6 to 7.0 (−1.4 to 7.5)**	−0.08 to 0.38**

* Approximately half of the 10–40° N estimate for total nitrogen deposition and nitrogen fixation given in Table 2.

** Using the Martel & Wunsch (1993) transport at 24° N.

basin quite close to balance. Further, there are indications from the Pacific Ocean that the rate of oceanic denitrification may change quite markedly on glacial-interglacial time-scales thus affecting the overall stock of nitrate (Ganeshram et al. 1995). Watermasses at different depths have residence times with respect to ventillation of 10s to 100s of years in the North Atlantic Ocean and any variability in nitrogen boundary fluxes on local scales will lead to heterogeneities in the oceanic transport rates as these signals propagate through the ocean.

Table 8. Mass balances of N and P in the North Atlantic Ocean north of approximately 36° N. Some estimates use a 40°N boundary. Data are abstracted from Tables 2 and 4. All fluxes are in units of 10^{12} moles y^{-1}.

North of 36° N–40° N latitude	N	P
Atmospheric deposition		
40–70° N	0.36	~0
Total atmospheric deposition	0.36	0
Exchange with continental shelves		
Western boundary, 40–70° N	−0.41	0.003
Eastern boundary, 40–70° N	−0.18	0.004
Total exchange with shelves	−0.59	0.007
Physical transport (negative is southward or westward)		
36° N (Rintoul & Wunsch 1991)	2.6 to 4.9	–
36° N (Martel & Wunsch 1993)	−2.0 to 3.5	−0.14 to 0.18
Arctic Sea	−0.3 to −2.8	−0.16 to −0.3
Estimated imbalance	2.7 to 7.5 (−1.9 to 6.1)*	0.03 to 0.49*

* Using the Martel & Wunsch (1993) transport at 36° N.

Summary

- The total standing stocks of nitrogen and phosphorus in the open ocean are large compared to the magnitude of the boundary exchanges in a single year. Changes in atmospheric deposition will only have local or ephemeral impacts on ocean ecosystems, either close to a pollution source or in the center of the gyre where nutrient depletion is stongest. Except for the Amazon outflow, nitrogen fluxes in rivers only meet a portion of the denitrification and burial fluxes on continental shelves; the remainder is supplied from oceanic nitrate pools. Increases in riverine fluxes of nitrogen could decrease the net on-shelf transport of nitrate; however, this would have little observable effect on the open ocean on time-scales of less than millenia.

- The ability to resolve nutrient transport in the ocean is still poor, in most cases because of limitations in data quality or quantity. Even the question of whether the North Atlantic exports nitrate to other basins cannot be adequately resolved at this time. The balance of flux estimates currently available indicates that there should be a net accumulation of nitrate in the North Atlantic Ocean and that this accumulation is related to processes that occur at low and mid-latitudes.

- We calculate that 3.7 – 6.4 × 10^{12} moles NO_3^- y^{-1} are created in the upper 1000 m of the Sargasso Sea. This nitrate comes from either nitrogen fixation or differential remineralization of dissolved organic nitrogen and phosphorus; we suggest that nitrogen fixation is the likely source. The rate of creation of nitrate is similar to a flux divergence observed by Rintoul & Wunsch (1991) and implies that the North Atlantic should either export nitrate to the south, have a much larger denitrification rate over the entire basin or be accumulating nitrogen. If nitrogen fixation occurs at the required rate, it requires an iron supply of the same order as the observed deposition. Thus interannual and decadal variations in dust deposition could play an important role in modifying the upper ocean nitrogen dynamics of the Sargasso Sea.

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