The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean

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Abstract. Five large rivers that discharge on the western North Atlantic continental shelf carry about 45% of the nitrogen (N) and 70% of the phosphorus (P) that others estimate to be the total flux of these elements from the entire North Atlantic watershed, including North, Central and South America, Europe, and Northwest Africa. We estimate that $61 \cdot 10^9$ moles y^{-1} of N and $20 \cdot 10^9$ moles y^{-1} of P from the large rivers are buried with sediments in their deltas, and that an equal amount of N and P from the large rivers is lost to the shelf through burial of river sediments that are deposited directly on the continental slope. The effective transport of active N and P from land to the shelf through the very large rivers is thus reduced to $292 \cdot 10^9$ moles y^{-1} of N and $13 \cdot 10^9$ moles y^{-1} of P.

The remaining riverine fluxes from land must pass through estuaries. An analysis of annual total N and total P budgets for various estuaries around the North Atlantic revealed that the net fractional transport of these nutrients through estuaries to the continental shelf is inversely correlated with the log mean residence time of water in the system. This is consistent with numerous observations of nutrient retention and loss in temperate lakes. Denitrification is the major process responsible for removing N in most estuaries, and the fraction of total N input that is denitrified appears to be directly proportional to the log mean water residence time. In general, we estimate that estuarine processes retain and remove 30–65% of the total N and 10-55% of the total P that would otherwise pass into the coastal ocean. The resulting transport through estuaries to the shelf amounts to $172-335 \cdot 10^9$ moles y^{-1} of N and $11-19 \cdot 10^9$ moles y^{-1} of P. These values are similar to the effective contribution from the large rivers that discharge directly on the shelf.

For the North Atlantic shelf as a whole, N fluxes from major rivers and estuaries exceed atmospheric deposition by a factor of 3.5–4.7, but this varies widely among regions of the shelf. For example, on the U.S. Atlantic shelf and on the northwest European shelf, atmospheric deposition of N may exceed estuarine exports. Denitrification in shelf sediments exceeds the combined N input from land and atmosphere by a factor of 1.4–2.2. This deficit must be met by a flux of N from the deeper ocean. Burial of organic matter fixed on the shelf removes only a small fraction of the total N and P input (2–12% of N from land and atmosphere; 1–17% of P), but it may be a significant loss for P in the North Sea and some other regions. The removal of N and P in fisheries landings is very small. The gross exchange of N and P between the shelf

and the open ocean is much larger than inputs from land and, for the North Atlantic shelf as a whole, it may be much larger than the N and P removed through denitrification, burial, and fisheries. Overall, the North Atlantic continental shelf appears to remove some $700-950 \cdot 10^9$ moles of N each year from the deep ocean and to transport somewhere between 18 and $30 \cdot 10^9$ moles of P to the open sea. If the N and P associated with riverine sediments deposited on the continental slope are included in the total balance, the net flux of N to the shelf is reduced by $60 \cdot 10^9$ moles y^{-1} and the P flux to the ocean is increased by $20 \cdot 10^9$ moles y^{-1} . These conclusions are quite tentative, however, because of large uncertainties in our estimates of some important terms in the shelf mass balance.

Introduction

The word "margin" appears commonly in papers dealing with exchanges between land and sea. It is a conveniently ambiguous term for an interface that is difficult to define. We use it here to refer to the whole complex border of environments between free-flowing fresh water and the edge of the continental shelf, including intertidal wetlands, estuaries, and the shelf. While it would be best to describe the outer boundary of the shelf by a marked change in water depth, as a practical matter we define the shelf as extending seaward to a depth of 100 or 200 m. Areas within each of these depths have been calculated (Pilson & Seitzinger, this volume), and one or the other is frequently used to fix the shelf-slope boundary (Eisma 1988).

If we define the oceans as beginning where fresh and salt water first meet (an admittedly elusive point), then the nitrogen (N) and phosphorus (P) fluxes reported by Howarth et al. (this volume) may be taken as the inputs to the North Atlantic from land. In what may have been the first attempt to develop nutrient budgets for the world ocean, Emery et al. (1955) worked from such a perspective and established a convention for later efforts (for example, the Paris Commission as discussed by Balls 1994). During the last 15–20 years, however, there has been a growing appreciation that intense biogeochemical exchanges in estuaries (including their wetlands) and on the continental shelf may influence markedly the net flux of N and P from land to the open ocean (Edmond et al. 1981; GESAMP 1987; Balls 1994; Howarth et al. 1995; Nixon et al. 1995). In this report we attempt to assess the magnitude of this influence around the land-sea margin of the North Atlantic so that we can estimate the net transport of N and P from land onto the continental shelf and the net exchange between the shelf and the open sea.

Very large rivers

Five major rivers with an average water flow exceeding $3000\,\mathrm{m}^3\,\mathrm{s}^{-1}$ discharge directly onto the continental shelf on the western side of the North Atlantic

Table 1. Estimated flux of total nitrogen and phosphorus in major rivers that discharge directly on the North Atlantic continental shelf.

	Water Discharge ² m ³ s ⁻¹	109 moles y ⁻¹	
		N	P
Mississippi-Atchafalaya ³	17,545	130	3.5
Grijalva-Usumacinta ⁴ (Western Gulf of Mexico)	3,265	13	0.05
Magdelena ⁴ (Central America)	8,000	9.5	0.6
Orinoco ⁵ (Central America)	28,000	39	2.3
Amazon ⁶	180,000	<u>223</u>	<u>47</u>
Total direct discharge on shelf ⁷		414	53

¹ The St. Lawrence is also a very large river (10,400 m³ s⁻¹), but it does not form a delta and contains an estuarine mixing zone at its mouth (Czaya 1981; Bugden 1981).

(Czaya 1981). Because the flows from these rivers are sufficiently great that fresh and salt water mixing takes place largely on the shelf, rather than in an estuarine embayment, we can consider the N and P they carry as direct additions to the shelf. Unfortunately, the fluxes of total N and total P in two of these rivers (the Grijalva-Usumacinta and the Magdelena) appear not to have been measured, and we have assumed that the discharge of N and P from the regions they drain is partitioned according to regional water discharge as described by Howarth et al. (this volume). The contributions of N and P from the Mississippi, the Amazon, and the Orinoco have been measured directly (Table 1). Together these five river systems appear to carry about 45% of the N and 70% of the P that Howarth et al. (this volume) calculate for the total riverine flux to the North Atlantic.

These fluxes are so large that it is useful to consider them in more detail rather than simply entering them in future tables as inputs to the shelf. This is particularly important for P, because a very large portion of the total P carried by the rivers is associated with suspended sediments. Most of this P will ultimately be buried with the sediments and thus not play an active role in what are geologically speaking short-term biogeochemical processes on the shelf and in the ocean (Froelich 1988).

² Czaya (1981).

³ Recent values calculated by Howarth et al. (this volume) from data summarized by Turner and Rabalais (1991).

⁴ Calculated assuming that the ratio of river nutrient discharge to regional nutrient discharge is equal to the ratio of river water discharge to regional water discharge as reported by Howarth et al. (this volume).

⁵ Lewis & Saunders (1989).

⁶ N from Solati et al. (1982); P from Devol et al. (1991).

⁷ As discussed in text, we estimate that 29% of this N and 75% of this P is buried in deltas and on the continental slope.

The fate of the sediment discharged by the very large rivers (Table 2) is not known with a great deal of certainty – some accumulates in the delta formed at the mouth of each of the rivers (Table 2), some may be deposited elsewhere on the shelf away from the delta, and some is carried over the shelf break and buried on the continental slope. For the purpose of this accounting, we assume that 50% of the sediment discharged from each river is buried in its delta as found for the Amazon (Kuehl et al. 1986). We further assume that the remaining sediment is deposited and buried on the slope, thus bypassing the shelf entirely.

Because there have been few reports of the N content of delta sediments, we based our estimate of N burial on the more numerous measurements of organic carbon and an assumed C/N ratio of 10 (molar). Meybeck (1982) reported a C/N (molar) ratio of 9.3–14 for marine sediment and DeMaster et al. (1994) found a range from 7.5 to 10 in rapidly accreting slope sediments off North Carolina. Trefry et al. (1994) reported a C/N (molar) ratio of 9.9 for particulate organic matter in the Mississippi River and Richey & Victoria (1993) found a mean ratio of 10.8 for fine particulates in the Amazon. Our use of a ratio of 10 may underestimate the N burial, however, since Aller & Aller (1986) reported a mean value of 7.4 in 22 samples of sediment (0–45 cm depth) from the Amazon continental shelf.

The organic carbon content of delta sediments has been measured for the Mississippi (1.4%, Trefry et al. 1994), the Orinoco (0.91%, van Andel & Postma 1954), and the Amazon (0.66%, Showers & Angle 1986). Following Berner (1982) we assumed a C value of 0.75% for delta sediments from the remaining two rivers. Based on these assumptions, we estimate that about $61 \cdot 10^9$ moles N y⁻¹ are buried in the deltas of the five very large rivers (Table 2), and that an equal amount of N from the rivers is buried on the adjacent continental slopes. This represents 29% of the total N discharged by the rivers (Table 1) and leaves 292 · 10^9 moles N y⁻¹ as a potentially active contribution to the continental shelf.

There have also been few measurements of total P in deltaic sediments. Unfortunately, while there is a relationship between organic P and organic C in sediments that appears to vary in a regular way with sedimentation rate (Ingall & Van Cappellen 1990), a large fraction of the river borne P is in inorganic particulate form (Jahnke 1992). For example, Richey & Victoria (1993) found no correlation between organic C and total P in particulate matter carried by the Amazon. As a result, we estimated P burial in a different way than we did N burial. Following Froelich (1988), who concluded that "... about 25% of the total phosphorus eroded from the continents is activated and enters the ocean in a biologically available form," we assume that 75% of the total P discharge (Table 1) will be buried in the large river deltas and on the

	Sediment discharge ¹	Delta area ²	109 moles y ⁻¹	
	10^{12} g y^{-1}	10^3 km^2	N	P
Mississippi-Atchafalaya	210	30	12	1.3
Grijalva-Usumacinta	96	17	3	0.02
Magdelena	220	1.7	7	0.2
Orinoco	150	21	6	0.9
Amazon	1200	100	33	17.6

Table 2. Estimated burial of nitrogen and phosphorus in major river deltas on the North Atlantic continental shelf. We assume that an equal amount of N and P is buried on the continental slope.

170

61

20

1876

² Amazon and Mississippi deltas from Czaya (1981), others from Mulholland (1981). The latter reports delta areas of $29 \cdot 10^3$ km² and $467 \cdot 10^3$ for the Mississippi and the Amazon, respectively.

continental slope. If this is correct, about $20 \cdot 10^9$ moles P y⁻¹ from the very large rivers will be buried in the deltas, $20 \cdot 10^9$ moles y⁻¹ will be buried on the continental slope, and $13 \cdot 10^9$ moles y⁻¹ will be an active input to the shelf.

It follows from these assumptions that the average P concentration on the buried sediments from the very large rivers should be $40 \cdot 10^9$ moles P y^{-1} divided by $1876 \cdot 10^{12}$ g y^{-1} of sediment or 0.02 mmol P g^{-1} . This is equivalent to 0.66 mg P g^{-1} , a value consistent with recent measurements of total P in marine sediments summarized by Howarth et al. (1995).

Aside from the five very large rivers, all of the remaining riverine fluxes of N and P from land must pass through estuaries before they reach the shelf. During the passage through these intensely metabolic systems, there is great potential for modification.

Estuaries

Total

Considering that the first attempt to develop a quantitative mass balance or budget for nitrogen in a marine system was carried out almost 90 years ago in the North Sea (Johnstone 1908), there have been surprisingly few efforts to describe the overall balance of total N and P in estuarine embayments

 $^{^1}$ From various sources summarized by Milliman & Syvitski (1992). The Grijalva-Usumacinta sediment discharge was calculated from Milliman and Syvitski's regression relating sediment discharge to runoff for high rivers using mean water discharge (1980–1983) and watershed data for the Usumacinta at Boca del Cerro, Mexico (UNESCO 1992). The resulting flux of $69 \cdot 10^{12}$ g y $^{-1}$ was increased by a factor of 1.39 to account for the higher water flow at the mouth of the combined Grijalva-Usumacinta river system (Czaya 1981). No estimate of combined watershed area was available.

around the North Atlantic. Fortunately, for this exercise we were able to find or assemble relatively complete mass balances for nine impressively diverse systems. They vary widely in size (24 km² to 375.10³ km²), mean depth (1 m to 55 m), water residence time (3 days to 20 years), and nutrient loading rate (230 mmol N m^{-2} y^{-1} to 13,400 mmol N m^{-2} y^{-1}). The systems represented include a coastal lagoon (the Guadalupe Estuary), drowned river estuaries (e.g., Delaware Bay), coastal embayments (Boston Harbor), and an inland sea (the Baltic). The sample also includes relatively pristine systems where non-point sources of N and P dominate (e.g., Ochlockonee Bay) as well as intensively developed estuaries where point source sewage discharges provide large amounts of nutrients (e.g., the Scheldt Estuary). Some of the systems experience hypoxic or anoxic conditions (e.g., Chesapeake Bay, Potomac Estuary, Scheldt, the Baltic), while others are relatively well mixed and characterized by oxygenated bottom water (e.g., Delaware Bay, Narragansett Bay). Some have extensive areas of intertidal salt marsh (e.g., Delaware Bay), while others do not (e.g., Narragansett Bay, Boston Harbor).

Despite the considerable efforts expended by many investigators, we can not claim to have a rigorously closed budget for N and P in any of these diverse systems. In no case have all of the inputs, outputs, and changes in internal storage of N or P been measured independently and contemporaneously (see discussion in Nixon et al. 1995). In most cases, the flux in which we are most interested, the net export of N and P to the shelf, has been calculated by difference. The Baltic Sea and the Scheldt are notable exceptions in which that flux has been measured or modeled and denitrification has been calculated by difference. The estuarine-shelf exchanges at the mouth of Chesapeake Bay have also been modeled (Cerco & Cole 1992) and agree well with the exchanges calculated by difference (Boynton et al. 1995).

In order to facilitate comparison among the systems, we have expressed all of the terms in each budget as a flux per unit area (Tables 3–11). It is important to emphasize that our sample only includes studies in which all of the various forms of N and P have been measured. There are many more estuaries in which the behavior of dissolved inorganic N and P has been observed, but these can not be taken as revealing anything about the exchange of total N or P. For example, it has been well established that dissolved reactive phosphorus accounts for only a small fraction of the total P flux in unpolluted rivers (Jahnke 1992; Howarth et al. 1995).

It is apparent from an inspection of the budgets that our sample of only nine coastal systems includes a wide range of biogeochemical behavior, from almost complete transfer of N and P between land and the shelf (e.g., Ochlockonee Bay and Boston Harbor) to almost complete interception of the flux from land (e.g., the Baltic Sea). Chesapeake Bay and the estuary of its tributary, the

Potomac River, appear to import P from the shelf (Boynton et al. 1995). In seeking to relate such behavior to various characteristics of the systems, we turned to limnology, where it has been shown that the retention of N and P in many lakes is largely a function of flushing rate, though the exact form of the relationship is described differently by various authors (Kirchner & Dillon 1975; Kelly et al. 1987; see brief overviews by Rigler & Peters 1995; Howarth et al., this volume). It is more difficult to estimate the effective flushing rate in estuaries than in lakes, but we were able to obtain at least a rough estimate of the mean fresh water replacement time for each system in our sample. Linear regressions of the fractional net transport of nitrogen and phosphorus from land to the coastal ocean as a function the log mean residence time suggest that this feature is also very important in influencing the net balance of N and P in estuaries (Figures 1 and 2).

This result was not necessarily expected because there are important differences between the behavior of N and P in fresh and salt water and in lake and marine sediments (Froelich 1988; Seitzinger 1988b; Nixon 1988; Caraco et al. 1990; Howarth et al. 1995). However, our conclusion is further supported (at least for N) by a recent independent study of the N balance in a Danish fjord by Nielsen et al. (1995), who found that 95% of the N entering that system from land was exported. Their published report described the fjord as having a water residence time ranging from 1.5 to 13 days, but they have provided us with a calculation of the time-averaged fresh water replacement rate of five days during the year of their study. Their export is thus consistent with the other systems shown in Figure 1. The behavior of N in the northern Adriatic Sea also fits with the pattern shown by estuaries and lakes in our sample (Degobbis et al. 1986).

Because the companion article by Howarth et al. (in this volume) discusses N retention in lakes as a function of the ratio of mean depth to water residence time according to the model of Kelly et al. (1987), we have also analyzed our data in that way. While the result (Figure 3) confirms that the N retention of estuaries is generally consistent with that of lakes and rivers (see Howarth et al., this volume), the inclusion of water depth did not result in a regression with a higher r^2 .

The relationship between flushing rate and export is less convincing for P (Figure 2). We excluded Chesapeake Bay and its tributary estuary, the Potomac, from the P export regression because they both appear to have a net input of P from the coastal ocean (Tables 4 and 8). This exceptional behavior appears to be due, at least in part, to very rapid sedimentation rates in these systems that are supported equally by sediment inputs from shoreline erosion and from rivers (Boynton et al. 1995). High rates of sediment deposition also make Chesapeake Bay and the Potomac appear to bury a larger fraction of

Table 3. The annual mass balance of total nitrogen and phosphorus in the Baltic Sea. Data are from Elmgren (1984), HELCOM (1993), Larsson et al. (1985), Shaffer & Rönner (1984), Wulff & Stigebrandt (1989), and Wulff et al. (1994). In some cases values have been recalculated to exclude the Danish Straits area. Units are mmol m⁻² y⁻¹.

	N	P
Inputs		
Direct atmospheric deposition ²	68	0.2
Nitrogen fixation ³	26	_
Rivers ⁴	109	3.1
Direct urban areas and industries ⁵	14	0.8
	217	4.1
Changes in storage		
Net accumulation in water ⁶	16	0.3
Net accumulation in sediment ⁷	11	3.0
Outputs		
Denitrification ⁸	161	_
Loss as gaseous N ₂ O ⁹	4	_
Fish landings ¹⁰	5	0.3
Coastal ocean, net exchange ¹¹	20	0.5

Inside the Danish Straits. Area = 374 600 km², mean depth = 55 m (Wulff & Stigebrandt 1989).

their N input than calculated for the other estuaries. With the exception of the upper end of the estimated range for N burial in Narragansett Bay, all of the other estimates of N burial are less than 10% of the input, while N burial in the Potomac is reported to be 35% of the input and for the Chesapeake as a whole, it is almost 40% of the input (Boynton et al. 1995) (see Tables 3-11).

In a previous comparison of denitrification rates and the inputs of dissolved inorganic nitrogen (DIN) to several estuaries, Seitzinger (1988b) found that denitrification removed a relatively constant 45% of the DIN input. If we express denitrification as a fraction of the total nitrogen input, however, it

Swedish Environment Protection Agency (1993: 142-143).

³ Larsson et al. (1985).

⁴ Swedish Environment Protection Agency (1993), minus direct loads from urban areas and industries.

HELCOM (1993).

⁶ Change between 1982–1986 and 1987–1991, Wulff et al. (1994).

⁷ N value from Larsson et al. (1985); P value calculated by difference.

⁸Calculated by difference. ⁹ Shaffer & Rönner (1984).

¹⁰ Finfish only (Elmgren 1984), content of nutrient elements calculated as in Table 14.

¹¹ Wulff & Stigebrandt (1989).

Table 4. The annual mass balance of total nitrogen and phosphorus in Chesapeake Bay, Maryland-Virginia. during 1985–1986. Data from Boynton et al. (1995). Units are mmol $m^{-2} y^{-1}$.

	N ·	P
Inputs		
Direct atmospheric deposition ²	113	2
Nitrogen fixation	?	0
Rivers (diffuse sources)	565	18
Direct sewage (point sources)	260	11
Coastal ocean ³	_0	<u>10</u>
	938	41
Changes in storage		
Accumulation in water	0	0
Accumulation in sediment	327	40
Outputs		
Denitrification	245	0
Fish landings	84	1.5
Coastal ocean ³	282	0

¹ Area = 11542 km^2 , mean depth (MLW) = 6 m.

³ P input and N output calculated by difference.

appears that N removal is largely a function of water residence time (Figure 4). Our finding that the fractional loss of N to denitrification increases with water residence time in estuaries is also consistent with the general behavior of five out of six Danish lakes studied by Andersen (1974) and with the unstratified lakes analyzed by Kelly et al. (1987).

Unfortunately, it is difficult to apply the relationships between flushing rate and N and P export in any exact way to the fluxes reported by Howarth et al. (this volume) because their results represent an aggregate flux through long stretches of coastline. Each region may contain numerous estuaries with highly variable flushing rates, many of which have never been estimated. As a practical expedient we have assumed that most estuaries are characterized by mean residence times of 0.5–12 months, and that they will acccordingly export some 35–70% of their total N input and about 45–90% of their total P input to the continental shelf. We have made an exception to this procedure for the Baltic Sea, where we reduced the N and P exported from the Baltic according to Table 3 in order to compute a net flux to the Northwest European Coast and North Sea. The consequence of these assumptions in combination with the burial of some of the N and P carried by the very large rivers is that the total riverine flux of N from land onto the total North Atlantic shelf is

² Smullen et al. (1982); 1976–1981 mean TN and TP in wet deposition.

Table 5. The annual mass balance of total nitrogen and phosphorus in Delaware Bay, Delaware-New Jersey¹ during the 1980s. Units are mmol m⁻² y⁻¹.

	N	P
Inputs		
Direct atmospheric deposition ²	100	3
Land drainage and sewage ³	<u>1800</u>	<u>155</u>
	1900	158
Changes in storage		
Accumulation in water	0	0
Accumulation in sediment		
Salt marshes ⁴	178	2
Subtidal ⁵	<u>77</u>	21
	255	23
Outputs		
Denitrification ⁶	825-1025	0
Fish landings	Small	Very small
Coastal ocean ⁷	620-820	135

 $^{^{1}}$ Area = 1 989 km², mean depth = 9.7 m (Polis & Kupferman 1973).

⁵ Based on a sediment input of $1.6 \cdot 10^6$ mt accumulating in subtidal fine-grained deposits (Biggs & Beasley 1988) with a nitrogen content of 0.13% (Cifuentes 1991) for upper bay depositional area sediments (Weil 1977). P deposition based on 800 μ g P g⁻¹ inorganic sediment in the upper bay depositional area (Strom 1976).

reduced to 50–67% of the value calculated by Howarth et al. (this volume) and the flux of P is reduced to 29–39% of the calculated total discharge from land (Table 12). The reduction in P flux is probably even greater since some estuaries trap all of the P from land and import P from the shelf (e.g., Tables 4 and 8).

² Direct wet DIN from Scudlark & Church (1994). They assumed dry deposition equal to wet. We assume DON equal to 50% of wet NO₃ and wet NO₃ equal to 50% of wet DIN based on Nowicki & Oviatt (1990). P based on recent regional AIRMON data.

³ From Jaworski & Howarth (in press). NOAA (1989) reported a total N input of 1630 mmol m⁻² y⁻¹ and a total P input of 190 mmol m⁻² y⁻¹.

⁴ N burial estimated assuming 10 mg N/g of marsh sediment based on various sources summarized by Nixon & Lee (1986) and $497 \cdot 10^3$ mt y⁻¹ of marsh sediment accumulation (Biggs & Beasley 1988). P burial estimated from 300 μ g P/g of marsh sediment (Strom 1976).

Calculated using denitrification rates in the Delaware River from (Seitzinger 1988a; $300 \,\mu\text{mol m}^{-2} \,h^{-1}$) and Delaware Bay proper (Seitzinger 1988b; $100 \,\mu\text{mol m}^{-2} \,h^{-1}$) and areas of 179 km² and 1819 km², respectively. Lower value obtained assuming the lower bay rate applied only to the area not classified by Biggs & Beasley (1988) as consisting of gravel or gravely sand. Lower bay rates measured in summer only.

Calculated by difference.

Table 6. The annual mass balance of total nitrogen and phosphorus in Narragansett Bay, Rhode Island. Data were collected at various times during the 1980s and early 1990s. Units are mmol m⁻² y⁻¹. From Nixon et al. (1995).

	N	P
Inputs	·	
Direct atmospheric deposition	90	0.4
Nitrogen fixation	~0	0
Rivers	1200	65
Direct sewage	550	40
Storm water runoff	20	_12
	1960	115
Changes in storage		
Accumulation in water	~0	~0
Accumulation in sediment	140–335	17–38
Outputs		
Denitrification	260-520	0
Fish landings		
Hard clams	10	0.6
Fin fish	3	0.2
Coastal ocean ²	765-1410	76–98

¹ Area = 328 km² including Mt. Hope Bay, mean depth (MLW) = 8.3 m (Pilson 1985)

The N and P balance on the continential shelf

Deposition from the atmosphere

In addition to inputs of N and P from the large rivers that discharge on the shelf and the net export from estuaries, there is a significant flux of N to the continental shelf from atmospheric deposition (Duce et al. 1991; Paerl 1995). We have estimated this term for each region of the shelf around the North Atlantic by multiplying the shelf area estimates of Pilson & Seitzinger (this volume) by mean area-specific wet and dry N deposition intensities provided by three different atmospheric transport/chemistry models (Prospero et al., this volume). The result suggests that atmospheric deposition may provide an amount of N to continental shelf waters of the North Atlantic equal to 5–10% of the net N flux from large rivers and estuaries, depending on one's choice of the lower or upper range of probable transport from estuaries and one's choice of depth to define the outer edge of the shelf (Table 13). The relative importance of the atmosphere as a pathway for N input varies markedly

² Calculated by difference. Each term rounded.

Table 7. The annual mass balance of total nitrogen and phosphorus in the Guadalupe Estuary, Texas¹ during a dry (1984) and a wet (1987) year. Data are from Brock et al. (1995) and Longley (1994). Units are mmol m^{-2} y⁻¹.

	N		P	
	1984	1987	1984	1987
Inputs				
Direct atmospheric deposition	40	40	3.6	3.6
Nitrogen fixation	48	48	0	0
Rivers	345	1900	49*	160*
Direct sewage	<u>115</u>	<u>70</u>	<u>17</u>	11
	548	2058	70	171
Changes in storage				
Accumulation in water	25	30	-7	2
Accumulation in sediment ²	_1	65	0.3	<u>_16</u>
	26	95	-6.7	18
Outputs				
Denitrification	320	320	0	0
Fish landings ²	35	85	2.2	5.3
Adjacent bays and gulf ³	167	1558	75	148

¹ Area = 551 km^2 , mean depth (MLW) = 1.4 m.

among regions. For example, along the North Sea – Northwest European Coast, atmospheric deposition may provide an amount of N equal to 40–110% of the N supplied by the estuaries (Table 13). In fact, the input from the atmosphere is even larger because dissolved organic N is not included in these estimates, and recent evidence indicates that this may be a significant component of the total N deposition from the atmosphere (Cornell et al. 1995).

Denitrification

In a well-known review of estimates of nitrate uptake by continental shelf sediments, Christensen et al. (1987) concluded that denitrification in such sediments was an important term in the oceanic and global N cycle. While

² P burial reported by Longley (1994) adjusted to revised N burial reported by Brock et al. (1995) using an N/P ratio of 4 (D. A. Brock, Texas Water Development Board., personal communication. Fish landings adjusted assuming N/P (molar) of 16.

³ Calculated by difference. Brock et al. (1995) used a numerical model to estimate a net N exchange for this term of 390 mmol m^{-2} y^{-1} in 1984 and 1500 mmol m^{-2} y^{-1} in 1987.

^{*} River and sewage P data from D. A. Brock (personal communication).

Table 8. The annual mass balance of total nitrogen and phosphorus in the Potomac Estuary, Maryland-Virginia¹ during 1985–1986. Data from Boynton et al. (1995). Units are mmol m^{-2} y^{-1} .

	N	P
Inputs		
Direct atmospheric deposition ²	113	2
Nitrogen fixation	?	0
Rivers (diffuse sources)	1277	5.6
Direct sewage (point sources)	705	20
Chesapeake Bay ³	0	<u>16</u>
	2095	44
Changes in storage		
Accumulation in water	0	0
Accumulation in sediment	837	42
Outputs		
Denitrification	330	0
Fish landings	10	1.8
Chesapeake Bay ³	918	0

¹ Area = 1210 km^2 , mean depth (MLW) = 5.9 m

³ P input and N output calculated by difference.

the summary compiled by Christensen et al. (1987) contains a number of errors and their calculations based on their own pore water nitrate profiles are not necessarily convincing, we agreed with their general conclusion that denitrification in shelf sediments was likely to be an important sink for N in the North Atlantic. For this reason a considerable effort was devoted to obtaining region-specific estimates of denitrification on the North Atlantic shelf. This was a considerable challenge because few measurements of denitrification have actually been made in the area. The details of the approach taken, the assumptions required, and the results obtained are presented elsewhere (Seitzinger & Giblin, this volume). Briefly, Seitzinger and Giblin first developed an empirical regression between primary production in the overlying water and sediment oxygen uptake. That regression was then linked to another regression relating sediment oxygen uptake to measurements of coupled nitrification and denitrification in shelf sediments. In this way, they were able to use relatively abundant primary production data to estimate region-specific benthic denitrification. We recognize that this model will underestimate total denitrification in areas where direct uptake of nitrate from the overlying water contributes significantly to denitrification in the sediments

² Smullen et al. (1982); 1976–1981 mean TN and TP in wet deposition.

Table 9. The annual mass balance of total nitrogen in Ochlockonee Bay, Florida 1 during normal flow conditions. Data from Seitzinger (1987) and unpublished measurements. Units are mmol m^{-2} y^{-1} .

	N
Inputs	
Direct atmospheric deposition ²	82
Nitrogen fixation	<3.5
Rivers ³	5910
Direct sewage	0
	5995
Changes in storage	
Accumulation in water	0
Accumulation in sediment ⁴	105–125
Outputs	
Denitrification	640
Fish landings	Very small
Coastal ocean ⁵	5230-5250

¹ Area = 24 km^2 , mean depth at low tide = 1 m.

⁵ Calculated by difference.

The important conclusion for our effort in this paper is that denitrification appears to remove more nitrogen from every region on the North Atlantic shelf except the Amazon and, perhaps, the Gulf of Mexico, than the combined flux from rivers and the atmosphere can provide (Table 14). For the North Atlantic shelf as a whole, coupled nitrification-denitrification in sediments appears to exceed the effective N input from land and atmosphere by a factor of about 1.4–2.3. The net loss of N on the western side of the North Atlantic is about two-three times that on the eastern side, in spite of a much larger input of N from land on the west (Table 14).

In addition to denitrification, there are two additional fluxes that can remove N and P from biological circulation on the shelf – fisheries landings and long-term burial in sediments.

Fisheries harvest

The North Atlantic contains some of the world's most productive fishing grounds, including the North Sea, the Grand Banks, Georges Bank, and the

² Hendry & Brezonik (1980), includes TON, NH₄, and NO₃ in bulk precipitation during 1976–1977.

³ DIN input of Seitzinger (1987) increased by a factor of 5 based on TN:DIN ratios measured in June (4:1) and November (6:1).

⁴ Based on ²¹⁰Pb profiles and measured N concentrations of sediments below 14 cm averaging $86 \mu \text{mol N gdw}^{-1}$. Range for different assumptions regarding ²¹⁰Pb input.

Table 10. The recent (1992–1994) annual mass balance of nitrogen and phosphorus in Boston Harbor, Massachusetts prior to sewage diversion. Units are mmol m^{-2} y^{-1} .

	N	P
Inputs ²		
Direct atmospheric deposition	200	0.3
Nitrogen fixation	0	0
Rivers	590	27
Groundwater	60	3
Storm water	85	4
Sewage	<u>8160</u>	<u>625</u>
	9095	660
Changes in storage ³		
Accumulation in water	0	0
Accumulation in sediment	185	22
Outputs		
Denitrification ⁴	910	0
Fish landings ³	Very small	0
Dredging ⁵	150	9
Coastal ocean ⁶	7850	629

¹ Area = 108 km^2 , mean depth = 5.8 m (Kelly 1991).

Gulf of Mexico. We estimated the removal of N and P in fish by averaging the recent (1987–1991) annual commercial landings from the United Nations Food and Agricultural Organization (FAO) statistical areas that cover the North Atlantic. While finfish account for about 85% of the total North Atlantic catch, we separated the landings of other groups that may differ in their content of N and P (Table 15). If we assume that 90% of the catch is actually taken from the continental shelves, it appears that commercial fishing may remove from the shelf an amount of N equal to 3.6–6.4% of the total input from land and atmosphere (Table 15). Fishing may return to land some 4.1–10% of the total P flux from land onto the shelf (Tables 12 and 15). These calculations underestimate the N and P removal in fish because they do not include recreational landings from the shelf. On the other hand, they overestimate the removal because the FAO data include estuarine commercial landings as well as those from the shelf. It seems likely that inshore commercial landings

² Alber & Chan (1994).

³ Kelly & Nowicki (1992); P storage calculated from N assuming an N/P ratio of 8.5 as in Narragansett Bay (Nixon et al. 1995).

⁴ Giblin et al. (1993).

⁵ Kelly & Nowicki (1992); P calculated from N assuring N/P ratio of 16.

⁶ Calculated by difference.

Table 11. The annual mass balance of total nitrogen and phosphorus in the western Scheldt Estuary. N data are from Billen et al. (1985) for 1973–1983. P data are less certain but represent approximate conditions for alow flow year (1991). P data from Billen & Servais (1991). Units are mmol m^{-2} y^{-1} .

	N	P
Inputs		
Direct atmospheric deposition	?	?
Nitrogen fixation	?	0
Rivers	7220	770
Direct sewage	3350	260
Direct agriculture	2830	10
	13400	1040
Changes in storage		
Accumulation in water	?	0
Accumulation in sediment	<u>1030</u>	540*
	1030	
Outputs		
Denitrification*	5420	0
Fish landings	?	0
Coastal ocean	6950	500

Area = 277 km², mean depth = 11.2 m (Billen, personal communication).

exceed the recreational catch on the shelf. In any case, the impact on the shelf N and P budgets is minor.

Burial exclusive of large river deltas

It is difficult to evaluate this term because of the complexity of sediment dynamics on continental shelves. We began by assuming that the burial of N and P only takes place in areas of sediment deposition, because of the general correlation between sedimentation rate and the burial rate of organic matter (Henrichs & Reeburgh 1987; Mayer 1994), and because sediments themselves also carry some inorganic N and P. The sediments being deposited may have been carried onto the shelf very recently by rivers, been eroded recently from headlands, or been eroded from much older deposits elsewhere on the shelf (Eisma 1981).

^{*} Calculated by difference by original authors.

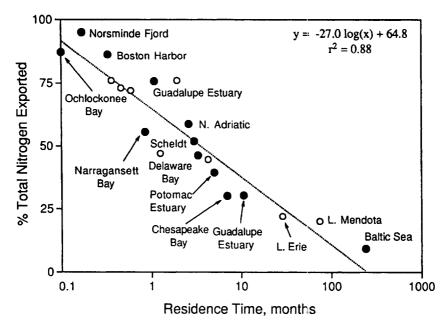


Figure 1. The percent of total nitrogen input from land and atmosphere that is exported from a sample of estuaries and lakes as a function of mean water residence time in the system. Estuarine data (solid points) from Tables 3–11. Norsminde Fjord export from Nielsen et al. (1995). Estuarine residence times from Seitzinger (1987) Ochlockonee Bay, FL; Signell & Butman (1992) Boston Harbor, MA; David Brock (personal communication) Guadalupe Estuary, TX in dry and wet years; Pilson (1985) Narragansett Bay, RI; Billen (personal communication) Scheldt Estuary; Polis & Kupferman (1973) Delaware Bay; W. Boicourt (personal communication) Potomac Estuary, VA-MD and Chesapeake Bay, VA-MD; C. Cerco, U.S. Army Corps of Engineers, recently provided a residence time estimate of 7.6 months for Chesapeake Bay based on a simulated dye study using a hydrodynamic model of the bay; Larsson (1986) Baltic Sea; K. Nielsen (personal communication) Norsminde Fjord. North Adriatic data from Degobbis et al. (1986). Lakes Erie and Mendota (open circles) from various sources summarized by Nixon (1988). Other lakes (unnamed open circles) from a study of six shallow Danish lakes by Andersen (1974). The regression line is for the combined data set. Separate regressions for estuarine and lake data were virtually identical.

Sediments carried by rivers

In their recent review of sediment discharge to the world ocean, Milliman & Syvitski (1992) provided a concise summary of our present state of knowledge:

What is the sediment flux to the sea? This question really has two parts: how much sediment is carried by rivers, and how much escapes the present-day land/estuarine environment? The answer to both is more or less the same – we don't know.

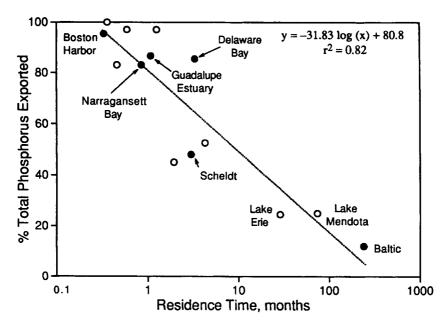


Figure 2. The percent of total phosphorus input from land that is exported from a sample of estuaries and lakes as a function of mean fresh water replacement time in the system. Data sources as in Figure 1. Regression line includes lakes and estuaries but excludes the Guadalupe in a low flow (long residence time) year.

Fortunately, the situation is not quite so difficult for the North Atlantic, where there appears to be good evidence that virtually all (90–95%) of the sediment carried by rivers on the east coast of the United States is deposited in estuaries rather than on the shelf (Meade 1972, 1982; Swift et al. 1981). The situation appears to be the same in the North Sea, where Eisma (1981) found that sediment deposition in estuaries (including the Wadden Sea and The Wash) was essentially equal to the input from rivers. While recognizing that some sediment escapes from the estuaries, especially during large floods, we assume that this flux is sufficiently small for the shelf as a whole that we can ignore it in subsequent calculations.

Sediments from coastal erosion

In the North Sea, this source appears to provide an amount of sediment equal to about 15% of that carried into the estuaries by rivers (Eisma 1988). We are not aware of any comprehensive estimate of this kind for the North Atlantic as a whole, and we are reluctant to extrapolate from the North Sea alone. As a practical matter, we simply acknowledge that coastal erosion may provide an unquantified, but almost certainly small, amount of sediment to the inner shelf. Moreover, even if the amount were known, we would still have to

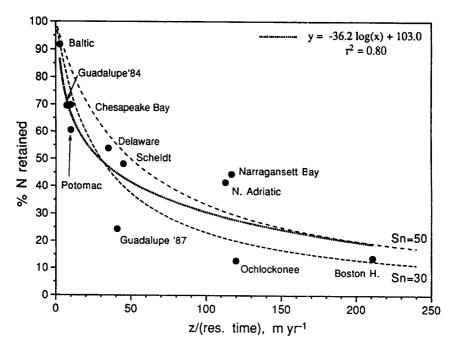


Figure 3. The percent of total nitrogen input from land and atmosphere that is "retained" (buried and denitrified) in various estuaries as a function of the ratio of mean depth (z, m) to fresh water residence time in the system. We have used retention rather than export and years rather than months for the residence time in this figure to be consistent with the discussion of Figure 6 in Howarth et al. (this volume). The broken lines were calculated using the model of Kelly et al. (1987) for mass transfer coefficients (Sn) of 30 and 50. The estuarine systems follow the pattern described for lakes, reservoirs and rivers.

determine the net increase (if any) in N and P concentration on the sediment between the time it was eroded and the time it was buried on the shelf. This would be necessary because Howarth et al. (this volume) did not include coastal erosion in their estimates of N and P flux from land.

Sediments resuspended from relic deposits

Again using the North Sea as an example, Eisma (1981, 1988) estimated that this source contributes as much or more sediment to depositional areas as do rivers. Overall, he calculated that some $14-24 \cdot 10^{12}$ g y⁻¹ of fine-grained sediment are redeposited on the bottom of the North Sea outside the estuaries. Major depositional areas include the Skagerrak, the Kattegat, and the German Bight (van Weering 1981; Lohse et al. 1995).

It is difficult to know how much N and P is buried as older deposits are resuspended, transported, and deposited again. Sediments in the large depositional area of the Skagerrak contain 3-6 times more organic C than

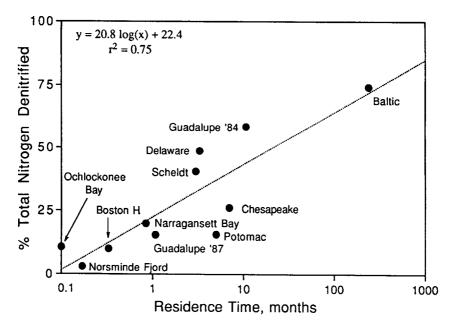


Figure 4. The fraction of total nitrogen input from land and atmosphere that is denitrified in various estuarine systems as a function of mean water residence time. Data sources as in Figure 1. The estimate for Delaware Bay is almost certainly too high because it is based on summer measurements only (see Table 5). Anoxic bottom waters over parts of Chesapeake Bay and the Potomac estuary may reduce the fraction of total N input that is denitrified.

adjacent sediments (van Weering 1981), but this may be due to grain size (Mayer 1994; Milliman 1994; Lohse et al. 1995) and we do not know if there was an increase in the concentrations of N and P on the sediments since they were eroded.

In the absence of specific information for all but a few of the various depositional areas on the North Atlantic shelf, we can only make a very rough beginning in estimating the potential magnitude of N and P burial. Since we are dealing with older sediment that may have been on the shelf for thousands of years (e.g., Bothner & Bacon 1987), the N and P of concern to us must enter the sediment from the deposition of organic matter formed in the water column above. In other words, in contrast to the active river delta sediments, we do not need to consider the mineral P associated with the redeposited sediments, since that P was on the shelf long before the time frame of our mass balance.

Deposition and burial of organic matter

As part of their effort to estimate denitrification on the North Atlantic shelf, Seitzinger & Giblin (this volume) reviewed and summarized numerous

Table 12. Estimated flux of total nitrogen and phosphorus from estuaries onto the continental shelf in various regions around the North Atlantic. The fluxes from large rivers that discharge directly on the shelf have also been included after correction for the estimated burial of N and P in large river deltas and on the continental slope. See text. Boundaries of the regions are given in Howarth et al. (this volume).

	10 ⁹ moles y ⁻¹	
	Total N	Total P
North Canadian Rivers	8-15	0.3-0.5
St. Lawrence Basin	16-33	0.3-0.6
Northeast Coast of U.S. ¹	13-26	1.0-1.9
Southeast Coast of U.S.	6–12	0.2-0.3
Gulf of Mexico ²	136-159	1.1-1.3
Central America and Caribbean Islands ³	33-43	1.4-2.2
Amazon Basin ⁴	<u>161–165</u>	13-14_
Total Western Atlantic	373-453	17.3-20.8
Northwest European Coast	11-22	0.4-0.8
North Sea	38-68	1.4-2.9
Southwest European Coast	5–10	0.8-1.6
Northwest Africa ⁵	<u>37–74</u>	1.3-2.5
Total Eastern Atlantic	91–174	3.9-7.8
Total North Atlantic	464-627	21.2-28.6

¹ Includes Bay of Fundy and part of Nova Scotia and the U.S. coast to Cape Hatteras, North Carolina.

measurements of primary production in the area. They also examined the relationship between primary production in the water and the consumption of organic matter by shelf sediments. While there is considerable variation, almost all of the data were consistent with the view that about 10–30% of the shelf primary production was consumed in or on the sediments. This is in agreement with more detailed studies of the U.S. shelf south of New England (Rowe et al. 1988) and the North Sea (Billen et al. 1990). As a working number, Seitzinger & Giblin (this volume) used 16% for their estimate of the fraction of primary production respired on the bottom. Given the scatter in the data, and considering that the deposition of organic matter on the bottom

² Effective contribution from the Mississippi plus Grijalva-Usumacinta = $113 \cdot 10^9$ moles N and $0.91 \cdot 10^9$ moles P.

³ Effective contribution from the Orinoco plus Magdelena = $22.5 \cdot 10^9$ moles N and $0.7 \cdot 10^9$ moles P.

⁴ Effective contribution from the Amazon = $157 \cdot 10^9$ moles N and $11.8 \cdot 10^9$ moles P.

⁵ Not including any net flux to the deep Atlantic from the Mediterranean (see Michaels et al. this volume).

Table 13. Estimated deposition of NO_y and NH_x (wet plus dry) from the atmosphere onto the continental shelf in various regions around the North Atlantic. Deposition rates are from Prospero et al. (this volume), shelf areas (0–100 m depth and 0–200 m depth) are from Pilson & Seitzinger (this volume). Boundaries of the regions are given in Howarth et al. (this volume).

10 ⁹ moles y ⁻¹			
NO _y		NO _y + NH _x	
0–100 m	0–200 m	0-100 m	0–200 m
3.5	6.4	4.9	9.0
4.7	7.8	6.6	11.0
8.8	14	11	18
2.7	3.0	3.9	4.4
11	13	18	21
1.9	2.4	4.6	5.8
1.8	1.9	5.4	_5.7
34.4	48.5	54.4	74.9
20	29	38	54
0.7	1.1	1.1	1.8
1.9	2.3		
41.1	58.2		
	NO _y 0-100 m 3.5 4.7 8.8 2.7 11 1.9 1.8 34.4 20 0.7 1.9	NO _y 0-100 m 0-200 m 3.5 6.4 4.7 7.8 8.8 14 2.7 3.0 11 13 1.9 2.4 1.8 1.9 34.4 48.5 20 29 0.7 1.1 1.9 2.3	NOy NOy + NF 0-100 m 0-200 m 0-100 m 3.5 6.4 4.9 4.7 7.8 6.6 8.8 14 11 2.7 3.0 3.9 11 13 18 1.9 2.4 4.6 1.8 1.9 5.4 34.4 48.5 54.4 20 29 38 0.7 1.1 1.1 1.9 2.3

 $^{^{1}}$ 0-100 m = 708,616 km² $0.200 \, \text{m} =$ 1,276,783 km² 2 0-100 m = 315,770 km² $0.200 \, \text{m} =$ 518,998 km² 3 0-100 m = 230.780 km² $0.200 \, \text{m} =$ 361.042 km² ⁴ 0–100 m = $0.200 \, \text{m} =$ 137,364 km² 123,338 km² 5 0–100 m = 500,926 km² $0.200 \, \text{m} =$ 573,565 km² 6 0–100 m = 474,755 km² 381.070 km² $0.200 \, \text{m} =$ 7 0-100 m = 389,562 km² 359,579 km² $0.200 \, \text{m} =$ 8 0-100 m = 1,181,318 km² 786,236 km² $0.200 \, \text{m} =$ 9 0-100 m = $33,986 \text{ km}^2$ $51,435 \text{ km}^2$ $0.200 \, \text{m} =$ 10 0–100 m = 319,325 km² $0.200 \, \text{m} =$ 392,888 km²

N.W. European coast includes Norway through France, excluding the Baltic.

can not be much larger than the amount respired, we assumed that deposition on average was equal to 25% of primary production. This is lower than the 32% estimated by Wollast (1993) for the world coastal zone, but higher than the findings of Billen et al. (1990), who estimated an average deposition of 25 g C m² y⁻¹ in the whole of the North Sea, a value equal to about 18% of the primary production according to Seitzinger and Giblin's review.

Unfortunately, there are few direct measurements of organic deposition on non-upwelling shelves, and even fewer measurements of net long-term

S.W. European coast includes Spain and Portugal.

Cape Hatteras divides N.E. and S.E. coast of the U.S.

Table 14. Estimated balance of nitrogen on the continental shelf in various regions around the North Atlantic excluding exchanges with the open ocean. Boundaries of the regions are given in Howarth et al. (this volume). Fluxes from the land are from Table 12, rates of atmospheric deposition are from Prospero et al. (this volume) as calculated in Table 13; denitrification rates are from Seitzinger & Giblin (this volume). Low and high ranges in atmospheric deposition and denitrification apply to shelf areas with 0-100 m or 0-200 m depth contours, respectively (Pilson & Seitzinger, this volume).

	109 moles y ⁻¹	7		
	Flux from	Atmospheric	Denitrification	Net input
	land ¹	deposition	loss	or (loss)
North Canadian Rivers	8–15	4.9–9.0	49–99	(29–82)
St. Lawrence Basin	16-33	6.6-11	94–155	(54-128)
Northeast Coast of U.S.	13–26	11–18	114–178	(77-147)
Southeast Coast of U.S.	6-12	3.9-4.4	105-117	(89-107)
Gulf of Mexico	136-159	18–21	171–195	6-(38)
Central America and Caribbean Islands	33–43	4.6–5.8	101-122	(53–83)
Amazon Basin	161–165	5.4-5.7	77-84	83–93
Total Western Atlantic	373-453	54-75	711–950	(204–502)
Northwest European Coast	49–90	38–54	165–258	(37-155)
Southwest European Coast	5-10	1.1–1.8	19–29	(7.9-22)
Northwest Africa	37-74	1.9–2.3	98-171	(22-132)
Total Eastern Atlantic	91–174	41–58	282-458	(67–309)
Total North Atlantic ²	464–627	95–133	993-1408	(271–811)

1 Does not include the N and P from very large rivers that we consider to be buried in deltas and on the continental slope.

² Seitzinger & Giblin (this volume) also calculated a denitrification loss in the shallow waters around Greenland & Iceland that amounted to an additional $22 \cdot 10^9$ moles y⁻¹

Table 15. Estimated removal of nitrogen and phosphorus in fisheries landings from the North Atlantic continental shelf. Values are based on mean annual landings from FAO statistical areas 21, 27, 31 and 34 during 1987–1991.

	Nitrogen Landings, 10 ⁹ mole		n and Phosphorus Removed ² es y ⁻¹	
	metric tons ¹	N	P	
Oysters	334,400	0.37	0.012	
Mussels	510,100	0.46	0.028	
Scallops	324,900	0.51	0.027	
Clams, etc.	498,200	0.96	0.024	
Squids, octopuses	286,900	0.41	0.018	
Lobsters	152,200	0.25	0.010	
Crabs	182,600	0.30	0.012	
Shrimp, prawns	480,600	1.20	0.034	
Fin fish	15,887,700	22.7-34.0	1.02-2.05	
Total	18,656,900	27.2-38.5	1.18-2.21	

¹ From FAO (1993).

burial as a fraction of deposition. Based on the work of Canfield (1989) and Blackburn (1991), we have assumed a C preservation equal to 1–5% of deposition, or between 0.25 and 1.25% of primary production. The fact that this leaves a balance between our deposition estimates and the respiration estimates of Seitzinger & Giblin (this volume) is of no real importance given the variability of all of the data. It is probably also useful to note that a net accumulation of organic matter in shelf sediments is neither inconsistent with, nor supportive of, the view of Smith & Hollibaugh (1993) that continental shelves are essentially in metabolic balance, with organic production equalling consumption. Even in shelf areas such as the Georgia Bight off the southeast coast of the U.S., where Hopkinson (1985) found a great excess of respiration over production, it is possible that a fraction of the shelf primary production is buried while a large flux of organic matter from land supports an overall heterotrophic carbon balance.

Our estimate of a total North Atlantic shelf deposition of $19 \cdot 10^{12}$ moles C y⁻¹ and burial of $0.2-1 \cdot 10^{12}$ moles C y⁻¹ can be compared in a very rough way to global estimates made by others if we consider that the North

² N composition from Vinogradov (1953): mussels = 7.2% fresh weight, oysters = 7.7%, clams = 2.7%, scallops = 2.2%, squid and octopuses = 2% (Pilson 1970), lobster and crabs = 2.3%, shrimp = 3.5%, fin fish = 2-3%.

P composition from Vinogradov (1953): mussels = 0.17% fresh weight, oysters = 0.11%, clams = 0.15%, scallops = 0.26%, squid and octopuses = 0.2%, lobsters and crabs = 0.2%, shrimp = 0.22%, fin fish = 0.2-0.4%.

Atlantic (0–200 m) contains about 20% of the world shelf area. Wollast (1993) concluded that $183 \cdot 10^{12}$ moles C y⁻¹ (2.2 · 10^{15} g C) were sedimented onto the world continental shelves, about twice as much as a simple prorating of our estimate would give. However, his value presumably includes estuaries and active river deltas while ours does not, and a global estimate must also include very productive coastal upwelling areas with high rates of organic deposition and accumulation. Smith & Hollibaugh (1993) concluded that $9 \cdot 10^{12}$ moles C y⁻¹ were put into long-term burial on the "coastal bottom" of the world ocean, a value 1.8–9 times greater than ours. Again, however, their estimate presumably includes estuaries, river deltas, and major upwelling areas that are excluded from our value. All of these estimates must be considered as very rough approximations.

We next calculated N burial assuming a C/N (molar) ratio of 10. Walsh (1983) found such a value over large areas of the Gulf of Mexico shelf outside the Mississippi Delta, though there was also considerable local variation. Unfortunately, it was more difficult to decide on an approximate C/organic P ratio, since it is evident from a recent review that that ratio varies widely as a function of sedimentation rate (Ingall & Van Cappellen 1990). It is possible, of course, that a comparable review would show that our choice of a constant value for the C/N ratio was also an oversimplification.

There have been relatively few measurements of deposition rates on the North Atlantic shelf. One 13,000 km² area of fine-grained sediments on the southern New England shelf has been studied in some detail (Twichell et al. 1981), and geochemical evidence indicated a modern deposition rate of about 25 cm/1000 years (Bothner et al. 1981). This rate suggests a C/organic P ratio of about 500 (Ingall & Van Cappellen 1990). On the other hand, deposition rates in the German Bight and the Skagerrak appear to be much higher, perhaps on the order of 0.5 cm y⁻¹ (Lohse et al. 1995). Eleven cores of fine-grained inner shelf sediments off the southeast U.S. coast dated using ²¹⁰Pb also showed high rates of deposition that averaged 0.9 cm y⁻¹ (Pomeroy et al. 1993). Sediments accumulating at these higher rates are characterized by a lower C/organic P ratio of about 250 (Ingall & Van Cappellen 1990). In the absence of a convincing area-weighted sedimentation rate, we assumed a total shelf C/organic P range of 250–500.

The results suggest that the burial of N on the shelf outside of major river deltas is very small (Table 16) and amounts to only about 1–7% of the total denitrification estimate calculated by Seitzinger & Giblin (this volume). The removal of P may be more significant, however, accounting for 1–20% of the net flux onto the shelf from estuaries and very large rivers (Table 12). In areas away from the large rivers, the burial of organic P may be particularly important. For example, in the North Sea, we estimated that $1.4-2.9 \cdot 10^9$

Table 16. Estimated potential burial of N and P in North Atlantic continental shelf (0–200 m) sediments exclusive of major river deltas. Burial calculated assuming 0.25–1.25% of the C fixed in the water column is preserved in long-term burial and that sediments accumulate with a C/N (molar) of 10 and C/organic P of 250–500.

	Primary production ²	Burial, 10 ⁹ moles y ⁻¹		
	10 ¹² moles C y ⁻¹	N	P	
North America	39.2	9.8-49	0.20-1.96	
Central and South America	10.8	2.7-14	0.05-0.54	
Europe	16.3	4.1-20	0.08-0.81	
N. W. Africa	8.9	2.2-11	0.05-0.44	
Greenland and Iceland	1.2	0.3-1.5	0.01-0.38	
	76.4	19-95	0.39-4.13	

¹ These estimates also do not include 50% of the sediments discharged by the very large rivers that we assume are deposited outside the deltas on the shelf or over the shelf-slope break. See Table 17.

moles of P were discharged from the estuaries (Table 12). Using Seitzinger & Giblin's (this volume) estimate for primary production of 32 mmol C m⁻² d⁻¹ (140 g C m⁻² y⁻¹), we calculated a P burial rate on the North Sea shelf of $0.07-0.70 \cdot 10^9$ moles P y⁻¹, or 2.4-50% of the input from land. It is obvious from the example, however, that large uncertainties very much limit our ability to develop a mass balance for the shelf.

Exchanges at the shelf break

If we summarize the estimates developed up to this point, it appears that there is a net flux of active P from the continental shelf to the open North Atlantic that is equal to $17.7-30.4 \cdot 10^9$ moles y^{-1} , or 24-41% of the value that Howarth et al. (this volume) estimate for the total P loss from land (Table 17). In addition there is an estimated $20 \cdot 10^9$ moles P y^{-1} buried on the continental slope with sediments from the large rivers. The situation with regard to N, however, is very different. The shelf budget developed thus far requires an additional large net source of N that is approximately equal to or greater than the combined input of N from large rivers, estuaries, and atmospheric deposition (Table 17).

There are two potential sources for the missing N – biological fixation directly on the shelf and the nutrient-rich deeper ocean waters off the shelf that Csanady (1990) termed the "slope sea." It is likely that the first is of little importance. Walsh (1988) estimated that N fixation on the entire shelf area of the world ocean was less than $100 \cdot 10^9$ moles N y⁻¹. Since the area of

² From Seitzinger & Giblin (this volume) who provide a more detailed geographical assessment. They used the shelf area within the 200 m depth contour.

Table 17. Comparison of the estimated fluxes of active N and P onto the North Atlantic continental shelf (0–200 m depth) from land and atmosphere with removal processes on the shelf. We estimate that an additional $61 \cdot 10^9$ moles y^{-1} of N and $20 \cdot 10^9$ moles y^{-1} of P are buried on the shelf in deltas of the very large rivers. We also assume that equal amounts of N and P associated with sediments carried by the very large rivers are deposited and buried directly on the continental slope.

	N	P
	Input 10 ⁹	moles y ⁻¹
From direct atmospheric deposition	133	Very small
From very large rivers	292	13
From estuaries	172-335	<u>11-19</u>
Total	597–760	24–32
	Removal 10	⁹ moles y ⁻¹
Organic matter buried on the shelf	19–95	0.4-4.1
Fisheries harvest	27-38	1.2-2.2
Denitrification ¹	1408	_0
Total	1454–1541	1.6-6.3

Does not include shallow areas around Greenland and Iceland.

shelf in the North Atlantic (0–200 m) accounts for about 20% of the world total, biological fixation probably supplies less than $20 \cdot 10^9$ moles N y⁻¹ compared to the apparent deficit of 690–940 \cdot 10⁹ moles N y⁻¹ (Table 17). The largest single source of N for the North Atlantic shelf as a whole must be the onwelling of deeper nutrient-rich water from the continental slope.

Onwelling of N and P from the slope

As long ago as the 1930s, a few oceanographers noted that the physical circulation on at least some parts of the North Atlantic shelf was such that the slope waters could potentially make an important contribution to the nutrient supply and productivity of the shelf. As Iselin (1939) explained:

The fact that the salinity is at a maximum near the bottom on the continental shelf shows conclusively that the coastal circulation has an off shore component at the surface and an in shore component beneath ... During the last few years physical oceanographers have begun to appreciate the important role which lateral turbulence plays in the sea ... Under the conditions of high stability often found in coastal waters, the isopicnal transport of nutrients should prove a most fruitful study ... The chemicals which are in this way pumped up from mid depths in the Sargasso Sea are transferred isopicnally across the Gulf Stream to the edge of the

continental shelf. Thus as the bottom water penetrates landward, it carries with it a good supply of nutrients...

More recent work has shown that the physical exchange processes can be more complicated than this early picture (e.g., Walsh et al. 1978; Csanady 1990; Verity et al. 1993) and few attempts have been made to measure or calculate the fluxes of nitrate onto various regions of the North Atlantic shelf. The results that are available range by a factor of three, from about 1.9 mmol N m⁻¹ of shelf break s⁻¹ off Nova Scotia to about 5.7 mmol m⁻¹ s⁻¹ off the southeast coast of the U.S. (Table 18). When averaged over the entire width of the shelf in each area, these slope-shelf transports translate into N inputs amounting to 0.3 to 1.1 mol N m⁻² y⁻¹ between eastern Nova Scotia and Florida (Table 18). Georges Bank and, perhaps, a few other special areas are more intensively enriched.

If similar rates of onwelling characterize the entire North Atlantic shelf (0–200 m), this process would supply 1.7– $6.2 \cdot 10^{12}$ moles N y⁻¹, far more than enough to meet the deficit of 0.6– $0.9 \cdot 10^{12}$ moles N y⁻¹ identified in Table 17. Unfortunately, the area of shelf between Nova Scotia and Florida where the most intensive effort has been made to quantify the slope-shelf exchange accounts for less than 10% of the total shelf area (0–200 m) in the North Atlantic (Pilson & Seitzinger, this volume).

We have also estimated the flux of nitrate onto the entire North Atlantic shelf using an empirical regression relating primary production (¹⁴C uptake) to the supply of dissolved inorganic nitrogen (DIN) in a variety of phytoplankton-based marine systems (Figure 5). The plot shown modifies earlier versions (Nixon 1992; Nixon et al. 1994) in that we have only included systems where all of the DIN inputs have been considered. There are numerous estuarine sites for which primary production measurements and N input inventories from land and atmosphere are available, but there are few studies that also provide estimates of the gross flux of DIN into the estuary from the coastal ocean. This version also includes recent measurements of ¹⁴C uptake from the Sargasso Sea and the North Pacific made using "clean techniques," as well as revised estimates of DIN input to those systems.

The review of primary production measurements given by Seitzinger & Giblin (this volume) provides an area-weighted mean value of 165 g C m⁻² y⁻¹ for the entire North Atlantic shelf. The relationship shown in Figure 5 suggests that this level of production would be associated with a DIN input of about 0.5 moles N m⁻² y⁻¹ over the total shelf area (0–200 m) of $5.6 \cdot 10^6$ km² (Pilson & Seitzinger, this volume). The total required flux of $2.9 \cdot 10^{12}$ moles DIN y⁻¹ might consist of 0.6– $0.8 \cdot 10^{12}$ moles N from land and atmosphere (if we ignore the fact that a significant but unknown fraction of the N flux from large rivers and estuaries is organic N) and 2.2– $2.3 \cdot 10^{12}$

	$mmol\ N\ m^{-1}\ s^{-1}$	$mol N m^{-2} y^{-1}$
Scotian Shelf ¹	1.9	0.32
Georges Bank ²		5.0
New York Shelf ³		4.6
New York Shelf ⁴	3.4	0.8
Mid Atlantic Shelf ⁵	4.0	1.1

Table 18. Estimates of the flux of nitrate from slope waters onto various regions of the North Atlantic continental shelf

5.7

5.6

1.0

Walsh et al. (1987); estimate for entire area within 60 m isobath.

Outer Southeast U.S. Shelf⁶

Southeast U.S. Shelf⁷

moles of DIN from the slope. These values are consistent with the range of $1.7-6.2 \cdot 10^{12}$ moles DIN y^{-1} we calculated for the flux from the slope water by extrapolating from the measurements off Nova Scotia and the east coast of the U.S. Considering the uncertainty in all of these numbers, we accept a range of $2-6 \cdot 10^{12}$ moles DIN y^{-1} as a reasonable working estimate for the gross flux onto the shelf from the deeper ocean.

Since dissolved inorganic phosphorus (DIP) is present in the slope water with a DIN/DIP ratio of approximately 16, we estimate that the DIN flux of $2-6 \cdot 10^{12}$ moles y⁻¹ would be accompanied by a DIP flux of $0.12-0.37 \cdot 10^{12}$ moles y⁻¹. This compares with the addition of only $0.02-0.03 \cdot 10^{12}$ moles of active P onto the shelf from large rivers and estuaries (Table 17).

The onwelled slope waters also contain particulate and dissolved organic N and P, but we do not know how to make a credible estimate of their flux onto the shelf. This may be of little consequence because we assume that the concentration of particulate organic matter in the deeper slope water is low and that the dissolved organic matter is sufficiently refractory that it is not metabolized to any significant degree during its relatively brief residence time on the shelf (e.g., about three months on the southeast U.S. shelf, Menzel et

¹ Houghton et al. (1978); flux per unit length of shelf at 50–100 m; area estimate for entire width of shelf.

³ Walsh et al. (1987). It is not clear how much of the entire shelf is included in this estimate of flux per unit area.

⁴ Flux per unit length of shelf-slope break from Walsh et al. (1987); flux per unit area for entire shelf calculated using a mean width between Long Island and Cape May of 139 km (Stommel & Leetma 1972).

⁵ Flux per unit length of 900 km long shelf from Csanady (1990); flux per unit area calculated for entire shelf area assuming a mean width between Nantucket shoals and Cape Henry of 113 km (Stommel & Leetmaa 1972).

⁶ Flux per unit area calculated assuming slope waters only influence the outer 1/3 of the shelf area (Verity et al. 1993).

⁷ Flux per unit length from Verity et al. (1993); flux per unit area calculated for entire width of shelf as given by Menzel et al. (1993).

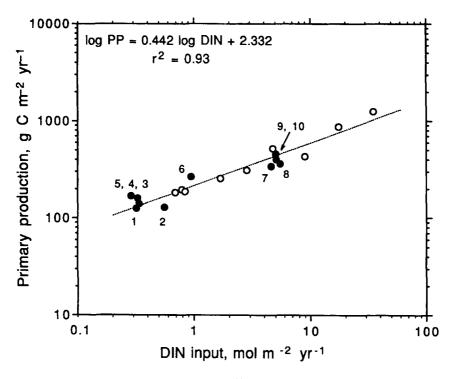


Figure 5. Primary production by phytoplankton (14C uptake) as a function of the estimated rate of input of dissolved inorganic nitrogen (DIN) per unit area in a variety of marine ecosystems. The open circles are for large (13 m³, 5 m deep) well-mixed mesocosm tanks at the Marine Ecosystems Research Laboratory (MERL) during a multi-year fertilization experiment (Nixon et al. 1986; Nixon 1992). Natural systems (solid circles) include (1) Scotian shelf - DIN from Houghton et al. (1978), production from Mills & Fournier (1979), (2) Sargasso Sea - DIN from Jenkins (1988), production from Lohrenz et al. (1992) mean of 1989 and 1990 values of 110 and 144 g C m⁻² y⁻¹, (3) North Sea – DIN from Laane et al. (1993) assuming that the ratio of DIN/TN in the input from the Atlantic equals that in the Channel, production from Seitzinger & Giblin (this volume), (4) the Baltic Sea - DIN and production from Rönner (1985), including DIN flux across the halocline, (5) North Central Pacific - DIN from Platt et al. (1984), production from Tupas et al. (1993, 1994) mean of 1992 and 1993 values of 150 and 185 g C m⁻² y⁻¹, (6) Tomales Bay, CA, DIN and production from Smith (1991), (7) Continental shelf off New York - DIN and production from Walsh et al. (1987), (8) Outer continental shelf off southeastern U.S., DIN and production from Verity et al. (1993), (9) Peru upwelling – DIN calculated from annual mean upwelling rate of 0.77 m d⁻¹ (Guillén & Calienes 1981) and an initial 20 µM concentration of NO₃ in upwelled water (Walsh et al. 1980), production off Chimbote from Guillén & Calienes (1981), (10) Georges Bank – DIN from Walsh et al. (1987), production from O'Reilly et al. (1987). The equation is a functional regression.

al. 1993). As a practical matter, there may be essentially no net exchange of dissolved organic N or P between shelf and slope, and we ignore these fluxes in our budgets.

This discussion of the additions of N and P to the shelf from the slope leads directly to the last term in the shelf budget — the flux of N and P off the shelf. We have already established that the loss of N from the shelf in denitrification and burial exceeds the input from land and atmosphere (Table 17), but the onwelling of DIN from the slope is potentially large enough to meet the deficit and leave a large amount of excess N on the shelf. The onwelling of DIP is also much larger than the potential export of terrestrial P from the shelf (Table 17). Since the concentrations of N and P on the North Atlantic shelf as a whole are presumably not increasing (except perhaps in some local areas near shore), we can calculate this last term in the shelf N and P budgets by difference. Before proceeding to do so, however, it is useful to make some effort to estimate the amount of shelf to slope transport that consists of organic N and P in the form of phytoplankton detritus.

Export of organic N and P from the shelf

There has been a considerable recent effort along the Atlantic Coast of the U.S. to measure the loss of organic matter from the shelf and its possible accumulation in slope sediments. Much of the motivation for this work has come from the suggestion that such burial may be an important sink in the global carbon budget (e.g., Walsh et al. 1981, 1985; Walsh 1991). Unfortunately, it is difficult to measure the rate and extent of burial and, as noted by Yoder & Ishimaru (1989), "the magnitude of off-shelf phytoplankton carbon transport, the processes affecting the transport rate and the significance of such processes to global budgets are in dispute ..." For example, while Walsh et al. (1987) estimated that 2.2 moles N m⁻² y⁻¹ were exported to the slope from the shelf off New York (52% of the N consumed in annual primary production), a more recent budget developed for the same area by Rowe et al. (1988) concluded that there "... was little evidence that substantial organic matter escapes from the continental shelf to the upper continental slope." It is also apparent that the flux of organic matter from the shelf is not uniform. Even in an area thought to be an important export region, such as the slope off Cape Hatteras, NC (USA), measurements have shown highly variable rates of carbon and nitrogen burial over relatively small (150-180 km) distances (DeMaster et al. 1994).

Based on detailed studies of the carbon budget of the mid-slope deposition center of the Middle Atlantic Bight, Anderson et al. (1994) recently concluded that less than 2% of the shelf primary production could be buried in slope sediments. If we assume that an export of 1–2% of primary production might be realistic for the North Atlantic shelf as a whole, then the total primary production of $76.4 \cdot 10^{12}$ moles C y⁻¹ estimated by Seitzinger & Giblin (this volume) would give a flux of $0.76-1.53 \cdot 10^{12}$ moles C y⁻¹ from the shelf

to the slope. If this is fresh organic matter with a Redfield C:N:P ratio of 106:16:1, there would be an associated loss of $115-230 \cdot 10^9$ moles of N and $7-14 \cdot 10^9$ moles of P. This would represent a return to the slope in organic form of about 2-12% of the onwelled DIN and DIP.

The Balance of Total N and P on the North Atlantic shelf

The various estimates summarized in Table 19 suggest a picture that is very different from textbook sketches that show N and P from land fertilizing the ocean. Denitrification in estuaries and on the continental shelf appears to return to the atmosphere an amount of N that exceeds the total N input from land and the atmosphere. If the estimates developed by Seitzinger & Giblin (this volume) and in this paper are approximately correct for the North Atlantic as a whole, denitrification also consumes between about 12 and 37% of the DIN brought onto the shelf from the deeper ocean. Overall, our budget suggests that the ocean provides a net flux of about 700–950 \cdot 10⁹ moles N y⁻¹ to the North Atlantic shelf (Table 19), an amount approximately equal to the total N input from all other sources combined. If N associated with river sediments buried on the continental slope is included in the balance, the net loss from the ocean would be reduced by about $60 \cdot 10^9$ moles y^{-1} .

The situation with regard to P is quite different. About 70% of the total flux of P from the North Atlantic drainage basin is carried by the five very large rivers that discharge directly on the shelf. Even allowing for the burial of a large amount of this P in the deltas of the rivers and in riverine sediments deposited over the shelf-slope break, the addition of active P from these systems is 2–8 times greater than the removal of P from the shelf in fisheries and the burial of organic matter on the shelf (Table 19). The combination of $11-19\cdot 10^9$ moles P that likely escape from estuaries, plus the $13\cdot 10^9$ moles of active P from the large rivers provides for a net export of P from the shelf to the ocean that amounts to about $17.7-30.4\cdot 10^9$ moles P y⁻¹ (Table 19). An additional $20\cdot 10^9$ moles P y⁻¹ may reach the ocean but remain buried on the slope.

Since the shelf appears to be such a strong sink for N while allowing P to pass from land to the ocean, there could be a marked reduction in the N/P ratio of water during residence on the shelf. The estimates compiled in Table 19 suggest that the ratio of DIN/DIP exported from the shelf might be somewhere between 7 and 13. However, the large range again emphasizes the very preliminary stage of the shelf budget developed in Table 19. While it is clear that there is a great potential for biogeochemical processes in estuaries and on the shelf to modify greatly the exchange of N and P between land and the ocean, it is also clear that our ability to quantify that influence is still far from satisfying. The next order of business should be to obtain

Table 19. A preliminary assessment of the annual mass balance of active N and P on the continental shelf (0–200m) of the North Atlantic Ocean. Units are 10^9 moles y^{-1} . These estimates do not include an additional $122 \cdot 10^9$ moles y^{-1} of N and $40 \cdot 10^9$ moles y^{-1} of P that are carried by five very large rivers and buried with riverine sediments in deltas and on the continental slope. See text.

	N	P
Inputs		
Direct atmospheric deposition ¹	133	Very small
Biological nitrogen fixation ²	~20	0
Estuaries ³	172-335	11–19
Very large rivers ⁴	292	13
Continental slope ⁵	2000-6000	120-370
•	2617–6780	144-402
Changes in storage		
Organic matter buried on shelf ⁶	19–95	0.4-4.1
Outputs		
Fish landings ⁷	27-38	1.2-2.2
Denitrification ⁸	1430	0
Continental slope		
As organic detritus ⁹	115-230	7–14
As DIN and DIP ¹⁰	824-5189	124-393

¹ From Table 13.

direct measurements of denitrification in a variety of shelf environments, to improve our estimates of P burial, and to extend our knowledge of shelf-slope exchanges to additional areas. There is also great room for improvement in our understanding of the amount and fate of N and P associated with the sediments carried by the large rivers.

² Prorated on the basis of world shelf rate from Walsh (1988).

³ From Table 12 minus footnote values.

⁴ From Table 1, minus burial in deltas and on the slope (see Table 2).

⁵ See Table 18 and Text.

⁶ From Table 16.

⁷ From Table 15.

⁸ From Table 14; includes shallow areas around Greenland and Iceland.

⁹ Assuming 1–2% of primary production exported See text.

 $^{^{10}}$ Calculated by difference. Ranges from maximum input minus minimum losses and vice versa. Thus, total flux to the slope = 1054– $5304 \cdot 10^9$ moles N y⁻¹ and 138– $400 \cdot 10^9$ moles P y⁻¹.

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