Sources and cycling of nitrogen in the Gulf of Maine

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Abstract

An analysis of water mass flows and nitrogen fluxes in the Gulf of Maine region shows that deep Slope Water that enters the Gulf through the Northeast Channel, and Scotian Shelf Water that enters at the surface, dominate the flux of nitrogen into the Gulf. A box model is developed that examines internal vertical nitrogen fluxes, and reveals that the flux of nitrogen into surface waters is sufficient to explain only about 59 gC m$^{-2}$ yr$^{-1}$ of new primary production, which is 20% of the total estimated Gulf of Maine primary production of 290 gC m$^{-2}$ yr$^{-1}$. This means that the Gulf-wide $f$ ratio (of "new" NO$_3$-based production to the total production based on both new NO$_3$ and recycled NH$_4$) is 0.20, which is more typical of oligotrophic oceans than a productive continental shelf sea like the Gulf of Maine. The expected $f$ ratio is nearer to 0.4, which would require an additional flux of new NO$_3$ into the Gulf equal to about 40% of the total flux already accounted for by all sources: Slope Water, Scotian Shelf Water, rivers and atmospheric deposition. This additional supply of "new" nitrogen is argued to be the result of water column nitrification. The box model also shows, surprisingly, that nutrients delivered to surface waters of the Gulf by Scotian Shelf Water are roughly equal to that of Slope Water. It is concluded that better estimates are needed of water flows into and out of the Gulf, along with more measurements of their nutrient loads, and that measurements should be made of water column nitrification rates. An overall conclusion is that the energetics of vertical mixing processes that deliver nutrients to the productive surface waters set the upper limit to biological production in the Gulf of Maine, and that construction of carbon and nitrogen budgets that consider only fluxes into and out of the Gulf, and not internal recycling, will be in error. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Gulf of Maine; nitrogen; geochemical cycle; models

1. Introduction

The Gulf of Maine is a continental shelf sea situated between Cape Cod, Massachusetts, and southwestern Nova Scotia. A number of shoals and banks effectively isolate the Gulf of Maine from the North Atlantic Ocean (Fig. 1); the most prominent of these barriers is Georges Bank. At depths exceeding 100 m, the exchange of waters and the materials they carry between the Gulf and the North Atlantic is confined to the Northeast Channel between Georges Bank and Browns Bank. Within the interior of the Gulf are three major deep basins: Georges, Jordan, and Wilkinson, which are relatively isolated from one another below the 200 m isobath. Georges Basin is the deepest of the three (370 m) and is an exten-
Fig. 1. Map of the Gulf of Maine, with features referred to in the text. The 60, 100, 200 and 2000 m isobaths are indicated, as are the 3 stations (21, 43 and 58) referred to in Fig. 4 and the Northeast Channel Stations (36 and 37) referred to in Fig. 3.

The northeastward extension of the Northeast Channel into the Gulf. These physical characteristics of deep basins and limited deep water exchanges with the Atlantic Ocean are coupled with other important features and processes that together dominate nitrogen fluxes and carbon cycling in the Gulf. They include: vertical mixing by tides (Garret et al., 1978); seasonal extremes in heat fluxes, which lead to winter convection and vertical stratification in summer; pressure gradients from the density contrasts set up by Slope Water (SLW) inflows and river runoff (Brooks, 1985; Pettigrew et al., 1996) and influxes of the cold, but fresher waters associated with Scotian Shelf Water (Smith, 1983). The result of all these processes is believed to be a fairly productive marine ecosystem in terms of nitrogen fluxes and organic carbon production.
The nature of the productivity of the Gulf’s inshore areas and offshore banks is well known (Bigelow, 1926, 1927; Bigelow et al., 1940). Levels of primary production in offshore waters, the least productive areas in the Gulf of Maine, average about 290 gC m$^{-2}$ yr$^{-1}$ (O’Reilly and Busch, 1984; O’Reilly et al., 1987). The principal source of nutrients that support this primary production has been thought to be primarily the influx into the Gulf of nutrient-rich deep Slope Water through the Northeast Channel (Ramp et al., 1985; Schlitz and Cohen, 1984; Townsend, 1991). Once delivered into the Gulf, the high concentrations of inorganic nutrients that accompany these deep SLW intrusions are delivered upward to the surface by various mechanisms and thus eventually are made available for planktonic primary production. Townsend, 1991 has reviewed the major nutrient flux mechanisms in the Gulf and discussed three important pathways that deliver new nitrogen to the surface: (1) vertical mixing by tides and upwelling in the eastern Gulf and on the southwest Scotian Shelf, (2) vertical fluxes across the seasonal pycnocline, and (3) winter convection, which supplies the standing stock of nutrients that fuels the spring phytoplankton bloom.

Upwelling of new nitrogen off the southwest Scotian Shelf and off the eastern Maine coast has been studied (Denman and Herman, 1978; Townsend et al., 1987; Brooks and Townsend, 1989), but very little is known about levels of primary production that result from the nutrient fluxes driven by either winter convection (which precedes the spring phytoplankton bloom) or from vertical mixing across the seasonal pycnocline at other times of the year. Ongoing research is presently directed at the possible role that internal waves might have in promoting vertical nutrient fluxes during the stratified season (Townsend et al., 1996). It is becoming apparent that internal waves may promote vertical nutrient fluxes by way of direct mixing across the pycnocline (Townsend et al., 1996) as well as by vertically oscillating populations of phytoplankton and nutrient-rich waters through an exponentially decaying light field (Pettigrew et al., 1997). Pettigrew et al., 1997 showed that, theoretically, the latter process could enhance specific primary production rates by as much 65% above measured rates during the stratified season in the offshore Gulf. This additional primary production would be “new” primary production (e.g. Dugdale and Goering, 1967) rather than “recycled” production, which normally domimates in stratified waters. Of the three vertical flux mechanisms identified winter convection may be the most important because of the potential importance of the spring bloom in these waters (Townsend and Cammen, 1988; Townsend et al., 1994a). To date, however, there have been no organized studies focused on Gulf-wide spring bloom phenomena.

The purpose of this communication is to examine the various fluxes of nitrogen into and out of the Gulf of Maine as they are controlled by advective exchanges with waters outside the Gulf, by atmospheric deposition, and by riverine fluxes, and then to examine how nitrogen is cycled internally in the Gulf.

2. Approach

In setting relevant bounds for this exercise, it is important to assess first the significance of smaller spatial scales to overall planktonic production. In particular, the importance of estuaries and near-shore environments should be evaluated. Townsend, 1991 estimated the rate of new primary production in the Gulf of Maine’s estuaries to be ca. $8.3 \times 10^{11}$ gC yr$^{-1}$. Averaged over the entire area of the Gulf of Maine ($1.03 \times 10^{11}$ m$^2$) in order to assess the contribution of estuaries, this estimate gives a primary production rate of only ca. 8 gC m$^{-2}$ yr$^{-1}$. Given that the average rate of planktonic primary production in the Gulf of Maine is on the order of 290 gC m$^{-2}$ yr$^{-1}$ (O’Reilly and Busch, 1984; O’Reilly et al., 1987), it must be concluded that for the purposes of evaluating the cycling of carbon and nitrogen in the Gulf of Maine proper, estuaries and inshore areas can be ignored. For this reason, the simplified view of the Gulf of Maine, shown in Fig. 2, is used for this analysis whereby we consider first the major fluxes of water that carry loads of nitrogen (as well as direct atmospheric fluxes), and then examine in more detail the internal cycling processes. Published data were used where possible, especially estimates of water mass fluxes, although some data are new, having only been collected during the past year.
Fig. 2. Plan and cross-sectional views of important fluxes of water and its accompanying materials in the Gulf of Maine. This forms the basic conceptual framework for examining total nitrogen entering the Gulf, and total nitrogen exiting the Gulf, as a first step in studying the internal cycling of carbon and nitrogen.

MSW = Maine surface water; MIW = Maine intermediate water; MBW = Maine bottom water (Hopkins and Garfield, 1979).

Using these data and the simplified approach in Fig. 2 we examine the various important storage parameters and the rates associated with each of the flows between them.

3. Nitrogen cycling

The first nitrogen budget for the Gulf of Maine was published by Schlitz and Cohen, 1984, which underscored the importance of Slope Water fluxes into the Gulf through the Northeast Channel. Based on Schlitz and Cohen’s work, Townsend, 1991 assessed the major oceanographic processes that affect nitrogen fluxes in the Gulf, as discussed above. Later, Christensen et al., 1995 examined the nitrogen cycle in the Gulf with particular attention to the importance of sediment denitrification. With the major sources and processes indicated in Fig. 2, the nitrogen budget for the Gulf of Maine can be reconstructed where we compare for the first time the relative importance of the various fluxes and internal cycling processes.

Nutrient budgets often are based on attempts to balance estimates of planktonic primary and secondary production with nutrient fluxes. In the case of nitrogen, it is important to include a consideration of internal recycling and to quantify the relative importance of “new” and “recycled” primary production. As was pointed out by Dugdale and Goering, 1967, “… measurement of primary production alone is not enough to assess the capacity of a region to support production at higher trophic levels in the food chain”. They pointed out that, in theory, ammonia can cycle indefinitely, if the phytoplankton populations incur no losses whatsoever to zooplankton grazing or sinking. Under such conditions the phytoplankton would just keep fixing organic carbon and sharing the nitrogen forever. Thus, only by phytoplankton taking up nitrate, or nitrogen that is “new” to the system from external reservoirs, could there be any possibility of “export” production to either higher trophic levels, or for vertical flux to deep water reservoirs or burial in the sediments. Eppley and Peterson, 1979 followed up with Dugdale and Goering’s work and placed it all in a global primary production and carbon cycling scheme. They argued that in order for the system to not run down, the nutrients lost by exports must be replaced by external inputs, e.g. by the injection of nutrients from deep water into the euphotic zone (or other sources, such as atmospheric inputs). They thus defined the $f$ ratio, which is the ratio of nitrate uptake by phytoplankton to the uptake of both nitrate and ammonium, e.g.

\[
f = \frac{[\text{NO}_3^-]}{[\text{NO}_3^-] + [\text{NH}_4^+]}\]

For oligotrophic open ocean waters the $f$ ratio is generally on the order of 0.1, meaning that only ca. 10% of the primary production is “new” production, and the remainder (90%) is “recycled” produc-
tion dependent on ammonia. Productive near-shore and neritic systems (more like the Gulf of Maine) would have a larger \( f \) ratio, which Eppley and Peterson, 1979 suggest falls between 0.30 and 0.46. No data on \( f \) ratios are available for the Gulf of Maine, but Cochlan, 1986 measured rates on the western Nova Scotian Shelf of 0.67 in March, 0.27 in April and 0.30 in July.

Based on these concepts of new and recycled primary production, we view our new nitrogen budget accordingly. That is, we examine: (1) the primary production that would result from fluxes of nitrogen into the Gulf of Maine \( (N_{in}) \), based on the Redfield ratio of C:N, (2) losses of potential carbon production as a result of internal denitrification of that initial nitrogen flux once entered \( (N_{de-N}) \) and (3) organic carbon equivalents of fluxes of nitrogen out of the Gulf of Maine \( (N_{out}) \), where:

Potential exports = \( (N_{in} - N_{de-N} - N_{out}) \)

This then allows an estimate of the potential annual new primary production that would be available for export to fisheries, or other forms of export, such as migratory species. The next step is to take the ratio \( (R) \) of the estimated potential primary production that would result from fluxes of new nitrogen into the surface waters to measurements of total primary production (which include both new and recycled), as:

\[
R = \frac{\text{N flux into MSW}}{290 \text{ gC m}^{-2} \text{ yr}^{-1}}
\]

Potential new PP = \( \frac{\text{Total measured PP}}{f \text{ ratio}} \)

where MSW is Maine surface water and PP is primary production. The ratio \( (R) \) is one way to estimate the \( f \) ratio discussed earlier for the Gulf as a whole over an annual cycle but it would not account for any internally recycled nitrogen that occurs by way of nitrification within the Gulf. That is, if any of the new nitrogen that enters the Gulf is remineralized and internally recycled back to nitrate, by way of internal nitrification processes, then the calculated \( f \) ratio \( (R) \) will be an underestimate. Therefore, forcing \( R = f \) ratio of 0.4 (chosen arbitrarily within the range 0.30 to 0.46 given for near-shore areas by Eppley and Peterson, 1979) necessitates our accounting for enough new nitrogen fluxes in the numerator of the above equation for it to equal 0.4. If we come up short—if our computed \( R < 0.4 \)—then we must concede that either the nitrogen flux estimates are in error, or that there is internal nitrification in the Gulf that “re-creates new nitrate”. A tally of input and output fluxes of nitrogen in the Gulf of Maine is given in the following sections.

### 3.1. Riverine sources of nitrogen

The volumes of river waters entering the Gulf of Maine region are given in Table 1, which shows that the greatest volume of river water comes from Maine and New Brunswick. Thus, we may take as representative concentrations of both dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) the values obtained by Mayer et al., 1996 which are on the order of 10\( \mu \)M nitrogen for three river systems in Maine (the Kennebec, Damariscotta and Sheepscot Rivers). The product of total river flow \( (8.049 \times 10^{10} \text{ m}^3 \text{ yr}^{-1}) \) and nitrogen concentration \( (1 \times 10^{-2} \text{ gatm}^{-3}) \) gives a flux of \( 5.7 \times 10^{7} \text{ gN yr}^{-1} \) into the Gulf.

### 3.2. Atmospheric deposition of nitrogen

Atmospheric deposition of nitrogen in the marine environment is receiving a great deal of attention in recent years (Lovett, 1994, Jickells, 1995; Paerl, 1995). On a global scale, the magnitude of the contribution of atmospheric fluxes of nitrogen is comparable with that from rivers, with rivers con-

<table>
<thead>
<tr>
<th>Province/state</th>
<th>Annual total (m³ yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nova Scotia</td>
<td>0.085 x 10¹⁰</td>
</tr>
<tr>
<td>New Brunswick</td>
<td>3.438 x 10¹⁰</td>
</tr>
<tr>
<td>Maine</td>
<td>3.302 x 10¹⁰</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>0.480 x 10¹⁰</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>0.744 x 10¹⁰</td>
</tr>
<tr>
<td>Total</td>
<td>8.049 x 10¹⁰</td>
</tr>
</tbody>
</table>
tributing a flux of between 1500 and 3570 × 10^9 moles N yr^{-1}, and the atmosphere contributing 2140 × 10^9 moles N yr^{-1} Jickells, 1995. Data from Lovett, 1994 show that the atmospheric (wet) deposition of NH_4 and NO_3 to the Gulf of Maine area is on the order of 10 kg NO_3 hectare^{-1} yr^{-1}, and 1.5 kg NH_4 hectare^{-1} yr^{-1}. This is equivalent to 0.0208 moles NO_3-N m^{-2} yr^{-1} and 0.0088 moles NH_4-N m^{-2} yr^{-1}. Numbers of Lovett, 1994 are of the same order of magnitude as those measured by R. Talbot and B. Mosher of the University of New Hampshire in their study of atmospheric deposition in the Gulf of Maine region (e.g., Mosher et al., 1996). They found that the total deposition of nitrogen, including both wet and dry phases of nitrate and ammonia, was about 0.09 moles N m^{-2} yr^{-1} in 1994 and 0.04 moles N m^{-2} yr^{-1} in 1995. Nixon et al., 1995 reported that Narragansett Bay receives about 0.09 moles N m^{-2} yr^{-1}. Thus, a value of 0.09 moles N m^{-2} yr^{-1} is taken as representative for this discussion.

### 3.3. Advecive fluxes of nitrogen

Fluxes of water into and out of the Gulf of Maine, as diagramed in Fig. 2, are summarized in Table 2. We see that the major fluxes are associated with the inputs from Scotian Shelf Water, which is a low salinity, cold water mass that enters the Gulf at the surface around southwestern Nova Scotia (Smith, 1983), and deep Slope Water that enters the Gulf along the bottom through the Northeast Channel (Hopkins and Garfield, 1979). The major outputs are associated with Maine intermediate water (MIW) and Maine surface water (Hopkins and Garfield, 1979). These major water masses will carry nitrogen into and out of the Gulf of Maine and thus impart control over the production of organic carbon. Using the water budget in Table 2, and known concentrations of nitrogen in the various water masses in the Gulf of Maine region, the advective fluxes of nitrogen identified in Fig. 2 can be evaluated. The water mass with the highest nitrogen concentrations is Slope Water (Schlitz and Cohen, 1984; Ramp et al., 1985) which can be operationally defined as waters with salinity > 34. Slope Water is shown in Fig. 3 for two stations sampled in the Northeast Channel in April of 1994. The near-surface waters at both stations are colder and fresher than waters beneath and no doubt reflect a contribution from Scotian Shelf Water. At Station 37, Slope Water is present below a depth of about 150 m, while at Station 36, it is present as two forms, beginning below a depth of about 40 m. The distinct water mass at Station 36 between 40 and 160 m (temperature > 9–10°C and salinity > 35) is described as upper Slope Water, or warm Slope Water (WSW) by Ramp et al., 1985. Beneath the WSW is a bottom water layer of Labrador Slope Water (LSW; Ramp et al., 1985; salinity > 35, temperature ca. 8.2°C). The dissolved inorganic nitrogen (DIN) concentrations at depth are noticeably higher at Station 36 than Station 37, and most likely reflect the contribution of higher nutrient concentrations in WSW than LSW at the same depth in the water column. Thus, the question becomes: what concentration of DIN can be ascribed to waters entering the Gulf of Maine through the Northeast Channel? The deep Slope Water has a nitrite + nitrate concentration as high as 21 μM (e.g. at Station 36). Shallower Slope Water DIN concentrations (nitrate + nitrite concentration at 34 psu salinity) are as low as 13 μM (at both Stations 36 and 37). A linear average would be 17 μM for Slope Water. The other major influx of water and nutrients into the Gulf is via Scotian Shelf Water, which has DIN concentrations on the order of 5 μM (Christensen et al., 1995).

### Table 2

Water budget for the Gulf of Maine (modified from Christensen et al., 1995; additional data from Ramp et al., 1985; Schlitz and Cohen, 1984; McAdie, 1994)

<table>
<thead>
<tr>
<th>Process</th>
<th>Volume (10^{12} m^3 yr^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inputs</td>
<td></td>
</tr>
<tr>
<td>Northeast Channel</td>
<td>8.7</td>
</tr>
<tr>
<td>Scotian Shelf Water</td>
<td>6.31</td>
</tr>
<tr>
<td>rivers</td>
<td>0.08</td>
</tr>
<tr>
<td>precipitation</td>
<td>0.08</td>
</tr>
<tr>
<td>Outputs</td>
<td></td>
</tr>
<tr>
<td>MSW</td>
<td>5.04</td>
</tr>
<tr>
<td>MIW</td>
<td>10.06</td>
</tr>
<tr>
<td>evaporation</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Evaporation is assumed to equal precipitation plus river inputs (which may not be true); MIW = Maine intermediate water; MSW = Maine surface water (Hopkins and Garfield, 1979). MSW and MIW output volumes assume that MSW extends from the surface to 25 m depth, MIW extends from 25 to 75 m depth, and that the sum of these two volumes equals NE Channel and Scotian Shelf Water inputs.
Fluxes out of the Gulf are associated with Maine surface water and Maine intermediate water (Hopkins and Garfield, 1979). Because Ramp et al., 1985 estimated Slope Water influxes through the Northeast Channel to be below 75 m depth, the outputs of MSW and MIW are assumed in this exercise to be associated with waters from 0–75 m depth, with MSW being 0–25 m and MIW being between the base of MSW and 75 m. The volume flows are computed as simple proportions, with no consideration given to possible variations in flow with depth. The estimated nitrogen loads accompanying these outputs of MSW and MIW do not include the dissolved organic nitrogen (DON) or particulate organic nitrogen (PON); DON concentrations can be similar to DIN in coastal waters, and an order of magnitude greater than PON (Sharp, 1983). Because no data are available on DON for the Gulf of Maine, it is
assumed that the flux of DON and PON into the Gulf is equal to the flux out; if true, these fluxes cancel out and are therefore not considered. There are, however, numerous data available on DIN concentrations in the Gulf. Annually averaged DIN concentrations are estimated to be 3.5 $\mu$M for MSW (which ranges from near 0 $\mu$M in summer to ca. 8 $\mu$M in winter), and 8 $\mu$M in MIW (Townsend and Christensen, 1986; Townsend et al., 1987). These data, and those in the literature cited, produce the approximate advective fluxes into and out of Gulf as given in Table 3.

Table 3 reveals that the bulk of the nitrogen flux into the Gulf of Maine is associated with Slope Water. The influence of this water mass throughout the Gulf of Maine can be seen in Fig. 4, which shows the differences in deep water nitrate concentrations as a function of proximity to the Northeast Channel source of Slope Water. The general trend is for deep waters in the western Gulf to have lower concentrations of nitrate.

### 3.4. Losses of nitrogen

In addition to the processes just discussed, whereby we arrive at the figures shown in Table 3, Christensen et al., 1995 have shown that some nitrogen is “lost” through other mechanisms: by the processes of denitrification, burial in the sediments, and other exports (such as that attributable to fisheries landings, migratory fishes, whales and birds, etc.). Christensen et al. showed that as the high nutrient, deep Slope Water spread at depth across the Gulf of Maine’s basins, there is an apparent loss of DIN from east to west. For example, their data show that DIN, plotted against phosphate, is depleted in the western Gulf (e.g., in Wilkinson Basin in the west as compared with Jordan Basin in the east; Fig. 1); silicate, on the other hand, does not show this depletion toward the west. Those data argue for significant sediment denitrification that acts to remove DIN from the overlying water column; this removal was estimated by Christensen et al., 1995 to be $33.1 \times 10^9$ gat N yr$^{-1}$. Loss of nitrogen as a result of burial is given as $5 \text{ gC m}^{-2} \text{ yr}^{-1}$; with a C:N ratio of 10, this converts to a burial rate for nitrogen of $4.4 \times 10^9$ gat N yr$^{-1}$ (Christensen, 1989).

The analysis presented in Table 3 shows that there is a net flux of nitrogen into the Gulf of Maine of $53 \times 10^9$ gat N yr$^{-1}$. The net flux term divided by the area of the Gulf ($1.03 \times 10^{11}$ m$^2$) gives an area-specific flux rate of 0.52 gat N m$^{-2}$ yr$^{-1}$.

### Table 3

<table>
<thead>
<tr>
<th>Flux</th>
<th>Volume $(10^{12} \text{ m}^3 \text{ yr}^{-1})$</th>
<th>[N] $(\mu\text{gat N l}^{-1})$</th>
<th>N flux yr$^{-1}$ $(10^9 \text{ gat N yr}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inflows</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>atmosphere (wet and dry)$^a$</td>
<td></td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>rivers $^b$</td>
<td>0.08</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>Scotian Shelf Water $^b$</td>
<td>6.31</td>
<td>5.0</td>
<td>31.5</td>
</tr>
<tr>
<td>Slope Water (NE Channel)$^b$</td>
<td>8.7</td>
<td>17</td>
<td>147.9</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>189.5</td>
</tr>
<tr>
<td><strong>Outflows</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSW $^c$</td>
<td>5.04</td>
<td>3.5</td>
<td>17.6</td>
</tr>
<tr>
<td>MIW $^c$</td>
<td>10.06</td>
<td>8.0</td>
<td>80.5</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td>98.1</td>
</tr>
<tr>
<td><strong>Other losses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>denitrification$^d$</td>
<td></td>
<td></td>
<td>33.1</td>
</tr>
<tr>
<td>burial$^e$</td>
<td></td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td><strong>Net flux</strong></td>
<td></td>
<td></td>
<td>+ 53.1</td>
</tr>
</tbody>
</table>

$^a$ From Talbot and Mosher, unpublished.
$^b$ Modified from Christensen et al., 1995 and McAdie, 1994.
$^c$ From Townsend and Christensen, 1986 and Townsend et al., 1987.
$^d$ From Christensen et al., 1995.
$^e$ From Christensen, 1989.

The fluxes are for the area of the Gulf, assumed to equal $1.03 \times 10^{11}$ m$^2$. 

The table above provides a summary of the fluxes of nitrogen into and out of the Gulf of Maine, based on the water budget in Table 2, and nitrogen concentrations as footnoted.
Multiplying by the Redfield ratio for carbon to nitrogen (5.67 by weight) gives a value of 3 gC m\(^{-2}\) yr\(^{-1}\) new net primary production that is available for transfer to higher trophic levels and subsequent export from the Gulf. This is equal to approximately 300,000 metric tons (MT) of carbon per year for the Gulf of Maine. But how realistic is this estimate of “exportable” production? Cohen and Grosslein, 1987 reported a value of 32 kcal/m\(^2\) for fish and squid production in the Gulf of Maine prior to the 1960s; this is converted by assuming 1 gC = 11.4 kcal, giving 289,000 MT carbon, which is close to our estimate, and lends some confidence to our calculations and assumptions.

The analyses in Table 3 can be used to construct a box model of nitrogen fluxes among the three water masses and bottom sediments in the Gulf, which is given in Fig. 5, and allows us to compare the nitrogen fluxes to measured rates of carbon fixation (primary production). The model shows that once we account for the inputs of DIN to the Gulf, into both Maine surface water (by atmospheric deposition, rivers, Scotian Shelf Water and Slope Water) and Maine bottom water (by Slope Water), and the outputs via fluxes of MSW and MIW, we arrive at a gross nitrogen flux into the productive surface waters of the Gulf (the MSW box in Fig. 5) of 41.6 \times 10^9 gat N yr\(^{-1}\) plus a vertical flux of 34.4 m \times 10^9 gat N yr\(^{-1}\) giving a total of 76 \times 10^9 gat N yr\(^{-1}\). This equals 0.74 gat N m\(^{-2}\) yr\(^{-1}\) when averaged for the area of the Gulf (1.03 \times 10^{11} m\(^2\)), and multiplying by the atomic weight of 14 for nitrogen, and the Redfield ratio of 5.67 (by weight), gives 59 gC m\(^{-2}\) yr\(^{-1}\) of potential new primary production. Divided by the total primary production of 290 gC m\(^2\) yr\(^{-1}\) gives an f ratio of only 0.20. We have already argued that the Gulf of Maine should have an f ratio of ca. 0.4, based on Eppley and Peterson, 1979. For this to be the f ratio, there would need to be a much greater flux of new nitrogen into the Gulf of approximately 152 \times 10^9 gat N yr\(^{-1}\), which is more similar to the gross inflows in Table 3, before exports are subtracted.
There are a couple possible sources of error that could explain this discrepancy between gross nitrogen fluxes into surface waters of the Gulf, as given by our box model \( (76 \times 10^9 \text{ gat N yr}^{-1}) \), and the expected flux, based on an \( f \) ratio of 0.4 and measured total primary production (twice the former, or \( 152 \times 10^9 \text{ gat N yr}^{-1} \)). One obvious error would be the assumption of an \( f \) ratio of 0.4. Could 0.20 be the actual value? To answer this question would require actual measurements of new and recycled primary production in the Gulf, and to date there have been none. Another source of error could be our flux estimates in Table 3. For example, Ramp et al., 1985 reported that their annually averaged estimated influx of Slope Water of \( 262 \times 10^3 \text{ m}^3 \text{ s}^{-1} \) has a standard deviation of \( 199 \times 10^3 \text{ m}^3 \text{ s}^{-1} \). (Their measurements also showed that the residence time of the deeper waters in the Gulf are on the order of 1 year.) But if we accept the average fluxes given in Table 3, then we need to provide an additional annual nitrogen flux into surface waters of ca. \( 76 \times 10^9 \text{ gat N yr}^{-1} \), which is shown by the dashed box in Fig. 5 as the presumed result of nitrification of vertically settling organic material into Maine intermediate water, and its subsequent vertical flux back into surface waters as an additional source of new nitrate.

The box model also illuminates the significance of Scotian Shelf Water relative to Slope Water: they are about equal. That is, much of the nutrient flux into the Gulf via Slope Water leaves the Gulf with exiting intermediate waters or is denitrified. Only 23% of the nitrogen that comes in via Slope Water through the Northeast Channel is delivered upward to the surface layer (euphotic zone) where it becomes available to phytoplankton.

### 4. Nitrification in the Gulf of Maine

Throughout this exercise we have been working with “new” primary production, based on gross flux estimates of “new” nitrogen into the Gulf of Maine by way of the fluxes listed in Table 3. The problem with this approach is that there is evidence that “new” nitrogen may be “created” within the Gulf itself, and that therefore not all is from external sources. Our analysis argues for significant nitrification, whereby regenerated ammonia is oxidized to nitrite and then nitrate, at an annual rate that approximates 40% of the total nitrate (DIN) inflows (\( = 76/189.5 \)). Evidence of nitrification in the water column is seen in Fig. 6 for the western Gulf of Maine. Fig. 6 shows a very slight maximum in ammonia concentration at about 20 m, which is likely the result of heterotrophic grazer activity at that depth, producing recycled nitrogen from shallow water-produced organic matter. There is also a subsurface maximum in nitrite (\( \text{NO}_2^- \)) at about 40 m,

![Fig. 6: Profiles of ammonia, nitrite, nitrate, phosphate and silicate at Station 21](image-url)
which is coincident with the beginning of the nitricline, where nitrate (NO\textsubscript{3}) increases steadily with increasing depth below that. This ‘‘primary nitrite maximum’’ is most likely evidence of bacterial nitrification of ammonia at that depth, as has been described in other areas (e.g., Ward et al., 1989; Dore and Karl, 1996). The nitrite maximum is very near to, or in, the pycnocline (Fig. 6), and thus may be readily mixed into the upper mixed layer, or utilized by phytoplankton at that depth, which is normally the depth of the subsurface chlorophyll maximum layer. The box model analysis in Fig. 5 leads us to believe that such nitrification processes are responsible for a remineralization and recycling rate on the order of once per year for each nitrogen atom that enters the surface waters of the Gulf of Maine as new nitrogen from outside (primarily via Slope Water, which enters through the Northeast Channel, and Scotian Shelf Water).

Data from Rakestraw, 1936 show that such a nitrite maximum is present throughout the Gulf of Maine for much of the year; the depth of highest concentration of nitrite in Rakestraw’s data is similar to that in Fig. 6. His data showed that the highest concentrations appear to be related to the spring and fall seasons, and may be related to a greater vertical flux rate of organic material at those times. The extensive distributions of nitrite seen in Rakestraw (1936) data would suggest that water column nitrification is an important, but poorly understood process going on in the Gulf of Maine.

5. Conclusions

A number of significant conclusions can be drawn from this exercise, beyond those already given in earlier works (e.g. by Schlitz and Cohen, 1984; Ramp et al., 1985; Townsend, 1991; Christensen et al., 1995). First, it is clear that we need better estimates of the advective flows into and out of the Gulf of Maine, along with more detailed measurements of nutrient loads associated with the major flows. Slope Water through the Northeast Channel, and to a lesser extent Scotian Shelf Water, dominate the flux of nitrogen into the Gulf, but even slight errors in either the magnitude of the flows, or the loads of nutrients, or both, can have very large effects on the estimated net nutrient flux. Indeed, the standard error that Ramp et al., 1985 reported for the flow of Slope Water through the Northeast Channel is 69\% of the mean. The magnitude of those possible errors will dictate the level of significance we ascribe to rates of water column nitrification in the Gulf. Second, we must also conclude that we need to evaluate much better the significance of nitrification in intermediate waters in the Gulf of Maine by way of actual field measurements. The rate we ascribe in our box model is much greater than other coastal measurements reported by Kaplan, 1983 in his review, and is closer to rates he reported for Chesapeake Bay. Our box model approach arrived at an estimate only by way of subtraction, and includes all the uncertainties that come with all our flux estimates. Nonetheless, we conclude that nitrification is probably occurring at a rate on the order of once per year (76/[34.3 + 41.6]; Fig. 5) for each nitrogen atom that enters the surface waters of the Gulf from outside, which is attributable primarily to Scotian Shelf Water and Slope Water, in roughly equal proportions. We must face the fact that detailed measurements of advective flows of water and nutrients into the Gulf are only one part of the story, and nitrogen budgets so based could be in large error if internal nitrification is not taken into account. Third, actual measurements are needed upon which to base a better estimate of the seasonally averaged $f$ ratio in the Gulf of Maine. Using a value of 0.4 in our box model produces an estimate of $76 \times 10^9$ gat N yr$^{-1}$ being recycled internally in the Gulf (the dashed box in Fig. 5); a larger or smaller $f$ ratio will produce a proportional change in this estimate. A fourth conclusion is somewhat of a surprise: that nutrients that enter the Gulf of Maine at the surface via Scotian Shelf Water are as important as those that enter via the deep Slope Water that comes through the Northeast Channel. Although the initial gross flux into the Gulf via Slope Water is much greater, only 23\% of it reaches the surface layer where it becomes available to phytoplankton (see Fig. 5). And herein lies our final and most interesting conclusion: that the energetics of vertical mixing processes that deliver nutrients to the productive surface waters effectively set the upper limit to biological production in the Gulf of Maine. That is, the influx of new nitrogen alone
cannot sustain all the observed primary production, because much of that new nitrogen exits the Gulf before being made available to the primary producers. It is the subsurface waters, in the intermediate water layer where we see the primary nitrite maximum, that likely exchanges most energetically with surface waters and provides the nutrients to support the relatively high rates of primary production in the Gulf of Maine.

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