CHAPTER 16

Nitrogen Biogeochemistry and Modelling of Carmarthen Bay

R. F. C. Mantoura, N. J. P. Owens and P. H. Burkill

16.1 INTRODUCTION

It is apparent from recent reviews of nitrogen in the marine environment (Fogg, 1982; Carpenter and Capone, 1983) that most studies have concentrated on oceanic (McCarthy and Carpenter, 1983) upwelling (Codispoti, 1983), shelf and estuarine waters (Nixon and Pilson, 1983), with relatively few purposeful studies of bays, as distinct systems. Bays in their various forms and sizes are probably the most common feature of coastal morphology (Davies, 1977; King, 1972) and there is evidence that productivity and biogeochemical cycling in bays may often be greater than their surrounding waters (e.g. Chesapeake Bay (McCarthy et al., 1977); Lyme Bay (Pingree et al., 1983); Swansea Bay (Mantoura and Morris, 1980)). In this chapter we propose to highlight the sources and biogeochemical cycling of nitrogen in Carmarthen Bay, South Wales, and to identify and model some of the critical properties and processes of bay systems.

16.1.1 Carmarthen Bay physiography

Carmarthen Bay (CB, Figure 16.1) is a shallow (average 17 m), macrotidal and vertically mixed (Uncles and Joint, 1983) 'headland-type' bay (Zenkovitch, 1977) situated in the northwest Bristol Channel (50°40'N, 04°30'W). In common with other bays in South Wales, Carmarthen Bay evolved during the postglacial rise in sea level associated with the Flandrian transgression in the late Quaternary (Owens and Bridges, 1980; Steers, 1976). The bay margins consist of: (1) extensive stretches of alluvial/glacial sandy beaches and dunes in the northern and eastern regions including the Burry Inlet; (2) crenulated cliffs of Nemurian and Devonian Old Red Sandstone on the northwestern margins; and (3) two Carboniferous limestone headlands (Caldy Island and Worms Head) at the bay mouth (Steers, 1976). Carmarthen Bay is exposed to prevailing south-westerly swells and waves, and it is their oblique approach and refraction round headlands that controls coastal sediment transport and accretion of beach sands in the northeast.
Figure 16.1. Location, physiography, bathymetry, bay boundaries and sampling stations of Carmarthen Bay, South Wales, in relation to the Bristol Channel and the United Kingdom. Monitoring cruise track in the Bristol Channel and the Celtic Sea Study Station CS-2 are also shown.
The area, mean depth and volume of Carmarthen Bay (including the Burry Inlet) are $5.65 \times 10^8$ m$^2$, 17.3 m and $9.8 \times 10^9$ m$^3$ respectively (Admiralty Chart No. 1076). Although the tidal sandflats together with the Burry Inlet account for 20% of the bay area they correspond to only 3.6% of the high water bay volume. The bathymetric contours run parallel to the coastline but are perturbed by a 15 km shallow (~5 m) sandbank (Helwick Sands) directed westwards from Worms Head (Figure 16.1c) and which is aligned with strong tidal residuals of the northern Bristol Channel (Uncles, 1982). Thus tidal exchange of bay water with the Bristol Channel occurs predominantly from the southwest between Helwick Sands and Caldy Island. The tides, which are semidiurnal ($M_2$) with average range of 5.0 m (7.2 m springs, 2.9 m neaps; Admiralty Tide Tables, 1980), flow in a rectilinear orientation (E–W) at ~ 100 cm/s outside the bay, and swing northeast around Caldy Island reducing to less than 40 cm/s within the bay margins (Uncles, 1982). The tidal excursions in the inner and outer parts of the bay are in the order of 3 km and 14 km respectively.

Land-derived nutrients enter the bay by two river systems: the Taf/Towy/Gwendraeth confluence in the north (average flow: $5.6 \times 10^6$ m$^3$/d) and the River Loughor via the Burry Inlet in the east (average flow: $1.6 \times 10^6$ m$^3$/d; Welsh Water Authority). Both estuaries are completely flushed with each tide (Moore, 1977). The circulation and dispersion of water in CB is dominated by tidal exchange with the Bristol Channel (BC; $8.3 \times 10^8$ m$^3$/d) rather than river discharge (average flow $7.2 \times 10^6$ m$^3$/d).

16.1.2 Field and experimental methods

Nutrient cycling measurements were carried out during six cruises aboard the RRS John Murray in August 1979, March, May, August and October 1980 and January 1981. Two different cruise tracks designed (1) to cover the spatial heterogeneity of CB via a grid of stations (Figure 16.1c), and (2) to characterize the surrounding waters in the Bristol Channel via a monitoring track (Figure 16.1b). The standard grid consisted on an $8 \times 10$ nautical mile ($12.8 \times 16$ km) rectangular array of 29 stations which were serially sampled within a tidal cycle along E–W tracks as shown in Figure 16.1c. The variables measured, together with an outline of methods used, are summarized in Table 16.1, and will be detailed in other papers. The variables were measured synoptically and are based on a classical flow model of coastal nitrogen cycling (Figure 16.2) and include the uptake (process No. 6) of dissolved nutrients (1) such as $\text{NH}_4^+$ and $\text{NO}_3^-$ by phytoplankton (2). These are grazed (7) by zooplankton (3), which in turn excrete (8) $\text{NH}_4^+$ and organic forms of N back to the dissolved pool (1). This pool is also supplied by remineralization (10) from bacteria (4) and by sedimentary upflux (9) from the benthos (5). Account is also taken of river (11) inputs into the bay, and the water exchange (12), which occurs at the southern boundary of CB with the Bristol Channel. An important study of this aspect was
Table 16.1. Nutrient cycling parameters determined in Carmarthen Bay

<table>
<thead>
<tr>
<th>Process No.</th>
<th>Description and variables</th>
<th>Measurement mode</th>
<th>Sampling/Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dissolved inorganic nutrients (NO₃⁻, NO₂⁻, NH₄⁺, PO₄³⁻, SiO₂⁻)</td>
<td>S S</td>
<td>Automated shipboard analyses</td>
</tr>
<tr>
<td></td>
<td>Dissolved organic nutrients (DOC, DON, DOP, R-NH₂, urea)</td>
<td>D</td>
<td>Automated shipboard analyses</td>
</tr>
<tr>
<td></td>
<td>Other parameters: S‰, T, turbidity</td>
<td>C C</td>
<td>Automated shipboard measurements</td>
</tr>
<tr>
<td>2</td>
<td>Phytoplankton species and abundance</td>
<td>D C</td>
<td>Lugols, in vivo fluorescence, Chlo-a spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Particulates (POC, PON)</td>
<td>C D</td>
<td>Filteration, gravimetry</td>
</tr>
<tr>
<td>3</td>
<td>Zooplankton species and abundance</td>
<td>D D</td>
<td>Lowestoft oblique hauls; size fractionation, carbon, nitrogen analyses</td>
</tr>
<tr>
<td>4</td>
<td>Bacteria</td>
<td>D</td>
<td>Most probable numbers</td>
</tr>
<tr>
<td>5</td>
<td>Benthos</td>
<td>D</td>
<td>Meio- and macrobenthic analyses of core + grab samples. AO analyses</td>
</tr>
<tr>
<td>6</td>
<td>Phytoplankton N assimilation</td>
<td>D</td>
<td>¹⁵N (NO₃⁻, NO₂⁻, NH₄⁺, urea) and ¹⁴C-HCO₃ shipboard incubations</td>
</tr>
<tr>
<td>7</td>
<td>Zooplankton grazing</td>
<td>D</td>
<td>Estimated indirectly; modelling</td>
</tr>
<tr>
<td>8</td>
<td>Nitrogen excretion</td>
<td>D</td>
<td>Shipboard incubations of 4 size classes for NH₄⁺, PO₄³⁻, urea, R-NH₂, DOC excretion</td>
</tr>
<tr>
<td>9</td>
<td>Benthic upflux (NH₄⁺, NO₃⁻, PO₄³⁻)</td>
<td>D</td>
<td>Shipboard incubation of sediment cores and pore water analyses</td>
</tr>
<tr>
<td>10</td>
<td>Microbial mineralization</td>
<td>D</td>
<td>¹⁵N-isotope dilution</td>
</tr>
<tr>
<td>11</td>
<td>River inputs</td>
<td>D D</td>
<td>Hydrochemical correlation and Water Authority Data</td>
</tr>
<tr>
<td>12</td>
<td>Exchange with BC</td>
<td>D D</td>
<td>Tidal circulation model</td>
</tr>
</tbody>
</table>

* C = continuous sampling; S = semi-continuous sampling; D = discrete sampling
that all the rate measurements were done on board the vessel, making it possible to directly compare the importance of the various components in the N cycle.

### 16.2 COASTAL BAY MIXING AND GROWTH LIMITING NUTRIENTS

Whereas phytoplankton production in eutrophic inland waters (rivers, lakes) is typically phosphorus-limited (Vollenweider, 1975), in marine waters it is nitrogen-limited (Ryther and Dunstan, 1971; Nixon and Pilson, 1983). Since nutrient conditions in coastal waters are intermediate between these two environments it is necessary, in the first instance, to establish which element is the potentially growth-limiting nutrient in coastal bay systems.

The nutrient distributions for the Bristol Channel region (see Table 16.2) indicate that river concentrations of NO$_3^-$ and PO$_4^{3-}$ are, respectively, up to 7000 and 270 times greater than those in the Celtic Sea. Further, the molar NO$_3^-$:PO$_4^{3-}$ ratios decrease from 22 in the River Severn to ~1 in the seasonally stratified waters of the Celtic Sea. Since growing phytoplankton exhibit N:P assimilations ratios of 16 (Redfield ratio) it follows that the potential growth-limiting nutrient is P in the river inputs and N in the Sea. Thus a switch from potential P-limitation to potential N-limitation must occur in intermediate coastal waters simply as a consequence of estuarine mixing of compositionally different end members. This switch occurs at a critical salinity ($S_c$) when the NO$_3^-$:PO$_4^{3-}$ ratios fall below the Redfield ratio of 16.

The nutrient ratio profiles resulting from estuarine and coastal mixing can be modelled, in the first instance, by using a simple two-component conservative
Table 16.2. Nutrients in the Bristol Channel and Celtic Sea: concentrations, (µmol/l)

<table>
<thead>
<tr>
<th>Location/year</th>
<th>NO₃⁻</th>
<th>PO₄²⁻</th>
<th>NO₃⁻:PO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>River Severn</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1971</td>
<td>323</td>
<td>15</td>
<td>21.5</td>
</tr>
<tr>
<td>1979</td>
<td>540</td>
<td>24</td>
<td>22.5</td>
</tr>
<tr>
<td>Average 1974–1980</td>
<td>360</td>
<td>16</td>
<td>22.5</td>
</tr>
<tr>
<td><strong>Swansea Bay</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>May 1977</td>
<td>39</td>
<td>1.4</td>
<td>28.5</td>
</tr>
<tr>
<td>Aug. 1977</td>
<td>15</td>
<td>0.6</td>
<td>39.6</td>
</tr>
<tr>
<td>Nov. 1977</td>
<td>30</td>
<td>1.3</td>
<td>23.0</td>
</tr>
<tr>
<td>Jan. 1978</td>
<td>38</td>
<td>1.3</td>
<td>29.2</td>
</tr>
<tr>
<td><strong>Carmarthen Bay</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aug. 1979</td>
<td>0.44</td>
<td>0.06</td>
<td>7.3</td>
</tr>
<tr>
<td>Mar. 1980</td>
<td>18.4</td>
<td>1.03</td>
<td>17.9</td>
</tr>
<tr>
<td>May 1980</td>
<td>17.8</td>
<td>0.58</td>
<td>30.7</td>
</tr>
<tr>
<td>Aug. 1980</td>
<td>3.2</td>
<td>0.42</td>
<td>7.6</td>
</tr>
<tr>
<td>Oct. 1980</td>
<td>8.6</td>
<td>0.64</td>
<td>13.4</td>
</tr>
<tr>
<td>Jan. 1981</td>
<td>18.3</td>
<td>1.01</td>
<td>18.1</td>
</tr>
<tr>
<td><strong>Celtic Sea (St CS2; Figure 16.1a)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>surf., Aug. 1983(d)</td>
<td>0.1</td>
<td>~0.05</td>
<td>~2.0</td>
</tr>
<tr>
<td>surf., Aug. 1983(n)</td>
<td>0.5</td>
<td>0.10</td>
<td>5.0</td>
</tr>
<tr>
<td>surf., Sept. 1984(d)</td>
<td>0.008</td>
<td>~0.04</td>
<td>~0.5</td>
</tr>
<tr>
<td>deep., Aug. 1983</td>
<td>5.6</td>
<td>0.65</td>
<td>8.6</td>
</tr>
</tbody>
</table>

(d) Day samples; (n) night samples.

![Graph showing Nitrogen Cycling in Coastal Marine Environments](image-url)
Figure 16.3. (a) Winter variations of \( \text{NO}_3^- : \text{PO}_{4}^{3-} \) ratio with salinity in the Bristol Channel (•, March 1980; +, January 1981) in relation to modelled conservative mixing curves (eqn. (3), data Table 16.2) computed for summer (curve 1) and winter (curve 2) end-member conditions. Curve 3 corresponds to a hypothetical mesotrophic river concentration of one-tenth the 1979 River Severn concentrations. (b) Variation of \( \text{NO}_3^- : \text{PO}_{4}^{3-} \) ratio with salinity in the outer Bristol Channel for July/August 1979, in relation to the nutrient ratio model expanded to include increasing degrees \( (\theta = 0.0-0.9) \) of \( \text{NO}_3^- \)-depletion by phytoplankton (eqn. 4). Data regionally discriminated into central BC (•, △), Swansea Bay (■), Carmarthen Bay (▲) and Celtic Sea (○).

mixing model of freshwater \((f)\) and seawater \((s)\). If the seawater end-member salinity is \( S_0 \), then the conservative \( \text{NO}_3^- \) concentration \( (N_c) \) at salinity \( S_i \) can be calculated from:

\[
N_c = N_f(1 - R) + N_sR
\]
where $N_f$ and $N_s$ are the NO$_3^-$ concentrations in freshwater and seawater end-members respectively, and $R = (S_f/S_0)$. Similarly for PO$_4^{3-}$:

$$P_c = P_f(1 - R) + P_s R$$

rearranging and combining equations (1) and (2):

$$\frac{N_c}{P_c} = \frac{N_f - R(N_f - N_s)}{P_f - R(P_f - P_s)}$$

Figure 16.3a shows the winter and summer variations in N:P ratio with salinity together with the model curves for the Bristol Channel derived from eqn. (3) and using the nutrient data in Table 16.2. Both the model curves and the data indicate a persistence of the river-derived potential P-limitation conditions (i.e. N:P $> 16$) up to surprisingly high salinities ($\sim 32\%_0$). This arises from the swamping effect of high concentrations of fertilizer-derived NO$_3^-$ in the River Severn. The switch to potential N limitation in the model curves appears at a critical salinity of 33.6$\%_0$ in winter and 34.0$\%_0$ in summer, and decreasing to $\sim 25\%_0$ for a hypothetical mesotrophic river input (curve 3, Figure 16.3a). Interestingly, since the average summer salinities for Swansea Bay and Carmarthen Bay are 33.0$\%_0$ and 34.2$\%_0$ respectively, the model would predict Swansea Bay to be potentially P-limited and Carmarthen Bay to be marginally NO$_3^-$-limited. However, to test this prediction the model must be expanded to include effects of nutrient uptake by phytoplankton on the residual NO$_3^-$ and PO$_4^{3-}$ concentrations. If $\theta$ is the proportion of conservative NO$_3^-$ ($N_c$) removed by phytoplankton assimilation, and assuming a Redfield nutrient assimilation ratio of N:P = 16, then eqn. (3) can be re-expressed in terms of a residual NO$_3^-$:PO$_4^{3-}$ concentration ratio ($N_i$:$P_i$):

$$\frac{N_i}{P_i} = \frac{N_c(1 - \theta)}{P_c - \theta N_c/16}$$

The effects of increasing $\theta$ (the proportion of NO$_3^-$ removed by phytoplankton) from 0 to 90$\%_0$ on the NO$_3^-$:PO$_4^{3-}$ ratio is shown in Figure 16.3b, together with corresponding data for July/August 1979. At salinities $< 30\%_0$ the data converge with the conservative mixing model ($\theta = 0.0$) and this simply reflects the low primary production which characterizes the turbid, light-limited conditions of the central Bristol Channel (Joint and Pomroy, 1981). At higher salinities elevated phytoplankton production results in steep increases in NO$_3^-$:PO$_4^{3-}$ ratios in the P-limited zone and decreases in the ratios in N-limited marine waters, with maximal divergence centred about the transitional salinity $S_c$ of 34.2-34.6$\%_0$. The expanded model identifies CB and the Celtic Sea to be N-limited in the summer, and Swansea Bay to be P-limited. This is in accord with the nutrient data, which have been recalculated in Figures 16.4a and b in terms of regional contours of the percentage NO$_3^-$ and PO$_4^{3-}$ depleted by phytoplankton blooms in the Bristol Channel. These show Swansea Bay to be essentially PO$_4^{3-}$-depleted (PO$_4^{3-}$ $> 90\%_0$, NO$_3^-$ $\sim 50\%_0$) and Carmarthen Bay to be predomi-
Figure 16.4. Percentage depletion of (a) $\text{NO}_3^-$ and (b) $\text{PO}_4^{3-}$ relative to central Bristol Channel obtained during monitoring survey (147 stations) in August 1979. The hatched line corresponds to the 33.6–34.2‰ critical salinity boundary separating potentially P-limited waters in the east from potentially N-limited waters to the west.

Figures 16.4a and b that the critical salinity boundary (34.2–34.6‰) occurs in the onshore well-mixed side of the shelf frontal systems (Pingree et al., 1978). The critical salinity boundary must have ecological implications linked with the role of nutrients in phytoplankton productivity and in species succession. Finally, the
data also suggest that bays are regions of enhanced nutrient depletion with the potential for coastal eutrophication.

16.3 BAY CIRCULATION AND RESIDENCE TIME

In biogeochemical processes there is a cyclic consumption of primary reactants and build-up of products. These become evident in bays when the time scales of the net biogeochemical processes are shorter than the water residence time in the bay. The water residence time ($\tau_w$) represents an upper time scale for bay-specific fluxes, and so basic hydrodynamic information on the influence of tidal advection and local runoff is fundamental in coastal biogeochemical studies.

Numerical models of horizontal advection and tidal mixing (Pingree et al., 1978) suggest that CB may lie in a transitional zone between vertically mixed waters and stratified waters (Simpson and Hunter (1974) stratification parameter

![Diagram](image)

Figure 16.5. (a) Tidally driven residual currents and gyres in Carmarthen Bay; derived from Uncles (1982). (b) Typical salinity distribution obtained in March 1980. Hatched lines correspond to bay boundaries used in bay-average model calculations.
However, we have never found any thermal or chemical stratification in the bay and conclude, in agreement with Uncles and Joint (1983), that vertical mixing time scales (1–4 hours) in these regions are too short to allow stratification to occur. The tidally driven residual circulation of CB is shown in Figure 16.5a, and arises from the combined effects of rectilinear tidal streams and the asymmetric bathymetry of the bay. Together these give rise to a net southwesterly inflow towards the bay centre and a return along the bay sides to the sea, in the form of two oppositely flowing gyres (Uncles, 1982). These gyres have implications on the spatial distribution of nutrients together with phytoplankton and zooplankton, and will be discussed in a later section.

The water residence time ($\tau_w$) for CB was calculated using the salt budget–river runoff method (Dyer, 1973; Pilson, 1985) which takes into account the contribution of advection and diffusion processes in the bay system. This is described by equation (5):

$$\tau_w = \frac{(1 - (\sum s_i v_i) / V \bar{S}_0) V}{Q_{fw}}$$

where $s_i$ and $v_i$ are the mean salinity and volume respectively of the $i$th grid of the bay of volume $V$, $\bar{S}_0$ is the mean salinity outside the bay and $Q_{fw}$ is mean daily freshwater runoff into CB. For example, using the March 1980 salinity distributions (Figure 16.5b) together with values for $\bar{S}_0 = 33.11\%$ and $Q_{fw} = 6.47 \times 10^6$ m$^3$/d we calculate by this method that water residence time ($\tau_w$) is 9.6 days. This compares favourably with water replacement time ($\tau_r$) of $12.7 \pm 1.4$ days which was derived from a tidally averaged residual transport model (Uncles, 1982) applied to the CB boundaries shown in Figure 16.1c. Since diffusion is neglected in the latter advection calculations it is to be expected that $\tau_r > \tau_w$.

### 16.4 Nitrogen Reservoirs, Speciation and Seasonal Variation

The seasonal distribution of dissolved, particulate and mobile sedimentary (0–4 cm) reservoirs of nitrogen ($N_d$, $N_p$ and $N_s$ respectively) in CB is shown in Figure 16.6. There is a pronounced seasonal change in $N_d$ resulting in a switch of the order of N reservoirs from $N_d > N_s > N_p$ in winter months (January–March) to $N_s > N_d > N_p$ in August. The corresponding variations in N species that make up $N_d$ are shown in Figure 16.7; these follow Harvey's (1966) classical NO$_3^-$ pattern derived for the English Channel.

Nitrate (NO$_3^-$) is the most abundant form of $N_d$ throughout the year, except in August, when it is markedly depleted to $< 0.5 \mu M$ NO$_3^-$ by the high biomass of phytoplankton (up to 4.2 $\mu g$ chlorophyll-$a$ per liter). Also shown is the half saturation constant ($K_s$) for the assimilation of NO$_3^-$ by phytoplankton obtained in August 1980. The fact that the ambient concentrations of NO$_3^-$ were periodically below the $K_s$ value is a strong indication that nitrogen could limit...
Figure 16.6. Seasonal variation of grid averaged (N = 29) and ranges (vertical bars) of N reservoirs in the mobile (0–4 cm) sediment (N_s), dissolved (N_d) and particulate (N_p) forms of nitrogen in Carmarthen Bay. Nitrogen associated with phytoplankton biomass (N_ph) and zooplankton (N_z) are shown in different scales.
primary production in CB. Also at this time, ammonia (NH$_4^+$) concentrations of 2.6 $\mu$M NH$_4^+$, indicating that active nitrogen recycling is occurring in mid-summer. Cycling is also apparent in October when concentrations of NO$_2^-$ reach 2 $\mu$M NO$_2^-$. This temporal sequence of nitrogen speciation (NH$_4^+ \rightarrow$ NO$_2^- \rightarrow$ NO$_3^-$) is evidence that nitrification contributes to the autumnal recovery of NO$_3^-$ levels in CB. However, most of the high winter NO$_3^-$ levels undoubtedly result from river discharges which originate from the N-fertilized arable catchments.

The contrasting winter and summer speciation of $N_d$ and $N_p$ are shown as pie diagrams in Figure 16.8. Speciation in summer is dominated (65.3%) by dissolved
organic nitrogen (DON), which would include recently exuded or excreted compounds such as amino acids, urea, purines, etc. and also the more refractory humic-type compounds. Although primary amines (R-NH₂, including amino acids) do peak in August 1980 (0.25 μM R-NH₂), their average annual concentrations are very low (0.08 μM R-NH₂). Similar results have been explained by Billen et al. (1980) and others as resulting from a dynamic balance between the production and the efficient heterotrophic utilization of dissolved amino acids. Urea, on the other hand, may have made a significant contribution to the DON, since on the one occasion (August 1980) when we measured urea, concentrations averaging 2.7 μM urea were found, and this could account for an average of 59.4% of DON.

The levels of particulate nitrogen (Nₚ), which accounted for between 7.3%
(May) and 25.6% (August) of total nitrogen (Figure 16.8) in the water column showed no obvious seasonal pattern (Figure 16.6). However, the contribution of phytoplankton-associated nitrogen \( (N_{ph}) \) calculated from chlorophyll-a \( (C:\text{chlo-a} = 50:1; \ C:N = 106:16) \) increases from 14.7% of \( N_p \) in January to 46.5% in August. Zooplankton nitrogen biomass \( (N_z) \) contributes a further 1.4–14.0% to \( N_p \), whereas the maximum contribution from bacteria is only 0.6%. Thus a significant proportion (28–85%) of particulate nitrogen is detrital rather than living.

### 16.5 BAY DISTRIBUTION AND ANOMALIES

The pronounced seasonal variation in \( \text{NO}_3^- \) concentrations shown in Figure 16.7 are also evident in the bay distribution of nitrogen species.

Typical summer distributions of \( \text{NO}_3^- \), \( \text{NO}_2^- \) and \( \text{NH}_4^+ \) in relation to chlorophyll, salinity and other nutrients in CB are shown for August 1979 and May 1980 in Figures 16.9a–h and 16.10a–d, respectively. There are pronounced onshore gradients of decreasing concentrations of \( \text{NO}_3^- \), \( \text{NO}_2^- \), \( \text{NH}_4^+ \) and \( \text{PO}_4^{3-} \). In most summer cruises (e.g. May, Figure 16.10) chlorophyll also shows onshore increases from < 1 to 4.2 µg chlo-a per liter, resulting in crescent-shaped fronts of high chlorophyll and low \( \text{NO}_3^- \) along the margins of the bay. In these regions the concentration isopleths of \( \text{NO}_3^- \), \( \text{NO}_2^- \) are orthogonal with respect to salinity, indicating non-conservative removal of nutrients during their passage time through the bay.

A quantitative estimate of \( \text{NO}_3^- \) depletion at any Station \( i \) in Carmarthen Bay may be obtained by comparison with the corresponding \( \text{NO}_3^- \) concentrations \( ([\text{NO}_3^-]_{BC}) \) in Bristol Channel waters of the same salinity (Figure 16.11). From this it is possible to estimate a \( \text{NO}_3^- \) anomaly \( (\Delta \text{NO}_3^-) \) from the equation:

\[
\Delta \text{NO}_3^i = [\text{NO}_3^-]_{BC} - [\text{NO}_3^-]_i
\]

Positive values of the anomalies indicate net production and negative values net consumption in the bay.

The bay distribution of \( \Delta \text{NO}_3^- \) in May (Figure 16.10) points to the inner, shallow, chlorophyll-rich regions of the bay as areas of maximum \( \text{NO}_3^- \) depletion. Further inshore, and within the local estuaries, \( \text{NO}_3^- \) concentrations must recover due to river inputs.

If the anomalies are then depth-weighted and summed for all stations \( i \), a bay average anomaly \( (\Delta \text{NO}_3^-) \) can be calculated which represents the net effect or balance between \( \text{NO}_3^- \) production (i.e. inputs from rivers, Bristol Channel, nitrification) and consumption by phytoplankton. Thus, at steady state, a bay-average net flux \( J_{\text{NO}_3^-} \) may also be derived from the equation:

\[
J_{\text{NO}_3^-} = \frac{\Delta \text{NO}_3^-}{\tau_w}
\]  

(7)
Figure 16.9. Nutrients, salinity (S, %) and temperature (°C) distributions in Carmarthen Bay in August 1979. Concentration units for NO$_3^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$, and Si in μM N, P, Si and chlorophyll-a in μg/litre.
Figure 16.10. The distribution of salinity ($S/\%_o$), chlorophyll-\textit{a} (Chlo-\textit{a}, $\mu g$/litre), nitrate concentration ($\mu M$) and nitrate anomalies ($\triangle NO_3, \mu M$) in Carmarthen Bay; May 1980.

Figure 16.11. The non-conservative distribution of nitrate ($NO_3$) concentration with respect to salinity in the central Bristol Channel (\textbullet) and in Carmarthen Bay (\textcircled{O}); data obtained in August 1979. The depletion of $NO_3$ in Carmarthen Bay is shown as an anomaly, $\triangle NO_3$. 
where $\tau_w$ is the mean water residence time (9.6 days) in the bay. For example, for $\text{NO}_3^-$ we calculate the August 1979 bay-average depletion fluxes to be $-0.42 \text{mm} \text{NO}_3^- \text{m}^{-3} \text{d}^{-1}$ which, given approximations and assumptions made above, is in remarkably good agreement with a value of $-0.79 \text{mm} \text{NO}_3^- \text{m}^{-3} \text{d}^{-1}$ derived from $^{14}$C primary production and Redfield conversion to nitrogen. Ammonia, on the other hand, has a positive anomaly in August 1979 of $\Delta \text{NH}_4^+ = +0.04 \text{mm} \text{NH}_4^+ \text{m}^{-3}$; thus there is a net efflux of $\text{NH}_4^+$ of $0.03 \text{mm} \text{NH}_4^+ \text{m}^{-3} \text{d}^{-1}$ from the bay to the Bristol Channel. The inclusion of these anomalies and bay-average flux calculations into a nitrogen budget for CB will be shown later.

### 16.6 NITROGEN ASSIMILATION AND AMMONIFICATION

$\text{NH}_4^+$ and $\text{NO}_3^-$ assimilation rates were obtained from simulated in situ incubations using $^{15}$N, and were carried out concurrently with $^{14}$C incubations to obtain carbon assimilation rates. Grid-averaged depth-weighted assimilation rates are shown in Table 16.3. Total nitrogen demand rates are based on the observed $^{14}$C assimilation rates calculated using the Redfield ratio of C:N assimilation of 6. The nitrogen assimilation rates obtained in this way are consistently lower than those obtained by the $^{15}$N incubations, and were considered to give a more reliable estimate of total nitrogen demand for

Table 16.3: Bay-averaged nitrogen assimilation and $\text{NH}_4^+$ remineralization

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Total nitrogen demand (mmol N m$^{-3}$ d$^{-1}$)</th>
<th>$\text{RPI}_{\text{NO}_3^-}$</th>
<th>$f_{\text{NO}_3^-}$</th>
<th>$\text{NH}_4^+$ remineralization rate (mmol NH$_4^+$ m$^{-3}$ d$^{-1}$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug. 1979</td>
<td>0.79</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mar. 1980</td>
<td>0.003</td>
<td>11.45</td>
<td>77</td>
<td>0.109</td>
</tr>
<tr>
<td>May 1980</td>
<td>0.13</td>
<td>3.93</td>
<td>87</td>
<td>0.103</td>
</tr>
<tr>
<td>Aug. 1980</td>
<td>0.24</td>
<td>1.76</td>
<td>28</td>
<td>0.103</td>
</tr>
<tr>
<td>Oct. 1980</td>
<td>0.06</td>
<td>4.10</td>
<td>68</td>
<td>0.176</td>
</tr>
<tr>
<td>Jan. 1981</td>
<td>0.11</td>
<td>8.68</td>
<td>71</td>
<td>0.080</td>
</tr>
</tbody>
</table>

* Relative preference index:

$$\text{RPI}_{\text{NH}_4^+} = \frac{\sigma\text{NH}_4^+/(\sigma\text{NH}_4^+ + \sigma\text{NO}_3^-)}{[\text{NH}_4^+]/([\text{NH}_4^+] + [\text{NO}_3^-])}$$

where $\sigma\text{NH}_4^+$ and $\sigma\text{NO}_3^-$ are assimilation of $\text{NH}_4^+$ and $\text{NO}_3^-$ and $[\text{NH}_4^+]$ and $[\text{NO}_3^-]$ are ambient concentrations.

* Proportion of total mass of N assimilated as $\text{NO}_3^-$:

$$f_{\text{NO}_3^-} = \frac{\sigma\text{NO}_3^-}{\sigma\text{NH}_4^+ + \sigma\text{NO}_3^-} \times 100$$
budgeting and modelling purposes. The reasons for choosing this approach are considered in detail by Ownes et al. (1986). Briefly, however, $^{15}$N assimilation rates are considered to overestimate the actual assimilation for the following reasons; firstly, non-phytogenic organic nitrogen cannot be excluded in the calculations, and secondly the $^{15}$N technique requires the addition of significant quantities of N, which in oligotrophic conditions stimulate phytoplankton assimilation. The $^{15}$N incubations do, however, provide reliable information on the relative proportions of $\text{NO}_3^-$ and $\text{NH}_4^+$ assimilated (Table 16.3). It can be seen that $\text{NH}_4^+$ was consistently preferred to $\text{NO}_3^-$. If, however, the total masses of nitrogen utilized by the phytoplankton are compared, it can be seen that, only during August 1980, less than 50% of the demand was met by $\text{NO}_3^-; \text{at other times of the year an average of 76% (range 59–92%) of the total nitrogen demand was met by } \text{NO}_3^-.

Ammonia remineralization rates obtained by $^{15}$N isotope dilution experiments were carried out at the same times as N assimilation rates. It can be seen from Table 16.3 that $\text{NH}_4^+$ remineralization rates are of the same order as the assimilation rates, and could supply all of the phytoplanktonic nitrogen demand apart from August 1980 when benthic fluxes became important. In all other cases CB would appear to be a net exporter of $\text{NH}_4^+$. This is made more apparent by the fact that on average only 25% of the total nitrogen assimilated is in the form of $\text{NH}_4^+$ (see Table 16.3). The imbalance between $\text{NH}_4^+$ assimilation and regeneration is most marked during October 1980. During this cruise pronounced positive $\text{NH}_4^+$ anomalies were also found, and are shown in Figure 16.12 together with the observed $\text{NH}_4^+$ remineralization rates. It can be seen that there is a general agreement between the spatial variability of $\text{NH}_4^+$ remineralization and the observed $\text{NH}_4^+$ anomalies.

![Figure 16.12. Bay-specific ammonia concentration anomalies (Δ$\text{NH}_4^+$, $\mu$M) and $\text{NH}_4^+$ remineralization rates (μM/d) by microplankton (< 200 μM), October 1980.](image)
16.7 BAY FRONTS

The origins of the high chlorophyll, low NO₃⁻ fronts which occur along the bay margins (Figure 16.10) are related to the phytoplankton growth conditions in these waters. The water column characteristics in CB may be viewed (see Figure 16.13) in terms of a radial, vertically mixed section, of linear bathymetry and constant photic depth \( (D_p) \). Under these conditions phytoplankton growth rate \( (\mu_x, \text{d}^{-1}) \) at a radial distance \( x \) from the bay centre is related to the vertically integrated light intensity \( I \) (Parsons and Takahashi, 1973) at that position by:

\[
\mu_x = \frac{\mu_{\text{max}} I}{(1/a + I)}
\]

where \( \mu_{\text{max}} \) is the maximum light-saturated growth rate, \( 1/a \) is a constant.

Figure 16.13. A conceptual model for the development of bay fronts along the margins of Carmarthen Bay. (a) Radial, vertically mixed section of the bay with linear bathymetry \( (Z) \) and a photic depth \( (D_p) \). (b) radial profiles of vertically integrated light intensity \( (I) \) relative to the intensity \( (I_o) \) of light incident at the sea surface and of phytoplankton growth \( (\mu_x, \text{d}^{-1}) \). (c) Comparative profiles of \( \mu_x \), reciprocal radial water residence time \( (\tau_x^{-1}) \) and the zone (hatched) of net phytoplankton production where \( (\mu_x - \tau_x^{-1}) > 0 \). (d) radial steady-state distribution of nutrients and chlorophyll.
be related to the incident light intensity $I_0$ by:

$$T = I_0(1 - e^{-kz})/kz$$  \hspace{1cm} (9)

where $k$ is the light attenuation coefficient (m$^{-1}$) and $z$ is the depth (m). For coastal waters Sinclair et al. (1981) have shown that $k \approx 1.44/D_s$, where $D_s$ is Secchi disc depth and so making the approximation that $D_p \approx 2D_s$ (Parsons and Takahashi, 1973) it follows that in deep water eqn. (9) reduces to:

$$T \approx 1.4I_0D_p/Z$$  \hspace{1cm} (10)

that is, phytoplankton production in deep waters is controlled by the ratio of photic depth $D_p$ to the water depth ($Z$). Upon moving towards the shallower more euphotic bay margins, $I \rightarrow I_0$ and production increases rapidly up to the light saturation limit ($\mu_{\text{max}}$) as shown in Figure 16.13b. However, phytoplankton production in these shallow margins is also subject to attrition from tidal dispersion and river runoff, such that if $\tau_x$ is the radial residence time of water in the bay section (Figure 16.13c) then net production can only occur if:

$$\mu_x - 1/\tau_x > 0$$  \hspace{1cm} (11)

It is evident from Figure 16.13c that $(\mu_x - \tau_x^{-1})$ goes through a maximum, which at steady state would give rise to a zone of high chlorophyll and lowered $NO_3^-$ concentrations (Figure 16.13d) eventually leading to $NO_3^-$ limitation. Furthermore, microbial recycling of N also appears to be coupled with chlorophyll fronts, since both $NH_4^+$ anomalies and remineralization rates increase towards the bay margins (Figure 16.12). These crescent-shaped bay fronts may be explained in terms of the optimal growth conditions which developed at the interphase between euphotic shallow waters along the bay margins, in which phytoplankton growth is limited by tidal washout, and a deeper more stable zone towards the bay centre in which production is light-limited. However, more exact predictions of bay fronts and their calibration would require hydrodynamic modelling of tidal dispersion, and circulation and nitrogen cycling rates.

### 16.8 ZOOPLANKTON EXCRETION

Studies of zooplankton in CB consisted of measurements of standing stocks and excretion activity of different size classes. The results for August 1979, which are summarized in Table 16.4, highlight the importance of the microzooplankton (100–280 mm) as comprising 51% of the total stock and exhibiting the highest specific excretion rates (663 $\mu$mol $NH_4^+$ N g$^{-1}$ d$^{-1}$). The impact of microzooplankton in terms of the N remineralization is even more important, as they contribute 86% of the total zooplankton $NH_4^+$ excretion. Microscopic analyses of these organisms showed the protozoan *Noctiluca scintillans* and naupliar stages of the neritic copepods such as *Acartia clausi*, *Pseudocalanus* sp. and *Temora longicornis*, to be present in this size fraction.
Table 16.4. Zooplankton standing stocks, their weight-specific excretion rates and in situ ammonia remineralization rates as a function of organism size. Carmarthen Bay, August 1979

<table>
<thead>
<tr>
<th>Remineralization Zooplankton size class</th>
<th>Biomass (µg/l)</th>
<th>Excretion rate (µmol NH₄-N g⁻¹ d⁻¹)</th>
<th>Rate (µmol NH₄-N m⁻³ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (100–280 µm)</td>
<td>24.57</td>
<td>663</td>
<td>16.29</td>
</tr>
<tr>
<td>2 (280–560 µm)</td>
<td>3.27</td>
<td>250</td>
<td>0.82</td>
</tr>
<tr>
<td>3 (560–1180 µm)</td>
<td>4.98</td>
<td>117</td>
<td>0.58</td>
</tr>
<tr>
<td>4 (&gt; 1180 µm)</td>
<td>14.71</td>
<td>86</td>
<td>1.26</td>
</tr>
</tbody>
</table>

\[ \sum = 18.95 \]

The micronekton component (size class 4, > 1180 µm) which often formed an appreciable proportion of the community biomass, made only a small contribution to the excretion flux. However, within the micronekton an important component are the gelatinous zooplankton such as ctenophores and medusae (Williams and Collins, 1985). In June 1978, for example, we observed high concentrations of the ctenophore *Pleurobrachia pileus* distributed at two centres within CB (see Figure 16.14). These centres coincided with the centre of residual current gyres (Figure 16.5a) suggesting that these weakly swimming organisms may be concentrated within the bay by residual circulation. In agreement with other studies (Kremer, 1975), we have measured unusually high specific excretion rates with these organisms, indicating that ctenophores also make a significant but episodic contribution to NH₄⁻ recycling in CB.

Figure 16.14. Isoptths of ctenophore (*Pleurobrachia pileus*) standing stocks (mg dry weight/m³) in Carmarthen Bay during June 1978
16.9 NITROGEN BUDGET

It is beyond the scope of this chapter to discuss the detailed seasonal and spatial patterns of individual N cycling processes in CB; these are published elsewhere (Owens et al., 1986). Nevertheless, it is useful to evaluate the relative importance of the various N cycling routes discussed previously, by reference to some of the bay-averaged fluxes. This is shown for August 1979 in Figure 16.15 in terms of an integrated steady-state budget for $\text{NO}_3^-$, $\text{NO}_2^-$ and $\text{NH}_4^+$ which has been assembled from measurements of individual N fluxes.

The phytoplankton demand rates for $\text{NO}_3^-$, $\text{NO}_2^-$ and $\text{NH}_4^+$ were calculated individually from bay-averaged anomalies ($\Delta \text{NO}_3^-$, $\Delta \text{NO}_2^-$, see Section 16.5) and from differences between measured $\text{NH}_4^+$ inputs (river; Welsh Water Authority; zooplankton; Table 16.4; benthos; Pomroy et al., 1983, microbial remineralization; Table 16.3 and losses from CB. Together, the calculated phytoplankton demand of 0.61 mmol N m$^{-3}$ day$^{-1}$ accounts for 77.2% of the nitrogen assimilation rate (0.79 mmol N m$^{-3}$ d$^{-1}$) derived independently from integrated $^{14}$C-primary production and Redfield conversion to equivalent N (see Section 16.6 and Table 16.3). The small difference may be associated with inaccuracies of...

![Nutrient Budget Carmarthen Bay August 1979](image)

Figure 16.15. Nitrogen budget of Carmarthen Bay derived for August 1979. Circles and boxes denote living and non-living reservoirs of nitrogen (mmol N m$^{-3}$) respectively and arrows denote nitrogen fluxes (mmol N m$^{-3}$ d$^{-1}$) between compartments. Microbial $\text{NH}_4^+$ remineralization rate shown was obtained in August 1980.
individual measurements and assumptions in calculations, or may reflect the assimilation of other forms of N (e.g. urea, amines) available to the phytoplankton. At any rate, the general accord serves to verify the mass balance calculations used in the model.

The principal source of N in CB in August 1979 is the advective input of NO$_3^-$ from the Bristol Channel (83%) with local rivers contributing only 17% of the nitrogen. Despite the comparable concentrations of NO$_3^-$ and NH$_4^+$, there appears to be a preferential assimilation of NO$_3^-$ over NH$_4^+$, suggesting that phytoplankton production is linked with advective supply of NO$_3^-$ from the BC. This contrasts with NH$_4^+$ inputs into CB which are almost entirely autochthonous (94.7%) and which arise mainly from benthic inputs (35%) and the microbial mineralization of NH$_4^+$ in the water column (50%). The latter contribution may be an underestimate, since this rate was based on results from August 1980 (Table 16.3) when primary production was significantly lower than August 1979. Either way, this does not alter the overall nitrogen flow pattern, emphasizing that phytoplankton N demand is fuelled primarily by NO$_3^-$ inputs from the Bristol Channel. Zooplankton excretion of NH$_4^+$ exceeds river inputs but provides a maximum of 12% of the phytoplankton N demand. Most of this internal regeneration of NH$_4^+$ is reassimilated by phytoplankton (82.5%) leaving a residual proportion (17.5%) of the NH$_4^+$ production to be lost by advective exchange with the Bristol Channel. Together this is evidence for very efficient recycling of reduced N in CB. In addition, the high N-trapping efficiency of the bay is also evident from the net exchange of inorganic N at the bay boundaries, since of the 0.43 mmol N m$^{-3}$ d$^{-1}$ entering the bay, mainly as NO$_3^-$, only 0.03 mmol N m$^{-3}$ d$^{-1}$ is lost as NH$_4^+$ to the Bristol Channel.

The quantitative fate of phytoplankton production is more difficult to estimate since direct measurements of grazing, sedimentation and horizontal transport were not made. However, assuming a zooplankton ration of 100% body dry weight per day, which is a median value for the size classes (Table 16.4) we investigated (Omori and Ikeda, 1984), we estimate that up to a third of the phytoplankton production in CB may be grazed by zooplankton. Uncles and Joint (1983) have shown that sedimentation of phytoplankton is unlikely to be important in the presence of the intense vertical mixing characteristic of the Bristol Channel; but the higher chlorophyll levels encountered in CB indicate that a proportion of the bay-enhanced N production must also be exported to the Bristol Channel. This role of CB, as a trap for dissolved N and a source for N production in summer, is reversed in winter when the increased river inputs and catabolic regeneration of N transform the bay into a net exporter of dissolved nitrogen into the Bristol Channel.

16.10 CONCLUSIONS

Bays, by their semi-enclosed nature, are hydrodynamically more stable regions of reduced current speeds and increased water residence times. They are also areas
in which nutrients are trapped and phytoplankton production is stimulated. In addition, bay waters are profoundly affected by cyclic inputs from shallow sediments and rivers. Tidal exchange and mixing exert major controls on the boundary conditions, frontal activity and time scales of biogeochemical cycling of nitrogen in temperate bays.

Although the results from our nitrogen cycling studies in Carmarthen Bay may also apply to other large macrotidal bays in the UK (e.g. Cardigan Bay, Lyme Bay, The Wash) there must, however, be a lower size limit below which a vertically mixed bay must lose its biogeochemical individuality due to efficient flushing. Since bays, in their various sizes (1–10³ km) and shapes (open, headland, Rias, log-spiral, etc.) are a widespread feature of coastal marine systems, there is an urgent need for some hydrodynamic systematics of bay types in terms of scaled parameters such as flushing, stratification, circulation, light availability and nutrient loading similar to the classification schemes available for lakes (Vollenweider, 1975; Hutchinson, 1957), estuaries (Dyer, 1973) and shelf seas (Pingree et al., 1979). Such a classification scheme would provide the basis for comparative nitrogen cycling studies of bays and the prediction of coastal eutrophication.

ACKNOWLEDGEMENTS

We would like to thank M. Woodward and R. Howland for excellent shipboard support, and C. Goodchild and P. Frickers for analytical assistance in the laboratory; Dr. R. J. Uncles for help in modelling, and the Master and Crew of the RRS John Murray for excellent services at sea. This project forms part of the Biogeochemistry Programme at IMER, and is partly funded by Department of Environment Research Contract NO. DGR 480/48.

REFERENCES


