Is the atmosphere really an important source of reactive nitrogen to coastal waters?

Lucinda J. Spokes, Tim D. Jickells*

School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Received 26 April 2004; received in revised form 19 July 2005; accepted 22 July 2005
Available online 6 September 2005

Abstract

Increasing inputs of reactive nitrogen have led to excessive phytoplankton growth in some coastal waters. Until recently, rivers were thought to be the most important nitrogen source but we now know that atmospheric inputs are large and can equal, or exceed, those from the rivers. These atmospheric nitrogen compounds have both agricultural sources (ammonia emitted from animal wastes) and combustion sources (nitrate derived from NOx emitted by vehicles and power stations). Our hypothesis is that atmospheric nitrogen deposition in summer to nutrient depleted, well lit, surface waters in coastal seas stimulates phytoplankton blooms. This paper summarises and compares studies conducted in the North Sea, the North East Atlantic Ocean and the Kattegat Sea. Budgeting approaches imply that the atmosphere can, under certain meteorological conditions and over short time periods, provide enough nitrogen to support a large increase in phytoplankton growth. This is not true in all areas and at all times and this emphasises the highly episodic nature of atmospheric deposition. However, productivity-based approaches suggest that atmospheric nitrogen inputs have little effect on phytoplankton growth. This may be because productivity in the North Sea and the Kattegat is controlled by internal recycling of nitrogen, even in the summer when inorganic nitrogen levels are very low. Over longer time scales, atmospheric inputs do increase the overall nitrogen stock in the water column. Reducing the input of nitrogen from the atmosphere will, therefore, reduce total nitrogen loads to coastal seas and hence may decrease eutrophication problems.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Air–sea interaction; Atmospheric deposition; Eutrophication; Nitrogen compounds; Nutrient fluxes; Phytoplankton

1. Introduction

Coastal seas are one of the most valuable resources on the planet but are threatened by human pressures. In Europe, high population densities, high levels of industrial activity and intensive agriculture mean that the pressures are...
particularly acute. We rely on the coastal region for mineral reserves, fisheries and recreation and so these areas have great economic importance. Humans have probably doubled the global fluxes of reactive species and increases in Europe are probably greater than this. At present humans convert \( \text{N}_2 \) to reactive nitrogen at the same rate as biological nitrogen fixation, double the preindustrial rate. Predictions are that anthropogenic nitrogen fixation will increase by \( \sim 60\% \) by 2020 (Galloway and Cowling, 2002; Jickells, 2002; Prospero et al., 1996). Most of the increase will be in Asia (Galloway et al., 1995). This increased nitrogen flux reaches coastal seas via the rivers, the atmosphere and by groundwater.

Increasing concentrations of nitrogen species have led to excessive phytoplankton growth in coastal waters (Nixon, 1995), some of which are harmful (Paerl, 1988; Zhang, 1994). Decay of these phytoplankton blooms leads to lower water column oxygen levels. Under extreme conditions, this can cause fish kills. Other undesirable effects include changes in phytoplankton species composition and hence changes to food web structures and carbon cycling. Many studies have attempted to assess the importance of the atmosphere as a source of reactive, biologically available nitrogen to coastal waters (Duce et al., 1991; Asman et al., 1995; Paerl, 1995; Galloway et al., 1996; Prospero et al., 1996; Jickells, 1998; Paerl et al., 1999; Schulz et al., 1999; Spokes et al., 2000; de Leeuw et al., 2003).

We suggest that atmospheric inputs are quantitatively important and potentially different in their effect on coastal ecosystems to riverine inputs. However, up until recently there has been almost no information on the impacts of atmospheric deposition on marine ecosystems. We hypothesise that high atmospheric deposition events in summer to nutrient depleted, well lit, surface waters in coastal seas may play a role in stimulating phytoplankton blooms. These blooms may be harmful and/or contribute to bottom water oxygen depletion. This paper compares studies conducted in the North Sea region, the North East Atlantic Ocean and the Kattegat Sea during the UK Natural Environment Research Council funded research Atmospheric Chemistry Studies in the Oceanic Environment (ACSOE) and European Union funded projects Atmospheric Nitrogen Inputs to the Coastal Environment (ANICE) and Marine Effects of Atmospheric Deposition (MEAD). The sampling locations are shown in Fig. 1. We present here a summary of our work so far and our current state of knowledge of the magnitude and importance of atmospheric nitrogen deposition to European coastal waters.

2. Processes

Rivers have, until recently, been thought to be the most important source of reactive nitrogen to the coastal seas though it should be noted that this riverine input does include a contribution from atmospheric deposition to the catchment, a point that will be considered later. We now know that inputs from the atmosphere to coastal waters are large and can equal, or exceed, those from the rivers (Duce et al., 1991; Rendell et al., 1993). Our initial hypothesis in these studies was that atmospheric inputs are important and potentially different in their effect on coastal ecosystems to riverine inputs. We know atmospheric inputs are
an important source of nitrogen but, unlike rivers, not phosphorous or silicon (Jickells, 1998). As we show below, atmospheric inputs are highly variable in space and time and that there are chemical reactions which occur in the atmosphere in the coastal region which alter the deposition of biologically available nitrogen to surface waters. However, until recently we had almost no information on the direct effects of atmospheric deposition on marine ecosystems, though clearly such a large external nitrogen input should lead to enhanced phytoplankton growth.

Atmospheric inputs are delivered to surface waters through dry deposition of gases and aerosol particles and in wet deposition. Reactive gases, such as nitric acid (HNO₃) and ammonia (NH₃), are removed from the atmosphere onto the land or sea surface and through reaction with atmospheric aerosols with rates of removal dependent on these reactions (Church and Jickells, 2004 and references therein). For aerosols, wet and dry deposition increases with particle size and also depends on wind speed and humidity (Pryor and Barthelmie, 2000). Under certain meteorological conditions, the atmosphere can deliver very high concentration short-lived pulses of material (Fig. 2) typically lasting only a day or so (Spokes et al., 1993; Prospero et al., 1996; Jickells, 1998; Spokes et al., 2000).

High atmospheric concentration events in Europe are, in general, associated with high-pressure systems over Northern Europe where the air is slow moving over a continental area of large emission sources. Pollutants accumulate in these airmasses and can then be advected over marine areas with associated high dry deposition. If rainfall occurs at the time, particularly high deposition can result (Spokes et al., 1993, 2000). The resulting events, while small in overall annual budget terms, may be able to promote phytoplankton blooms under nutrient depleted summer conditions (Owens et al., 1992; Michaels et al., 1993; Paerl, 1985). Winter water column productivity in temperate latitudes is low due to limitation by light and temperature, and productivity in the spring is controlled by nutrients which enter the surface waters during winter deep mixing. Blooms do occur in temperate waters in the summer when water column nutrients are very low and these may be triggered by inputs of nitrogen from the atmosphere. Since atmospheric inputs do occur all year round, the flux of nitrogen from the air may not only trigger summer blooms but also contribute to the water column nitrogen standing stock and hence the magnitude of the spring bloom, and both situations are considered here.

There is a range of nitrogen species in the atmosphere. In this review, we consider gas-phase ammonia and nitric acid and aerosol and rainwater-phase nitrate and ammonium and water soluble atmospheric organic nitrogen (WSAON) compounds in both rain and aerosols since we believe no other nitrogen components contribute significantly to atmospheric nitrogen inputs. We now briefly review the different behaviour of these different forms of nitrogen.
There are significant emissions of ammonia from marine waters (e.g. Quinn et al., 1988); however, in an anthropogenically perturbed environment, ammonia is primarily generated from agricultural livestock wastes and to a lesser extent from fertiliser production and application (Buijsman et al., 1987). The resultant high atmospheric ammonia levels drive the ammonia flux into, rather than from, seawater. The oxidation of ammonia in the atmosphere is so slow it is essentially irrelevant (Høv et al., 1994) but it is rapidly removed close to source by dry deposition since it has a high-deposition velocity. Ammonia is an important neutralising species, readily reacting with acids in the atmosphere to form ammonium aerosols, increasing the lifetime of reduced nitrogen in the atmosphere. The reaction of NH₃ with H₂SO₄ is preferred over reaction with HNO₃ so NH₄NO₃ is only formed if NH₃ concentrations are high relative to H₂SO₄.

Aerosol nitrate over Europe and North America is mostly anthropogenic in origin and is formed from high temperature oxidation of nitrogen in internal combustion engines, power stations and during industrial activity. The emission, transport and oxidation of the precursor species NO and NO₂ (collectively known as NOₓ) over Europe is now quite well described (Pacyna et al., 1991; Høv et al., 1994; Høv and Hjollo, 1994; EMEP www.emep.int/index.html; Hertel et al., 1995, 2002). These species are oxidised to nitric acid by the OH radical resulting in NO₃ lifetimes of a day or so (Seinfeld and Pandis, 1998). HNO₃ is an important contributor to atmospheric acidity but is partially neutralised by NH₃ in a reversible reaction to form submicron NH₄NO₃ aerosols. This slow oxidation of NO₃ to nitric acid and nitrate means that oxidised nitrogen species have relatively long atmospheric lifetimes and undergo efficient long-range transport before deposition.

A knowledge of the aerosol chemical composition is important because formation of both NH₄NO₃ and NH₄Cl is potentially reversible reactions while formation of ammonium sulphate salts is not (Allen et al., 1989). Thus, NH₄NO₃ and NH₄Cl formed in polluted continental air have the potential to dissociate as HNO₃, HCl and NH₃ concentrations fall as a result of chemical reactions and via dilution as the airmass moves away from the sources. HNO₃, HCl and NH₃ emitted by such dissociation can then go on to react with other species within the marine boundary layer. Ottley and Harrison (1992) report that there is evidence that NH₄NO₃ and NH₄Cl can, however, persist under conditions when dissociation is predicted over the Southern North Sea. This may reflect slow dissociation kinetics or that organic films on aerosols make simple inorganic thermodynamics inappropriate (Allen et al., 1989; Keene et al., 1998).

Reaction of HNO₃ with coarse mode seasalt aerosol as marine and polluted continental air-masses mix, shifts nitrate from the fine mode fraction to the coarse mode as non-volatile sodium nitrate (e.g. Harrison and Pio, 1983; Brimblecombe and Clegg, 1988; Wall et al., 1988; Pakkanen, 1996):

\[
\text{NaCl}(s) + \text{HNO}_3(g) \rightarrow \text{HCl}(g) + \text{NaNO}_3(s)
\]

This reaction increases the deposition of aerosol nitrate by forming large particles which are more efficiently removed from the atmosphere in dry and wet deposition. In marine airmasses, over 80% of the nitrate occurs as coarse mode aerosol, greater than 1.0 µm in diameter (Spokes et al., 2000). Reaction with seasalt aerosol in the coastal region not only affects the deposition of nitrate. Rosenfeld et al. (2002) show that mixing of seasalt aerosol with pollutant-rich continental air in the coastal region enhances precipitation from these airmasses. Thus, seasalt helps to clean the atmosphere of atmospheric pollution and as a consequence of this enhances the deposition of a variety of nutrients and contaminants to the water surface (Spokes et al., 2000, 2001).

There is growing evidence that a significant proportion of ammonium exists in the coarse mode and thus deposits much faster than predicted based on an entirely fine mode component for the species. Our previous studies (Spokes et al., 2000; Yeatman et al., 2001) show that around 30% of the ammonium occurs in the coarse mode. We suggest, therefore, that in the coastal region the deposition of ammonium is enhanced by up to factor of six as a result of reaction with seaspray and conversion onto the coarse mode aerosol.
How the coarse ammonium forms is as yet unsure, but it has been suggested (see above) that in coastal environments, NH$_4$NO$_3$ does not dissociate on reaching the coastal zone but rather is transferred to coarse mode seasalt aerosol through physical processes, such as coagulation or scavenging (Allen et al., 1989; Ottley and Harrison, 1992; Keene et al., 1998; von Salzen and Schlunzen, 1999; Yeatman et al., 2001). This coagulation process produces both coarse mode ammonium and nitrate and through increasing the deposition velocity increases the deposition of both aerosol nitrate and ammonium, both of which can be used by phytoplankton as nutrients.

The sources of WSAON are still uncertain. Evidence suggests that they are principally continental in origin, that they contribute significantly to the total soluble nitrogen flux (Cornell et al., 1995, 2003) and that a significant fraction is available to phytoplankton as a nitrogen sources (Timperley et al., 1985; Peierls and Paerl, 1997; Seitzinger and Sanders, 1999). Organic nitrogen is not always measured in campaigns but studies (e.g. Cornell et al., 2003; Neff et al., 2002) suggest it is important and represents, on average, one-third of the total atmospheric nitrogen load.

Many of the atmospheric chemical reactions of nitrogen discussed above are not well described in models of atmospheric chemistry, transport and deposition at present (de Leeuw et al., 2001). Furthermore, wet deposition is often the main route of removal and this, as a result of its highly episodic nature, is extremely difficult to model well. Hence, the magnitude of atmospheric nitrogen deposition to coastal seas is not particularly well known at present. Advances in atmospheric chemical and meteorological modelling as a result of the ANICE and MEAD projects (de Leeuw et al., 2001; Spokes et al., submitted for publication) along with advances in computing power have gone some way to improving our estimates of nitrogen deposition to coastal seas but further work is required. Table 1 gives examples of our best estimates of the atmospheric nitrogen flux around the North Atlantic region. The magnitude of the flux depends, of course, on the proximity of the region to the continental source areas. In general, inputs of nitrate and ammonium are comparable in size with this ratio varying slightly with the relative source strengths of ammonia and NO$_x$ in the region of interest. The relative importance of reduced and oxidised nitrogen emission sources can, of course, change with time as industries change, e.g. the expansion of the intensive pig industry in the southeastern USA has led to a much higher ammonium/nitrate ratio in deposition in this region over the last 20 years (Paerl et al., 2001).

Atmospheric nitrogen added to coastal waters is almost entirely anthropogenic in origin and thus

Table 1
Estimates of atmospheric nitrogen inputs to coastal environments in the North Atlantic Ocean region

<table>
<thead>
<tr>
<th>Location</th>
<th>Deposition flux (mol m$^{-2}$yr$^{-1}$)</th>
<th>% Nitrate</th>
<th>Significance versus other land inputs (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>German Bight</td>
<td>0.20</td>
<td>70</td>
<td></td>
<td>Schulz et al. (1999)</td>
</tr>
<tr>
<td>Chesapeake Bay</td>
<td>0.092</td>
<td>58</td>
<td></td>
<td>Meyers et al. (2001)</td>
</tr>
<tr>
<td>Southern North Sea</td>
<td>0.071</td>
<td>59</td>
<td>27</td>
<td>Rendell et al. (1993)</td>
</tr>
<tr>
<td>Delaware Bay</td>
<td>0.075</td>
<td>50</td>
<td>5</td>
<td>Church et al. (1982), Scudlark and Church (1993) and Russell et al. (1998)</td>
</tr>
<tr>
<td>Kattegat Sea</td>
<td>0.069</td>
<td>38</td>
<td>30</td>
<td>Asman et al. (1995)</td>
</tr>
<tr>
<td>Irish West Coast</td>
<td>0.06</td>
<td>35</td>
<td></td>
<td>Spokes et al. (2000)</td>
</tr>
<tr>
<td>Great Bay Maine</td>
<td>0.048</td>
<td>54</td>
<td></td>
<td>Meyers et al. (2001)</td>
</tr>
<tr>
<td>North Atlantic Shelf</td>
<td>0.023</td>
<td>40</td>
<td>20</td>
<td>Galloway et al. (1996)</td>
</tr>
<tr>
<td>Puget Sound</td>
<td>0.021</td>
<td>57</td>
<td></td>
<td>Meyers et al. (2001)</td>
</tr>
<tr>
<td>Bermuda</td>
<td>0.017</td>
<td></td>
<td></td>
<td>Michaels et al. (1993)</td>
</tr>
</tbody>
</table>

Note: The studies by Rendell et al. (1993) and Spokes et al. (2000) are the only ones to explicitly include organic nitrogen. Cornell et al. (2003) suggest that organic nitrogen will enhance deposition total nitrogen by 10–20%, probably more in remote regions.
represents a human induced perturbation of the ecosystem. In open ocean waters, where excessive algal growth is not a problem, increases in atmospheric N inputs can increase production and therefore increase the amount of atmospheric CO₂ fixed (Jickells, 2002).

3. Methods

Details concerning gas, aerosol and rain collection are given in Geernaert et al. (1998), Spokes et al. (2000) and Pryor et al. (2002). In summary, size segregated aerosols were collected using a high volume aerosol sampler with sampling periods of around 12 h. Rain samples were collected on an event basis using manually deployed funnels and wet deposition fluxes were determined directly. Gas-phase measurements were made with denuders and fluxes calculated using profile techniques and determined directly by Relaxed Eddy Accumulation. Analysis was by ion chromatography, fluorimetry and colorimetry. Measured aerosol concentrations were converted to fluxes using the approach given in Spokes et al. (2000, 2001). Duce et al. (1991) suggest that the deposition velocity values used in this present study are uncertain by a factor of three and this leads to uncertainty in our dry aerosol flux estimates. Other uncertainties in atmospheric flux estimates result from the large temporal variabilities in atmospheric concentrations and the problems of extrapolating from time limited campaigns to long-term averages.

4. Results

There are several ways of assessing the importance of atmospheric nitrogen inputs. Here, we show the approaches we have used in these studies.

4.1. Atmospheric deposition to river watersheds

We first consider the extent to which atmospheric nitrogen deposition to river watersheds contributes to riverine nitrogen inputs to the Southern North Sea.

Major sources of inorganic nitrogen in rivers include runoff from agricultural fertiliser use, discharge from sewage works and from industry and as a result of atmospheric deposition to the watershed. Boyer et al. (2002) suggest that atmospheric deposition is the second most important nitrogen source, after agriculture, to river catchments in the northeastern US. Using equations developed by Caraco and Cole (1999) it is possible to estimate the contribution of the atmospherically derived inorganic nitrogen to the total riverine inorganic nitrogen input and compare this to the direct atmospheric deposition of inorganic nitrogen to the Southern North Sea.

The relationship developed by Caraco and Cole (1999) predicts nitrate export by rivers as a function of point source inputs from sewage (with this related to urban population density) and to non-point source inorganic nitrogen inputs to the watershed from fertiliser use and atmospheric deposition.

\[
\text{NO}_3\text{ export} = \text{river export} \times ([\text{point source inputs} \\
+ (\text{watershed export} \times \text{watershed inputs})])
\]

where the river and watershed export values represent the fraction of inorganic nitrogen which is exported from the system. The best fit to the actual data was achieved using:

\[
\text{NO}_3\text{ export} = 0.7[1.85 \times \text{urban population density} \\
+ (0.4 \times \text{river runoff}^{0.8} \\
\times (\text{atmospheric deposition} \\
+ \text{fertiliser use})]],
\]

where 1.85 is the total human sewage production in kg N person\(^{-1}\) yr\(^{-1}\). Comparisons of model results to data show significant agreement.

The equation predicts 30% nitrate retention within the river and that the fraction of nitrate retained in the watershed is dependent on river runoff. At high flows (1 m yr\(^{-1}\)) 60% of the inorganic nitrogen added to the watershed is retained, whereas at a runoff of just 0.1 m yr\(^{-1}\), 94% of the inorganic nitrogen added to the watershed is retained. Runoff is defined as the river flow in m\(^3\) yr\(^{-1}\) divided by the catchment area in m\(^2\).
Around 20% of the inorganic nitrogen exported by rivers is not nitrate (occurring instead as nitrite and reduced nitrogen species, primarily ammonium). To determine the total amount of inorganic nitrogen discharged from the rivers, the nitrate export in kg N km\(^{-2}\) yr\(^{-1}\) can be converted to a total dissolved inorganic nitrogen (DIN) riverine export in kg N yr\(^{-1}\) (Kroeze and Seitzinger, 1998; Seitzinger and Kroeze, 1998):

$$\text{DIN}_{\text{export by rivers}} = 1.19 \times \text{NO}_3 \text{ export} \times \text{watershed area}.$$

In this study, we have calculated the export of nitrogen from the rivers arising from atmospheric deposition to the watershed as a fraction of the total river flux. Values for atmospheric wet + dry inorganic nitrogen deposition have been obtained from EMEP model data. The calculated atmospherically derived inorganic nitrogen export has then been compared to measured inorganic nitrogen export values for the major European rivers draining into the Southern North Sea (Table 2) using data from the 1999 OSPAR Comprehensive Study of River Inputs and Direct Discharges.

On average, 16.2% of the nitrogen entering the Southern North Sea from the rivers results from atmospheric deposition to the watershed. In a similar analysis, Castro and Driscoll (2002) found that total atmospheric inputs (watershed runoff plus direct deposition to the estuary) accounted for between 15% and 42% of the total nitrogen inputs to 10 estuaries on the east coast of the USA.

The EMEP model calculates an average direct nitrogen deposition to the Southern North Sea of 1040 kg km\(^{-2}\) yr\(^{-1}\) (www.emep.int/index.html). The area of the Southern North Sea considered is 190,944 km\(^2\) (Hydes et al., 1999) giving an average direct atmospheric nitrogen input of 199 kt yr\(^{-1}\). This compares well with the value of 228 kt yr\(^{-1}\) determined through atmospheric measurements (Rendell et al., 1993). Combining the EMEP atmospheric flux with the atmospherically derived component of the riverine nitrogen flux gives a total atmospheric nitrogen flux of 319 kt yr\(^{-1}\) to the Southern North Sea. The measured riverine N flux (subtracting the calculated atmospherically derived component) is 625 kt yr\(^{-1}\) which suggests that ~34% of the total nitrogen entering the Southern North Sea is atmospheric in origin.

Studies in the Humber and Thames estuaries (Sanders et al., 1997, 2001) have shown considerable seasonality in the riverine flux of water into the Southern North Sea with highest water flows in winter. As a consequence of this, highest nutrient fluxes also occur in winter. Prandle et al. (1994) calculate the flushing time of the Southern North Sea (to 56°N) as 240 days which suggests that these nutrients added in winter will still be available to phytoplankton to fuel the spring bloom.

### Table 2

<table>
<thead>
<tr>
<th>River system</th>
<th>Atmospheric inorganic nitrogen deposition to watershed (kg km(^{-2}) yr(^{-1}))</th>
<th>DIN export through the rivers which results from atmospheric deposition (kt yr(^{-1}))</th>
<th>Total riverine DIN export (atm + sewage + fertiliser) (kt yr(^{-1}))</th>
<th>% Export which is atmospheric in origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhine</td>
<td>2187</td>
<td>62</td>
<td>350</td>
<td>18</td>
</tr>
<tr>
<td>Elbe Estuary</td>
<td>2001</td>
<td>24</td>
<td>131</td>
<td>19</td>
</tr>
<tr>
<td>Weser</td>
<td>2132</td>
<td>12</td>
<td>71</td>
<td>17</td>
</tr>
<tr>
<td>Schelde</td>
<td>3072</td>
<td>6</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>English East Coast</td>
<td>1708</td>
<td>23</td>
<td>153</td>
<td>15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>126</strong></td>
<td><strong>745</strong></td>
<td></td>
<td><strong>74</strong></td>
</tr>
</tbody>
</table>

*Note: English East Coast rivers include the Humber, the Thames and the Wash Embayment. These three river systems make up 75% of the total riverine inputs from the English East Coast to the Southern North Sea.*
4.2. Budget approach comparing the magnitude of different nitrogen inputs to coastal waters

In a simple budgeting approach, Rendell et al. (1993) compared the different nitrogen inputs to the entire North Sea. The results showed that over annual time scales, input from the North Atlantic Ocean dominates the total inorganic nitrogen input to the North Sea but the atmosphere comprises ~28% of the land-based input. Our studies conducted as part of the MEAD project in the Kattegat Sea suggest that, on an annual basis, ~24% of the external biologically active inorganic nitrogen load comes from the atmosphere (Ærtebjerg et al., 2003; Spokes et al., submitted for publication). During the summer, as river flows decrease, the relative importance of the atmosphere increases with atmospherically derived inorganic nitrogen comprising around 40% of the external nitrogen load to surface waters (Ærtebjerg et al., 2003). These approaches inevitably treat the coastal region considered as a single ‘box’ for budgeting purposes while in practice, there are very strong regional gradients (e.g. de Leeuw et al., 2001; Hertel et al., 2003).

We have also used a budgeting approach on data collected as part of the ACSOE project in the Eastern Atlantic Ocean (Spokes et al., 2000). Fig. 3 shows rain and aerosol concentrations at Mace Head on the west coast of Ireland in May 1997 emphasising the episodic nature of the process. Converting these measured values to the total nitrogen rain and aerosol flux (inorganic + organic) gives a nitrogen input of 11 mmol m$^{-2}$ month$^{-1}$. The measured water column mixed layer depth offshore of Mace Head was 30 m and surface water nitrate concentrations were 1.3 mmol m$^{-3}$. During this time the atmosphere could, therefore, have supplied ~30% of the standing stock of surface water inorganic nitrogen.

4.3. Primary production approach—use of Redfield ratios

The Redfield ratio shows that phytoplankton use nutrients in well-defined ratios. These ratios show that for every mole of nitrogen used, 6.625 mol of carbon are assimilated (Redfield et al., 1966). Assuming all the atmospheric nitrogen is bioavailable, we can use this relationship to convert the calculated atmospheric nitrogen flux to surface waters into carbon incorporated by phytoplankton. This approach assumes that productivity in the receiving waters is nitrogen limited. This has been explicitly demonstrated in the Kattegat (Spokes et al., submitted for publication) and in the North Sea (Riegman et al., 1990). N/P ratios in atmospheric deposition tend to be very high both in these areas (Jickells, 1998) and more generally (Baker et al., 2004).

4.3.1. Using literature values or modelled estimates of primary production

Until recently, there were no simultaneous measurements of the atmospheric nitrogen flux and surface water biological production. We have previously, therefore, compared calculated atmospheric fluxes with literature values or modelled
estimates of primary production (Spokes et al., 2000). Using model primary production values from Sathyendranath et al. (1995) and new production estimates (Buesseler, 1998) results showed that in May 1997, 30% of new production in Atlantic waters off Ireland could have been supported by atmospheric nitrogen inputs. Atmospheric concentrations during this time were high as a result of meteorological conditions which allowed the transport of air over polluted source regions in continental Europe and Southeast England prior to arrival at the west coast of Ireland (Fig. 3). This study confirmed the fundamental importance of high concentration episodic inputs of nitrogen associated with transport of polluted air.

Comparing calculated atmospheric fluxes determined from studies in the Southern North Sea (Fig. 4) with measured primary production during the 1991 UK NERC North Sea Project suggests that in June 1998 ~2% of the surface water production could be supported by atmospherically derived nitrogen. In August 1999, the atmosphere could supply enough nitrogen to support ~6% of the surface water production. The increased importance of the atmosphere in 1999 compared to 1998 was the result of a very high concentration pulse of material associated with flow across the strong nitrogen source regions of Continental Europe and the UK (de Leeuw et al., 2003).

If we consider the just high concentration event centred on 26 August 1999 (shown in Fig. 4b), the average daily flux of wet + dry nitrate and ammonium was 0.8 mmol m$^{-2}$ d$^{-1}$. Assuming Redfield stoichiometry this amount of nitrogen could fix 5.3 mmol m$^{-2}$ Cd$^{-1}$. Average primary production measured in August during the NERC North Sea Project was 36 mmol m$^{-2}$ Cd$^{-1}$ suggesting that this single high concentration atmospheric event could support ~15% of surface water productivity.

Although comparisons are always made between atmospheric data and biological measurements made in the same season this approach assumes that the measured atmospheric flux and the

![Fig. 4. Aerosol and rainwater concentrations of nitrate and ammonium at Weybourne, on the north Norfolk coast of England overlooking the Southern North Sea. Samples were collected during the EU ANICE project with (a) showing data for June 1998 and (b) August 1999. The extremely high concentrations observed in both the aerosol and rainwater phase centred on 26 August 1999 (note the differences in scales between the two figures) are associated with transport of pollutants from the UK and continental Europe. Data from de Leeuw et al. (2001, 2003).](image-url)
productivity values are representative of this season in other years. With the limited data we have, it is impossible to determine whether this is the case. To overcome this we need to make simultaneous measurements in the atmosphere and in the water column.

4.3.2. First simultaneous measurements of the atmospheric flux and water column processes

As part of the ACSOE North East Atlantic Experiment in June 1998 measurements of rain and aerosols (Fig. 5) were made simultaneously with biological parameters. Only clean air that had spent at least 5 days over the ocean prior to sampling was encountered during this campaign resulting in an average inorganic wet + dry nitrogen flux of just 0.014 mmol m\(^{-2}\) d\(^{-1}\). During this time the measured biological nitrate uptake rate was 8.3 mmol m\(^{-2}\) d\(^{-1}\) (Jickells et al., in preparation). The atmospheric flux, therefore, represents <0.2% of nitrate uptake suggesting that in June 1998 the atmosphere was not an important source of nitrogen to the North East Atlantic and upwelling of nitrogen from deep waters is likely to be the most important external source of nitrogen to surface waters during this time.

During the MEAD campaigns measurements of surface water productivity were made in the Kattegat whilst atmospheric sampling was conducted at Bua on the southwest coast of Sweden. In August 2000, the average inorganic wet + dry nitrogen flux was 0.15 mmol N m\(^{-2}\) d\(^{-1}\) which, assuming all the nitrogen is available to phytoplankton, results in the assimilation of 1.02 mmol C m\(^{-2}\) d\(^{-1}\). Measured production in surface waters was 40–170 mmol C m\(^{-2}\) d\(^{-1}\) (Spokes et al., submitted for publication) and therefore atmospheric inputs had the potential to support just 0.6–2.5% of measured production during this time. In May 2001, the inorganic wet + dry nitrogen flux was 0.26 mmol N m\(^{-2}\) d\(^{-1}\). The average measured nitrogen input demand was 2 mmol N m\(^{-2}\) d\(^{-1}\) (Spokes et al., submitted for publication) and thus the atmosphere can supply enough nitrogen to provide 13% of this demand.

Retrospective analysis of long-term monitoring data from the Kattegat region conducted during the MEAD project (Hasager et al., 2003; Carstensen et al., 2004; Spokes et al., submitted for publication) suggests that the cumulative input of nitrogen from the atmosphere is larger than the cumulative input of nitrogen from deep water entrainment on an annual time scale in the Kattegat. Thus, the atmosphere is an extremely important overall nitrogen source to this region and will contribute towards eutrophication problems in the area. However, the results of this retrospective analysis and mesocosm experiments suggests that even the extreme high atmospheric deposition events seen in this region are not large enough to trigger algal blooms and that summer blooms in the region are most likely the result of entrainment of nutrient-rich deep water during wind driven mixing events (Hasager et al., 2003; Carstensen et al., 2004).

5. Conclusions

Inputs of biologically available nitrogen from the atmosphere to coastal waters are comparable
to riverine nitrogen inputs. Here, we consider the impact of atmospheric inputs using several different approaches. These approaches are all useful but lead to different conclusions.

Budgeting approaches imply that the atmosphere can, in some situations, provide enough nitrogen to potentially produce a large increase in phytoplankton growth. This is not true in all areas and at all times, emphasising the highly episodic nature of atmospheric deposition and the strong gradients away from source regions. Atmospheric deposition effects also need to be considered on various time scales. Firstly, there are direct effects of atmospheric deposition where short-lived high-deposition events appear to increase primary productivity. Secondly, atmospheric deposition enhances the overall nitrogen stock in the water column potentially fuelling primary production on the longer term and may contribute towards eutrophication problems in some coastal regions. In addition, atmospheric nitrogen deposition on land augments riverine nitrogen inputs to coastal waters adding further to the longer-term effects of elevated nitrogen.

However, productivity-based approaches seem to show that atmospheric nitrogen inputs are less important. This maybe because productivity in the Kattegat and in the North Sea (Weston et al., 2004) is controlled by internal recycling of nitrogen even in the summer when there is little inorganic nitrogen in the water column. In both environments, there are large organic and particulate nitrogen reservoirs in the water column. These can be recycled into ammonium and urea to drive production and, in a well-mixed water column, these regenerated nutrients remain potentially available to the biological community. The atmosphere provides a source of new nitrogen to the water column which is rapidly converted to organic nitrogen and joins this recycled nitrogen pool. The amount of new nitrogen added is small compared to the total pool of organic nitrogen even allowing for the variability and uncertainty in both the atmospheric input and the biological productivity. However, new nitrogen is assumed to drive export production (Dugdale and Goering, 1967) and in regions where there is stratification, atmospheric nitrogen inputs may contribute to carbon export to deep waters. Atmospheric inputs also contribute to the total nitrogen load in surface waters and, as mentioned above, may enhance eutrophication problems. Although not considered in this paper, biological nitrogen fixation of atmospheric N₂ gas is also a potential new nitrogen source to coastal waters.

The conclusions from the two approaches reflect the subtle differences in the questions posed. Even though productivity-based approaches appear to indicate that atmospheric nitrogen inputs do not significantly enhance summer biological production, reducing the load of nitrogen to surface waters will decrease total nitrogen loads and hence may reduce eutrophication problems.

What is the best way to achieve reductions in atmospheric nitrogen loads? Atmospheric nitrogen inputs arise largely from the handling of animal wastes (NH₃) and from combustion processes (NOₓ). NOₓ must first be converted to nitric acid and nitrate aerosols before significant oxidised nitrogen deposition can take place. This oxidation takes hours to days in the atmosphere allowing long-range transport to occur, so the impact of oxidised nitrogen deposition is widespread. In contrast, NH₃ deposition is very rapid and the main impacts are very close to the source of ammonia and, therefore, local. Thus, the environmental management of atmospheric deposition requires two very different strategies and scales. These are, in turn, very different to the management of riverine nitrogen inputs from fertiliser use and sewage discharge.

References


Asman, W.A.H., Hertel, O., Berkowicz, R., Christensen, J., Runge, E.H., Sorensen, L.L., Granby, K., Nielsen, H., Jensen, B., Gryning, S.E., Sempreviva, A.M., Larsen, S.,


