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The role of air-sea exchange in the marine nitrogen cycle

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Abstract

This contribution to the Spot-On volume considers the magnitude and composition of atmospheric nitrogen inputs to the oceans and then goes on to consider the impacts of these inputs. Effects in open ocean and coastal areas are probably different. Offshore atmospheric inputs may produce a small enhancement of overall ocean productivity and hence CO_2 drawdown. In coastal waters atmospheric inputs contribute significantly to overall eutrophication pressure, but evidence that they trigger algal blooms is limited. Management of atmospheric inputs to coastal waters to mitigate eutrophication pressures requires that emissions be managed over a wide area reflecting the efficient long range transport of atmospheric nitrogen. Strategies for management of oxidised and reduced nitrogen deposition will be different reflecting their different rates of deposition.

1 Introduction

Atmospheric inputs represent a significant component of the global nitrogen cycle and provide a relatively fast and efficient mechanism by which nitrogen released in one component of the Earth system can impact areas remote from the source regions. In this short article I will attempt to summarise our knowledge of the nature, cycling and magnitude of atmospheric nitrogen inputs to the oceans and then go on to speculate on the effects of these inputs. In considering effects it is convenient to consider open ocean and coastal systems separately.

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2 Atmospheric deposition to the oceans

2.1 Sources

Atmospheric nitrogen is traditionally considered in terms of two main components, oxidised and reduced nitrogen. The chemical behaviour of these components relevant to their atmospheric inputs is described very briefly here. More extensive discussions are available in Paerl et al. (2002); Raes et al. (2000); Spokes and Jickells (2005) or in standard texts such as Seinfeld and Pandis (1998). Oxidised nitrogen is dominated by emissions of NO and NO_2 (usually referred to as NO_x since they can interchange rather easily) which react relatively quickly (hours to days) to form nitric acid which can then react to form nitrate aerosol. Reduced nitrogen emissions are dominated by NH_3 gas and this gas is a major base in the atmosphere and reacts rapidly and sometimes reversibly with acids such as HCl, H_2SO_4 and HNO_3. In addition there are components such as relatively inert N_2 gas, the main gas in the atmosphere, and the long lived trace gas N_2O which will be covered by others in this symposium volume. Recently it has become clear that organic nitrogen is also important and will be discussed later.

Table 1 provides an estimate of global nitrogen fluxes, both natural and anthropogenic. Such compilations are necessarily best estimates and exclude sources that may be important locally or episodically. For instance Uematsu et al. (2004) and Huebert et al. (1999) recently noted the importance of nitrogen emissions associated with volcanic activity. The global nitrogen cycle has been massively perturbed by human activity (Galloway et al., 2004) and this includes the atmospheric component. Not only have total atmospheric nitrogen emissions changed over the last few hundred years associated with a doubling of overall global nitrogen fluxes (Galloway et al., 1995) but the nature of sources continue to change as global patterns of agriculture and industry evolve (e.g. Galloway et al., 2004; Fowler et al., 2004, Paerl et al., 2002). Table 1 presents estimates of the NO_x and NH_3 atmospheric emission sources, and emphasises that about 80% of current emissions are anthropogenic. Anthropogenic NO_x emissions are dominated by those associated with fossil fuel combustion while

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anthropogenic NH_3 emissions are associated with agricultural activity, particularly the handling of waste from intensive animal husbandry. The emission pattern is dominated by sources in highly populated and/or intensively farmed regions particularly in the Northern Hemisphere.

2.2 Reactions

As noted above, NO_x is oxidised on a time scale of hours to days depending on atmospheric conditions to HNO_3 which is then reactive with other gases and aerosols and can also be rapidly removed by deposition. Ammonia gas is also highly reactive in the gas phase and does not require an oxidation step prior to reaction. The result of these differences is that ammonia tends to be deposited closer to sources with NO_x only undergoing deposition after oxidation (Spokes and Jickells, 2005). For instance it is estimated that 71% of UK NO_x emissions are exported to the North Sea and beyond, while only 25% of ammonia emissions are exported (NEGTAP, 2001). This pattern is also seen in the eastern USA, but differences between oxidised and reduced nitrogen behaviour are less. This may reflect differences in emission patterns or climatology (Paerl et al., 2002), stressing the importance of dealing with different regions individually. This difference in behaviour between oxidised and reduced nitrogen has important implications for management strategies (see later).

Over land the primary reactions controlling the behaviour of oxidised and reduced nitrogen are acid base reactions forming aerosols from gas phase species. Such reactions result in the formation of fine (<1 μm diameter) aerosols (Raes et al., 2000). Some of the resulting aerosol species are semi-volatile and hence ammonium nitrate and ammonium chloride can dissociate to their component gases as ambient concentrations of those gases fall during transport and mixing. In certain environments such as near deserts, alkaline soil dust aerosol makes an important contribution to the aerosol and in such environments, these particles will also react with acids. Soil dust aerosol is usually formed by mechanical processes in arid areas and results in coarser aerosol particles (>1 μm). In addition when continental air masses are mixed

with seasalt aerosols near the coast there is a reaction between seasalt and nitric acid:

$HNO_3 + NaCl \rightarrow NaNO_3 + HCl$.

Seasalt is formed mechanically which also creates coarser aerosol particles, and hence this reaction shifts nitrate from fine mode to coarse mode. It also releases HCl which can then liberate free halogen radicals which can influence ozone cycling (e.g. Ayers et al., 1999). The importance of these reactions of nitric acid with dust and seasalt is that they serve to move the nitrate onto coarser aerosol particles. Atmospheric deposition rates increase rapidly with particle size. Kane et al. (1994) and Russell et al. (2003) have estimated that the reaction with seasalt increases deposition rates of nitrate in the marine environment by increasing particle size and deposition rates and this offsets the effects of the removal of highly reactive nitric acid (Pryor and Sørenson, 2002).

2.3 Deposition

Atmospheric deposition occurs by wet and dry deposition, the latter including both dry deposition of particles and gases. Gas deposition depends on concentration gradients across the air-sea interface and the equilibrium distribution between the phases (Henry's Law constant). Nitric acid concentrations in seawater are extremely low so deposition is a one way process, and nitric acid is rapidly and efficiently deposited (Pryor and Sørenson, 2002). For ammonia the situation is more complex as discussed below. Paerl et al. (2002) suggests that nitric acid dominates over nitrate, and ammonium over ammonia in both the eastern USA and Northern Europe, possibly because of efficient reaction of ammonia with sulphuric acid which is usually the dominant acid in the atmosphere. Norman and Leck (2005) find ammonia and ammonium concentrations to be generally similar with a slight dominance of ammonium in a large scale study covering much of the Atlantic Ocean. Reactions of seasalt with nitric acid mean that nitrate probably dominates over nitric acid in the remote marine boundary layer (Keene et al.,

1998), although the distinction between these species can be difficult to achieve with many sampling strategies.

For all the other species of interest here we are essentially considering wet and dry aerosol deposition, a process whose rate increases rapidly and non-linearly with aerosol particle size. Hence the importance of reactions of acid species with seasalt and dust as discussed above for creating coarse mode nitrate in the marine atmosphere as opposed to a fine mode dominance in the terrestrial atmosphere. There is also now evidence of some coarse mode ammonium in the marine atmosphere (Spokes and Jickells, 2005).

The relative importance of wet and dry deposition obviously varies greatly on short time scales since rainfall is episodic and varies spatially on longer time scales with global rainfall patterns. Relative proportions of wet and dry deposition from many campaigns lasting weeks have been reported, but these are still subject to the vagaries of the weather. Long term average wet deposition estimates are available for some sites though these are usually only for inorganic components, and these suggest that wet deposition dominates (Table 3). Since wet deposition is dominant and intrinsically episodic, and because atmospheric circulations such as frontal system can sometimes concentrate atmospheric contaminants in wet deposition, it follows that atmospheric deposition is episodic, often highly so (e.g. Spokes and Jickells, 2005), an issue of importance when assessing impacts.

2.4 Fluxes to the oceans

Dentener has used model simulations to estimate atmospheric N fluxes to the oceans in general and to different ocean basins (Galloway et al., 2004). The model simulations allow estimates of past fluxes as well illustrating the changing deposition pattern with time. The model estimates are very similar to early estimates of Duce et al. (1991) which were based on extrapolation of data from measured sites across the oceans. The agreement of these two approaches gives confidence in the overall fluxes, although there is inevitably an element of model tuning to match existing data. Galloway

et al. (2004) report the overall nitrogen fluxes to the ocean to be 2.4×10^{12} mol yr^{-1} representing about a third of total nitrogen emissions to the atmosphere. This estimate excludes organic nitrogen. Oxidised nitrogen is estimated to dominate total deposition (1.5 (nitrate) vs 0.9 (ammonium)$\times10^{12}$ mol yr^{-1}) again reflecting the preferential removal of ammonia emissions close to sources compared to emissions (Table 1).

The ammonia fluxes to the oceans are complicated by an internal recycle. In surface seawater ammonium is produced and consumed by marine biological processes. At the pH of seawater a small percentage of the ammonium is present as dissolved ammonia and this maintains an air-sea exchange equilibria with atmospheric ammonia gas. This emission cycle has been suggested to be an important climate regulation process via the formation of ammonium sulphate aerosol, the sulphate being derived from marine biogenic emission of DMS (Liss and Galloway, 1993; Bigg et al., 2003; Norman and Leck, 2005). This process is estimated to have resulted in a small net flux of ammonia from sea to land in the pre-industrial period (Galloway et al., 1995). On a global basis this has probably now been reversed (Galloway et al., 2004). Any ammonia emitted from the oceans is probably re-deposited fairly rapidly and hence predominantly in the oceans due to the rapid dry deposition and reactions of ammonia. Hence this cycle is not included in the overall N fluxes to the ocean above. However, this essentially internal cycle within the nitrogen cycle may still be important in process such as marine aerosol formation and pH control (Liss and Galloway, 1993; Norman and Leck, 2005). Isotopic evidence suggests that in remote ocean areas far from terrestrial ammonia sources, this marine recycled ammonia may become particularly important (Jickells et al., 2003). This isotopic approach offers a method to correct for any ammonia emitted from the oceans present in aerosols within the marine boundary layer.

2.5 Organic nitrogen

It is now clear that organic N represents a significant component of atmospheric N deposition. Most studies to date have focussed on organic matter that is either soluble in rainwater or easily extracted by water from aerosols (Cornell et al., 2003) but one study also considered insoluble organic N and noted it to be much more abundant than the soluble organic fraction (Russell et al., 2003). The nature and sources of atmospheric organic nitrogen are largely unknown, and it is undoubtedly composed of a wide range of organic material. Although in some areas some highly biologically labile components such as urea and amino acids appear to be important, much more refractory components such as humic material may also be important (Cornell et al., 2003). In both remote and more contaminated areas the organic nitrogen has an important fine mode aerosol component suggesting it is formed from gas to particle reactions, although a coarse mode primary from primary sources is also seen. (Cornell et al., 2001; Mace et al., 2003c; Russell et al., 2003). Seitzinger and Sanders (1999) have suggested that a significant fraction of atmospheric organic nitrogen may be bioavailable.

Comparison of results from several studies around the world provide some clues as to sources of the water soluble aerosol organic nitrogen (Table 2). Much higher concentrations appear to be associated with air flows from land, rather than from the oceans, suggesting that terrestrial sources, rather than, for instance, recycled marine organic matter, dominate. Biomass burning may also be important as a source. Existing studies do not identify any simple relationship between organic and inorganic nitrogen in the atmosphere which would be anticipated if the organic material had clear and simple anthropogenic sources. For instance, in sites with relatively high concentrations of nitrate from contaminant sources such as the Delaware coast, organic nitrogen concentrations are not exceptionally high (Russell et al., 2003) and Cape et al. (2004) in an extensive study at 7 sites in the UK and Neff et al. (2002) found no simple relationship to other inorganic nitrogen components. It is therefore not possible to say with any confidence if this organic nitrogen is of predominantly natural or anthropogenic origins.

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It probably has a mixed origin, and indeed it is perfectly possible that the C framework may be of natural origin and the N of anthropogenic origin, reflecting formation by atmospheric reactions. This would be consistent with some of the very limited available C and N isotopic data for atmospheric aerosol water soluble organic nitrogen (Kelly et al., 2005).

Although the data base is small, Cornell et al. (2003) report a review of a wide range of individual studies from many different environments which suggest on average organic N constitutes about 35% of total atmospheric nitrogen. More recent results are broadly consistent with this value with reported values from remote sites ranging from 17–46% (Mace et al., 2003a, b, c) and for 7 sites in the UK (rainfall only) 24–40% (Cape et al., 2004). Neff et al. (2002) also suggest a figure of 30%. Assuming organic nitrogen represents 35% of total nitrogen deposition, if inorganic atmospheric nitrogen deposition is 2.4×10^{12} moles yr^{-1} the organic component will be an addition 1.3×10^{12} moles yr^{-1}, giving a total flux of 3.7×10^{12} moles yr^{-1}. Note this assumes scavenging rates and deposition velocities for atmospheric organic and inorganic nitrogen are similar. This can be compared with a river flux 3.4×10^{12} moles yr^{-1}, the latter representing total riverine nitrogen. This further emphasises the importance of atmospheric deposition and that reduced, oxidised and organic nitrogen are all of importance in overall atmospheric nitrogen deposition. Furthermore, the budgets for the North Atlantic of Galloway et al. (1996) suggest that fluvial nitrogen inputs to the oceans are denitrified on the shelf and that the shelf region is a sink rather than a source of nitrogen for the open oceans. Their analysis leaves atmospheric inputs and nitrogen fixation as the dominant inputs of nitrogen to the open ocean.

3 Effects of atmospheric deposition

Atmospheric inputs are therefore comparable to fluvial inputs and of the same order of magnitude as marine nitrogen fixation, so it is logical to ask what effect this input has on the marine ecosystem. In considering this question it is useful to separate the

impact on the open ocean from coastal waters because the latter are subject to high nitrogen loadings in general including atmospheric inputs. It is not possible to consider impacts of nitrogen alone since phytoplankton primary production requires a range of nutrients – N, P, Si and Fe particularly, plus light. Human activity mobilises large amounts of gas phase nitrogen as NH_3 and NO_x. Since P and Si have no significant gas phase components, their atmospheric fluxes are minor and little perturbed by human activity (e.g. Jickells, 1998; Baker et al., 2003, 2006[1]). Iron fluxes are similarly probably little modified by human activity, but the effective trapping of fluvial iron within coastal systems means that atmospheric inputs of iron represent a major source of this key nutrient to ocean waters and the absence of this input contributes to the development of high-nutrient-low-chlorophyll (HNLC) regions in the oceans such as in the Southern Ocean (Falkowski et al., 1998; Jickells et al., 2005). Thus in assessing atmospheric inputs, the balance of nutrient inputs, in addition to simply the nitrogen inputs, must be considered. The atmosphere is also an important transport route for a wide variety of contaminants to the marine system (Duce et al., 1991) albeit at relatively low levels. The combined effects of nutrient and contaminant addition have never been studied in this context, although we know that small changes in the availability of copper for example can have significant effects on phytoplankton species composition (Moffett et al., 1997).

3.1 Oceanic areas

Atmospheric inputs of fixed nitrogen can probably only directly affect waters that at least seasonally show nutrient depletion. HNLC regions such as the Southern Ocean will not respond directly to atmospheric nitrogen inputs since there is already excess nitrate in the water column. Atmospheric nitrogen inputs to these regions are modest

[1]Baker, A. R., Jickells, T. D., Biswas, K. F., Weston, K., and French, M.: Atmospheric aerosols along the AMT transect – sources and cycling of atmospheric nutrients, Deep-Sea Res. II, submitted, 2006.

(Galloway et al., 2004) anyway and may contribute in a small way to the concentrations in deepwater when water masses in this region sink. Atmospheric iron inputs in such regions although small may of course be very important (Jickells et al., 2005). Hence in considering atmospheric nitrogen inputs it is simplest to really only consider the central gyre regions and the temperate ocean waters subject to seasonal macro nutrient depletion. Primary production in these waters is clearly nutrient limited, though not necessarily limited by nitrogen supply or at least not only by nitrogen supply (e.g. Mills et al., 2004). Baker et al. (2003; 2006[1]) consider the balance of atmospheric nutrient supply through the Atlantic Ocean, demonstrating that the aerosol is a very minor source of phosphorus and silicon compared to its role supplying iron. Furthermore meteorological processes mean that atmospheric inputs of Fe and N are co-located over the tropical Atlantic (Baker et al., 2006[1]). A similar situation probably occurs in the Pacific Ocean as the Asian dust plume passes over the industrial zone of China, Japan and Korea. (Galloway et al., 2004; Jickells et al., 2005), an area likely to see large increases in nitrogen flux in coming decades with increasing industrialisation in this region (Galloway et al., 2004). Note the co-deposition of nitrogen and iron is not always the case, with, for example, the major nitrogen plume from the northern United States not being associated with significant dust transport. Given the minor role of silicon as a nutrient in ocean gyre regions, co-deposition of nitrogen and iron translates into the atmospheric input pushing the system toward phophorus limitation, both by supplying inputs with a high N/P ratio and supplying Fe which can stimulate nitrogen fixation. The same situation has been argued to occur in the Mediterranean and contribute to the situation of extreme oligotrophy seen in the eastern Mediterranean (Carbo et al., 2005). This means, ironically, that the small atmospheric phosphorus flux may be relatively important compared to the much higher (in absolute and Redfield ratio terms) atmospheric nitrogen flux.

In considering the effects of atmospheric inputs on marine systems, it is obvious that the effects will vary from place to place depending on the gradients in atmospheric nitrogen inputs, the ambient water column nitrogen concentrations and the nitrogen

requirements of the euphotic zone community. Impacts may take many forms but the easiest question to pose is whether the atmospheric inputs are going to significantly modify primary productivity and hence potentially have ecological consequences. One way to address this is to consider the situation in the Sargasso Sea near Bermuda. This is a relatively oligotrophic gyre region which at least for significant periods of time receives relatively high nitrogen inputs arising from the continental USA (Galloway et al., 1996), and hence is an area where impacts are relatively likely to occur, if anywhere. This implicitly assumes that the system is nitrogen limited whereas in fact it may be phosphorus limited (Wu et al., 2000) or show complex patterns with different nutrient limitation of different communities (e.g. Mills et al., 2004). Only long term wet deposition data are available for the Bermuda site and hence total nitrogen deposition will probably be 30% higher based on Table 3. It is clear from Table 4 that atmospheric inputs, with or without dry deposition, are small compared to new primary production and hence large scale impacts are unlikely. Sources of nitrogen to sustain new production at this site have been extensively discussed (e.g. Jenkins and Doney, 2003).

Although this calculation specifically implies that the impacts of atmospheric deposition are likely to be small, this is not the only way to consider the impacts of atmospheric inputs in this area and more generally.

Atmospheric inputs are episodic as noted earlier. Michaels et al. (1993) therefore carefully evaluated if individual atmospheric deposition events could significantly alter primary and new production in the Sargasso Sea. They concluded that this was very unlikely and that ambient water column nitrogen cycling rates and standing stocks are large compared to atmospheric inputs, even on the short term and even allowing for seasonality at this site. Bange et al. (2000) used cruise data on aerosol nitrogen concentrations to estimate the relative importance of atmospheric inputs in sustaining new production in the Indian Ocean. They estimate atmospheric deposition rates approximately half those in Table 4 and estimate that atmospheric nitrogen could support 0.1–17% of new primary production, the range covering different times and areas within the region.

Pahlow and Riebesell (2000) have reported temporal trends in deep ocean Redfield ratios with increasing N/P ratios in the deep waters of the North Atlantic from the 1960s to the 1990s which they suggest could be the result of atmospheric nitrogen deposition. This effect would allow long term impacts of atmospheric nitrogen deposition far from areas of deposition as deepwater returns to the surface at high latitude. The required atmospheric fluxes to modify deep water Redfield ratios are at the upper end of those in Table 4, but it is clear that atmospheric inputs could be contributing to the trend reported. However, Pahlow and Riebesell (2000) do specifically assume the North Atlantic to be nitrogen limited, which as noted earlier may not be the case. They also in their analysis eliminate changes in circulation as a potential cause of the changes seen, but this conclusion may require reconsideration in the light of recent evidence of changes in circulation pathways in this region (Bryden et al., 2005).

An alternative coupling of the iron and nitrogen cycles involves stimulation of nitrogen fixation, since iron is a key nutrient for nitrogen fixing enzymes (Capone et al., 2005; Jickells et al., 2005; Mills et al., 2004). The role of nitrogen fixation will be dealt with elsewhere in this special volume, but it should be noted that dust inputs to the tropical North Atlantic are at a maximum in summer when nutrient conditions in surface waters are most oligotrophic, although there is no direct evidence that this dust input affects fluxes to the deep ocean in this region (Jickells et al., 1998). Galloway et al. (1996) suggest that nitrogen fixation is the dominant external input of nitrogen to the North Atlantic. Pahlow and Riebesell (2000) attribute changes in deep water Redfield ratios in the Pacific to changes in atmospheric iron (dust) input to an iron limited ecosystem.

This consideration of the Sargasso Sea region leads to the same conclusion as Michaels et al. (1993), that atmospheric nitrogen inputs are small compared to internal nutrient stocks and cycles within the euphotic zone under most conditions. This region is a central ocean gyre region of rather low ambient water column nutrient concentrations downwind of large atmospheric emissions and if the direct impacts of atmospheric inputs are modest in this region then they will be modest in other areas. However, the analysis of Pahlow and Riebesell (2000) points to a different kind of effect, and that

is on the larger scale inventory of ocean nitrogen. Atmospheric inputs of nitrogen are comparable to riverine inputs (Galloway et al., 2004) and both can increase the overall stock of nitrogen within the oceans. This nitrogen stock is large so that short term effects of inputs will be modest and hence large scale effects on ocean productivity will be small and may be offset by changes in denitrification. However, it is also possible to consider the atmospheric input as a low level fertilisation effect on the oceans. Hence, in Table 5 I consider the extent to which the atmospheric inputs of nitrogen to the oceans might increase overall new production in the oceans and hence oceanic CO_2 uptake. In making this rather preliminary calculation I have assumed that all atmospheric inputs fall into nitrogen limited marine euphotic zone systems. This is clearly not the case and hence the impact is an upper limit. However, as is clear from most of the major emission regions do in fact pass over nitrogen deficient ocean areas; Galloway et al. (2004) estimate that 85% of atmospheric deposition to the oceans is into the North Atlantic, North Pacific and Indian oceans, for example. Assuming that all the atmospheric input falls into N limited waters and stimulates new primary productivity according to Redfield stoichometry implies an increase in ocean productivity equivalent to 0.15 $Gt\,yr^{-1}$ CO_2 uptake as a result of anthropogenic N release. This represents 5–10% of all ocean CO_2 uptake and is therefore not trivial in a global sense, though all of the assumptions make this an upper limit, except the exclusion of organic nitrogen. Houghton et al. (1996) reach a broadly similar figure and conclusion.

3.2 Coastal systems

Atmospheric deposition rates of nutrients including nitrogen and contaminants are in general higher into coastal waters than to open ocean areas because these are closer to sources. However, the magnitude of atmospheric fluxes varies over at least two orders of magnitude (Jickells, 2005) between relatively pristine environments such as the Alaskan Shelf (0.9 $mmol\,N\,m^{-2}\,yr^{-1}$) to areas close to major centres of habitation and industrial activity (e.g. North Sea 70 $mmol\,N\,m^{-2}\,yr^{-1}$). Theses are annual averages and again it should be stressed that short term events can yield much high fluxes, and

sub-regions of a large area like the North Sea may receive higher fluxes.

There are some additional complications in coastal areas. The higher ammonia concentrations in the atmosphere and complex ammonia cycling in the atmosphere and nutrient rich waters mean that air-sea exchange fluxes for ammonia can be particularly complex (Walker et al., 2004; Sørenson et al., 2004). In addition the seasalt/nitric acid reactions (see earlier) take place as the terrestrial and marine air masses mix (Spokes and Jickells, 2005). Air sea exchange of reactive gases such as ammonia is dependent on small-scale meteorological phenomena. Rapid changes in surface roughness and complex coastal topography make the coastal zone particularly complex meteorologically with the formation of jets, seabreezes etc. (Žager et al., 2005) which means that the whole coastal zone needs to be treated as a complex intermediate zone both physically and chemically, and not as either an extension of the terrestrial or oceanic ocean/atmosphere system.

Assessing the impacts of atmospheric deposition to coastal waters is complicated by the importance of other inputs such as rivers and groundwater (Jickells, 1998, 2005; Paerl et al., 2002). These are not completely independent because a significant component of the fluvial nitrogen input may be derived from atmospheric inputs to the catchment. This issue is particularly important in regions with relatively small estuaries compared to their catchment area and hence where direct atmospheric deposition to the estuary is inevitably small (Valigura et al., 2001). For instance, the contribution of atmospheric inputs to the total fluvial nitrogen input ranges from 7–61% for 34 estuaries on the US east and gulf coasts (Castro et al., 2001), and in most of these estuaries direct atmospheric deposition makes a secondary contribution to the total atmospheric deposition, the proportion being related to the estuarine area versus the watershed area (Castro et al., 2001). Spokes and Jickells (2005) show that for the major North Sea rivers, atmospheric deposition may contribute 15–20% of total fluvial nitrogen. The importance of atmospheric deposition to river catchments as a contribution to eutrophication pressures leads to the concept of “airsheds”, areas where atmospheric emissions influence a coastal water body (Paerl et al., 2002). These airsheds can be

15–200 times larger than the watershed, creating complex challenges for strategies for management of coastal eutrophication.

In the case of large coastal seas such as the North Sea and the Baltic, direct atmospheric deposition to marine waters is also important. For instance, Brion et al. (2004) estimate that atmospheric inputs exceed riverine inputs of nitrogen to the North Sea (1631 vs 805 kT N yr^{-1}), although their atmospheric input estimate is substantially high than that of Rendell et al. (1993) based on direct measurements (412 kT N yr^{-1}), which is similar to the estimate of Rodhe et al. (2005) 350 kT N yr^{-1}, perhaps emphasising the uncertainties in these estimates. Both Brion et al. (2004) and Rodhe et al. (2005) agree that the biggest input of N to the North Sea is from offshore (6476 and 3619 kT N yr^{-1}, respectively) although this value is probably the most uncertain and most difficult to estimate in any budget. In the Baltic Sea, Voss et al. (2004, and references therein) estimate atmospheric N inputs at 185 kT N yr^{-1} compared to riverine inputs of 830 kT N yr^{-1}. Exchanges with the North Sea in this case are also significant sources of N (e.g. Spokes et al., 2006) and for the Baltic Sea in particular nitrogen fixation is also very important (Voss et al., 2004). Direct atmospheric inputs are also important in other areas such a the East China Sea where Zhang and Liu (1994) estimate atmospheric (inorganic) nitrogen inputs to be 1.8 times fluvial inputs and 2 times for P, although fluvial fluxes dominated for Si. As noted earlier, this is a region where fluxes are expected to increase considerably in coming decades.

Thus atmospheric nitrogen sources are clearly significant compared to other terrestrial nitrogen sources, and as noted earlier these inputs have been significantly increased by human impact. However, assessing the impact of atmospheric inputs does require that other inputs, such as those from offshore and from nitrogen fixation are considered. In addition different responses can be anticipated from different coastal biogeochemical communities in response to nutrient loadings depending on the hydrography of each coastal area (e.g. Jickells, 1998; Paerl et al., 2002). Hence it is very difficult to generalise except to the extent that primary productivity in many most coastal waters is nitrogen limited (Jickells 1998; Paerl et al., 2002), and hence any

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input of nitrogen will enhance productivity.

Pearl (1995) has shown that atmospheric inputs can represent a significant component of external inputs of nitrogen to a wide variety of systems and (Paerl, 2002) has shown that atmospheric deposition at high but plausible concentrations can alter productivity. Paerl (2002) and Paerl et al. (2002) also showed that supplying the nitrogen in different forms can alter the phytoplankton response.

Spokes and Jickells (2005) have considered various strategies to assess the significance of atmospheric nitrogen inputs. They point out that budget approaches which indicate the relative importance of atmospheric nitrogen inputs may not on their own always be the most appropriate method to assess the impact of atmospheric deposition on primary productivity. Thus as noted already for offshore waters, much of the primary productivity in coastal waters is sustained by internal recycling on a variety of time scales. Hence atmospheric (and indeed other) inputs may be small compared to productivity requirements for nitrogen and in the short term standing stocks of phytoplankton, bloom development and primary production may not be affected by atmospheric deposition events. However, atmospheric inputs do increase standing stocks of nitrogen and in this way contribute to the overall magnitude of algal activity. In addition, while atmospheric deposition events may usually not be large enough to stimulate blooms, they may play an important role in sustaining them (e.g. Kononen, 2001).

In a detailed study of the role of nitrogen deposition in the Kattegat, Spokes et al. (2006) showed again that atmospheric inputs were only a small part of the overall nitrogen cycle, although their relative importance changed seasonally. On their own atmospheric inputs were unlikely to stimulate blooms but again can contribute to the overall eutrophication pressure in the area. These authors went on to evaluate management options for reducing nitrogen loading and associated eutrophication pressures noting that different strategies were required for ammonia/ammonium and nitric acid/nitrate because of their different sources and deposition characteristics. Thus local regulation would be most effective for ammonia/ammonium while regional strategies would be required for nitric acid/nitrate and since both were important, large

scale integrated management strategies would be needed. The results of Valigura et al. (2001) for the eastern United States are similar and suggest this is a general conclusion on management strategies. The scale of airsheds (Paerl et al., 2002) requires that management strategies for coastal eutrophication must consider management of agricultural and combustion based emissions of nitrogen throughout the air shed and watershed.

4 Conclusions

Atmospheric nitrogen inputs to the oceans are comparable to riverine inputs in magnitude on a global basis and thus an important part of the global nitrogen budget. These fluxes have also be greatly perturbed by human activity. In general atmospheric nitrogen inputs are small compared to internal ocean nitrogen fluxes and so are unlikely to cause large scale changes in phytoplankton activity. However, such changes are locally possible under special circumstances and atmospheric nitrogen inputs do contribute to the productivity of the oceans and coastal waters.

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Table 1. Atmospheric emissions of fixed nitrogen 1993 10^{12} moles N yr^{-1} (based on Galloway et al., 2004).

Activity	NO_x	NH_3
Anthropogenic		
Biomass Burning*	0.5	0.6
Agricultural Activity	0.2	2.8
Fossil Fuel Combustion	1.5	0.01
Industry	0.5	0.2
Natural		
Soils, vegetation and animals	0.2	0.3
Lightening	0.4	–
Natural fires[$]	0.06	0.06
Stratosphere exchange	0.04	0.04
Ocean exchange	0.4	
Total	3.4	4.5

* Some of the tropical biomass burning included here could be natural.
[$] Under "natural fires" only high latitude forest fires are included.

Table 2. Aerosol water soluble organic nitrogen concentrations in aerosols at some selected locations.

Location	Concentration nmol m^{-3}	
Delaware coast	6.9	Russell et al. (2003)
Amazonia wet season	3.5	Mace et al. (2003a)
Dry (burning) season	61	Mace et al. (2003a)
Mediterranean	29	Mace et al. (2003b)
Tasmania		
ocean sector	0.95	Mace et al. (2003c)
land sector	3.6	Mace et al. (2003c)
Hawaii		
ocean sector	3.3	Cornell et al. (2001)
land sector	28.5	Cornell et al. (2001)

Table 3. Percentage of total deposition which is wet from a variety of long time series measurements.

Site	% Wet Deposition*	Reference
40 US East Coast Watersheds	61%	Meyers et al. (2001)
Kattegat	79%	Carstenson et al. (2005)
Southen North Sea	55%	Chester et al. (1994)
World Oceans	71%	Duce et al. (1991)

*only Southen North Sea estimate includes organic nitrogen

Table 4. Atmospheric nitrogen inputs vs new primary production for the Sargasso Sea.

Sargasso Sea Annual Budget	mmol N m^{-2} yr^{-1}
New production	670–780*
Atmospheric input (wet)	5.8–29[#]

* Jenkins and Doney (2003)
[#] Knap et al. (1986)

Table 5. Estimation of the fertilisation effects on CO_2 uptake of anthropogenic nitrogen deposition on the oceans.

Global atmospheric inorganic N Flux	2.4×10^{12} moles yr^{-1} ,
80% Anthropogenic (Table 1),	
Equivalent to 1.9×10^{12} mole N yr^{-1} Ocean fertilisation.	
Assuming this all falls on N limited areas and Redfield stoichiometry,	
Equivalent to 0.15 Gt CO_2 uptake yr^{-1}	