Dry deposition of reactive nitrogen to marine environments: recent advances and remaining uncertainties

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Abstract

Many highly productive marine ecosystems exhibit nitrogen limitation or co-limitation. This article is a status review of research into the exchange of nitrogen between the atmosphere and these ecosystems with a particular focus on reactive nitrogen compounds. A summary of research conducted over the past ten years is presented and a perspective given as to remaining uncertainties and research needs. Looking toward development of coastal management modeling tools, we illustrate the processes that need to be resolved in order to accurately simulate the flux from the atmosphere and provide guidance on the required resolution of such models.

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1. Introduction

Many marine ecosystems, particularly ones with high primary productivity, exhibit nitrogen (N) limitation or co-limitation (Herbert, 1999). Hence there is interest in quantifying the current N flux to marine ecosystems for use in eutrophication studies (Meyer-Reil and Koster, 2000; Smith et al., 1999) and developing prognostic tools to quantify flux spatiotemporal variability and future flux scenarios. Recent studies have indicated increased confidence in estimates of internal N cycling (Herbert, 1999) and riverine loads of N (Stalnacke et al., 1999; Unlceas et al., 1998) but the atmospheric component of the flux remains poorly constrained (Valigura et al., 2001) despite indications that it makes a significant contribution in both coastal and open ocean environments (Huesemann et al., 2002) particularly during periods of low nutrient concentrations (Rendell et al., 1993).

Understanding of the atmospheric N flux and development of prognostic tools for policy based scenario building has been largely limited by

1. Limitations in our observational capabilities from which we may obtain data sets of the exchange and the process level understanding necessary for development of prognostic numerical models.
2. The lack of validated, comprehensive numerical models to assess spatial and temporal variability.

Many research projects have been undertaken during the last decade focused on quantifying N exchange with coastal waters and the biochemical response. However, there is a geographic bias to this research which has been largely conducted in northern Europe (e.g., Baltic Sea (see www.io-warnemuende.de/Projects/Basys/), North Sea (de Leeuw et al., 2001), and the Kattegat Strait (Sørensen et al., 2002b)), the coasts of North America (Valigura et al., 2001) and the seas around Japan (Murano et al., 1998).

Herein, we present a brief summary of the status of knowledge, some new developments and highlight some issues that may form the basis of future investigations. For brevity we omit many details of the exchange processes (documented elsewhere, e.g. Wesley and Hicks, 2000; Geernaert and Geernaert, 1998). We also neglect direct fixation of molecular N (Herbert, 1999) and wet deposition of N compounds (Scudlark et al., 1994) as mechanisms for N input and focus on dry deposition of the most abundant, soluble and biologically available...
fixed reactive N species: nitric acid (HNO₃), ammonia (NH₃), nitric oxide (NO), nitrogen dioxide (NO₂), and particle bound nitrate (NO₃⁻) and ammonia (NH₄⁺). Dry deposition of these compounds comprises 20–40% of the N flux dependent upon the study area (Geernaert et al., 2000).

2. Atmosphere–surface exchange of reactive nitrogen

2.1. Oxides of nitrogen

Oxides of nitrogen (NOₓ = NO + NO₂) have traditionally been considered minor components of the addition of atmospheric N to marine ecosystems due to (i) their relatively short atmospheric lifetimes and (ii) low deposition velocities (v_d). Laboratory studies indicate v_d to sea water for NO₂ of ≈6 × 10⁻³ cm s⁻¹ (Duyzer et al., 1993) (at least two orders of magnitude less than typical values for NH₃). However, few in situ measurement of NO₂ deposition to water surfaces exist and the high abundance of NO in urban atmospheres (Fenger, 1999) means NO₂ may significantly contribute to N deposition downwind of coastal conurbations. Direct flux estimation for NO and NO₂ is now possible via eddy covariance (Walton et al., 1997; Pilegaard et al., 1995) and should be undertaken to provide in situ observations of v_d.

2.2. Nitric acid

Nitric acid has been shown to significantly contribute to total N deposition to a range of surface types due in part to its high solubility. With respect to marine environments a major uncertainty regarding HNO₃ fluxes is associated with reaction on sea spray droplets which acts as a competing sink to surface removal and leads to complex vertical gradients of concentration and flux divergence (Geernaert, 1998; Geernaert et al., 1998). This reaction may be particularly important in the coastal zone where surf activity enhances total sea spray concentrations (de Leeuw et al., 2000), and while it does not impact the total N deposition, it greatly modifies the spatiotemporal patterns due to the discrepancy in v_d for HNO₃ versus particle NO₃⁻ (Pryor and Sørensen, 2000). The phase transfer is largely determined by the droplet surface area (and accommodation coefficient) and competition with other acidifying gases (Erickson et al., 1999), and hence is very sensitive to trace gas concentrations, the formulation of the sea spray source function (Guelle et al., 2001) and the vertical distribution of sea spray relative to trace gases. It has typically been assumed that NO₃⁻ formed from this reaction is associated with coarse mode particles that have high v_d and thus that the phase transfer tends to result in higher near source deposition. This view is being increasingly challenged by observations and modeling which suggest a more complex picture and even that transfer to the particle phase may reduce deposition in the coastal zone under some conditions (see Fig. 1, Pryor et al., 2001a; Pryor and Sørensen, 2000; de Leeuw et al., 2001). These findings are particularly relevant in light of new research indicating that the flux of sub-micron sea spray may previously have been under-estimated in source parametrizations (Nilsson et al., 2001) and hence that sea spray surface area may be dominated by smaller (less readily depositing) particles.

2.3. Ammonia

To date, a major limitation on our understanding of atmosphere–surface exchange of trace N compounds has been the lack of instrumentation capable of measuring atmospheric NH₃ at ambient concentrations or directly measuring the flux thereof. With respect to the former, the recently developed WEDD systems (Sørensen et al., 1994; Pryor et al., 2001b) represent a significant advancement. These systems are capable of continuously measuring NH₃ concentrations in the concentration range which characterize many marine environments. With respect to flux measurement, fast response sensors capable of accurately measuring ambient concentrations of NH₃ and HNO₃ at the second or
sub-second timescales are not yet available. However, development of relaxed eddy accumulation (REA) methods (Businger and Oncley, 1990) has facilitated direct flux measurement of HNO₃ (Pryor et al., 2002) and NH₃ (Sørensen et al., 2002b). These improved measurement capabilities are key to understanding the full complexity of NH₃ exchange. As shown in Fig. 2 the WEDD based REA system operated during the MEAD experiment (Sørensen et al., 2002b) is able to resolve the flux over averaging periods of minutes versus gradient approaches using denuders or filter packs which require much longer sampling periods.

Although it has long been known that atmospheric concentrations of NH₃ in the atmospheric marine surface layer are small compared to water concentrations (Asman, 1994), only recently has it been possible to measure (and therefore consider in detail) the bi-directionality of NH₃ fluxes (Sørensen et al., 2002a) and most current atmospheric models continue to treat the sea surface as a perfect sink for NH₃. However, Sørensen et al. (2002a) showed that for a small variability in seawater pH of 7.9–8.1 the atmosphere–surface exchange of NH₃ was modified by 1/3 and that including modest gradients of dissolved NH₄⁺ into model calculations for the North Sea can decrease NH₃ deposition to the coastal zone by a factor of 5. These findings illuminate the importance of recent instrumentation innovation and the necessity for coupling marine and atmospheric models at appropriate spatial scales in order to correctly determine the air–sea concentration gradients.

2.4. Particle bound N

In terms of particle flux measurement, no instrumentation is currently available that can offer direct measurement of the size and composition resolved particle fluxes. Hence it remains common place to use the concentration method to determine particle N deposition where measured size resolved concentrations are multiplied by modeled $v_d$ for the appropriate particle diameter and the results integrated over the particle size spectrum (Pryor et al., 1999). There are two principal sources of error in this approach (excluding those which arise due to violations of assumptions inherent in micrometeorological techniques such as those regarding the constant flux layer):

- Sampling artefacts where the collected deposit may be subject to reactions and/or evaporation/condensation during the sampling period (Pio and Lopes, 1998).
- Uncertainties in the model used for estimation of $v_d$.

Although detailed numerical models exhibit relatively good agreement with data sets available from laboratory measurements (e.g., Larsen et al., 1995) the uncertainty is factor of two (Pryor and Sørensen, 2002a).

![Fig. 2. Half-hour average NH₃ fluxes determined using the WEDD based REA system (shown by the symbols) and the fluxes calculated from gradients (solid bars) derived using diffusion denuders as measured at Bua on the SW coastline of Sweden during three days of the MEAD experiment when consistent onshore winds were observed. Negative fluxes represent surface uptake.](image)

![Fig. 3. Relative abundance of NH₄⁺, NO₃⁻ and Na⁺ as a function of particle size (in the model layer extending from 2 to 22 m above the surface) for a simulation conducted using the CHEM-COAST multi-layer trajectory model (Pryor et al., 2001a) where simulation conditions are as in Fig. 1 except after 3 h (70 km from the coast) the column experiences a relatively high NH₃ environment (molar concentrations 100 times those of the initial NH₃ and 10 times the initial HNO₃) for 3 h. Under these conditions NH₃ is taken up into acidified sea spray droplets causing an NH₄⁺ peak in the coarse mode aerosol. Note: Concentrations are shown as abundance relative to the maximum bin averaged concentration per m³ of air at the end of the simulation.](image)
2000). Additionally, most numerical models do not adequately resolve the ambient particle size distribution and hence often apply a single \(d_a\) (see discussion in Pryor, 2002).

The bi-modality of \(\text{NO}_3^-\) in marine particles has long been the subject of research (Foltescu et al., 1996; Yvon et al., 1996) but the presence of \(\text{NH}_3^+\) in the coarse mode of marine particles received relatively little attention until Yeatman et al. (2001) suggested this feature arises largely due to coagulation of accumulation mode particles. Given the low coagulation efficiency of these particles (Binkowski and Roselle, 2002) it is possible that this feature actually arises due to uptake of \(\text{NH}_3\) onto coarse mode sea spray particles acidified by uptake of \(\text{S}\) and \(\text{N}\) gases. This postulate is exemplified by the scenario depicted in Fig. 3 where an air parcel which initially has high acidic gas concentrations enters a marine environment and subsequently experiences elevated \(\text{NH}_3\) concentrations (such as might characterize a coastal zone).

3. Concluding remarks

As outlined above, considerable progress has been made during the last decade in understanding the physicochemical controls on air–sea exchange of \(\text{N}\) compounds. However many questions remain with respect to our process-level understanding and there is a need for development of numerical models of the \(\text{N}\) exchange which incorporate the physical, chemical and biological processes and can capture the appropriate scales of variability with respect to for example; atmospheric flow, sea spray emission, heterogeneous chemistry and the variability of sea water \(\text{pH}\) and \(\text{NH}_3^+\) concentrations particularly in the coastal zone.

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