

## Air-Sea Exchange of Nitrogen and Iodine

A Contribution to subproject CAPMAN

Tim Jickells, Alex Baker, Sarah Cornell, Lucinda Spokes and Stuart Yeatman.

*School of Environmental Sciences, University of East Anglia,  
Norwich, NR4 7TJ, U.K*

### Summary

Most of the research described here aims to improve our understanding of the transport, deposition and impact of atmospheric nitrogen on marine ecosystems. Recent highlights of our work include:

1. an improved description of the interactions between sea salt, nitric acid and ammonia in the coastal marine atmosphere,
2. the first report of the speciation, size distribution and composition of organic nitrogen in the remote marine atmosphere,
3. the demonstration of the utility of nitrogen isotopes for tracing the sources and transformations of nitrogen in the coastal marine atmosphere,
4. the quantification of the significant contribution of atmospheric nitrogen deposition to the nitrogen requirements of coastal phytoplankton.

In addition we have a significant programme of research into iodine cycling in the coastal marine environment. Recently we have shown the importance of marine macroalgae as a source of gas phase methyl iodide to the coastal marine atmosphere and also described the speciation of aerosol iodine.

### Aims of the Research

The overall aim of the research is to better understand atmospheric transport and deposition processes in the marine environment and its effect on marine ecosystems.

### Activities During the Year

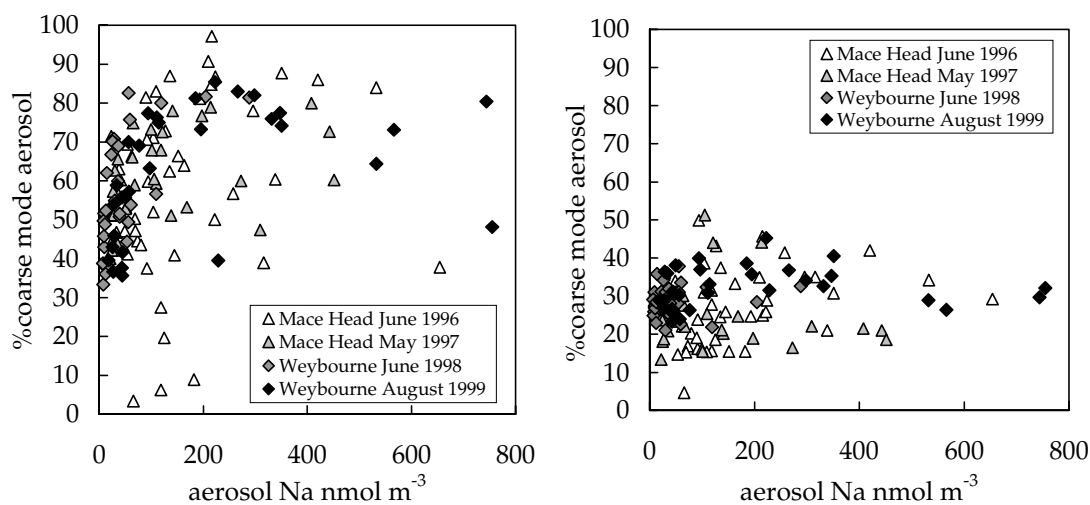
The main field campaigns have been involved with the EU funded FP5 project MEAD (Marine Effects of Atmospheric Deposition) in the Kattegat. In addition we have been analysing samples and data from previous campaigns, particularly those of the EU FP4 project ANICE (Atmospheric Nitrogen Inputs to the Coastal Ecosystem) and the UK NERC ACSOE project (Atmospheric Chemistry Studies in the Oceanic Environment).

### Principal Results

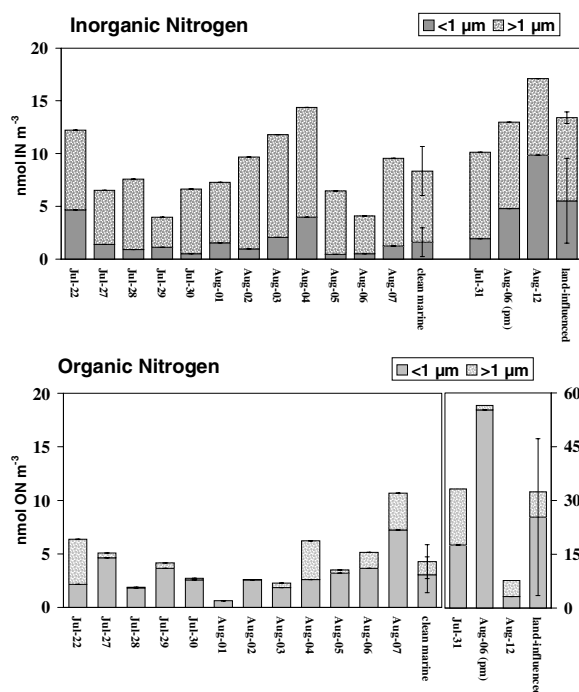
#### *Nitrogen*

The deposition rate of fixed nitrogen depends critically on the size distribution of the component of interest in the aerosol. In the coastal zone, air masses of marine and continental origin interact. We have shown that during such interactions the size distribution of continentally derived nitrate and ammonium are significantly altered. This arises from interactions of gas phase nitric acid and ammonia and fine mode aerosol salts containing ammonium and nitrate with coarse mode seasalt. We have documented that in general 40-100% of the nitrate is found in the coarse mode (<1.0  $\mu\text{m}$  in diameter) and under polluted continental conditions 19-51% of the ammonium is as coarse mode aerosol at sites around the North European coast (*Figure 1*). This is the first such systematic documentation of this size shift for ammonium. We have gone on to show that these reactions significantly enhance deposition rates of these

nitrogen species, and that such deposition is a quantitatively significant nitrogen source for the phytoplankton living in the coastal sea waters of this region under nutrient depleted summer conditions (Spokes *et al.*, 2000; Yeatman *et al.*, 2001a, de Leeuw *et al.*, in press). We also show that such deposition is dominated by the relatively rare highly polluted episodes.



**Figure 1.** Percentage coarse mode nitrate (left hand plot) and ammonium (right) in aerosols collected at Mace Head on the west coast of Ireland and at Weybourne on the North Norfolk coast of the U.K. as a function of aerosol sodium concentration. At both sites, and at the Meetpost Noordwijk 9 km off the Dutch Coast, coarse mode nitrate and ammonium are a significant fraction of the inorganic nitrogen aerosol load. Under less polluted conditions, such as those seen on the southwest coast of Sweden, little coarse mode ammonium is seen.



**Figure 2.** Size segregated aerosol from Oahu, Hawaii, shows the tendency for inorganic and organic nitrogen to be found on different sized particles, with most of the organic nitrogen on fine mode aerosol. The 3 days when local island air was sampled are shown on the right-hand side of each plot, separately from the clean, trade wind aerosol.

We have previously shown that organic nitrogen is an important component of aerosols and rainwater, and we have now shown that organic nitrogen is significant in clean marine air sampled on the coast of Hawaii. This organic nitrogen is primarily associated with fine mode aerosol, less than 1.0  $\mu\text{m}$  in diameter (Figure 2, Cornell *et al.*, in press). Urea appears to be an important component of this organic nitrogen, possibly derived from long range transport from Asia where it is used extensively as a fertiliser. Since the organic nitrogen appears to remain associated with fine mode aerosol, while the inorganic nitrogen is transferred to the coarse mode, the atmospheric residence time of organic nitrogen will be greater than that of inorganic nitrogen and hence more liable to undergo long range atmospheric transport.

Nitrogen has two stable isotopes  $^{14}\text{N}$  and  $^{15}\text{N}$ , the former being the most abundant. Isotopic fractionation of the nitrogen relative to the ratio in atmospheric  $\text{N}_2$  can occur during chemical

reactions such as combustion processes. Measurement of isotopic ratios in aerosols can, in theory, allow different sources of aerosol fixed nitrogen to be differentiated, as has been done previously for sulphur. We have conducted the first large scale systematic study of nitrogen isotopes in aerosols and documented that there are indeed systematic differences in isotopic composition for both nitrate and ammonium between locations and between air masses of different origin at the same location (*Table 1*, Yeatman *et al.*, 2001 b,c).

**Table 1.** Isotopic Composition of Aerosol Nitrate Measured at Weybourne on the North Norfolk Coast of the U.K. classified by air-parcel trajectory into different source regions.

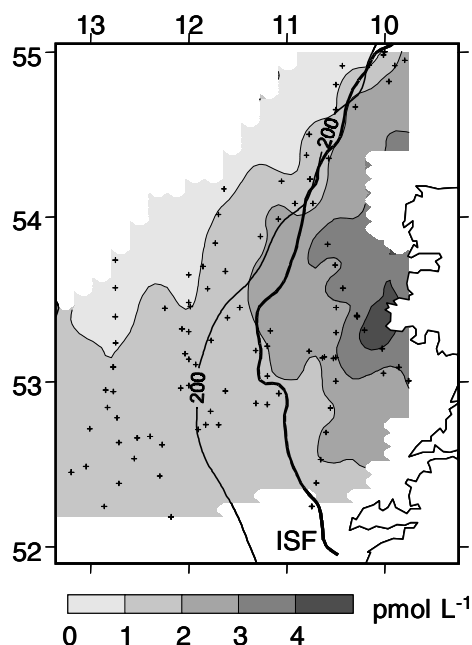
	Average Nitrate Concentration (nmol m <sup>-3</sup> )	$\delta^{15}\text{N}$ ‰
Northern UK	41	+15 ± 3
Southern UK	82	+10 ± 3

Since these are the first such studies reported, the processes controlling the isotopic fractionation are still not fully determined, but the methodology opens the way to a new way by which sources can be apportioned. This use of stable isotope ratios promises to be a valuable tool in air pollution and eutrophication management.

### Iodine

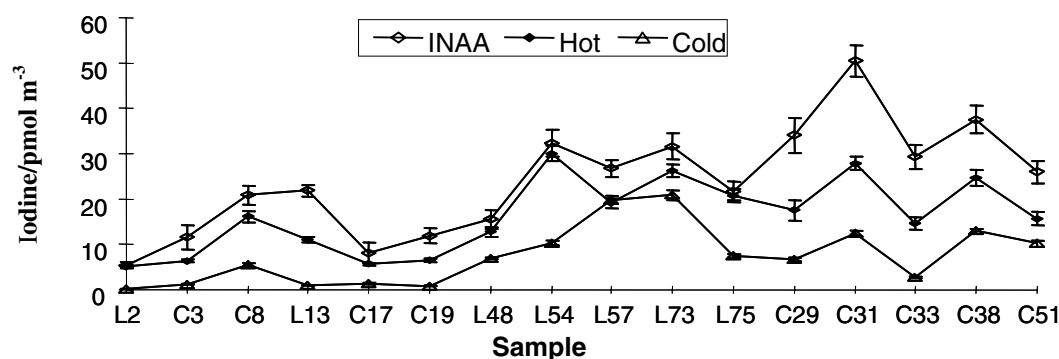
We have been involved in a large study of trace gas emissions from waters offshore of the west coast of Ireland. The study showed that the patterns of distribution of various important trace gases such as methyl iodide, dimethylsulphide and isoprene are all different, suggesting different mechanisms by which these gases are formed and released from the water column, although all are connected to phytoplankton activity. This means that it is not possible to scale the emissions of one gas from another with confidence. The pattern of methyl iodide

concentrations in the water imply that macroalgae growing in the coastal waters are a major source (*Figure 3*). Other organohalogen gases are also released from these macroalgae and the resulting release of iodine gases can produce significant quantities of IO radicals with important consequences for atmospheric oxidation reactions in the coastal atmosphere (Baker *et al.*, 2000a, Carpenter *et al.*, 1999).



**Figure 3.** Concentration of methyl iodide in surface waters off the west coast of Ireland, May 1997.

Atmospheric iodine chemistry is complex and poorly understood, but extensive recycling of iodine from the aerosol phase has been proposed to take place. Such recycling assumes the presence of iodide in the aerosol phase. We have conducted a study of the speciation of aerosol iodine in the coastal marine environment. We find that about half of the inorganic iodine is present as iodate and the remainder as iodide. In addition we identified for the first time a significant component that we believe to be high molecular weight and low volatility organic iodine (*Figure 4*, Baker *et al.*, 2000b).



**Figure 4.** Total aerosol iodine (INAA) and inorganic iodine extracted into aqueous solution at 95°C (Hot) and 20°C (Cold). ‘Hot’ concentrations are generally higher than ‘Cold’, possibly because boiling destroys organo-iodine compounds in the aqueous extracts. Based on solubility considerations, non-extracted iodine (Total minus Hot) is also probably organic. (see Baker *et al.*, 2000b).

## Acknowledgements

This work was funded, in part, by the EU, by an NERC Ph.D. studentship to Stuart Yeatman and by two NERC Research Grants.

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