

**Biogeochemical cycles of ammonia and dimethylsulphide in the marine environment. University of East Anglia, 2001.**

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Ammonia and dimethylsulphide (DMS) are important constituents of the reduced sulphur and nitrogen cycles in the marine environment. Various aspects of these individual cycles including their atmospheric interaction were investigated.

During the 5th and 9th Atlantic Meridional Transect (AMT) research cruises from the UK to the Falkland Islands and the UK to Uruguay respectively, basin scale variability in seawater DMS and the dissolved and particulate forms of its biochemical precursor dimethylsulphoniopropionate (DMSP) were investigated. Highest concentrations were predominantly found in Northern and Southern temperate regions and at the North African upwelling. During AMT 5, a comprehensive suite of chemotaxonomic phytoplankton pigments was correlated with surface DMS and DMSP. The results showed that 19'Hexanoyloxyfucoxanthin, chlorophyll  $c_3$  and chlorophyll  $c_1c_2$  correlated well with particulate DMSP and that these correlations were better than that of particulate DMSP with total chlorophyll  $a$ . DMS and its oceanic flux did not correlate well with either the accessory pigment pool or chlorophyll  $a$ . These findings imply that remote sensing may only be useful for mapping DMS *via* particulate DMSP.

Ammonia gas and  $NH_4^+$ ,  $nssSO_4^{2-}$  and MSA in aerosol and rainwater were measured between 30°N to 30°S during AMT 9. Ammonia fluxes were calculated using estimated seawater ammonium concentrations. It was found that although finely balanced, the ocean was an overall source of ammonia with a flux of  $1 \pm 1 \mu\text{mole m}^{-2} \text{d}^{-1}$ . The overall ratio of the ammonia flux to the DMS flux was  $\sim 0.3$ , a factor of 3 lower than the overall aerosol  $NH_4^+/nssSO_4^{2-}$  ratio. For one deposition event in the North Equatorial Counter Current, an inorganic nitrogen budget showed that the atmosphere could fuel up to 8% of the new nitrogen requirement.

Aerosol samples from Halley Base, Antarctica between April and December 1998 were analysed for  $NH_4^+$ ,  $nssSO_4^{2-}$  and MSA. Seasonal signals were discernible for each species providing further evidence that biological activity in the ocean is a likely source for these compounds. Mean  $NH_4^+/nssSO_4^{2-}$  and MSA/ $nssSO_4^{2-}$  ratios were 0.7 and 0.4, respectively. A significant sulphate fractionation was found to occur in some winter samples under high sea salt loading. This provides further evidence that sulphate fractionated brine on sea ice surfaces and frost 'flowers' may be an important source of winter time coastal Antarctic aerosol, in addition to open ocean water. This process has important implications for the calculation of  $nssSO_4^{2-}$ .

The process of ammonium photo-production from dissolved organic matter was examined. A fulvic acid was isolated from coastal seawater and irradiated in a seawater matrix with artificial sunlight. Ammonium was produced in significantly elevated amounts over dark controls and was concurrent with a decrease in absorption at 350 nm. The absorptivity normalised production rate was  $0.8 \text{ nM } (NH_4^+) \text{ m h}^{-1}$ . With this production rate it was estimated that the impact of photochemically produced ammonium upon the required daily phytoplankton nitrogen demand in both coastal and open ocean environments would be minimal but that the impact upon the ocean to atmosphere flux of ammonia may be significant.