

Amino acids in the atmospheric and marine environments: distributions and the influence of chiral characteristics

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Atmospheric deposition is now well recognised as a major source of both inorganic and organic nitrogen for many aquatic ecosystems. Until now approximately 70-90% of the dissolved organic nitrogen (DON) fraction of aerosols has remained uncharacterised. In the present study D and L amino acids were determined in urban and remote Atlantic aerosol samples and surface sea water using HPLC. Aerosol samples were collected from the Liverpool Campus, the Taiwan Port and from the Atlantic Ocean during the Atlantic Meridional Transect AMT12, 13, 14 cruises. Dissolved free amino acids (DFAA), dissolved hydrolysable amino acids (DHAA), and particulate amino acids (PAA) were determined in each sample. The peptidoglycan derived D- enantiomer of aspartic acid (D-Asp), glutamic acid (D-Glu), serine (D-Ser), and alanine (D-Ala) were found in significant amounts in all dissolved and suspended aerosol samples. Plant derived D-enantiomers of leucine (D-Leu) and isoleucine (D-Ile) were found mainly in the Liverpool samples whilst the signature of bacterial content was notably higher in marine samples.

The contribution of bacterially-derived compounds to the DON pool was assessed, using amino acid enantiomeric (D/L) ratios. The results also indicated a significant bacterial input to DON. The distribution of D-amino acids in the samples suggested a potential, additional input from other sources; plant materials and terrestrial substances.

This work is the first direct and complete quantification of D-amino acids in dissolved and particulate components of the atmosphere and provides molecular evidence for microbial and higher plant contribution to the organic nitrogen content of the atmospheric aerosol.

The final part of the thesis deals with isomer selective adsorption of amino acids by components of natural sediments. This selectivity can also be seen to a lesser degree in the minerals quartz, montmorillonite and kaolin. Adsorption reactions were performed using racemic amino acid mixtures and, after equilibrium, deviations from a D/L ratio of 1 were measured and in many cases were found to be significant. This was particularly pronounced at pH 4.0 where selective removal of the L-isomers by adsorption onto sediment fractions was almost total. Changes in both the nature and degree of selectivity were also observable in different sediment size fractions. At this stage it has not been possible to identify the primary adsorbent producing this selectivity but experiments with these candidate sediment components, quartz, kaolin and montmorillonite have demonstrated some selective behaviour. The existence of natural chirally selective components in sediment may indicate a new approach to development in chiral catalysis and synthesis.