Biogenic halocarbons and light alkyl nitrates in the marine environment. University of East Anglia, 2002.

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The ocean plays a significant role in the trace gas composition of the atmosphere, via sea-to-air emissions, which are controlled by biotic and abiotic production and consumption processes occurring within the water column. Both the halocarbons and alkyl nitrates affect the 'oxidising capacity' of the atmosphere, primarily as a result of their influence on ozone concentration. Halocarbons have been shown to be produced biogenically by various species of microalgae in laboratory studies. However, the production processes and their fluxes in the open ocean are poorly characterised. In general, the alkyl nitrates have a predominantly anthropogenic source, but atmospheric measurements in the remote troposphere have led to assumptions of an oceanic source of the light alkyl nitrates. The aims of this project were therefore to contribute to the knowledge of the occurrence, distribution and dynamics of biogenic halogenated gases in seawater, and to test the hypothesis that the ocean is a source of the light alkyl nitrates.

Existing instrumentation at UEA was modified to enable the analysis of a suite of halocarbons and light alkyl nitrates in seawater and air samples. Three major fieldwork campaigns were undertaken; two North-South Atlantic Ocean transects (AMT 9 and Anreise) and an *in situ* iron enrichment experiment in the Southern Ocean (EisenEx). Seawater and air concentrations of methyl iodide (CH_3I), chloroiodomethane (CH_2ClI), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), methyl nitrate (CH_3ONO_2) and ethyl nitrate ($C_2H_5ONO_2$) have been reported. In addition to the field measurements, determinations of the seawater Henry's Law constants for the alkyl nitrates and methyl iodide were carried out.

Calculations of the % saturation of the compounds in seawater have established that the ocean is a source of $MeONO_2$ and $EtONO_2$. Data from the Atlantic Ocean suggests that the tropical ocean is a major source area. A simple box model calculation indicates that the oceanic flux of $MeONO_2$ could constitute a significant component of the atmospheric budget in the equatorial region. For the biogenic halocarbons, the ocean was found to be consistently supersaturated with respect to CH_3I and CH_2ClI but in general, the pelagic ocean was a sink for $CHBr_3$.