AFI Fieldwork report

Project: AFI5/01

Title: Alkyl nitrates and organo-halogens in the Antarctic: Production in seawater and role in atmospheric chemistry

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Field personnel/ PDRA: Dr Claire Hughes (UEA)

Rothera marine assistants: Paul Mann; Helen Rossetti

Location: Rothera Research Station, Adelaide Island, Antarctic Peninsula (November 2005 – April 2006)

Objectives:

The overarching objectives of this project are to improve our understanding of the mechanisms by which alkyl nitrate and organo-halogen gases are produced in seawater, and assess the atmospheric impact of the sea-to-air flux of these compounds. To work towards this, the specific aim of this field campaign was to determine alkyl nitrate and organo-halogen concentrations in the upper 100m of the water column during a seasonal cycle at the Rothera Time Series (RaTS) site. These data will allow us to investigate possible relationships between trace gas concentrations and ancillary parameters indicative of biological, physical and chemical processes. All trace gas samples were extracted from seawater by purging and the resulting samples analysed for selected alkyl nitrates and organohalogens using a gas chromatograph – mass selective detector (GC-MSD) set-up in the Bonner Laboratory at Rothera between November 2005 and April 2006.

Highlights:

Time series of trace gas concentrations -

Trace gas samples collected by Paul Mann from the RaTS site during the summer and winter seasons of 2005 were analysed. Additionally, seawater samples were collected and analysed for alkyl nitrates and organohalogens by Claire Hughes during the 2005/ 2006 summer season. Sampling was not possible between mid-October and late December 2005 as the sea-ice remaining in the bay was not safe enough to traverse but was too abundant to launch a boat. Despite the delay in the start of sampling the results obtained were very interesting. They show that there is a large increase in the concentration of some trace gases (e.g. bromoform – $CHBr_3$, dibromomethane – CH_2Br_2) during the Antarctic summer and that this increase coincides with break-up of the sea-ice and the onset of the phytoplankton bloom which occurs in Marguerite Bay (the location of the RaTS site) during this period. These findings could suggest that the microalgae play some role in the production of these trace gases at this location and that sea-air flux of these compounds during the summer months contributes to changes in the atmospheric chemistry such as ozone depletion that are known to occur during this time.

Trace gas depth profiles -

Samples were collected from 0, 5, 10, 15, 25, 50 and 100 m at the RaTS site using a Niskin bottle hand winched to the various depths. In total 12 depth profiles were obtained between 4 January and 4 March 2006. In general all trace gas depth profiles were similar to those obtained from other ocean regions showing higher concentrations in the surface ocean, decreased concentrations at depth and in some cases sub-surface maxima. Over the coming months the observed changes in alkyl nitrate and organohalogen concentrations at the various depths will be analysed and compared to physical parameters such as temperature and salinity indicative of water mass movement, biological parameters indicating changes in microalgal abundance and health, and nutrient concentrations.

Mystery compound –

In the chromatograms obtained from the analysis of the seawater samples using the GC-MSD, there was a mystery peak with a retention time of 6.8 minutes and a mass to charge ratio (m/z) of 46. Whereas all other

identified peaks were on the order of 10^3-10^5 peak area units, this compound was found at 10^6-10^7 peak area units which (if it has similar sensitivity) may suggest that it occurs at very high concentrations. It is interesting that a similar unidentified peak with the same m/z and retention time was found by a UEA colleague in air samples collected at Halley. We will be attempting to identify and quantify this compound and assess its potential impact on atmospheric chemistry. Although there are many known naturally produced compounds that can cross the sea surface and impact processes occurring in the atmosphere there may be many unidentified compounds that could also have an important influence.

Sampling from the Niskin bottle at the RaTS site (L-R, Claire Hughes and Helen Rossetti)

Hand winching the Niskin bottle to collect depth profile samples (Paul Mann)