Fieldwork Report (2008/2009 Rothera field season)

The production of ozone-depleting bromocarbon gases in near-shore Antarctic waters (AFI8/22, Liss)

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1. ***Background*** - Bromine (Br) is known to play an important role in atmospheric ozone chemistry. In the atmosphere this element becomes part of several molecules that comprise inorganic Br_y (e.g. BrO and HOBr) which is known to participate in reactions that regulate ozone (O_3) concentrations (von Glasow *et al*., 2002). This occurs through direct catalytic loss, and reduced O_3 production resulting from the formation of halogen nitrates and the associated reduction in nitrogen oxides (von Glasow *et al.*, 2004). The two major sources of Br to the atmosphere are the long-lived organic halons and methyl bromide (CH_3Br) from anthropogenic sources (Wingenter *et al*., 1998), and the relatively shorter-lived biogenic bromocarbons such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) which are produced principally in the marine environment (reviewed by Quack and Wallace, 2003).

   Previously we observed large increases in the concentrations of $CHBr_3$ and CH_2Br_2 during the summer microalgal bloom which occurs annually at the Rothera Time-Series (RaTS) site located in Marguerite Bay, 4 km offshore from Rothera (Hughes *et al*., 2009). The aim of this field season was to:

   a) Re-establish a time-series of seawater and air bromocarbon measurements at the RaTS site.
   b) Carry-out incubation studies to assess production and loss rates of the two compounds.
   c) Isolate single-species microalgal cultures to determine which organisms are responsible for bromocarbon formation.

2. ***Sampling*** - For these studies, sampling was carried out from a small RIB using a Niskin bottle hand winched to depth. The air and water samples were analysed using a Markes Thermal Desorpiton Unit (TDU) and UltrA autosampler coupled to an Agilent gas chromatograph-mass spectrometer (GC-MS). Tables 1-3 below show details of air and water sampling events, and incubation studies carried out during the 2008/2009 summer field season at Rothera. The simultaneous collection of air and surface water data can be used to calculate the direction and rate of flux of the bromocarbons across the sea-to-air interface. Figure 1 shows all seawater $CHBr_3$ concentrations measured at the RaTS site (15 m) as part of this and our previous AFI project (AFI5/01). It is apparent from this plot that the concentrations reached during the 2008/2009 summer were far lower than those measured during previous years. The lower bromocarbon concentrations measured during the 2008/2009 summer coincide with lower chlorophyll *a* concentrations, which visual observations suggest may be due to increased abundances of krill and more 'top-down' control of the algal population in Marguerite Bay.

3. ***Algal isolations –*** Whilst at Rothera samples of seawater were collected from the upper water-column of the RaTS site and examined under the microscope. From these samples, single microalgal cells were isolated using a micro- or capillary pipette, washed in sterile seawater medium and placed in well-plates in an incubator to encourage cellular division and growth. In total, over 100 single

cells were isolated and will be returned to UEA to be used in laboratory experiments designed to assess bromocarbon production by different microalgal species and how this production varies with changing environmental conditions. Figure 2 a-e show pictures of some phytoplankton cells isolated using this technique.

Table 1. RaTS bromocarbon sampling events showing the water-column depths sampled, and specific CTD site visited. The dates on which air samples were collected simultaneously are indicated.

Date	Sampling depths (m)	CTD site	Air
04-Nov-08	0	1	
05-Nov-08	15	1	✓
07-Nov-08	0,15	2	✓
12-Nov-08	0,15	1	
14-Nov-08	0,15	1	✓
24-Nov-08	0,15	1	✓
27-Nov-08	0,5,10,15,50,100	1	✓
04-Dec-08	0,5,10,15,25,50,100	2	
10-Dec-08	0,5,10,15,25,50,100	1	
12-Dec-08	0	1	✓
15-Dec-08	0	1	✓
18-Dec-08	0,5,10,15,50,100	1	✓
27-Dec-08	0	1	✓
30-Dec-08	0,5,10,15,25,50,100	1	✓
05-Jan-09	0	1	✓
08-Jan-09	0,5,10,15,25,50,100	1	✓
15-Jan-09	0	1	✓
19-Jan-09	0,5,10,15,25,50,100	1	✓
22-Jan-09	0	1	✓
29-Jan-09	0,5,10,15,25,50,100	1	✓
02-Feb-09	0	1	✓
05-Feb-09	0,5,10,15,25,50,100	1	✓
09-Feb-09	15	1	✓
12-Feb-09	0,15	1	✓
18-Feb-09	0,15	1	✓

Table 2. RaTS incubation studies designed to assess bromocarbon production rates. Given are the dates on which the samples were collected and the incubations were started, and the depths incubated. On 28 November a samples of ice-algae was incubated to assess production by this community.

Date	Depths incubated (m)
05-Nov-08	15
14-Nov-08	0,15
28-Nov-08	Ice algae
04-Dec-08	0,15
10-Dec-08	0,15
18-Dec-08	0,15
30-Dec-08	0,15
8-Jan-09	0,15
19-Jan-09	0,15
29-Jan-09	0,15
5-Feb-09	0,15

Table 3. RaTS incubation studies designed to assess bromocarbon breakdown rates. Given are the dates on which the samples were collected and the incubations were started, and the depths incubated.

Date	Depths incubated (m)
22-Nov-08	0
25-Nov-08	0
08-Dec-08	0
15-Dec-08	0,15
27-Dec-08	0,15
05-Jan-09	0,15
15-Jan-09	0,15
22-Jan-09	0,15
02-Feb-09	0,15

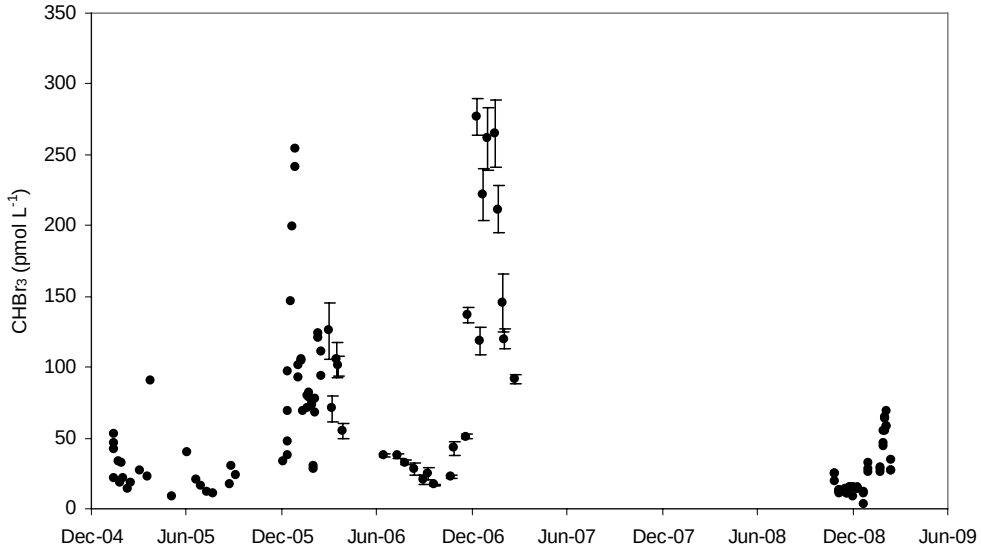

Figure 1. Seawater concentrations of $CHBr_3$ measured at the RaTS site (15 m)

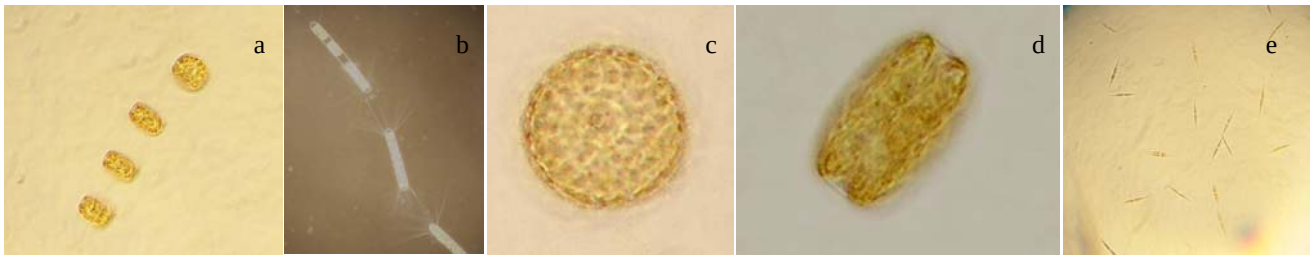

Figure 2. Photographs of microalgae isolated from the water-column at the RaTS site during the 2008/2009 summer season. Preliminary identification suggests that the algae shown are a) *Thalassiosira gravida*, b) *Corethron*, c) *Coscinodiscus/Thalassiosira* (valve view), d) *Coscinodiscus/ Thalassiosira* (girdle view), and e) *Pseudonitzschia*.

References

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