Impact of combined iodine and bromine release on the Arctic atmosphere (COBRA): Final report

<u>Summary:</u> Experimental data was generated during a 4-5 week (measurements from 10th Feb - 9 Mar 2008) field campaign at a mobile field station set up by COBRA scientists on the eastern coast of Hudson Bay, near the Centre d'Études Nordiques, Kuujjuarapik (55°18´N, 77°44´W). The site was located at the sea ice edge, which was frozen throughout the campaign. COBRA produced a large high quality data set on the composition, properties and fluxes of gases and aerosols within a "bromine hot spot" of the Arctic boundary layer. Measurements in air included halogen oxide radicals (BrO and IO), organic halogens, ozone, nitrogen oxides, OH and HO_2 radicals (funded and reported separately *via* NERC grant of project partner Prof D Heard), and micrometeorological fluxes of sensible & latent heat, ozone and ultrafine aerosol. Measurements of biogeochemical parameters were also made in sea-ice, brine, seawater and of frost flowers, including their surface area enhancement.   Finally, transport properties of organic halogens within brine channels of sea-ice were investigated post-campaign using a cold chamber.

Location of COBRA field site on the east coast of Hudson Bay, Canada

Iodine present in Arctic air: (paper arising – Mahajan et al., 2010)

Before the IPY, a marked difference had become apparent between the Arctic and Antarctic regions: high levels of boundary layer iodine (IO) were observed at Halley Bay [Saiz-Lopez et al., 2007] and Neumayer [Frieß et al., 2001] in Antarctica, and satellite measurements revealed the widespread occurrence of iodine chemistry over the Antarctic continent [Saiz-Lopez et al., 2007a; Schönhardt et al., 2008]. In contrast, IO had not been detected in the Arctic boundary layer [Hönninger et al., 2004; Tuckermann et al., 1997], although integrated column measurements indicated the possible presence of IO in the Arctic troposphere [Hönninger, 2002; Wittrock et al., 2000]. During COBRA, episodes of elevated levels of IO (up to 3.4 ± 1.2 ppt) accompanied by a variety of iodocarbons were observed *for the first time*. Air mass back trajectories show that the observed iodine compounds originate from open water polynyas that form in the sea ice on Hudson Bay. A combination of Long Path-DOAS and Multi Axis-DOAS observations suggested that the IO is limited to about 100 m in height. The observations were interpreted using a one-dimensional model, which indicated that the iodocarbon sources from these exposed waters could account for the observed concentrations of IO. These levels of IO deplete O_3 at rates comparable to bromine oxide (BrO) and, more importantly, strongly enhance the effect of bromine-catalyzed O_3 depletion in the Arctic boundary layer, an effect which has not been quantitatively considered hitherto. However, the measurements and modeling results indicate that the effects of iodine chemistry are on a much more localized scale than bromine chemistry in the Arctic environment.

Iodine in sea-ice and importance of emissions from open water polynyas compared to brine channels: (papers arising – Shaw et al., submitted, 2011; Atkinson et al., in prep., 2011)

Post-campaign, several experiments were conducted with artificial sea ice in a cold chamber to assess the potential for dissolved gaseous halocarbons to percolate through brine channels within sea-ice to the overlying air. Physico-chemical properties of the hypersaline brine, sea-ice and the underlying seawater were measured to quantify the vertical transport of a comprehensive range of volatile organic iodinated compounds (VOICs), including CH_3I, C_2H_5I, $2\text{-}C_3H_7I$ and $1\text{-}C_3H_7I$, at air temperatures of -3 and -14 °C. The results suggested that VOIC gas transfer velocities from diffusion through the sea-ice alone are at least ~60 times lower at an air temperature of -3 °C than gas exchange from leads and polynas during the winter (assuming a sea-ice fractional coverage of 0.1), and are negligible at -14 °C. This is consistent with the discussion above concerning the potential sources of IO during COBRA. Further, assuming 100 % brine channel fractional connectivity and a diffusion coefficient (*D*) of 5 x 10^{-5} cm^2 s^{-1} at -3 °C, the timescale of diffusion through 50 cm of first year sea ice is ~145 days. This has significant implications for *in situ* VOIC losses within the brine from chlorination, hydrolysis and photolysis processes. Thus, in the absence of any significant biogenic production of halocarbons within the brine network, there

should be a negligible flux through the sea-ice. However, measurements of ice-cores taken from within a few km of the coast of Hudson Bay showed that some diatom and iodine enhancement was occurring in the ice, despite being very early in the spring for biological activity.

Agreement between ground-based and satellite vertical columns of BrO; BrO largely confined to BL: (paper arising – Oetjen et al., in prep, 2011)
Significantly enhanced tropospheric BrO was observed during a bromine explosion event over Kuujjuarapik from three instrumental platforms: the MAX-DOAS and LP-DOAS instruments, and the satellite instrument GOME-2. With the LP-DOAS, maximum BrO surface concentrations of 28 ppt were detected (close to the maximum levels ever seen in the Arctic). Excellent agreement was found for the BrO tropospheric vertical column densities measured by the MAX-DOAS and GOME-2. The combination of all three sets of measurements revealed that the bulk of the BrO was confined to the boundary layer. BrO maps from GOME-2 in combination with trajectory simulations show that the origin of the bromine was the northwest of Hudson Bay, about 1300 km from Kuujjuarapik. Travel times from the source to the location of the ground-based measurements were about two days. A 1-dimensional boundary layer model showed that the observed levels of BrO and O_3 could only be maintained after this time period if O_3 had mixed in from the free troposphere, and there was replenishment of active bromine within the boundary layer.

Unlikely frost flower source of BrO: (paper arising – Obbard et al. 2010)
Measurements of the surface area enhancement of frost flowers, analyses of their ionic content, and comparison of frost flower photographs with the meteorological records showed that, contrary to expectation, frost flowers were not dispersed by strong winds, that although broken pieces of frost flowers were observed after a strong wind they had only been blown a few cm, and that wind-blown snow could collect between frost flowers. The surface area enhancement was also found to be at the low end of previous estimates. We concluded that frost flowers were rarely the direct agent for the observed rapid enhancement of reactive bromine in the polar boundary layer. This lends strong support to speculation by Yang et al. (2010) that salt-laden wind-blown snow was more often the direct agent. Again contrary to expectation, there was no bromide enhancement in the flowers or brine, despite temperatures often being below the eutectic crystallisation point of sodium chloride (-24 °C).

NO_x release from snow- and ice-covered surfaces related to terrain: (paper arising – Moller et al. 2010)
The presence of nitrogen oxides in the remote Arctic and sub-Arctic has been attributed to emissions from the snowpack (Jones et al., 2001; Beine et al., 2002) but this process is not yet fully explained or understood. Release from snow in particular may prove important since this re-release of species to the gas phase has implications for the use of ice cores in paleo-atmospheric chemistry studies and our treatment of deposition as a removal process. In addition snow-pack emissions may have a substantial impact on the seasonality of tropospheric concentrations and on the oxidative capacity over snow-covered areas where mid-latitude emissions are often transported and processed. During COBRA, NOx mixing ratios ranged from near zero to 350 pptv with emission from snow believed to be the dominant source. The amount of NOx was observed to be dependent on the terrain over which the airmass has passed before reaching the measurement site. The 24 h average NOx emission rates necessary to reproduce observations were calculated using a zero-dimensional box model giving rates of ~ 7×10^8 molecules cm^{-2} s^{-1} and ~4×10^8 molecules cm^{-2} s^{-1} for land based and sea-ice based trajectories, respectively. These emissions are higher than those suggested by previous studies and indicate the importance of lower latitude snowpack emissions. The difference in emission rate for the two types of snow cover shows the importance of snow depth and underlying surface type for the emission potential of snow-covered areas.

Both downward and upward ozone fluxes (paper arising Muller et al., in prep., 2011):
The measured eddy covariance ozone fluxes varied from -20 (downward flux) to +90 (upward flux) ng m^{-2} s^{-1}, suggesting strong chemical perturbation within the local surface layer. Ozone deposition velocities (v_d) ranged from about +0.5 mm s^{-1} (deposition) to -1.5 mm s^{-1} (emission). The order of magnitude of deposition velocities is similar to previously observed deposition velocities to snow surfaces (Helmig et al., 2007) but the occurrence of such a high percentage of negative deposition

velocities has not been reported before. The median of v_d for all deposition events (downward flux) is 0.13 mm s^{-1}. The data were subjected to the strict quality control measures described by Muller et al. (2009) for eddy covariance ozone flux measurements and so represent clear differences. Some limited ozone concentration profile measurements by other groups also support a strong ozone flux divergence within the surface layer, which highlights the underlying complexity of interpreting any observed ozone fluxes adequately in this region. Local *in situ* ozone-halogen photochemistry was identified as weakly controlling the ozone flux and horizontal advection and vertical mixing were considered important in influencing fluxes during the campaign.

Re-suspension of snow-ice particles (paper arising Whitehead et al. in prep., 2011):
Large re-suspension fluxes of snow-ice particles as a function of particle size were also measured using optical particle spectrometers as were ultrafine particle fluxes using condensation particle counters. The size distribution measurements showed no nucleation events occurring within the measurement period. The median ultrafine particle fluxes were depositional and at the detection limit of the instrumentation, supporting the lack of any nucleation events. Several blowing snow events provide sufficient data to record size segregated resuspension fluxes from the sea ice. A clear change in resuspension flux with particle size was recorded. Significant differences in the threshold friction speed for resuspension was also found for the clear sea ice surface and snow covered surface cases. These data are being used to parameterise the number, area and mass of ice particle resuspension fluxes.

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