1 Introduction

Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere (SHIVA)

- Halogenated very short-lived substances (VSLs) are emitted from oceans by microalgae and macroalgae.
- Ascending warm air over tropical oceans transports halogenated VSLs to the stratosphere.
- Halogens are responsible for global-scale catalytic ozone depletion and formation of the Antarctic ozone hole.
- The SHIVA measurement campaign combines ship-based, aircraft-based and ground-based measurements in and over the South China Sea and the Sulu Sea, and around the coast of Malaysian Borneo (see map in section 4).
- Aims: 1) Reduce uncertainties in amount of halogenated VSLs reaching the stratosphere, and associated ozone depletion; 2) Investigate effects of changing climate on these processes.

Tropospheric Iodine Chemistry

- Iodine-containing organic compounds (e.g. CH$_3$I, CH$_2$I$_2$, and I$_2$) are produced by marine organisms and released from the oceans, providing the main source of iodine to the atmosphere (Saij-Lopez et al., 2011).
- Photolysis of these compounds yields I atoms which react with ozone to form IO (Wolfe et al., 1999).
- Iodine oxides are responsible for new particle formation (Mfgeers et al., 2006; Saij-Lopez et al., 2008).
- Iodine chemistry impacts NO$_x$ and HO$_x$ ratios (Saij-Lopez et al., 2011).

4 Results

Map of cruise track coloured by measured I$_2$ mixing ratio. Highest values were observed in the Sulu Sea. Diurnal stations were at point A, near Kuching, and point B, near Kota Kinabalu.

3 I$_2$ denuder tube sampling system

- I$_2$ is an important measurement when considering sources of IO in the marine boundary layer.
- Measurements made using the University of Mainz coupled diffusion denuder system for separation and quantification of I$_2$, ICI and HOI (Huang et al., 2010).
- Glass tubes coated on inside with 1,3,5-Trimethyloxene for ICI and HOI, and a-cyclodextrin for I$_2$.
- Air pumped through tubes at 500 mL min$^{-1}$ for 30 minutes per sample.
- Tubes positioned on the port side of the front deck of the ship.
- Analysis of concentration by gas chromatography ion trap mass spectrometry (GC/MS).
- I$_2$ Limit of detection = 0.17 pptv (for 30 minute samples at 500 mL min$^{-1}$) (Huang et al., 2010).

Night-time IO measurements

- IO was detected above the limit of detection on 10 out of the 11 nights during which the LIF instrument was operational during the cruise.
- Reactions of I$_2$, CH$_3$I and CH$_3$I$_2$ with the nitrate radical, NO$_3$, have been proposed as a night-time source of IO (Chambers et al., 1992; Nakao et al., 1995; Saij-Lopez et al., 2006).
- Significant levels of IO have been measured at night in other locations (e.g. 2.5 pptv at Mace Head (Saij-Lopez et al., 2006)) but measurements of IO at night in an open ocean environment have not previously been reported.

Comparison with concurrent IO measurements

- IO was measured by the University of Heidelberg cavity-enhanced DOAS (CE-DOAS) (Pfeifer et al., 2012) and the University of Bremen multi-axis DOAS (MAX-DOAS) (Wittrock et al., 2012) during the cruise.
- Reasonable agreement between LIF and MAX-DOAS (no clear detection by CE-DOAS).
- Elevated IO measured by MAX-DOAS in Sulu Sea, as for LIF measurements.
- MAX-DOAS: mean IO = 1.0 pptv, max = 2.3 pptv.