Reactive Iodine Species in the Western Pacific Marine Boundary Layer

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1 Introduction

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

- Halogenated very short-lived substances (VSLS) are emitted from oceans by macroalgae and microalgae
- Ascending warm air over tropical oceans transports halogenated VSLS to the stratosphere
- Halogens are responsible for global-scale catalytic stratospheric ozone depletion and formation of the Antarctic ozone hole
- The SHIVA measurement campaign combines ship-borne, 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_3I, CH_2I_2) and I_2 are produced by marine organisms and released from the oceans, providing the main source of iodine to the atmosphere (Saiz-Lopez *et al.*, 2011)
- Photolysis of these compounds yields I atoms which react with ozone to yield IO (Alicke *et al.*, 1999)
- Iodine oxides are responsible for new particle formation (McFiggans *et al.*, 2004; Saiz-Lopez *et al.*, 2006)
- Iodine chemistry impacts NO_x and HO_x ratios (Saiz-Lopez *et al.*, 2011)

$$CH_3I + h\nu \rightarrow CH_3 + I$$
$$CH_2I_2 + h\nu \rightarrow CH_2 + 2I$$
$$I_2 + h\nu \rightarrow 2I$$
$$\mathbf{I + O_3 \rightarrow IO + O_2}$$
$$IO + h\nu \rightarrow I + O$$
$$IO + XO \rightarrow I + X + O_2$$
$$IO + IO \rightarrow OIO$$
$$OIO + h\nu \rightarrow I + O_2$$

- Atmospheric models predict a contribution to ozone loss from open ocean sources of iodine, and laboratory studies suggest an ozone-initiated route for release of iodine-containing compounds from the ocean (Martino *et al.*, 2009), in addition to strong coastal emissions
- Significant IO concentrations have been measured in open ocean locations (e.g. Read, *et al.*, 2008; Mahajan *et al.*, 2010; Großmann *et al.*, 2012, Dix *et al.*, submitted), but uncertainty surrounds the importance of open ocean iodine chemistry (Mahajan *et al.*, 2012)
- The SHIVA project offers an excellent opportunity to measure IO in both coastal and open ocean environments, in the tropical marine boundary layer

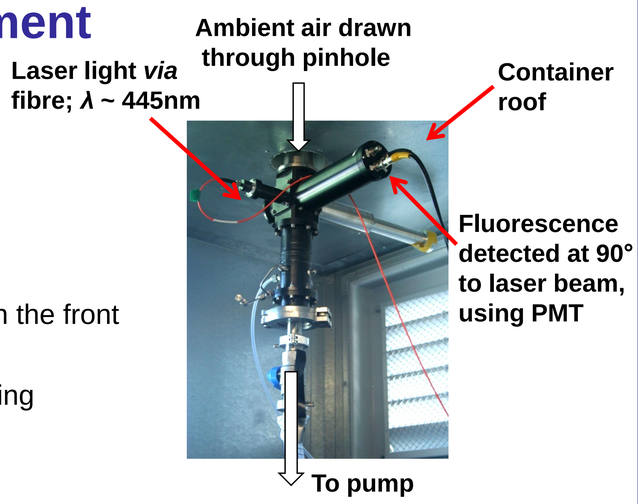
SO218 SHIVA Scientific Cruise onboard Research Vessel 'Sonne'

- 15th November – 29th November 2011
- Singapore to Manila, Philippines, *via* northern coast of Malaysian Borneo (South China Sea) and Sulu Sea
- 26 scientists from the SHIVA consortium, the University of Malaya (Kuala Lumpur, Sarawak and Sabah), and the University of the Philippines Diliman, Quezon, providing a suite of oceanic and atmospheric measurements

Research Vessel *Sonne* during SO218 scientific cruise. Arrows mark position of LIF, MAX-DOAS and CE-DOAS IO instruments during cruise. Photo: Johannes Lampel.

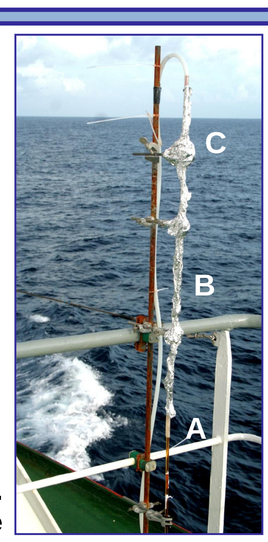
2 The Leeds LIF IO Instrument

- Ambient air drawn directly into detection cell through a pinhole, at ~ 150 Torr (Whalley *et al.*, 2007; Commane *et al.*, 2011)
- Laser light at λ ~ 445 nm excites IO radicals
- Fluorescence at λ ~ 512 nm is detected using a photomultiplier tube (PMT) and photon counter
- Instrument located in a 10 ft shipping container on the front deck of the ship, to sample clean air
- Limit of detection = 0.3 pptv for 30 minute averaging period



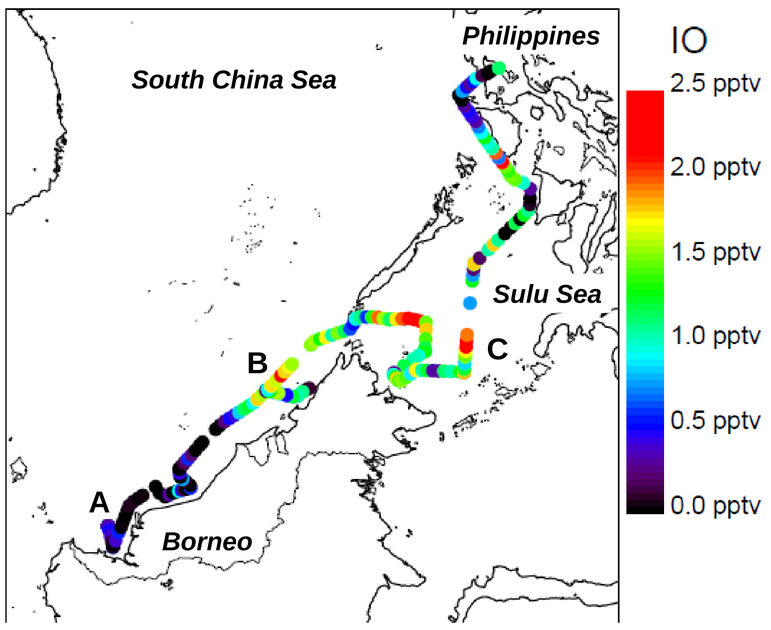
3 I_2 denuder tube sampling system

- Measurements of I_2 and HOI+ICl (activated iodine compounds) using the University of Mainz coupled diffusion denuder system (Huang *et al.*, 2010)
- Glass tubes coated on inside with 1,3,5-Trimethoxybenzene for ICl and HOI, and α-cyclodextrin for I_2
- Ambient air drawn through tubes at 500 mL min^{-1} for 30 minutes per sample. I_2 Limit of detection = 0.17 pptv (Huang *et al.*, 2010)
- Tubes positioned on the port side of the front deck of the ship
- Analysis of concentration by gas chromatography ion trap mass spectroscopy (GC/MS)

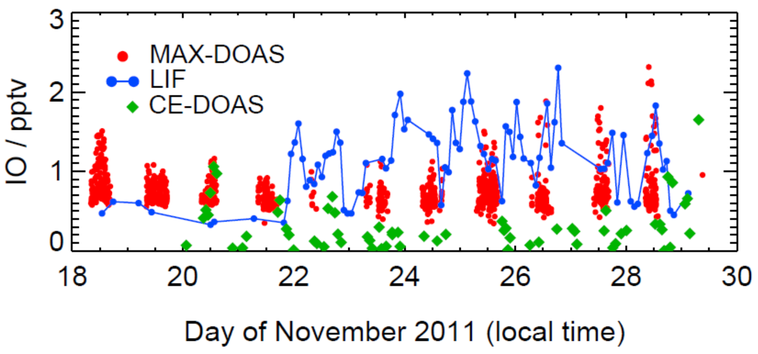


Denuder tubes set up on port side of front deck. A = blank tube; B = ICl/HOI tube; C = I_2 tube

4 Results



Map of cruise track coloured by IO mixing ratio measured by LIF instrument. Highest values were observed in the Sulu Sea (point C). Diurnal stations were at point A, near Kuching, and point B, near Kota Kinabalu.



Time series of IO measured by MAX-DOAS (red), LIF (blue) and CE-DOAS (green) during SHIVA cruise. CE-DOAS did not detect IO above limit of detection. Elevated IO was measured by MAX-DOAS and LIF during second part of cruise, though the day-to-day agreement varies.

IO LIF measurements

Daytime mean IO = 1.2 pptv
Daytime maximum IO = 2.2 pptv
Night-time mean IO = 1.3 pptv
Night-time maximum IO = 2.4 pptv
IO Cruise average = 1.2 pptv

Maximum IO

- Maximum IO mixing ratio of **2.4 pptv** measured around **18:00** on 26th November
- Location was in middle of Sulu Sea, point 'C' on map, an area known for high biological activity

I_2 measurements

Daytime mean I_2 = 1.3 pptv
Daytime maximum I_2 = 5.4 pptv
Night-time mean I_2 = 3.5 pptv
Night-time maximum I_2 = 12.7 pptv
I_2 Cruise average = 2.0 pptv

Maximum I_2

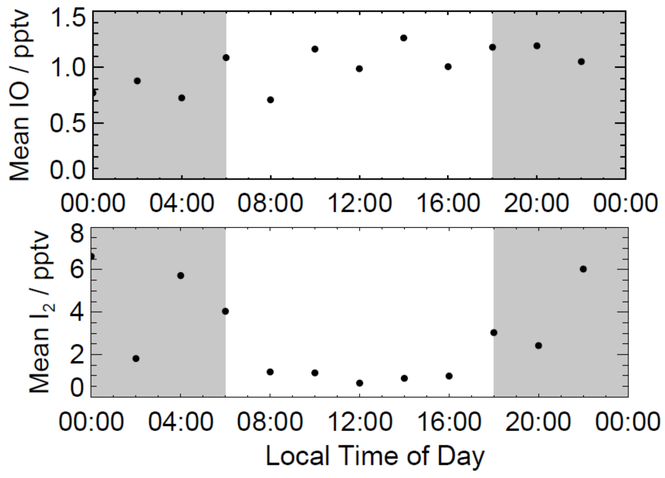
- Maximum I_2 mixing ratio of **12.7 pptv** measured around **22:00** on 18th November during diurnal station near Kuching (point 'A' on map) where several large rivers flow into the sea

Night-time IO measurements

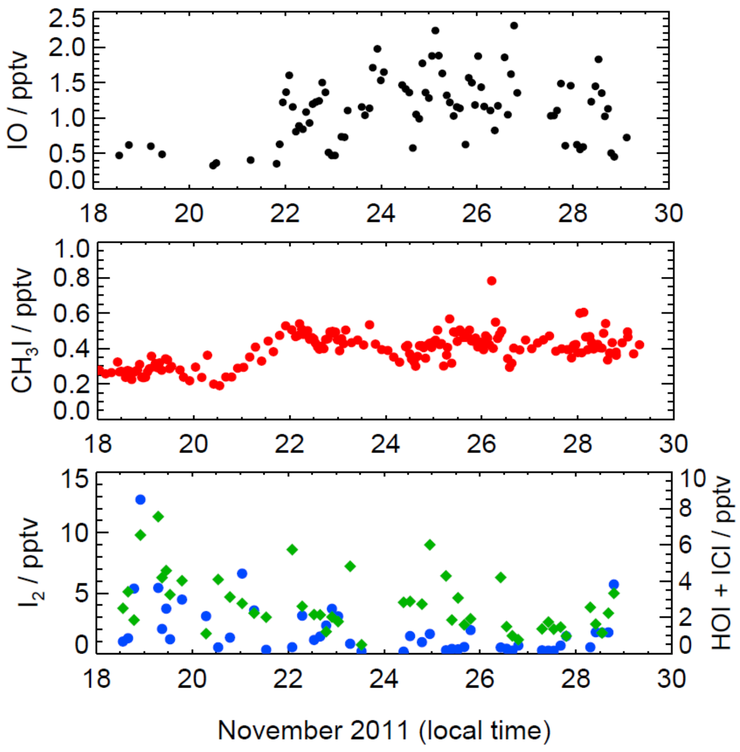
- IO was detected above the limit of detection on 10 out of the 11 nights during which the LIF instrument was operational during the cruise
- Reactions of I_2, CH_3I and CH_2I_2 with the nitrate radical, NO_3, have been proposed as a night-time source of IO (Chambers *et al.*,1992; Nakano *et al.*, 1995; Saiz-Lopez *et al.*, 2006)
- Significant levels of IO have been measured at night in other locations (e.g. 2.5 pptv at Mace Head (Saiz-Lopez *et al.*, 2006)) but measurements of IO at night in an open ocean environment have not previously been reported

Comparison between IO measurements

- IO was measured by the University of Heidelberg cavity-enhanced DOAS (CE-DOAS) (Pöhler *et al.*, 2012) and the University of Bremen multi-axis DOAS (MAX-DOAS) (Wittrock *et al.*, 2004) during the cruise (see DOAS poster for details)
- Comparison of the three measurements is given in time series (left)
- No clear detection of IO by CE-DOAS
- MAX-DOAS and LIF saw elevated IO during second half of cruise especially in Sulu Sea (see map)
- MAX-DOAS: mean IO = 0.7 pptv; max = 2.3 pptv
- LIF mean IO = 1.2 pptv; max = 2.4 pptv



Mean diurnal profiles of IO (top) and I_2 (bottom), showing higher I_2 values at night (shaded) than in the day, due to photolysis



Time series of IO (black), CH_3I (red), I_2 (blue), HOI + ICl (green) for days when LIF instrument was operational. IO and CH_3I are both elevated during the second half of the cruise.

5 Summary

- Significant levels of IO measured during daytime and night-time in the tropical marine boundary layer by University of Bremen MAX-DOAS and Leeds LIF instruments
- I_2 and HOI + ICl measurements made by Mainz the coupled diffusion denuder system
- Open-ocean and coastal environments encountered during the cruise, with higher IO detected in the biologically rich Sulu Sea
- Maximum IO (2.4 pptv) similar to concentrations measured in this region previously (e.g. 2.2 pptv by MAX-DOAS during TransBrom project; K. Großmann *et al.*, 2012)

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