Measurements of IO in the tropical marine boundary layer using laser-induced fluorescence spectroscopy

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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

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

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)

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

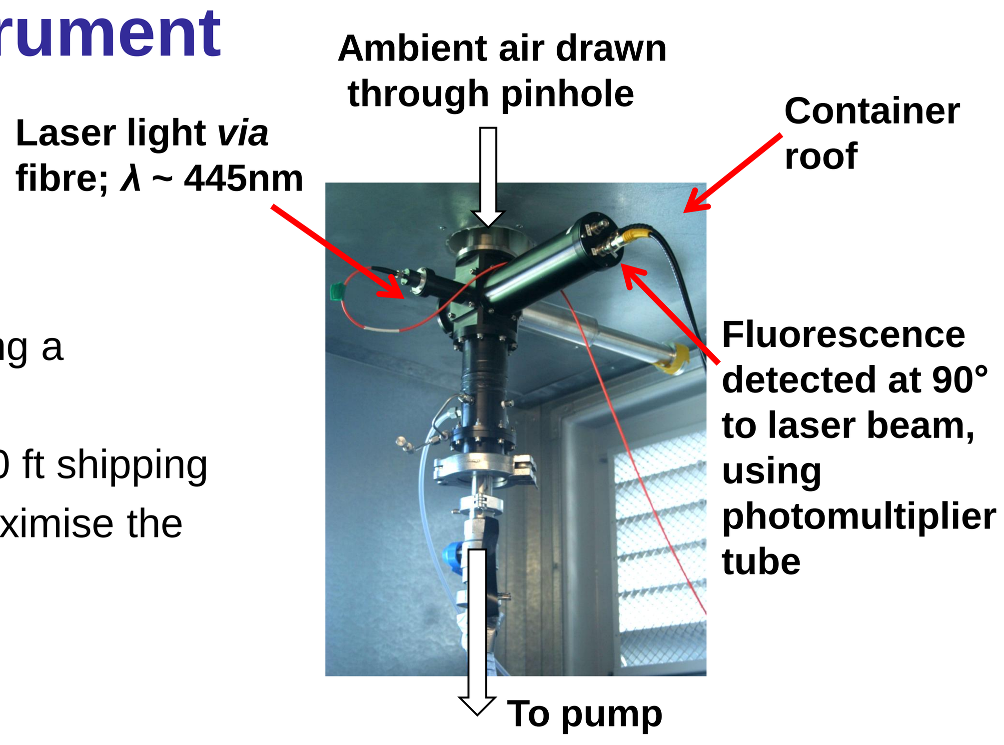
- Atmospheric models predict a contribution to ozone loss from open ocean sources of iodine, and laboratory studies suggest an ozone-initiated route for release of iodine-containing compounds from the ocean (Martino *et al.*, 2009), in addition to strong coastal emissions
- Significant IO concentrations 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


Research Vessel *Sonne* during SO218 scientific cruise. Arrow marks position of LIF IO instrument in shipping container. Photo: Torsten Bierstedt.

2 The Leeds LIF IO Instrument

- Ambient air is drawn directly into a 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 and photon counter
- Instrument located in a specially designed 10 ft shipping container on the front deck of the ship, to maximise the chance of sampling clean air.
- Calibration by flowing nitrogen, CF_3I and N_2O down an aluminium tube containing a mercury pen-ray lamp:

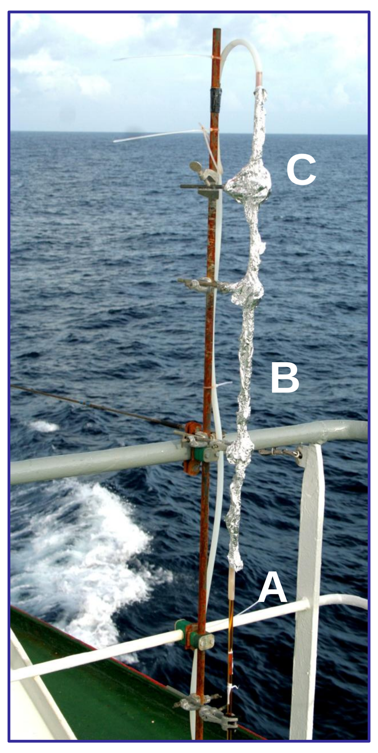
$$N_2O + h\nu \rightarrow N_2 + O(^1D)$$
$$O(^1D) + N_2 \rightarrow O(^3P)$$
$$CF_3I + O(^3P) \rightarrow IO + CF_3$$



- The instrument was calibrated before, during and after the cruise
- Limit of detection = 0.3 pptv for 30 minute averaging period

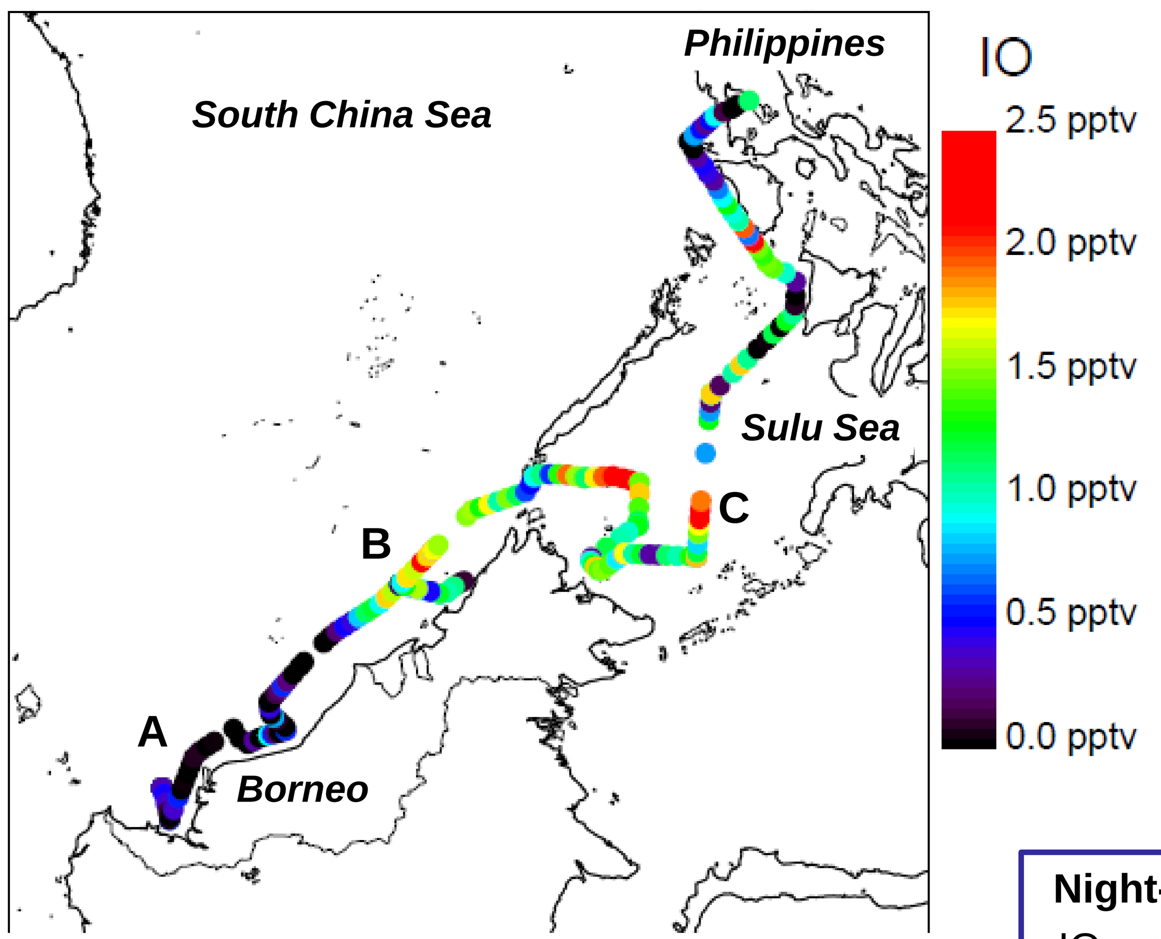
3 I_2 denuder tube sampling system

- 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, ICl and HOI (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
- 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)
- I_2 Limit of detection = 0.17 pptv (for 30 minute samples at 500 mL min^{-1}) (Huang *et al.*, 2010)



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 measured IO mixing ratio. Highest values were observed in the Sulu Sea. Diurnal stations were at point A, near Kuching, and point B, near Kota Kinabalu.

IO measurements

12 days of 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

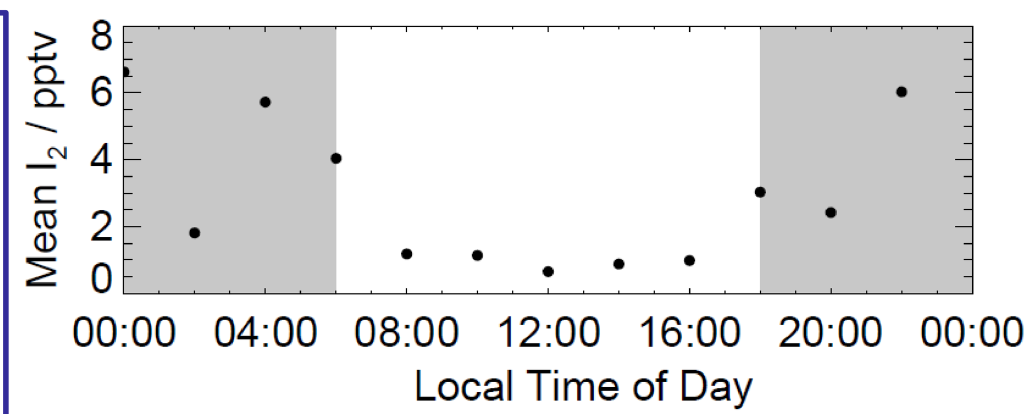
- Maximum IO mixing ratio of **2.4 pptv** measured around **18:00** on 26th November
- Location was in middle of Sulu Sea, point 'C' on map, an area known for high biological activity

I_2 measurements

12 days of 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

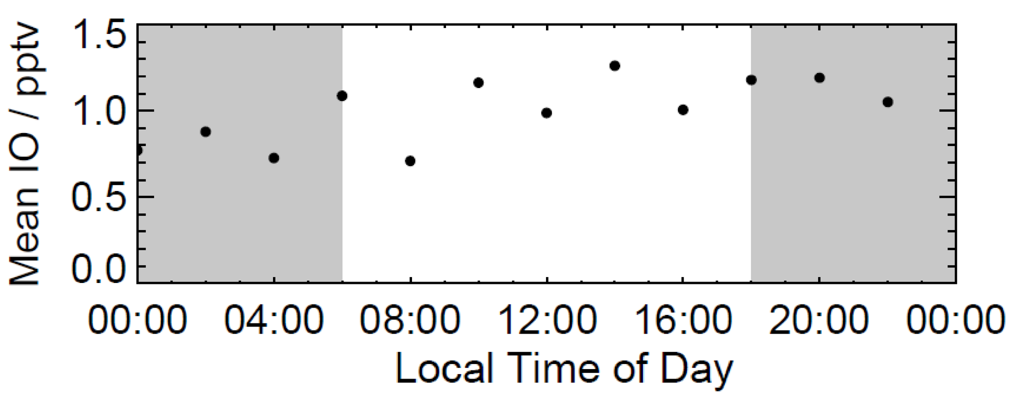
- Maximum I_2 mixing ratio of **12.7 pptv** measured around **22:00** on 18th November during diurnal station
- Location was northern coast of Borneo, near Kuching (point 'A' on map) where several large rivers flow into the sea



Diurnal profile of I_2 for the whole cruise, showing higher values at night (shaded) than in the day, due to photolysis

Night-time IO measurements

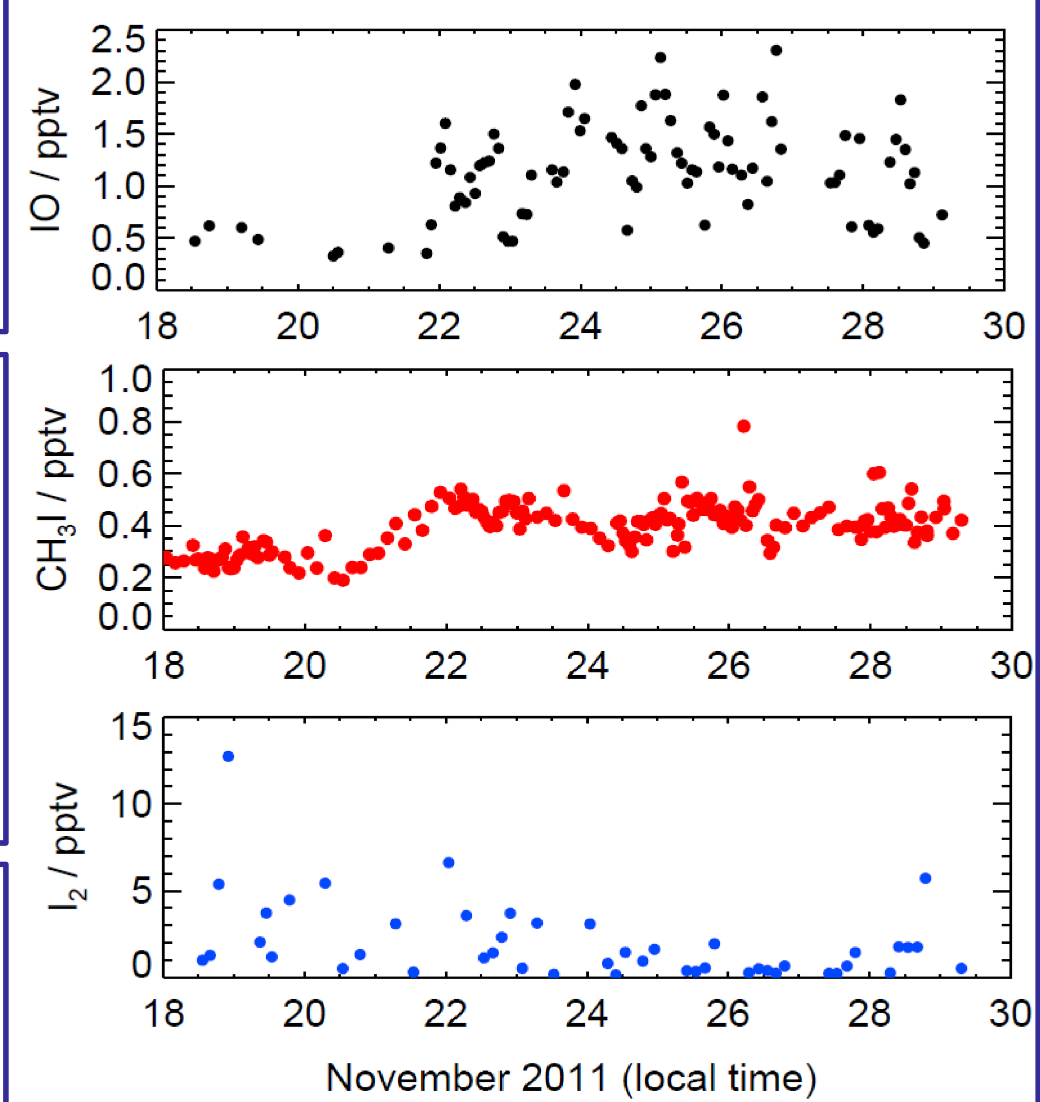
- IO was detected above the limit of detection on 10 out of the 11 nights during which the LIF instrument was operational during the cruise
- Reactions of I_2, CH_3I and CH_2I_2 with the nitrate radical, NO_3, have been proposed as a night-time source of IO (Chambers *et al.*,1992; Nakano *et al.*, 1995; 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



Diurnal profile of IO for the whole cruise, showing similar values during day and night (shaded).

Comparison with concurrent 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
- 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



Time series of IO (black), CH_3I (red) and I_2 (blue) for days when LIF instrument was operational. IO and CH_3I are both elevated during the second half of the cruise. CH_3I data courtesy of Elliot Atlas

5 Summary and Outlook

- Significant levels of IO measured in-situ during daytime and night-time in the tropical marine boundary layer
- Open ocean and coastal environments encountered
- 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)
- Box modelling will be used to predict IO concentrations based on measurements of longer-lived species

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