

## SOLAS Open Science Conference 2009

### Discussion Session Report:

#### Does a halogen-ozone exchange feedback exist and dominate MBL reactive iodine atom sources?

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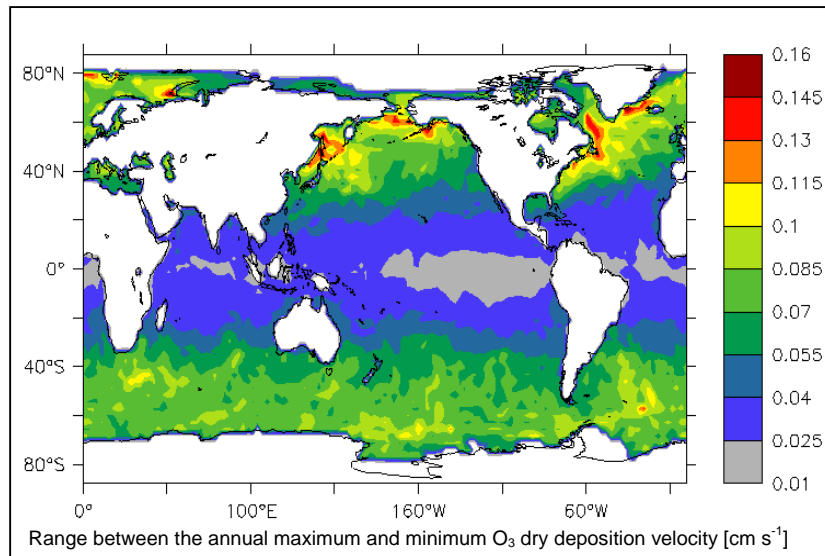
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**This discussion session aimed to explore: 1. the evidence for a feedback mechanism involving increased ozone removal in the marine boundary layer (MBL) resulting from reactions at the sea surface that may not only increase O<sub>3</sub> deposition to the oceans but enhance emission of reactive, ozone-depleting halogens to the MBL; 2. how the proposed feedback compares in terms of O<sub>3</sub> depleting potential with our understanding of water-column processes that also provide a source of reactive halogens to the MBL.**

This discussion session builds on the ESF-COST Action 735: “O<sub>3</sub> in the Marine Boundary Layer” meeting held in York, UK in June 2009 (Carpenter et al. SOLAS Newsletter December 2009).

*Evidence for the possible existence of a significant O<sub>3</sub>-depleting positive feedback mechanism takes several forms, both direct and indirect:*

1. observations of O<sub>3</sub> deposition velocities ( $v_d$ ) are substantially faster, by a factor of  $\sim 40$ , than would be expected if only dissolution of O<sub>3</sub> in seawater is considered. Observed deposition velocities can be accounted for by allowing for chemical enhancement of ozone deposition. Ozone deposition may be enhanced by reactions of ozone with iodide ([Garland et al. 1980) and with organic matter (Schwartz 1992).
2. mechanistic representation of oceanic ozone dry deposition in a chemistry-climate model (Fairall et al. 2007) constrained with global fields of iodide, DMS and chlorophyll (Ganzeveld et al. 2009), and including sea-surface reactions between ozone and iodide and organic matter, illustrates a potentially important role for biogeochemistry in determining ozone oceanic uptake, particularly in tropical waters.



3. The reaction of ozone with dissolved iodide that may enhance ozone deposition to the oceans (Garland et al. 1980), has been shown experimentally to produce volatile organoiodine compounds in natural seawater containing dissolved organic matter (Martino et al. 2009). This further reaction potentially represents a ubiquitous source of iodine to the MBL.
4. Another source of reactive halogens to the MBL may involve oxidation of halogen anions by photosensitisers, e.g. chlorophyll or aromatic carbonyl compounds, to their radical forms which then leads to the formation of organic halogens (Reeser et al. 2009, Jammoul et al. 2009). This light enhanced reaction is facilitated by O<sub>3</sub> at the sea surface and is another potential ozone depleting mechanism.

*Additional (so far unpublished) evidence of ozone depleting mechanisms at the sea surface and possible atmospheric consequences of increased reactive halogen emissions were presented in a series of 'poster summaries':*

1. Results from a 1D model of the MBL (MISTRA) fail to explain high levels of IO observed at Cape Verde without involving an ozone-driven, sea surface mechanism to produce sufficient reactive iodine (Sommariva and von Glassow SOLAS poster). The model was informed by seawater & air measurements carried out upwind of Cape Verde during the RHaMBLe cruise in 2007. Results from the MISTRA model agree well for BrO, but modelled iodocarbon fluxes cannot reproduce the high IO Cape Verde measurements without employing an additional sea-surface, ozone-depleting mechanism.
2. Enhanced reactive halogen emission may impact on the fate of DMS in the MBL. Results from a modelling study using a global 3D CTM coupled to a detailed aerosol microphysics scheme, suggest reaction with BrO contributes 16 % of the global annual DMS sink (Breider et al. SOLAS Poster). Additionally, DMS potentially increases the acidity of sea-salt aerosols causing enhanced Br emission from the sea-salt and effectively accelerating DMS oxidation in a feedback mechanism.
3. The first direct observations of glyoxyl (CHOCHO) and IO over the remote ocean using a novel Ship Multi AXis DOAS (CU SMAX-DOAS) instrument, demonstrate enhanced concentrations over biologically active oceanic regions (Volkamer et al. SOLAS Poster). The observations highlight large uncertainties in satellite derived estimates (SCIAMACY and OML data). Strong correlations between CHOCHO and IO in the MBL, support an extension of the reaction scheme described by Reeser et al. 2009.
4. Observations as part of a pH-manipulation, mesocosm experiment in Bergen, Norway, illustrated a decrease in water column, net production of volatile organoiodine compounds at reduced pH (Hopkins et al. SOLAS Poster). However, understanding the full consequences of this response requires knowledge of the relative magnitude of the variety of sources of reaction halogens to the MBL, including water column versus sea surface, ozone depleting processes.

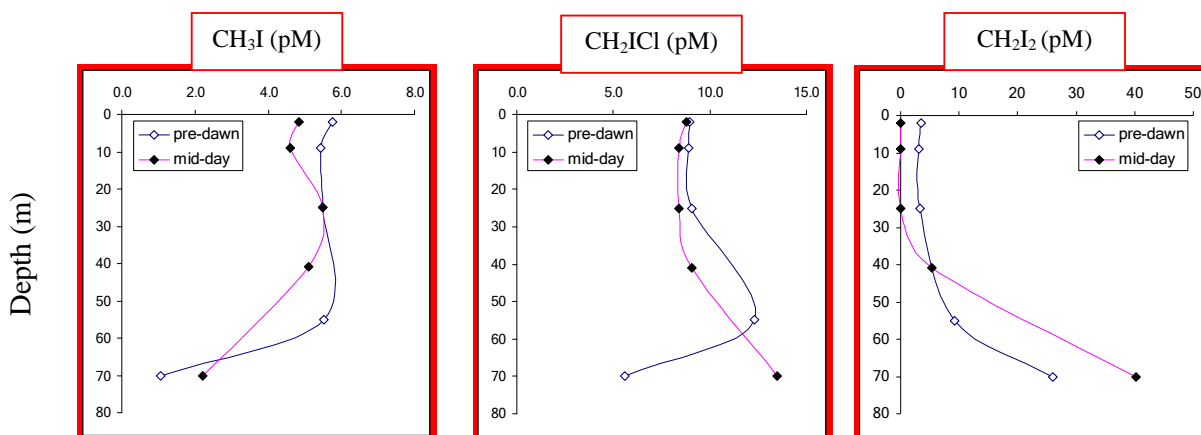
*Points raised in the discussions included:*

1. Patterns of IO concentrations in relation to potential sources. The two sea-surface reactive halogen reaction schemes may result in different diel patterns of IO in the MBL. Measurements at Cape Verde (e.g. Read et al. 2008), illustrate a 'top hat' profile with the peak in IO during midday. This may favour a photosensitive reaction source (e.g. Reeser et al. 2009) in contrast to the Martino et al. 2009 scheme, which if prevalent might be expected to result in a build up of IO precursors overnight, resulting in a large peak early in the day. The same may be true of water column based sources which may generally decrease during daylight due to in-water photolytic loss or transformations. High temporal resolution observations of IO, and potential precursors in the atmosphere and at source

may help to identify the principal mechanisms underlying reactive iodine input to the MBL.

2. Water column processes and relative magnitude of potential sources. Processes controlling water column concentrations of volatile organoiodine compounds remain poorly understood and efforts are just starting to address the regional variability in water column and atmospheric observations by compiling a collaborative database (HALOCAT, Bell & Quack). If sufficiently active, sea-surface generation of organoiodine might be expected to be observable as elevated concentrations near the surface in water column depth profiles. This is not apparent in for instance, lagrangian water column measurements in the Cape Verde region (Figure 2. Archer et al. unpublished ). Net loss of  $\text{CH}_3\text{I}$  and  $\text{CH}_2\text{I}_2$  concentrations through the mixed layer between pre-dawn and midday, illustrate photolytic losses. No obvious enhancement of these compounds, identified as products of the Martino et al. (2009) reaction scheme, is apparent at a depth of 2m. However, a modeling exercise is required to assess the potential for sea-surface reaction derived organoiodine to mix down into the water column.

**Figure 2.** Water column depth profiles of volatile organoiodine compounds measured at a ‘semi-lagrangian’ station northeast of Cape Verde, Tropical Atlantic.



It is possible to make a preliminary assessment of the relative magnitude of the sea-surface and water column sources of volatile organoiodine compounds: Martino et al. (2009) estimated a flux to the atmosphere of reactive iodine of  $2.5 \times 10^7$  atoms  $\text{cm}^{-2} \text{s}^{-1}$  derived from the sea-surface reaction involving  $\text{O}_3$ , iodide and organic matter in North Sea water. Interestingly, this is comparable to an estimated, annual average flux estimate of  $3.0 \times 10^7$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ , based on an annual study of the near-surface water column concentrations of  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{ICl}$ ,  $\text{CH}_2\text{I}_2$ ,  $\text{C}_2\text{H}_5\text{I}$  and  $\text{CH}_2\text{IBr}$  in the western English Channel (Archer et al. 2007).

3. In trying to develop an understanding of the halogen-ozone removal feedback the following major uncertainties were identified:
  - a) There is limited knowledge of the global fields of iodide concentrations with which to constrain modeled estimates of enhanced ozone deposition. Major uncertainties exist in the anti-correlation between nitrate and iodide (Campos et al. 1999) that has been used to estimate global iodide concentrations. At the very least, recent observations of iodide concentrations should be used to inform models.

- b) Flux of I<sub>2</sub> from the oceans may be a significant omission in budgets of reactive iodine sources. Is the life-time in the water column sufficiently long to allow surface-produced I<sub>2</sub> to exchange to the atmosphere?
  - c) Current estimates of the yields of reactive iodine and enhanced ozone deposition from sea-surface reactions (Martino et al 2009, Reeser et al. 2009) are laboratory based and may err on the side of upper limits. How do factors such as photochemistry, surfactants, wind speed, surface turbulence effect the ozone-depleting reactions and yields of reactive iodine.
  - d) When current models of tropospheric ozone (e.g. Saiz Lopez et al. SOLAS presentation) include enhanced deposition at the sea surface, unrealistically low levels of O<sub>3</sub> are generated in a matter of years; meaning the chemically enhanced deposition velocities may create an unrealistically large sink.
  - e) Halogen emissions are spatially highly variable (Volkamer et al. SOLAS Poster), which questions the role of a ubiquitous seas-surface process generating reactive iodine. Understanding this variability is needed to fully understand the relevance of the proposed feedback. Does IO occur over the open oceans, Volkamer et al. demonstrate it does over the tropical East Pacific, greater regional coverage is required.
  - f) The theory proposed by Reeser et al. (2009) does not necessarily link ozone destruction with reactive halogen production: photolysis of chlorophyll can release excited halogen radicals that recombine to form reactive halogens without involving O<sub>3</sub>. Therefore, according to this mechanism, the extra halogens can be accounted for without the existence of positive ozone destruction feedback mechanism.
  - g) We still require a greater understanding of the water-column processes that lead to reactive iodine emission and experimental approaches that allow the relative magnitude of sea-surface and water column sources to be assessed, including their temporal and regional variability.
4. How to progress? One exciting proposition is the proposed TOAST expedition to the Galapagos Island *Isabella* and associated research cruises (Plane et al. Proposal to UK NERC); to specifically study the interaction between ozone fluxes and halogens.

**We would like to thank all those who attended and contributed to this Discussion Session and hope it stimulates some ideas and kicks-off further collaborative research in this field.**