

Scientific report on COST Action 735 workshop “Ozone in the remote marine boundary layer”

Lucy Carpenter¹, Roland von Glasow², Laurens Ganzeveld³, Rolf Sander⁴, Steve Archer⁵, Liz Coleman⁶, Christian George⁷, Saso Gigorovski⁸, Jeff Hare⁹, Dwayne Heard¹⁰, Manuela Martino², Johannes Ofner¹¹, John Plane¹⁰, Xin Yang¹²

¹Department of Chemistry, University of York, UK ²School of Environmental Sciences, University of East Anglia, UK ³Department of Environmental Sciences, Wageningen University and Research Centre, Netherlands, ⁴Max-Planck Institute of Chemistry, Germany, ⁵Plymouth Marine Laboratory, UK ⁶CCAPS, National University of Ireland, Galway, ⁷Institut de Recherches sur la Catalyse et l'Environnement de Lyon UMR, France, ⁸Universités d'Aix-Marseille, France, ⁹Cooperative Institute for Research in Environmental Sciences (CIRES), USA, ¹⁰School of Chemistry, University of Leeds, UK, ¹¹University of Bayreuth, Germany, ¹²Centre for Atmospheric Science, University of Cambridge.

Summary:

The workshop consisted of 3 inter-related sessions on the control of ozone in the remote marine boundary layer by halogen-related processes and by deposition to the sea surface. Presentations of new laboratory, field and modelling studies were followed in each session by discussion and identification of major scientific issues as detailed below.

Session 1: Reactive halogen species in the remote marine boundary layer

The six presentations in this session discussed some of the main uncertainties related to reactive halogen chemistry in the remote marine boundary layer. They include the actual source mechanism and rates for the release of photolysable iodine from the ocean in order to explain the measurements of IO at the atmospheric observatory on the Cape Verdes. The presentations by John Plane and Roland von Glasow showed that organic iodine precursors are unlikely to provide enough iodine to explain the measurements. The reaction of O₃ with dissolved iodide on the ocean surface (Martino et al., GRL, 2009) might play an important role in providing the required iodine flux. The vertical profile of radicals (OH, HO₂, IO, BrO) remains largely unknown and – as outlined by Dwayne Heard and others - field measurements are required in order to examine whether model predictions are realistic. Vertical profiles of radicals within the MBL and also at the transition between MBL and free troposphere are required, as are measurements close to the ocean surface with higher vertical resolution. These measurements could possibly be made with aircraft and/or zeppelins.

Global model studies of bromine chemistry in the troposphere and especially MBL as presented by Rolf Sander (Mainz) and Xin Yang (Cambridge) indicated areas with rather large BrO mixing ratios (e.g. the Southern Ocean) where no measurements are available. The Mainz model, that uses explicit sea salt aerosol chemistry, could reproduce BrO levels measured at Cape Verde, however the Cambridge model that uses a parameterisation for the release of bromine from sea salt underestimates BrO here by a factor of about 10. The use of parameterisations instead of full sea salt chemistry schemes in models, the treatment of meteorology and especially the absence/presence of precipitation (i.e. wet deposition), and the limited resolution of global models were identified as possible causes for model-model and model-field data differences. These discrepancies in surface BrO also raise the need for more information about bromine depletion/enrichment factors in sea salt aerosol.

Models still seem to underestimate reactive chlorine amounts in the MBL, but data is sparse. If high Cl-atom concentrations are in fact present, this should be visible in hydrocarbon ratios and possibly also in DMS. This should be investigated with data from the Cape Verde Observatory. It is important to check whether the implications of the wide-spread presence of halogen chemistry in the MBL is indeed consistent with available observations including bromide enrichment factors, ozone, OH/HO₂ and NO/NO₂ ratios, effects on DMS/DMSO etc.

Important uncertainties remain with regard to rate coefficients of higher iodine oxide gas-phase and aqueous-phase chemistry as well as non-pH dependent reactions on aerosol surfaces and the ocean. The gas phase rate coefficient for the $\text{CH}_3\text{O}_2 + \text{IO}$ reaction is another large uncertainty, especially in low-NOx environments. Furthermore, halogen and organic compound reactions still have considerable uncertainties. For example the role of DOM (in the surface ocean but also in airborne aerosol) for aqueous halogen chemistry is “known” but little kinetic information is available.

Session 2: Production and loss of volatile halogen compounds in seawater and at the sea-water surface

New laboratory data (as presented by Christian George) suggests that there are a range of potential mechanisms for supplying reactive halogens from the sea surface to the atmosphere. Photosensitisers, e.g. excited triplet states of aromatic ketones (a component of DOM), have been shown to oxidise halogen anions to their radical forms, which in turn will lead to the formation of organic halogens in the presence of organic compounds in the sea surface microlayer. The oxidation is enhanced in the presence of atmospheric O_3 , which acts as an electron acceptor, thus promoting the cationic form of the photosensitiser. A further implication of this mechanism is that O_3 deposition to high DOM-containing marine regions may be higher than previously thought, and needs to be studied under irradiated conditions (see also session 3). An additional role of atmospheric O_3 is in the direct oxidation of I^- in the sea surface microlayer, which has recently been shown to result, presumably *via* HOI/I_2 , in potentially significant production of reactive organoiodine compounds including CH_2I_2 , CHClI_2 and CHI_3 (presented by Manuela Martino). These reactions occur in the dark when seawater is exposed to O_3 , but so far it is not known whether they are enhanced by solar irradiance, due to the complicating factor that polyhalogenated organoiodine compounds are extremely photolabile. New field data suggests that sea-air fluxes of organoiodines, calculated from subsurface seawater data and corrected for photolytic degradation in surface seawater (presented by Lucy Carpenter), are not sufficient to supply enough atmospheric iodine to account for the concentrations of iodine oxide (IO) recently observed at the Cape Verde Observatory (see Session 1). These field observations lend support to the existence of additional mechanisms for supply of reactive halogens to the remote MBL. Further, direct measurements of marine bacterial oxidation of CH_3I suggest that biological degradation of reactive organoiodine is insufficient to significantly deplete concentrations in the water column (presented by Steve Archer). However, other undefined biological processes may be involved and rates of bacterial oxidation of polyhalogenated reactive organoiodine compounds may differ from those of monohalogenated compounds.

Key questions raised in this session include:

- What are the rates of $\text{X}^- \rightarrow \text{X}$ oxidation in the marine environment, i.e. in the presence of marine DOM? What can be used as good mimics for marine DOM photosensitisers?
- What is the relative importance of the dark ($\text{O}_3 + \text{I}^- + \text{DOM}$) and light (photosensitiser + $h\nu + \text{O}_3 + \text{I}^- + \text{DOM}$) reactions for production of reactive volatile iodine from the seasurface to the atmosphere?
- What are the biological production mechanisms for reactive organoiodines in the water column and what controls organoiodine variability in surface seawater?
- The possibility of direct I_2 emissions from the open ocean.
- What are the key biological processes that produce or degrade reactive organoiodines in the water column and how much do they contribute to controlling organoiodine variability in surface seawater?

Session 3: O₃ deposition to sea surface

This session addressed in more detail the importance of, and issues involved in, the removal of ozone by uptake by the ocean. The session on oceanic ozone deposition consisted of presentations by Laurens Ganzeveld (invited expert) and Liz Coleman on, respectively, a global and regional scale modelling exercise of the relevance of oceanic ozone deposition followed by a presentation by Jeff Hare (invited expert) on ship-borne ozone eddy correlation measurements. The modelling presentations showed the impact of including a more mechanistic representation of oceanic ozone uptake according to Fairall et al. (2007) compared to commonly applied constant uptake rate approaches. The mechanistic exchange model considers atmospheric- and waterside turbulence, diffusion, bubble-bursting, temperature dependent dissolution and chemical enhancement of ozone uptake. The latter is explicitly simulated considering ocean water biogeochemical properties including chlorophyll-*a* and iodide concentrations and the temperature dependent reaction rates of ozone with these components. Chlorophyll-*a* concentrations are inferred from satellite based observations whereas the global scale analysis by Ganzeveld et al. (2009) uses iodide concentrations that are inferred from an ocean water nitrate concentration climatology and observed nitrate-iodide concentration (anti) correlations. Comparison of the simulated ozone dry deposition velocity (V_{dO_3}) with the limited number of observations indicates that the mechanistic model simulates realistic V_{dO_3} values for remote sites but underestimates the coastal V_{dO_3} excluding the role of chlorophyll. Both the global and regional scale analysis including the role of chlorophyll-ozone chemical interactions (using a highly parameterized reaction rate) suggest a substantial change (decrease) in marine boundary layer ozone concentrations compared to the constant surface uptake approach. Changes in marine boundary layer ozone concentrations are, however, much smaller compared to those anticipated based on previously done sensitivity analysis using a range of constant uptake rate constants. This surprising result indicates the importance of compensating effects which are more properly considered in the mechanistic oceanic ozone exchange model compared to the commonly applied constant uptake approach; enhanced reactivity associated with enhanced tropical iodide concentrations is counteracted by reduced solubility (high temperatures), reduced chemical enhancement in high-latitude regions is counteracted by enhanced atmospheric and waterside turbulence, enhanced uptake for high wind speed conditions is counteracted by effective supply of ozone by advection and entrainment.

Further validation of these simulations of oceanic ozone deposition can profit from the recently collected ship-borne eddy correlation ozone flux observations presented by Jeff Hare. The observations of five cruises with the US research vessel *Ronald Brown* indicate that the oceanic V_{dO_3} is generally very small and contains a large uncertainty requiring long-term averaging of the observations. Experimental challenges include measuring close to the detection limit, accounting for the interference of water vapor, missing a part of the flux (~10% based on comparing measured and modeled co-spectra) and determining the lag time (based on analysis of the covariance between the ozone and vertical wind component) associated with the long inlet tubing. The observed mean dry deposition velocities for the five campaigns, which have covered a wide range of meteorological and biogeochemical regimes, seem to be on the low side of previously observed range. The observations also do not show such a clear dependence of V_{dO_3} on wind speed for some of the campaigns. Identification of other correlations and, consequently, of controlling processes (e.g. V_{dO_3} -SST) is also complicated by the large scatter in the observations.