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Sea-air fluxes and 1-D ocean modelling of volatile photolabile iodocarbons

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Recent research carried out at the Cape Verde Observatory has demonstrated that reactive iodine chemistry can contribute significantly to photochemical ozone depletion within the marine boundary layer of the atmosphere. Organoiodine compounds emitted from the oceans have been proposed as a major source of atmospheric iodine, however there is currently considerable ambiguity associated with estimates of iodocarbon sea-air fluxes, and hence the global importance of these gases as an I atom source to the atmosphere remains unclear. During the MAP (Marine Aerosol Production) and RHaMBLe (Reactive Halogens in the Marine Boundary Layer experiment) cruises in the Atlantic Ocean during summer 2006 and 2007 respectively, we made simultaneous measurements of a range of iodocarbons in surface seawater (2 - 6 m depth) and in marine air, using two GC-MS systems. Our measurements suggest that the dihalomethanes CH_2I_2, CH_2IBr and CH_2ICl may provide a combined global I atom source which is comparable to that of CH_3I, and are the dominant organic source of iodine in the marine boundary layer. However, since the dihalomethanes are rapidly photolysed within the top few metres of the water column, deriving sea-air fluxes for these short-lived gases based on their sub-surface seawater concentrations is more complex than for the longer-lived iodocarbons such as CH_3I. Consequently, we have developed an oceanic mixed layer model to predict the difference between the true surface and sub-surface dihalomethane concentrations, based on a combination of meteorological, biological and physical ocean parameters, in order to obtain more accurate sea-air fluxes for these gases.