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Dissolved organic matter in the surface microlayer: a heterogeneous iodine source over the open ocean

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Reactive halogen species (chlorine, bromine, iodine) have a globally significant effect on the concentration and lifetimes of climatically active gases (CH4, O3, DMS) and may alter the boundary conditions to regional atmospheric CTMs. Iodine radicals are thought to be produced primarily from photolysis of alkylhalides. However, recent laboratory data suggests the potential for additional sources that might involve heterogeneous reactions of ozone and/or light mediated redox chemistry (Martino et al., 2009; Sakamoto et al., 2009; Reeser et al., 2009). Whether these mechanisms are operative and relevant on global scale is presently not clear, partly due to the lack of observations over the open ocean. Further mechanistic insights can be derived from investigating the accelerating/inhibiting role of organic compounds on halogen abundance. Here we present recent field evidence from two ship cruises (2008 and 2009) and a first research flight (2010) over the remote tropical Pacific Ocean. Previous our observations of up to 140 ppt glyoxal (Sinreich et al., 2010) are found to correlate with elevated concentrations of iodine oxide (IO) on synoptic scales more than 5000km from continental land. While oxygenated VOC are known to be rapid sinks for bromine and chlorine radicals, this reaction is endothermic for iodine radicals. The positive correlation we observe between glyoxal and IO gives field evidence that halogen activation is enhanced (not suppressed) by organic matter. The source mechanism for iodine activation is discussed in light of the consistency of field data, recent laboratory data, spatial correlations of isoprene, 9 monoterpenes, formaldehyde, bromine oxide and IO, as well as glyoxal as an indicator species for heterogeneous reactions of dissolved organic matter (DOM) in the surface microlayer. Finally, a lower limit for the global iodine source is estimated.