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Halogen Chemistry in the Marine Boundary Layer

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Although the role of halogens in destroying stratospheric ozone has been well known for more than two decades, the subtler impact of halogens in the marine boundary layer is only now becoming recognised. This paper will focus on iodine and bromine. Important atmospheric sources of iodine include the biogenic production and air-sea exchange of iodocarbons (e.g. CH2I2, CH2IBr) and molecular iodine (I2). The uptake of O3 and photochemical reactions in the sea-surface microlayer appear to be significant sources of volatile iodine compounds. The major source of bromine (and chlorine) is the release of bromide ions from sea-salt aerosol. The subsequent atmospheric chemistry of these halogens (1), changes the oxidizing capacity of the marine boundary layer by destroying ozone and changing the hydroxyl radical concentration; (2), reacts efficiently with dimethyl sulphide and mercury (in the polar regions); and (3), leads to the formation of ultra-fine particles which may contribute to cloud condensation nuclei (CCN) and hence affect climate.

This paper will report observations of I, IO, OIO, I2 and BrO in several contrasting marine environments. To complement these field campaigns we have carried out wide-ranging laboratory studies, including: the formation and growth kinetics of iodine oxide nano-particles, and their uptake of water and sulphuric acid; the redox kinetics of iodate/iodide ions in aerosols; and the action of O3 in releasing I2 from aqueous iodide. The significance of these laboratory results will then be explored using atmospheric models.