Novel iodine chemistry in the marine boundary layer

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[1]   The atmospheric chemistry of iodine is important for several reasons, including the influence of iodine oxides on the oxidising capacity of the troposphere, the formation of new particles, and the enrichment of iodine in marine aerosols and the transport of this essential dietary element to the continents. It is shown here that a substantial iodine source is I_2, most likely emitted from macro-algae at low tide. This source accounts for the daytime production of new particles in the coastal marine boundary layer, and also explains the discovery of significant night-time levels of iodine oxides.   *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/ atmosphere interactions; 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere— composition and chemistry. **Citation:** Saiz-Lopez, A., and J. M. C. Plane (2004), Novel iodine chemistry in the marine boundary layer, *Geophys. Res. Lett.*, *31*, L04112, doi:10.1029/ 2003GL019215.

1.   Introduction

[2]   Recent observations of the iodine oxides IO [*Alicke et al.*, 1999; *Allan et al.*, 2000a] and OIO [*Allan et al.*, 2001] in the marine boundary layer (MBL) have demonstrated the importance of iodine chemistry in the atmosphere. Iodine affects the oxidising capacity of the atmosphere in at least three ways. First, the iodine oxides are involved in ozone-depleting cycles in the troposphere [*Davis et al.*, 1996; *McFiggans et al.*, 2000] and stratosphere [*Solomon et al.*, 1994]. Second, IO is an efficient oxidiser of dimethyl sulphide (DMS) [*Nakano et al.*, 2003], which is emitted by phytoplankton in the ocean. Third, the uptake of inorganic iodine compounds, such as HOI and INO_3, on sea-salt aerosols liberates chlorine and bromine into the gas phase; these halogens are also ozone-depleting and their atoms and oxides are highly reactive towards certain organic compounds [*McFiggans et al.*, 2002]. Another aspect of iodine chemistry is that the higher iodine oxides, such as I_2O_5, condense from the gas phase very readily, and this may explain the substantial bursts of new particles in the daytime marine atmosphere [*O'Dowd et al.*, 2002].

[3]   The surprisingly high levels of iodine oxides that have been observed are partly explained by the discovery that a range of alkyl iodides (e.g., CH_2I_2, CH_2ICl, CH_3I) evade from the ocean, and then photolyse readily to produce I atoms and hence IO by reaction with O_3 [*Carpenter et al.*, 1999]. However, even though the rapid cycling of iodine compounds through sea-salt particles back into the gas phase helps to maintain the concentration of IO [*Vogt et al.*, 1999], the source of alkyl iodides does not seem to be sufficient [*McFiggans et al.*, 2000]. In this paper we will demonstrate that molecular iodine, I_2, is another major source of atmospheric iodine.

2.   DOAS Measurements of Iodine Species

[4]   Observations of I_2, OIO, IO and NO_3 (the nitrate radical) were made at the Mace Head Atmospheric Research Station on the west coast of Ireland (53°20′ N, 9°54′ W) during August 2002. The concentrations of these species were measured by the technique of Differential Optical Absorption Spectroscopy (DOAS) [*Allan et al.*, 2000a; *Allan et al.*, 2000b; *Allan et al.*, 2001]. The DOAS instrument consists of a Newtonian telescope housing both the transmitting and receiving optics. An absorption path, 8.4 km long and about 20 m above the sea, was set up by installing an array of corner-cube reflectors on an island 4.2 km west of the observatory [*Allan et al.*, 2000a]. The light beam, powered by a 450 W xenon arc lamp, was folded back to the receiver and then directed through a quartz fibre optic bundle to a 0.5 m Czerny-Turner spectrometer (Acton Research model SP-556-i, grating 1200 grooves mm^{-1}), and dispersed onto a two-dimensional charge coupled detector (Princeton Instruments model NTE2, front-illuminated chip with an open electrode structure). A spectral resolution of 0.25 nm was employed in the three wavelength ranges used for this study.

[5]   Spectra of the atmospheric light beam, scattered sunlight, and the xenon lamp, were recorded every 10 s and averaged for 30 min (I_2, OIO and IO) or 20 min (NO_3) to produce a differential absorption spectrum. Details of the spectral deconvolution procedure are provided elsewhere [*Allan et al.*, 2000a; *Allan et al.*, 2000b]. Literature reference spectra for OIO [*Himmelmann et al.*, 1996], IO [*Harwood et al.*, 1997] and NO_3 [*Yokelson et al.*, 1994] were adapted to the spectrometer instrument function. The I_2 reference cross section was measured in our laboratory at a pressure of 1 atm N_2 and at a resolution suitable for DOAS retrievals [*Saiz-Lopez et al.*, 2004], in contrast to the last study reported in the literature [*Tellinghuisen*, 1973]. The spectrum is available from the corresponding author on request.

[6]   Figure 1 shows examples of reference spectra for these molecules that have been fitted to atmospheric spectra, after other known absorbers in the atmosphere (e.g., NO_2 and H_2O) have been subtracted out. The top panel shows the clear identification of I_2 from the band structure of its $B^3\Pi(0_u^+) - X^1\Sigma_g^+$ electronic transition. Note that I_2 and OIO were measured simultaneously in the $535-575$ nm wavelength region, IO in the $425-448$ nm region, and NO_3 in the
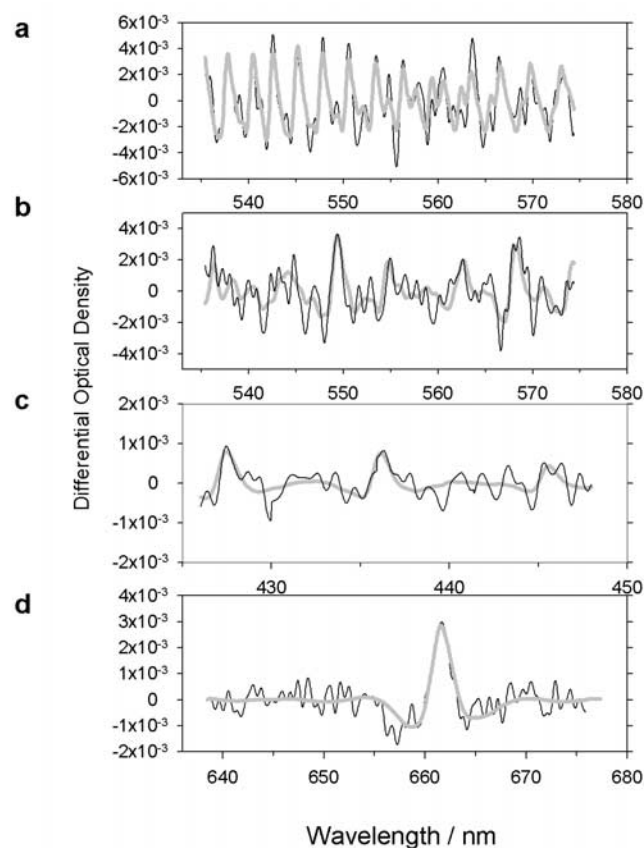
Figure 1. Examples of atmospheric spectral fits. The black line is the atmospheric optical density (OD) spectrum with all the known absorbers (apart from the species of interest) fitted and subtracted; the grey line is the fitted reference OD spectrum of the final species. This procedure yields: a. $[I_2]$ = 88.5 ± 4.1 ppt; b. $[OIO]$ = 2.5 ± 0.4 ppt; c. $[IO]$ = 3.0 ± 0.4 ppt; d. $[NO_3]$ = 11.5 ± 0.4 ppt.

$640–768$ nm region. It should be noted that the mixing ratios reported here are *averaged* over the optical path.

3. Results and Discussion

[7] The DOAS instrument normally operated in a single spectral region for each daytime or night-time period. Figure 2 illustrates a selection of observations from 34 days of near-continuous measurements. Panels (a) and (b) show night-time and daytime measurements of I_2 and OIO; panel (c) shows data on IO. The respective tidal heights are also plotted in these panels. Panel (d) illustrates two nights of NO_3 measurements.

[8] The I_2 mixing ratio varied from below the instrumental detection limit of about 3 parts per trillion by volume (ppt), to maximum levels of 93 ppt at night and 25 ppt during the day. As shown in Figure 2a, the I_2 mixing ratio exhibited large pulses that were highly correlated with low tide. This behaviour, observed over 16 nights and 3 days of measurements, is most likely due to strong emissions of I_2 from exposed macro-algae at low tide. For example, *Laminaria* kelp accumulates high concentrations of I^- ions from seawater, which become oxidised to hypoiodous acid (HOI) and I_2 in the plant [*Kupper et al.*, 1998; *Truesdale and Canosamas*, 1995]. Previous work has shown that

elevated levels of alkyl iodides, such as CH_3I, CH_2ICl and CH_2I_2, also occur in the coastal MBL at low tide [*Carpenter et al.*, 1999]. Notwithstanding the strong correlation with tidal state, significant I_2 levels (up to 25 ppt at night) were also observed at high tide in westerly winds. This may indicate that atmospheric I_2 is also produced over the open ocean, possibly by the reaction of O_3 with iodide ions in the sea surface microlayer [*Garland and Curtis*, 1981].

[9] During the day, the rapid photolysis of I_2 (photolytic lifetime ≈ 10 s, determined in our laboratory) indicates that, on a local scale, there will be a substantial production of iodine oxides at low tide. This could well be responsible for
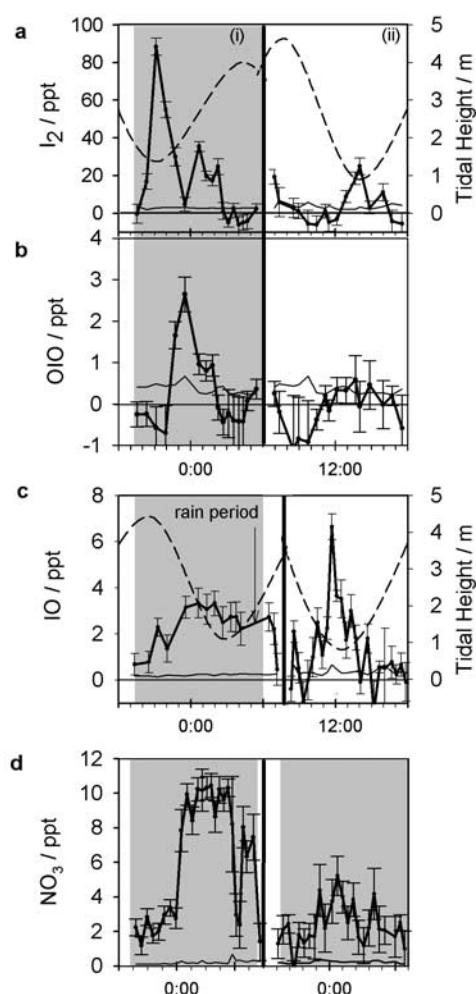

Figure 2. Mixing ratio profiles of I_2, OIO, IO and NO_3, measured at Mace Head, Ireland, during August 2002. The mixing ratios, together with 2σ uncertainties, are shown in black. The detection limit of the instrument, and the tidal height, are plotted as thin black and thick broken lines, respectively. Two approximately 12-h periods, labelled (i) and (ii), are shown for each species. (a) I_2, (i) August 20/21, (ii) August 26. (b) OIO, measured simultaneously with the I_2 in (a). (c) IO, (i) August 28/29, (ii) August 24. (d) NO_3, August 19/20, August 21/22. The abscissa shows Greenwich Mean Time, with tick marks every hour. The grey and white backgrounds correspond to periods of night and day, respectively.

the bursts of new particles which are commonly observed in the coastal MBL [*O'Dowd et al.*, 2002]. During these bursts, the observed rate of production of 3 nm-sized particles can reach about 5×10^4 particles cm^{-3} s^{-1}. Assuming that each of these particles contains about 500 I_2O_5 molecules, then this requires an I atom formation rate of 5×10^7 cm^{-3} s^{-1}. This rate would be produced by the daytime photolysis of about 10 ppt of I_2, typical of the daytime mixing ratios observed at low tide during the campaign.

[10] The night-time mixing ratios of OIO ranged from below the detection limit (≈ 0.5 ppt) to a maximum of 3 ppt. OIO is mainly produced by the self reaction of IO [*Allan et al.*, 2001]. However, it has a large photolysis cross section between 500 and 620 nm, so that during the day its lifetime is only about 1 s [*Ashworth et al.*, 2002]. Indeed, throughout the campaign OIO was not observed above the detection limit during daytime (see Figure 2b(ii)). In accord with our previous measurements [*Allan et al.*, 2001], OIO sometimes exhibited a small peak immediately after sunset, when its photolysis ceased; it then disappeared over about 1 h, probably due to uptake on aerosol. However, when a significant pulse of I_2 occurred at night, OIO built up to a peak about 2 h later (Figure 2b(i)). This clear correlation between I_2 and OIO, the time lag between them, and the fact that the mixing ratio of I_2 is at least an order of magnitude larger than that of OIO, strongly suggests that I_2 is the source of the OIO. We consider this further below.

[11] The mixing ratios of IO ranged from below the detection limit (≈ 0.5 ppt) to a maximum of 7 ppt. As shown in Figure 2c(ii), the daytime IO mixing ratio usually peaked around low tide, as has been reported previously [*Alicke et al.*, 1999]. However, during this campaign we also measured IO on two nights. Figure 2c(i) shows one of these nights where IO was clearly above the detection limit, peaking at 3 ppt around midnight. Figures 2c(i) and (ii) both show the pulse of IO that typically occurred for about an hour after dawn. This is most likely caused by the rapid photolysis of the inter-halogen species IBr and ICl [*McFiggans et al.*, 2002; *Vogt et al.*, 1999]. These species can build up during the night, following the uptake of inorganic iodine species such as INO_3 and HOI on sea-salt aerosol [*Mössinger and Cox*, 2001].

[12] An intriguing question raised by the night-time observations reported here is how IO and OIO are generated in the absence of sunlight. As discussed above, the iodine source is most likely I_2. Although the gas-phase reaction between O_3 and I_2 is too slow [*Vikis and Macfarlane*, 1985] to be important in the MBL, the reaction between NO_3 and I_2 has a reasonably fast rate constant ($k = 1.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 285 K [*Chambers et al.*, 1992]), and is assumed to yield INO_3 and I [*Atkinson and Wayne*, 2000]. Atomic I would then react rapidly with O_3 to form IO. Figure 2d shows the NO_3 mixing ratio measured during two nights when air masses arrived at Mace Head from the oceanic sector (west/northwest wind direction), conditions similar to those when I_2, OIO and IO were measured in Figures 2a–2c. NO_3 mixing ratios averaging 7 ppt were observed under these conditions [*Allan et al.*, 2000b]. At night in relatively clean air, the main loss process for IO is probably recombination with NO_2 to form INO_3 ($k = 4.0 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 285 K [*Allan and Plane*,

2002]). During the night shown in Figure 2c(i), the average NO_2 mixing ratio (measured in the same spectral region as IO) was 70 ppt. Taking I_2 and NO_3 mixing ratios of 50 and 7 ppt, respectively, then the steady-state mixing ratio of IO would be 2 ppt, which is in sensible accord with the observed levels.

[13] The iodine oxides, at the mixing ratios measured in this environment, have a significant impact on the oxidising capacity of the MBL. The average rate of O_3 depletion, catalysed by the IO self-reaction [*McFiggans et al.*, 2000], ranged from about 0.06 ppb h^{-1} at night to 0.11 ppb h^{-1} during the day. These rates of O_3 loss are significant when compared, for instance, to observed daytime loss rates of $0.3-0.4$ ppb h^{-1} during summer at Cape Grim (Tasmania), another remote coastal location [*Ayers et al.*, 1992]. IO has also been shown recently to react more rapidly with DMS than previously measured [*Nakano et al.*, 2003]. Taking the average daytime IO mixing ratio of 3 ppt, and an average OH mixing ratio of 0.06 ppt measured during summer at Mace Head [*Carslaw et al.*, 1999], shows that IO will oxidise DMS about 3 times faster than OH in this environment.

[14] In summary, the present work has demonstrated that large concentrations of I_2 can occur in the coastal MBL. The clear correlation of I_2 with tidal state indicates that emissions from exposed macro-algae are responsible. A crude estimate of the contribution of coastal emissions of I_2 to the global iodine budget can be made by assuming that all the emission occurs within the DOAS optical path (i.e., 4.2 km offshore), and that at every low tide a 1 km high boundary layer is filled with 50 ppt of I_2 (based on the night-time measurements when I_2 is not rapidly removed by photolysis). This corresponds to 1.5 Mg I yr^{-1}, per km of coastline. Assuming that 20% of the earth's total coastline (1.6×10^6 km) lies within temperate latitudes where I_2-producing macro-algae are abundant, then the integrated flux is 0.5 Tg I yr^{-1}. This may be compared with estimates of $0.4-1.0$ Tg I yr^{-1} for the emission of I_2 from the action of O_3 at the sea surface [*Garland and Curtis*, 1981], and $1-2$ Tg yr^{-1} for the global emission of CH_3I from the ocean [*Davis et al.*, 1996].

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