

In situ measurements of molecular iodine in the marine boundary layer: the link to macroalgae and the implications for O₃, IO, OIO and NO_x

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Abstract. Discrete in situ atmospheric measurements of molecular iodine (I₂) were carried out at Mace Head and Mweenish Bay on the west coast of Ireland using diffusion denuders in combination with a gas chromatography-mass spectrometry (GC-MS) method. I₂, IO and OIO were also measured by long-path differential optical absorption spectroscopy (LP-DOAS). The simultaneous denuder and LP-DOAS I₂ measurements were well correlated ($R^2=0.80$) but the denuder method recorded much higher concentrations. This can be attributed to the fact that the in situ measurements were made near to macroalgal sources of I₂ in the intertidal zone, whereas the LP-DOAS technique provides distance-averaged mixing ratios of an inhomogeneous distribution along the light-path. The observed mixing ratios of I₂ at Mweenish Bay were significantly higher than that at Mace Head, which is consistent with differences in local algal biomass density and algal species composition. Above algal beds, levels of I₂ were found to correlate inversely with tidal height and positively with the concentrations of O₃ in the surrounding air, indicating a role for O₃ in the production of I₂ from macroalgae, as has been previously suggested from laboratory studies. However, measurements made ~150 m away from the algal beds showed a negative correlation between O₃ and I₂ during both day and night. We interpret these results to indicate that the released I₂ can also lead to O₃ destruction via the reaction of O₃ with I atoms that are formed by the photolysis of I₂ during the day and via the

reaction of I₂ with NO₃ radicals at night. The results show that the concentrations of daytime IO are correlated with the mixing ratios of I₂, and suggest that the local algae sources dominate the inorganic iodine chemistry at Mace Head and Mweenish Bay.

1 Introduction

The role of iodine chemistry in ozone depletion events and marine aerosol formation has received considerable attention in the past few years (Saiz-Lopez et al., 2007; Read et al., 2008; Huang et al., 2010; O'Dowd et al., 2002; Vogt et al., 1999; Seitz et al., 2010). The precursors for these iodine-related atmospheric processes have been proposed, from early studies, to be iodocarbons such as CH₃I, CH₂I₂, CH₂ClI, CH₂BrI, C₂H₅I, C₃H₇I, or C₄H₉I (Carpenter et al., 1999). However, recent field measurements show that molecular iodine (I₂) is probably the dominant source of atmospheric iodine in certain coastal regions. A maximum I₂ mixing ratio of 93 parts per trillion by volume (pptv) at night and of 25 pptv during the day was observed during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX) field campaign at Mace Head, Ireland in summer 2002 using long-path differential optical absorption spectroscopy (LP-DOAS) (Saiz-Lopez and Plane, 2004). During daylight, I₂ molecules in the atmosphere photolyze to I atoms which then react with O₃ to form iodine oxide (IO). A clear anti-correlation between IO and tidal height and a correlation between IO and solar irradiation were also observed at Mace Head (Carpenter et al., 2001; Saiz-Lopez et al., 2006a). The



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self-reaction of IO is thought to result in the formation of higher iodine oxides like OIO or I₂O₄ and finally leads to new particle formation (Hoffmann et al., 2001; O'Dowd and Hoffmann, 2005; Pirjola et al., 2005). Also, IO radicals play a key role in a number of other important tropospheric processes, including NO_x and HO_x chemistry.

Biogenic emission of I₂ by macroalgae has been suggested to be one of the most important processes responsible for the observed tropospheric iodine levels in coastal locations (McFiggans et al., 2004; Pirjola et al., 2005; Palmer et al., 2005). A recent study shows that iodine is accumulated in macroalgae (e.g., *Laminaria digitata*) in the form of iodide, which can react with O₃ when the plants are exposed to the ambient air at low tide, leading to the direct release of I₂ into the atmosphere (Küpper et al., 2008). However, the correlations between I₂ emissions and algal species are still poorly understood, especially under ambient conditions, so that the impacts of biogenic emission of I₂ on tropospheric photochemistry on regional and global scales remain an open question.

Currently, data on ambient I₂ are still quite scarce, and most of the measurements have been carried out by long-path differential optical absorption spectroscopy (LP-DOAS) (Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2006a; Peters et al., 2005). This technique provides spatial average concentrations along the DOAS light-path (usually several kilometres in length), thus is incapable of resolving inhomogeneous distributions of I₂. However, it has been proposed that the spatial variability of the sources of reactive iodine leads to significant spatial variations in the concentrations of iodine species. Thus, the DOAS measurements cannot clearly identify the sources of the iodine species (Peters et al., 2005; von Glasow and Crutzen, 2007). Therefore, "point" in situ measurements of gaseous I₂ are highly desirable to better identify the potential source of molecular iodine. A broadband cavity ring-down spectrometer (BCCRDS) was deployed during the NAMBLEX campaign, and the application of this system to point measurements of ambient I₂ has been demonstrated (Bitter et al., 2005). Recently, incoherent broadband cavity-enhanced absorption spectroscopy (IB-BCEAS) has been developed in the laboratory for gaseous I₂ measurements (Vaughan et al., 2008). However, the detection limits of these spectrometric methods are relatively high (~20 ppt), which makes the clear identification of daytime I₂ still difficult. In addition, the initial concentrations from direct I₂ emissions are not accessible by LP-DOAS method since the light-path runs mostly at a height of several meters above the ground and the rapid photolysis of I₂ during daytime causes a vertical concentration gradient. However, model studies have predicted that even very low concentrations of I₂ under daytime conditions could strongly affect the marine atmosphere (Peters et al., 2005).

In this paper, we present the results of a 5-week field campaign carried out at Mace Head and Mweenish Bay located at the West Coast of Ireland in August/September 2007. Ambient I₂ mixing ratios were measured by a diffu-

sion denuder system combined with a gas chromatography-mass spectrometry (GC-MS) with precolumn derivatization method and by the DOAS technique for comparison. The correlation between I₂ concentrations at different measurement sites, ozone concentrations, tidal height, and occurrence of different algal species were investigated. Also the impact of iodine on nighttime chemistry was studied.

2 Experimental

2.1 Diffusion denuder sampling in combination with GC-MS measurements

The collection of I₂ on diffusion denuder tubes (6 mm i.d. × 50 cm length, Huang and Hoffmann, 2009) is based on the rapid formation of inclusion complexes of I₂ with the combined coatings α -cyclodextrin (α -CD) and iodide (I⁻). To obtain denuders coated uniformly with the coating reagents, nine 0.5 mL aliquots of coating solution (2.5 mg mL⁻¹ α -CD and trace ¹²⁹I⁻ in methanol) were slowly pipetted into the openings of the brown denuder tube which was held at an angle of about 10° relative to the horizontal plane. During the coating procedure the tubes were rotated and flushed with nitrogen for drying (flow rate 0.5 L min⁻¹). Afterward, the coated denuders were sealed with polypropylene (PP) end-caps and stored under refrigeration until sampling. At the sampling site, the denuders were set vertically to eliminate particle deposition due to gravitational settling. The interference iodine species were isolated by coupling a 1,3,5-trimethoxybenzene-coated denuder upstream of the α -CD/I⁻-coated denuder (Huang and Hoffmann, 2009), and an untreated glass tube of specific length (15 cm) with the same diameter as the denuder tube was coupled to the denuder inlet, used as a subduction zone to adjust the laminar flow of the sampled air into the denuder. Ambient air was sampled through the denuder system by a membrane pump located downstream of the denuder for 30–180 min at a flow rate of 500 mL min⁻¹. Once the sampling was completed, the open ends of the tubes were again sealed with PP end-caps and kept under refrigeration until subsequent laboratory measurements.

In the laboratory, the samples were eluted with five 2.0 mL-portions of ultrapure water into a 25-mL calibrated flask. Amounts of 500 μ L of phosphate buffer (pH 6.4), 100 μ L of 2,4,6-tribromoaniline (2.5 mg L⁻¹, internal standard), 400 μ L of sodium 2-iodosobenzoate, and 300 μ L of *N,N*-dimethylaniline were then added. The solution was diluted to about 23 mL with ultrapure water and subsequently shaken at room temperature for about 120 min. 2.0 mL of sodium acetate solution (20% *m/v*) was then introduced, and the solution was diluted to the mark with ultrapure water. Finally, the solution was extracted with 100 μ L of cyclohexane. 1.0 μ L of the solution was injected into a gas chromatography with an ion-trap mass spectrometer (Trace GC/PolarisQ,

Thermo Finnigan Italia S.p.A., Rodano, Italy). A fused-silica capillary column (30 m×0.25 mm i.d., d_f : 0.25 μm , Rtx-5MS, Restek Co., Bad Homburg, Germany) was used for chromatographic separation. High-purity helium (99.999%) was used as a carrier gas at a constant flow of 1.0 mL min⁻¹. The temperature of the injector was set to 250 °C and the transfer line was 300 °C. The temperature of the GC oven was programmed as follows: initial temperature 50 °C (hold 3 min), 30 °C min⁻¹ to 220 °C (hold 3 min). The MS was operated in the electron impact (EI) ionization mode with an acceleration energy of 70 eV. A solvent delay of 4.5 min preceded the MS spectra acquisition in the selected ion monitoring (SIM) mode in the following sequence: 4.50–6.00 min, m/z : 77, 121; 6.00–7.50 min, m/z : 119, 247; 7.50–11.67 min, m/z : 250, 329, 331. The blanks were estimated by measuring the unsampled denuders which were sealed throughout the campaign and were found to be within the ranges of the limit of detection (0.17 pptv).

2.2 DOAS measurements

DOAS is a well established technique to identify and quantify trace gases by their narrow band absorption structures (Platt and Stutz, 2008). In this study, two active LP-DOAS instruments were used (Seitz et al., 2010). A light beam generated by a high pressure Xe-arc lamp (type: XBO500, Osram) was passed through a telescope of 1.5 m focal length then through the open atmosphere to an array of quartz prism retro-reflectors (63 mm diameter each). For the measurements at Mace Head the light-path (6.8 km, one-way) crossed Roundstone Bay to Roundstone about 10 m above sea level at high tide, where the reflector (consisting of 76 quartz prisms) was located. At Mweenish Bay, a light-path (2.0 km, one-way, 39 quartz prisms) was established crossing Mweenish Bay at about 5 m above sea level at high tide. For both instruments the reflected light was analyzed by a spectrometer (Acton Spectra Pro 300, $f = 4.1$, 1900 gr mm⁻¹ and an Acton Spectra Pro 500, $f = 6.9$, 600 gr mm⁻¹ grating for the measurements at Mace Head and Mweenish Bay, respectively). The detector used was a 1024 pixel photodiode array detector (type: S3904-1024, Hamamatsu). O₃ was measured in 320±40 nm, IO in 430±40 nm, I₂ and OIO in 550±40 nm, and NO₃ in 630±40 nm. For the analysis of the LP-DOAS data the software DOASIS (Kraus, 2005) was used to simultaneously fit the different references to the atmospheric spectrum using a non-linear least-squares method (e.g., Stutz and Platt, 1996). In addition, a polynomial was included to account for broad band structures due to scattering in the atmosphere. IO was analyzed in the wavelength range between 416 and 439 nm. The IO cross section (Spietz et al., 2005) as well as references of NO₂ (Voigt et al., 2002) and H₂O (Rothmann et al., 2005) were included in the IO fitting procedure. The evaluation of I₂ was performed in the wavelength range 530 to 567 nm and the cross sections of I₂ (Saiz-Lopez et al., 2004), references of OIO (Bloss et al.,

2001), NO₂, O₄ (Greenblatt et al., 1990) and H₂O were considered during the fit. O₃ was analyzed between 315 and 342.5 nm (Mweenish Bay) and 332.5 and 343.75 nm (Mace Head) and the cross sections of O₃ (Voigt et al., 2001), BrO (Wilmouth et al., 1999), SO₂ (Vandaele et al., 1994), HCHO (Meller and Moortgat, 2000), NO₂, O₄ and HONO (Stutz et al., 2000) were included in the fitting procedure. NO₃ was analyzed between 618 and 626 nm and 657 and 664 nm and fitted using NO₃ (Yokelson et al., 1994) and H₂O cross sections.

2.3 Online GC-MS measurements

CH₃I, C₂H₅I, CH₂BrI, CH₂ICl and CH₂I₂ were analysed automatically from 3 L of dried air using a Perkin Elmer (USA) Turbomass GC-MS system connected to a Perkin Elmer Automated Thermal Desorption unit (ATD). Air samples were measured every 45 min during 5 days of measurement between the 29 August and the 11 September 2007. Analytes were trapped onto a 3-stage carbon-based adsorbent micro trap (Air monitoring trap, Perkin Elmer, UK) held at -30 °C. The micro trap was then flash heated to 360 °C, injected onto a 60 m DB5 GC column (Supelco), then analysed by the MS in single ion mode. The GC-MS was calibrated against a gas standard prepared in-house containing low-pptv mixing ratios of the target halocarbons in zero grade nitrogen (BOC, UK) at 100 bar in an Aculife cylinder (10 L, CK Gases). This gas standard was quantified in our laboratory against a permeation tube system (Wevill and Carpenter, 2004) immediately after the campaign. The method is discussed in more detail in Hornsby et al. (2009).

2.4 Sampling sites

The denuder sampling systems and LP-DOAS instruments were positioned at the Mace Head Atmospheric Research Station (53.32° N, 9.90° W) and at Mweenish Bay (53.31° N, 9.83° W) (see Fig. 1). Also, at Mace Head, in situ measurements of reactive halocarbons were carried out by the online GC-MS system. The Mace Head site is well known for atmospheric events with regard to iodine chemistry. A detailed description of this measurement site can be found elsewhere (Carpenter et al., 2001). Mweenish Bay is located about 7 km southeast of the Mace Head research station in an area of large seaweed beds. The algae species present differ from those at Mace Head, with the brown algae *Ascophyllum nodosum* and *Fucus vesiculosus* being dominant (Irish Seaweed Centre, 2001). In addition, Mweenish Bay has a higher seaweed density. Denuder sampling was carried out in the intertidal zone at Mweenish Bay-II for 30 consecutive days (6 August–4 September, 2007) and at Mace Head for 6 consecutive days (28 August–2 September, 2007). To explore the concentration levels of I₂ from direct biogenic emissions, several samples were taken by denuder during low tide in the central zone of algal beds (Mweenish Bay-I). The

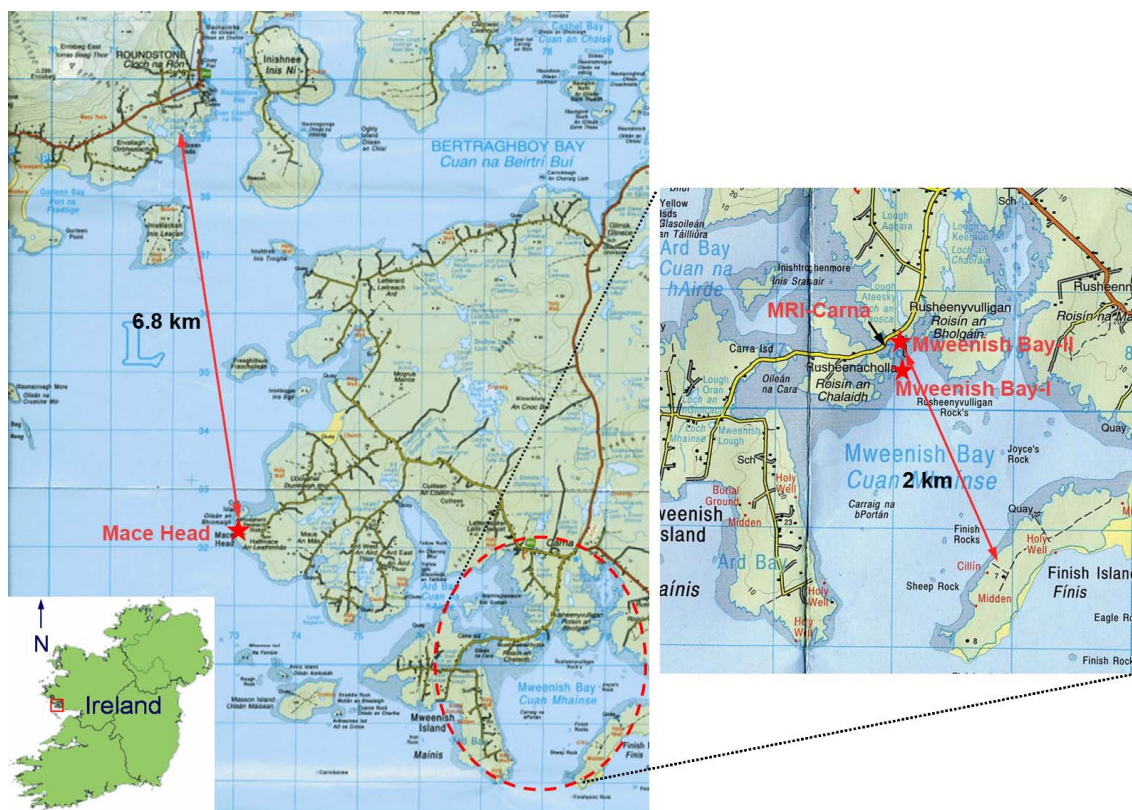


Fig. 1. The denuder sampling sites (☆) and the light paths of the LP-DOAS measurements at Mace Head and Mweenish Bay, Ireland.

distance between Mweenish Bay-I and Mweenish Bay-II is about 100–150 m.

3 Results and discussion

3.1 Iodine emissions from macroalgae

Although laboratory-based studies have observed the direct emissions of I_2 from macroalgae (e.g., *Laminaria*) (Sellegrì et al., 2005; Küpper et al., 2008; Dixneuf et al., 2009), the levels of I_2 emissions under atmospheric conditions have not been clarified so far. To address this question we used diffusion denuders which can provide “single-point” in situ measurements of I_2 to collect samples at the central zone of algal beds (Mweenish Bay-I) during low tide. Since I_2 is rapidly photolyzed to iodine atoms during daytime, the denuder tubes were set up directly above the algal beds with a very short vertical distance of around 5 cm between the seaweed and the denuder inlet to minimize the potential influence of photolysis. Figure 2a shows the results of 5-day measurements within a period of 21 days, at a fixed sampling site. The mixing ratios of I_2 were observed to fluctuate with a range between 110 and 302 ppt. This fluctuation could be attributed to algae themselves and the surrounding atmosphere. Küpper et al. (1998) report that young plantlets of

seaweed have a larger capacity of iodine uptake than adult plants. Thus, within these 21 days the changes of physiological conditions of algae can lead to the differences of iodine level accumulated in the seaweed and thereby the emission level of I_2 into the air. Other factors such as solar radiation, temperature, and ozone concentration may also have contributed to the observed fluctuation of I_2 emission. A plot of the I_2 mixing ratio observed at Mweenish Bay-I against the measured O_3 (Fig. 2b) shows that the emissions of I_2 increase with increasing O_3 mixing ratio. This finding (although the data set is very limited) is in close agreement with the result from a chamber experiment (Palmer et al., 2005) as well as the recently suggested mechanism in which I_2 emissions are supposed to be regulated by the ozone-scavenging reaction of the accumulated iodide on the algae surfaces (Küpper et al., 2008).

Given the short atmospheric lifetime of I_2 and the dilution effect during air transport (Saiz-Lopez et al., 2004, 2006b; Palmer et al., 2005), the I_2 mixing ratio downwind of the seaweed beds could be lower. As expected, the mixing ratios of I_2 observed at Mweenish Bay-II (i.e., further far away from the seaweed beds) decreased significantly compared to the enhanced levels observed at Mweenish Bay-I (Fig. 2a). These comparison results were associated with northwesterly/southwesterly winds which passed over the algal beds with speeds $<7.7 \text{ m s}^{-1}$. When the wind came from

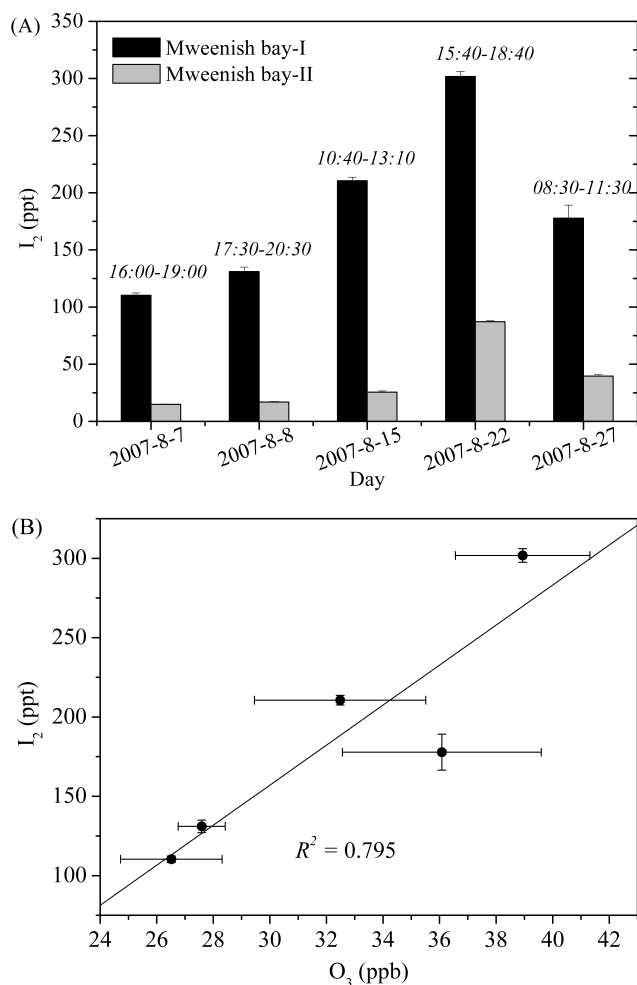


Fig. 2. Comparison of the mixing ratio of I₂ between Mweenish Bay-I and Mweenish Bay-II (A), and the correlation between the emission of I₂ and O₃ in the surrounding air at Mweenish Bay-I (B), measured directly above the algal beds.

northeasterly (land) direction the levels of I₂ measured at Mweenish Bay-II decreased further to around 5 ppt, which indicates that local algae is the dominant emission source of I₂ under the ambient conditions in the coastal area.

Over the course of this study the concentration levels of I₂ observed at Mace Head were significantly lower than that at Mweenish Bay-II. The maximum mixing ratios for daytime and nighttime measurements at Mace Head were 29 ppt and 141 ppt, respectively, and the values at Mweenish Bay-II were 87 ppt and 193 ppt, respectively. The discrepancies of I₂ levels between Mace Head and Mweenish Bay can be attributed to the higher biomass density at Mweenish Bay than at Mace Head and the difference on algae species composition present at these two locations (Irish Seaweed Centre, 2001). It suggests that the algae species *Ascophyllum nodosum* and *Fucus vesiculosus* at Mweenish Bay are strong I₂ sources and that Mweenish Bay is a “hot spot” of iodine atmospheric chemistry.

Since algae are an important source of ambient I₂ and the biomass of algae exposed to air is related to the tidal height, the tidal effects on I₂ emissions were investigated during daytime and nighttime throughout the campaign at Mweenish Bay-II. A plot of I₂ mixing ratio as a function of tide height exhibits a clear anticorrelation (Fig. 3), which is in agreement with the recent observations at Mace Head (Bale et al., 2008; Saiz-Lopez et al., 2006a). It is apparent that the levels of I₂ are higher at low tide during nighttime due to its accumulation in the absence of solar photolysis. Nevertheless, we also observed that I₂ mixing ratios at Mweenish Bay-II were maintained at levels of around 15–18 ppt even when strong westerly winds occurred ($> 10.8 \text{ m s}^{-1}$, from sea direction), irrespective of the state of tide as well as day or night. Given that a certain amount of macroalgae at the nearby rocky upper littoral zone was still exposed to the atmosphere during high tide, these values (15–18 ppt) could represent the background level of I₂ at the coastline.

The concentrations of reactive organic iodine species measured at Mace Head by an online GC-MS technique are compared to I₂ observed by the denuder/GC-MS method in Fig. 4. Clearly, the concentration of I₂ is much higher than that of the iodocarbons for both daytime and nighttime measurements. Therefore, it is clear that I₂ is the predominant iodine precursor at Mace Head. However, like the emissions of I₂, the biogenic emissions of iodocarbons are also algae species dependent, and high concentration levels of iodocarbons have been reported at Brittany, a French Atlantic Coast (Peters et al., 2005). Therefore, it is difficult to tell whether I₂ is the predominant source of iodine in coastal areas other than Mace Head.

3.2 Implications for O₃, IO, OIO and NO_x

IO mixing ratios were measured by LP-DOAS at both Mweenish Bay and Mace Head during the campaign. The average and maximum values of daytime IO were 3.4 ± 1.0 and 9.5 ± 0.8 ppt for consecutive 30-day measurements at Mweenish Bay, and 1.1 ± 0.3 and 4.4 ± 0.6 ppt for consecutive 9-day measurements at Mace Head, respectively. Note that the maximum mixing ratios were observed around noon. A plot of three sets of data measured at Mweenish Bay indicates that daytime IO concentration levels increase with the increase of I₂ concentrations and of the solar irradiation, as shown in Fig. 5. A similar trend was also observed at Mace Head by Commane et al. (2008) during this campaign. These provide good evidence for the photochemical production of IO from coastal emissions of I₂. Figure 5 also shows that I₂ concentrations increase with enhanced solar irradiation. Since enhanced biological activity and biogenic emissions of iodine species have been suggested to correlate with solar irradiation together with warmer temperature (Carpenter et al., 1999), I₂ emissions can be expected to be more elevated when low tide periods coincide with maximum solar irradiation exposure.

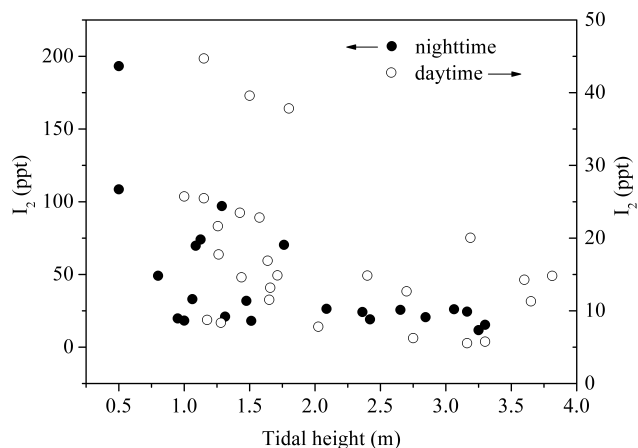


Fig. 3. The mixing ratio of I_2 as a function of tidal height at the sampling site Mweenish Bay-II.

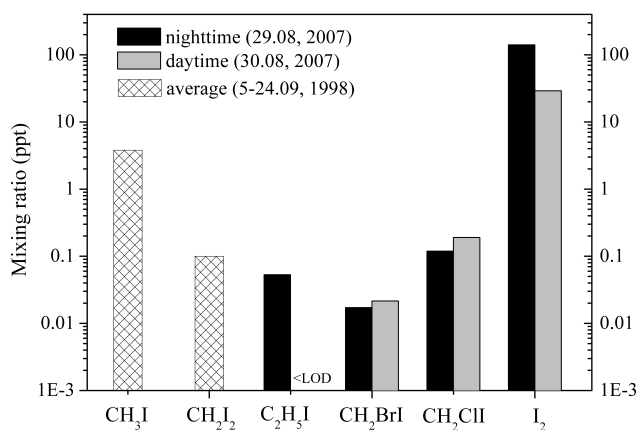


Fig. 4. Typical mixing ratios of reactive organic iodine species and I_2 at Mace Head. The average CH_3I and CH_2I_2 mixing ratios during the 1998 PARFORCE campaign at Mace Head (also given in Carpenter et al., 2003) are included since these two species were not measured during the campaign in 2007. The limits of detection (LODs) for CH_3I , C_2H_5I , CH_2BrI and CH_2ClI are 0.2, 0.1, 0.02 and 0.04 ppt, respectively. The bar is missing if the mixing ratio is below the LOD. Note the logarithmic scale.

Recent models predict that bromine- and iodine-induced ozone destruction can also occur in the troposphere (Vogt et al., 1999; von Glasow et al., 2004), and observations of IO and BrO have been linked to extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean (Read et al., 2008). However, reduction in the tropospheric ozone burden through iodine emitted from coastal marine sources has not been verified by observations so far. During the 5-week field observations at Mweenish Bay, the mixing ratio of ozone decreased in several days from the normal levels of ~ 40 ppb down to as low as 12 ppb. Since the measurements by denuders did not cover all these ozone destruction events observed by LP-DOAS and the time resolution of the

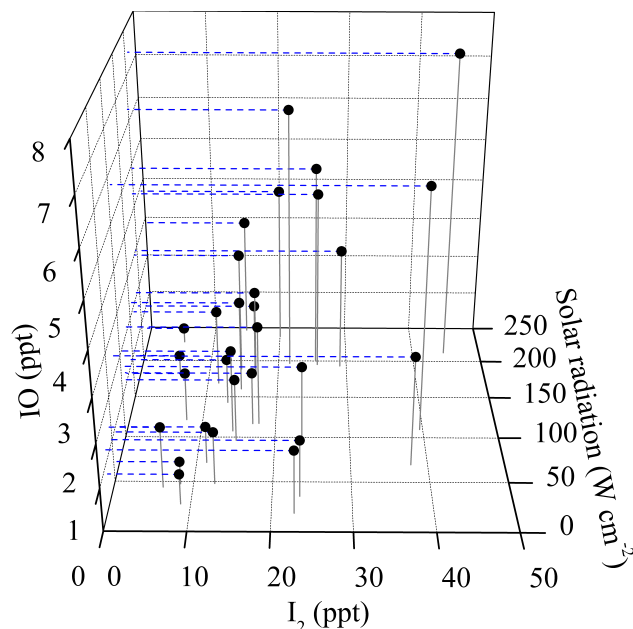


Fig. 5. Observed daytime IO mixing ratios as a function of solar radiation and I_2 . Measurements were taken at Mweenish Bay.

two techniques was different, we use the mean O_3 concentrations observed at the timescales of I_2 measurements to investigate the correlations between these two ambient constituents. The results show that the O_3 concentration decreased in general with the increase of I_2 concentration for daytime observations (Fig. 6), which is consistent with the observations shown in Fig. 5 and strongly supports the viewpoint that photochemical production of daytime IO is related to concentration levels of O_3 . For nighttime observations, a clear anti-correlation of O_3 with I_2 was observed, as shown in Fig. 6. Surprisingly, the O_3 concentrations dropped significantly to around 15 ppb when a high level of I_2 mixing ratio was observed around midnight. Here, it should be noted that the correlation between O_3 and I_2 shown in Fig. 6 is opposite to that shown in Fig. 2b. This can be attributed to the difference in the sampling locations. The positive correlation presented in Fig. 2b was measured directly above the algal beds, therefore, can be the consequence of the ozone-scavenging reaction of iodide on the algae surfaces at low tide (i.e., $I^- + O_3 \rightarrow I_2$) (Küpper et al., 2008). However, the negative correlation presented in Fig. 6 was measured in the intertidal zone about 150 m from the algal beds. In this case, the emitted I_2 will mix up and react with other atmospheric constituents, leading to the O_3 destruction.

The chemistry of iodine at nighttime is still uncertain. The gas-phase reaction of I_2 with O_3 is too slow (Vikis and Macfarlane, 1985) to lead to significant O_3 destruction. A suggested reaction (Chambers et al., 1992; Saiz-Lopez et al., 2006a) for the formation of atomic iodine (Reaction R1) at night is

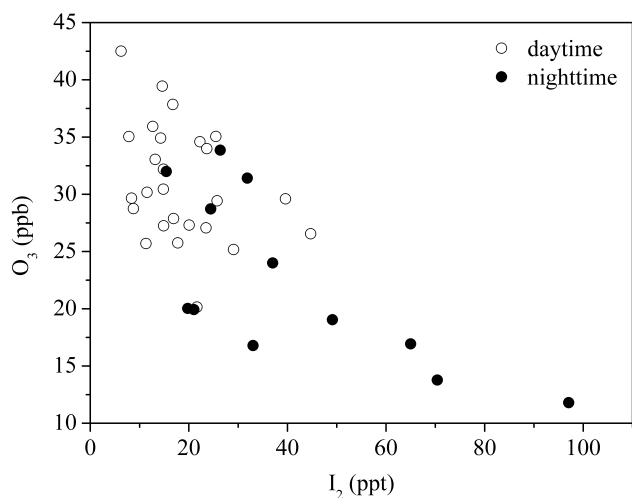


Fig. 6. Plot of O_3 versus I_2 during ozone destruction events at Mweenish Bay.



Based on quantum chemical calculations this reaction has recently been proposed to be the major source of iodine oxides at night (Kaltsoyannis and Plane, 2008). The resulting atomic iodine will then react rapidly with O_3 to form IO (Reaction R2). The IO produced can react with NO_3 (Reaction R3) with a rate coefficient of $9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Dillon et al., 2008), which will lead to additional NO_3 consumption and will compete with IO+IO for nighttime OIO formation.



Our observations during nighttime at Mweenish Bay show that, with the increase of I_2 concentrations, the NO_3 concentrations decrease (Fig. 7). The results indicate the importance of nitrate radicals for nighttime iodine chemistry in the coastal marine boundary layer (MBL). However, it should be noted that the lower O_3 levels at higher I_2 levels would also indicate a lower source of NO_3 given the production pathway of NO_3 (Reaction R4).



It also should be noted that the observed O_3 loss rate for both daytime and nighttime measurements (Fig. 6) is much higher than the value predicted by model simulations by Saiz-Lopez et al. (2006a, b). A possible explanation could be that other halogen compounds which have the similar diurnal pattern as I_2 also contribute to the O_3 loss. Indeed, the activated iodine compounds, ICl and HOI, showed a strong correlation with I_2 (Huang and Hoffmann, 2009).

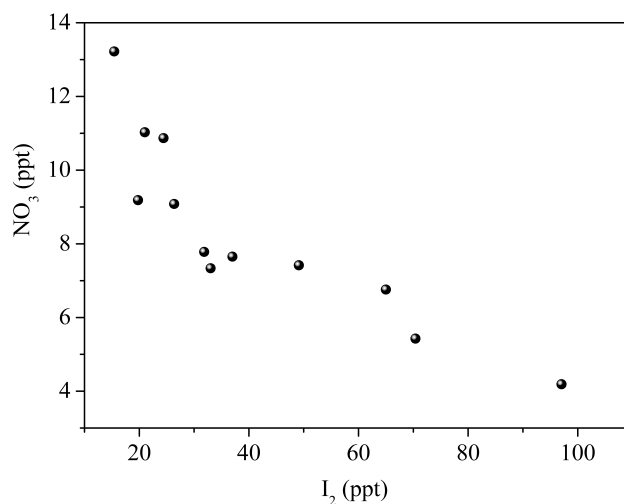


Fig. 7. NO_3 as a function of I_2 at night at Mweenish Bay.

During the campaign OIO was also measured at Mweenish Bay and Mace Head. Unambiguous identification of the absorption structure of OIO was not realized although it was observed several times above the detection limit (average, 12.5 ppt at Mweenish Bay and 3.3 ppt at Mace Head, respectively). The measurement of OIO in the spectral region of 500–600 nm has some principal problems (Peters et al., 2005), leading to high residual structures and therefore high errors and high limit of detection. To date the only unambiguous daytime OIO measurements is made in the Gulf of Maine (Stutz et al., 2007). At Mace Head (Peters et al., 2005; Saiz-Lopez et al., 2006a), Cape Grim (Allan et al., 2001), and Roscoff (Mahajan et al., 2009), OIO has been observed during the nighttime but never in the daytime.

3.3 Data evaluation

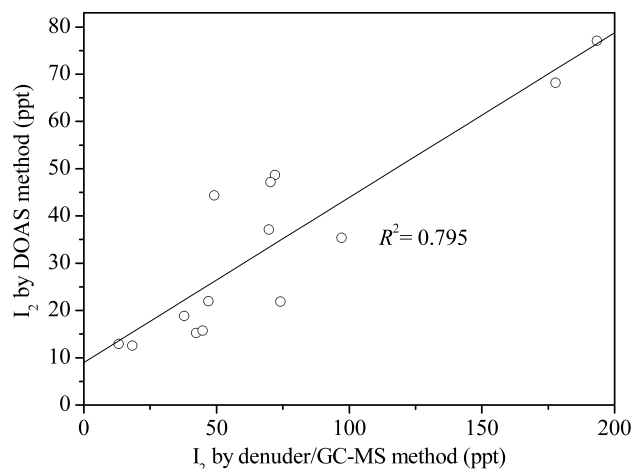
Gas-phase reactive inorganic iodine species (I_2 , IO, and OIO) have been observed at Mace Head previously (Table 1). A maximum mixing ratio of I_2 of 93 ppt at night and 25 ppt during the day was observed by LP-DOAS during the NAMBLEX campaign (Saiz-Lopez and Plane, 2004). In situ measurements of daytime I_2 were also performed at Mace Head using BCCRDS (Bitter et al., 2005) and at a nearby location (Mweenish bridge) using denuder tubes in combination with ICP-MS analysis (Saiz-Lopez et al., 2006b), which reported much higher mixing ratios of daytime I_2 compared to the LP-DOAS measurements (see Table 1). A more comprehensive comparison between “single-point” in situ and LP-DOAS measurements was carried out at both Mace Head and Mweenish Bay during the campaign. Note that average values of LP-DOAS measurements within the same sampling period of denuder measurements at Mweenish Bay-II and Mace Head were used for comparison because of the different time resolution of the two techniques. As shown in

Table 1. Observations of reactive inorganic iodine species (I_2 , IO, and OIO) at Mace Head and Mweenish Bay, Ireland, by different techniques.

Species	Location, year	Technique	Spatiality	Max. conc. (ppt)		Reference
				Daytime	Nighttime	
I_2	Mace Head, 1998	LP-DOAS	14.4 km	–	61.3±12	Peters et al. (2005)
	Mace Head, 2002	LP-DOAS	8.4 km	25	93±3	Saiz-Lopez and Plane (2004)
	Mace Head, 2002	BBCRDS	“point” in situ	94±20	–	Bitter et al. (2005)
	Mweenish bridge, 2003	Denuder/ICP-MS	“point” in situ	115	–	Saiz-Lopez et al. (2006b)
	Mace Head, 2007	Denuder/GC-MS	“point” in situ	29.1±1.0	140.7±5.6	this work
	Mace Head, 2007	LP-DOAS	13.6 km	–	94.4	this work
	Mweenish Bay-I, 2007	Denuder/GC-MS	“point” in situ	301.8±4.3	–	this work
	Mweenish Bay-II, 2007	Denuder/GC-MS	“point” in situ	87.2±1.8	193.3±9.3	this work
	Mweenish Bay, 2007	LP-DOAS	4.0 km	–	–	this work
IO	Mace Head, 1997	LP-DOAS	14.4 km	6.7±0.5	–	Alicke et al. (1999)
	Mace Head, 1998	LP-DOAS	14.4 km	7.2±0.3	–	Hebestreit (2001)
	Mace Head, 2002	LP-DOAS	8.4 km	7.0±0.5	3	Saiz-Lopez and Plane (2004)
	Mace Head, 2007	LIF	“point” in situ	33.8±3.3	–	Commene et al. (2008)
	Mace Head, 2007	LP-DOAS	13.6 km	4.4±0.6	–	this work
	Mweenish Bay, 2007	LP-DOAS	4.0 km	9.5±0.8	–	this work
	Mace Head, 1998	LP-DOAS	14.4 km	–	9.2±3.3	Peters et al. (2005)
OIO	Mace Head, 2002	LP-DOAS	8.4 km	< 4	10.8	Saiz-Lopez et al. (2006a)
	Mace Head, 2002	BBCRDS	“point” in situ	–	13±4	Bitter et al. (2005)
	Mace Head, 2007	LP-DOAS	13.6 km	–	–	this work
	Mweenish Bay	LP-DOAS	4.0 km	–	–	this work

Fig. 8, the denuder method recorded much higher concentrations of I_2 than the LP-DOAS method, for both daytime and nighttime measurements. This can be attributed to the facts that denuder method provides “single-point” measurements in the intertidal zone, whereas the LP-DOAS technique provides distance-averaged mixing ratios of a rather inhomogeneous distribution along the light-path (i.e., 4–14 km). As described above, the local algal sources dominate the inorganic iodine chemistry at Mace Head and Mweenish Bay. However, under the conditions of Mace Head and Mweenish Bay, the seaweeds extend only over a short distance of the DOAS light-path and most of the light-path extended over the open sea. In addition, a vertical I_2 concentration gradient caused by its rapid photolysis during daytime and by diffusion at night is expected. The vertical distance between the denuder inlets and the sea level is shorter than that between the DOAS light-path and sea level. Thus, the inhomogeneous spatial distribution of I_2 can be responsible for the observed discrepancies of I_2 mixing ratios.

The maximum mixing ratios of daytime IO measured by LP-DOAS at Mace Head are consistent with previous observations. However, the levels observed at Mweenish Bay are significantly higher than that at Mace Head. These results suggest that Mweenish Bay is a biological “hot spot” of iodine atmospheric chemistry. It should be noted that LP-DOAS averages over a few kilometers and the time resolution of denuder sampling is greater than tens of minutes.

**Fig. 8.** Comparison of I_2 mixing ratios measured by denuder/GC-MS and LP-DOAS.

This does not allow measurements at the spatial and temporal scales at which the iodine species (I_2 , IO, and OIO) are produced. Therefore, it can be expected that the actual peak values of these three iodine species could be higher than those reported here. This is supported by comparison results of IO measurements by LP-DOAS and laser-induced fluorescence (LIF) spectroscopy at Mace Head (Commene et al., 2008). Since the LIF technique provides “point” in situ measurements with a very high time resolution (10 s–5 min),

the maximum mixing ratios of IO observed by LIF are significantly higher than that measured by LP-DOAS, with a maximum value of 34 ppt reported. Considering the limit of detection of the denuder/GC-MS method (0.17 ppt for a sampling duration of 30 min at 500 mL min⁻¹) as well as the concentration levels at the west coast of Ireland, we suggest a shorter sampling time for example 10–30 min for further field measurements in algae-rich coastal areas. This would allow a more detailed study of the diurnal variation of ambient I₂ and a better understanding of the release mechanisms and atmospheric impact of I₂.

4 Summary

A diffusion denuder in combination with a GC-MS method has been used for “single-point” in situ measurements of I₂ at the West Coast of Ireland. The observations show that above algal beds, the emissions of I₂ from macroalgae are correlated with the surrounding O₃ concentration levels. Comparison of I₂ measurements was carried out at Mace Head and Mweenish Bay, and the results indicate that the mixing ratios of I₂ are correlated with species and biomass of local algae and that Mweenish Bay is a biological “hot spot” of iodine atmospheric chemistry. An anticorrelation between I₂ concentration levels and tidal height was observed for both daytime and nighttime measurements. In addition, the mixing ratios of I₂ were also measured by LP-DOAS and compared to the denuder/GC-MS measurements. The results show that local coastal emissions are the main source of ambient I₂ and that the denuder/GC-MS method can be used to better identify the potential source of I₂.

Measurements made ~150 m away from the algal beds showed a negative correlation between O₃ and I₂ during both day and night. The levels of I₂ and the intensity of solar irradiation significantly effect the mixing ratios of daytime IO and consequently the potential for O₃ destruction. During nighttime, the involvement of NO_x in the reaction cycles of I₂ is suggested to be responsible for the enhanced O₃ destruction. Further laboratory-based studies and field measurements are required to clarify the importance of the nighttime atmospheric chemistry of iodine.

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