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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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“Single-point” in situ measurements of molecular iodine (I_2) were carried out in the coastal marine boundary layer (MBL) using diffusion denuders in combination with a gas chromatography-mass spectrometry (GC-MS) method. Comparison measurements were taken at Mace Head and Mweenish Bay, on the West Coast of Ireland. The observed mixing ratios of I_2 at Mweenish Bay are much higher than that at Mace Head, indicating the emissions of I_2 are correlated with the local algal biomass density and algae species. The concentration levels of I_2 were found to correlate inversely with tidal height and correlate positively with the concentration levels of O_3 in the surrounding air. However, the released I_2 can also lead to O_3 destruction via the reaction of O_3 with iodine atoms that are formed by the photolysis of I_2 during the day and via the reaction of I_2 with NO_x at night. IO and OIO were measured by long-path differential optical absorption spectroscopy (LP-DOAS). The results show that the concentrations of both daytime and nighttime IO are correlated with the mixing ratios of I_2 . OIO was observed not only during the day but also, for the first time at both Mace Head and Mweenish Bay, at night. In addition, I_2 was measured simultaneously by the LP-DOAS technique and compared with the “single-point” in situ measurement. The results 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; O’Dowd et al., 2002; Vogt et al., 1999). The precursors for these iodine-related atmospheric processes have been proposed, from early studies, to be iodocarbons such as CH_3I , CH_2I_2 , CH_2ClI , CH_2BrI , C_2H_5I , C_3H_7I , or C_4H_9I (Carpenter et al., 1999). However, recent field measurements show that molecular iodine (I_2)

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is probably the dominant source of atmospheric iodine in certain coastal regions. A maximum I_2 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 a long-path differential optical absorption spectroscopy (LP-DOAS) (Saiz-Lopez and Plane, 2004). During periods of daylight, I_2 molecules in the atmosphere photolyze to I atoms which then react with O_3 to yield 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 self-reaction of IO is thought to result in the formation of higher iodine oxides like OIO or I_2O_4 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 I_2 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 O_3 when the plants are exposed to the ambient air at low tide, leading to the direct release of I_2 into the atmosphere (Küpper et al., 2008). However, the correlations between I_2 emissions and algal species are still poorly understood, especially under realistic ambient conditions, so that the impacts of biogenic emission of I_2 on tropospheric photochemistry on regional and global scales remain an open question.

Currently, data on ambient I_2 are still quite scarce, and most of the measurements were 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 I_2 . However, it has been proposed that the spatial variability of the sources

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of reactive iodine leads to significant spatial variations in the concentrations of iodine species. Thus, the DOAS measurements can lead to ambiguity in the identification of the source 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 (BBCRDS) was deployed during the NAMBLEX campaign, and the application of this system to “point” in situ measurements of ambient I₂ has been demonstrated (Bitter et al., 2005). Recently, incoherent broadband cavity-enhanced absorption spectroscopy (IBBCEAS) 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 the spectrometric methods 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 diffusion denuder system combined with a gas chromatography-mass spectrometry (GC-MS) with pre-column derivatization method and by the DOAS technique for comparison. The correlation between I₂ concentrations at different measurement sites, ozone concentrations, tidal height, occurrence of different algal species were investigated. Also the impact of iodine on nighttime chemistry was investigated.

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2 Experimental

2.1 Diffusion denuder sampling in combination with GC-MS measurements

Ambient I₂ samples were taken by diffusion denuder tubes (6 mm i.d. × 50 cm length). The collection of I₂ 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, 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. Fi-

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nally, the solution was extracted with 100 μL of cyclohexane. 1.0 μL 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 \times 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.

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. The setup of the LP-DOAS systems used was a further development of the coaxial mirror system introduced by Axelson et al. (1990). The light beam was sent 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 between 530 and 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 3L 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 4 min during 5 days of measurement between the 29 August and 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 flashed 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-

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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 (53.25° N, 9.80° W) and the Mweenish Bay (53.32° N, 9.73° W) (see Fig. 1). Also, at Mace Head, in situ measurements of reactive iodine species 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 brown species *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 consecutive 30 days (6 August–4 September 2007) and at Mace Head for consecutive 6 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 algae beds (Mweenish Bay-I). The distance between Mweenish Bay-I and Mweenish Bay-II is about 100–150 m.

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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*) (Sellegri 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 algae beds (Mweenish Bay-I) during low tide. Since I_2 is rapidly photolyzed to iodine atoms during daytime, the denuder tubes were set up exactly above the algae 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 concentrations of I_2 observed are fluctuant with a range between 110 and 302 ppt. This fluctuation could be attributed to algae themselves and the surrounding atmosphere. In the literature, Küpper et al. (1998) reported that young plantlets of seaweed have 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. Certainly, other factors such as solar radiation, temperature, and ozone concentration may also contribute 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).

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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), I_2 mixing ratio beyond the seaweed beds could be lower. As expected, the mixing ratios of I_2 observed at Mweenish Bay-II decreased significantly compared to the enhanced levels observed at Mweenish Bay-I (Fig. 2a). These comparison results were associated with north-westerly/southwesterly winds which passed over the algae beds with low speeds ($<15 \text{ m s}^{-1}$). When the wind came from northeasterly (land) direction the levels of I_2 measured at Mweenish Bay-II decreased further to around 5 ppt, which indicates further that local algae is really an unambiguous emission source of I_2 under the ambient conditions in the coastal area.

Over the course of this study the concentration levels of I_2 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 I_2 levels between Mace Head and Mweenish Bay could be attributed to the higher biomass density at Mweenish Bay than at Mace Head and the difference on algae species present at these two locations (Irish Seaweed Centre, 2001). It suggests that Mweenish Bay is a “hot spot” of iodine atmospheric chemistry.

Since algae is an important source of ambient I_2 and the biomass of algae exposed to air is related to the tidal height, the tidal effects on I_2 emissions were investigated during daytime and nighttime throughout the campaign at Mweenish Bay-II. A plot of I_2 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 I_2 are higher at low tide during nighttime due to its accumulation in the absence of solar photolysis. Nevertheless, we also observed that I_2 mixing ratios at Mweenish Bay-II were maintained at levels of around 15–18 ppt when strong westerly winds occurred ($>21 \text{ m s}^{-1}$, from sea direction). The locally emitted I_2 certainly will dilute in an expanding air mass. However, this interesting episode occurred 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 whenever the high tide occurred, these values (15–18 ppt) could represent the background level of I_2 at the coastline.

The concentrations of reactive organic iodine species measured at Mace Head by an online GC-MS technique are compared to I_2 observed by the denuder/GC-MS method in Fig. 4. Clearly, the concentration of I_2 is much higher than that of the iodocarbons for both daytime and nighttime measurements. Therefore, it is clear that I_2 is the predominant iodine precursor at Mace Head. However, like the emissions of I_2 , 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 I_2 is the predominant source of iodine in coastal areas other than Mace Head.

3.2 Implications for O_3 , 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 I_2 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 I_2 . Figure 5 also shows that I_2 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), I_2 emissions can be expected to be more elevated when low tide periods coincide with maximum solar irradiation exposure.

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Ozone destruction is of utmost concern for halogen-related studies which has been well documented in the stratosphere (von Glasow and Crutzen, 2007). Nevertheless, 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). Most recently, extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean has been observed (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 ratios of ozone decreased in several days from the normal levels of ~ 40 ppt down to as low as 12 ppt. Since the measurements by denuders did not cover all these ozone destruction events observed by LP-DOAS and the time resolution of the 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 O_3 concentration decreases 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 on the observation condition. The positive correlation presented in Fig. 2b was measured exactly above the algae 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 algae beds. In this case, the emitted I_2 will mix up and react with other atmospheric constituents, leading to the O_3 destruction.

The nighttime iodine chemistry is still not quite clear. The gas-phase reaction of I₂ with O₃ is too slow (Vikis and Macfarlane, 1985) to lead to significant O₃ destruction. A suggested reaction (Chambers et al., 1992) for the formation of atomic iodine at night is:



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 O₃:



10 Our observations during nighttime at Mweenish Bay show that, with the increase of I₂ concentrations, the NO₃ concentrations decrease, whereas, the concentrations of IO increase (Fig. 7). The results support the reactions described above and also indicate the importance of nitrate radicals on the nighttime iodine chemistry in the coastal marine boundary layer (MBL). Nevertheless, it should be noted that the observed O₃ 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 I₂ also contribute to the O₃ loss. Indeed, the activated iodine compounds, ICI and HOI, showed a strong correlation with I₂ (Huang and Hoffmann, 2009).

20 During the campaign OIO was also measured at Mweenish Bay and Mace Head. However, unambiguous identification of the absorption structure of OIO was not realized in most cases. 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 (average, 12.5 ppt at Mweenish Bay and 3.3 ppt at Mace Head, respectively). Nevertheless, OIO was observed several times above the detection limit. The observed maximum levels of OIO were 29.3 ppt at Mweenish Bay and 10.1 ppt at Mace Head for nighttime measurements, and 38.2 ppt

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at Mweenish Bay and 6.5 ppt at Mace Head for daytime measurements. The nighttime OIO could be formed via the reactions of either IO + IO or IO + NO₃ (Saiz-Lopez et al., 2006a). However, the formation mechanism of daytime OIO is not clear so far, and the observations of daytime OIO are still very scarce (Stutz et al., 2007).

3.3 Data evaluation

Gas-phase reactive inorganic iodine species (I₂, IO, and OIO) have been observed at Mace Head previously (Table 1). A maximum mixing ratio of I₂ 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). Exemplary in situ measurements of daytime I₂ were also performed at Mace Head using BBCRDS (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 I₂ 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 Fig. 8, the denuder method recorded much higher concentrations of I₂ than the LP-DOAS method, for both daytime and nighttime measurements. This can be attributed to the facts that denuder method provides “single-point” in situ measurements in the intertidal zone; however, 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 algae 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 I₂ concentration gradient caused by its rapid photolysis during daytime and by diffusion at night is expected. The vertical

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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 and nighttime OIO measured by LP-DOAS at Mace Head are consistent with previous observations. However, the concentration levels of these two iodine species 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 the time resolution of both LP-DOAS measurement and denuder sampling is greater than tens of minutes. This does not allow measurements at the timescales 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 (Commane et al., 2008). Since the LIF technique provides “point” in situ measurements with higher time resolution (10–5 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 help to obtain a better time resolution and to get a more detailed study of the diurnal variation of ambient I_2 and a better understanding of the release mechanism and atmospheric impact of I_2 .

4 Conclusions

A diffusion denuder in combination with a GC-MS method has been used for “single-point” in situ measurements of I_2 at the West Coast of Ireland. The observations show that the emissions of I_2 from macroalgae are correlated with the surrounding O_3 con-

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centration levels. Comparison of I_2 measurements was carried out at Mace Head and Mweenish Bay, and the results indicate that the mixing ratios of I_2 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 I_2 concentration levels and tidal height was observed for both daytime and nighttime measurements. In addition, the mixing ratios of I_2 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 I_2 and that the denuder/GC-MS method can be used to better identify the potential source of I_2 .

The potential implications of I_2 for IO, OIO, O_3 , and NO_x were studied. During daytime, the concentration levels of I_2 and the intensity of solar irradiation affect the production of daytime IO and consequently the potentiality of O_3 destruction. However, during nighttime the involvement of NO_x in the reaction cycles of I_2 are found to be responsible for the enhanced O_3 destruction. Certainly, more laboratory-based studies and field measurements are required to clarify the importance of the nighttime atmospheric chemistry of iodine.

Acknowledgements. This work was supported by the European Union under the FP6 project (Contract No. 018332): Marine Aerosol Production (MAP), the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) within the graduate program 826 “Trace Analysis of Elemental Species: Development of Methods and Applications”, the European Science Foundation INTROP exchange scheme and the European Community EUSAAR Infrastructure fund, as well as NERC grant NE/D006538/1. The authors are grateful to Colin O’Dowd (NUI, Galway) for leading the field campaign and to the Martin Ryan Institute, especially Richard Fitzgerald, for the support during the field measurements. KEH acknowledges NERC for award of a studentship.

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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	19.6	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	4.0	90.7	97.9	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	2.3±0.7	this work	
Mweenish Bay, 2007		LP-DOAS	4.0 km	9.5±0.8	4.7±1.1	this work	
OIO	Mace Head, 1998	LP-DOAS	14.4 km	–	9.2±3.3	Peters et al. (2005)	
	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	6.5±1.9	10.1±4.4	this work	
	Mweenish Bay	LP-DOAS	4.0 km	38.2±6.3	29.3±8.6	this work	

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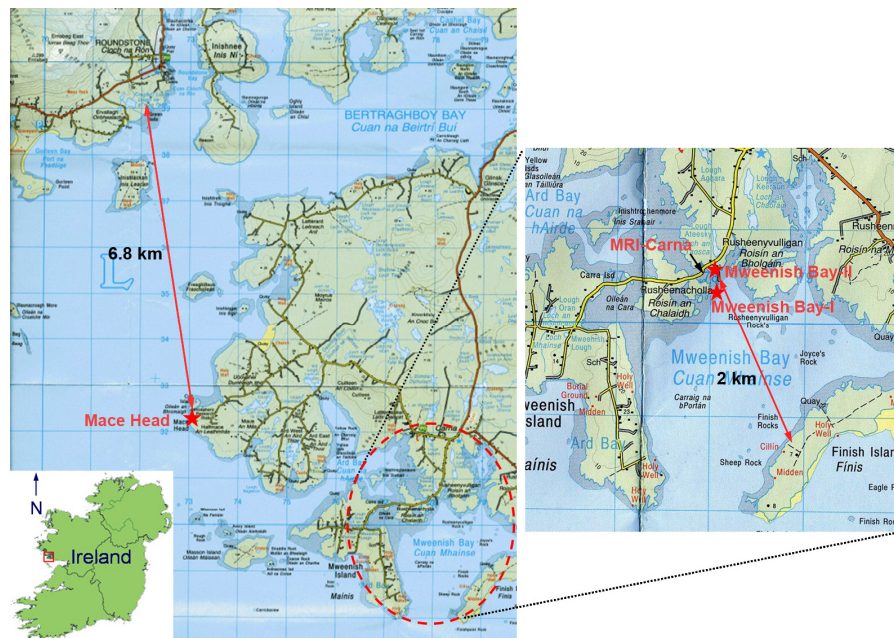


Fig. 1. The denuder sampling sites (★) and the light paths of the LP-DOAS measurements at Mace Head and Mweenish Bay, Ireland.

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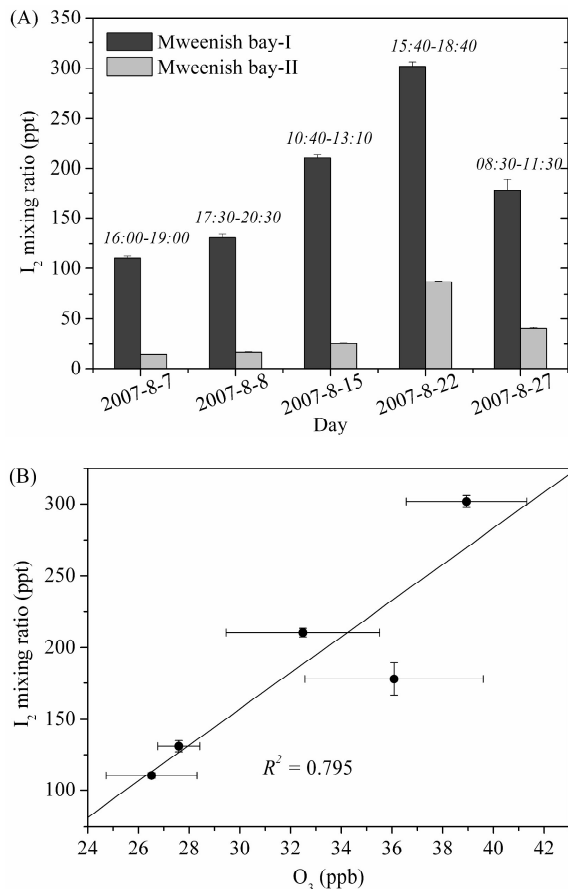


Fig. 2. Comparison of the mixing ratio of I_2 between Mweenish Bay-I and Mweenish Bay-II (A), and the correlation between the emission of I_2 and the concentration of O_3 in the surrounding air at Mweenish Bay-I (B). Note that I_2 and O_3 were measured by denuder/GC-MS and LP-DOAS, respectively.

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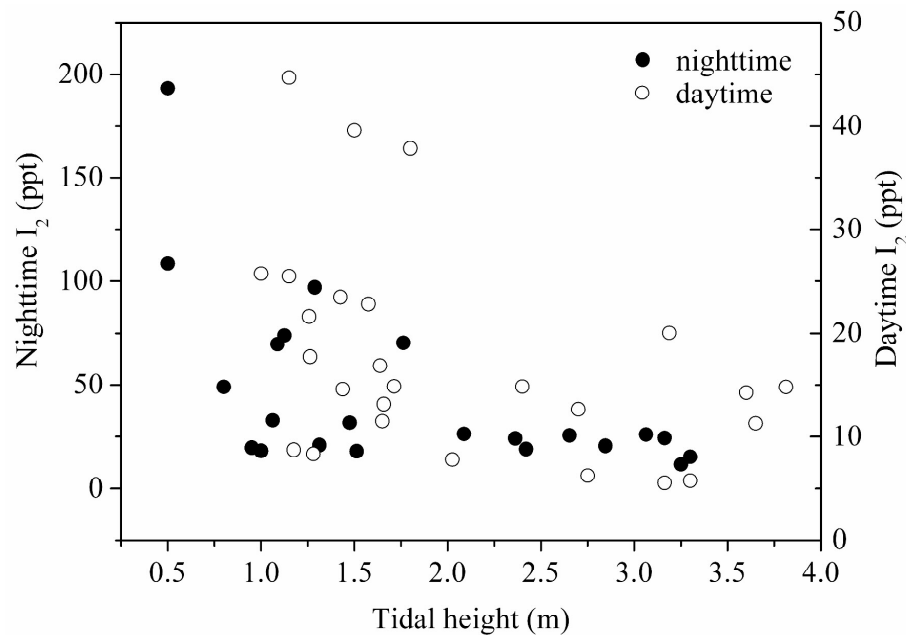


Fig. 3. The mixing ratio of I₂ as a function of tidal height at the sampling site Mweenish Bay-II. Note that I₂ was measured by denuder/GC-MS.

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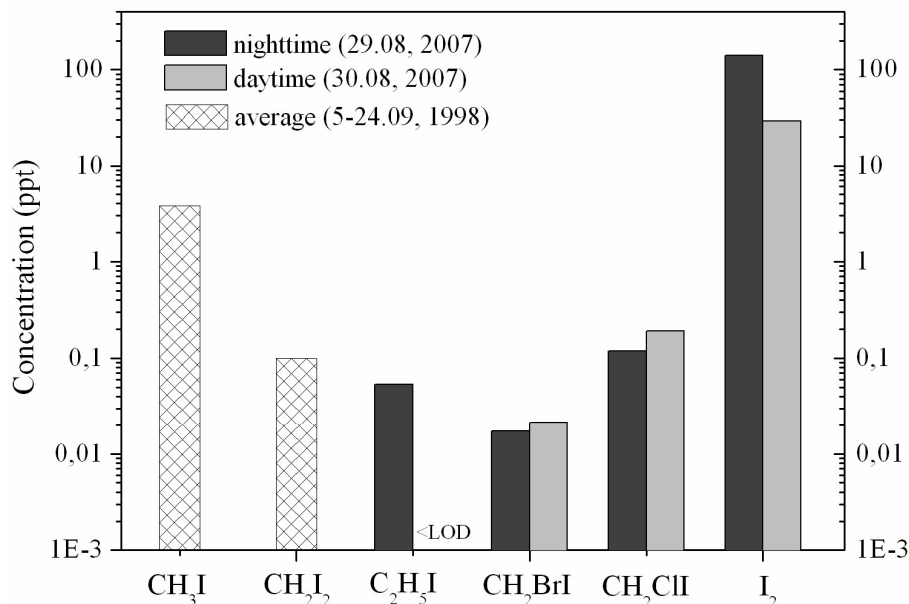


Fig. 4. Typical concentrations of reactive organic iodine species and I₂ at Mace Head. The average CH₃I and CH₂I₂ concentrations during the 1998 PARFORCE campaign at Mace Head (also given in Carpenter, et al., 2003) are included since these two species were not measured during the campaign in 2007. The limits of detection (LODs) for CH₃I, C₂H₅I, CH₂BrI and CH₂ClI are 0.2, 0.1, 0.02 and 0.04 ppt, respectively. The bar is missing if the concentration is below the LOD. Note the logarithmic scale.

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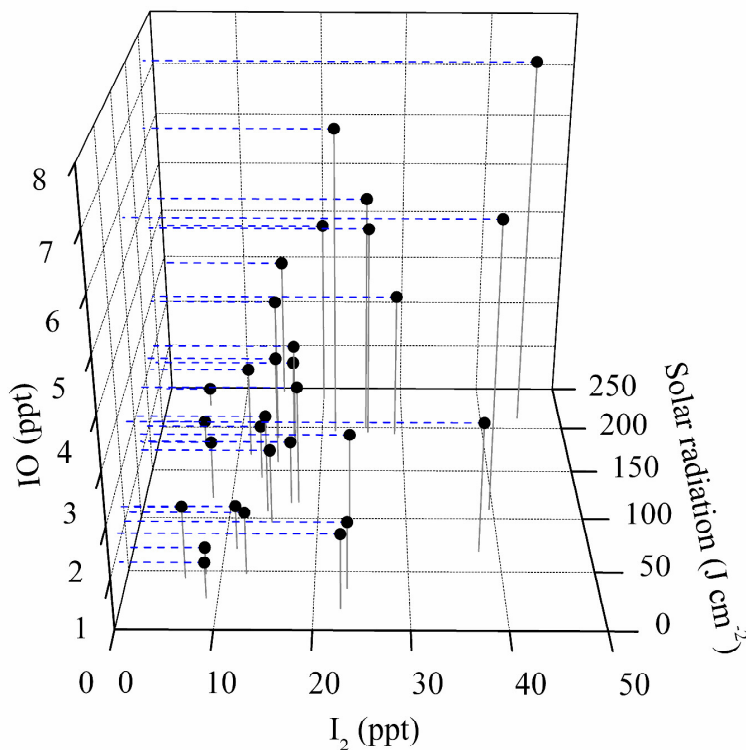


Fig. 5. The observed daytime IO as a function of the solar radiation and the concentration of I₂. Measurements were taken at Mweenish Bay. IO and I₂ were measured by LP-DOAS and denuder/GC-MS, respectively.

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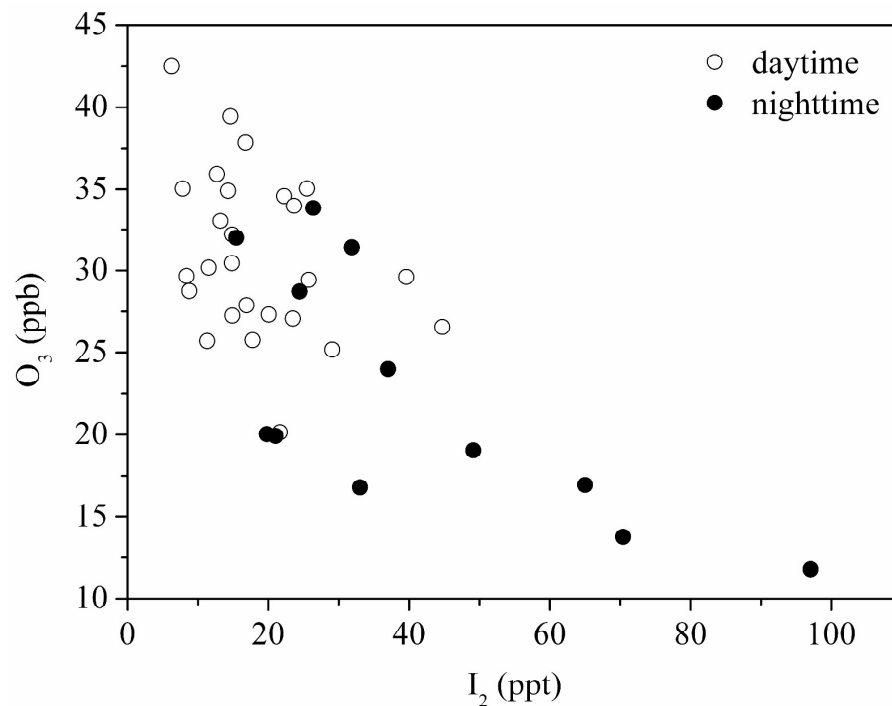


Fig. 6. Plot of O_3 versus I_2 during ozone destruction events at Mweenish Bay. Note that O_3 was measured by LP-DOAS, and I_2 by denuder/GC-MS.

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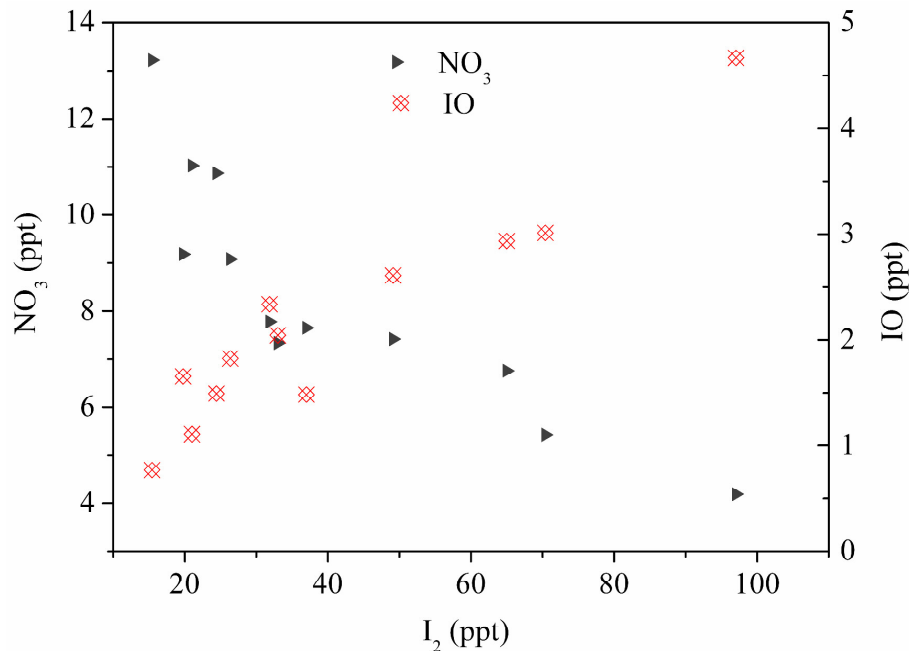
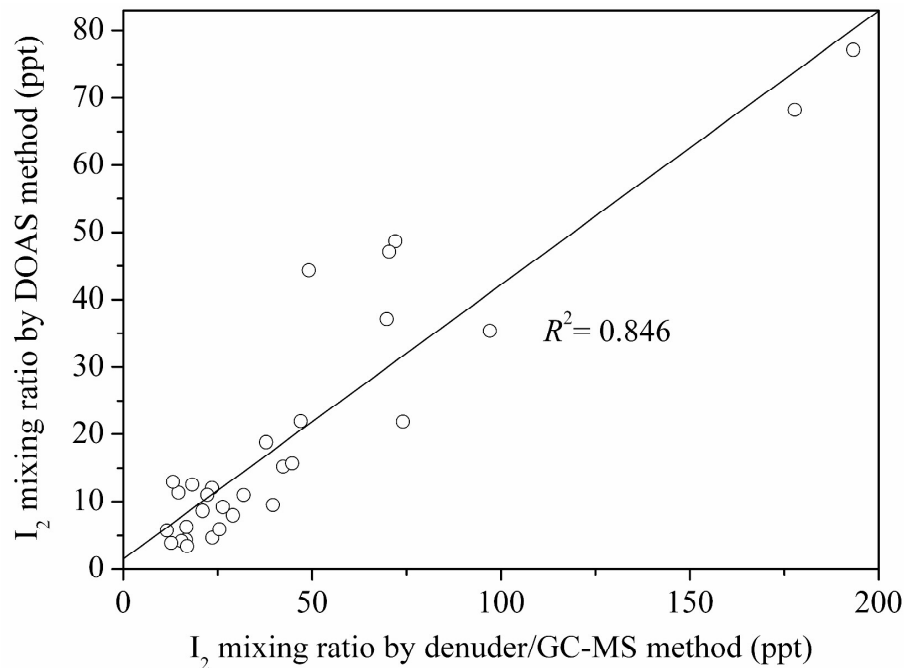


Fig. 7. IO and NO_3 as a function of I_2 at night at Mweenish Bay. Note that IO and NO_3 were measured by LP-DOAS, and I_2 was measured by denuder/GC-MS.

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**Fig. 8.** Comparison measurements of I₂ between denuder/GC-MS and LP-DOAS.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)