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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Iodine monoxide at a clean marine coastal site: observations of high frequency variations and inhomogeneous distributions" *by* R. Commane et al.

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Reviewer 2: We thank the reviewer for their very helpful and constructive comments. We present our detailed response to the questions raised and have made the corresponding changes in the new draft of the manuscript.

Major comments: **(Comment1) The paper includes a highly detailed discussion on the LIF instrument, which is not necessary. The measurement technique, albeit another version of the particular instrument used, has been used in the past and hence perhaps need not be discussed in such detail in the paper.**

- The instrumental description (sections 2.2 to 2.2.2) have been reduced in length but details

particular to this instrument have been retained.

(C2) The title of the paper suggests a detailed discussion on the observations and more information about the IO distribution, which has not been dealt in detail in the paper. I would suggest adding more information about the IO inhomogeneity, which is discussed in only one paragraph. There is work done in the past suggesting and even showing the inhomogeneity in iodine compounds around Mace Head (e.g. Saiz-Lopez, 2006, Seitz et al., 2010). These should be discussed in further detail in the paper. The present manuscript does not offer many improvements on the past work, with the only novel part being point observations of IO to confirm the inhomogeneity in the iodine spatial distribution, which has been observed by other instruments in the past (e.g. for I2).

- Section 4.2 has been changed to focus on 'Inhomogeneities in IO distribution' and the section has been extended to include a more substantial discussion on the inhomogeneities observed in IO through comparison with the LIF and LP-DOAS observations. The previous work of Saiz-Lopez et al. (2006) and Seitz et al. (2010) have been discussed and compared to the results obtained here. A discussion of the high variability seen in the IO data on short timescales compared to the longer time average of the LP-DOAS data has also been included.

(C3) Maybe rather than a simple schematic representation of the distribution of macroalgae in the intertidal zone, the authors can improve on the past estimates by using bathymetry data, which should be available or macro-algae distribution maps if available. This will also help shed more light on the inhomogeneity and source strengths of the different regions.

Figure 1: The authors maybe would like to consider replacing this figure since it is a very rough approximation. Maybe a google map will show more details on the macroalgae distribution.?

- A detailed seaweed distribution map has been included and macro-algae distributions have been discussed. Unfortunately neither googlemaps nor google earth provide any details on the macro-algae distribution at Mace Head.

Comments on 1 s data: If the authors suggest that the highest mixing ratio was 49 pptv

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and are confident about the 1 s data, why are they using the 60 s data for the figures? If there is good data available, please show it. It may be confusing for the reader with half the paper referring to 49 pptv as the highest, but the other half referring to 29 pptv.
Page 4544, line 16-20: Are the authors confident on the 1 s data variability? If the variability is real, it needs much more discussion. This would shed more light on the distribution of the sources.
Why are the high-frequency variations not discussed? The only effort to discuss these is on page 4544, but can be further expanded upon.
- The authors are confident of the 1 s data and the associated variability at the daytime lowest tides. However, the high limit of detection associated with the 1 s data (LOD = 9-11 pptv; 2σ) precludes the use of the 1 s data at all but the highest mixing ratio/lowest daytime tides. In order for the entire tidal cycle to be considered the data was averaged to 60 s (LOD = 1-2 pptv; 2σ). For comparison with the LP-DOAS IO data, both datasets were averaged to a common time basis so the LIF data presented in Section 4 is averaged to 10 minutes. A note on the temporal averaging has been added to the manuscript. Section 3.1: 'Temporal variability of IO' has been expanded with some overlap with Section 3.1.2: 'Temporal offset from Low tide' removed. The 1 s data has been discussed further.

(C5) The introduction and the whole paper in general may need some more work and the right references should be cited.
- The introduction has been reviewed and references have been checked throughout the text to ensure accuracy. Iodine observations from other mid-latitude locations have also been included and discussed.

(C6) An inclusion of a table with past observations of iodine compounds at Mace Head is also recommended to put the new point measurements in context.
- Table with observations of IO at mid-latitude coastal sites has been included.

Minor Comments:
Page 4534 Line 26: Include more references for simultaneous observations of iodine compounds and particle formation.

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- more references included

Page 4535 Line 5: The exact pathway of iodine particle formation is still under discussion. Mention this and provide further references to other studies.
- brief discussion added (with reference to Saunders et al 2010)

R1 and R2 are not necessary. If the authors want to show a simple iodine chemistry scheme, I suggest a figure or more reactions rather than leaving it incomplete.
- Reactions R1 and R2 have been removed.

Page 4535, line 17: Should be (MHARS)
- The acronym MHARS has been removed in favour of the NOAA/AGAGE standard of MHD.

Page 4535 lines 13-15: Bale et al measured only at Mace Head. If the authors want to generalize this to 'coastal areas', include other I atom observations, eg. Mahajan et al, 2001 (ACP) or modeling studies estimating I atoms from Roscoff.
- A reference to the Mahajan et al. (2011) measurements of I atoms in Galicia has been added.

Page 4535, line 228: Insert references for LP-DOAS observations.
- references have been added

Page 4536: The authors define Mace Head as a clean marine site. Can they provide more details to substantiate this claim? For e.g. Heard et al, 2006 (ACP) mention that there were periods of clean marine air and polluted continental air observed at Mace Head. Were there NOx or CO observations to show that the air was 'clean' over the campaign?
- The reference to clean has been removed from the first paragraph of section 2.1. The air quality is then discussed in more detail in the second paragraph. NO was measured using a TECO Trace Analyser with a limit of detection of 50pptv and NO was not recorded above this limit during the measurement period discussed here. The analyser recorded a short-lived pollution event when a speedboat passed the site but this occurred during a calibration of the LIF system and so has not been considered here.

(MC7) Page 4537 line 8: What dataset was used to calculate the back trajectories?

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- Back trajectories were calculated using the HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model. This has been included in the text (with reference: NOAA Air Research Laboratory: Draxler and Hess, 1998). Multiple ensemble back trajectories were re-run for the preparation of the updated manuscript.

(MC8) Page 4544, line 11: Kaltsoyannis and Plane did not suggest that growth of particles proceeds through higher oxides and nor were Furneaux et al. the first to observe IO for the first time with IOPs.
- The Kaltsoyannis and Plane reference has been changed to Saunders et al 2010, which proposes a mechanism for particle growth. Furneaux et al 2010 present point obervations of IO with particles but the references have been changed to include a reference to Saiz-Lopez2006 as well.

Page 4546 lines 3-5: What do the authors mean that determining the relationship between IO and particles was difficult at Roscoff? It has been characterized in detail in the past ((MCFiggans et al., 2010, Leigh et al., 2009). If they are suggesting that it is in fact easier at Mace Head, why is it not done here?
- Unfortunately, as stated in the text, no aerosol measurements were made during the observation period described here so further interpretation of the in situ IO relationship with particles was not possible at Mace Head. The text has been changed to include this and the reference to Roscoff has been removed.

Page 4546, line 8. (MCFiggans et al did not measure I2. The observations were made by Saiz-Lopez and Plane, 2004
- corrected

Page 4546, lines 10-18: Discuss in more detail. Dixneuf et al., 2009 (ACP) have carried out studies on emission of time dependence of I2 from different species.
- The Dixneuf et al 2009 paper was already discussed in Section 3.2.1 but the discussion has been expanded.

Page 4546, line 25: Please quantify.

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- a paragraph on the magnitude and location of the O3 destruction has been added to Section 4.3.2. An approximate time/location of maximum ozone loss has been quantified for this study but a more complete model is required to fully understand the chemistry involved in ozone destruction. A modelling study by Bloss et al. (Bloss et al, 2009, Geophysical Research Abstracts, Vol.11, EGU-2009-5944) is working to quantify this effect.

Page 4547, line 8: Reference.
- added

Page 4547, line 14: Observations were not made by Saiz-Lopez et al 2006, but by Saiz-Lopez and Plane, 2004.
- The observations were made in Saiz-Lopez and Plane 2004 but the modelling work to determine the extent of the spatial averaging (which I am referring to here) was described in Saiz-Lopez et al 2006.

Page 4548 line 15: The light is diffracted by the spectrometer as opposed to analyzed.
- corrected

Page 4548: The IO cross-section is reported by Gomez-Martin et al., 2005 , which was a companion paper and not Spietz et al., 2005.
- both references have been included for completeness

Why was I2 not measured with LP-DOAS during the campaign?
- I2 was measured by LP-DOAS during the campaign but only one night of measurments coincided with the LIF observations. A peak of 65 pptv was observed on 29 August. Assuming the average LIF/LP-DOAS IO ratio from the 28 and 29 August daytime low tide of 10 holds true for night-time I_2, then up to 650 pptv I_2 could be present in the area close to the LIF sampling point. This point has been included in the discussion of inhomogeneities of iodine.

Page 4551 line 5: Roscoff is not a polluted site according to the EPA standards.
- the term polluted has been replaced with semi-polluted (up to 8 ppbv NO2 observed, Furneaux et al, 2010) to provide a comparison with the 'clean' marine air (NO < 50 pptv, this study)

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sampled at Mace Head.

Page 4551, line 23: What about the O3 loss rate at 50 ppt? Have the authors done any calculations to estimate the O3 loss or do they just use the MCFiggans estimates from 2004?
- the O3 loss rate from 50 pptv has been calculated and the locations of potential iodine precursors discussed.

Page 4552 line4: Could this be a reason for the reduced LIF/LPDOAS ratio rather than an increased inhomogeneity? Bathymetry maps or macroalgae distribution will show if this was the case.
- Multiple particle back-trajectory models were re-run every 6 hours for the August 28-30 measurement period. These calculations suggest that the air on 30 August arrived at the site from a slightly more westerly direction than August 28-29, but did not vary in direction during the day on 30 August. Measurments of wind direction at a nearby Mace Head Meteorology station, confirmed this constant wind direction. The reduction in the LIF/LP-DOAS ratio decreases at tide heights below 0.3m, which is a short time around low tide, and this time coincides with the exposure of hyperborea at the retro-reflector end of the light path, as well as at the edges of two islands close to the light path. The manuscript has been updated with this information.

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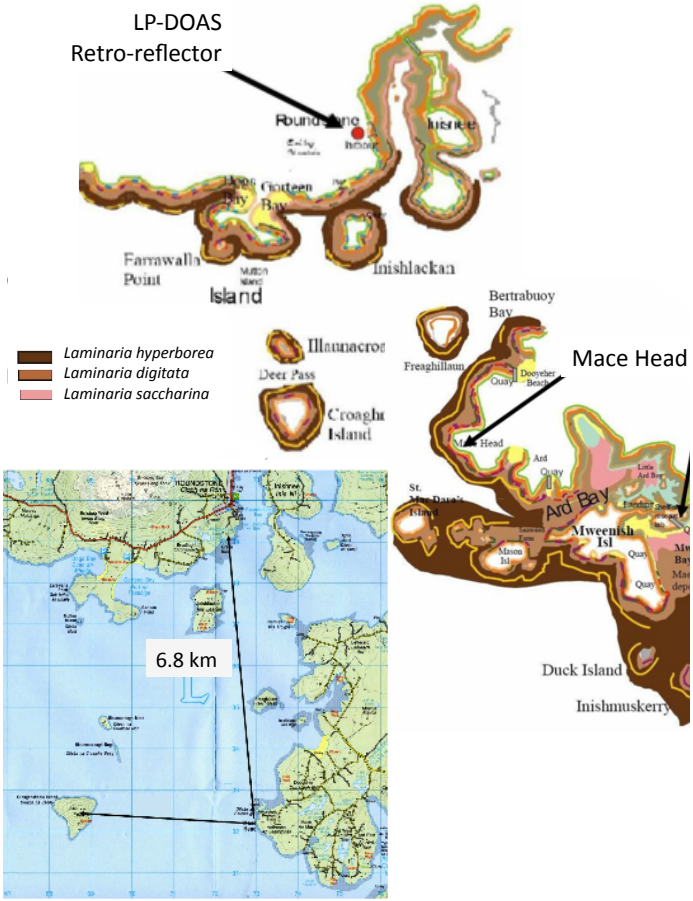

Fig. 1.

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