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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Measurements of iodine monoxide at a semi polluted coastal location" *by* K. L. Furneaux et al.

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The manuscript describes LIF measurements of IO made during the RHaMBLe campaign performed near Roscoff at the NW coast of France in the fall of 2006 (other RHaMBLe data from the Roscoff campaign were published by e.g. McFiggans et al. 2009, Leigh et al. 2009, and Mahajan et al. 2009, Whitehead et al. 2009) and thus presents an important data set. LIF is a relatively new, very sensitive technique for IO measurement and is shown to be extremely useful for the purpose. Overall the manuscript presents no fundamentally new conclusions from the data, however there are many interesting findings supporting earlier observations to warrant publication in ACP. In detail I have reservations with several of the conclusions and should like to recommend changes as detailled below (A-D). In addition there are numerous minor

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errors or unclear points, which are summarised in a separate list at the end of this report (1-15).

Referee Comment A) Nighttime IO: From the stated measurement errors of the LIF instrument, and even more so from the histograms shown in figure 11, it is unlikely that the nighttime IO observations are actually significantly different from zero. For instance the histograms in fig. 11, though showing mean online IO levels around +1 ppt, exhibit several ppt wide probability distributions, thus the deviation of the mean from zero is not significant. Accordingly the discussion of nighttime IO sources should be removed from the manuscript (it is a repetition of arguments given by Kaltsoyannis and Plane 2008).

Author Comment: Owing to all three referees' comments section 3.3 will be modified – we would still like to present the nighttime data – we will no longer draw strong conclusions on the presence of IO at night from this dataset, however, and the discussion on differences between different nights (page 25753, lines 16 – 20) will be removed.

Referee Comment B) The discussion of the differences between LIF and long-path DOAS measurements (section 3.4.1) is not convincing as given. Apparently only slight differences in the wind directions on Sept. 8 and 9 (this is in fact said twice in lines 12, p 25755 and 1+2, p25756) are causing differences in the LIF/DOAS ratio of a factor of 2, why? Perhaps a figure showing the algae fields crossed by the trajectories at the two days could help. Why are the differences on Sept. 17 so large?

Author Comment: the highest time resolution that a calculated trajectory from Hysplit or BADC, which we have ready access to, is 30 minutes. So assuming the wind speed was 3 ms-1 this would be about 5.4km from sample point to the next point along the trajectory path. So we would get a straight line between these 2 points but nothing more detailed. If we consider the local wind direction, on the 9th this is slightly more south easterly, meaning that the direction is more inline with the DOAS light path axis as opposed to slightly more off axis as was the case on the 8th – this change in wind

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direction means that the LP-DOAS instrument should detect higher [IO] on the 9th. The slower wind-speeds on the 9th, compared to the 8th, means that [IO] are reduced via chemical processing more on the 9th before reaching the LIF inlet, so the LIF-IO instrument detects lower [IO] on the 9th vs 8th. The meteorological conditions experienced on the 17th – slack winds originating from the west where macroalgae beds were sufficiently far from the LIF inlet that IO had mostly reacted away before sampling ensured that the LIF instrument detected very little IO. Owing to the positioning of the DOAS light path, macroalgae bed C, (fig. 1) was much closer to the LP-DOAS sampling axis than the LIF sampling point and was able to detect significant IO originating from this region.

Referee Comment C) In section 3.5 a linear relationship between IO levels and particle formation is suggested. What is the basis for this and if Fig. 17 actually show a linear relationship what is the explanation? From R4-R9 one would expect a quadratic or higher dependence of the particle formation rate on the IO concentration since the IO self reaction and halogen oxide cross reactions are involved.

Author Comment: We agree that a quadratic dependence (or higher) of particle formation on IO concentration should exist – we will re-plot Fig.17, fitting the data to a more appropriate line of best fit.

Referee Comment D) The model calculations on the impact of IO on HOx partitioning are not new and not backed by HOx measurements so no new results or insight are presented here and the reference to the several previous studies is sufficient. Thus section 4 could be deleted.

Author Comment: Although the impact of IO on HOx partitioning has been modelled previously, this impact has generally only been considered under low NOx conditions, such as those encountered at Mace Head (e.g. Bloss et al., Geophys. Res. Lett., 32, L06814, doi:10/1029/2004GL022084, 2005.) or in coastal Antarctica (Saiz-Lopez et al. Atmos. Chem. Phys. 8, 887-900, 2008. The impact of IO on HOx under the

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semi-polluted conditions over a wider range of NOx such as experienced at Roscoff has been less widely studied, is more complex, and warrants discussion here.

Minor points: 1) It would be informative to the reader if RHaMBLe and Roscoff were mentioned in the abstract. This will be included in the revised manuscript

2) Section 2.2: The Ti:Sapphire laser probably was frequency doubled? Yes, this detail will be added to the manuscript.

3) P. 25745, line 9: the 184.9 radiation was provided by a Hg lamp? Yes, this detail will be added to the manuscript.

4) Section 2.3, page 25746, the statements in lines 17 and 19 on permanent heterogeneous loss of IO and recycling of IO appear to be in contradiction, clarify. We feel that the description of how the model treats heterogeneous loss of species to aerosols is adequately explained in the manuscript – in the model halogenated species are irreversibly lost to aerosols, this may mean that the recycling of IO in the model is a lower estimate (rather than a contradiction) as there are aqueous phase processes that can result in the re-release of gaseous halogen species which are not considered by the model. Peters et al (ACP, 2005) estimate that the recycling of reactive iodine by aerosol processing is responsible for roughly 10% of modelled IO.

5) page 25746, Equations (1): In the centre Eq. “A:y” should probably read “Ay”, in the right Eq. w should probably be omega (as used in the centre equation). This will be revised.

6) Page 25748, relationship between IO and TH: Why should there be an exponential relationship? Is not rather the contour of the coast the determining factor, i.e. the relationship of additionally exposed kelp area per meter of tidal height change. In other words the orography of the intertidal area is important. The conclusion about similar IO production pathways in lines 13/14 is therefore not correct. We agree with the referee that the contour of the coast could contribute to the observed relationship –

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other factors, for example, the time that the seaweed is exposed may also contribute to the amount of I2 released. We will include a discussion of these factors on pg 25748 in the revised manuscript.

7) Page 25748, line 20: ... flatter diurnal profile ... ‘diurnal’ will be added

8) Sentence at the bottom of page 25748, top of page 25749: This is clouding the issue, apparently solar radiation is essential to photolyse I2. To me the conclusion rather appears to be that there are no alternative sinks of I2, thus less solar radiation leads to higher I2. Owing to comments by referee 3, this discussion section has been re-phrased as follows: ‘On days when IO originated from macroalgae source regions further afield, (for example from macroalgae beds C & D, fig. 1) the dependence of IO concentration upon solar irradiation becomes reduced owing the short photolytic lifetime of I2. We can compare the IO diurnal profile from two days in the campaign during which IO originated from two different source regions; the tidal minimum occurred at different times on each day. The 8 September was a clear day, providing a flat j (I2) profile throughout the day, once it had risen from zero at dawn, the IO displays a large variation around the tidal minimum. The wind prevailed from macroalgae area A, close to the LIF inlet (Fig. 1) on this day. On 14 September solar irradiation was more variable and low tide fell late in the afternoon (wind prevailed from just north of macroalgae area C). On both of these days IO peaked at the tidal minimum. On 14 September, IO did not peak at solar noon / peak j (I2). Under this scenario, chemical cycling of IO extends its lifetime beyond that of I2 (with respect to photolysis) and diminishes its dependence upon solar irradiation.’

9) page 25750, 1st line: There is another, even higher NO2 spike at about 9:50 (Fig. 9), corresponding to a another dip in NO2. We will mention this spike in NO2 in the manuscript – although as with the spike later in the day, the spike at 9:50 also occurs when there is a dip in j(I2).

10) Page 25751 (and 25741) lines 27/28: what is a "point source technique“? ‘point

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source' refers to the measurement of an individual air parcel (in-situ measurement) as opposed to a measurement of air averaged over the DOAS path length.

11) Page 25752, delete R17 and replace by ref. to R2. This will be addressed.

12) Pages 25752 and 25752: Refs. to Mahajan et al. 2009, there are two publications by Mahajan et al. 2009, ref. needs a, b. This will be revised.

13) Page 25757, the statement in lines 11+12 is obvious and should be deleted. These lines will be deleted

14) Section 3.5: The instrument description belongs into section 2. This description will be moved to section 2 in the revised manuscript.

15) Page 25762, paragraph in lines 10-16: These are no new results, delete para. We refer the referee to the author's response to comment D above.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 25737, 2009.

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