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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In situ measurements of molecular iodine in the marine boundary layer: the link to macroalgae and the implications for O_3, IO, OIO and NO_x" *by* R.-J. Huang et al.

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The authors thank E. Saltzman, T. J. Dillon, J. C. Gomez Martin, and the anonymous referee for their time to review our manuscript and particularly for their valuable comments and suggestions that have significantly improved the manuscript. We have made most of the changes suggested by the reviewers and have outlined these in detail below.

Comments from E. Saltzman (Referee)

This paper presents unique in situ measurements of I2 over coastal algal beds. This is an important addition to the study of coastal iodine emissions, which has hereto-

fore largely been dominated by long path spectroscopic measurements. The paper presents two very interesting observations – 1) the positive correlation between O3 and I2 near the sea surface in the presence of macroalgae, which is presumably reflecting the source mechanism for I2, and 2) the negative correlation of O3 and I2 away from the surface, which presumably reflects catalytic ozone destruction related to iodine chemistry. I think this new data is definitely worth publishing, and I think the interpretations offered are generally reasonable. However, there are several issues which should be addressed prior to publication.

Response: None

Some specific comments:

General comment - I am a bit at a loss to understand the meteorological situation here or what the authors envision as the air flow field. Is the studied being carried out in a two-dimensional flow field? Is there evidence to support this? Is the air flow onshore all the time (no seabreeze)? Is the ozone loss reasonable in view of the short transit time between the kelp and the ozone sensor? How much time is there? I'm pretty confused here as to whether the same air is being measured by the various techniques and what the temporal relationship is between them. Defining the meteorological framework is essential to the conclusions of the study.

Response: When measurements were taken exactly over the central zone of seaweed beds, comparison measurements were also taken downwind of (i.e., further far away from) the seaweed beds. These measurements were associated with northwesterly/southwesterly winds which passed over the seaweed beds. The advection time is in the order of a few tens of seconds. We have actually realized that the ozone loss rate can not be explained during such short advection time if I2 is considered as the only O3 sink. Therefore, as already stated in the text, we believe other halogen compounds which have the similar diurnal pattern as I2 (e.g., ICl and HOI, see Huang and Hoffmann, 2009) may also contribute to the ozone loss rate.

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Section 2.1 beginning - Huang and Hoffmann, 2009 needs to be cited here as a place for the reader to find out how/why this technique works, and to see how it has been validated. Detection limits need to be explicitly stated and justified, if only with reference to earlier paper. Some actual field evidence of this would greatly strengthen the paper.

Response: The reference “Huang and Hoffmann (2009)” has been cited at the beginning of Section 2.1. Also the detection limit (0.17 pptv) is now included.

Section 3.1 P6 line 2 “expanding air mass” is unclear. Does this mean that emissions are wind speed dependent? I did not understand the point of this statement.

Response: We tried to explain the dilution effect during air mass transport by using “expanding air mass”. In the revised text the phrase “The locally emitted I2 certainly will dilute in an expanding air mass” has been replaced by “The locally emitted I2 certainly will dilute in an evolving air plume during air mass transport”.

p6 sentence beginning “Ozone destruction is of utmost concern: : :” An artificial argument is posited here, between stratospheric and tropospheric halogen chemistry. There really is no contradiction, and no need for "Nevertheless...". This paragraph could just start with “Recent models: : :”

Response: Following the reviewer’s suggestion, the change has been made.

p6 14 lines from bottom: I think I would say that halogen-mediated ozone destruction was “suggested” not “observed” by Read et al.

Response: “observed” has been replaced by “suggested”.

p7 line 13 - I believe there have been other field measurements supporting the existence of this reaction. My recollection is that Saiz-Lopez and co-workers observed IO and NO3 at night and derived a rate constant for this reaction. Perhaps in their Antarctic Science paper?

Response: The reaction of I2 with NO3 is also supported by Saiz-Lopez et al. (2006a).

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We have added this reference in the revised text. Saiz-Lopez et al. (2006a) calculated that a rate coefficient for the reaction of IO with NO3 of >7 $\times$ 10^{-12} cm^3 $molecule^{-1}$ s^{-1} would be needed to explain the nighttime chemistry. Recently, Dillon et al. (2008) reported an updated coefficient for this reaction of 9 $\times$ 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, derived from laboratory studies. The reaction IO + NO3 will lead to additional NO3 consumption and compete with IO + IO for OIO formation. This piece of information has been added in the text.

p7 3 lines from bottom: “Exemplary” is not the right word here. I am not sure exactly what you mean.

Response: The word “exemplary” has been deleted.

p9 line 3-4. This sentence does not make sense and should be rewritten. Measurements were made during daytime, but so what? What are potential implications and how do they differ from regular implications? Also, “concentration levels” is redundant. Just levels is fine.

Response: The phrase “The potential implications of I2 . . .and consequently the potentiality of O3 destruction.” has been deleted from P9, Ln 3-5. The sentence “The levels of I2 and the intensity of solar irradiation affect significantly the mixing ratios of daytime IO and O3” has been added in its place.

Figure 4. axis label and caption. "ppt" is a unitless measure of mixing ratio, not a concentration.

Response: “Concentration” has been replaced by “mixing ratio”.

Comments from Anonymous Referee 2

This manuscript describes primarily diffusion denuder measurements of molecular iodine (I2) over seaweed beds near Mace Head, Ireland. The measurements are compared to long-path DOAS observations, which are inherently path averaged over long distances. The results are generally consistent with current understanding of coastal

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marine iodine chemistry (i.e. that molecular iodine is produced in hotspots very near seaweed beds and is diluted and photolysed giving lower inferred concentrations along DOAS paths than are observed directly over the seaweed beds). Interestingly, molecular iodine appears to be produced by ozone (there is a higher mixing ratio of molecular iodine with higher ozone on short length scales $\approx$ 5 cm) but molecular iodine is inversely correlated with ozone on longer length scales (e.g. DOAS path averaging length scales). These results appear to be able to constrain the timescale of possible iodine-induced ozone loss. In general, the work appears to be sufficiently careful and adds data to the discussion regarding iodine chemistry in marine coastal areas. It should be published, although there are some points that the authors should consider in their revision of the manuscript.

Response: None.

P392, line 7: In most of the manuscript, the authors use the phrase "hotspot of iodine chemistry" to describe Mweenish Bay. In this section, they say that the higher mixing ratios of molecular iodine are "indicating the emissions of I2 are correlated with local algal biomass density and algae species". This statement appears to be too strong in comparison with the text's discussion. A wording of "is consistent with differences in algal biomass density" appears more appropriate.

Response: Following the reviewer's suggestion, this sentence has been rewritten.

P367 line 26: The word "flashed" should probably be "flash"

Response: Has been changed.

P369 line 13: The phrase "are fluctuant" should probably be "to fluctuate"

Response: Has been changed.

P373 line 10, and Figs. 6 and 7: Although it is observed that as I2 increases, NO3 decreases, there is also a relationship between the formation rate of NO3 and ozone (one needs NO2 and O3 to form NO3). Thus, the lower ozone levels at higher I2 levels

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would also indicate that there is a lower source of NO3. Can the authors discuss this concept, and also, have they observed the NO2 levels and found them to be invariant such that they are not important for the observed NO3 fluctuations?

Response: We agree with the reviewer that the reaction NO2 + O3 -> NO3 + O2 should be included to explain the lower mixing ratio of NO3 observed during lower ozone levels. The reaction IO + NO3 -> NO2 + OIO has also been included (see response to referee 1). It is a pity we can not see the trend of NO2 levels during the ozone destruction events.

P375, line 27: I believe that "form" should be "from"

Response: Change has been made.

P384 – Fig. 2: It is interesting to note that the I2 mixing ratio would go to zero at around 18 ppbv of ozone if the linear correlation of this plot were extrapolated to I2 = 0. Can the authors discuss whether they believe that the plot is actually linear at lower ozone mixing ratio, or if they have a mechanistic reason for the linear correlation without a zero intercept?

Response: We have realized that, based on the limited data set shown in Fig. 2b, it is risky to draw a conclusion that the plot of I2 against O3 is linear at lower ozone mixing ratio. However, a positive correlation between I2 emission and the quantity of O3 available has been observed in a seaweed chamber experiment (Palmer et al., 2005). Here, we tried to explain that such positive correlation can also occur under the real atmospheric conditions. Certainly, more field observations are needed to clarify this issue.

Overall, although this paper does not resolve the outstanding controversies in marine iodine chemistry, it does add some interesting data points to the discussion that can assist in understanding the process. Clearly more laboratory work is needed to work out mechanisms and in addition, more field observations (particularly at other coastal re-

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gions) to see if the Mace Head area is representative or anomalous for coastal marine iodine chemistry.

Response: None

Additional revision

1. As stated in Atmos. Chem. Phys. Discuss., 10, C8-C9, 2010, we were not able to unambiguously identify OIO during the campaign. Therefore, the OIO mixing ratios have been deleted in the revised manuscript.
2. The unit of wind speed shown in the discussion version should be knot instead of m/s. We have changed the values by multiplying by 0.5144 to deliver the number with unit of m/s in the revised manuscript.
3. We recently realized that Figure 8 is incorrect, as the data set from DOAS has been updated. The correct figure has been included in the revised version. This update will not affect the conclusions we have drawn. We apologize for any inconvenience this may have caused.

References:

Dillon, T. J., Tucceri, M. E., Sander, R., Crowley, J. N.: LIF studies of iodine oxide chemistry, Part 3. Reactions IO + NO3 -> OIO + NO2, I + NO3 -> IO + NO2, and CH2I + O2 -> (products): implications for the chemistry of the marine atmosphere at night, Phys. Chem. Chem. Phys., 10, 1540–1554, 2008.

Saiz-Lopez, A., Shillito, J. A., Coe, H., and Plane, J. M. C.: Measurements and modelling of I2, IO, OIO, BrO and NO3 in the mid-latitude marine boundary layer, Atmos. Chem. Phys., 6, 1513–1528, 2006a, www.atmos-chem-phys.net/6/1513/2006/.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 361, 2010.