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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The spatial distribution of the reactive iodine species IO from simultaneous active and passive DOAS observations" *by* K. Seitz et al.

Anonymous Referee #1

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General Comments

This article presents simultaneous measurements of IO by LP-DOAS and MAX-DOAS instruments at an Irish coastal site in a region which is well known for the presence of iodine compounds. In using both techniques and especially by applying two different light paths in the LP-DOAS measurements, the authors find good evidence for the IO being mainly located over the intertidal area. Several days of measurements are presented and analysed. While IO is detected over all days shown in the manuscript, the detection of OIO and I_2 has not been significant. A further main result of the study is the correlation of enhanced IO columns with the occurrence of particle nucleation

events.

While some findings (such as the correlation of IO with solar radiation and low tide) mainly confirm results of previous field studies in this region, the analysis of the different LP-DOAS light paths and the comparison of IO columns with particle density measurements, contribute new information and new data sets to the field of research. In the presentation of the particle measurements, the authors need to give considerably more information, as these constitute an important part of the article which is also advertised in the abstract. In general, putting some more effort into the presentation of the results and the comparison of the active and passice DOAS techniques will further improve this article. I believe that some more clarity and a revision according to the comments below is possible on the basis of the already presented data of this study (meaning no further data sets or revisions of the data evaluation will be necessary).

The article is largely well written and well understandable. The measurement results are interesting to the research community of RHSs, the study fits well into the scope of the ACP journal and I therefore recommend the publication of this manuscript after the following aspects have been addressed.

Specific Comments

A. Main comments

1. The particle measurement method is not described. Although the nucleation events and particle concentrations as well as the correlation with IO columns are mentioned in the abstract, which assigns some importance to the particle measurements, only very little information is given in the text of the article, in three lines within the site description paragraph. The method should be properly explained in an individual paragraph in section 2 (and possibly additional paragraphs also in section 3 and/or 4 on data analysis and discussion of the results).

The declared correlation between particle concentration and IO mixing ratios is an im-

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portant result of the manuscript. This result is emphasized in abstract and conclusions and should therefore be supported by a clear figure. When comparing Fig.2 with Figs. 5 and 6, this correlation can be estimated, the data set is thus present and it should be possible to demonstrate the mentioned correlation directly. An additional, purposeful plot would be helpful, at least showing particle concentration and IO mixing ratios together.

2. Section 2.1 and 2.2: Please give some information on the integration times for both techniques. In the LP-DOAS case, please state the time difference between the alternating paths.

3. In section 4.1 the polynomial order and an "offset" within the MAX-DOAS retrieval are discussed as influencing the retrieval of OIO and I_2. The meaning of the "offset" in the retrieval is not explained or mentioned. Please add some information in section 3.1 on this (stray light?).

4. Section 4.1 discusses the increase of IO dSCDs for decreasing viewing angle and a steep vertical gradient of IO is identified in the interpretation of this finding. In this argumentation, the authors should be more specific and quantitative. Generally, a decrease of dSCD with increasing elevation angle is also expected for a constant profile (box profile) up to a certain altitude. Here, the analysis and the finding of a "strong vertical gradient" (p. 21379, l.5) depends on the strength of the increase, so that some quantitative information becomes necessary. How strong does the IO dSCD increase for increasing viewing angle? E.g. also: which increase in IO dSCD would still agree with a box profile of the IO mixing ratio? I believe that it is difficult to retrieve specific profile information of IO from these measurements, but even more the authors should be somewhat more precise and cautious then in their interpretation. The statement in p.21379, l.12 is unfortunately not true, otherwise the authors could quantify the vertical gradient. I am convinced, that the vertical gradient of IO mixing ratios influences their measurements and may lead to the observed decrease in dSCDs for increasing elevation angle - however, the vertical gradient is not measured directly, which is

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unfortunately quite a difficult task. Maybe the sentence can be reformulated.

5. p. 21381, l.13-15: What is the difference between the two fibres used? In writing "well mixed" - are the authors referring to polarization issues? Do the fibres have different lengths? Why does this cause a negative bias for the IO results? Please just give some more information on this.

6. The structuring of section 4 is not ideal, as 4.2 contains the results from the LP-DOAS and additionally also the comparison with the MAX-DOAS and the interpretation following from this (starting p.21381, l.17). I suggest an additional paragraph 4.3 for the comparison and interpretation.

7. Section 4.2 (maybe becoming 4.3?) might need some revision. Little information is given and one part of this section is by content repeated twice: parts (p. 21381, l.22-29) and (p.21382, l.10-15) contain very similar information and nearly the same wording.

In the comparison between LP-DOAS and MAX-DOAS (starting p. 21381, l.17) it needs to be made clear right at the beginning, that agreement between the column densities is not expected, as the light paths between the two methods are considerably different.

The statement on p. 21381, l.19-21 is not entirely correct, as far as I understand. The MAX-DOAS dSCDs are not generally higher than the LP-DOAS column values. This statement is mainly true for the MAX-DOAS 2° direction. However, the 4° elevation values are rather similar or lower than the LP-DOAS results. In this part, some more detailed and careful comparison of the measurement results will help.

In the discussion of higher IO columns in the MAX-DOAS results, the statement that "light reflecting from the surface and passing very high concentrations, causes the higher signal" might need more reflection, ideally some quantitative information. I agree that this light path contributes to the measured signal. However, is a major contribution to the signal expected? Radiative transfer calculations should be able to estimate the

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contribution from this pathway. Can the authors provide block air mass factors for their measurements?

8. In the Conclusions, the sequence of argumentation seems somewhat confused (starting p. 21382, l. 22). Shouldn't the line of logic should run in the following way? IO column results from the LP-DOAS long light path agree well with those from the short distance. Hence, one understands that the IO distribution is inhomogeneous along the long light path, meaning that a confinement of IO to the intertidal area can be inferred. In addition one can suspect, that on the short light path, the IO also might be inhomogenously distributed (which cannot be seen directly from the measurements, but might well be the case). If the IO is not homogenously distributed over the intertidal area, then the previously found model results on IO concentrations and nucleation events agree with the findings in the present study.

B. Additional Comments

- p. 21373, l.25: As not all RHS are listed in Peters et al (2005), maybe rewrite "... observations of RHS can be found in Peters et al. (2005)." to read "... observations of important RHS (IO, OIO, I_2 and BrO) can be found in Peters et al. (2005)."

- p. 21373, l.26: It is not clear that the expression "All above mentioned measurements..." actually only refers to the few lines above and not to the first half of this page 21373, where studies are cited which actually use other than LP-DOAS techniques. Please be more specific here, saying (e.g.) that the measurements which were conducted at Mace Head were using the LP-DOAS method.

- p. 21375, l.3: Here, "f" is used for the f-number (f/) and below (l.21) for the focal length. Please write in l.3 "(f/6.9,...)" or "(f-number = 6.9,...)" and in addition give the focal length (f = 500 mm, I guess?) of the Action 500pro.

- p. 21376, l.8: As Fig.1 does not show the seaweed density, the reference to Fig.1 should be relocated to earlier in the sentence, e.g., to behind "Mweenish Island".

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- pp. 21377-21378: In the description of the electronic-vibrational absorption bands of IO, OIO and I_2, for IO and I_2 the term electronic transition (with spectroscopic notations given) is used, while for OIO it says vibrational bands (without giving the spectroscopic notation). This is correct, but misleading. As the absorption bands are in any of the three cases electronic transitions into different vibrational levels, please use similar descriptions for each, e.g. write "vibrational bands" on p. 21377, l. 17 and p. 21378, l.1 for IO and I_2, respectively, as for OIO.

- p. 21380, l.12-13: Do you mean "with only minor differences" or "although also some differences are found"?

- p. 21380, l.29: The sentence "Until 2 Sep, the column densities are about the same." would be better understandable if one would add "as for the long light path".

- Fig.1: Please give a legend to the colours of the figure, probably the green colour is the intertidal area, but definite assignment is always helpful. (If possible a higher quality figure would be desirable.)

- Fig.2, figure caption: The name/abbreviation "Nano-SMPS" is not explained.

- Fig.2: The axis label is missing on the x-axis (Julian Day) as well as the label on the colour bar (particle concentration cm^{-3}). The information is given in the caption but should always be placed on the figure also.

C. References:

p. 21372, l.26: I think in this place, reference to the article from Barrie et al. 1988 would be appropriate. (Reference: Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, Nature, 334, 138–141, 1988.)

p. 21373, l.4: Please give references for the statement that at mid latitudes and Antarctica IO plays a role in the ozone destruction process, e.g. Read et al. 2008, or others. (Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard,

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D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J., and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical atlantic ocean, Nature, 453, 1232–1235, 2008.)

p. 21373, l.19-20: Please give a reference to this statement.

Technical Corrections

p. 21375, l.24: “stabilized” should read “stabilize”

p. 21377, l.17: “band” should read “bands”. For better reading maybe include the word “situated” or similar at the end of the sentence.

p.21378, l.8: “ring” should read “Ring”

p.21380, l.26: either “concentrations ... are” or “concentration ... is”

p. 21382, l.3: either “from intertidal areas” or “from the intertidal area”

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 21371, 2009.