

***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 #2

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Anon reviewer #2 Atmos Chem Phys Discuss 9, 21371-21398, 2009; The spatial distribution of the reactive species IO from simultaneous active and passive DOAS observations; K Seitz et al.

General comments:

This paper reports on efforts to measure three reactive iodine species (molecular iodine and the IO and OIO radicals) in the marine boundary layer. The atmospheric chemistry of these species is an active area of research because (i) reactions of the IO radical, in particular, perturb partitioning in the NO_x and HO_x radical families that control so much of tropospheric chemical processing, including ozone production/loss rates, and (ii) the

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OIO radical (formed by the self-reaction of IO) can condense to form aerosol particles and is thought to be responsible for the phenomenon of coastal “nucleation bursts” of ultra-fine particles. These nucleation bursts were first identified at Mace Head on the west coast of Ireland, and only recently have they been observed in other coastal regions e.g. the present work and at Roscoff on the northern coast of France during the RHAMBLE campaign (J. D. Whitehead, et al, Atmos. Chem. Phys. Discuss., 9, 20567-20597, 2009).

A particular strength of this work is that the authors have deployed four spectroscopic instruments viewing different absorption paths through the atmosphere in order to provide spatial information on the source of reactive iodine species. In coastal regions, it seems likely that the source is molecular iodine emitted by seaweeds exposed to the atmosphere at low tides and, although I₂ could not be unambiguously detected in this work, comparison of the IO amounts in the different LP-DOAS parts and their strong tidal signatures would seem to confirm the seaweed source. Although the present measurements were made at the Martin Ryan Institute only some 6 km away from Mace Head, the extra observations of IO and coastal particle nucleation are significant because the seaweed speciation around two sites is different, yet both give rise to an active iodine chemistry.

The greater IO slant column densities in the 2 degree MAX-DOAS viewing angle compared to higher angles certainly suggests a strong ground-based source for this relatively short-lived species. This is discussed well qualitatively, but it seems to me (I'm not a MAX-DOAS expert) that there is a lot of quantitative data contained within the slant column differences which has not been exploited. For example, what is required to retrieve vertical profiles of IO? Can this be done within the scope of this paper? It would be very interesting.

It is a shame that I₂ and OIO could not be measured above the present instruments' detection limits. OIO is notoriously difficult to detect, and although I₂ has a helpfully structured absorption spectrum it too has often not been observed by previous inves-

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tigators even in the presence of strong IO signals. Thus the absence of I2 and OIO data is not a substantial flaw in this work. However discussion on this topic would be improved considerably by including a summary of the I2 and OIO concentrations observed by previous studies (with references), and thus whether the authors might expect to have seen I2 and OIO above the detection limits of their various instruments. [It is not acceptable simply to refer readers to Peters et al (2005) in line 25 p21373 and expect them to form their own conclusions]. For example, the I2 detection limit quoted for the shorter LP-DOAS path (282 pptv; top of page 21380) is rather larger than any ambient I2 mixing ratio detected to my knowledge.

I agree with Referee #1 that much more could and should have been included about the particle observations and their relationship to the measured IO time series. After all, this is a major reason for doing this work! It is too important to limit to just one sentence in the site description when introducing figure 2 and one further sentence in section 4.2 discussing the LP-DOAS measurements.

Specific comments:

The paragraph “The most likely source of reactive iodine... source of RHS” needs references (line 16 onwards on p21373).

Line 26 p21373: “All of the above mentioned measurements were carried out using active LP-DOAS”. Not true. Bale et al used resonance fluorescence of iodine atoms and Saiz-Lopez et al includes measurements of I2 by denuder tubes and broadband cavity ringdown spectroscopy.

Line 25 p21374: It is not necessary to reference the Merten (2008) PhD thesis if the pertinent information can be found in the Merten et al 2009 publication.

Line 1 p21375: are the prisms 63 mm dia each, or the retro-reflectors? I agree with Ref #1's comment about f-numbers. Please also include the focal length of the spectrometer, typical spectral resolution and typical integration times for each observation

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(these could equally go into section 3).

Line 15 p 21376: Only limited justification is given for choosing to concentrate on the core five-day period. What happened outside these days? – any useful data here too?

Spectral fitting for IO (second paragraph in section 3.1): there is also an absorption band of H₂O around 445nm. Was this included in the fit?

Line 5 et seq p 21380: I agree that the observation of similar IO column densities in the two LP-DOAS paths suggests a common localised source. Yet for the lowest tide on the 30th Aug, systematic differences were observed and attributed to another seaweed bed becoming uncovered at the far end of the longer DOAS path (top of p 21381). Is it possible to use these data and the seaweed habitat map (Fig 3) to deduce approximate source strengths (e.g. per unit length) for the two emitting areas? After all, they comprise different seaweed species which might be expected to emit differently.

Line 17 et seq 21380: comparisons with simultaneous IO measurements at Mace Head, whilst interesting background information, cannot be considered quantitative because IO is too short-lived to be transported between these measurement sites.

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

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