

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

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General comments:

The paper by Furneaux et al. provides a very detailed analysis of determinations of IO radicals in the marine boundary layer, obtained primarily using a laser induced fluorescence (LIF) instrument. Comparisons are drawn with measurements made by long-path differential optical absorption spectroscopy (LP-DOAS) and multi-axis (MAX) DOAS instruments co-located in Roscoff as part of the reactive Halogens in the Marine Boundary Layer (RHAMBLE) project in September 2006. In addition, the time sequences of IO data are compared with measurements of NO<sub>x</sub> and particle number, and discussed within the context of tide heights, prevailing winds, and locations of likely sources of atmospheric iodine compounds. The interpretation of the field mea-

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measurements is supported by box model calculations incorporating iodine chemistry. The result is a thorough and convincing account of the iodine chemistry in the MBL at the Roscoff site and its impact on local HOx levels.

#### Specific comments:

Much of the analysis and discussion in the paper revolves around the LIF measurements of IO and it is clear that this technique provides an excellent method to monitor this radical at pptv mixing ratios in air (provided the excitation is to  $v=2$  of the A2II state to avoid quenching of fluorescence by fast predissociation [1]). The experimental methods, instrument calibration, and sources of error were the subject of a previous paper by Heard and co-workers, but it would be useful to have a short summary of the accuracy and precision of the LIF determinations in section 2. The only places I found mention of uncertainties in absolute determinations of IO were in the captions to figures 6 and 10, and the meaning of a 23% 1-sigma calibration error was not wholly clear. In places in the text, comparison is drawn with the outcomes of IO measurements at Appledore Island (e.g. page 25749) that suggests some conflicting outcomes. A robust and complete model for the iodine chemistry and its interconnection with NOx should—in principle—be able to rationalise both the Roscoff and the Appledore Island observations. What might account for the differences that are highlighted? Figure 9 shows a decline in IO concentrations when there is a spike in the NO2 concentration, and the implication of the discussion is that IO is removed at high NOx levels. The time series data in figure 9, however, appear to indicate that the fall in IO occurs a short time before the observation of high NO2 concentration instead of being coincident. This apparent time lag in the NO2 rise may be a consequence of the way the measurements of IO and NO2 are made, but merits some comment.

I was not wholly convinced by the analysis of the night-time data (section 3.3, page 25752) to extract IO mixing ratios and to argue that they lie above zero, although within the 1-sigma error bars that pass through zero (figure 10). The limit of detection shown in figure 10 is well below the calibration uncertainty on the instrument. The deductions

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on page 25753, lines 16 – 20, therefore seem precarious considering the data on which they are based.

On page 25755, comparisons are not made with the CRDS data of Wada et al. [2] on the grounds that there are too few coincident measurements. This is mostly fair because the CRDS data, with an open-path instrument, generated a limited number of data sets, which are of lower quality than the LIF data, and with poorer limits of detection. What may merit some comment, however, is that the CRDS measurements provide a direct determination of absolute IO mixing ratios (as long as baseline losses from aerosol and Rayleigh scattering are correctly treated, and the absorption cross section at the monitoring wavelength is established) and, on the 8th September, at low tide, suggested IO mixing ratios that are as high as 40 pptv. These levels are clearly considerably higher than the mixing ratios determined by the LIF instrument and displayed in figure 6 for the same date, despite being located close together.

[1] S.M. Newman, W.H. Howie, I.C. Lane, M.R. Upson, and A.J. Orr-Ewing, *J. Chem. Soc. Faraday Trans.* 94, 2681-2688 (1998). [2] R. Wada, J.M. Beames and A.J. Orr-Ewing, *J. Atm. Chem.*, 58, 69 – 87(2007).

Technical and typographical corrections:

Page 25742, line 3: add "of" after "number" Page 25746, equation (1): the colon in the second equation is unnecessary; in the third equation the italic  $w$  should be an  $\omega$  for consistency with the second equation and the text. Page 25758, line 19: "4 September order" should read "4th order" Page 25762, line 1: the wording should be improved so that a distance is not compared to a lifetime. Pages 25795 and 25796: the axes labels for particle number are prepared in different styles. My preference would be to include a factor of 104 or 105 in the axis label, and to change the number scale so that it does not include these powers of 10. Figure 1: A distance scale bar would be informative. Figure 8: the need to display both the solid and dashed red line data was not clear, nor was the reason for the choice of 50 and 60 s time intervals. What are the uncertainties

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in the modelled values?

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