Atmos. Chem. Phys. Discuss., 9, C11143–C11148, 2010
www.atmos-chem-phys-discuss.net/9/C11143/2010/

Atmospheric Chemistry and Physics Discussions

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

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Received and published: 25 February 2010

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 NOx 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- surements 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: Referee Comment: 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 A2_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.

Author Comment: the following statement will be included in section 2: 'The accuracy of the measurement is equal to 23% (1σ). The uncertainties in the absolute IO concentration generated during calibration arise from uncertainties associated with the chemical yield of IO from the reaction O(3P) with CF3I, the lamp flux determination (from O3 actinometry), the concentration of N2O present and estimates of the chemical loss of IO between point of generation and LIF sampling. Other uncertainties relate to the laser power measurement and the variability in the absorption cross-section of the IO bandhead at the laser spectral bandwidth for the wavelength precision ($\pm$0.001 nm) achievable by the wavemeter used to control the laser wavelength (Whalley et al, 2007). The signal variation observed at a constant [IO] (equal to $\sim$5%) represents the random error associated with the instrument precision.'

Referee Comment: 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 high-

lighted?

Author Comment: As discussed in the manuscript (pgs 25750 -25751), the apparent discrepancy between the IO-NOx relationship observed by the LIF-IO-Roscoff measurements and LP-DOAS-Appledore Island measurements may, in part, be caused by the different measurement techniques used to detect IO. The modelling study conducted for Roscoff suggests that the anti-correlation observed between IO and NOx using LIF may not be caused solely by chemical reactions and we suggest that the spatial heterogeneity of NOx sources (Roscoff town) and IO sources (macroalgae beds) may also contribute to the anti-correlation. Spatially averaged IO and NO2 measurements from LP-DOAS could smooth out the spatial heterogeneity of IO and NOx sources, masking the anti-correlation. A 1-D model, which includes both the IO and NOx source variability and the detailed chemistry, would be required to rationalise the observations fully – such a modelling study is beyond the scope of this paper (and is likely to be highly uncertain with respect to the extent of spatial variability of the source regions assumed). The comparison of LIF-IO observations with the zero dimensional box modelling study (in which only chemistry is considered) combined with the arguments presented here should help rationalise the observations of IO under elevated NOx conditions both at Roscoff and Appledore Island.

Referee Comment: 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.

Author Comment: Although the minima of the IO dip occurs before the maxima of the NO2 spike, the start of the rise (NO2) and fall (IO) are simultaneous – the scale at which the NO2 is plotted may mask this slightly (we will improve the scale in the revised manuscript). Other factors controlling [IO] – macroalgae exposure, solar irradiance,

wind-speed could all contribute to the apparent time-lag in the peak NO2/dip in IO.

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

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: 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.

Author Comment: The CRDS IO measurements from the Wada et al, 2007 paper suggest that IO concentrations were as high 54 ± 14 pptv (30 s time resolution) on the 8th September from one measurement which peaked before low tide, so this is clearly much higher than the IO concentrations reported in this manuscript. At lowest tide the

CRDS measurements between ∼25 - ∼35 pptv for a 30 s data-point is in relatively good agreement (within error) with the low-tide LIF [IO] of ∼ 15 pptv for a 150 s data-point. The CRDS IO instrument's cavity was at a height of ∼ 85 cm whilst the LIF inlet was at a height of 3.5 m and was positioned slightly further from the water's edge (∼3.5 m cf ∼2 m) – potentially there may have been a strong vertical gradient in [IO] but we are cautious to draw strong conclusions from this comparison.

Technical and typographical corrections: Referee comments: 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 ! 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.

Author Comment: The suggestions above will be incorporated into the revised manuscript

Referee Comment: 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 in the modelled values?

Author Comment: The purpose of displaying both the solid and dashed line was to demonstrate the sensitivity of the model to interaction time between IO and NOx – this timescale also corresponds to the transit time from macroalgae bed A in fig 1 at wind-speeds of ∼5 – 6 ms-1 that we believe was the source of IO on several days of the campaign. Regarding model uncertainty with respect to modelled IO, it is difficult to determine an absolute uncertainty as many of the parameters the model is constrained to, for example intial [I2] are unknown. For modelled OH and HO2, section 4, a 2σ

standard deviation of 30 – 40% for OH and 25 – 30% for HO2 has been estimated using a Monte Carlo technique coupled with Latin Hypercube Sampling (LHS) for similar models incorporating the MCM scheme (Sommariva et al., ACP, 2004).

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