

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

**K. L. Furneaux et al.**

lisakw@chem.leeds.ac.uk

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The manuscript by Furneaux et al. describes in-situ measurements of IO by LIF at Roscoff, France, in 2006. The manuscript has several objectives. Measurements by the LIF IO instrument are compared to LP-DOAS and MAX-DOAS observations. In addition, the data is interpreted with respect to dependence of iodine chemistry on tidal height, NO<sub>x</sub>, and meteorological parameters. The correlation of new particle formation and the presence of IO is also investigated. Finally, model calculations on the impact of iodine on HO<sub>x</sub> chemistry are presented. This is an interesting manuscript that contains unique IO observations. The data interpretation follows, in large, strategies performed in previous publications. Generally I recommend this manuscript for publication in ACP. However, a number of aspects of the manuscript need to be refined/clarified before its

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final acceptance.

Detailed comments and questions: Referee Comment: Section 3.2: The argument that IO is more dependent on the macroalgae source than on solar irradiation is misleading, after all IO mixing ratios are very low at night. The reason why the authors do not see a dependence is that most I2 is photolyzed between time of emission and time of detection. I recommend rephrasing this section by explaining why one would not expect a dependence on solar irradiance during the day if the I2 source is more than 30 - 60 seconds upwind of the IO measurements.

Author Comment: As suggested by the referee we will rephrase section 3.2 as follows: 'On days when IO originated from macroalgae source regions further afield, (for example from macroalgae beds C & D, fig. 1) the dependence of IO concentration upon solar irradiation becomes reduced owing the short photolytic lifetime of I2. We can compare the IO diurnal profile from two days in the campaign during which IO originated from two different source regions; the tidal minimum occurred at different times on each day. The 8 September was a clear day, providing a flat j (I2) profile throughout the day, once it had risen from zero at dawn, the IO displays a large variation around the tidal minimum. The wind prevailed from macroalgae area A, close to the LIF inlet (Fig. 1) on this day. On 14 September solar irradiation was more variable and low tide fell late in the afternoon (wind prevailed from just north of macroalgae area C). On both of these days IO peaked at the tidal minimum. On 14 September, IO did not peak at solar noon / peak j (I2). Under this scenario, chemical cycling of IO extends its lifetime beyond that of I2 (with respect to photolysis) and diminishes its dependence upon solar irradiation.' The following sentence will be removed: 'Overall, IO was found to have a stronger dependence on tidal height compared to solar irradiation. This suggests that the IO concentration is more dependent on the macroalgae source of iodine compounds than the availability of solar radiation'

Referee Comment: Figure 5: I am not sure that I understand Figure 5. In Figure 6 there are clear times of high J(I2) with low IO. These times do not show up in Figure

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5. Was some kind of filtering performed? If the authors mean “averaging”, by “binning” then should there not be an error bar, as in Figure 4?

Author comment: The average IO concentration was calculated for each 0.01 s<sup>-1</sup> j(l2) bin, error bars will be added to show the variability of the [IO] in each bin. The data when [IO] is low but j(l2) is high is included in the IO data that has been averaged – these data reduce the average [IO] observed at the highest j(l2).

Referee Comment: Section 3.3, and Figures 8 and 9: The authors state that IO was not observed at high NO<sub>x</sub>. However, Figure 9 shows at least one event of 14ppb NO<sub>2</sub> in the presence of 3ppt of IO. While the IO-NO<sub>2</sub> dependence in Figure 5 looks convincing one has to wonder if this is in part an artifact of the 60min averaging. Why was this interval chosen and how would the curve look if it were not averaged? Also, why are there not times of low IO AND low NO<sub>x</sub> in figure 8?

Author Comment: Hourly averaging around peak [IO] was chosen to ensure that the anti-correlation observed was not an artefact of the diurnal cycling of these two species – NO<sub>x</sub> levels were highest in the morning and evening, correlating with the local traffic flow, whilst [IO] were generally greatest around noon, when the tide was low. This data selection criteria means that times of low IO are not included – for information we include a plot of all IO data vs NO<sub>x</sub> which highlights that a negative relationship exists between these two species and includes times when there is low IO and NO<sub>x</sub>.

Referee Comment: Page 25752 A reference to a paper describing the LP-DOAS system should be added.

Author Comment: This will be added to the revised manuscript

Referee Comment: Section 3.3 The definition of the detection limit used in this manuscript should be added. I am puzzled that so many negative mixing ratios of the LIF and the LP-DOAS fall outside of the detection limit range (see also Table 2).

Author Comment: The definition of the LOD will be added to the revised manuscript.

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The LOD of the LIF instrument is calculated from the following equations:

$$\text{LOD} = (\text{SNR}/\text{CIO} * \text{Pw}) * \text{SQRT}(1/m + 1/n) * \sigma_b$$

where SNR is the signal-to-noise ratio, CIO is the instrument sensitivity in counts s<sup>-1</sup> mW<sup>-1</sup> molecule<sup>-1</sup> cm<sup>3</sup>, Pw is the laser power entering the cell in mW, m is the number of data acquisition points taken when the laser is tuned to the on-line wavelength, n is the number of data points taken when measuring the background signal, and  $\sigma_b$  is the sample standard deviation of the background signal:

$$\sigma_b = \text{SQRT}(1/t(\text{Slb} + \text{Ssb} + \text{Sds}))$$

where t is the time period for the acquisition of a single data point in seconds, Slb is the laser scatter signal, Ssb is the background signal arising from solar scattered light, and Sdc is the dark count signal of the CPM. In the paper we have used a SNR equal to 1, so this LOD should encompass 68.3% of the data, using this definition there will be times when data fall both above and below the positive and negative LOD. DOAS LOD: The minimum detectable optical density for the DOAS data is estimated using the root mean-square (RMS) across the spectral window under consideration. The value of the root mean square shows the statistical fitting of the reference spectra to the atmospheric spectra as it is a measure of the noise in the residual after the analysis. If the species under study is under the detection limit of the instrument, the least squares fitting routine used for retrieving individual molecular absorption will still reproduce the best fit to the atmospheric spectra, sometimes resulting in negative concentrations. However, the error in the measurement is calculated using the chi-square, which can still be low due to low noise in the spectra. For more explanation please see Plane and Saiz-Lopez (2006) (Plane, J. M. C. and Saiz-Lopez, A.: Analytical Techniques for Atmospheric Measurement- Editor: Heard, D. E., vol. Chapter 3, Blackwell, Oxford, 2006.).

Referee Comment: The argument for the presence of IO at night is not very convincing. The statistical analysis of the LIF data in Figure 11 is very qualitative. The nocturnal

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LP-DOAS measurements shown in Figure 12 are more often negative than positive. I also do not understand how the LP-DOAS can measure with a 0.9ppt error if the negative values are -2 to -4ppt. One would expect the error to be more in the range of 2ppt during this night. The text suggests also that I<sub>2</sub>, IO and NO<sub>3</sub> were never measured during the same night. Considering how variable all of these species are, the argument that one should see IO formed from I<sub>2</sub> + NO<sub>3</sub> during the night of Sept. 8-9 is not convincing.

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. In response to the errors associated with the DOAS measurements we refer to the referee to the response above that deals with the LOD derivation of the instruments.

Referee Comment: Section 3.4 The authors argue convincingly that the LIF and the LP-DOAS do not measure the same airmass. This begs the question of why the observations of the two instruments are compared in a more quantitative way in Figure 13? Interestingly, the fact that LIF and LP-DOAS measured similar amounts of IO on Sept 9 was interpreted by assuming that the LP-DOAS intercepted air from more extensive macroalgae fields. Does this mean that LP-DOAS data can sometimes be interpreted as true mixing ratios? This would contradict the general belief that, due to the inhomogeneous release of I<sub>2</sub>, LP-DOAS data are lower than the true IO levels.

Author Comment: We will remove figure 13 from the manuscript as, as the referee states, if the two instruments are sampling different air-masses we do not really gain any information from such a detailed comparison – there are too many uncertainties to draw strong conclusions. In response to the second query, we will refine the statement 'the LP-DOAS intercepted air from more extensive macroalgae fields on the 9th' and will include further discussion of IO levels detected on this day (and the 8th) in the revised manuscript:

'The local wind direction on the 9th is slightly more southerly than on the 8th, and, as such, the air flowed along the DOAS light path on the 9th, whilst on the 8th the air flowed slightly off axis. Assuming that on both days the air parcels intercepted similar levels of I2 emissions, we would expect the DOAS instrument to detect higher levels of [IO] on the 9th than on the 8th. The slower wind-speeds on the 9th, compared to the 8th, results in lower [IO] detected by LIF on the 9th as there is more time for chemical processing between emission and detection, which leads to a reduction in [IO], so the LIF-IO instrument detects lower [IO] on the 9th than on the 8th.'

The Roscoff coastline differs from the more widely studied Mace Head coastline in that, as shown in Figure 1, the macroalgae beds are dotted around the bay rather than in a narrow, well defined strip. The wind direction was also variable during the RHaMBLe campaign, and, as discussed in the manuscript, this can influence the [IO] measured by LIF – for example if an air mass does not pass over a macroalgae bed before reaching the LIF inlet IO will not be detected by the instrument – this is not the case for the LP-DOAS – if the light path passes directly over an exposed macroalgae bed, the LP-DOAS would detect IO irrespective of wind direction.

Referee Comment: Figure 14: The CMAX-DOAS observed IO near high tide. This seems to contradict earlier statements on the dependence of IO on tidal height.

Author Comment: The CMAX-DOAS measurements can provide greater spatial coverage than the LIF or LP-DOAS instrument, it is possible, therefore, that the IO measured by the CMAX-DOAS is not solely from macroalgae beds labelled in figure 1 and is instead originating from sources further around the Brittany coastline also.

Referee Comment: Page 25758, line 19. Remove the word "September" and replace with "th".

Author Comment: This will be addressed

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

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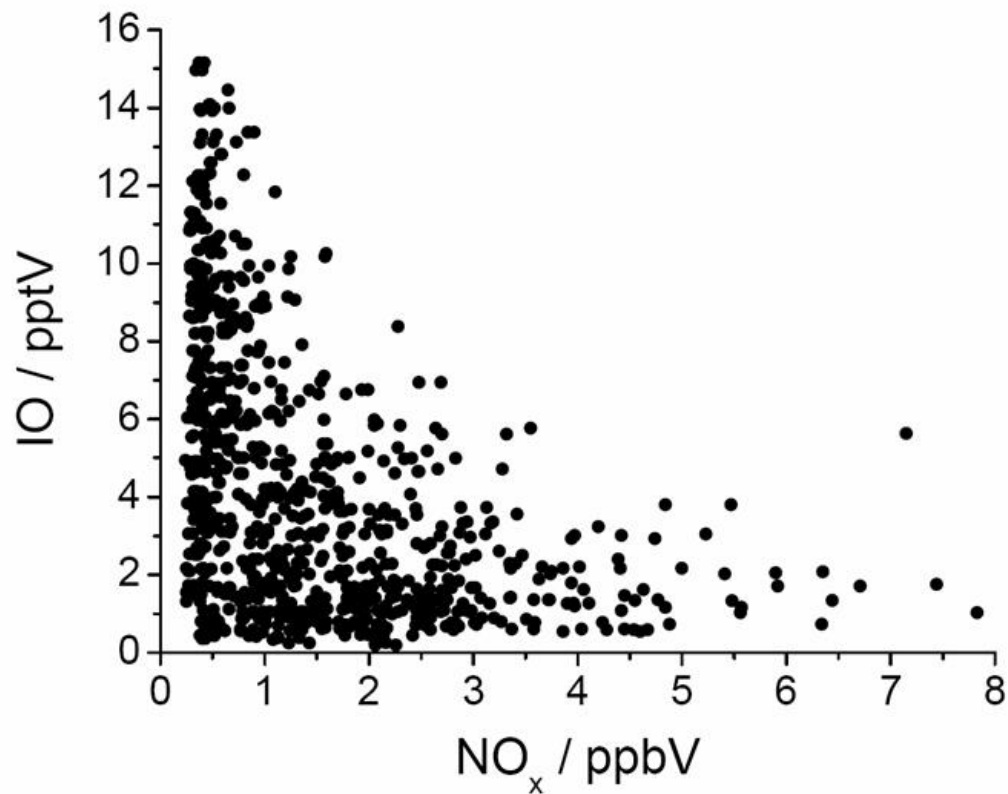


Fig. 1. NO<sub>x</sub> vs IO

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