**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Modelling multi-phase halogen chemistry in the coastal marine boundary layer: investigation of the relative importance of local chemistry vs. long-range transport" *by* D. Lowe et al.

D. Lowe et al.

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We would like to thank Referee 1 for their helpful comments. Below are our responses.

Major Comments:

1. *I suggest the inclusion of a full table of reactions with the manuscript in the supplementary text... Additionally, the references for the individual reactions should be mentioned, rather than citing only Saiz-Lopez et al (2008) for table 1.*

We will include a full table of reactions in the supplementary material.

The reactions listed in table 1 are described in Saunders and Plane (EC, 2005), however they offer a range of minimum reaction rates (from 1.0×10^{-12} to 1.0×10^{-13} cm^{3}molecules^{-1}s^{-1}) for these reactions, depending on the rates of other reactions in the system. Saiz-Lopez et al (ACP, 2008) chose the higher of these two reaction rates (Mahajan et al (GRL, 2009) chose a rate of 6.0×10^{-13} cm^{3}molecules^{-1}s^{-1} instead), which we adopted for our study after their choice. We will add the reference to Saunders and Plane (EC, 2005) in Table 1, but will retain our reference to Saiz-Lopez et al (ACP, 2008) too.

2. *Have the authors also considered photolysis for higher oxides of iodine proposed by Saiz-Lopez et al. (2008)? It would be worth mentioning the effect of this photolysis on the I2/IO ratio and the emission strength. Also the latest laboratory results indicate that reactions of higher oxides with O3, ending with production of I2O5 might not take place at the rate constants used in this study (Saunders et al., ZPC, 2010; Mahajan et al., ACP, 2010). Please update the reaction scheme used as this would affect the IO levels.*

(Changes to the chemistry scheme have all been considered together - please see our reply to Major Comment 3, below).

3. *The prediction of 5-2.5 times the OIO detection limit estimated by Mahajan et al. (2009) is surprising. Even though there would be much lower levels in the total column of the LP-DOAS, these predicted levels are much higher than the model predictions by Mahajan et al. (2009). Has the photolysis of OIO with a quantum yield of 1 been included in this study (Gómez Martin et al., GRL, 2009)? I believe this would also have implications on the emission strength necessary for generating the observed levels of I2.*

Our OIO mixing ratios immediately above the I$_2$ source are high, but for very localised sources this would not necessarily be seen by the LP-DOAS. Mahajan et

al (GRL, 2009) estimate that the measured I_2 and IO mixing ratios should be multiplied by a factor of ≈ 3.4 in order to make comparisons with their model results, so the peak OIO mixing ratios that we predict are (especially with the correction in our choice of the vertical levels to compare with the LP-DOAS measurements, as noted in the reply to your Minor Comment 9) fully in-line with the measured mixing ratios.

We had not, in the original work, considered the photolysis of the higher oxides of iodine (nor included the thermal dissociation of I_2O_4 either). These reactions we have now included in the model. The photolysis of OIO was also, in the original study, calculated with a quantum yield of 0.1. This has now been changed to assume a quantum yield of 1, as suggested. The effects of these changes on the gas-phase iodine mixing ratios are shown in Figure 1 (which should be compared with Figure 9 in our original paper). IO mixing ratios increase slightly, resulting in little change in the I_2 : IO ratio. OIO mixing ratios, in contrast, increase by around 10%, matched by a similar decrease in I_xO_y mixing ratios. This change in gas-phase chemistry is principally driven by the inclusion of the I_2O_4 thermal dissociation reaction — the changes inI_xO_y and OIO photolysis rates only have a minor influence on the gas-phase compositions. These changes to the chemistry scheme will be included in the paper as the new base case; with updates to Figures 3–9 and minor corrections to the text to reflect the changes in iodine compound mixing ratios.

Saunders et al. (ZPC, 2010) do show that IOP formation occurs without the involvement of ozone; however they do also demonstrate that the addition of ozone increases IOP formation (although it is unclear that the postulated $I_xO_y + O_3$ reactions are the cause of this increase, and their results do show that gas-phase I_2O_5 is not important to IOP formation, if it even occurs at all). While there is progress being made on the theories of how these IOP form, these theories are not yet fully mature (Mahajan et al, ACP, 2010). To investigate the effect that

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changing the method of forming IOP's would have on our modelling study we created a model version without the $I_xO_y + O_3$ reactions, but instead with the I_xO_y polymerisation reactions

$$I_2O_3 + I_2O_4 = IOP \tag{1}$$

$$I_2O_4 + I_2O_4 = IOP \tag{2}$$

and the pseudo-uptake of I_2O_3 and I_2O_4 to the condensed phase (for the sake of model development speed these go to a gas-phase species "IxOy_cond", rather than being added directly to the condensed-phase, however the reaction rate is calculated using the size-resolved aerosol microphysical properties). Lab kinetic studies indicate that these higher oxides polymerise at, essentially, the collision frequency (pers. comm. John Plane), so we have adopted a reaction rate of 1.0×10^{-10} cm^{3}molecules^{-1}s^{-1} for Reactions 1 and 2, and an uptake coefficient of 1.0 for the pseudo-uptake to the aerosol phase. The differences these changes make to the iodine gas-phase chemistry are shown in Figure 2 — IO and OIO mixing ratios increase in column layers 3–5, but not enough to change the NO_3 mixing ratio, or the I_2:IO ratio.

Because there is so small a dependence of the iodine chemistry on the formation route of IOPs, and because it is outside of the scope of this paper to investigate the formation of IOPs, we feel that we are justified in continuing to use the reactions of the higher iodine oxides with ozone in order to simulate the removal of active iodine from the gas-phase via primary particle production. We will, however, add some additional explanatory text to our paper in the first paragraph of the "Microphysics and Chemistry" section, referencing Saunders et al (ZPC, 2010) and Mahajan et al (ACP, 2010), and explaining that the most up to date lab studies, and theories of IOP formation, do not support the formation of gas-phase I_2O_5, but that we are using these reactions simply in order to simulate the removal of reactive iodine from the gas-phase via IOP formation.

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We have conducted a small experiment to examine the influence of the $I_xO_y + O_3$ reaction on the gas-phase iodine chemistry though. We have reduced these reaction rates by a factor of 10 (to 1×10^{-13} cm^{3}molecules^{-1}s^{-1}. These changes result in an $\approx$50% increase of OIO mixing ratio in the lowest model layer, increasing with height to an $\approx$100% increase in the fifth layer of the model (Figure 3). The peak I_xO_y mixing ratios are reduced by 10–15%, and tail off more rapidly than in the new base case model. IO mixing ratios are much less changed, with small increases which are only become noticeable in the higher model levels. I_2 mixing ratios, and the I_2 : IO ratio, remain unchanged.

4. *Why are the model results compared only with the LP-DOAS observations by Mahajan et al. (2009), while the observations by in situ instruments like LIF (Whalley et al., 2007) and CRDS (Wada et al., 2007) not considered (they are mentioned only in the introduction)? I think that using the in situ observations would help further constrain the emission sources and also help check wether the LP-DOAS column measurements are influenced more by the local sources, thus helping model the I_2:IO ratio. A figure comparing the model results to observations should be included.*

We compared our model only with the LP-DOAS measurements because we were, primarily, interested in investigating the reported I_2:IO ratio. The test-case we chose for this study was not one which suitable for comparisons with in-situ measurements because of the distance between the main I_2 source and "Roscoff", and we felt that such a comparison did not fit with the focus of the rest of the paper, so these were not presented.

However, we have selected another I_2 emission scenario, for the purpose of making comparisons with the in-situ measurements. This has strong emissions closer too (though not at) Roscoff (Figure 4); the original iodine emission scenario does have emissions at Roscoff, but these are 10^3 times smaller than the peak emissions in the centre of the trajectory. We have plotted the vertical profiles of IO,

I_2, OIO, NO, NO$_2$ and NO$_3$ + N$_2$O$_5$ for model runs using both emission scenarios, and both with, and without, the I + IONO$_2$ reaction (Figure 5). For comparison, the FAGE LIF measured a maximum IO mixing ratio of 30 ± 7.1 pmol mol^{-1}; while the BBCRDS measured a maximum I_2 mixing ratio of 50 pmol mol^{-1} (McFiggans et al, ACP, 2010). There are clear differences between the two iodine emission scenarios. IO, I_2 and OIO mixing ratios show stronger vertical gradients within the lowest 5 metres of the model column in the original emission scenario, because of the small I_2 emissions next to Roscoff in this scenario. The vertical profiles are smoother in the second emission scenario, because there has been time for the column to become more mixed, but for our model run with the I + IONO$_2$ reaction the mixing ratios of IO, I_2 and OIO still show a strong vertical gradient, and have mixing ratios over 7, 15, and 0.4 pmol mol^{-1} in the lowest 10 metres of the column. These results suggest that either a strong local I_2 source is needed (stronger than is suggested by local seaweed surveys), or a recycling mechanism is needed to maintain the high I_2 and IO mixing ratios. In all scenarios we observe that OIO mixing ratios are below detection limits, and that variations in NO and NO$_2$ mixing ratios are smaller than those variations which we observe with changing wind direction (and so source term). The NO$_3$ + N$_2$O$_5$ mixing ratio is, however, significantly increased to over 8 pmol mol^{-1} within the lowest 10 metres of the model column. This is measurable, and confirmation of it's presence, or lack thereof, within similar iodine bursts in a polluted environment would confirm, or disprove, the importance of the I + IONO$_2$ reaction.

5. *The authors mention that the I_2/IO ratio can be reproduced even without considering reaction 1. For this, they point to the prediction of a ratio of 4, 1-3 m above the sea level and suggest that a strong but spatially limited I_2 source could reproduce the observed ratio 'if only a couple of meters below the light path'. The observation by Mahajan et al. (2009) were made at a height of 7-10 m above the mean sea level, meaning that this observation height would be much larger and*

not smaller during low tide. Hence, I find it surprising that the authors mention they can reproduce the observations when the modelled ratio on levels 3 (6-10 m) and 4 (10-15 m) is about 2-2.5. If a higher ratio can in fact be produced without any recycling as the authors suggest, this would be a result of faster mixing of I2 to the height of observation. A sensitivity study on the model response to vertical mixing would be a good way to check this.

We've run three testcases investigating the sensitivity of the I_2:IO ratio to vertical mixing — for which we've multiplied our vertical mixing ratios by factors of 0.5, 2, and 5. We found that, while the vertical mixing rate does change the absolute mixing ratios of I_2 and IO through the column, there is little effect on the actual I_2:IO ratio. The influence of these changes are shown in the the files `Iodine_x0.5_vert_tran.pdf`, `Iodine_x2.0_vert_tran.pdf`, and `Iodine_x5.0_vert_tran.pdf`, included in the supplementary material for this reply.

What did have a large effect on I_2:IO ratio was the photolysis rate — as described in Minor Comment 5 below.

Minor Comments:

1. *P19431 Line 13 and Line 21: DOAS observations of halogen compounds are described twice.*

   We have removed the first paragraph describing the DOAS measurements.

2. *P19432 Line 6: Source strength should be 1 x 10^{11} molecule cm^{-2} s^{-1} and not 1 x 10^{-11} molecules cm^{-2} s^{-1}.*

   We have corrected the source strength description.

3. *Use units accepted by IUPAC and keep them constant in the manuscript, e.g using ppt, pptv and pmol mol^{-1} interchangeably is not recommended.*

   These units have now been tidied up.

4. *Page 19437 Line 6: Why have the authors chosen 23rd September for the model run? A brief explanation would be useful.*

   We picked the 23rd September for our photolysis profile (not for any other aspect of the model run) because we wanted to use a profile which was as close to clear sky conditions as possible.

5. *Page 19437 Line 6: 'The photolysis rates are calculated under near clear sky conditions'. Although these conditions might be true for 23rd September, the I_2/IO ratio observed by Mahajan et al. (2009) is over the whole campaign. The sensitivity of the ratio, and the source strength necessary for reproducing the observed levels of I_2 and IO, to the range of photolysis rates observed during the campaign should be presented.*

   To investigate the dependence of the I_2:IO ratio on photolysis rates we have rerun the base case over the "Roscoff" leg using photolysis data from the 14th September, when cloud cover had reduced the actinic flux by 40-50% in the hour between 11am and 12am (see actinic flux figure in supplementary material). We have also reduced the I_xO_y photolysis rates by 50%, to 0.03. These reductions in photolysis lead to an increase in I_2, while decreasing IO, OIO, and I_xO_y mixing ratios. These changes lead to an increase in the I_2:IO ratio at levels 4 and 5 to around 2–3 (Figure 6).

   We have also run this reduced photolysis model for comparison with in-situ measurements, in the same manner as the model runs used in answering Major Comment 4. This also shows an increase in I_2 mixing ratios to over 30 $pmol\,mol^{-1}$, along with decreases in IO and (to a lesser extent) OIO mixing ratios (Figure 7).

   We will add a new section to the results section of the paper discussing the influence of photolysis rates on the iodine compound mixing ratios.

6. *Page 19439 Line 9: Why is the emission scenario used from 10th September but not photolysis rates? Wouldn't it be easier to keep the day constant considering changing conditions like wind speed, direction and more importantly, tidal height?*

We chose the 10th Sept because it was the greatest emission of I2 according to the model in Leigh et al (ACP, 2010). Because we are most interested in looking at the general trends of the emissions, rather than trying to examine a specific day (the I_2/IO ratio that we are comparing our model results against are calculated from averages for the whole campaign) we felt that this was a justifiable approach.

7. *Page 19439 Lines 8 and 18: It is not clear whether the modelled airmass reaches the measurement site at 12 pm or 12:30 pm.*

The modelled airmass reaches the in-situ site at 12pm, model time. We will make this clearer in the text.

8. *Page 19441 Line 22: 'I$_2$ sources could be anything from 2-3 m to 15-20 below the LP-DOAS light path'. I find this sentence contentious considering that LP-DOAS light path was 7-10 m above the mean sea level (hence if anything, this height would be more during low tide). Additionally, if the authors have detailed bathymetry information of the region at high resolution, this height should be easy to calculate.*

The bathymetry data (see file `bathdata_DOAS_lightpath.xls` in the supplementary material) shows that the sea-bed heights along the DOAS light-path vary between -8 and +6 metres (compared to mean sea level). Our statement about the range of distances of possible I_2 sources below the DOAS light-path is accurate and will be left as is.

9. *Page 19441 Line 20: I think the authors mean levels 3 and 4 at heights of 3-6 m and 6-10 m. This is also seen in figure 10, the values of which match the text but for levels centred at 4.5 and 8 m (e.g. 70 pmol mol^{-1} of IO represents the level*

centred at 4.5 m). However, the observations should be checked with layers 4 and 5 at heights 6-10 m and 10-15 m. Please check this is indeed the case.

Levels 3 and 4 are indeed at heights of 6-10m and 10-15m as you point out! We have corrected our text to use the values from levels 4 and 5 rather than those from levels 3 and 4 for both this section and for the I_2 recycling section.

10. *There are 1 minute data available for NO$_2$ and NO. Have the authors checked through these for signatures indicated by the model?*

We have compared the in-situ LIF IO measurements with the NO$_2$/NO data — however the effect of local meteorology is a strong influence on the measurements (air-masses coming from Roscoff town have high NOx and low IO, while the reverse is true of air-masses from the Channel), which makes distinguishing any influences of iodine on NOx difficult. Ideally we would want to have 2 (or more) measurement sites, one upwind of the iodine sources, the other downwind, in order to be able to distinguish any such influences.

11. *Similarly, the BrO modelling suggests that there should be a large depletion in O$_3$ if the BrO is generated by sea salt rather than a 'beach source'. I believe this was not observed and should be mentioned.*

The BrO modelling suggests that there would be lower ozone mixing ratios with a sea-based, rather than beach-based, bromine source — however this difference is much less than the ozone destruction caused by the iodine emissions and wouldn't, we believe, be distinguishable in the measurements.

12. *Table 2: Fluxes for organoiodides and organobromides are considered but not discussed in the manuscript. What were these constrained with and what was their effect?*

References for the emissions listed in Table 2 have now been added. The emission fluxes of organoiodides and organobromides from the sea are much lower

than the emissions of I2 from the exposed macroalgae sources, and so have little effect on the campaign iodine compound measurements.

13. *Table 5: The symbols are not defined in the manuscript.*

    The caption of Table 5 has been expanded to fully describe the symbols.

14. *Figure 2: Is this scenario reproduced using conditions in Leigh et al. (2010), if so, reference it, or mention how this was calculated.*
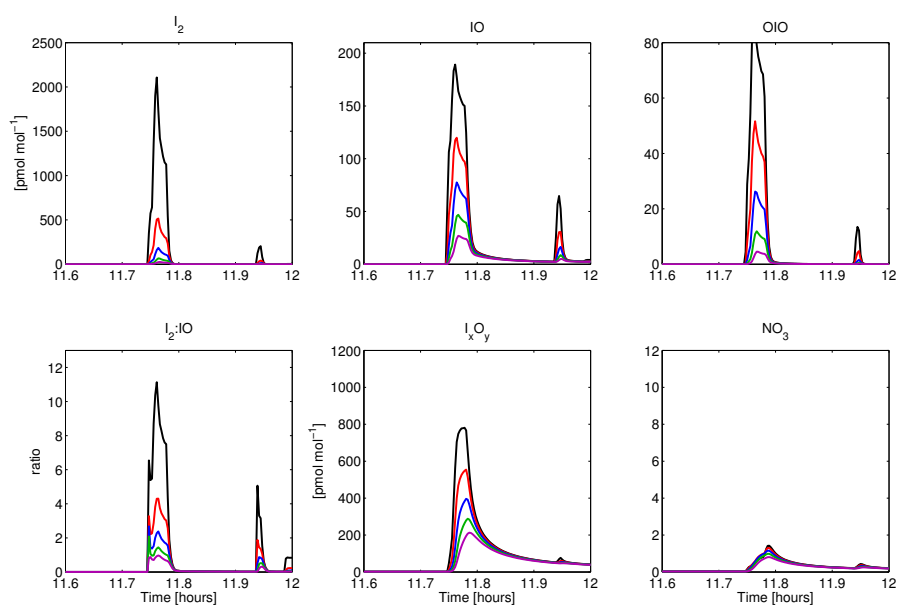
    The scenario in Figure 2 is created using the model of Leigh et al (2010), We have expanded the caption to note this.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C11165/2010/acpd-10-C11165-2010-supplement.zip

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19429, 2010.

Fig. 1. Mixing ratios of I2, IO, OIO, IxOy, NO3, and ratio of I2:IO, in the lowest five layers of the model column for the new base case, low tide, model run. Same colouring as Figure 9 in our ACPD paper.
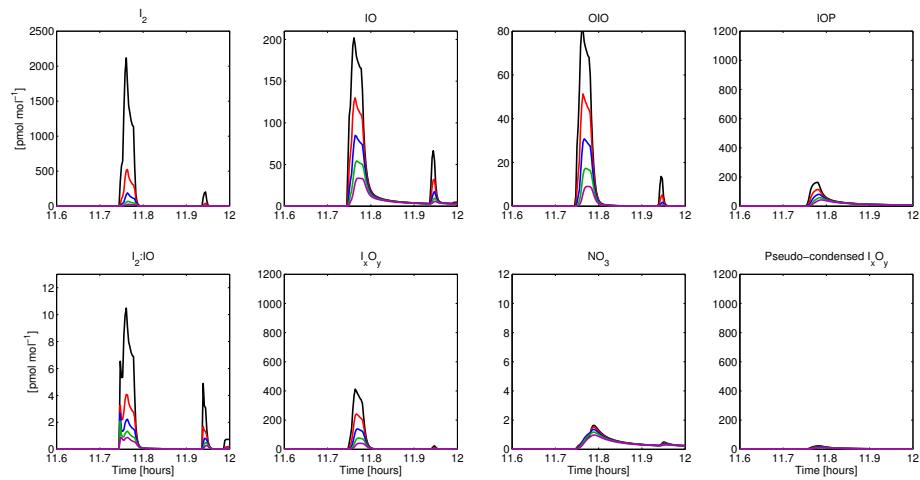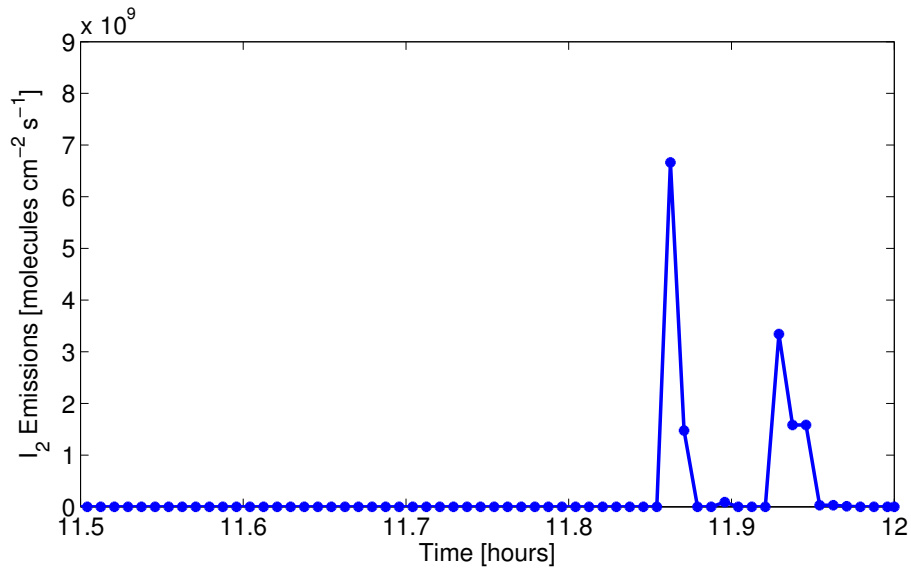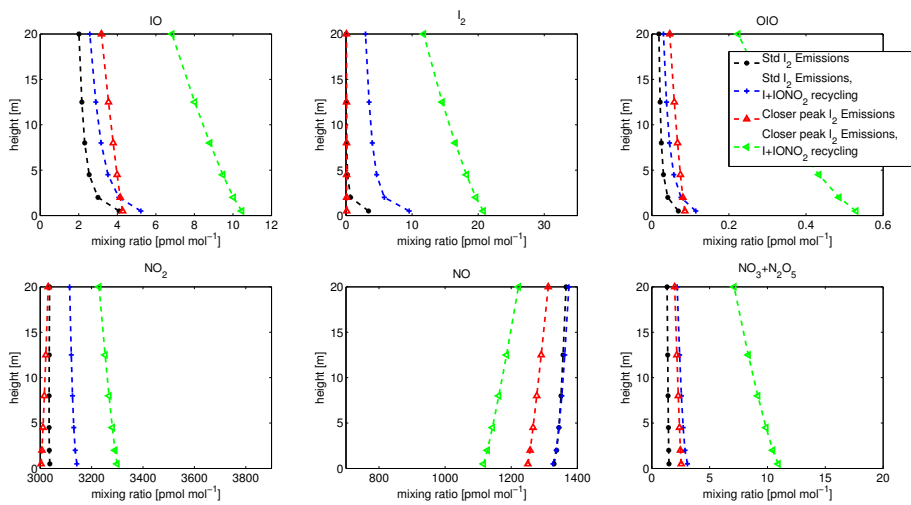
Fig. 2. Mixing ratios of I2, IO, OIO, IxOy, NO3, IOP, condensed IxOy, and ratio of I2:IO, in the lowest five layers of the model column for the IxOy polymerisation model run.
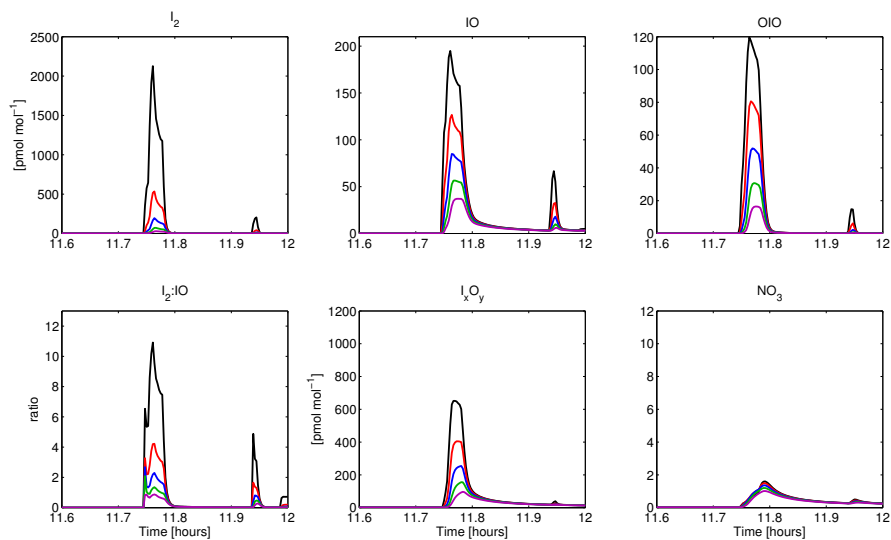
Fig. 3. Mixing ratios of I2, IO, OIO, IxOy, NO3, and ratio of I2:IO, in the lowest five layers of the model column for the lower IxOy+O3 reaction rate model run. Note change in OIO y-axis scale.

Fig. 4. I2 emissions used for the "close emissions" scenario. Calculated using a back trajectory from the Roscoff measurement site at 12:34:30 on 10th September 2006 (Leigh et al., ACP, 2010).
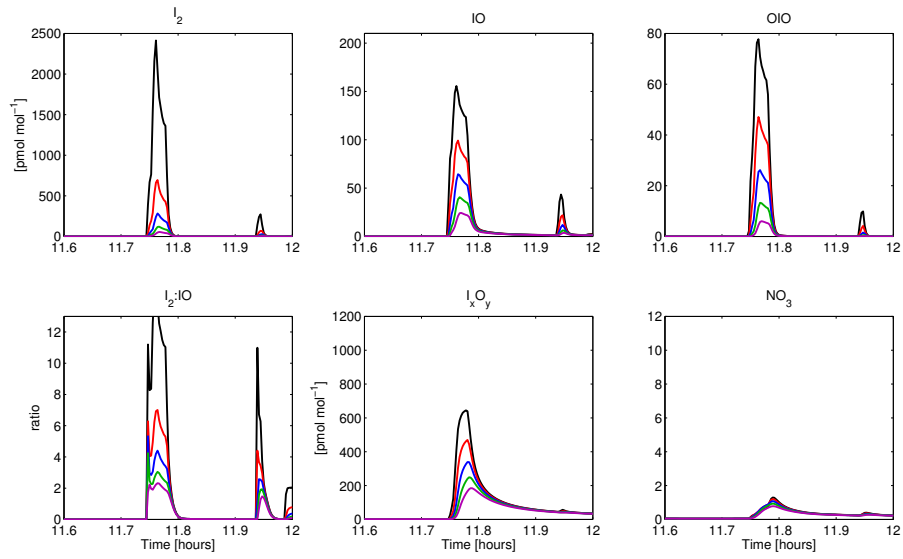
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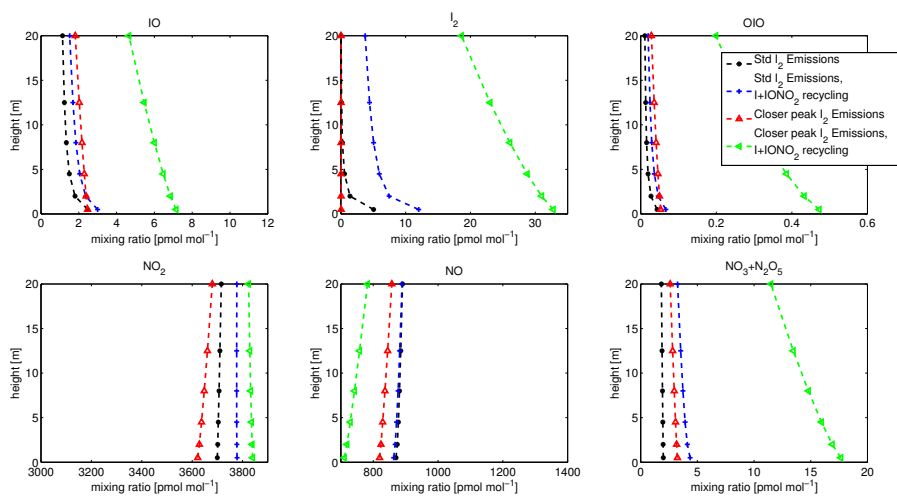**Fig. 5.** Vertical profiles of I2, IO, OIO, NO, NO2 and NO3+N2O5 mixing ratios at Roscoff.

Fig. 6. Mixing ratios of I2, IO, OIO, IxOy, NO3, and ratio of I2:IO, in the lowest five layers of the model column for the low tide model run using the reduced photolysis rates from the 14th September 2006.

Fig. 7. Vertical profiles of I2, IO, OIO, NO, NO2 and NO3+N2O5 mixing ratios at Roscoff, using the reduced photolysis rates from the 14th September 2006.