

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.

Anonymous Referee #1

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This paper presents a modelling study of iodine and bromine compounds, the measurements of which were made at Roscoff, France. The modelling analysis complements and expands over the recent manuscripts that have tried to elucidate the chemistry of iodine and bromine in semi-polluted environments, which is not very well characterised to date. Therefore I recommend the manuscript is published in ACP, after the authors have addressed a few important points that are detailed below.

Major comments:

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1) I suggest the inclusion of a full table of reactions with the manuscript in the supplementary text. The reaction scheme used here is from three works in the past: Pechtl et al. (2006), Saiz-Lopez et al. (2008) and Lowe et al. (2009). It is not easy to understand which reactions are included from which study, except for higher iodine oxide reactions that are detailed in table 1. Additionally, the references for the individual reactions should be mentioned, rather than citing only Saiz-Lopez et al (2008) for table 1.

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 I_2/IO ratio and the emission strength. Also the latest laboratory results indicate that reactions of higher oxides with O_3 , ending with production of I_2O_5 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.

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 I_2 .

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 whether the LP-DOAS column measurements are influenced more by the local sources, thus helping model the $I_2:IO$

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ratio. A figure comparing the model results to observations should be included.

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 I_2 to the height of observation. A sensitivity study on the model response to vertical mixing would be a good way to check this.

Minor comments:

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

2) P19432 Line 6: Source strength should be 1×10^{11} molecule $\text{cm}^{-2} \text{s}^{-1}$ and not 1×10^{-11} molecules $\text{cm}^{-2} \text{s}^{-1}$.

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.

4)Page 19437 Line 6: Why have the authors chosen 23rd September for the model

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run? A brief explanation would be useful.

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.

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?

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

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.

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.

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10) There are 1 minute data available for NO_2 and NO . Have the authors checked through these for signatures indicated by the model?

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.

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?

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

14) Figure 2: Is this scenario reproduced using conditions in Leigh et al. (2010), if so, reference it, or mention how this was calculated.

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