

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.

douglas.lowe@manchester.ac.uk

Received and published: 16 December 2010

We thank Rolf Sander for his helpful comments, below are our replies.

Scientific Comments:

1. *The introduction contains very long descriptions of the models by Leigh et al. (2009) and Mahajan et al. (2009a). Since this is not a review paper, I don't think it is necessary to describe the models of other studies.*

C11183

As this paper builds on the findings of these two studies we feel that some description of their studies should be retained, although these have been cut down.

2. *p. 19440, l. 9: Does the value of 0.8 really refer to the molar Cl/Na ratio or is it the chlorine enrichment factor compared to sea water composition? Note that the molar Cl/Na ratio of sea water is not equal to one.*

The value of 0.8 is the molar Cl/Na ratio, not the chlorine enrichment factor compared to sea water composition. However, as the molar Cl/Na ratio is close to unity for the fresh “sea-salt” aerosol that we emit, it can be taken as a close proxy for chlorine enrichment for this study. It should be noted, though, that instead of explicitly accounting for all major cations in primary seasalt we only consider Na⁺ (ignoring Mg²⁺, Ca²⁺ and K⁺) owing to the model complexity and the low relative concentration of the other cations. This is not expected to play a substantial role in the chemistry, but may have led to the confusion in the terminology. This is now explicitly stated in the paper.

3. *p. 19441, last paragraph: Could you briefly mention what in your opinion is the reason for the discrepancy between measured and modeled OIO?*

The difference between measured and modelled OIO is, we believe, down to non-heterogeneity of OIO in the sampling volume of the DOAS instrument - the averaging of OIO mixing ratio along the whole light-path will reduce the OIO measurement, since the OIO contribution in our model takes the maximum I₂ emissions. The I₂ emissions contributing to the OIO along the rest of the light-path are likely to be lower.

4. *p. 19441, l. 27: What is the meaning of the word “only” in “only 5-2.5 times the detection limit”? If it is above the DL, it should still have been detected.*

If the local mixing ratio is 5-2.5 times the detection limit but is spatially very heterogeneous, with very low mixing ratios along the rest of the LP-DOAS light path,

C11184

then it is possible that averaging along the light path would reduce the total mixing ratio of OIO to below the detection limit.

5. *p. 19442, l. 10-11: I don't understand "before increasing equally markedly at the end of the bursts". As far as I can see from Fig. 3, reactive chlorine and bromine remain low until the next burst starts at about 11.93.*

Reactive bromine has a fairly straight forward inverse relationship with I — with (relatively) large decreases in mixing ratio during the I₂ bursts, before returning to the previous mixing ratios afterwards. Reactive chlorine mixing ratios also decrease during the iodine bursts, but because of the release of chlorine compounds from the seasalt particles during the bursts it's mixing ratios increase markedly immediately after both iodine bursts (and during the latter third of the first iodine burst, as iodine mixing ratios drop). The timings of these events isn't, unfortunately, very clear from Figure 3, because of the amount of information that this Figure contains. Figure 1 gives a clearer indication of the timing of these changes.

6. *conclusions, last paragraph: If NO_x is not uniformly distributed, it would also be possible that local patches of BrO exist in areas with low NO_x.*

The LP-DOAS instrument measured BrO and NO₂ concurrently — their analysis of the measurements showed no consistent relationship between the BrO and NO₂ mixing ratios. It is possible that the NO_x mixing ratios were non-uniform along their light path, allowing localised build up of BrO, however I don't think we can determine if this is the case or not from the measurements available. What would be useful is in-situ concurrent measurements of BrO and NO_x, which would allow us to get a better handle on their relationship.

Technical Comments:

C11185

1. *Please add the physical units to all quantities, especially to Tables 1 and 5, and also to Equations (2) and (4).*

Physical units have been added.

2. *Please define all acronyms that you use, e.g.: "PD-FiTE", "LT".*

PD-FiTE and LT have been expanded, as has ACASA too.

3. *p. 19430, l. 24: Change "Odown" to "O'Dowd".*

This has been corrected in our reference records.

4. *p. 19431, l. 10: The sentence starting with "Which" seems to be incomplete.*

The "Which" sentence carries on from the previous sentence (but in a disjointed manner). We have made the connection clearer.

5. *p. 19431, l. 27-28: Change "pptv" to "pmol/mol" here (and also elsewhere).*

These have been corrected.

6. *p. 19434, l. 13-14: I agree with the other reviewer that the complete chemistry mechanism should be published in a supplement instead of just citing other papers on which it is based.*

We will provide the whole chemistry mechanism in the supplementary material.

7. *p. 19436, l. 3: Is K_e proscribed or prescribed?*

It is prescribed. This has now been corrected!

8. *p. 19437, l. 26: Are the numbers describing the composition based on mass fractions or molar fractions?*

The percentages given for the initial aerosol compositions are based on mass fractions. To clarify this in the text we have replaced the phrase "dry composition" with "dry mass fraction" (and replaced the percentages with fractions).

C11186

9. p. 19443, l. 3: The word "if" is probably missing here.

This has been added.

10. p. 19444, l. 19: The word "are" is probably missing here.

This has been added.

11. Tables 3 and 4: Please gives the references from where these values are obtained. If they are your own estimates, please mention it in the table captions.

We have added references to Tables 3 and 4 where appropriate, and indicated where the values are our own estimates.

12. Table 5: Is the denominator of the function really dr ? I think it should probably be $d\ln r$ or $dlgr$.

The denominator is indeed $d(\ln(r))$ - this has now been corrected.

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

C11187

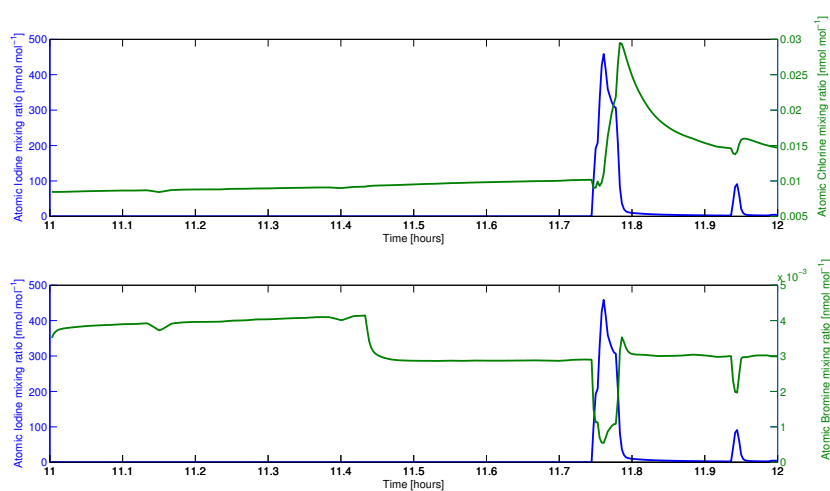


Fig. 1. Top panel: I (blue) and Cl (green) mixing ratios in lowest column layer. Bottom panel: I (blue) and Br (green) mixing ratios in lowest column layer.

C11188