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Interactive Comment

Interactive comment on "Coastal zone production of IO precursors: A 2-dimensional study" *by* "L. J. Carpenter et al."

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General comments

The paper provides a timely discussion of processes important to current studies in the coastal MBL. The participation of reactive halogen species in MBL chemistry has been subject to extensive investigation in recent years and observational support of hypotheses concerning such chemistry in mid-latitudes has been largely based on measurements taken at coastal locations. Precursors of reactive inorganic iodine, CH_2I_2 likely making the largest contribution, are produced in abundance by seaweeds in the intertidal zone. It is therefore important to establish whether iodine mediated chemistry (e.g. ozone destruction, ICl- and IBr-initiated Cl and Br activation from seasalt etc.) is a general open ocean MBL phenomenon or whether intertidal emissions of iodocarbons are sufficient to explain coastal measurements. The paper presents a modelling study

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which attempts to address this problem by replicating CH_2I_2 measurements made during a field study at a coastal location by varying intertidal and more remote fluxes. The problem is difficult to constrain but the paper takes a methodical approach using the available data and generally appropriate assumptions. The paper is well written and coherent and the methodology is, on the whole, well-developed and supported by good observational evidence. There are, however, areas of fundamental importance in the approach and conclusions which should be addressed.

Specific comments

The first point may be readily addressed and is one of terminology. It is, however, crucially important. Throughout the manuscript, fluxes of CH_2I_2 not emanating from the local intertidal zone are frequently referred to as 'open ocean'. Averaged open ocean fluxes may be interpreted as those which could be important on regional or even global scales. The coastal shelf off the west coast of Ireland is many tens of kilometers offshore and must be traversed before reaching the coastal zone from the open ocean. Fluxes from within the coastal shelf region are indistinguishable from the open ocean. In addition, there are numerous islands and coastal regions several kilometers distant from the measurement site. Only if it is certain (by means of local flow modelling for example) that there were no inputs of CH_2I_2 from these potential sources can it be suggested that the fluxes are from non-coastal regions. It is suggested that 'open ocean' be replaced by 'non-local'throughout the manuscript.

The second point is more difficult to address and impacts directly on a major conclusion. The modelling study uses a diurnally averaged eddy-diffusivity. That this may be inappropriate is recognised in the discussion of figure 11a where it is noted that the uplift of the nighttime plume may be overestimated. By corollary, daytime vertical mixing will be underestimated and the predicted difference between day and night CH_2I_2 will also be underestimated. Scaling the fluxes to reproduce the nighttime concentration with realistic diurnal diffusivity fluctuation may therefore predict the observed diurnal fluctuations without requiring non-local emissions. Before attempting to explain

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the discrepancy in modelled and observed concentrations by non-local fluxes it is appropriate to vary the eddy diffusivity throughout the day to see whether agreement could be obtained by using a realistic diurnal diffusivity variation. Alternatively, but more difficult, if it could be shown that daytime overprediction (when fluxes are scaled to match nighttime observations) increased with the photolability of the species, this would indicate the assumption in the paper was correct. However this would require the assumption that the ratio of local to non-local fluxes was identical for all species; this is a large assumption.

The last major point also concerns the meteorology at the measurement site. It has been reported by other workers that significant stratification frequently occurred at the measurement site during the field project. Such internal boundary layer formation would cause abrupt changes in the vertical diffusivity gradient. It is not suggested that such details should be considered in the present study, but it should be stated whether strong stratification was present in the period under consideration. If so, where was the measurement location in relation to the height of the lowest layer and how does this compare with the vertical grid resolution in the model. In any case, mention should be made of the possibility that IBL formation could affect the conclusions.

The following points are more minor detailed comments:

p196 ln 9. As I understand it, the box model is a 1 box 0-dimensional model in which it is assumed that concentrations result from fluxes at the same location and there is no consideration of transport. It is not used in a Eularian famework.

p199 In this section, where the vertical windspeed dependence and roughness lengths are described, I feel it would be useful to state that the extent of the very variable sloping complex terrain will vary with tidal height and so contribute to local roughness length uncertainties / variability.

p200 ln 8. It states that 'it is clear from Figure 1...' Figure 2 shows better that there is a relationship between IO, tidal height and daylight. It may appear to be true from Figure 1, but there is contradictory data (peak IO is higher on 14th than 9th and 12th, although the peak appears after dusk - NB is there an explanation for this?), and

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cannot be said to be clear.

p200 The construction of Figure 2 should be described. What does each each datapoint represent and what do the error bars indicate? Figure 1 shows peak IO values much higher than those shown in Figure 2. Also, the peak nighttime values (above detection limit) from 12th and 14th September do not appear.

p200 The sentence starting on line 15 is unclear and should be rephrased.

p200 ln 17. The Hebestreit reference is missing.

p200 ln 24. Figure 4 shows a constant offset of 0.06 ppt in CH_2I_2 concentration which is attributed to 'offshore' sources. This may be the best evidence for non-tidal sources and could be stressed elsewhere in the paper to reinforce the argument for such a source.

p200 ln 26-27. Whilst I agree that it is likely that iodine photochemistry will change the IO relationship with tidal height, it is not obvious that the daytime CH_2I_2 exhibits a very convincing linear dependence on tidal height. This will be the most important IO precursor in this study. What is the R^2 of the linear fit of daytime CH_2I_2 to TH? Would a linear relationship between CH_2I_2 and IO be expected anyway, since CH_2I_2 will give up 2 I atoms on photolysis and IO formation requires one?

p201 ln 8. Can the authors suggest a physical basis for an linear inverse flux relationship with tidal height?

p201 ln 15 onwards. I have difficulty in following the argument. Since the contribution of flux variation to concentration fluctuation is dependent on vertical stability how can it be stated that the relationship derived from the best fit using a box model assuming instantaneous mixing is an appropriate one to use in a model using explicit vertical mixing? I agree that a tidal relationship to flux is appropriate but cannot see how a general relationship can be inferred from a box model.

p202 ln 10. The final vertical grid spacing has extremely poor resolution at the height where measurements were taken. A logarithmically-spaced vertical grid would be more appropriate, or a sensitivity to fine resolution near the ground should be made if comparisons are to be made with measurements. Such a resolution sensitivity should

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also be investigated if a diurnally-varying K is used.

p202 ln 22. A pair of fluxes required to 'match the measurements' is given. What criterion was used to decide whether the 'match' was a good one?

p203 ln 2. How was the average concentration between 200 m and 5 km determined? What was the spatial resolution of the measurements? Were they taken at the same time as the coastal measurements?

p203 ln 5. Was the quoted Henry's law a measured or estimated value?

Figure 3 shows a significant number of CH_2I_2 concentrations > 0.2 ppt. These are not shown in Figure 4. What does each point, and its associated error bars, represent in Figure 4?

Whilst the above criticisms may appear harsh, I believe the study to be an extremely important one. If it is possible to address the major points and derive the same conclusions, this work would make a significant contribution to our understanding of mid-latitude coastal (/shelf) halogen chemistry. It is of great importance to establish whether there is indeed a significant non-coastal iodine source but I am unsure whether there is currently sufficient data available - this paper is making a superb attempt to squeeze out the most from that data which is available.

Interactive comment on Atmos. Chem. Phys. Discuss., 1, 193, 2001.

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