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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Concurrent observations of atomic iodine, molecular iodine and ultrafine particles in a coastal environment" *by* A. S. Mahajan et al.

Anonymous Referee #1

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This paper describes measurements of reactive iodine species, 3-9 nm particle number concentration and supporting observations of NOx and O3 at a coastal environment. Measured data are presented for a relatively short period (1 week), and are interpreted using a 1-D model to simulate the evolving evolution of iodine species, and predicted iodine aerosol precursors, under various emission scenarios, to attempt to reconcile the observed levels of I, I2 and particles. The measurement combination makes a novel contribution to our understanding of the marine iodine system. While some difficulty is experienced in attempting to match the modelled and observed behaviour, the hypotheses suggested to account for the discrepancy should be testable using either future or possibly archived field and/or laboratory datasets.

The topic of the paper is suitable for ACP, and the manuscript is largely clearly written. Subject to consideration of the points below, I support publication.

Science Issues

-The authors state that I, I2 and ultrafine particles showed a clear tidal (anti)correlation, and analyse their data accordingly, but this is not always the case for the particles – e.g. early in the morning on the 3rd, 4th and 5th of may, particle bursts are apparent while the tide is high. More consideration should be given to other possible contributions to the observed particle data, e.g. other marine or terrestrial contributions; back trajectory analyses for these periods may be of use. The statement that the source for (particles) is tidal in the conclusions should be qualified.

-The key metric the models seek to reproduce is the I/I2 ratio. From figure 5 this seems to be extremely dependent upon height (the colour contours are on a logarithmic scale) – how does the modelled value change over the 0-3m range ? I wonder if the likely impacts of local topography, change in surface roughness over the intertidal range, would greatly perturb the vertical mixing, particularly up to the (fairly low) 1.5 m measurement height, and considering the substantial measurement uncertainty.

-The postulated reaction of iodine atoms with species X may be somewhat unlikely given the (lack of) measurements of any such process in the literature (although it is fair enough to advance this possibility as a hypothesis). There have been some measurements of rate constants for I atoms with various VOCs (although arguably not the most abundant species in the MBL) – see e.g the NIST kinetics database, particularly at elevated temperatures (combustion systems); extrapolation to ambient temperatures leads to very low rate constants. This reaction would triple the gaseous iodine atom sink (above that due to O3 and NOx) – what impact does this then have upon the iodine (I2) source strengths required to reproduce the observations ?

-The impact of NOx upon iodine chemistry through reservoir formation depends upon the stability of the reservoirs, i.e. the partitioning of iodine between I/IO and INO3 etc,

not (solely) the formation rate constants, as stated in section 4.3. Consideration to the partitioning of iodine should be given here. It should be made clear that the NOx influence argument assumes that the iodine source strength is constant across the timeseries. I am curious as to why the INO3 in figure 6 does not peak at ground level (where IO maximises) ?

-Measurement error is of course always possible, particularly with new instruments such as that used here, and the authors appear to have carefully considered the potential known uncertainties. Some aspects of this discussion (p.27242) could however be more precise – what does “ratio of sensitivities stays fairly constant” actually mean in % terms ? To what extent did lamp ageing occur and affect the results (within the short timeseries presented here) – in the accompanying AMTD paper, there is some discussion of an issue with lamp failure towards the end of the measurements.

Minor Points

-It would be helpful to outline the tidal range (vertical and horizontal) encountered within the text (e.g. section 2) in addition to showing tide range on the figure, and to compare this with those for Mace Head and Roscoff Section 3 p. 27232 It is not clear to me how the timeseries in Fig 2 relates to the statement that I2 and I were observed on 4 days and 1 night ?

-What is the sensitivity of the NOx monitor ? Were all the measurements co-located ? The O3 trace seems very noisy – this plot (Figure 2 panel d) would be clearer with longer averaging applies to these data.

-Wind direction was not *always* within 30’ of North, as inspection of Figure 2 shows.

-What spin-up time was used for the model (for non-iodine species) ? The model results will be sensitive to many parameters, input conditions etc, rather than just two as stated on p. 27235.

-The phrase “50% cloudy” implies intermittent patchy cloud cover within clear sky – but

I presume the authors actually divided constant photolysis frequencies for all species by 2, this wording should be clarified. Similarly “clear sky” would be clearer than “0% cloudy”.

-p.27239 clarify that correlations relate to observed not modelled quantities

-p. 27242 line 21 loss not lost; line 24 I would say “current” rather than “undergoing”; line 26 were not where; p. 27243 “extend” rather than “contribute to expand geographically”.

-Figure 5 caption “scenarios”

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27227, 2010.