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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.

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Response to review by anonymous referee 1.

We thank the referee for comments on the manuscript. Here we detail the response to the questions raised and have made the corresponding in the manuscript.

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

R1.1) 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.

RESPONSE: Ultrafine particles do indeed show an anti-correlation with the tide as is mentioned in the manuscript. This can be seen clearly in figure 2c, where none of the particle burst events are observed at high tide. We think the referee is referring to figure 3, which shows larger particles (diameter > 30 nm) during high tide. These could result from anthropogenic emissions and not due to iodine chemistry. Back trajectories for these periods were studied but did not offer any further insight to the appearance of ultrafine particles (3-9 nm) during low tide and hence have not been detailed in the paper.

R1.2) 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.

RESPONSE: The I2/I ratio is sensitive to the height of the measurement as the referee correctly points out. A decrease of 0.5 m to the apparent measurement height would result in an increase in the ratio by approx. 30%, whereas an increase in the height by the same amount would result a decrease of the ratio by approx. 15%. However, such an effect would show dependence on wind speed, which was not observed. This is now mentioned in the manuscript (Line 351).

R1.3) 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?

RESPONSE: A presence of such a reaction, although unlikely, has large impacts on the strength of the iodine source. This has already been presented in the manuscript as scenario 5, and the source strength necessary to reproduce the observations is $\sim$4.5 times the source without any extra loss of I atoms. (Line 323)

R1.4) 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)?

RESPONSE: The referee appears to have misinterpreted section 4.3 describing the impact of NOx chemistry on iodine compounds. The aim of this section is not to discuss the partitioning of iodine between the different iodine compounds, but to underline that NOx has a strong effect on the formation of IOPs. This happens because of the formation of IONO3 as a reservoir species and is clear from section 4.3 and figure 6. For studying the impact of NOx, we keep all variables, but the NOx concentrations, constant in the model runs. Figure 6 does not have a height axis but describes all observations as a particular height in the model as described in the caption.

R1.5) 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.

RESPONSE: To be more precise, the ratio of sensitivities remained within 4% of the averaged value for a single lamp under the same settings of pressure, temperature and position of the collection and collimating optics, over a period of 20 days, and within 20% for 4 different lamps of the same batch. During the campaign, first symptoms of lamp ageing (dependence on housing temperature and lower background scatter signal) where observed the 6th of May, and therefore only data until the 5th of May is considered. The absence of I and I2 signal the 4th and 5th of May, when particle bursts were still observed, could have been in part caused by a decrease of sensitivity to both I and I2 due to lamp ageing, although these two days there were no exposed algae beds in the vicinity of the detector. Further details are now incorporated into the manuscript (Line 496).

Minor Points

-R1.6) 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?

RESPONSE: A comparison between tide heights to previous studies is now included (Line 80). I2 and I were observed conclusively over the detection limit only on 4 days and 1 night. The figure also indicates this.

-R1.7) 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.

RESPONSE: Details of the NOx monitor are included (Line 141). The instruments were indeed co-located. This has now been made clear in the manuscript (Line 139).

R1.8) Wind direction was not *always* within 30' of North, as inspection of Figure 2 shows.

RESPONSE: Changed to 'mostly'.

R1.9) 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.

RESPONSE: The model was in steady state before the injection of the iodine species (Line 263). It was noticed that iodine chemistry is most sensitive to the two parameters stated in the manuscript and hence the effect of the other input parameters, which are not determining, can be excluded to focus on the evolution of iodine species.

R1.10) 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".

RESPONSE: The photolysis is not just assumed to be divided by a factor of 2. A description of the calculation of the photolysis rates is detailed in the model description paper which is cited in the manuscript (Saiz-Lopez et al., 2008, ACP). However the referee is right in assuming that the model does not consider patchy skies, which is now made clear (Line 289).

R1.11) p.27239 clarify that correlations relate to observed not modelled quantities

RESPONSE: No, they do refer to measurements. We do not model particles in the study.

R1.12) 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".

RESPONSE: Changed

R1.13) Figure 5 caption "scenarios"

RESPONSE: We do not think this is necessary.

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