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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 comment by R. Saunders

We thank R. Saunders for his comments on the manuscript. Presented here are detailed responses and changes are made accordingly in the revised manuscript.

This paper reports some very interesting new measurements of iodine-containing gas-phase and aerosol species at a previously unexplored coastal site in Spain. The reported correlations between the measurements are complex but the different modelling scenarios do go some way to explain the observed trends.

R3.1) The main comment/observation/question I would like to direct to the authors is the relatively low total ultrafine particle numbers (1-2 $\times$ 10ˆ4 cmˆ(-3)) detected during 'bursts'. Although clearly significantly higher than the background levels reported, such levels are 1-2 orders of magnitude smaller than those reported during similar daytime low-tide events at Mace Head, Ireland and at Roscoff, Brittany. Firstly, I think that this point should be clearly stated in the paper, particularly as a quantitative comparison is made for the I2 and I atom mixing ratios. Are the lower numbers likely to be a reflection of the relative sizes/density/ages of the seaweed beds, ambient NOx levels, meteorological conditions, geographical considerations, or a combination of these or other factors? Apologies if I have not fully understood the modelling/analysis section and the authors infer that the lower particle numbers are related to the reported anomalously high levels of I2 and I2/I (is this the case?), but I would suggest that a more detailed comparison of such factors from Mace Head (or Roscoff) and this 'new' site would make the picture clearer for the reader.

RESPONSE: The ultrafine particle concentrations observed at Galicia were indeed much lower than previous reports from Mace Head and Roscoff. This has now been stated clearly in the manuscript (Line 57, line 228). We think the reason behind the low particle concentrations at Galicia could be the size of the seaweed bed. For example, the exposed seaweed was observable in a bed of only 40 m in width, where as in Roscoff, this bed was about 1 km wide. The other reason could be the distance of the seaweed beds responsible for the particles from the measurement site, which could result in the air mass reaching the measurement site before or after the ultrafine particle number peaks. The high I2/I ratio and the I2 and I concentrations place a constraint as to when the air mass containing the particles could arrive at the measurement site, as explained in scenario 4 and 5 (Line 426).

R3.2) Reference is also made to the lack of a typical 'banana' particle growth plot as observed in other studies but no further discussion is made of this point. It would be fruitful (sorry, couldn't resist the pun) if some discussion was included to provide insight

into why non-banana type growth might occur at this coastal site and not others, which presumably accounts for the lower particle growth rates at this site?

RESPONSE: We think that the absence of a classic banana growth curve is related to the earlier question. It could indicate that the air mass reaching the measurement site does not contain the 'fully grown' particles, in which iodine has been injected a long time before in the air mass. Other studies in the past have detailed scenarios under which banana growth curves should be observed and are now cited in the manuscript. However, lower growth rates than Roscoff and Mace Head cannot be ruled out. (Line 436)

R3.3) My final comment relates to the authors suggestion of a 'mystery' organic species/group which could account for removal of iodine. Having made the sug- gestion, a fairly thorough job of ruling things out is done but there is only a vague, generalised comment on what it could be. One possible candidate group which I would flag up are the benzene-1,2 and -1,3 diols (catechol and resorcinol respectively) which have direct anthropogenic (industrial/combustion) sources and are also oxidation by-products of PAHs. These species are water soluble and react readily through aromatic substitution with iodine (Willard and Wooten, 1950). There is essentially no atmospheric abundance data available for these species but it's unlikely that 1-2 ppbv mixing ratios suggested in the modelling analysis are realistic. However, the aromatic 1,2 diol group has been identified in humic-like substances (HULIS) which constitute an important fraction of secondary organic aerosol or SOA (Graber and Rudich, 2003; Ofner et al., 2010). It is this functional group which is thought to be responsible for the fixing of iodine in natural waters to form non-volatile iodine-containing organics (e.g. Francois, 1987; Reiller et al., 2006), and so could also play a role in the uptake of iodine by SOA with a HULIS component?

It might be stretching things a bit but I note that the measurement period was only a few weeks after the severe storm ('Xynthia') hit NW Spain causing reported damage to the local eucalyptus and pine forests which are used for timber and pulp production. The

combustion or pulping of these tree types are known to result in the release of organics including HULIS (e.g. Gonçalves et al., 2010). If there was any increased clearance of storm-damaged trees by burning or pulping in the period between the storm and the measurements, this may have increased background levels of secondary organics in the gas and aerosol phases, and also that of background primary organic aerosol (POA) in fine and coarse modes i.e. at sizes beyond those measured. Both HULIS-containing POA and SOA could play a possible role as a sink for iodine? How does the ultrafine background level of 1700 cm^(−3) compare with those reported at Mace Head/Roscoff?

RESPONSE: The exact type of the species X is not easy to determine and all the suggestions made in the above comment could be valid options, but there are no laboratory studies available in the literature to substantiate these hypothetical reactions. We have now expanded the section involving the species X by including some of the above hypothesised pathways, but think that this is pure speculation and hence want to limit our discussion on the possible reactions (Line 337).

We had not considered the effect of the storm on the increase in the background aerosols. However, the total aerosol surface area observed at Galicia was not very different from observations at Roscoff and hence it would be surprising if this was a major factor.

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