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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Direct evidence for coastal iodine particles from Laminaria macroalgae - linkage to emissions of molecular iodine" *by* G. McFiggans et al.

G. McFiggans et al.

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The authors would like to thank Dr Malin for her constructive comment and alternative perspective on the paper. The issue of the ozone concentrations used in the experiments is not so clear as it should be in the manuscript.

Firstly, it is rightly pointed out that the control of ozone levels is indeed difficult in the exposure experiments. In the experiments where ozone was directly flowed into the primary reactor, the steady-state mixing ratio of ozone for a given lamp exposure and flow rate in an empty primary reactor was initially significantly lower on addition of a Laminaria specimen; for example, only a few ppb measured at outlet compared with 200 ppb for an empty reactor. The mixing ratio in the reactor reached this temporary steady state after some 10 minutes depending on flow rate, as did the measured par-

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ticle size distribution. The particle production diminished after several tens of minutes exposure to such high ozone levels. This would be entirely consistent with the triggering of cell death apart from the fact that at least partial (and often full) recovery of the particle production was observed after switching off the ozone lamp for several hours. For example, switching off the lamp after an afternoon experiment and re-exposing the specimen to ozone the next morning led to particle production on the same scale as the initial exposure the previous afternoon. Often, high ozone exposure for even 12 hours would not prevent recovery. This was all the more surprising since the macroalgae had not been returned to water in the intervening period. The reported ozone levels are those after the reactor once particle production has ceased entirely. As stated in the manuscript, the results presented are those from fresh or fully recovered specimens, meaning that the particle properties illustrated in the table and figures 2 to 5 are those produced during the initial exposure stage of the experiment at the steady state reduced ozone measured at the output. Single intact specimens were used (though cut strips of the fronds have been used with similar effect). The above points are clarified in the amended script.

More importantly, it was not necessary to expose the specimen to ozone to initiate particle formation. Similar levels of particle production were observed flowing the ozone into the secondary reactor, the Laminaria only exposed to zero air. The comparable response indicates that the particle precursor is not only released as a result of ozone exposure but that ozone is required in the particle formation mechanism itself.

Concerning the abstract statement that ultrafine iodine-containing particles are produced by intertidal macroalgae exposed to ambient levels of ozoneŤ: this is an accurate statement, but not fully drawn out in the original script. It is mentioned that Şa range of ozone mixing ratios from zero to around 300 parts per billion (ppbv) was used for the experiments, and in the table caption ...In many cases particle production was observed at very much lower mixing ratios (a few tens of ppb), though this was not always repeatable, being dependent on the number of previous exposures, light levels

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etc... The higher mixing ratios are used to extend the breadth of the produced distribution to enable measurement by the wide range of instrumentation. A more extensive set of experiments with controllable light levels and better flow control is planned to enable greater repeatability. In any case, particle production was observed at mixing ratios of a few tens of ppb.

The confusion between the reported ozone mixing ratios in the table and in figure 2 is due to the sequence of the experimental programme. Figure 2 shows results from the original in situ experiments at Mace Head when an ozone monitor was not continuously employed: control of the concentration was done by manually controlling the voltage on a PenRay lamp. The duration and intensity of lamp exposure was constant between experiments, but flow control was better in the experiments at UMIST and a bespoke ozone generator, more suitable flow design and continuous use of a monitor allowed better ozone control and measurement. The mixing ratio in the Mace Head experiments could not be more accurately reported than ...around 300 ppb... Table 1 reports the results from the UMIST experiments. Unfortunately, not all the sampling instrumentation available at Mace Head was available at UMIST due to fieldwork commitments, so size distributions for all the conditions in table 1 are not available. The variability indicated by the error bars in figure 2 is entirely legible in the original documents and on screen in the online version. I am not sure why this cannot be printed and perhaps this can be answered at the ACP office. Plotting all curves on the same figure is confusing, but I have such a figure if anybody would find it useful.

Finally, the particle burst phenomenon is only observed at low tide when Laminariales are fully exposed to the air. I agree entirely with the referee and Dr Malin that molecular iodine (and indeed HOI) will likely rapidly react with DOM when the kelps are submerged and that they are only fully exposed infrequently. This is borne out by the lack of particles formed in the experiments exposing submerged specimens to ozone. The vast majority of iodine emitted by the kelp beds will therefore not be available to the atmosphere as molecular iodine. However, the coastal low tide atmospheric molecular

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iodine that is observed is the source of the new ultrafine particles, even if itŠs not the major fate of the iodine emitted from Laminaria the most of the time.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 939, 2004.