

***Interactive comment on “Iodine speciation in rain, snow and aerosols and possible transfer of organically bound iodine species from aerosol to droplet phases” by B. S. Gilfedder et al.***

**B. S. Gilfedder et al.**

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We would like thank Roland von Glasow for the time taken to review our paper and particularly for his astute comments and suggestions that have significantly improved the previous version of this manuscript. We have attempted to address these comments below.

Dr. R. Von Glasow: Title: I'm not sure if the second part of the title is adequately discussed in the paper. I suggest to either to do this or to drop the second part of the title.

Answer: This suggestion has been accepted with the new title shortened to 'Iodine speciation in rain, snow and aerosol particles'. We only included the second part of

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the title to highlight the fact that the unknown IC-ICP-MS peaks observed earlier (e.g. Gilfedder et al 2007) in rain and snow samples were most likely derived from aerosols rather than uptake from the gas phase. However, Dr. von Glasow is correct that this is unnecessary and so the title has been modified accordingly.

Dr. R. Von Glasow: p. 7978, l. 22: Maybe add that this indicates either a long lifetime of these components or a very rapid cycling.

Answer: Yes this is a possibility for the unidentified organically bound iodine species. As yet we are unsure which is correct (or even what these iodine species are); rapid production and loss so that a pseudo steady state is obtained, or if these species are simply resistant to decomposition. Both of these possibilities have been added to the revised abstract as suggested.

Dr. R. Von Glasow: This has already been suggested a few years ago

Answer: In the body of the manuscript we now fully reference the work of Baker (2005) with regards to the reaction between organic matter and HOI, however this is probably inappropriate in the abstract. Therefore, we have left the reference out of the abstract, but we have highlighted the fact in the discussion that Baker (2005) was the first to suggest this reaction for iodination of organics in aerosols.

Dr. R. Von Glasow: For iodine this mechanism is not important to deplete particles compared to seawater

Answer: Dr. R. Von Glasow is correct that field measurements have shown iodine accumulation in particles rather than depletion and therefore degassing of iodine following oxidation of iodide should not be an important mechanism for iodine loss (as it is for bromine). However, given the rapid kinetics of iodide oxidation (diffusion controlled) iodide should be released to the gas phase very rapidly after formation, whereas iodine accumulation in aerosol is facilitated by iodine oxides/iodo-organics. Indeed, earlier modeling study by McFiggans et al., (2000) required iodine release from aerosols to

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maintain observed IO levels in the remote marine boundary layer. Therefore we have modified the manuscript to reflect that it is halide (I-/Br-) ions that should be rapidly released from the aerosol particles during ageing and acidification.

Dr. R. Von Glasow: p. 7980, l. 2/3: This is a finding that has been reported many times before, so I suggest to add "e.g." before the references.

Answer: this change has been made and one or two additional references have been added.

Dr. R. Von Glasow: Please explain in more detail how the snow sampling was made. Was it surface snow or taken from a snow pit? What time of year (or better: what date) where the samples taken?

Answer: The snow sampling has now been described in more detail, including additional information such as sampling depth (as relevant to the snow pit samples taken from Greenland) and month of sampling. We considered putting all sampling dates in, however this would have become to overbearing on the flow of the paper (for example, there were over 16 individual snow sampling dates from Lake Constance over a period of 2 years). However the critical information of the month and year has been included. Also, the samples from Mt. Taranaki were taken in the middle of august and were the last remnants of the winter snow. These samples were quite old and could have been subject to numerous processes (particularly partial melting and recrystallisation) that could have affected their chemistry. The TSI and iodide concentrations in these samples were also approaching the detection limit, as shown by the chromatogram in Figure 9 and Table 3. Therefore it is difficult to draw strong conclusions from these data, and we only included it as there is very little snow data from the southern hemisphere. These points have been highlighted in the revised version of the manuscript.

Dr. R. Von Glasow: p. 7984, l. 7: You refer to "results" but it is not clear for the reader where, or rather if, they are discussed. Please add.

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Answer: Rather than 'results' we should have more correctly worded this phrase to read 'calculations'. This statistical exercise was aimed at testing if there was any significant effect (with known degree of uncertainty) of day/night processes on iodine speciation. The significant diurnal differences observed for iodide and possible explanations have been fully discussed in the discussion section (e.g. p7988 l. 25).

Dr. R. Von Glasow: p. 7984, l. 26: Change "minima" to "minimum".

Answer: Change made

Dr. R. Von Glasow p. 7986, l. 28: Doesn't this suggest that there might be either additional, terrestrial sources for iodine (as other particulate marine tracers like Na+ do show a strong decrease with distance from the coast) or, possibly more likely, that there is a very active recycling of iodine species between the gas and aerosol phases that increases the lifetime of atmospheric iodine over the lifetime of aerosol particles? We have found this in our model studies for bromine and chlorine (e.g. Pechtl and von Glasow, 2007) and it would be perceivable that this is happening for iodine as well. In order to test this "multiphase iodine recycling" in a numerical model more kinetic information about organic iodine species is required. Possibly such a recycling - if indeed occurring- could involve photochemical reactions as you list on p. 7988. As you state yourself (top of p. 7991), your sampling might be inadequate to resolve if there is either a day-night difference in the gas-aerosol partitioning or if even faster (light-dependent?) recycling reactions is occurring. If there is indeed light-dependent recycling between the gas and aerosol phase going on, you might "freeze" the chemical composition during sampling when you store the sample dark. Maybe you could add some discussion on this point.

Answer: These are all very interesting and important points raised by Dr. Von Glasow and certainly warrant future studies on iodine speciation and the effect of photolytic processes on aerosol/gas phase partitioning. Unfortunately we don't have definite answers (i.e. backed up by lab/field data) for many of the questions raised here, and

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thus we must speculate a little more on possible reaction mechanisms. We hope the reviewers can forgive the rather large degree of speculation in the discussion section of this paper, which is simply a function of how little we know about organically bound iodine. To address the points raised by Dr von Glasow, a significant terrestrial iodine flux is a possible solution for the lack of any strong iodine concentration gradient between the ocean and continental areas. There have been a number of works recently that have found some terrestrial emissions of volatile iodine compounds (mostly focused on methyl iodide), for example, Manley et al., (2007), Sive et al., (2007) and Keppler et al., (2000). The question is if these fluxes are large enough to negate the iodine losses due to progressive washout. Also, due to CH<sub>3</sub>I's relatively long half life (compared to other volatile iodine compounds) it will be diluted over most of the troposphere and distributed over large distances. However, until more is known about the terrestrial sources, and absolute fluxes, we have included this as a possible explanation for the lack of any strong iodine gradient. This leaves the possibility for rapid cycling between gas/particle phases. At the current state of the science I believe this is probably the most likely answer, that is, that there is some kind of dynamic-equilibrium between gas phase and droplet/particle phase that is established during transport. Indeed, it is interesting to compare the gaseous iodine concentrations to aerosol iodine concentrations in some older studies that measured volatile and particulate iodine simultaneously e.g. Rancher and Kritz, (1980), Moyers and Duce, (1972) and Duce et al., (1965). All of these authors found significantly higher iodine concentrations in the gas phase compared to the particulate phase. Moyers and Duce, (1972) even found good correlations between gaseous iodine concentrations and particulate iodine concentrations, suggesting that there is indeed a role for cycling between gas and particle phases. Thus if organic material could bind insoluble reactive iodine species such as I<sub>2</sub>, then due to concentration gradients more iodine could be progressively taken up out of the gas phase. Again, this would depend on kinetic factors as well, such as the rate of iodine binding to organic material, and so we must conclude that more work is needed in this area. We have added a brief statement in the revised manuscript of

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possible particle-gas phase cycling for maintaining the iodine levels in droplets during transport. However we have not elaborated on this point to a large extent due to the already rather speculative nature of the paper.

In response to the comment 'If there is indeed light-dependent recycling between the gas and aerosol phase going on, you might "freeze" the chemical composition during sampling when you store the sample dark. Maybe you could add some discussion on this point'.

We hope that we do indeed freeze the speciation in the samples after sampling, as we aim to measure the speciation as it is occurring in the atmosphere rather than post sampling changes. Also note that the samples were taken over at least a few hours and up to 12 hour periods, and thus the speciation that we present is in fact an average over this sampling time. We also believe that the sampling method would be able to determine day/night differences (if taken on sunny days). The largest problem lies with the extraction procedure in that we only measured the soluble iodine. For a robust test of day-night concentration/speciation differences we need to measure total iodine, soluble iodine and the inorganic iodine species. The problem with measuring total iodine is that it requires access to nuclear reactor for NAA analysis. We have tried to commission such analysis as part of a separate project but the results were unreliable (about 50-100% too high, and only had a detection limit of 1 mg/kg) and thus we are currently working on modifying the method of Gilfedder et al., (2007) for total iodine quantification in aerosol samples. We hope to clarify such obscurities in the near future.

Dr. R. Von Glasow p. 7990, R6: This had already been suggested by Baker, 2005.

Answer: as stated above the paper by Baker, 2005 as now been referenced as the first suggesting the nucleophilic HOI + organic reaction.

Dr. R. Von Glasow p. 7990, I. 23: Are you really referring to R4 here - how is R4 dependent on the organic substrate?

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Answer: this was a mistake from an earlier version of the manuscript (we have added and deleted many equations over the course of this manuscript). We should have written (R6).

Dr. R. Von Glasow p. 7991, l. 7-9: I assume that this implies that your "total iodine", as reported in text and tables, is "total soluble iodine". If this is the case, please make this more explicit in the text and captions to the tables. Are there any indications for an appreciable amount of insoluble iodine? Maybe you can refer to studies by Duce et al that used neutron activation to measure the "real" total iodine to put your "total (soluble) iodine" numbers into perspective.

Answer: Yes indeed we did only measure 'total water soluble iodine' rather than total iodine in the aerosol filters. We did not adapt the terminology of Baker for total soluble iodine abbreviated as TSI as TSI inc. is a relatively well known manufacturer of atmospheric analytical equipment, which may lead to confusion. However, as TSI and also SOI are more accurate and other workers are tending to prefer these abbreviations we have adopted this terminology in the revised version of the manuscript.

The second part of the question 'Are there any indications for an appreciable amount of insoluble iodine?' is more difficult to answer. I have checked through the older literature for real total iodine concentrations as analyzed by NAA (e.g. (Duce et al., 1965; Duce et al., 1963; Winchester and Duce, 1967; Seto and Duce, 1972; Moyers and Duce, 1972; Rancher and Kritz, 1980). The median TSI in our study was 1.5-6 times higher than total iodine in these works (note that in the revised version of the paper we have summed the TSI, SOI iodide and iodate concentrations over all impactor stages for comparison with literature levels and also for presentation of basic statistics e.g. median etc). However, a quantitative comparison between our data and these older studies presents three major problems:

1) In some of these studies the aerosol size distribution sampled was not stated (e.g. (Rancher and Kritz, 1980). This means that we cannot know which aerosol classes

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were included in the sampling and analysis. Our sampling was between 0.085 and 10  $\mu\text{m}$  and for a quantitative comparison we require the other studies to sample aerosols in this size range. 2)When the aerosol size range is given as in most of the papers by Duce and co workers the lower limit of aerosol sampling was 0.3  $\mu\text{m}$ , again not in our range. As the works of Duce et al find the highest concentrations in their smallest size classes this could be a reason for the discrepancy between the results. Also related to size class problems is the definition of the aerosol diameter cutoff size. Some authors prefer to use the size at which 100 % of the aerosols are retained on the filter, whereas others use 50 %. This obscures comparisons between our and other studies. 3)The locations of the other records are not in the vicinity of our sampling location (mostly in the Pacific, tropical Atlantic or Arctic). As such, it is difficult to compare between areas with such differing amounts of biological activity. We are confident that the concentrations of TSI and SOI measured in our samples is accurate, as aerosol samples from the MAP campaign have been measured by ICP-MS both in our lab and in the Mainz lab (Mainz speciation by GE-ICP-MS; some of the results of the Mainz samples were presented at the Nucleation and Atmospheric Aerosols 17th International Conference, Galway, Ireland, 2007 and can be found in the proceeding of that conference under 'Iodine Speciation in Marine Boundary Layer' by Senchao Lai). Moreover, the aerosol samples were taken with two different types of impactors, the Berner impactor and the virtual impactor (PM 2.5). While it was not possible to analyse exactly the same samples due to limited sample volume, the iodine concentrations measured in both labs were in the same range. This leaves the question of why our results are so much higher than found previously. The most likely answer is that biological productivity in the Atlantic (as observed by SEAWIFS chlorophyll) during MAP 2006 was very high. A second possibility is a costal influence. The costal influence hypothesis is negated, however, by the offshore Celtic Explorer data, which did not differ significantly to the iodine levels observed at Mace Head. In summery, we are currently unsure why the concentrations in our samples are so much higher than previous measurements and direct analysis of total iodine in aerosol filter samples is required for a comparison

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between SOI and non soluble organically bound iodine concentrations. Dr. R. Von Glasow p. 7992, l. 6-8: 'The composition of nucleation clusters should not expected to be the same as those of the larger particles that you sampled' Answer: It is true that many other compounds and molecules would have been added our aerosol samples since iodine induced nucleation. However, current knowledge of aqueous phase iodine chemistry predicts that once iodine oxide (iodate) is formed it should not react further with the other molecules in the aerosols and therefore the original oxides should be preserved. However, due to the very low absolute concentrations of iodine in the nucleating clusters (i.e. 3 nm particles contain very little absolute iodine) there is no way that we can detect these oxides, and most of the iodine must come from gas phase deposition during aerosol growth. According to the modeling work of Pechtl et al., (2007), which is currently the most comprehensive treatment of atmospheric iodine chemistry, the vast majority of iodine should be taken up as HIO<sub>3</sub>. Therefore in the revised conclusion of the manuscript we have stated that iodine should be taken up as iodine oxides, but that we have not found any large concentrations of oxides in our aerosol and precipitation samples.

Dr. R. Von Glasow; Spelling of Mt. Egmont

Answer: Thank you pointing out this rather embarrassing spelling error. Indeed we did not mean a mountain of eggs, and my grandparents in Taranaki would be rather offended if they had seen this mistake. The correct spelling has now been added to the manuscript (both Maori and Anglo-Saxon).

Dr. R. Von Glasow: Table 3: Isn't it surprising that in the Mt Egmont sample only 10% organic iodine was found whereas in Summit snow - even at 1m snow depth - it was a lot higher? Could you speculate about possible differences? Is the age of the snow comparable, what about post-depositional effects incl. snow photochemistry or lack thereof if deposition in winter?

Answer: We have responded to most of these comments above. But also note that the

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IC column used for the Greenland snow samples was brand-new and so in very good condition, which is why the peaks were less noisy than observed in the snow samples from Mt. Taranaki at similar concentrations. Future studies are needed to investigate the role of snow photochemistry on iodine speciation, but could be an important factor controlling iodine concentrations in snow deposits.

Dr. R. Von Glasow: Figure 2: Caption: Change "doted" to "dotted" or rather "dashed".

Answer: The changes have been made as well as the suggested corrections to references have also been made.

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