

***Interactive comment on “Iodine speciation and cycling in limnic systems: observations from a humic rich headwater lake (Mummelsee)” by B. S. Gilfedder et al.***

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

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Reply to reviewer 1:

First of all we would like apologize for the lengthy delay of our response. Secondly we would like to thank the reviewer for the constructive comments on the manuscript, which improved the previous version. We have attempted to address the comments below.

1.0 Reviewer 1: Although superlatives are used to express the significance of examining iodine speciation in freshwater systems, the reader is not given a reason for this scientific pursuit.

1. 1 Answer: We have now included a section at the start of both the abstract and the manuscript outlining the importance of iodine as a trace element in biogeochemical cycles. We highlight the fact that iodine is a vital nutrient for all mammals and despite the efforts of the WHO up to 2 billion people currently have insufficient iodine in their diet. We also point out that there are a number of radioactive iodine isotopes formed during nuclear fission, and that the mobility and cycling of these isotopes can perhaps be studied using natural stable  $^{127}\text{I}$  as a surrogate.

2. 0 Reviewer 1: The most defensible conclusion, regarding the building evidence for the prevalence of organo-I in this (and possibly other) freshwater systems, needs to be "front and center".

2.1 Answer: We agree with the reviewers interpretation and have attempted to address this point by (1) reorganizing some parts of the paper, particularly moving the organically bound iodine section in the discussion to the start of the discussion and the inorganic species more to the end, (2) brought the role of biology in the iodination of organics to the forefront. We have also highlighted the fact that biological iodination may be direct (occurring within the organism) and indirect (e.g. oxidizing iodide to  $\text{I}_2$ , by for example an exoenzyme,  $\text{I}_2$  then reacts with humic matter forming C-I bonds in an abiotic reaction). (3) suggested that most of the iodination is microbiologically driven based on literature and the observation that there is a rapid formation of organo-I when the lake is frozen over and oxygen is reintroduced into the anoxic hypolimnion. At this time there would have been no light under the thick layer of ice and snow and therefore we can rule out a significant contribution from photosynthetic organisms. (4) as the reviewer suggests, the re-release of iodide into the lake is also probably biologically driven. This has now been added to the manuscript, and backed up with I/C ratios (as suggested by the second reviewer). The I/C ratios display 6 times lower level in the sediment compared to the lake water, and are very variable in the top part of the core suggesting preferential deiodination of the organic substrate during sediment mineralisation.

3.0 Reviewer 1: Can we see a (propagated) error on the organic I concentrations (at least one example) on Fig. 3a?

3.1 Answer: We have now added error bars in the first depth profile for all iodine species including the propagated error for organically bound iodine. This was only done to the first profile to avoid the graphs becoming overcrowded. In this approach the reader can still get a feel for the error, but at the same time the temporal trends are still clear.

4.0 Reviewer 1: It would have been interesting to see DOC (and possibly POC) analyses for the water column. It might also have been interesting to look at filtered and unfiltered samples for I measurements to examine whether or not POI is present.

4.1 Answer: Yes this would have been interesting and also useful in helping with interpretation. We did in fact measure a few depth profiles (3) for DOC, however due to sample age and analytical problems we were not able to produce reliable data for more dates. These three profiles were used to calculate the I/C ratio mentioned above. Particulate iodine would have also been very interesting. We did try this once, however a particle blocked the capillary in the ICP-MS nebuliser (which is rather expensive), and therefore we did not attempt any more unfiltered samples. We also attempted to install a sediment trap in the lake, however the line to the float was cut/undone by a tourist, and therefore we were not able to sample any falling sediment.

5.0 Reviewer 1: The overall organization does not flow well.

5.1 Answer: As mentioned above, and as recommended by the reviewer, we have brought the organically bound iodine section further forward in the discussion and highlighted the role of biological activity in the Mummelsee's iodine cycle. The discussion of trends in the sediment core has been removed as recommended, as more data is needed to backup the speculations made in the previous version of the manuscript.

6.0 Reviewer 1: p. 36: Discuss the reason(s) for the prevalence of iodate in the inflow water.

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6.1 Answer: This is not such an easy question to answer, as we are currently unsure why iodate dominates inorganic speciation in the spring. Rain and snow from the Mummelsee consistently has very low iodate, and therefore it can not be a direct precipitation signal. However, it is also difficult to oxidise iodide to iodate in the soils (due to high organic matter content) or ground water. Perhaps there is a small amount of leaching of iodate from the bedrock, however due the already speculative nature of the paper we have left this out of the final version. It is hoped that we can conduct future studies to try to elucidate this processes.

7.0 Reviewer 1: p. 37, lines 9, 10: explain this point in greater detail or leave it out altogether if no insight is to be gained in the observed pattern.

7.1 Answer: As we do not know the reason for this spike in iodine concentrations we have left the sentence out as recommended.

8.0 Reviewer 1: p. 40 The work of Amachi, 2005 is not properly characterized (i.e., not simple 'absorption' of iodide)

8.1 Answer: We thank the reviewer for pointing out this misinterpretation. The reference has been corrected and we have added that it is active uptake, rather than passive absorption as seen by enrichment factors  $>6000$  times.

9.0 Reviewer 1: Grammar, spelling, readability: Need more paragraph breaks

9.1 Answer: we would like to think that with the new structure the readability has increased significantly. We have also adapted the grammatical/spelling changes suggested by the reviewer where appropriate. In some cases the offending sentences have been removed during the revision.

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