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Biogeosciences Discussions

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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Response to Reviewer 2

First of all we would like to thank the second reviewer for the informative comments on our manuscript that significantly improved the previous version. We would also like to apologies for the length of time it has taken us to finalise the revised version. Answers and comments to each point raised by the reviewer are given in detail below.

Reviewer 2: Pick a focus, elaborate more deeply on the chosen focus and consult a professional linguist.

Answer: We have significantly revised the previous version of the manuscript, such as

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highlighting the importance of biological influences on iodine cycling and speciation in the lake. We have moved the organically bound iodine discussion to the start of the discussion to highlight that nearly all of the iodine in the lake is bound to humic material.

Reviewer 2: Please provide scientific name of Norway spruce

Answer: We have now added this to the manuscript

Reviewer 2: Is the pH of the lake really a result of acidification and not due to the land use (i.e. Norway spruce?). It seems odd if the bedrock is acid with poor buffering capacity and the catchment is dominated by Norway spruce that the pH should be 6-7, something is odd in the description.

Answer: we mention in the overview of the study site that the lake had previously been affected by acid deposition. Acid rain was historically a very significant problem in the Black Forest and is relatively well documented. For example, Thies (1990), found that for the Mummelsee the pH had been lowered due to acid deposition rather than land use practices. While the reviewer is correct that a catchment planted with Norway spruce should result in lower pH, our measurements found that the pH was between 6-7. Excluding errors with the pH equipment, it may be that there is more buffering capacity in the catchment than previously thought. We have now made clear in the site overview section that lowering of pH due to acid deposition was a historic problem, and that the 6-7 pH values were recorded by us.

Reviewer 2: Please provide age of the forest and previous land-use pattern

Answer: the forest is a managed forest with selective logging. This has now been added to the site overview section. The actual age of the forest stand is unknown.

Reviewer 2: Figure 1 is unclear. Is this the topography of the catchment or the lake bottom?

Answer: This is the bathymetry of the lake. This has now been made clear in the caption to the figure. We have also added the approximate sampling location to the

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lake map.

Reviewer 2: 1.1. does not say anything about the methods, please elaborate more in detail. For example: Where in the lake were the samples collected, at how many locations, with what type of equipment, how much water was collected and how were the samples stored until analysis? Oxygen "standard techniques" please provide details of probe etc Sediment corer. Please provide details, size, origin, material

Answer: We have now enlarged the sampling and analytical section to include the points mentioned by the reviewer. During the reformatting of the paper we have also restructured the methods so that there is now an initial section on the study site, followed by a new section on the water sampling and analysis and finally a section on the sediment sampling and analysis.

Reviewer 2: How did you certify only minimal disturbance to the core?

Answer: We visually checked the core during collection. There did not appear to be any disturbance, such as re-suspension into the overlying water or mixing within the core. However, as we have no other evidence for lack of disturbance other than visual observations this statement has been removed from the manuscript.

Reviewer 2: Figure 1. Change color coding. Difficult to see difference between 0 m and rain.

Answer: We have modified the colours in this figure so that the different chromatograms can be distinguished.

Reviewer 2: Why does I- chromatograph at so different times?

Answer: the exact retention time of iodine species in the ion chromatograph is dependent on a number of factors such as age of the exchange column, room temperature and eluent flow rate and concentration. The chromatograms presented in Figure 2 are from a number of different dates to highlight differences in iodine speciation during different redox conditions. Therefore, the exact conditions in the column for each chro-

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matogram (most affected by column age) were slightly different for between samples resulting in different retention times. This has how been added to the caption of figure 2.

Reviewer 2: Figure 3. The graph is too much. Compile the information somehow.

Answer: We have attempted to make this graph more readable without loosing vital information. Some of the element profiles of less importance (i.e. Si, Al, Mn) have been relegated to the supplementary material with a link in the appropriate place. This has allowed us to enlarge the iodine speciation data. We have left the Fe data in the paper as it represents redox changes in the lake and is used in the interpretation of results.

Reviewer 2: You could plot the iodine-to-carbon ratio for the sediment column. This would help your discussion on organo-iodine

Answer: the reviewer is thanked for this tip, indeed when we plot the I/C ratio in the sediment it is immediately obvious that the top part of the core is actively involved in sediment mineralization and deiodination with large variations. In contrast in the deeper depth the I/C ratio tends to a constant value, suggesting that deiodination has ceased or at least is progressing at the same rate as carbon mineralization. It is also interesting to compare the I/C ratio in the sediment to the overlying water column. It was found that the I/C ratio in the sediment is about 6 times lower than in the water column, which we interpret as further evidence of the iodine flux into the hypolimnion originating from mineralization of organic matter at the sediment-water interface. These points have been added to the revised version of the paper.

Reviewer 2: You several times say "interestingly"; but it is not obvious why the statement that follows is particularly interesting.

Answer: All reference to "interestingly" have now been removed except for once case, where we observe no organo-I in the highly anoxic bottom waters during the May 2006 turnover. We find this interesting, as all other samples over the entire year contained ˜80 % or more organically bound iodine.

Reviewer 2: When discussing whether or not the organo-iodine in the sediment originates from the water column, it would help with data on iodine-to-carbon ratio in the water column and relate this to the same in the sediment core.

Answer: This has mostly been covered above. In short, we believe that the lower I/C ratio in the sediments compared to the overlying water column is evidence for mineralization of the sediments and preferential iodine release during this process.

Reviewer 2: You claim that speciation gives a more holistic understanding of the system but you fail to explain in what sense this is true (i.e. simply put: that the whole is more than the sum of the parts)

Answer: We have now included an explanation as to why speciation is vital to obtain a better understanding of the iodine cycle. In particular, each iodine species behaves differently in the environment, and that iodine’s mobility and bioavailability is not fully captured by only analyzing total iodine.

Reviewer 2: Are there no studies of iodination in freshwater or by freshwater organisms? If not, clarify the challenges of extrapolating from marine environments.

Answer: We are only aware of the study by Rädlinger and Heumann, (2000), who studied iodide conversion to organo-I in waste waters. Therefore the only option is to draw from marine analogs until more is known about biological influence on iodine speciation in fresh waters.

Reviewer 2: Line 15 You write: "It is suggested that the negative flux during November is due to major mortalities in lake biology due to the cooling of the lake water associated with the oncoming winter. The falling organic debris could then scavenge iodide from the hypolimnion." In the light of the previously forwarded arguments that iodination is driven by biological processes, it is hard to understand why the physical movement of

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"falling organic debris" would render scavenging of iodide. If the iodination is driven by organisms, the scavenging should follow either the amount or the activity of the biota.

Answer: The reviewer is correct that our previous interpretation is floored in that it is very unlikely that falling debris could physically remove iodide from the hypolimnion. We have now modified the interpretation. We believe the most likely process is that the falling organic matter (derived from mortalities related to cooling of the lake water before winter) is an ideal substrate for microorganism (e.g. bacterial) proliferation. This bacteria residing in the falling organic matter may than then take up the iodide and convert it to organo-I, or indirectly (e.g. exo-enzymatically) oxidize the iodide to I2, which subsequently can bind to the abundant humic material.

Reviewer 2: P 44. More thorough calculation on how the iodate may be explained by inflow, please

Answer: while this calculation could account for the iodate during the summer and autumn, it could not account for the rapid increase in iodate with lake turnover. Therefore it has been removed from the manuscript.

Reviewer 2: P 46, line 20 You write: "in the anion chromatograms from both the spring inflow and the lake suggests that the iodine is bound to high molecular weight, non-ionic carbonaceous species. "In my view, this supports formation of HOI and unspecific iodination of the organic matter as the underlying process. In general, it is rather fuzzy what you mean by abiological and biological formation. I would say that exo-enzymatically driven formation of HOI, followed by abiotic iodination of organic matter is a biotic process although it encompasses an abiotic step. You do not at all discuss exo-enzymatic iodination, although it is well known that many organisms are able to produce such enzymes.

Answer: In the previous version of the manuscript we considered biological production of reductants/oxidants that react with iodate/iodide to form I2/HOI with subsequent formation of organo-I as non biological. However, on the recommendation of the reviewer

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we have now changed the manuscript to include this as a biological reaction. We have also included a clear definition of this to ensure that the reader understand what we interpret as "biological" and "abiotic".

Reviewer 2: Terminology "abiological" I prefer the more widely accepted term "abiotic"

Answer: this has now been changed.

Reviewer 2: You do not really use the sediment data. I suggest you compile this information and only present what you actually use and skip the rest. The paper is overloaded as it is.

Answer: based on the comments by reviewer 1 we have removed the interpretation of the sediment data. We still include the sediment data in the results section however, as it aids with the interpretation of iodide lease back into the lake, particularly by using the I/C ratio as suggested by the reviewer.

Reviewer 2: Conclusion This is not really a conclusion, it is more a summary of the results.

Answer: this end section has now been changed to summary as suggested

Reviewer 2: "Terrestrial aquatic system" is a rather odd term.

Answer; we have now changed this to "freshwater environments"

Rädlinger, G. and Heumann, K.G., Transformation of iodide in natural and wastewater systems by fixation on humic substances, Environmental Science and Technology 34(2000), pp. 3932-3936.

Thies, H., Acidification studies at northern Black Forest cirque lakes. In: H. Lang and A. Musy, Editors, Hydrology in Mountainous Regions 1: Hydrological measurements, the water cycle, IAHS, Lausanne, Switzerland (1990).

Interactive comment on Biogeosciences Discuss., 5, 25, 2008.

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