

## ***Interactive comment on “Halogens in porewater of peat bogs – the role of peat decomposition and dissolved organic matter” by H. Biester et al.***

**H. Biester et al.**

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Final author's comments to comments of the referees

Anonymous Referee #1

Referee's comment: In sampling description, it would be interesting to know how many samples were taken at each depth and locations and on how many locations at each site. I would also like to see some error estimates (e.g. standard deviations between the samples at each depth) to be able to better estimate how significant are the deviations between different depths and different parameters. It would be important, because new sampling system was used.

We have taken only single cores and a single porewater set at each site. We therefore cannot give estimates of spatial variation of halogen concentration in porewater. It is of course desirable to take multiple cores and porewater sets at each site, but we did not have a budget for such a very cost and time intensive approach. We also like to remind

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that sampling in the Magellanic Moorlands is extremely extensive due to the absence of any infrastructure.

Referee's comment: In the description of the chemical analysis (p. 1463, lines 6-9), it was unclear, why the Rhenium was used instead of Rhodium. Why shifting does not affect all the peaks? More information about the shifts and the analytical mass of Rhenium should be given.

Has been changed. Shifting was indeed the wrong term. The signal showed interferences dependent on the amount of DOC.

Referee's comment: Amounts of organobromine and organoiodine (p. 1463, lines 13-16) were calculated from the difference between total and inorganic species. Could some error estimates of the method (e.g. standard deviations between parallel samples) be given? Are there any references to this kind of method?

As mentioned above we have no parallel samples. The measurements were validated by the use of reference materials and a reference of the method is given (see method section).

Referee's comment: A few words about carbon and nitrogen, peat and rainwater sampling could be added even if detailed description of the method can be found elsewhere.

We added this information to the Material and Methods section.

Referee's comment: p. 1466 line 3: It was assumed that there is as much organochlorine in lakes and rivers in Sweden as in porewaters in this study and based on that it is said (even in conclusions) that most chlorine is inorganic. It is also said, that in the study by Asplund (1991) highest organochlorine concentrations have been measured in streams draining peatlands. Based on that, I would assume that concentrations in Peatlands and in porewaters would be higher. Could you clear your assumption?

The reviewer is right, but data on organochlorines in peat porewater is not available and our assumption is based on data from a small number of studies. However, even

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if the organochlorine content is higher we don't think that it will reach a level comparable to those of organobromine or organoiodine, so that chloride will remain to be the predominant chlorine species in peat porewater.

Referee's comment: Table 2 and p.1466 lines 10-14: It is said that wide range of halogen ratios is found in porewaters. Are the ratios stable in rainwater? Could the ranges of ratios in rainwater also be added to the table 2?

We have made only three measurements of halogen concentrations in rain (means are given). One of these measurements, which was made after a longer dry period (1 week) and predominately easterly winds show slightly higher halogen concentrations, but no significant changes in halogen ratios. However, short term changes in the halogen ratios in rain would be averaged out by the retention process in peat and by the large amount of halogens released from peat. The individual peat sections cover hundreds of years, periods, which we can't cover by rain measurements anyway.

Answers to comments of referee Gunilla Öberg

Referee's comment: The general assumption that chloride is inert in soil and thus can be used as an internal tracer of water movement is commonly used in hydrological and hydrochemical studies. The past years of research has revealed that chloride participates in a complex biogeochemical cycle - hence the inertness of chloride is questioned. The present paper takes its point of departure in these findings and argues that the fact that the concentration of chloride (and the other halogens) is higher in pore-water than in rain proves that these elements originate from decomposing peat. However, without knowledge of evapotranspiration and run-off, it is not possible to determine how high the concentration of the halides ought to be if they were to originate solely from precipitation. It is well known that high evapotranspiration in combination with low run-off renders a considerable increase in chloride concentrations. I assume that the investigated bogs do have outlets since they otherwise would be prone to saltification. It is quite possible that the authors are right in their conclusion, but the data

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does not stand for scrutiny without information on evapotranspiration and run-off, hence basic hydrological information should be included and internalised in the text.

We agree with the reviewer that knowledge of basic hydrological data would be a great merit to better validate our assumptions about the sources of halogens in porewater. Unfortunately such data is not available for the bogs in the Magellanic Moorlands and it is not an easy task to obtain this data; several years of measurement are necessary and a major problem is that some of these bogs are several kilometres in extension and hydrological conditions in bogs can be very heterogeneous. However, raised bogs usually have a positive water balance, which means that evapotranspiration is lower than precipitation and that there is continuous outflow. We therefore believe that a 20 to 30-fold enrichment of halogens in porewater compared to rain could not be caused by evapotranspiration alone. We have now discussed this aspect in the manuscript.

Referee's comment: The distribution between organohalogenes in peat, halides in peat, organohalogenes in pore water and as halides in the pore water at any site in the investigated bogs is bound to be the result of at least four processes: 1. input by vertical movement, 2. output by vertical movement, 3. halogenation 4. dehalogenation. (input and output by horizontal movement can probably be omitted). As the text stands now, the authors mainly confine the discussion to dehalogenation. Halogenation is brought in on page 1469 (page 10 in the ms) and vertical transport is concluded to be of minor importance on unclear grounds. The input of organohalogenes by atmospheric deposition can most likely be assumed to be of minor importance based on the reasoning in Asplund and Grimvall, 1989. However, vertical transport within the peat-bog is likely to occur (as I assume that the investigated bogs do have outlets for reasons given above). The authors should interpret their results in the light of the complexity guiding the halogen cycle rather than focussing on one out of four major processes. If this is done, the paper has the potential of becoming truly interesting.

In those points we do not agree with the reviewer. Vertical transport of solutes in peat bogs is of minor importance and the predominant movement of water is lateral trans-

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port, this has been shown in many studies on bog hydrology. Groundwater recharge below raised bogs has been measured to be  $< 30$  mm/yr. Halogenation of peat has been discussed in a previous paper (Biester et al., 2004) and the major point in our presented study was dehalogenation or better peat as a source of halogens in peat porewater and especially the role of DOC. We also don't think that atmospheric deposition of organohalogen is of minor importance for all halogen. To our knowledge Asplund and Grimvall (1989) have not investigated bromine and iodine. Large amount of iodine in the atmosphere occur as organic iodine (e.g. iodomethane) and we also found organoiodine in rain samples from our study sites.

Referee's comment: Redox does most likely play a crucial role in the natural halogen cycle. The authors touch upon this issue and do, between the lines, conduct an interesting discussion. However, the line of reasoning disappears in the overwhelming and unstructured body of text. I suggest that the authors refine this discussion and make it a major point of the paper and omit as much as possible of other more speculative threads. The text is a bit raw and repeats itself several times. It should be structured such that repetition is avoided.

It is true that redox plays a crucial role in the natural halogen cycle. We are not sure about the meaning of this statement. Redox is comparatively uniform (permanently anaerobic) in the catotelm, which covers the major part of a bog. We discussed that reductive dehalogenation is the predominant dehalogenation mechanism to be expected in anaerobic environments (especially for chlorine). We do not know which speculative threads are exactly meant but we restructured the manuscript and eliminated some of them.

Referee's comment: It is confusing that the authors repeatedly stress that "organohalogen in porewaters are not considered in this study" (e.g. line 25) at the same time as one of the major issues discussed is organohalogen in porewater based on data from the present study.

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The statement that organohalogens in porewaters are not considered in this study relates to the study of Shotyk (1997) so “that” instead of “this” must be used. The other context is probably that we stated not to have measured “organochlorines”. What we have measured (or calculated) were organobromine and organoiodine).

Referee’s comment: The method section should be more elaborated such that it is possible to evaluate the results without having to scrutinize previous papers. No need to go into details but more information than presently given should be given. It is a bit difficult to understand from the information given, what was measured and how. This is of crucial interest since the major focus deals with speciation and distribution patterns among organically bound, adsorbed in peat, dissolved organic and ionised halogens.

We have added information on that in the Materials and Methods section

Referee’s comment: When discussing enzymatic halogenation, reference should be given to Asplund G et al. 1993 A chloroperoxidase-like catalyst in soil: detection and characterization of some properties. Soil Biol Biochem 25:41-46 Ortiz-Bermudez et al. 2003. Appl. Env. Microbiol. 69:5015-5018 When discussing halogens in peat, reference should be given to Asplund and Grimvall, 1989

Some of the references are now included in the manuscript.

Answers to comments of referee Christian Blodau

Referee’s comment: Specific comments: The study relies on a number of implicit assumptions that are critical regarding the validity of these findings. In the reviewer’s opinion the shortcomings of these assumptions are not so severe as to reject their validity. The assumptions have to be carefully evaluated, though, and they have to be made more transparent. First, the authors imply that concentration equals or is at least tightly correlated to “release”. As the authors point out in the abstract “Results show that the release of bromine and iodine depend on the degree of peat degradation &#711; E”. In fact the authors measured only concentrations. Concentrations are,

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however, only representative for sources and sinks if transport is slow. Assuming that advective transport is very slow, which is likely in the catotelm, owing to the decrease of hydraulic conductivity by orders of magnitude with depth (Fraser et al. 2001), diffusion remains as a transport process. Concentration and production are, under steady state conditions, then related to each other by a differential equation, encompassing:  $p$ : porosity;  $D_{s,i}$ : sediment diffusion coefficient for dissolved species  $i$ ,  $C_i$ : concentration of dissolved species  $i$ ;  $R_i$ : production rate of dissolved species  $i$  (see e.g. [Berg et al., 1998]). Release will only be indicative for production if  $D_{s,i}$  becomes very small. Then, concentration gradients become large, if the differential equation is to be satisfied with a given  $R_i$ . Now this is an assumption that is difficult to justify for inorganic species. In fact, pore water modelling approaches are based on the interaction of diffusion and production. In such models, production is associated with changes in concentration gradients, rather than with high concentrations [e.g. Berg et al., 1998]. Fortunately, DOM has much smaller diffusion coefficients than inorganic species that are typically encountered in pore waters (Cornell et al., 1985). This is particularly true for large humic molecules. Thus, the occurrence of the observed concentration peaks reflects the fact that bromine and iodine are primarily bound to fairly immobile DOM molecules. Hence concentration peaks also reflect production. This assumption does not hold true for chloride, though. Hence the authors likely observe much smaller changes in chloride concentration because of the much larger diffusion coefficient of inorganic chloride. The authors should, in the reviewer's opinion, state their assumption (release  $\ddot{Y}$  concentration) explicitly in the method section and justify their assumption with the small diffusion coefficients of DOM and the organic nature of bromine and iodine in the pore waters, e.g. based on Cornell and colleagues' work.

The aspects of solute transport in pore water addressed by the reviewer are very important and have been neglected in the previous version of our manuscript. We have now implemented this general concept of solute transport and discussed our results based on the suggestions made by the reviewer.

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Referee's comment: Second, the authors only use C/N ratios as a proxy for decomposition degree. The study relies on a clear indication how decomposition degree relates to these ratios. The authors thus should elaborate in more detail (page 1470, line 5-10) on how C/N ratios are related to other indicators of decomposition (van Post index, humification indices using FTIR spectroscopy,  $^{13}\text{C}$ -NMR spectroscopy, fluorescence spectroscopy) to make their case. Studies by Kalbitz et al., might serve as a reference. The study would certainly have gained in strength if some simple humification indices had been determined in addition.

Most humification indices are based on changes in the quality of organic matter such as colour, proportion of aromatic components or changes in carbon isotopic composition etc.. C/N ratios have been used in several peat studies to describe differences in the degree of peat decomposition. Decomposition is here used as a process, which includes both humification and mass loss through mineralisation of organic matter. Especially, mineralisation, which is an important process for enrichment or depletion of chemical elements in peat, is to our opinion not adequately described by the term humification or indices used to estimate humification. That is why we prefer to use C/N ratios instead of humification indices as nitrogen has been shown to be enriched during mineralisation of organic matter. We have determined the amount of active carbon in our peat profile; a measure similar to humification indices, where high amounts of active carbon indicate a relatively high degree of humification. In our peat profiles amounts of active carbon show a positive correlation with low C/N ratios (high decomposition). Moreover, recent studies by Borgmark and Schoning show good correlation between humification indices and C/N ratios.

Borgmark, A., Schoning, K.: A comparative study of peat proxies from two eastern central Swedish bogs and their relation to meteorological data, *J. Quaternary Sci.*, (in press). ISSN 0267-8179.

Referee's comment: In the reviewer's view, the study raises significant questions about the controls on halogen dynamics in peats. It would be highly beneficial if, in fu-

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ture studies, an experimental, reductionistic approach could be taken to identify more clearly the factors that control halogen release and immobilization. This could, for example, be done by carrying out incubation and column experiments with peats having different degrees of decomposition and humification, exposure to different redox conditions etc.. This way some of the complexity of factors and processes that affect halogen dynamics could be eliminated and field studies such as the one presented here could be more easily interpreted. Also, the question of transport of bromine and iodine in pore waters of peatlands - which is critical to the interpretation of field data - could be investigated separately from mobilization and immobilization mechanisms.

In principal we agree with the suggestion of the reviewer.

Technical and minor comments: p. 1463, line 20: peat dating, (add comma). Has been changed

p. 1466, line 4: Are there any data on chlorine/organochlorine concentrations in peat pore waters in published studies? This would strengthen the argument that chlorine is predominantly chloride in the pore waters. Unfortunately not (to our knowledge)

p. 1466 line 18: “halogen ratios” - specify which halogen ratios are meant. Has been changed

p. 1466, line 24 “in pore water (84-324).” New sentence: “He concluded”. Has been changed

p. 1467, line 1: “The influence.” It is not clear what the influence is on. Has been changed

p. 1468, line 3: replace “process” by “mechanism”. Has been changed

p. 1468, line 23: “iodoine” replace by “iodine”. Has been changed

p. 1471, line 17: Reference for the reductive dehalogenation of chlorine is missing. p. 1472, line 22: “organobromine-“ replace by “organobromine”. Has been changed

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p. 1473, line 4: I do not see data on organic species in table 1. It says “total concentrations” in the heading. Values in the table are total concentrations. Percentages of organically bound iodine and bromine.

p 1473, line 24: “Halogen concentrations” replace by “Halogen concentrations in the peat” as the peat is meant. Has been changed

p. 1474, line 5: sipping techniques and depth resolution- see also Blodau and Moore (2002) for an evaluation of a sipping vs. dialysis technique Has been added

p. 1474, line 10: ”of only slightly decomposed” - it is unclear what is meant by “slightly”- is there, for example a van Post index available? We mean relatively slight, compared to peat sections, which show a higher degree of decomposition.

References Cornel P.K., Summers R.S., Roberts P.V. (1985) Diffusion of humic acid in dilute aqueous solution. J. Colloid Interface Sci. 110, 149-164.

Has been added

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Interactive comment on Biogeosciences Discussions, 2, 1457, 2005.

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