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

C. Blodau (Referee)

christian.blodau@uni-bayreuth.de

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General comments:

The study by Biester et al. is concerned with the concentration and concentration dynamics of inorganic and organic halogens, i.e. chlorine, bromine and iodine, in peats and peat pore waters of three peatlands in Patagonia, South America. Furthermore, the authors aim at elucidating to what extent decomposition of peat and release of dissolved organic matter control the concentration patterns of the investigated halogens in peat pore water profiles.

The topic is of significant interest for climate change research. In ombrotrophic peatlands, halogens concentrations may reflect either changes in atmospheric deposition regimes or in peat decomposition patterns. The former view is based on the assumption that halogens are conservative in peats, whereas the second view more strongly

considers chemical interactions between peat matrix and halogens. Bromine and iodine primarily occur in their organic forms and should be co-released with dissolved organic matter (DOM), a process that is connected to the decomposition degree of peats. Chlorine is moreover believed to be released by reductive dehalogenation. The suite of halogens might provide an indicator for environmental change that is analytically relatively easily accessible. The value of halogens as indicators for environmental change is currently debated, as is also pointed out by the authors. The contribution is thus timely and of significance for the audience of Biogeosciences.

The paper meets the standards regarding style, conciseness, and organization that can be expected from a contribution to an international journal. The applied methods are state of the art and suitable regarding the objectives of the study. The use of suction samplers to obtain detailed concentration profiles down to larger peat depths, instead of using piezometers, is a novel approach and avoids some of the shortcomings of the latter method, such as an insufficient depth resolution, and long equilibration times at low hydraulic conductivity. The group has moreover a long experience in the investigation of halogens and peatlands, and the results of the study can be related to previous investigations at the studied sites. The sites themselves are very suitable for a study as undertaken, as they are remote from any influence by humans.

The main findings of the study are:

(I) Organobromine and -iodine are dominant forms of the elements in peat pore water, whereas this is not the case for organochlorine.

(II) Concentrations of bromine and iodine in the porewaters are negatively correlated with the degree of decomposition as indicated by lowered C/N elemental ratios.

(III) Concentrations of bromine and iodine in the porewaters are correlated to DOM concentrations, whereas this not the case for chlorine.

The study thus confirms the intimate connection of halogen chemistry to diagenetic

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processes in the peats and suggests that halogens could be used as indicators for climate related changes in peat decomposition degree. It is, therefore, a significant contribution that deserves publication.

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 degradationĚ". In fact the authors measured only concentrations. Concentrations are, 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; Ds,i: sediment diffusion coefficient for dissolved species i, Ci: concentration of dissolved species i; Ri: production rate of dissolved species i (see e.g. [Berg et al., 1998]).

Release will only be indicative for production if Ds,i becomes very small. Then, concentration gradients become large, if the differential equation is to be satisfied with a given Ri. Now this is an assumption that is difficult to justify for inorganic species. In fact, pore water modeling 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

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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 ~ 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.

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, 13C-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.

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 future 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.

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Interactive Comment

Technical and minor comments:

p. 1463, line 20: peat dating, (add comma).

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.

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

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

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

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

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

p. 1471, line 17: Reference for the reductive dehalogenation of chlorine is missing.

p. 1472, line 22: “organobromine-“ replace by “organobromine”.

p. 1473, line 4: I do not see data on organic species in table 1. It says “total concentrations” in the heading.

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

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

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?

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.

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Fraser, C.J.D., N.T. Roulet, and P.M. Lafleur (2001): Groundwater flow patterns in a large peatland, J. Hydrol., 246, 142-154.

Berg, P., N. Risgaard-Petersen, and S. Rysgaard (1998): Interpretation of measured concentration profiles in sediment pore water, Limnology and Oceanography, 43 (7), 1500-1510.

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