**Biogeosciences
Discussions**

Interactive comment on "A Holocene record of mercury accumulation in a pristine lake in Southernmost South America (53 S) – climatic and environmental drivers" *by* Y.-M. Hermanns and H. Biester

Y.-M. Hermanns and H. Biester

y-m.hermanns@tu-bs.de

Received and published: 3 October 2011

We thank referee 2 for the helpful comments on our manuscript and answer as follows. RC: referee comment, AR: author response

RC 1: However, the literature concerning mechanisms regulating export of terrestrial DOM to lakes is less comprehensive, especially as regards the balance between terrestrial POM, DOM, and aquatic primary production as OM sources to lakes. Good reviews by J.J. Cole etal. 2007. Ecosystems 10: 171-84, Y.T. Prairie 2008. Can. J.

Fish. Aquat. Sci. and L. Tranvik et al. 2009. Limnol. Oceanogr. 54: 2298-2314 provide the perspective that most carbon influx to lakes in forested catchments is derived from terrestrial DOM (about 10x more than POM influx). It would be useful to review these studies, to better refine the specific expectations for change in DOM (and Hg) flux arising under different climate regimes

AR 1: We agree with the referee, that DOM often is the dominant form of carbon fluxes into forested lakes and definitely plays an important role in Lake Hambre as well. We will add this to the introduction section following the reviewer's advice. Aditionally we withdraw our statements about the ratio of DOM to bulk OM in section I (page 6569, line 13-29, page 6571, line 13-15). Nevertheless the sediments of Lake Hambre clearly reveals to be a mixture of aquatic and terrestrial material as shown in the manuscript and terrestrial plant remains as well as Nothofagus leaves in the sediments clearly account for a significant contribution of particulate terrestrial OM in this particulate lake.

RC 2. p. 6558, l. 13-25. The paper suffers from imprecise predictions for the relationship between climatic variation, terrestrial development, and Hg transport. For example, if Hg influx was regulated by DOM inputs, then the two should covary most strongly, when there are substantial changes in DOM flux – specifically, immediately after soils develop. Similar hypotheses could be described for each of the previously documented climatic changes (more precipitation, more DOM influx, more Hg influx, etc.). As it stands, the objectives are poorly defined, beyond a 'let's investigate' statement. This becomes more of a problem in the Discussion, where the authors expend considerable energy debating all possible mechanisms, rather than critically testing the central hypothesis

AR 2: The aim of our study was not to make clear predictions for the relationship between climatic variation, terrestrial development, and Hg transport. Despite that this is the final aim of this kind of research we doubt that this can be done from a single study site and we do not know any study which has already shown that for the Holocene

or even shorter periods. Moreover, it was not our primary aim to investigate solely the relationship between DOC and Hg fluxes to our lake. Instead we intended to investigate the variability of Hg accumulation in this remote lake in the Southern Hemisphere and this is the first time this has been shown (this is why we started with a 'let's investigate' approach). We are a bit surprised that the reviewer did not comment on that (see also comments of reviewer 1). As a second aim we tried to explain the observed variations in Hg accumulation by a multi-proxy approach using PCA which does not include only OM source proxies (as in most other studies) but also a larger number of elements which allow a deeper insight into the geochemical processes in the lake and its catchment. In this respect, the strong focus on the influence of different sources of organic matter on Hg accumulation in the introduction is probably misleading, while more information should have been given about other potential processes controlling Hg fluxes, which have been suggested to play an important role in previous studies (e.g. atmopheric deposition, minerogenic fluxes). According to that we will change the introduction and state our objectives more clearly.

The statement of the reviewer that "if Hg influx was regulated by DOM inputs, then the two should covary most strongly, when there are substantial changes in DOM flux" is doubtful if not wrong. This assumption would imply that the system is such simple that the soil organic matter stores fixed amount of Hg which is only released to the lake by DOM, the Hg content in DOM is constant, and DOM is the only organic matter source to the lake. In this case both parameters would covary strongly. However, in natural systems the catchment Hg pool is not stable, but depends on the amount of atmospheric Hg deposition. As both the accumulation of organic matter (and DOM production) and Hg deposition may vary independently, covariance between DOC and Hg fluxes cannot be expected. Things become even more complicated if bulk organic matter in sediments is regarded, as considerable amounts of the lake's organic matter are from within-lake production; so the amount of organic matter in the lake is not the limiting factor for Hg accumulation in the sediments and covariance between OM and Hg cannot be expected invariably. This is why we used other "proxies" such as

copper and lithogenic elements, which are independent from the OM source but clearly indicate, that catchment soils (not direct atmospheric deposition) are the source of Hg. Therefore, we believe that the processes causing changes of Hg fluxes to a lake are multiple and complex and it is probably a too simplified approach to base the discussion solely on the relation between DOM and Hg.

RC 3 a). Methods, p. 6559-6560 – In general, the methods seems very well done and reliable. In particular, the chronology is superb and the data density sufficient to investigate the statistical relationships among the various geochemical proxies. Unfortunately, I think the central problem of the paper is that the authors lack a unique metric to measure the various unique sources of organic matter to the sediments. For example, fossil diatoms or pigments (either extracted and quantified or measured by fluorescence) could be used to follow changes in lake production (See general books edited by J.P. Smol et al. Tracking Environmental Change Using Lake Sediments. Vol 3,. Kluwer), while recent work suggests that stable isotopes can be useful metrics of DOM influx, at least over the Holocene (e.g., Bunting et al. 2010. Limnol. Oceanogr. 55: 333-345, McKnight et al. 1997. Biogeochem. 36: 99-124). While C/N ratios are proposed, they are mainly useful for interpretations of large-scale variation (10-20:1 ratio changes), and are much more problematic for finer details, particularlywhen there are high amplitude changes in terrestrial DOM influx, aquatic production,or algal composition. As a result, the narrative flips back and forth on whether the C/N is a good index of terrestrial OM or not – leading to excessive speculation and an unconvincing argument.

AR 3 a): The referee is right in saying that C/N ratios are a rather rough estimate of varying contributions of terrestrial and aquatic organic material. However, the reliability of their use has been proven in many studies (see Smol et al.). Moreover the C/N variations changes in our record (as shown in Figs.3, 4 and 5 between the different sections as well as short term changes such as the cyclic variations in section II or the strong variations at the beginning of section III) are no random noise but significant

and reliable and in combination with changes in the total C concentrations clearly allow estimations on changes in fluxes of the terrestrial OM. Moreover we use other typically organically bound elements as additional proxies (such as Cu). The coincidence of Cu and Hg with the variations in C concentrations in section II, as represented by PC1, clearly confirms Cu and Hg as representatives of organically bound transport into the lake. Our answer regarding the suggestion of using fossil diatoms or pigments additionally is that it was not our intention to focus specifically on changes in aquatic bioproductivity as a transport vector in the sediment (see also AR 2). The question rather is how Hg enters the lake, because autochtonous production of organic matter without an additional supply of Hg from a source outside the lake cannot significantly influence the accumulation of Hg, simply due to mass balance reasons. At least in our lake, as indicated by the high C concentrations in the sediments, the availability of organic matter is not the limiting factor for the transport of Hg into the sediments. So we believe that no additional information can be obtained by using more OM source proxies. Even if we can quantify the contribution of the different OM sources (which is not easy), this does not allow a quantification of Hg from different sources, because this would imply that the Hg content in DOM from soils is constant over time, which is not the case (Hg/C ratios, see refences in the manuscript, e.g. Meili 1991). According to the referees advice on the rather speculative narrative flips back and forth on whether the C/N is a good index of terrestrial OM or not we will delete those speculations (e.g. page 6569, line 13-29, page 6570 line 20-26). Regarding the remark on using stable isotopes as a proxy of DOM fluxes: The cited studies clearly depict that a careful evaluation of interelations, for example by using a reliable calibration data of endmembers, is needed, which we do not have for this particular region. Anyhow, it's an interesting aspect worth to pursue in further studies.

RC3 b) I also think the authors need to use a constrained cluster analysis to better justify their three zones. I don't think it will change the story much, but it would provide a more objective demarcation of zones.

AR 3 b) Cluster analysis (among user statistical methods) might be another appropriate method to visualize the three zones in the cores. However, as the reviewer stated, this will not change the story why we like to omit further statistical analyses.

RC 4: Results and Discussion. While I understand that the combination of Results and Discussion section is a common practise, I felt that this paper has ended up too long and speculative as a result of this narrative being in one section. In particular, details concerning the basic geochemistry tend to get repeated by stepping through OM, metals, Hg and statistics sections one at a time. Also, because there are no obviously testable objectives or hypotheses (point 1 above), the narrative is somewhat longer than needed, as it attempts to address all possible explanations.

AR 4: Our aim was to establish a reliable and comprehensive analysis of environmental and climatic changes in the study area prior to discussing the broad variety of potential factors controlling the accumulation Hg in our particular lake. This is somewhat time- and space-consuming, but provides a comprehensive evaluation on how environmental changes affect Hg accumulation through thousands of years, which has not yet been shown before. Anyhow, we will skip reiterations and reduncancy if they are not mandatory.

RC 5: Transitions among core Sections, Fig. 3, 4 and associated narrative. The most problematic aspect of the data is the apparent evidence that major changes in OM influx occur without corresponding changes in Hg deposition, such as occurs when local forest starts to develop at the base of the core, or between zones I and II. If OM were essential to transport Hg and regulate its influx, then I would have expected particularly strong covariance at these intervals. While it's possible there are extenuating mechanisms which override OM control (as touched on in the later Discussion), the more parsimonious explanation is that OM flux is not really that important – at least in these conditions.

AR 5: We do not agree with the referee in that the lack of a corresponding change

in OM and Hg fluxes especially at the transition between the different core sections is "problematic". Instead we think that it is rather logical. In a short term, precipitation events will transport OM and complexed Hg out of a soil, leading to a common increase in both. In a long term it should be clear, however, that a rise in OM production and fluxes can not result in a long term increase in Hg fluxes, if there is no additional Hg available for complexation and transport. A release of Hg from minerals or atmospheric fluxes of Hg onto the catchment's surface are not necessarily lineary related to the development of the catchments vegetation. We discussed those interelations in-depth on page (6571, line 25 – page 6572, line 10), which is probably placed too far down. For a better understanding we will add this aspect in section 3.4.1. We have also already commented on the expected lack of covariance between Hg and OM above (AR 2).

RC 6: p. 6563-6564. Although it's common to discuss the general relationship between proxies, I would find the arguments more convincing if statistical comparisons where used, rather than vague statements that match are 'quite good' (e.g., p. 6564, l. 14). Simple linear detrending of the time series, followed by Pearson correlation analysis would be fine, if the authors are assuming common regulatory mechanisms underlying the temporal variations.

AR 6: Maybe there is some misunderstanding. In this section we only discuss that mean Zr values in the sediment match approx. those in catchment rocks (time-independent), which needs no statistical evaluation. The overall relationship between Zr and C/N (and others) is already shown by the PCA results and needs to our opinion no further statistical analyses.

RC 7: p. 6563, l. 15, and l. 26. While it is probable that temperature and precipitation had an effect, these arguments are not convincing. Similarly, p. 6565, l. 17-24 is not useful – as it says that sediments are a mix of terrestrial and aquatic OM (which is both obvious and vague)

AR 7: We agree with the referee and will delete the related paragraphs.

RC 8: p. 6566, l. 22-26, Table 3, and Methods. There is insufficient information provided to evaluate whether the soil and substrate survey was sufficiently comprehensive to allow general statements about "the catchment". Is Hg evenly distributed, or have past streams incised to deeper strata and accessed a 'point source' of Hg?

AR 8: The referee is right in his concerns weather the soil samples are representative for the whole catchment. However, the catchment is very small and we tried to depict the soil samples as represantative as possible. The parent rock material is uniform throughout the catchment, wherefore the rock sample gives reliable values as well. As mentioned in the section "2.1 study site" there are no inflowing streams but some gullies accounting for intermittent inflow of surface runoff during high precipitation events (page 6559, line 6-7). Anyhow, there is no morphological evidence for past streams incising into deeper strata. Moreover we analyzed the soils depth dependend (Table 3) and Hg concentrations decrease in deeper soil sections

RC 9: p. 6568-6572. Insufficient data were provided to evaluate whether the PCAs captured enough variance to be useful. At least in one case (Section II), the overall explained variation in the PCA is low (31%...on how many axes?), suggesting that the variation in proxies was not explained well be linear relationships. More importantly, I found the PCA data greatly over-interpreted and unconvincing. While the authors expend considerable effort evaluating the reasons for differences in relationships among Hg, C, N and erosion indicators in PCAs for sections 1, 2 and 3, again, I was left with the impression that they were trying to "save" a central hypothesis which had only weak support, rather than critically evaluate the mechanism.

AR 9: We do not agree that our PCA is over-interpreted and unconvincing. However, the referee is right in that more detailed information could have been given on how many of the overall data variance in each section is explained by the given amount of extracted principle components. We will add that on page 6568, line 10. In sections I, II and III 75 %, 81 % and 82 % of the respective data variance is explained by 3, 4 and 5 principle components, respectively. This clearly depicts that there exists a significant

relationship between our proxies and that our results are useful and convincing. We used the Kaiser-criterion (Eigenvalues >1) to decide how many axes to extract and will add that in the methods section. Especially the high and significant factor loadings of of Hg, Cu and Y in one single PC in every core section depict clearly that there is a significant relationship between all three elements under different environmental conditions. The factors controlling most of the Hg's variance show very high factor loadings (> 0.8) for Hg, which is high, regarding that sedimentation in lakes is affected by a broad variety of different processes. Regarding the value of 31% the referee probably misunderstood the meaning of the sentence. This means that PC1 explains 31 % of the overall data variance (all proxies), while alltogether the 4 extracted principle components explain 81 % of the overall data variance in section II.

RC 10: p. 6572-73, section 3.5. Due to the high degree of speculation, I found several of the basic conclusions to be overstated (e.g., 6572 l. 17-19; 6573, 19-20).

AR 10: Since this is the interpretation of our data we do not agree with the referee regarding his concerns about the basic statements. Again, the most important finding and aim of our study was to show that Hg accumulation in this remote area has been constant on the long term throughout the Holocene, but that short term variability can even surpass the factor of anthropogenic forcing. These findings, we believe, are important as a reference for natural variability of Hg deposition and Hg fluxes in lake systems (see also comments of reviewer 1). The discussion on the possible processes and reasons for the short term changes in Hg accumulation might be in some places speculative, but due to the large multi-element/proxy data set used we believe that the interpretations are more robust than if only a Hg-DOM approach is used. However, words like "strong" or "tight" are probably too intense, not adequate for a scientific statement and not necessary for the understanding. We will therefore delete them.

RC Summary: The paper suffers from having a great central hypothesis, but an incomplete set of proxy metrics needed to test it. As a result, the paper is excessively long and speculative. The best means of resolving this issue would be to provide additional

C3419

time series, particularly of OM sources. Alternately, the authors could focus on more statistical and critical testing, possibly resulting in the OM control mechanisms being rejected (with this data set).

AR Summary: We already commented on the "missing" clear hypothesis and the incomplete set of proxy metrics. Again, a resolving time series may resolve different OM sources, but not the sources and processes controlling the fate of Hg. Instead we believe that our PCA results give more valuable information on that, than time series analysis could. We hope that our reply (especially AR 2 and AR 3a) clearly reveals our intention on organizing this manuscript the way we did and that the broad variance of used proxies is sufficient. We intended to provide a long term Hg record with a comprehensive evaluation of several different potential factors controlling Hg accumulation and we clearly depict a new aspect (OM fluxes control Hg fluxes on a short term, but not on a long term), including new ways of using a multi-proxy data set. Regarding the referees concerns on the statistics the additional information on the explained variances should be convincing. Results are clear and significant and reliable (see AR 9). Of course it is the first paper stating that DOM fluxes controll Hg accumulation in lake sediments and further research is needed to carefully test if this interrelation is applicable to other settings. One potential approach is the DOM reconstruction using isotopes for example, as suggested by the referee.

C3420