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Biogeosciences
Discussions

Interactive comment on "Mn seasonal upwellings recorded in Lake Tanganyika mussels" *by* D. Langlet et al.

D. Langlet et al.

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We group our answers to both referees in five points, with systematic references to each related referee question or comment. We appreciated the very constructive and helpful comments of both referees, which greatly improved the manuscript.

1 Comments about the Mnd data in lake water

1.1 About the manganese dissolved data (Mnd)

Referees Comments: D Dettman §1.1; S Severmann §3 "I would very much like to see the Mn dissolved data. Why are these not included?" (D Dettman §1.1)

Contrary to the particulate fraction of lake surface water, for which we disposed of a quite continuous set of data analysis extending from February 2002 to December 2003, data concerning the dissolved fraction (Mnd) are fragmentary for year 2002 because of storage problems in Mpulungu. The Mnd series is rather complete from March 2003 to October 2004 (missing points between December 2003 and March 2004). Then, the monitoring of both dissolved and particles is only available between March and December 2003. Because of the missing Mnd points in 2002 and the poor constraints of shell growth rate, the dissolved data are not helpful to decipher whether Mn peaks in "young" shells collected in March 2003 (i.e. the higher growth rate and the most precise profiles) were related to dissolved Mn incorporation or to the assimilation of increasing quantities of Mn-rich particles. However, we agree that it is important to show these data to support our arguments. A recent review of phytoplankton biomass estimations collected during the CLIMLAKE Project (Descy et al., 2005) suggests that major increases of Mn in shells might reflect the incorporation of Mn-enriched digestible food particulates. This hypothesis is discussed below and in the revised version of the manuscript.

"The authors say that there is a sustained increase in Mnd during upwelling - it would be nice to see the numbers." (D Dettman §1.1)

In the dissolved fraction, there is a clear seasonal contrast of Mnd in surface waters with a sustained increase during the dry season 2003 and 2004. To be consistent with shell data, results of dissolved fraction analysis are given as (Mn/Ca)d molar ratios (Fig. 3a, revised manuscript). Ratio values rose from 0.01 to 0.08 in July 2003 and 0.14 in September 2003, and from 0.02 to 0.14 in June 2004 and 0.19 in July 2004. As for (Mn/Al)p dissolved Mn typically displayed a bimodal peak pattern. The second peak is more intense than the first although it was not concordant with the most pronounced water cooling. In the dissolved fraction, both are delayed by about 1.5 month.(The text above is included in "Results" §3.1 of the revised manuscript; see also "Discussion" §4.1 revised manuscript).

1.2 About the alignment of the surface cooling and Mn peaks in water

Referees Comments: D Dettman §1.3. ; S Severmann §6 "The upwelling and Mnp

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does not seem to agree very well" (D Dettman §1.3.) "The maxima in particulate load seems to occur mostly after the upwelling " (S Severmann §6)

Reduced Mn2+ is not thermodynamically stable in surface water but a time lag is very likely between the supply of reduced Mn2+ and its precipitation in oxic surface layers because at least six biogeochemical processes could conjugate their effects to disturb Mn precipitation and dissolution (see BGD manuscript p. 1459). (1) High sunlight intensity on lake Tanganyika should affect directly the Mn2+ concentration in the surface water by photo-inhibiting the manganese oxidizing micro-organisms (Sunda and Huntsman, 1990). (2) Sunlight has also been shown to exert a stimulatory effect on the reductive dissolution of Mn natural oxides produced by the microbial activity in seawater (Sunda and Huntsman, 1994). (3) The increase of primary production during the dry season should increase the activity of heterotrophic bacteria that catalyze the reduction of Mn-oxides (non soluble MnO2 or Mn(OH)x) as a source of oxygen for decaying the organic matter (Souchu et al., 1998). These conditions favor the reduction and the dissolution of the Mn-oxides or Mn2+ bounded to biological debris. (4) By contrast, an increase of biological activity concomitant with a supply of Mnd in surface waters likely enhances the production of Mn-rich particles, while green algae can efficiently take up and concentrate Mn2+ intracellularly (Sunda and Huntsman, 1985). (5) Moreover, photosynthetic activity in dense algal population generates high pH ($>$9) which, in turn, favors oxides or carbonates precipitations in organic-rich microenvironments (Richardson et al., 1988). (6) Finally, the nutrient supply from deep layers during the dry season may also enhance the precipitation of Mn-phosphate and carbonates (MnHPO4 and MnCO3) (Branchu, 2001).(The text above is included in "Discussion" §4.1, revised manuscript).

"Why were these two years so different (Mnp in water)?" (D Dettman §1.3.)

The CLIMLAKE Project (Descy et al, 2005) has detailed limnological changes during the upwellings. All monitorings (water temperature in pelagic area Fig. 3d; air temperature, wind speed monitoring and main nutrients concentration data not shown) indicate

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that the upwelling event was more intense in 2003 than in 2002. For instance, the major increase of Chl a in 2003 was higher than in 2002 (Fig. 3b, revised manuscript) in response to the higher nutrient supply. Apart from the main peak, a relatively high secondary peak occurred in September, 30th, 2003, at the end of the dry season and could explain that Mnp levels in water remained high for a few months after the 2003 upwelling (Fig. 3a, revised manuscript).(The text above is included in "Discussion" §4.1, p. 9, revised manuscript).

"The most pronounced surface cooling in May 2002 and July 2003 do not align with lows in the bottom water temperature" (S Severmann §6)

The discrepancy between the pelagic and bottom temperature graphs was due to a slight shift due to the graphic alignment of the two series for which sampling periods are very different. To avoid this problem and to show a longer record of bottom temperatures (from 01/29/2002 to 5/4/2004), we replace the continuous record by the biweekly record of bottom temperature at the bivalve site (Fig. 3c; Revised manuscript).

1. 3 About the deep Mn profile in the pelagic area.

Referees Comments: S Severmann §5

The deep profile (0-1400m) of dissolved and particulate Mn illustrates the chemical stratification of the lake with deep anoxic layers below 250m that constitute a large reservoir isolated from external influences. However, we follow the suggestion of both reviewers and decide to replace the deep profile of dissolved and particulate Mn by the monitoring of dissolved Mn in the coastal area.

2 Comments about the staining experiment

Referees Comments: D Dettman §1.4. ; S Severmann §4 (see § 2.2 "Staining experiment", pp.3-4, revised manuscript) "Details of this experiment are not presented" (S Severmann §4)

In July 2002, we put 13 individuals in a bath in which we added manganese chloride

(MnCl2, 4H2O) at 25 ppm (dissolved Mn2+) for 12 hours. Shells were put back in the site for 8 month. We retrieved all specimens in March 2003 and we managed a second experiment. Ten days after, we sacrificed five specimens (including shell V10) and prepared shells sections for analysis by cathodoluminescence (Langlet et al., 2006). P. spekii shells presented contrasts of CL with in general high CL intensity in older parts of the shells that could indicate an ontogenic increase of Mn with age. No luminescent line attributed to our staining experiment was observed. Below, we explain why the staining experiment has failed.

"... simply failed to grow new shell or take any Mn into the body fluids during 12 hours" (D Dettman §1.4)

It is true that the individuals may have failed to grow new shell layer during the staining experiment, due to stress or sluggish growth. Besides, Mn should have been incorporated in growth layers but the resulting low CL intensity (low concentrations and/or to thin lines) might be under the detection limit of the technique used (i.e. "cold-cathode"). All three factors could have combined their effect to bias the staining procedure.

"Is there any alternative explanation why the staining experiment may have failed" (Comment S. Severmann §4)

Another factor could be metabolic. Although a staining time of 12 hours in elevated concentrations of Mn is long compared to the 4 hours experiment successfully realized on the Japanese oyster Crassostrea gigas (Langlet et al., 2006), a longer experimental exposure might be required to mark P. spekii shells. Indeed, a lag phase and equilibration period up to several days was reported for the freshwater bivalve Hyridella depressa, which was experimentally exposed to elevated water concentrations of Mn2+ (20ppm) for 2 to 6 days (Jeffree et al., 1995). Moreover, an injection method directly in the pallial cavity or better in the extrapallial fluid cavity may be more efficient to mark the shell. In the latter case, the injection may reduce the active sequestration of Mn in soft tissues before being release in the mineralization fluid (extrapallial fluid).

"Why would staining with dissolved Mn not work in the particular species, although it has previously been successfully demonstrated for other species of freshwater and marine bivalves?" (Comment S. Severmann §4)

To our knowledge, only three studies deal with Mn2+ marking. Two of these concerned marine bivalves: the black-lip abalone Haliotis rubra (Hawkes et al., 1996); the Japanese oyster Crassostrea gigas (Langlet et al., 2006) and the freshwater bivalve Hyridella depressa, which was experimentally exposed to elevated water concentrations of Mn2+ (20ppm) for 2 to 6 days (Jeffree et al., 1995). The marking was successful for the marine bivalves. In the case of the freshwater bivalve, for which the extrapallial fluid is isolated from the external medium, a more important regulation of the trace metal composition of the extrapallial fluid compared to marine bivalves (Wada and Fujinuki, 1976) would lead to reduce efficiency of the Mn-marking. In the particular case of P. spekii the regulation should be important, the Mn being sequestrated in soft tissues at very high concentrations (6544 μg.g-1, dry weight) compared to the shell (Chale, 2002). For instance, concentrations in P. spekii tissues are two orders of magnitude higher than those reported for the mangrove oyster Crassostrea rhizophorea (61 μg.g-1, dw) known for its strong Mn accumulation pattern (Silva et al., 2006).

3 Comments about time in shells

3. 1 About the age of Pleiodon specimens

Referees Comments: D Dettman §1.4. ; S Severmann §2 "The authors should (Ě) give an estimate of their age" (D Dettman §1.4) "to have more detailed information about the growth rates of the shells" (S Severmann §2)

Growth pattern of Pleiodon (Cameronia) spekii was expected to be determined by repeated size measurements of tagged specimens over the two-year survey. However, it remains imprecise because of the extremely sluggish growth of the specimens collected. The shell length increase over a 8 month interval between two missions was not large enough compared to the precision of the measurement (caliper). Moreover,

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only six dead specimen with a length $<$ 80mm (i.e. juvenile stages) were found. Some investigations in the collection of the Royal Museum for Central Africa have shown that small shells were rare. As no other studies focused on the ecology and biology of P. spekii we cannot propose a reference growth curve for this species. The temporal framework in which geochemical profiles have to be interpreted is only deduced from one shell measurements (V10) and the analogy between [Mn] variations in shells and in water. Age of shells is given as a relative age with respect to the length/weight curve (the 3 individuals V10, V72 and V-E are younger than V61 and V34).(see "Study site & shell collection", §2.1, revised manuscript)

3. 2 About a sclerochronological approach of Pleiodons' shell.

Referees Comments: D Dettman § 2.1. § 2.4. "How well is the timing of events in the shell really documented?" (D Dettman § 2.1) "Is there any indication that growth banding is associated with upwelling events (based on a comparison of visible banding and the long records shown in Figure 6)? In Kigoma, near the center of the lake, banding is virtually absent in Pleiodon." (D Dettman § 2.4.)

Color and transparency contrasts in thin shell sections of P. spekii from the South and the North of the Lake are attributed to variations in shell microstructure (crystallographic changes in aragonite). Generally, they consist in a diffuse rather than a distinct boundary and do not constitute clear banding, as one can observe in freshwater shells living in higher latitudes. These variations in microstructure properties cannot be associated with upwelling events. Indeed, the luminosity profile (ImageJ software) realized in the shell section of MPU-V10 for which we have an estimation of time has shown that contrasts of transparency are associated neither with an annual cycle, nor with Mn content. In conclusion, the timing of events is not documented by independent markers (i.e. sclerochronological marker). Only two successive size measurements of specimen V10 allowed us to give an estimation of the mean growth rate along a 8 month period for this shell.

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"...to put a very precise landmark in Figure 5b" (D Dettman §2.1)

On Figure 4a (revised manuscript), a black arrow and a doted line was added to pin-point the position of the laser shot 172 that corresponds to the main Mn peak on shell V10.

3.3 About the possibility of multiple [Mn] peaks per year.

Referees Comments: D Dettman §2.2.

The correlation pointed out between V61 and V22 on Fig. 5 was based on the similarity of Mn peaks (shape and relative intensity with respect to low values preceding the peaks) and the hypothesis that Mn cycles were annual. If peaks of Mn in shells results of an increase in digestible organic Mn-rich particles, it implies that both (Mn/Ca)d and the phytoplankton biomass increase in coastal waters. These conditions are present during the dry season, especially at the beginning of the upwelling (see § 1.1, this AC), but not in the rest of the year. The possibility of multiple (Mn/Ca)shell peaks per year cannot be precluded because of the lack of any time marker in shells, but this option is unlikely if we consider shell V10 for which current oxygen isotopic preliminary results confirm our time scale estimates.(see "Discussion" p. 11, revised manuscript). We agree with the referees that stable isotopes analysis should be helpful for deciphering geochemical archives in shells.

3. 4 About the years 1996 - 1997.

Referees Comments: D Dettman §2.3. ; S Severmann §7

1997-98 El Ninõ event is considered as the strongest in the XXth century. In Lake Tanganyika unfortunately, there is a lack of measurements and observations, even for fisheries or meteorological database, during this exceptional El Ninõ event. It should have led to a strong increase in rainfall and anomalous high temperatures in lake surface waters, theoretically reducing the intensity of the upwelling.

3. 5 About distance scale in figure 5

Referees Comments: D Dettman §2.1. ; S Severmann §2 "(...) 2.9mm/8 month appears to be inconsistent with figure 5b, which (...) implies a growth of 15mm over the 8-month period" (S Severmann §2)

The problem was due to a scale error that was corrected. Successive size measurements on shell V10 (umbo-margin) indicated that shell increased of 7.6mm in 8 month. Because of the shell curvature, it corresponds to a distance of about 9.7 mm on the laser-sampling axis.

4 Comments about the quantification of the skeletal [Mn] signals

Referees Comments: D Dettman §1.1, §2.1; S Severmann §1

"Is (the Mnd seasonal increase) large enough to contribute to the particulate uptake suggested by the authors as the primary control? Is the change large enough to be the cause of the 3 to 4 fold increase in shell [Mn]?" (D Dettman §1.1)

As noticed in the BGD version (p.1460, lines 1-7), "a rapid and positive response of Mn levels in the aragonitic shells of P. spekii to the elevation of particulate and/or Mnd in water is consistent with the freshwater bivalves sensitivity to this element in both temperate and tropical conditions". Such sensitivity is consistent with the very high level of this element in the soft tissues of P. spekii, which demonstrated its the capacity to accumulate this element with respect to the surrounding water, Our data cannot be used to provide precise and quantitative information about the distribution factor between shell and water and no related study exists in the literature for Mn incorporation in inorganic or biogenic aragonite, but we argue that the 6 to 20 fold increase of (Mn/Ca)d in surface water may induce the 3 to 4 fold Mn/Ca increase in the shell. The way to obtain such an increase has to be discussed. Indeed, skeletal Mn/Ca peak (Fig. 4a, b, c, revised manuscript) may coincides with the 2002 upwelling according to V10 measurements but bimodal pulses of coastal (Mn/Ca)d during the dry season 2002 (Fig. 3a, revised manuscript) could not properly explain the single peak observed in shells (Fig. 4, revised manuscript). In the previous version, we suggested that the particulate uptake (Mnp) was the primary control of skeletal Mn/Ca variations but, as for Mnd, the observed pattern of Mn/Al increases in particles (Mn/Al)p during the dry season 2002 and 2003 (Fig. 3a, revised manuscript) do not follow the pattern observed in shells. An alternative hypothesis is now proposed taking into account phytoplankton blooms. As mentioned in in BGD version (p.1461, lines 1-8), peaks of skeletal Mn have been reported for Mytilus edulis (Vander Putten et al., 2000) in temperate marine ecosystem and for Isognomon ephippium in tropical mangroves (Lazareth et al., 2003). In both cases, peaks were supposed to be related to phytoplankton's blooms and increases of Mn-rich particles rather than a direct uptake of Mnd. This hypothesis was consistent with the delay of a few weeks observed between the increased run-off of freshwater carrying high contents of nutrients and Mnd in the tropical estuary and the appearance of high Mn concentrations in I. Ephippium (Lazareth et al., 2003).("Discussion" §4.2 and §4.3, p. 9-11, revised mansucript)

"Why would the peak show up in the shell before the strong increase (Mnp) apparent in September 2002?" (D Dettman §2.1)

In 2002, the first peak of (Mn/Al)p in water occurred on July, 9th and the second in September, 3rd (Fig. 3a, revised version). This matches with the date attributed to the main Mn/Ca peak in shell V10, i.e. "June-July 2002". The agreement is even larger if the Mn incorporation is controlled by the peak of chlorophyll a, which occurred in June, 26th 2002 (Fig. 3b, revised version).

"(...) and why does the MPU-E shell return to low [Mn]shell values after a spike in June 2003?"(D Dettman §1.3)

According to our hypothesis of a control by phytoplankton blooms, the last and highest Mn/Ca spike (laser shot n°7) measured in shell MPU-E in the last formed layers (shell collection: 18th July, 2003) is related to the sharp peak of chlorophyll a measured in water on 1st July 2003. Such a sudden increase of chl a likely triggers the physiological activity of P. spekii, resulting in a rapid increase of Mn/Ca in shell. After the spike, the

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rapid return to low Chl a values may have induce the same pattern for Mn/Ca in shell.

Referees Comments: D Dettman §3 ; S Severmann §1 "Ideally samples from the upwelling site should be compared to a background site" (S Severmann §1)

We agree that a "background site" would be important, but it is tricky because due to the internal waves, we could observe a lot of secondary upwellings along the coasts up to the northern part of the lake.

"(...) a consistent offset between the drilled samples in MPU-10 and the laser transect data." (D Dettman §3.2)

An error was done that was corrected in Fig. 4a (revised manuscript). Most of the laser data are in the range of the drilled samples, considering that each micromilled sample (SN HR-ICP-MS analysis) represent an average value of about five laser points (LA ICP-MS analysis). On the micromill profile, one point diverges significantly from the laser profile. This probably results from the presence of a small Mn-rich impurity in the powder sample, which was not sampled at the higher spatial resolution performed by the laser ablation.

"Do some of the peaks disappear if Mn concentrations are normalized to Ca, and would this improve the agreement between laser-ICP data and microdrill data?" (S Severmann §1)

Calcium is used as an internal standard to correct signal instability (in both laser and ICP-MS energy) and matrix effects in raw counts calculations (following Toland et al., 2000), postulating that Ca is uniformly distributed along the shell as quasi-pure aragonite (99% of $CaCO_3$) (BGD lines 10-13 p.1457). Consequently, the peaks are not affected if Mn concentrations are normalized to Ca. To be consistent with other studies dealing with geochemistry of bio-carbonates, we propose to convert our results into Mn/Ca ratios.

"Can the authors comment on the large difference in [Mn]shell for the two shells in

Figure 6? Why are the overall patterns and concentrations so different?" (D Dettman §3.1)

In contrast to the referee comment, we sustain that the overall patterns of Mn in the shells presented in Fig.6 are similar, despite difference in the concentrations levels. Indeed, the relative variations of content (i.e. the ratio between the lowest and the largest value of each peak) are quite similar in the last 7 Mn cycles (see table 1, this AC). It supports the idea that skeletal [Mn] is a potential proxy of the primary production in relation with limnological changes in surface waters. The comparison of the area under the skeletal [Mn] curves, evocated by D Dettman, may give some hints on how shell data could be quantified and then used as a quantitative proxy. Even if such investigations are promising, we are limited by the actual resolution of the laser (50μm) that gives us too a few analyses by peak to be reliable. The improvement of the laser methodology with more energetic beam (for instance the 157nm LA-ICP-MS) and a more sensitive mass spectrometer may allow to future use of surface peak measurements as a mean to quantify relative change in the upwelling intensity.(see "Discussion" §4.3, revised manuscript).

"I am missing a more thorough discussion of alternative explanations, such as vital effects" (S Severmann §1)

At the moment, one can only speculate on the nature of additional "vital effects" varying with age and controlling Mn incorporation in shells. Age-mediated changes in the metabolic activity might be involved in the ontogenic trend observed for skeletal Mn in P. spekii. Rosenberg and Hugues (1991) noted that Mg/Ca composition within the shell of the blue mussel Mytilus edulis increased with the shell curvature, since the metabolic efficiency decreased. They proposed that a metabolic gradient could control the shell geochemistry and contribute to the control of the shell 'shape. It is also possible that the detoxification mechanisms in soft tissues became less efficient with age leading to the sequestration of increasing quantity of Mn in the shell. Changes in Mn/Ca ratios in shells of P. spekii may be related to the onset of gametogenesis and energy relocation for spawning. As the biology of this freshwater tropical specie remains unknown, we cannot give any indication about the age from which shells become sexually mature and about the reproduction strategy (continuous spawning vs. seasonal spawning).(The text above is included in the "Discussion" p. 12, revised manuscript).

5 About the data tables

"I am a big fan of data tables" (S Severmann §7) The CLIMLAKE database will be made available once each partner has completed the publications of this multidisciplinary project.

6 About the editorial corrections

The text has been corrected taking into account all corrections provided by the referees. Figures 4 and 6 were enlarged to make an easier reading. The title was changed accordingly to the suggestion of D Dettman: "Manganese content records seasonal upwelling in Lake Tanganyika mussels" The Hecky reference was corrected (the title was missing).

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Peak............MPU-V61.....MPU-V22.....% of variation

peak #1 (2002)..2.41........2.37........2%

peak #2 (2001)..3.36........3.33........1%

peak #3 (2000)..1.63........1.53........6%

peak #4 (1999)..1.66........1.59........4%

peak #5 (1998)..2.6.........1.79.......31%

peak #6 (1997)..1.45........1.14.......21%

peak #7 (1996)..2.08........2.21........6%

peak #8 (1995)..2.50........2.28........9%

Table 1: Pleiodon spekii. Relative variations of the last eight Mn/Ca peaks (i.e. ratio between maximum value and the lowest value preceding each peak) from the ventral margin to the umbo on shell V61 and V22 (see Fig. 5, revised manuscript). A year was attributed to each peak based on the hypothesis of an annual Mn cycle in shell.

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