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Biogeosciences Discussions

Interactive comment on "Heavy metal uptake in foraminiferal calcite: results of multi-element culture experiments" *by* D. Munsel et al.

D. Munsel et al.

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We appreciate the effort of the reviewer put into our manuscript, which greatly benefited from his/her comments. Each of the comments was addressed separately.

Answers to Anonymous Referee #2

Comment 2.1: The authors defend the choice of multi-metal cocktails by indicating that these are closer to the natural situation. However, such a strategy seems premature in a situation where no coefficients are known for Ni and Mn from mono-metal experiments.

Answer: The reviewer is right, but in systems influenced by for instance hydrothermal activity show enrichment of more than one trace metal. Our not yet published data

of palaeo foraminifera show considerable enrichment of these trace metals and thus we conducted these multi-element experiments to see how the response of a multi-element cocktail is on living foraminifera. Nonetheless mono-metal experiments would be a good and concise addition to our experiments.

Comment 2.2: Due to the strongly deviating values for all metals at the highest metal concentrations, the authors decide not use these values fort he calculation of partition coefficients of Ni, but they do include them for Cu, although the trends are very similar. This discutable choice has a heavy impact on the calculated PC's, and is neither explained nor defended.

Answer: The reviewer is right by saying that we excluded the data of the highest Ni concentrations for the calculation of the PC's. But for Cu we also excluded the according data as the trend is similar to that of Ni. In our figure 3 it seems as if Cu is included, but it isn't – coincidently the calculated Cu value for the 20x tank is identical to the one from the 5x tank in case of the LA-ICP-MS measurements and very close together in case of the μ-synchrotron XRF measurements. In the revised manuscript the line of the Cu-μ-synchrotron XRF graph going through the 20x Cu concentration is removed and in the text it is clarified that for the PC calculations the highest concentrations are not included. Unfortunately this line was misleading the reviewer.

Comment 2.3: In order to explain the surprisingly low foraminiferal metal concentrations at higher concentrations, the authors evoke toxic effects and/or chemical competition/exclusion effects. Unfortunately the arguments raised on favour of these mechanisms are not convincing. Of course, in case of mono-metal experiments, the second possibility could have been excluded. It appears that the experimental approach has been too ambitious in view of the present rather limited state of knowledge.

Answer: The arguments raised to favour the mentioned mechanisms have not been reported yet for foraminifera. We had to adapt arguments proved for other marine life and tried to explain similar processes we observed. An indicator for toxic effects is

revealed by the observed reduced chamber formation of the foraminifera (see table 2) in the highest concentration tank.

Comment 2.4: The paragraph on the use of metal contents in foram tests to better constrain environmental pollution (p. 956, l. 5-13) is an interesting side-line, somewhat marginal in this paper.

Answer: Referee # 1 wanted clarification for this passage. So we added some references recommended by Referee # 1 and rewrote some of the text in the revised version of our manuscript. This also should be of the same tenor of Referee # 2.

Comment 2.5: P. 960, l. 8. How did the authors determine that all foraminifera were alive at the end of the experiments?

Answer: See comment 1.6 to referee # 1.

Comment 2.6: P. 960, l. 15-16. The authors say they will not consider Mn concentrations later in the paper. This is not true since they discuss them extensively later on.

Answer: See comment 1.36 to referee # 1.

Comment 2.7: The description (paragraph 3.4) and discussion (paragraph 4.1) of the partition coefficients are extremely fast, and the finally proposed values have been chosen rather arbitrarily. I have several minor comments and questions here: - l. 7: calculated PC's for Cu range between 0.08 (not 0.1) and 0.25.

Answer: This was corrected in the revised manuscript to 0.08. In the revised manuscript the Discussion was also restructured and the passage about partition coefficients is now titled 4.3. Also a new part about the calculation of the coefficients was added in the Method section (now found as 2.3).

Comment 2.8: l. 8: how was the "very uncertain estimate" of at least 2.4 for Mn determined?

Answer: The PC of Mn was estimated by calculating (Mn/Ca) (calcite)/(Mn/Ca) (sea water) using the lowest Mn measurements (in this case LA-ICP-MS). But since Mn scatters very broad, it only can be termed an estimate.

Comment 2.9: l. 12-15: a systematical decline of Ni and Cu at the highest concentrations: rather surprisingly, the results of the highest Cu concentrations are no longer considered (but this is never said), whereas the highest Ni concentrations are still used to define the PC's.

Answer: The highest Ni concentrations are not being used to define the PC's. It is the same with the highest Cu concentrations as both display the same trend and are considerably lower than the 10x concentrations. In the revised version of our manuscript it is clearly pointed out that for the calculation only the 1x-10x concentrations are being used (see also comment 1.8 to referee # 1).

Comment 2.10: l. 20: 0.1 should be 0.08.

Answer: This was corrected in the revised manuscript.

Comment 2.11: l. 21: "DCu was found to be 0.18". How was this calculated? Apparently, it is the average of 0.12 and 0.25, being the PC's medians of the 1) 5x and 20x and 2) of the 10x concentration? How was the error envelope calculated?

Answer: The value of 0.18 was indeed calculated as the mean of the medians – but only of the 1x to 10x concentrations (= 0.175 – then rounded to 0.18) and not using the 20x concentration! Unfortunately the error envelope was calculated wrong in the first version of the manuscript and was corrected in the revised version. The procedure is described in the new section 2.3 of the revised manuscript using the calculated standard deviation of the mean.

Comment 2.12: l. 22: the average value for LA-ICP-MS (0.12) is obtained in exactly the same way.

Answer: Yes.

Comment 2.13: l. 22: the final average DCu of 0.17 is based on a simple average of the LA-ICP-MS and XRF. Are the authors sure it is a good idea to calculate the average value of two different measuring methods, and present it (in the Abstract) as THE partition coefficient for Cu. This is all not very convincing to me.

Answer: Since the values of both methods are close together, the calculation of a total mean (including a new calculation of the error envelope in the revised manuscript) is absolutely an appropriate way as by this calculation possible systematic errors of both methods are being reduced.

Comment 2.14: l. 24: the DCu of 0.17 is lower than the value found by de Nooijer et al. However, the lower value is mainly obtained by the fact that they take into consideration the values obtained for the highest metal concentrations, which they do not do for Ni!

Answer: No! We did not use the highest concentration pool for the PC calculations – neither for Ni nor for Cu.

Comment 2.15: Another question: what range of experimental metal concentrations was used by de Nooijer et al.?

Answer: For their highest concentration they used 17.8 mol/L, which would be equivalent to a 100-fold concentration of the sea water we used in our experiment. This is included in the revised manuscript.

Comment 2.16: P. 962, l. 3-7: Here, the values obtained at 20x are not considered. Again the choice of the finally proposed value looks very arbitrarily.

Answer: As mentioned before, we didn't use the values of the 20x tank - neither for Cu nor for Ni when calculating the PC's.

Comment 2.17: p 962, l. 22-27: because all forams survived (how did the authors test this?), under all conditions new chambers were formed, and no malformed chambers were observed, the authors conclude that the culture conditions were "reasonably good". This statement contradicts the strong suggestion of environmental stress at

higher metal concentrations in chapter 4.3.

Answer: The whole paragraph was rewritten in the revised manuscript. About the vitality test for the foraminifera – see the comments 1.6 and 1.10 to referee # 1. It is also included in the revised manuscript.

Comment 2.18: The case made for toxic levels of metal concentrations in the 20x experiment is not very convincing, but it is hard to see how the authors could have done better. They should indicate (p.963, line 27) above what exact concentration Ni inhibits calcite precipitation in the study of Bachmeier et al. Along the same lines, it would be useful to know what maximum Cu concentrations were used by de Nooijer et al. and le Cadre and Debenay (p. 964, l. 4).

Answer: We added this information as far as it was written in these studies. Regarding the fact that Cu is an essential trace element it is more probable that Ni is responsible for the toxic effect. Considering the study of le Cadre and Debenay (2006) – see answer to comment 1.33 of Referee # 1.

Comment 2.19: The antagonism between Mn and Cu (p. 964, line 21 and further) is not very convincing either. The authors suggest that this antagonism is partly responsible for Cu and Mn concentrations, "at least in the 5- and 10-fold" concentrations. I fail to see why. In the 10x concentration both Mn and the other two metals increase. Conversely, the contrasting results for the 20x (increase in Mn, decrease in the other two) could indeed be indicative of such an antagonism. The whole paragraph is somewhat confusing.

Answer: That's why parts of this paragraph were rewritten in the revised manuscript.

Comment 2.20: The last paragraph of section 4.3 is very speculative.

Answer: This is correct. We stated in the revised manuscript that we speculate about that topic as there are no published data regarding these effects in foraminifera, we used studies considering other marine life and tried to transform the known facts to our

observations. To perform experiments focussing on these effects would go well beyond the scope of this paper, but could be indeed a key to explain our observations.

Interactive comment on Biogeosciences Discuss., 7, 953, 2010.