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Biogeosciences Discussions

Interactive comment on "Methylated arsenic and antimony species in suspended matter of the river Ruhr, Germany" *by* L. Duester et al.

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Authors response to referee comment3 bgd-2008-0031

This is the authors reply to the comment of referee 3. As general comment the remarks by anonymous referee 3 are less helpful to enable a constructive improvement of the publication. However we address them step by step as follows:

Referee comment1: In this article the authors measure the inorganic and organic arsenic and antimony in a fraction of suspended material in the River Ruhr, Germany, over a period of a year. The authors seem to be very familiar with the analytical techniques needed for the quantification of the alkyl forms of As and Sb.. Authors reply: Thank you for this comment; this is one of our key competencies.

Referee comment2: ..but, unfortunately, they seem to ignore nearly everything about the study of colloids and particles. Moreover, the sampling method used facilitates the modification of the sample (at least, it remains to be proved that it is not the case).

Authors reply: We are happy to reinsert our data re. particle size distribution of the samples, which was not included in the initial manuscript submission (wet analyses, CILAS 1180 laser particle analyser, measured in 100 classes broken down to 20 classes, presented as Q3). This data was not originally presented as we considered that the information that can be drawn from the results of these particle size analyses was limited. Indeed, there was very little variation in the particle size composition with 90 % at a particle diameter of 49 - 58 μm through out the year. (please see also comment5). An in depth study of colloids and particles was 1. not possible due to the limitations of sample size available to use (see response to the comments of referee1), moreover such analyses was outside of the remit of this study. As well recognised by both referees 1 and 2, this aims of this study were to (i) examine potential changes in the seasonal cycle of the methylarsenic und methylantimony species content in the suspended material and (ii) compare the biogeochemical behaviour of arsenic and antimony within this specific environment. We agree with referee, and as further detailed in our response to comment 6, that use of this low cost and easy to handle sampling technique does have sampling bias problems associated with it. In this case, certain particle size classes (particularly those $<$ 0.1 μm) will likely be less effectively captured than larger diameter particles. Particle diameter sampling bias is however a common feature of all methods currently in use for sampling suspended matter in streams, whether on an intermittent or continuous basis (e.g. in continuously working monitoring stations). Furthermore, it should be noted that the two most common alternatives used for monitoring purposes, filtration and centrifugation, are interference-prone, and in contrast to the method used in this study require significant maintenance and are expensive to operate. An additional and significant advantage of the sedimentation system is that even in times of low suspended particular matter content this method delivers enough material for various analyses and that the sampling within the stream (location and orientation) is of a

BGD

5, S675–S680, 2008

representative kind over the year.

Referee comment3: For these reasons, the conclusions of the study, based on the results shown, have little, if any, value. In case of a traditional referee evaluation procedure, I would not recommend the acceptation of this article. Authors reply: Whilst we recognise the right of the referee to recommend the acceptance or refusal for publication of the article, based on the individual comments of this reviewer we are of the opinion that the reviewer was assessing the article narrowly and solely with reference to their field of expertise. We have addressed all individual comments made by referee 3 and we would further point out that positive expressions of support for the publication of this article have already been received from two independent referees (see comments from referee 1 and referee 2)

Referee comment4: Some points to be considered by the authors are: - There is no mention of the existence of colloidal particles when it is well-known that, because of its high specific surface, they are often responsible for the adsorption of trace elements and organic pollutants. Authors reply: Sentence added, in please see comment 6.

Referee comment5: - The characterization of the "suspended matter" is virtually non-existent in the article. No way of knowing which is the particle size range considered, the composition of the inorganic and organic particles, the TSS or total suspended particle concentration, the changes in all these parameters with time, etc Authors reply: Please see our previous statements to referee 1 comment 1 (the Corg. and total C data will be inserted) and to referee 3, comment 2.

Referee comment6: - The sampling method used looks very prone to sampling artefacts. Have the authors tested whether As and Sb speciation remains unchanged after two weeks in the "floor of the basin? It is obvious that the physicochemical (pH, Redox, particle type and concentration) and biological conditions in the "floor of the basin" are radically different from the ones in the river! This "floor of the basin" looks as an excellent chemical and biological reactor... Authors reply: As mentioned before the

BGD

5, S675–S680, 2008

sampling method causes problems but in contrast to the alternatives working with high pressures (e.g. filtration) the sample remains relatively unaffected from physical forces (e.g. pressure and shear forces). The following paragraph is added to the methods part: The room in which the sedimentation basin is placed is tempered. With this sampling technique certain particle size classes (particularly those < 0.1 μm) will likely be less effectively captured than larger diameter particles (Figure 3). Particle diameter sampling bias is however a common problem of all methods currently in use for sampling suspended matter in streams in continuously working monitoring stations. Furthermore, it should be noted that the two most common alternatives used for monitoring purposes, filtration and centrifugation, are interference-prone, and in contrast to the method used in this study require significant maintenance, are expensive to operate and change the sample composition via physical forces (e.g. shear forces). An in depth study of different particles size classes (especially of the fraction < 0.1 μm) was not possible due to the limitations of sample material available and the amount of sample needed for the splitting of the sample and the pH-gradient technique.. Hence the most important influencing variables concerning the behaviour of bioreactor are the water temperature, the amount of living organisms (micro organism and algae) and the nutrient supply.

Taking these factors together, the highest quantity of metalloid organic species should be, as a logical consequence of the referee’s suggestion, detected during the warm water period (19 - 21°C, data will de inserted) in July and August. This instance did not occur.

Referee comment7: - Knowing which particles are seen by turbidimeters remains a difficult issue. In particular, the weight of the phytoplankton on the response obtained may be highly variable. However, what is nearly sure is that humics do not play any role (essentially turbidimeters do not see humics) as wrongly mentioned by the authors. Turbidity is a rather unspecific parameter and using it as the authors do in the article (without having any measurement at least of particulate carbon) is, at best, doubtful.

BGD

5, S675–S680, 2008

Authors reply: Agreed. The sentence will be changed to: Turbidity is an indicator of the suspended matter concentration.

Referee comment8: - No information about general parameters such as pH, conductivity, DOC of the waters is given. Authors reply: In The TC and TOC data will be inserted to the final manuscript version (DOC data is not available because of the previously mentioned limitations in sample amount.) Our previous studies have indicated no correlation between pH or conductivity and methylAs or methylSb content (Duester, Vink, Hirner 2008; Duster, Hartmann, Luemers, Hirner, 2007 and Duester, Diaz-Bone, Hirner 2005). Conductivity and pH was not measured in the sedimentation basin, but in the river water, statistical correlation of these data with reference to methylAs or methySb content is given.

Referee comment9: - The way how the relationship between flows and turbidity is managed is weak and not consistent from the statistical point of view. For instance, the way how "strong rain events" are dealt with is unclear. The links with melting periods are not well established. Establishing correlations between flows and turbidity, turbidity and TSS, turbidity and phytoplankton (has productivity been measured?), temperature and POC, etc. should be a first step in the study. These correlations are extremely easy to set (if the necessary parameters have been measured). Authors reply: Please see our response to referee2 comments.

Referee comment10: - Bacteria may play a role in methylation. No information is given concerning them in the study. Why? Authors reply: As the referee him/herself mentions (comment12) this is a descriptive study. Speculation concerning the primary group methylators will not be undertaken by the authors.

Referee comment11: - The use of Pb and Fe as "indicators" is unclear. Indicators of what? Pollution? Watershed inputs? Authors reply: The sentence was removed during the review process (see referee2).

Referee comment12: Since this study is in itself a descriptive one, and that many pa-

BGD

5, S675–S680, 2008

Interactive Comment

rameters do not seem to have been measured, it is not possible to extract any mechanistic conclusion regarding methylation processes, as the authors do. Authors reply: In comment 10 the referee tries to tease out a comment on processes. With one exception, which has already been removed following a comment by referee 2, the authors have not made any process related statements or conclusions.

In conclusion, despite the comments of reviewer 3, we share the opinion of the reviewers 1+2 that our descriptive study is of interest to an international audience, particularly as the data set is not as weak as suggested by reviewer 3. We will insert TOC, TC, temperature and particle size distribution even though we think that the amount of information which may be derived from this additional data is low. We believe that the study is of value towards a better understanding of the Methyl- Sb- and As-species distribution in rivers. The key issues of this study were to (i) examine potential changes in the seasonal cycle of the methyl arsenic und methyl antimony species content in the suspended material and (ii) to compare the biogeochemical behaviour of arsenic and antimony within this specific environment. In our opinion the study achieves these aims.

Interactive comment on Biogeosciences Discuss., 5, 1361, 2008.