

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

L. Duester et al.

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Authors response referee comment2 bgd-20

Please find attached our responses to the very constructive and useful comments of referee 2.

Reviewer comment 1: This field study measures inorganic and organic As and Sb in suspended particles of the River Ruhr in Germany. The objectives 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. Results show that patterns of the methylated species of As and Sb are different to each other and it was concluded that the occurrence of these two organic xenobiotics is not related. The

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methods are well described and the authors seem to be familiar with their analytical techniques for As and Sb species identification. Authors comment: No comment required.

Reviewer comment 2: There is an issue with the pooling of biogenic and geogenic material as suspended solids. In my mind, plankton should not be used as 'suspended solids'; (see below). Authors comment: This topic is answered in detail below.

Reviewer comment 3: As for other organometals, such as organic Hg, it is interesting that inorganic As and Sb concentrations cannot predict any of the methylated species. This should be discussed further in the present study including statistical analysis to better understand how concentrations of methylated As and Sb species differ with regard to inorganic concentrations throughout this seasonal study. Authors comment: From our point view it is always doubtful to perform statistical evaluation with very small data sets, in our case $n=2 \times 12$. This is nowadays often neglected as the results look meaningful but the statistical background is from it basis weak. However there is no statistical correlation between the methylated species content and the total content (As $r^2=0,16$; Sb $r^2=0,08$) in this small data set.

Reviewer comment 4: Moreover, it should be underlined that this study is purely observational in nature and cannot conclusively discuss processes involved in methylation. Authors comment: We agree with this statement and we didn't include any discussion concerning processes of methylation. One misleading phrase was removed (see below).

Reviewer comment 5: Lastly, although this paper is mainly descriptive, it would be necessary to put these results into environmental perspectives with regard to availability/biohazards of these xenobiotics in freshwater systems. Authors comment: The data concerning the environmental impact of methyl- arsenic and antimony is consciously excluded from this publication, as from our opinion it would 'inflate'; this

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small study unnecessarily. General information can be found at Duester et al. 2008; detailed at Dopp, E.; Hartmann, L. M.; Florea, A. M.; von Recklinghausen, U.; Rabbieh, S.; Shokouhi, B.; Hirner, A. V.; Rettenmeier, A. W., Trimethylantimony dichloride causes genotoxic effects in Chinese hamster ovary cells after forced uptake. *Toxicology in Vitro* 2006, 20, (6), 1060-1065 and Dopp, E.; Hartmann, L. M.; Florea, A. M.; Rettenmeier, A. W.; Hirner, A. V., Environmental distribution, analysis, and toxicity of organometal(loid) compounds. *Critical Reviews in Toxicology* 2004, 34, (3), 301-333.

Specific comments:

Reviewer comment 6: p. 1363, l. 3 Add 's' to 'centre';
Authors comment: Changed

Reviewer comment 7: p. 1363, l. 9 I suggest changing 'biological activity' with 'autochthonous sources (e.g., microorganisms)';
Authors comment: We agree. This is more specific and hence better.

Reviewer comment 8: p. 1363, l. 12 It is not clear what exactly comprises suspended solids? In particular, can aquatic organisms really be called suspended solids because most of them are motile and don't depend, in large, on external suspension forces. I recommend using the term 'particles' rather than 'solids';
Authors comment: We agree and will use the term suspended particulate matter (solids and bio material, e.g. algae or decaying vegetation)

Reviewer comment 9: p. 1367, l. 8 The authors may want to replace 'yearly' with 'annual';
Authors comment: Changed.

Reviewer comment 10: p. 1367, l. 14 peak concentrations of chlorophyll-a were clearly associated with phytoplankton development: It is not clear how peak concentrations were associated with phytoplankton development. How was the phytoplankton development measured? Moreover, what did the term 'peak'; in the second part of this sentence refer to? The wording is misleading and occurred during the in-

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terior review process. Please excuse this mistake from our side. Authors comment: The sentence is changed to: In this study, peak concentrations of chlorophyll-a (used as indicator for phytoplankton development), was between April and August, whereas two distinct maxima were seen for turbidity measurements (November/December and February); the February turbidity peak was associated with the peak flow rate of the Ruhr (Fig. 2a).

Reviewer comment 11: p. 1368, l. 25 This study did not examine methylation processes, but concentrations of organic As and Sb species. Thus, no conclusions about methylation of As and Sb can be made. Authors comment: We accept this comment and the sentence will be changed to: It may therefore be concluded that organo arsenic concentration in the current, which was observed in the spring and early summer months occurring simultaneously with the increase of the chlorophyll-a content, does not result in significant extend from biological process during the winter period.

Reviewer comment 12: p. 1369, l. 1 I assume the authors refer to H_2O ; water. Authors comment: Yes we do. Thank you.

Reviewer comment 13: p. 1369, l. 16 H_2O ; This coincides with the lowest flow rates (when strong rainfall events are ignored) H_2O ; . Is this correlation statistically significant? Why were strong rain events ignored? Are more careful examination is warranted. Authors comment: It is not statistically significant. Hence we removed this sentence from the publication. Strong rain events were ignored in connection to the mean lowest flow rates as one elevated rain event during the mentioned months occurred.

Reviewer comment 14: p. 1369, l. 19-26 This is a run-on sentence and it does not discuss results. Moreover, it is not clear how Pb or Fe can be H_2O ; indicator elements H_2O ; ; for what? Moreover, how can the source of MeSb, presumably of terrestrial origin, be functionally related with Sc? Authors comment: A definitive source for the particulate matter collected in the sedimentation bowl in winter cannot be deduced

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via indicator elements monitored in this study. Future studies therefore require that the analysis incorporates elements that can be used for standardisation of the metalloid concentrations, e.g. via scandium to characterise the proportion of contaminants not bound to clay minerals.

Reviewer comment 15: Table 2+3. Please explain the abbreviated terms in the figure caption. Authors comment: The abbreviations are explained in the abstract and introduction, but we agree that an amendment in the heading is useful.

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