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

Anonymous Referee #3

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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 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). 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 acceptance of this article.

Some points to be considered by the authors are:

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- 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.

- 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.

- 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...

- 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.

- No information about general parameters such as pH, conductivity, DOC of the waters is given.

- 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

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the necessary parameters have been measured).

- Bacteria may play a role in methylation. No information is given concerning them in the study. Why?
- The use of Pb and Fe as "indicators" is unclear. Indicators of what? Pollution? Watershed inputs?

Since this study is in itself a descriptive one, and that many parameters do not seem to have been measured, it is not possible to extract any mechanistic conclusion regarding methylation processes, as the authors do.

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