

## ***Interactive comment on “Geochemical controls on the partitioning and hydrological transport of metals in a non-acidic river system” by J. Thorslund et al.***

### **Anonymous Referee #1**

Received and published: 30 September 2014

Dear Editor,

Please find my comments on the manuscript hess-2014-222, entitled: “Geochemical controls on the partitioning and hydrological transport of metals in a non-acidic river system”. Author(s): J. Thorslund et al.

First I will give general comments then precise ones.

#### General comments

The manuscript presents a study on geochemical controls on metallic trace element transport in a non-acidic river. With only two surveys which add up to 10 samples, the

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authors discussed the speciation control of some trace element using both analytical results and model results. The main aim of this study is not very relevant because it is well known that, under pH around 8 to 10, trace elements are mainly transported as associated to oxyhydroxide phases. In addition, some important thermodynamic concepts were not considered. This work could be interesting if some specific results were assessed. I am sorry but I do not think that the data which have been collected for this study could provide the authors with interesting results. If the paper addresses relevant scientific questions within the scope of HESS, ideas, scientific methods and assumptions are not valid. My opinion will be to reject this paper.

Please find some specific comments below.

#### Other comments

1. Introduction P9717Ln19-22. “The dissolved form, especially the dissolved inorganic fraction, is considered to be the most toxic form of the majority of metals. . .”. I am sorry but this assertion is false. The most bioavailable forms are the lipophilic ones, not the ionic ones. In addition, the references on this theme are not appropriate.

3.1 Field methods and sample collection You collected only five samples in June 2012 and five in September 2013? Trace element concentration is very much variable in a river. Are you sure that your samples are representative? The same remark is valid for flow measurement.

I suppose that analyses made on unfiltered samples gave the total concentration values. But you use only an acidification with HNO<sub>3</sub> at pH = 1 or 2. Also you did not really measure the “total” concentration of each trace metal, you have measured forms that were associated to calcite + amorphous oxyhydroxide + forms adsorbed on crystalline solids.

Samples were stored at room temperature?

To be valid, the alkalinity measurement must be made the day of sampling to avoid

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any equilibration of the solution carbonate system with the atmosphere (and samples stored at 4°C).

3.2 Analytical methods You give the detection limits, in Table A1, but not the concentration values which have been measured. How it can be used? You always present data as relative values (%) never as direct values.

Table 4. You express alkalinity as mg/L. It is more accurate to express it as eq/L or meq/L. You can give the electrical conductivity of water in order to help the reader. This gave a rapid view of the ionic strength.

3.4 Modeling approach P9725Ln5. Equation (4). The equation that you have used corresponds to the limit of stability of water before water is oxidized to O<sub>2</sub>. By using this relation, you assume that this reaction regulate the redox condition of the river water. This is not realistic.

Table 2. Table caption. You write: " Some elements only had one state in the program " no. These elements are only present under one oxidation state in natural environment.

For oxyhydroxide, what concentration of binding sites have you chosen? What active surface area? With what LogK? According to which criterion? And for organic matter, what have you chosen as complexation characteristics?

I have stopped the review here because a lot of work is needed before the discussion part.

Kind regards,

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Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 9715, 2014.