

HESS - Final responses to R1 and R2

Our detailed, point-by-point response to the referee comments follows below and includes references to where in the manuscript the corresponding changes were made. We think that we could address and answer all relevant questions raised through the review. However, key comments from reviewer 1, such as for instance “*ideas, scientific methods and assumptions are not valid*”, “*This work could be interesting if some specific results were assessed*”, and “*the references on this theme are not appropriate*” could not be accounted for in the revised manuscript, since the reviewer did not support them as can be expected by logical arguments or other references. Furthermore, as shown below, such reviewer #1 judgments are contradicted by published journal papers as well as judgments of reviewer #2.

Notably, in response to converging criticism from both reviewer #2 and #1 regarding data representativeness and (too limited) number of sampling locations, we considerably expanded the number of analysed locations from 5 to 17, including also observations from an adjacent river basin. We hope that, with the present modifications, this paper can be acceptable for publication in HESS.

Response to Referee #1 comments.

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 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.

→ The main objective is much broader than implied above: investigating geochemical controls on large-scale water-borne spreading of metals in non-acidic systems. The speciation studies which have been conducted in non-acidic systems have mainly been focused on one or a few metals, at local to multiple scales (e.g. Moldovan and Henry., 2005, Avilés et al., 2006, Sjöstedt et al., 2009), whereas the focus of multiple metals on a larger scale in non-acidic systems are lacking. To our knowledge there are only a few papers with this perspective (Pandey et al., 2014 and Sungur et al., 2014). It follows that there are still considerable knowledge gaps on geochemical controls and transport of metals in non-acidic river systems. For instance, our results show that transport associated with oxyhydroxide phases is not the main control of all trace metals, but that organic material plays an important role controlling the mobility of several metals.

Regarding modelling approach and underlying concepts, the thermodynamic concepts used within Visual MINTEQ builds upon the model code MINTEQA2. This code was developed by USEPA, and has been used in over 200 published papers in ISI's Web of Science. Visual MINTEQ is a state-of-the-art code that has been used to study mass distribution in a wide range of problems, including soil solutions (e.g. Gustafsson et al., 2003), rivers (e.g. Butler et al., 2009) and lakes (e.g. Sjöstedt et al., 2010).

Furthermore, one of our objectives (i) was to evaluate the model performance under these non-acidic conditions and we have now showed, with an expanded dataset (see below), good agreement (76%) for most metals with this approach, including both river and surface water ponds.

The analysis was based on 150 samples: from 5 sampling locations in 2012, revisited in 2013. For each sampling location in 2013, we took six samples for metal analysis (three replicates with filtered samples and three replicates with unfiltered samples), six replicate samples for organic carbon (three for DOC/TOC), three replicate samples for major ion analysis. In total, for each considered river location, we took 15 samples, which then adds up to 150 samples. Further, for each sampling location we modelled and analyzed 25 metals and other key geochemical parameters for each considered location. Compared to similar studies that combine hydrology and geochemistry, this number is quite substantial (e.g. Butler et al., 2009, Yun et al., 2001).

Furthermore, in response to specific review comments on this issue (see below), we now considerably expanded the number of analysed locations from 5 to 17, including nine riverine sampling locations (5 more from the Tuul River and four from another high pH river in the region) and three pond sampling locations from the mining area, expanding the number of analysed samples from 150 to 330.

Specific comments

1. Introduction "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.

→ Whereas the lipidic form is known to be highly bioavailable, the point made from our large-scale metal spreading perspective (where transport processes differ considerably between dissolved and suspended phases) is that dissolved forms are more toxic than suspended forms. We have now additionally added another more general toxicological reference on this theme stating that as a rule, the ionic form is the most toxic (Chapman 1992).

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.

→ As briefly mentioned previously, we addressed the comment of sample representativeness through substantially extending our dataset and geochemical analysis, with additionally nine riverine samples (five more from the Tuul River and four from another high pH river in the region) and three pond samples from the mining area (See e.g. section 3.1, Table 1, Table 4) from the 2013 sampling campaign. Hence, with this new dataset, we include more river sampling locations, additional high-pH systems and a new sub-catchment, hence extending the analysis to include a wider range of conditions.

Further, we now added additional comparisons of our snapshot measurements with long term flow and metal concentration data (PxxLnxx). A comparison of metal concentrations with available monthly averages showed that there were periods during which the metal concentrations were higher than during the here reported snapshot campaigns (Thorslund et al., 2012). For flow measurements, monthly

average discharge at the Zaamar site vary between 15-54 m³s⁻¹ (Thorslund et al., 2012), whereas long term (1945-2007) average discharge in Tuul River is 27 m³s⁻¹ (GEMStat, 2011).

I suppose that analyses made on unfiltered samples gave the total concentration values. But you use only an acidification with HNO₃ 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.

When running the unfiltered and filtered samples a v-groove nebulizer were used to ensure that also particles were included in the measurements. V-groove nebulizers have shown that it is possible to do analysis even of slurries (see for example Bings et al. 2014 and references therein).

Samples were stored at room temperature?

→ Due to field conditions and logistics, we did not have cooling possibilities in the field. Samples were kept dark and as cool as possible. Average temperatures during the field campaigns were relatively low (below 10°C).

To be valid, the alkalinity measurement must be made the day of sampling to avoid any equilibration of the solution carbonate system with the atmosphere (and samples stored at 4°C).

→ The alkalinity measurements can be uncertain, however, since we kept the samples without contact with the atmosphere, degradation within the samples would be the main cause of alkalinity change. For the speciation modeling, we tested the model performance by varying the alkalinity between the two years results and this did not significantly impact the modeled speciation.

3.2 Analytical methods. You give the detection limits, in Table A1, but no values which have been measured. How it can be used? You always present data as relative values (%) never as direct values.

→ We have now added all average concentration data and DL to our supplementary information and hence removed Table A1 (included in SI).

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.

→ This has now been changed accordingly, to meq/L (see Table 4) and the new points values have also been added here.

3.4 Modeling approach. Equation (4). The equation that you have used corresponds to the limit of stability of water before water is oxidized to O₂. By using this relation, you assume that this reaction regulate the redox condition of the river water. This is not realistic.

→ It is well known that measuring pe in natural waters is a difficult task (e.g. Stefansson et al., 2005) and that the results may vary considerably based on which method is used. The estimation method used in our manuscript, equation (4), has been assumed reasonable for O₂ saturated waters (Stumm and Morgan, 1996) and has been used for estimating pe in river systems in other published work (e.g. Wällstedt et al., 2010). The estimated values should be considered as maximum values, since the redox reaction for O₂ is slow and the pe-values of natural waters are in reality often lower than the theoretical values (Langmuir, 1997). This has now been added in the text (P14Ln320-323). Additionally, a test run where pe was lowered by 50 % for each sampling location, showed that only Mn speciation results were significantly impacted (predicted to be 100 % more dissolved with lower pe). Notably, Mn was already identified in the manuscript as a metal which we cannot predict at this stage (P13Ln353-357 and P17Ln480-482) and for the metals that could be predicted well, pe was of minor importance (for instance, As and V were on average predicted to be 9 % more dissolved with lower pe).

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.

→ This was wrongly expressed and has been removed from the table caption text.

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?

→ For both organic matter complexation with the Stockholm Humic Model (SHM) and adsorption to ferrihydrite and gibbsite, default databases in Visual minteq were used. The only exception is vanadate adsorption to ferrihydrite where the adsorption constants were changed according to Wällstedt et al., 2010. Even though this was mentioned in the text, we agree that this information may not have been totally clear. This has now been clarified. However, since the scope of this paper was not to give a full description of the model settings, but rather to give an overview of model input, basic parameter settings and assumptions, the Modelling Approach section is kept relatively short.

More specifically; The active surface area of ferrihydrite (Dzombak and Morel, year) is 600 m² g⁻¹. For Gibbsite (Karamalidis and Dzombak, 2010) this value is 32 m² g⁻¹. The log K values for these solids are shown in Table 3. Log K values for adsorption onto these solids are default and can be found in the complexation databases in the models (feo_dlm_2008_vdb and Gibbsite_dlm_2010.vdb).

Response to Referee #2 comments.

This is in general a very good paper that I can without hesitations accept for publication. The research question, while not entirely new, provides new insights for the region of the Tuul river, which was

previously poorly investigated with regard to the study question. Due to ongoing but changing mining practices, the mobilization and transport of various substances, including heavy metals, are a relevant issue from the environmental perspective. I would suggest the authors, where meaningful, to refer to a series of papers recently published in a special issue on Water in Central Asia in the journal Environmental Earth Sciences.

→ We fully agree that the Tuul River has not previously been investigated for this purpose, and that present results give new insights on environmental effects on mining. We also would like to highlight that the model approach and main findings can apply to other non-acidic systems beyond the Tuul River. We use the Tuul River as a focus reach where both mass flows and speciation estimations are conducted, since this site includes the Zaamar Goldfield, which is a previously identified source zone (e.g. Thorslund et al., 2012, Chalov et al., 2014). This application example is used to study more general research questions about metal spreading and partitioning in non-acidic systems. To make the contribution more general we have now additionally considered another high pH river system and some surface water ponds in the region, extensively expanding our sampling from five to 17 locations. One of the main objectives of this study was to test model performance in these type of systems, compared to measured data. With the now extended dataset, we show that model predictions work well for a majority of the modeled data in all of these systems (76 %). We believe that the general objective, methodological approach and findings of this paper have been further enhanced with this expansion of the dataset.

Regarding additions of suggested references, we already refer to the study by Pfeiffer et al. (2014) (P22Ln538-542) and we have additionally added a reference to Hofmann et al. (2014) to the manuscript, in the discussion regarding metal pollution in Mongolia.

Referee #1 second comment

The subject of this paper could be interesting if the tools that have been used were relevant. The number of samples is too small to be representative of the water quality. This remark is also true for the flow measurements. In addition, the thermodynamic code was not used in an appropriate manner. Kind regards

→ These issues were raised in the general comment and specific comment 3.1 of Referee #1. See our response to these comments.

Referee #2 second comment

I can understand the point of reviewer #1 regarding the limited number of samples/discharge measurements. While I would not go as far as saying that this disqualifies the paper, the authors could in a revised version more explicitly describe the limitations of the study as it is

→ We have, as mentioned, now substantially expanded our study by adding twelve more samples for the model approach. For mass flows of metals, we still have the focus of the Zaamar site, since this region previously have been quantified as having a large impact on net transport in the Tuul River and this is also where data for comparison in this highly unmonitored region do exist (Thorslund et al., 2012).

In the end of the conclusions (P26Ln665-671), we now clarify the limitations of the present findings, that: “Although further model development is needed, for instance developing sorption databases, the present results show that the applicability of this approach can work well on non-acidic systems. However, we suggest that the combination of transport quantifications and this geochemical modelling need to be applied in other non-acidic systems with different geochemical conditions, to further increase the understanding of controls governing metal spreading and fate”.

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