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Geochemical controls on the partitioning and hydrological transport of metals in a non-acidic river system

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Abstract

The speciation of metals, i.e. in which chemical form they occur, controls their mobility, bioavailability and toxicity. The overall objective of this study is to extend the knowledge on the spreading of metals in non-acidic river systems; this knowledge is currently much more limited than the knowledge on metal behavior under acidic conditions that for instance are found in acid mine drainage systems. We combine novel measurements of metal spreading under distinctly high-pH conditions (up to 9.6) in the Tuul River at the Zaamar Goldfield mining site (Upper Lake Baikal Drainage Basin, Mongolia) with a geochemical modelling approach (Visual MINTEQ). Total mass flows of several metals (Al, Cd, Fe, Mn, Pb and V) showed net increases over the mining site, with metals in suspension generally dominating the total export from the site. Model results showed that a main difference from acid mine drainage geochemistry is that the prevailing high pH causes precipitation of ferrihydrite and gibbsite, which removed between 90 to 100% of Fe and Al from solution. This notably influenced the behavior of As, Pb and V since their solubilities are controlled by sorption onto ferrihydrite. The combined effects from such geochemical processes (precipitation, sorption) hence explain the high impact of suspended transport to total transport under high pH conditions. Arsenic furthermore showed dissolved concentrations above health risk-based guideline values in several locations and can thus be of main toxic concern in the upper Lake Baikal Drainage Basin. Moreover, present modelling showed that in particular the solubility of Fe, Pb and Zn can increase considerably as DOC concentrations increase due to metal-organic complexation. In high pH systems, seasonality of DOC concentrations can therefore have a major influence on the spreading and toxicity of these metals, as can DOC trends caused by land use change. Present results also suggest that the behavior of Cr, Cu and Mo would be much better understood if a dependable adsorption database for hydroxyapatite could be developed.

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1 Introduction

Metals can become exposed to the environment through natural processes, such as weathering of soil and bedrock, and through anthropogenic processes, such as mining, industry and agriculture. They can enter aqueous systems through wash out from surface soils, diffuse groundwater inflow, metal mobilization from enriched sediments, leaching from agricultural areas and mine tailings, catastrophic tailings dam failure and discharge of industrial and mining effluents (e.g. Hudson-Edwards, 2003; Macklin et al., 2006; Mighanetara et al., 2009; Inam et al., 2011). Material mobilization via bank and bed erosion under conditions of geomorphic adjustment can dominate pollutant transport under certain conditions (Lewin and Macklin, 1986; Chalov et al., 2014). Once metals are released into aquatic systems they persist in the environment, since they are non-degradable. Metals held in alluvial stores may therefore continue to pose a threat to ecosystems, long after their initial release, and alluvial sediments may possibly constitute the most significant source of catchment heavy metal pollution (Dennis, 2005; Alexeevsky et al., 2013).

Mounting evidence over the last decades have shown that the speciation of metals (i.e. in which chemical form they occur) controls their mobility, bioavailability and toxicity (e.g. Tessier and Campbell, 1979; Tack and Verloo, 1995; Tipping, 1998; Fytianos, 2001; Landner, 2005). The dissolved form, especially the dissolved inorganic fraction, is considered to be the most toxic form of the majority of metals (e.g. Gundersen and Steinnes, 2001; Nystrand et al., 2012), since it can readily be taken up by organisms and biota (e.g. Törnqvist et al., 2011; Raguz et al., 2013). Many chemical factors and parameters need to be accounted for in determining the speciation, such as pH, redox conditions, oxidation state of the metal and available surfaces for adsorption (e.g. Palleiro et al., 2013). An advantage of equilibrium speciation models is the possibility to predict dominating forms and evaluate controlling mechanisms, such as sorption and precipitation reactions (Lund et al., 2008). Frequently used speciation models include WHAM (Tipping, 1994), PHREEQC (Parkhurst and Appelo, 1999) and Visual

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MINTEQA (Gustafsson, 2009), which are used for both groundwater and surface water applications (e.g. Tipping and Lawlor et al., 1998; Butler et al., 2004; Gustafsson et al., 2009; Korfali and Davies, 2004; Wällstedt et al., 2010; Nystrand et al., 2012). They have the ability to represent surface complexation reactions and binding to organic matter, which are all central to metal transport and partitioning between the water and sediment phase (e.g. Butler et al., 2008).

Although there are many studies on speciation modeling of metals in aqueous systems (e.g. Eary, 1999; Butler et al., 2004; Balistrieri et al., 2007; Gustafsson et al., 2009; Nystrand et al., 2012), the majority of them have focused on metal behavior under acidic or near neutral conditions rather than metal behavior under high pH conditions. Some exceptions are for example a study by Sjöstedt et al. (2009) who measured and modeled the speciation of Al, As and Mo in Swedish lakes that had been limed to near neutral pH and a study by Moldovan and Hendry (2005) who modeled the speciation of As, leaching from uranium mining, up to pH 11. In addition to speciation modeling studies, others have highlighted pollution problems of metals in non-acidic systems (see e.g. Tarras-Wahlberg et al., 2000; Sjöblom et al., 2004; Grosbois et al., 2009; Zak et al., 2009), often showing high metal concentrations in particles but low concentrations in the dissolved form, hence indicating that geochemical controls and dominating processes might differ from well-studied acidic pollution sources.

Furthermore, understanding geochemical controls in combination with physical transport of metals could greatly enhance metal transport and fate predictions (Foster and Charlesworth, 1996; Destouni et al., 2010; Persson et al., 2011). For example, geochemical processes (e.g. adsorption) influence whether or not certain physical processes (e.g. suspended sediment transport; Chalov et al., 2012) will be important for the overall transport of metals. There are however relatively few studies that address these combined effects of physical and chemical controls on metals in aqueous systems (e.g. Caruso et al., 2008; Malmström et al., 2008).

The overall objective of this study is to extend the knowledge on the spreading of metals in non-acidic river systems. We combine novel site specific measurements with

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a geochemical modelling approach (Visual MINTEQ), specifically aiming at (i) evaluating the performance of using this modeling approach by comparing observations and model predictions, (ii) identifying dominating solids and predict the capacity of these solids to sorb and/or co-precipitate other metals that are transported in suspension and (iii) identify dominant controls keeping metals in solution, such as soluble complexation.

As an application example, we consider the distinctly high-pH conditions (Pietron, 2012; Thorslund et al., 2012; Chalov et al., 2012, 2014) of the Tuul River, at Zaamar Goldfield, in Mongolia. It is the largest gold mining site within the Tuul River basin, comprising a widespread source zone. The Tuul River connects to the Orkhon–Selenga River system and is a highly polluted river in the upstream Mongolian part of the transboundary Russian–Mongolian Lake Baikal drainage basin. The many mining companies within Zaamar Goldfield, as well as illegal mining, is considered to have serious impact on the water quality within the river basin (Altansukh and Davaa, 2011; Chalov et al., 2012; Thorslund et al., 2012) and could possibly have an impact on downstream Selenga river and Lake Baikal. Although total (suspended and dissolved) concentrations and mass flows of several metals within this system were high, dissolved concentrations were generally low. In the downstream regions of the Lake Baikal drainage basin however, increasing metal pollution of both sediments and biota has been reported (e.g. Rudneva et al., 2005; Khazheeva et al., 2006). Investigating controls on metal partitioning between the sediment and water phase is thus of particular importance for this system, since metals originating from Zaamar Goldfield could potentially be transported all the way to the vicinity of Lake Baikal that hosts a unique ecosystem and comprises a huge water resource.

2 Site description

The mining areas of Zaamar Goldfield are located along the Tuul River valley, between Latitude: 48°17'50" N and Longitude: 104°24'65" E (Fig. 1) (AATA, 2008),

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approximately 600 km upstream of the Lake Baikal inlet (AATA, 2008). The Tuul River is a tributary to the Selenga River, a transboundary river between Mongolia and Russia, which is by far the largest river draining into Lake Baikal (Lee et al., 2006), discharging about 30 km³ of water and 3.5 million tons of sediments annually into the lake area. Before the Selenga River flows into Lake Baikal there is the Selenga delta, covering an area of about 1200 km² (USGS, 2011).

Annual average discharge of the Tuul River is 27 m³ s⁻¹ (1945–2007), but maximum discharges in the summer period can reach values of around 80 m³ s⁻¹, whereas decreasing discharges are marked throughout the coldest months of the year (November–March). After the junction of the Tuul River with the Orkhon River, discharges on average increase by an order of magnitude and in the downstream Selenga River, annual average discharge reaches just over 1000 m³ s⁻¹ (GEMStat, 2011; MCA, 2011). The average yearly precipitation in the region is between 200 and 250 mm. The climate of the region is semi-arid with warm and dry summers (averaging temperatures of 20 °C), although intense rainfalls do occur, and cold winters (averaging temperatures of –20 °C) (AATA, 2008).

The geology of the area includes sedimentary, igneous, and metamorphic rock formations, such as sedimentary sand and siltstones, igneous gabbros, and metamorphic schists. The region is also naturally consisting of calcium bicarbonates to a large degree (Altansukh and Davaa, 2011) and there are strong interactions between surface waters and groundwater, due to extensive areas of alluvial unconfined aquifers in the river valleys (Zandaryaa et al., 2008). This impacts the Tuul River quality and quantity, which is fed by groundwater inflows with high water-rock interactions; affecting the pH values throughout Zaamar Goldfield to be high (Lee et al., 2006; Zandaryaa et al., 2008).

Zaamar Goldfield is the largest gold mining site within the Tuul basin and the extensive source zone contains both alluvial and hard rock mining that stretches for about 45 km along the floodplain of the Tuul River (Lee et al., 2006). The many mining activities over widespread areas and the lack of control of tailing and leakage from settling

(S) concentrations and Chloride concentrations were set to equal measured Sodium (Na) concentrations.

The redox potential (pe) was estimated according to Eq. (4) for both years, which is assumed representative for well oxygenated waters (Stumm and Morgan, 1996).

$$pe = 20.77 + \frac{1}{4} \log pO_2 - pH \quad (4)$$

where pO_2 was assumed to equal 0.2 atm (i.e. the O_2 content in the atmosphere is 20.95 %), similar to what Wällstedt et al. (2010) used in their study.

The solids that were allowed to precipitate when their respectively solubility constant was exceeded are shown in Table 3. These were chosen based on (i) knowledge about common solids for the present geological conditions at the study site, and (ii) model outputs of “saturation indices”, indicating which minerals could precipitate, based on site specific data and thermo dynamical calculations.

Adsorption to ferrihydrite and gibbsite was estimated using the DLM (diffuse layer model) according to Dzombak and Morel (1990) and Karamalidis and Dzombak (2010) respectively. The DLM is a surface complexation model that simulate the distribution of each metal ion between the dissolved form and adsorbed to a solid (Gustafsson et al., 2009). Both of these minerals were selected due to their high measured particulate concentrations and their sorption capacities. Published data on the solubility of gibbsite varies and is mainly a function of pH, sulfate, fluoride and DOC concentrations. The main difficulty lies in that it is hard in natural systems to separate amorphous $Al(OH)_3$ from gibbsite. Because of this difficulty the solubility of Al is restricted and its database in Visual MINTEQ is more limited than for ferrihydrite. ferrihydrite is an iron mineral which is a frequently used solid for adsorption in Visual MINTEQ and the adsorption database for this solid is thus extensive. Ferrihydrite is well known for its metal retention capacity due to large surface sites for adsorption and has been shown to correlated well with measured data (e.g. Sjöstedt et al., 2010; Nystrand et al., 2012; Tiberger et al., 2013). Adsorption constants for Vanadium adsorption to ferrihydrite was

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change according to Wällstedt et al. (2010). All other parameter values in this menu were kept on default.

For simulation of complexation of the metals with dissolved organic matter the “Stockholm humic model” (SHM) was used. This model uses a discrete-site approach to represent the metal-humic complexation, similar to the model described by Tipping (1994). The default ratio of 1.65 between active DOM (i.e. the part of the organics that binds to the metals) and DOC (dissolved organic Carbon) was assumed representative and thus not changed. All of the DOM was assumed to be fulvic acid, based on earlier studies (e.g. Khai et al., 2008; Sjöstedt et al., 2010; Wällstedt et al., 2010; Gustafsson et al., 2014), which is also set as default in the model.

4 Results

4.1 Tuul River water chemistry

Geochemical parameter values, used for the model input, representative for the five sampling locations along the Tuul River reach (T5–T6a) are shown in Table 4. The pH shows in all cases alkaline conditions, with values ranging between 9.6 (T5a) to 8.5 (T6) in the 2012 campaign and between 9.2 (T5a) to 7.6 (T5a) in the 2013 campaign. DOC concentrations vary between 10–12 $mg\ L^{-1}$ throughout the measured river locations. TOC concentrations were on average only a few percent higher than DOC concentrations, hence dissolved organic matter is dominating the total organic matter composition. Estimated alkalinity values are very high, especially from field measurements in 2013. However, changing the alkalinity values in the model input did not change the speciation of selected metals, indicating low sensitivity for this parameter.

Dissolved and total riverine concentrations for the selected metals in the 2012 and 2013 campaigns are shown in Fig. 2a–k. In case of no detectable results, the midpoint of the possible concentration range is shown in a lighter color for illustrative purposes (see Table A1 for DL values). The results show that concentration levels are generally

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in the same order of magnitude during both snapshot measurements (2012 and 2013), with the exception of total concentrations of Al, Cd and Mn which are up to one order of magnitude greater in the 2012 campaign. The differences between particulate and dissolved concentrations are greatest for Al, Fe and Mn with particulate concentrations being on average 178, 35 and 25 times greater than dissolved concentrations in the 2012 campaign respectively 42, 18 and 5 times greater in the 2013 campaign. As, Cd, Cr, Cu and Mo, have dissolved concentrations within the same order of magnitude as their total concentrations. V and Zn show varying behaviour, both having higher dissolved and particulate concentrations depending on sampling point. Overall, total concentrations show a net increase over the site, with increased values at the most downstream point (T6a) compared to the upstream points (T5, T5a), with the exception of Zn and Mo. Several metals (Al, As, Fe and Mn) show total (unfiltered) concentrations that exceeds WHO and Mongolian health risk-based guideline values (Table B1). As additionally shows dissolved (filtered) concentrations exceeding these health risk-based guideline values.

4.2 Riverine mass flows

Dissolved and total (dissolved + suspended) mass flows at the five locations along the Tuul River from the campaigns in 2012 and 2013 are shown in Fig. 3a–k (note the different scales on the y-axis). The first location (T5) is not included in the 2013 campaign due to discharge data missing. Taken together, the majority of metals from both campaign years show net increasing total mass flows over Zaamar Goldfield, with values being higher at the most downstream point (T6a) than the most upstream (T5, T5a) points. Due to above mentioned high dissolved and total concentration differences, differences between dissolved and total mass flows are generally high, with total mass flows being up to two orders of magnitude higher than dissolved mass flows, especially for Al, Fe and Mn. Similarly, dissolved mass flows of As, Cd, Cr, Cu and Mo are generally of the same magnitude as total mass flows. Total mass flows of most metals

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(As, Cr, Cu, Fe, Mo, Pb, V and Zn) were higher in the 2013 campaign than in the 2012 campaign (median: 5 times higher).

4.3 Modeling results

4.3.1 Comparing observations and model predictions

Figure 4 compares measurement and modeling results on the dissolved fraction (percentage) of considered metals and sampling locations in the (a) 2012 and (b) 2013 campaign. Cr, Cu and Mo were always predicted to be 100 % dissolved while Mn was predicted to be 100 % precipitated throughout the study, although measured dissolved fractions were changing with location (see Tables C1 and C2 for values). This is further discussed later (Sect. 5). For all other metals (Al, As, Cd, Fe, Pb, V and Zn; Fig. 4) model predictions in both campaign years agreed well with measurements (within 20 % difference between measured and modeled results) for the majority of metals and locations (73 % of all data points in 2012 and 82 % in 2013). Large discrepancies (i.e. > 20 % difference) between measured and modeled results were more common in the 2012 campaign (27 % of all data) than in the 2013 campaign (18 % of all data). The overall best agreement was for Al and Fe (< 5 % average difference between measured and modeled results) whereas the least good agreement was for Cd (35 % average difference).

4.3.2 Speciation of metals

Refined speciation modeling results for the Tuul River reach is shown in Fig. 5a–g (2012) and Fig. 6a–g (2013). Here the measured “dissolved” fraction of the total concentration is divided into two fractions; “dissolved inorganic” and “bound to DOM”. These model results hence together make up was measured as “dissolved” (filtered samples). Furthermore, the modeled “sorbed” and “precipitated” fractions together correspond to the measured “total” fraction (unfiltered samples).

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Al and Fe were predicted to dominantly occur as particulate gibbsite and ferrihydrite (90–100%), respectively, throughout the river sections, for both campaign years. A small fraction of Fe (up to 5%) was predicted to occur as soluble organic complex (bound to DOC). As, Pb and V were predicted to sorb to ferrihydrite, on average by 10% (As) respectively 40% (Pb and V), but with highest predicted sorption to ferrihydrite of 60%. However, the dissolved inorganic forms of As (hydrogen arsenate; HAsO_4^{2-}) and V (hydrogen vanadate; HVO_4^{2-}) were predicted to dominate in both years. At location T6 (2012), Pb was predicted to sorb more to gibbsite than to ferrihydrite. This location had a very high measured particulate Al concentration (see Fig. 2). The concentration was twice as high as the concentration of Fe, reaching over $6000 \mu\text{g L}^{-1}$. Zn was predicted to sorb only to gibbsite throughout all modelled locations, on average by adsorbing 50% (in 2013) to 80% (in 2012) to gibbsite. Cd was predicted to bound strongly to DOC in both years, on average by 75%, although with some sorption to gibbsite (mainly in the 2012 campaign). Pb and Zn were also predicted to bind to DOC, on average by 55% respectively 40% in the 2013 campaign and about 20% less in the 2012 campaign. Overall, comparing the speciation between the two field campaigns suggest that Cd, Pb and Zn had higher average solubility during the latter occasion in 2013 (i.e. more modeled as either dissolved inorganic and/or bound to DOM) with 15% (Cd) and 20% (Pb and Zn).

The modelling runs where pH was lowered to 6 respectively 3.5 generally increased the dissolved fraction of most metals. At pH 3.5, 100% dissolution of all previously adsorbed or precipitated metals were predicted, compared to their speciation at site specific pH. At pH 6, Al, Cd, Fe and Zn increased their dissolution. Zn was predicted to dissolve most in all model runs, on average with 50% more dissolution than site specific pH, but up to 80% more dissolution in T6a (from pH 8.5 to pH 6). Dissolution of ferrihydrite on average increased by 16%, which was more than for Al (5%) and Cd (6%). However, for As, V and Pb their dissolved fraction instead decreased by changing the pH to 6, on average by 11% (As) and 19% (Pb, V), due to increased sorption to ferrihydrite.

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Increasing the DOC concentration by 50% from measured values in 2012 resulted in predicted increased overall dissolution of all investigated metals, with greatest impact on Fe, Pb and Zn solubility; up to 10%. This increase in DOC concentrations correspondingly lead to predicted increased Fe-organic complexation, with a few percent.

5 Discussion

The main chemical parameter controlling solubility of metals in aqueous systems is often considered to be pH (e.g. Bourg and Loch, 1995). Agreement between the present observations of high concentrations of metals in suspension and predicted precipitation and/or sorption controls, show that dissolution is generally limited for several metals under the alkaline conditions that prevail at Zaamar Goldfield. Through the scenario modelling where pH was altered from actual site conditions, it becomes apparent that there is a strong pH dependence of several metals in this system. The scenario modelling at pH 3.5 represents pH conditions common at many well studied acid mine drainage sites (e.g. Elliot et al., 1998; Saria et al., 2006). Under such conditions, practically all metals are dissolved. Model predictions at the pH 6 scenario compared to site conditions also changed the speciation of the metals, however with higher sensitivity for some (Zn, V, Pb and Fe) than for others (Al, As, Cd). The substantial dissolution of Zn between site conditions and pH 6 suggest that it is very sensitive to fluctuations in pH. This agrees with results from for instance Chen et al. (1997), who also showed Zn to be pH sensitive, with a significantly decreasing solubility above pH 6.5, where all dissolved Zn was removed from solution due to adsorption.

Adsorption is a main process responsible for limiting dissolved forms of metals in natural systems (e.g. Zhao et al., 2011). A high affinity of “divalent base metals”, including Cd, Cu, Pb and Zn, to adsorb to solid phases, such as Al and Fe-hydroxides is common (e.g. Early, 1999). In the here modeled system, adsorption to Al (gibbsite) was predicted to limit Cd and Zn solubility, with highest impact on Zn and minor influence on Cd. Further, as Pb was predicted to adsorb to gibbsite instead of ferrihydrite where Al

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concentrations reached double Fe concentrations this solid could also control Pb solubility. Studies on the adsorption to gibbsite under high pH conditions are not abundant, however Weerasooriya et al. (2001) showed sorption of Pb to gibbsite, in the same range as predicted here, with up to 50 % sorption to gibbsite at pH 9, supporting our results. Otherwise, sorption of metals to ferrihydrite is commonly reported (e.g. Shultz et al., 1987; Jung et al., 2005; Sanchez-España et al., 2006) and was here predicted to be the main solid for adsorption of As, Pb and V. The degree of sorption of these metals were all predicted to increase as the input pH was changed to 6, suggesting these metals to be more soluble at the non-acidic site conditions than at pH 6. However, results from the predictions at pH 3.5, showing complete dissolution of previously sorbed metals, indicate that sorption is not an active control under acidic mine drainage conditions. Several other studies have shown highest adsorption of these metals to ferrihydrite at circum-neutral pH. For example, Sanchez-España et al. (2006), showed 90–99 % adsorption of As and Pb to ferrihydrite within the pH range 7–8. Further, Jung et al. (2005) indicated 95 % adsorption of Cd, Pb and Zn onto ferrihydrite at pH 7. This suggest that adsorption onto ferrihydrite mainly limits dissolved forms of these metals at circum-neutral pH, but with adsorption still occurring at the very high pH conditions predicted in our study; with up to 50 % sorption of As, Pb and V to ferrihydrite.

Although locations with high adsorption of As and V was predicted here, these metals were overall dominantly found in their dissolved inorganic fractions (HAsO_4^{2-} and HVO_4^{2-}), indicating higher bioavailability of these compared to the others. As is well known to be highly dissolved at alkaline conditions (e.g. Early, 1999), especially in combination with non-humid climates (Smedley and Kinniburgh, 2002), which agrees with our results. Wällstedt et al. (2010) found, using the same modeling approach as this study, that both As and V were dominated by their dissolved fractions in streams with pH above 6.9. Further, since dissolved As concentrations reached above concentrations commonly found in freshwaters (Smedley and Kinniburgh, 2002) and health risk-based guideline values (WHO) in several locations, this metal is of additional toxic concern. A recent paper on As contamination in Mongolia (Pfeiffer et al., 2014) also

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show high As concentrations in several regions, with highest values in areas of gold mines (including Zaamar Goldfield), highlighting this problem.

Model results also suggested that dissolved organic matter (DOC) influenced the speciation of several metals. DOC mainly controlled the dissolved form of Cd in both campaign years and Pb in 2013 and also impacted Zn. Many studies (e.g. Christensen et al., 1996; Hagedorn et al., 2000; Sauvé et al., 2000) have suggested DOC to be an important controlling factor for metal transport and fate in natural systems. A modeling approach by Weng et al. (2002) showed that metal complexes with organic matter could lead to dissolved metal concentrations of up to two orders of magnitude greater than without DOC, especially at alkaline conditions. This was most pronounced for Pb and Cu, whereas for Cd and Zn the effects were smaller. Antoniadis and Alloway (2002) however found that complexation with DOC significantly increased the dissolved concentrations of Cd and Zn; a result that agrees with the model results from this study. Additionally, binding of Fe and Al to organic matter has been shown to affect the binding of other metals as well. High concentrations of Fe and Al were shown by Tipping et al. (2002) to dominate the space at the organic material, thus increasing the dissolved concentrations of other metals which could no longer stay in a complex with the organic material. This was seen for Fe in our modeled system; with the scenario of increased DOC concentrations by 50 %, Fe-organic complexation also increased. This was also predicted to increased the dissolved fraction of previously adsorbed metals to ferrihydrite. If site specific DOC concentrations were higher than the here assumed values for the 2012 campaign, more metal-organic complexes could exist in our system than what was predicted, suggesting that the systematic under-prediction of the dissolved fraction for many metals in 2012 (Fig. 4a) could be related to DOC. Several studies (e.g. Schelker et al., 2012; Raymond and Saiers, 2010) have showed DOC fluctuations with up to several 100 %, for instance due to land use changes (deforestation) and storm events. Since data on DOC variability in the studied region is scarce (Yoshioka et al., 2002), it is possible that real DOC concentrations in 2012 were much higher than in 2013.

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Table 1. Sampling information (locations, names and dates) for water samples collected in and around the Zaamar mining areas during 2012 and 2013.

Sample	Date	Location	Longitude (decimal degrees)	Latitude
T5	24 Jun 2012 14 Sep 2013	Tuul River, upstream of Zaamar site	104.523	48.014
T5a	24 Jun 2012 14 Sep 2013	Tuul River, start of Zaamar site	104.306	48.158
T5b	23 Jun 2012 12 Sep 2013	Tuul River, at Zaamar site	104.325	48.229
T6	23 Jun 2012 11 Sep 2013	Tuul River, at Zaamar site	104.420	48.332
T6a	23 Jun 2012 11 Sep 2013	Tuul River, downstream of Zaamar site	104.512	48.389

9745

Table 2. Chosen oxidation states of the various components for the input file in Visual Minteq. Since samples were collected from river water, well oxygenated conditions were assumed and thus oxidized forms of the elements were chosen. Some elements (Al, Ca, K, Mg, Na, Ni, P, Pb, Si, Zn) only had one state in the program and could thus not be altered.

Al^{3+} , As(V) , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr(VI) , Cu^{2+} , Fe^{3+} , K^+ , Mg^{2+} , Mn^{2+} , Mo(VI) , Na^+ , Ni^{2+} , $\text{P (PO}_4\text{)}$, Pb^{2+} , $\text{S (SO}_4\text{)}$, Cl^- , $\text{Si (H}_4\text{SiO}_4\text{)}$, V(V) , Zn^{2+}
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9746

Table C1. Comparison of measured and modeled dissolved fractions of the selected metals in 2012.

	Al	As	Cd	Cr	Cu	Fe	Mn	Mo	Pb	V	Zn
% Dissolved measured											
T5	0.3	96.5	NA	NA	67.5	3.5	6.	84.5	72.3	88.7	57.4
T5a	0.3	93.4	NA	10.	26.1	2.4	2.	33.5	NA	73.1	24.7
T5b	3.6	85.7	87.1	39.4	NA	3.7	89.1	88.9	NA	78.	28.1
T6	1.1	NA	67.5	21.2	NA	2.3	2.6	41.2	12.1	62.8	44.5
T6a	4.	92.2	86.9	35.1	NA	2.7	4.5	80.5	NA	82.2	64.4
% Dissolved modelled											
T5	2.63	72.3	NA	NA	100	2.54	0.00	100	48.4	55.0	45.3
T5a	1.77	39.8	NA	100	99.8	0.21	0.00	100	NA	37.1	5.76
T5b	1.29	94.5	90.2	100	NA	0.82	0.00	100	NA	75.6	23.5
T6	0.05	NA	53.0	100	NA	0.46	0.00	100	19.4	52.8	3.08
T6a	0.78	98.6	91.4	100	NA	2.03	0.00	100	NA	89.2	24.2

9751

Table C2. Comparison of measured and modeled dissolved fractions of the selected metals in 2013.

	Al	As	Cd	Cr	Cu	Fe	Mn	Mo	Pb	V	Zn
% Dissolved Measured											
T5	2.49	NA	NA	66.8	55.2	8.8	10.6	NA	53.4	40.7	70.2
T5a	2.55	NA	45.1	92.8	83.7	6.7	42.3	NA	57.2	64.9	48.3
T5b	6.07	NA	NA	74.8	69.9	7.5	25.1	82.0	50.9	57.5	105
T6	0.92	76.4	76	102	62.3	2.2	15.6	77.4	40.7	45.0	31.0
T6a	11.9	NA	NA	75.4	83.6	3.7	11.7	NA	37.8	45.8	48.7
% Dissolved Modelled											
T5	1.54	NA	NA	100	100	4.27	0.00	NA	71.0	63.9	71.9
T5a	0.60	NA	97.0	100	100	7.23	0.00	NA	67.0	56.6	75.0
T5b	0.29	NA	NA	100	100	2.66	0.00	100	58.0	49.1	51.0
T6	0.63	85.0	91.0	100	100	1.21	0.00	100	41.1	53.7	32.0
T6a	0.29	NA	NA	100	100	1.58	0.00	NA	45.2	49.7	21.0

9752

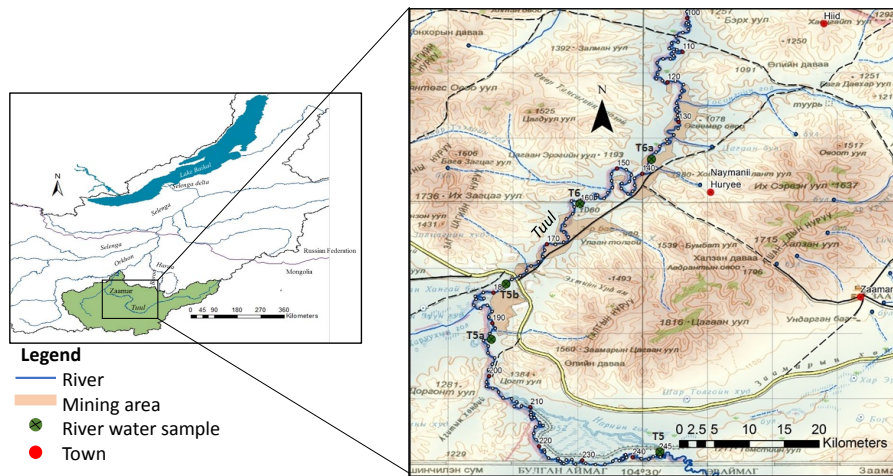


Figure 1. Map of the Baikal Basin with the Zaamar mining area (zoomed) located in the Mongolian part of the basin, along the Tuul River (author J. Thorslund).

9753

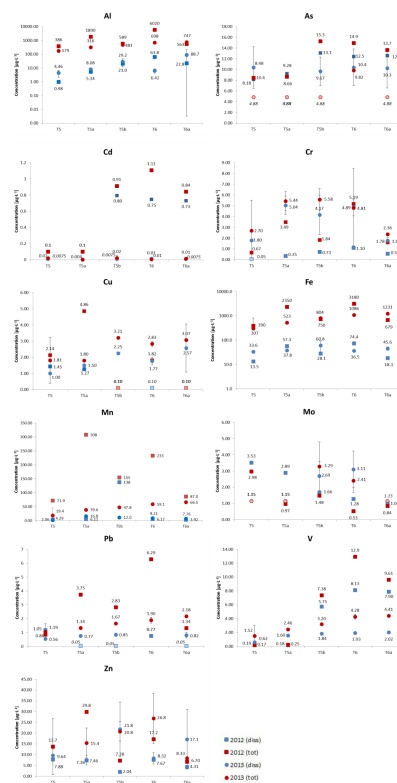


Figure 2. Dissolved (blue) and total (red) concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Pb, V and Zn at the five sampling locations along the Tuul River and the Zaamar Goldfield, from the sampling campaigns in 2012 (squares) and 2013 (circles).

9754

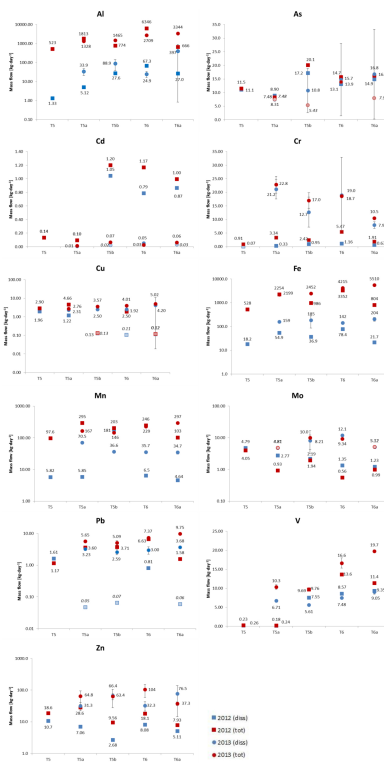


Figure 3. Estimated dissolved (blue) and total (red) mass flows, in kg per day, of Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Pb, V and Zn at the five sampling locations (T5–T6a) along the Tuul River and the Zaamar Goldfield, from the sampling campaigns in 2012 (squares) and 2013 (circles).

9755

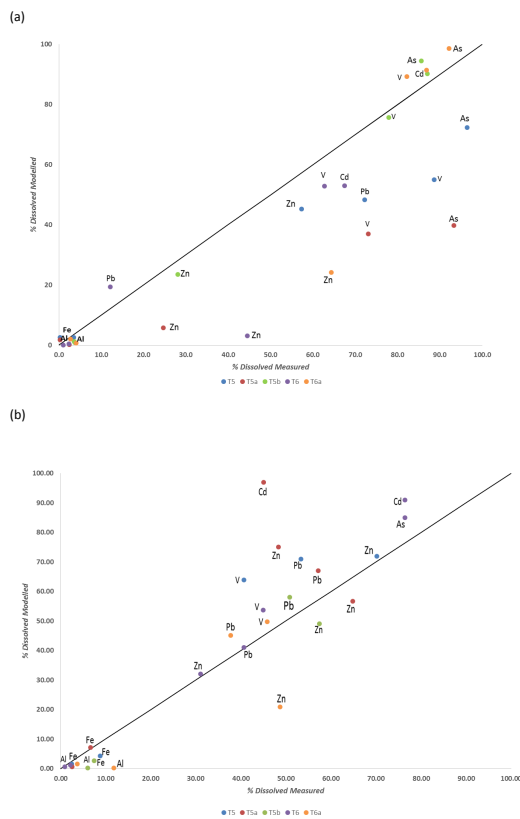


Figure 4. Comparison between measured and modeled results for the dissolved fractions (percentage) of metals in the (a) 2012 campaign and the (b) 2013 campaign.

9756

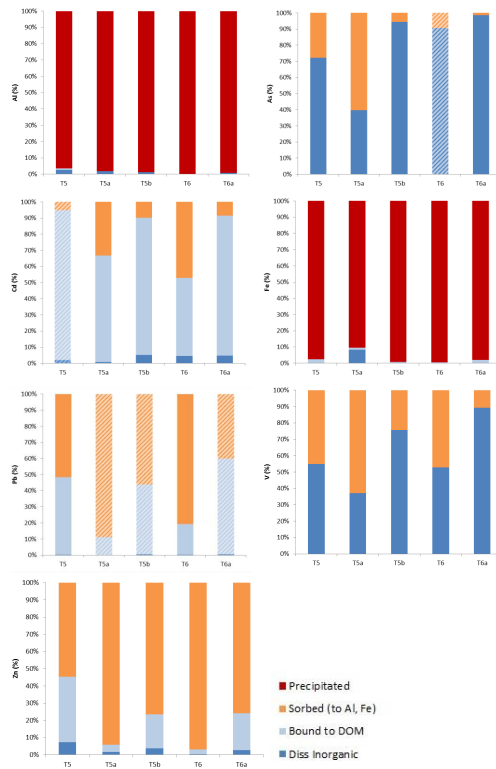


Figure 5. Predicted speciation of selected heavy metals between “dissolved inorganic”, “bound to DOM”, “sorbed” and “precipitated” in the five sampling locations along the Tuul River in the 2012 campaign. Dashed lines indicate model prediction from detection limit (DL) concentrations.

9757

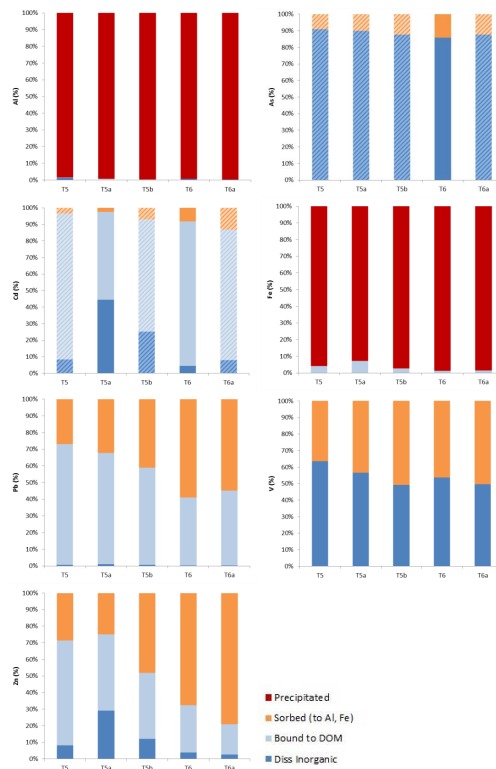


Figure 6. Predicted speciation of selected heavy metals between “dissolved inorganic”, “bound to DOM”, “sorbed” and “precipitated” in the five sampling locations along the Tuul River in the 2013 campaign. Dashed lines indicate model prediction from detection limit (DL) concentrations.

9758