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., the chemical forms in which the metals occur, controls their mobility, bioavailability and toxicity. The overall objective of this study is to expand the knowledge of the spreading of metals in non-acidic river systems. This knowledge is currently much more limited than that of the behaviour of metals under acidic conditions (e.g., in acid mine drainage systems). We combine novel measurements of metal spreading under distinctly high-pH conditions (up to 9.6) along two rivers and in surface water ponds (in the Upper Lake Baikal Drainage Basin, Mongolia) with a geochemical modelling approach (Visual MINTEQ). One of the two rivers, the Tuul River, flows through a major gold mining site and was selected as a focus reach for mass flow quantifications, to investigate the impact of a large mining site on the transport of metals. Total mass flows of several metals (Al, Cd, Fe, Mn, Pb and V) showed net increases across the gold mining site, with metals in suspension generally dominating the total export from the site. The model results indicated that a primary difference between non-acid and acid mine drainage geochemistry is that the prevailing high pH in the former causes the precipitation of ferrihydrite and gibbsite, which removes between 90 and 100 % of the Fe and Al from solution. This effect additionally influenced the behaviour of As, Pb and V, for which the solubilities were predicted to mainly be controlled by sorption onto ferrihydrite. The combined effects of such geochemical processes ( precipitation and sorption) thus explain the high impact of suspended transport relative to total transport under non-acidic conditions. Furthermore, As showed dissolved concentrations above the health risk-based guideline values in several locations and thus is of main toxic concern in the Upper Lake Baikal Drainage Basin. Moreover, the present modelling showed that the solubility of Fe, Pb and Zn, in particular, can increase considerably, due to metal-organic complexation, as dissolved organic carbon (DOC) concentrations. In non-acidic systems, the 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. The present results also suggest that the behaviour of Cr, Cu and Mo would be much better understood if a dependable adsorption
database for hydroxyapatite could be developed, since it seems likely that this mineral controls their solubilities.

Keywords: metals, spreading, speciation, river system, alkaline, geochemical modelling, solubility, Lake Baikal
1 Introduction

Metals can become exposed to the environment through natural processes, such as the weathering of soil and bedrock, and through anthropogenic processes, such as mining and other industrial activities and agriculture. Metals can enter aqueous systems through washout from surface soils, diffuse groundwater inflow, metal mobilisation from enriched sediments, leaching from agricultural areas and mine tailings, catastrophic tailings dam failure and the discharge of industrial and mining effluents (e.g., Hudson-Edwards 2003, Macklin et al., 2006, Mghanetara et al., 2009 and Inam et al., 2011). Material mobilisation via bank and bed erosion under conditions of geomorphic adjustment can dominate pollutant transport under certain conditions (Lewin and Macklin 1987 and Chalov et al., 2014). Once metals are released into aquatic systems, they persist because of their non-degradable nature. Metals held in alluvial stores may therefore continue to pose a threat to ecosystems long after their initial release, and alluvial sediments may constitute the greatest source of catchment heavy metal pollution (Alexeevsky et al., 2013).

Mounting evidence in recent decades has shown that the speciation of metals (i.e., the chemical forms in which they occur) controls their mobility, bioavailability and toxicity (e.g., Tessier and Campbell 1979, Tack and Verloo, 1995, Tipping, 1998, Fytianos 2001 and 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., Chapman et al., 1992, Gundersen and Steinnes, 2001 and Nystrøm et al., 2012) because it can be readily taken up by organisms and biota (e.g., Törnqvist et al., 2011 and Raguz et al., 2013), in contrast to many suspended forms. Many chemical factors and parameters must be accounted for in determining the speciation of metals, such as pH, redox conditions, the oxidation state of the metal and the available surfaces for adsorption (e.g., Palleiro et al., 2013). An advantage of equilibrium speciation models is their ability to predict predominant forms of metals and evaluate the mechanisms controlling speciation, 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 MINTEQ (Gustafsson 2009), which are used in 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 and Nystrand et al., 2012). These models have the ability to simulate surface adsorption reactions and the complexation of metals with organic matter, which are 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 modelling of metals in aqueous systems (e.g., Eary 1999, Butler et al., 2004, Balistrieri et al., 2007, Gustafsson et al., 2009 and Nystrand et al., 2012), the majority of these studies have focused on metal behaviour under acidic or near-neutral conditions rather than under high-pH conditions. Some exceptions include a study by Sjöstedt et al. (2009), who measured and modelled 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 modelled the speciation of As, leaching from uranium mining, up to a pH of 11.

However, speciation studies focusing on large-scale spreading of multiple metals across scale in non-acidic hydrological systems are rare (Pandey et al., 2014 and Sungur et al., 2014), although a lot of research many studies have highlighted pollution problems of metals in these environments (see, e.g., Tarras-Wahlberg et al. 2000, Sjöblom et al., 2004, Grosbois et al., 2009 and Zak et al., 2009), often. Non-acidic systems often showing high metal concentrations in particles but low concentrations in the dissolved form, thereby indicating that the geochemical controls and dominating processes might differ from well-studied acidic pollution sources water systems.

Furthermore, understanding geochemical controls in combination with the physical transport of metals could greatly enhance predictions of metal transport and fate (Foster and Charlesworth 1996, Destouni et al., 2010, Persson et al., 2011). For example, geochemical processes (e.g., adsorption) influence whether certain physical processes (e.g., suspended sediment transport; Chalov et al., 2012) will be important in the overall transport of metals. However, relatively few studies have addressed these combined effects of physical and chemical controls on metals in aqueous systems (e.g., Caruso et al., 2008 and Malmström et
The overall objective of the present study is to extend the knowledge on the spreading of metals in non-acidic river systems. We combine novel site-specific measurements with a geochemical modelling approach (Visual MINTEQ), specifically aiming to (i) evaluate the performance of this modelling approach by comparing observations and model predictions, (ii) identify dominant solids and predict the capacity of these solids to sorb and/or co-precipitate other metals that are transported in suspension and (iii) identify the dominant controls keeping metals in solution, such as soluble complexation.

As application examples, we consider the distinctly high-pH conditions of the Tuul and Sharyngol Rivers, which are both influenced by mining activities and located in the upstream Lake Baikal basin, Mongolia (Pietron 2012, Thorslund et al., 2012, Chalov et al., 2012 and Chalov et al., 2014). We also consider small surface water ponds within the largest mining site in Mongolia, comprising a widespread source zone; namely the Zaamar Goldfield which is located along the Tuul River and comprises 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 the Zaamar Goldfield, as well as illegal mining, are considered to have a serious impact on the water quality within the river basin (Altansukh and Davaa 2011, Chalov et al., 2012 and Thorslund et al., 2012) and may have an impact on the downstream Selenga River and Lake Baikal. Although total (suspended and dissolved) concentrations and estimated mass flows of several metals within this system were high, the dissolved fractions were generally low (Thorslund et al., 2012). 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 and Khazheeva et al., 2006). Investigating controls on metal partitioning between the sediment and water phase is thus of particular importance for this system because metals originating from the Zaamar...
Goldfield may be transported all the way to the vicinity of Lake Baikal, which hosts a unique ecosystem and represents a major water resource.

2 Site description

The Tuul River and the Sharyngol River are both located in the upstream Lake Baikal basin, Mongolia (see Fig. 1 and Table 1 for sampling locations and coordinates). The Sharyngol river basin is about half the size of the Tuul River basin (MCA 2011). Both rivers are tributary rivers to the Orkhon-Selenga river system, with the transboundary Selenga River being by far the largest river draining into Lake Baikal (Lee et al., 2006), discharging approximately 30 km$^3$ of water and 3.5 million tons of sediments annually into the lake. Before the Selenga River flows into Lake Baikal, it flows through the Selenga delta, covering an area of approximately 1200 km$^2$ (USGS 2011).

The mining areas of the Zaamar Goldfield are located in the Tuul River valley, between latitude 48°17'50" N and longitude 104°24'65" E (Fig. 1) (AATA 2008), approximately 600 km upstream of the Lake Baikal inlet (AATA 2008). The Tuul River is a tributary of the Selenga River, a transboundary river between Mongolia and Russia and by far the largest river draining into Lake Baikal (Lee et al., 2006), discharging approximately 30 km$^3$ of water and 3.5 million tons of sediments annually into the lake. Before the Selenga River flows into Lake Baikal, it flows through the Selenga delta, covering an area of approximately 1200 km$^2$ (USGS 2011).

The annual average discharge of the Tuul River is 27 m$^3$/s (1945-2007), but maximum discharges in the summer period can reach approximately 80 m$^3$/s, whereas lower discharges occur throughout the coldest months of the year (November-March). Below the confluence of the Tuul River with the Orkhon River, discharges increase on average by an order of magnitude, and in the downstream Selenga River, the annual average discharge reaches just over 1000 m$^3$/s (GEMStat 2011, MCA 2011). The Sharyngol annual average discharge is much lower than for the Tuul River, with long term average (1977-2007) of only 1.7 m$^3$/s (MCA 2011). The average annual precipitation in the region is between 200 and 250 mm. The
climate of the region is semi-arid with warm and dry summers (average temperatures of 20 °C), although intense rainfall does occur, and cold winters (average temperatures of -20 °C) (AATA 2008).

The geology of the area includes sedimentary, igneous, and metamorphic rock formations, such as sedimentary sandstones and siltstones, igneous gabbros, and metamorphic schists. The region also naturally contains 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 condition impacts both the Tuul and Sharyngol River quality and quantity because the river is fed by groundwater inflows with high water-rock interactions. These interactions cause the pH values throughout the Zaamar Goldfield region to be very high (Lee et al., 2006 and Zandaryaa et al., 2008).

Both of these rivers are also impacted by mining activities, with placer gold mining in the Tuul river basin and open pit coal mining in Sharyngol (MCA 2011). The mining areas of the Zaamar Goldfield are located in the Tuul River valley, between latitude 48°17’50” N and longitude 104°24’65” E (Fig. 1) (AATA 2008), approximately 600 km upstream of the Lake Baikal inlet (AATA 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 approximately 45 km along the floodplain of the Tuul River (Lee et al., 2006). The abundant mining activities over a widespread area and the lack of control of tailing and leakage from settling ponds contribute to both diffuse and direct pollution of soil, groundwater and surface water (Zandaryaa et al., 2008). High levels of metals have been measured in the Tuul River (Lee et al., 2006 and AATA 2008), and previous mass balance quantifications have shown a net increase in metal loading over the mining zone, especially of metals in suspension (Thorslund et al., 2012).
3 Methods of data collection and analysis

3.1 Field methods and sample collection

Water samples were collected during two field campaigns, one in June 2012 and one in September 2013. In the first year, only a focus reach of the Tuul River, at five locations around the Zaamar Goldfield, was sampled. This reach was chosen due to previous quantifications in this region and independent quantifications exist for them, for instance showing that Zaamar is as an important source zone with high transport of metals. During the second year, sampling of the five locations around Zaamar Goldfield and the Tuul focus reach sampling was repeated. In addition, sampling of 12 more locations with high pH in the region was performed; five additional ones from the Tuul River (T2, T3, T4, T6b, T7) four from Sharyngol River (S1, S2, S3, S5) and three from ponds at the Zaamar site (P1, P3, P4). The pond water consists of waste water from washing out the gold from metal enriched sediments.

Information on the sampling locations, including coordinates, is shown in Table 1 and Fig. 1. Relatively low water discharges were observed during the June 2012 campaign (Q = 13–15 m³/s), whereas substantial flooding with floodplain inundation was documented during the September 2013 field campaign (Q = 45–52 m³/s). The hydrometeorological conditions also varied between the seasons, e.g., relatively dry weather during the 2013 campaign and abundant rainfall in the 2012 campaign.

The sampling procedure included grab sampling of water in plastic polypropylene bottles (500 ml) just below the surface of the sampled water. All sampling bottles were rinsed with the selected water before collecting the sample for analysis. The bottled water was then transferred into two high-density polypropylene test tubes (10 ml): one unfiltered sample and one filtered sample (filtered through a sterile 0.20 µm pore membrane filter, prewashed with sample water). In the 2013 campaign, three replicates of both filtered and unfiltered samples were collected. All test tubes were sterile and rinsed thoroughly with the sampled water before collecting the sample for analysis. The samples were acidified (1%) with concentrated HNO₃.
(65 %) to preserve them for analysis and prevent the precipitation of metals. In the following
text, unfiltered metal concentrations are referred to as total concentrations, while the filtered
concentrations are referred to as dissolved fraction, using a similar nomenclature as for
TOC/DOC.

The temperature and pH were measured in situ, directly in the rivers and ponds, using a
Hannah Instrument (HannahNorden, Sweden, Kungsbacka) HI 9828 meter (2012) and an HI
98108 (2013). The meters were calibrated with pH 7 and pH 10 solutions before each
measurement campaign and then recalibrated during the campaigns. For the 2012 campaign,
the alkalinity was measured at Moscow State University using the standard titration method,
whereas for the 2013 campaign, alkalinity was measured using a Total Alkalinity test kit (HI
38014) directly in field.

Additionally, in the 2013 campaign, samples for total and dissolved organic carbon
(TOC/DOC) were collected from all locations. Samples were collected in 30 ml high-density
polypropylene test tubes (three replicates) and samples for DOC analysis were filtered with
0.22 µm pore membrane filters. All samples were acidified (1 %) with concentrated acid
HNO₃ (65 %) and wrapped in aluminum foil to prevent light from penetrating the samples.
These procedures were all performed directly in the field. In 2013, samples were also
collected for anion (F⁻, Cl⁻, NO₃⁻, SO₄²⁻, Br⁻) analysis in 10 ml high-density polypropylene test
tubes (three replicates), without further preparations.

### 3.2 Analytical methods

All samples discussed in the present paper were analysed at Stockholm University. The metal
concentrations were determined by inductive coupled plasma optical emission spectrometry
(ICPOES) with a Thermo iCAP 6500 Duo analyser to determine the contents of the following
metals: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Sr, Ti,
V and Zn. The analysis of samples followed standard procedures using a micro concentric
nebuliser and, in some cases, an ultra sonic nebuliser, CETAC USN U5000AT⁺, to obtain
better detection limits.
TOC/DOC concentrations were determined using an NPOC (non-purgeable organic carbon) measurement in a Shimadzu TOC-L CPH analyser. The major anion analysis was performed by liquid chromatography using the IC20 Dionex following standard Swedish procedures (EN-ISO 10304-1:2009).

3.3 Discharge measurements and mass flow estimates

Discharge was measured at the five sampling locations around the Zaamar Goldfield along the focus reach of the Tuul River (T5, T5a, T5b, T6, T6a), both in 2012 and 2013 and at the same places and times as the collection of water samples for chemical analysis. The measurements were made by wading, by boat or from bridges (depending on the depth of each river section). Velocities were measured with a hydrometric propeller (ISP-1) at 0.6 m depth (from the surface) at each width increment. When the depth exceeded 1.5 meters, an Acoustic Doppler Profiler (ADP) was used, which measures water level and velocity in horizontal profiles across a channel.

The discharge of each cross-section was calculated according to Eqs. (1) and (2):

\[ Q = \sum_{n} V_n \cdot A_n \cdot k \]  

(1)

where \( V_n \) is the velocity of each width increment and \( A_n \) is the area of each rectangular subsection, using the Trapezoidal rule; and

\[ A_n = \frac{d_n + d_{n-1}}{2} \cdot (b_n - b_{n-1}) \]  

(2)

The coefficient \( k \) in Eq. (1) is used when the expression is applied to non-steep banks; here, \( k \) is equal to 0.7 (Bykov and Vasil'ev 1972). In Eq. (2), \( d \) is the depth of each subsection and \( b \) is the distance from the bank.
The discharges, $Q$, were multiplied with the concentrations, $C$, according to Eq. (3) to yield estimates of the dissolved and total metal mass flows, $M_f$, for the five cross-sections along the Tuul River.

$$M_f = C \cdot Q \quad (3)$$

The simultaneous measurements of pollutant concentrations and discharges were made to obtain snapshot values of loads along the river reach and across the Zaamar mining site.

3.4 Modelling approach

Eleven metals were selected from the analytical results dataset for further interpretation and modelling purposes: Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Pb, V and Zn. These metals were selected because they are often found at mining sites (e.g., Hudson-Edwards 2003) and because of their potential toxicity to humans and biota. Mercury (Hg) is a metal that is often associated with mining activities but was excluded here because it requires different analytical procedures from those performed here, i.e., the fluorescence method. Furthermore, previously reported measurements have repeatedly shown that Hg concentrations have been low and in many cases below detection limits in recent years (2006-2011) (Thorslund et al., 2012).

The geochemical equilibrium model Visual MINTEQ vers. 3.0 (Gustafsson 2011) was used to model the speciation of the eleven selected metals. This model calculates the chemical composition of various inorganic ions in aqueous systems at a single point (e.g., a water sample) under the assumption of a chemical equilibrium state. For inorganic complexes, the thermodynamic default database in Visual MINTEQ was used, which is mostly based on the NIST compilation (Smith et al., 2003).

Complexation of the metals with dissolved organic matter was modelled using the ‘Stockholm humic model’ (SHM) (Gustafsson, 2001) with its default database. 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 was assumed to be representative based on a
study by Sjöstedt et al. (2010) and thus not changed. All of the DOM was assumed to be fulvic
acid based on previous studies (e.g., Khai et al., 2008, Sjöstedt et al., 2010, Wällstedt et al.,
2010 and Gustafsson et al., 2014).

The input variables for each sampling point were the following: total concentrations of all
elements analysed (see Table 2 for the selected oxidation states), major anion concentrations,
$\text{pH}$, alkalinity ($\text{HCO}_3^-$), temperature, $\text{pe}$ (redox potential) and DOC (see Table 4 for input
values). Previous studies (e.g., Nystrand et al., 2012) have shown that modelling results are
more accurate if they are based on concentrations of a relatively large number of elements in
the input data because this provides a better representation of the chemistry in the water
sample (ionic strength and complex binding is then better represented) and thus decreases
uncertainties in model calculations. The concentration data of all elements determined in the
ICP-OES analysis were therefore used as input variables (see Sect. 3.2). However, in the
subsequent sections, the model outputs for the eleven selected metals are presented and
furthered discussed.

The DOC and major anions were not measured during the field campaign in 2012. Thus, for
the modelling of the 2012 data, the DOC values from the 2013 campaign were used. In
addition to this, $50\%$ higher DOC values than the measured ones were simulated for in
scenario simulations of all locations to investigate the sensitivity to changing DOC
concentrations, as well as a test simulation one some locations where DOC
concentrations were excluded assumed to equal zero. Because sulphate ($\text{SO}_4^{2-}$) and chloride
($\text{Cl}^-$) concentrations were not measured in the 2012 campaign, they had to be approximated.
Sulphate concentrations were assumed to be equal to half of the measured sulphur ($\text{S}$)
concentrations, and chloride concentrations were set to equal the measured sodium ($\text{Na}$)
concentrations.

The $\text{pe}$ was estimated according to Eq. (4) for both years, which is assumed to be
representative of well-oxygenated waters (Stumm and Morgan 1996).
\[ \text{pe} = 20.77 + \frac{1}{4} \log P_{O_2}^* \cdot \text{pH} \quad (4) \]

where \( P_{O_2} \) is assumed to equal 0.2 atm (i.e., the O2 content in the atmosphere is 20.95 %), similar to the value used by 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).

The solids that were allowed to precipitate when their respective solubility constants were exceeded are shown in Table 3. These solids were chosen based on (i) knowledge of common solids for the present geological conditions of the study site and (ii) model outputs of ‘saturation indices’, indicating which minerals could precipitate based on site-specific data and thermodynamic calculations. For ferrihydrite, \( \text{Fe}_2\text{O}_3 \cdot 1.8\text{H}_2\text{O} \), the solubility constant selected was one for ‘aged’ ferrihydrite with \( \log *K_s = 2.69 \) at 25 °C (Smith et al., 2003). This is in the lower range of constants reported for ‘amorphous iron hydroxide’, ‘hydrous ferric oxide’, etc. (\( \log *K_s = 2.5–5 \); Tipping et al., 2002). This model approach has previously been shown to produce reliable modelling results for Fe that agree well with analytical results (Sjöstedt et al., 2013). Ferrihydrite is an iron mineral that is frequently used as a 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 specific surface area and has been shown to correlate well with measured data (e.g., Sjöstedt et al., 2010, Nystrand et al., 2012 and Tiberg et al., 2013).

For Gibbsite (C), the solubility constant with \( \log *K_s = 7.74 \) at 25 °C (Smith et al., 2003) was selected. The published data on the solubility of gibbsite vary and are mainly a function of pH, sulphate, fluoride and DOC concentrations. The main difficulty lies in that it is difficult to separate amorphous Al(OH)3 from gibbsite in natural systems. Because of this difficulty, the solubility of Al is restricted, and its database in Visual MINTEQ is more limited than for ferrihydrite.
For modelling of adsorption, ferrihydrite and gibbsite were chosen as possible solid phases, due to their high measured particulate concentrations and their sorption capacities. The adsorption was estimated using the diffuse layer model (DLM) using the default database in Visual Minteq based on Dzombak and Morel (1990) and Karamalidis and Dzombak (2010) respectively. The only exception was vanadate adsorption to ferrihydrite where the adsorption constants were changed based on Wällstedt et al (2010).

To test the impact of varying conditions on model predictions, both pH and pe were changed from site specific values for each sample location. Model simulations were conducted for two different acidic pH conditions: pH 3.5 and pH 6 and pe was lowered by 50 %.

### 4 Results

#### 4.1 Tuul River water chemistry

The representative geochemical parameter values, used for the model input, of the sampling locations along the Tuul River (T2, T3, T4, T5, T5a, T5b, T6, T6a, T6b, T7), the Sherengol River (S1, S2, S3, S5) and ponds (P1, P3, P4) are shown in Table 4. The pH indicates neutral to alkaline conditions in all cases, with average values of 8.3 (Tuul), 8.2 (Sherengol) and 8.7 (ponds). The DOC concentrations are similar for all sampled locations, however are within the same range with average values being slightly higher for the Sherengol River (10.7) than for the Tuul River (10.4 mg/l) and the ponds (9.6 mg/l). The TOC concentrations were on average only a few per cent higher than the DOC concentrations; hence, the DOM dominates the total organic matter composition. The estimated alkalinity values are very high, especially from the field measurements in 2013.

Dissolved and total riverine concentrations for the focus reach of the reach of Tuul River that was sampled both years (T5, T5a, T5b, T6, T6a), representing the proximity of Zaamar Goldfield the mining site (upstream, at site, downstream), are shown in Fig. 2 a to k. The results show that concentration levels are generally 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, respectively, than dissolved concentrations in the 2012 campaign and 42, 18 and 5 times greater, respectively, in the 2013 campaign. As, Cd, Cr, Cu and Mo have dissolved concentrations in the same order of magnitude as their total concentrations. V and Zn show varying behaviour, both having higher dissolved and particulate concentrations depending on the sampling point. Overall, the total concentrations show a net increase over the site, with higher values for 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 exceed WHO and Mongolian health risk-based guideline values (Appendix A). Additionally, As exhibits dissolved (filtered) concentrations exceeding these health risk-based guideline values. Nevertheless, a comparison with data on monthly average concentrations for the Tuul River during summer or autumn months of 2005, 2006 and 2008 indicate that concentrations can be higher in this system (Thorslund et al., 2012) than observed during the here considered 2012 and 2013 campaigns.

4.2 Riverine mass flows

The dissolved and total (dissolved + suspended) mass flows around Zaamar Goldfield at the Tuul River focus reach (T5, T5a, T5b, T6, T6a) from both campaigns are shown in Fig. 3 a to k (note the different scales on the y-axis). The first location (T5) is not included in the 2013 campaign due to missing discharge data. Taken together, the majority of metals from both campaign years show net increasing total mass flows across the Zaamar Goldfield, with values being higher at the farthest downstream point (T6a) than the farthest upstream (T5, T5a) points. Due to the previously noted large dissolved and total concentration differences, the differences between dissolved and total mass flows are generally high, with total mass flows up to two orders of magnitude higher than dissolved mass flows, especially for Al, Fe and Mn. Similarly, the dissolved mass flows of As, Cd, Cr, Cu and Mo are generally of the same
magnitude as total mass flows. The total mass flows of most metals (As, Cr, Cu, Fe, Mo, Pb, V and Zn) were higher in the 2013 campaign than in the 2012 campaign (median: 5 times higher). Furthermore, this net export of several metals from the Zaamar site was shown in Thorslund et al. (2012), quantified from reported monthly average data. These mass flows of metals at the same locations during summer or autumn months of 2005, 2006 and 2008, in many cases showing were often even higher mass flows than during the present 2013 campaigns.

4.3 Modelling results

4.3.1 Comparing observations and model predictions

Fig. 4 compares the measured and modeled results for 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, whereas Mn was predicted to be 100 % precipitated throughout the study, although measured dissolved fractions changed with location (see Appendix B for values). Due to the lack of static model sensitivity output for these metals, they are excluded from Fig. 4 but further discussed below (Sect. 5). Model predictions for Cd did not always correlate well with measured data (30 %, average difference between measured and modelled results). However, for all other metals (Al, As, Fe, Pb, V and Zn; Fig. 4), model predictions in both campaign years agreed well with measurements (within a 20 % difference between measured and modelled results) for the majority of metals and locations (67 % of all data points in 2012 and 76 % in 2013), with larger discrepancies between the measured and modelled results in 2012 than in 2013. The overall best agreement was for Al and Fe (< 5 % average difference between measured and modelled results).

4.3.2 Speciation of metals

Refined speciation modelling results for the Tuul River around Zaamar Goldfield focus reach from 2012 are shown in Fig. 5 and the results from the more extensive sampling campaign in 2013 are shown in Fig. 6 a to g. Here, the measured 'dissolved' fraction is comparable to the
sum of the modelled two fractions: ‘dissolved inorganic’ and ‘bound to DOM’, while the
modelled ‘sorbed’ and ‘precipitated’ fractions together correspond to the measured ‘total’
fraction (unfiltered samples). Due to high measured alkalinity in some locations in 2013, a
test run for these locations where alkalinity was lowered to the 2012 values was performed.
However, changing the alkalinity values in the model input did not significantly change the
speciation of selected metals, indicating a low sensitivity to this parameter.

Precipitation of gibbsite and ferrihydrite was predicted as the dominant control of Al and Fe,
with the particulate fraction generally reaching 90-100 %, for both campaign years. The only
exception to these results were predictions for the most upstream Tuul river locations (T2, T3)
sampled in 2013 (Fig. 6), where showing 40-50 % were predicted to occur as soluble organic
complexes (Bound to DOC). Compared to the other locations, where only minor fractions of
Fe (up to 5 %) were predicted to exist as complexes with organic matter, pH was the main
difference (being lower at the upstream locations), potentially limiting precipitation.

Adsorption to ferrihydrite and gibbsite controlled the speciation of the rest of the metals to
various degrees according to the modeling results, mainly limiting the dissolution of V, Pb
and Zn. The latter was consistently predicted to sorb only to gibbsite, on average showing
adsorbed fractions of 50 % (in 2013) and 80 % (in 2012). The overall highest sorbed fractions
in 2013 was predicted for the Sharyngol River and the ponds, with all Zn being sorbed at
location P4. Pb and V were predicted to sorb to ferrihydrite, on average by 40 % (2012) to 60
% (2013). The sorbed fraction reached over 70 % in several locations, with pond P4 showing
the overall highest results. At location T6 (2012), Pb was predicted to sorb more to gibbsite
than to ferrihydrite. This was also seen for V at location P4, although all other locations
showed sorption to ferrihydrite only. These locations had a very high measured particulate Al
concentration (see Fig. 2 and SI). Contrasting cases of low sorbed and high dissolved fractions
of V, Pb and Zn includes one of the ponds (P1) and the most upstream Tuul River locations
(T2, T3).
Dissolved inorganic forms (mainly HAsO$_4^{2-}$) were predicted to dominate almost consistently for As in both years, on average governing its solubility by 75%. However, the different ponds locations showed varying predictions a wide range of predicted conditions, both including the highest (P1; 90%) and lowest (P4; 2%) soluble fractions, in the latter case with sorption to ferrihydrite limiting the solubility. Contradicting, In contrast to the 2013 predictions, V was in 2012 dominated by the dissolved inorganic fraction, hydrogen vanadate (HVO$_4^{2-}$).

Complexation with organic matter largely governed the solubility of Cd, in both years, where on average by 63% (2013) to 75% (2012) was modelled as “Bound to DOM”. Pb and Zn were also predicted to bind to DOC, on average by 50% and 30%, respectively, in the 2013 campaign and by approximately 15% less in the 2012 campaign compared to 2013. Overall, a comparison of the speciation between the two field campaigns suggests that Cd, Pb and Zn had higher average solubility during 2013 (i.e., a larger quantity modelled as either dissolved inorganic and/or bound to DOM), with 5% (Cd), 15% (Pb) and 25% (Zn). The impact of when the DOC concentrations were increased by 50% in the model, in order to investigate the influence of the uncertainty in DOC concentrations, an increased fraction of all investigated metals was modelled as dissolved, with the greatest impacts on Fe, Pb and Zn solubility, on average increasing by 65%, 40% and 30% respectively, but with values reaching over 80% increase for all these metals compared to site specific conditions. Scenario simulations assuming 0% DOC for Tuul River locations (T2, T3, T4, T6b, T7) decreased the agreement between measured and modeled results for V and Pb. When DOC was accounted for, differences between measured and modeled dissolved fractions were 9% (V) and 3% (Pb). Without DOC this difference increased to 28% (V) respectively 53% (Pb).

The model simulations where pH was lowered to 6 and 3.5 generally increased the dissolved fraction of most metals. At pH 3.5, 100% dissolved fractions of all previously adsorbed or precipitated metals was predicted, compared to their speciation at site-specific pH. Lowering
the pH to 6 had a large impact on the modelling results for Al, Cd, Fe and Zn, where a larger fraction was modelled as dissolved compared to at site-specific pH. Zn was the element most influenced by the lower pH, where the fraction modelled as dissolved was on average twice as large, and in some sites, especially in the ponds, as much as five times higher compared to at site-specific pH. Ferricydrate and gibbsite followed the same pattern, where a model run with pH 6 results in a much higher fraction modelled as dissolved compared to at ambient pH, up to 25 times higher for the river locations and even higher in ponds. However, due to the small dissolved fractions in the original model runs for Al and Fe, this overall impact is minor. For As, V and Pb, the fraction modelled as dissolved instead decreased slightly by changing the pH to 6, due to increased sorption to ferricydrate.

5 Discussion

The main chemical parameter controlling the solubility of metals in aqueous systems is often considered to be pH (e.g., Bourg and Loch, 1995). The agreement between the present observations of high concentrations of metals in suspension and the predicted precipitation and/or sorption controls shows that dissolution is generally limited for several metals under the alkaline conditions that prevail in the studied region. The pH 3.5 modelling scenario simulates pH conditions common at many well-studied acid mine drainage sites (e.g., Elliot et al., 1998 and Saria et al., 2006). Under such conditions, practically all metals are dissolved. The model predictions of the pH 6 scenario compared to site conditions also changed the speciation of the metals. The substantial difference on the fraction of Zn modelled as dissolved between the site conditions and pH 6 suggest that this metal is very sensitive to fluctuations in pH. This finding agrees with results from Chen et al., (1997), for instance, who also showed Zn to be pH sensitive, with a significantly decreasing solubility above pH 6.5, at which all dissolved Zn was removed from solution due to adsorption. Adsorption is a main process controlling metal solubility in natural systems (e.g., Zhao et al., 2011). The 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). Our modelling results indicated that adsorption to Al (gibbsite) was an important controlling factor only for Cd and Zn solubilities, with the greatest impact on Zn and a minor influence on Cd. Furthermore, because Pb and V were predicted to adsorb to gibbsite instead of ferrihydrite, when Al concentrations reached similar or higher concentrations as Fe, gibbsite could also control Pb and V solubility. Studies of 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, which supports our results. Otherwise, the sorption of metals to ferrihydrite is commonly reported (e.g., Shultz et al., 1987, Jung et al., 2005 and Sanchez-España et al., 2006) and was here predicted to be the main solid for adsorption Pb and V, and in some locations also for As. The degrees of sorption of these metals were all predicted to increase when the input pH was changed to 6, suggesting, in agreement with literature, that these metals are less soluble at pH 6 than at site conditions (e.g. Dzombak and Morel 1990). However, the results from the predictions at pH 3.5, which show a complete dissolution of previously sorbed metals, indicate that sorption is not an active control under acidic mine drainage conditions. Several other studies have shown the 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. Moreover, Jung et al. (2005) indicated 95 % adsorption of Cd, Pb and Zn onto ferrihydrite at pH 7. These findings suggest that adsorption onto ferrihydrite mainly limits dissolved forms of these metals at circum-neutral pH, but adsorption still occurs at the very high pH conditions predicted in our study, with up to over 70 % sorption of Pb and V to ferrihydrite. For As, the analytical results show that the dissolved fraction is generally dominating (Fig 2). This is in agreement with the modelling results, which indicate that it is the dissolved inorganic fraction ($\text{HAsO}_4^{2-}$) that is the dominating form (Fig 5 and 6). This indicates a higher bioavailability of this metal compared to the others. As is well known to be highly soluble in alkaline conditions (e.g., Early 1999), especially in combination with non-humid climates
(Smedley and Kinniburgh 2002), which agrees with our results. Based on a similar modelling approach as in the present study, Wällstedt et al. (2010) suggested that the dissolved inorganic fraction was the dominating form of As in streams with pH above 6.9. Furthermore, because dissolved As concentrations reached concentrations above those commonly found in freshwaters (Smedley and Kinniburgh 2002) and health risk-based guideline values (WHO) in several locations in the present study, this metal is of toxic concern in the study area. Recent papers on metal contamination in Mongolia (Hofmann et al., 2014 and Pfeiffer et al., 2014) also shows high dissolved As concentrations in several high pH regions, with elevated values in areas of gold mines (including the Zaamar Goldfield), highlighting this problem.

The model results also suggested that DOC influenced the speciation of several metals. Our scenario results showing that the model performance was considerably lower assuming zero DOC concentrations instead of site-specific values are consistent with those of Ahmed et al. (2014). The study highlights that organic matter concentrations can have large impact on metal speciation in non-acidic systems, due to increased negative charge on the humic molecules, which enhances the complexation capacity with the positively charged metal ions.

With site-specific DOC concentrations, metal-organic complexation was modelled as the main controlling factor for Cd solubility and DOC also influenced the solubility of Pb and Zn. Many studies (e.g., Christensen et al., 1996, Hagedorn et al., 2000 and Sauvé et al, 2000) have suggested that DOC is an important controlling factor for metal transport and fate in natural systems. A modelling approach by Weng et al. (2002) showed that complexation with organic matter could lead to dissolved concentrations of Pb of up to two orders of magnitude greater than those without DOC, especially in alkaline conditions, and with significant effects also on the solubility of Cd and Zn. 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, the 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 of the organic matter, thereby increasing the dissolved concentrations of other metals, which could
no longer remain in a complex with the organic material. This condition was observed throughout for Fe in our modelled system; when DOC concentrations were increased by 50 %, Fe-organic complexation also increased, by between 50 % and 80 %, while a larger fraction of metals previously modelled as adsorbed to ferrihydrite was modelled as dissolved. If site-specific DOC concentrations were higher than our 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, and Raymond and Saiers 2010) have shown that DOC concentrations fluctuate up to several 100 % due to land use changes (deforestation) and storm events, for instance. Because data on DOC variability in the studied region is scarce (Yoshioka et al., 2002), it is possible that real DOC concentrations in 2012 were higher than in 2013.

As noted in the results (sect. 4.3), the modelled speciation of Cr, Cu, Mn and Mo did not agree well with the measured fractionation. A possible reason for this disparity could be the impact of adsorption onto precipitates not included in the model. Apatites, a group of phosphate minerals, have commonly been suggested to be the main solids limiting the dissolved form of several metals in natural systems (e.g., Chen et al., 1997). Notably, hydroxyapatite, which is a natural calcium phosphate mineral within the apatite group, may be an important solid providing adsorption sites in our study region, because it was oversaturated (i.e., would precipitate if added as a possible solid phase) according to the model throughout the modelled locations. The measured concentrations of particulate calcium and phosphorous, which are chemical constituents of the mineral, were also considerable in the Tuul River, suggesting that the mineral may be present in the system. However, it would be premature to add this mineral to the model as a possible solid for adsorption due to the current lack of an adsorption database for this phase. Nevertheless, several previous studies (e.g., Corami et al., 2008, Chen et al., 2010, Feng et al., 2010 and Corami et al., 2012) have pointed to the importance of this solid for the adsorption of metals, including Cr, Cu and Mo. For example, the adsorption of Cr to hydroxyapatite was shown experimentally by Asgari et al. (2012) to remove high fractions
of dissolved Cr up to a pH of 11. Hence, hydroxyapatite may serve as an active control on several metals, including Cr, Cu and Mo, in non-acidic systems.

Linking the results from the analytical fractionation and the speciation modelling with the measured concentrations and mass flow quantifications highlights the strong correlation between the modelled forms of precipitated Fe and Al and their high impact on suspended total transport. The potential capacity of sediments to hold much more metals than a corresponding volume of water is well known (e.g. Horowitz, 1991). The combined effects of mining activities that stir up metal-rich bottom sediments, and the non-acidic environment that cause precipitation of Al and Fe and enhance adsorption of several other metals, lead to an overall large export of several metals in suspension from the site. This situation is in line with previous site assessments (Thorslund et al., 2012), suggesting a net contribution of metal loads transported from the Zaamar Goldfield compared to the natural mass flows. Because the concentrations of the metals did not vary as much as the discharges, the discharge would be the main factor controlling the magnitude of the mass flows. The impact of discharge on pollutant loads was also noted by Basu et al. (2010).

Considering the combined influences of land use alterations (expansion of mining areas) and projected climate changes (increased frequency of peak flow events; Altansukh and Davaa 2011), which will likely result in increased discharge and erosion in the Lake Baikal Drainage Basin, one can expect that the transport of metals from the Zaamar site to the connected river system will also increase. Increasing organic matter concentrations have also been found to correlate with increasing discharge (e.g. Lewis and Grant 1979), which could enhance solubility for several metals in suspension. The transport of metals to downstream regions, where geochemical conditions might be different (e.g., Yoshioka et al., 2002) could potentially also increase the solubility and bioavailability of metals in suspension. This does not only apply for this system, but can be of general relevance for spreading and fate of metals in non-acidic systems. This potential highlights the need for further studies focusing on the large-scale implications of coupled hydrodynamic (governing the magnitude of suspended
sediment transport) and geochemical (governing the mobility of metals between the sediment and water phases) processes.

6 Conclusions

Under non-acidic conditions, riverine suspended mass flows typically constitute the dominant component of total mass flows, as observed during our snapshot measurements in the Tuul River. Total mass flows showed net increases across the Zaamar Goldfield, reflecting the export of several metals (Al, Cd, Fe, Mn, Pb and V) from this mining site to the downstream river system. The main geochemical control limiting the solubility of metals in this non-acidic system, identified through speciation modeling, was the precipitation of ferrihydrite and gibbsite, which removed between 90 and 100% of the Fe and Al from solution. This effect additionally influenced the speciation of V, Pb and Zn because their solubilities are to large extent controlled by sorption onto these solids; with sorption to ferrihydrite removing between 40 to 60% of V and Pb from solution and sorption to gibbsite removing up to 80% of Zn from solution. Observations and model estimations suggest considerable impacts of sorption for prevailing conditions in rivers and in surface water ponds.

Simulations also suggest that organic matter constitutes a dominant control keeping several metals (Cd, Pb and Zn) in solution. In non-acidic environments, most metals have relatively low solubilities in the absence of DOC and the predictions where DOC concentrations were increased highlight the possibility of considerably increased metal-organic complexation for several metals, in particular Fe, Pb and Zn. In non-acidic systems, the seasonality of DOC concentrations (which can vary by several 100%) can therefore have a major influence on the spreading and toxicity of these metals and need to be accounted for in both field measurements and speciation modeling. The solubility of these metals could change considerably in response to climate and land use changes that impact DOC concentrations, such as the increasing frequency of storm events, agricultural expansion and deforestation.
Under present site conditions, As was the only metal where the dissolved form was dominating throughout most locations. It was predominantly modelled to occur in its dissolved inorganic form (HAsO$_4^{2-}$) and showed measured dissolved concentrations above health risk-based guideline values in several locations. This metal is thus of primary toxic concern in the Upper Lake Baikal Drainage Basin.

For most metals, the simulated results of dissolution fractions generally agreed well (differences within 20% for the dissolved fractions) with observations in the considered systems. However, with this current model approach, predictions of Cr, Cu, Mn, Mo and Cd (in some locations), were not satisfactory. An identified possible reason for this discrepancy is that the model do not account for the influence of sorption to hydroxyapatite, an apatite mineral known to have high sorption capacity. Nevertheless, no adsorption database is currently available for hydroxyapatite, which hinders appropriate sorption quantification. The potential importance of this mineral for metal partitioning under non-acidic conditions in general and for the investigated Tuul River in particular is emphasised by the fact that this mineral’s constituents were observed on site, with conditions being favourable for its precipitation.

Overall, the model approach used in this application that accounted for surface complexation, including binding to common solids and dissolved organic matter, worked well for 76% of the large number of simulated metals. Further, the modelled speciation for the Tuul River focus reach supports the conducted load estimations and the export of metal enriched suspended sediments from the Zaamar site to downstream regions. Although further model development is needed, for instance developing sorption databases, the present results show that the applicability of this approach can work well to both surface and river systems in non-acidic systems, is identified to work well. 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.
### Appendix A

Table A1. Maximum permissible concentration levels (µg/l) in drinking water according to the World Health Organization (WHO 2006) and the Mongolian State Standard (AATA 2008).

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
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<tbody>
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<td>WHO</td>
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<td>10</td>
<td>3.00</td>
<td>50</td>
<td>2000</td>
<td>300</td>
<td>400</td>
<td>70</td>
<td>10</td>
<td>200</td>
<td>3000</td>
</tr>
<tr>
<td>Mongolian</td>
<td>500</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>300</td>
<td>100</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>5000</td>
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### Appendix B

#### Table B1. Comparison of measured and modelled dissolved fractions of the selected metals in 2012.

<table>
<thead>
<tr>
<th>% Dissolved</th>
<th>Al</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>T5</td>
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<td>96.5</td>
<td>NA</td>
<td>NA</td>
<td>67.5</td>
<td>3.5</td>
<td>6.0</td>
<td>84.5</td>
<td>72.3</td>
<td>88.7</td>
<td>57.4</td>
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<td>T5a</td>
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<td>93.4</td>
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<td>10.0</td>
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<td>4.2</td>
<td>2.0</td>
<td>33.5</td>
<td>NA</td>
<td>73.1</td>
<td>24.7</td>
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<tr>
<td>T5b</td>
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<td>85.7</td>
<td>87.1</td>
<td>39.4</td>
<td>NA</td>
<td>3.7</td>
<td>89.1</td>
<td>88.9</td>
<td>NA</td>
<td>78.0</td>
<td>28.1</td>
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<td>T6</td>
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<td>NA</td>
<td>67.5</td>
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<td>NA</td>
<td>2.3</td>
<td>2.6</td>
<td>41.2</td>
<td>12.1</td>
<td>62.8</td>
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<td>2.7</td>
<td>4.5</td>
<td>80.5</td>
<td>NA</td>
<td>82.2</td>
<td>64.4</td>
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<td>% Dissolved</td>
<td>Al</td>
<td>As</td>
<td>Cd</td>
<td>Cr</td>
<td>Cu</td>
<td>Fe</td>
<td>Mn</td>
<td>Mo</td>
<td>Pb</td>
<td>V</td>
<td>Zn</td>
</tr>
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<td></td>
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<td>T5</td>
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<td>100</td>
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<td>55.0</td>
<td>45.3</td>
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<td>0.00</td>
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<td>24.2</td>
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#### Table B2. Comparison of measured and modelled dissolved fractions of the selected metals in 2013.

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<th>% Dissolved</th>
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<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>Pb</th>
<th>V</th>
<th>Zn</th>
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<td></td>
<td></td>
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<td>NA</td>
<td>NA</td>
<td>30.8</td>
<td>53.2</td>
<td>NA</td>
<td>86.0</td>
<td>63.9</td>
<td>66.4</td>
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<td>Cr</td>
<td>Cu</td>
<td>Fe</td>
<td>Mn</td>
<td>Mo</td>
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<td>V</td>
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Author contribution

J. Thorslund did model simulations and manuscript preparation, with contributions from all coauthors. J. Thorslund, J. Jarsjö and S. Chalov developed research ideas, including field preparations, measurements and modelling approach. T Wällstedt was responsible for modelling aspects, including parameter settings. M. Mörh was responsible for analytical methods, sampling handling and analysis. M. Lychagin contributed to geochemical interpretation.

Acknowledgements

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Tiberg, C., Sjöstedt, C., Persson, I., and Gustafsson, J.P.: Phosphate effects on copper(II) and lead(II) sorption to Ferrihydrite, Geochem Cosmochim Ac., 120, 140–157, 2013.


USGS.: Lake Baikal’s Selenga River Delta: Biodiversity, Conservation and Sustainable Development. Institute of General and Experimental Biology, Siberian Branch, Russian Academy of Sciences, Ulan-Ude, Russia.


Table 1. Sampling information (locations, names and dates) of the water samples collected in the Tuul and Sharyngol rivers and the surface water ponds in 2012 and 2013.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Location</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2</td>
<td>2013-09-08</td>
<td>Tuul River, Ulaanbaatar</td>
<td>107.056</td>
<td>47.973</td>
</tr>
<tr>
<td>T3</td>
<td>2013-09-08</td>
<td>Tuul River, downstream Ulaanbaatar</td>
<td>106.767</td>
<td>47.957</td>
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<td>T4</td>
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<td>105.198</td>
<td>47.862</td>
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<td>2012-06-24</td>
<td>Tuul River, upstream of Zaamar site</td>
<td>104.523</td>
<td>48.014</td>
</tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>Tuul River, start of Zaamar site</td>
<td>104.306</td>
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<td>Tuul River, at Zaamar site</td>
<td>104.325</td>
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<td>Tuul River, downstream of Zaamar site</td>
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<td>Tuul River, just before conjunction with Orkhon River</td>
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<td>Sherengol River, upstream mining area</td>
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<td>Sherengol River, downstream mining area</td>
<td>106.403</td>
<td>49.239</td>
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Table 2. Selected oxidation states of the various components for the input file in Visual Minteq. Because samples were collected from river water, well-oxygenated conditions were assumed, and thus oxidised forms of the elements were chosen.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺, As (V), Ca²⁺, Cd²⁺, Co²⁺, Cr(VI), Cu²⁺, Fe³⁺, K¹⁺, Mg²⁺, Mn²⁺, Mo(VI), Na¹⁺, Ni²⁺, P (PO₄), Pb²⁺, S (SO₄), Cl⁻, Si (H₄SiO₄), V(V), Zn²⁺</td>
<td></td>
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Table 3. Reactions and reaction constants of the possible solid phases allowed to precipitate if their solubility constant (log Ks) is exceeded (equations from Visual Minteq).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction</th>
<th>Log Ks (25°C)</th>
</tr>
</thead>
<tbody>
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<td>Aluminium hydroxide (soil)</td>
<td>Al(OH)₃ + 3H⁺ = Al³⁺ + 3H₂O</td>
<td>8.29</td>
</tr>
<tr>
<td>Calcite</td>
<td>CaCO₃ + 2H⁺ = Ca²⁺ + CO₂(g) + H₂O</td>
<td>-8.48</td>
</tr>
<tr>
<td>Ferrhydrite (aged)</td>
<td>Fe(OH)₃ + 3H⁺ = Fe³⁺ + 3H₂O</td>
<td>2.69</td>
</tr>
<tr>
<td>Gibbsite (C)</td>
<td>Al(OH)₃ + 3H⁺ = Al³⁺ + 3H₂O</td>
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</tr>
<tr>
<td>Manganite</td>
<td>MnOOH + 3H⁺ = Mn²⁺ + 2H₂O</td>
<td>25.3</td>
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</table>

Table 4. Measured geochemical parameters in all sample locations from 2012 and 2013. a) calculated according to Equation (4).

<table>
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<th>Parameter/ Site</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>Pe⁰⁺</th>
<th>Alkalinity (meq/l)</th>
<th>DOC (mg/l)</th>
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<td></td>
<td>2013</td>
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Figures

Figure 1. Map showing the two sampled rivers; Tuul River (A) and Sharyngol River (B) within the Lake Baikal Basin. A zoomed map with the Zaamar mining area located along the Tuul River where ponds were sampled and where mining areas are marked is shown in C (Author: J. Pietron).
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).
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 focus reach and the Zaamar Goldfield from the sampling campaigns in 2012 (squares) and 2013 (circles). In the case of no detectable results, the midpoint of the possible concentration range is shown in a lighter colour for illustrative purposes (see SI for DL values).
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 focus reach and the Zaamar Goldfield from the sampling campaigns in 2012 (squares) and 2013 (circles).
Figure 4. Comparison between measured and modelled results for the dissolved fractions (percentage) of metals in the (a) 2012 campaign and the (b) 2013 campaign.
Figure 5. Predicted speciation of the selected metals (‘dissolved inorganic’, ‘bound to DOM’, ‘sorbed’ or ‘precipitated’) for the five sampling locations along the Tuul River in the 2012 campaign.
Figure 6. Predicted speciation of the selected metals (‘dissolved inorganic’, ‘bound to DOM’, ‘sorbed’ or ‘precipitated’) in the five sampling locations along the Tuul River in the 2013 campaign.