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PAPER

Gold mining impact on riverine heavy metal transport in a sparsely monitored region: the upper Lake Baikal Basin case†

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Mining and ore excavation can cause the acidification and heavy metal pollution of downstream water systems. It can be difficult to assess the load contributions from individual mining areas, which is commonly required for environmental impact assessments. In the current study, we quantified the net impact of the unmonitored mining activities in the Zaamar Goldfield (Mongolia) on heavy metal transport in the downstream Tuul River–Selenga River–Lake Baikal water systems. We also noted that the Zaamar site shares the conditions of limited monitoring with many rapidly developing regions of the world. The heavy metal concentrations and flow data were obtained from historical measurement campaigns, long-term monitoring, and a novel field campaign. The results indicate that natural mass flows of heavy metals in dissolved form increased by an order of magnitude because of mining. Prevailing alkaline conditions in the vicinity of Zaamar can limit the dissolution, maintaining the on-site concentrations below health-risk based guideline values. However, suspended river concentrations are much higher than the dissolved concentrations. The placer gold mining at the Zaamar site has increased the total riverine mass flows of Al, As, Cu, Fe, Mn, Pb and Zn by 44.300, 30.1, 65.7, 47.800, 1.480, 76.0 and 65.0 tonnes per year respectively. We suggest that local to regional transformation and enrichment processes in combination with suspended sediment transport from numerous existing upstream mining areas contribute to high concentrations of dissolved heavy metals in downstream parts of the Selenga River, including its delta area at Lake Baikal. Furthermore, single hydrological events can increase the suspended load concentrations by at least one order of magnitude. Overall, the Selenga River Basin, which drains into Lake Baikal, should be recognised as one of the world's most impacted areas with regard to heavy metal loads, and it contributes to 1% and 3% of the world flux of dissolved Fe and Pb, respectively.

1. Introduction

The pollution of water systems affects humans and the natural environment worldwide. A key water management challenge is to identify the main anthropogenic pollution sources and to assess their downstream environmental and socio-economic impacts. For instance, such assessments are needed to identify cost-effective remediation measures that can mitigate the adverse impacts of the sources of pollution (*e.g.*, Baresel and Destouni).[1] However, the impact of inland sources on downstream recipients

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Environmental impact

Mining in remote, unmonitored regions can impact downstream, populated areas because of the waterborne transport of heavy metals over large distances. We determined the net impact of a large gold mining site in the Lake Baikal Basin on the riverine transport of heavy metals. We established the relative contributions of dissolved and suspended matter fluxes, the possible contribution of groundwater discharge, and the extent to which transport was affected by natural hydrological (rainfall) events. Because the Zaamar site is unlikely to be unique, the results suggest that as yet unmonitored mining areas in large river basins may have a large influence on the waterborne metal fluxes of these basins.

depends on the varying conditions in the different water systems along the contaminant transport pathways that connect source to recipient, including groundwater, rivers, lakes, and reservoirs. Dependable assessments may also need to take into account that conditions can vary within each system due to spatio-temporal hydrological, hydrogeological, and geochemical heterogeneities and that transport can occur in multiple phases (*e.g.*, as dissolved or suspended materials). Additionally, most contaminants are influenced by transformation and retardation processes that act along the flowpaths and can contribute to a natural attenuation of the pollution loads.[2,3] These processes include dispersion, sorption, dissolution–precipitation, and chemical reactions. Due to the complexity of and interactions between different processes in different water systems,[4,5] the generation of transport predictions, which are needed to understand the net impact of inland pollution sources on recipients, is scientifically challenging.[6–8]

The release and spread of heavy metals are associated with mining and ore excavation[9,10] and the oxidation of sulphide-rich minerals such as pyrite,[11] which lead to acid mine drainage. Heavy metal pollution and spreading occur when metals from excavated rocks are washed and leached to nearby waters. Anthropogenic disturbances have resulted in an increase of the global river-borne heavy metal flux.[7] However, in contrast to many other human activities, mining can occur in remote and sparsely populated regions that are not well monitored; nevertheless, this remote activity can have a large environmental impact on more populated downstream areas due to the long-distance transport of waterborne contaminants.[12–14] The overall consequences of many of the world's mining regions for downstream recipients are presently unknown due to the combined effects of complex transport processes, large transport distances, and absent or incomplete monitoring and impact assessments.

The current study increases our knowledge of the large-scale impact of mining waste by examining the Selenga River Basin, which comprises an area of 447 000 km^2, extends from northern Mongolia into southern Siberia in Russia, and has its outlet at Lake Baikal. The Selenga River Basin and Lake Baikal are located in the upstream section of the Yenisey River system, which discharges into the Arctic Ocean. The volume of Lake Baikal is the largest of any lake in the world at approximately 23 000 km^3 (representing 20% of all unfrozen freshwater globally), the lake hosts a unique ecosystem,[15] and it is an important regional water resource.[16] Mining is well developed in the region (*e.g.*, Karpoff and Roscoe;[17] AATA;[11] Byambaa and Todo[18]), and heavy metals have been shown to accumulate in biota and sediments of the Selenga River delta and Lake Baikal (*e.g.*, Boyle *et al.*;[19] Rudneva *et al.*;[20] Khazheeva *et al.*[21]); however, the underlying cause-and-effect relationships between mining and downstream pollution are poorly understood. In particular, gold mining is a relatively acute source of water pollution in the Lake Baikal region[5] and has been shown to increase the suspended sediment loads elsewhere in Siberia.[6] Most gold production occurs within the Zaamar Goldfield area,[18] which is located in the Tuul River valley in northern Mongolia.[17] Currently, more than 80 mines operate within the site.[11] The primary type of mining performed in this region is placer mining (*i.e.*, the mining of alluvial deposits); hard rock mining also occurs.

This study aims to determine the net impact of the unmonitored mining activities of the above-mentioned Zaamar mining site on heavy metal transport in downstream river reaches, including possible contributions from the groundwater system and the relative partitioning of heavy metals into the dissolved and suspended phases. As previously noted, the complex processes that are involved can result in prediction uncertainties at the large size scale considered. We reduced and quantified these uncertainties by combining available environmental datasets with novel field measurements and analysing them with mass flow estimations and statistical quantifications. Through mass balance closure, the net riverine heavy metal loading from the extensive Zaamar site could be determined. We expect that the approach used here to quantify large-scale contaminant transport can be implemented at many sites where monitoring is limited (*e.g.*, many rapidly developing regions of the world) to clarify key aspects of the spread of pollution (*e.g.*, Bayer-Raich *et al.*;[2] Jarsjö *et al.*;[22] Darracq *et al.*;[23] Destouni *et al.*;[24] Persson *et al.*;[3] and Chalov *et al.*[59]).

2. Theoretical considerations

Fig. 1a illustrates a conceptual hydrological model of a coupled groundwater–surface water system that is consistent with earlier catchment-scale models (Jarsjö *et al.*;[25] Darracq *et al.*;[23] Destouni *et al.*;[24] and Persson *et al.*[3]). In this example, the gaining river is fed by diffuse flows of groundwater and/or small, non-permanent streams. The contaminant source zone, consisting of a single mining site, is located completely within the river basin; therefore, the contaminant mass cannot be lost to other rivers. In this case, the impact of the mining site can be evaluated by analysing the contaminant mass flow (brown arrows in Fig. 1a), *i.e.*, the contaminant mass passing along the river reach per unit time. Specifically, the net mass flow contribution from the mining site can be evaluated from changes in mass flow between measurement locations (Fig. 1b; green circles) upstream and downstream of the mining site. The mass flow contributions of unmonitored river branches (Fig. 1b; black circle) can be estimated in a similar way, given that there are upstream and downstream monitoring data in the main river, relatively close to the confluence point. Notably, a corresponding analysis of river concentration data alone may not yield conclusive results because the river concentrations may not rise downstream of a mining site due to increasing dilution from unpolluted areas (blue arrows in Fig. 1a).

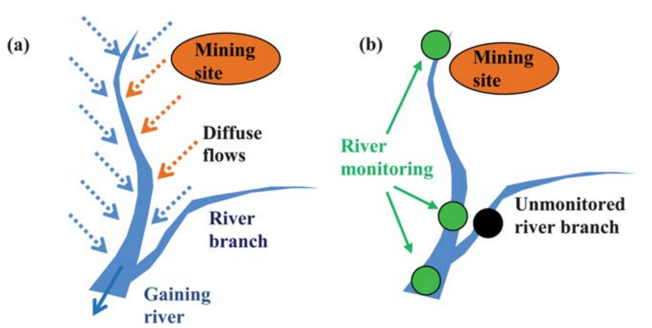

Fig. 1 Conceptual model of (a) a coupled groundwater–surface water system, and (b) its possible monitoring.

Mass flows are the products of local concentrations and discharges, according to eqn (1):

$$\mathrm{Mf} = C_i \times Q_i \tag{1}$$

where C_i is the pollutant concentration at the control plane for a given time t_i and Q_i is the water discharge through the control plane for a given time t_i.

To allow accurate mass flow estimations, pollutant concentrations and discharge values should optimally be measured simultaneously over a long time period and from the same sampling point (*e.g.*, Littlewood[26] and Li *et al.*[27]). However, comparable data can be scarce due to time and cost constraints.[26] These data discrepancies lead to uncertainties in mass flow estimations and are a key problem in the field of hydrology.[27]

The standard equation above (eqn (1)) required adjustments to compensate for a lack of simultaneous concentration and discharge data. The resulting eqn (2), which is used in the calculations of the current study, differs from eqn (1) because it is based on the mean values $\bar{C}$ and $\bar{Q}$ of repeated concentration and discharge measurements, respectively, produced over a certain time period. By using eqn (2), mass flows can be estimated from measurements of concentrations and discharges even if they are not simultaneous, provided that the data represent the same time period.

$$\mathrm{Mf} \approx \overline{C} \times \overline{Q} = \left(\frac{1}{n}\sum_{i=1}^{n} C_i\right)\left(\frac{1}{m}\sum_{j=1}^{m} Q_j\right) \tag{2}$$

In eqn (2), C_i are the instantaneous concentration values and Q_j are the instantaneous discharge values representative of the considered time period. In addition, n is the number of concentration samples, which may or may not differ from the number of discharge measurements, m, obtained during the considered time period. The standard deviation of Mf obtained from eqn (2) can be furthermore approximated by eqn (3):

$$\sigma_{\mathrm{Mf}} \approx \mathrm{Mf} \times \sqrt{\left(\sigma_C/\bar{C}\right)^2 + \left(\sigma_Q/\bar{Q}\right)^2} \tag{3}$$

where the standard deviation σ_x of a sample set x that consists of q samples with the mean value $\bar{x}$ is defined as eqn (4):

$$\sigma_x = \sqrt{(n-1)^{-1}\sum_{1}^{q}\left(x_i - \overline{x}\right)} \tag{4}$$

In addition, note that in the present case, $q = n$ for $x = C$ and $q = m$ for $x = Q$.

3. Site description

The pollutant source area considered in this study, the Zaamar Goldfield, is situated between lat: 47°20′–50°40′ N and long: 103°50′–108°50′ E in the northern part of central Mongolia,[28] approximately 230 km northwest of the capital city, Ulaanbaatar[11] (Fig. 2). The Zaamar Goldfield is located within the Tuul River Basin, which has an area of 49 840 km^2 and is part of the Orkhon–Selenga River Basins, which contribute approximately 50% of the total lake inflow to Lake Baikal.[29] The distance from the Zaamar Goldfield to Lake Baikal is approximately 600 km.[11] Gold mining activities occur over a distance of approximately 20 km along the river valley floodplain.[18] The Tuul River is the most polluted river in Mongolia, arguably due to the mining of the placer gold deposits.[30] High levels of heavy metals have been measured in the Tuul River, where concentrations have been detected that exceed both local (Mongolian State Standard 4586-98 Water Quality Standard) and global guidelines (WHO).[11,28] Gold mining in Zaamar has been active since the 1970s.[17] Presently, the area has the greatest gold production in Mongolia, with 147 tonnes generated from 1998 to 2007.[11] The largest and newest gold mine in the Zaamar Goldfield is the Big Bend Placer Gold Mining Project (“Big Bend”). The primary source of gold is placers that were deposited by the river during the Quaternary period[28] and are found both in terraces (deposits located above the water table) and alluvia (deposits located below the water table).[11] Other sources of gold are within hydrothermal veins and alteration zones.[28]

Mining in Zaamar is dependent on surface water from the Tuul River, which is used for the separation of gold from sediment.[28] The separation is performed either mechanically with a dredge (“wet mining”) or with the washing of excavated placers with high-pressure water (“dry mining”).[17,28] The geology within the Zaamar area consists of sedimentary, igneous, and metamorphic rock formations, including sedimentary sand and siltstones, igneous gabbros, and metamorphic schists.[11,17,28]

The climate of the area is semi-arid, although the region close to Lake Baikal has a microclimate that is influenced by the lake and surrounding high mountains.[11] The winters are cold, with temperatures averaging −20 °C, whereas the summers are relatively warm and dry, with temperatures averaging 20 °C.[31] The long-term monitored average discharges of the Tuul, Orkhon, and Selenga Rivers vary by an order of magnitude, with the Selenga discharge being the greatest. The discharge of the principal Selenga River can reach more than 2500 m^3 s^{-1} in the vicinity of its Lake Baikal delta (with an average annual value of 1040 m^3 s^{-1}), whereas the maximum Tuul River discharge is approximately 80 m^3 s^{-1} near its junction with the Orkhon River (with an average annual value of 26 m^3 s^{-1}).[32,33] During autumn and winter (November–March), the freezing temperatures cause the discharges to decrease significantly in all the rivers. The above-mentioned maximum discharges typically occur in the summer (June–August) because of the summer rainy period.[33] The average yearly precipitation in the region is between 200 and 250 mm.[11,28]

4. Methods of data collection and analysis

Data on the river flow, pollutant concentration, and water quality along the Tuul–Orkhon–Selenga River system were obtained from previous measurements conducted in October 2005, June 2006, and July 2008;[11,28] from long-term monitoring data;[32–35] and from the results of a novel screening campaign that was conducted in June–August 2011. The discharge and concentration data were combined to yield estimates of monthly averages and standard deviations (see Section 2, eqn (2) to (4)) of the dissolved and total (including suspended matter) heavy metal mass flows over river cross-sections at five locations and the suspended sediment loads at four of the five locations.

The cross-sections analysed are located in the Zaamar mining site (a main pollution source zone) and both upstream

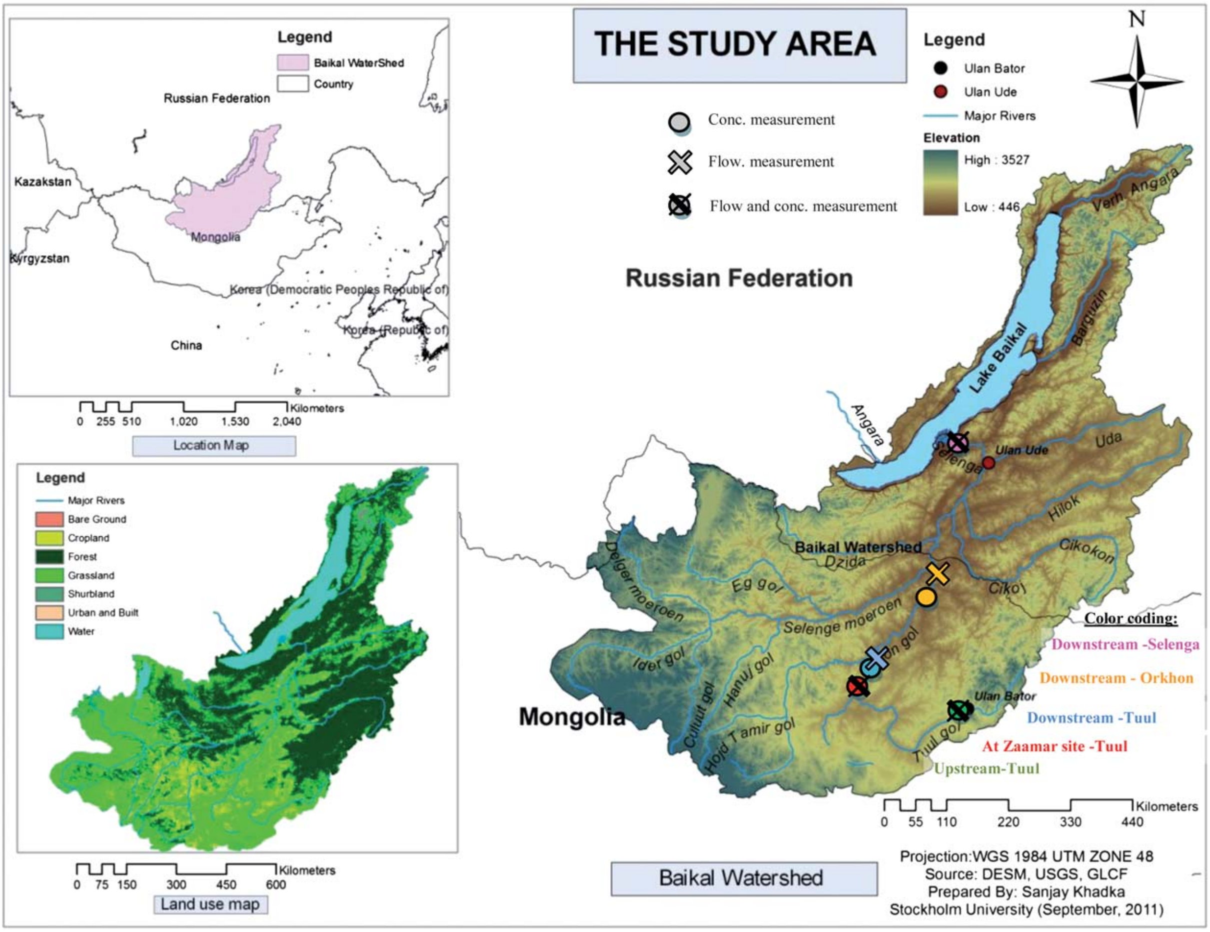

Fig. 2 Map showing the Zaamar Goldfield area (circled in red), the Tuul river, the Orkhon river, the Selenga river, and Lake Baikal (Sanjay Khadka, 2011). Also illustrated are the locations of concentration (colored circles) and discharge (crosses) measurements relative to the Zaamar Goldfield.

and downstream of it, which enabled the assessment of the relative source zone contributions to the observed pollution loads (see Section 2 and Fig. 1) and the mass flows into the Selenga River delta close to the main downstream recipient of pollution; Lake Baikal. Fig. 2 depicts the following five river cross-section sites that were analysed: (i) "*Upstream* (*Tuul*)," located at the Tuul River approximately 200 km upstream of the Zaamar site in the Ulaanbaatar region (sampling points 1 and 29–35;[28] sampling point S110[11]); (ii) "*At site* (*Tuul*)," located at the Tuul River within the Zaamar Goldfield (sampling points 2–5 and 12;[28] sampling points S120–S140[11]); (iii) "*Downstream* (*Tuul*)," located at the Tuul River downstream of the Zaamar Goldfield before the confluence with the Orkhon River (sampling points 7 and 10;[28] sampling point S150[11]); (iv) "*Downstream* (*Orkhon*)," located at the Orkhon River farther downstream of Zaamar than (iii), between the Tuul–Orkhon confluence and Sukhbaatar (sampling points 20–31);[28] and (v) "*Downstream* (*Selenga*)," located at the Selenga River close to its Lake Baikal outlet and upstream of its delta (lat: 52°3′23″ N, long: 106°40′1″" E). In contrast to locations (i)–(iv), the Selenga data originate solely from long-term monitoring[32] and from the latest publicly available five-year measurement series (1999–2003 or 1998–2002, depending on the substance).

Table 1 describes how the different discharge, metal concentration, and suspended sediment concentration data were combined for the derivation of the mass flows and suspended sediment loads presented in the Results section. Although discharges were not measured simultaneously as part of the reported concentration measurement campaigns in October 2005, June 2006, and July 2008, the table shows that independently reported discharge data were available for these months and years from sites close to the location of the concentration measurement in most cases (see also Fig. 2). In several instances, the flow conditions were estimated from the available data on the average long-term conditions for the month in question. In most cases, although it was possible to estimate the average flow $\bar{Q}$ for a given month, measurements of the actual (snapshot) flow were unavailable (except from the 2011 campaign reported in this study). We addressed the associated uncertainty with the equation $\sigma_Q = \bar{Q} \times \mathrm{CV}$ to calculate the standard deviation of $\bar{Q}$ for the month of measurement from the reported[34] month-specific coefficients of variation (CVs) of Q, in the Orkhon River. This decision was based on the assumption that the reported CVs (at the location of the measurement station) are representative of the studied stretch of the Tuul–Orkhon River system. Furthermore, by deriving the month-specific means and standard deviations of concentration C, σ_C, from the reported multiple concentration

Table 1 Information on discharge and concentration data measurements at (time and location) the four different sampling locations relative to the Zaamar site, as well as in Selenga close to the Lake Baikal outlet (see Table S1 in the ESI† for values)

River	Sample site location relative to Zaamar	Month and year of concentration *C* measurement	*C* data source	No of *C* samples	Month and year(s) of discharge *Q* measurement	*Q* data source	Comments
Tuul	Upstream	Oct 2005	Lee *et al.* 2006	3	Oct 2005	MIMH[a]	*Q* represents the average value for the specific month and year
Tuul	Upstream	Jun 2006	Lee *et al.* 2006	3	Jun 2006	MIMH[a]	*Q* represents the average value for the specific month and year
Tuul	Upstream	Jul 2008	AATA 2008	1	Jul 2008	MIMH[a]	*Q* represents average discharges from Ulaanbaatar station. *C* was measured further downstream
Tuul	Upstream	Jul 2011	This study	*d*[b]	Jul 2011	This study	*Q* represents the snapshot from 27 Jul 2011
Tuul	At site	Oct 2005	Lee *et al.* 2006	4	Oct 2008	AATA 2008	*Q* from measurements at 11 sections along the river, within the Zaamar Goldfield site
Tuul	At site	Jun 2006	Lee *et al.* 2006	4	Jul 2008	AATA 2008	*Q* from measurements at 14 sections along the river. *C* was measured in a different year
Tuul	At site	Jul 2008	AATA 2008	3	Jul 2008	AATA 2008	Independently measured *Q* within the Zaamar site
Tuul	At site	Jul 2011	This study	*d*[b]	Jul 2011	This study	*Q* represents the snapshot from 26 Jul 2011
Tuul	Downstream	Oct 2005	Lee *et al.* 2006	2	Oct 1971–2007	MCA 2011	*Q* represents the average value for the specific month and the time period. *Q* from measurements in Tuul river, at the intersection between Tuul and Orkhon
Tuul	Downstream	Jun 2006	Lee *et al.* 2006	2	Jun 1971–2007	MCA 2011	As above
Tuul	Downstream	Jul 2008	AATA 2008	1	Jul 1971–2007	MCA 2011	As above
Tuul	Downstream	Aug 2011	This study	*d*[b]	Aug 2011	This study	*Q* represents the snapshot from 6 Aug 2011
Orkhon	Downstream	Oct 2005	Lee *et al.* 2006	6	Oct 2005	MIMH*	*Q* represents the average value for the specific month and year
Orkhon	Downstream	Jun 2006	Lee *et al.* 2006	6	Jun 2006	MIMH*	*Q* represents the average value for the specific month and year
Selenga	Downstream	Aver 1998–2003 (Jun, Jul, Oct)	GEMStat 2011	[c]	Aver 1998–2003 (Jun, Jul, Oct)	GEMStat 2011	*Q* and *C* represent long term average conditions for the period 1998–2003

[a] MIMH = Mongolian Institute of Meteorology and Hydrology. [b] *d* = SSC was obtained from depth integrated water sampling with a GR-16M bottle sampler at the midstream. [c] Continuous, varying due to substance (Fe/Pb).

samples (see the "No. of *C* samples" column in Table 1), we could determine the standard deviation of the monthly mass flow, σ_{Mf}, from eqn (3), with eqn (2) then yielding the associated average monthly mass flow.

Seven heavy metals, Al, As, Cu, Fe, Mn, Pb and Zn, were selected for pollution analysis because of their association with mining activities (*e.g.*, Jain and Sharma,[36] Nordstrom,[37] and Weng *et al.*[38]). These selected metals comprise all of the metals for which the necessary information was available in the different campaigns (from 2006 to present) and which were above detection limits. Cr, Cd and Hg are also commonly associated with mining but were not included because they were repeatedly found to be below the detection limits (0.6, 0.5 and 0.8 μg L^{-1} respectively). The analytical procedures of the previous campaigns (in 2005, 2006, and 2008) included analysis of sample duplicates, blanks and standards. The RSD (percentage relative standard deviation) values of duplicate sample analysis were found to be less than 5%.[28] All water samples for dissolved heavy metal analyses were filtered (through a 0.45 μm pore membrane) and acidified (HNO_3) prior to analysis).[11,28] Additionally, the hydrological conditions of metal transport in the area were studied during a new measurement campaign (July–August 2011) that complemented the reporting of historical heavy metal and discharge data with observations of the short-term changes in several basic parameters (water levels and discharges, turbidity, pH, and suspended sediment concentrations). The observations were performed at the Tuul, Orkhon, and Selenga Rivers both upstream and downstream of the Zaamar Goldfield. Discharges were gauged from bridges, by boat, or while wading in two directions. Flows were measured from bridges with a hydrometric propeller ISP-1 at one-fifth the depth of each width increment. For depths greater than 1.5 metres, an acoustic Doppler current profiler (ADCP) was used. The total water discharges were calculated by multiplying the discharge flow velocity by the cross-sectional area of the river being studied. A Hanna Instruments HI 9828 meter was used to measure the pH close to and downstream of the Orkhon River's convergence with the Tuul River. Turbidity measurements were performed in stretches of both the Tuul and the Orkhon Rivers using a portable HACH 2100P meter. Turbidity was measured on-site from depth-integrated water samples collected at the midstream with a GR-16M bottle sampler. Samples collected for measuring the suspended sediment concentration (SSC) were filtered through a pre-weighed membrane and paper filters with the Millipore filtration system, then oven-dried and reweighed. The suspended sediment loads (SSLs) were calculated by multiplying the sediment load velocities by the average SSC values and the cross-sectional areas of the rivers. Additionally, measurements during an extreme hydrological event (2011-07-28 to 2011-07-30) were obtained more frequently than in prior studies, including four turbidity measurements at five points of a cross section (28^{th} of July at 17:00, 29^{th} of July at 10:00, 17:00 and 30^{th} of July at 08:30), four water level measurements (same time as turbidity measurements) and three SSC samples (28^{th} of July at 17:00, 29^{th} of July at 17:00 and 30^{th} of July at 08:30), which enabled an evaluation of the responses of stream flow and water quality to this individual event, resulting from heavy rainfall.

5. Results

5.1 Water quality

The pH measurements of both the Tuul River and the Orkhon River (downstream of the confluence of the Tuul River and the Orkhon River) revealed basic (alkaline) conditions in all cases, with values varying between 7.2–9.0[11] and 7.7–9.0, respectively (novel campaign 26 June to 7 August 2011).[28] The turbidity was high in both the Tuul and Orkhon Rivers, varying between 85.5 and 493.0 NTU in the Tuul River stretches close to the Zaamar site (26 and 27 June 2011) and between 69.7 and 105.0 NTU in the Orkhon River downstream of its confluence with the Tuul River (7 August 2011).

The dissolved and total (dissolved + suspended) concentrations of each heavy metal (Al, As, Cu, Fe, Mn, Pb and Zn) from the previous measurement campaigns (October 2005, June 2006, and July 2008) at the four locations in the vicinity of the Zaamar site, upstream (Tuul), at site (Tuul), downstream (Tuul), and downstream (Orkhon), are shown in Fig. 3a–g. The results displayed in Fig. 3 show that, with few exceptions (Pb and Zn), the dissolved concentrations were significantly higher during the June and July campaigns than in October, indicating a relatively pronounced effect of seasonality (note the non-overlapping error bars of the data from the summer and autumn campaigns). All dissolved concentrations for the investigated elements increase in the Tuul River downstream of the mining site. Generally, the dissolved concentrations are also lower upstream of the mining site than at the site. However, a notable exception is in October 2005, when dissolved concentrations of Mn, Pb and Zn were lower at the site than upstream of it.

Furthermore, the results show significant differences between the dissolved and total concentrations, with total concentrations that are up to two orders of magnitude higher than the dissolved concentrations due to high concentrations of suspended heavy metals. Dissolved concentrations are generally well below the WHO health risk-based guideline values,[39] the exception being Mn that is above the guideline value and As that is relatively close to the guideline value.

The average concentrations of both Fe and Pb are higher in the Selenga River than in the rivers closer to the Zaamar site. For instance, the average dissolved Fe concentrations in the Selenga River exceed the health risk-based guidelines[39] during the times of year when the Zaamar site measurements were conducted (June, July, and October). However, the average dissolved Pb concentrations did not exceed the WHO limit during these months. The highest average concentrations of Fe and Pb (1420 $\mu g\ L^{-1}$ and 8.75 $\mu g\ L^{-1}$, respectively) are obtained in July and February, respectively.

5.2 Mass flows

The coloured lines in Fig. 4a–g show the dissolved and total (dissolved + suspended) mass flows of Al, As, Cu, Fe, Mn, Pb and Zn in October 2005, June 2006, and July 2008 at the four studied locations along the Tuul and Orkhon Rivers (note the logarithmic scales on the *y*-axes). The dissolved and total mass flows of Al and Fe (Fig. 4a and d) increased along the flow direction of the Tuul River, with no exception. Further downstream, in the Orkhon River, the dissolved mass flows of Al and Fe (Oct 2005 and June 2006) decreased, which means that some of the suspended particles were deposited. For total mass flows, the net increase in the Tuul River over the full extent of the site (estimated from the difference between the mass flows of the downstream Tuul location and the upstream Tuul location) was 44.300 tonnes per year and 47 800 tonnes per year for Al and Fe, respectively. For dissolved mass flows, the average net increase was 610 tonnes per year for Al and 800 tonnes per year for Fe.

The other heavy metals, As, Cu, Mn, Pb and Zn (see Fig. 4), also showed higher mass flows downstream of the site than upstream of it, with no exception. There was a net increase over the full extent of the site for all elements (dissolved and total). However, the dissolved mass flows in the middle of the mining site were at times (at least in one measurement series per element) lower than upstream of the site. Mn was the only element that showed, for all dissolved measurement series, lower mass flows in the middle of the site than upstream of it. For total mass flows, Zn was the only element where the mass flows were lower in the middle of the site than upstream of it. The net increases over the full extent of the site for total mass flows were: 30.1 tonnes per year (As), 65.7 tonnes per year (Cu), 1480 tonnes per year (Mn), 76.0 tonnes per year (Pb) and 65 tonnes per year (Zn). The average net increases for dissolved mass flows were: 9.79 tonnes per year (As), 6.18 tonnes per year (Cu), 650 tonnes per year (Mn), 1.5 tonnes per year (Pb) and 10.3 tonnes per year (Zn).

Altogether, the results shown in Fig. 4 reveal higher dissolved and total mass flows in the Tuul River downstream of the mining site, than in the upstream location, for all the investigated heavy metals. These overall trends of net increasing mass flows over the Zaamar site are in contrast to the concentration trends shown in Fig. 3, which differ among the different heavy metals. Furthermore, the mass flows of dissolved metals were higher in the summer measurement campaigns (June and July) than in the autumn ones (October). A similar pattern was shown earlier for heavy metal concentrations (Fig. 3). In addition, analogous to the concentration results, the total mass flows are significantly higher than the corresponding mass flows of dissolved metals. Average suspended transport (based on the July 2008 series) accounted for between 44% and 99% of the total transport of all the heavy metals, with As and Mn having the lowest suspended

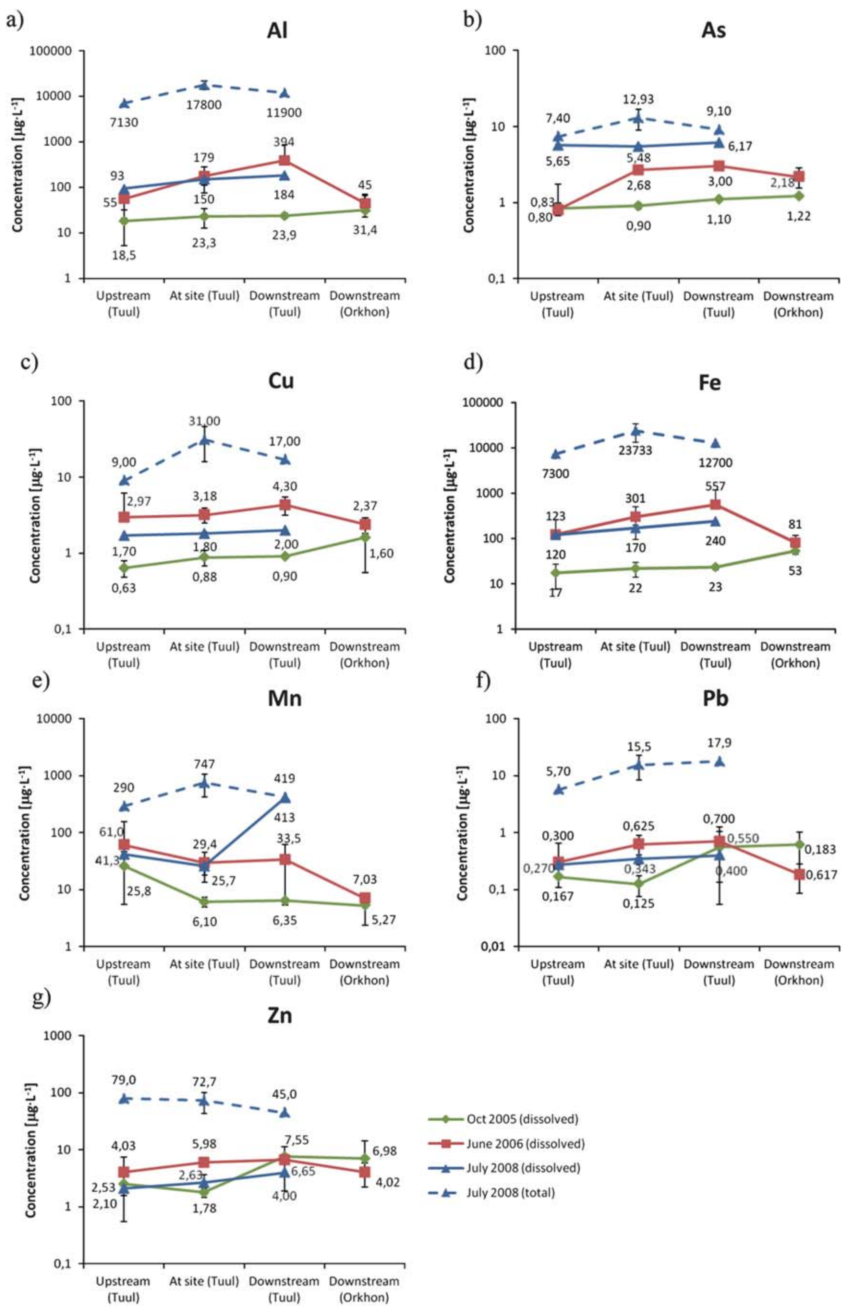

Fig. 3 Concentrations (dissolved and total) of Al, As, Cu, Fe, Mn, Pb and Zn at the four different sampling points along the Tuul and Orkhon rivers, located upstream of, at, and downstream of the Zaamar Goldfield. The three different series represent different time periods and seasons. The data originates from Table S1 (see ESI†) (Lee *et al.* 2006; AATA 2008).

transport (44% and 45%) and Fe and Al having the highest (both 99%).

The mass flows of dissolved metals in the Selenga River close to its delta at Lake Baikal (where Fe and Pb data were available) were 2 orders of magnitude greater than the corresponding mass flows of Fe and Pb in the Tuul River downstream of the site. The estimated mass flows of the Selenga River in July were 46.600 tonnes per year for dissolved Fe and 173 tonnes per year for dissolved Pb, compared to 1600 tonnes per year for dissolved Fe and 2.82 tonnes per year for dissolved Pb measured downstream of the site. The mass flows of dissolved metals in the Selenga River were substantially higher during the summer months. The average annual Fe and Pb mass flows were estimated to be approximately 23.800 and 96 tonnes per year, respectively.

6. Discussion

The pollution of the Tuul–Orkhon–Selenga River system has been investigated in a number of earlier studies (*e.g.*, Khazheeva *et al.*;[21] Zandaryaa *et al.*;[5] Altansukh;[30] Byambaa and Todo[18]). Research has shown that there are several pollution sources along the river system, in addition to mining sites, that are the

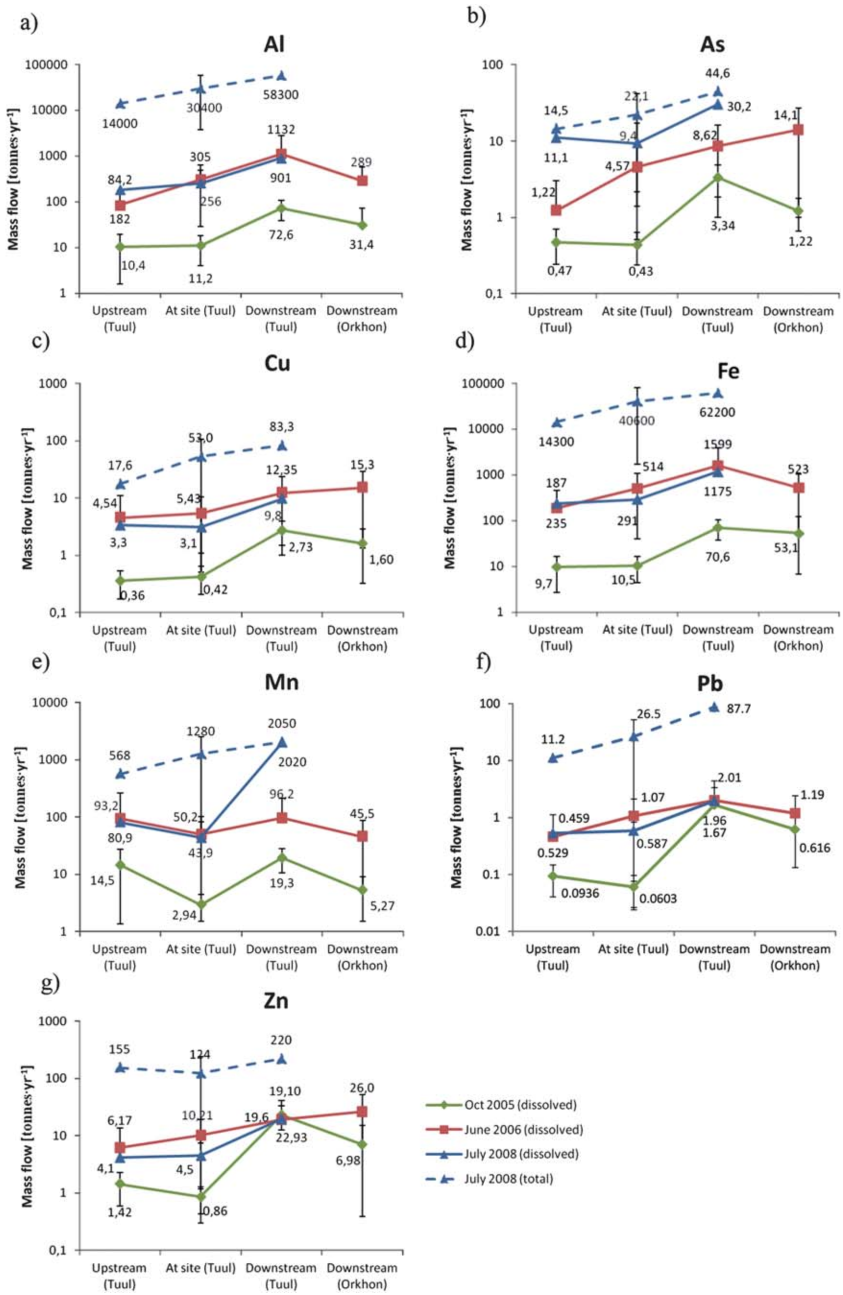

Fig. 4 Estimated mass flows, in tons per year, of Al, As, Cu, Fe, Mn, Pb and Zn at the four different sampling points along the Tuul and Orkhon rivers. Sampling point number two is at the Zaamar Goldfield. The data originates from Table S1.†

result of rapid urbanisation and industrial expansion in the area (*e.g.*, Farrington[40] and Altansukh[30]). However, the individual contributions of these source zones to the downstream heavy metal pollution of the Tuul River have previously not been quantified. The novel estimates presented here specifically regard the total riverine heavy metal flows entering the Zaamar Goldfield, resulting from natural processes and anthropogenic activities in the upstream (sub-) catchment area, plus the net mass flow changes over Zaamar. Although there are no other mining sites in the area upstream of Zaamar, it hosts the capital city of Ulan Bator. Data from Lee *et al.*[28] suggest that the mass flows of dissolved heavy metals are approximately twice as high in the Tuul River just downstream of Ulan Bator City than upstream of it. Since there are no major cities or industrial areas along the Tuul River upstream of Ulan Bator, this implies that the impact of the urban activities approximately results in a doubling of the natural mass flows of dissolved heavy metals. Our present results show that the modified (by human activities) mass flows of dissolved heavy metals that enter the Zaamar Goldfield increase six-fold over the mining area. Furthermore, the Zaamar contribution is an order of magnitude higher than the natural mass flows that presumably would prevail upstream of Zaamar under natural conditions, without the anthropogenic influence from the city of Ulan Bator.

For comparison, Grosbois *et al.*[41] report impacts of a principal gold mining district in the Upper Isle river basin of France, where 37 tons of gold were extracted in the 20th century, generating over 1 400 000 tonnes of mining waste. They found on average three times as high concentrations of dissolved heavy metals in the Upper Isle mining district than in a reference tributary through an undisturbed region of similar geochemical conditions. The riverine As concentration was high in the Upper Isle district (14 $\mu g\ L^{-1}$, compared to 3.8 $\mu g\ L^{-1}$ at Zaamar), due to high background concentrations (120 $mg\ kg^{-1}$) in soils of the region.[41] Whereas the riverine Fe and Zn concentrations were approximately the same at the Upper Isle mining district and at Zaamar (250 to 260 $\mu g\ L^{-1}$ for Fe and 4 to 5 $\mu g\ L^{-1}$ for Pb), the Pb concentration is slightly higher at Zaamar (0.5 $\mu g\ L^{-1}$, compared to 0.16 $\mu g\ L^{-1}$ at the Upper Isle mining district). At both locations, the neutral to high pH values (6.1 to 7.5 at Upper Isle; 7.5 to 9.0 at and downstream of Zaamar) are likely to considerably constrain the dissolved concentration levels, which is discussed in more detail in a separate paragraph below. At Zaamar, the riverine transport of dissolved As, Fe, Pb and Zn is generally much higher than in the Upper Isle district, despite the similar concentrations, since the river discharges on average are an order of magnitude higher through the Zaamar site. Whereas untreated mining waste impoundments have been identified as a main source of heavy metal loading in the Upper Isle district,[41] the mining waste should be more accessible for transport in the Zaamar region, due to the practice of dredge mining and the presence of hundreds of open waste heaps in the valley of the Tuul River.

The present results and those of Grosbois *et al.*[41] show considerable increases above background levels of dissolved heavy metal concentrations at the mining sites, as discussed above. However, the results also suggest that, in the investigated alkaline to neutral river water of the mining areas, there is a prevalence of dissolved heavy metal concentrations below the WHO health-risk based guideline values,[39] with relatively few exceptions. Available investigations of mining impacts in neutral to alkaline river waters generally converge on supporting this pattern.[42–46] For instance, Zak *et al.*[46] considered the Litavka River (average annual flow 2.6 $m^3\ s^{-1}$; pH 7.1 to 7.6) in the Czech Republic, which is impacted by the Příbram Ore Region where 3500 tonnes of Ag, 480 000 tonnes of Pb, 260 000 tonnes of Zn and 80 000 tonnes of Sb have been produced, mainly during the 20th century. They report dissolved concentrations of Cu between 3.4 and 6.3 $\mu g\ L^{-1}$, Pb between 0.5 and 1.0 and Zn between 4 and 167 $\mu g\ L^{-1}$, which are below the WHO guideline values. Sanchez España *et al.*[43] showed that high dissolved heavy metal concentrations (in particular of Al, Cu, Fe, Mn, Pb, and Zn) in acid mine drainage waters precipitated to a large extent after being neutralized in the Odiel River water of southern Spain, leaving only high dissolved concentrations of Cu and Zn (that are relatively soluble) in the downstream river water. Similarly, Tarras-Wahlberg *et al.*[42] considered the occurrence of Cd, Cu, Pb and Zn in the gold mining impacted Puyango River of Ecuador, which is characterized by neutral to alkaline waters. They showed that the measured total (unfiltered) concentrations were high for all investigated elements, whereas the dissolved concentrations were only considerable, *i.e.* above WHO standards, for Cu and Zn.

In terms of on-site conditions, the dissolved riverine mass flows were lower at the Zaamar site than both upstream and downstream of it, in contrast to the suspended concentrations. However, water is physically removed from the river in the mining process, which contributes to increases in the diffuse flows through groundwater and small streams or channels; such flows are not detected by on-site river monitoring. If the diffuse flows with their dissolved metals feed the river downstream of the source zone (as outlined in the principal sketch of Fig. 1), they will be detected by river monitoring downstream of the site. Therefore, the elevated dissolved mass flows in the river downstream of the Zaamar site, which were consistently higher than those in the upstream area, are likely to have entered the river through diffuse flows from groundwater and small channels. Such groundwater loading of rivers with metals has also been shown to be important in the vicinity of the Pacific Mine in Utah (USA), an abandoned silver and lead mine.[47] Monitoring upstream and downstream of a mining area has been demonstrated to be effective at other sites[48] and can provide evidence of the relative importance of point sources *versus* diffuse pollution sources.

The present results demonstrate that, despite the fact that the neutral to high pH of the Tuul river limits the dissolved phase concentrations and transport, the direct input from the Zaamar Goldfield to the total (suspended + dissolved phase) transport can be high, on the order of 44 000 tonnes per year for Al, 30 tonnes per year for As, 70 tonnes per year for Cu, 48 000 tonnes per year for Fe, 1500 tonnes per year for Mn, 80 tonnes per year for Pb and 65 tonnes per year for Zn. In addition to high concentrations of contaminated, suspended sediments, the considerable water discharges in the Tuul River at the Zaamar site constitute a precondition for supporting such mass flows. For comparison, a recent estimate of the historical mining activity contribution to the total waterborne mass flow of metals to surface waters in England and Wales was 551 tonnes per year for Fe, 72 tonnes per year for Mn, and 18.5 tonnes per year for Pb.[13]

A key question is to what extent the heavy metals that are attached to suspended particles can become bioavailable and hence adversely impact downstream aquatic ecosystems. Since toxic effects are primarily related to the ionic state of metals, metals in suspended material and sediments will mainly become bioavailable if they undergo phase transformations and/or reactions. In the considered Selenga River Basin, a gradient in pH exists between the investigated river water of the Zaamar area and the downstream recipient of Lake Baikal, as shown by the non-overlapping ranges of the measured pH values (7.5 to 9.0 in river waters of the Zaamar area and 7.3 to 7.5 in Lake Baikal).[49] Furthermore, studies of the Selenga River Delta region of Lake Baikal have documented the occurrence of acid rains (pH 4.1).[50] Low-pH environments, in combination with the large-scale trend of decreasing pH in the flow direction, can contribute to dissolution of heavy metals that originally were transported in suspension close to high-pH headwater areas. In large parts of the Selenga River Basin, arid conditions prevail, which also means that dissolved heavy metals can be enriched through evapo-concentration. More generally, Tarras-Wahlberg *et al.*[42] point out that sediment-bound heavy metals, and in particular Pb, can become bioavailable through dissolution in the gastronomic tract of larvae. Taken together, we suggest that such local to regional transformation and enrichment processes in combination with suspended sediment transport from numerous existing upstream mining areas (such as the here quantified high transport from the Zaamar area) contribute to the documented (see *e.g.*, Khazheeva *et al.*[51]) high concentrations of dissolved heavy metals in downstream parts of the Selenga River, including its delta area at Lake Baikal.

The present results indicate that total mass flows were considerably higher in the summer (June and July) than in the autumn (October), implying significant effects of seasonal hydrological changes. However, the lack of available water quality data obtained on a daily or hourly basis in this region diminishes our understanding of the influence of individual hydrological events on total mass transport. However, a period of intense rainfall occurred during the reported field campaign in the present study (June and August 2011), in which approximately 50 mm of precipitation (approximately 20% of the average annual precipitation) was observed over a three-day period (Fig. 5). The recorded event formed one of two distinct flow peaks during the hydrological year of 2011 (Fig. 5a). Fig. 5b also shows that the water level of the Orkhon River increased by more than 2 metres in response to this event. Notably, the results of the novel measurements of total SSC revealed a greater than 10-fold increase (from approximately 160 g m^{-3} to 2400 g m^{-3}) following this hydrological event (Fig. 5b). Considering the combined effects of the increases in SSC and discharge in response to these high water levels, it is possible that relatively large portions of the total annual sediment transport can occur within limited periods of time. Unless such events are explicitly considered in water quality monitoring, the total annual mass flows are likely to be underestimated. These results of increased SSC support the conclusions of Whyte and Kirchner,[52] Gallo *et al.*,[53] Obermann *et al.*,[54] and Zak *et al.*,[46] which assert that discharge variations and the associated turbidity changes have large impacts on both the dissolved and the suspended phases of pollution transport. For instance, Whyte and Kirchner[52] considered total Hg fluxes in a stream downstream of the Gambonini mine in California, and showed that 30 of 82 kg Hg transported during a two-month period was released during 28 hours, in response to an intense two hour rainstorm event.

In order to identify relevant measures for the mitigation of adverse impacts of mining, one also needs to consider possible future changes in ambient conditions that can influence the water-borne transport, including on-going and projected future hydro-climatic changes. Trend analysis of hydrological changes in the Tuul River Basin since 1945 revealed increased peak flow values and decreased low flow values, with a considerably increased variability in daily flows.[55] Since the SSC of Tuul River was observed to distinctly increase at high flows, this suggests that the transport potential of sediment-borne pollutants from the Zaamar Goldfield can exhibit an increasing trend. In addition, the trend of intensified mining activities observed at the Zaamar site during the past decade is not foreseen to change in the near future. More generally, the high temporal variability that characterises the hydrology of the Tuul–Orkhon–Selenga River system is consistent with river systems functioning under strong anthropogenic pressures (*e.g.*, Meybeck and Vörösmarty).[7] The available long-term monitoring data from the Selenga River close to its Lake Baikal outlet reveal flows of dissolved Fe and Pb that correspond to 1% and 3% of the recently estimated total dissolved worldwide flux of Fe and Pb, respectively, from rivers to the ocean (Viers *et al.*).[6] These numbers are high, considering that the Selenga River Basin covers only 0.4% of the earth's ocean-drained land area; they suggest that the basin should be acknowledged as one of the world's most impacted areas with regard to heavy metal loads. Currently, this status is only recognised by Russian literature sources (*e.g.* Garmaev and Khristoforov).[56]

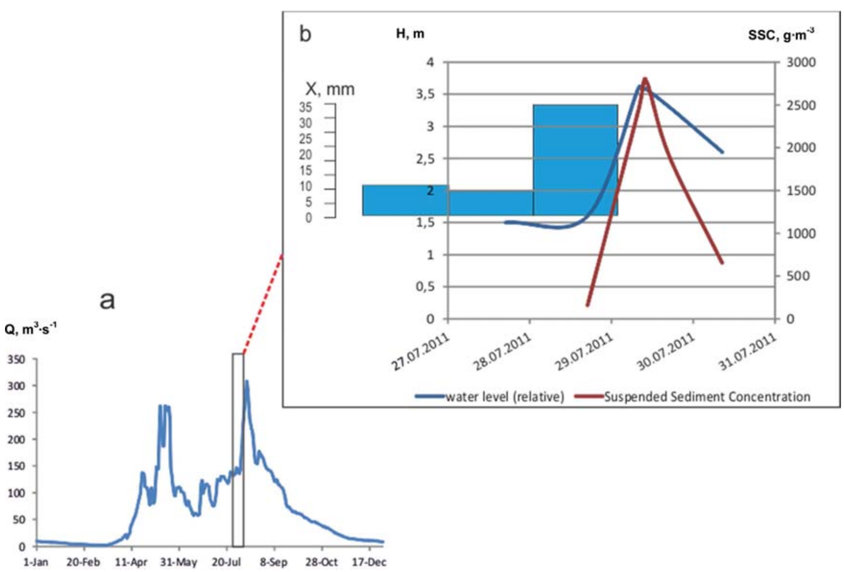

Fig. 5 Water discharge (*Q*) changes during 2011 at the downstream gauging station Suhaabator of the Orkhon river (a) and the corresponding water level (*H*) and suspended sediment concentration (SSC) fluctuations at the Orkhon upstream station Kharkhorin during 27.07–31.07 due to abundant precipitation (*X*) (b).

One methodological contribution of this work was to demonstrate how relatively limited data from long-term monitoring and individual measurement campaigns on discharge, concentrations, and their variability can be combined to yield conclusive evidence of mass flow changes over source zones. In particular, by quantification of mass flows over consecutive control planes, including one upstream and one downstream of the extensive source zone, the net change (erosion or deposition) over a relatively long distance (tens of kilometres) could be determined. This information may be difficult to obtain from local estimates of sedimentation or erosion rates, since one must then consider the sum of contributions that can vary significantly over such long distances. Furthermore, as recognised in previous works (*e.g.*, Jarsjö and Bayer-Raich;[57] Alary and Demougeot-Renard[58]), an absence of clear trends in concentration data alone can be explained by dilution and mixing effects, such as the mixing of waters from different sub-catchment areas or aquifer regions. It is likely that these effects have contributed to the results shown here; whereas the integrated mass flow signal showed consistently higher mass flows downstream of the source zone than upstream of it, the underlying concentrations showed diverging and less pronounced differences between the upstream and downstream locations.

7. Conclusion

This study highlights the importance of the Zaamar Goldfield, which is located in the upper Lake Baikal Basin, as a significant contributor to downstream heavy metal mass flows. The natural mass flows of heavy metals in dissolved form were estimated to increase by an order of magnitude because of mining. The contribution of diffuse flows with groundwater appears to be important for dissolved transport of heavy metals. The results also suggest that the prevailing alkaline conditions in the vicinity of Zaamar can limit the dissolution, maintaining the on-site concentrations below health-risk based guideline values. However, suspended river concentrations are much higher than the dissolved concentrations. The overall impact of the mining activities on downstream water systems must hence be dominated by the fate of the heavy metals that are attached to particles in suspension. The extensive Selenga River Basin, which drains into Lake Baikal, should be considered among the world's most impacted areas with regard to heavy metal loads, as it contributes 1% and 3% of the world flux of dissolved Fe and Pb, respectively. Unmonitored areas of large river basins such as the Zaamar site and the Tuul River can make considerable contributions to high metal fluxes.

More generally, the combination of high export of suspended sediment and decreased pH in downstream water systems can contribute to the dissolved concentrations generally being considerably higher farther downstream of a mining site than on it, as exemplified here. This is because heavy metals in suspension can undergo phase transformation (dissolve) and become bioavailable during and after being transported to downstream regions, as a result of hydrological and hydrogeochemical variability and gradients (*e.g.*, in pH). Furthermore, the fact that the suspended phase transport increased by at least an order of magnitude during a single hydrological event implies that total mass flows may be underestimated unless the measurement frequency is sufficiently high (at least one measurement per day) to capture such events. In the considered river, high flow events have been seen to become increasingly frequent in recent times, which show more generally that monitoring strategies may need to be adapted considering on-going and projected future trends of hydro-climatic change.

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